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INSTITUT INTERNATIONAL DE PHYSIQUE SOLVAY

DIXIÈME CONSEIL DE PHYSIQUE
tenu à l'Université de Bruxelles
du 13 au 17 septembre 1954

LES ÉLECTRONS DANS LES MÉTAUX

RAPPORTS ET DISCUSSIONS

publiés par les Secrétaires du Conseil
sous les auspices de la Commission Administrative de l'Institut

R. STOOPS
Editeur
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1955

LE DIXIÈME CONSEIL DE PHYSIQUE SOLVAY

Le dixième Conseil s'est tenu à Bruxelles, du 13 au 17 septembre 1954, dans les locaux de l'Institut de physique appliquée, à l'Université.

Les membres de ce Conseil, dont on trouvera la liste ci-après, ont pris une part active à la discussion des rapports qui avaient été proposés. Les travaux ont été interrompus le mercredi 15 après-midi, pour permettre la visite du Musée Napoléonien installé dans la Ferme du Caillou, sur le champ de bataille de Waterloo; ils se sont terminés le 17 par le banquet traditionnel offert aux participants par la Famille Solvay et la Commission administrative de l'Institut, avec la présence effective des Autorités Universitaires de Bruxelles.

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(septembre 1954)

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The Collective Description of Electron Interaction in Metals

by **DAVID PINES**
University of Illinois

I

I have been asked to report on the collective description of electron interactions, which David Bohm and I have developed in a series of papers over the past few years (1). Because the approach is a new and rapidly developing one (so much so that the majority of applications using it have yet to appear in print) it is difficult for me to give a balanced summation at this time. For that reason this report will be more in the nature of a progress report; I shall review the basic development of the collective description, with emphasis on the underlying physical picture and then discuss present and projected applications of the theory. I shall begin with a brief historical introduction, which stresses the problems arising in the treatment of electron interaction on the basis of the conventional Hartree-Fock theory, and conclude with some speculations on the general validity of the collective description of electron interactions.

The first sections of this report may thus be regarded as a « guide » to Papers II, III and IV, in that we consider the physical basis for the collective description, and sketch the mathematical derivation of the Hamiltonian which is used as a starting point for discussing electron interaction in metals. We then discuss in some detail the correlation energy and consider the influence of correlation and exchange on the state density, magnetic susceptibility and bandwidth of electrons in metals. We confine our attention, for the most part, to the alkali metals, for which a free electron model is particularly appropiate. We also discuss the excitation of collective oscillations by a fast charged particle and the damping of these oscillations by interaction with the core electrons. Finally, we discuss the role of electron-electron interactions in determining the electron-phonon interaction in metals.

II

The usual treatment of electron motion in metals is based on an independent electron model, in which the motion of a given electron is assumed, in first approximation, to be independent of the motion of all the other electrons. The effect of the other electrons on this electron is then represented by a smeared-out potential, which may be determined by using a self-consistent field method. In its simplest version, the Hartree approximation, in which all correlations in the position and energy of the electrons due to their mutual interaction are neglected, this model is quite successful qualitatively and, in many cases, quantitatively. Examples of its success include the specific heat, X-ray band-width and magnetic behavior of the alkali metals.

The success of the simple Hartree approximation is surprising for two reasons. First, on physical grounds, we might expect electronic correlations to play an important role in metals. For the Coulomb interaction is a long-range interaction, so that many hundreds of particles interact simultaneously, leading us to anticipate a high degree of long-range correlation in their motion. Second, we might expect that any improvement in the Hartree theory which takes into account electronic correlations would lead to even better agreement between theory and experiment. Such is not the case. In fact, if we use the Hartree-Fock approximation, in which correlations in the motion of electrons of parallel spin are introduced via the exclusion principle, we find that the agreement between theory and experiment for the above-mentioned metallic properties is completely destroyed.

It is certainly necessary to take into account electron correlation in a description of a metal. For the Hartree approximation fails quite badly in one respect — the calculation of the cohesive energy of metals. Consider the free electron gas model of a metal (²), for which the energy of the system in the Hartree approximation is just the Fermi energy, and is, per electron :

$$\mathrm{E} = 2.21/r_s^2 \ ry \tag{1}$$

where r_s is the inter-electronic spacing in units of the Bohr radius. The cohesive energy calculated from (1) is much too small in comparison with the experimental values, since the electrons spend too much time close together in unfavorable potential fields. Any correlation in the electronic motion which acts to reduce this tendency will lead to a reduction in the system energy, and hence an improved value for the cohesive energy. The success of the Hartree-Fock approximation in this respect is due to the fact that the exclusion principle keeps electrons of parallel spin apart, so that the system energy becomes :

$$E = 2.21/r_s^2 - .916/r_s \; ry , \tag{2}$$

the additional term representing the average exchange energy per electron.

The origin of some of the difficulties associated with the Hartree-Fock approximation may be seen by considering the expression for the energy of a given electron of wave-vector k. This is :

$$E(k) = k^2/2m - \frac{e^2 k_o}{2x} \left\{ 2 + \frac{k_o^2 - k^2}{k_o \, k} \ln \left| \frac{k_o + k}{k_o - k} \right| \right\} \tag{3}$$

where k_o is the wave vector of an electron at the top of the Fermi distribution, and the last term represents the effect of exchange and is the source of much anguish. For instance, consider the density of states in energy of the electron gas. This may be written :

$$\frac{dn}{dE} = \left(\frac{dn}{dk}\right) \Big/ \left(\frac{dE}{dk}\right) = \frac{k^2}{\pi^2} \Big/ \left(\frac{dE}{dk}\right) \tag{4}$$

Then on substituting (3) into (4), we find that because of the exchange term the density of states at the top of the Ferni distribution vanishes; more generally its effect is to reduce drastically the density of states near the top of the Fermi distribution. This reduction profoundly affects the theoretical predictions for a large number of metallic phenomena. For instance, Bardeen ([3]) has shown that the specific heat is altered from a linear dependence on temperature to a $T/\ln T$ dependence, a result which is not in agreement with experiment. The theoretical predictions of the diamagnetic susceptibility, and, indeed, all perturbation-theoretic calculations (which depend on $[dn/dE]_{E = E_0}$) would also be adversely affected.

We might hope that the day could still be saved for our « improved » one-electron theory by our making yet another improvement. In the Hartree-Fock theory, no correlations between electrons of anti-parallel spin have been taken into account. Such correlations are, however, needed, since (2) still yields too little cohesion. We might hope that the Coulomb interactions, which lead to such correlations, could consistently be treated as a small perturbation, and that by taking these into account by conventional second order perturbation theory methods, we might eliminate the foregoing difficulties with exchange effects. If we do this, we obtain an additional term in the cohesive energy due to the correlations between electrons of anti-parallel spin, which is :

$$\mathrm{E}^{(2)} = -\frac{1}{2} \sum_{\vec{k}\vec{k}'\vec{\Delta k}} \left[\frac{4\pi e^2}{(\Delta k)^2}\right]^2 \frac{m}{\vec{\Delta k}\cdot(\vec{k}-\vec{k}'+\vec{\Delta k})}$$

where Δk is the momentum transfer in the « virtual » interaction of two electrons of wave vector $\vec{k}$ and $\vec{k}'$. There is an analogous term for the one electron energy $\mathrm{E}(k)$. Unfortunately, rather than eliminating the difficulties with exchange, these terms themselves diverge!

The cause of this second set of contradictions is again the long-range of the Coulomb interaction. For this in turn makes possible very small momentum transfers between very distant electrons, and it is these small momentum transfers which lead to the divergence of our perturbation-theoretic expression above, as well as to the exchange difficulties (4). Thus we appear to have gone full circle. We start with a theory which we should not expect to work. It does work in its very simplest version. But on improving it, we find that it does not work, and for just the reasons that might have initially discouraged us.

One way out of this dilemma was proposed by Wigner (5) some twenty years ago. He calculated the correlation energy (6) by using determinental wave-functions in which the wave function of an electron of given spin is assumed to depend on the positions of all the electrons of opposite spin. His method, which represents a departure from the independent electron model, could only be applied to an electron gas of very high density ($r_s \lesssim 1$). He calculated the correlation energy in this case, and then developed an approximate formula for the region of actual metallic densities ($2 \lesssim r_s \lesssim 5.5$) by extrapolating his result in such a way as to approach the correct value of the correlation energy for very low densities ($r_s \gg 5$) (⁷). Wigner obtained the result :

$$E_{corr.} = -0.58/(r_s + 5.1)\ ry\ , \qquad (5)$$

which he estimated to be accurate within 20 %. Wigner also suggested that Coulomb correlations would counteract the exchange difficulties discussed earlier, and demonstrated the possibility of this for the specific heat and ferromagnetism of the free electron gas. There is little doubt about the correctness of Wigner's approach; there remains, however, the difficulty involved in carrying out detailed calculations for the effects of electron interactions on phenomena in the region of actual metallic densities.

III

Let us turn now to a consideration of electron interaction from the viewpoint of the collective description. This approach starts from a point of view diametrically opposed to the one-electron model, from a recognition and exploitation of the correlated electronic motion brought about by the long-range of the coulomb interactions. The nature of this correlated motion can be understood simply from a study of the classical analogue of the electrons in a metal, the plasma (⁸).

A plasma is an ionized gas consisting of a suitably high density of free positive and negative charges, which can be regarded for many purposes as a gas of point electrons moving through a uniform background of positive charge. Experimental and theoretical investigations of the electrons in a plasma show that they display a high degree of correlation (⁹). In consequence of this, the plasma is more nearly like a medium analogous to a liquid, in that it tends to remain in an approximately neutral field-free state, and to sustain oscillations about that equilibrium state. If a static disturbance is set up by, for instance, an imbalance of charge density in a particular region, then the highly mobile electrons will rush into the affected area and consequently shield out the disturbance by restoring the balance of charge density. There is a limit to the distance within which such a disturbance can be screened out, arising from the competition between the potential energy of interaction which favors screening and the random thermal motion of the individual electrons which opposes it. The characteristic length for which such screening occurs is the well-known Debye length (¹⁰) which is given by :

$$\lambda_{\mathrm{D}} = (k\mathrm{T}/4xne^2)^{1/2} \tag{6}$$

where T is the temperature of the electron gas, n its density, and e is the electron charge. For a typical gaseous discharge of electron density 10^{12}/cc and average electron kinetic energy ~ 3 ev. :

$$\lambda_{\mathrm{D}} \cong 10^{-3} \text{ cm.}$$

The oscillations, which resemble sound waves, may be viewed as arising in the following way. Consider our previous imbalance of charge density. The electrons rush into the affected area to screen out the disturbance. In so doing, they acquire a certain amount of kinetic energy, so they overshoot the area; the imbalance remains, the electrons are attracted back, overshoot, etc., and we have a longitudinal oscillation. The frequency of these oscillations is the plasma frequency.

$$\omega_p = (4xne^2/m)^{1/2} \tag{7}$$

where m is the electron mass. ω_p is $\sim 5 \times 10^{10}$ sec^{-1} for the gaseous discharge cited above. Langmuir, who first investigated this oscillatory phenomenon in gaseous discharges, called the discharge a plasma, because of its resemblance in this respect to a jelly.

The starting point in the collective description is an analysis of this correlated collective behavior brought about by the Coulomb interactions. In Paper II where the electron gas was treated classically, it was shown that the density fluctuations in the electron gas furnish a particularly appropriate tool for such an analysis. For a gas of point electrons, these are given by :

$$\rho_k = \int d\vec{x}\,\rho(\vec{x})\,e^{-\overrightarrow{ik}\cdot\vec{x}} = \int d\vec{x}\sum_i \delta(\vec{x} - \vec{x}_i)\,e^{-\overrightarrow{ik}\cdot\vec{x}} = \sum_i e^{-\overrightarrow{ik}\cdot\vec{x}_i}$$

In the long wave-length limit, the equations of motion of the ρ_k are approximately given by :

$$d^2\rho_k/dt^2 + \omega^2\rho_k = 0$$

so that in this limit the ρ_k describe approximately oscillatory behavior with the plasma frequency. Closer analysis shows that the ρ_k can be split into two components, one of which characterizes pure collective behavior, predominates at long-wave lengths (wave-lengths greater than the Debye length) and represents the collective oscillations. For wave-lengths shorter than the Debye length, collective oscillation cannot be maintained, and here the other component, which characterizes individual particle behavior, predominates. The individual particles component represents a collection of individual electrons surrounded by co-moving clouds of charge which act to screen out the field of any given electron within a Debye length. Thus one finds that the electron gas is capable of both collective and individual particle behavior : that for phenomena involving distances greater than the Debye length, the system behaves collectively and is best characterized by a set of harmonic oscillators representing the plasma oscillations; for smaller distances the electron gas is best described as a collection of individual particles which interact weakly by means of a screened Coulomb force. Although these conclusions were reached on the basis of a classical analysis, we shall see that they are for the most part appropriate in the quantum domain (11). Here too, screening and collective oscillation emerge as the hall-marks of the long-range correlated behavior; the only major modification occurs in the choice of a screening length. We shall find that for electrons in metals, $\omega_p \sim 10^{16}$, $\hbar\omega_p$ is a few electron volts, and the screening length is of the order of the interparticle spacing.

A quantum-mechanical generalization of the density fluctuation method is straightforward, and is given in Paper III. However, for detailed calculation of the system wave-functions and energy a Hamiltonian formalism is required, and the greater part of Paper III was devoted to the development of that formulation. We here sketch briefly an alternative way of carrying out this development.

Our basic Hamiltonian for the free electron gas model is (12) :

$$\mathrm{H} = \sum_i p_i^2/2m + 2\pi e^2 \sum_{ijk} \frac{e^{i\vec{k}\cdot(\vec{x}_i-\vec{x}_j)}}{k^2} - 2\pi n e^2 \sum_k \frac{1}{k^2}. \tag{8}$$

where the first term corresponds to the electron kinetic energy the second to their Coulomb interaction and the third to a subtraction of their self-energy. Once again, we first seek to analyze the correlated behavior of the electrons and then to investigate the character of the electron motion once the collective aspects are isolated. For this purpose we wish to introduce in addition to our individual particle co-ordinates a set of field variables, which we hope to relate to the collective oscillations of the system as a whole. We may anticipate from the analysis in Paper II that we can introduce only a limited number of these co-ordinates corresponding, say, to wave-vectors less than some k_c, since there is a minimum wave-length for which oscillation may be maintained. We may do this by adding a field energy term.

$$\mathrm{H}_{field} = \sum_{k<k_c} \frac{\overset{*}{p}_k \;\, p_k}{2} \tag{9}$$

to the Hamiltonian (8), provided we impose the following subsidiary condition on the combined system wave function :

$$p_k\psi = 0 \;\; (k < k_c) \tag{10}$$

This subsidiary condition serves two functions : it guarantees that the system energy is unaltered by the addition of (9) to our Hamiltonian (8) and it guarantees that we have not changed the total number of degrees of freedom in our system through the introduction of the field variables, p_k.

We may accomplish our goal of separating out the long-range correlated part of the electronic motion provided we can relate these field variables to that component of the density fluctuation which describes pure collective oscillation. This program may be carried out by a series of canonical transformations. As a first step, we are led to relate the p_k to the ρ_k, since for long-wave lengths the density fluctuations are almost entirely collective in character. The appropriate transformation is generated by :

$$\mathrm{S} = \sum_{k<k_c} \left(\frac{4\pi e^2}{k^2}\right)^{1/2} q_k \, \rho_{-k} \tag{11}$$

where q_k is the co-ordinate conjugate to the plasma field « momentum », p_k. After this transformation the subsidiary condition (10) becomes :

$$(\mathrm{P}k^{-i\,(4\pi e^2)^{1/2}} \rho - k)\, \Psi' = 0 \qquad (k<k_c) \tag{12}$$

providing the desired relationship. The Hamiltonian becomes :

$$\mathrm{H} = \sum_i \frac{p_i^2}{2m} + \sum_{k<k_c} \frac{\overset{\times}{pk}\; pk \; + \; \overset{2}{\omega p}\, \overset{\times}{q_k}\, q_k}{2} + \sum_{ik<k_c} \left(\frac{4\pi e^2}{m}\right)^{1/2} \vec{\varepsilon}_k \cdot \left(\vec{pi} - \frac{\vec{k}}{2}\right) q_k e^{i\vec{k}\cdot\vec{x}_i}$$

$$+ 2\pi e^2 \sum_{\substack{i \pm j \\ k > k_c}} \frac{e^{i\vec{k}\cdot(\vec{x}_i - \vec{x}_j)}}{k^2} - 2\pi n e^2 \sum_{k<k_c} \left(\frac{1}{k^2}\right) + \frac{2\pi e^2}{m} \sum_{\substack{i \\ (\vec{k},\vec{l}<k_c) \\ \vec{k} \pm -\vec{l}}} \varepsilon_k \cdot \varepsilon_l q_k q_l e^{i(\vec{k}+\vec{l})\cdot\vec{x}_i} \tag{13}$$

where $\vec{\varepsilon_k}$ denotes a unit vector in the k direction. In obtaining (13), use is made of the subsidiary condition (12) to simplify certain terms (13).

The first three terms in (13) describe the kinetic energy of the electrons, the energy of the plasma field, and an electron-plasma interaction. The effective coupling constant of this interaction is :

$$g^2 = \left\langle \left(\frac{\vec{k} \cdot \vec{p}_i}{m \, \omega p} \right)^2 \right\rangle_{\text{AV}} \cong \frac{\beta^2}{2r_s}$$

where we average over the particle momenta and the collective field wave vectors, and we have introduced :

$$\beta = k_c / k_o \, .$$

This interaction is comparatively weak, reflecting the fact that for wave-lengths greater than k_c^{-1} the ρ_k describe almost pure collective oscillation (14).

The fourth term in (13), which we shall denote by $H_{s.r.}$, represents the short-range part of the Coulomb interactions. To see this we carry out the indicated summation, and find :

$$H_{s.r.} = \frac{1}{2} \sum_{i \neq j} \frac{e^2}{\left|\vec{x}_i - \vec{x}_j\right|} \left\{ 1 - \frac{2}{\pi} \, \mathrm{S}i \, (k_c \left|\vec{x}_i - \vec{x}_j\right|) \right\} \qquad (14)$$

where :

$$\mathrm{S}i(y) = \int_o^y dx (\sin x/x) \, ,$$

from which it follows that $H_{s.r.}$ describes screened electron interaction with a range $\sim k_c^{-1}$. A plot of $H_{s.r.}$ is given in figure 1.

The last term in (13) is quite small. It describes equivalently a complicated electron-plasma interaction or a non-linear plasma-plasma interaction, depending on whether or not the subsidiary condition (12) is explicity applied in connection with it. Its smallness might be anticipated on the physical ground that it depends on a product of two field variables and on the electron co-ordinates; these latter are distributed over a wide variety of positions, so that the various components entering into the term tend to cancel. The neglect of this term (to which we have given the sobriquet « random-phase approximation ») (15) is justified in detail in Paper III.

With this approximation, we see that we are well on our way toward the completion of our program to isolate the correlated collective electron behavior. For in (13) we have redescribed the long-range part of the Coulomb interactions in terms of the organized oscillations they bring about. These oscillations are still not quite independent, since there remains a term describing electron-plasma interaction. However because the electron-plasma coupling is weak, we may readily transform to a new set of co-ordinates in which the collective oscillations are now isolated. The required transformation is a standard perturbation-theoretic canonical transformation which eliminates this interaction term in first order. This transformation is carried out in Paper III, and there we obtain the follow-

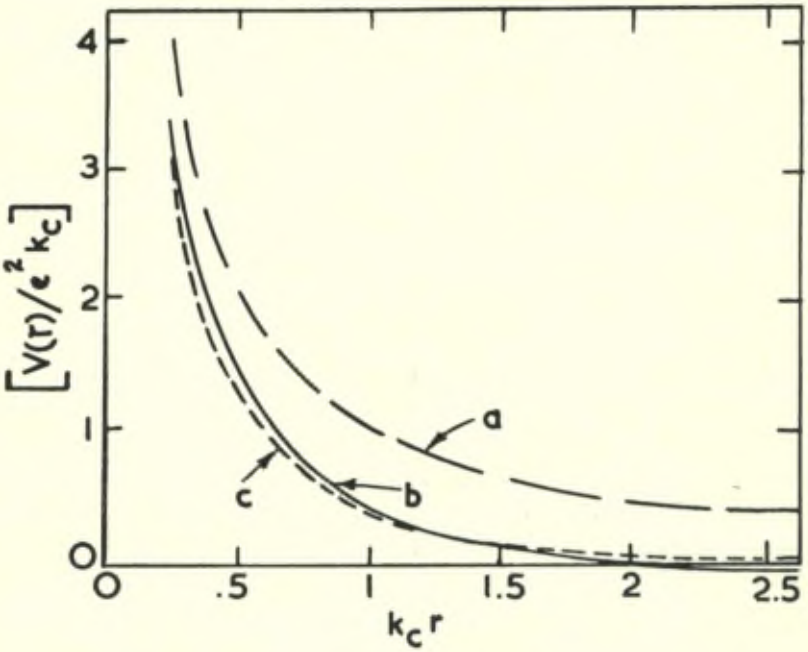

Fig. 1. — $H_{s.r.}(r)$ compared with $\frac{e^2}{r}$ and $\frac{e^2}{r}\exp(-k_c r)$

(*a*) — — $V(r) = \frac{e^2}{r}$

(*b*) ——— $V(r) = H_{s.r.}(r)$

(*c*) - - - - - - - - $V(r) = \frac{e^2}{r}\exp(-k_c r)$

ing Hamiltonian, which will serve as a starting point in our discussion of electron interaction in metals :

$$H = \sum_i \frac{p_i^2}{2m}\left(1 - \frac{\beta^3}{6}\right) + \sum_{k<k_c}\left\{\frac{p_k^* p_k + \omega^2 q_k^* q_k}{2} - \frac{2\pi n e^2}{k^2}\right\} + 2\pi e^2 \sum_{k>k_c} \frac{e^{i\vec{k}\cdot(\vec{x}_i - \vec{x}_j)}}{k^2} + H_{r.p.} \qquad (15)$$

where :

$$\omega \cong \omega_p\left(1 + \frac{3}{10}\frac{k^2 v_o^2}{\omega_p{}^2} + \frac{k^4}{8m^2\omega_p{}^2}\right) \qquad (16)$$

v_o being the velocity of an electron at the top of the Fermi distribution. The subsidiary condition (12) becomes one which does not involve the field variables, and is given by :

$$\sum_i \frac{\omega^2}{\omega^2 - (\vec{k}\cdot\vec{p}_i/m - k^2/2m)^2}\,\psi = 0 \qquad (k<k_c) \qquad (17)$$

The effects of the electron-plasma interaction are slight as might be expected. There is an increase in the electronic effective mass to $m/(1 - \beta^3/6)$ (16). This increase is usually quite small, since β is customarily rather less than unity. From (16) we see that the frequency of the collective oscillations is increased and becomes slightly k dependent. Finally, it leads to a quite weak long-range electron-electron interaction which we have denoted by $H_{r.p.}$. As pointed out in Paper III, $H_{r.p.}$ represents that part of a screened interaction which is present beyond the screening length, and may be neglected in comparison to $H_{s.r.}$.

At this point, on the basis of the Hamiltonian (15), we can resolve the first of the basic puzzles we mentioned earlier, that dealing with the role of long-range electron correlations in metals. For we see that these long-range correlations do in fact exist, but that their effect can be isolated and re-expressed rather simply in terms of the collective oscillations of frequency ω they bring about. This is the great advantage of the collective description, that through the introduction of the concept of collective oscillation it enables us to account in comparatively simple fashion for the quite complicated long-range correlations brought about by the Coulomb interactions. These oscillations are now quite independent, since they no longer interact with the electrons or appear in the subsidiary condition. Furthermore the frequency of the collective oscillations is so high that the energy in a quantum of plasma oscillation is greater than that of an electron at the top of the Fermi distribution for all metals. As a result collective oscillations will not be excited at ordinary temperatures, and hence will not play a dynamic role in a description of a metal under ordinary conditions. (We discuss the excitation of plasma oscillations in metals by external fast charged particles in Sec. VII.)

The remainder of (15) describes a collection of individual electrons interacting via a short-range interaction $H_{s.r.}$. The existence of this screened interaction is also a consequence of the long-range correlations; these are in fact such that the field of any given electron is screened out within a distance k_c^{-1}, so that the effective electron-electron interaction is only over this range. For the k_c observed in metals ($k_c \lesssim k_o$), the range of this interaction is of the order of the interparticle distance, so that one would not expect it to affect the otherwise free electronic motion greatly. Thus as far as our study of the Hamiltonian is concerned, we see that the long range correlations give rise to collective oscillations we don't usually observe, and through their screening action lead us directly to the concept of the electron gas as a collection of rather weakly interacting independent particles ([11]).

There remain the subsidiary conditions (16) which act only on the electronic wave-functions. These subsidiary conditions are a necessary evil. For we have now gone to a representation in which we have n' independent collective co-ordinates, where :

$$n' = k_c^3/6\pi^2 = (\beta^3/6)\,n \tag{18}$$

so that we must of necessity impose a comparable number of subsidiary conditions on our total system wave-function. The physical content of the subsidiary conditions is that they act to reduce greatly the long-wave length density fluctuations of the electrons, corresponding to the fact that the bulk of these have been redescribed in terms of the collective oscillations. Actually the subsidiary conditions have very little effect on the system behavior. For, as is shown in III, they will not affect the ground state wave function, since this turns out to satisfy them automatically. The excited state wave functions will be affected, but because the number of subsidiary condition turns out to be quite small compared to the total number of degrees of freedom in the system, i.e.

$$(n'/3n) \leqslant 1 \,, \tag{19}$$

we do not expect their effect to be very large.

Thus on the basis of the Hamiltonian (15) we should expect, on physical grounds, that an independent electron model would provide quite a reasonable approximation for the motion of electrons in metals. There remains the problem of the self-consistency of the Hartree approximation. We may anticipate that this problem is now also resolved, because in (15) the residual electron-electron interaction is of comparatively short range, whereas the difficulties which arose in connection with our attempts to go beyond the simple Hartree picture were associated with the long-range character of the interactions. We demonstrate the truth of this assumption in Sec. V.

IV

In this section we wish to sketch the calculation of the ground state energy of the free electron gas according to the collective description, and discuss the correlation energy of the alkali metals. In determining the ground state energy, we also determine the screening parameter k_c^{-1} (or alternately the number of collective degrees of freedom n'). This hitherto arbitrary parameter is chosen in such a way as to minimize the resultant system energy.

Our procedure in calculating the ground state energy is to treat the short-range electron interaction term $H_{s.r.}$ in (15) as a small perturbation. Thus we neglect its effect on the system wave-function in first approximation, and take its effect on the system energy into account by using conventional second-order perturbation theory. In this case our ground state wave-function is :

$$\psi_o - \psi_o^{osc} \varphi_o \tag{20}$$

where ψ_o^{osc} represents a products of simple harmonic oscillator wave functions, one for each collective oscillation wave-vector up to k_c, and φ_o is the usual Slater determinant made up of free electron wave functions appropiate to the ground state of our system (17). The calculation of the ground state energy is quite straightforward using (20), and we obtain for the ground state energy per electron :

$$E = (2.21/r_s^2)\,(1-\beta^3/6) + \}(n'/n)\,[\langle\omega\rangle_{AV}/2] - 1.222\ \beta/r_s\{$$
$$- 0.916/r_s\,\}1 - (4/3)\,\beta + \beta^2/2 - \beta^4/48\{\ ry\ . \qquad (21)$$

The first term is the Fermi energy modified by the increased electronic mass. The second term represents the difference between the zero point energy of the collective oscillations and the self-energy of the charge distribution the oscillations here redescribe.

$\langle\omega\rangle_{AV}$ is the average frequency of collective oscillation, obtained by averaging the dispersion relation (16) over all $k < k_c$. For the β we encounter, the second term is always negative and represents a gain in energy brought about by the reduction of the long wave length density fluctuations due to the long range correlations in electronic motion. The term is the third exchange energy arising from $H_{s.r.}$. It is smaller in magnitude than the exchange energy associated with the Coulomb interactions because of the shorter range of $H_{s.r.}$.

We may then define a long-range correlation energy for the electron gas as the difference between (21) and (2). We use the adjective « long-range » because in determining (21) we have only taken into account the long-range coulomb correlations as described by the collective oscillations. We then determine the screening length k_c^{-1} by minimizing this long-range correlation energy with respect to β ([18]). These calculations are also straightforward, and the results are given in figure 2, where we show the variation of the long-range correlation energy with β for some typical values of r_s, and figure 3, where we plot β_{min}, that value of β which minimizes $E_{corr}^{l.r.}$, as a function of r_s.

It is worth noting that although the magnitude of the long-range correlation energy is small, there has taken place a considerable redistribution in the energy gain to be assigned to correlations between electrons of parallel spin versus those of anti-parallel spin. There is a reduction in the energy gain to be attributed to correlations between electrons of parallel spin, and a corresponding, but somewhat larger, increase in the energy gain assigned to correlations between electrons of anti-parallel spin. This redistribution has its origin in the reduction of the exchange energy contribution. It is what one should expect, for if the electrons tend to stay apart (because of long-range correlations) in the absence of exchange

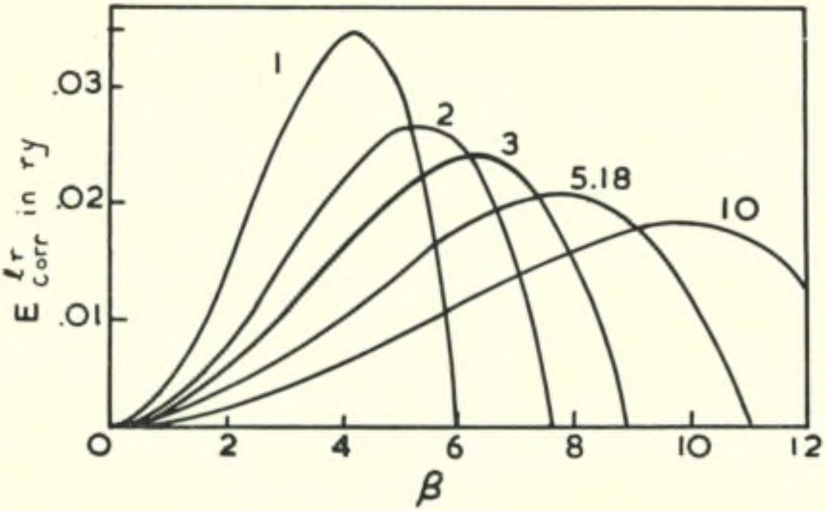
$E^{\ell r}_{corr}$ in ry
.03
.02
.01
1
2
3
5.18
10
0
2
4
6
8
10
12
β

Fig. 2

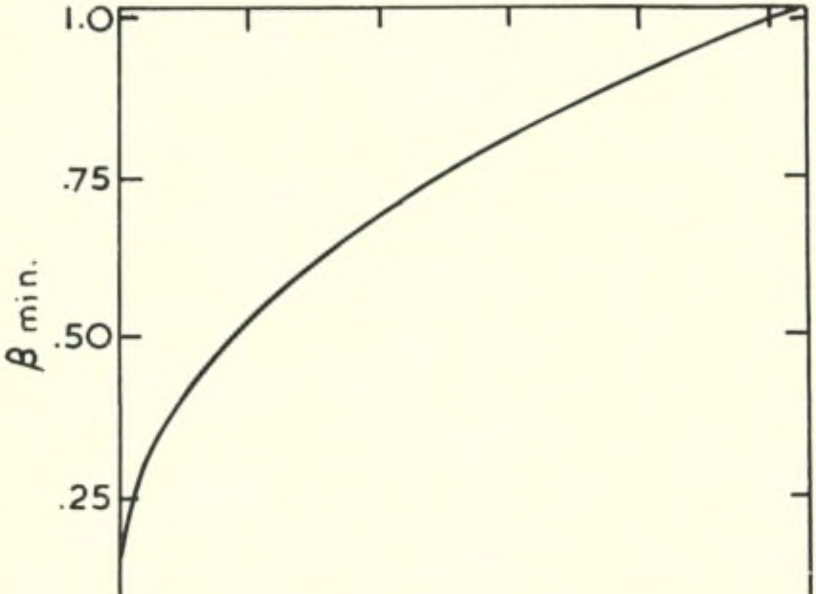
β min.
1.0
.75
.50
.25
0
0
2
4
6
8
10
r_s

Fig. 3

effects, then when these are taken into account they should not play as important a role as in a gas of uncorrelated electrons. Thus there is rather less difference in the behavior of electrons of parallel and anti-parallel spin on our model, corresponding to the fact that the long-range coulomb correlations are spin independent.

We see that for the electronic densities encoutered in metals (r_s roughly between 2 and 5.5), β_{min} runs between about 0.5 and 0.8. Hence the relative number of collective degrees of freedom, $(n'/3n)$, we introduce to describe the long range correlations runs between $\sim 1/48$ for $r_s = 2$ and $\sim 1/12$ for $r_s = 5.5$. Thus at most only ~ 8.5 % of the individual electron degrees of freedom are replaced by collective degrees of freedom. The effective electron-plasma coupling constant ε^2 may likewise be shown small, being $\sim 1/14$ for $r_s = 2$ and $\sim 1/16$ for $r_s = 5.5$.

We may now improve our calculation of the ground state energy by taking into account $H_{r.s.}$. We do this within the framework of the conventional second-order perturbation theory (19). We find that the divergency difficulty encoutered earlier with the Coulomb interactions has disappeared, and that $H_{s.r.}$ may be regarded to a good degree of approximation as giving rise to comparatively small changes in the system energy and wave-functions.

The dominant term in the correlation energy arising from $H_{s.r.}$ turns out to be associated with electrons of anti-parallel spin. According to perturbation theory, the interaction energy due $H_{s.r.}$ for two electrons of anti-parallel spin with wave-vectors k and k' may be written as :

$$\mathrm{E}\,(\vec{k},\vec{k}') = -\sum_{p>k_c}\left(\frac{4\pi e^2}{p^2}\right)^2 \frac{m}{\vec{p}\cdot(\vec{k}-\vec{k}'+\vec{p})}$$

where the exclusion principle further requires that :

$$\left|\vec{k}+\vec{p}\right| > k_o \quad ; \quad \left|\vec{k}'-\vec{p}\right| > k_o$$

If we now sum this over all electrons $\vec{k}'$ of anti-parallel spin, we obtain the effect of short-range correlations on E(k). We find :

$$\mathrm{E}(k)_{corr.} = -\frac{1}{2\pi^4}\,\frac{\int d\vec{p}\int d\vec{k}'}{p^4\,\vec{p}\cdot(\vec{k}-\vec{k}'+\vec{p})} \quad ry. \qquad (22)$$

where we have changed the sums to integrals, the momenta are measured in units of k_o, and the allowed regions of integration are specified by :

$$\left|\vec{k}+\vec{p}\right| > 1 \quad ; \quad \left|\vec{k}'-\vec{p}\right| > 1 \quad ; \quad k' < 1 \quad ; \quad p > \beta \qquad (23)$$

The expression for the total short-range correlation energy per electron for electrons of anti-parallel spin is then obtained by averaging (22) over all electrons in the Fermi distribution and dividing by two, so that no interactions are counted twice. This is :

$$\mathrm{E}^{s.r.}_{corr.} = -\frac{3}{16\pi^5} \frac{\int d\vec{p} \int d\vec{k} \int d\vec{k}'}{p^4 \vec{p}\cdot(\vec{k}-\vec{k}'+\vec{p})} \qquad (24)$$

where the regions of integration are specified by (23) and ($k < 1$).

The corresponding correction to the exchange energy between electrons of parallel spin is per electron :

$$\mathrm{E}^{exch.}_{corr.} = -\frac{3}{16\pi^5} \frac{\int d\vec{p} \int d\vec{k} \int d\vec{k}'}{\vec{p}\cdot(\vec{k}-\vec{k}'+\vec{p})} \left\{\frac{1}{p^4} - \frac{f(\vec{k}-\vec{k}'+\vec{p})}{p^2(\vec{k}-\vec{k}'+\vec{p})^2}\right\} \qquad (25)$$

where :

$$f(\gamma) = 0 \qquad \gamma < k_c$$
$$f(\gamma) = 1 \qquad \gamma > k_c$$

and we have the same restrictions on our regions of integration as for electrons of anti-parallel spin. We should in general expect that E^{exch}_{corr} is considerably smaller than $\mathrm{E}^{s.r.}_{corr}$, since it represents a perturbation correction to the already reduced exchange energy. An examination of the integral bears this out, since the two terms in the integrand tend to cancel one another over much of the region of integration. We have not yet succeeded in carrying out the indicated integration for E^{exch}_{corr} and so we make here what is perhaps the principal approximation in our calculation of the correlation energy, which is to neglect E^{exch}_{corr} entirely.

We have evaluated the integrals in (24) and obtain the following expression for $\mathrm{E}^{s.r.}_{corr}$, (21).

$$\mathrm{E}^{s.r.}_{corr.} = -\left\{+.0254 - .0626\,ln\beta + .00637\beta^2\right\} ry. \qquad (26)$$

We may then combine this result with our long-range correlation energy to obtain the total correlation energy :

$$E_{corr.} = E_{corr.}^{s.r.} + E_{corr.}^{l.r.}$$

In figure 4, we plot E_{corr} as a function or r_s, and, for comparison, the Wigner expression Eqtn (5) as well. Our result and the Wigner

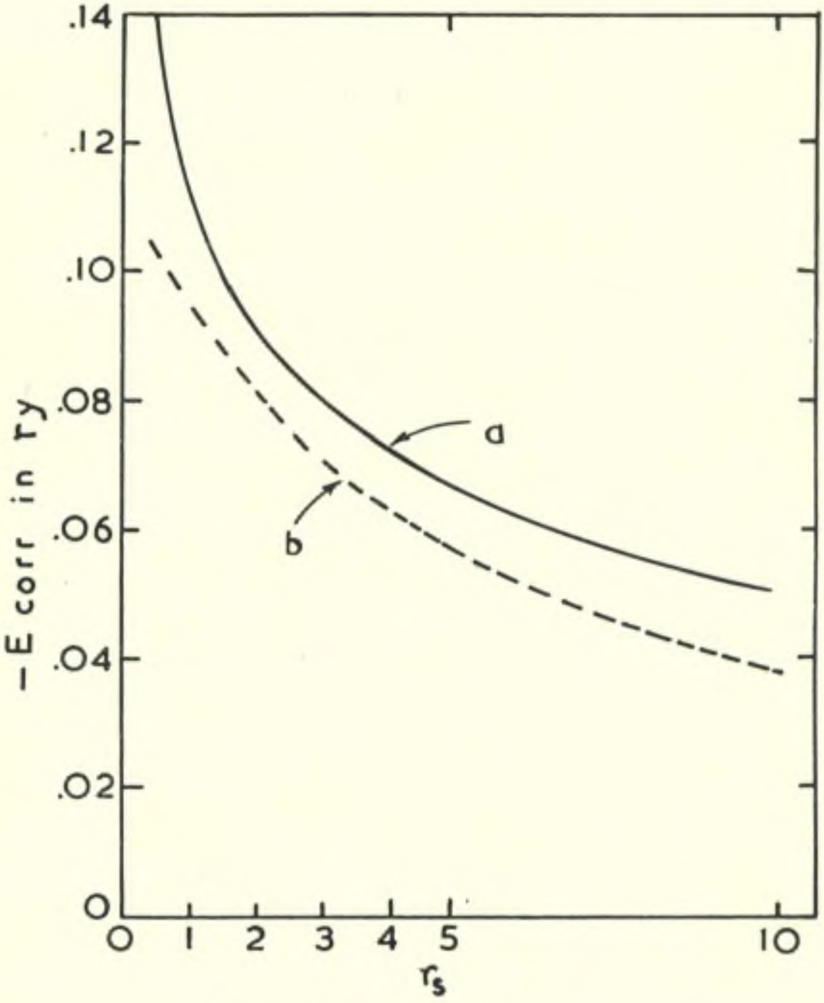

Fig. 4. — Correlation energy as a function of density.
(*a*) ——— $E_{corr.}$ In collective description.
(*b*) - - - - - - $E_{corr.}$ Due to Wigner.

expression may be seen to agree to within about 10-20 % over the region of actual metallic densities (22).

There are two important sources of error in our results for the correlation energy. These arise in our calculation of $E^{s.r.}_{corr}$. The first is connected with the validity of perturbation theory in our treatment of $H_{s.r.}$. We may estimate this by calculating the probability of finding the system in an excited state in consequence of the interaction $H_{s.r.}$. This probability is :

$$\delta = \sum_n \frac{|(H_{s.r.})_{no}|^2}{(E_n - E_o)^2}$$

where the sum is over all possible intermediate states. We have estimated δ and obtain :

$$\delta = \frac{r_s^2}{29}\left(\frac{.39}{\beta} - .35 + .075\beta\right)$$

δ varies from $\sim .065$ for $r_s = 2$ to $\sim .20$ for $r_s = 5.5$. Thus for high densities, where the Fermi energy is considerable, δ is small and use of perturbation theory in treating $H_{r.s.}$ appears quite valid. For the low density limit (represented by Cs/δ is rather larger and our use of perturbation theory is on the verge of becoming questionable.

The second source of error relates to our neglect of the exchange corrections (25). We may estimate this by considering the correlation energy in the high density limit of our electron gas (in the region of $r_s \precsim 1$). In this region we may expect that our neglect of (25) might be on most questionable grounds. For here β is quite small, the « unperturbed » exchange energy [the last term in (21)] is at its maximum, and hence corrections to it might be expected to be most important. This is also the region in which Wigner's expression for the correlation energy (5) may be expected to be quite accurate. Thus it is gratifying to note that our expression agrees with that obtained by Wigner to within about 20 % for $r_s = 1$. Taking both the above-mentioned effects into account, we are inclined to estimate the accuracy of our correlation energy calculation as about 15 % for the region of actual metallic densities.

It is also interesting to consider the correlation energy in the low density of the electron gas. Here we should expect that our description of the long-range interactions in terms of the plasma oscillations is an excellent one, since the plasma-electron coupling constant, $g^2 = \beta^2/2r_s$, approaches zero as we go to very large r_s. In this limit the frequency of the plasma oscillations is ω_p, and it is energetically favorable to introduce the maximum number of longitudinal collective degrees of freedom, $n' = n$. Furthermore for such large r_s the short-range correlation energy (although we cannot calculate it by using perturbation theory) becomes rather smaller than the long-range correlation energy. This long-range correlation energy in the very low density limit is :

$$\frac{-.458\,\beta^2 + .019\,\beta^4}{r_s} = \frac{-.68}{r_s}$$

Thus our result for the correlation energy, neglecting short-range correlations, agrees quite well with the exact low density limit of $-.88/r_s$ (7), and gives us further confidence in the validity of our approach.

Thus far we have neglected the periodic field of the lattice in treating the electron interactions. Actually we can readily take it into account in the effective mass approximation (23) in which the sole effect of the periodic field is to change the electron mass from m to some m^*. This approximation should be quite good as far as the long-wave length interactions are concerned; on the other hand one would not expect it to work at all for short-wave-length interactions, for which band-band transitions come into play. For this reason, we have adopted the following procedure in calculating the correlation energy in the effective mass approximation. We replace m by m^* throughout in our treatment of the long-wave length interactions, and hence in our determination of $E^{l.r.}_{corr}$ and β_{min}. However we use the free electron mass in calculating $E^{s.r.}_{corr}$ because this seems the only consistent approach within the framework of the free electron gas approximation (24). It is clear that to obtain the effect of lattice periodicities on the short-range correlation energy, one should calculate $E^{s.r.}_{corr}$ with Bloch functions rather than plane waves.

With the above-mentioned procedure, we see that the correlation energy is rather intensitive to the values of the effective mass adopted. For $(m^*/m) > 1$, the long-range correlation energy is increased (due to the reduction in the zero-point energy of the collective oscilla-

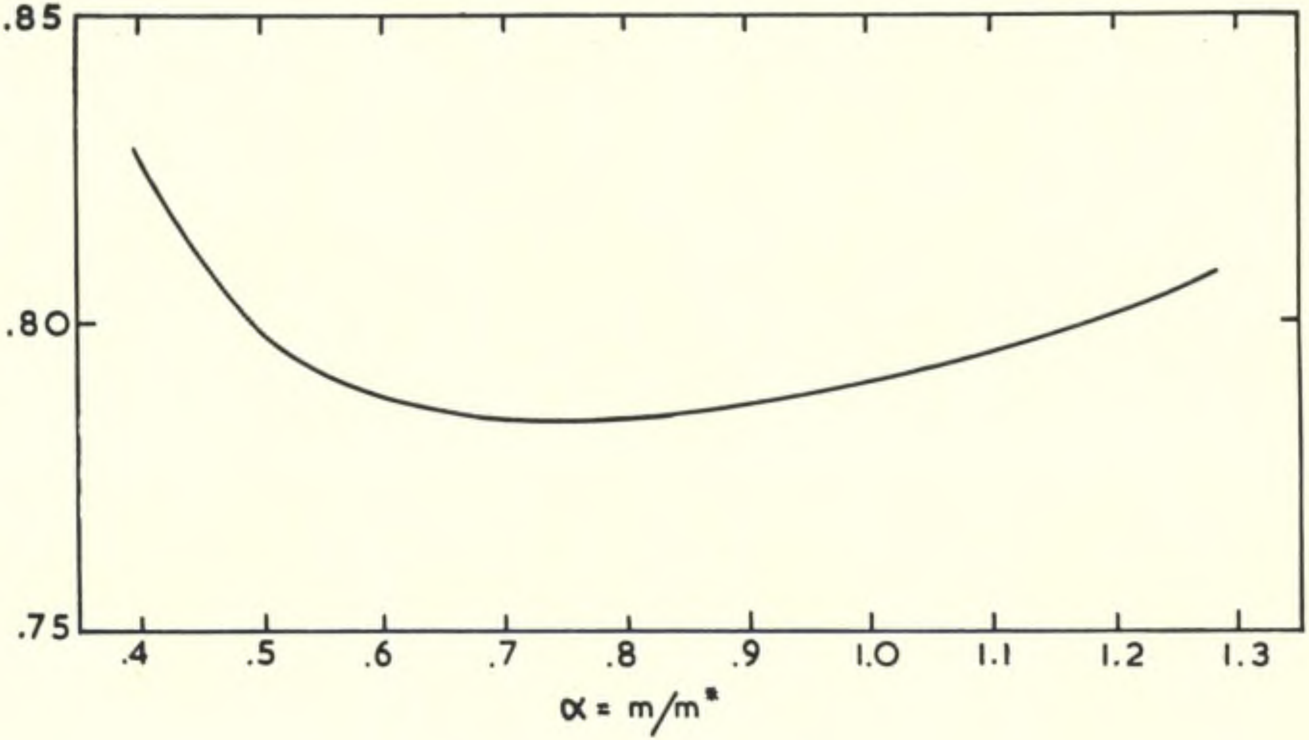

Fig. 5. — Correlation energy as a function of m^* for lithium.

tions), as is β. But this implies a decrease in the screening length ($[\beta k_0]^{-1}$) which in turn produces a decrease in the short-range correlation energy and so compensates the increase in the long-range correlation energy. For $(m^*/m) < 1$, the roles are simply reversed. The resultant variation in the correlation energy with effective mass is show in the case of lithium in figure 5. In table 1 we list the correlation energy as calculated for the alkali metals, using effective mass values due to Harvey Brooks (25). For comparison we also list the Wigner values obtained using (5).

Our values when combined with the binding energy calculations of Brooks (26) yield results for the cohesive energy which agree with experiment within the estimated accuracy of our correlation energy calculation.

TABLE 1

Correlation energy for the alkali metals

	Li	Na	K	Rb	Cs
r_s	3.22	3.96	4.87	5.18	5.57
m^*/m	1.45	.98	.93	.89	.83
β_{min}	.73	.68	.73	.73	.73
$E^{l.r.}_{corr}$ (ry)	— 0.030	— 0.021	— 0.019	— 0.018	— 0.017
$E^{s.r.}_{corr}$ (ry)	— 0.049	— 0.052	— 0.049	— 0.049	— 0.049
E_{corr} (ry)	— 0.079	— 0.073	— 0.068	— 0.067	— 0.066
E_{Wigner} (ry)	— 0.069	— 0.064	— 0.058	— 0.056	— 0.054

V

We now consider the influence of exchange and correlation on the one-electron energy curves $E(k)$, and use these results to discuss the electronic specific heat and the x-ray band width in metals. The influence of the long-range correlations on the $E(k)$ curves has been discussed in Paper IV. Their major effect is associated with the « reduction » of the effective electron interaction to its screened Coulomb character, which, as anticipated, eliminates the difficulties associated with the influence of exchange on the $E(k)$ curves (27). There is also a slight effect due to the increased effective mass of the electrons (28). According to Paper IV, we have for electrons of effective mass m^* :

$0 < k < 1 - \beta$

$$E(k) = \frac{3{,}68}{r_s^2} k^2 \left(1 - \frac{\beta^3}{6}\right)\left(\frac{m}{m^*}\right) - \frac{.611}{r_s}\left\{2 - 4\beta + \frac{1 - k^2}{k} ln \frac{1 + k}{1 - k}\right\} ry. \qquad (27)$$

$1 - \beta < k < 1$

$$E(k) = \frac{3{,}68}{r_s^2} k^2 \left(1 - \frac{\beta^3}{6}\right)\left(\frac{m}{m^*}\right) - \frac{.611}{r_s}\left\{1 - 2\beta + \frac{\beta^2 + 3k^2 - 1}{2k} + \frac{1 - k^2}{k} ln \frac{1 + k}{\beta}\right\} ry. \quad (28)$$

where k is measured in units of k_o. We see from (28) that there is no longer any anomalous behavior of $E(k)$ or its derivatives in the region of $k = 1$, since the logarithm now depends on β rather than $1 - k$.

The effect of short range correlations on $E(k)$ is given by Eqtn. (22). We have not yet been able to obtain an explicit expression for the dependence of E on k because certain of the integrations in (22) must be performed numerically (29). Calculations are now under way to determine $E(k)$ and its derivatives at a few selected points, but have not been completed at the time of writing this report. We anticipate that the effect of short-range correlations on the one-electron energies is not a drastic one, so that we proceed to discuss their properties as predicted by (27) and (28).

The influence of exchange and the long-range correlations on the electronic specific heat may be calculated using (4) and (28). One obtains for the ratio of this modified specific heat, C_e, to that calculated on the simple Hartree model, C_o,

$$\frac{C_e}{C_o} = \left[1 - \frac{\beta^3}{6} + \frac{m^*}{m}\frac{r_s}{12{,}07}\left\{2 ln \frac{2}{\beta} + \frac{\beta^2}{2} - 2\right\}\right]^{-1} \qquad (29)$$

(Of course a similar ratio applies for the state density at the top of the Fermi distribution.) In Table 2, we give (C_e/C_o) for the alkali metals.

TABLE 2

Specific heat of the alkali metals :

(C_e/C_o) is the ratio of the calculated specific heat to the free electron value.

	Li	Na	K	Rb	Cs
(m^*/m)	1.45	.98	.93	.89	.83
β_{min}	.73	.68	.73	.73	.73
C_e/C_o	.96	.93	.96	.96	.96

We see that the combined effect of long-range correlations and exchange is to produce only a slight decrease in the electronic specific heat from that obtained on a free electron model.

On the basis of the E(k) curves for a metal one may compute the width of the conduction electron band, which is measured experimentally in soft-X-ray emission spectra. As has been pointed out by Jones (^{30}), the existence of an effective screened coulomb potential goes a long way toward removing discrepancies between the calculated (according to the Hartree-Fock model) and measured values of the band width. On the simple Hartree model, the width of this band is just the maximum energy of the Fermi distribution, and the experimental results are generally in accord with this prediction. On the Hartree-Fock model according to Koopmans' theorem the band-width is E(1) — E(O), which using Eqtn. (3) leads to an additional band-width :

$$\Delta_{\mathrm{H.F.}} = \frac{1.222}{r_s} \quad ry.$$

This term is appreciable and quite destroys the qualitative agreement between theory and experiment. If we now assume that Koopmans' theorem applies in the collective description (^{31}) we may calculate the band width from (27) and (28), obtaining an additional band width which is :

$$\Delta^{l.r.}_{corr.} = \frac{-.613}{r_s^2}\,\frac{\beta^3\, m}{m^*}\;\frac{-.611}{r_s}\;(2\beta + \beta^2/2).$$

This reduction in the band-width arises primarily from the reduction in the exchange energy. There is also a small correction coming from the increased effective mass of the electrons. The resultant total width is very much closer to the Fermi width, as may be seen in Table 3, where we tabulate the various contributions to the width for certain alkali metals.

TABLE 3

Band width of certain alkali metals

Column (*b*) is the band-width on the simple Hartree model; (*c*) and (*d*) represent the effect of exchange and long-range correlations respectively. (*e*) is the calculated total band width; (*f*) the experimental « reduced » band-width. Units: Col.(*b*)-(*f*) e.v.

	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)	(*f*)
	m^*/m	$\Delta_{\mathrm{F.}}$	$\Delta_{\mathrm{H.F.}}$	$\Delta^{l.r.}_{corr}$	Δ_{tot}	Δ_{expt}
Li	1.45	3.33	5.16	— 4.68	3.81	3.7
Na	.98	3.26	4.20	— 3.51	3.95	2.5
K	.93	2.27	3.41	— 3.10	2.58	1.9

(*) These values are taken from A.H. Wilson, The Theory of Metals, Cambridge University Press (1953).

We see that the theoretical band-widths are still rather larger than the measured values for Na and K, while that for Li agrees rather well. One possible reason for the remaining discrepancies may be the effect of the short-range correlations on the band-width. However, a rough preliminary estimate of this effect indicates that it is rather small and in the wrong direction (32). Another source of these discrepancies may be an effect discussed recently by Raimes (33). This concerns the method of derivation of an effective band-width from the experimental soft X-ray curves The usual procedure, leading to a « reduced » band-width, is to assume that the E(k) curve is parabolic in the region of $k = 0$, and so extrapolate that basis : i.e. using a density of state curve varying as $\sqrt{E}$. However due to correlation and exchange the E(k) curve is not parabolic in this region; if one takes seriously the effects of exchange, one should want to extrapolate this curve on this basis of (27), and thus obtain rather different « reduced » values for the band-width. This effect will in general increase the « reduced » experimental band-width, a change which is in the direction of improving the agreement between theory and experiment. For example, for sodium Raimes estimates this increased band-widths as $\sim .6$ e.v.

The effect of exchange and correlation on the work function of metals may be estimated by arguments quite similar to those used above, but we shall not enter on that here. One may also estimate the diamagnetism of the conduction electrons from their E(k) curves, and this is done in the following section.

VI

We have calculated the effect of electron-electron interactions on the magnetic susceptibility of the conduction electrons. There are two contributions to this susceptibility; a paramagnetic part associated with the polarization of the electron spins, and a diamagnetic part due to the orbital motion of the electrons. Let us consider the paramagnetic susceptibility, χ_p, first.

We have computed χ_p at 0°K using the method of Sampson and Seitz (34), which requires a knowledge of the way in which the energy of the electron system changes as the population of electrons of up and down spin varies. Our calculation for χ_p differs from that of SS in that we use the expressions for the correlation energy developed in IV, rather than the earlier Wigner expression. We further assume that the effective screening length, k_c^{-1}, is not altered by a shift in the spin populations. Physically, this assumption appears quite reasonable, since the screening length is determined primarily by the long-range correlations, which are in turn relatively insensitive to the electron spin aligment. A more detailed investigation verifies the validity of this approximation.

In general we might anticipate that exchange acts to increase χ_p, since the exchange energy is increased as we increase the number of electrons of parallel spin. By the same token, the short-range correlation energy will act to decrease χ_p, since any lining up of spins will decrease the contribution to the energy made by electrons of anti-parallel spin. The long-range correlation energy contribution opposes exchange and decreases χ_p because, as mentioned earlier, it acts to reduce the correlation energy to be associated with electrons of parallel spin.

Our results may be put in the form :

$$\chi_p = -(2n\mu_e^2/a) \tag{30}$$

where μ_e is a Bohr magneton, n is the density of conduction electrons, and α is given by :

$$\alpha = (20/9)\ \mathrm{E_F} + (8/9)\ \mathrm{E}_{exch} + \alpha_{l.r.} + \alpha_{s.r.} \tag{31}$$

the latter terms representing the effect of long-range and short-range correlations on χ_p. Table 4 gives the various contributions to α for the alkali metals, together with values of χ_p obtained using (30) and, for comparison, those obtained in the free electron approximation, and calculated by SS. We see that Coulomb correlations do not quite compensate for exchange, so that the resultant susceptibility is always rather higher than the free electron value. We estimate the accuracy of our theoretical values for χ_p as about 20 %.

TABLE 4

χ_p for the alkali metals

Units : Rows (*c*)-(*g*) Ryd, Rows (*h*) (*j*) and (*j*) c.g.s. units × 10—⁶.

Metal	Li	Na	K	Rb	Cs
(*a*) $(m^*/m)^*$	1.45	.98	.93	.89	.83
(*b*) β	.73	.68	.73	.73	.73
(*c*) 20/9 $\mathrm{E_F}$	.326	.319	.221	.207	.191
(*d*) $(8/9)\mathrm{E}_{exch}$	—.253	—,206	—.167	—.157	—.146
(*e*) $\alpha_{l.r.}$	.023	.015	.014	.014	.013
(*f*) $\alpha_{s.r.}$	.108	.111	.109	.109	.108
(*g*) α	.204	.239	.177	.173	.166
(*h*) χ_p	1.87	.85	.61	.53	.44
(*i*) χ_p^{free}	1.17	.64	.48	.44	.38
(*j*) $\chi_p^{(SS)}$	2.92	1.21			

(*) These values of the effective mass are due to Harvey Brooks (private communication).

A direct measurement of χ_p for lithium has been carried out recently by Schumacher, Carver, and Slichter (35). This was accomplished by measuring the total area under the absorption curve for conduction electron spin resonance, which is simply related to χ_p. They obtained a high degree of accuracy by comparing the absorption of the electron resonance with that of the nuclear resonance in the same sample at the same frequency, in this fashion eliminating most of the difficulties associated with an absolute intensity measurement. Their result is $\chi_p = 2.0 \pm 0.3 \times 10^{-6}$ cgs volume units. Our theoretical result of $\chi_p = 1.87 \times 10^{-6}$ cgs volume units is in good agreement with this experimental result, an agreement which is substantially better than that obtained with the free electron approximation or that of SS. Experiments are now under way to measure χ_p for sodium.

The technique of nuclear magnetic resonance provides another, somewhat less direct, way of measuring χ_p. In metals, the nuclear paramagnetic resonance frequency is greater than that observed when the nucleus is in a non-metallic compound. The frequency shift, which is of the order of a few tenths of one percent for the alkali metals, is due to the polarization of the conduction electron spins, and the consequent magnetic field, ΔH, produced by these electrons at the nucleus. ΔH is to a good degree of approximation just $8\pi/3$ times the mean density of spin moment at the nucleus. Following Tones, Herring, and Knight (36), we may express the fractional shift in nuclear resonance frequency as :

$$(\Delta H/H) = \frac{hc\Delta\nu I\Omega_o}{\mu_I\mu_e\,(2I+1)}\left(\frac{P_F}{P_A}\right)\chi_p \tag{32}$$

by dividing our expression for ΔH by the Fermi expression for the hyperfine splitting Δν for an *s* electron in the free atom. Here μ_I is the nuclear moment, and I the nuclear spin and Ω_o the atomic volume. (P_F/P_A) is the ratio of the mean probability density at the nucleus of an electron on the Fermi surface of metallic lithium to that of an S-electron in the lithium atom. Thus to the extent that one can calculate or measure P_F/P_A, one can determine χ_p from a knowledge of this frequency shift (36 a). In Table 5, we give the values of χ_p obtained in this fashion for those metals for which an estimate of P_F/P_A is available, as compared to the theoretical values listed in Table 4.

TABLE 5

χ_p as derived from the nuclear resonance shift

Nucleus	Observed(a) Shift ΔH/H (per cent)	P_F/P_A	$\chi_p = 10^6$(cgs) (from ΔH/H)	$\chi_p = 10^6$(cgs) (theory)
Li^7	.0261	.50(b)	1.82	1.87
Na^{23}	.112	.81(c)	.83	.85
Rb^{85}	.650	1.0 (d)	.53	.53

(*a*) H.S. Gutowsky and B.R. McGarvey, *J. Chem. Phys.*, **20**, 1472 (1952).
(*b*) Walter Kohn (Private communication).
(*c*) Townes, Herring, and Knight, *Phys. Rev.*, **77**, 852 (1950).
(*d*) Estimated from measurement of T_1 by D. F. Holcomb and R.E. Norberg (Private communication).

In view of our estimated 20 % accuracy in the calculated χ_p, the agreement between theory and experiment is surprisingly close.

The possible ferromagnetism of the free electron gas may also be discussed using the SS method (37). If one only takes exchange into account, the free electron gas would be ferromagnetic at $r_s \simeq 6$ (the point at which 8/9 E_{exch} cancels 20/9 E_F, and χ_p becomes formally infinite). However, as Wigner (5) has pointed out, Coulomb correlations act to prevent the free electron gas from displaying ferromagnetic behavior, essentially for the reasons discussed earlier in connection with their effect on χ_p. This may easily be established be extending the foregoing calculations into the low density region; in fact, we find that as the electron density decreases, the electron gas becomes less, rather than more paramagnetic.

The effect of exchange and correlation on the diamagnetic susceptibility, χ_d, of the conduction electrons, may be readily calculated in the case that the major contribution to this susceptibility (at $T = 0^\circ$ K) is given by (38) :

$$\chi_d = -\frac{e^2 k_o}{3h^2 c^2}\left\{\frac{2}{3}\,\frac{d^2 E(k)}{dk^2} + \frac{1}{3k}\cdot\frac{dE(k)}{dk}\right\}_{k=k_o} \tag{33}$$

where E(k) is the energy of an electron of wave-vector k. For the case of free electrons of effective mass m^*, (33) yields the familiar Landau-Peierls formula :

$$\chi_F = -\frac{e^2 k_o}{12\pi^2 c^2 m^*}\,. \tag{34}$$

In the Hartree-Fock theory, (33) diverges because of the anomalous behavior of the E(k) curves. However when we take into account long-range Coulomb correlations this divergence is removed and we may readily calculate the effect of exchange on χ_d using (28). Our results for lithium and sodium are given in Table 6. We see that the combined effect of exchange and long-range Coulomb correlations is to increase χ_d. We have not yet completed our calculation of the effect of short-range correlations on χ_d.

TABLE 6

χ_d for lithium and sodium

Columns (*b*) and (*c*) represent contributions from the Fermi energy and exchange combined with long-range Coulomb correlations; (*d*) χ_d the resultant diamagnetic susceptibility. Units : columns (*b*)-(*d*) in cgs volume units × 10^6.

	(*a*)	(*b*)	(*c*)	(*d*)
	(m^*/m)	χ_F	$\chi_{exch}^{l.r.}$	χ_d
Lithium	1.45	.185	.015	.200
Sodium	.985	.220	.017	.237

By combining the results of the direct measurement of χ_p with the balance measurements of χ_o, the total static magnetic susceptibility of the metal, it is possible to obtain an experimental estimate of χ_d (39). Unfortunately, the present scatter in the measurements of both χ_o and χ_p prevents us from estimating χ_d to much more than an order of magnitude. This may be seen in Table 7, where we list some of the limiting values of χ_o and χ_p, and the resultant derived χ_d.

TABLE 7

Experimental estimates of χ_d for lithium and sodium

Units : c.g.s. volume units × 10^6.

	χ_o	χ_p	χ_{ion}(a)	$\chi_d{}^{expt}$	$\chi_d{}^{th}$
Li	1.35(b) 1.95(c)	2.0+.3(f)	—.05	—.60+.3 .0+.3	—.20
Na	.51(d) .63(e)	.83+.16(g)	—.18	—.14+.16 —.02+.16	—.24

(*a*) The ion core susceptibilities are taken from J.H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, 1932), p. 359.
(*b*) S.R. Rao and K. Sarithrin, *Proc. Ind. Acad.*, **6,** 207 (1942).
(*c*) C. Starr and A.R. Kaufman, *Phys. Rev.*, **59,** 476 (1941).
(*d*) K. Honda, *Ann. d. Physik.*, **32,** 1027 (1910).
(*e*) C. Lane, *Phil. Mag.*, **8,** 354 (1929).
(*f*) Schumacher, et al, Reference (35).
(*g*) Estimated from (ΔH/H) in table 5.

It may be hoped that greater experimental precision in the determination of χ_o and χ_p (including a direct measurement of χ_p for Na) will make possible a closer comparison between experiment and theory for χ_d in the near future and thus provide the first check on the Landau-Peierls formula.

VII

Thus far we have treated the collective oscillations as being in their ground state, which they will be in lieu of any external excitation mechanism. Such a mechanism is provided by a fast charged particle passing through the metal. As pointed out in II and IV, a fast particle ($V \gg v_o$) as it passes through a metal will leave behind it a wake consisting of collective oscillations which carry energy away from the particle. This wake resembles the Cerenkov radiation observed when fast electrons go through a dielectric. Because the plasma oscillations are quantized, the charged particles will tend to give up energy in discrete amounts, corresponding to the basic plasma quanta. Thus an analysis of fast electrons emerging from a thin metallic film will show, in the forward direction, electrons which have lost no energy, excited one plasma quantum, two quanta, etc. (40). Such discrete energy losses in multiples of a basic quantum were first observed by Ruthemann (41) and Lang (42) and provide direct experimental evidence for the existence of plasma oscillation in metals.

The theory for the excitation of plasma oscillations is discussed in detail in II and IV, so we shall only summarize the results briefly here. The excitation of plasma oscillations may be regarded as the mechanism by which the particle loses energy in the long-range Coulomb collisions (impact parameters $> k_c^{-1}$) with the conduction electrons. The energy loss per unit path length to the collective oscillations is approximately :

$$(dT/dX)_{coll} = \frac{4\pi n Z^2 e^4}{MV^2} \ln\left(\frac{k_c V}{\omega_p}\right) \qquad (35)$$

where Ze, M and V are the charge, mass, and velocity of the fast charged particle. Energy loss to the long-wave length oscillations

($\omega \cong \omega_p$) is preferred. From (35) one may calculate the mean free path for the excitation of a plasma quantum, which is :

$$\lambda = \frac{\omega_p}{(dT/dX)_{coll}} \cong \left(\frac{E_o}{\omega_p}\right)\left(\frac{m}{m^*}\right)\frac{1}{Z^2}\frac{1}{ln\,(k_c V/\omega_p)}\,A \qquad (36)$$

for a non-relativistic incident particle of energy E_o.

There is excellent agreement between the theory outlined above and the pioneer experiments of Ruthemann and Lang on the scattering of kilovolt electrons by thin metallic films. They found groups of electrons emerging from Be and Al which had participated in several energy loss acts, for which the basic quantum was 19.0 e.v. and 14.7 ev. respectively. These values agree surprisingly well with our calculated values of ω_p (under the assumption that all the valence electrons are free) of 18.8 e.v. and 15.9 e.v. The mean free path for the excitation of a plasma quantum estimated from Lang's data is ~ 185 A, which confirms very well our theoretical value of ~ 160 A for the 7.6 kilovolt electrons used in his experiment.

Furthermore, Ruthemann and Lang did not find a similar set of discrete energy losses in Ag, Cu and Ni, but instead observed only one rather broad line. This brings us to the question of whether the damping of plasma oscillations in these metals could give to such a broad line. It is clear that interaction with the lattice vibrations or the motion of individual electrons does not offer a likely damping mechanism, since in both these cases the coupling constant for this interaction is quite weak. However for these metals, the ion core is much larger than for Be and Al, and the interaction of plasma oscillations with the core electrons offers attractive possibilities for a damping mechanism. Herring ([43]) has suggested that the broadening may be due to strong coupling between the *s* electrons and overlapping core *d* electrons. This could produce a rapid transfer of energy from the plasma oscillation in the *s* band to a single *d* electron and thus lead to an appreciable energy width for the oscillations. P.A. Wolff ([44]) has carried out calculations in the Hartree approximation which tend to confirm Herring's suggestion. This coupling between the «*s*» and «*d*» electrons also produces a shift in the frequency of the plasma oscillations, which Wolff has estimated in several cases with results again in qualitative agreement with experiment.

As is so often the case, when further experiments in this field were carried out the above semi-quantitative agreement between theory and experiment began to fade away. Since 1948 a number of workers have investigated characteristic energy losses of kilovolt

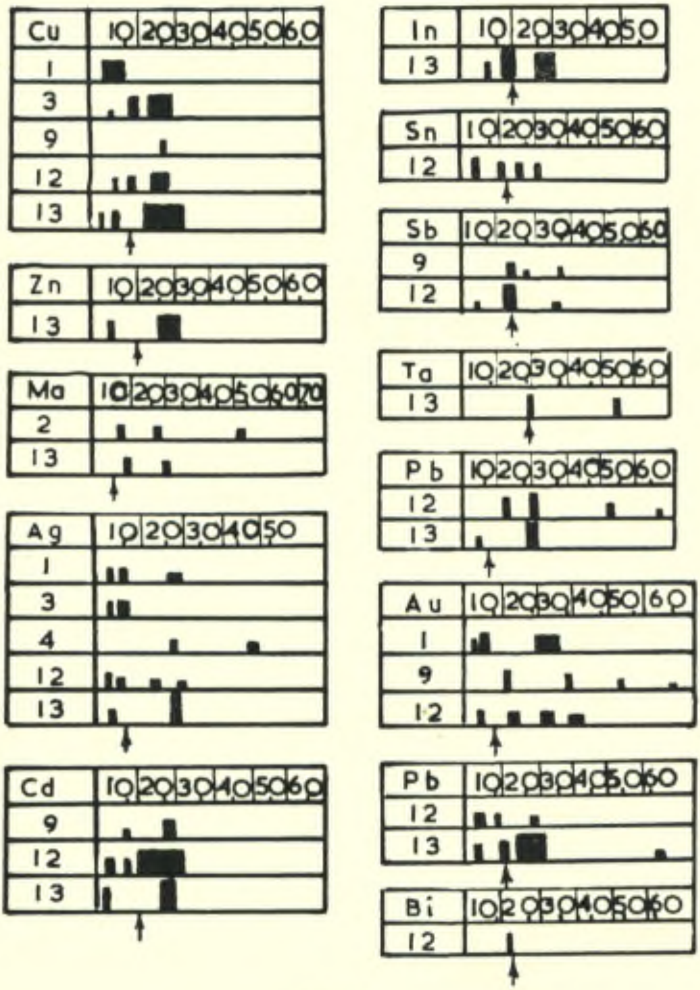

Fig. 6

Fig. 6 and 7. — Characteristic energy losses in metals. The position of a pip indicates the value of the energy loss in ev., the height the relative intensity, and the breadth the apparent width of the loss in question The plasma frequency is indicated by an arrow ↑. The code numbers and references are given in a table on the page following these figures.

electrons in solids, for the most part using electrostatic focussing techniques familiar from electron microscopy. Their findings have tended to indicate that the above simple theoretical account of the energy loss mechanism is open to considerable question. These difficulties seem to arise from the observation of a great multiplicity of lines of widely varying widths in both metals and insulators, and the observation of discrete energy losses under circumstances in which plasma oscillations are unlikely to play a role.

Recently L. Marton (46) has reviewed the experimental situation with regard to these characteristic energy losses, and in figures 6 and 7 we present the major part of his summary of the experimental

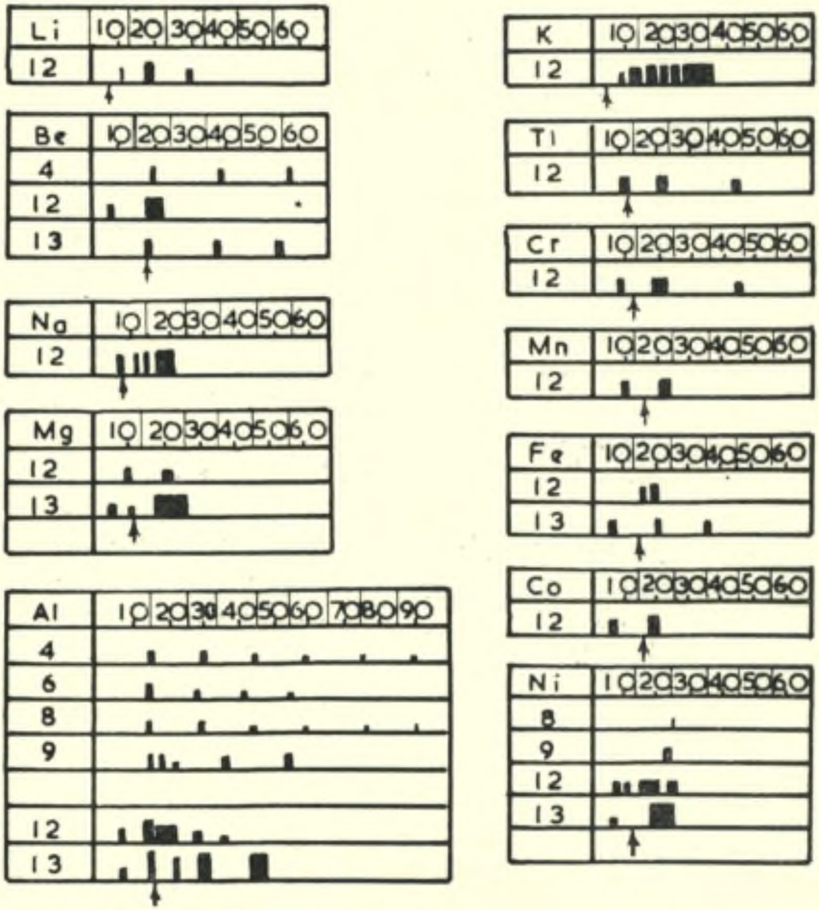

Fig. 7

findings for metals (46). It may be seen from these figures that at least part of the difficulty in interpreting these results is experimental, for there is considerable scatter in energy loss values between different experiments carried out on the same metal. There are possibly two reasons for this. One is that the samples in question may have been of varying degrees of purity. It is quite difficult to prepare very pure thin films (of ~ 100 A thickness) and oxide coatings, for instance, could be partially responsible for the observed sample variations. Another is that the film thickness and bombarding energy vary from one experiment to another. This will certainly affect the number of plasma lines observed, since according to (35) the excitation probability for these oscillations varies in inverse proportion to the particle energy, and for sufficiently high energy particles incident on very thin films, one might not expect to see any plasma lines at all.

Characteristic energy losses similar to those observed in metals have also been observed in insulators and semi-conductors. In several cases (47), experiments have been carried out for both a metal and its oxide (or sulphide), and essentially the same sets of energy losses have been observed. In these instances, plasma oscillations of the conduction electrons are certainly not responsible. However it is possible that one may be observing excitation of plasma-like oscillations of the core electrons (48). For if the core electrons may initially be regarded as possessing a characteristic frequency ω_o, then as a result of their Coulomb interaction, this frequency is altered to $(\omega_o^2 + \omega_p^2)^{1/2}$. (A derivation of this dispersion relation is sketched in Sec. IX.) If ω_p is large compared to ω_o, we would say that the oscillations are primarily plasma-like. It is not clear to what extent this phenomenon has been observed in these characteristic energy loss experiments, although we might expect it to play a role in both this and other metallic phenomena.

Of course it is quite likely that some other energy loss mechanism may be involved in certain of these cases. An argument in favor of this is that often under the existing experimental conditions one would not expect to observe excitation of plasma oscillations. Consider the experiment of Marton and Leder (49), in which they bombard with 30 kev electrons a sodium film (on collodion) which is no more than 100 A thick. The mean free path for excitation 6 e.v. plasma oscillations is in this case, according to (36), about

1200 A. Thus, although they have not measured line intensities, it seems highly unlikely that they have observed electrons which in passing through this thin film have excited several plasma quanta, an interpretation which is required on the simple plasma theory.

This brings us to the question of alternate energy loss mechanisms. The most likely alternative appears to be the excitation of a single core electron; however for many metals one might expect that this would take more energy than is observed given up in a single act. Another possibility is the excitation of a conduction electron band-band transition, although this might be expected to give rise to much broader lines than those observed. The extent to which either of these mechanisms plays a role is at present not clear, although there has been a tentative identification of certain of the very large energy loss acts ($\sim$ 50 ev) with known x-ray transitions.

We are confident of our identification of certain of the discrete energy losses in Al and Be as excitation of plasma oscillation, because here the core effects are small, a number of equally speced lines are observed, and the agreement between theory and experiment is highly satisfactory. Mg might also be put in this category, since it too possesses a small ion core, and the observed energy losses in multiples of 10 e.v. are in good agreement with the plasma quanta of $\sim$ 10.6 e.v. We have indicated the plasma frequency, computed under the assumption that all valence electrons are free, for the metals listed in figures 7 and 8 and it may be seen that in general agreement varies from one metal to another. It is clear that the characteristic energy losses of kilovolt electrons furnish a great deal of interesting information concerning electrons in solids, and it is to be hoped that in the near future theoretical and experimental clarification of the energy loss mechanisms will sharpen this new tool.

We might add that fast charged particles on passing through the metal also give up energy in close Coulomb collisions (impact parameters $< k_c^{-1}$) with individual conduction electrons. The energy loss per unit path length due to these individual electron collisions is roughly comparable to that due to the collective oscillations. For heavy metals, both mechanisms are quite unimportant compared to the energy given up in collisions with core electrons. However for the very light metals (Li and Be) for which the number of conduction and core electrons are comparable, the contribution to the stopping power from the conduction electrons is appreciable. As discussed in Paper IV, experiments on the stopping power of these metals tend to confirm the above theoretical description (50).

VIII

We now consider the influence of electron-electron interactions on the electron-phonon interaction in metals. We shall here give a brief summary of the approach to this problem which has been developed by the writer in collaboration with John Bardeen, an approach which is based on a generalization of the methods described earlier for treating electron interactions in a uniform background of positive charge. We further limit ourselves to a derivation and discussion of the basic Hamiltonian which obtains when electron-electron interactions have been properly taken into account.

The importance of electron-electron interactions in this problem arises from the general tendency of the electrons to screen out the field of the ions. Suppose we consider a given conduction electron. It first of all interacts with the ions, whose motion may be described in terms of the phonon field. For long wavelength phonons, however, this interaction is radically altered by the field due to the other electrons, which in the course of responding to the ionic motion move in just such a way as to produce a field which very nearly cancels the ionic field. Bardeen (51) established this by treating the electrons in the Hartree approximation, and thereby obtaining a self-consistent solution for the coupled motion of the ions and electrons. As one might expect, the phonon frequency is also greatly influenced by the electron response to the ionic motion. This problem has been discussed by Staver and Bohm (52), who treated the ions and electrons as a set of coupled plasmas. Working with the equations of motion, and using methods closely related to those applied in II, they obtained the dispersion relation for the phonon field as modified by the electron-electron interactions.

Recently, Nakajima (53) has also investigated the role of electron interactions in determining the phonon frequencies and electron-phonon interaction. He has given a self-consistent field treatment by means of canonical transformations; however he finds it necessary to make a number of approximations, which are essentially equivalent to the Hartree approximation and neglect of electron-electron correlations, so that the range of validity of his method is in question. The recent investigation by Bardeen and the writer represents an endeavour to go beyond the Hartree approximation in treating the electron interactions and enables one, for instance, to consider the exchange terms neglected by Nakajima. It was, in part, aimed at clarifying the role that electron-electron interactions might play in superconductivity, and represents an extension of the work of Bohm and Staver.

The basic Hamiltonian for describing the motion of electrons and phonons may be written as :

$$\mathrm{H} = \sum_i \frac{p_i^2}{2m} + \sum_k \frac{\mathrm{P}_k^{*}\,\mathrm{P}_k + \Omega^2\,\mathrm{Q}_r^{*}\,\mathrm{Q}_k}{2} + \sum_k \mathrm{V}_k\,\mathrm{Q}_k\rho_{-k} + \sum_k \frac{2\pi e^2}{k^2}\rho_k\,\rho_{-k}. \quad (37)$$

Here m is the effective mass of the electrons in the periodic field of the lattice, Ω is the frequency of the phonons in a uniform background of negative charge, Q_k and P_k are the phonon co-ordinates and momenta, and the ρ_k are as before the Fourier components of the electron density. We restrict ourselves to long-wave length interactions, for which the effective mass approximation may be expected to be valid. We further confine our attention to the longitudinal phonons which dominate the electron-phonon interaction. In the very long-wave length limit we may expect that the electron-ion and ion-ion interactions are to some extent Coulombic. To the extent that they are, the « bare » phonon frequency is :

$$\Omega^2 \cong \Omega_p^2 = \frac{4\pi n \mathrm{Z}^2 e^2}{\mathrm{M}} \quad (38)$$

while the coefficient of the electron-phonon interaction term is :

$$\mathrm{V}_k = -i\Omega\sqrt{\frac{4\pi e^2}{k^2}} \quad (39)$$

We now seek to take into account the effect of the long-range electron-electron interactions. Once again let k_c denote the maximum wave vector of the plasma oscillations we shall introduce to describe these long-range interactions. We are then led to consider separately the long-wave length phonons, their interaction with the electrons, and the long-range electron-electron interactions (all corresponding to Fourier components with wave vectors less than k_c). We return later to a discussion of the short-wave length phonons and electron interactions. As in the absence of ionic motion, we may as a first step, add to the Hamiltonian a term which describes the « kinetic energy » of the plasma field.

$$\sum_{k<k_c} \frac{p_k^{*} p_k}{2}$$

provided we impose the following subsidiary condition on the combined system wave function :

$$p_k \psi = 0 \ .$$

The essential point at which our redescription of the electron interactions in terms of plasma oscillations departs from that in which phonon field is neglected is in the circumstance that because the electrons are also in interaction with the phonons, we should expect that it is only some linear combination of electronic density fluctuations and phonon field variables which properly describe « pure » plasma oscillation. We may take this new circumstance into account by carrying out an « expanded » canonical transformation, which relates the plasma field variables to the phonons as well as to the electronic density fluctuations. The appropriate transformation is generated by :

$$S = \sum_{k<k_c} \left[\left(\frac{4\pi e^2}{k^2} \right)^{1/2} q_k \rho_{-k} + i U_k q_k Q_{-k} \right]$$

Here q_k is the co-ordinate conjugate to the plasma field momentum, P_k, and μ_k is a real constant to be determined. After this transformation, the Hamiltonian becomes :

$$\begin{aligned} H = {} & \sum_i \frac{p_i^2}{2m} + \sum_{k<k_c} \frac{P_k^{*} P_k + (\Omega^2 - U_k^2) Q_k^{*} Q_k}{2} + \sum_{k<k_c} \frac{p_k^{*} p_k + (\omega_p^2 + U_k^2) q_k^{*} q_k}{2} \\ & + \sum_{k<k_c} \left\{ V_k - i \left(\frac{4\pi e^2}{k^2} \right)^{1/2} U_k \right\} Q_k \rho_{-k} + \sum_{k<k_c} U_k P_k^{*} q_k + \sum_{k<k_c} \left(\frac{4\pi l^2}{m} \right)^{1/2} \hat{\varepsilon}_k \cdot \left(\vec{p}i - \frac{\vec{k}}{2} \right) q_k e^{i\vec{k} \cdot \vec{x}_i} \\ & + \sum_{k>k_c} \frac{P_k^{*} P_k + \Omega^2 Q_k^{*} Q_k}{2} + \sum_{k>k_c} V_k Q_k \rho_{-k} + \sum_{k>k_c} \frac{2\pi e^2}{k^2} \rho_k \rho_{-k} \end{aligned} \tag{40}$$

and the subsidiary condition is :

$$\left[p_k - i\left(\frac{4\pi e^2}{k^2}\right)^{1/2} \rho_{-k}\, k + \mathrm{U}_k\, \mathrm{Q}_{-k}\, k\right]\psi = 0 \quad (k < k_c) \qquad (41)$$

In obtaining (40), use is made of the subsidiary condition (41) to effect simplification of certain terms, and the « random phase » approximation has been applied.

The first three terms in the Hamiltonian (40), describe the kinetic energy of the electrons, the phonon field, and the plasma field. The next three characterize the electron-phonon interaction, the plasma-phonon interaction, and the plasma-electron interaction, while the remaining terms characterize the short-wave length phonons, their interaction with the electrons, and the short-range electron-electron interaction. We see that we have here re-described the long-wave length electron-electron interactions in terms of the plasma oscillations, which however are not yet « isolated », in the sense that there remains a plasma-electron and plasma-phonon interaction, and the plasma field variable still appears in the supplementary condition. However, as is the case in the absence of ionic motion, the coupling between the electrons and the plasma oscillations is weak; further, because of the disparity in the plasma and phonon frequencies, the coupling between the plasma waves and the phonon is likewise weak. Both the plasma-electron and plasma-phonon interaction may thus easily be taken into account by appropriate canonical transformations; when this is done, the remaining terms in the Hamiltonian are essentially unaltered, so that we may discuss them here by neglecting the foregoing coupling terms.

We thus see that the explicit effect of the long-range electron-electron interactions is to change the long-wave length phonon frequencies to :

$$(\Omega')^2 = \Omega^2 - \mathrm{U}_k^2 \qquad (42)$$

and the effective long-wave length electron-phonon matrix element to :

$$\mathrm{W}_k = \mathrm{V}_k - i\left(\frac{4\pi e^2}{k^2}\right)^{1/2} u_k. \qquad (43)$$

The u_k are thus proportional to the field on a given electron due to all the other electrons, and describe the response of all the other electrons to the ionic motion. We are not free to take the u_k as arbitrary constants, but must choose them in such a way that our treatment is self-consistent. In this context, the requirement of self-consistency appears in the following guise. The electrons and phonons are not only coupled in the Hamiltonian, but also through the subsidiary condition (41), and the requirement of self-consistency is just the requirement that in eliminating the electron-phonon interaction in the Hamiltonian, we eliminate it in the subsidiary condition as well.

When the electron-phonon interaction may be treated by perturbation-theoretic methods, the u_k may be determined by carrying out a straight-forward canonical transformation. We find for W_k, (and hence u_k),

$$W_k - V_k = -\frac{4\pi e^2}{m} \sum_i \frac{W_k}{\left(\omega_s - \frac{k \cdot p_i}{m}\right)^2 - k^4/4m^2} \tag{44}$$

where ω_s is the actual phonon frequency, and is given by :

$$\omega_s^2 = (k^2/4\pi e^2)\, W_k^* V_k \tag{45}$$

These results are in agreement with those of Nakajima, and prove that for long wave lengths his neglect of exchange effects and electronic correlations is justified. In the adiabatic approximation ($\omega_s \rightarrow 0$), (44) also reduces to the result of Bardeen for the effective matrix element for the scattering of electrons by phonons. In the limit of long-wave lengths, we may solve (44) for W_k obtaining :

$$W_k \cong \frac{V_k}{1 + \frac{4\pi n e^2}{m}\left(\frac{3m^2}{k^2 P_0^2}\right)} \approx V_k \frac{k^2 V_0^2}{3\omega_p^2} \tag{46}$$

Thus the effective matrix element for long-wave length interactions is drastically reduced. Similarly we have :

$$\omega_s^2 \cong \frac{1}{3} \frac{k^2 V_0^2}{\omega_p^2} \Omega_p^2 = \frac{1}{3} k^2 V_0^2 Z^2 \frac{m}{M} \tag{47}$$

Thus the velocity of sound, taking account only Coulomb interactions, is :

$$S = \frac{1}{\sqrt{3}} v_o \frac{Zm}{M}. \tag{48}$$

This is just the result obtained by Staver, and as shown by him, is in fairly good agreement with the experimental observations. The extent of this agreement ($\sim 20\ \%$ for the alkali metals, no worse than a factor of two for any metal) indicates that one can get a good order of magnitude estimate by such simple Coulombic considerations. (Of course a far more accurate calculation of the elastic constants, and hence of s, may be carried out for the monovalent metals using the Wigner-Seitz method.) It should be noted that the dispersion relation (47) is quite different from the bare phonon dispersion relation (38).

When the electron-phonon interaction is strong, so that perturbation-theoretic methods become inapplicable, we have not been able to obtain an explicit solution for the u_k. However the Hamiltonian (40), continues to be valid, so that, one could for instance treat the effect of the electron-electron interactions through the introduction of some suitable empirical coupling constant, W_k, thus implicitly choosing the appropriate u_k. One could then attempt to use the resulting effective Hamiltonian in calculations bearing on conductivity and superconductivity.

Thus far we have discussed only long-wave length phonons and electron-phonon interactions ($k < k_c$). What is the situation with respect to the short wave-length interaction? Here life is unfortunately much more complicated. First, the effective mass approximation is no longer valid, so that effects associated with the periodic field of the lattice, such as Umklapprozesses and virtual band-band transitions must be taken into account. Second, for the short-range electron-electron interactions exchange effects are important. When these come into play, it is no longer possible to treat in simple fashion the effect of electron interactions on the electron-phonon interaction, and we have not been able to carry out an explicit calculation of their influence for this problem. However, we may expect that for wave-lengths in the vicinity of k_c the effect of the short-range electron-electron intreactions is rather similar to that produced by the long-range interactions we have been discussing, since the cut off is not in fact a sharp one. For this reason it may well turn out that the expression derived by Bardeen ([51]) is a good approximation for all wave-lengths, since it has the right behavior in both the very long and very short wave-length limit, the latter case corresponding to essentially no screening.

The effect of electron-electron interactions on superconductivity may be discussed on the basis of the following considerations. Let us suppose that their effect on the effective matrix element for the electron-phonon interaction has been included properly — as may be done, as discussed earlier, through the introduction of a semi-empirical coupling constant (54). The remaining effect of the electron-electron interactions is to bring about short-range collisions between the electrons. This, however, may be regarded as a relatively small perturbation on the motion of a given electron. One may be led to this conclusion on the basis of the criteria, discussed earlier in this report, for the applicability of conventional second-order perturbation theory to this short-range electron-electron interaction term in the Hamiltonian. On the other hand, in just those elements which are superconductors, the electron-phonon interaction is a violent one — so much so that the electrons involved cannot be treated by perturbation — theoretic methods. Thus we should expect that compared to such a strong interaction, the comparatively weak electron-electron interaction may properly be neglected. It may play a small role in determining the energetics of the transition, but it should not materially influence it in first approximation.

IX

We should now like to discuss, in rather speculative fashion, the extent to which the simple model put forth in the preceding sections need be modified to apply for all metals. We have consistently neglected two important effects : the periodicity of the lattice and the structure of the ion-core. The first we have taken into account in the effective mass approximation which is essentially equivalent to neglecting the effect of band-band transitions, an approximation which we should expect to be rather good for long-wave length phenomena. It is not too difficult to formulate the collective description using Bloch waves (55); however detailed calculations must be carried out for each metal considered, and as yet none have been completed. It would also be highly desirable to carry out a calculation of the short-range correlation energy using Bloch waves rather than plane waves; such a calculation should yield a better value for the correlation energy, and make possible an estimate of the error encoutered in the plane wave approximation.

Our second approximation is probably the more serious one, particularly for the heavy metals. For as Herring has suggested, the core electrons can interact strongly with the plasma oscillations, provided they have an effective frequency near ω_p. A rather simple model for the treatment of this interaction may be developed to the extent that the core electrons may be characterized by a set of oscillators of frequency ω_l. In this case, one can treat their interaction with the plasma oscillations using the same Hamiltonian and techniques as were developed to treat the electron-phonon interaction in Section VIII. The only difference between the two problems is the different dispersion relation for the core electrons which replace the phonons of Section VIII. Because the « oscillators » in this problem may be of much higher frequency, they will affect the frequency of the collective oscillations much more strongly than did the phonons. Those $\omega_l < \omega_p$ will act to raise the plasma frequency; those $\omega_l > \omega_p$ to depress it, so that the shift in frequency may vary in both direction and magnitude from metal to metal.

The above model is now under investigation, particularly with regard to the extent that the plasma-ion core interaction will affect the general conclusions about electron interaction in metals reached on the basis of the collective description of the free electron gas. It is our present belief that these will not be materially altered; that the effective electron interaction will continue to be screened out at a distance of about the inter-particle spacing, and that the correlation energy will be about the same. If the effective screening is unchanged, we may expect that our conclusions concerning the effect of election interactions on the electronic specific heat, bandwidth, magnetic susceptibilities, etc., will apply quite generally.

Of course the foregoing conclusions apply only to the conduction or valence electrons, with the additional assumption that lattice effects may be treated in the effective mass approximation. We may expect a rather different situation to obtain in the case of the core electrons. Suppose we first consider the tightly bound electrons. For these too, plasma effects may be important; as we have remarked, plasma oscillations may even take place in insulators. To see this, let us consider again the simple model in which we have core electrons characterized by some frequency ω_o. We may write their Hamiltonian as :

$$H = \sum_k \frac{P_k^* P_k + \omega_o^2 Q_k^* Q_k}{2} + \sum_{i \neq j\, k} \frac{2\pi e^2}{k^2}\, e^{i\vec{k}\cdot(\vec{x}_i - \vec{x})}$$

where the second term represents the Coulomb interaction between these core electrons on different ion sites. If we then expand this interaction term about the equilibrium positions of the electrons (i.e. $\vec{x}_i = \vec{x}_{oi} + \delta\vec{x}_i$) and express the $\delta\vec{x}_i$ in terms of the oscillator co-ordinates Q_k, we find that our Hamiltonian (neglecting constant terms) becomes :

$$H = \sum_k \frac{P_k^* P_k + (\omega_o^2 + \omega_p^2) Q_k^* Q_k}{2}$$

Thus the effective frequency of the core electrons is shifted to : $(\omega_o^2 + \omega_p^2)^{1/2}$, and to the extent that ω_p 'is comparable with ω_o, we may anticipate that plasma effects will play an important role. The above dispersion relation has been derived by D. Gabor (48) by a rather different method. As have mentioned, plasma oscillations of core electrons may be responsible for certain of the characteristic energy losses observed in metals and insulators.

The intermediate case, of the not-quite-so-bound core electrons, is more difficult to treat. Here we deal with quasi-free electrons of quite high effective mass. We may anticipate that their collective behavior is likewise intermediate between that of the « free » conduction electrons and the tightly bound core electrons, but a more careful consideration of this problem is required.

REFERENCES

(1) D. Bohm and D. Pines, *Phys. Rev.*, **82,** 625 (1951), *Phys. Rev.*, **85,** 338 (1952), *Phys. Rev.*, **92,** 609 (1953) and D. Pines, *Phys. Rev.*, **92,** 626 (1953), hereafter referred to as I, II, III and IV, respectively.

(2) In the free electron gas model, which we adopt throughout this report, the metal is described as a system of electrons moving in a uniform background of positive charge. The great advantage of the free electron gas model is that it admits of exact (or reasonably so) solution in the various approaches employed for the treatment of electron interactions. To calculate the cohesive energy of a metal this model must be improved by taking into account the binding energy of the electrons due to the periodic field of the lattice. The cohesive energy in the Hartree approximation is then $E_o + 2.21/r_s^2$ where E_o is a constant and is the difference between the binding energy of the lattice for the most tightly bound electron, and the ionization energy of the free atom. The influence of the periodic field may also be taken into account in the effective mass approximation, and this is done in Sec. IV.

(3) J. Bardeen, *Phys. Rev.*, **50,** 1098 (1936).

(4) This may readily be seen from the expression for the exchange contribution to $E(k)$ which is $-4\pi e^2 \sum_{k'} \frac{1}{|k' - k|^2}$

(5) E.P. Wigner, *Phys. Rev.*, **46,** 1002 (1934), *Trans. Faraday Society*, **34,** 678 (1938).

(6) We define correlation energy as the difference between the energy calculated in the Hartree-Fock approximation and that calculated using any better approximation.

(7) Actually this is not quite the correct interpolation formula. For this expression corresponds to a low density correlation energy of $-(.58/r_s)\ ry$, whereas the actual low density limit should be $(-.88/r_s)\ ry$, as Wigner himself points out in a footnote in the second paper of reference 5. This will have the effect of increasing somewhat his values for the correlation energy.

(8) Historically the first utilization of the « plasma » aspects of the electron gas in a metal is due to Kronig and Korringa *Physica*, **10,** 406 (1943), who treated the effect of electron-electron interaction on the stopping power of a metal for fast charged particles. However their treatment is open to objection, in that they describe the electron gas as a classical fluid, with an artificially introduced coefficient of internal-friction. The stopping power problem is discussed from the viewpoint of the collective description in IV.

(9) L. Tonks and I. Langmuir, *Phys. Rev.*, **33,** 195 (1929).
H.J. Merrill and H.W. Webb, *Phys. Rev.*, **55,** 1191 (1939).
D. Bohm and E.P. Gross, *Phys. Rev.*, **75,** 1851 and 1864 (1949).

(10) The Debye length was first introduced in connection with screening processes in highly ionized electrolytes. See P. Debye and E. Huckel, *Physik. Z.*, **24,** 185 (1923). In terms of the plasma frequency, it may be expressed as $\lambda_D = (\langle V^2 \rangle_{AV} / \omega_p^2)^{1/2}$.

(11) At first sight, one might expect the Fermi statistics to make a significant difference. However they do not in first order because we are dealing with

phenomena involving distances long compared to the de Broglie wave length of the electrons for which exchange effects should be comparatively unimportant.

(12) We carry out our Fourier expansions in a box of unit volume. We further work in a system of units in which $h = 1$.

(13) This Hamiltonian and subsidiary condition, if k_c is taken as infinite, correspond to that familiar from quantum electrodynamics when the Coulomb interactions are described in terms of a longitudinal vector potential. This is the starting point of III.

(14) The condition that the coupling be weak, $g^2 \ll 1$, is essentially the condition that collective oscillations can only occur for wave-lengths greater than the Debye length. (See footnote 5). This provides one criterion for the choice of k_c.

(15) We might alternately regard this as a linear approximation.

(16) It should be noted that these particles are not those we started out with; rather, they correspond to « bare » electrons plus an associated cloud of plasma oscillation. It is this cloud which is responsible for the increased mass of our particles.

(17) In terms of the original electron co-ordinates, this is a many-particle wave function; it may be visualized as a product of φ_0 and a symmetric function which describes the long-range electronic correlations in rather complicated fashion, as may be seen by re-tracing the various canonical transformations.

(18) One might argue that we should determine β_{min} by minimizing the total energy, which would include the short-range correlation energy arising from $H_{s.r.}$ (Eqtn. 25). However because of the uncertainty in the knowledge of $E^{s.r.}_{corr}$, and because of the fact that $H_{s.r.}$ represents a small short-range perturbation on the system wave functions and hence should not affect β_{min} appreciably, we consider it best to consider only $g^{l.r.}_{corr}$.

(19) Actually, a certain amount of caution should be exercised in applying perturbation theory to a many-particle system, for although the perturbating term may appear small, if it involves a very large number of particles it may cause the system energy and wave-functions to deviate a great deal from their unperturbated values. Our use of perturbation theoretic techniques here is equivalent to the assumption that only two-body collisions are important, an assumption which appears justified in view of the short-range character of force.

(20) A treatment of correlation energy which begins on the basis of the perturbation theoretic expressions (24) and (25) for unscreened Coulomb interactions has been given by W. Macke, *Zeits. für Naturforschung*, **5a,** 192 (1950). By making certain approximations, he is able to obtain a finite result using perturbation theory. However, his approach seems open to objection on several counts. These include his use of perturbation theory for a many-particle long-range interaction, and a questionable application of variational techniques.

(21) Note that in the limit of $\beta \to 0$ we have the logarithmic divergence mentioned earlier.

(22) The agreement would be even closer if Wigner's interpolation formula were revised along the lines indicated in footnote 7.

(23) G.H. Wannier, *Phys. Rev.*, **52,** 191 (1937); J.C. Slater, *Phys. Rev.*, **76**, 1692 (1949); E.N. Adams II, *Phys. Rev.*, **85,** 41 (1952) and J. *Chem. Phys.*, **21,** 2013 (1953).

(24) For the same reason we have not taken into account the increase m to $m/(1 - \beta^3/6)$ in our calculation of $E^{s.r.}_{corr}$.

(25) Private communication. We should like to thank Prof. Brooks for communicating his results to us in advance of publication.

(26) H. Brooks, *Phys. Rev.*, **91**, 1027 (1953).

(27) Actually a screened Coulomb interaction was proposed empirically by P.T. Landsberg [*Proc. Phys. Soc.* (London) **A 162**, 49 (1949)] who introduced it in order to obtain agreement between theory and experiment for the tail of the soft X-ray emission spectrum. Wohlfarth [*Phil. Mag*, **41**, 534 (1950)] then showed that such an interaction would eliminate the specific heat difficulties cited above. The principle difficulty associated with the use of an empirical screened Coulomb potential was its disastrous effect on the cohesive energy.

(28) This effect was inadvertently omitted in IV. I should like to thank Dr. S. Raimes for bringing this omission to my attention.

(29) We were able to carry out the integrations in (24) only by doing the $\vec{k}$ and $\vec{k}'$ integrations first; these have a symmetry and simplicity which is lost if one essays the p integration at an early stage.

(30) H. Jones, *Phys. Rev.*, **94**, 1072 (1954).

(31) Koopman's theorem would apply if the screening length k_c were unaffected by the removal of an electron from the metal. However k_c does vary somewhat with density, so that Koopman's theorem may be expected to prove only approximately valid. However, as pointed out by H. Jones (private communication), even though it is only approximately valid, we might hope that rather accurate energy differences could be calculated using it, since the effect on k_c of taking an electron from the bottom of the Fermi distribution to the top is surely very slight.

(32) A very rough estimate of the effect of short-range correlations may be obtained by calculating $\underset{corr}{E(o)}$ (which may be done simply because the Pauli principle restriction is here $p > 1$) and estimating E(1) by an argument due to Seitz [*The Modern Theory of Solids*, (McGraw Hill, New York, 1940), p. 343], which gives $\underset{corr}{E(1)} = E^{s.r.}_{corr} - 1/3\ (\delta E^{s.r.}_{corr}/\delta r_c)$. One then finds that short-range correlations tend to increase the band-width by $\sim .1$ *ev* for the alkali metals.

(33) S. Raimes, *Phil. Mag.* (to be published).

(34) J.B. Sampson and F. Seitz, *Phys. Rev.*, **58**, 633 (1940), hereafter referred to as SS.

(35) R. Schumacher, T. Carver, and C.P. Slichter, *Phys. Rev.* (to be published).

(36) C.H. Townes, C. Herring, and W. Knight, *Phys. Rev.*, **77**, 852 (1950).

(36*a*) Alternately, one can derive P_F/P_A from $\Delta H/H$ if one has confidence in a given value for χ_p.

(37) For a discussion based on a somewhat different approach, see IV.

(38) A.H. Wilson, *The Theory of Metals*, Cambridge University Press, 1953, p. 175. In obtaining (33) we have assumed that the energy surfaces are spherical.

(39) Thus $\chi_o = \chi_o + \chi_d + \chi_{ion}$ where χ_{ion} represents the static ion core susceptibility.

(40) Observations should be made in the forward direction to reduce scattering effects.

(41) G. Ruthemann, *Ann. Phys.*, **2**, 113 (1948).

(42) W. Lang, *Optik*, **3**, 233 (1948).

(43) Conyers Herring (Private communication).

(44) P.A. Wolff, *Phys. Rev.*, **92**, 18 (1953).

(45) L. Marton, invited paper at Washington meeting of *Amer., Phys. Soc.*, (1954).

(46) We should like to thank Dr. Marton for sending us this summary.

(47) L. Marton and L. Leder (private communication).

(48) This possibility was first suggested by D. Gabor, *Phil. Mag.* (to be published).

(49) L. Marton and L.B. Leder, *Phys. Rev.*, **94**, 203 (1954).

(50) A discussion from a somewhat different point of view of conduction electron polarization effects in the stopping power of light metals has been given by H.A. Kramers, *Physica*, **13**, (1947) and A. Bohr, *Danske Videnskab Selskab. Mat. fys. Medd.*, **24**, No. 19 (1948).

(51) J. Bardeen, *Phys. Rev.*, **52**, 688 (1937).

(52) D. Bohm and T. Staver, *Phys. Rev.*, **84**, 836 (1952); T. Staver, *Ph. D. Thesis*, Princeton University, 1952 (unpublished).

(53) T. Nakajima, Abstract book Intl. Conference on Theoretical Phys., Kyoto, Japan (1953).

(53*a*) In Eqtn. (38), Z and M are the ionic charge and mass.

(54) This is the starting point for the theories of Frohlich [*Phys. Rev.*, **79**, 845 (1950)] and Bardeen [*Phys. Rev.*, **80**, 567 (1950)].

(55) The formalism developed by Adams (reference 23) is particularly useful in this respect.

Code No.	Investigation	Primary energy (ev)	Method of observation	Method of analysis
1	Rudberg (*a*)	100-400	Reflection	Magnetic
2	Haworth (*b*)	20-200	Reflection	Magnetic
3	Fransworth et al (*c*)	10-100	Reflection	Magnetic
4	Ruthemann(*d*)	2000, 8000	Transmission	Magnetic
6	Moore (*e*)	8,000	Transmission	Magnetic
8	Lang (*f*)	7,600	Transmission	Magnetic
9	Mollenstedt(*g*)	35,000	Transmission	Electrostatic
12	Marton and Leder (*h*)	30,000	Transmission	Electrostatic
13	Kleinn (*i*)	35,000	Reflection	Electrostatic

(*a*) E. Rudberg, *Phys. Rev.*, **50**, 138 (1936).

(*b*) L. Haworth, *Phys. Rev.*, **48**, 88 (1935).

(*c*) Farnsworth and Turnbull, *Phys. Rev.*, **53**, 944 (1938).

(*d*) G. Ruthemann, Ref. 41.

(*e*) A. Moore (private communication to L. Marton).

(*f*) W. Lang, reference 42.

(*g*) W. Mollenstedt, *Optik*, **5**, 499 (1949) and *Z. Angew. Phys.*, **3**, 187 (1951).

(*h*) L. Marton and L. Leder, reference 49.

(*i*) W. Kleinn, *Ph. D. Thesis*, Eberhard-Karls Univ. (Tubingen) (1953), (unpublished).

Discussion of Prof. PINES' report

Mr. Mott. — I want to be quite sure what your potential energy is. You have two terms; one is the electrostatic contribution between electrons, with the long-wave Fourier components cut out; the other is the potential energy of oscillators.

Mr. Pines. — That is correct. What I have done is to re-express that part of the potential energy corresponding to long wave-length Coulomb interaction in terms of the plasma oscillations.

Mr. Fröhlich. — Concerning the total number of degrees of freedom, is it correct to say that since the specific heat is nearly the same as for the free electron model, most of the degrees of freedom are still contained in the « individual » electrons (e.g. 0.9 of the total)?

Mr. Pines. — The situation is essentially as follows. We have n' independent collective degrees of freedom, which will not be excited at ordinary temperatures, and which represent about 5 % of the total number of degrees of freedom. We also have our system of $3\,n$ individual particle degrees of freedom, but with subsidiary conditions imposed on the electronic wave functions. It will, I believe, be quite difficult to carry out a detailed treatment of the specific heat of the electron gas taking into account these subsidiary conditions, for we should need remarkably good wave functions to satisfy them. However, in a general way, we can say that these conditions act to reduce the number of individual electron degrees of freedom to $3\,n - n'$, so that the specific heat of the electron gas should be somewhat less than the Sommerfeld value, insofar as this particular effect is concerned.

Mr. Kittel. — I would like to emphasize that the approximation $m^* — m$ is of doubtful value in comparisons of the estimated plasma frequency with the observed value of the discrete energy losses in films.

Mr. Pines. — I think this depends very much on the metal under consideration. For light metals it may well turn out to be a good approximation. For here we should expect ion-core effects to be relatively slight since the core itself is small and the core electrons are tightly bound. Here also the influence of band-band transitions may not be too important, since the plasma frequency is rather high, and may in fact be large compared to the frequency of these virtual transitions for which the oscillator strengths are appreciable. In this circumstance I should expect $m^* \gtrsim m$.

Mr. Seeger. — I wish to raise the question of plasma-oscillations corresponding to interaction of electrons in different cores.

Can we expect to obtain plasma oscillations of core electrons in real metals, because the electrostatic interaction of cores will be very effectively shielded by the conduction electrons? Can the remaining van der Waals interaction give rise to plasma-oscillations?

Mr. Pines. — The case I was discussing was that of an insulator, where the interaction between electrons on different cores may be of importance and may lead to plasma oscillation. I agree that the interaction between these different core electrons in a metal will be affected by the shielding action of the conduction electrons. As a result I would expect that the core electron frequencies are here more strongly affected by the core-electron-conduction electron interaction than by the core electron-core electron interaction.

Mr. Fröhlich. — In insulators, the relation of longitudinal to tranverse frequencies can (for very long waves) be expressed in terms of the dielectric constant. I think that your expression would reduce to the former, i.e. essentially lead to a calculation of the dielectric constant.

Mr. Seeger. — The T^5 law of electrical resistance at low temperatures comes from T^3 law of the lattice specific heat and from the assumption that the matrix element of a transition is proportional to the frequency ω of the phonons scattering the electrons and therefore, by virtue of $\hbar\omega \sim kT$, proportional to T. This assumption usually is justified by supposing that the displacement of an atom simply shifts bodily the whole potential due to that atom with it. If there is some screening of the charge due to the motion of ions should we not expect the T^5 law to be changed to some high power law? How strong is the experimental evidence for the T^5 law really?

Mr. Pines. — There certainly is a screening of the ionic change motion due to the conduction electrons. However it will not modify the T^5 law at very low temperatures, as Bardeen showed in his 1937 paper.

Mr. MacDonald. — Following Dr. Seeger's question, if the electron-lattice interaction is only altered in magnitude and if the effective lattice wave velocity, although altered in magnitude, may still be assumed constant for long wave oscillations (i.e. no dispersion at sufficiently low frequencies), then, the T^5 law for electrical resistance will still be valid for sufficiently low temperatures although, of course, the effective temperature below which it holds goods may be altered.

Mr. Aigrain. — It appears that in some semiconductors such as in Sb, with high enough electron densities for the electron gas to be degenerate, the ratio of plasma quantum energy to Fermi energy, which goes as $(\frac{m^*}{m} r_s)^{1/2}$ might be smaller then 1, because m^* is very small. The situation will then be very complicated, as the type of interaction which then sets in is analogous to the coupling with acoustic waves which occurs in superconductivity.

Mr. Pines. — This is certainly an interesting limiting case. For in just this region the coupling constant for the electron-plasma interaction may be greater than unity, since $g^2 \cong \beta^2(E_F/\hbar\omega_p)^2$ and β will be of order unity. Your analogy is then very well taken, since in both this case and superconductivity we have electrons strongly coupled to a longitudinal field. And I certainly agree that the situation will be complicated, for under these circumstances we can no longer carry out a separation of the collective and individual particle motion in the manner I have outlined.

Mr. Kittel. — 1) Prof. Kip at Berkeley has observed in preliminary experiments a plasma resonance in Germanium near 20° K; the resonance was at a microwave frequency;

2) The Debye length under these conditions is of the order of a micron. In the detailed application of plasma theory to semi-conductors, it will be necessary to consider the case when the mean free path is comparable with or less than the Debye length.

Mr. Aigrain. — In the case of In Sb, the mean free path is very large (a fraction of a micron at room temperature for lattice collisions), so that the Debye length would presumably be smaller than the mean free path.

Mr. Van Vleck. — Does your conclusion that a free electron model is incapable of yielding ferromagnetism apply regardless of the value of the effective mass which is used.

If so, it would seem that the Stoner band-model of ferro-magnetism cannot be selfconsistent. Thus ferro-magnetism must be attributed to short range intra-atomic coupling which is present when two electrons are coïncidently on the same atom, a refinement which is not included in the ordinary band theory.

Mr. Pines. — I have not looked at free electron ferromagnetism in the limit of very high effective mass. However I think a more realistic model within the framework of the free electron approach would be to consider an assembly of holes of high effective mass and of electrons of ordinary mass, taking into account the interactions between these, and the resultant correlated electron-hole behavior. I am planning to treat such a model in the very near future, just to see whether it exhibits any features resembling ferromagnetism.

Mr. Seeger. — I think that Pines' results on the impossibility of ferromagnetism in an electron gas have the following significance for the general theory of ferromagnetism : Pines has proved that an electron gas of *s*-electrons (i.e. electron gas not having degenerate eigenvalues for the one-electron wave-functions), does not become ferromagnetic at any density of the electron gas. Still dealing with electrons in one band only, his calculations could in principle be improved in essentially two respects, neither of which will lead to ferromagnetism. The first is that one could superimpose several determinantal wave-functions of somewhat smaller multiplicity than the one of highest multiplicity usually considered, and carry out a configuration interaction between these determinental wave-functions. As such a configuration interaction will have the effect of reducing the importance of exchange terms further, it can only reduce the chance of obtaining ferromagnetism. The second improvement would be to take into account the existence of atoms and to use Bloch functions instead of plane waves.

This would be essential in a theory which attributes ferromagnetism to an interatomic energy. If there is, however, no orbital degeneracy, and only one state is relevant, we cannot have triplet configurations.

So this modification of the theory cannot lead to ferromagnetism either.

From these considerations, it appears that, if we wish to use Pines' model for the study of ferromagnetism, we have to employ wave functions with orbital degeneracy, i.e. *p*, *d*, *f*, etc., functions. The supplementary condition in the Bohm and Pines theory will no longer be automatically satisfied, however.

Furthermore, in dealing with the short-range interaction we have to consider the multiplet problem. The simplest way to test the usefulness of the plasma oscillation approach and the validity of these considerations appears to be to determine the magnetic susceptibility at 0° K for a gas of 3*d*-electrons (e.g. using the Seitz method) and to see under which condition of band width and occupation of the band the paramagnetic susceptibility becomes infinite.

Mr. MacDonald. — It is perhaps of some interest to mention that the equilibrium spontaneous fluctuations (« noise ») that should be observed in an electron stream emitted from a cathode at temperature T, accelerated through a potential $\varnothing$, and then allowed to drift in zero field for a sufficiently long time, may be shown (1) to be given by :

$$\overline{\delta I_\omega^2} = \frac{kT}{2\varnothing}\left\{1+\frac{\omega^2}{\omega_p{}^2}\right\}\frac{eI}{\pi}\,\Delta\omega,$$

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(1) McDonald, D.K.C., *Phil. Mag.* **42**, 515 (1951).

where $\overline{\delta I_\omega^2}$ is the mean square current fluctuation in a band width $\Delta\omega$, I is the mean current flow, and e the electronic charge. For low frequencies ($\omega \ll \omega_p$) the noise is then reduced (by $\frac{kT}{2\Phi}$) below the value ($\frac{eI}{\pi}\,\Delta\omega$) characteristic of a purely random flow corresponding to the well-known phenomenon of « space charge reduction of noise » in thermionic valves, and this arises indeed (e.g. (1), (2)) from the coherent compensation by the space charge, or « plasma », of random irregularities in the electron-flow.

However, as the frequency of observation, ω, is increased towards the value $\frac{\omega}{e\pi} = \frac{v_0}{\lambda_D}$, where v_0 is the effective velocity of the beam ρ λ_D the Debye wavelength, the fluctuations then approach the value characteristics of a purely random current (i.e. having no compensation present).

Mr. Pippard. — Lindhard has shown by a classical calculation that there is a « natural » value for k_c such that plasma oscillations of greater k are highly damped.

How is such a consideration related to your choice of k_c for energetic reasons?

Mr. Pines. — I haven't seen Lindhard's calculation, so I cannot comment on his choice of k_c. As far as I know the « natural » choice of k_c for this problem would be the quantum analogue of the inverse Debye length, viz. $\sim(\omega_p/V_0)$. Incidentally, this too is a choice for « energetic » reasons, representing as it does a competition between the influence of potential and kinetic energy on the motion of the electron. This value of k_c is actually quite close to that I obtain by minimizing the system energy. My reason for carrying through the latter procedure is that I thereby obtain somewhat better system wave functions, and hence a more accurate value for the correlation energy and other metallic properties.

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(1) North, D.O., Et. al. *R.C.A. Rev.*, **4**, **5**, (1940).
(2) Schottky, W. & Spenke, E., *Wiss. veröff. Siem. Werk*, **16**-127 (1937).

Mr. Jones. — X-*ray Band widths of polyvalent metals.*

Dr. Pines(1) has shown, in his report, that there are several properties of the alkali metals which are not in accord with the predictions of a theory based on the Hartree-Fock treatment of the conduction electrons. One of the most striking failures of such a theory is in the interpretation of the observed soft X-ray emission bands from metals. Since there are good data on observed band widths for polyvalent as well as monovalent metals, it may not be without interest to consider these also in the light of the new theory. For divalent and trivalent metals, the Fermi surface must lie close to the Brillouin zone boundaries, and the electrons in this region at any rate, must presumably behave differently from free electrons. It is not, therefore, a foregone conclusion that the free electron plasma theory, which works so well for sodium, would also be applicable in such cases. The following figures, however, appear to show that, as far as band widths and cohesive energies are concerned, the polyvalent metals behave in much the same way as the alkalis.

For Beryllium, magnesium and aluminium Skinner(2) gives the following results for the soft X-ray emission bands :

	Be	Mg	Al
Observed band widths.	13.8	6.2	11.8 e.v.
Free electron widths	14.6	7.3	11.9 e.v.

For beryllium Herring and Hill (3) have calculated the Hartree eigenvalues of the electrons in the periodic field of the lattice. The energy interval of these eigenvalues between the highest occupied state and the lowest is a little over 12 e.v. No results are available for magnesium, but for aluminium some unpublished calculations by the cellular method, along the lines of the calculations which Howarth (4) has made for copper, show again that the overall band width is approximately the same as that given by the free electron model, although individual states differ appreciably from free electron states. From these and other examples, such as copper, the general conclusion appears to be that the band width, as measured by X-ray emission, agrees most closely with the Hartree band width which neglects exchange effects between the conduction electrons themselves.

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(1) Pines, D., The collective description of electron interactions in metals.

(2) Skinner, H.W.B., *Phil. Trans. Roy. Soc.*, Vol. 239, 95 (1940).

(3) Herring, C., and Hill, A.G., *Phys. Rev.*, 58, 132 (1940).

(4) Howarth D.J., *Proc. Roy. Soc.*, A 220, 513 (1953).

In the Hartree-Fock theory the effect of exchange is to lower the energy of the bottom of the band to a greater extent than the energy of the top. The excess is given by $a(p)$ where p is the momentum of an electron at the Fermi surface.

For the three metals mentioned these excess widths amount to 8.8 e.v. for beryllium, 6.3 e.v. for magnesium and 8.0 e.v. for aluminium. These values are free electron exchange energies; the true value are unknown, but Herring and Hill estimate that for beryllium the exchange energy is not more than 10 % different from free electron value.

It is clear therefore that the screening out of the exchange broadening must occur as effectively for a nearly filled band as it does for completely free electrons.

Some further information can be obtained by considering the cohesive energies of these metals. The observed values are given in the first line below :

	Be	Mg	Al
Observed cohesive energy . .	3.2	1.6	2.6 e.v. per atom
Exchange energy	13.2	9.3	17.9 e.v. per atom

Although calculations of the cohesive energy of these metals, along the lines of the Wigner-Seitz calculation for sodium are neither so accurate nor reliable as the work on sodium, they do lead to approximately the right values of the total energies. In these calculations the contributions from exchange are as shown in the second line above. Since the exchange energy is so much larger than the observed cohesive energy in all cases we see that any reduction of the exchange term must be rather accurately compensated by some effects. In other words, although the band must not be broadened by exchange effects its centre of gravity must be depressed by an amount which is closely equal to that given by the exchange interaction. It is the great beauty of the Bohm and Pines theory that in the free electron approximation there is just this compensation for the reduced exchange interaction by the long range correlation between all electrons. It appears that this result should also hold for metals with filled or almost filled bands.

(1) Raimes S., *Phil. Mag.*, 43, 327 (1952).

Mr. Van Vleck. — The contribution of Dr. Pines on correlation effects seems to me extremely valuable. When a theory is sufficiently important it is often instructive to derive the results in another way. It is therefore of some interest to examine how the type of approximation employed by Dr. Pines appears when presented in the language of a pure mathematician who is conversant only with the Ritz approximation in distinction from the physicist who utilizes the techniques of field theory, harmonic oscillators, canonical transformation with subsidiary conditions, and the like.

It is however doubtful whether without the physical insight provided by these techniques the requisite mathematical transformations would ever have been found.

Let us consider for simplicity the case that all the plasma oscillations are in the lowest state of zero point energy. Then the Pines procedure can be interpreted in a purely mathematical language as meaning that the dependent variable of the Schrödinger equation is changed from ψ to ψ' defined by :

$$\psi = \psi' \prod_{(k<k_c)} \exp \Big\} - a_k(\sum_i e^{-\overline{ik} \cdot \overline{r_i}})^2 \Big\{$$

Then if last term of Pines' eq. (13) is neglected, which he shows unimportant, ψ' satisfies a differential equation with a screened Coulomb force.

The value of a_k is determined by the requirement that the energy be a minimum.

I would like to ask the following questions :

How is the cancelling of the average potential of the electrons by the nuclei taken into account?

Mr. Pines. — Exclusion of the $k = 0$ from the Pines eq. (8).

Mr. Van Vleck. — In the Pines theory in the calculation of the cohesive energy should the Wigner correction be included for the fact that the nuclear spacings are discreet whereas the average electronic spaces are uniform?

Mr. Pines. — Yes.

Mr. Van Vleck. — In calculations with the cellular method is the Wigner addition of a potential $1/2\ e\rho r^2$ to include electron-electron forces in the unit cell a supplementary effect in addition to the correlation energy or is it redundant with the Pines approximation?

Mr. Pines. — It is redundant.

Mr. Mott. — I think that Dr. Pines is very much to be congratulated on giving the correct explanation of the interaction between two electrons in a metal. It has of course been known empirically for a long time that screening of this type had to be introduced; I think the first paper which uses it is one by Baber (1) on the term in the electrical resistance of metals, which varies as T^2, due to the interaction between electrons and positive holes in metals such as palladium and platinum where both are present. There is then the work of Heisenberg and his collaborators (2) who point out a breakdown of the second order perturbation theory, and work such as that of Landsberg (3) and Lee-Whiting (4) on the slowing down of electrons in metals when they have energy well above that of the Fermi limit.

I would like now to deal with Kittel's remark that it is surprising that the calculated and observed energies of the plasma agree so well for beryllium and aluminium, when one uses in the formulae the mass of a free electron and not the effective mass. I do not agree that this is surprising, for the following reasons.

May I first derive the frequency of the plasma vibration in a very simple way. Let there be N free electrons per unit volume in the metal. If at any point one of them is displaced a distance X, its equation of motion is :

$$m\ddot{X} = eE\ , \tag{1}$$

where E is the electric field. The field E is related to the polarisation P by the equation :

$$E + 4\pi P = 0\ .$$

---

(1) Baber W.G., *Proc. Roy. Soc.*, A **158** (1937), 383.
(2) Heisenberg W., 1947, *Z. Naturforsch*, *2a*, 185.
(3) Landsberg P.T., *Proc. Phys. Soc.*, A **62**, 806.
(4) Lee-Whiting G.E., *Proc. Roy. Soc.*, A **212**, (1952), 362.

If we suppose that all electrons are displaced by the same distance X at a given point, then :

$$\mathrm{P} = \mathrm{N}\, e\, \mathrm{X}\,.$$

Thus (1) becomes :

$$m\ddot{\mathrm{X}} + 4\pi \mathrm{N} e^2 \mathrm{X} = 0\,.$$

This is a simple harmonic equation of motion with characteristic frequency $\underline{\omega}_o$, where :

$$\underline{\omega}_o{}^2 = 4\pi \mathrm{N} e^2/m\,.$$

We expect that the quantised energies should be $(n + \frac{1}{2})\, \hbar\omega_o$, where n is an integer.

Now in a real metal, for simplicity a monovalent metal, one can describe each electron as a series of oscillations, each with frequency $\underline{\omega}_r$ and with oscillator strength f_r. Then we may write :

$$\Sigma f_r = 1 - f_o\,,$$

where f_o is the oscillator strength of frequency zero, so that $\mathrm{N}f_o$ is the effective number of free electrons. We may then treat the material as though it contained $\mathrm{N}_r = \mathrm{N}f_r$ bound electrons with frequency ω_r as well as $\mathrm{N}f_o$ free ones. The equation of motion of a bound electron is :

$$m\,(\ddot{\mathrm{X}}_r + \underline{\omega}_r{}^2\, \mathrm{X}_r) = e\mathrm{E}\,,$$

whence, if $\underline{\omega}$ is the frequency of vibration,

$$\begin{aligned} \mathrm{X}_r(-\,\underline{\omega}^2 + \omega_r{}^2) &= e\mathrm{E}/m \\ &= \frac{4\pi e^2}{m}\, \Sigma f \mathrm{X}_r\,. \end{aligned}$$

Multiplying by $f_r/(\underline{\omega}_r{}^2 - \underline{\omega}^2)$, summing over all r and dividing by $\Sigma f_r \mathrm{X}_r$, we find for the frequency ω of the free vibrations :

$$1 = \left[\frac{f_o}{\underline{\omega}^2} - \sum_i \frac{f_r}{\underline{\omega}_r{}^2 - \underline{\omega}^2}\right] \omega_r{}^2\,, \tag{2}$$

where as before $\underline{\omega}_o{}^2 = 4\pi \mathrm{N} e^2/m$. It will be seen that :

a) This equation has a solution for insulators as well as for metals. It seems therefore that plasma vibrations should be observed for insulators just as much as for metals, and it would be extremely interesting if experiments could be made for instance with thin films of metallic oxides;

b) For both, ω is the frequency for which the dielectric constant vanishes.

The validity of the model depends on the absorption due to single electron transitions not being too strong; i.e. if ω coincides with one of the values ω_0, there should be little damping here.

Turning now to the conduction electrons of metals such as Be or Al, it is probable that the quantum energies for electrons to jump into the next zone will be small compared with ω_r; thus formula (2) becomes :

$$1 = \omega_0^2 \left[\frac{1}{\omega^2} + \Sigma \frac{f_r \omega_r^2}{\omega^4} \right]$$

or :

$$\omega^2 \simeq \omega_0^2 \left[1 + \Sigma \frac{f_r \omega_r^2}{\omega_0^2} \right]$$

Assuming $\hbar\omega_r$ to be of the order 2 eV, we should thus expect ω to differ by not more than one per cent. from ω_0.

For the metals Cu, Ni, Ag, the energies required to excite perhaps the first two or three d electrons will be less than $\hbar\omega$; they must be included, which is certainly the origin of the large values of ω for these metals. Finally the agreement with experiment in the case of Al can perhaps be improved by including the influence of the L shell. This would modify formula (2), if we neglect the correction for bound electrons, in the sense :

$$\omega^2 = \omega_0^2 \left[1 - \frac{Z_L \omega_0^2}{\omega_L^2} \right]$$

where z is the number of electrons in the L shell and $\hbar\omega_L$ a mean excitation potential. If $\hbar\omega_L$ is of the order 100 eV or more and $z \sim 8$, a correction of the right order is introduced.

Mr. Fröhlich. — In insulators, the frequency of longitudinal waves can be easily derived in a macroscopical way if the wave length is sufficiently large.

Let P be the polarisation and ω_0 the frequency that would be obtained in the absence of an electronic field. Thus :

$$\ddot{P} + \omega_0^2 P = \frac{\varepsilon - 1}{4\pi} \omega_0^2 E$$

Where ε is the dielectric constant.

In an insulator for a longitudinal wave : $D = 0$ i.e. $E = -4\pi P$ and hence :

$$\ddot{P} = -\varepsilon\omega_o^2 P$$

According to Pines thus :

$$\varepsilon\omega_o^2 = \omega_o^2 + \omega p^2$$

i.e.

$$\varepsilon - 1 = \frac{\omega p^2}{\omega_o^2} = \frac{4\pi N e^2}{m\omega_o^2}$$

which is well known.

Mr. Pippard. — Prof. Mott derives the plasma frequencies by consideration of a plane slab. Whey should the shape of the body matter? An alternative derivation gives a shape-independent result. If we modify Ohm's law to allow for the electron inertia, introducing a relaxation time thus :

$$\underline{J} = \frac{1}{\tau}(\sigma\underline{E} - \underline{J}) \, ,$$

we may combine the equation with the Maxwell equations :

$$\text{div } \underline{J} = -\rho' \qquad\qquad \text{div } \underline{E} = 4\pi\rho$$

to yield an equation for the charge density :

$$\rho'' + \frac{1}{\tau}\rho'' + \frac{4\pi\sigma}{\tau}\rho = 0$$

This represents a plasma oscillation of frequency :

$$\omega_p{}^2 = \frac{4\pi\sigma}{\tau} = \frac{4\pi n e^2}{m}$$

damped by electron-lattice collisions.

Mr. Gorter. — It is probably accidental that the expression for $\lambda(= c/\omega_p)$ is equal to the penetration depth of a magnetic field into a system of free electrons which plays an important role in the theories of superconductivity.

An Extension of the Hartree-Fock Method to Include Correlation Effects

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In his introductory lecture, Professor Pines has pointed out that the ordinary Hartree-Fock scheme for treating electrons in metals shows an essential weakness in its neglect of the coulomb repulsion between the individual electrons and that it is highly important to try to include also this correlation effect in investigating many metal properties. The plasma model, developed by Bohm and Pines, seems to be one way out of this difficulty, but, in this remark, I would also like to report a recent attempt to include correlation effects in the independent electron model by a direct extension of the conventional Hartree-Fock scheme.

I. — EIGENVALUE PROBLEMS AND GENERALIZED DENSITY MATRICES

We would like to start by making a few comments about some simplifications of the standard method of treating a many-electron system. Let N be the number of electrons, and $X_i = (R_i, s_i)$ the space-spin co-ordinate of electron i. An arbitrary physical quantityΩ is then represented in the x-space by a hermitean operator Ω_{op}, which is symmetric in the N co-ordinates and expandable in the form :

$$\Omega_{op} = \Omega_{(o)} + \sum_{i} \Omega_i + \frac{1}{2!} \sum_{ij}{}' \Omega_{ij} + \frac{1}{3!} \sum_{ijk}{}' \Omega_{ijk} + \dots \qquad (1)$$

where $\Omega_{(o)}$ is a constant, Ω_i is a one - electron operator, Ω_{ij} is a two electron interaction operator, Ω_{ijk} is a three-electron interaction operator, etc. The necessity of considering also many-particle operators in the electron theory will be explained below. The basic problem is then to find the eigenvalues to :

$$\Omega_{op}\Psi = \omega\Psi$$

for antisymmetric wave functions $\Psi = \Psi(X_1 X_2 \ldots X_N)$, and this problem is usually solved by applying the variation principle :

$$\delta \langle \Omega_{op} \rangle_{Av} = 0$$

In evaluating the average value of Ω_{op}, some simplifications are now possible by introducing a generalized form of the conventional density matrices. Physically $|\Psi|^2$ gives the probability density in the N-electron x-space, and, by successively integrating this quantity, we obtain the series of conventional density matrices ending with :

$$\Gamma(X_1, X_2) = \binom{N}{2}\int|\Psi|^2(dx'_{12}) \qquad (4)$$

= density matrix of second order, giving probability density for finding one particle at point X_1 and another at point X_2, all the others having arbitrary co-ordinates,

$$\Gamma(X_1) = N\int|\Psi|^2(dx'_1) \qquad (5)$$

= density matrix of first order, giving probability density for finding one particle at point X_1, all the others having arbitrary co-ordinates. Here the symbol $dx'_{12..p}$ indicates that we should integrate (sum) over all co-ordinates X_i except $X_1, X_2 \ldots X_p$. These conventional density matrices may be used for computing average values of quantities Ω which are *diagonal* in the x-space, and, in deriving them, we have utilized only the absolute value $|\Psi|$ of the wave function.

The *complex* wave function Ψ describes, however, the entire physical situation and not only the situation in the x-space but even the situations in the complementary spaces, according to transformation theory. In order to calculate the average value of an arbitrary physical quantity Ω_{op}, we must therefore try to preserve this complex character also in the density matrices. This can be done by doubling the number of their co-ordinates and defining the new matrices by the relations :

$$\left.\begin{aligned}
&\gamma(X'_1|X_1) = N\int\Psi^*(1'2\,3\,\ldots\,N)\Psi(1\,2\,3\,\ldots\,N)(dx'_1)\,,\\
&\Gamma(X'_1X'_2|X_1X_2) = \tbinom{N}{2}\int\Psi^*(1'2'3\,\ldots\,N)\Psi(1\,2\,3\,\ldots\,N)(dx'_{12}),\\
&\Gamma(X'_1X'_2\,\ldots\,X'_p|X_1X_2\,\ldots\,X_p)\\
&\qquad = \tbinom{N}{p}\int\Psi^*(1'2'\,\ldots\,p'\,\ldots\,N)\Psi(1\,2\,\ldots\,p\,\ldots\,N)(dx'_{12-p}),\\
&\Gamma(X'_1X'_2\,\ldots\,X_N{}'|X_1X_2\,\ldots\,X_N) = \Psi^*(1'2'\,\ldots\,N')\Psi(1\,2\,\ldots N),
\end{aligned}\right\}\tag{6}$$

with the connection formula :

$$\begin{aligned}&\Gamma^{(p-1)}(X'_1X'_2\,\ldots\,X'_{p-1}|X_1X_2\,\ldots\,X_{p-1})\\ &= \frac{p}{N+1-p}\int\Gamma^{(p)}(X'_1X'_2\,\ldots\,X'_{p-1}X'_p|X_1X_2\,\ldots\,X_{p-1}X_p)\,dx_p\,.\end{aligned}\tag{7}$$

These generalized density matrices are *hermitean* with respect to the two sets of indices and *antisymmetric* within each set, e.g. :

$$\begin{aligned}\Gamma(X_1X_2|X'_1X'_2) &= \Gamma^*(X'_1X'_2|X_1X_2)\,,\\ \Gamma(X'_1X'_2|X_2X_1) &= -\Gamma(X'_1X'_2|X_1X_2)\,.\end{aligned}\tag{8}$$

Due to the antisymmetry property, every matrix having at least two indices within the same equal will vanish identically, e.g. :

$$\Gamma(X'_1X'_2|X_1X_2) = 0\,,\ \text{ for } X'_1 = X'_2 \text{ or } X_1 = X_2\,,\tag{9}$$

and the quantity $\Gamma(X_1X_1|X_1X_1)$ is therefore vanishing of the second order, giving rise to the well-know « Fermi hole ».

The generalized density matrices may now be used for evaluating expectation values, and, by using (1) and (6), we obtain the basic formula :

$$\begin{aligned}\langle\Omega_{op}\rangle_{Av} = \int\Psi^*\Omega_{op}\Psi(dx) &= \Omega_{(o)} + \int\Omega_1\gamma(X'_1|X_1)dx_1\\ &+ \int\Omega_{12}\Gamma(X'_1X'_2|X_1X_2)dx_1\,dx_2\\ &+ \int\Omega_{123}\Gamma(X'_1X'_2X'_3|X_1X_2X_3)\,dx_1\,dx_2\,dx_3 + \ldots\,,\end{aligned}\tag{10}$$

where we also have introduced the convention that every operator Ω_{ij} should work on X_i and X_j but *not* on the primed co-ordinates X'_i and X'_j and that, after the operations have been carried out, we should put $X'_i = X_i$, $X'_j = X_j$, etc.

We note that, for the calculation of expectation values, we do not need the knowledge of the entire wave function but only the knowledge of the generalized density matrix of the same order as the highest many-particle operator in the physical quantity under consideration.

As an example, we will consider the unrelativistic Hamiltonian of a system of N electrons moving in the field of a frame-work of fixed nuclei :

$$\mathscr{H}_{op} = \frac{e^2}{2} \sum_{gh} Z_g Z_h / r_{gh} + \Sigma \left\{ P_1^2/2m - e^2 \sum_{g} Z_g / r_{ig} \right\} + 1 \sum_{ij}{}' e^2/r_{ij} , \quad (11)$$

where Z_g is the atomic number of the nucleus at the position g. For the expectation value of the energy, we then obtain :

$$\begin{aligned} \langle \mathscr{H}_{op} \rangle_{AV} = {} & \frac{e^2}{2} \sum_{gh} Z_g Z_h / r_{gh} + \frac{1}{2m} \int P_1^2 \gamma(X'_1 | X_1) \, dx_1 \\ & - e^2 \sum_{g} Z_g \int \frac{\gamma(X_1)}{r_{ig}} \, dx_1 + e^2 \int \frac{\Gamma(X_1 X_2)}{r_{12}} \, dx_1 dx_2 , \end{aligned} \quad (12)$$

with a simple interpretation of each term; we note that the generalized form of the first-order density matrix is used in evaluating the kinetic energy of the electrons. Neglecting the zero-point motion of the nuclei, we have here considered them as classical particles, but, by introducing generalized density matrices for several kinds of particles, the quantum-mechanical motion of the nuclei may be easily formally included.

Other quantities characteristic for the electronic system are spin S (measured in units of $\hbar$) and the electric moment D, defined by :

$$\begin{aligned} S^2 = \sum_{ij} S_i \, . \, S_j & = - N(N-4)/4 + \sum_{ij}{}' (1 + \sigma_i \, . \, \sigma_j)/4 \\ & = - N(N-4)/4 + \tfrac{1}{2} \sum_{ij}{}' P_{ij}^s , \end{aligned} \quad (13)$$

$$D = \sum_{i} e R_i , \quad (14)$$

where, according to Dirac, $P_{ij}{}^s$ is the operator for interchanging the spin co-ordinates s_i and s_j . According to (10), their expectation values are then given by :

$$\langle S^2 \rangle_{AV} = - N(N-4)/4 + \int \Gamma(R_1 s_1 , R_2 s_2 | R_1 s_2 , R_2 s_1) \, dx_1 \, dx_2 , \quad (15)$$

$$\langle D \rangle_{AV} = e \int R_1 \gamma(X_1) \, dx_1 . \quad (16)$$

II. — THE CONVENTIONAL HARTREE-FOCK APPROXIMATION

We have seen above that the expectation value of a physical quantity is determined by the generalized density matrix of the same order as the highest many-particle operator entering in the quantity, but otherwise we cannot expect that the lower order density matrices should characterize the entire physical situation. It is therefore somewhat surprising to find that, in the conventional Hartree-Fock approximation, the first-order density matrix :

$$\gamma(X'_1|X_1) \tag{17}$$

describes fully the state under consideration.

In the Hartree-Fock scheme, the total wave function is approximated by a single Slater determinant :

$$\Psi = (N!)^{-\frac{1}{2}} \det \{\psi_k(X_l)\} , \tag{18}$$

where ψ_k ($k = 1, 2, \ldots N$) is a set of one-electron functions or spin-orbitals, which must not necessarily be orthonormal :

$$\int \psi^*_k(X_1)\psi_l(X_1)dx_1 = d_{kl} . \tag{19}$$

If D is the matrix formed by these non-orthogonality integrals, D_1 its determinant ($\pm$ 0), one easily finds :

$$\int |\Psi|^2(dx) = \det \{d_{kl}\} = D_1, \tag{20}$$

giving the normalization integral necessary for our calculations. The determinant of the inverse matrix D^{-1} is further D_1^{-1}.

The set (ψ_1 , ψ_2 , ... ψ_n) may be considered as a *vector* in a specific non-orthogonal representation of the Hilbert space, and we note that a linear transformation of this set changes the determinant (18) only by a constant factor and leaves all density matrices (6) invariant. The physical situation can therefore depend only on the invariant « length » of this vector, defined by :

$$\rho(X_1 , X_2) = \sum_{kl} \psi^*_k(X_1)\psi_l(X_2)d^{-1}_{lk} . \tag{21}$$

A quantity of this type was first introduced by Fock (1) and investigated in detail by Dirac (2) for the orthogonal case ($d_{kl} = \delta_{kl}$) . The matrix ρ fulfills the relations :

$$\rho^2 = \rho , Tr(\rho) = N , \tag{22}$$

where Tr (= Trace) indicates formation of diagonal sum.

Let us now evaluate the generalized density matrices corresponding to the normalized wave function (18). For $p = \mathrm{N}$, we obtain :

$$
\begin{aligned}
&\Gamma(X'_1 X'_2 \ldots\ldots X'_N | X_1 X_2 \ldots\ldots X_N) \\
&= (N!)^{-1} \det \left| \psi_k^*(X'_i) \right| \det \left| \psi_l(X_j) \right| \det \left| d_{ek}^{1-} \right| \\
&= (N!)^{-1} \det \left| \sum_{kl} \psi_k^*(X'_i)\, \psi_l(X_j)\, d_{ek}^{-1} \right| \\
&= (N!)^{-1} \det \left| \rho(X'_i, X_j) \right| . \qquad (23)
\end{aligned}
$$

Using (7) and (22), we find by successive integrations :

$$\Gamma(X'_1 X'_2 \ldots\ldots X'_p | X_1 X_2 \ldots\ldots X_p) = (p!)^{-1} \det \left| \rho(X'_i, X_j) \right| \text{ (order } p\text{)}, \quad (24)$$

ending with :

$$\Gamma(X'_1 X'_2 | X_1 X_2) = \frac{1}{2!} \begin{vmatrix} \rho(X'_1, X_1) & \rho(X'_1, X_2) \\ \rho(X'_2, X_1) & \rho(X'_2 X_2) \end{vmatrix} , \qquad (25)$$

$$\gamma(X'_1 | X_1) = \rho(X'_1, X_1) .$$

If the total wave function is approximated by a single Slater determinant, all the generalized density matrices and hence the entire physical situation is determined by the first-order density matrix $\gamma(X'_1|X_1)$, which is identical with the fundamental invariant (21). We observe further that the knowledge of the individual spin-orbitals ψ_k in (18) is completely unnecessary.

In another paper (3) treating complete configurational interaction, we have shown that the relation $\Gamma^2 = \Gamma$ is not only a necessary but also sufficient condition for the possibility of expressing the total wave function as a single Slater determinant. The matrix Γ has then only the eigenvalues 0 or 1, indicating that there exist N « natural spin-orbitals » which are all fully occupied.

In the Hartree-Fock approximation, the basic formula (10) now takes the form :

$$
\begin{aligned}
\langle \Omega_{op} \rangle_{Av} = \Omega_{(o)} &+ \int \Omega_1\, \gamma(X'_1|X_1) dx_1 \\
&+ \frac{1}{2!} \int \Omega_{12} \begin{vmatrix} \gamma(X'_1|X_1) & \gamma(X'_1|X_2) \\ \gamma(X'_2|X_1) & \gamma(X'_2|X_2) \end{vmatrix} dx_1 dx_2 \qquad (26) \\
&+ \frac{1}{3!} \int \Omega_{123} \begin{vmatrix} \gamma(X'_1|X_1) & \gamma(X'_1|X_2) & \gamma(X'_1|X_3) \\ \gamma(X'_2|X_1) & \gamma(X'_2|X_2) & \gamma(X'_2|X_3) \\ \gamma(X'_3|X^1) & \gamma(X'_3|X_2) & \gamma(X'_3|X_3) \end{vmatrix} dx_1 dx_2 dx_3 + \ldots\ldots
\end{aligned}
$$

In order to find the best density $\gamma(X'_1|X_1)$ for approximating an *eigenstate* to the physical quantity represented by the operator (1), we will now apply the variation principle (3) directly to the quantity Γ. A few words may here be said about the auxiliary conditions. Since Γ fulfills the relation $\Gamma^2 = \Gamma$, it may, according to von Neumann (4), be considered as a « projection operator » defining a particular subspace of the Hilbert space. If Λ is an arbitrary hermitean matrix, its *orthogonal projection* within this subspace is given by :

$$\lambda = \Gamma\Lambda\Gamma\,. \tag{27}$$

From $\Gamma^2 = \Gamma$ we obtain directly $\Gamma\,.\,\delta\Gamma\,.\,\Gamma = 0$, telling us that $\delta\Gamma$ is without orthogonal projection within the sub-space defined by Γ. The « scalar product » of $\delta\Gamma$ and Λ must then be zero :

$$\mathrm{Tr}(\delta\Gamma\,.\,\Lambda) = 0\,,$$

which gives the necessary auxiliary condition.

By varying Γ and using (3), (26) and (28), we obtain the condition :

$$\Omega_{eff}(1)\gamma(X_2|X_1) = \lambda(X_2|X_1)\,. \tag{29}$$

Here the *effective* one-electron operator $\Omega_{eff}(1)$ is defined by :

$$\begin{aligned}\Omega_{eff}(1) = \Omega_1 &+ \int\Omega_{12}\begin{vmatrix}1 & P_{12}\\ \gamma(X'_2|X_1) & \gamma(X'_2|X_2)\end{vmatrix}dx_2\\ &+ \frac{1}{2!}\int\Omega_{123}\begin{vmatrix}1 & P_{12} & P_{13}\\ \gamma(X'_2|X_1) & \gamma(X'_2|X_2) & \gamma(X'_2|X_3)\\ \gamma(X'_3|X_1) & \gamma(X'_3|X_2) & \gamma(X'_3|X_3)\end{vmatrix}dx_2dx_3 + \ldots.,\end{aligned} \tag{30}$$

where P_{12} is the ordinary permutation operator for interchanging the co-ordinates X_1 and X_2, etc., to be written to the right of the Γ-factors in expanding the determinants. One can also write :

$$\begin{aligned}\Omega_{eff}(1) &= \Omega_1 + V_{op}(1)\,,\\ V_{op}(1) &= \int\Omega_{12}(1-P_{12})\gamma(X'_2|X_2)dx_2\\ &\quad+\frac{1}{2!}\Big|\Omega_{123}(1-P_{12}-P_{13})\begin{vmatrix}\gamma(X'_2|X_2) & \gamma(X'_2|X_3)\\ \gamma(X'_3|X_2) & \gamma(X'_3|X_3)\end{vmatrix}dx_2dx_3 + \ldots.,\end{aligned} \tag{31}$$

where $V_{op}(1)$ gives the *average* field on one electron due to its interaction with the total electronic cloud.

By choosing an orthogonal representation in which the matrix $\lambda(X_2|X_1)$ takes diagonal form, one can easily show that the condition

(29) is equivalent to the ordinary Hartree-Fock equations for the individual spin-orbitals. However, the condition (29) may also be used as an independent basis for the whole theory.

It may be shown that Koopman's theorem (5) may be generalized to Hamiltonians of the form (1) containing also many-electron interactions, and the spin-orbital energies ε_k being the eigenvalues of the effective Hamiltonian H_{eff} (1) may therefore be interpreted as the negative ionization potentials. For the excitation of a single electron we have further, in a first approximation, the formula :

$$\langle \overline{\mathscr{H}}_{op} \rangle_{AV} - \langle \mathscr{H}_{op} \rangle_{AV} = \overline{\varepsilon}_j - \varepsilon_1 , \tag{32}$$

where $\overline{\varepsilon}_j$ is an eigenvalue to the effective Hamiltonian $\overline{H}_{eff}$ (1) associated with the excited state, and ε_i is an eigenvalue to the effective Hamiltonian H_{eff} (1) associated with the ground state. More details have been given in another paper (3).

III. — EXTENSION OF THE HARTREE-FOCK SCHEME TO DEGENERATE SYSTEMS

Before discussing the correlation problem, we will investigate how the Hartree-Fock scheme should be applied to a system which shows spin or orbital degeneracies. In this case, a solution based on a *single* Slater determinant represents usually a rather poor approximation, and it is therefore highly desirable to improve this approach.

For the sake of simplicity, let us just consider the eigenvalue problem :

$$\mathscr{H}_{op}\Psi = E\Psi , \tag{33}$$

where $\mathscr{H}_{op}$ is the basic Hamiltonian for our N-electron system, expandable in the form :

$$\mathscr{H}_{op} + \mathscr{H}_{(o)} + \sum_i \mathscr{H}_i + \frac{1}{2} \sum_{ij} \mathscr{H}_{ij} , \tag{34}$$

and containing only zero-, one-, and two-electron operators. Let the degeneracy be classified by the hermitean operator α_{op} commuting with $\mathscr{H}_{op}$ and having the eigenvalues $\alpha_1 , \alpha_2 , ... \alpha_n$, which are assumed to be known. It is then possible to expand an eigenfunction to $\mathscr{H}_{op}$ for a degenerate level into eigenfunctions to α_{op} :

$$\Psi = \sum_{k} \Psi_k \, , \tag{35}$$

Since we have $(\alpha_{op} - \alpha_k)\Psi_k \equiv 0$, a factor $(\alpha_{op} - \alpha_k)$ will anihilate the term Ψ_k in this expansion. The operator

$$O_p = \prod_{k \pm p} (\alpha_{op} - \alpha_k)/(\alpha_p - \alpha_k) \tag{36}$$

will therefore annihilate all terms except the one for $k = p$, and we obtain :

$$O_p\Psi = \Psi_p \, , \tag{37}$$

which means that O_p takes out the « orthogonal projection» of Ψ on the eigenstate of α_{op} having the eigenvalue α_p . We have further $(\alpha_{op} - \alpha_p)O_p \equiv 0$ and :

$$O_p{}^2 = O_p \, , \tag{38}$$

showing that O_p is really a « projection operator » in the sense of v. Neumann (4).

It seems now natural to try to extend the conventional Hartree-Fock scheme by approximating the eigenfunction Ψ to (33) not by a single determinant but by a *projection of such a determinant* corresponding to a definite eigenvalue of α_{op} :

$$\begin{cases} \Psi = O\Psi_o \\ \Psi_o \qquad\qquad = \text{single determinant.} \end{cases} \tag{39}$$

Forming the average energy, we obtain :

$$\begin{aligned} \int\Psi^* \mathscr{H}_{op}\Psi(dx) &= \int\Psi_o{}^*(O^{+}\mathscr{H}_{op}\, O)\Psi_o(dx) \\ &= \int\Psi_o{}^*(\mathscr{H}_{op}\, O)\Psi_o(dx), \end{aligned} \tag{40}$$

$$\int\Psi^*\Psi(dx) = \int\Psi_o{}^*(O^{+}O)\Psi_o(dx) = \int\Psi_o{}^*O\Psi_o(dx) \, . \tag{41}$$

This means that we obtain the same average energy as for a *single* determinant Ψ_o and a « composite Hamiltonian » of the form :

$$\Omega_{op} = \mathscr{H}_{op}O \, , \tag{42}$$

where we also have to take the normalization into proper account. There seems to be two equivalent ways of describing the degenerate state : either by a simple Hamiltonian $\mathscr{H}_{op}$ and a complicated wave function Ψ , or by a simple wave function Ψ_o and a composite

Hamiltonian Ω_{op}. Compare the two equivalent ways of describing time-dependence in the Schrödinger and Heisenberg pictures, respectively. The composite Hamiltonian (42) may now be expanded in the form (1), and we note that it usually contains many-electron interaction operators of high orders. The wave function Ψ'_o is the simplest antisymmetric wave function based on the idea that the particles are moving independently of each other, but, due to the degeneracy, there are now new couplings between the electrons in the form of many-body forces. The physical situation is entirely described by the first-order density $\gamma_o(X'_1|X_1)$, which is determined by the Hartree-Fock condition (29) with an effective Hamiltonian given by (30) and (31). However, even the normalization condition (41) must now be taken into account.

The main importance of this scheme depends on the fact that it preserves some of the simplicity and physical visuality which is characteristic for the ordinary Hartree-Fock approximation.

IV. — CORRELATION EFFECTS

The basic idea of the « independent-particle model » is that, in a first approximation, one can neglect the mutual interaction between the N-electrons in constructing the total wave function and assume that the electrons are moving independently of each other in a set of N-spin-orbitals $\psi_k(X)$. The total wave function is then a simple product. However, between the electrons i and j there is in reality a repulsive coulomb potential $\mathscr{H}_{ij} = e^2/r_{ij}$ which, particularly for small distances $r_{ij} \gtrsim 0$, becomes tremendously large. This repulsive potential tries naturally to keep the electrons apart, and, since this « correlation » between the movements of the particles is entirely neglected in forming the product wave function, the corresponding total energy is affected by an error usually called the « correlation energy ».

The situation is somewhat chaged by the antisymmetrization procedure, which transforms the product into the determinant (18). The corresponding second-order density matrix $\Gamma(X'_1X'_2|X_1X_2)$ is now antisymmetric in each set of its indices, and, for the diagonal element, we obtain in particular :

$$\Gamma(X_1X_2) = 0 \text{ for } X_1 = X_2, \qquad (43)$$

showing that the probability density for two particles with the same to be in the same place is zero of at least the second order; cf. (9). The antisymmetry requirement thus acts as if there would be a rather strong repulsion between electrons with the same spin at small distances, and this consequence of the Pauli principle automatically diminishes the error due to the neglect of the coulomb correlation. The exchange energy will therefore take care of a rather large part of the correlation energy, referring to particles with parallel spins.

The main problem is evidently to take the correlation between electrons having different spins into proper account. On this point I would like to stress that the Hartree-Fock scheme in its conventional form does not take full advantage of the degrees of freedom for the electronic motion, provided by the independent-particle model. In constructing e.g. the singlet ground state of an electronic system, one starts usually from the assumption of the existence of a certain number of *orbitals* in ordinary space, which are then assumed to be occupied each by two electrons having opposite spins; the corresponding determinant (18) represents then really a singlet state. In treating the atoms of the periodic system, this assumption was natural for historical reasons as a consequence of the Pauli-principle in its original formulation, but, from the point of view of correlation, it is energetically rather unfavourable since it compels electrons having opposite spins to be in the same orbital i.e. in the same places in ordinary space leading to a high coulomb repulsion.

One way of improving the conventional scheme would be to make us free from the idea of « doubly filled orbitals », and to let the best *spin-orbitals* be determined by the variation principle (^{3}). The possibility of having different orbitals for different spins was first mentioned by Hartree and Hartree (^{6}), but it was never used by them. The importance of this possibility for the description of magnetic properties has recently been stressed by Slater (^{7}), and self-consistent-field calculations for atoms on this basis have actualy been carried out by Pratt. At the Shelter Island Conference in 1951, Mulliken (^{8}) pointed out the importance of finding a generalization of the self-consistent-field procedure from « closed-shell » to « open-shell » configurations with the number of orbitals doubled.

The new theory can be developed without any additional assumptions, and one has only to let the N undetermined spin-orbitals $\psi_k(x)$ be occupied each by *one* electron. The Slater determinant (18) then does not usually represent a pure spin state, but the total wave function may now simply be formed by taking a *projection* of this determinant giving the spin state of required multiplicity. The spin degeneracy problem may therefore be solved by the procedure outlined in Section III.

Measuring the spin in units of $\hbar$, we know that S^2 has the eigenvalues $l(l+1)$, where $l = N/2$, $N/2 - 1$, ... 0 or 1/2, depending on whether the number N of electrons is even or odd. According to (36), the projection operator for selecting a state of multiplicity $(2l+1)$ is :

$$^{(2l+1)}O = \prod_{k \pm l} \{ S^2 - k(k+1) \} / \{ l(l+1) - k(k+1) \}, \quad (44)$$

and the basic wave function takes then the form :

$$^{(2l+1)}\Psi = (N!)^{-\frac{1}{2}}\, {}^{(2l+1)}O \det \{ \psi_k(X_i) \}. \quad (45)$$

The physical situation may be described by a first-order density matrix $\gamma_0(X'_1|X_1)$, and this matrix (or the individual spin-orbitals) may be determined by the variation principle (3), leading to a self-consistent-field problem. Instead of getting doubly filled orbitals, we will now find that, due to the coulomb repulsion, there is a tendency for electrons with opposite spins to try to avoid each other by having their orbitals localized in different parts of the ordinary space·

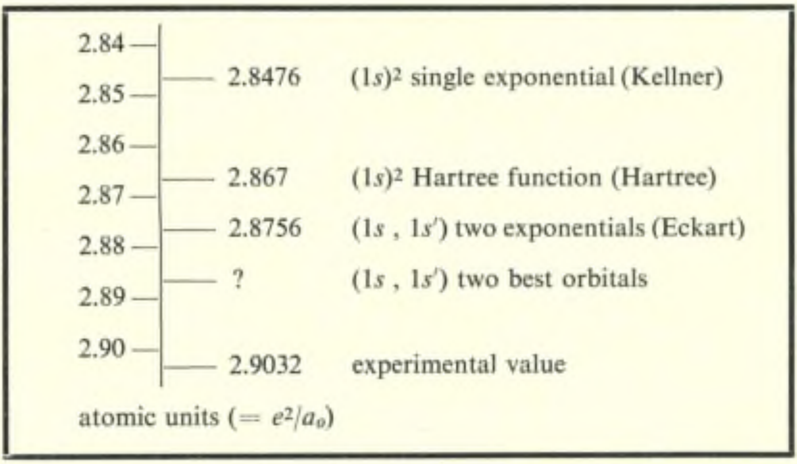

Fig. 1. — *Helium atom, ground state.*

In order to get familiar with the method, let us start by looking at some atomic and molecular applications. The helium atom in its ground state has conventionally the configuration $(1s)^2$, but it turns out that a configuration of the type $(1s\ ,\ 1s')$ will be energetically lower. Eckart's result with two simple exponentials showed a lower energy than Hartree's result with the best $1s$-orbital, and calculations going on at present indicate that further improvements of the $(1s\ ,\ 1s')$ -result are possible. The spin-orbitals obtained in this connection are characterized by the fact that they have their maxima in different regions of space and that one of the electrons tends to keep the other electron outside itself. In addition to this « in-out effect », there is also an « angular effect », which may be included by using angle-dependent spin-orbitals and a projection operator for creating an S-state, constructed according to (36).

Next, we will consider the diatomic molecules with two electrons, as the hydrogen molecule or the π-electron problem of ethylene. Due to the coulomb repulsion, there will now be an « alternant effect », trying to keep the two electrons on separate atoms (9), and an « in-out effect », trying to keep one electron outside the other, when they happen to be on the same atom. As far as we know, the « in-out effect » has not previously been used in the theory of molecules or crystals. It seems to be rather important, since the coulomb integrals associated with two electrons concentrated in the *same* orbital on one atom are certainly too large, due to

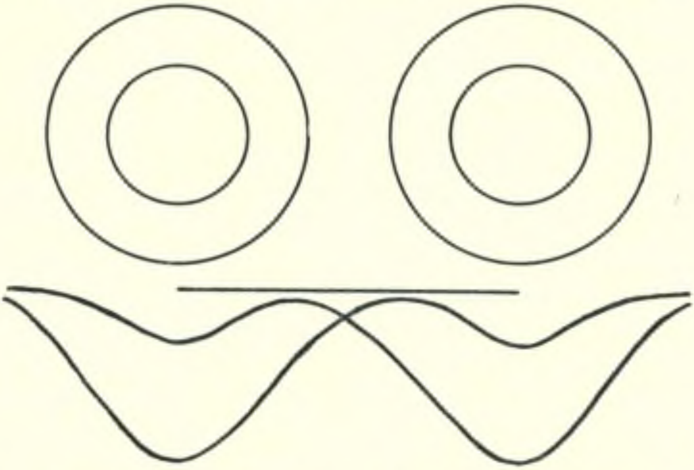

Fig. 2. — *Two orbitals showing " alternant effect " and " in-out effect " for a two-electron problem in a diatomic molecule.*

the neglect of the coulomb correlation. The problem of these «ionic» coulomb integrals has been particularly emphasized by Moffitt (10) in treating the oxygen molecule and by Pariser and Parr (11) in investigating some conjugated organic compounds, and these authors have proposed that the values of the ionic integrals should be corrected by comparison experimental data. Spouer (12) and the writer found similarly that, in a π-electron theory for ethylene based on the atomic Hartree-Fock functions for carbon, the singlet-triplet separation comes out much too large, and that the error could be localized mainly to the ionic $(\pi\pi/\pi\pi)$-integral. By introducing the « in-out effect », the value of the coulomb integrals will now be essentially diminished, and, by using the variation principle, the correction may be performed purely theoretically without the aid of empirical data. The effect is probably just as important in metals.

After these preparations, let us now consider the electrons in metals. By investigating the cohesive energy, we can get an idea of the strength of our extension of the Hartree-Fock scheme for treating the coulomb repulsion, since, as Professor Pines pointed out, the energy calculations are very sensitive to correlation effects. It is characteristic for a « naive » metal theory, where the total wave functions is approximated by a *single* Slater determinant built up of Bloch orbitals doubly filled within a particular Fermi surface, that the curve for the cohesive energy as a function of the lattice parameter shows an entirely wrong asymptotic behaviour for separated atoms. The model permits electrons of opposite spins to accummulate on the same atom and give rise to negative and positive ions, having higher energy together than the dissociation products occurring in nature, where the coulomb repulsion prevents the excessive formation of ions. Making us free from the idea of doubly-filled orbitals, we may determine the new spin-orbitals by applying the variation principle. We can get a connection with the conventional theory by developing the new spin-orbitals in the system of ordinary and virtual Bloch spin-orbitals; the expansion coefficients may be determined by a self-consistent-field procedure (3).

The resulting wave function will leave the electrons distributed on both sides of the conventional Fermi surface with some electrons excited above the surface by the influence of the coulomb repulsion. This method seems to be able to take so much of the correlation

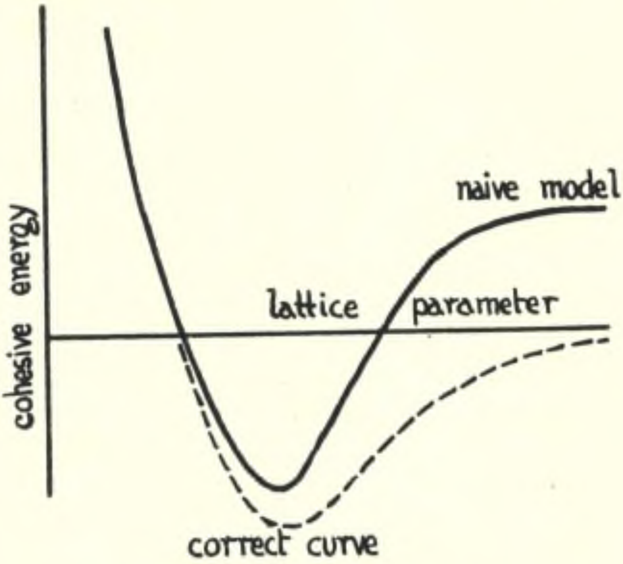

Fig. 3. — *Cohesive energy of a metal.*

into account that the energy curve will get at least a correct asymptotic behaviour.

As an example, we will consider an *alternant system* (13), as a body-centered cubic crystal, which is constitued by two equivalent interpenetrating subsystems, I and II.

It is a characteristic feature of such a system that the conventional Bloch spin-orbitals occur in pairs, j' and j'', with orbital energies ε_j' and ε_j'' belonging to symmetric places in the lower and the upper half of the energy band, respectively. The excited orbital Ψ_j'' may be obtained from the lower orbital Ψ_j' by changing the sign of the co-efficients of the atomic orbitals Φ_μ of one of the subsystems, let us say II :

$$\begin{aligned} \Psi_j' &= \sum_{\mu}^{\mathrm{I}} \Phi_\mu c_{\mu j} + \sum_{\mu}^{\mathrm{II}} \Phi_\mu c_{\mu j}\,, \\ \Psi_j'' &= \sum_{\mu}^{\mathrm{I}} \Phi_\mu c_{\mu j} - \sum_{\mu}^{\mathrm{II}} \Phi_\mu c_{\mu j}\,. \end{aligned} \tag{46}$$

The best new spin-orbitals should be obtained by expanding them in the total system formed from all orbitals Ψ_j in (47), but, in a first approximation, we will be satisfied by forming the combinations :

$$\begin{aligned} \Psi_{j\text{I}} &= a\Psi_j' + b\Psi_j'' = (a+b)\overset{\text{I}}{\underset{\mu}{\Sigma}}\Phi_\mu c_{\mu j} + (a-b)\overset{\text{II}}{\underset{\mu}{\Sigma}}\Phi_\mu c_{\mu j} \, , \\ \Psi_{j\text{II}} &= a\Psi_j' - b\Psi_j'' = (a-b)\overset{\text{I}}{\underset{\mu}{\Sigma}}\Phi_\mu c_{\mu j} + (a+b)\overset{\text{II}}{\underset{\mu}{\Sigma}}\Phi_\mu c_{\mu j} \, . \end{aligned} \tag{47}$$

Since the normalization condition for orthonormalized atomic orbitals Φ_μ takes the form $a^2 + b^2 = 1$, we may put $a = \cos\theta$ and $b = \sin\theta$ and describe the influence of the coulomb repulsion by an angle θ ; we note the following special cases :

$\theta = 0$: ordinary bonding Bloch orbitals
$\theta = 45^\circ$: purely alternant orbitals (48)
$\theta = 90^\circ$: ordinary antibonding Bloch orbitals.

For $0 < \theta < 90^\circ$ the orbitals Ψ_{j_I} are semi-localized on system I and the orbitals Ψ_{j_II} on system II, and these « alternant » orbitals have therefore the property desired here. As a simple example, we may consider the lowest orbitals for a linear chain, as shown in figure 4.

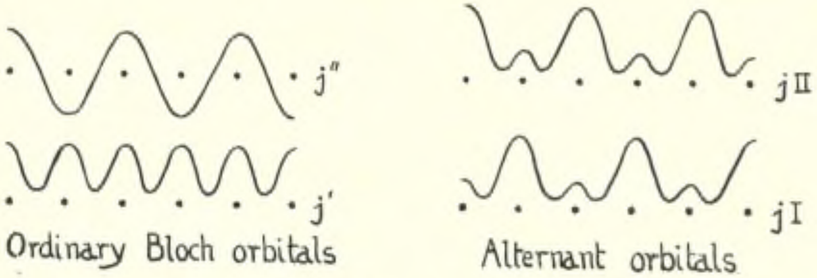

Fig. 4.

Alternant orbitals for different values of *j* are always orthogonal, whereas orbitals belonging to the same *j* are usually non-orthogonal :

$$\int \Psi_{j_\text{I}} \Psi_{j_\text{II}} dx = \cos 2\theta \, . \tag{49}$$

For the sake of simplicity, we will assume that the number of electrons equals the number of alternant orbitals available, and, in order to obtain as low repulsion energy as possible, we will then fill each orbital of type I by an electron with plus spin and each orbital of type II by an electron with minus spin, in this way trying to localize electrons of opposite spins in different regions of ordinary space; the corresponding Slater determinant will be denoted by Ψ_o. If, for separated atoms, we let θ tend to the value $\theta = 45^{\circ}$, the construction of the wave function Ψ_o prevents the accummulation of electrons of opposite spins on the same atom, and the corresponding energy curve shows then a correct asymptotic behaviour. We have now only to check that the same holds for the various pure spin state functions, obtained by taking projections (39) of Ψ_o. For $\theta = 45^{\circ}$, the discussion is simplified by the fact that *all* the alternant orbitals become strictly orthogonal, cf. (49), and the energy of the state of multiplicity $(2l + 1)$ is then simply given by the formula :

$$\langle \mathscr{H}_{op} \rangle_{AV} = \int \Psi_o^* \mathscr{H}_{op} \Psi_o (dx) - \frac{l(l+1) - n}{2n_2} \sum_{j,k} (j\mathrm{I}, k\mathrm{II} | \mathscr{H}_{12} | k\mathrm{II}, j\mathrm{I}). \quad (50)$$

Since the exchange integrals in the last sum tend to zero for $\theta = 45^{\circ}$ and separated atoms, our theorem is proved.

For $\theta = 0$ and $l = 0$, the wave function under consideration reduces to the well-known single determinant having all the bonding orbitals doubly occupied. This means that, by varying θ, we may obtain a depression of the entire energy curve of the « naive » theory, and, in particular cases, the improvement of the energy minimum may be appreciable. In this way, part of what is conventionally called correlation energy for electrons of opposite spins will be taken into account in a very simple way, and θ could therefore be called the « correlation angle ». In forming the energy in the general case $(\theta \pm 45^{\circ})$, one has to note the existence of the non-orthogonality integral (49).

Numerical results for metals are not yet available, but calculations on the free-electron model as well as on the LCAO-method are in progress. However, it should be mentioned that, in an application to the mobile electrons of the ground state of the benzene molecule which behave similarly to the valence electrons of a metal, Thoh and Yoshizumi (14) have obtained a depression of the energy minimum for $\theta \approx 23^{\circ}$ of about 2.35 *e*V, which amounts to 85 % of the depression obtained by using configurational interaction between nine determinants; there is also a fairly good resemblance between the two total wave functions found in so different ways. The whole approach seems therefore to be rather promising, but, of course, it is still too early to say whether it will be possible to save the « independent-particle model » along this line and to remove the Hartree-Fock method in treating metallic properties, as was just failure of the stressed by Professor Pines.

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Resistance of Metals at Low Temperatures

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1. INTRODUCTION

The report is written essentially from the standpoint of an experimentalist engaged in this field and is intended to draw attention to those theoretical questions which appear to be of major interest in the interpretation of experimental data and the planning of further research. On the one hand, we are concerned with those problems to which as yet final answers have not been given and on the other with specific discrepancies between theory and experiment which have not yet been resolved.

The application of quantum theory together with the concept of Fermi statistics of conduction electrons by such workers as Houston, Bloch, Sommerfeld, Wilson, Mott, Fröhlich and others to electron transport in metals constituted of course a great advance in our understanding of these processes. Thus in the case of resistance due to thermal vibrations it was found (Grüneisen, 1931, 1933; Meissner and Voigt, 1930; Meissner, 1935) that what is now called the Grüneisen-Bloch law, namely :

$$R \propto \frac{T^5}{\Theta^6} \int_0^{\theta/T} \frac{x^5 dx}{(e^x - 1)(1 - e^{-x})} \tag{1}$$

appeared to describe rather well the experiments for a number of metals over a fair range of temperature. Although equation (1) was originally derived analytically by Bloch as the low-temperature limit only ($T/\theta \rightarrow 0$), more recently Sondheimer (1950) and Rhodes (1950) have said that equation (1) should not depart from the true expression by more than 10 %-15 % in the region $T/\theta \sim 1$.

Nevertheless, in the detailed comparison of theory and experiment an empirical factor $(1 + aT + bT^2)$ was frequently introduced, while in some cases the data was related to the Bloch formula only through an estimation, in the upper temperature region, of θ, the characteristic temperature. Consequently, the degree of agreement obtained does not provide an entirely convincing criterion for judging the adequacy of the theory.

As $T/\theta \rightarrow 0$, equation (1) gives $R \rightarrow T^5$ and the validity of this prediction was at first questioned. However, after some consideration (cf. Peierls, 1930, 1931) it was agreed that in general if thermal equilibrium of the lattice were maintained R should depend on T^5 — which can be tested fairly readily. (See fig. 1 and 2.)

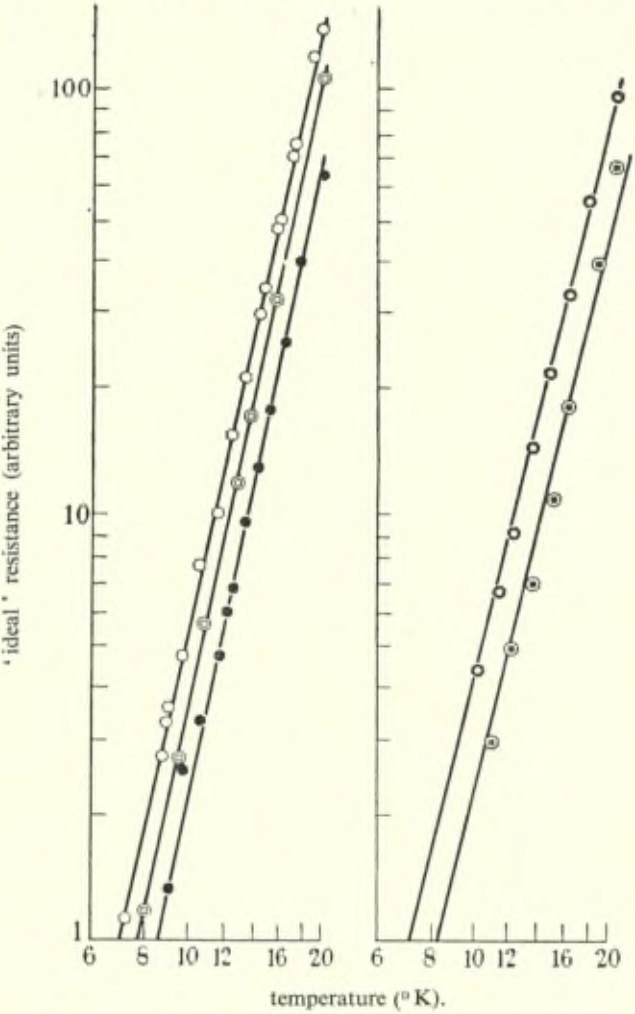


Fig. 1.— Logarithmic plot of electrical resistance of sodium and lithium due to thermal vibrations. Circles are experimental points on various specimens. The straight lines for sodium correspond to $R \propto T^{4 \cdot 85}$, and for lithium to $R \propto T^{4 \cdot 55}$. (After MacDonald and Mendelssohn, 1950.)

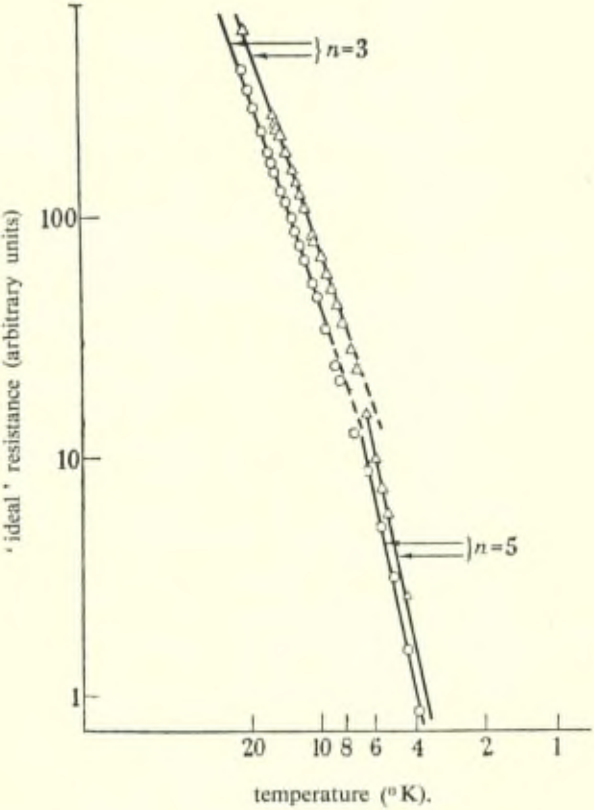
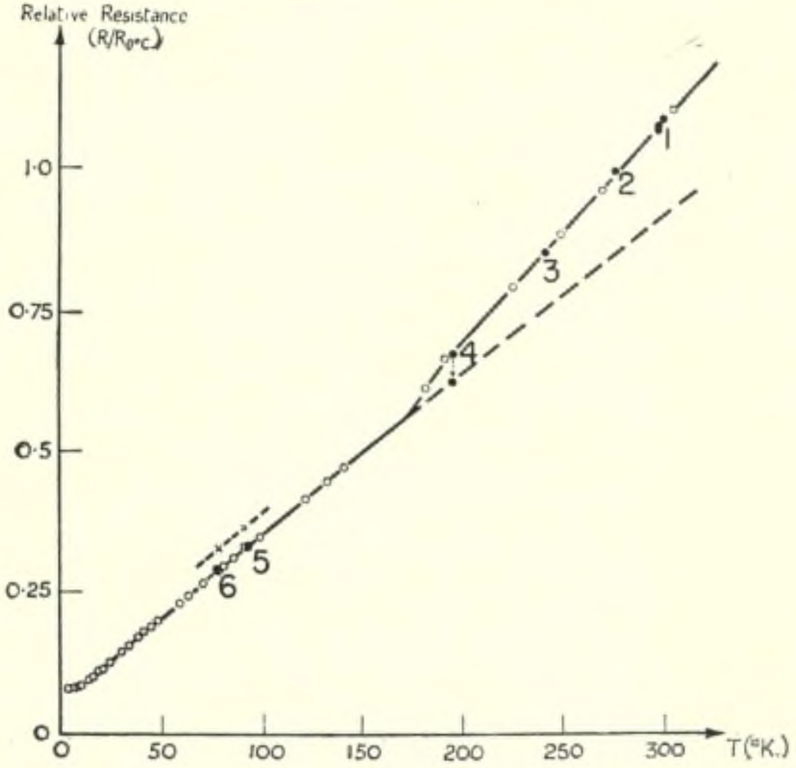


Fig. 2. — Logarithmic plot of electrical resistance of potassium due to thermal vibrations. Circles and triangles are experimental points on different specimens. (After MacDonald and Mendelssohn, 1950.)

Since the war, the notable increase in low-temperature facilities has enabled more detailed and systematic data to be obtained and considerable discrepancies between theory and experiment have been revealed. The writer with his group has been concerned particularly with the monovalent metals in the belief that until we can claim a reasonably thorough understanding of these theoretically simple metals we cannot reasonably expect to interpret in any fundamental manner the more complex structures. Thus, for example, the behaviour of caesium is markedly different in kind from that of sodium; rubidium exhibits an unexplained resistive « transition » around 180° K (fig. 3) and the Group IB metals (Cu, Ag, Au) present some puzzling problems, as will be seen later.

It will be evident that one cannot adequately isolate electrical conductivity from the other electron transport processes and these will also be considered to some extent in this report.



Electrical resistance of Rubidium.

O : Observations on cryostat experiment.

● : Observations in fixed-temperature baths :
(1) Room-temperature.
(2) Ice point.
(3) Liquid ammonia.
(4) Solid carbon dioxide (arrow shows range of time-dependent resistance).
(5) Liquid oxygen.
(6) Liquid nitrogen.

× : Observed points in liquid oxygen and nitrogen after very rapid cooling.

Fig. 3. — Electrical resistance of rubidium showing anomalous « transition» around 200° K. (After MacDonald, *Phil. Mag.*, 1952). (See also Kelly and Pearson, *Can. Jour. Phys.*, (1954), for subsequent investigations of thermal expansion, crystal structure etc.)

2. RESISTANCE COMPONENT
DUE TO THERMAL VIBRATIONS OF THE LATTICE

Apart from the specific « scaling » parameter θ, the Bloch-Grüneisen equation predicts for all metals a universal temperature-dependence of the electrical resistance due to thermal vibrations. Departures would be expected to arise from (inter alia) the following factors, each of which has already received considerable attention and is potentially of great importance. In this report, however, we shall simply give references with particular emphasis on the more recent papers.

a) *Varying ion-electron scattering properties from metal to metal.*

Houston, 1929; Nordheim, 1931; Sauter, 1942; Houston, 1951.

b) *Asphericity of Fermi surface* (E *not* $\propto |k|^2$) .

Vonsovsky and Smirnov, 1934; Supek, 1940 (cf. also Titeica, 1935) (see also Skinner, 1940).

The structure of the Fermi surface has still not been determined with certainty even in the monovalent metals. When convenient, we are inclined to state that the surface must be almost spherical; on the other hand, the variation in sign of thermo-electric power even in the alkali metals demands a considerable divergence in structure from the simple « free-electron » model. At this Congress, Pippard (cf. Pippard, 1950, 1954; Sondheimer, 1954) is reviewing the information which may be gained from study of the « anomalous skin effect » and the de Haas-van Alphen effect.

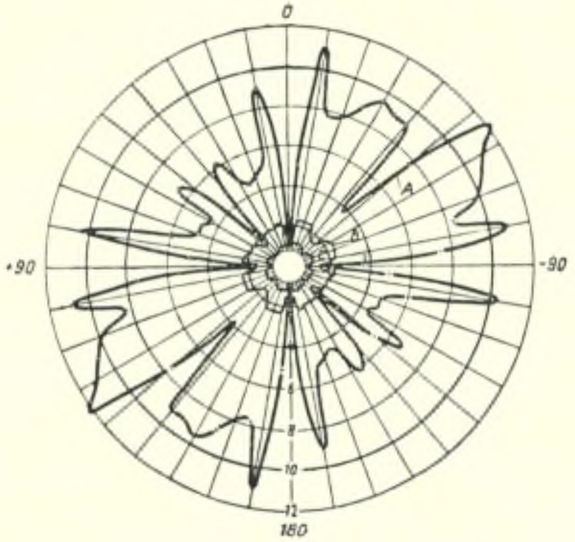
c) *Non-uniform relaxation-time.*

(Cf. e.g. Justi and Kohler, 1939.) This is perhaps not separable in principle from b) above.

The structure of the Fermi surface and the characteristics of the relaxation-time together determine the *magneto-resistance* where many problems remain unsolved (e.g. Wilson, 1936, 1953, and the recent review by MacDonald and Sarginson, 1952, on galvanomagnetic effects).

Because of the immediate entry of the term $eH\tau/mc$ into the Boltzmann equation (which is thus equivalent to a dependence on

H/R), magneto-resistance is, indirectly, most significant in pure metals at low temperatures where R is small. Striking anisotropic variations of large magnitude can then be observed in single crystals (e.g. Justi and Scheffers, 1936; see fig. 4) for which detailed interpretation is still lacking.



Relative resistance increase $\Delta p/p$ of a gold crystal rod cut parallel to the cubic edge in a transverse magnetic field as a function of angle of rotation. Curve A, $T = 4.2^\circ$ K, $H = 18.6$ kG; curve B, $T = 20.4^\circ$ K, $H = 35.2$ kG; curve C, $T = 20.4^\circ$K, $H = 21.7$ kG.

(*After* Justi and Scheffers 1936)

d) *Departure of frequency-spectrum from the Debye model.*

(Cf. e.g. Blackman, 1951, and earlier papers; Bauer, 1953; Cornish and MacDonald, 1951.)

e) *The influence of anharmonicity of lattice vibrations.*

(Cf. Born and Brody, 1921; Born, 1933; Damköhler, 1935; Smirnov, 1934; Dugdale and MacDonald, 1954.)

f) *The immediate influence of thermal expansion* (on θ and the electron-ion interaction energy).

(E.g. Smirnov, *loc. cit.*; Mott, 1934; Mott and Jones, 1936; Meixner, 1940; Kelly, 1954; Kelly and MacDonald, 1953.)

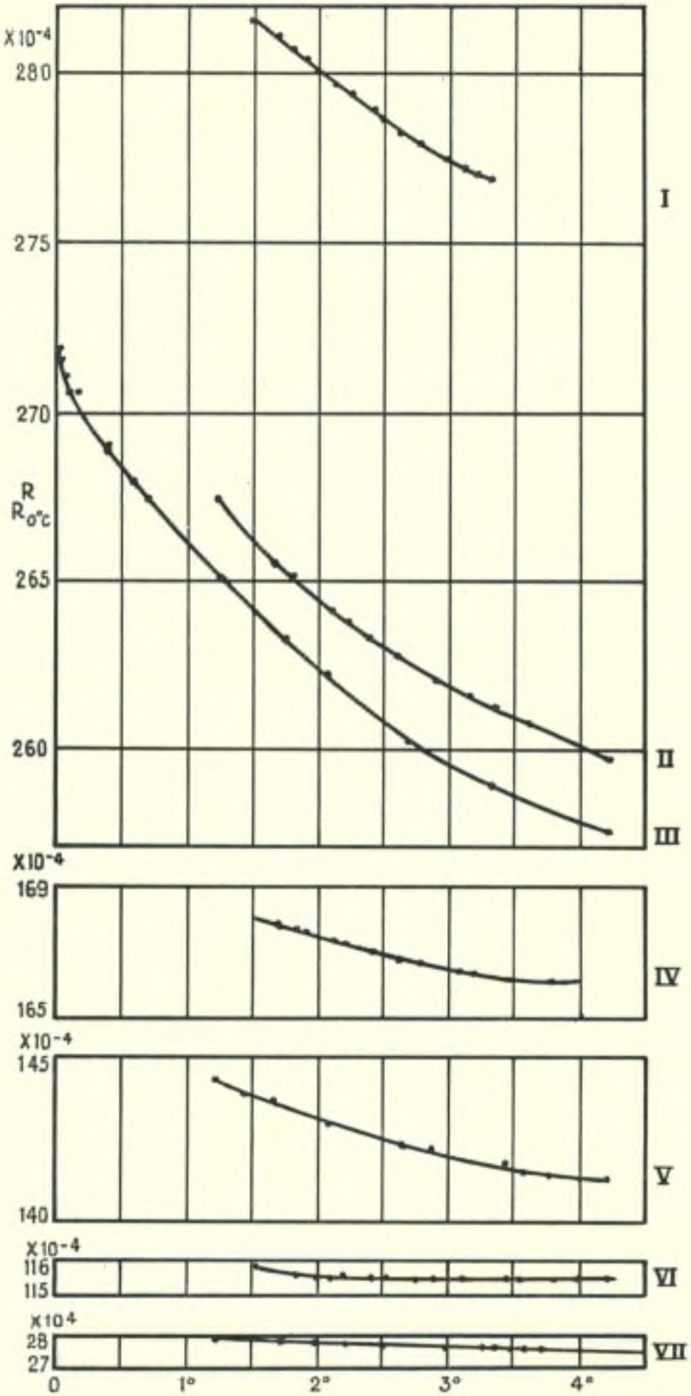


Fig. 5. — Variation of resistance of silver specimens in the region of temperature $\sim 4°$ K to $\sim .1°$ K as observed by Mendoza and Thomas (1951).

Since, in general, theories of electrical resistance are based on a constant-volume model, we may omit consideration of f) if we correct all experimental data to the appropriate volume at $T = 0$. This calls for adequate data on R as a function of volume, some of which is already available from Bridgman's (1946) classical work, although this is essentially confined to the room-temperature region.

g) *Resistance due to electron-electron scattering* (see below).

3. RESISTANCE COMPONENT DUE TO STATIC IMPERFECTIONS

After Bloch and Houston had shown that electrons would not be scattered in a perfectly periodic lattice (including the influence of zero-point energy) it was evident that the « residual » resistance, as $T \to 0$, must be ascribed to static imperfections (physical and/or chemical) in the lattice. This, of course, had been familiar experimentally since the statement of Matthiessen's rule (Matthiessen, 1860; Matthiessen and Vogt, 1864) of the approximate additivity of « residual » and thermal components of resistance. Many workers such as Linde and Borelius (e.g. Johannson and Linde, 1930, 1936; Linde, 1932; Borelius, 1937) have made detailed studies of the resistivity of alloys, and this work has seen expansion recently with the wider availability of very low temperatures. On the theoretical side Nordheim (*loc. cit.*) and Mott (1936), in particular, have contributed to a considerable general understanding of the data, having discussed, for example, the influence of homovalent and heterovalent impurity scattering.

However, on the volume-dependence of residual resistance our knowledge is rather scanty both experimentally and theoretically (cf. e.g. Frank, 1935; Lenssen and Michels, 1935). This information would be of particular value, for example, in the analysis of *thermoelectric behaviour* (q.v.) at low temperatures.

A particularly puzzling feature is that of the *minimum of electrical resistance* at low temperatures. First observed systematically in gold by de Haas and van den Berg (de Haas et al, 1933; van den Berg, 1938) it has since been found definitely in a few other metals by workers in Oxford, Bristol (fig. 5), Leiden (fig. 6), and Ottawa (refs. in MacDonald, 1952); although occurring in the IB elements,

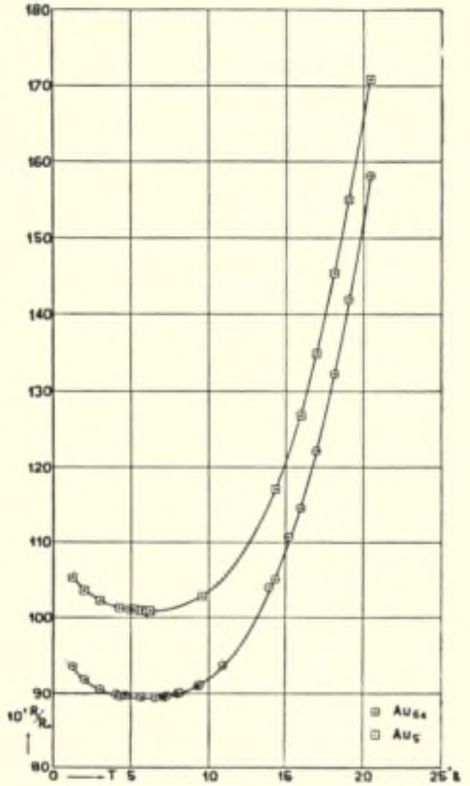


Fig. 6. — Electrical resistance of two specimens of gold as observed by de Haas and van den Berg. (See van den Berg, 1938). For more recent work at Leiden, see Gerritsen and Linde, (1951, 1952).

the phenomenon is not evinced by the alkali family. It appears now to be generally agreed that the resistance minimum would *not* occur in the ideally pure metal. Detailed study of copper shows that it will arise from introduction of a remarkably small atomic concentration of a rather wide range of specific « impurity » elements (e.g. Mn, Fe, Co, Ga, In, Si, Ge, Sn, Pb and Bi), while Ag, Au and probably Ni will *not* produce the effect.

There is also some appreciable evidence linking the mechanical properties of the metal with the resistive minimum (Blewitt et al, 1954; Pearson, 1954). Blewitt on the one hand has suggested that grain boundaries alone are sufficient to produce the minimum. On the other hand it appears that the distribution of responsible solute atoms in relation to grain boundary structure is an important factor in producing a resistance minimum (Pearson, *loc. cit.*).

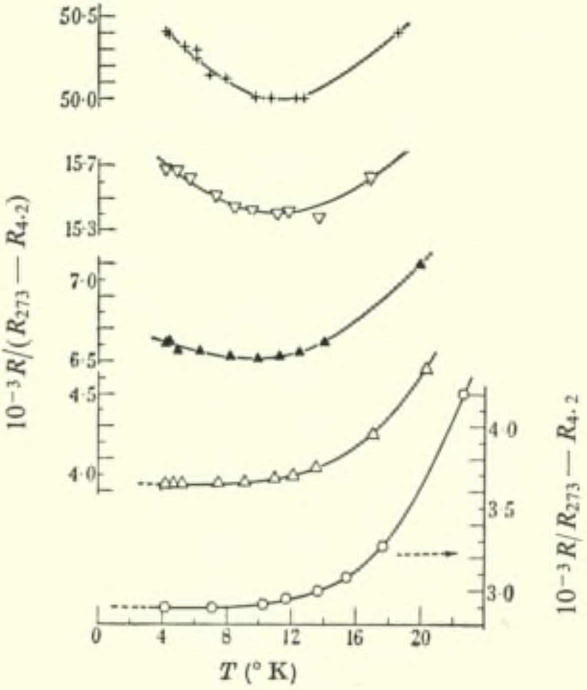


Fig. 7*a*. — Relative electrical resistance of pure copper and copper-tin alloys. Legend for experimental points as in figure 7*b*. (After MacDonald and Pearson, 1953.)

The phenomenon is also closely linked with very marked anomalies in the thermoelectric behaviour at low temperatures (MacDonald and Pearson, 1953, 1954; MacDonald, 1953 [fig. 7*a*, 7*b*]). This thermoelectric behaviour is indeed so striking that one is inclined to regard it perhaps as the major effect from which we may garner the most information, using it then to explain the resistive behaviour.

In the purest available metals, the electron mean free path increases by a factor 10^3 - 10^4 as the temperature is lowered from room temperature to that of liquid helium. Thus, for example, in the purest sodium a mean free path in the order of 1/10 mm can be attained. Consequently, the geometrical boundaries of the specimen may

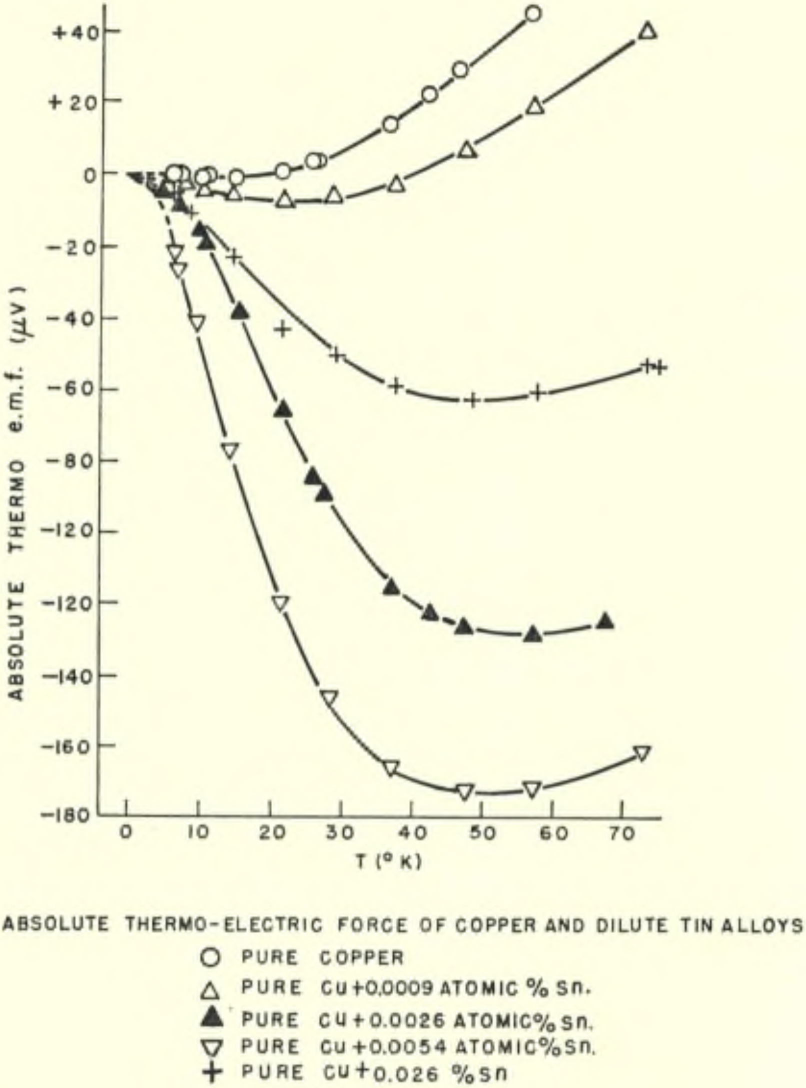


Fig. 7*b*. — (After MacDonald and Pearson, 1953).

readily contribute to the scattering. Studies of such *size-effects* (e.g. Andrew, 1949; Chambers, 1950; Dingle, 1950; Fuchs, 1938; MacDonald and Sarginson, 1950; Sondheimer, 1950*b*) both with and without application of a magnetic field are capable in principle of giving information about the electron momentum, mean free path and scattering characteristics at a metallic surface. Although in some experiments a simple assumption of diffuse electron-scattering seems sufficient, it appears that this is not adequate in all cases (e.g. see fig. 8).

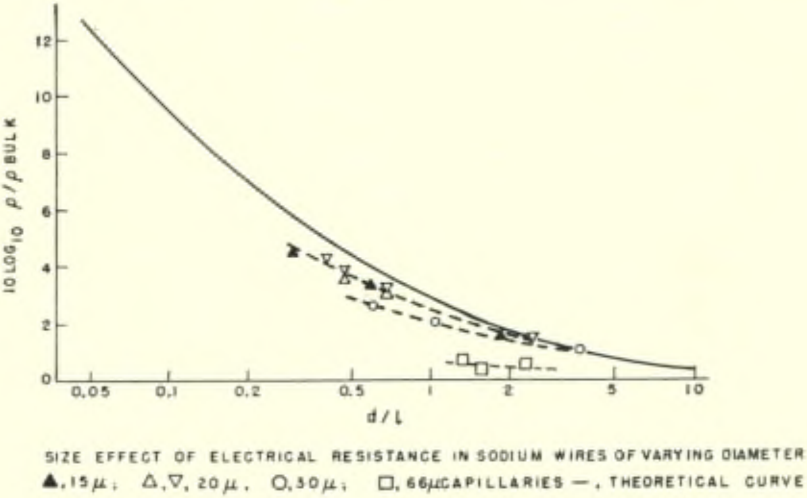


Fig. 8. — *d* : Effective diameter of wire; *l* : Electron mean free path. (After MacDonald and Sarginson, 1950).

High-frequency electromagnetic measurements (« skin-effect » and « anomalous skin-effect » — e.g. Pippard, 1947; Reuter and Sondheimer, 1948; Chambers, 1952) may be considered as closely allied to this field and may also in principle (cf. Pippard : this Congress) yield fundamental information about conduction electron characteristics.

Nevertheless, the very dependence of these effects on surface properties which are still not fully understood would indicate some caution in making deductions about electron behaviour in a bulk metal.

4. ELECTRON TRANSPORT UNDER A THERMAL-GRADIENT

It has been pointed out above that striking « anomalous » thermoelectric effects in dilute copper alloys, in particular, show a strong correlation with the « anomalous » resistive minimum. If, therefore, we wish to understand the latter, it appears we must also focus attention on the interpretation of thermoelectric power and, more generally, on the influence of a thermal gradient on electron diffusion and conduction phenomena. Peierls appears to have been the first to question the adequacy at low temperatures of the « Blochscheannahme » — that during electrontransport (in that case electrical conductivity) we may assume with sufficient accuracy that the *lattice* remains essentially in thermal equilibrium. This leads to consideration of lattice-relaxation processes and Peierls introduced the « Umklappprozess » for electrons as a mechanism for maintaining a momentum-balance. In the course of this process, a conduction electron of selective de Broglie wavelength imparts its momentum *directly* to the rigid lattice, suffering an internal Bragg reflection, instead of dissipating its momentum through the more « usual » intermediary of thermally-excited lattice waves (« phonons »). Such Umklappprozesse in the case of monovalent metals seem rather improbable at low temperatures, although of course we are as yet without secure knowledge of the shape of the Fermi surface and its relation to the Brillouin zone structure (see 2, b), above). More recently, Houston (1939) and Peierls (private discussion) have suggested that multiple electron-processes ought also to be considered (cf. also Klemens, 1951*a*), but in any case our knowledge is most uncertain; to quote Wilson (1953) : « ... the subject is still very obscure ».

When a temperature-gradient is applied it is evident that the lattice equilibrium is to some extent directly disturbed but the « conventional » theory of electron-transport assumes that this perturbation may be neglected in relation to the electronic effects. If this be so, we can then show (e.g. Mott and Jones, *loc. cit*) that the absolute thermoelectric power of a metal, S, arising solely from electron diffusion is given rather generally by :

$$S = \frac{\pi^2 k^2 T}{3e}\left(\frac{d \log \sigma(E)}{dE}\right)_{E=\zeta} \tag{2}$$

(E = conduction-electron energy
ζ = Fermi-level
σ = electrical conductivity)

As usual, more detailed consideration is necessary when $T/\theta \sim 1$ (cf. Sondheimer, 1947) but the modification to equation (2) is unlikely to be serious. From (2) we may discuss the relationship of S to resistivity (particularly in alloys) (e.g. Friedel, 1952; Mott and Jones, *loc. cit.*; MacDonald and Pearson, *loc. cit*) and also note that generally S should approach zero linearly with T as $T \rightarrow 0$. Rather frequent disagreement is found with the latter prediction, in particular (cf. also Pullan, 1953; Borelius, 1953), and we are thus led to ask where the theory may be wanting.

Gurevich (1945, 1946), was first to consider the « *first-order* » thermoelectric effect which could arise from the dragging of conduction electrons by the lattice phonon-current under a thermal gradient. (Makinson, 1938, had previously assessed as negligible the contribution from this process to *thermal conductivity* in metals.) Interest in this effect has very recently grown rapidly (Frederikse, 1953; Blatt*; Herring*, 1954; Klemens*, 1954; MacDonald, 1954), both in semi-conductors and metals.

The various theoretical approaches (Herring, Klemens, MacDonald) agree essentially that the absolute thermo-electric power due to phonon-electron interaction will be given by :

$$S \sim \frac{C}{N_e.e} (\alpha) \; ....$$

where :

C is the specific heat of the solid
$N_e.e$ is the density of mobile charges
α is a numerical factor between 0 and 1 governed by the relative importance of phonon-electron scattering to other phonon-scattering processes.

For $T > \Theta$ and in a monovalent metal we have :

$$S \sim \frac{3k}{e} . \alpha ,$$

which assuming free electrons as carriers, gives :

$$S \simeq -250\alpha \ \mu V/^{\circ}K .$$

The observed absolute thermoelectric power of sodium around room temperature is : $\sim$ 5-6 $\mu V/^{\circ}K$, and we must therefore certainly assume that phonon-electron scattering is of little importance at higher temperatures — in agreement with the usual conception that

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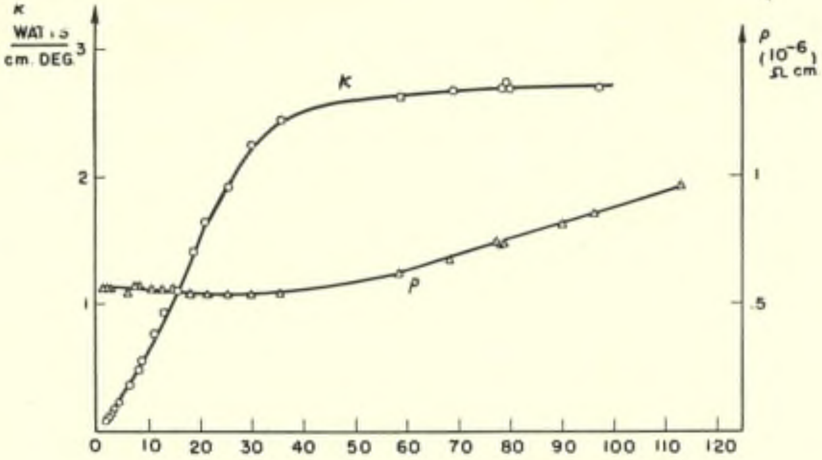
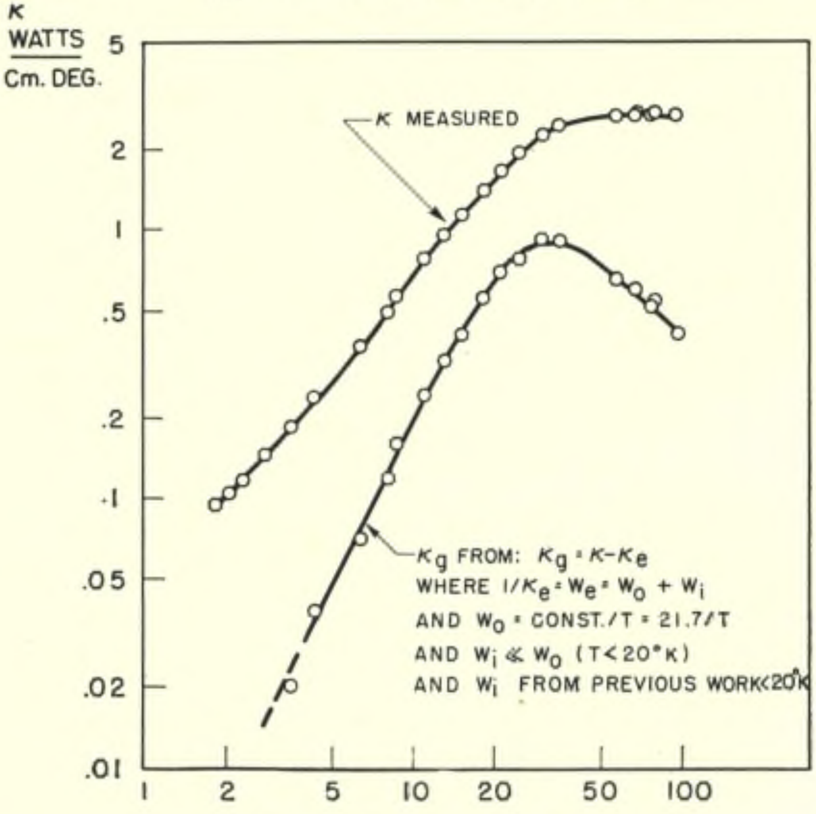
(*) I am grateful to these gentlemen for private communications and for letting me see MSS before publication.



White & Woods : Cu - 0.056% Fe alloys.

Fig. 9*a*. — Thermal conductivity (κ) and electrical resistivity (ρ) of a dilute copper-iron alloy. (After White and Woods).



White & Woods : Cu - 0.056% Fe alloys.

Fig. 9*b*. — Computed lattice component of thermal conductivity (κg) from measurements of White and Woods on a dilute copper-iron alloy.

at high temperatures lattice anharmonicity forms the major limitation to lattice heat flow. At low temperatures, it is generally assumed that in metals and dilute alloys phonon-electron scattering becomes the dominant factor. Thus, a recent elegant experiment by White and Woods (1954) (see fig. 9*a* and 9*b*), on a very dilute Cu-Fe alloy shows clearly that below about 30° K phonon-electron scattering rapidly becomes the limiting factor in lattice thermal conductivity. Now for $T \ll \theta$, again in a monovalent metal, we have :

$$S \sim -\left(\frac{T}{\theta}\right)^3 . 2 \times 10^4 . \alpha \ \mu V/^\circ K \ ....$$

and if, as the thermal conductivity results suggest, α is now of order unity :

$$S \sim -\left(\frac{T}{\theta}\right)^3 \times 10^4 \ \mu V/^\circ K \ ....$$

For copper at $T \simeq 16^\circ K$ ($\theta \simeq 320^\circ K$) this gives $S \sim -1 \mu V/^\circ K$ while in the pure metal the observed value is of the order $+ 0.1 \mu V/^\circ K$ at this temperature. On the other hand, as seen in figure 7*b* for Cu-Sn alloys, certain very small solute additions do produce rather large negative thermoelectric powers up to *several* $\mu V/^\circ K$ magnitude, but it is then difficult to propose any mechanism whereby these very small impurety concentrations could so dramatically « catalyse » phonon-electron scattering.

We may also note that for sodium ($\theta \simeq 180^\circ K$) the predicted values at 20°K and 10°K would be about $-15 \mu V/^\circ K$ and $-2 \mu V/^\circ K$ while the observed values are $-0.8 \ \mu V/^\circ K$ and $\sim -0.4 \ \mu V/^\circ K$, following in this case rather well a *linear* dependence with temperature as predicted by the « conventional » theory.

This field thus presents a number of problems and arouses fresh interest in phonon-electron and other phonon interaction processes.

We are also led to ask how far we are justified in speaking of a thermodynamic electron-temperature. In the statistical theory, due originally to Lorentz, it is assumed that even under a thermal gradient we can assign at each point, x, of the conductor a unique temperature to the electron distribution-function so that we may write:

$$\left(\frac{\delta f}{\delta x}\right)_{px} \approx \left(\frac{df_o}{dT}\right) \cdot \left(\frac{dT}{dx}\right)$$

where f_o is the thermodynamic unperturbed distribution. On the other hand, following Lorentz, electron-electron collisions are specifically assumed to be negligible whereas one might have surmised that a sufficiently *short* electron-electron relaxation-time would be necessary to ensure the validity of using an electron temperature. (The extreme case of an accelerated « electron-beam » in a valve points the difficulty.) There are also questions involved in the statement of the Boltzmann equation for electrons in a metal under a thermal gradient which might give cause for concern. Baber (1937) discussed the contribution to metallic resistance which could arise from electron-electron collisions (cf. also Abrahams, 1954), and Fröhlich (e.g. 1946) has considered the role of electron-electron interaction more specifically in relation to dielectric behaviour. It seems, however, that a careful and detailed combined discussion or assessment of :

a) Electron-electron relaxation;

b) Electron-lattice (including phonon-electron) relaxation;

c) Lattice relaxation (phonon-phonon, etc.),

would be most valuable at the present time.

The latter process is of course the direct source of *thermal resistivity in insulators* and has been treated in recent years by Peierls (1929) and Klemens (1951*b*) in terms of a phonon-statistical model. Since, however, thermal resistivity due to lattice anharmonicity increases with temperature, one might expect that a rather direct *classical* analysis should be possible giving a quantitative result at higher temperatures linked directly, in particular, with the thermal expansion of the solid. This problem is being considered in detail by the author and his colleagues at Ottawa.

It may also be that a careful examination of modern resonance techniques (nuclear, electron-spin and « cyclotron » resonance) as developed by Bloch, Purcell, Gutowsky, Kittel, Kip and others, although difficult in their application to metals, would enable more direct experimental information on the relaxation processes to be gathered. Research is, of course, very active in these fields.

If, despite the foregoing, we assume that existing electron transport theory is indeed reasonably adequate for the understanding of metals and we therefore interpret data by equation (2) above (or a suggested generalisation: MacDonald and Pearson, *loc. cit.*), we are then faced with very large values for the energy-dependence of electron-scattering in many dilute alloys. Although the possibility of a quasi-Ramsauer effect in solids has been suggested to account for this behaviour, it appears that theory at present has no fundamental explanation to offer.

* * *

In this brief account, we have tried first to summarise those aspects of the theory which have for some time past remained unsatisfactory and, secondly, to survey more fully the problems raised by recent experimental work to which answers are eagerly awaited.

I am grateful to Drs. W.B. Pearson and J.S. Dugdale for reading and commenting on this report and to Dr. Dugdale for many helpful discussions.

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Discussion of MACDONALD's report

Mr. Mott. — You have used an alloy instead of a pure metal in order to have an electronic part of the thermal resistance which can be calculated according to the Wiedemann-Franz law. Do the impureties play no part in determining the interaction between phonons and electrons?

Mr. MacDonald. — The primary reason for using an alloy is in order to reduce the intrinsic electronic component of thermal conductivity sufficiently that the lattice component significant, and a suitable very *dilute* alloy (of high electron-scattering) was chosen so that one could be reasonably certain that the matrix is still essentially that of pure copper.

The dilution is sufficiently great that it appears most unlikely that the impurity atoms can significantly influence the phonon-electron scattering but any proposed influence would be of interest.

Mr. Fröhlich. — I think Peierls' Umklapp processes are very essential to obtain a stationary state in any transport phenomenon involving electrons and phonons. Processes in which momentum alone is conserved can never lead to stationary conditions, as was realized by Peierls long ago, because an external electrical field feeds momentum to the system of electrons which can be removed only by processes in which momentum is transferred to the center of gravity of the lattice.

I wish to mention on this occasion that another model, often used in classical physics, cannot lead to stationary conditions. It is the model based on elastic scattering of electrons on hard spheres. Here momentum conservation does not lead to difficulties but energy cannot be conserved because the field F feeds energy into the system of electrons ($\propto F^2$) which cannot be removed by elastic scattering.

Mr. MacDonald. — I agree with Professor Fröhlich in the case of the isothermal lattice with no physical or chemical impureties present. When, however, a temperature gradient is present, so that with anharmonic forces there is a differential atomic separation, then it appears that *each* atom will absorb momentum in sustaining this differential separation.

Mr. Pines. — I would think that it would take a very strong thermal disturbance to distort the lattice in such a way as to destroy the periodicity which will inevitably lead to « Umklappprozessen ». The condition for the existence of Umklappprozessen is essentially that for Bragg reflections; and both should exist under most circumstances usually encoutered.

Mr. Matthias. — I did not understand the discontinuity in the thermo-electric power of lithium between 30° and 40° K. Has it not been measured between 60° and 70° K where the phase transition of lithium occurs?

Mr. MacDonald. — We are not ourselves able yet to give a reason for the discontinuity between 30° K and 40° K, although X-ray investigations, being published by Dr. W.B. Pearson, have been carried out.

I believe Dr. Pearson has made thermoelectric measurements at the higher temperatures without observing any anomaly but I cannot be certain at present how far up the measurements went.

Mr. Meissner. — As Dr. MacDonald has said so much on the thermoelectric power, perhaps the following may be of interest : As you know, Benedicks believed he had found the so called « 1st Benedicks effect ». To make sure whether the effect exists, we have made experiments in the following manner : we have taken polycrystalline toroids of very pure Au, Pt and Ag and annealed them very well. In high vacuum, a small piece of the toroid was heated, and, on the one side of the heated region a small piece of the toroid was cooled. So we had a large gradient of temperature in one direction, and a small gradient in the other direction. If the effect exists, one should get a current in the toroid. Measurements of this current by a suspended magnetic needle showed the 1st Benedicks effect at all points of the toroid. The thermoelectric power caused by small inhomogeneities was eliminated.

Mr. Pippard. — According to Pullan's measurements, the thermoelectric power of Ag depends markedly on the degree of annealing. It may be that the apparent Benedicks effect is a result of uneven annealing of the ring.

Mr. Aigrin. — Herpin studied the Benedicks effect in single crystal materials a few years ago. His results showed a very small Benedicks effect superimposed on much larger thermoelectric effects due to inhomogeneity, in spite of all care to avoid inhomogeneity. So it looks as if the Benedicks effect exists but is very small.

Mr. Prigogine. — En connection avec le rapport de M. MacDonald, je voudrais attirer l'attention sur le fait que les forces harmoniques jouent également un rôle très important dans l'établissement de l'équilibre thermique. (Klein & Prigogine, *Physica*, **19,** 1053 (1953), L. Van Hove, à paraître, *Phys. Rev.*) Considérons pour simplifier le cas d'une chaîne linétaire caractérisée par les distances relatives entre les particules et les vitesses de celles-ci. Appelons y_{2n+1} les distances relatives, moins la distance d'équilibre, y_{2n} la vitesse de la même particule. Ces grandeurs étant convenablement normalisées.

Alors, la solution des équations du mouvement se met sous la forme (Schrödinger, *Annalen der Physik*, **44,** 316, 1914) :

$$y_n(t) = \sum_{\nu=-\infty}^{\nu=+\infty} y^o_\nu \mathrm{J}_{n-\nu}(t) \qquad (1)$$

le temps étant également normalisé de manière appropriée. La forme (1) de la solution permet de discuter très simplement la «propagation» des conditions initiales dans le réseau. A l'instant initial, on a trivialement :

$$[\mathrm{J}_k(o) = 1\ ,\ \mathrm{J}_k(o) = 0\ ,\ k \text{ entier positif}]\ y_n = y^o_n. \qquad (2)$$

Lorsque le temps augmente, de plus en plus de conditions initiales contribuent à la valeur de $y_n(t)$. Le problème de l'établissement de l'équilibre thermique peut alors s'énumérer comme suit : Nous ne connaissons initialement que les possibilités des variables : $y_n\ (= y^o_n)$ qui sont donc des variables aléatoires. Nous voulons étudier l'evolution de leur loi de possibilité et montrer que lorsque $t \to \infty$ on a la loi de distribution gaussienne caractéristique de l'équilibre thermique :

$$e^{-y_n^2/2} \text{ pour } t \to \infty\,. \qquad (3)$$

Nous n'entrerons pas dans les détails de la démonstration qui a été publiée ailleurs. Notons seulement que cette propriété apparaît comme liée directement au théorème central du calcul des probabilités : au bout d'un temps très grand, le variable aléatoire y apparaît comme la somme d'un très grand nombre, pratiquement infini, de variables aléatoires dont chacune donne une contribution qui, prise individuellement, est négligeable.

On peut même démontrer que dans le cas d'une chaine linéaire, la manière dont l'équilibre est atteint est en $|t|^{-1/2}$ tandis que dans le cas de réseaux à trois dimensions, elle est en $|t|^{-3/2}$.

Ces systèmes quoique non ergodiques au sens de la théorie habituelle, jouissent aussi d'une propriété *d'ergodicité locale* très intéressante.

Il y a toutefois une restriction très importante liée à la nature du système (pas de forces anharmoniques). Si les différents modes normaux n'ont pas initialement la même énergie, ces différences subsistent au cours du temps et le système ne peut atteindre l'équilibre thermique.

Nous devons donc nous limiter à des distributions initiales telles que l'équipartition de l'énergie entre les modes normaux soit déjà réalisée. L'analyse de cette condition montre qu'il faut, pour cela, considérer des distributions initiales de y_1, ... y_t .... *factorisées*, c'est-à-dire telles que :

$$f(y_1{}^o \,....\, y_t{}^o) = \Pi f_1(y_1{}^o) f_2(y_2{}^o) \,.... \tag{4}$$

En d'autres termes, les variables aléatoires y_n^o doivent être des variables indépendantes.

Moyennant cette restriction, les considérations que nous venons de présenter donnent une sorte de théorème H qui n'introduit, une fois que la spécification initiale du système est donnée, plus aucun élément probabiliste, mais seulement les équations de la mécanique.

Mr. Gorter. — I should like to call attention to a series of experimental and theoretical investigations being carried out by Gerritsen, Linde & Korringa* on the properties of various solid solutions

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(*) Cf. J. Korringa and A.N. Gerritsen, Leiden Comm. Suppl. 106; *Physica* **19** (1953), 457.

in the noble metals Cu, Ag and Au. In most of these alloys, the usual minimum of the electrical resistance was observed, which shifts from T = 0 to higher temperatures when the impurety concentration is increased. Incidentally, Van den Berg and Van de Marel studied a similar minimum in a gold single crystal. When a paramagnetic impurety (Mn, Cr, Fe) is introduced, usually a pronounced maximum is found in the resistance below the temperature of the minimum. It is plausible to ascribe this maximum to two (or one) resonance bands for the scattering of conduction electrons, situated near the Fermi limit. The whole effect quantitatively is described by the magnitude, position and width of the supposed resonance bands. At zero concentration, the bands apparently coincide with the Fermi limit, while they move away from it when the paramagnetic impurity concentration increases. The width remains at first constant but afterwards increases rapidly with the concentration.

The authors, so far, have not been able to give a satisfactory theory of the introduction of the resonance bands by the impurity atoms. It is reasonable, however, that when the impurities are paramagnetic, interaction leads to decomposition of the single band at the Fermi limit into two bands.

A very strong decrease of the resistance is found in the alloys with magnetic impurities in strong parallel or perpendicular magnetic fields.

This decrease may be explained by the same picture. The presence of the levels should lead to an anomalous thermo-electric behaviour of the character presented by the data.

Measurements of other properties of the alloys mentioned have also been started. In particular, study of the specific heats may be instructive. An anomaly in the specific heat of Cu-Mn alloys has been observed recently at the University of Leeds.

Some Experiments on the Thermal Conductivity of Metals

by **K. MENDELSSOHN**, Oxford

After the war a programme of systematic investigations on the transport phenomena in metals was started at Oxford. Work on the electrical conductivities at low temperatures of the alkali metals and the alkaline earths (1) showed that sodium represents a good approximation to an « ideal » metal with quasi-free electrons while the other metals, including lithium, exhibited a more complex behaviour. A survey of this and more recent work has been given in Dr. Mac-Donald's report. These experiments have now been supplemented by detailed and comprehensive measurements, covering the whole periodic system, of the thermal conductivities which have greatly increased our knowledge of the part played by the metal electrons in the transport effects.

In this contribution I shall not deal with the general features of the heat conductivity data, about which fairly exhaustive reports exist (2) or are in preparation (3), but merely describe a few recent experiments. These have been selected to with a view to showing how the work on thermal conductivities is often of the greatest help in the analysis of complex phenomena.

There is first of all the peculiar minimum, at a few degrees above absolute zero, in the electrical resistance of certain specimens of gold, magnesium and copper which has been mentioned at this conference. The question arises whether there exists a corresponding effect in the thermal conductivity which at the lowest temperatures seems to obey in general the Wiedemann-Franz law quite well. Routine measurements on magnesium (4) provided actually some indication of an anomaly since the heat conduction at $\sim 4^{\circ}$ K did not extrapolate to the value zero at absolute zero. However, since the effect is small and also appears to be structure dependent, the only convincing evidence can be provided by simultaneous determination, on the same specimen, of the electrical *and* the thermal conductivities. The result of this, somewhat difficult, experiment obtained

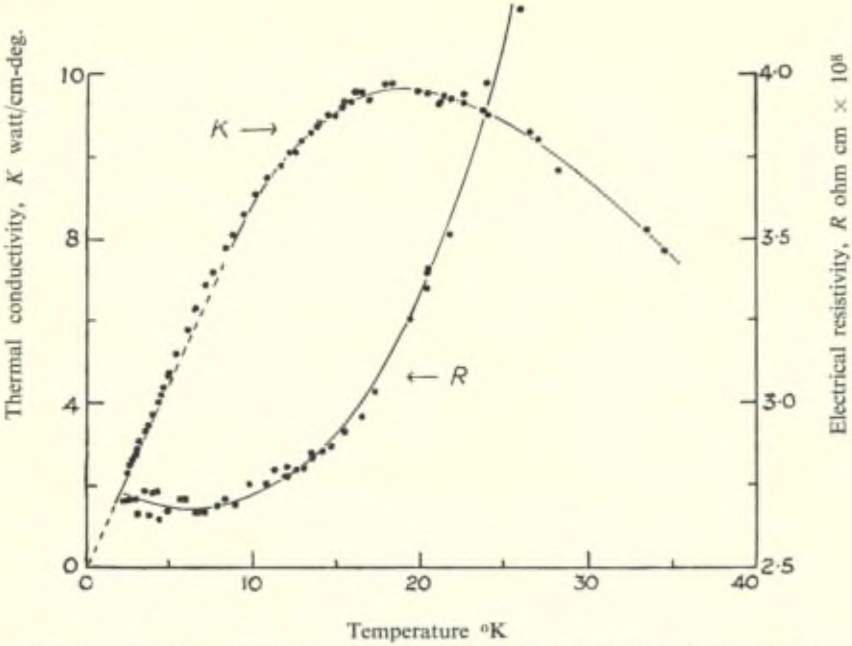

Fig. 1. — The thermal conductivity *K*, and the electrical resistivity *R*, of a magnesium specimen showing the departure of *K* from linearity in the region of the electrical resistance minimum.

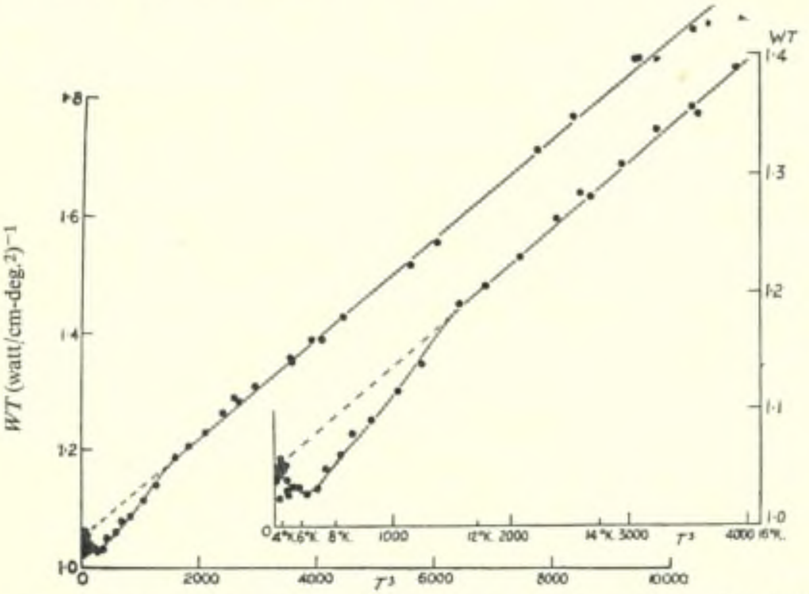

Fig. 2. — The graph of *WT* against T^3 showing the minimum in the value of *WT*. Inset, the lower half of the curve on a larger scale.

by Rosenberg (5) shows that in the region of the resistance minimum the thermal conductivity, K, indeed appears to be slightly increased. This effect becomes much more striking when one plots T/K against T^3. Since $1/K$ can in this temperature region be represented as $const./T + const.\ T^2$, the plot should yield a straight line. The plot of the experimental points in this diagram, as is shown in figure 2, is well represented by such a straight line up to temperatures of about 20° K with a very marked minimum in the region of the electric anomaly.

However, apart from the interesting result that the thermal as well as the electrical resistance shows a minimum, the heat conductivity data lead to a quite unexpected conclusion. Since $K = L/T/R$, where R is the electrical resistance, the well known fact that at low temperatures the heat conductivity of a metal is proportional to T means that in this region R is temperature independent. L is the Lorenz number, and as it is found that within the limits of experimental accuracy the thermal anomaly corresponds to the electrical one, its value is constant over the temperature range of the whole minimum. It can be seen from figure 2 that the value of T/K at absolute zero is an extrapolation of the straight line above 12° K, which is indicative of the residual resistance. It thus appears from the heat conductivity measurements that there is not, as has generally been assumed, a rise of the electrical resistivity above the normal residual value at the lowest temperatures. Instead, the residual resistance being determined by the straight line in the $T/K - T^3$ diagram, the minimum denotes an anomalous drop of the electrical resistance *below* the residual value. This conclusion is, of course, based on the validity of Matthiesen's rule which, while empirical, has nevertheless been found quantitatively correct in the case of sodium. Whether there is any connection between this minimum and the phenomenon of superconductivity must remain an open question.

Another question which has arisen in connection with the resistance minima has, however, been definitely settled by the heat conductivity results. It has sometimes been suggested that in such metals as magnesium the electrical resistance may possibly rise further at lower temperatures and eventually reach infinity at absolute zero. Resistance measurements below 1° K (6) have failed to decide the issue. The coincidence of the lowest measured points in the $T/_K - T^3$

diagram with the intercept of the straight line at absolute zero leaves now little doubt that at this temperature the electrical resistance will have a finite value.

The next two experiments to be mentioned, while different in character, give information about the same quantity, the lattice conduction K_g. A comparison of these two experiments then allows an estimate of the scattering of phonons by the free electrons. The first type of measurement is the determination of the heat conductivity of metals in high magnetic field. Some metals show a marked decrease in thermal conductivity with increasing magnetic field and, while there exists no very satisfactory theoretical interpretation of the experimental results, it can be safely assumed that this is a decrease in the electronic heat conduction K_e. It is also clear that the conduction of heat by phonons, being uninfluenced by the magnetic field, must set a final limit to the extent to which the total heat conductivity of the metal can be decreased. Figure 3 shows

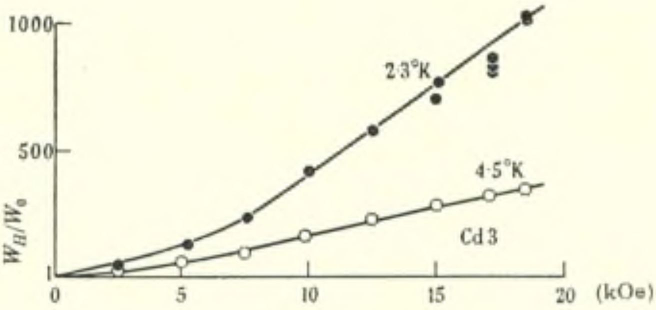

Fig. 3. — Variation of the thermal resistance of cadmium with magnetic field.

the results for a cadmium single crystal (7) where the ratio of the thermal resistance W_H in a magnetic field to W_o, that in zero field, is plotted against the strength of a transverse field. At the lowest temperature (2.3° K) and the highest available field (18.5 *k*0*e*), the thermal resistivity is increased by more than a thousand times. Above 7.5 *k*0*e* the change of W_H/W_o with H is linear and there is no indication of a saturation effect. This means that the contribution of the phonon conduction must be still negligible, amounting to certainly less than one percent of the total heat conductivity.

A quite different possibility to determine K_g is provided by observations on superconductors. In a pure metal the heat conductivity in the superconductive state is at any temperature smaller than that in the normal state. This can readily be understood from the fact that the conduction electrons which pass into the superconductive state cease to contribute to the entropy (8). It is known from a comparison of the measured electronic entropy in the normal state and the entropy defect when the metal becomes superconductive that with decreasing temperature the number of these « superconductive electrons » increases and that at absolute zero all conduction electrons have passed into the superconductive state (9). For this reason the heat conductivity of a superconductive metal near absolute zero is of special interest since one may expect the electronic heat conduction to become small in comparison with that of the lattice.

The result of such a measurement on a lead single crystal (10) is shown in the logarithmic plot of figure 4. The observations which have been extended to less than 1/20 of the transition temperature demonstrate that in this temperature region the heat conductivity of the metal is proportional to T^3. This is the temperature dependence which has been postulated by theory for a dielectric crystal (11). This, together with the absolute value of the heat conduction, indicates that below 1° K in the lead single crystal heat is carried by the phonons only and that electronic conduction has become negligibly small. Accordingly, at low enough temperatures, a superconductor behaves like an insulator as far as its heat conductivity is concerned.

It is of interest to compare the two values of K_g, that obtained from superconductivity and the upper limit derived from the measurements in high magnetic fields. Such a comparison, which will certainly be correct within one order of magnitude, can be made by extrapolating the K_g-value of lead to 2.3° K and to substitute the measured heat conductivity constants of cadmium for those of lead. The two values for K_g obtained in this way then differ by a factor of 500 to 1,000, that derived from the superconductivity results being the larger.

The reason for the enormous discrepancy between the two K_g-values is due to the different part played by the conduction electrons in both cases. In the heat conduction in high magnetic fields, the ability of the electrons to transport heat is greatly diminished but

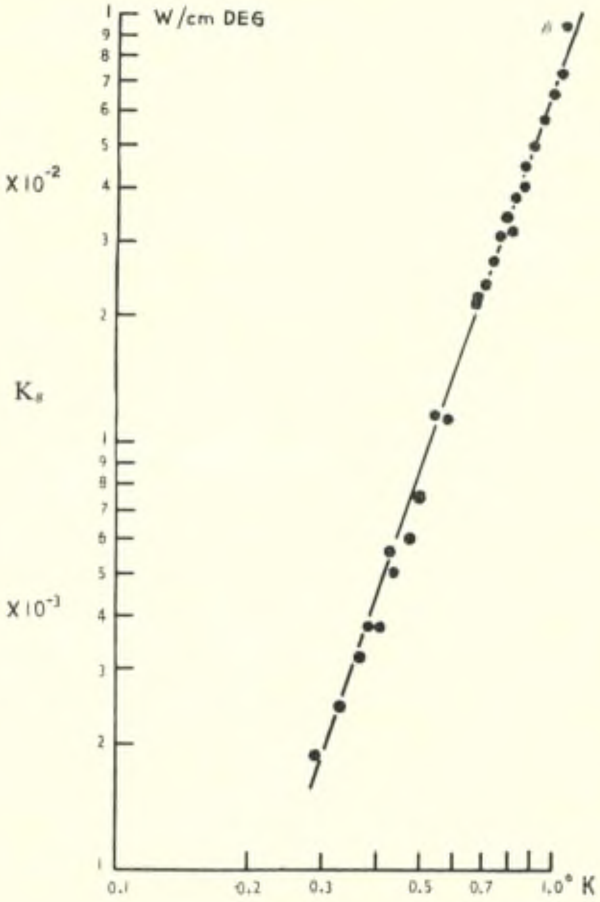

Fig. 4. — Heat Conductivity of a lead single crystal in the superconductive state below 1°K.

the electrons retain, of course, their function as scattering centres for the phonons. In the superconductor, too, the electrons carry no heat but they have also ceased to scatter lattice vibrations. In fact, under the conditions studied in these experiments the reduction of K_g by scattering of phonons on electrons had roughly the same value as K_e in the normal metal. We are thus faced with the surprising result that, at least at low temperatures, the conduction electrons in a metal lower through scattering the lattice conduction by about the same amount as they themselves contribute to the heat conductivity.

Finally I like to mention another series of experiments which have only been started recently but which also promise to give new information on the behaviour of electrons in metals. These are heat conductivity measurements on semi-conductors. Owing to the technical possibilities offered by these substances, good specmiens of silicon and particularly germanium are now becoming available. The samples vary from extremely pure single crystals with a negligible number of current carriers to specimens showing definitely metallic behaviour. As the number of conduction electrons is gradually increased from sample to sample, it should therefore be possible to trace step by step their contribution to the heat conduction as well as their scattering properties. The great advantage of this work will be that it can all be carried out on the same substance which moreover permits comparison with such an ideal dielectric as the

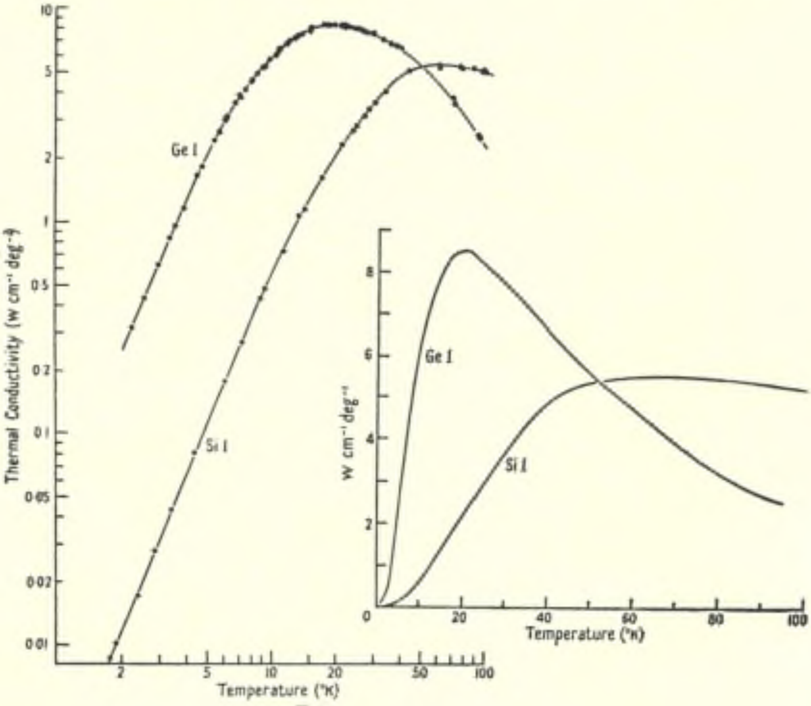

Fig. 5. — The thermal conductivity of germanium and silicon in the range 2 to 100° K plotted on a logarithmic scale. The inset shows the same curves plotted on a linear scale.

diamond with which it shares the same crystal structure. The first results, obtained on very pure germanium and silicon (12), are shown in figure 5. They strongly resemble the observations on diamond (13), showing the form to be expected for a pure dielectric crystal. Quantitative analysis reveals that the mean free path of the phonons is determined by the size of the crystal which in the case of the germanium specimen was identical with its geometric dimensions. The beginning of the series has thus been successful in starting with a sample for which the typical properties of an insulator could be established. Only further experiments can show whether it will be possible to change these properties gradually to those of a metal.

In this short and necessarily incomplete survey no more than a sketchy account of the work on thermal conductivities could be given. However, I hope that I have been able to show the usefulness and the future potentialities of this type of experiment for the study of the behaviour of metal electrons.

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Experimental Methodes for Determining the Fermi Surface

by **A. B. PIPPARD**

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I. INTRODUCTION

Although in elementary treatments of the theory of metals the assumption of a free, or quasi-free, electron gas is made, it soon becomes clear when comparison is attempted of the results of experiment with the theoretical predictions that the model is at best very approximate, except perhaps for the alkali metals and the noble metals of group 1. In order to achieve better agreement the influence of the periodic field of the lattice on the electronic motion must be considered, and at this stage serious difficulties of calculation arise. Between the delineation of the Brillouin zone structure and the quantitative explanation of any single property of a real metal lies an expanse of almost uncharted country, and any information which can serve as a guide must be seriously examined. Perhaps the main experimental obstacle to an understanding of the true behaviour of a metal is that most properties which are strongly influenced by the detailed electronic structure depend on so many factors that it is virtually impossible to sort them out from the experimental data. Thus, to take as an example a phenomenon whose very existence depends on departures from the free-electron model, a complete explanation of the magneto-resistance effect involves knowledge of the form of the energy surfaces in the neighbourhood of the Fermi energy and of the relaxation time at all points of the Fermi surface; to put it in another way, one needs to know the polar distribution of electron trajectories as well as the Fermi velocity, effective mass tensor and relaxation time for all directions of motion. These parameters are so intimately mingled in the general theory of the magnetoresistance effect that they could not be extricated from the experimental results. There are, however, two phenomena, the Anomalous Skin Effect and the de Haas-van Alphen Effect, which have recently been seen to offer a means of attack on the problem, since certain aspects of the effects are interpretable in terms simply of the geometrical form of the Fermi surface, uncomplicated by other factors. Moreover the connexion between the geometry and the observed behaviour is such that a systematic survey of the anisotropy of the effects in single crystals promises to be sufficient to determine the Fermi surface completely, at any rate in the simpler metals. Of course, this by itself is not nearly enough — it is only a beginning; but it is at least a beginning. Unfortunately at the present time is not possible to quote any positive successes of these methods of attack. The labour involved in a systematic study of even a single metal is very considerable, and none is complete yet. We can do no more, therefore, than present the theory of these effects in so far as it is relevant to our particular problem, and point out, with the aid of what data are available, the way in which they may be applied and the sort of difficulties, experimental and theoretical, which are likely to occur in practice.

There are two basic assumptions common to both theories which should be pointed out at the very beginning. The first is that interactions between the electrons may be neglected, so that the electron assembly may be treated as a perfect gas obeying Fermi statistics, but having an arbitrary dependence of energy E on wave-number $\underline{k}$. The second assumption is that the electrons may be treated semi-classically, quantisation being introduced where necessary by means of the Bohr-Sommerfeld-Wilson rule. Where, as in the theory of the de Haas-van Alphen effect for ellipsoidal energy surfaces, comparison may be made between the predictions of the semi-classical theory and of an exact wave-mechanical treatment, there appear to be no discrepancies. The validity of the first assumption, however, cannot be simply ascertained, and must be justified, if at all, either by a more searching theoretical treatment or by appeal to experiment. If the assumption should prove false the method of analysis used will be equally invalid; but in any case under these conditions the whole question of what is meant by the Fermi surface will need re-examination.

II. THE ANOMALOUS SKIN EFFECT

The phenomenon which has since come to be called the « anomalous skin effect » was first observed by H. London (2), and after the war investigated experimentally by Pippard (3), Chambers (4) and Fawcett (5) in Cambridge, and by a number of other workers (6) elsewhere. The quantitative theory for an isotropic metal was given first by Reuter and Sondheimer (7), and later refinements have been made by Holstein (8) and Dingle (9). Recently Sondheimer (10) has extended the theory to cover ellipsoidal energy surfaces, and Pippard (11) has used the results of Sondheimer's work to justify a more geometrical approach which may be applied to Fermi surfaces of any shape. We start with a brief outline of the phenomenon and its interpretation in an isotropic metal.

If a high frequency current is carried by a plane surface ($\underline{J} = J_x(z)$, $\underline{\varepsilon} = \varepsilon_x(z)$, $\underline{H} = H_y(z)$) the fields and currents are confined to a thin layer at the surface, whose thickness may readily be determined if « normal » conductivity be assumed, i.e. if $\underline{J}$ and $\underline{\varepsilon}$ may be related by Ohm's Law in the form $\underline{J} = \sigma\underline{\varepsilon}$; σ here is the d.c. conductivity. For according to Maxwell's equations, for an oscillation of angular frequency ω :

$$d^2\varepsilon/dz^2 = 4\pi i\omega J \tag{1}$$

if we neglect displacement current, put the magnetic permeability equal to unity, and work in electromagnetic units. Combining this equation with Ohm's Law, we have :

$$d^2\,\varepsilon/dz^2 = 4\pi i\omega\sigma\varepsilon\ , \tag{2}$$

with the solution, for a semi-infinite slab :

$$\varepsilon = \varepsilon(o)e^{-kz},\ \text{ where } k = (1+i)\sqrt{2\pi\omega\sigma}\ . \tag{3}$$

Thus the fields and current decay exponentially into the metal, with an extinction distance (skin depth) :

$$\delta_r = 1/R(k) = (2\pi\omega\sigma)^{-\frac{1}{2}}\ . \tag{4}$$

The property which can be measured experimentally is the surface impedance, which is defined by the equation :

$$Z = \varepsilon\,(o)/\int_o^\infty J dz\ .$$

In the normal skin effect it follows from (3) and Ohm's Law that :

$$Z = k/\sigma = (1+i)(2\pi\omega/\sigma)^{1/2},$$

so that the real part of Z, the surface resistance R, is given by the equation :

$$R = (2\pi\omega/\sigma)^{1/2} = 2\pi\omega\delta_r \, . \tag{5}$$

Equation (5) exhibits the relation between R and δ_r , and we shall adopt this as a definition of the skin depth in cases where the field does not decay exponentially. It is simply a convenient measure of the thickness of the surface layer to which most of the field is confined.

Expertimentally it is usually found that at microwave frequencies $10^9 - 10^{11}$ cycles/sec.) $R \sim \sigma^{-1/2}$ at ordinary temperatures, in accordance with (5), but that as the temperature of a pure metal is lowered, so that σ increases, R begins to vary more slowly with σ than is predicted by (5), and with a really pure metal R becomes independent of σ as the latter rises to the very high values then attainable. It is this departure from (5) which constitutes the anomalous skin effect, and the explanation of the effect is to be found in the very long mean free path, l, of conduc-tion electrons in pure metals at low temperatures. For example in the purest obtainable tin, below 5^0 K_0 $\sigma = 1$ e.m.u. and $l = 10^{-2}$ cm, while for a 3 cm wavelength oscillation ($\omega = 2\pi \times 10^{10}$) :

$$\delta_r \sim 1.6 \times 10^{-6} \text{ cm.}$$

Thus $l \gg \delta_r$ so that during the course of one free path most electrons will spend only a minute fraction of the time in a region where the field is non-vanishing. Under these circumstances the assumption that $J = \sigma\varepsilon$ is quite inadmissible, and a new approach to the conduction equation is required. At any point in the metalthe electrons there contributing to the current may have passed through a highly varying field, and acquired additional momentum therefrom, and the current must be calculated by a suitable integration of the contributions due to the electric field in the whole surrounding region. For an isotropic metal the appropriate refinement ([12]) of Ohm's Law is as follows :

$$\underline{J} = \frac{3\sigma}{4\pi l} \int \frac{\underline{r}(\underline{r} \, . \, \underline{\varepsilon}) e^{-r/l}}{r^4} \quad d\tau \, , \tag{6}$$

in which $\underline{r}$ is the radius vector from the volume element $d\tau$ to the point at which $\underline{J}$ is to be calculated. It is readily seen that if $\underline{\varepsilon}$ is sensibly constant over a distance of the order of l (6) reduces to the form $\underline{J} = \sigma\underline{\varepsilon}$.

The substitution of (6) in (1) and the solution of the resulting integro-differential equation was first made by Reuter and Sondheimer (⁷). Their solution showed good agreement with the experimental results (a particularly careful study was made by Chambers (⁴) at a wavelength of 25 cm), and thus provided an explanation of the asymptotic approach of R to a constant value. The region of behaviour in which l is so much greater than δ_r that R has effectively its limiting value R_∞ is known as the « extreme anomalous limit », and it is in this region that the behaviour of the metal becomes tractable by more intuitive methods.

When l is much greater than δ_r only those electrons which move nearly parallel to the surface can execute a substantial fraction of a free path within the surface layer which contains the field. It is only such electrons that are fully effective in the conduction process, and we may tentatively divide the electrons into two groups according as their components of velocity normal to the surface are greater or less than $\beta\delta_r/\tau$; here τ is the relaxation time, related to the mean free path by the formal definition $l = V_0\tau$, V_0 being the Fermi velocity, and β is a numerical constant whose value can only be determined by an exact analysis. If the normal velocity is less than $\beta\delta_r/\tau$, the electron spends more than a fraction $1/\beta$ of its free path in the field at the surface, and is regarded as effective in the conduction process, while the remaining electrons, spending less time in the field, are regarded as ineffective and completely ignored. Further, we assume that the effective electrons move parallel to the surface, in a constant field, so that if f is the effective fraction of electrons the effective conductivity may be written as simply $f\sigma$. This crude simplification of the theory, known as the « ineffectiveness concept », can only be justified by comparison with the exact theory, but we shall see that the justification appears to be sound. If the Fermi surface is spherical the value of f is easily calculated to be $\frac{3}{2}\beta\delta_r/l$, so that we insert into the theory of the normal skin effect an effective conductivity :

$$\sigma_{eff} = \tfrac{3}{2}\beta\delta_r\sigma/l\,. \tag{7}$$

Combining (7) with (4) we have :

$$\delta_r = (3\pi\omega\beta\sigma/l)^{-1/3},$$

and for the surface resistance :

$$R = \left(\frac{8\pi^2\omega^2 l}{3\beta\sigma}\right)^{1/3} \tag{8}$$

An anternative form for R which will prove of use in the general theory follows from (7) and (8) :

$$R = (4\pi^2\omega^2\delta_r/\sigma_{eff})^{1/3} . \tag{9}$$

It will be seen from (8) that the expression for R contains σ only in combination with l, and as σ/l is a constant for a given metal R is independent of σ. This (8) is applicable, if at all, only in the extreme anomalous limit, and the expression we have derived is the value of R_∞ . Now according to Reuter and Sondheimer :

$$Z_\infty = (1 + \sqrt{3}i)(3\pi^2)^{1/6}(\omega^2 l\sigma)^{1/3} ,$$

so that (8) may be made to have the correct value by choosing :

$$\beta = 8\pi/3^{3/2} = 4.836 .$$

The ineffectiveness concept thus provides a physical model for the constancy of R when $l \gg \delta_o$ but it is not surprising that the form of the expression derived is correct, since it is the only possible form, for dimensional reasons, having this property. The real test of the concept as a useful simplification lies in its application to anisotropic Fermi surfaces, to see whether it predicts the right anisotropy of the surface resistance, i.e. whether β can be assumed constant for all shapes of the Fermi surface. Fortunately Sondheimer (^{10}) has extended the exact theory to include one or more spheroidal Fermi surfaces, and his result may be compared with that predicted by the ineffectiveness concept (^{11}). It is found that there is complete agreement, so that we may proceed with some confidence to use the concept to derive a general expression for R_∞ in terms of the form of the Fermi surface. The derivation of the formula for R_∞ in the case of spheroidal surfaces will not be given here; it may be obtained from the general result which we now derive.

We shall treat in detail only the hypothetical case of a two-dimensional metal, which enables all the main points to be made simply, and merely quote the corresponding result for a real three-dimensional metal. In the two-dimensional metal the energy surfaces are curves in momentum space (p-space), either closed or terminating on zone boundaries and capable of redistribution into closed curves in a reduced zone scheme. The normal to a curve at any point gives the direction of motion of the electron represented by that point, and we shall assume that V_o and τ may vary arbitrarily along the Fermi surface. It is convenient to describe the curves at each point by the radius of curvature, ρ and the direction of the normal, $\varnothing$, relative to some axis fixed with respect to the crystal axes. Within the Fermi surface the density of occupation is $2/h^2$ per unit area of momentum space and of metal.

If the fixed axis is inclined at an angle θ to the edge of the metal the electrons which suffer greatest displacement by the electric field are those in the vicinity of the curve $\varnothing = \theta$, as, for example, in figure 1, and in general this curve will not be a straight line. When an electric field is applied parallel to the edge there will if necessary be set up a normal field to prevent current flow normal to the edge. The resultant field cannot in general be parallel at all points to the curve $\omega = \theta$ so that the displacement in p-space of the effective electrons will not necessarily be along the curve. Since electrons which do not lie on or near the curve are displaced less there will be an apparent bunching of electrons at some points and thinning-out at others. These changes of density in momentum space are, however, compensated for by changes of density in ordinary space so that, by Liouville's theorem, the density in phase-space remains

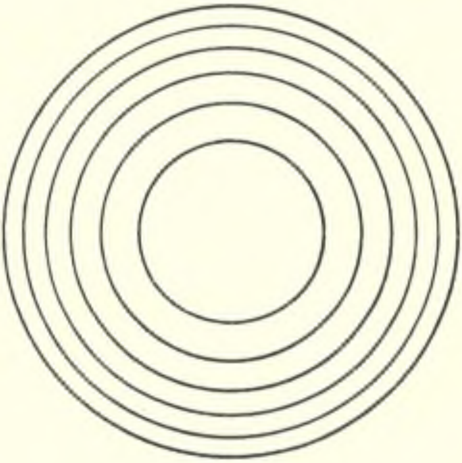

Fig. 1

constant. If, therefore, we confine our attention to those electrons which occupy a given area of ordinary space (as we must do in calculating the current density), the density of occupation of the corresponding momentum space will remain constant. Hence, in spite of this additional complication, there is no need to consider the current as arising from any effect other than deformation of the Fermi surface. Moreover, we are interested only in displacements of the Fermi surface normal to itself, and therefore, when we apply the ineffectiveness concept, only in the displacement of the effective electrons which is caused by ε_x, the component of $\underline{\varepsilon}$ parallel to the edge of the metal.

Consider then the region around the point P in figure 1, the region occupied by the effective electrons at the Fermi surface. If V_o and τ are the electronic velocity and relaxation time respectively at P, the effective electrons must move within an angle $2\beta\delta_r/(\nu_o\tau)$, and occupy a length of arc $2\beta\delta_r|\rho|/(\nu_o\tau)$. Under the influence of a constant field $\underline{\varepsilon}$ the equilibrium displacement of the Fermi surface normal to itself will be $e\varepsilon_x\tau$, and there will be a similar displacement at the other end, P′, of the line $\varphi = \theta$. Effectively therefore, the electrons occupying an area $2\beta\delta_r e|\rho|\varepsilon_x/\nu_o$ are transferred from P′ to P, having their velocities reversed in sign. The current density is consequently given by the expression :

$$J_x = 8\beta\delta_r|\rho|e^2\varepsilon_x/h^2\,,$$

so that :

$$\sigma_{eff} = 8\beta\delta_r|\rho|e^2/h^2. \tag{10}$$

Hence from equation (9) :

$$R = \left(\frac{\pi^2\omega^2h^2}{2\beta|\rho|e^2}\right)^{1/3} = \frac{\sqrt{3}}{2}\left(\frac{\pi\omega^2h^2}{2|\rho|e^2}\right)^{1/3} \tag{11}$$

The surface resistance in the extreme anomalous limit is thus seen to depend only on $|\rho|$, and not on ν_o or τ. From a study of R as a function of θ it is clearly possible to deduce immediately the relation between $|\rho|$ and φ for the Fermi surface, since $|\rho|$ is always determined at the point at which $\varphi = \theta$ and :

$$|\rho| = \frac{3^{3/2}\pi\omega^2h^2}{1\sigma e^2R^3}\,. \tag{12}$$

Thus a plot of $1/R^3$ against θ is also, apart from a scaling factor, a plot of $|\rho|$ against φ, from which, by graphical construction if necessary, the shape of the Fermi surface may be found.

The extension of this result to a real metal is straightforward and we shall merely quote the result, but first we must note that caution must be exercised in applying the ineffectiveness concept in this case. For any given surface, oriented arbitrarily with respect to the crystal axes, the surface resistance is necessarily, on account of the linearity of the system, a second-rank tensor. If we choose x and y axes on the surface to coincide with the axes of the tensor, then for current flowing at an angle φ to the x-axis the corresponding resistance :

$$R(\varphi) = R_x \cos^2\varphi + R_y \sin^2\varphi \,, \tag{13}$$

R_x and R_y being the principal resistivities of the surface. Now it may be shown that the ineffectiveness concept is only valid when applied to the calculation of R_x or R_y, and not at intermediate angles. This does not matter, however, since (13) automatically fills in the gaps. In general it is not possible to derive by simple arguments the orientation of the principal axes of the surface with respect to the crystal axes, and this would have to be done by experiment in any application of the method (except of course for certain orientations of the surface for which the principal axes are fixed by symmetry requirements).

It is easy to show that along a principal axis the metal behaves as a stack of two-dimensional metals. For example, if we wish to calculate R_x, we may section the Fermi surface by planes normal to the y-axis; on any one of these plane sections there will be points where the normal to the Fermi surface lies parallel to the surface of the metal, and these will be the effective regions of the section. If at any one of these points the radius of curvature, in the plane of the section, is ρ_y then the contribution of the section to the surface resistance may be written. following (11) :

$$d(R_x^{-3}) = \frac{\beta e^2 |\rho_y| dy}{\pi^2 \omega^2 h^3} \,,$$

and by integration :

$$R_x = \left\{ \frac{\pi^2\omega^2h^3}{\beta e^2\int|\rho_y|dy} \right\}^{1/3} , \tag{14}$$

the integral extending over all parts of the Fermi surface where the normal lies parallel to the surface of the metal. A similar result obtains for R_y , and so from (13) we have, substituting for β :

$$R\ (\varphi) = \frac{\sqrt{3}}{2} h \left(\frac{\pi\omega^2}{e^2}\right)^{1/3} \left\{ \left(\int|\rho_y|dy\right)^{-1/3} \cos^2\varphi + \left(\int|\rho_x|dx\right)^{-1/3} \sin^2\varphi \right\} . \tag{15}$$

From this result, and the method of derivation, it will be seen that the anomalous skin effect selects a certain limited region of the Fermi surface in the form of a band, and measures a particular average of the curvature on the band. Thus by studying crystals oriented differently with respect to the surface the variation of the property over the surface is determined, and by perseverance the shape of the surface may be constructed. There are, however, obvious difficulties in application which need further discussion, but this we shall leave until a later section. Before passing on to the other methods of obtaining information about the surface it is of interest to quote a result arising from the theory just presented, which was given first, in not quite exact form, by Chambers (4). If the principal resistivities of the surface are determined for all orientations of the crystal axes relative to the surface, the average value of $1/R^3$ so found is related to the total free area, S, of the Fermi surface in *p*-space, by the equation :

$$\overline{R^{-3}} = 2e^2S/(3^{3/2}\pi\omega^2h^3) . \tag{16}$$

It is probable that, unless the Fermi surface is highly anisotropic, $\overline{R^{-3}}$ is not greatly different from $(\overline{R})^{-3}$ and may be measured by means of a polycrystalline sample. Thus the method enables S to be determined fairly easily. We shall touch on this point again later.

The de Haas-van Alphen effect

It was found by de Haas and van Alphen (13) that at very low temperatures the magnetic susceptibility of bismuth in high fields ($\sim 10k$G) showed a periodic variation with field strength. At first regarded as a peculiarity of bismuth, the effect has since been demonstrated in many other metals, Zn (Marcus) (14), Ga, Sn, Cd, In, Sb, Al, Hg, Tl, Graphite (Shoenberg) (15), Mg, Be (Verkin, Lazarew and Rudenko (16), who also observed the effect in some metals already listed), As (Berlincourt) (17) and Pb (Shoenberg) (18). An explanation of the effect was first given by Peierls (19) for a free electron model, and the theory has been subsequently refined by many workers (20). We shall not be concerned here with a general discussion of the details of the theory, to which references are given by Shoenberg (15), but mainly with those aspects which directly concern the study of the Fermi surface, and we shall draw largely on the ideas recently expounded by Onsager (21).

In order to clarify the later discussion it will be convenient to consider first the theory of the effect in a two-dimensional free-electron metal, in which at O°K the electrons are uniformly distributed within a circle in p-space, having radius p_o corresponding to a Fermi energy $E_o = p_o^2/2m$. The density of the states in p-space will be Q/h^2 per unit area, if Q is the area of the metal considered, and electron spin is neglected for the moment. From the semi-classical viewpoint the trajectories of the electrons are straight lines in the absence of a magnetic field, but when a field is applied normal to the plane of the metal the trajectories are bent into circles of radius $p/(eH)$. We shall continue to use the symbol $\underline{p}$ to represent the kinetic momentum, $m\underline{v}$, but it is important to remember that in a magnetic field it is not $\underline{p}$ but $\underline{p} + e\underline{A}$ which is the momentum conjugate to the positional coordinate $\underline{r}$. Thus we apply the quantization rule to the orbit of a free electron in the form :

$$\int (\underline{p} + e\underline{A}) \,.\, d\underline{r} = (n + \tfrac{1}{2})h \,.$$

If we take the centre of the orbit as origin, $\underline{A}$ may conveniently be written as $\frac{1}{2}\underline{H} \times \underline{r}$, while the electronic velocity takes the form :

$$\underline{v} = -\frac{e}{m}\,\underline{H} \times \underline{r} = -\,2e\underline{A}/m \,.$$

Then :

$$\int \underline{p}(\underline{p} + \underline{A}) \,.\, d\underline{r} = -\,e \int \underline{A} \,.\, d\underline{r} = e\Phi,$$

where Φ is the magnetic flux contained within the orbit. It follows then that only those orbits are permitted which contain half-integral multiples of the fundamental unit of flux, h/e,

$$\Phi = (n + \tfrac{1}{2})h/e \, .$$

Correspondingly the only permitted values of $|\underline{p}|$ are those given by the equation :

$$p^2 = (n + \tfrac{1}{2})eh\mathrm{H}/\pi \, ,$$

and the permitted energies are : $(n + \frac{1}{2})eh\mathrm{H}/m$, i. e. $(2n + 1)\beta\mathrm{H}$,

β being the Bohr magneton. The distribution of states in p-space is thus altered by H from one which is virtually continuous and uniform to one which consists of a series of circles, as in figure 2,

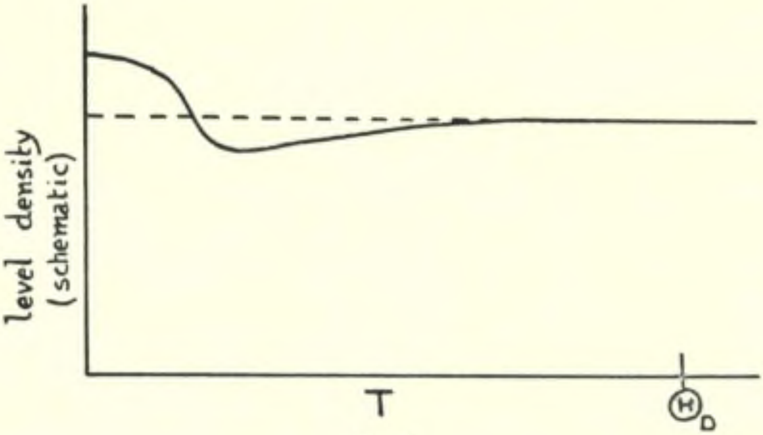

Fig. 2

the area between successive circles being $eh\mathrm{H}$; and the continuum of energy levels is likewise split into a discrete set with an even spacing of $2\beta\mathrm{H}$. The mean density of states remains constant, however, since each of the new energy levels is highly degenerate, having a capacity of $ae\mathrm{H}/h$. The multiplicity of states of the same energy may be thought of as due to the possibility of locating the centres of equivalent orbits at different points in the metal.

So far we have neglected the spin of the electron, and this must now be considered. In a typical orbit of energy $(2n + 1)\beta H$ two electrons of opposite spins may be contained, having spin energy of $\pm \beta H$. Thus the total energy of the electron is either $2n\beta H$ or $2(n+1)\beta H$ according to the aligment of the spin, and as a result the permitted energy levels form an evenly spaced set $E = 2n\beta H$, having a degeneracy $2aeH/h$ except for the lowest $(n = 0)$ which has a degeneracy aeH/h. The way in which spin reconstitutes the energy levels without essentially altering their character is characteristic only of the free-electron model; if the orbital motion is modified by the ionic lattice so that, for example, the effective mass of the electrons is altered, the separation of the orbital levels will be governed by an effective magneton $\beta_{eff} = eh/(2m_{eff})$, and each level will be split by spin into two with separation $2\beta H$. It is, however, the orbital effect which gives rise to the principal features of the de Haas-van Alphen effect, and we shall not consider the effect of spin except in the free-electron model.

In figure 3 the energy levels for the two-dimensional metal with and without a magnetic field are compared. In this particular case

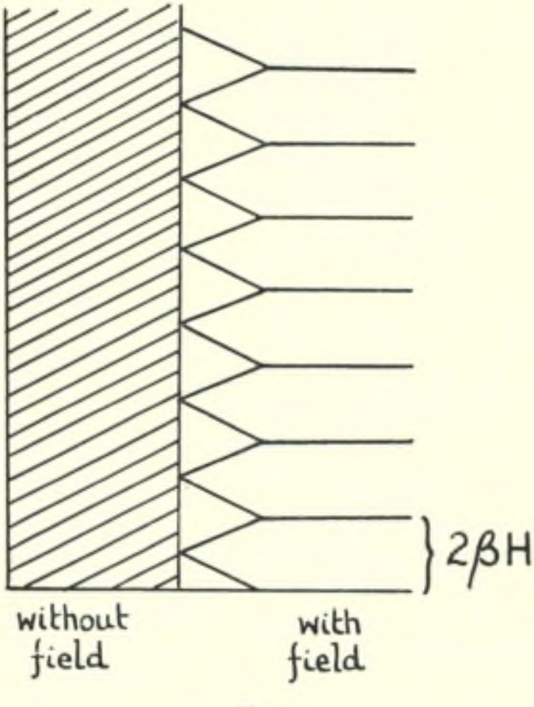

Fig. 3

the density of states in the continuum, when $H = 0$, is uniform, and it is immediately clear that the only groups of electrons whose mean energy is affected by the field are those with energies less than βH, which can go into the lowest state of zero energy, and those at the very top of the filled band. Since the number in the former group is $N\beta H/E_o$, N being the total number of electrons, and on the average they lose energy $\frac{1}{2}\beta H$, the total energy, U, is decreased through the modification to this group by an amount $N\beta^2H^2/(2E_o)$. Since the magnetic moment $M = -dU/dH$, we see that this effect gives rise to a constant paramagnetic susceptibility $N\beta^2/E_o$, which is just the ordinary paramagnetism. The behaviour at the top of the band is more complicated. Here the coalescence of energy levels cannot reduce U, and only when there is a level at a depth βH below the Fermi level is U the same as in the absence of a field; otherwise $U(H) > U(O)$. The energy thus fluctuates periodically with H, and the magnetic moment, $-\delta U/\delta H$, shows corresponding fluctuations. We have here, in a simple model, the origin of the de Haas-van Alphen effect. It is easy to work out the details of the variation of M, but we shall not do so here, for this highly artificial model gives a very exaggerated picture of the magnitude of the effect. In a real metal the variations of U are not nearly so rough as the model suggests, for a variety of reasons :

a) In a real metal, motion along the direction of H is not quantized, except by virtue of the finite dimensions of the specimen;

b) The energy levels are broadened by collisions of the electrons with the lattice;

c) At temperatures above 0° K the Fermi surface is not sharp.

The net result of these modifying influences is to smooth out the fine details of the variation of U with H, reducing the amplitude of the variation and eliminating practically everything but the lowest harmonic component. In practice, therefore, what is usually observed (except sometimes in very pure specimens at the lowest temperatures) is a smoothly periodic variation of M with H. In fact, since the periodicity is governed by the condition that U is unaltered whenever $E_o = (2n + 1)\beta H$, the measured magnetic moment shows a constant period when plotted against $1/H$, and approximates closely to a sine curve. This is something of a simplification of the true picture, since a number of components of different periodicity are often observed, and the amplitude of the oscillations may in addition vary slowly with H. The multiple periodicities will affect us closely in what follows, but we shall henceforth disregard the slow change in amplitude, only remarking that it may be accounted for, at least qualitatively, in a more refined theory.

Before leaving this simple picture to examine a more general theory we may remark that the effects (*b*) and (*c*) noted above provide criteria for the observation of the de Haas-van Alphen effect. For if collision broadening is so extensive as to bridge the gap between successive discrete levels, or if the thermal excitation similarly extends over two or more levels, the periodic variation of U will be much reduced. Thus if the mean time between collisions of electrons with the lattice is τ, from the uncertainty principle we expect collision broadening to be of the order of h/τ, and this must be made less than $2\beta H$ if the effect is not to be seriously diminished. In fact Dingle (22) has shown that collision broadening reduces the effect by a factor $\exp\,(h/(2\tau\beta H))$. Similarly the result of a non-zero temperature is to reduce the effect by a further factor whose principal term is $\exp\,(\pi^2 kT/(\beta H))$. In consequence observations are only possible in rather pure metals (for which τ is large) at temperatures below a few degrees Absolute.

We now consider the generalization of the theory along the lines pointed out by Onsager (21), dealing first with the two-dimensional metal, whose extension to three dimensions involves no new principles. If an electron is represented in *p*-space at a point on the closed curve $E(p) = $ constant, its velocity in real space is $\text{grad}_p E$ and is directed along the normal to the curve. Thus in the presence of a magnetic field the Lorentz force $e\underline{H} \times \underline{v}$ lies along the curve, and the resulting motion of the electron is such as to make its representative point trace out the curve of constant energy. Moreover the speed with which the point moves along the energy curve is given by $\underline{\dot{p}}$, i.e. $e\underline{H} \times \underline{v}$, so that it is at all times proportional to the velocity $\underline{v}$ and perpendicular to it. It follows then that the trajectory in real space is of the same form as the curve of constant energy, but reduced in scale by a factor eH and rotated through a right angle. In calculating the phase integral $\int(\underline{p}+e\underline{A})\,.\,d\underline{r}$ we may therefore write :

$$\int \underline{p}\,.\,d\underline{r} = eH \int \underline{r} \times d\underline{r} = 2eH \times \text{area of orbit.} = 2e\Phi\,,$$

where Φ is the flux contained within the orbit. Also, with the same sign convention, $\int e\underline{A} \, . \, d\underline{r} = -e\Phi$, so that the quantization condition implies, just as for the circular orbit, that $\Phi = (n+\frac{1}{2})h/e$. From this it follows immediately that the permitted trajectories in p-space are those energy curves whose areas are $(n + \frac{1}{2})he\mathrm{H}$.

If, then, the area of the Fermi curve $\mathrm{E}_o(\underline{p})$ is A the energy will be periodic with respect to the magnetic field, equivalent points in different cycles being reached when, for example, $\mathrm{A}=(n + \frac{1}{2})\, he\mathrm{H}$, or $1/\mathrm{H} = (n + \frac{1}{2})he/\mathrm{A}$; the magnetization curve will have a constant period of he/A when M is plotted against 1/H, and from such a curve A is immediately deducible. It is this general result which gives the de Haas-van Alphen effect its potential importance as a tool for determining the form of Fermi surface.

The extension of the argument to a real three - dimensional metal is straightforward. The trajectory of an electron in p-space will be unaffected by the third dimension, parallel to H, which is unquantized, and will follow the intersection of the energy surface with a plane perpendicular to H. Thus so far as quantization is concerned the metal may be thought of as a stack of two-dimensional metals, each with its appropriate value of A depending on the component of momentum parallel to H, which we shall take as parallel to the Z-axis. The resulting variation of U with 1/H will consist of a continuous spectrum of periodicities, which will to some extent smooth out the contributions of different groups of electrons. The periodic behaviour will not, however, be completely eliminated, since there will in general be a value, $p_z^{'}$, or p_z for which A takes an extremal value, and the contributions from this region will dominate the behaviour. For example if we consider such conditions that the phase of the oscillation $\varphi\,(= 2\pi\mathrm{A}/(he\mathrm{H}))$ is high, a very small relative variation of A from its extreme value A_o will give rise to a significant change in φ, and we need only consider, as we shall see immediately, the contributions from the neighbourhood of the extremum, where we may write as an adequate approximation :

$$\mathrm{A} = \mathrm{A}_o \pm \alpha p^2,$$

in which $\alpha = \frac{1}{2}\left|(d^2\mathrm{A}/dp_z^2)_{p=0}\right|$, and $p = p_z - p_z^{'}$. Let us now assume that for an infinitesimal strip, dp, considered as a two-dimensional metal, the variation of dU with $1/H$ has the simple form :

$dU = dU_o + B \cos (Ax + \varepsilon)\, dp$, where $x = (heH)^{-1}$ and ε is a constant phase correction.

Then for the whole metal :

$$U = U_o + B \int_{-\infty}^{\infty} \cos \{(A_o \pm \alpha p^2)x + \varepsilon\}\, dp\,.$$

The integral converges fairly rapidly as p increases (Cf. the Cornu spiral), so that the only part of the Fermi surface which contributes significantly is that for which φ lies within a few cycles of its extreme value φ_o ($= 2\pi A_o/heH$) and :

$$U = U_o + B \sqrt{\frac{\pi}{\alpha x}} \cos (\varphi_o + \varepsilon \mp \pi/4)\,. \qquad (17)$$

Thus the de Haas-van Alphen oscillations observed in a real metal should be the same as those predicted for a two-dimensional metal having an energy curve identical with the extremal cross-section in the real metal, except for an amplitude factor and an extra phase correction depending on whether the extremal section is a minimum or a maximum. It should be remembered, however, that we have given a far from complete analysis of the problem and have neglected some of the factors which influence both phase and amplitude. We shall not try to refine the analysis any further here, partly because it is the periodicity which has the most direct application to the problem in hand. It may be that other aspects of the effect will eventually prove of value, but at the moment it does not seem very likely. It is worth noting at this stage, however, that a detailed comparison between theory and experiment can be made with certain metals (see e.g. Shoenberg) (11), and such comparison is desirable in order to ascertain whether there are any discrepancies which require further refinement of the theory. At present it does not seem that anything very definite can be said concerning amplitudes and phases, except that the temperature variation of the amplitude is in reasonable accord with prediction. But on the most important point, the predicted constant period of the oscillations when plotted against 1/R, there is complete confirmation of the theory for all metals studied so far.

Let us now consider the trajectory in real space of an electron, which will move so as to keep a constant component p_z of momentum parallel to the field. In the free-electron model this implies that the trajectory will by a uniform circular helix, but in general the motion will not be so regular. For as the electron executes one cycle of its revolution about $\underline{H}$, the velocity $\underline{v}$ will not necessarily be constant, and in consequence V_z will vary, though of course the variations will be exactly repeated in each cycle. If the z-axis does not coincide with a crystal axis the asymmetry of the helix will in general give rise to a component of magnetic moment perpendicular to $\underline{H}$, and the crystal will in consequence experience a couple, whose magnitude, G, is given by $-(\delta U/\delta\theta)_H$, θ being the orientation of the crystal with respect to an axis of suspension normal to $\underline{H}$. if U is expressed by (17), we have immediately :

$$G = B\nu\pi\left\{\frac{\sqrt{heH}}{2\alpha^{3/2}}\frac{d\alpha}{d\theta}\cos\left(\frac{2\pi A_o}{heH} + \varepsilon \mp \pi/4\right) + \frac{2\pi}{\sqrt{heH\alpha}}\frac{dA_o}{d\theta}\sin\left(\frac{2\pi A_o}{heH} + \varepsilon \mp \pi/4\right)\right\}$$

In this expression the coefficient of the second term is larger than that of the first by a factor of the order of $2\varnothing_o$, so that, except in such high fields that φ_o is quite small, the first term is negligible and G has the same periodicity as U. This result is of great importance since it is often more convenient to measure the couple acting on a specimen than to determine its susceptibility.

Experimental techniques

It is desirable at this stage to say a little about the experimental techniques which are available for studying the anomalous skin effect and the de Haas-van Alphen effect, and to point to some of the difficulties which are likely to limit the application of the methods. In order to keep the discussion realistic let us first consider what would be observed with copper if it were an ideal free-electron metal; this will indicate roughly what conditions must be satisfied for useful results to be obtained with real metals. The number of conduction electrons per cm^3 (taking 1 electron per atom) is 8.5×10^{22}, and the radius of the Fermi sphere in p-space is 1.4×10^{-19} gm.cm/sec. With these values the expected surface resistance at a frequency of 10^{10} cycles/sec (wavelength 3 cm) in the extreme anomalous limit is 5.2×10^{-3} ohm, which is quite convenient for measurement by either resonance or calorimetric methods, as will be discussed later. The skin depth corresponding to this resistance (equation 5) is 1.3×10^{-5} cm. Now at room temperature the mean free path of the conduction electrons in copper is about 4.2×10^{-6} cm, so that, since in order to attain something near the extreme anomalous limit l must be about 100δ, or more, it will be necessary to use copper of such purity that the residuaal resistance is 300 times less than the room temperature resistance. It is clear, therefore, that the peculiar simplicity of the anomalous skin effect only manifests itself in the purest of materials.

For the same metal the period of the de Haas-van Alphen oscillations, plotted against 1/H, is 1.7×10^{-9} Gauss^{-1} so that even in a field as high as 10^5 Gauss the spacing of the oscillations is only 17 Gauss. This means that a highly refined technique will be necessary to observe the effect in a metal such as we are considering, and shows also that the effect observed at lower fields cannot, except in special cases, represent the contribution of the major part of the Fermi surface. We shall return later to the interpretation of these oscillations found in lower fields, but it is of interest before leaving the free electron model to consider the conditions of temperature and purity necessary to observe the rapid oscillations. If we confine our attention only to a diametrical plane of the Fermi sphere, which is the region determining the periodicity of the effect, we may treat it as two-dimensional metal and quote the results derived above, that the effect of working at a temperature T with collision time τ is to reduce the amplitude by a factor exp $\}(\pi^2 kT + h/2\tau)/(\beta H)\{$. If a field of 10^5 Gauss, then, there will be significant loss of amplitude if the temperature is higher than 1°K or to collision time shorter than 5×10^{-12} seconds, which is 200 times longer than the collision time in copper at room temperature. It is therefore clear that for the observation of the effect due to the major part of the Fermi surface of most metals the required conditions of field strength, temperature and purity are only realisable with an effort. Moreover we can understand how it is that the effects observed hitherto have usually corresponded to Fermi surfaces apparently much smaller than would be expected if all the conduction electrons were contributing, since only rarely have the conditions for observing the latter been met.

So far as experimental methods are concerned there are two principal methods which have been investigated for each effect, and these can be described briefly. The surface resistance at microwave frequencies may be measured by a reconance method, in which the quality factor, Q, is determined for a resonator constructed of the metal, or by measuring the heat generated in a metal plate when a microwave beam is reflected from it. The first method is in principle absolute, if the design of the resonator is simple enough for the relation between Q and R to be calculated theoretically. The calorimetric method is not easy to make absolute on account of the difficulty of measuring the intensity of the incident beam, but, as Fawcett has shown, it is possible to make comparative measurements by allowing the same beam to fall on the test surface and on a standard comparison surface which may be separately calibrated. Apart from one or two experimental difficulties which will be mentioned when we discuss some results the measuring techniques present no major obstacles, and the chief difficulty lies in the preparation of specimens. A complete survey of the anisotropy of R, from which the Fermi surface may be constructed, demands the preparation of single crystal surfaces of known crystal orientation, and the geometry of the apparatus must be such that the current flow at all, or nearly all, points on the surface is in a constant direction. This implies that plane surfaces must be used, and it is difficult to arrange for these to be very small unless the wavelength used for measurement is also small. In addition, since the current is confined to a depth of about 10^{-5} cm, the surface must be extremely smooth. The deformations introduced by mechanical polishing are sufficiently serious to cast doubt on any results obtained with specimens so polished, and probably electrolytic polishing is the only satisfactory way of preparing the surfaces. It is unfortunate that there are few metals (tin is the outstanding example) which can be both readly crystallised and well polished electrolytically, so that advances in this method must wait upon technical advances in the preparation of specimens.

The de Haas-van Alphen effect is not handicapped in this way, being a body effect, so that surface polish is immaterial. On the other hand the crystals used must be much more nearly perfect than for resistance studies; for the phase of the oscillations may be a very rapid function of orientation, and the presence of disoriented crystallites may smooth out the effect altogether. It is for this reason that we have paid scant attention to the theoretical estimate of the amplitude of the effect — in the most interesting cases, when all the electrons are contributing, the phase in any attainable field is usually so high that the inevitable mosaic structure of even the best crystals modifies the amplitude to some extent. But even without this diminution of amplitude the oscillations of magnetic moment are so small as to require special care in their detection. The direct measurement for example, of susceptibility or differential susceptibility by standard methods appears to be impraticable except in a few special cases. Most of the work to date has been done by means of a torsion balance, to determine the oscillations in the couple experienced by the specimen in a constant field. This method has its blind spots, since there is no couple when the field lies along a symetry axis of the crystal, but it is extraordinary how close to ($< 1^{\circ}$) a symmetry axis the couple can still be detected usually. The principal defect of this torsion method is the purely practical difficulty of setting up and maintaining steady a uniform field greater than about 20,000 Gauss, and in fact very little work has been done in fields higher than this by the method. Recently Shoenberg ([18]) has devised an ingenious technique for measuring the differential susceptibility in very high fields. The specimen, a thin single-crystal wire, is placed in a solenoid (wound so as to produce a highly uniform field), which is shock-excited by the discharge of a battery of condensers through its windings. The field rises to something over 10^5 Gauss and decays again within a few milliseconds. But while the field varies smoothly, the magnetization of the specimen shows a high-frequency ripple if de Haas-van Alphen oscillations are present, and these may be picked up and amplified, and their frequency determined. By comparison of this frequency with the measured rate of change of the field the periodicity of the oscillations is found. The striking of the method is that it is particularly sensitive to the oscillations of shortest period, since these give rise, other things being equal, to the greatest rate of change of magnetization. On the other hand, to detect a ripple of period 17 Gauss in a field of 10^5 Gauss demands very high homogeneity of the field. Although this may be attained by careful winding of the solenoid there is another factor of importance, the skin effect in the specimen. The changing field does not penetrate immediately throughout the specimen, since circulating eddy currents are set up, and there may well be inhomogeneity of field within the specimen from this cause. As a result it is necessary to use very fine wires as specimens, and even then to rely considerably on the magneto-resistance effect to cut down the magnitude of the eddy currents. The method has been shown to work successfully for tin and lead, which have a high magneto-resistance effect, but so far no results have been obtained for any other metals. In spite of these difficulties, however, Shoenberg's method shows high promise as the only known way of extending de Haas-van Alphen measurements into the range of fields where the results should be really interesting.

Applications

From the theory it will be seen that the two methods have this in common, that they select certain regions of the Fermi surface and give information about its geometrical properties. In the anomalous skin effect the regions selected are those where the normals are parallel to the surface of the specimen, i.e. those parts that form the edge of the shadow which the Fermi surface would cast under normal illumination, and the information provided is of the mean curvature in planes perpendicular to the surface of the specimen. In the de Haas-van Alphen effect what is measured is the extremal area of the Fermi surface when intersected by planes normal to the magnetic field. A very important difference between the methods is that in the latter each portion of the Fermi surface or surfaces which has an extremum of area gives rise to its own periodicity, so that the contributions of different Brillouin zones are separable, while in the former no such separation is possible. It seems, then, that the interpretation of the de Haas-van Alphen effect is likely to be rather easier than that of the anomalous skin effect, if a complete set of data for all orientations is obtained. But even this, to judge from measurements already made, may prove difficult, and the results of both experiments together would be a considerable improvement on one only.

At present no such complete sets of data exist and it is hard to predict how troublesome their analysis will be when they are obtained, and how much help will be provided by other information, e.g. the known Brillouin zone structure and the number of electrons which must be fitted into the zones. The only metal for which the anomalous skin effect has been studied in any detail is tin. Fawcett's results on this metal are not yet quite complete, but it is hoped to be able to present them at the conference. There is no doubt about the high anisotropy of the Fermi surface in tin, for the surface resistance at 8 mm wavelength varies over a factor of more than 2. From equation 14 it will be seen that this implies variations of the « average curvature » $\int|\rho|dy$ over a factor of 10 or more. Fawcett has shown that his results, so far as they go, are approximately consistent with a model Fermi surface consisting of 3 separate ellipsoids, each very flat, and each with its smallest axis directed along one of the tetrad or dyad axes. But there is some difficulty in fitting these ellipsoids into the very complicated Brillouin zone structure, and at the moment the prospect of arriving at an acceptable interpretation of the results is not very promising. It is satisfactory, however, that the periods of the de Haas-van Alphen oscillations to be expected from this model do not differ greatly from those found in the preliminary survey of tin which Shoenberg has conducted with his new high-field method. It is to be hoped that a more detailed study of the latter will clarify the situation, although it must be admitted that tin is so complex that it is not the metal which one would choose in testing these new methods, if it were not for the comparative ease of preparation of suitable specimens. A relatively simple metal like copper offers much more hope of successful analysis by means of the anomalous skin effect, and there is a reasonable chance that the technical problem of preparing specimens can be surmounted.

Before leaving the topic of the anomalous skin effect it is worth mentioning that the combination of its results with specific heat measurements enables the mean reciprocal Fermi velocity to be determined. If we designate by dS an element of the Fermi surface in p-space, we may define the mean reciprocal Fermi velocity $\overline{1/v_o}$ by the equation :

$$\overline{1/v_o} = \frac{1}{S}\int\frac{dS}{v_o} = \frac{1}{S}\int dS/|\mathrm{grad}_p E| .$$

Now the density of states at the Fermi level is :

$$\frac{2}{h^3}\int dS/|\mathrm{grad}_p E|$$

per unit volume of metal, from which it follows that the coefficient γ

of the electronic specific heat per unit volume is given by :

$$\gamma = \frac{2\pi^2k^2S}{3h^3}\,\overline{1/\nu_o}\,.$$

Hence from (16) :

$$\overline{1/\nu_o} = \frac{\gamma e^2}{\sqrt{3}\pi^3\omega^2k^2\;.\;\overline{1/R^3}}$$

or for a not too anisotropic metal :

$$\overline{v}_o = \frac{\sqrt{3}\pi^3\omega^2k^2}{\gamma e^2\overline{R}^3}\,, \tag{18}$$

in which $\overline{R}$ is the surface resistance of a polycrystalline specimen at frequency ω. Equation 18 leads to the following table of values of $\overline{V}_o$:

Metal	γ(ergs deg^{-2}cm^{-3})	$\omega^2/\overline{R}^3$ (e.m.u.)	$\overline{v}_o$ (cm/sec^{-1})	ν'_o (cm/sec^{-1})
Cu	1.05×10^3	28.3	1.07×10^8	1.56×10^8
Ag	0.94	15.8	0.67	1.38
Cd	0.42	10.5	0.99	1.61
Al	1.24	37.5	1.20	2.00
Sn	1.14	17.4	0.61	1.88
Pb	1.98	17.3	0.35	1.81

Of these values, probably those for Cu, Al and Sn are the best; the others may be in error by as much as 50 % owing to the uncertainties in $\overline{R}$ and γ, and are likely to be underestimated. It should be remembered that (18) is only approximate, since we have altered the forms of the averages, and in a highly anisotropic metal like tin the resulting error may be significant. Nevertheless the values obtained are not unreasonable in comparison with v'_o, the values for a free-electron gas having the same number of valence electrons.

It will be seen from these figures that the relaxation time, $\tau(= l/v_o)$, may become quite long at low temperatures. For example in the purest tin l may be as long as 10^{-2} cm, so that $\tau \sim 1.6 \times 10^{-10}$ sec. Now in Fawcett's experiments the angular frequency ω was 2.5×10^{11}, so that $\omega\tau \sim 40$. It might be thought that the theory given above, which ignores relaxation effects, would be quite inadequate under these conditions, but Reuter and Sondheimer have shown that in the anomalous skin effect the criterion for neglecting relaxation effects is not that $\omega\tau \leqslant 1$ but that $\omega\tau' \leqslant 1$, where τ' is the time taken by an electron in traversing the skin depth normally. Thus $\tau'/\tau = \delta_r/l \sim 10^{-3}$ in these experiments, and $\omega\tau' \sim 1/25$, so that relaxation is still rather unimportant. When, at infra-red frequencies, relaxation effects dominate the behaviour, the anomalous skin effect becomes fairly simple once more, as Holstein(8) has shown, and the absorption coefficient of the metal for normally incident radiation should be $\frac{3}{4}\,v_0/c$. It would seem that this might provide an alternative method for measuring v_0, but such results as are available are not encouraging, the absorption coefficient being two or three times as great as expected. The explanation of this is not known.

We turn now to a brief survey of the experimental results on the de Haas-van Alphen effect. Little need be said about the details of the results, but there are a few general points of interest. The effect is observed for many metals in comparatively weak fields ($\sim 10^4$ Gauss), and the period of the oscillations, when plotted against 1/H is much longer than might be expected. It is clear that, with a few exceptions, the greater part of the free Fermi surface is not concerned in these oscillations, since they correspond to an effective number of conduction electrons which is far too small to account for the conductivity. It seems certain, then, that in such metals as tin, zinc and mercury there are inner Brillouin zones which are almost filled, except for some very small pockets, presumably at corners of the zones. The theory developed above applies equally well to holes as to electrons, so that what is measured by the period of the oscillations is the extremal areas of the holes. It is noteworthy that the angular variation of the period in these cases follows closely what would be expected for an ellipsoid, so that it is likely that the behaviour of these holes may be justifiably treated by the « quasi-free» theory, in which a mass-tensor, independent of energy, is associated with the holes. To take a specific example, the low-field effect in tin shows two long periods, which beat with one another in a most delightful way (Berlincourt) (23); this probably means that the various pockets in the corners of the inner zones may be combined into two nearly ellipsoidal surfaces. In Fawcett's measurements of the anomalous skin effect these surfaces were probably unobserved, being too small to make an effective contribution to the conduction in comparison with the main Fermi surface or surfaces, which only appear in the de Haas-van Alphen effect at very high field strengths.

The angular variation of the periods in tin shows that the ellipsoids are highly elongated, and this effect is even more strikingly shown by graphite, which has two long periods in the ratio 4 : 3. The angular variation of these periods is consistent with their being caused by cylindrical Fermi surfaces (21), oriented parallel to the hexagonal axis. There is a Brillouin zone for graphite in the form of a hexagonal prism which contains 4 electrons, and this is presumably not quite full, having pockets along each edge of the prism. Bragg reflection at the ends of the prism would effectively extend such pockets indefinitely and thus give rise to a nearly cylindrical Fermi surface. It is uncertain whether the two periods observed correspond to maximum and minimum areas of a slightly wavy cylinder, or to two separate Fermi surfaces, the other being that of the electrons which overlap into the next zone. A more elaborate variant of this structure has been found by Berlincourt (24) in cadmium; the periods observed are similar to those which would be produced by two cylindrical surfaces with their axes inclined at 28.5° to the hexagonal axis. There are difficulties, however, about interpreting the results in this way, since from the symmetry properties of cadmium it is necessary to consider at least six such surfaces with their axes disposed evenly around a cone of semi-angle 28.5°; it is then hard to see why the oscillations from each do not beat with one another when the field does not lie along the hexagonal axis. In fact no such beats are observed except those interpretable in terms of only two cylinders.

Recently Gunnersen has obtained results for aluminium which do not seem to be explicable in terms of ellipsoidal surfaces, but the data are not yet sufficiently extensive to enable a suitable surface to be devised. It seems likely from the metals studied so far, as is not unexpected, that although the oscillations of long period (corresponding to small surfaces) may be adequately interpreted by the ellipsoidal model, those due to larger portions of the Fermi surface require a more refined model; and if the behaviour of cadmium is in any way typical it may be that the invention of plausible surfaces to explain the results may involve considerable imaginative ingenuity. There is no evidence yet that the theory of the effect is seriously at fault — for example all oscillations studied are of constant period in 1/H — and at present it would be wise to attribute lack of success in accounting for the cadmium results to failure of imagination rather than of the basic premisses. It is possible, of course, that future work may reveal behaviour which cannot be accounted for by the present theory, and may thus show up the inadequacies, if any, of the single electron model, but it cannot be said at the moment that there is any significant evidence for the breakdown of the theory.

This account of the two effects has concentrated, necessarily, on their potentialities as a research tool rather than on their successes, and I should like to take the opportunity of the comparative informality of a conference report to close on a more personal note. It is difficult for an experimental physicist who is not familiar with the enormous literature on the theory of metals to appreciate how valuable would be the contribution to the subject which these proposed methods might make, nor to be certain that he has not overlooked some vital point which might throw doubt on the validity of the suggested method of interpretation. If the experiments could be performed easily there would be no excuse for not performing them, but unfortunately in the present case the experiments are long and difficult. It is for this reason that I welcome the opportunity afforded by the Solvay conference to bring these proposals forward for general discussion by experts. If, as I believe, the results which careful and patient experimenting could achieve will throw new light on the electronic structure of metals, then I hope the approval of the theorists will encourage the experimenters to push forward and overcome the technical obstacles.

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Discussion of PIPPARD's report

Mr. MacDonald. — In the case of non-glancing electrons, in the anomalous skin effect, is it obvious why one can neglect the loss of momentum on scattering at the surface?

Mr. Pippard. — No, it is not obvious, and in fact there is theoretically a small dependence, amounting at most to about 12 %, on the scattering properties of the surface. The effect is small for two reasons; first, electrons which are not moving at glancing angles spend only a small fraction of a free path in the field, and secondly, what is much more important, it may be shown that the field-configuration is such that an electron arriving at the surface from well within the metal has lost to the field near the surface practically all the momentum which it acquired from the field at a greater depth; in the limit, as $l \to \infty$, $\int_0^\infty \mathrm{E}dz \to 0$, so that non-glancing electrons strike the surface with the same momentum as they possessed originally before entering the field. Under these conditions it does not matter whether the surface reflects specularly or scatters diffusely. The small effect predicted by the detailed theory is presumably the effect of surface conditions on those glancing electrons which made their last collision within the skin depth.

It may be noted that in this respect the anomalous skin effect differs markedly from the superficially similar phenomenon, the d.c. conductivity of thin films. In the latter the surface conditions are all-important.

According to Chambers' experiments the surface appears to scatter electrons diffusely.

Mr. Fröhlich. — Would the theory of the anomalous skin effect be affected if electron-electron collisions were taken into account?

Mr. Pippard. — Yes, in contrast to normal conductivity electron-electron collisions could have a most important effect in the anomalous skin effect. The theory shows that the whole phenomenon is dependent on most of the electrons spending only a small fraction to the time between successive lattice collisions in the region occupied by the field. If electron-electron collisions were frequent the trajectory of an electron between successive lattice collisions would not be a straight line but a very tortuous « Brownian » path, and a far higher proportion of the electrons would be effective. In fact the result of electron-electron collisions would be an increase of the surface conductivity towards the value predicted by the theory of the normal skin effect. Experimentally there is no evidence of any departure of the behaviour from that predicted by the Reuter-Sondheimer theory which neglects electron-electron collisions, and I think one may conclude that the mean free path for such collisions at low temperatures is considerably greater than 10^{-2} cm.

This experimental result may be understood in terms of the Bohm-Pines theory, according to which the cross-section for electron-electron interactions is of the order of 10^{-15} cm^2. In a metal having 10^{22} conduction electrons per cm^3 the mean free path for electron-electron collisions would be about 10^{-7} cm if the electrons constituted a classical gas. But because of the fact that they are a degenerate Fermi gas the mean free path should be very much greater. In the first place only a fraction approximately equal to T/T_o (T_o is the degeneracy temperature) occupy the « Fermi tail » and are able to change their momentum by collision; in the second place even these electrons are greatly restricted as to the possible collisions they may make, since there are no unoccupied states of smaller momentum into which one of the electrons may be scattered. A rough calculation shows that this reduces the scattering cross-section by a further factor T/T_o. Since therefore for most metals at helium temperatures $T/T_o \sim 10^{-4}$, we are led to predict a free path of about 10 cm for electron-electron collisions, which should therefore be quite negligible in comparison with the electron-lattice collisions.

Independent confirmation of this conclusion comes from the thermal conductivity at low temperatures, which usually agress well with the value predicted by the Wiedemann-Franz law and the theoretical Lorenz constant. Electron-electron collisions would reduce the thermal conductivity of a free-electron gas without affecting the electrical conductivity, and so again we must suppose the free path for electron-electron collisions to be much greater than that for electron-lattice collisions.

Mr. Mendelssohn. — Is there a correlation between the results on the anomalous skin effect in tin and the anisotropic transport effects in the bulk metal?

Mr. Pippard. — No close correlation is to be expected, for whereas the anomalous skin effect depends under extreme conditions solely on the geometry of the Fermi surface, the d.c. conductivity is conditioned also by the values of the free path and Fermi velocity all over the surface. In addition the bulk properties have a simple tensorial character and do not reflect the local variations in the shape of the Fermi surface as does the anomalous skin effect.

Mr. Mendelssohn. — Considering the rather complicated structure of the two metals which have been discussed in detail, Cd and Sn, it is clearly most desirable to test the methods on a metal in which the Fermi surface is closer to a sphere. The obvious choice for the anomalous skin effect would be Na, but probably the experimental difficulties in preparing a suitable surface would be prohibitive. The next best choice seems to be Au, which is rather better than Cu and of which single crystals can be made.

Mr. Onsager. — In the theory of the de Haas-van Alphen effect the introduction of the kinetic momentum $\underline{p} - \frac{e}{c}\underline{A}$ for an electron in a magnetic field is admittedly a swindle. The components of this vector do not commute, so that they cannot even be specified simultaneously.

This particular swindle is standard practice. We have some reason to hope that it will cause no great harm, but the questions involved have not been analyzed thoroughly.

Some years ago, when Dr. O. E. Robinson and I looked into the theory of the de Haas-van Alphen effect, we found out how the « one electron » zone theory could indeed account for nearly tubular sections of the Fermi surface, of the type indicated by the data. As it turned out, we had just re-discovered a long-known consequence of the zone theory, which had received scant attention.

In the neighbourhood of a zone boundary the effective mass in one direction normal to the boundary can easily be small. Similarly, two small components of the mass tensor may occur near the line of intersection of two Bragg reflexions, if they are of equal strength or nearly so.

The case of graphite makes a good illustration. To simplify matters we consider first a single sheet of carbon atoms. The first Brillouin zone for this two-dimensional crystal is a hexagon, the second completes a star of David. The corners of the hexagon are the points of trigonal dihedral symmetry (2/3, 1/3) and (1/3, 2/3). Three corners meet at each of these points when the Brillouin zones are reassembled in the reduced zone scheme. The dihedral group has one and two dimensional representations, and with two atoms (regions of low potential energy) in each cell, the sign of the Bragg reflexions is such that the lowest state belongs to a two dimensional representation. Accordingly the points (2/3, 1/3) and (1/3, 2/3) are contact points where the energy levels of the first two Brillouin zones coincide. In the reciprocal lattice of the three dimensional crystal, the contact points are extended into contact lines parallel to the hexagonal axis.

If the energy were constant along the contact lines then the lowest zone would be exactly filled to that level, and graphite would be a semi-conductor with vanishing energy of excitation. If we were allowed to assume a gentle variation of the energy along the contact lines, then the Fermi surface would consist of two spindles, one enclosing a region of holes near the top of the first zone, the other enclosing the spillover of electrons into the bottom of the second zone, and we should have a beautiful explanation of Shoenberg's two periods.

However, it does not seem easy to find a perturbation which would lead to this desirable result. On the contrary, Johnston looked into the complications which arise from the alternate stacking of the graphite sheets, which brings in some more group theory. His analysis indicates that there ought to be a triplet of additional low-shaped contact lines surrounding each of the two symmetry lines, and it is very difficult to match his conclusions with the observed de Haas-van Alphen effect.

I have tried to correlate the magnetic data with the zone theory for other metals too, and I am none too happy about the results. Nevertheless, Berlincourt's data for Cadmium amount to a much greater catastrophe for the theory; it seems impossible to account for this results in termes of any fixed Fermi surface. If we really have to consider a Fermi surface which follows the direction of the magnetic field like a weather-vane, then we might perhaps suspect a coupling with the phonon field. The elastic properties of a hexagonal crystal have cylindrical symmetry.

Mr. Pippard. — It may be worth recalling an idea introduced by Born and Cheng in their abortive theory of superconductivity. They suggested that in a Brillouin zone which was nearly filled it might be more favourable (as a result of the Coulomb interactions) to have a few corners considerably unoccupied than to have all corners less, but equally, empty. If such a situation is possible it might provide a neat explanation of what Onsager calls the « weather-vane » effect in Cd. For a magnetic field might be sufficient to determine which of the corners were unoccupied, so that the Fermi surface, having lower symmetry than the crystal, would have its orientation tied to the direction of the field. Pherhaps this idea would bear re-examination.

Mr. Jones. — The difficulty with Cd is to explain the occurence of cylindrical Fermi surfaces which are inclined to the hexagonal axis.

Mr. Seeger. — Shoenberg did not observe a de Haas-van Alphen effect in Ge. Under what conditions would we expect the de Haas-van Alphen effect to be observable in semi-conductors?

Mr. Pippard. — Shoenberg's specimen of Ge was very pure indeed, and probably did not contain nearly enough free electrons to give rise to any noticeable magnetic effects.

Mr. Aigrin. — In order to observe de Haas-van Alphen phenomena one has to have a highly degenerate electron gas. Thus, only very impure semi-conductors could show this phenomenon. On the other hand, the anomalous skin effect could probably be studied on semiconductors with only slightly degenerate electron atmospheres. The long relaxation time in some of these semi-conductors would presumably help in observing the phenomenon.

Mr. Pauli. — I should like to raise the general question of magneto-resistance. How far is the empirical dependence of electrical resistance on the magnetic field strength H theoretically explained? Perturbation theory leads to a proportionality of the change of resistance with H^2 for small field strengths in accordance with experiment. But for larger field strengths, one finds very often empirically a region where this change of resistance varies linearly with H. I remember that from about 1920 till 1935 this was not explained theoretically. Has this situation improved since?

Mr. Onsager. — On the subject of magneto-resistance my memory is none too good, and I should be grateful for corrections or supplementary facts; but at least, I seem to recall some intriguing details. The resistivity of Bi is proportional to the magnetic field over a very wide range, and it is practically unaffected by impurities. On the other hand, the resistance of Cd (I think) at low temperatures is proportional to the square of the magnetic field; in this case the addition of impurities reduces the resistivity. At very low temperatures the resistivity of Bi, as a function of the magnetic field, exhibits oscillations, two in one period of the de Haas-van Alphen effect; similar oscillations were found in recent measurements of the Hall effect.

Mr. Seeger. — The Wilson theory of magneto-resistance gives a $\frac{H^2}{H_o^2 + H^2}$ law which correctly describes the quadratic dependence of magneto-resistance on the magnetic field H but fails to account for the often observed linear rise at higher field.

Mr. Kittel.— I believe that it would be valuable to carry out magneto-resistance measurements on single crystals of the simpler metals, such as Cu, Ag, Au and the alkali metals. While such measurements would give one the combined effects of anisotropy of the Fermi surface and of the relaxation time, it might be possible to estimate how much of the effect arises from the relaxation time by studying the magneto-resistance when phonon scattering is dominant and when impurity scattering is dominant. Existing theoretical work on magneto-resistance appears to be valid only in the range $\omega_c\tau \leqslant 1$ where $\omega_c = \frac{eH}{m^*c}$ is the cyclotron frequency in the field H.

MacDonald. — The theory of magneto-resistance is of course only strictly valid when $\omega_c\tau \leqslant 1$; for example, in pure sodium at helium temperatures this is already violated for fields of the order of 1 Kgauss.

The production of suitable small single crystals of the alkali metals for magneto-resistance measurements is not easy and appears particularly difficult for rubidium and caesium; it is aldo difficult to obtain these metals, particularly the former, in a sufficiently pure form for the anisotropy of magneto-resistance to be significant (since the overall effect depends on $\omega_c\tau$ i.e. on H/ρ where ρ is the resistivity). Measurements of the magneto-resistance of the alkalis on essentially poly-crystalline material were published in Proc. Phys. Soc. (1950) and confirm strongly that sodium has the least-deformed Fermi-surface.

Mr. Gorter. — The anomalous magneto-resistance in Bi, mentioned by Onsager, was discovered by Schubnikov and de Haas a few years before the de Haas-van Alphen effect.

Would it be promising to study this resistance effect in order to find the periodicities by a device similar to Shoenberg's high field method?

Mr. Pippard. — Olsen at Zürich has published preliminary measurements of the magneto-resistance of copper in very high fields, produced impulsively like Shoenberg's. It would seem very worth while following up Gorter's suggestion.

Mr. Pauli. — Are the theoretical situations concerning the magnetic susceptibility and the magneto-resistance really analogous? In the former the relation between mean free path and the mean curvature of the orbit does not play any role; in the latter, however, it does.

Mr. Pippard. — Perhaps a combination of Shockley's tube-integral method for the magneto-resistance with Onsager's treatment of the de Haas-van Alphen effect would lead to a deeper understanding of the periodic variations of resistance in strong magnetic fields.

Mr. Fröhlich. — The magneto-resistance in strong fielfs, and in particular the question of whether it should show saturation, might be treated by taking the magnetic field into account in zero order (by the use of circular orbits) and then treating the electric field and the lattice vibrations as perturbations.

Resonance Experiments
and
Wave Functions of Electrons in Metals

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The are three principal types of resonance experiments which give information bearing on the wave functions in solids :

a) Cyclotron resonance;
b) Nuclear spin resonance;
c) Electron spin resonance.

We shall discuss separately the three fields.

1. CYCLOTRON RESONANCE

Cyclotron resonance absorption of radiofrequency power occurs when the orbital rotation frequency of a conduction electron moving in an applied constant magnetic field is approximately equal to the frequency of the *rf* electric field. The first successful experiments (1) were performed in germanium crystals. Reviews of results for electrons and holes in germanium and silicon were given by Kip, Lax, and Kittel at the recent semiconductor conference (2) in Amsterdam. The experiments have been successful in determining accurately the effective masses, symmetries, and degeneracies of the band edges of the conduction and valance bands in germanium and silicon.

In principle cyclotron resonance is ideally suited to the determination of the actual energy surfaces in crystalline solids. In practice it appears that the successful application of the method is probably limited to semi-conductors and insulators. There have been two objections, both connected with high charge-carrier concentration, raised against the possibility of observing cyclotron resonance in metals and in the known superconductors. I would not suggest that both objections have been proved conclusively, because to my knowledge no satisfactory solution of the relevant transport problems have been given, but it is a fact that our experimental attempts to observe cyclotron resonance in metals and superconductors have not been successful. The difficulties appear to include the following :

1) The coherent motion of electrons in cyclotron resonance produces a rotating electric polarization P in the specimen. If the dimensions of the specimen are finite there is produced a depolarizing field $E_d = - LP$, where L is the geometrical « demagnetization » factor in the plane of the motion. The effect of depolarization can be measured by the magnitude of the depolarization frequency ω_d defined by :

$$\omega_d = (LNe^2/m^*)^{1/2} , \tag{1}$$

where N is the carrier concentration and m^* the effective mass. The condition for the existence of a cyclotron resonance is that the angular frequency ω employed in the measurement should be much greater than ω_d . A critical concentration N_d may be defined by the relation :

$$N_d = m^*\omega^2/Le^2 . \tag{2}$$

Using 1 cm wavelength, $m^* = 0.1$ m, and $L = 4\pi/3$ as for a sphere, we find $N_d \approx 10^{12}$ cm^{-3}. By improving the geometry we might expect to get N_d up to perhaps 10^{14} cm^{-3}, but this is still far below the concentrations of the order of 10^{22} cm^{-3} obtaining in the common metals.

2) As the electrons diffuse within the *rf* skin depth δ they will see the *rf* field in randomly-varying amplitudes and phases if the mean free path Λ is comparable with δ ; also, as the electrons revolve in circular orbits different parts of the orbits will see the *rf* field in different phases. These circumstances will probably obscure the cyclotron resonance, although the transport problem has not been solved for $\Lambda \gtrsim \delta$. A solution has been given by Donovan and Sondheimer (3) for $\Lambda \ll \delta$ and $\omega\tau \ll 1$. At microwave frequencies the classical skin depths in pure monovalent metals at helium temperatures are of the order of 10^{-5} cm, whereas the mean free paths may be of the order of 10^{-3} cm or more. The orbital radius for electrons of velocity 10^8 cm/sec at microwave frequencies is also of the order of 10^{-3} cm, much larger than the actual skin depth.

2. NUCLEAR SPIN RESONANCE

Nuclear spin resonance experiments on pure metals give information relating to conduction electron wave functions in a number of ways, including :

a) Knight shift.

b) Nuclear spin-lattice relaxation times.

c) Nuclear exchange coupling via conduction electrons.

Knight Shift

In 1949, Knight (4) observed a shift in the nuclear magnetic resonance frequencies in metals from the frequencies observed for the same nucleons in chemical compounds in the same constant magnetic field. Townes (5) suggested that the Knight shift was caused by the hyperfine interaction of the nuclear magnetic moment with the magnetic moment of the conduction electrons. Values of the shift as large as 2 percent of the resonance frequency have been reported for the heavy elements; in Na^{23} the shift is 0.10 percent.

We indicate briefly the theoretical derivation of the Knight shift, under the assumption that the electron charge distribution has cubic symmetry about the nucleus. For this to be true we must have the nucleus in a position of cubic crystal symmetry and we must neglect the electron spin-orbit interaction, as this interaction tends to lower the symmetry of the charge distribution. When the charge distribution has cubic symmetry the classical dipolar part of the hyperfine interaction averages to zero and we are left with the contact or Fermi part of the hyperfine interaction :

$$\mathscr{H} = -\frac{16\pi}{3}\frac{\mu_B\mu_I}{I}|\Psi(0)|^2 \mathrm{I} \cdot \mathrm{S}, \qquad (1)$$

where $|\Psi(0)|^2$ is the electron probability density at the nucleus. In a representation in which S_z is diagonal the diagonal matrix element of $\mathscr{H}$, averaged over the N conduction electrons per unit volume, is :

$$\overline{\mathscr{H}} = -\frac{8\pi}{3}\frac{\mu_I}{NI}|\Psi_k(0)|^2 I_z M_z, \qquad (2)$$

where M is the magnetization of the conduction electrons, and

$|\Psi_k(0)|^2$ is averaged over the Fermi surface. E_1. (2) may be interpreted by saying that there is an effective magnetic field :

$$\Delta H = \frac{8\pi}{3N} |\Psi_k(0)|^2 M_z , \tag{3}$$

acting on the nuclear moments. The fractional shift is :

$$\frac{\Delta H}{H} = \frac{8\pi}{3N} |\Psi_k(0)|^2 \chi_s , \tag{4}$$

where χ_s is the Pauli *spin* susceptibility, per unit volume. We know that :

$$\chi_s = \mu_B^2 n(W_F) , \tag{5}$$

where $n(W_F)$ is the density of states at the Fermi surface.

It is convenient and instructive to express the shift in terms of the free atom value of $|\Psi_a(0)|^2$, as this is known accurately from atomic beam measurements. We define :

$$\xi = |\Psi_k(0)|^2 / |\Psi_a(0)|^2 . \tag{6}$$

The Knight shift in effect gives us direct experimental values of the product $\xi\chi_s$. Experimental values for monovalent metals are given in table 1. A summary of observed shifts is presented in table 2, as kindly collected for me by Professor Knight.

TABLE 1

$\xi\chi_s$ Values from the Knight Shift.

Metal	$\xi\chi_s \times 10^6$ experimental	$\chi_s \times 10^6$ calculated for free electrons, $m^* = m$	ξ derived from preceding columns
Li	0.85	0.80	1.1
Na	0.59	0.65	0.91
Rb	0.52	0.47	1.1
Cs	0.58	0.45	1.3
Cu	0.69	0.98	0.70
Ag	0.57	0.87	0.65

TABLE 2

Summary of Experimental Values of the Knight Shift.

Element	Isotopes	ΔH/H (percent)	μ Nuclear Magnetons	I
Li	7	0.025	3.26	3/2
Be	9	~0	− 1.18	3/2
Na	23	0.10	2.22	3/2
Al	27	0.16	3.64	5/2
Si	29		− 0.555	1/2
V	51	0.55	5.15	7/2
Cu	63, 65	0.23	2.23, 2.39	3/2
Ga	69, 71	0.45	2.01, 2.56	3/2
Rb	85, 87	0.65	1.35, 2.75	5/2, 3/2
Nb	93	0.85	6.17	9/2
Rh	103		0.0881	1/2
Ag	107, 109	0.52	−0.113, −0.130	1/2
Sn	117, 119	α0, β0.75	−0.913, −0.995	1/2
Te	125	~0	0.882	1/2
Cs	133	1.5	2.58	7/2
Tl	203, 205	(1.0), 1.5	1.61, 1.63	1/2
Pb	207	1.2	0.584	1/2
Hg	199	2.5	0.499	1/2

The only good determination of spin susceptibility is that made by Slichter and coworkers (6) for lithium. They find $\chi_s = 2.0 \pm 0.3 \times 10^{-6}$, for which $\xi = 0.44$. Recent calculations of ξ for lithium have been made by Kohn (7), who finds $\xi = 0.46$, and Jones and Schiff (8), who find $\xi = 0.39$.

An interesting recent development is the measurement by Knight of the temperature dependence of the metallic shift in sodium. His preliminary results are shown in figure 1. It is unlikely that ξ depends significantly on temperature, except for effects of thermal expansion. The remarkable behavior of the shift at low temperatures is interpreted most plausibly as a change in the density of states. The density of states appears to decrease as the temperature is lowered from liquid nitrogen temperature, increasing somewhat again just above 1° K. The drop in the density of states is perhaps contrary to what one might expect from an electron-phonon interaction theory, although P. Marcus has suggested informally that the sign predicted by the theory is not unambiguous.

If the crystal has lower than cubic symmetry the Knight shift may be anisotropic — that is, the shift may depend on the angle

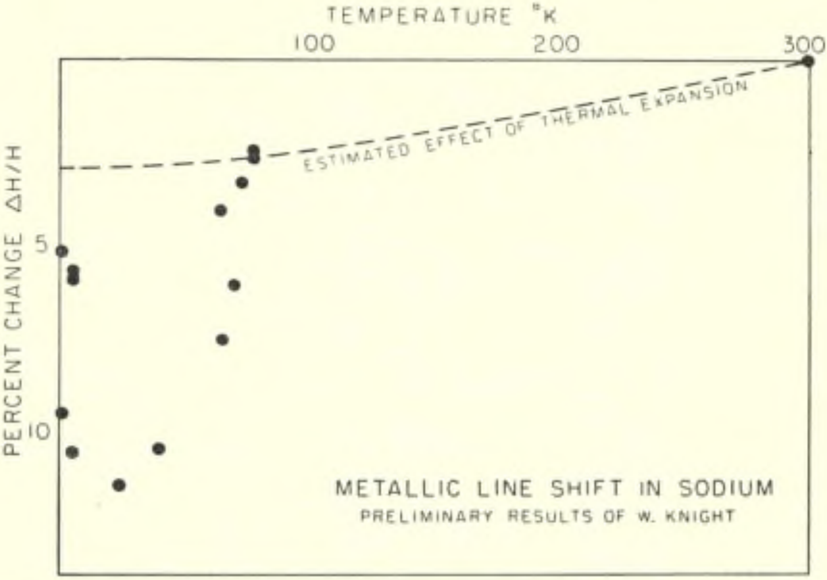

Fig. 1

between the constant magnetic field and the crystal axes. An anisotropy effect of 3 percent of the mean shift was observed in white tin by Bloembergen and Rowland (⁹), who have indicated the connection with the *p*-character of the wave function and the anisotropy in the electron *g*-value.

Nuclear spin-lattice relaxation time

Frequently in metals the dominant mechanism of energy exchange between the nuclear spin system and the lattice is by means of the hyperfine coupling of the nuclear magnetic moments with the conduction electrons. This process was discussed first by Heitler and Teller (¹⁰); the detailed theory was given by Korringa (¹¹). Neglecting the mixture of *p* and higher angular momentum states in the conduction band functions at the Fermi surface, Korringa finds a simple relationship between the Knight shift and the spin-lattice relaxation time T_1 :

$$T_1 \left(\frac{\Delta H}{H}\right)^2 = \frac{\hbar}{\pi k T}\left(\frac{\mu_B I}{\mu_I}\right)^2. \tag{7}$$

A comparison of experiment and theory is given in table 3. The only experimental data presented were obtained by Norberg (¹²)

using the spin-echo method; it is hoped that these values are more trustworthy than values by other methods.

TABLE 3

Test of the Korringa relation between Knight shift $\Delta H/H$ and spin-lattice relaxation time T_1.

	T_1T products, sec-degree K	
	From measured shift and Korringa relation	From experimental relaxation time
Li^7	65	45
Na^{23}	3.8	4.8
Rb^{85}	0.68	0.86
Rb^{87}	0.060	0.075

Any *p*-wave contribution to the conduction electron wave functions will introduce a dipolar contribution to the relaxation time, even though for cubic crystals there is no *p*-wave contribution to the Knight shift. An especially large effect on T_1 will occur when *p*-states from inner shells are mixed in. The effect of *p*-wave mixing is to replace the equality sign in the Korringa relation by an inequality:

$$T_1 \left(\frac{\Delta H}{H}\right)^2 \geq \frac{\hbar}{\pi k T} \left(\frac{\mu_B I}{\mu_I}\right)^2 . \tag{8}$$

Indirect nuclear exchange coupling

Ruderman and Kittel (13) have shown recently that there exists in metals a coupling between the magnetic moments of two nuclei via their hyperfine interaction with conduction electrons. The resulting interaction has the form :

$$\overline{H} = \sum_{i>j} \sum_{j} A_{ij} \mathbf{I}_i \cdot \mathbf{I}_j$$

— that is, it is an indirect exchange interaction — provided that the contact part of the hyperfine interaction is dominant. The interaction constant A_{ij} is given by, in the effective mass approximation :

$$A_{ij} = \frac{\Omega^2 m^* \xi_i \nu_a(i) \xi_j \nu_a(j)}{2\pi(2I_i + 1)(2I_j + 1)} \left(\frac{1}{R_{ij}} \right)^4 [2k_m R_{ij} \cos(2k_m R_{ij}) - \sin(2k_m R_{ij})]. \quad (9)$$

Here Ω is the atomic volume; $\nu_a(i)$ is the atomic hyperfine structure splitting of atom i; R_{ij} is the distance between atoms i and j; k_m is the magnitude of the wave vector at the Fermi surface.

The principal experimental evidence for the existence of an $\mathbf{I}_i \cdot \mathbf{I}_j$ coupling in metals is that the widths of nuclear spin resonance lines in the heavier metals with mixed isotopes are broader than expected from magnetic dipolar interactions alone, even for nucleons with $I = 1/2$ for which nuclear electric quadrupole broadening cannot exist. Bloembergen and Rowland (^{14}) report widths in tin and thallium of the order of five times the calculated dipolar widths. Sogo and Jeffries (^{15}) find that the width peak-to-peak of the absoption derivative of the Ag^{109} resonance in natural silver is 115 ± 15 cps, whereas the calculated dipolar width is 50 cps. It has also been found by Bloembergen (^{16}) that the line width in metallic thallium varies quite strongly with the isotope abundance, as shown in table 4.

TABLE 4

Nuclear line widths in thalium metal with various isotopic abundancies of $T/^{203}$ and $T/^{205}$, after Bloembergen.

(H_0 = 5560 oersted; T = 77° K)

Tl^{205} abundance percent	Width between points of maxima slope, kc/sec	
	Tl^{205}	Tl^{203}
98.7	20	—
90.5	23	—
70.5	33	∼ 60
52·1	54	54
14.0	> 60	27

Van Vleck (^{17}) has studied the effect of exchange and dipolar interactions on line width. In particular, he gives results for the interesting situation which arises when the crystal consists of two magnetic ingredients with gyromagnetic factors sufficiently different that the resonances for the two species do not overlap. The nuclear exchange interaction between unlike nucleons tends to broaden the resonance line, whereas the exchange interaction between like nucleons tends to sharpen the resonance line with respect to the width caused by the dipolar interaction alone. Bloembergen's results illustrate very well the broadening effect of unlike nucleons. He estimates $|A|$ for nearest neighbor unlike nucleons as 23 kc/sec in thallium.

Ruderman and Kittel estimate $|A|$ as 40 cps in silver, using $m^* = m$ and $\xi = 1$. This leads to a width in quite good agreement with the observed width, although the agreement is improved for $\xi = 0.8$. If we analyze the Knight shift in silver with $m^* = m$, we find $\xi = 0.7$. It should be noted that the Knight shift involves the product $\xi\chi_s$, while the exchange broadening involves $\xi^2\chi_s$. In principle the two effects together will determine ξ and χ_s separately.

In metals with 3 or more valence electrons it is likely that the *s*-wave contribution to the hyperfine interaction is not large in comparison with the *p*-wave contribution. For the same reasons that the equality in the Korringa relation may not hold, we could expect anisotropic exchange terms in the nuclear interactions, even in cubic crystals. As Bloembergen first suggested, the excessive line widths in pure isotopic thallium and in lead, which contains only one magnetic isotopic species, are probably caused by anisotropic exchange interactions associated with individual Bloch states. Theoretical calculations on the effect are now in progress. It is not unlikely that the effect will be a useful guide to the amount of *p*-character at the Fermi surface.

3. ELECTRON SPIN RESONANCE

Electron spin resonance experiments on conduction electrons in metals provide information about the state of the conduction electrons in several ways, including :

a) Intensity of the resonance signal.
b) Shift in the *g*-value.
c) Overhauser shift accompanying saturation.
d) Spin-lattice relaxation time.
e) Electron diffusion effects on the line shape.

Signal Intensity

The first successful experiments on conduction electron spin resonance were carried out by Griswold, Kip, and Kittel (18), who worked with fine particles of sodium at a frequency of 9240 Mc/sec. They found that the signal intensity decreased on cooling from room temperature to 77° K; the decrease was attributed to a decrease in the *rf* skin depth. The fact that the signal intensity did not vary as T^{-1} was cited as evidence that the signal was not caused by paramagnetic impurities on the surface of the particles.

The only determined attempt to obtain an accurate measurement of spin susceptibility is that carried out for lithium by Schumacher, Carver, and Slichter (19). They find $\chi_s = 2.0 \pm 0{,}3 \times 10^{-6}$ cgs volume units. Their experimental method is very clever — the number of metal atoms in the *rf* field is determined by carrying out a nuclear resonance experiment at the same frequency as the electron resonance experiment, so that the same number of atoms are exposed to the *rf* field in the two experiments.

Preliminary results by G. Feher on beryllium suggest that the spin susceptibility here may only be a small fraction of the free electron value. This result, if confirmed, would not be surprising, in view of the two valence electrons per atom. The small value of the Knight shift in beryllium also suggests that the spin susceptibility is small.

The *g*-shift

The spectroscopic splitting factor g is defined by the equation :

$$\hbar\omega = g\mu_B H\,. \tag{10}$$

The g-shift is defined as the difference between the observed g and the free electron value 2.0023 :

$$\Delta g = g - 2.0023\,. \tag{11}$$

The g-shift is a measure of spin-orbit effects on the conduction electron wave functions. The shift is of the order :

$$\Delta g \sim -\lambda/\Delta\,, \tag{12}$$

where λ is spin-orbit interaction and Δ is an interband energy difference. A positive Δg is characteristic of holes, whereas a negative Δg is characteristic of electrons. The g-shift is one feature of wave functions at the Fermi surface which is relatively insensitive to exchange and correlation effects. The shift was first calculated by Yafet (20). A summary of experimental and theoretical values of Δg is given in table 5. It is interesting that the value for beryllium suggests that holes have the major effect.

TABLE 5

Experimental and Theoretical Values of Δg

	Experimental	Theoretical
Li	$\Delta g \leq 10^{-4}$ (Feher and Kip)(21)	-2×10^{-5} (Argyres and Kahn)(22)
Na	$\Delta g = -(8 \pm 2) \times 10^{-4}$ (Feher and Kip)(21)	-3×10^{-4} (Yafet)(20) -7×10^{-4} (Brooks)(23)
K	$\Delta g = -(7 \pm 5) \times 10^{-3}$ (Levy and Browne)(24)	-4×10^{-3} (Brooks)(23)
Cs	$\Delta g = -7 \times 10^{-2}$ (Levy and Browne)(24)	-6×10^{-2} (Brooks)(23)
Be	$\Delta g = +(9 \pm 1) \times 10^{-4}$ (Feher and Kip)(21)	—

Overhauser shift

Overhauser (25) has discovered the remarkable result that under appropriate conditions the population distribution of nuclear spins in a metal among the nuclear magnetic sublevels is determined essentially by the magnitude of the electronic magnetic moment μ_B, rather than by the nuclear moment μ_I. His conditions are that the electron spin resonance of the conduction electrons should be saturated, and that the principal spin-lattice relaxation mechanism of the nuclear spins should be the $\mathbf{I} \cdot \mathbf{S}$ hyperfine coupling with the conduction electrons. The predicted enhancement of nuclear polarization on saturating the electron resonance has been detected experimentally in metallic lithium by Carver and Slichter (26).

It was further suggested by Overhauser that there should be, especially in metals, an important shift in the position of the electron spin resonance line as the line is saturated. The shift is the result of the hyperfine interaction with the nuclear moments. At temperatures over 1° K the nuclear moments under equilibrium conditions cause a shift in the position of the electron spin resonance in metals by less than 1 part in 10^5. However, if the nuclear polarization is enhanced by a factor of the order of 10^3 by the Overhauser effect, the electron shift may be of the order of 1 in 100, which should be observable. To my knowledge, it has not yet been looked for experimentally under favorable conditions.

We can easily derive an expression for the Overhauser shift in the position of the electron spin resonance, assuming that the hyperfine (Heitler-Teller-Korringa) mechanism of nuclear relaxation is dominant. The average hyperfine interaction, from Eq. (1), is :

$$\mathscr{H} = -\frac{16\pi}{3}\frac{\mu_B\mu_I}{I}|\Psi(0)|^2 S_z\bar{I}_z\,. \tag{13}$$

Now, for $I = 1/2$:

$$\bar{I}_z \approx \frac{\mu_B H}{2kT}s\,, \tag{14}$$

where s is the fractional saturation $(1 \geq s \geq 0)$, and we assume $|s\mu_B| \gg |\mu_I|$. We define an effective field ΔH by :

$$\mathscr{H} = -\Delta H 2\mu_B S_z\,, \tag{15}$$

so that :

$$\frac{\Delta H}{H} = -\frac{8\pi}{3}\frac{s\mu_B\mu_I}{kT}|\Psi(0)|^2 \tag{16}$$

or, in terms of the free atom hyperfine constant a in $\mathscr{H} = a\mathbf{I}\,.\,\mathbf{S}$:

$$\frac{\Delta H}{H} = \frac{as}{4\xi kT}\,, \tag{17}$$

where ξ is defined by Eq. (6).

In sodium for $s = 1$ we have, using the result for arbitrary nuclear spin I :

$$\frac{\Delta H}{H} = \frac{I(I+1)}{3}\frac{as}{\xi kT} \sim \frac{0.1}{T}. \tag{18}$$

At 5° K and 1 cm wavelength, $\Delta H \sim 200$ oersteds, which is enormous. It is important to carry out the measurement in such a way that the resonance line does not run away because of the shift. A determination of the shift at known s will determine ξ directly. This would be of great value in estimating the non-s character of wave functions at the Fermi surface.

Spin-lattice relaxation.

In sodium, potassium, and cesium the electron spin resonance line width increases as the temperature increases. In lithium and beryllium the width is independent of temperature, but (at least in lithium) varies from sample to sample and is known to be sharper in the purer samples. At the present time the principal causes of electron spin-lattice relaxation are believed to include :

a) Overhauser (27) mechanism-interaction between the magnetic moment of one electron and the field caused by the translational motion of a second electron.

b) Elliott (28) mechanism-electron spin flipping caused by spin-orbit effects in the collision of a conduction electron with thermal phonons and with impurities and imperfections.

The experimental and theoretical situations are not yet fully clear. It is possible that both the Overhauser and Elliott mechanisms are important. Brooks (29) has pointed out that Overhauser's original estimates of relaxation times are too long because of the use of plane waves as conduction electron wave functions. It may be that at helium temperatures the Overhauser mechanism is dominant in very pure specimens, while the Elliott mechanism may be dominant at high temperatures and in impure specimens.

Elliott has found a most interesting and suggestive expression relating the spin-lattice relaxation time T_1 with the conductivity relaxation time τ_R for electron collisions :

$$T_1 = \alpha \frac{\tau_R}{(\Delta g)^2}, \tag{19}$$

where α is a numerical factor which for phonon collisions may be of the order of 0.03; Δg is the g-shift of the conduction electron resonance and enters because the amount of down spin, in a conduction electron wave function which is essentially spin up, is proportional to Δg. The square enters through the transition probability for spin-reversal during a conductivity collision process. In an impurity collision it is likely that Δg to be used in (19) is not the observed value, but rather a value appropriate to the local state of the impurity atom. Thus a heavy impurity atom may be more effective in causing spin flips than a light impurity atom. Elliott's mechanism appears to give a fair account of the temperature dependence of the line width observed in a silicon semiconductor (30).

In lithium the purest sample has $T_2 = 6 \times 10^{-8}$ sec, and the width is independent of temperature (31). The latter circumstance makes it seem likely that the width is controlled by impurity scattering, although it seems to be difficult to reconcile the width with the reputed purity of the metal. The line width in beryllium is presumably dominated by impurity scattering, and some specimens give no observable resonance.

The details of the temperature dependence of the lines in sodium, potassium, and cesium are not yet worked out in sufficient detail to permit a decision to be made between the Overhauser and Elliott mechanisms. The sharpest widths at 4° K which we have found in these metals are : Na, 0.1 oersteds; K, ~ 5 oersteds; Cs, ~ 10 oersteds. The ratio of widths in Na and K is roughly compatible with the ratio of the $(\Delta g)^2$, but the Cs line appears to be much sharper relatively than expected on the Elliott mechanism. For this reason we prefer to regard the Cs results as still tentative.

Feher examined Al and Mg carefully at 300 Mcs between 4° K and 300° K, and Pd and W between 77° K and 300° K. No resonance was observed. In impure Al a resonance was seen, but not in the purest material. It may be that a small energy denominator causes a large *g*-shift in metals for which the Fermi surface is in part close to the boundary of a Brillouin zone.

Electron diffusion effects on the line shape.

It was noticed by Griswold (32) that conduction electron resonance could be observed at microwave frequencies in thick plates of alkali metals. It had been thought previously that the rapid diffusion ($\sim 10^{-9}$ sec) of electrons out of the skin depth would broaden the resonance line proportional to the reciprocal of the diffusion time, so that it was not expected that a line could be observed in thick plates at high frequencies. However, the line observed by Griswold has a normal width but an unusual shape, and the intensity is quite weak.

These results where explained by Dyson (33), who obtained an exact solution to the line shape problem in the normal skin effect region. His results have been extended to the anomalous skin effect region (34) which obtains in the measurements at low temperatures. Physically, it may be said that the reason why a sharp line is observed is that the electrons diffusing out of the skin depth may have a very good chance of diffusing back in a number of times before the spin relaxes.

We give now a qualitative explanation of Dyson's principal result when the electrons diffuse in and out of the skin depth many times in one relaxation time.

We let : U = spin relaxation time;
D = diffusion time through layer of thickness δ .

If $U \ll D$, the electron loses its memory of motion many times in one passage through the skin depth, and hence it does not know it is diffusing. The absorption will then be proportional to $\chi_1 + \chi_2$ as in the case of impurities in a metal.

If $U \gg D$, we have Dyson's case. The electron goes in and out of the skin many times before losing its memory, so that it is the average magnetization that we see. Let H now be in the x-direction, E in the y-direction :

$$M_x = C \int_0^{-\infty} B_x(z) dz \, . \tag{20}$$

Here C is a constant of proportionality which we estimate later. From the Maxwell equations :

$$\frac{\delta E_y}{\delta z} = \frac{i\omega}{c} B_x \, . \tag{21}$$

Therefore :

$$M_x = \frac{ic}{\omega} C E_y(0) \, , \tag{22}$$

and the surface impedance is :

$$Z = \frac{E_y(0)}{H_x(0)} = \frac{E_y(0)}{B_x(0) - 4\pi M_x} \tag{23}$$

We note that M_x is independent of z because of the diffusion. We write :

$$Z_o = E_y(0)/B_y(0). \tag{24}$$

This appears unconventional, but we shall soon see that B should be used rather than H. Now for small χ, we can make the expansion:

$$Z = Z_o + 4\pi Z_o \frac{M_x}{B_x(0)}\,; \tag{25}$$

$$Z = Z_o + \frac{4\pi ic}{\omega} C Z_o^2\,. \tag{26}$$

We now assert that Z_o is the same as $E_y(0)/H_x(0)$ if there were no magnetization. This follows from the eddy current equation for B. We have :

$$\frac{\partial^2 H_x}{\partial z^2} = \frac{4\pi\sigma\omega i}{c^2} B_x \tag{27}$$

With uniform magnetization we can substitute B_x for H_x in the above equation. Hence Z_o is the surface impedance for this case of $\mu = 1$.

The problem has been reduced to the determination of the constant C. Its phase will strongly affect the absorption. We make a rough estimate of C. Consider an electron in the surface layer : from the equation of diffusion we obtain the result that the probability of finding an electron at position z at time t, if it were at $z = 0$ at $t = 0$, is given by :

$$G(z, t) = \frac{1}{(4\pi Dt)^{1/2}} e^{-z^2/4Dt}\,, \tag{28}$$

where D is the diffusion coefficient. For large t this varies as $t^{-1/2}$. Thus the probability after time t that the electron is to be found in the skin is of the order of :

$$\delta/(\pi Dt)^{1/2} \approx (\mathrm{D}/t)^{1/2}\,, \tag{29}$$

where D is the diffusion time defined in (35) below. The fraction of the time spent in the skin layer is $(\mathrm{D}/\mathrm{U})^{1/2}$. We can roughly write the magnetization as a product of the frozen susceptibility times the fraction of the time spent in the skin layer, times the average field.

$$M_x \approx \chi_{frozen}(\mathrm{D}/\mathrm{U})^{1/2} \frac{1}{\delta}\int_0^{-\infty} B(z)dz\,. \tag{30}$$

Thus we identify C as $\chi_{frozen}(\mathrm{D}/\mathrm{U})^{1/2} \,.\, (1/\delta)$.

Now :

$$\chi_{frozen} = \frac{1}{2}\chi_0\omega_0 U \frac{1}{(\omega - \omega_0) + i/U} \tag{31}$$

or :

$$\chi_{frozen} = \frac{1}{2}\chi_0\omega_0 U \frac{U(\omega - \omega_0) - i}{1 + U^2(\omega - \omega_0)^2} . \tag{32}$$

The absorption is proportion to Re Z and its variation during traverse of the resonance will be proportional to :

$$\frac{(\omega - \omega_0)}{1 + U^2(\omega - \omega_0)^2} . \tag{33}$$

Thus diffusion gives us an antisymmetrical line, as observed by Feher and Kip (31). Exact calculation by Dyson shows that the absorption is proportional to :

$$\mathrm{I}m\left(\frac{1}{1 - i(\omega - \omega_0)U}\right)^{1/2} , \tag{34}$$

which produces our result if U is small. The occurrence of an antisymmetrical absorption signal is good evidence that the magnetic moments are diffusing.

The diffusion theory of line shape has been verified in all detail in the experimental work of Feher and Kip. The shape of an observed line gives in effect an experimental determination of the diffusion constant D, defined as :

$$D = \frac{3\delta^2}{2v\Lambda} \tag{35}$$

where δ is the skin depth, v the velocity at the Fermi surface, and Λ is the mean free path. A determination of D is essentially a determination of an average of $v\Lambda$. Similarly, the electrical conductivity :

$$\sigma = \frac{Ne^2\Lambda}{m^* v} \tag{36}$$

determines an average of Λ/m^*v.

One would expect the time taken to diffuse out of the skin depth to depend on the cyclotron frequency if $\omega_c\tau \gg 1$. No appropriate experiments in this region have been reported. It would seem possible in principle to determine the cyclotron frequency in a metal from a study of the spin resonance line shape and its dependence on the orientation of the static field normal to the surface.

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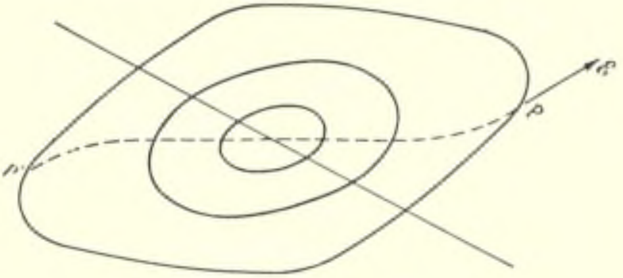

Fig. 2

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(34) C. Kittel, see appendix to reference (31).

Discussion of KITTEL's report

Mr. Pines. — Even if there is no *p*-wave mixing, the Korringa relation may not be valid. Thus, electronic correlations affect the spin susceptibility χ_s (and hence the Knight shift) and the relaxation time T_1 in different ways. Their effect on χ_s is a fairly subtle one which cannot be simply expressed as a change in state density.

On the other hand, it is probably a good approximation to assume that the effects of correlations on T_1 is well represented by their effect on the state density.

These considerations are borne out by the experiments of Norberg and Holcomb (*) on the alkali metals. Using their experimental values of T_1 we find that :

$$T_1(\Delta H|H)^2 > \frac{h}{\pi k T}\left(\frac{\mu_B I}{\mu_I}\right)^2 .$$

This inequality has the opposite sign to that predicted by Eq. (8) of Prof. Kittel's paper and thus cannot be interpreted as an effect of *p*-wave mixing. (To put it another way, they find an experimental T_1 which is greater than that expected from the Korringa relation and would thus require an additional relaxation mechanism which is « substractive » rather than « additive ».)

Their results are, however, simply interpreted as a correlation effect, since both the values of T_1 and the Knight shift are independently consistent with the theoretical calculations of Pines for χ_s and Kohn, and Townes, Herring and Knight for $|\Psi^*_k(0)|^2$.

Mr. Fröhlich. — I should like to comment on the temperature shift of the Knight shift. Kittel suggested that this must be due to a temperature change in the level density of electrons near the Fermi surface. Such a temperature dependence has recently been derived theoretically by Buckingham and Schafroth on the basis of electron-lattice displacement interaction, which, if strong enough, is responsible for superconductivity.

(*) R.E. Norberg and D.F. Holcomb, *Physical Review* (to be published).

Theoretically the density-temperature dependence is as in the diagram.

Mr. Pippard. — Are there sufficient data on γ and χ to see whether they agree as they should?

Mr. Kittel. — I do not believe that there is a sufficient number of examples in which the same metal has been investigated by both methods to make a comparison significant.

Mr. Pines. — It seems to me that it will be difficult to separate out the various factors which may alter γ from the free electron value. Among these are the influence of the lattice periodic field (which alters the effective mass), short-range electron correlations, and the reduction in the number of electronic degrees of freedom (in consequence of the existence of plasma degrees of freedom), as well as the electron-phonon interaction under discussion.

Mr. Pippard. — If weak coupling between electrons and lattice vibrations can modify the electronic specific heat, should not the effect be even more marked for superconductors in magnetic fields greater than critical?

There is no strong evidence that this occurs.

Mr. Mott. — Could Professor Fröhlich tell us whether the experiments still suggest that there are materials in which γ (the electronic specific heat) is abnormally large, and whether it fits with his theory of the strong interaction?

Mr. Fröhlich. — I am not sure of the present state regarding experiments. Various investigators definitely assert that the electronic specific heat of sodium, though given by γT, leads to a level density which is larger by a factor between one and two than would follow from an effective mass equal to the electronic mass m.

I think that this is due to the interaction with the phonon field, as I mentioned earlier (paper by Buckingham & Schafroth).

Mr. Mott. — Could Professor Fröhlich indicate why he expects that superconducting alloys would give an abnormally large value of γ while the value for superconductors in the magnetic field seems quite normal?

Mr. Fröhlich. — The value of γ need only be larger by a relatively small factor, say two. To check this experimentally, it would be necessary to measure γ (i.e. the level density) at a temperature of the order of the Debye temperature (e.g. by the temperature dependence of the Knight shift).

Mr. Mendelssohn. — Regarding the electronic specific heat of the alkali metals, it has to be remembered that, owing to the low Debye Θ, the lattice contribution is still high at helium temperatures while the γ values to be expected are low. This means that it is difficult to separate the two terms with good accuracy. It is to be hoped that the specific heats of these metals will be measured below 1° K where the electronic component will be dominant.

No such experiments have yet been made, but they are probably feasible. The position, so far, has been obscured by the fact that in a number of metals, small specific heat anomalies have been reported, some of which were later found to be spurious.

As to the question wether the specific heat of a superconductor which has been rendered normal by a magnetic field shows a differentγ value from that above the transition point, the evidence on tin and tantalum shows that the γ values are equal. However, it has to be remembered that *both* measurements of the γ value have, in these cases, been obtained at temperatures well below Θ.

Mr. Gorter. — It may be useful to point out that the energy difference ΔU_0 between the normal and the superconducting state at $T = 0$ is much smaller than RT_c. From a generally accepted analysis of the caloric and magnetic data, one finds in fact $\Delta U_0 \approx \gamma T_c^2/4$. As has been remarked by Dr. Matthias T_c increases experimentally with γ. ΔU_0 thus apparently increases even more rapidily with γ. This pronounced dependence of ΔU_0 on the density of energy levels near the Fermi-limit seems one of the first facts to be explained by a theory of superconductivity.

Mr. Pines. — As Professor Kittel has pointed out, the experimental and theoretical situations with regard to the electron spin-lattice relaxation time are not yet completely clear. However, Y. Yafet at the University of Illinois has recently completed a theoretical investigation of T_1 for sodium. He finds $T_1 \sim 6 \times 10^{-9}$ sec. a result in good agreement with experiment. Yafet also finds that the dominant mechanism is yet another one investigated by Overhauser, the interaction between the magnetic moment of the electron and the electric field of the phonons, an interaction of the form $A\underline{\sigma} \times \underline{\rho} \,.\, \underline{\nabla \varepsilon}$ where $\underline{\varepsilon}$ is the electric field of the lattice vibrations. Yafet does not make the plane wave approximation of Overhauser, but instead takes into account the modulations in the electronic wave functions introduced by the ion core, and in so doing obtains a substantially shorter relaxation time than that calculated by Overhauser. The ion core modulations seem quite generally important because the dominant relaxation mechanisms (either that above or that proposed by Elliott) depend on a gradient coupling and hence on the details of the wave function quite near the ions.

Yafet finds that, for pure metals, the Overhauser spin-phonon coupling is more important than the Elliott mechanism in determining the relaxation time and yields a width proportional to T. On the other hand, when even slight amounts of heavy impurities are present, the Elliott mechanism may take over and lead to a temperature-independent line width. Thus our conclusions are in general agreement with those of Professor Kittel concerning relaxation mechanisms, except that we do not believe that the Overhauser electron-electron interaction mechanism plays an appreciable role.

Mr. MacDonald. — We are well aware of the interest and importance of the specific heats of the alkali metals but is should be remembered that there are very considerable experimental difficulties even in the higher temperature ranges. Following the pioneer investigations of Simon and his collaborators, L.G. Carpenter & Steward, and other workers on Li, Na and K, D.H. Parkinson of R.R.E., Great Malvern, has recently made some careful and extensive measurements on Na in the liquid helium region, while H. Preston Thomas and T.M. Dauphinée at Ottawa have been working on Na, K and Rb over a wide temperature-range. The alkali metals themselves present a particular problem of course, in handling and maintenance in a high state of purity, etc.; in addition, however, accurate specific heat measurements below, say, 4° K are exceedingly difficult because of such problems as adsorption and desorption of relatively minute quantities of helium gas and so on.

As an example of the extreme care and attention to detail required in this sort of experimental work, I might mention the excellent series of experiments by J.A. Morrison, together with Los, Dugdale and others, in the field of surface chemistry. In order to determine contributions from surface phenomena a consistent accuracy in measurement of $\sim 0.1\ \%$ has had to be maintained, and more recently, Morrison has been facing the problems of extending such work to the liquid helium range.

Solutions solides primaires dans les métaux

par **J. FRIEDEL**

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Le but de ce rapport est l'étude théorique des solutions solides métalliques, et en particulier des solutions diluées et désordonnées. L'analyse expérimentale des limites de phases a conduit Hume-Rothery (1) à distinguer dans ce domaine plusieurs facteurs dont l'action semble être plus ou moins additive. Ce sont essentiellement la *taille* des constituants, définie par exemple par le rayon de la sphère atomique du corps pur; et leur place dans le tableau périodique, définie par leur *valence* et la *période* à laquelle ils appartiennent.

L'effet de valence, en général prépondérant, sera particulièrement développé.

TAILLE

Dans les solutions de *substitution*, le facteur de taille peut être défini par la différence δ des rayons r_s, r'_s des sphères atomiques des deux constituants. Dans un modèle grossier souvent utilisé [(2), (3), (4), (5), (6), etc.], les atomes de soluté et la matrice sont traités comme des milieux continus, homogènes et isotropes doués des propriétés élastiques *macroscopiques* des constituants purs. Un trou sphérique de rayon r_s est créé dans la matrice; une sphère de rayon r'_s représentant un atome dissous est introduit, et les deux sphères sont amenées en contact à un rayon intermédiaire a. Un tel modèle donne les résultats suivants.

1. Terme d'énergie libre dû aux contraintes élastiques.

Le travail fourni σ *par atome dissout* dans l'opération précédente est naturellement positif et proportionnel à δ^2. Il est *petit*, d'habitude une faible fraction d'un ev. au moins. Il est plus précisément de l'ordre kT_s (T_s température du solidus) pour $\delta/a \simeq \pm 0{,}15$. Comme Hume-Rothery l'a remarqué expérimentalement, il commence donc, pour ces valeurs du facteur de taille, à jouer un rôle dans les diagrammes de phases près du point de fusion des alliages.

2. Interaction entre atomes dissous.

Si le volume d'alliage est assez grand pour pouvoir être traité comme infini, la dilatation et la contrainte hydrostatique dues à l'introduction d'un atome dissous sont nulles dans la matrice. L'énergie (libre) d'interaction de deux atomes dissous est donc *nulle*, car elle se réduit, par suite de la symétrie sphérique, au travail de la contrainte hydrostatique due à l'un des atomes quand l'autre est introduit.

Les atomes de soluté peuvent cependant interagir des deux façons suivantes.

2.1. *Interactions à courtes distances.* — Deux atomes dissous en position de premiers voisins ont des sphères atomiques qui se coupent; le modèle employé n'est alors plus valable. Des interactions à courte distance, *entre premiers voisins*, sont donc possibles. Des mesures récentes sur l'alliage AuNi (7) semblent indiquer que ces interactions sont faibles pour un couple isolé d'atomes dissous. Les interactions peuvent par contre être assez fortes, dans des groupements d'un *grand* nombre d'atomes dissous, pour relâcher une grande partie de l'énergie élastique. Les groupements favorables sont, à faibles concentrations, des disques minces (8), (9), tels que les zônes de Guinier-Preston (10), donc correspondent à une attraction entre atomes dissous; à fortes concentrations, ils correspondent à un état ordonné, donc à une répulsion entre atomes dissous.

2.2. *Dilatation de la matrice.* — Deux atomes dissous interagissent en fait à longues distances quand le volume V d'alliage est fini. Quand V tend vers l'infini, l'énergie d'interaction devient indépendante de la distance et tend vers zéro de façon telle que l'énergie d'interaction d'un atome dissous avec *tous* les autres soit finie à concentration c finie. Cette énergie ne correspond à aucune force si la concentration est uniforme.

Quand un atome de soluté est introduit dans l'alliage, son volume augmente en effet de $w = 4\pi r'_{s}2\ (r'_{s} - a)$. Comme le volume total de matière n'est pas changé par l'introduction de contraintes internes, le volume V de matrice est réduit de $- w$ par atome dissous, soit de $-\, w \dfrac{cV}{v}$ à concentration c, si $v = \dfrac{4\pi}{3} r_s^3$ est le volume atomique. Ce changement de volume est obtenu par le jeu de forces « images » à la surface de l'alliage, donc est uniforme (sauf près de la surface) s'il n'y a *pas* de gradient de concentration [(5), (13)]. La matrice a alors une dilatation uniforme et finie à concentration finie (*) :

$$e = -\frac{1}{V}\left(w\frac{cV}{v}\right) = -\frac{w}{v}\,c.$$

Cette dilatation facilite la dissolution d'un nouvel atome de soluté, donc réduit σ à concentration croissante. Un simple calcul donne, pour le travail *par atome dissous* (12) :

$$\sigma = A\delta^2\,(1 - 2\frac{\chi'}{\chi}c)\,,$$

où le coefficient A est fonction des constantes élastiques :

$$A = 6\pi a/[\chi' + (1+\upsilon)\,\chi/2\,(1-2\upsilon)]\,. \qquad (1)$$

χ et χ' sont les compressibilités des deux milieux, υ le coefficient de Poisson de la matrice.

Le travail *par atome d'alliage* :

$$\Sigma = \int_0^c \sigma\,dc = A\delta^2 c\,(1 - \frac{\chi'}{\chi}\,c), \qquad (2)$$

a par suite une courbure *négative* $\delta^2\Sigma/\delta c^2$ aux deux extrémités du diagramme de phases ($c \to 0$ et $c \to 1$). La différence entre $\Sigma(c)$ et sa tangente à l'origine représente l'énergie (libre) d'interaction entre atomes dissous. Il n'y correspond aucune force, quand la concentration est uniforme, parce que la dilatation e est alors uniforme.

3. Termes d'énergie et d'entropie dus aux contraintes élastiques.

Le travail Σ est la part de l'énergie libre de formation de l'alliage *qui n'est pas due à l'entropie de position* ou aux facteurs, négligés ici, de valence et de période. Σ varie avec la température essentiellement comme l'inverse des compressibilités [Eq. (1)], donc décroît

(*) L'étude de la diffusion des rayons X a permis de mettre cette dilatation en évidence dans Au Ni (7).

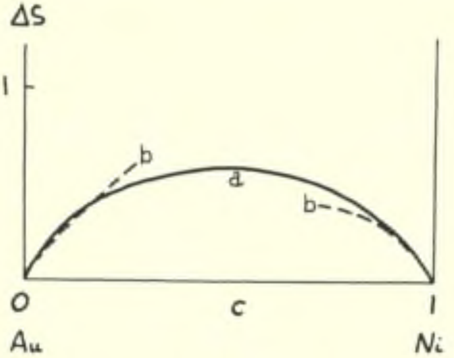

Fig. 1. — Anomalie d'entropie de formation des alliages AuNi à 900° C (en 10^{-3} ev/o/at)
a) Résultats expérimentaux; *b*) Formules (2), (3).

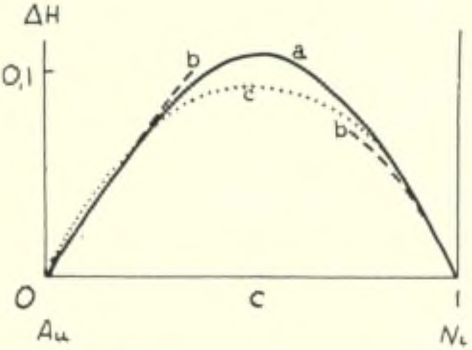

Fig. 2. — Chaleur de formation des alliages AuNi à 900° C (en ev/at)
a) Résultats expérimentaux; *b*) Formules (2), (3); *c*) Formule de Lawson.

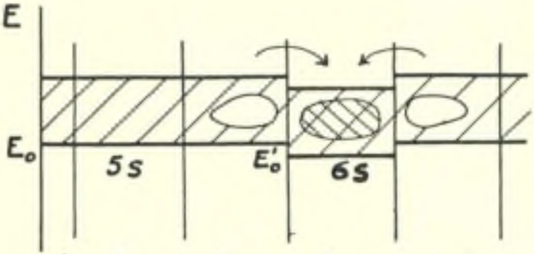

Fig. 3. — Dissolution de l'or dans l'argent.

à température croissante et donne un terme positif dans l'*entropie* de formation :

$$\Delta S = - \delta\Sigma/\delta T > 0 . \qquad (3)$$

Une anomalie positive de ce type semble caractéristique des alliages à fort facteur de taille [(13), (14)]. La figure 1 donne par exemple des mesures récentes pour AuNi (14), un alliage à fort facteur de taille ($\delta/a = 0{,}14$) et faibles facteurs de valence et de période. La courbe donne l'entropie, en 100^{-3} eV/0/atome, diminuée de l'entropie de position, supposée de hasard. Les deux courbes pointillées sont déduites de (1), (2), (3) et des variations des constantes élastiques avec la température; elles sont en accord satisfaisant avec l'expérience. La correction due au faible ordre à courte distance observé dans ces alliages (7) serait très petite.

La figure 2 compare avec l'expérience l'*énergie* (ou mieux l'enthalpie) de formation $\Delta H = \Sigma + T\Delta S$ du même alliage. On voit que ΔH (en eV/atome) est positif et petit; qu'il a une courbure négative et qu'il a l'ordre de grandeur de la chaleur mesurée. La courbe ponctuée correspond à une formule approchée établie par Lawson (3) qui se déduit de (2) et (3) en prenant des valeurs moyennes pour les constantes élastiques des deux constituants et en négligeant leurs variations avec la température.

PÉRIODE

L'effet de période est petit lui aussi, tout au moins dans les alliages de *substitution* entre éléments assez lourds. Dans l'alliage AgAu par exemple, les deux constituants ont même valence, presque même taille, et des bandes de conductibilité de structures très similaires (fig. 3) : le bas des bandes a un caractère *s*, une masse effective voisine de l'unité et des énergies E_0, E'_0 voisines; car la grande différence des potentiels auxquels ils sont soumis, est compensée par une différence dans le nombre de leurs nœuds (5*s*, 6*s*) qui traduit une différence d'énergie cinétique.

Un atome d'or dissous dans l'argent peut donc être supposé raisonnablement avoir, dans son polyèdre atomique, des électrons de conductibilité avec la même structure que dans l'or pur. L'énergie de dissolution est nulle dans cette approximation.

En fait, par suite de la différence des énergies E_0 , E'_0 , les électrons de conductibilité sont un peu diffusés par les atomes d'or, ce qui accroît leur *résistivité*. La différence des niveaux de Fermi attire un peu vers les atomes d'or les électrons de valence des atomes d'argent voisins : la bande de conductibilité est un peu *polarisée*, l'électronégativité des éléments étant liée à l'énergie de leur niveau de Fermi (à tailles égales). Enfin ce réarrangement de charge stabilise le système, donc produit une énergie de dissolution *négative*.

Ces effets ont été étudiés par Mott (15) et Huang (16). Ils sont faibles dans le cas général où le bas des bandes de conductibilité a des énergies peu différentes.

VALENCE

Nous étudions maintenant des solutions interstitielles quelconques ou des solutions de substitution où le soluté et le solvant ont des valences différentes. Les facteurs de « taille » et « période » sont supposés négligeables ou pouvant être traités séparément.

Nous disposons ici d'un modèle électronique simple, dû à Mott (15) et susceptible de généralisations. C'est une approximation de Thomas Fermi, particulièrement appropriée pour l'étude des densités électroniques au voisinage du niveau de Fermi. Nous en exposons les conséquences en ce qui concerne la forme des bandes d'énergie, la position des niveaux de Fermi, la répartition des électrons dans l'espace; nous en tirons certaines conclusions concernant en particulier l'interaction des atomes de soluté et le moment magnétique des alliages ferromagnétiques.

Les corrections de corrélation sont difficiles à évaluer dans cette méthode, qui ne convient donc pas au calcul des énergies de dissolution. Elle ne permet pas non plus d'étudier les états liés ni de calculer les phases des fonctions électroniques, donc les propriétés électriques des alliages. D'autres méthodes, rappelées en fin de chapitre, peuvent être alors utilisées.

1. Le modèle utilisé.

Les hypothèses faites une fois précisées, le potentiel dans l'alliage est calculé.

1.1. *Hypothèses faites.*

Le modèle repose sur l'emploi d'*orbitales moléculaires* et d'une approximation de *Thomas Fermi* généralisée : les électrons de valence de l'alliage sont supposés se mouvoir tous dans le même potentiel, somme du potentiel périodique du solvant pur et d'une perturbation V_p' et V_p est traitée comme localement constante. Les densités ρ , ρ_o au point $\mathbf{r}$ des électrons d'énergie inférieure à E dans l'alliage et le solvant pur sont alors liées par la relation :

$$\rho(E, \mathbf{r}) \simeq \rho_0(E - V_p\,, \mathbf{r}). \tag{4}$$

L'équation de Poisson donne alors, si E_M et $E_M + \Delta E_M$ sont les niveaux de Fermi du solvant pur et de l'alliage, et si l'on néglige les termes de *corrélation* (*)

$$\Delta V_p = -4\pi\ [\rho(E_M + \Delta E_M\,, \mathbf{r}) - \rho_0(E_M\,, \mathbf{r})] \simeq 4\pi\ [\rho_0\ (E_M\,, \mathbf{r}) - \rho_0(E_M + \Delta E_M - V_p\,, \mathbf{r})]\,.$$

$\Delta E_M - V_p$ sera supposé assez petit pour qu'une approximation du *premier ordre* suffise. Enfin la densité $\partial\rho_0(E_M\,, \mathbf{r})/\partial E_M$ dans le solvant pur au niveau de Fermi est supposée assez constante dans l'espace pour être prise égale à la densité $n_0(E_M)$ des *états* de la structure de bande du solvant pur. D'où :

$$\Delta V_p \simeq 4\pi n_0\ (E_M)(V_p - \Delta E_M)\,. \tag{6}$$

Cette équation permet de calculer V_p , connaissant ses conditions aux limites. Nous supposerons ici les atomes de soluté assez bien *dispersés* pour que l'on puisse découper le métal en polyèdres contenant chacun un atome de soluté en son centre et de volumes à peu près égaux. Si les atomes de soluté sont représentés par des charges ponctuelles Z et Z électrons supplémentaires (Z = 1 pour l'hydrogène intersticiel ou le zinc dans le cuivre, etc.) et que l'on remplace les polyèdes par des sphères de même volume et de rayon R, la perturbation vérifie les conditions suivantes :

$$\begin{aligned} &V_p = \partial V_p/\partial r = 0 \qquad \text{pour } r = R \\ &V_p \to -Zr^{-1} \text{ pour } r \to 0\,, \end{aligned} \tag{7}$$

où r est la distance à une charge Z. Les deux premières conditions sont dues à la neutralité des sphères et à la symétrie sur une paroi du polyèdre.

(*) Les unités atomiques $e = m = \hbar = 1$ sont utilisées.

Notons pour finir qu'avec les approximations faites ici, l'alliage a la *même structure de bandes* que le solvant pur, simplement décalée dans l'échelle des énergies d'un terme égal à la perturbation moyenne. Les densités d'états d'énergie inférieure à E dans l'alliage et le solvant pur, N(E) et $N_0(E)$, sont en effet reliées par :

$$\begin{aligned} N(E) &= V^{-1} \int \rho\,(E, \mathbf{r})\, d\tau = V^{-1} \int \rho_0\,(E - V_p\,, \mathbf{r})\, d\tau \\ &= N_0(E) - V^{-1} \frac{dN_0}{dE} \int V_p d\tau = N_0(E - \Delta E_0) \qquad (8) \end{aligned}$$

avec :

$$\Delta E_0 = V^{-1} \int_v V_p d\tau = \text{const.}$$

V est ici le volume de l'alliage.

Cette approximation que nous dénommerons celle des « bandes rigides » est représentée figure 4*a*. Elle est souvent utilisée pour étudier la densité des états au niveau de Fermi et le déplacement du niveau de Fermi par rapport à la structure de bande [(17), (18)]. Il faut noter que cette approximation rentre dans le cadre du modèle développé ici, et ne suppose pas V_p constant.

Il est important de comprendre que si la perturbation V_p est très localisée, cette approximation n'est bonne que dans les bandes

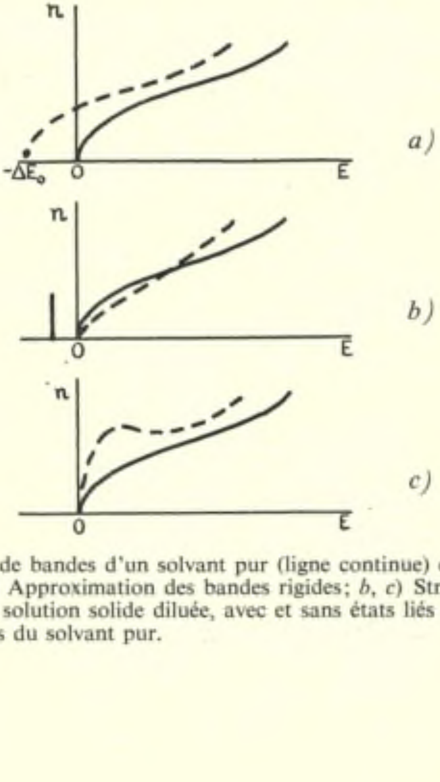

Fig. 4. — Structures de bandes d'un solvant pur (ligne continue) et d'un alliage (ligne pontillée). *a*) Approximation des bandes rigides; *b*, *c*) Structures réelles possibles pour une solution solide diluée, avec et sans états liés dans la bande d'énergies interdites du solvant pur.

d'énergies du solvant pur et assez loin des limites de bandes, c'est-à-dire pratiquement près du niveau de Fermi seulement (cf. §4). Dans des solutions solides diluées en particulier, l'alliage ne peut présenter que des états liés discontinus dans les bandes d'énergies interdites du solvant pur; ses structures de bandes possibles sont illustrées, figures 4*b* et *c*.

1.2. — *Calcul de la perturbation* V_p .

L'équation (6) et les conditions aux limites (7) donnent, aux dilutions infinies, le résultat classique (15).

$$V_p = -Zr^{-1}\exp(-qr) \tag{9}$$

avec :

$$q^2 = 4\pi n(E_{0M}) \text{ et } \Delta E_M = 0 . \tag{10}$$

L'atome de soluté attire donc ou repousse localement des électrons de façon à neutraliser sa charge Z à courte distance, de l'ordre de quelques q^{-1}. Le paramètre d'écran q ne dépend que de la densité des états $n_0(E_M)$ au niveau de Fermi; il est de l'ordre de l'unité atomique pour les métaux mono- et polyvalents comme le cuivre ou l'aluminium : l'atome dissous ne perturbe que les premiers et peut être seconds voisins.

A concentrations finies, on trouve (12) :

$$V_p = E_M - \frac{Z}{r}\,\frac{qR\,\mathrm{ch}\,q\,(R-r) - \mathrm{sh}\,q\,(R-r)}{qR\,\mathrm{ch}\,qR - \mathrm{sh}\,qR} \tag{9}$$

avec :

$$\Delta E_M = Zq/(qR\,\mathrm{ch}\,qR - \mathrm{sh}\,qR) \tag{10}$$

La variation du niveau de Fermi avec la concentration c est représentée figure 5, pour le cuivre ($q = 1{,}15$). La *tangente horizontale à l'origine vient de ce que le niveau de Fermi ne peut changer tant qu'une partie du solvant n'est pas perturbée.*

Ce résultat est général quelle que soit la perturbation.

V_p est alors juste assez fort pour déplacer au-dessous du niveau de Fermi E_M les Z électrons supplémentaires introduits par atome de soluté.

Le déplacement du niveau de Fermi à plus fortes concentrations est lié à l'interaction des atomes de soluté : V_p , devant s'annuler à distance R finie, diminue; il ne peut donc déplacer au-dessous

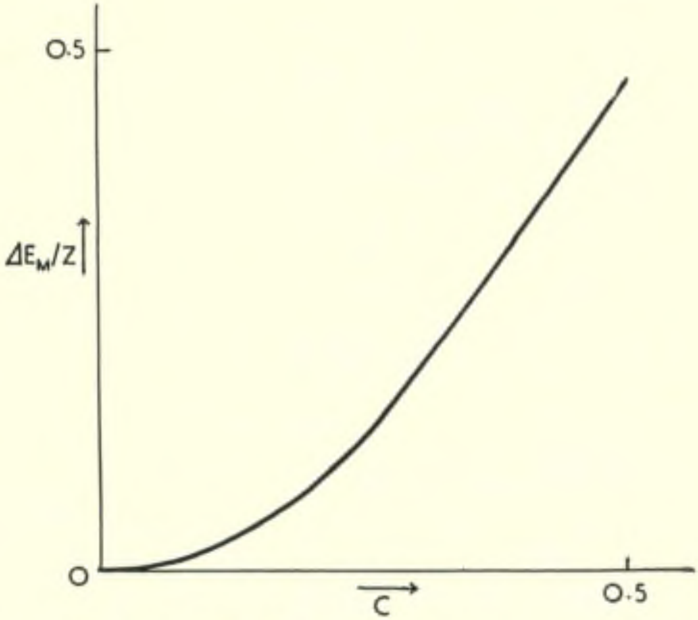

Fig. 5. — Déplacement ΔE_M du niveau de Fermi avec la concentration *c* pour le cuivre (en ev par atome).

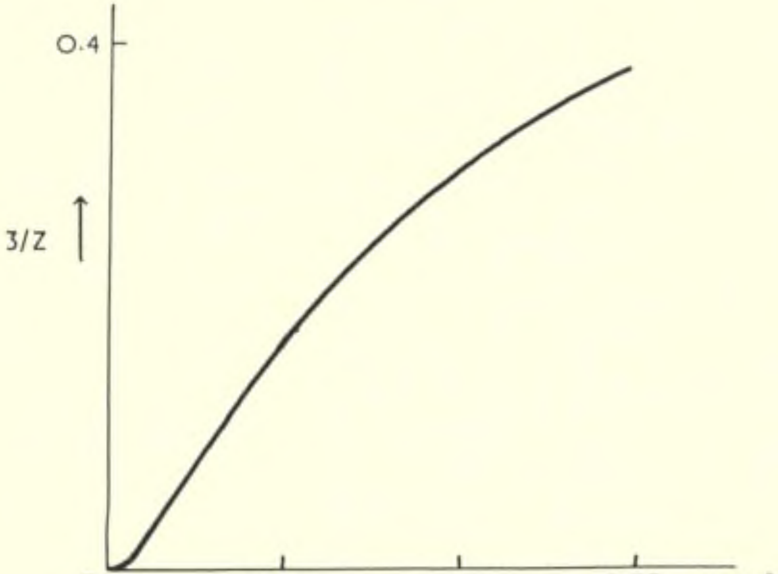

Fig. 6. — Variation de l'écran délocalisé *z* avec la concentration.

du niveau de Fermi E_M qu'une charge inférieure à Z; la différence z doit être obtenue par un déplacement ΔE_M du niveau de Fermi.

On a effectivement :

$$z = Z - \int_0^R [\rho(E_M, \mathbf{r}) - \rho_0(E_M, \mathbf{r})\, 4\pi r^2 dr = \frac{1}{3} q^2 R^3 \Delta E_M \qquad (11)$$

La charge z a une densité *uniforme*; le reste $Z - z$ de l'écran est fortement *localisé* autour de l'atome de soluté, car la densité de charge correspondante :

$$\rho(E_M, \mathbf{r}) - \rho_0(E_M, \mathbf{r}) = -q^2 V_p$$

et sa dérivée s'annulent, d'après (6), à la limite des polyèdres.

La figure (6) donne z/Z en fonction de $(qR)^{-3} = (qr_s)^{-3}c$. Pour les métaux, (qr_s) est au moins de l'ordre de 10^{-2}. Donc z/Z est toujours bien inférieur à l'unité, même aux fortes concentrations : les électrons de conductibilité de l'alliage ont une densité qui est *loin d'être uniforme*.

Cette conclusion est confirmée par la faible stabilité des réseaux ordonnés tels que les laitons β : si les électrons de valence avaient une densité de charge uniforme, la différence de charge des ions Cu^+ et Zn^{++} donnerait lieu à une forte énergie de Madelung qui stabiliserait l'état ordonné. La faible énergie de transformation ordre-désordre observée correspond au contraire à une faible délocalisation : $z \simeq 0{,}15$ (19), en bon accord avec la courbe de la figure 6 (12).

2. Interactions entre atomes de soluté.

L'énergie d'interaction due au facteur de valence s'exerce uniquement à assez faibles distances, et correspond donc à une force non nulle. Cette force et la courbure de l'énergie $\varepsilon(c)$ de formation de l'alliage, qui lui est liée, sont proportionnelles à la charge supplémentaire Z de soluté (attraction pour $Z < 0$, répulsion pour $Z > 0$); ces conclusions sont comparées aux résultats expérimentaux.

2.1. — *Distance maximum d'interaction.*

Tant que les atomes de soluté n'interagissent pas, le niveau de Fermi reste constant et l'écran est bien localisé ($\Delta E_M = z = 0$). L'interaction commence quand les courbes des figures 5, 6 quittent nettement l'axe des abscisses, soit pour une concentration :

$$c > c_0 \simeq (qr_s/10)^3 \qquad (12)$$

et une distance entre atomes de soluté $2\ R > 2\ R_0 \sim 20\, q^{-1}$.

Le tableau suivant donne des valeurs typiques de R_0 et c_0 :

	Cu	Al	Tl	Fe	Ni
q	1,15	1,4	1,0	3,2	4,75
Rr/rs	3,3	2,4	2,8	1,2	0,8
c_0 %	3	7,5	4,5	60	> 100

Les valeurs de q ont été déduites, à l'aide de (10), des densités d'états $n_0(E_M)$ mesurées par les chaleurs spécifiques de basse température (^{20}); ce processus semble justifié par les analyses de Bohm et Pines (^{25}).

Les valeurs du tableau donnent un bon ordre de grandeur : le «déplacement de Knight» des atomes de thallium dans les alliages(*) TlSn, mesuré par résonance magnétique nucléaire (^{21}), reste constant jusqu'à une concentration $c_0 \simeq 3$ % d'étain, ce qui indique que, jusqu'à cette concentration, une bonne partie des atomes de thallium n'est pas perturbée et le niveau de Fermi reste constant.

Dans les métaux de transition comme le fer, le nickel, $n_0(E_M)$ et q sont forts, et la distance d'interaction $2R_0$ est de l'ordre de la distance interatomique : les atomes de soluté n'interagissent que très faiblement. Quand les deux métaux purs ont même structure cristalline et des paramètres voisins, les atomes de soluté sont pratiquement dans le même état que dans le soluté pur : l'énergie de formation de l'alliage est pratiquement nulle, et la solution complètement désordonnée. Les alliages entre métaux de transition, FeNi par exemple, sont précisément un exemple classique de ces solutions solides idéales [(^{22}), (^{23})].

2.2. — *Courbure de l'énergie de formation de l'alliage.*

Tant que les atomes de soluté n'interagissent pas, leur énergie de dissolution est une constante et l'énergie ε de formation de l'alliage est proportionnelle à la concentration. L'interaction des atomes de soluté est liée à la *courbure* de $\varepsilon(c)$.

(*) AB signifie B dissous dans A.

Dans l'approximation du § 1, l'interaction entre atomes de soluté déplace de ΔE_M la bande de conductibilité, sans changer sa forme. L'énergie de formation de l'alliage s'écrit donc :

$$\varepsilon = \text{const.}\ c + (p + Zc)\Delta E_M\,, \qquad (13)$$

si le solvant a p électrons de conductibilité par atome. Le changement avec c de l'interaction de V_p avec la charge d'écran, qui n'apparaît pas dans cette expression, est négligeable (12).

La variation de ΔE_M avec c, représentée figure 5, montre que l'on doit s'attendre, du fait du facteur de valence, à une énergie de formation *dont la courbure* $\partial^2\varepsilon/\partial c^2$ *a le signe et est proportionnelle* à Z pour c petit. La courbure doit de plus être pratiquement *nulle* à concentration inférieure à la valeur c_0 définie au § 2.1. Ces conclusions ne sont évidemment valables qu'à concentrations assez faibles; l'énergie de formation $\varepsilon(c)$ d'une phase AB de substitution devrait donc varier suivant l'un des trois types de la figure 7, si le facteur de valence est prépondérant et si B est à la droite de A dans le tableau périodique.

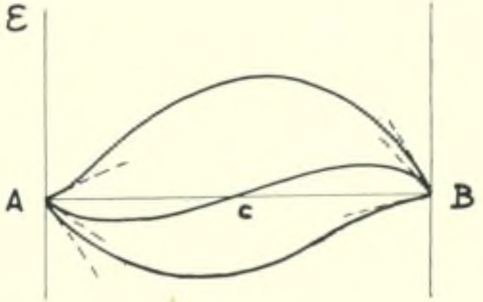

Fig. 7. — Formes prévues pour l'énergie de formation d'un alliage de substitution AB.

La courbure de $\varepsilon(c)$ a effectivement le signe Z dans la plupart des alliages étudiés jusqu'ici, quand le facteur de taille n'est pas trop fort [cf. (12)].

Les figures 8 et 9 montrent par exemple la courbure positive de $\varepsilon(c)$ pour les solutions solides **Ag**Cd et la courbure négative et croissant avec Z des solutions liquides **In**Ag, **Sn**Ag qui ont été récemment mesurées dans le but de vérifier cette théorie (24). Les effets de taille peuvent être négligés ici : ils sont peu importants pour l'alliage solide, et disparaissent en grande partie par fusion [(12), (28)]. Les formules

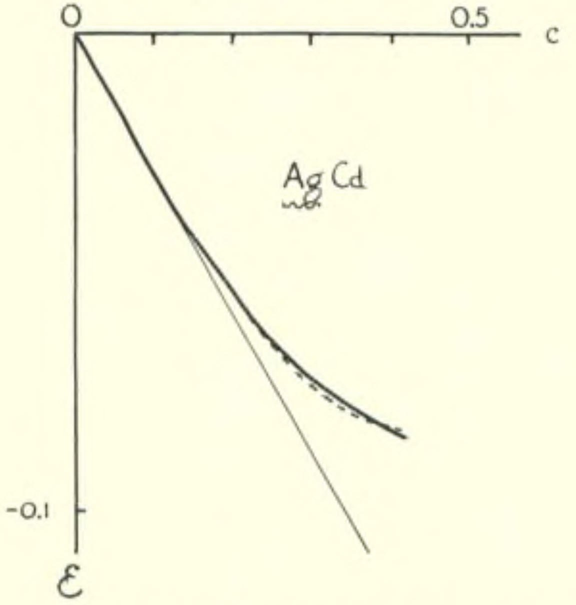

Fig. 8. — Energie de formation ε (*c*) pour **Ag**Cd solide (en ev/at.)
a) Résultats expérimentaux; *b*) Equation (13) avec $q = 1,75$.

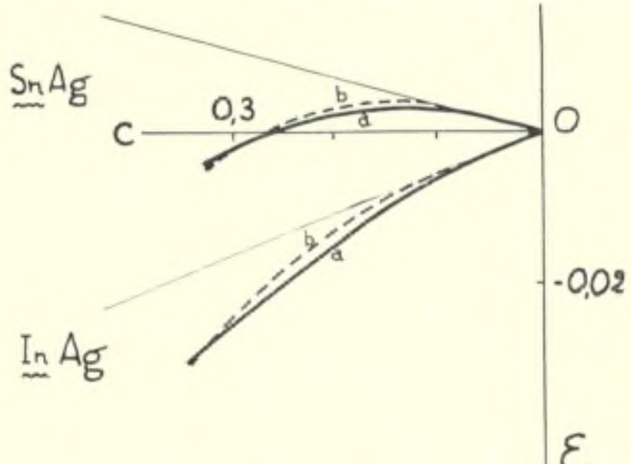

Fig. 9. — Energies de formation ε (*c*) des alliages **Sn**Ag, **In**Ag liquides (en ev/at)
a) Résultats expérimentaux; *b*) Equation (13) avec $q = 1,7$ (**Sn**Ag) et 1,75 (**In**Ag).

(10) et (13) permettent donc de déduire de la courbure mesurée de $\varepsilon(c)$ une valeur q_{exp} du paramètre d'écran. Le tableau suivant montre que les valeurs obtenues de cette façon (12) sont du bon ordre de grandeur, quoique supérieures aux valeurs q de l'équation(10):

	Z	q	$q'(1)$	q exp
CuZn	1	1,15	$1{,}6_5$	$1{,}6_5$
AgCd	1	0,9	1,8	$1{,}7_5$
AlZn	— 1	1,4	$1{,}5_5$	$1{,}7_5$
InAg	— 2	1,1	1,6	$1{,}7_5$
SnAg	— 3	1,1	$1{,}5_5$	1,7

La différence peut provenir en grande partie de ce qu'on a négligé dans V_p les termes de *corrélation* (échange et corrélation de Coulomb). Il leur correspond une répulsion entre électrons de conductibilité qui rend l'écran moins efficace, que ce que donne l'approximation de Hartree. Un traitement de l'échange dans l'approximation de Hartree Fock, valable pour une bande de conductibilité *parabolique* de *masse effective unité*, donne effectivement un écran plus concentré [cf. (12), (26), (27)],

$$q'(1) = q(1)(1 - 3/2\pi k_M)^{-\frac{1}{2}} ,$$

en meilleur accord avec les valeurs expérimentales k_M est ici le moment des électrons au niveau de Fermi. Une étude plus correcte de la corrélation par les méthodes de plasma (22) serait intéressante.

2.3. — *Force d'interaction.*

La courbure de l'énergie $\varepsilon(c)$ de formation de l'alliage due au facteur de valence correspond à une force d'interaction entre atomes de soluté, *attractive pour* $Z < 0$, *répulsive pour* $Z > 0$.

1) Si, en effet, la courbure est négative ($Z < 0$, fig. 10), un alliage de composition c tend à se décomposer, à basse température, en *deux* phases de même structure, mais de compositions différentes c_1, c_2 : les atomes de soluté *s'attirent* (*) de façon à réduire l'énergie

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(*) Un tel raisonnement suppose que les phases c_1, c_2 puissent être traitées indépendamment, donc que les énergies d'interaction s'annulent à grandes distances. Tel n'est *pas* le cas pour les interactions élastiques étudiées dans la première partie.

de l'alliage de la quantité *ab*. Ainsi la coexistence de deux phases cubiques à faces centrées dans **AlZn** au-dessous de 350° C est certainement due à la courbure de $\varepsilon(c)$ décrite plus haut (29), non à une anomalie de l'entropie (30).

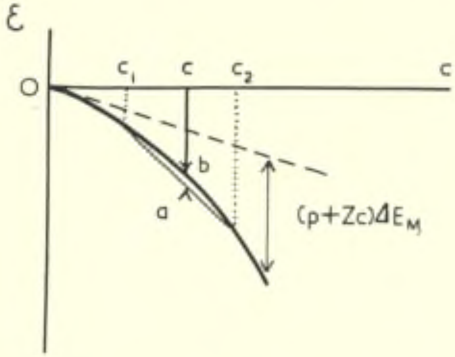

Fig. 10. — ε (c) avec une courbure négative.

Une phase de structure cristalline différente est souvent plus stable aux fortes concentrations c_1. On peut alors s'attendre à ce que, par trempe et vieillissement de la solution solide, des zones de fortes concentrations se forment dans la solution pendant une période transitoire avant la précipitation d'une phase plus stable. Le stade initial des *amas* de Guinier-Preston a été expliqué de cette façon (31). Effectivement les amas s'observent de façon générale dans des alliages à $Z < 0$ (12).

A températures plus élevées, l'agitation thermique tend à disperser les atomes, et l'on doit s'attendre à une redissolution en une phase unique, avec une légère tendance au groupement des atomes de soluté. Cette attraction locale a été observée aux rayons X pour **AlZn** (32) et **AlAg** (33).

2) Inversement, avec une courbure positive de $\varepsilon(c)$ $(Z > 0)$, les atomes de soluté doivent se *repousser*. A basse température, la nucléation d'une nouvelle phase doit se faire sans enrichissement préalable de la solution solide.

Cet « ordre local » explique sans doute pourquoi dans **CuAl**, certaines lignes de résonance nucléaire magnétique disparaissent beaucoup plus vite, par effet quadrupole, dans les atomes de cuivre que dans ceux d'aluminium quand la concentration en aluminium augmente (30). La destruction de cet ordre local explique probablement l'anomalie de chaleur spécifique observée pour **CuZn** (35). On sait également que les atomes intersticiels de carbone ($Z = 4$) se repoussent dans le fer (36) et que leur solubilité diminue quand on augmente la teneur en éléments à $Z > 0$ (Ni, Cu [cf. (22)]. Il en est de même pour l'hydrogène intersticiel ($Z = 1$) dans les alliages à base de cuivre, d'argent, d'or, d'aluminium et de palladium [cf. (12)].

3. Alliages ferromagnétiques.

Nous montrerons sur cet exemple que le modèle des « bandes rigides » conduit bien aux mêmes conclusions que l'étude des écrans localisés (37).

1) Quand plusieurs bandes se chevauchent au niveau de Fermi, le modèle des bandes rigides rappelé au § 1.1 montre que les Z électrons supplémentaires introduits avec chaque atome de soluté remplit les diverses bandes *en proportion de leurs desnités* $n_0\mathbf{j}(E_M)$ au niveau de Fermi.

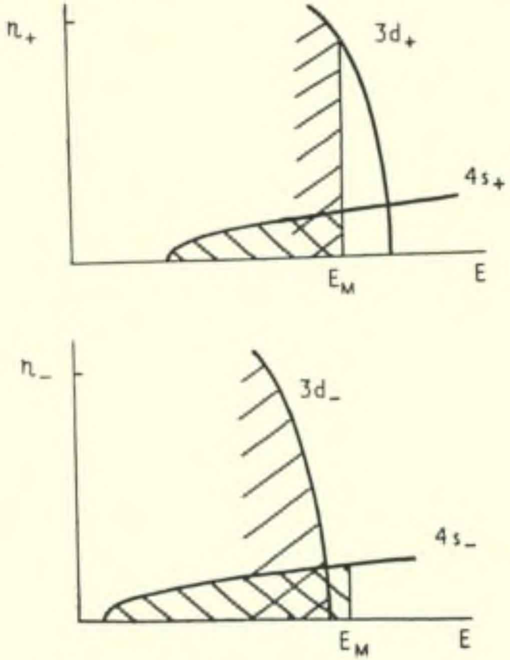

Fig. 11. — Structure de bandes proposée pour le nickel et le cobalt ferromagnétiques

Les moments magnétiques des alliages ferromagnétiques sont expliqués de cette façon en supposant que les interactions d'échange décomposent la structure de bandes en deux moitiés de spins opposés et de densités n_+, n_- très différentes au niveau de Fermi [(18), (38), (39), etc.]. Les figures 11 et 12 rappellent les structures de bandes proposées pour le nickel, le cobalt et le fer pur respectivement. Dans les deux cas, une seule moitié de la bande étroite $3d$ a une forte densité d'états au niveau de Fermi, l'autre étant pleine dans Ni, Co, et présentant dans Fe un minimum de densité au niveau de Fermi. Les mesures de chaleur spécifique à basse température (donnant $n_+ + n_-$) et d'absorption optique (donnant $n_s \simeq 2n_+$) montrent que $n_+/n_- \simeq 60$ pour le nickel et le cobalt. Les Z électrons supplémentaires par atome de soluté iront donc pratiquement tous dans la structure de bande ayant la plus forte densité, réduisant de Z l'excès d'électrons d'un spin dans le nickel et le cobalt, l'augmentant de Z dans le fer. Le moment magnétique *moyen* μ par atome d'alliage varie donc de façon linéaire avec la concentration c :

$$\mu = \mu_A + \alpha c Z \mu^d , \tag{14}$$

avec $\alpha = 1$ pour Fe, — 1 pour Ni, Co (μ_A moment magnétique de la matrice, μ_0 magnéton de Bohr). Ces deux lignes droites sont observées expérimentalement pour Z et c pas trop forts (fig. 13).

2) Il est équivalent de dire que chacune des bandes qui se chevauchent contribue à l'écran d'un atome de soluté Z la charge :

$$Z_j = \int_0^R [\rho_j (E_M + \Delta E_M , \mathbf{r}) - \rho_{0j} (E_M , \mathbf{r})] \, 4\pi r^2 \, dr = n^d{}_j (E_M) Z / n_0 (E_M),$$

proportionnelle à sa densité d'états $n_{0j}(E_M)$ au niveau de Fermi, et change d'autant le moment magnétique de cette bande. L'équation (14) en découle. Mais ce point de vue nous permet de préciser les moments individuels des atomes de soluté et de solvant : dans les alliages ferro-magnétiques, l'écran est fortement *localisé* sur l'atome de soluté, même à fortes concentrations (§ 2.1); il est produit ici par la moitié de la structure de bandes qui a de beaucoup la plus forte densité d'états au niveau de Fermi, donc donne aux atomes de soluté un moment :

$$\mu_B = \mu_A + \alpha Z \mu_0 , \tag{15}$$

et ne change pas le moment μ_A des atomes de la matrice.

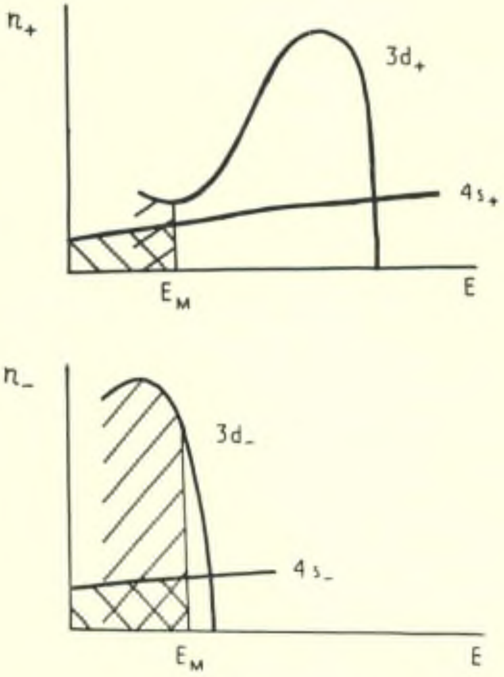

Fig. 12. — Structure de bandes proposée pour le fer ferromagnétique.

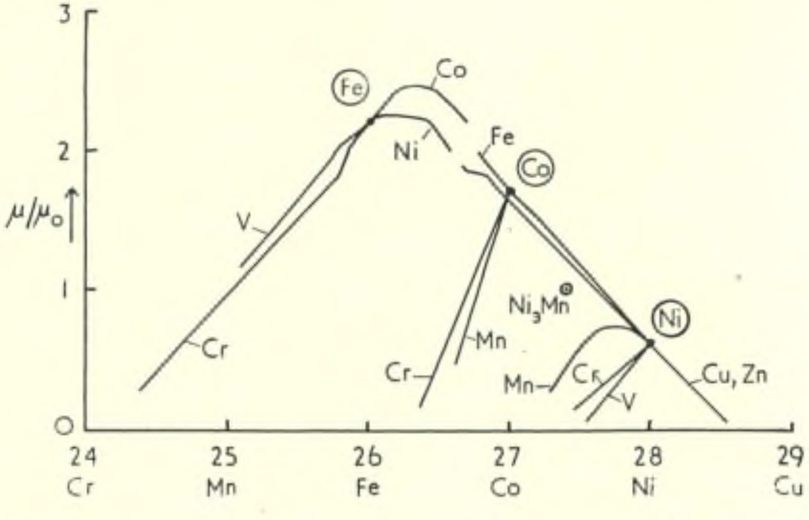

Fig. 13. — Moments magnétiques des éléments ferromagnétiques et de leurs alliages (d'après Slater, Pauling, Bozorth).

Pour **NiFe** par exemple, le moment du nickel doit rester sensiblement constant jusqu'à des concentrations assez fortes, et celui du fer doit en différer par $-Z = 2$ magnétons de Bohr. Ces moments doivent peu dépendre de l'ordre dans des alliages tels que Ni_3Fe. Ces prédictions semblent en assez bon accord avec les moments mesurés par diffraction de neutrons (40).

Le tableau suivant donne les valeurs de μ_A et de $\mu_B - \mu_A$(*), en magnétons de Bohr, ainsi obtenues pour un certain nombre d'alliages.

AB	100*c*		μ_A	$\mu_B - \mu_A$	Z
NiFe	0		0,6 ±	—	— 2
	25	ord.	0,6 ± 0,1	2,35 ± 0,2	»
	25,7	désord.	0,6 ± 0,1	2,31 ± 0,2	»
	39,9	»	0,6 ± 0,15	2,06 ± 0,2	»
	50,1	»	0,65 ± 0,2	1,93 ± 0,2	»
NiMn	25	ord.	0,30 ± 0,05	2,88 ± 0,20	— 3
CoFe	0		1,7	—	— 1
	50	ord.	1,7 ± 0,2	1,1 ± 0,2	»
CoCr	9,0	désord.	1,1 ± 0,15	0,96 ± 0,15	— 3
	13,6	»	0,65 ± 0,15	0,91 ± 0,15	»
FeCr	0		2,2	—	— 2
	15,2	désord.	2,2 ± 0,1	— 2,85 ± 0,10	»
	29,1	»	2,1 ± 0,1	— 2,38 ± 0,07	»
	46,4	»	1,75 ± 0,15	— 1,62 ± 0,11	»

L'interprétation des mesures utilise un facteur de forme calculé pour le fer pur; l'erreur supplémentaire qui en découle n'a pas été estimée et peut être forte dans les alliages tels que Ni_3Mn.

L'accord avec les valeurs prédites est donc satisfaisant, sauf pour **Co**Cr et peut-être **Fe**Cr. Le faible moment μ_A observé pour Ni_3Mn, comme d'ailleurs le faible moment moyen **Ni** Mn, sont probablement dus à l'expansion du réseau du nickel quand du manganèse y est dissous (41). Cette expansion rend probablement les électrons 4*s* plus instables, sans guère changer l'énergie des électrons 3*d*, d'où

(*) Une autre interprétation des mesures est possible pour les alliages désordonnés.

un remplissage de la bande $3d$ qui réduit le moment de l'alliage. Les alliages CoCr et Ni_3Mn désordonnés seront examinés plus loin (§ 4).

4. Autres approximations.

Le modèle développé jusqu'ici semble justifié par son accord raisonnable avec l'expérience dans des domaines variés. Il comporte cependant des points discutables, et en particulier (cf. § 1) :

1. Le développement du premier ordre en $\Delta E_M - V_p$.
2. L'approximation du type Thomas-Fermi.
3. L'emploi d'orbitales moléculaires.

L'examen de ces points critiques conduit à perfectionner le modèle et à développer d'autres approximations.

4.1. — *Développement du premier ordre en* $E_M - V_p$.

Nous avons remplacé, dans l'équation (5), la différence :

$\rho_p(E_M + \Delta E_M - V_p , r) - \rho_0(E_M , r)$ par $(\Delta E_M - V_p)(\partial\rho_0/\partial E_M)$.

L'erreur ainsi faite peut être estimée en tenant compte des termes du second ordre en $\Delta E_M - V_p$ ou même en conservant la différence exacte des densités ρ_0 dans le cas d'un gaz d'électrons libres (12).

On trouve ainsi, pour un gaz d'électrons, un *paramètre d'écran* q du même ordre de grandeur que précédemment, mais qui *croît avec* Z. L'écran est en particulier plus concentré autour d'une charge Z positive que d'une charge négative. Ces conclusions sont inversées pour un gaz de trous positifs.

Cette variation de q avec Z a deux causes différentes :

a) Dans une bande à forte densité ou à faible masse effective, elle est liée aux termes du second ordre en $\Delta E_M - V_p$, c'est-à-dire à la pente $\partial n_0/\partial E_M$ de la bande au niveau de Fermi.

b) Dans une bande à faible densité ou à forte masse effective, elle est due à ce qu'une perturbation répulsive ($Z < 0$) ne peut repousser plus d'électrons qu'il n'y en a initialement dans la bande; une perturbation attractive au contraire ($Z > 0$) peut attirer autant d'électrons que l'on veut dans des états liés d'énergie inférieure à celles de la bande.

Un atome d'argent dissous dans le palladium par exemple ($Z = 1$) ne peut pas repousser de son polyèdre atomique plus que les 0,6 trous positifs $4d$ qui s'y trouvaient initialement. Le reste de l'écran doit être obtenu par répulsion de trous positifs des atomes de palladium voisins ou par attraction d'électrons de conductibilité $5s$. Ces deux mécanismes donnent un écran moins concentré que ne le prédit l'approximation de premier ordre; il conduisent à des interactions assez fortes des atomes d'argent entre eux et avec d'autres impuretés, en accord avec l'expérience (42).

La *structure de bandes* de l'alliage, d'autre part, n'a plus une forme rigide : elle se déforme un peu quand la concentration croît. En général, des bandes qui se recouvrent tendent à s'interpénétrer davantage; la densité d'états au niveau de Fermi est plus faible que ne le prévoit l'approximation des bandes rigides (12). Ce dernier point pourrait être vérifié par des mesures de chaleur spécifique à basses températures sur des alliages simples tels que **Cu**Zn, Ga, Ge etc., où la différence devrait croître comme Z^2 à faibles concentrations.

4.2. — *Approximations de Thomas Fermi et de Tibbs.*

Le remplacement dans l'équation (5) de $\rho(E, \mathbf{r})$ par $\rho_0\,(E - V_p, \mathbf{r})$ est justifié tant que V_p varie lentement dans l'espace et que les énergies $E - V_p$ sont assez différentes d'une limite de zone E_0 : V_p doit varier peu sur une longueur d'onde k^{-1} des électrons d'énergie $E - V_p$; comme cette longueur d'onde devient infinie à une limite de zone ($k = 0$), la variation de V_p sur une longueur d'onde k^{-1} doit être bien inférieure à la différence d'énergie $E - V_p - E_0$ à la limite de zone; d'où :

$$|\nabla V_p| < |E - E_0 - V_p| k = (2\mu)^{1/2} |E - E_0 - V_p|^{3/2} \qquad (16)$$

si μ est la masse effective de la bande (43).

L'approximation est ainsi *très satisfaisante pour les états du continuum*, en particulier près du niveau de Fermi. Car ces états satisfont la condition (16) sauf à très courtes distances des impuretés, où leur densité est faible et les autres approximations faites ne sont de toutes façons pas valables. Ceci explique que les rayons d'écran calculés dans cette approximation pour des impuretés dans un gaz d'électrons libres ne diffèrent que de 5 à 10 % de ceux obtenus avec l'équation exacte de Schrödinger (12).

Cette approximation n'est cependant pas très bonne pour un électron *lié* à un centre d'impureté : l'énergie $E\ E_0 - V_p$ définie dans la condition (16) s'annule alors dans une région d'assez forte densité de l'état lié.

Dans ce cas, et aussi quand on veut une valeur du *déphasage* des fonctions d'ondes dans la bande de conductibilité, il est peut-être préférable d'utiliser l'approximation suivante, justifiée par Tibbs (44). Soit w la fonction d'onde d'un électron libre de masse *unité* et d'énergie $E - E_0$ se mouvant dans le champ de potentiel V_p :

$$\Delta w + 2\,(E - E_0 - V_p)\,w = 0 \qquad (17)$$

Si $\Psi_0(E_0)$ est une fonction de Bloch d'énergie E_0 ,

$$\Psi = \Psi_0\,w \qquad (18)$$

est une forme approchée pour la fonction d'onde d'un électron d'énergie E dans le réseau perturbé. Ceci néglige un potentiel correctif $\delta V_p = -\dfrac{\nabla w \nabla \Psi_0}{w \Psi_0}$, qui peut être petit dans les deux cas qui nous intéressent :

1) Si E_0 est le *centre d'une zone s de masse effective voisine de l'unité*, $\nabla\Psi_0$ est nul dans presque tout l'espace (15). L'approximation (18) est alors valable pour des perturbations assez quelconques et des énergies E assez différentes de E_0. Elle a été employée pour étudier les propriétés électriques d'impuretés dans des métaux tels que le cuivre où la surface de Fermi est contenue tout entière dans une seule zone de Brillouin (15).

2) L'approximation peut aussi être satisfaisante pour un *état lié* à la perturbation V_p . Il faut pour cela que sa fonction d'onde w ne prenne que de faibles valeurs dans la région périphérique V_1 où $K^2 = 2(E - E_0 - V_p)$ est négatif. L'erreur commise sur son énergie E en négligeant le potentiel correctif δV_p dans V_1 :

$$\int_{V_1} w \nabla w^* \Psi_0^* \nabla \Psi_0 d\tau \,,$$

peut alors être négligée. L'équation (17) donne d'autre part $w \simeq$ const. exp $(-i\mathbf{kr})$ si V_p ne varie pas trop violemment dans l'espace; l'erreur commise sur E dans la région centrale V_2 où K^2 est positif s'écrit donc approximativement const. $\int_{V_2} \Psi^*_0 \nabla \Psi_0 d\tau$; ceci s'annule si E_0 est une limite de bande et si V_2 est au moins de l'ordre d'un volume atomique (15). L'approximation de Tibbs doit donc s'appliquer raisonnablement à des états liés à des perturbations *localisées*, telles que celles rencontrées dans les alliages, tout au moins *pour des énergies* E *assez voisines d'une limite de bande* E_0, de façon que la partie centrale V_2 définie plus haut soit de l'ordre d'un volume atomique.

Les résultats obtenus dans ces deux cas sont brièvement résumés*.

4.2.1. — *Résistance et pouvoir thermoélectrique.*

Il est aisk de montrer que, pour une masse effective égale à l'unité, la méthode de Thomas Fermi de premier ordre utilisée aux § 1, 2, 3 est équivalente au calcul dans l'équation (18) des déphasages des fonctions w par l'approximation de Born (37).

L'approximation de Born a été utilisée par Mott pour calculer la résistivité $\Delta\rho$ d'impuretés dans les métaux (15). On trouve ainsi, à dilutions infinies, donc avec $V_p = Zr^{-1} \exp(-qr)$:

$$\Delta\rho = \frac{9\pi^2 Z^2 c}{2 r_s^3 k_M^6}\left[\ln\left(1+\frac{1}{y}\right) - \frac{1}{1+y}\right], \tag{19}$$

où c est la concentration, $\frac{1}{2}k_M^2$ l'énergie de Fermi et $y = q^2/4k^2_M$.

$\Delta\rho$ est due à la partie centrale de V_p, et la formule (17) est donc encore valable à fortes concentrations, en accord avec l'expérience : $\Delta\rho$ est effectivement proportionnel à c et à Z^2 dans les solutions solides primaires de Zn, Ga, Ge, As... dans le cuivre par exemple. L'accord quantitatif est d'autre part bien meilleur (fig. 14) si l'on calcule exactement à partir de V_p les déphasages à l'infini η_l des fonctions w_l de différentes symétries; choisit le paramètre q dans V_p de façon que la charge d'écran Z_0 soit égale à Z ; et déduit des déphasages η_l la valeur correspondante de la résistivité $\Delta\rho$. On utilise pour cela les relations [(16), (37)] :

$$\Delta\rho = c\,\frac{4\pi}{k_M^2}\,\Sigma[(2l+1)\sin^2\eta_l - 2l\sin\eta_{l-1}\cos(\eta_l - \eta_{l-1})] \tag{20}$$

et

$$Z_0 = \frac{2}{\pi}\,\Sigma\,(2_l + 1)\eta_l\,. \tag{21}$$

(*) Les conditions d'explications de l'approximation de Tibbs sont beaucoup mieux remplies dans les métaux et les sels ioniques que dans les semi-conducteurs. Pour ceux-ci, les méthodes plus complexes développées par Wannier, Slater, Adams, etc (37) semblent indispensables, contrairement à ce qui avait été suggéré par l'auteur [cf. (43), (45), (46)].

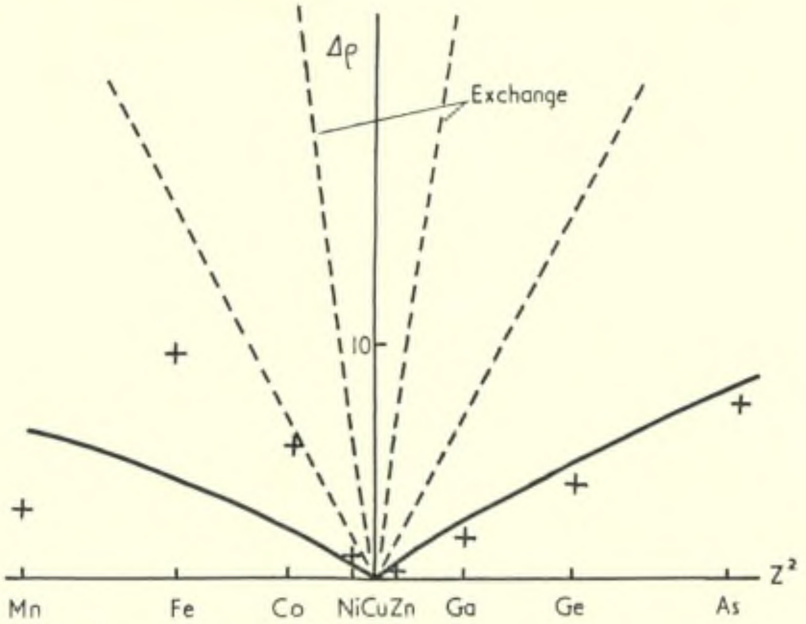

Fig. 14. — $\Delta\rho$ pour 1 at. % en $\mu\Omega$ cm. pour les alliages de cuivre.
Croix : résultats expérimentaux.
Courbes pointillées : formule (20) avec et sans échange.
Courbe continue : calcul plus exact.

Le même procédé a été employé pour une lacune considérée comme une impureté de charge égale à $-p$, s'il y a p électrons de conduction par atome. Un potentiel constant dans une sphère de rayon r_s donne (47) :

$$\Delta\rho = \mathrm{A}.100\ c/k_{\mathrm{M}}\ ,$$

avec A = 0,925; 0,790 et 0,725 pour p = 1,2 et 3 respectivement. D'autres formes pour V_p donnent des valeurs analogues (48).

Le pouvoir thermoélectrique dû aux impuretés s'écrit, au-dessus de la température de Debije (37) :

$$\Delta S = S_0 \left(1 - \frac{\Delta x}{x_0}\right) \Big/ \left(1 + \frac{\rho_0}{\Delta\rho}\right) \tag{22}$$

si ρ_0, S_0 sont la résistivité et le pouvoir thermoélectrique du solvant pur :

$$x_0 = -\ \tfrac{1}{2}\ k_{\mathrm{M}}\ (\partial ln\rho_0/\partial k)_{k_{\mathrm{M}}}$$

et

$$\Delta x = -\ \tfrac{1}{2}\ k_{\mathrm{M}}(\partial ln\Delta\rho/\partial k)_{k_{\mathrm{M}}}\ .$$

Pour les solutions solides dans le cuivre, l'argent et l'or, $\Delta\rho$ est proportionnelle à c, donc Δx constant; $\Delta\rho/\rho_0 c$ est une constante assez forte vis-à-vis de l'unité, donnant à $\Delta S(c)$ une forte concavité vers l'axe des concentrations. Cette concavité est effectivement caractéristique de ces alliages; la valeur correspondante et constante de Δx est en assez bon accord avec la valeur déduite de (19) :

$$\Delta x = 3 - \{(1 + y)[(1 + y) ln(1 + \tfrac{1}{y}) - 1]\}^{-1} .$$

La résistivité et le pouvoir thermoélectrique des solutés de $Z < O$ dans le cuivre, l'argent et l'or (Ni, Pd, Pt, Co, Fe, etc.), ne suivent pas ces règles simples. Les valeurs anormales observées sont peut-être dues à un effet du type Ramsauer-Townsend lié à la présence, près du niveau de Fermi, d'états « presque liés » issus de la bande $3d$.

4.2.2. — *Ecran produit par une bande pleine.*

Une bande pleine située au-dessous du niveau de Fermi (fig. 15) peut fournir un *écran localisé* autour d'un atome de soluté, si la perturbation V_p produite par celui-ci est assez répulsive ($Z < O$) pour soustraire de la bande un état lié d'énergie supérieure à celle du niveau de Fermi.

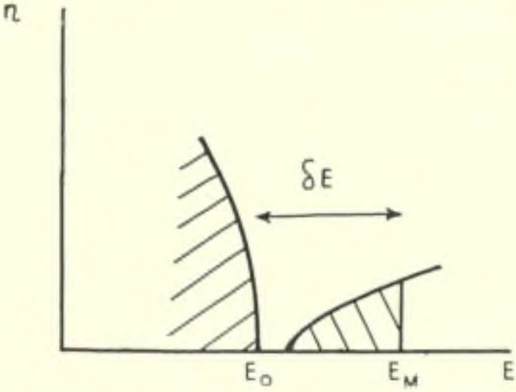

Fig. 15. — Une bande pleine au-dessous du niveau de Fermi.

Dans l'approximation de Tibbs, la bande pleine se comporte comme la bande parabolique d'un gaz de « trous positifs » *de masse unité*. Pour un tel gaz, un état lié apparaît dans :

$$V_p = - Zr^{-1} \exp(- qr) \text{ pour } - Z \geq 0{,}7\, q \ (^{49}).$$

La valeur minima de $|Z|$ pour qu'une bande pleine participe à l'écran de l'impureté est donc de l'ordre de 0,7 q à dilutions infinies et pour une distance δE nulle du sommet de la bande au niveau de Fermi; elle croît avec δE, elle décroît quand la concentration c croît car dans ce cas le niveau de l'état lié s'élargit en une bande (*) et d'autre part le niveau de Fermi baisse donc δE diminue de ΔE_M.

Dans les alliages ferromagnétiques à base de nickel ou de cobalt, les moments magnétiques ne suivent la loi linéaire en fonction de c du § 3 que pour Z et c petits. La baisse des moments observée pour Z et c plus grands (fig. 13) peut être due à ce que la demi-bande $3d$ pleine de la figure 11 commence à participer à l'écran. La concentration limite décroît bien comme prévu, quand $-Z$ croît pour un solvant donné (**Ni**Fe, **Ni**Mn) et s'annule pour une valeur de $-Z$ comprise entre 3 et 4 pour le nickel, 1 et 2 pour le cobalt. δE est très petit dans ce cas, et les valeurs de q calculées au § 1 donnent les valeurs limites respectives $-Z = 3{,}2$ et 2,7, en assez bon accord. Pour des valeurs plus fortes de $-Z$, la demi-bande $3d$ pleine fournit un trou positif lié à l'atome de soluté B, dont le moment magnétique μ_B doit donc différer de $Z - 2$ magnétons de Bohr de celui de la matrice μ_A :

$$\mu_B = \mu_A - (Z - 2)\mu_0 \, .$$

Pour **Co**Cr ($Z = -3$), la différence $|\mu_B - \mu_A|$ mesurée est effectivement voisine de μ_0 (cf. § 3).

Dans les alliages à base de cuivre, de zinc, de gallium, q a des valeurs semblables et la bande $3d$ est à une distance δE croissante du niveau de Fermi. Des éléments à Z *négatif* doivent donc se dissoudre avec des couronnes d pleines jusqu'à des valeurs croissantes de $-Z$. Les règles de Hume-Rothery et les propriétés magnétiques semblent bien indiquer que cette limite est comprise entre 1 et 2 pour Cu, Ag, Au; 3 et 4 pour le Zn; peut-être 6 et 7 pour le Ga, s'il se comporte comme l'Al. Pour le cuivre, la valeur $q = 1{,}15$ donne $-Z \gg 0{,}8$, en bon accord. On sait d'autre part que la limite croît avec la concentration : les atomes de cobalt se dissolvent avec des couronnes $3d^{10}$ complètes dans la phase **Zn**Coζ(7 % Co), mais avec des couronnes incomplètes $3d^9$ dans la phase γ(14 % Co) [cf. (12)].

(*) Des états liés à des amas d'atomes d'impuretés peuvent aussi apparaître.

Des impuretés à Z *positif* assez fort peuvent inversement soustraire des états liés à la bande de conductibilité. Dans le cuivre, c'est peut-être le cas du zinc, certainement celui du Ga, du Ge, etc. Comme nous l'avons déjà souligné, ces états liés correspondent, dans l'approximation des bandes rigides, à la partie de la bande de l'alliage d'énergie inférieure au bas de la bande du solvant pur.

4.3. — *Orbitales moléculaires et atomiques.*

Tous les électrons de valence ont été traités jusqu'ici dans un même potentiel moyen V. Des électrons liés, s'ils existent, sont ainsi traités dans le champ de leur propre charge, évidemment une mauvaise approximation.

On tient peut-être mieux compte des forts termes de corrélation, surtout pour $Z > 0$ fort, en supposant que, aux dilutions infinies, les atomes de soluté se dissolvent comme des atomes interstitiels neutres (H dans Cu) ou comme des ions substitués à des ions de même charge du solvant (Zn^+, Ga^+... dans Cu^+) (37). Certains électrons de valence sont ainsi traités dans des orbitales « atomiques » liées aux impuretés et soumises à un potentiel essentiellement *différent* du potentiel moyen V.

Les chaleurs de dissolution obtenues de cette façon sont d'un ordre de grandeur raisonnable, si l'on admet que les atomes ou ions de soluté ont la même structure qu'à l'état gazeux et que le reste des électrons de conductibilité est peu perturbé par l'introduction de l'impureté. On a pu vérifier sur **CuH** que le potentiel agissant sur la bande de conductibilité en soustrait autant d'états liés qu'il y a d'électrons de valence liés aux atomes interstitiels introduits (ou aux ions substitués); ces électrons « font donc partie » de la bande de conductibilité au sens de Hume Rothery. Le fort diamagnétisme de l'aluminium dissous dans le cuivre s'explique aussi quantitativement; ce modèle simplifié suppose par contre que le zinc et l'antimoine se dissolvent comme des ions paramagnétiques dans le cuivre et l'argent, en contradiction avec l'expérience [(51), (52)].

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Discussion of FRIEDEL's report

Mr. Pippard. — I do not quite understand why it is valid to equate the work done to the change in free energy in such a process as inserting a solute atom into a hole in the matrix. Is the process reversible in a thermodynamic sense?

I feel there is a difference between the sequence of events considered by Friedel and that which would actually occur when such a substitution were effected in nature, and that the difference may be significant to the calculation of the free energy.

M. Friedel. — σ serait le travail fourni si l'on pouvait fixer l'atome de soluté en un point donné. Il faut y ajouter un terme dû à l'entropie de position du soluté pour avoir l'énergie libre totale et un processus réversible. L'opération décrite dans le texte n'est donc pas réalisable en pratique; ce n'est qu'un moyen qui me semble tout à fait justifié, de calculer la partie de l'énergie libre qui ne dépend pas de l'entropie de position.

Mr. Bragg. — In Dr. Friedel's calculations of the energy associated with a foreign atom in a metal, he treats the structure as an elastic continuum. A spherical hole is cut out and is filled either with a sphere of larger size which expands the structure or with one of smaller size on to which the surrounding material collapses. The expression for the resulting strain energy is proportional to δ^2, where $\delta = r_s - r'_s$, and so is the same for a given δ whether this is positive or negative.

This function, it seems to me, is at variance with the physical reality. We are dealing with atoms in contact, pushed together by the intrinsic pressure, and held apart by forces of repulsion which rise very abruptly as the atoms approach.

The repulsive force can only be assumed to vary linearly with distance for very restricted ranges and we are interested here in cases when the atoms differ considerably in size.

In such cases, a foreign atom of larger size greatly distorts the surrounding lattice, setting up strains which extend to many atomic distances, whereas one of smaller size hardly disturbs the lattice at all. It rattles in its hole, so to speak. This is very well shown by the bubble model.

The right expression for the strain energy must be bery different for δ positive or negative; it cannot be quadratic in δ.

M. Friedel. — Les approximations de l'élasticité classique employées dans le rapport négligent dans l'énergie de distorsion les termes en δ/a de puissance supérieure à 2; comme le souligne Sir Lawrence Bragg, elles ne sont pas valables pour des facteurs de taille trop forts.

Pour avoir une idée de l'erreur ainsi commise, on peut introduire un terme non quadratique dans l'énergie E de distorsion de l'atome de soluté :

$$E = \text{const.}\left(\frac{a - r'_s}{r'_s}\right)^2\left[1 - A\,\frac{a - r'_s}{r'_s} + O_2\left(\frac{a - r'_s}{r'_s}\right)\right],$$

tout en conservant les approximations classiques pour la matrice, qui est moins violemment déformée. Le coefficient A est lié à la constante γ de Grüneisen; on a facilement [cf. (1)] : $A = 2\gamma - 5/3$.

On trouve (2) que la correction ainsi faite multiplie l'énergie élastique totale σ par un facteur $(1 - G\delta/a)$ où :

$$G = \frac{(6\alpha - 4)\gamma - 5\alpha + \frac{10}{3}}{(1 + \alpha)^2} \simeq \frac{248 - 20}{27},$$

car le coefficient :

$$\alpha = \frac{(1 + \nu)\,\chi}{2(1 - 2\nu)\chi'}$$

est voisin de 2 (ν coefficient de Poisson; χ et χ' compressibilités).

Les valeurs expérimentales de γ sont telles que b est *positif* : l'énergie de dissolution est plus faible pour δ positif (atome dissous plus petit) que δ négatif (atome dissous plus grand).

Mais cette correction est *assez faible* : b est inférieur ou égal à 2 car γ est au plus égal à 3 (1). Les raisons physiques en sont les suivantes :

1) Le coefficient A de dissymétrie entre compression et dilatation n'est pas très fort ($A \leq 4, 3$).

2) La distorsion de l'atome dissous n'est qu'une fraction de la distorsion totale. On a, pour $\frac{\delta}{a}$ assez petit [cf. (2)] :

$$\frac{\sigma}{\mathrm{E}} \simeq \frac{\delta/a}{(a - r'_s)/r'_s} \simeq \alpha + 1 \simeq 3 \, .$$

La correction serait plus importante dans un modèle à deux dimensions comme celui des bulles, où l'atome dissous doit prendre une part plus importante de la distorsion totale.

Enfin, si la substitution d'un atome plus petit ne contractait pas (ou peu) la matrice qui l'entoure, le paramètre cristallin moyen de l'alliage, mesuré aux rayons X ou par la densité, devrait présenter aux faibles concentrations une *tangente horizontale* aux faibles concentrations (ou tout au moins de fortes déviations par rapport à la loi de Vegard). Le modèle élastique classique prévoit au contraire une variation linéaire du paramètre avec la concentration qui semble mieux en accord en général, avec l'expérience [(3), (4)].

Mr. Seeger. — Was the contribution to entropy due to the lowering of elastic constants by the solute atoms (cf. Zener, *Acta Cryst.*, 1949), been taken into account?

M. Friedel. — Le terme d'entropie considéré dans le rapport, est précisément celui qui produit la baisse des constantes élastiques des alliages étudiée par Zener. La seule différence est que Zener ne considérait que les déformations dans la matrice, tandis qu'ici les déformations des atomes dissous ont été aussi introduites.

Mr. Seeger. — Does the theory give information on the initial slopes of the energy versus concentration curves?

M. Friedel. — Les corrections de corrélation dans l'approximation de Thomas-Fermi sont en général trop fortes et incertaines pour permettre un calcul raisonnable des « énergies de dissolution » (*pentes* initiales des courbes d'énergie de formation ε en fonction de la concentration c). Une étude de la corrélation par les méthodes de plasma de Bohm et Pines serait sans doute intéressante. Le succès de Fumi dans le cas des lacunes est sans doute dû à ce que la formation d'une lacune ne change pas le nombre d'électrons de valence, et probablement très peu leur corrélation. Mais c'est un cas très particulier qui ne s'étend qu'aux éléments de transition dissous dans d'autres métaux sans leur fournir d'électrons de conduction (**Cu**Ni, Fe, Co, etc.)

M. Néel. — 1) Je voudrais signaler qu'il existe toute une série de résultats expérimentaux auxquels il serait intéressant d'appliquer la théorie du Dr. Friedel : il s'agit des solutions étendues, solides ou liquides (*), des métaux magnétiques dans des métaux non magnétiques. On a ainsi dissous Ni, Co, Fe, Mn, Cr... dans Cu, Au, Ag, Zn, Sn, etc. Les solutions obtenues sont généralement paramagnétiques et obéissent à la loi de Curie-Weiss, et on peut en déduire des valeurs assez précises du moment atomique. L'application de la théorie à ces différents cas fournirait certainement des renseignements importants.

2) Ne convient-il pas aussi de tenir également compte de la variation de l'écartement des deux bandes 3*d* en fonction du remplissage de la bande supérieure?

Intuitivement, on s'attendrait à voir apparaître des trous dans la bande inférieure au moment où la bande supérieure serait presque pleine.

M. Friedel. — Le point intéressant suggéré par le professeur Néel ne peut jouer qu'à concentrations finies et assez fortes pour que les atomes de soluté interagissent fortement. Jusque là en effet, pour **Co**Cu par exemple, l'écartement des bandes et leur position par rapport au niveau de Fermi sont fixées par les propriétés de la portion non perturbée de solvant.

On sait par contre que, dans des alliages tels que **Cu**Co où subsistent des trous *d* liés aux atomes de cobalt, ceux-ci ont un paramagnétisme de Curie-Weiss, qui indique que les trous ont indifféremment l'une ou l'autre direction de spin. Une étude théorique des concentrations intermédiaires serait peut-être plus facile en partant du côté riche en cuivre.

Mr. H. Jones. — *Magnetic properties of alloys containing small amounts of transition metals.* — As a contribution to the discussion

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(*) Thèse de L. Weil en particuler.

on the electron configurations in alloys, I would like to mention some recent experiments, and also some older measurements, on the magnetic properties of alloys cohtaining small amounts of the transition metals, for example, iron, cobalt and manganese. These alloys may be solid solutions of the transition metals in copper, silver or gold for instance, or they may be phases which contain small proportions of a transition metal, e.g. MnAl.

I will state at once the conclusions which it seems can be drawn from these measurements and then give a few examples to support these inferences. The first conclusion is that the number of the electrons in the 3d configuration of the transition metal atom increases steadily with the electron concentration in the valency band of the alloy. The second conclusion is that the effective valency of the transition metal in any alloy, as determined by the magnetic measurements, agrees very well with that required to explain the existence of the structure on the basis of the filling of the well marked Brillouin zone derived from the Xray powder photograph.

Consider the alloys of cobalt first. Hildebrand (5) has measured the susceptibility of cobalt dissolved in copper and gold to the extent of about one atomic percent. The results are well described by a Curie-Weiss law and the effective magneton number is about 5.4 for Co in Cu and 4.6 for Co in Au. If it may be supposed that the orbital contribution to the magnetic moment is quenched in the alloy, the effective magneton number is given by $\sqrt{4S(S+1)}$. When $S = 4/2$ the magneton number is 4.9 which suggests a configuration *3d* for Co in Cu or Au, which implies that the Co is trivalent in these metals where the electron concentration is 1.0 per atom.

In the gamma brass structure Co_5Zn_4 where the electron concentration is 1.7, the paramagnetic susceptibility leads to a magneton number 1.9. The configuration *3d* with $S = 1/2$ would give a value 1.73. This configuration corresponds to the zero valency required by the Hume-Rothery rules. Recently, the susceptibility of the alloy Co.Al has been measured by Foex and Wucher (6) who find a week paramagnetism, less than that of pure aluminium, and almost temperature independent. Thus, we must conclude that the cobalt atoms are in the configuration *3d*. The electron concentration in this alloy in the valency band is 2.27. The CoAl structure gives rise to a very strongly marked and very symetrical Brillouin zone whose total volume corresponds to 2.33 electrons per atom.

Alloys having small amounts of Co in β-brass have been prepared by Hime-Rothery and Haworth (7). Their magnetic properties have not been measured, but if the limit of the β-phase is traced in the ternary diagram and it is assumed that the electron concentration is constant along this boundary the effective valency of the Co can be deduced. It is found to be 1.0. In other words, the configuration is 3*d* when the electron concentration is 1.5 per atom.

All these results can be summarized as follows :

3d configuration	$3d^6$	$3d^8$	$3d^9$	$3d^{10}$
electron concentration in electrons per atom . .	1.0	1.5	1.7	2.27
Valency band width . . .	7.0	8.3	9.2	10.2 e.v.

Similar results hold for manganese and chronium. Thus, for instance, G. Güstafsson (8) following earlier measurements by Néel (9) shows that manganese dissolved in Cu. Ag and Au gives rise to a paramagnetism which follows a Curie-Weiss law with effective magneton numbers between 4.9 and 5.9. Most of the measurements lying nearer the latter. This corresponds to a configuration 3*d* since the magneton number for $S = 5/2$ is 5.9.

The magnetic properties of the gamma brass structure Mn, Zn, have not been measured, but the Hume-Rothery rules suggest a configuration 3*d*. Foëx and Wucher show that Mn Al has a paramagnetic susceptibility a little greater than that of pure Al; and which increases slightly with temperature. This is a typical Pauli paramagnetism, not the Curie-Weiss type. These results therefore would be compatible with a configuration Sd^{10}. The negative valency which this implies leads to an electron atom ratio in the valency band which agrees well with the strongly marked Brillouin zone characteristics of this structure.

The case of iron is particularly interesting. Concentration less than one per cent Fe in Au lead to a magneton number of 3.6 which agrees well with the 3.87 of the 3*d* configuration (10).

In the gamma brass structure the magnetic measurements are rather sketchy and one cannot deduce the configuration from them. The Hume Rothery rules would require $3d$ of course.

Foëx and Wucher show that FeAl is paramagnetic with a susceptibility which follows a Curie-Weiss law, and which gives an effective magneton number for Fe of 1.67. The configuration $3d$ would give 1.73. This result is very interesting because it was predicted essentially by the zone theory of this phase. The zone corresponding to the strong lines of the Kray powder photograph of this alloy, and of the associated phases with nearly the same composition, has a volume of approximately 2.0 electrons per atom. If the Fe atoms had taken the $3d^{10}$ configuration, like other transition metals studied by Foëx and Wucher, the valency electron concentration would have been too low, viz. 1.74, whereas with $3d^9$ the zone is nearly complete since the electron atom ratio is now 2.0.

M. Néel. — Est-il sûr que dans de telles solutions, le moment orbital soit complètement bloqué?

Mr. Jones. — Perhaps the electric fields due to the neighbouring metal ions is sufficiently strong to quench the orbital contribution.

Mr. Bragg. — Has the energy barrier for a multiple vacancy been calculated? One would expect this to be very much smaller (perhaps 10 or 20 times smaller) than that for the movement of a single vacancy. For instance, if two neighbouring atoms are missing, the structure has now got two vacancies side by side. A new regular form is assumed in which one atom is symmetrically between the others. By allowing this atom to move into one of the vacant sites, and another atom to replace it, the vacancies move an atomic distance with a very small disturbance of the surrounding structure. With rigid atoms for instance, there is no disturbance at all. One could expect such clusters of vacancies to have a very high mobility.

Mr. Fumi. — The suggestion that vacancy pairs should have a lower activation energy for migration than single vacancies was put forward on a physical basis by Seitz (11). Dienes (12) and Bartlet and Dienes (13) have respectively computed and estimated these energies for NaCl and for Cu : the results indicate that the activation energy for migration of a vacancy pair should be between 1/2 and 1/3 of the corresponding energy for a single vacancy. Calculations indicate also that the binding energy of vacancy pairs in NaCl(14) and in Cu (13) should be of the order of several tenths of an ev.

The experimental evidence for the role of vacancy pairs in the transport of matter within solids is, however, rather dubious. In the case of ionic solids, in particular the alkali halides, where one has fairly sensitive experimental methods to study this role, such as the analysis of the deviation from the Einstein relation between ionic conductivity and diffusion coefficient for the alkali ion in the intrinsic range of temperatures (15), or the comparison between the diffusion coefficients of the alkali ion and of the halogen ion (16), it seems that vacancy pairs do not play an important role.

Mr. Seeger. — The increase of cohesive energy E going from the noble metals to the neighbouring transition metals is so large, particularly in the case of Ag-Pd, that it does not seem possible to overcompensate the decrease in binding due to *s*-electrons by an increase in the van der Waals contribution of *d*-electrons :

$$(E_{Ni} - E_{Cu} = 4000 \text{ cal/at}, \; E_{Pd} - E_{Ag} = 42\,000 \text{ cal/at}$$
$$E_{Pt} - E_{Au} = 35\,000 \text{ cal/at})$$

The van de Waals energy should be rather smaller for an ion core with a hole in it than for a complete shell.

As binding energy, reciprocal compressibility and melting points rise to a maximum in the middle of the long period of this periodic chart (in much the same way as they show maxima for diamond, silicon and germanium in the chart period), one is quite naturally led to the idea that homopolar binding by *d*-electrons is responsible for the high cohesive energies of the transition metals, since homopolar binding is most effective for a half-filled shell. This view is in contrast to the majority of theories of ferromagnetism which assume that there is hardly any connection between ferromagnetism, which is due to the *d*-electron, and chemical binding, for which the conduction electrons are mainly responsable. A theory which is based on a rather intimate connection between chemical binding and ferromagnetism in the transition elements will be reported in a separate contribution.

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The creation and Motion of vacancies in Metals

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The experimental study of the Kirkendall effect has shown that for a number of metals the transport of matter within the solid does not occur by an exchange process either of the traditional two atom type or of the Zener ring type (1) : lattice defects are involved in an essential way in the diffusion process in these metals. The experiments have not yet told us on the other hand whether the defects involved are single vacancies, interstitials, more elaborate versions of these defects such as vacancy pairs or crowdions, or perhaps more extended regions of disorder in the lattice. On the theoretical side, the only quantitative calculations on the activation energies of creation and motion of simple defects in metals are those of Huntington and Seitz (2) which show fairly convincingly that for Cu vacancies are the important defect of thermal origin. To contribute to an understanding of the process of matter transport within a metal it appears useful to calculate these energies for a number of metals. To achieve this end it seems best to try and construct simple models for the processes of creation and motion of defects in metals.

The work I have started in this direction this year at the University of Bristol has been concerned so far only with vacancies and I will report here the preliminary results I have obtained. The method I have followed to compute the energy to create a vacancy is based on the use of a formula due to Dr. Friedel which relates the phase shifts of the conduction electrons at the Fermi level to the excess or defect charge of the impurity they screen in a given matrix (3).

Let us consider a metal sphere in which the electrons are free to move. The process of creation of a vacancy can be schematized as the removal of an ion from the centre of the sphere and its distribution over the surface. We consider two contributions to the energy change undergone by the free conduction electrons in the process, namely the one due to the lack of an ion at the centre of the sphere and the one due to the expansion of the metal box. If we impose to the unperturbed and perturbed electron waves the condition that they vanish at the surface of the sphere, the energy change $\Delta E'_{el}$ of the electrons connected with the negative phase shifts $\eta_l(k)$ induced by the repulsive field $V(r)$ of the vacancy is :

$$\Delta E'_{el} = -2\int_0^{k_F} \Sigma\,(2l+1)\,\frac{\hbar^2 k\eta_l(k)}{mR}\,\frac{R}{\pi}\,dk$$

where :

$$\frac{-\hbar^2 k\eta_l(k)}{mR}$$

is the energy change of the lth component of the wave associated with the electron of wave number k, R is the radius of the metal sphere, R/π the density of l states in k space, and k_F is the wave number at the Fermi level. The Born approximation :

$$\eta_l(k) = -\pi\frac{m}{\hbar^2}\int_0^\infty V(r)\,[J_{l+\frac{1}{2}}(kr)]^2\,r\,dr$$

and Friedel's identity written in the Born approximation :

$$\frac{k_F m}{\hbar^2\pi^2}\int_0^\infty V(r)4\pi r^2 dr = -1$$

together with the summation properties of Bessel functions of half-integer order allow us to rewrite :

$$\Delta E'_{el} = \frac{2}{3}E_F$$

The energy change connected with the expansion of the metal box can also be computed easily. The energy of the N electrons in our box of volume V is $\frac{3}{5}NE_F$, and the change in this energy upon an expansion δV is $\Delta E''_{el} = -\frac{2}{3}\,\frac{3}{5}NE_F\,\frac{\delta V}{V}$ since $E_F \propto V^{-2/3}$. For a monovalent metal for which the number of atoms in the metal sphere equals the number N of conduction electrons we have :

$$\Delta E''_{el} = -\frac{2}{5}E_F\,.$$

In total :

$$\Delta E_{el} = \frac{4}{15}E_F\,.$$

The change in surface energy is negligible being of the order of $N^{-1/3}$.

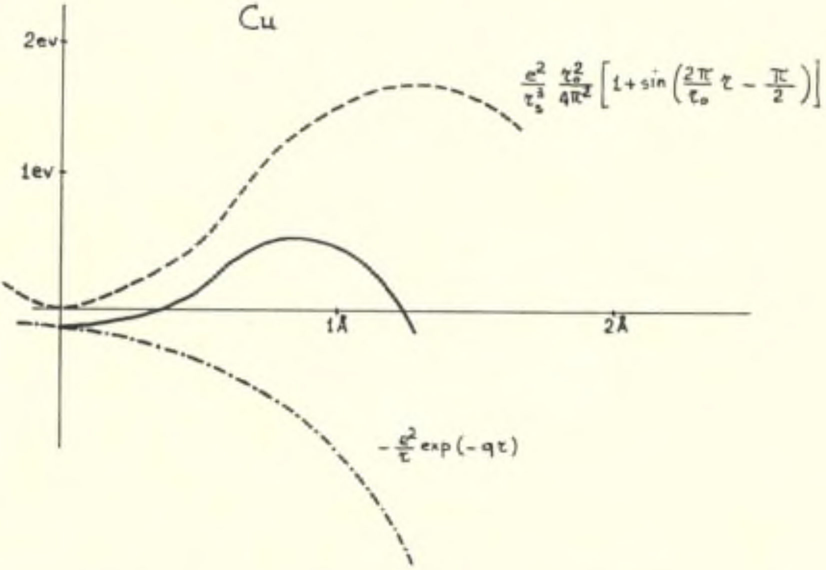
Table I gives the numerical values of ΔE_{el} for three monovalent metals for which we feel fairly confident following the work of Huntington and Seitz that vacancies are the defects responsible for the transport of matter. The values of $\frac{4}{15} E_F$ should thus be compared with the difference between the experimental values for the total activation energy and for the energy of migration : the first is obtained from measurements of self-diffusion (4) and the latter, rather more dubiously, from radiation damage experiments (5). It is apparent that in all three cases the theoretical value is an upper limit of the experimental energy of creation and is not much too large : it should be noted that the theoretical value would not be an upper limit if one did not use the most recent values for the activation energies for self-diffusion in Cu and in Au. The fact that $\frac{4}{15} E_F$ should be an upper limit for the experimental energy of creation of a vacancy is reasonable. Indeed we have used the Born approximation which for repulsive fields yields too large values for the phase shifts when they are bigger than abou $\frac{\pi}{10}$, as Friedel has shown (6) : thus we compute too large a value for $\Delta E'_{el}$. The fact that we have not considered the changes in the ion-ion interactions upon creation of a vacancy is perhaps not very important since we gain some energy from the decrease in repulsive interaction, but we must do work against the van der Waals forces which are probably important in metals such as Cu. These two contributions likely balance each other within very few tenths of an ev. For Cu the decrease in repulsive energy is $\sim .4$ ev : the work to be done against van der Waals forces is certainly smaller than the 1 ev van der Waals contribution

TABLE I

	E_F(ev)	4/15 E_F(ev)	U_{total}(ev)	$U_{migration}$(ev)
Cu	7.1	1.9	2.02	0.9
Ag	5.52	1.47	1.98	0.7
Au	5.56	1.48	1.97	0.7

to the cohesion since the presence of a vacancy polarizes the neighbouring Cu^+ and thus increases the van der Waals interaction between them. In any case these considerations obviously show that there is room improvement in the first order approximation we have described and work along this line is in progress.

To calculate the energy to move a vacancy in a monovalent metal we consider the metal to be composed of atomic spheres each uniformly occupied by one electron with the metal ion at the centre. We consider two contributions to the energy change of an ion which moves from the equilibrium position to the saddle point between the equilibrium position and the neighbouring vacancy : these two contributions are illustrated graphically in figure 1 for Cu. The top curve gives the variation in the electrostatic energy of the moving ion within its atomic sphere, on which we have imposed the condition of periodicity of the lattice. The bottom curve gives the change in electrostatic interaction between the moving ion and the vacancy field screened by the conduction electrons : for the screening constant q we do not take the Fermi-Thomas (or Born approximation) values by Mott (7) but the values computed numerically by Friedel (6). To the activation energy for migration of ∼ . 7 ev that one obtains by summing the two curves one should add the increase in ion-ion



repulsion which amounts to a few tenths of an ev. The fact that the theoretical value should here too be somewhat larger than the experimental value is not surprising since among other things we have neglected the rearrangement of the conduction electrons during the motion of the ion.

The preliminary results I have described seem to indicate that it may be possible to construct physical models for the processes of creation and motion of simple defects in metals capable of yielding with fair ease and accuracy the relative activation energies. The main point which needs to be clarified is the role that play in these processes the attractive interactions between *d*s hells discussed by Professor Mott (8) in his contribution.

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Neutron Diffraction Studies of Transition Elements and Their Alloys

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I. INTRODUCTION

During the past several years, Dr. M. K. Wilkinson and I have been studying the neutron scattering characteristics of transition elements and certain of their alloy systems. Since the neutron possesses a small but definite magnetic moment (only about 10^{-3} that of an electron), it is capable of interacting with any atomic magnetic moments present within a scattering sample; and this interaction shows itself as a scattering contribution to the diffraction pattern. It was to be hoped that information obtained from the scattering process would illuminate the electronic structure present in these elements and alloys and thus offer some guidance in the formulation of theories of metallic structure in general.

Some of the neutron scattering results have already appeared in the literature and only brief mention of these will be made, whereas the more recent work in the course of present publication will be summarized more fully. These studies to be included in the present review can be conveniently distributed into three groups : 1) various transition elements at normal or low temperatures; 2) the ferromagnetic elements iron and nickel at high temperatures up through their Curie transition and, 3) some typical alloys of the elements.

II. TRANSITION ELEMENTS

Neutron diffraction studies on W, Mo, Nb, V, Cr, Mn, Fe, and Co have been reported in the literature (*) and a brief mention of these findings will be given here. Among these, the first six-

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(*) C.G. Shull and M.K. Wilkinson, *Rev. Mod. Phys.*, **25**, 100-107 (1953).

named are known to be non-ferromagnetic and particular attention was paid in the investigation to a search for possible antiferromagnetic or paramagnetic scattering.

a) **W, Mo, Nb and V**

All of these were examined in the polycrystalline form at temperatures as low as liquid hydrogen or liquid helium. In no case were any superstructure diffraction lines indicative of an antiferromagnetic lattice observed. Moreover the appearance of the diffuse scattering was such as to rule out the presence of paramagnetically-coupled magnetic moments of strength indicated by the electronic distribution in the free atoms. From the observed intensities it was possible to set an upper limit of a few tenths of a Bohr magneton as the maximum atomic magnetic moment seen in neutron scattering in either ordered or disordered orientation. This upper limit is very much smaller than the free atom electronic structure would predict, for instance $3\mu_B$ for vanadium or $4\mu_B$ for niobium.

b) **Cr and Mn**

Both of these elements exhibit superstructure line intensity at reflection positions not permitted for nuclear scattering. Accordingly they are considered to be antiferromagnetic and from measurements of the antiferromagnetic intensities at various temperatures, the Néel temperatures for Cr and α-Mn were determined as 475°K and 100°K. For the chromium body-centered cubic case, weak antiferromagnetic intensity was found at the (100) reflection position and from this intensity at low temperature, the strenght of Cr moment was evaluated as $0.4\mu_B$. Because of the lattice complexity in α-Mn, it was not possible to describe the magnetic structure or the antiferromagnetic magnetic moment; but from the paramagnetic scattering level, it could be stated that the effective moment was small, perhaps $0.6\mu_B$.

c) **Fe and Co**

Early studies (*) on these ferromagnetic elements had shown the presence of magnetic scattering which for a simple ferromagnetic lattice is to be found superimposed on the normal nuclear reflections. The ferromagnetic part of the lattice reflections has been determined

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(*) C.G. Shull, E.O. Wollan and W.C. Koehler, *Phys. Rev.*, **84**, 912-921 (1951).

by observing the portion which exhibits the magnetic form factor in angular dependence. By placing the observed intensities on an absolute scale, the total scattering is found to consist of an isotropic nuclear part and an angularly dependent part representing the magnetic form factor. Extrapolation of the form factor portion to zero scattering angle (unit form factor) permits determination of the average ferromagnetic moment. Within the significance of the form factor extrapolation, these moments are the same as those observed from magnetization saturation for Fe and Co. The ferromagnetic scattering can also be recognized by studying the change in reflection intensity when the scattering sample is magnetized. Theory predicts a dependence of the neutron scattering upon sample magnetization and this has been confirmed in a variety of experiments.

In more recent work (*) attention has been given to the possible presence of superstructure intensity or ferromagnetic disorder scattering in the Fe pattern. It is well known that the ferromagnetic elements uniformly exhibit non-integral values for their ferromagnetic moments and it has always been attractive to ascribe this to a distribution of integral moments among the atoms in the lattice. If such a distribution were to exist within a magnetic lattice, then the neutron diffraction pattern should contain magnetic superstructure intensity if the distribution is ordered or magnetic disorder scattering if the distribution is of random nature. Neither of these magnetic scattering effects has been found in the case of Fe so that, as far as neutron scattering is concerned, all of the local moments appear of the same strength. Of course if the distribution is a rapidly changing one, such that during the passage time of a neutron accross the magnetic force field of the scattering atom ($\sim 10^{-13}$ seconds) the atom takes on all possible integral moments, then the neutron scattering would not exhibit the suspected disorder. This implies transition times of the order 10^{-14} seconds or smaller and such may not be unreasonable.

III. FERROMAGNETIC ELEMENTS AT HIGH TEMPERATURE

The studies on the ferromagnetic elements have recently been extended into the high temperature region above the Curie temperature. As is well known, the paramagnetic susceptibility data for Fe and Ni have long been considered anomalous with respect to

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(*) C.G. Shull and M.K. Wilkinson, *Rev. Mod. Phys.*, **25**, 100-107 (1953).

the ferromagnetic magnetization so that it was considered of interest to compare the results of paramagnetic neutron scattering with that obtained below the Curie temperature. Furthermore there exists a fundamental uncertainty as to whether paramagnetic scattering is observable in such transition metals. One band theory interpretation would allow for no atomic moment above T_c and hence no paramagnetic scattering would be expected. Additionally it can be suspected that electron spin relaxation effects might influence or eliminate the paramagnetic scattering.

For these reasons, nickel and iron have recently been studied at temperatures up to about 1 000° C, well above their Curie temperatures of 348° C and 770° C respectively. This was performed through use of a specially-designed high-vacuum furnace which could be mounted directly on a neutron diffraction spectrometer. Typical of the diffraction patterns obtained in this experiment are those shown in figure 1. These are patterns for iron taken at room temperature

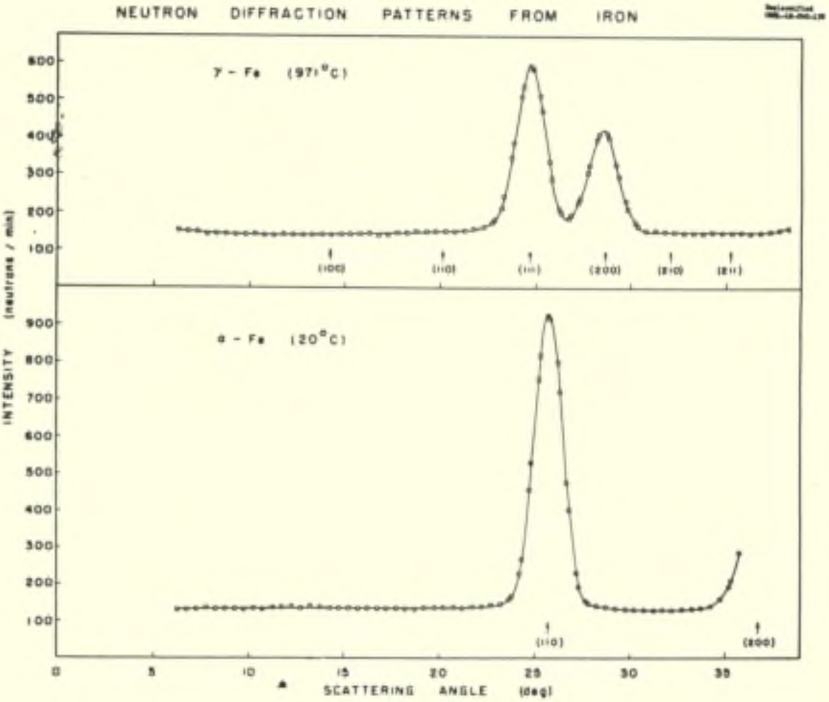


Fig. 1. — Neutron diffraction patterns taken for iron at 20° C and at 971° C showing the transformation from α-Fe to γ-Fe.

showing body-centered-cubic reflections and at 971° C where the face-centered-cubic reflections of γ-iron are obtained. It is of interest that no magnetic superstructure lines are found in the γ-iron pattern showing that the face-centered-cubic structure is definitely not antiferromagnetic.

Of most interest in the high temperature patterns is the appearance of the diffuse scattering which should contain ferro-magnetic discorder scattering and paramagnetic scattering. Figure 2 illustrates a portion of the diffuse scattering for iron obtained at various temperatures up to 922° C and, for comparison, the calculated change in diffuse level caused by the extra paramagnetic scattering which is to be expected at the highest temperatures. According to the theory of magnetic scattering of neutrons the diffuse level, should change by an amount whose cross section contains a term in S^2 where S is the spin quantum number to be associated with the atomic magnetic moment. In the calculation, the ferromagnetic value for S of 1.11 has been used. The experimental curves have been corrected for the thermal diffuse scattering expected at the various temperatures so that their differences should represent magnetic discorder or

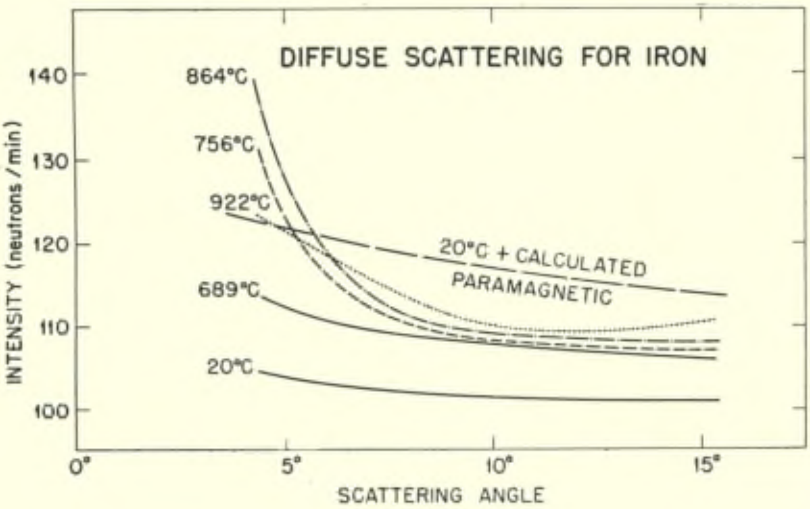


Fig. 2. — Diffuse scattering produced by iron at various elevated temperatures. The experimental curves have been corrected for thermal diffuse scattering and the upper curve represents the sum of the room temperature curve and the expected paramagnetic scattering.

paramagnetic scattering. Although there appears to be a definite paramagnetic scattering, its intensity level other than in the small angle scattering region is somewhat smaller than that calculated on the basis of the ferromagnetic moment. This reduction in the paramagnetic scattering level is considered to result from the inelastic nature of the paramagnetic scattering when the Curie temperature (1043° K for iron) approaches the neutron temperature (1183° for this experiment). Such behaviour has been found for other magnetic lattices includind several ionic substances wherein the magnetic moments are considered the same above and below T_c. Thus a paramagnetic scattering is seen to exist for iton at high temperatures and the absolute intensity is thought to be consistent with the ferromagnetic moment.

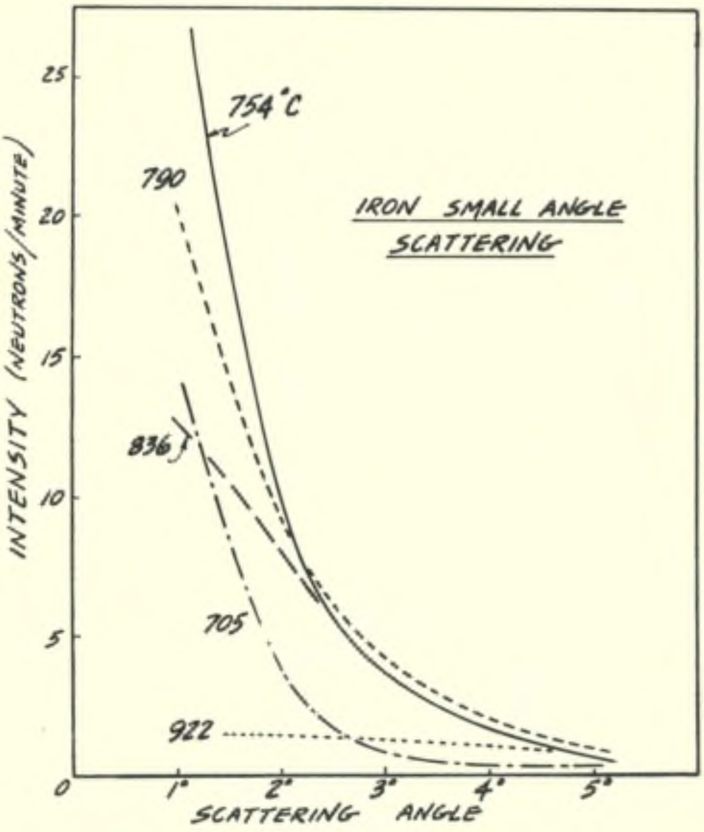


Fig. 3. — Small angle scattering of neutrons by iron at various elevated temperatures.

There is to be noted in the high temperature pattern of figure 2 the development of an intense small angle scattering and further detail of this is shown in figure 3. In obtaining the small angle scattering characteristics, the spectrometer resolution was improved, at the expense of intensity, until significant data could be obtained at scattering angles into about one degree. A pronounced small angle scattering was found to develop at temperatures above 600° C, build up to a maximum at the Curie temperature and then fall back down above T_c. This is attribued to a disruption of the size of the magnetically coherent regions as T_c is approached followed by a gradual transformation into short range order scattering above T_c. Application of conventional small angle scattering theory to the data at 754° C (close to T_c) yields magnetically coherent regions whose size extends only a few unit cells and this would get smaller as the temperature exceeds T_c. Even at the highest temperature studied there still appears residual short range order.

Similar studies on nickel have also shown the presence of paramagnetic scattering above T_c but again with an intensity somewhat less than that calculated with the ferromagnetic moment.

IV. ALLOYS OF TRANSITION ELEMENTS

Neutron diffraction data have been obtained for a series of ferromagnetic binary alloys of transition elements in order to obtain information about the individual atomic moments existing in the alloy mixture. In a disordered binary alloy with random distribution of the two species of atoms at the lattices sites, a magnetic disorder scattering would be expected if the atoms possessed different magnetic moments. On the other hand an ordered alloy with different atomic moments should exhibit magnetic superstructure intensity at the superlattice reflection positions. It can be shown that both of these magnetic scattering effects will be described in absolute intensity by an expression containing a term $(\mu_1 - \mu_2)^2$ where μ_1 and μ_2 are the individual atomic moments in the ordinary binary alloy. Thus a determination of either the magnetic disorder scattering or of the magnetic superstructure intensity can be used to furnish the difference of the atomic moments. This information when combined with the average magnetic moment obtained from ferromagnetic saturation data can then be used to evaluate the individual moments. Unfortunately there exists an algebraic sign ambiguity in the moment difference since the magnetic intensity is given by the square of the moment difference and this results in two permissible sets of solution for the individual moments. There are experimental means for removing this ambiguity which involve the use of polarized neutron beam technique but as yet these experiments have not been performed.

The determination of either the magnetic disorder scattering or the magnetic superstructure intensity offers some difficulty because they are usually superimposed on a much larger nuclear scattering contribution. The extraction of the magnetic part can however be performed by taking the diffraction pattern with an unmagnetized sample and then also with the sample magnetized in a direction for which magnetic scattering theory prescribes no magnetic scattering. This difference in scattered intensity can then be used as a measure of the magnetic scattering.

The alloy systems to be discussed here are shown in figure 4 superimposed on the Slater-Pauling curve. Here is plotted the average magnetic moment as determined in ferromagnetic saturation for various elements and alloys versus the outer electron concentration. The two alloy systems Fe-Cr and Ni-Fe fall along the main sequence

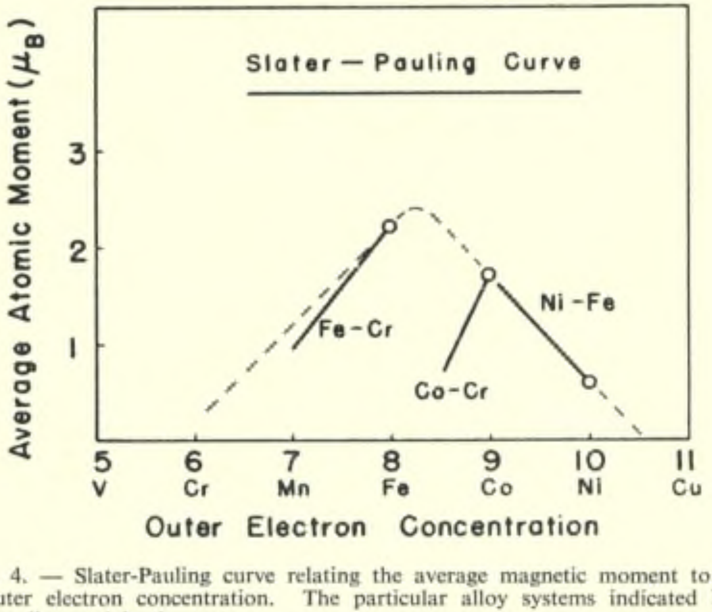


Fig. 4. — Slater-Pauling curve relating the average magnetic moment to the outer electron concentration. The particular alloy systems indicated here are discussed in the text.

of the curve whereas the magnetization obtained for the Co-Cr system deviates markedly from the general behaviour. Various disordered alloys in the regions shown for these three systems have been studied along with two ordered alloy phases, Ni_2Fe and Ni_3Mn.

a) **Fe-Cr Series**

Three alloys in this series containing 15.2, 29.1 and 46.4 atomic percent chromium in the disordered state have been examined. Figure 5 shows the magnetic disorder scattering in absolute units

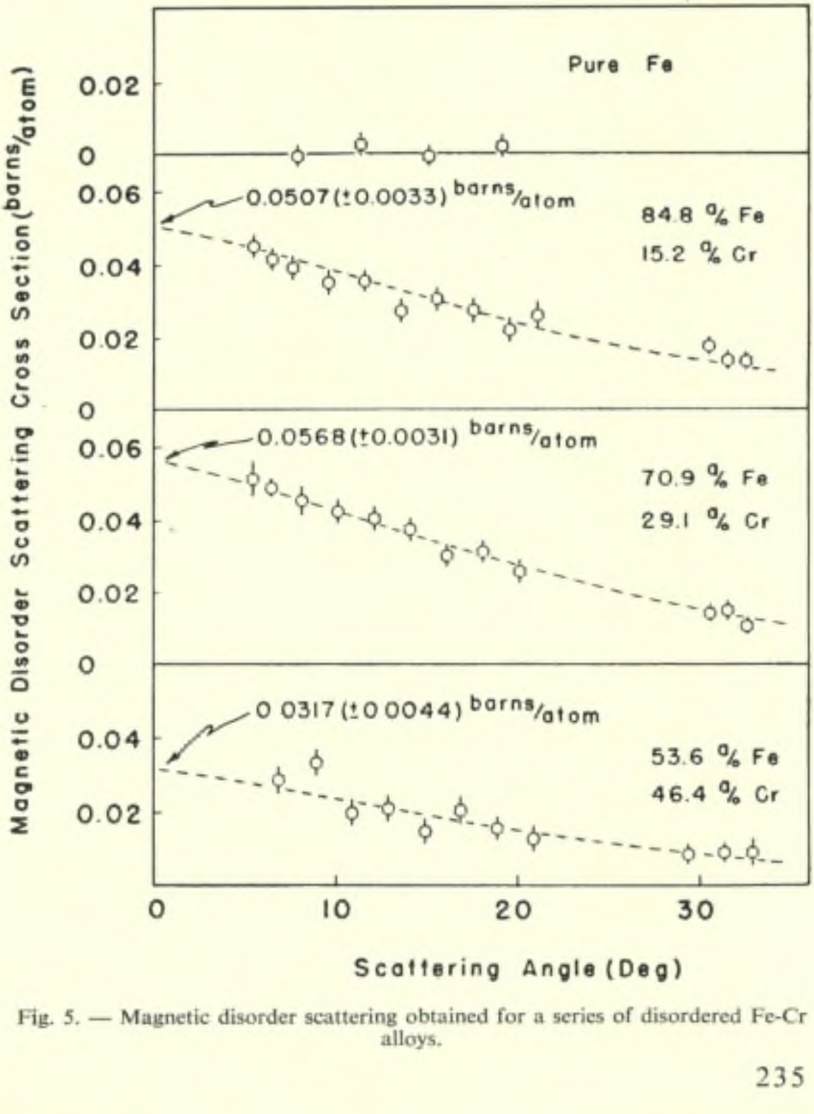


Fig. 5. — Magnetic disorder scattering obtained for a series of disordered Fe-Cr alloys.

of scattering cross section as a function of scattering angle that has been observed for these alloys along with that obtained for pure iron for comparison. The magnetic disorder scattering for iron is seen to be absent or very small relative to that determined for the alloys. As is to be expected, the disorder scattering falls off with increasing scattering angle because of the magnetic form factor and the curves drawn through the experimental points represent the best fit of the Steinberger-Wick theoretical form factor to the data. From the intercept values at zero scattering angle, the difference in the magnetic moments for iron and chromium have been evaluated

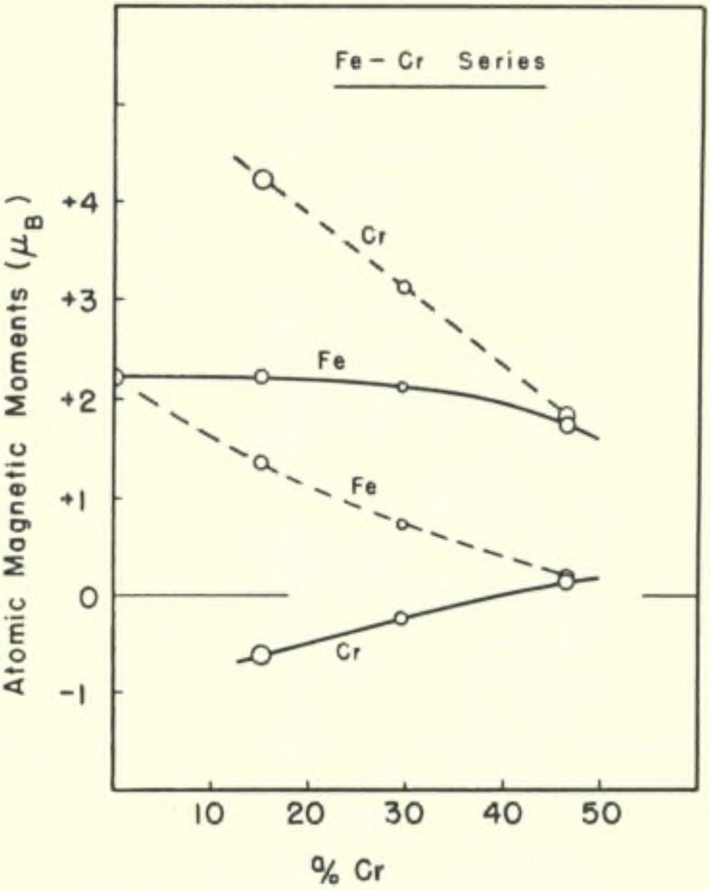


Fig. 6. — Atomic magnetic moments in disordered Fe-Cr alloys. Alternative solutions are represented by the points connected either by the solid lines or by dashed lines.

as 2.85 ± 0.10, 2.38 ± 0.07, and 1.62 ± 0.11 Bohr magnetons for the three alloys of increasing Cr composition respectively. Combining these difference values with the saturation magnetic moments yields the individual moments shown in figure 6. Because of the above-mentioned algebraic sign ambiguity, two sets of solutions are possible and these alternative solutions are represented by the points connected either with the solid curves or with the dashed curves. Either solution indicates that the iron magnetic moment is decreased upon chromium addition.

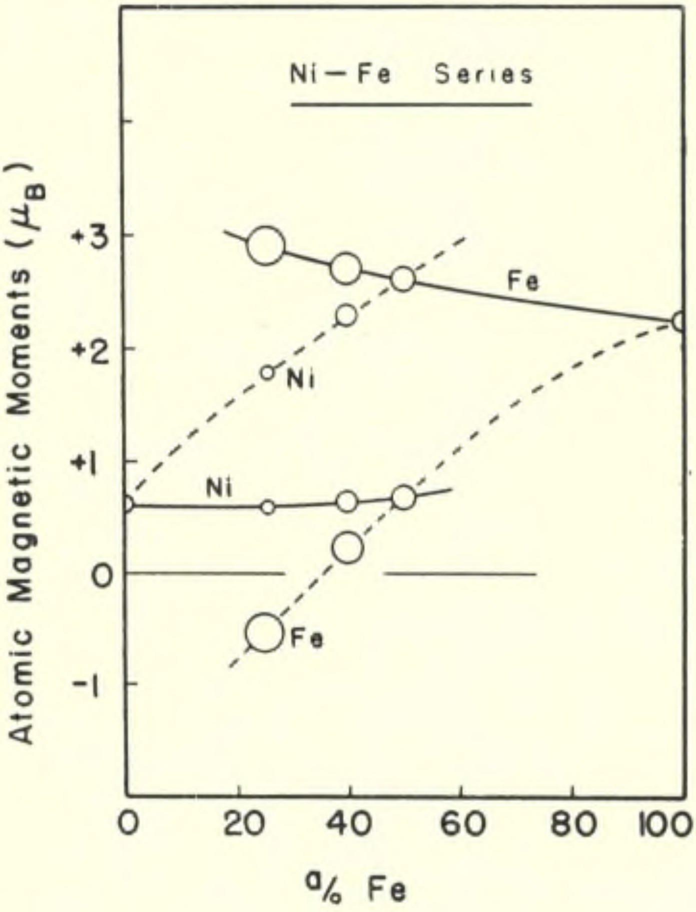


Fig. 7. — Atomic magnetic moments in disordered Ni-Fe alloys. Alternative solutions are represented by the points connected either by the solid lines or by the dashed lines.

b) Ni-Fe Series

Three alloys in this series containing 25.7, 39.9 and 50.1 atomic percent iron have been studied. All of these were investigated in the disordered state and in addition the first-listed alloy was given an extended heat treatment to form the ordered Ni_3Fe superstructure. In the same fashion as described for the Fe-Cr series above, the magnetic disorder scattering was determined for the disordered samples and from these cross sections the moment differences of 2.31, 2.06 and 1.93 Bohr magnetons (each significant to about 0.2) were obtained for the three alloys respectively. Figure 7 represents the alternative sets of individual moments and it is seen that for either set the nickel moment is increased upon the addition of iron.

For the ordered alloy, Ni_3Fe, the magnetic scattering is to be sought at the superlattice reflection positions and figure 8 illustrates

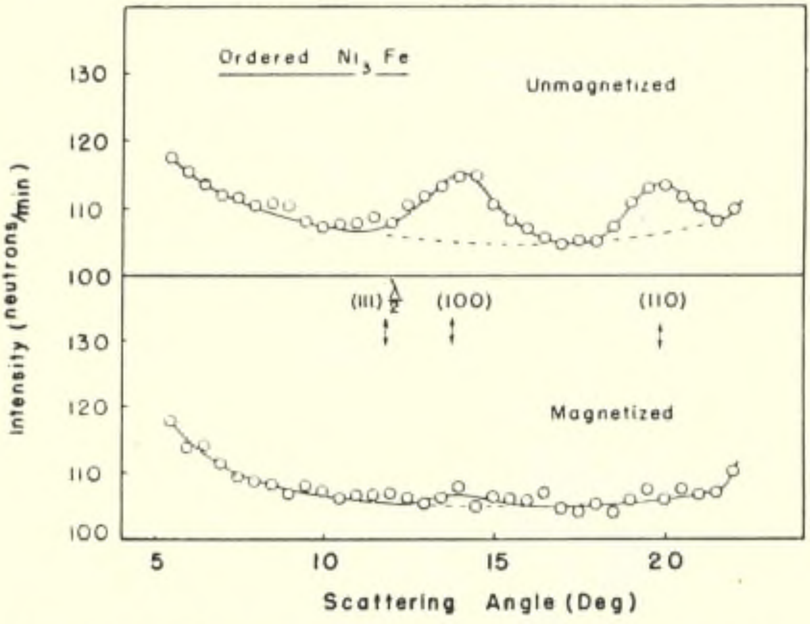


Fig. 8. — Portions of the diffraction pattern for ordered Ni_3Fe showing the superlattice reflections (100) and (110). The top pattern contains both nuclear and magnetic scattering whereas the bottom pattern contains only nuclear scattering.

portions of the diffraction pattern taken with the sample unmagnetized and magnetized. The change in intensity for the (100) and (110) superlattice reflections represents the magnetic superstructure castter-ing and from these absolute intensities, the difference in the two magnetic moments has been evaluated as 2.35 ± 0.20 Bohr magnetons. Very interestingly this difference is closely the same as that found for the disordered alloy of the same composition and since the saturation moments for the disordered and for the ordered alloys are nearly the same, this implies that the individual moments are the same irrespective of the state of order. In other words, this suggests that the individual moments are determined by the overall lattice composition and not by the local surroundings of a particular atom.

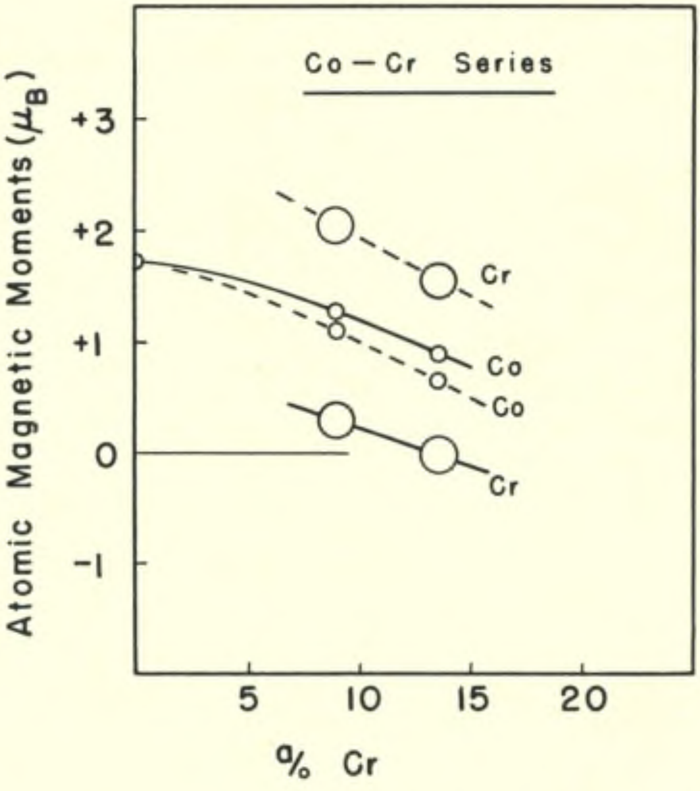


Fig. 9. — Atomic magnetic moments in disordered Co-Cr alloys. Alternative solutions are represented by the points connected either by the solid lines or by the dashed lines.

c) Co-Cr Series

This set of alloys is a particularly interesting one because it deviates markedly from the Slater-Pauling curve shown in figure 4. It has been suggested by a number of authors that this anomalous behaviour is a consequence of the introduction into the cobalt lattice of a large antiparallel moment for chromium since this would then decrease the magnetization in a sensitive fashion. Two disordered alloys containing 9.0 and 13.6 atomic percent chromium have been studied and from the magnetic disorder scattering the moment differences have been evaluated as 0.96 ± 0.15 and 0.91 ± 0.15 Bohr magnetons respectively. The individual atomic moments have been calculated and are represented in figure 9. For either data solution, it is seen that the cobalt moment falls rapidly as chromium is added and hence that it is not necessary to assume a large antiparallel chromium moment to account for the magnetization effects. If the former picture had been correct, a very much larger disorder scattering (about forty times larger than was observed) would have been expected.

d) Ordered Ni_3Mn

This alloy is known to order in the same fashion as Ni_3Fe and in the ordered state it is ferromagnetic with an average magnetic moment of 1.02 Bohr magnetons. From studies of the magnetic superstructure intensities similar to those described above for Ni_3Fe it has been established that the difference of the two moments has the value of 2.88 ± 0.20 Bohr magnetons. Calculation of the individual moments leads to the alternative solutions :

$$\mu_{Mn} = + 3.18 \ (\pm\ 0.25), \ \mu_{Ni} = + 0.30 \ (\pm\ 0.05)$$

or :

$$\mu_{Mn} = - 1.15 \ (\pm\ 0.25), \ \mu_{Ni} = + 1.73 \ (\pm\ 0.05) \ \mu_B.$$

In contrast to the ferromagnetism in the ordered state, the disordered alloy is known to be non-ferromagnetic at room temperature. Neutron diffraction patterns for disordered samples of Ni_3Mn show a broad diffuse peak in the background scattering suggestive of residual short range order. Undoubtedly this diffuse peak contains nuclear contribution and it may also contain a magnetic component. Unfortunately the latter cannot be established by the methods described in this report since the sample is not ferromagnetic.

Hence at the present time it cannot be said that the individual moments in Ni_3Mn are independent of the state of order as was concluded for the case of Ni_3Fe.

e) General conclusions from alloy studies

It has been demonstrated in the above experiments that there exists within alloys, differences in the magnetic moments among the various atomic species and moreover that these atomic magnetic moments differ from the values known to exist in the pure element form. A change in composition is found to alter the individual moments although the quantitative significance of these changes in terms of electron concentration cannot be too well established because of an algebric sign ambiguity associated with the data results.

In all cases the magnetic scattering which is observed for the alloy systems, whether of disordered or of superstructure form, exhibits a magnetic form factor dependence on scattering angle which is satisfactorily matched with that characteristic of pure iron. Thus the magnetic electron shells responsible for the atomic moments in the alloys must not differ much among the various transition elements included in this study.

In the case of Ni_3Fe, the magnetic scattering data suggest that the individual atomic moments are determined by the composition and not by the state of chemical order within the alloy. It follows that the local electron concentration surrounding an atom is not as effective in determining its magnetic moment as is the overall concentration throughout the alloy. It would be highly desirable to have similar data available on other ordered and disordered systems to see if this were a general rule.

Discussion of SHULL's report

Mr. Van Vleck. — I should like to discuss the bearing of Dr. Shull's experiments on the band width of the *d* electrons. In ferromagnetic materials an atom does not on the average have an integral number of Bohr magnetons, and this fact means that an atom is continuously redistributing itself between a variety of configurations. Nickel, for instance, has a saturation moment of about 0.5 Bohr magneton per atom. This state of affairs can be interpreted as meaning that the atom is 50 percent of the time in the configuration d^9 (1 Bohr magneton) and 50 percent in the configuration d^{10} (no moment). Actually, it can also be in configurations d^8, d^7, . . . , and the presence of these higher configurations accentuates fluctuation effects even more.)

The coherent scattering is determined by the average moment per atom. The fluctuations of the atomic moments from their average values give rise to incoherent, inelastic scattering. Actually, no appreciable inelastic scattering is observed in the ferromagnetic materials studied by Shull. This indicates that the fluctuations in the atomic moments must be fairly rapid. The frequency of these fluctuations is measured by the band width associated with the *d* electrons. The existence of such a structure does not imply that the *d* electrons conform to the free electron model but is instead an inevitable consequence of the fact that the electrons are necessarily handed from atom to atom since each atom is a mixture of configurations of different polarity. The scattering will be inappreciable only if the fluctuation frequency is sufficiently high, i.e. the band width sufficiently great. If the band width is negligible, the ratio of the total incoherent to coherent scattering is : $(\overline{S_Z^2} - \overline{S}_Z^2)/\overline{S}_Z^2$ where S_Z and $\overline{S_Z^2}$ are respectively proportional to the mean and mean square moment of an atom in the direction of magnetization. As the band width is widened, this ratio progressively decreases.

It has sometimes been stated in the literature (by me, for instance) that the criterion that the incoherent radiation be inappreciable is that the time of flight of the neutron through the atom be long compared with the fluctuation time between the various configurations. This at first sight seems reasonable, as then fluctuation effects would average out while the neutron traverses the atom. In Shull's experiments the time of flight is of the order 10^{-13} seconds, corresponding to a band width of the order 10^3 wave numbers, and if the actual band width is to large compared with that associated with this characteristic time, the band width would have to be of the order 10^4 cm^{-1}. A band width as large as 10^4 cm^{-1} is irreconcilable with other physical phenomena, as will be detailed later. The use of the time of flight as a criterion for the critical band width is, however, incorrect, and the problem must be tackled from a quantum-mechanical rather than an intuitive classical standpoint. The inelastic processes giving rise to the incoherent scattering involve a transition from one level to another inside a *d*-band, and an exchange of energy between the neutrons and the *d*-band. The energies of Shull's neutrons are about $2k$T, and processes in which the neutrons impart energy to the *d*-band are not possible if the energy involved is over $2k$T. The converse process in which the neutron acquires energy at the expense of the excitation energy of the *d*-band is appreciably only if the energy transfer does not exceed kT. Thus most of the incoherent scattering can be ruled out on energetic grounds as long as the band width is large compared to $2k$T. On the basis of such considerations, the band width should be about 10^2 to 10^3 cm^{-1} to suppress most of the inelastic scattering. It should, however, be emphasized that these considerations are reliable only qualitatively. Two effects working in opposite directions may be mentioned which should be taken into account in a more exact quantitative study. Even if the over-all band-width is$>2k$T, some inelastic transfer processes will still persist involving changes in band energy $<2k$T; the question is how important is this residual effect. On the other hand, even for energetically permitted processes there is some reduction in intensity because the atomic form is smaller for inelastic than for elastic processes.

A band width as large as 10^3 cm^{-1} or .1 volt is not too easy to reconcile with other physical evidence. For one thing, ferromagnetism cannot exist if the band width is too large, for the favorable exchange energy necessary for ferromagnetism is secured only at the expense of a greater sacrifice of band energy, so that the ground state is not ferromagnetic. One would expect such suppression of ferromagnetism to begin to enter as soon as the band energy becomes comparable with or exceeds the band energy. Inasmuch as Curie temperatures, which are a measure of exchange energy, are of the order 10^3 degrees or 10^3 cm^{-1}, this figure can be regarded as roughly an upper limit to the permissible band width. The observed widths of ferromagnetic resonance lines also set an upper limit to the allowable size for a *d*-band structure. The finite width of ferromagnetic resonance lines is caused by the fluctuations in the local fields associated with dipolar interaction (or rather pseudo-dipolar interaction, i.e. interaction of the same angular dependence as that arising from classical electromagnetic forces, but stemming instead from quantum-mechanical spin-orbit effects). The more rapidly the spins redistribute themselves among the different lattice sites, the more the fluctuating fields tend to average out, and the narrower the resonance lines. The order of magnitude of the line breadth is[1] :

$$\Delta\nu \sim C^2/\nu$$

where C is the constant of the pseudo-dipolar interaction, and ν is the fluctuation frequency in the redistribution of the spins, i.e. essentially the band width. According to Kittel and Abrahams*, Ç is about 3 cm^{-1} and the values of $\Delta\nu$ observed by Bloembergen** are about 10^{-1} cm^{-1}. Hence, if ν exceeds 10^2 in order of magnitude, the expected line widths should be appreciably smaller than observed. Because of uncertainties in C and in numerical factors, a value of ν as high as 10^3 cm^{-1} cannot definititely be excluded.

A band width as high as 10^3 cm^{-1} is thus barely acceptable from the standpoint of the two phenomena discussed in the preceding paragraph, while anything much lower would lead to appreciable incoherent scattering. There is thus something of a dilemma. Our discussion, however, has been only qualitative, and exact calculations of the precise amount of the incoherent scattering for a given band-pattern are highly desirable.

(*) See C. Kittel and E. Abrahams, *Rev. Mod. Phys.*, **25**, 237 (1953) Eq. (21) These authors deal explicitly with fluctuations in local fields caused by spin waves. However, when there are still more rapid fluctuations caused by transfer of polarity from one lattice site to another, the appropriate frequency to use in the denominator of their equation is that associated with the *d*-band migration structure rather than the frequency characteristic of the spin waves.

(**) N. Bloembergen, *Phys. Rev.* **78** : 572 (1950).

Mr. Kittel. — The ferromagnetic resonance line widths in ferrites and in pure iron (presumably approximately d^8) are comparable in magnitude.

I doubt if all ferromagnetic line widths can be explained by configuration hopping.

Mr. Bragg. — Would it not be possible to discover the arrangement of the magnetic polarities in mangenese by a process of trial and error as in X-ray analysis?

The number of measured diffractions is not large, and by incorporating the various combinations of plus and minus phases in the customary Fourier summation, one should be able to recognize the combination which gives a physically acceptable answer.

Mr. Shull. — The presently available patterns for alpha-manganese permit recognition of only four magnetic reflections and with such a complicated structure (58 atoms in the unit cell) probably not much progress can be made in this direction. When patterns with better resolution and intensity become available then such a procedure may turn out to be very useful.

Mr. Mott. — Can I ask Dr. Shull what he means by a « rapid » exchange; how rapid?

Mr. Shull. — In its simplest form, the transit time of a low neutron across the magnetic force field of an atom is about 3.10^{-13} seconds so we should like exchange periods a good deal smaller than this. These matters are touched on in Professor van Vleck's comments.

Mr. Mott. — I agree with Professor Van Vleck, that the time of flight Δt has nos relation to the problem.

If one tries to form a wave packet, out of the wave functions of the neutron, representing neutrons with energies in the range ΔE where $\Delta E . \Delta t \sim h$ one obtains values of the order of one electron volt, and so considerably greater than the total energy of the neutron.

Incoherent scattering is, as Van Vleck says, inelastic scattering. It will occur either :

a) if the neutron has enough energy to excite large numbers of excited states of the crystal, and thus if the energy of the neutron is of the order $k\theta$, where θ is a Curie or Néel temperature;

or :

b) if the temperature T of the lattice is of the order θ, so that the neutron can change its momentum and excite a new electronic state of the crystal without any large change of energy.

Mr. Gorter. — Dr. Shull ascribes the maximum of small angle scattering at the Curie temperature to short range order. He mentioned that similar scattering must be expected to occur near the Bragg reflection angles. This has been investigated in the Norwegian-Dutch reactor in Kjeller with single crystals of Fe_3O_4 , but the results have not yet appeared. On account of the observed asymmetry of the scattering however, this is ascribed to inelastic scattering rather than to short range order effects. I feel a bit unhappy that the two results, which peak in the same way at the Curie temperature, are described in so very different ways.

Mr. Shull. — The angle scattering effects which have been observed in the case of iron at high temperatures are known to be closely of elastic nature, whereas the Kjeller experiments (as well as equivalent experiments by Lowde at Harwell) are known to be of inelastic nature as Professor Gorter has mentioned. I do not believe that these observations are incompatible because the degree of inelasticity may very well depend strongly on the angle of scattering. More than likely both types of observations can be accounted for as different limiting cases of a complete unified theory.

Mr. Bragg. — I am interested in Dr. Shull's picture of the metal in the neighbourhood of the Curie point. As I understand it, the low angle scattering indicates that ordered domains become smaller and smaller as the Curie point is approached from the low temperture side. But in the usual treatment of the order-disorder phenomenon, it is envisaged that long-range order persists up to the critical temperature, though its degreee is diminishing. At the critical temperature, it passes abruptly into short range order. How do we reconcile these two pictures of the phenomenon?

Mr. Shull. — As the Curie temperature is approached from the low temperature side, the degree of long range magnetic order is lessened just as in the chemical ordering case. This is seen in both cases as a reduction in the coherent scattering. On the other hand the magnetic small angle scattering interpreted as a degeneration of the size of the magnetically coherent regions does not appear to have its analog in the chemical case. Almost certainly these magnetically coherent regions are of dynamic type (and hence there has been some objection to calling them domains) so that this difference may not be too surprising since there does not appear a chemical analog to the spin wave picture.

Mr. Onsager. — The concentration of the scattering in the forward direction has esentially the same significance regardless of whether order is present or not. Above the Curie point this phenomenon indicates that neighbouring atoms tend to assume the same orientation of their spins; below the Curie point it depends on a tendency for neighbouring atoms to assume the same orientation more frequently than atoms which are far apart.

Mr. Mendelssohn. — It is interesting to correlate Dr. Shull's data on neutron scattering with the occurrence of superconductivity. It might be expected that an internal magnetic field in the metal would inhibit superconductivity, which we know to be quenched by fairly small fields of the order of a few hundred gauss. On the other hand, other conditions besides the absence of a field will probably have to be fulfilled to make a superconductor. Denoting with *m* the observed antiferromagnetic scattering, and with *S* the occurrence of superconductivity, we can tabulate the results as follows :

	m	*S*	
expected behaviour	+	+	forbidden
	—	— +	superconductivity possible but not necessary
Metal			
V	—	+	
Nb	—	+	
Cr	+	—	
Mn	+	—	
Mo	—	—	These metals form superconducting compounds
W	—	—	

This shows that Cr and Mn which should not become superconducting according to this rule, indeed do not.

V and Nb which are superconductors show no antiferromagnetic scattering. The known occurrence of superconductivity in metals can therefore be used to predict the absence of antiferromagnetic neutron scattering. The metals which might possibly show antiferromagnetism but should not do so, according to the correlation, are Os, Ru, Re, U, Ti, Ta, La, Hf and Zr. There are also a great number of intermetallic compounds falling into this category of which especially Mo_3Ir and the series Rh Zr found by Matthias to be superconducting should be mentioned. These may be expected not to be antiferromagnetic, as has indeed been found for V_3Si which is a superconductor.

Mr. Pippard. — While agreeing with the likelihood of a correlation of the sort proposed by Mendelssohn, I am not convinced by this argument.

I do not think that local magnetic fields such as must be present in antiferromagnetics can play much part in inhibiting the superconducting condensation. Is it not more probable that the magnetic transition is so much more energetic than the superconducting transition that if the former can occur, it will do so and control the way in which the electrons order themselves? A second (superconducting) type of ordering process would not then be expected.

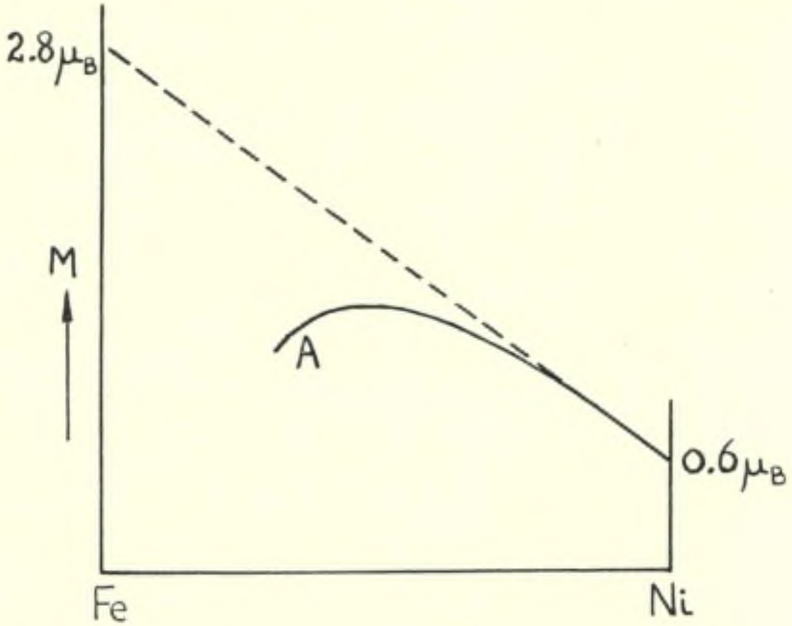
Mr. Mott. — Faut-il s'attendre à l'existence de champs magnétiques internes importants dans les antiferromagnétiques par suite de l'existence des parois de séparation entre les domaines élémentaires?

Mr. Néel. — 1. Nos connaissances sur les parois des domaines élémentaires antiferromagnétiques sont encore beaucoup trop incomplètes pour qu'il soit possible de donner une réponse précise au Prof. Mott, car les parois sont assimilables à des feuillets magnétiques, mais on ne connaît ni leur puissance, ni leur contour.

Néanmoins, l'existence de champs internes de quelques centaines de gauss paraît vraisemblable.

2. Dans sa détermination des moments magnétiques atomiques des constituants A et B d'un alliage binaire, Mr. le Dr. Shull suppose que tous les moments de A sont parallèles entre eux, ainsi que tous les moments de B. Or, dans deux des séries étudiées Fe-Ni et Fe-Cr, ce n'est pas du tout certain, car il existe de très fortes raisons de penser que, dans les alliages en question, les interactions Fe-Fe et Cr-Cr sont négatives et provoquent dans la série Fe-Ni, l'apparition de quelques moments Fe en sens inverse de l'aimantation générale, et, dans la série Fe-Cr l'orientation en sens inverse de quelques moments Cr.

En fait, c'est par l'existence d'une quantité croissante d'atomes de fer orientés en sens inverse de l'aimantation générale qu'il est possible d'interpréter la forme de la courbe qui représente la variation avec la concentration de l'aimantation à saturation des ferronickels. Cette courbe a l'allure générale représentée par la figure 10.



L'interprétation de la baisse du moment résultant dans la région A par le retournement du moment de quelques atomes de fer est d'ailleurs confirmée par le fait que, dans la région paramagnétique, la variation avec la concentration de la constante de Curie est à peu près linéaire.

Si l'on adopte ce point de vue, il faudrait reconsidérer l'interprétation des expériences de diffraction de neutrons et il n'est pas impossible que dans ces conditions les moments magnétiques atomiques du fer et du nickel dans les Fe-Ni et les Fe-Cr deviennent indépendants de la concentration.

C'est pourquoi il serait extrêmement intéressant d'étudier, avec les neutrons, les alliages ferromagnétiques dans lesquels ces retournements de moment ne se produisent pas, c'est-à-dire les alliages dans lesquels les interactions A-A, A-B, et B-B, sont toutes positives : par exemple, les Fe-Co et les Co-Ni.

Mr. Smit. — L'antiferromagnétisme partiel des ions de fer proposé par le Prof. Néel dans les alliages de nickel avec du fer causera une susceptibilité différentielle à la température du zéro absolu, dans des champs magnétiques élevés. Cette susceptibilité différente de zéro est observée indirectement*, par la mesure du changement de la résistivité dans un champ magnétique dans les alliages nickel-fer pour des concentrations du fer supérieures à 40 %. En conséquence, il ne semble pas probable que la diminution considérable du moment magnétique pour des faibles concentrations de fer puisse être expliquée par le modèle proposé par le Prof. Néel.

Mr. Onsager. — An atom which changes the orientation of spins on its neighbours is a larger scattering object than a single atom, and it ought to have a different form factor.

Mr. Shull. — If there is any sort of correlation from one spin to neighbouring spins, then this surely will influence the observed form factor as Prof. Onsager has suggested.

(*) J. Smit, *Physica*, **17**, 612 (1951), *Comm. Kam. Onnes*, Lab. Leiden, 186*a*.

Antiferromagnétisme et métamagnétisme

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1. INTRODUCTION

Nous nous proposons d'examiner dans cet exposé dans quelle mesure il est possible d'interpréter les propriétés des substances métamagnétiques en les considérant comme antiferromagnétiques. Ces substances, ainsi appelées en 1939 par J. Becquerel (1) et dont $CoCl_2$, $NiCl_2$, $FeCl_2$ constituent de bons exemples, obéissent dans la région paramagnétique à une loi de Curie-Weiss avec un point de Curie paramagnétique nettement positif, mais lorsque la température s'abaisse, même largement, au-dessous de ce point, elles ne deviennent pas ferromagnétiques à tel point que dans des champs de 30.000 Oe aucun indice de saturation n'est observable : la susceptibilité commence à croître avec le champ magnétique mais tend ensuite vers une valeur constante. En outre, ces substances présentent une faible hystérésis et une faible rémanence.

L'idée de rechercher l'origine de ces différentes manifestations dans un arrangement antiparallèle des moments atomiques n'est pas nouvelle : Landau (2) avait déjà suggéré une explication dans cette voie. Starr de son côté (3) a proposé une théorie basée sur la formation de groupements antiparallèles plus ou moins développés. Il nous semble cependant encore actuellement que la meilleure méthode et, en tout cas, la plus simple pour traiter de tels problèmes, est la méthode du champ moléculaire que nous avons déjà largement utilisée dans des problèmes variés (4), (14). Nous savons qu'elle est discutable et qu'elle fournit, notamment dans le cas de la chaîne linéaire, des résultats incorrects (5) mais sa simplicité la rend d'autant plus indispensable que les autres méthodes sont absolument inapplicables aux problèmes complexes qui nous occupent ici.

C'est également par raison de simplicité que nous supposerons que le moment orbital est complètement bloqué et que nous ne nous préoccuperons pas de la nature exacte de la décomposition des niveaux par le champ cristallin. L'interprétation que nous proposons ici se présente donc comme une première approximation.

Comme il est d'usage, nous divisons le réseau des ions magnétiques en deux sous-résaux et nous représentons les interactions d'échange à l'intérieur d'un même sous-réseaux et entre les deux sous-réseaux par deux champs moléculaires différents; enfin, nous tenons compte des couplages magnétocristallins en exprimant l'énergie correspondante par des formules analogues à celles que l'on emploie pour les ferromagnétiques, notamment ceux qui sont uniaxes. Dans toute la suite les expressions de l'énergie, de l'aimantation, etc., seront toujours rapportées à un mole, à moins d'indication contraire.

2. ÉTUDE DE LA SUSCEPTIBILITÉ DANS UNE DIRECTION PERPENDICULAIRE A LA DIRECTION D'ANTIFERROMAGNÉTISME

Etudions d'abord rapidement quelques-uns des aspects du problème du couplage magnéto-cristallin dans les antiferromagnétiques. Considérons pour simplifier une substance uniaxe et désignons par θ et θ' les angles que font avec l'axe les directions des aimantations spontanées des deux sous-réseaux. Adoptons comme expression de l'énergie magnétocristalline :

$$W_c = \frac{K}{2}(\sin^2\theta + \sin^2\theta') . \qquad (1)$$

Cette formule suppose que les deux sous-réseaux sont couplés indépendamment l'un de l'autre au réseau cristallin. Cette hypothèse n'a rien de nécessaire et on peut imaginer des mécanismes faisant apparaître des termes en $\sin\theta \sin\theta'$ et en $\cos\theta \cos\theta'$ dans l'expression de W_c . Nous avons adopté la forme (1) par simplicité et parce qu'elle permet de rendre compte des faits expérimentaux, tout au moins en ce qui concerne les substances étudiées ici.

Pour l'énergie d'échange W_e , nous adoptons l'approximation du champ moléculaire et en désignant par M/2 l'aimentation spontanée de chacun des sous-réseaux, nous obtenons :

$$W_e = \frac{1}{4} n M^2 \cos(\theta - \theta') ,$$

où n est essentiellement positif puisqu'il s'agit d'une substance antiferromagnétique.

Si K est positif, la position d'équilibre stable du système, en l'absence de champ extérieur, correspond à $\theta = 0$, $\theta' = \pi$; le moment résultant des deux sous-réseaux est nul. La direction de l'axe est une direction privilégiée d'antiferromagnétisme.

L'aimantation M/2 de chacun des sous-réseaux doit être considérée comme l'aimantation spontanée prise sous l'action d'un champ moléculaire égal à $(n + n')$ M/2 où le premier terme nM/2 provient des interactions entre les deux sous-réseaux, le second terme n'M/2 provenant des interactions à l'intérieur d'un même sous-réseaux, la somme $n + n'$ devant naturellement être positive. Le calcul de M/2 est alors identique à celui qu'on effectue dans la théorie de Weiss pour un ferromagnétique dont le coefficient de champ moléculaire est égal à $n + n'$. Notamment la variation thermique de M est la même que celle du ferromagnétique correspondant.

Appliquons maintenant un champ magnétique extérieur H suivant une direction perpendiculaire à l'axe; il faut alors ajouter à l'énergie un terme :

$$W_m = -\frac{1}{2} \mathrm{MH} (\sin\theta + \sin\theta') .$$

La configuration d'équilibre s'obient en écrivant que l'énergie totale $W_c + W_e + W_m$ est minimum et on déduit l'aimantation résultante :

$$J = \frac{H}{n + \frac{2K}{M^2}} \tag{2}$$

Si K est petit devant nM^2, cette expression montre que la susceptibilité perpendiculaire à l'axe s_n, sensiblement égale à $1/n$, reste indépendante du champ et de la température T, dans la mesure où on peut négliger la variation thermique de n. En particulier, l'aimantation reste proportionnelle au champ jusqu'au voisinage de la saturation : cette propriété très remarquable des substances antiferromagnétiques les différencie très nettement des substances paramagnétiques obéissant aux lois de Langevin et Brillouin pour lesquelles la courbure de J = B (T) devient très sensible lorsqu'on atteint la moitié de la saturation. Malheureusement, dans la plupart des antiferromagnétiques, $\underline{n}$ est trop grand pour qu'on puisse atteindre une fraction notable de la saturation avec les champs magnétiques disponibles qui ne peuvent guère dépasser 30.000 Oe et il n'est pas possible de mettre en évidence cette propriété. Cependant, W.E. Henry (6) a étudié entre 1° et 4° K, et jusqu'à 30.000 O*e*, l'aimantation de l'antiferromagnétique $CuCl_2 . 2H_2O$ pour lequel $\underline{n}$ est particulièrement petit : il a trouvé que dans ces limites l'aimantation était indépendante de la température et proportionnelle au champ à 2 % près. Comme il a atteint environ la moitié de la saturation et que dans ces conditions la loi de Brillouin avec $j = 1/2$ conduit à des écarts à la proportionalité de 8 % on peut en conclure à l'exactitude des prévisions de la théorie élémentaire de l'antiferromagnétisme.

Lorsque K n'est plus négligeable devant nM^2, la formule (2) montre que la susceptibilité perpendiculaire peut dépendre notablement de la température. Très souvent dans les substances ferromagnétiques, l'expérience montre que la constante d'anisotropie K décroît avec la température beaucoup plus rapidement que le carré M^2 de l'aimantation à saturation : c'est par exemple le cas du nickel et du fer. Si le même phénomène se produit chez les antiferromagnétiques, K/nM^2 diminue lorsque la température s'élève, de sorte que la susceptibilité perpendiculaire croît en même temps que la température : c'est peut-être ce qui se produit dans le cas du FeF_2 étudié par Stout et Matarrese (7).

3. ÉTUDE DE LA SUSCEPTIBILITÉ PARALLÈLE A LA DIRECTION D'ANTIFERROMAGNÉTISME

Etudions maintenant l'action d'un champ magnétique appliqué dans une direction parallèle à l'axe. L'énergie magnétique prend alors la forme :

$$W'_m = -\frac{1}{2} MH (\cos \theta' + \cos \theta) .$$

Comme nous le préciserons plus loin, lorsque MH est suffisamment petit devant K, la configuration d'équilibre du système correspond toujours à $\theta = 0$ et $\theta' = \pi$, de sorte que les changements de l'aimantation résultante proviennent des changements de l'aimantation spontanée elle-même produite par le champ H et non plus des changements d'orientation des aimantations spontanées des deux sous-réseaux. Ce phénomène a été étudié par F. Bitter (8). L'aimantation correspondante est alors donnée par :

$$J = \frac{H}{n - \frac{n+n'}{2}\frac{M}{T}\frac{dT}{dM}}, \tag{3}$$

dans laquelle la dérivée dT/dM est prise le long de la courbe de variation thermique de l'aimantation spontanée M. La susceptibilité correspondante, c'est-à-dire la susceptibilité parallèle S_p, nulle au zéro absolu, tend vers $1/n$, c'est-à-dire vers la valeur de la susceptibilité perpendiculaire, lorsque la température atteint la température de transition T_n à laquelle M et dT/dM s'annulent tous les deux.

4. DÉCOUPLAGE DE LA DIRECTION D'ANTIFERROMAGNÉTISME ET DE L'AXE DU CRISTAL

Lorsqu'on augmente l'intensité d'un champ magnétique appliqué parallèlement à l'axe, les phénomènes se compliquent par des changements d'orientation de l'aimantation spontanée des deux sous-réseaux. Le système prend les trois configurations successives reprérepréséntées sur la figure 1 : la configuration I est la configuration initiale avec $\theta = 0$ et $\theta' = \pi$. La configuration II correspond à $\theta = -\theta' = \theta_0$ avec $0 < \theta_0 < \frac{\pi}{2}$: lorsque θ_0 est voisin de $\frac{\pi}{2}$, la direction d'antiferromagnétisme est devenue perpendiculaire à la direction de l'axe. Enfin, la configuration III correspond à $\theta = \theta' = 0$ et le système est aimanté à saturation dans la direction de l'axe. Pour simplifier l'étude, nous supposons que la température est

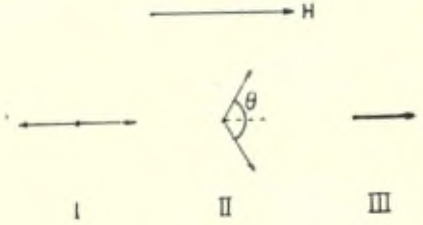

Fig. 1. — Les trois types possibles dans la disposition de l'aimantation spontanée des deux sous-réseaux d'une substance anti-ferromagnétique.

suffisamment voisine du zéro absolu pour qu'il soit possible de négliger les effets, indiqués plus haut, de la variation de l'aimantation spontanée M/2 de chacun des sous-réseaux sous l'influence du champ H.

L'énergie totale du système est égale à $W_c + W_e + W_m$. L'étude de la stabilité des différentes configurations est un problème élémentaire qui n'appelle aucune remarque particulière. Il suffit d'en donner ici les résultats que nous exprimons en fonction de deux coordonnées réduites : un champ réduit $h = 2H/nM$ et un paramètre $r = 2K/nM^2$, égal au rapport de l'énergie de couplage à l'énergie d'échange.

Remarquons d'abord que l'aimantation J du système est égale à 0 dans la configuration I et à M dans la configuration III. Dans la configuration II, on trouve à l'équilibre :

$$\cos \theta_0 = \frac{h}{2(1-r)} ,$$

d'où on déduit J par la relation $J = M \cos \theta_0$. Dans le cas où r est inférieur à 1/2, on trouve ensuite que la configuration I est la plus stable lorsque h^2 est inférieur à $4r(1-r)$; puis c'est la configuration II lorsque h^2 est compris entre $4r(1-r)$ et $2(1-r)$ et la configuration III lorsque h^2 est supérieur à $2(1-r)$. Dans le cas où r est supérieur à 1/2, la configuration II n'apparaît plus et on passe directement de I à III lorsque h^2 devient supérieur à 1. Les diagrammes d'aimantation correspondant à ces deux éventualités sont représentés schématiquement sur la figure 2, en traits pleins.

Le passage de la configuration I à la configuration II pour $h^2 = 4r(1-r)$ correspond à une brusque rotation de la direction d'antiferromagnétisme; nous avions déjà signalé (9) en 1936 ce brusque découplage de la direction d'antiferromagnétisme lorsque le champ magnétique atteignait une certaine valeur critique. En 1952, ce phénomène fut retrouvé expérimentalement par C.J. Gorter, N.J. Poulis et al. (10). Dans notre calcul de 1936, nous avions supposé que K était petit devant nM^2, de sorte que la valeur du champ critique correspondait simplement à $h^2 = 4r$.

5. HYSTÉRÉSIS PARAMAGNÉTIQUE

La considération des états les plus stables qui fait l'objet du paragraphe précédent n'épuise pas le problème car on peut montrer qu'il existe des états métastables. Lorsque r est inférieur à 1, on peut résumer ainsi les résultats de la discussion. Lorsqu'on opère par champs croissants à partir de 0, la configuration I reste stable jusqu'à ce que h^2 atteigne la valeur $4r(1 + r)$: quand r est inférieur à 1/3 on passe alors à la configuration II, mais quand r est supérieur à 1/3 on passe directement à la configuration III. D'une manière analogue, lorsqu'on opère dans des champs décroissants depuis une valeur très élevée, on constate d'abord un passage réversible de la configuration III à la configuration II, puis un passage irréversible de la configuration II à la configuration I lorsque h^2 atteint la valeur $4r(1-r)^2/(1+r)$. Lorsqu'on fait osciller le champ magnétique appliqué entre 0 et une valeur élevée, l'aimantation décrit un véritable cycle d'hystérésis tel que ceux qui sont schématiquement représentés en pointillé sur la figure 2. Il est intéressant de remarquer que lorsque r est petit, l'abscisse du centre du cycle d'hystérésis est proportionnelle à $r^{1/2}$ tandis que la largeur du cycle est proportionnelle à $r^{3/2}$. Comme en général l'énergie magnétocristalline est beaucoup plus petite que l'énergie d'échange, l'amplitude de ces phénomènes d'hystérésis doit être le plus souvent négligeable, puisque r, rapport de ces deux énergies, est alors très petit.

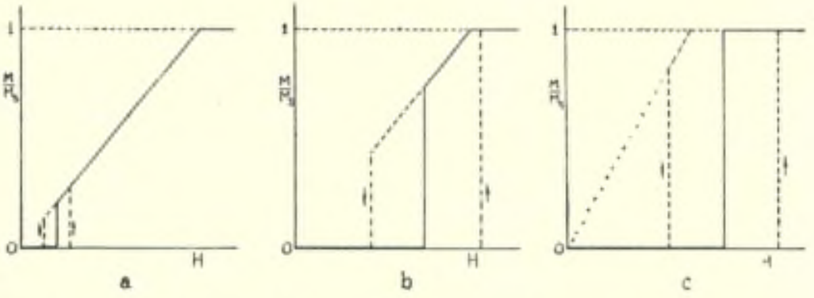

Fig. 2. — Cycles d'hystérésis schématiques d'une substance antiferromagnétique.

On peut même se demander d'ailleurs si de tels phénomènes d'hystérésis sont possibles. En effet, la situation que l'on rencontre ici est analogue à celle des corps ferromagnétiques, dans lesquels l'énergie magnétocristalline devrait donner naissance, en principe, comme l'avait montré Akulov (11), à des phénomènes d'hystérésis importants, avec des champs coercitifs de plusieurs centaines d'oersteds pour du fer ou du nickel. L'expérience montre au contraire qu'il est facile d'abaisser le champ coercitif du fer jusqu'à quelques centièmes d'oersted. L'explication de ce paradoxe est simple : il existe toujours, après aimantation dans un sens, des îlots extrêmement petits aimantés en sens inverse et, par suite de la structure des parois de Bloch, la direction de l'aimantation spontanée passe graduellement d'une direction d'aimantation à la direction antiparallèle, à l'intérieur des parois qui séparent les îlots de la phase principale. Il y a donc toujours possibilité d'un passage réversible d'une phase à l'autre de sorte que la substance, à l'exception de très petits îlots résiduels, se trouve toujours dans la phase la plus stable.

Il est bien possible que les choses se passent de la même façon dans les substances antiferromagnétiques. On peut concevoir, en effet, l'existence dans les antiferromagnétiques de véritables domaines élémentaires (12), à l'intérieur desquels la direction d'antiferromagnétisme conserve une orientation invariable, séparés par des régions étroites, les parois, dans l'épaisseur desquelles cette direction change progressivement d'orientation. Dans les substances qui possèdent plusieurs directions d'antiferromagnétisme, il convient de distinguer, comme pour les substances ferromagnétiques, deux catégories de parois, les parois à 90° qui séparent deux domaines à directions différentes d'antiferromagnétisme et les parois à 180° qui séparent deux domaines dont les directions d'antiferromagnétisme sont identiques, *mais avec des orientations antiparallèles.* Ces orientations antiparallèles correspondent à l'inversion des sens d'aimantation des deux sous-réseaux. Quand la substance possède une seule direction d'antiferromagnétisme, elle ne possède également que des parois à 180°.

Il résulte de ces considérations qu'il n'est jamais possible, sous les réserves faites ci-dessous, d'avoir affaire à un échantillon macroscopique contenant un seul domaine élémentaire : même si la direction d'antiferromagnétisme est partout la même, les deux orientations antiparallèles seront représentées et nous aurons une série de domaines séparés par des parois à 180°. Si nous appliquons maintenant un champ magnétique parallèle à la direction d'antiferromagnétisme, l'intérieur des domaines sera dans la configuration I par rapport au champ magnétique. Mais dans l'épaisseur des parois, il y aura des régions, qui, relativement au même champ, seront dans la configuration II. Il sera donc toujours possible à la phase II de croître d'une manière réversible aux dépens de la phase I : un tel processus exclut naturellement la possibilité d'hystérésis.

Si la substance est fragmentée en grains de dimensions inférieures à l'épaisseur de paroi, ces grains ne contiendront cependant qu'un seul domaine élémentaire et le raisonnement précédent n'est plus applicable : on peut espérer observer ainsi des phénomènes d'hystérésis et on peut rapprocher ce phénomène de l'augmentation du champ coercitif des ferromagnétiques produites par la subdivision en grains très fins (13). Il y a cependant une différence essentielle : le point $H = 0$ est ici toujours en dehors du domaine d'hystérésis de sorte que les cycles d'hystérésis que l'on obtient en faisant varier le champ entre deux limites symétriques $-H$ et $+H$ sont des cycles en nœud de cravate, dont les deux branches sont confondues à l'origine.

6. LA VARIATION AVEC LE CHAMP DE LA SUSCEPTIBILITÉ DES SUBSTANCES ANTIFERROMAGNÉTIQUES POLYCRISTALLINES

La description des phénomènes que nous venons de donner se rapporte au cas où la température est très basse et où la susceptibilité parallèle, dans un champ petit vis-à-vis de $r^{1/2}$, est sensiblement nulle. Lorsque la température se rapproche de la température T_n du point de transition, cette susceptibilité croît et tend vers $1/n$. En gros, nous devons obtenir une succession de phénomènes du même genre que ceux que nous avons déjà décrits : la principale différence réside dans le fait que la susceptibilité de la configuration I possède alors une valeur finie, au lieu d'une valeur nulle.

Il serait également utile mais fastidieux d'étudier ce qui se passe lorsqu'on applique un champ magnétique oblique par rapport à la direction d'antiferromagnétisme initiale. Nous avons déjà étudié (9) le cas où r est petit devant l'unité, pour lequel l'hystérésis est négligeable en tout état de cause. La figure 3 représente les valeurs de la susceptibilité en fonction du champ, pour différentes valeurs de l'angle que fait la direction du champ avec la direction initiale d'antiferromagnétisme : la figure est tracée en coordonnées réduites, H_o^2 est égal à $4r$ et χ_m est égal à $1/n$, avec les notations adoptées ici. Comme nous l'avions déjà indiqué dans le même mémoire (9), la

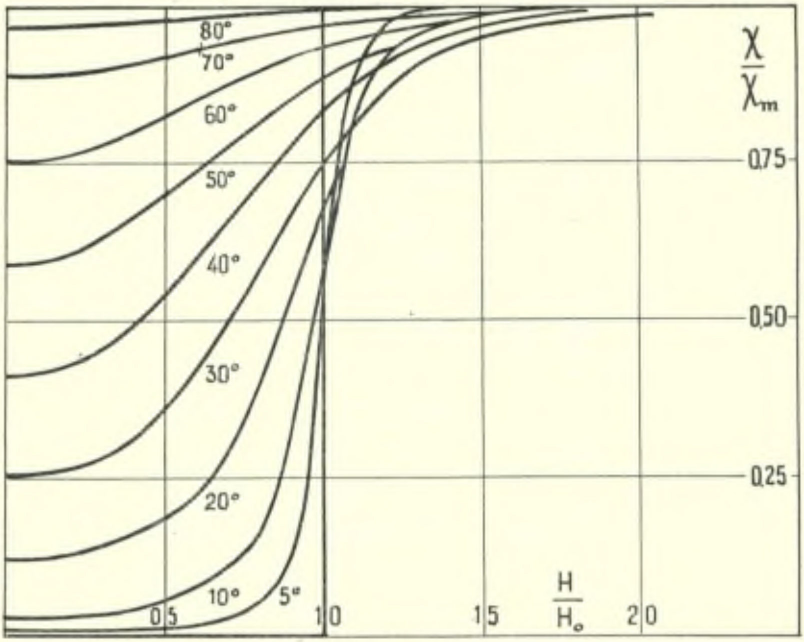

Fig. 3. — Susceptibilité magnétique en fonction du champ, pour différentes orientations de la direction privilégiée d'antiferromagnétisme. — *Annales de Physique* (1936), t. 5, p. 232 (Néel).

susceptibilité moyenne d'une substance polycristalline s'obtient en faisant la moyenne pondérée des différentes courbes obtenues précédemment : quand le champ est très petit, la susceptibilité est alors égale à $2/3n$. Cette susceptibilité augmente ensuite avec le champ et l'allure de la courbe est intermédiaire entre celles qui correspondent aux angles de 50° et de 60°.

Tous ces résultats se rapportent à des températures voisines du zéro absolu pour lesquelles la susceptibilité parallèle s_p est nulle. Les calculs ont été étendus par Nagamiya et Yosida aux températures plus élevées (16). En particulier, si l'on se limite aux termes en H^2, la susceptibilité moyenne $\underline{s}$ est donnée par :

$$S = \frac{1}{3} S_n + \frac{2}{3} S_p + \frac{2(S_n - S_p)^2 H^2}{15K} + \dots \tag{4}$$

Il importe de remarquer que la rotation de la direction d'antiferromagnétisme, impliquée dans les phénomènes décrits ici n'est pas la cause unique de l'augmentation de la susceptibilité avec le champ, tout au moins quand il s'agit de substances, comme celles qui appartiennent au système cubique, dans lesquelles il existe, par raison de symétrie, des directions privilégiées d'antiferromagnétisme non parallèles entre elles. Dans ce cas, une paroi à 90° sépare deux domaines élémentaires dont les suceptibilités sont en général différentes. L'application d'un champ magnétique équivaut à l'application sur la paroi d'une pression proportionnelle au carré du champ et à la différence des susceptibilités correspondant à la direction du champ appliqué. Si les deux domaines étaient parfaitement identiques du point de vue énergétique, la paroi devrait se déplacer librement dans un champ même faible, de sorte que le domaine de plus grande susceptibilité devrait croître et absorber le domaine de plus faible susceptibilité. Lorsqu'il s'agit par exemple d'une substance cubique dont les axes quaternaires sont les directions privilégiées d'antiferromagnétisme spontané, il résulte de ce processus que finalement et dans tous les domaines, la direction d'antiferromagnétisme occupe celui des trois axes quaternaires qui est le plus près d'être perpendiculaire au champ appliqué. Si tel est le cas, on peut en conclure que la susceptibilité au zéro absolu doit être égale à 0,975 s_0 en désignant par s_0 la valeur de la susceptibilité à la température de transition, tandis qu'avec une répartition isotrope des directions d'antiferromagnétisme on obtient comme nous l'avons vu 0,667 s_0. Or l'expérience (15), notamment dans le cas de MnO, CoO, etc., est nettement en faveur de cette dernière valeur; il doit donc exister un mécanisme qui empêche les domaines mal orientés de se résorber au profit des domaines bien orientés.

A l'image des phénomènes ferromagnétiques, il est logique de supposer qu'il existe des perturbations qui font apparaître des différences d'énergie entre deux directions primitivement équivalentes de la direction d'antiferromagnétisme. En admettant par exemple que l'énergie W'' de perturbation soit de la forme :

$$W'' = C \sin \frac{x}{L}$$

et qu'il existe une paroi normale à Ox pour $x = \pi k L$ où k est un entier, on trouve (16) que la variation de la susceptibilité en fonction du champ est donnée par l'expression :

$$S = \frac{1}{3} S_p + \frac{2}{3} S_n + \frac{(S_p - S_n)^2 H^2}{3\pi C} + \ldots . \qquad (5)$$

Cette expression est formellement équivalente à l'expression (4). Normalement, il est logique de s'attendre à ce que l'énergie C de perturbation soit petite vis-à-vis de l'énergie principale K de couplage magnétocristallin de sorte que le terme en H^2 dans (5) doit être plus grand que le terme correspondant en (4). L'application de la formule (5) aux variations avec le champ de la susceptibilité de MnO, mises en évidence par Bizette(15), fournit une valeur de C qui est de l'ordre de 6.10^6 erg/mole. Cette valeur est considérablement plus élevée que les énergies de perturbation observées pour les corps ferromagnétiques, tout au moins pour ceux qui n'ont pas reçu de traitement spécial pour cela. A priori, elle paraît difficile à justifier.

Il faut remarquer cependant que l'apparition de l'ordre antiferromagnétique fait apparaître une déformation (17) qui est de caractère rhomboédrique pour MnO, FeO, NiO et de caractère tétragonal pour CoO : elle est due au caractère anisotrope des arrangements antiferromagnétiques. Il s'agit en somme d'une *magnétostriction d'échange* (18) : cette magnétostriction due aux forces d'échange passe généralement inaperçue dans les ferromagnétiques car elle ne provoque qu'une déformation isotrope de la maille; ici au contraire la déformation est anisotrope et dépend de celui des quatre axes ternaires auquel les plans des sous-réseaux sont perpendiculaires. L'amplitude de ces déformations est relativement grande de l'ordre de 1 à 5 pour mille, en valeur relative. De pareilles déformations dans les corps ferromagnétiques donnent naissance à des énergies magnétoélastiques qui sont de l'ordre de 10^6 erg/mole, c'est-à-dire de l'ordre de grandeur obtenu plus haut; il peut en être de même ici.

Dans l'état actuel de nos connaissances, il ne paraît pas possible de préciser davantage.

7. LA COURBE D'AIMANTATION D'UNE SUBSTANCE ANTIFERROMAGNÉTIQUE POLYCRISTALLINE

Il reste à examiner quelle peut être l'allure de la courbe d'aimantation d'une substance polycristalline composée de cristallites orientés au hasard. Lorsque l'axe du cristal est perpendiculaire à la direction du champ, on obtient la droite d'aimantation OD (fig. 4) de pente $1/n(1+2r)$. Lorsque l'axe du cristal est parallèle au champ, on obtient lorsque r est assez petit, le diagramme d'aimantation OABC, avec une pente terminale de BC égale à $1/n(1-2r)$. Pour des orientations intermédiaires, les résultats sont plus compliqués. Le résultat final s'obtient en principe en effectuant une moyenne pondérée de toutes ces courbes. Mais cette manière de faire implique le droit de négliger les interactions magnétiques entre les différents cristallites. C'est légitime lorsque l'aimantation est faible mais beaucoup plus discutable lorsqu'on approche de la saturation. Quoi qu'il en soit, on doit finalement obtenir une courbe d'aimantation moyenne analogue à la courbe OE tracée en traits pleins sur la figure 4, avec une pente initiale égale aux deux tiers de celle de OD.

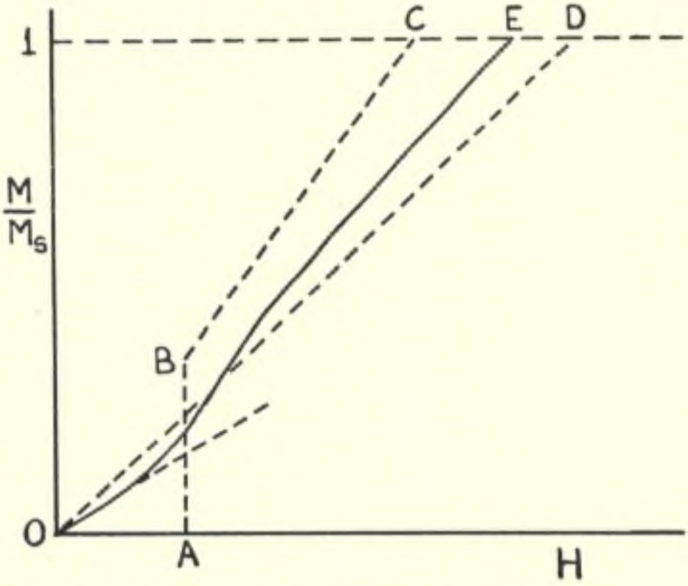

Fig. 4. — Variation schématique de la susceptibilité d'une substance polycristalline.

8. APPLICATION DE LA THÉORIE AUX CHLORURES ANHYDRES

Nous examinerons dans ce chapitre l'interprétation des propriétés magnétiques des chlorures anhydres des métaux de transition et tout particulièrement de $NiCl_2$, $CoCl_2$ et $FeCl_2$. Leurs propriétés avaient paru assez singulières pour que de Haas et Schultz (19) d'une part, Becquerel d'autre part (1) les aient considérés comme constituant une classe spéciale de substances magnétiques : les *métamagnétiques.* A la lumière de nos connaissances actuelles, il semble qu'il s'agisse d'un antiferromagnétisme particulièrement bien caractérisé.

On constate d'abord que $NiCl_2$, $CoCl_2$, $FeCl_2$ présentent respectivement à 50° K, 25° K, 24° K, le maximum de susceptibilité caractéristique des substances antiferromagnétiques. A ce maximum correspond très exactement (20) (53° K, 24,9° K, 23,5° K) une anomalie

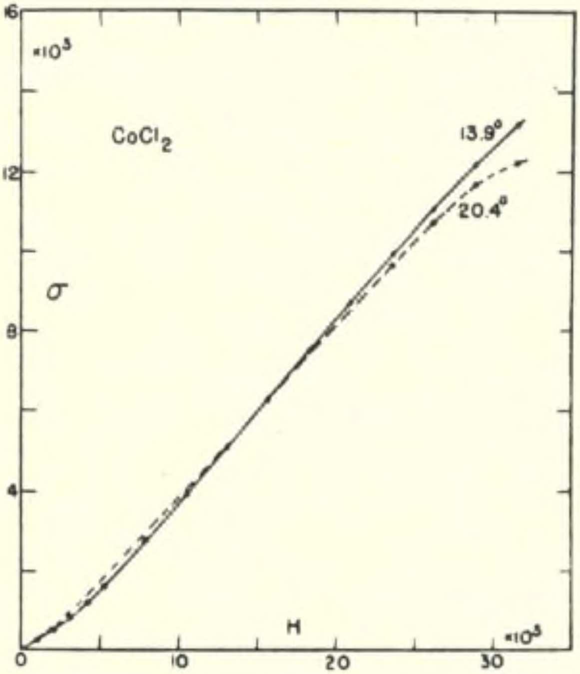

Fig. 5. — Aimantation de $CoCl_2$, d'après Starr, Bitter et Kaufmann. — *Physical Review* (1940), t. 58, p. 977 (Starr, Bitter et Kaufmann).

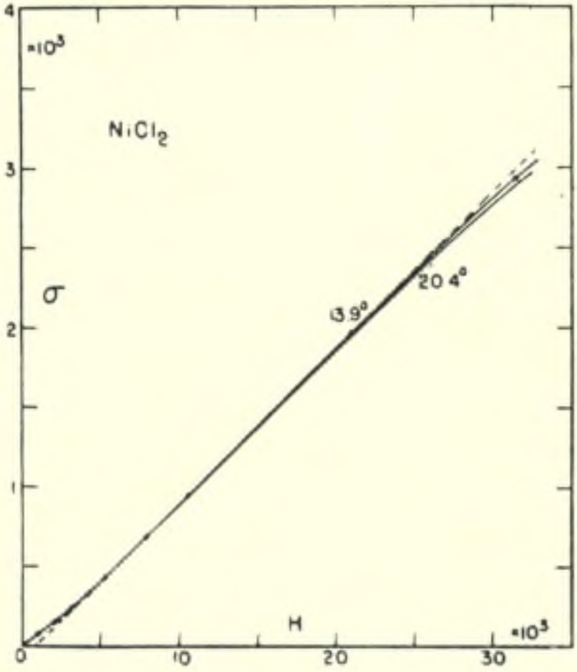

Fig. 6. — Aimantation de $NiCl_2$, d'après Starr, Bitter et Kaufmann. — *Physical Review* (1940), t. 58, p. 977 (Starr, Bitter et Kaufmann).

de chaleur spécifique, semblable à celle des antiferromagnétiques classiques (MnO, FeO, etc.). En ce qui concerne plus spécialement $NiCl_2$ et $CoCl_2$, de Haas et Schultz ont montré qu'à 20° K, c'est-à-dire au-dessous de la température de transition, leur susceptibilité magnétique commençait par varier paraboliquement en fonction de la température puis devenait constante au-dessus de 20.000 Oe. Ces observations sont entièrement confirmées par celles de Starr, Bitter et Kaufmann (21) (fig. 5 et 6). Tous ces auteurs ont été frappés par l'allure rectiligne de la courbe d'aimantation dans les champs élevés et l'absence d'indice de saturation, pour des aimantations qui, dans le cas de $CoCl_2$, atteignent pourtant les 2/3 de la saturation absolue correspondant à tous les ions magnétiques présents. Cette allure rectiligne correspond précisément, comme nous l'avons vu plus haut, à ce qu'on doit attendre d'une substance antiferromagnétique : les courbes de Starr et d'autres correspondent d'ailleurs exactement à la courbe de notre figure 4. La courbure initiale, observée dans les champs inférieurs à 10.000 Oe, correspond donc au découplage de la direction d'antiferromagnétisme par rapport à la direction privilégiée initiale.

L'étude des courbes expérimentales permet d'obtenir l'ordre de grandeur des différentes quantités mises en jeu. D'après la pente de la courbe $J = f(H)$ et l'estimation de la valeur du champ critique, on trouve pour ces deux chlorures des valeurs de $\underline{n}$ respectivement égales à 10 et à 2,6 et des valeurs de K voisines de 1.10^6 erg/mole et de 2.10^7 erg/mole, à la température de 14° K. A 20° K pour $CoCl_2$, K n'est plus que de 0,5 à $1,10^7$ erg/mole. Rappelons à ce propos que les constantes d'anisotropie des métaux ferromagnétiques purs varient de 3.10^6 erg/mole pour le nickel à 2.10^8 erg/mole environ pour le cobalt; les valeurs que l'on obtient ici sont du même ordre de grandeur.

Si l'on admet au surplus que les moments à saturation de $NiCl_2$ et de $CoCl_2$ sont respectivement voisins de 2 et de 3 μ_B, on trouve pour ces deux chlorures des valeurs de $\underline{r}$ voisines de 0,0016 et de 0,054.

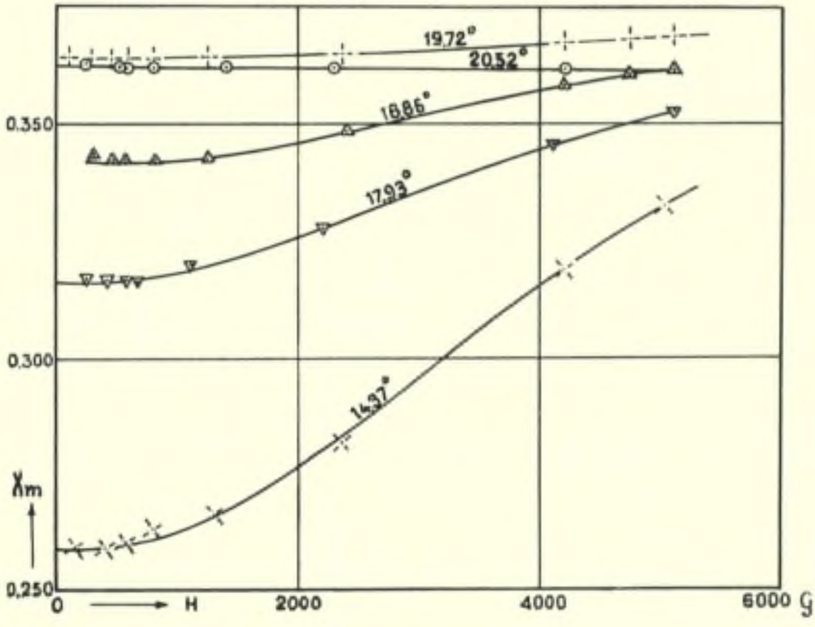

Fig. 7. — Susceptibilité du chlorure mixte $CoCl_2$. $MgCl_2$, d'après de Haas et Schultz. — *Journal de Physique*, (1939), t. 10p. 7 (De Haas, Schultz).

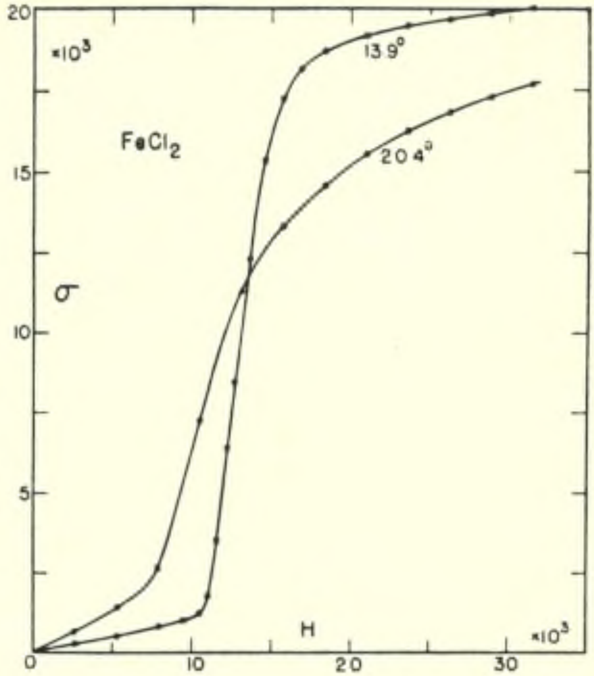

Fig. 8. — Aimantation de $FeCl_2$, d'après Starr, Bitter et Kaufmann. — *Physica Review* (1940), t. 58, p. 977 (Starr, Bitter et Kaufmann).

On obtient une preuve supplémentaire du caractère antiferromagnétique de ces substances et du rôle du découplage de la direction d'antiferromagnétisme, en examinant la variation avec le champ de la susceptibilité du chlorure mixte $CoCl_2$. $MgCl_2$ étudiée par de Haas et Schultz (fig. 7) : on remarquera l'analogie étroite de la courbe correspondant à la température de 14,37° K avec la courbe moyenne déduite de notre théorie, correspondant à une inclinaison comprise entre 50° et 60° de la direction d'antiferromagnétisme sur la direction du champ (fig. 3).

Les chiffres cités plus haut montrent que la valeur de $\underline{r}$ augmente beaucoup en passant du nickel au cobalt : il faut donc s'attendre pour le fer à des valeurs de l'ordre de grandeur de l'unité et par conséquent à des courbes d'aimantation ressemblant à celle de la figure 2*c*, avec une discontinuité ou tout au moins une variation très rapide de l'aimantation l'amenant à une valeur voisine de la saturation. C'est bien exactement ce qui se passe pour le chlorure ferreux, à la température de 13,9° K pour lequel, d'après les observations de Starr et autres (21), l'aimantation moléculaire passe très rapidement, comme le montre la figure 8, de 1.500 à 20.000 au voisinage de 12.000 Oe, alors que la saturation absolue doit être de l'ordre de 22.000 (4 magnétons de Bohr). En admettant que cette courbe corresponde au cas $r = 1/2$ avec un champ réduit critique $h = 1$, on en déduit que $\underline{\mathrm{n}}$ doit être voisin de 1 et K voisin de $1{,}3.10^8$ ergs/mole. Ces deux valeurs se rangent d'une manière très satisfaisante à côté des valeurs obtenues pour $CoCl^2$ et $NiCl^2$.

Il faut faire remarquer cependant que la susceptibilité de $FeCl_2$ semble tendre au zéro absolu vers une valeur voisine de zéro tandis que la théorie approchée du ferrimagnétisme donne les 2/3 de la susceptibilité maximale. Mais Starr, Bitter et Kaufmann font remarquer qu'il s'agit de cristaux en paillettes dont les plans tendent, dans les conditions de préparation des ampoules étudiées, à s'aligner à angle droit du champ appliqué. Il est donc possible que dans ces échantillons la direction d'antiferromagnétisme soit partout assez voisine de la direction du champ, au lieu d'être orientée au hasard. On s'explique ainsi d'une part que la susceptibilité tende vers zéro au zéro absolu, comme la susceptibilité parallèle, et d'autre part que la discontinuité d'aimantation à 12.000 Oe soit aussi brutale.

Les autres chlorures de la série sont aussi manifestement des substances antiferromagnétiques. $CuCl_2$ possède à 70° K environ un maximum de susceptibilité et sa susceptibilité au zéro absolu tend vers une valeur sensiblement égale aux 2/3 de la susceptibilité maximale. La valeur correspondante de $\underline{\mathrm{n}}$ est voisine de 400. $CrCl_2$ possède également à 40° K environ un maximum de susceptibilité qui donne $n = 70$. Seul $MnCl_2$ suit la loi de Curie jusqu'à des températures extrêmement basses et un point de Curie paramagnétique à — 3°3 d'après Starr et autres (21) et à + 3° ou + 4° K d'après Lallemand (24) et Fehrenbach (25). On peut donc en conclure que la valeur de n est sensiblement nulle.

9. VARIATION DES INTERACTIONS EN FONCTION DU NUMÉRO ATOMIQUE

Le tableau suivant rassemble les valeurs de $\underline{n}$ et de K obtenues pour les différents chlorures du type MCl_2 :

TABLEAU

M	Cu	Ni	Co	Fe	Mn	Cr
K	?	1.10^6	2.10^7	$1,3.10^8$	?	? erg/mole
n	400	10	2,6	1	0	70
n'	20?	86	23	27	0	—20

Ces dichlorures sauf $CuCl_2$ possèdent la structure en couches parallèles de $CdCl_2$. Les ions M forment des réseaux hexagonaux à deux dimensions dans lesquels chaque ion possède six voisins. Ces plans sont séparés par deux couches d'atomes de chlore. La structure antiferromagnétique la plus vraisemblable consiste donc en couches successives d'atomes M aimantés alternativement en sens inverse. Nous devons compléter la description des interactions en représentant les interactions d'échange à l'intérieur d'une même couche par un champ moléculaire de coefficient $\underline{n'}$; ce champ est donc égal à $1/2n'M$. Dans la région paramagnétique, située au-dessus du point de transition, le champ moléculaire agissant sur la substance, pour une aimantation moléculaire égale à J, vaut.. $(n'—n)J/2$ de sorte que $n'—n$ est lié à la constante de Curie C et au point de Curie paramagnétique Θ par la relation de $(n'—n)C = 2\Theta$. Des expériences de Starr, Bitter et Kaufmann, on déduit les valeurs de n' données dans le tableau précédent. La diminution régulière de $\underline{n'}$ quand on passe du nickel au chrome est assez frappante ainsi que le minimum accusé de $\underline{n}$ au voisinage du manganèse et du fer. Le champ moléculaire de coefficient $\underline{n}$ s'exerce par l'intermédiaire des atomes de chlore; il s'agit donc d'actions de superéchange. Il est assez intéressant de constater que le signe de ces interactions, signe négatif, se conserve du cuivre jusqu'au chrome, alors que le nombre des électrons de la couche 3d varie de 8 à 3.

On remarquera, en examinant le tableau précédent, que seul le chlorure de cuivre constitue une exception à la régularité d'évolution de n et n' en fonction du numéro atomique : il ne faut pas s'en étonner car, comme nous l'avons déjà dit, sa structure cristalline est différente. On remarquera en outre que les interactions entre les couches, proportionnelles à $-n$, sont importantes : elles sont en fait du même ordre de grandeur que les interactions à l'intérieur d'une même couche. Or les couches magnétiques sont séparées par deux couches de chlore : il s'agit donc ici de superéchange d'ordre supérieur du type M-Cl-Cl-M. En réalité, on connaissait déjà dans les ferrites (12) un superéchange du type M-O-O-M, relatif aux interactions entre les atomes placés sur les sites tétraédriques (sites A) mais l'interprétation en était moins directe que dans le cas des chlorures où elle s'impose de toute évidence.

Indépendemment de toute considération théorique, ces faits montrent qu'il existe des actions importantes d'orientation entre atomes magnétiques qui s'exercent à travers deux atomes intermédiaires. D'autre part, on ne voit pas a priori pourquoi de telles actions ne s'exerceraient pas également dans les métaux ferromagnétiques. Si c'était le cas, au lieu des 8 ou 12 voisins dont on tient compte conventionnellement, il faudrait en envisager 100 ou 150, peut-être davantage. On s'expliquerait alors pourquoi l'approximation du champ moléculaire de Weiss, très apte par sa nature même à traduire les effets d'un grand nombre de voisins, représente beaucoup mieux les phénomènes que les premières approximations des théories plus rigoureuses. On s'expliquerait aussi pourquoi l'étude précise des effets de fluctuations au voisinage du point de Curie, dans le cas du nickel, indique comme probable (22) le rôle d'un très grand nombre de voisins : de l'ordre de plusieurs centaines.

10. LE CAS DE QUELQUES AUTRES SUBSTANCES

D'autres substances ont été rangées parmi les métamagnétiques comme le chlorure chromique $CrCl_3$. Ce corps possède une anomalie de chaleur spécifique au voisinage de 17° K mais la susceptibilité continue à augmenter à mesure que la température s'abaisse : à 13,9°K, elle est pratiquement infinie dans les champs faibles, mais diminue avec le champ à l'inverse de ce qui se passe pour les chlorures. Un tel comportement correspond au cas où $\underline{n}'$ est nettement positif et $\underline{n}$ nul. On obtient ainsi des plans ferromagnétiques aimantés à saturation et indépendants les uns des autres. Or, la théorie des ondes de spin montre qu'un ferromagnétique à deux dimensions ne présente pas de rémanence : l'expérience montre en effet que $CrCl_3$ ne présente pas de rémanence appréciable. L'énergie à dépenser pour aimanter à saturation ce corps est de l'ordre de 1.10^8 erg/mole, à 13,9° K; si on suppose qu'il s'agisse d'un corps uniaxe composé de cristallites orientés au hasard on en déduit une constante K d'anisotropie égale aux 3/2 de la valeur précédente, soit $1,5.10^8$ erg/mole, en accord d'ordre de grandeur avec les résultats obtenus plus haut.

Le carbonate ferreux CO_3Fe, ainsi que des espèces minérales voisines, mésitite, sidérose, etc., possèdent des propriétés analogues (1), (15) à celles des chlorures également explicables par un antiferromagnétisme.

Le cas de CrF_3 et CO_3Co est un peu différent. Il s'agit selon Bizette (15) de substances dont les points de Curie paramagnétiques sont situés respectivement à —133° K et —63° K mais qui deviennent ferromagnétiques vers 70° K et 15° K. Il s'agit probablement alors de ferrimagnétisme : il existe en effet une analogie extrêmement étroite entre l'allure de la variation thermique de la susceptibilité de ces deux substances et celle du chromite CoO, Cr_2O_3 étudié par McGuire, Howard et Smart (23), qui possède un point de Curie paramagnétique à —700° K et qui devient ferromagnétique à 110° K. Dans ce chlorure, l'hyperbole caractéristique de la variation thermique de l'inverse de la susceptibilité des ferrimagnétiques dégénère pratiquement en deux droites mais cette hyperbole est particulièrement belle pour le chromite voisin CuO, Cr_2O_3 .

En résumé, la théorie classique de l'antiferromagnétisme permet de rendre compte d'une manière très satisfaisante de la plupart des propriétés magnétiques des substances qui avaient été rangées jusqu'ici dans la catégorie des corps métamagnétiques. Il reste simplement à rendre compte maintenant des faibles rémanences et thermorémanences que présentent ces substances.

11. ÉPAISSEUR ET ÉNERGIE DE PAROI DANS LES SUBSTANCES ANTIFERROMAGNÉTIQUES

Nous nous proposons dans ce chapitre d'examiner d'un peu plus près la question des parois dans une substance antiferromagnétique, mais pour simplifier et préciser le problème, nous nous limiterons au cas d'une substance uniaxe dans laquelle les ions magnétiques sont répartis en couches successives, d'équidistance $\underline{d}$, perpendiculaires à l'axe. Nous supposons que les interactions sont positives à l'intérieur d'une même couche et négatives entre deux couches successives. Enfin, nous admettons que l'axe est la direction privilégiée d'antiferromagnétisme. Dans un cristal donné, nous pouvons répartir d'une manière définitive en deux sous-réseaux A et B tous les sites occupés par les atomes magnétiques : le sous-réseau A est constitué par les sites appartenant aux couches d'ordre impair, le sous-réseau B par les autres. Lorsque l'ordre antiferromagnétique s'établit dans la substance, par exemple en la refroidissant à travers la température de transposition T_n, deux situations locales peuvent se présenter : l'une est la situation Q dans laquelle les atomes du sous-réseau A ont l'orientation + et les atomes du sous-réseau B l'orientation —, l'autre est la situation Q′, dans laquelle ce sont les atomes du sous-réseau B qui ont l'orientation +. Nous avons donc affaire à deux catégories Q et Q′ de domaines élémentaires séparés par des parois présentant quelques analogies avec les parois à 180° des substances ferromagnétiques, parois qui séparent deux domaines aimantés en sens inverse.

Avant d'aller plus loin, il convient de remarquer qu'il y a beaucoup de chances pour que les dimensions des domaines d'espèce Q ou Q′ soient beaucoup plus petites que les dimensions des domaines ferromagnétiques. La raison en est l'absence complète du rôle unificateur du champ magnétique dû à ce que les aimantations spontanées des domaines sont nulles et à ce que les deux espèces de domaines Q et Q′ possèdent dans un champ magnétique le même potentiel thermodynamique. Par contre, les forces perturbatrices, qui tendent à empêcher la fusion de deux domaines d'espèces différentes en un seul domaine plus grand, sont du même ordre de grandeur qu'il s'agisse de ferromagnétiques ou d'antiferromagnétiques. En effet, ces forces perturbatrices sont les forces magnétocristallines ou magnétoélastiques qui gênent au même titre la libre rotation de la direction d'antiferromagnétisme ou de la direction de l'aimantation spontanée : or l'étude des chlorures nous a montré que la constante K d'anisotropie possédait effectivement des valeurs comparables dans les antiferromagnétiques et dans les ferromagnétiques. Nous devons donc nous attendre à ce qu'il existe beaucoup de domaines et beaucoup de parois dans une substance antiferromagnétique.

Dans une substance uniaxe, il convient de distinguer deux espèces de parois de séparation entre les domaines : celles qui sont parallèles à l'axe et celles qui sont perpendiculaires. Les parois parallèles ne possèdent aucune propriété remarquable aussi nous n'en parlerons pas davantage. Il n'en est pas de même des parois perpendiculaires dont nous allons nous occuper maintenant. Si le passage d'un domaine Q à un domaine Q′ s'effectue brutalement, on voit immédiatement que, de part et d'autre du plan idéal qui constitue la paroi, les deux couches adjacentes possèdent des aimantations spontanées de même sens. Cette situation correspond à une augmentation de l'énergie potentielle égale à $nM^2d/2V$ erg/cm², en utilisant les mêmes notations qu'au début de ce travail et en désignant par V le volume moléculaire. Or le passage de la situation Q à la situation Q′ consiste essentiellement en une rotation de 180° de la direction d'antiferromagnétisme et la paroi idéale que nous avons considérée plus haut est donc caractérisée par une brusque rotation de la direction d'antiferromagnétisme effectuée en passant d'une couche à la suivante. Comme nous allons le montrer, l'énergie de paroi est moindre si cette rotation de 180° est répartie sur p couches successives, c'est-à-dire sur une épaisseur $D = pd$. Dans ce cas en effet l'énergie d'échange est égale à $\pi^2 nM^2d^2/8VD$ à laquelle il convient d'ajouter une énergie magnétocristalline égale à KD/2V. La somme de ces deux énergies est minimum pour :

$$D = \frac{\pi M}{2}\left(\frac{n}{K}\right)^{1/2}$$

ou encore approximativement $D = 2dr^{-1/2}$ avec les mêmes notations que plus haut.

Pour les trois chlorures étudiées plus haut, $NiCl_2$, $CoCl_2$, $FeCl_2$, les épaisseurs D de paroi ainsi obtenues sont respectivement égales à $50d$, $5d$ et $3d$ où d est voisin de 5,8 Å. L'énergie de paroi E s'en déduit aisément. On trouve :

$$E = \frac{KD}{V} = \frac{2Kd}{Vr^{1/2}} \text{ erg/cm}^2 . \qquad (6)$$

Pour ces trois exemples, on trouve des énergies de paroi qui sont respectivement de l'ordre de 0,075, 0,15 et 0,5 erg/cm². Elles sont notablement plus faibles que les énergies de paroi des ferromagnétiques ordinaires mais c'est tout à fait normal puisque les énergies d'échange sont plus faibles.

12. MOMENT MAGNÉTIQUE DE PAROI DANS LES ANTIFERROMAGNÉTIQUES

Revenons maintenant à la paroi idéale infiniment mince séparant deux domaines d'espèces Q et Q′ : nous avons déjà fait remarquer que les deux couches d'atomes magnétiques adjacentes à la paroi possédaient des aimantations spontanées de même sens. Supposons maintenant que nous déplacions la paroi parallèlement à elle-même d'une distance $\underline{d}$ égale à l'équidistance des couches : il suffit pour cela de faire passer l'une des couches adjacentes de la situation Q à la situation Q′, c'est-à-dire de renverser son aimantation. Dans cette opération nous avons fait varier le moment magnétique total du système d'une quantité $2m$, en désignant par $\underline{m}$ le moment magnétique par cm² d'une couche, soit $m = \mathrm{M}d/\mathrm{V}$. Tout se passe donc comme si la paroi possédait un moment magnétique superficiel égal à $\underline{m}$, susceptible d'être retourné sans dépense d'énergie. Dans cet exemple nous constatons que le moment $\underline{m}$ possède deux orientations stables antiparallèles séparées par une barrière de potentiel de hauteur égale à $\mathrm{K}d/\mathrm{V}$. Le champ coercitif correspondant est de l'ordre de K/M.

En réalité, comme nous l'avons montré dans le paragraphe précédent, les parois possèdent une certaine épaisseur D et il en résulte que la véritable valeur m' du moment magnétique superficiel de paroi est inférieure à m. En admettant qu'à l'intérieur de la paroi, les aimantations spontanées des couches atomiques successives tournent toujours du même angle quand on passe d'une couche à la suivante, on peut montrer que m' est de l'ordre de m/p, en désignant par p le nombre de couches constituant la paroi. Mais cette approximation, qui donne un résultat convenable dans le calcul de l'énergie de paroi, n'est pas légitime ici. Quand on tient compte de l'allure réelle de la rotation de l'aimantation spontanée à l'intérieur de la paroi, on trouve que m' devient une fraction négligeable de m dès que p dépasse 5 ou 6.

On peut donc s'attendre, lorsque *p* est petit, c'est-à-dire lorsque *r* est grand, à ce que les substances antiferromagnétiques possèdent un petit moment magnétique permanent provenant de la présence des parois. Il est donc possible que le moment permanent des substances métamagnétiques, tout au moins dans le cas de $FeCl_2$ et $CoCl_2$, provienne de ce mécanisme.

Il est également possible que les cristaux de ces substances contiennent des dislocations, qui, en créant des discordances dans l'alternance des plans aimantés antiparallèlement, donnent naissance à un moment magnétique permanent : chaque ligne de dislocations correspondrait ainsi à une ligne de doublets magnétiques.

13. LE CAS DU SESQUIOXYDE DE FER $Fe_2O_3\alpha$

L'interprétation de ses propriétés magnétiques pose des problèmes difficiles : expérimentalement, les courbes d'aimantation dans les champs magnétiques forts s'expriment (26) par la relation :

$$\sigma = \sigma_s + \chi_s H \,, \tag{7}$$

qui exprime la superposition d'un paramagnétisme de susceptibilité χ_s et d'un ferromagnétisme d'aimantation spontanée σ_s .

La variation thermique de la susceptibilité est analogue à celle d'un antiferromagnétique dont le point de transition serait situé à 675° C. Cette interprétation est confirmée par la présence d'une anomalie de chaleur spécifique à cette température ainsi que par la diffraction des neutrons qui a permis en outre de déterminer (27) la structure des sous-réseaux. On sait enfin qu'au dessous de 250° K la direction d'antiferromagnétisme est celle de l'axe ternaire et qu'au dessus de 250° K elle est située dans le plan de base (28). Tout ceci est très normal.

L'interprétation de σ_s est beaucoup plus difficile à cause de la petitesse même de cette quantité qui est de l'ordre de 0,01 μ_B à 0,02 μ_B pour une molécule Fe_2O_3 alors que le moment magnétique total des ions ferriques présents est de 10 μ_B. L'expérience met en outre en évidence une forte anisotropie (28) : les plus grandes valeurs de σ_s s'observent dans les directions du plan de base et au-dessus de 250° K. Enfin σ_s disparaît à 675° C. On a pensé un moment (26) que l'existence de ce ferromagnétisme était liée à la présence d'impuretés ou à des défauts de stoechiométrie mais cela paraît maintenant peu probable.

Il semble assez séduisant de rapprocher les propriétés de Fe_2O_3 de celles des substances métamagnétiques examinées plus haut et d'en attribuer le ferromagnétisme au moment magnétique propre des parois de séparation entre les domaines élémentaires antiferromagnétiques et au rôle des dislocations : en effet, aussi bien pour les métamagnétiques que pour Fe_2O_3, σ_s est une fraction faible et du même ordre de grandeur que l'aimantation à saturation absolue. Cependant, ces théories du ferromagnétisme parasite semblent dans un état trop primitif pour qu'il soit possible de discuter dès maintenant ces hypothèses d'une manière valable : il faut attendre de nouveaux progrès théoriques et expérimentaux.

14. PROPRIÉTÉS MAGNÉTIQUES DES FERRITES DE TERRES RARES

Ces ferrites, de formule générale $Fe_2O_3 \,.\, M_2O_3$ où M est un élément de la série des terres rares, ont été découverts à Strasbourg par Forestier (29) et ont fait l'objet d'une première étude de Guiot-Guillain (30). L'étude des propriétés magnétiques a été ensuite reprise d'une façon plus précise à Grenoble (31).

D'une manière générale, les propriétés magnétiques de ces composés correspondent, comme dans le cas de $Fe_2O_3\alpha$, à la superposition d'un ferromagnétisme, d'aimantation spontanée égale à σ_s, et d'un ferromagnétisme de susceptibilité égale à χ_s. Les figures 9 et 10 résument les résultats obtenus dans l'étude de la variation thermique de ces deux quantités, pour les trois ferrites correspondant à M = Gd, Dy et Fr. La variation thermique de l'aimantation spontanée σ_s est très remarquable : σ_s, d'abord très grand à la température de l'hydrogène liquide, décroît ensuite très rapidement, s'annule à une certaine température T_c qui dépend beaucoup de la nature de M, croît à nouveau, passe par un maximum et s'annule enfin définitivement en un point de Curie situé au voisinage de 550° K. Il semble même que, pour le ferrite de gadolinium, σ_s réapparaisse encore au-dessus. La température T_c est certainement une tempéra-

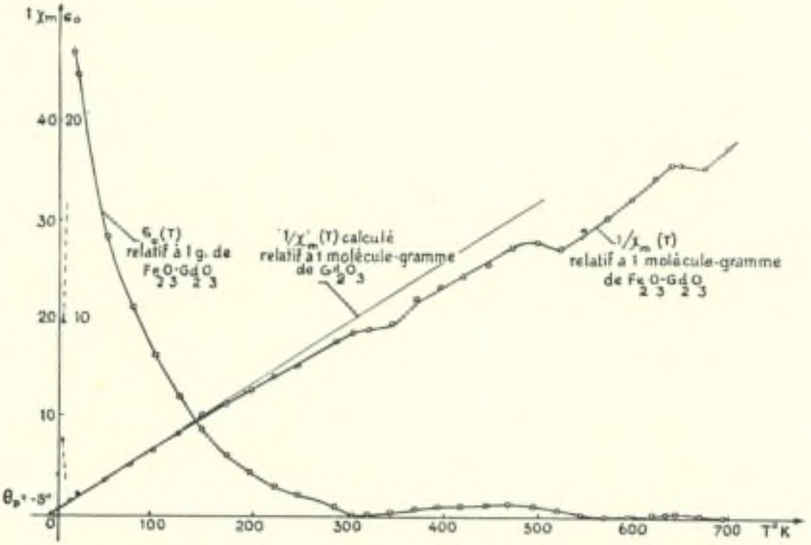

Fig. 9. — Aimantation spontanée et susceptibilité de Fe_2O_3 . Gd_2 O_3 , d'après Pauthenet et Blum. — *Comptes rendus Ac.Sc.* (1954), t. 239, p. 33 (Pauthenet, Blum).

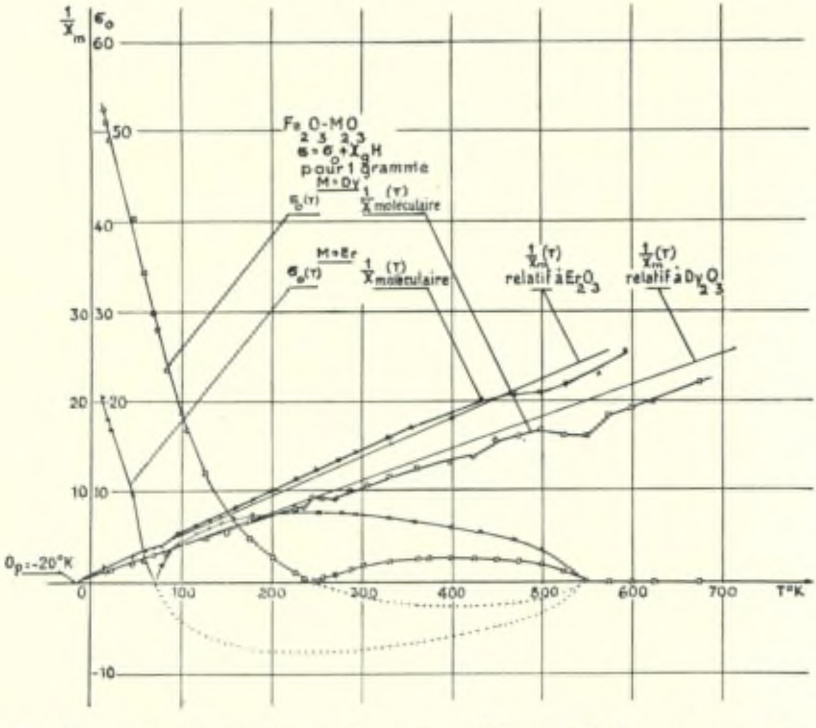

Fig. 10. — Aimantation spontanée et susceptibilité de Fe_2O_3 . Dy_2O_3 et de $Fe_2O_3Er_2O_3$, d'après Guiot-Guilain, Pauthenier et Forestier. — *Comptes rendus Ac. Sc.* (1954), t. 239, p. 155 (Guiot-Guillain, Pauthenier et Forestier).

ture de compensation : l'expérience montre en effet qu'en communiquant, en dessous de T_c, une certaine aimantation rémanente à des ferrites de dysprosium et d'erbium, et en chauffant ensuite la substance dans un champ magnétique nul, on observe une inversion spontanée de l'aimantation.

Il convient sans doute d'interpréter ce phénomène selon le mécanisme que nous avions envisagé autrefois dans la théorie du ferrimagnétisme (12) : il s'agit de deux sous-réseaux aimantés spontanément en sens inverse et évoluant d'une manière différente en fonction de la température : la température de compensation est celle où les aimantations spontanées des deux sous-réseaux sont égales et opposées. La présence d'une température de compensation prouve donc qu'il existe au moins deux sous-réseaux. Rappelons que ces ferrites constituent le second exemple de substances présentant une inversion thermique de l'aimantation spontanée : le premier exemple, un ferrite de lithium et de chrome avait été trouvé par E.W. Gorter (32).

Quand à la susceptibilité paramagnétique χ_B , elle prend des valeurs qui, quoique plus grandes, sont voisines de la susceptibilité des ions M^{+++} correspondants, dans les oxydes M_2O_3 ou dans les sels.

15. APPLICATION DE LA THÉORIE DU CHAMP MOLÉCULAIRE

L'ensemble de ces propriétés complexes peut s'interpréter en première approximation en supposant qu'il existe dans ces ferrites deux sous-réseaux, couplés par un champ moléculaire négatif (33).

Un premier sous-réseau A est formé par les ions Fe^{+++} et possède des propriétés magnétiques voisines de celles de $Fe_2O_3\alpha$; son aimantation J dans un champ H peut donc s'écrire sous la forme :

$$J_A = \sigma_A + \underline{a}H .$$

Le point de Curie σ_A serait situé au voisinage de 550° K; les valeurs de $\underline{a}$ seraient de l'ordre de grandeur de la susceptibilité de Fe_2O_3 .

Le second sous-réseau B est formé par des ions M^{+++} faiblement couplés entre eux et possède ainsi des propriétés presque purement paramagnétiques, caractérisables par une susceptibilité b donnée par une loi de Curie-Weiss :

$$b = \frac{C}{T - nC}$$

où C est la constante de Curie des ions M^{+++}.

Si nous supposons maintenant qu'il existe entre les deux sous-réseaux des interactions susceptibles d'être représentées par un champ moléculaire de coefficient m, on obtient une aimantation totale résultante de la forme (7) avec des coefficients donnés par les relations :

$$\sigma_s = \sigma_A \frac{1 + bm}{1 - abm^2} \quad ; \quad \chi_s = b + \frac{a(1 + bm)^2}{1 - abm^2} \quad , \tag{8}$$

Ces deux formules permettent de rendre compte assez bien des résultats expérimentaux. En particulier, la température de compensation T_c correspond au moment où l'égalité :

$$1 + bm = 0$$

est satisfaite. En outre, on conçoit que si a est petit, χ_s soit voisin de b.

Il est possible de déduire de la comparaison des formules (8) avec les résultats expérimentaux, les valeurs des paramètres σ_A et a, caractéristiques des propriétés magnétiques du sous-réseau A. On trouve alors que, pour une molécule, σ_A est de l'ordre de 0,5 μ_B pour le ferrite de gadolinium et de l'ordre de 1,5 μ_B pour les deux autres ferrites, tandis que la saturation absolue correspond à 10 μ_B. Il semble ainsi que l'analogie des propriétés magnétiques du sous-réseau A avec celles de $Fe_2O_3\alpha$ soit une analogie de pure forme, tout au moins en ce qui concerne l'aimantation spontanée. En effet celle-ci est de l'ordre du dixième de la saturation totale pour le sous-réseau A et de l'ordre du millième pour $Fe_2O_3\alpha$. Il n'est pas certain que le mécanisme soit le même dans les deux cas.

L'analyse des résultats expérimentaux montre aussi que les interactions entre les moments magnétiques des ions M sont négatives : la température de Curie, égale à nC, est en effet de — 8° K pour Gd et de — 20° K pour Dy et Er. Conformément à ce que nous savons des corps antiferromagnétiques, il faut s'attendre à ce qu'aux températures faibles devant $-n$C, le sous-réseau B se fragmente en deux sous-réseaux B′ et B″ antiparallèles. L'expérience montre qu'il se passe bien quelque chose de ce genre : en effet, comme le montre la figure 9, l'aimantation spontanée et la susceptibilité magnétique du ferrite de gadolinium diminuent toutes les deux quand on passe de 14° K à 4° K : il existe donc entre ces deux températures un maximum de susceptibilité. Le réseau du ferrite de gadolinium est donc, au dessous de 4° K, décomposé en 4 sous-réseaux au moins : les deux réseaux secondaires B′ et B″ des ions Gd et au moins deux sous-réseaux secondaires pour les ions Fe.

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Discussion du rapport du Prof. NÉEL

Mr. Pauli. — I believe that the concept of a « molecular field » proportional to the magnetization is hiding rather than explaining the problem of ferromagnetism or antiferromagnetism, as it cannot be directly connected to a model for the interaction of magnetic atoms.

As is well known, the exchange interaction between atoms seems to be a satisfactory model for such phenomena. Moreover, in the case of ferromagnetism in the neighbourhood of saturation at deep temperatures, the spin waves of F. Bloch are a good approximation to evaluate the consequences of the model. The situation, however, is different for antiferromagnetic substances where even the ground state is not exactly known. Nevertheless, different authors, more recently P.W. Anderson tried to apply the spin wave method also to the antiferromagnetics. The approximations involved in this method have been investigated more closely by Kuba and Schafroth. But I would like very much to know the opinion of the experts, whether they consider the spin wave method really to be justified in the case of antiferromagnetism.

M. Néel. — Il n'est pas toujours facile d'exploiter les résultats que fournit une théorie rigoureuse. En ce qui concerne par exemple la loi d'approche à la saturation des substances paramagnétiques en fonction de la température, les travaux expérimentaux des physiciens de Strasbourg avaient conduit à la loi empirique :

$$J = J_s (1 - aT^2 + ...) \tag{1}$$

en désaccord d'ailleurs avec les résultats de la théorie du champ moléculaire. La théorie des ondes de spin permit alors à Bloch de montrer que la loi d'approche devait prendre la forme :

$$J = J_s (1 - aT^{3/2} - bT^{5/2} + ...) \tag{2}$$

Beaucoup de travail fut dépensé pour montrer que les résultats expérimentaux étaient mieux représentés par (2) que par (1), sans que les conclusions fussent très décisives. En fait, on montra bientôt qu'il fallait, dans la loi (2) intercaler un terme en T^2 entre les termes en $T^{3/2}$ et $T^{5/2}$ et finalement, Schafroth a donné très récemment à la loi d'approche théorique la forme :

$$J = J_s\,(1 - aT^{6/4} - bT^{7/4} - cT^{8/4} + \ldots\ldots) \,. \tag{3}$$

Mr. Fröhlich. — I also have difficulties in seeing how the spin wave concept can be applied to the case of anti-ferromagnetism until one finds the wave function of the ground state.

Mr. Mott. — Does one know whether the specific heat of any antiferromagnetic material behaves at low temperatures like e^{-T}/θ , or like $T^{3/2}$ (or T^2) by which I mean some form that would indicate a spin wave?

M. Gorter. — A Leyde, on a fait des calculs sur l'antiferromagnétisme dans des cristaux, qui sont plus ou moins pareils à ceux qui sont présentés par M. Néel. Je ne signalerai que quelques points d'intérêt où les calculs se touchent :

Je désire d'abord attirer l'attention sur une petite différence de nomenclature. Kramers, Hulthén, Van Vleck et après eux, d'autres auteurs, parmi lesquels nous nous comptons, ont appelé antiferromagnétiques, d'une part, les interactions tendant à orienter deux spins égaux voisins dans des directions opposées, et, d'autre part, les substances où ces interactions provoquent la formation de sous-résaux de magnétisation égale mais opposée. Néel, au contraire, admet dans les antiferromagnétiques des interactions qui tendent à rendre parallèles les spins d'un seul sous-réseau.

M^me^ van Peski a fait des calculs sur des substances de symétrie rhombique et cubique au zéro absolu de la température. Elle fait ressortir que l'on peut introduire les anisotropies de façons différentes. Pour le cas rhombique, on peut écrire avec Néel et Yosida :

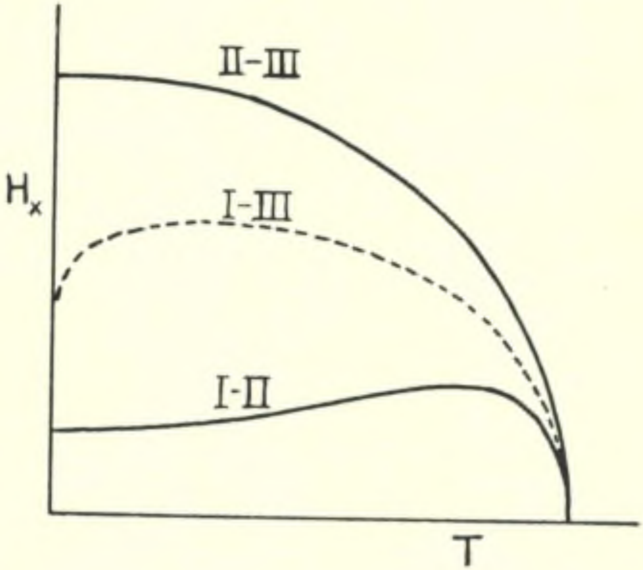
$$2U = n(M_o M^1) - KM_x^2 - KM_x'^2$$

mais aussi bien avec Haantjes et moi-même :

$$2U = n_x M_x M'_x + n_y M_y M'_y$$

si l'on choisit les coefficients n, K, n_x et n_y de manière à rendre identiques les deux expressions pour des champs faibles (où $M' \approx -M$) ils ne le sont plus pour les champs forts où la transition entre les configurations II et III se présente (où $M' = M$). Dans le cas d'une symétrie cubique, on a même le choix entre trois expressions équivalentes. Ces calculs, qui paraîtront bientôt, donnent plus de détails que ceux de Néel, mais ils se bornent à des anisotropies faibles.

Enfin, je signale que dans le diagramme H_x : T d'une substance rhombique, la courbe d'équilibre entre les configurations I et III (calculée par Garrett) et celle entre II et III se dessinent facilement entre $T = 0$ et la température de Néel. Elles présentent des transitions du second ordre dans la nomenclature d'Ehrenfest. La transition entre les configurations I et II, au contraire, est du premier ordre et donne donc une chaleur de transition. Il semble que, dans le cas d'une anisotropie faible, les trois courbes se terminent au point $H = 0$; $T = T_N$ et qu'en conséquence, la transition I-III ne se réalise pas.



Mr. Gorter. — Recently, four or five papers have appeared on antiferromagnetism at very low temperature according to the spin wave theory. They lead to the conclusion that, in a anisotropic substance, the specific heat should vanish not with a power of T, but exponentially. Likewise, the spontaneous magnetisation of the sublattices and the susceptibility should exponentially approach their values at $T = 0$. This general result is confirmed by the data, but the numerical agreement with some of the computations is only mediocre.

M. Néel. — Les deux formes d'énergie indiquées par le professeur Gorter, à savoir, en se limitant à deux dimensions :

$$2U = n_x M_x M'_x + n_y M_y M'_y \tag{1}$$

$$2U = n(MM') - KM_x^2 - KM'^2_x \tag{2}$$

paraissent correspondre à des mécanismes différents : la forme (1) correspondant à la superposition d'interaction d'échange et d'interactions dipolaires magnétiques, la forme (2) à des interactions d'échange superposées à un couplage avec le réseau cristallin. A priori, on peut utiliser l'une ou l'autre. C'est à l'expérience de décider.

Mr. Fröhlich. — I would like to show that the band model of the electronic state in solids may be wrong in certain cases. Consider a single crystal of N atoms each having one *s*-electron. Then an energy band containing 2N levels (2 for spin) to be filled by N electrons. Hence the system as a whole, forms a continuum of $\binom{2N}{N} \approx 2^{2N}$ states. If we imagine the lattice distance $\underline{a}$ to become very large, then, this is wrong. For, in this case, the lowest state is one in which there is one electron per atom, which is 2^N fold degenerate, and $2^N \ll 2^{2N}$. If $\underline{a}$ is very large, then, the interaction between neighbours is negligeable. To obtain all 2^{2N} states, it is necessary to consider also states with two electrons (and none). However, if $a \rightarrow \infty$ then these states containing (negative and positive) ions have a higher energy than the 2^N states mentioned before. If $\underline{a}$ is reduced, then interaction between neighbours becomes of importance leading to a splitting of degenerate states, and at sufficiently small all 2^{2N} states should form a continuum, and the band model becomes valid. These considerations show that the correlation energy may be of great importance in investigating the distribution of energy levels.

Mr. Aigrin. — It may be worth to add just one or two remarks to Prof. Fröhlich's comments. As the atoms will get closer together, coming in from infinite separation, the 2^N lowest lying states are not expected to widen much into a band, since they only differ by spin reversals. But the next higher set of levels will be much widened. As soon as one of the levels in this set is below those of the first set, then the ground state will be a conductive one, so the transition from insulator to metal will be very sudden.

It would be very interesting if these phenomens could be studied in impurity states in semiconductors. Unfortunately the impurity atoms are spaced at random, so that the density of levels in any calculated band extends to infinite negative energies (with an exponentially decreasing level density). Thus some of the levels in the second set of Prof. Fröhlich will always, at any concentration, lie below the non-ionic levels, and band theory whould then be valid at all distances. This is connected with the finite probability for finding large clusters of impurity atoms, which may have vanishing ionization energy. This, of course, spoils any possibility to study experimentally dilute lattices in the form of impurity atoms in semiconductors.

Superconductivity

by **H. FRÖLICH**

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In order to explain the properties of the superconductive state clearly the model of a metal in which the electrons are treated as free has to be refined by introduction of an interaction between conduction electrons. Until recently it was generally accepted that this interaction does not involve the ionic lattice. In 1950, however, it has been shown (Fröhlich, 1950) that the interaction of the electrons with the lattice vibrations, first introduced by F. Bloch (1928) in order to account for ordinary conductivity, necessarily leads to an interaction between electrons carried by the field of lattice displacements. Thus without introducing a new hypothesis it had been shown that an interaction between electrons exists which hitherto had been (unjustifiably) neglected. It could be shown that the dynamic part of this interaction may strongly influence the properties of electrons near the Fermi surface provided a certain interaction parameter F satisfies $F > 1$. The value of this F could be estimated from the magnitude of ordinary conductivity at high temperatures, and it was found that for most superconductors F is larger than for normal metals, a property closely connected with the empirical fact that at high temperatures most superconductors are poor normal conductors. The conjecture was, therefore, advanced that the dynamic part of the interaction of electrons through the field of lattice, displacements is responsible for superconductivity. This conjecture was soon afterwards strongly supported by the discovery of the isotope effect.

Attempts to give a satisfactory treatment of this interaction in the case $F > 1$ lead to serious mathematical difficulties (e.g. Bardeen, 1951; Fröhhlich, 1953) which have not been overcome yet. The case $F < 1$ has, however, now been treated in a satisfactory way (Buckingham and Schafroth, 1954). It leads essentially to an increase in electronic level density at low temperatures as compared with that at high temperatures. As a result the electronic specific heat at low temperatures should be of the form $C_v = \gamma T$ with a factor γ, however, which is larger than the γ_0 that would be obtained by using numbers of free electrons deduced from high temperature measurements (e.g. from Hall effect).

In view of the above-mentioned difficulties it has so far been impossible to decide whether the interaction mentioned actually yields the main properties of superconductors. It might be argued that although the isotope effect proves the importance of the lattice displacements, the whole model normally used in the electron theory of metals is inadequate. It must be remembered in this connection that this theory is based on a hypothesis rather than on a derivation from first principles.

It seems of importance, therefore to find a limiting case of the usual model which permits a simple treatment of the electron-lattice interaction and still shows features of a superconductor. This has been carried out recently (Fröhlich, 1954*a*). A one dimensional model with cyclic boundary condition (i.e. a circle) has been used in the case of fairly strong interaction. Such a model is unrealistic, of course, because there is no magnetic field in one dimension, and for other reasons which make it difficult to generalize a one dimensional case. If the basic assumptions are correct, however, then one should expect that such a model still shows some of the main features of superconductors namely the absence of scattering of electrons on impurities or lattice defects, at the absolute zero of temperature, $T = 0$, and the replacement of the linear electronic specific heat by a term proportional to exp (— const/T). For sufficiently large values of the interaction constant F it has been found that these properties actually follow from the model. Moreover the solutions can be described in terms of simple physical concepts. It is found that the lattice displacement of a certain wave number W_0 is strongly excited and hence leads to an energy gap in the single electron spectrum. The value of W_0 is chosen such as to make the number of states below the gap equal to the total number of electrons. It is necessary of course that $2\pi/W_0$ is a length smaller than the lattice distance. In the lowest state of the system then the single electron spectrum is similar to that in an insulator, but there exists a very essential difference : the whole system has still one degree of freedom available which enables the electrons together with the lattice displacement W_0 to move through the lattice with a velocity v

which is quantized according to $v = 2\pi n\hbar/(\mathrm{L}m)$, ($\mathrm{L}$ = length of the region, $n = 0, \pm 1, \pm 2$ ....), provided v is sufficiently smaller than the velocity of sound s. Such an organized motion can be described as the electrons riding on the wave of the lattice displacement. For the total electronic density fluctuates with the period W_0, and the position of these fluctuations is fixed relative to the lattice displacements only and not relative to the lattice points as it is in an insulator. The gap leads to a stabilization of this configuration and prevents elastic scattering of electrons by impurities or lattice defects. The specific heat clearly behaves as $\exp(-\mathrm{W}/k\mathrm{T})$ as $\mathrm{T} \rightarrow 0$ if W is the gap width.

With rising temperature some electrons get excited across the gap. This reduces the magnitude of the periodic density fluctuations of the electrons which in turn reduces the amplitude of the lattice displacement and hence the gap width. A situation arises similar to that in systems showing second order transitions, and in fact Kuper (1954) has shown that this type of transition actually follows.

Clearly as mentioned before the one dimensional case has many unrealistic features. It is important to emphasise, however, that it does not involve any new assumptions but represents a limiting case of the ordinary model of free electrons, interacting with the lattice displacements. It is of interest and importance to notice that the use of a self consistent method which converges in this limit suppresses the isotope effect because such a method does not take account of dynamic properties. It is from an analysis of this feature, I think, that further progress will be made. Let us classify first the theoretical results obtained so far :

Approximation :	Perturbation theory Dynamic terms	Self consistent field method Strong coupling, one dimensional
Result :	Isotope effect	Superfluidity, specific heat.

Thus perturbation theory, as in many other cases, gives a correct order of magnitude of the energy of the ground state, but probably leads to very bad wave functions. The self consistent field (Hartree) method suppresses dynamic features of the interaction, but yield some detailed properties in a satisfactory way. This method cannot, however, be applied in a straight-forward way to three dimensions. Clearly it is desirable to find a new method which forms a link between the two methods discussed so far, e.g. by introducing dynamic features into the self consistent field method. A similar problem arises in the much simpler case of a single electron in an ionic crystal (cf. Fröhlich, 1954*b*). Here two methods have been applied, both using the variational principle so that it is easily possible to decide which one yields the better energy. A dimensionless coupling parameter α can be introduced such that $\alpha < 1$ permits application of perturbation theory. It is then found that even for $\alpha > 1$ is the energy of the ground state obtained in perturbation theory a good approximation although the wave functions may be very incorrect. This energy depends on the dynamic properties of the lattice, and only when $\alpha \gtrsim 10$ is it superseded by the quasi-static Hartree method. The latter was first applied by Landau to the present case. It requires a total wave function which is a product of an electronic function and a lattice function. The electron function is concentrated around a given point, say $\underline{r}_0$, in space, and the lattice displacement is produced in a self consistent way by the electron cloud, considered as a static charge distribution.

The concentration of the electron function around a fixed point r_0, is, of course, undesirable because the probability of finding the electron in the lattice must be independent of the position. It might seem at first that this could easily be remedied by overlapping many such wave packets but this is not so. In fact the difficulty is very essentially connected with the Hartree method. To show this consider the very simple case of a two body problem e.g. the hydrogen atom. Neglecting spin this is a problem in six degrees of freedom. For an exact treatment one introduces centre of gravity and relative coordinates, $\underline{r}_c$ and $\underline{r}$ respectively (three degrees of freedom each). The wave function is a product of the form :

$$\Psi = e^{i\underline{k}\cdot\underline{r}_c}\,\psi(\underline{r})$$

where $\psi(\underline{r})$ is negligibly small if $\underline{r}$ is large compared with the Bohr radius. This means that the probability of finding the electron at a large distance from the proton is negligibly small. Nevertheless the probability of finding the electron (proton) at a given position irrespective of the position of the proton (electron) is a constant because of the dependence of Ψ on $\underline{r}_e$. In Hatree approximation, however, one would have :

$$\Psi_{\mathrm{H}} = \psi_e(\underline{r}_e - \underline{r}_0)\psi_p(\underline{r}_p - \underline{r}_0)$$

where both functions ψ_e and ψ_p, depending on the coordinates of the electron and the proton repectively, are large only near an arbitrary point $\underline{r}_0$. It would be incorrect to mutiply this function by $\exp(i\underline{k} \cdot \underline{r}_0)$ and to treat $\underline{r}_0$ as a further available variable because all six degrees of freedom have already been made use of. This difficulty is closely connected with the fact that in the wave function Ψ_{H} the total momentum of the system is not on principal axes in contrast to the exact solution Ψ ; in other words the motion of the two particles does not show any correlation.

To go back to the case of the single electron in an ionic crystal, clearly it would be desirable to introduce a centre of gravity coordinate $\underline{x}_{\mathrm{L}}$ of the lattice displacements (it better would be differently denoted because lattice waves do not carry momentum, *cf.* Fröhlich, 1954*b*, § 3). This might make it possible to introduce a motion of $\underline{x}_{\mathrm{L}}$ relative to the electron although the remaining degrees of freedom (of the lattice) could be treated in a self consistent way. Such a treatment would reintroduce some dynamic features into a self consistent field method. It remains to be seen whether this programme can be realized.

Finally I should like to suggest certain experiments which would be helpful in connection with the questions discussed here. As mentioned before, Buckingham and Schafroth (1954) have shown that for normal metals the electronic specific heat is of the form $C_v = \gamma T$ where the factor γ is larger than γ_0 which is the value which would follow with the use of the number of free electrons measured at high temperature (e.g. from the Hall coefficient). Furthermore γ increases with increasing interaction constant F until F reaches a critical value $F = 1$ when the metal becomes a superconductor and a qualitative change in C_v takes place. It would be of interest to investigate the electronic specific heat, together with the Hall coefficient at high temperatures, for alloys whose composition can be changed gradually leading from normal to superconductive materials. It should be expected then that F should increase as the composition is approached in which the material becomes superconductive. On the other hand γ/γ_0 is a direct measure for F. Alloys with the required compositional properties have been found by B. Matthias (1953).

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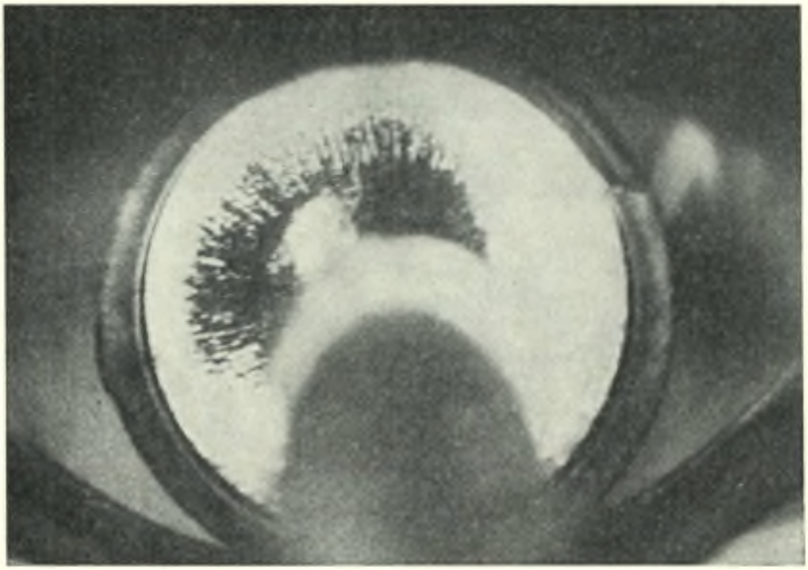

Fig. 1

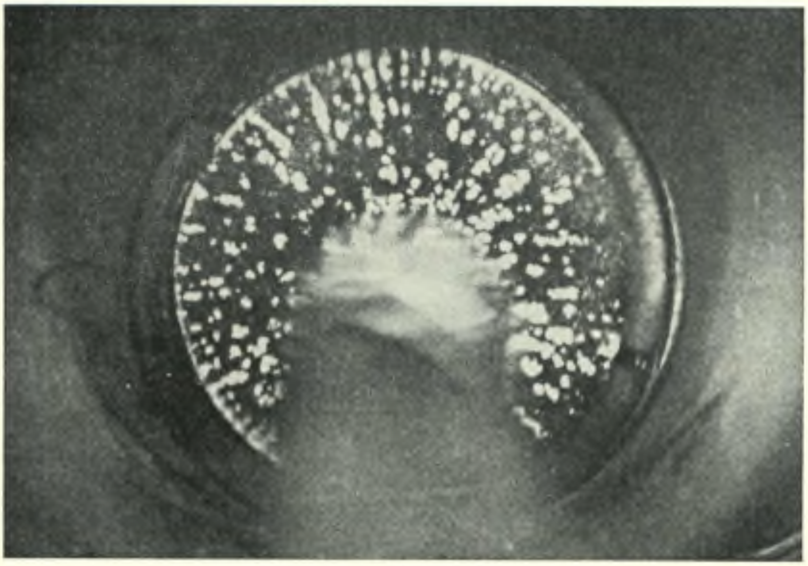

Fig. 2

Discussion of FRÖLICH's report

Mr. Gorter. — 1) Does your one-dimensional model really give superfluidity in the sense that the introduction of irregularities does not give rise to any scattering or reflection?

2) The energy difference ΔU_o between the normal and the superconducting state at $T = 0$ is only of the order of $10^{-6}eV$. If this is the order of magnitude of the energy gap for single electrons, one should expect notable excitation of electrons at temperatures 1 000 times below the transition temperature.

3) In connection with this, I should like to inquire also about Dr. Kuper's calculation mentioned in your report. Has he found a sharp transition temperature for a 1-dimensional model?

Mr. Fröhlich. — 1) The gap in the one-electron spectrum prevents elastic scattering of individual electrons provided the velocity of flow of the system as a whole is small compared with the velocity of sound.

2) We can write $\Delta U_o \simeq n(kT_c)^2/\zeta$ where T_c is the transition temperature, ζ is an energy of the order of 1 electron-volt, and n is the total number of electrons. The energy gap is, however, *not* of the order $\Delta U_o/n = (kT_c)^2/\zeta$ but of the order kT_c, as required. It means that only nkT_c/ζ electrons near the top of the Fermi surface have their energy depressed by about kT_c each.

3) The calculation is not exact near the transition temperature.

Mr. Pippard. — I am not very happy about the point of view, to which both Prof. Fröhlich and Prof. Gorter appear to subscribe, that superconductivity originates in the appearance of current carriers which are not scattered by lattice irregularities. In the first place, I do not believe that in a 2- or 3-dimensional model it will be possible to avoid scattering entirely. If an organised current can flow in any one direction then there is equal facility for the current to flow in any other direction; the collective motion of electrons and lattice waves may be influenced much less than single electrons by irregularities, but surely the influence cannot ever be vanishingly small, so that some measure of resistance will still remain, even though it may be exceedingly minute. In a superconductor, however, particularly a singly-connected superconductor, the resistance is known to vanish entirely. I feel therefore that the Meissner effect is the essential property which gives rise to perfect conductivity.

Even if the conductor were perfect, in the sense of possessing an infinite free path for the current carriers, its behaviour, as Lindhard has pointed out, would still be very different from that of a superconductor. For a system of free electrons, if they are not at rest at the moment of application of a magnetic field, cannot confine the field to a thin penetration layer. The field slowly enters the material, the time taken for it to reach a depth α being proportional to α^3; this is very different from what is observed with superconductors. Here again we have to invoke the Meissner effect to explain how the field is kept out, and if we do invoke the Meissner effect we do not have to worry any more about lattice collisions. For the Meissner effect shows the stable state of the superconductor to be one in which the applied magnetic field is excluded; this being so, electron-lattice collisions can only help to maintain the currents which keep the field out — they can never lead to any destruction of the stable state.

Mr. Fröhlich. — I think Prof. Gorter's question was not meant to imply that a perfect conductor is equal to a superconductor but rather that one of the properties of a superconductor must be the inability of irregularities to reduce a current (by elastic scattering of individual electrons). The fact which Pippard mentions, namely that a gas of free electrons — none of which is scattered by irregularities — does not form a superconductor, is no doubt correct but not relevant to the present discussion. The one-dimensional case, discussed here, does at $T = 0$ not contain any free electrons but might rather be described as a huge molecule consisting of all the electrons of the metal. A single electron can then clearly not be scattered because to do so would require first to detach it from the « molecule » which requires an energy of the order of the gap width.

I agree that irregularities do influence the behaviour of electrons even in a superconductor. But to describe this influence as elastic scattering would imply that the electrons are free.

In the two or three dimensional case singly connected superconductors are essentially different from multiply connected ones because only the latter can exhibit a permanent current without an external magnetic field. Even a normal singly connected diamagnetic metal carries in the presence of an external magnetic field currents which are not destroyed by scattering of electrons. It would, therefore, require a special proof that the properties (permanent current) of multiply connected superconductors follow simply from the magnetic behaviour of singly connected ones.

Mr. Meissner. — I should like to mention the following : We have made experiments on the contact-resistance between two lead cylinders. The thickness of the non-superconducting layer was more than 10^{-3} mm. But currents up to 10 amps. went without resistance through the contact. Do you not believe that it is difficult to understand this result on the basis of your theory?

Mr. Fröhlich. — I am afraid the theory is not sufficiently developed to consider this question.

Mr. Pines. — I should like to bring up for further discussion one of the questions raised by Prof. Fröhlich, namely, whether a free electron-phonon interaction model is adequate for a treatment of superconductivity. It seems to me that the adequacy of such a model depends on whether long wavelength or short wavelength electron-interactions are of primary importance in superconductivity. (Let me define long wavelength as wavelengths greater than approximately three interatomic distances.) If the long wavelength interactions are dominant, then the simple model is probably adequate, since ion-core effects are then not of primary importance.

This is presumably a question which can be decided experimentally. Thus, the thin film experiments indicate that wavelengths greater than 100 Å are not of great importance. On the other hand, I believe that recent experiments suggest that short wavelengths effects are not essential — that the superconducting properties are not sensitive to the structure of the ion-core. There is perhaps another argument in favor of the long wavelength interactions. We know that the motion of electrons is correlated over quite long distances in the superconducting state, and it is perhaps more satisfactory aesthetically to picture this as arriving from a long wavelength interaction.

Mr. Fröhlich. — The question whether long or short wavelength phonons are of principal importance is, no doubt, of great importance but I cannot say anything definite about it at the moment. In the one-dimensional case short waves only are essential but there is no reason why this should hold for 2 or 3 dimensions. One might be tempted to suggest that the wavelength is of greatest importance for which $hs/\lambda = kT_c$ (S = velocity of sound, T_c = transition temperature). If $s = 3 \times 10^5$ cm/sec, $T_c = 7^o$, then :

$$\lambda = \frac{6.6 \times 10^{-27} \times 3 \times 10^5}{7 \times 1.4 \times 10^{-16}} = 2 \times 10^{-6} \text{ cm},$$

i.e. a very long wave.

Mr. Mendelssohn. — As for the influence of size on superconductivity, it seems that all the available information points to a radical change of superconducting properties as dimensions of the order of the penetration depth are approached. Some of these changes indicate that, in order to maintain superconductivity, fairly large aggregates of electrons must co-operate.

Regarding the relation between normal conductivity and superconductivity, the greater simplicity of the latter phenomenon is, of course, already shown by the lower entropy. However, there is also the greater symmetry of the electrodynamic equations in the case of a superconductor.

In an old theory of Kronig's, which assumed a three-dimensional electron lattice passing through the ionic lattice, it turned out that such a process was, owing to the potential barrier, impossible. However, it would work in the one-dimensional case. Perhaps Prof. Fröhlich could say what prospect exists that in his theory superconductivity will not vanish when one goes from the one-dimensional to the three-dimensional case.

Mr. W. Meissner. — *Neue Messungen über magnetische Eigenschaften der Supraleiter.* Frühere Versuche verschiedener Forscher über die Abhängigkeit der Eindringtiefe eines longitudinalen Magnetfeldes in cylindrische Supraleiter in Abhängigkeit von der Feldstärke ergaben folgendes : Schon von Feldstärken an, die erheblich kleiner als die Hälfte der kritischen Feldstärke bei der Messtemperatur sind, steigt die Eindringtiefe ziemlich stark an. Désirant und Shoenberg, die, z.B. eingehende Versuche hierüber anstellten, führten als Grund für dies unerwartete Ergebnis folgendes an : Entweder ist es durch Unregelmässigkeiten an der Oberfläche des Supraleiters bedingt oder es liegt an dem Einfluss der Enden des nicht unendlich langen Zylinders. In solchen Zylindern muss ja schon aus thermodynamischen Gründen nach von Laue beim Übergang zur Supraleitung ein komplizierter Zwischenzustand eintreten, in dem einzelne kleine supraleitende Bereiche vorhanden sind.

Um zunächst einmal den letzteren Umstand zu beseitigen, habe ich durch meinen Mitarbeiter Herrn Näbauer Versuche an Bleitoroiden anstellen lassen, in denen durch eine entsprechende Bewicklung ein in sich geschlossenes circulares Magnetfeld erzeugt wird, so dass keine Wirkung von Enden eintreten kann. Das Bleitoroid war ein Einkristall in Form eines Hohlcylinders von etwa 10 cm Höhe, 5 cm Durchmesser und 0,15 cm Wandstärke. Um Oberflächenwirkungen möglichst herabzusetzen, war die Oberfläche so lange elektrolytisch poliert, bis keine polykristallinen Stellen mehr festzustellen waren. Der Hohlzylinder hatte 3 übereinanderliegende Wicklungen von teils mehreren tausend Windungen, zu deren Herstellung eine besondere Wickelmaschine konstruiert und gebaut wurde. Um ohne Anwendung von Elektronenröhren-Verstärkern grosse Messgenauigkeit zu erzielen, wurde ein von meinem Mitarbeiter, Herrn Doll auf meine Veranlassung gebautes, unter Verwendung von neuzeitlichen Materialen höchst empfindlich gemachtes Panzergalvanometer verwendet. Es wurde sowohl für ballistische wie für flux-metrische Messungen benutzt.

Die Versuchsanordnung zeigt Fig. 1 in der die übereinanderliegenden Wicklungen der Deutlichkeit nebeneinander gezeichnet sind. Die innerste Wicklung S_1 aus Kupferdraht dient zur ballistrischen oder fluxmetrischen Messung des Magnetflusses $\varnothing$ und damit der Eindringtiefe δ die mittlere Wicklung P_1 zur Erzeugung eines kleinen kommutierbaren Messfeldes (Kommutator K), die äusserste Wicklung M zur Erzeugung eines konstanten Magnetfeldes. P_1 und M waren im Gebiet des flüssigen Heliums auch bei stärkeren Magnetfeldern supraleitenden Blei-Wismut-Draht. Das wie das Bleitoroid im flüssigen Helium liegende Kompensationstoroid aus Isolier-

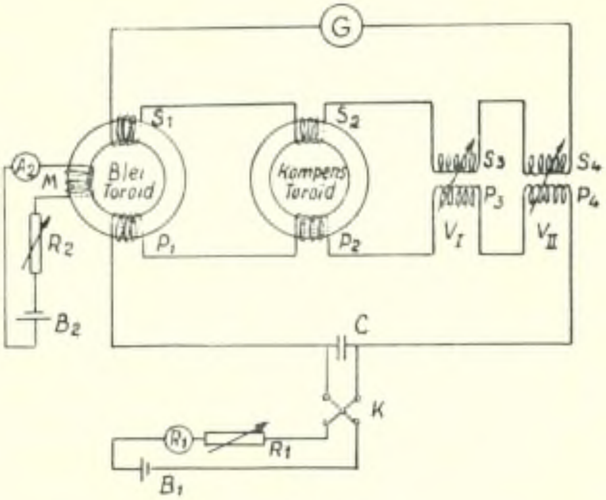
G
S1
S2
S3
S4
P1
P2
P3
P4
A2
M
Blei Toroid
Kompens Toroid
R2
B2
C
K
R1
R1
B1
VI
VII

Fig. 1

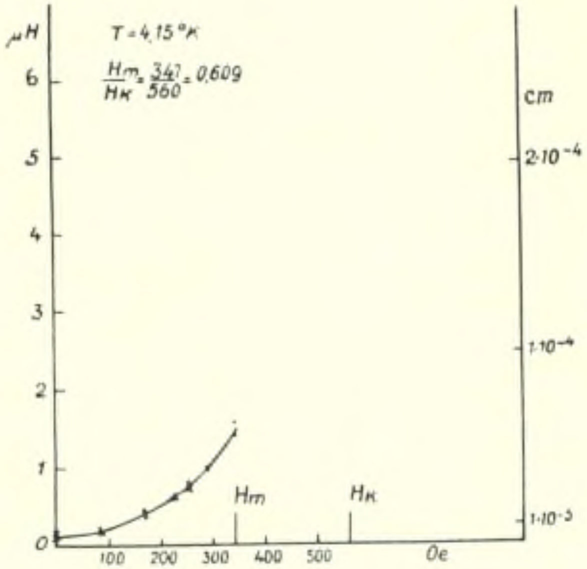
μH
T = 4,15 °K
Hm/HK = 341/560 = 0,609
cm
2·10⁻⁴
1·10⁻⁴
1·10⁻⁵
6
5
4
3
2
1
0
100
200
300
400
500
Hm
HK
Oe

Fig. 2

material mit Wicklungen S_2 und P_2 dient dazu, den Hauptteil des zwischen Blei und Wicklung S_1 liegenden Flusses wegzukompensieren. Der Rest wird durch die hintereinander geschaltete Gegeninduktionstüten V_1 und V_2 beseitigt. Diese werden auch bei den ballistischen Messungen verändert, bis der Galvanometeranschlag wieder null war (Nullmethode).

Die Ergebnisse der zunächst angestellten ballistischen Messungen (Mess-strom durch K kommutiert) zeigen die Figuren 2 bis 6 :

Fig. 2. — Steigerung des Magnetfeldes H bis auf 0,609 H_t und Wiederabschwächen auf null. Wie bei früheren Forschern starkes Anwachsen der Eindringtiefe δ (rechte Ordinate), etwa auf das zehnfache. Keine Hysteresis. Ordinate gibt nur die *Änderung* von δ auch in den folgenden Figuren.

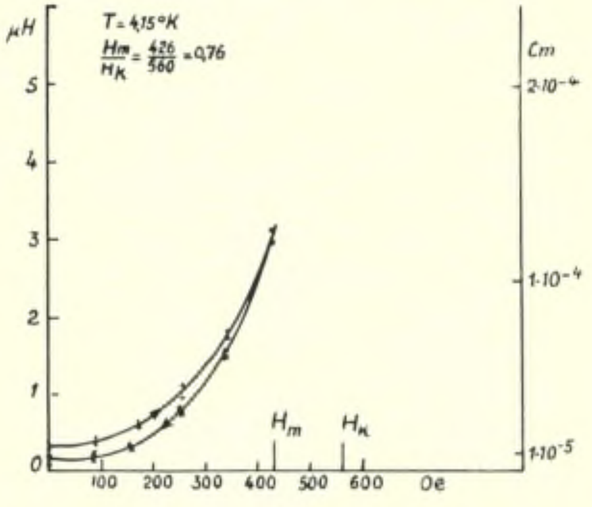

Fig. 3

Fig. 3. — Steigerung von H auf 0,76 H_t. Weiteres Ansteigen von δ und Hysteresis.

Fig. 4. — Steigerung von H auf 0,91 H_t. Noch stärkere Hysteresis.

Fig. 5 I. — Bis H = 75 Oe bleibt δ konstant. Vor der Messung H = 0.

Fig. 5 II. — Vor der Messung H_t einmal überschritten. Wegen Stark streuender Messpunkte H 60mal kommutiert von H_t an mit auf null abnehmender Stärke. Sodann Aufnahme von 5 II.

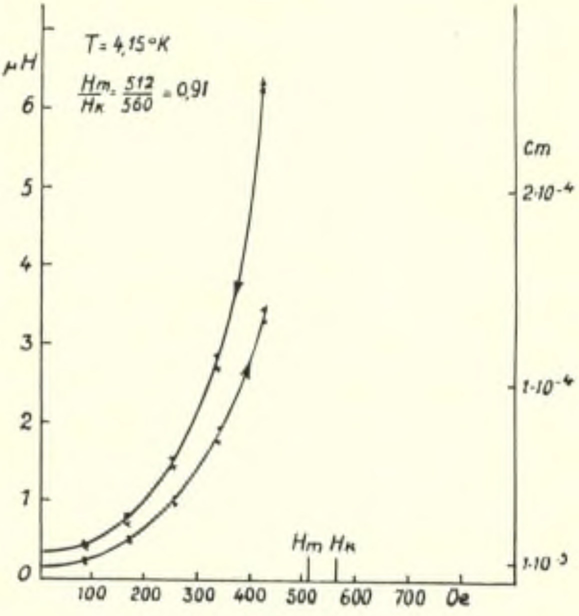
T = 4,15 °K
$\frac{H_m}{H_K} = \frac{512}{560} = 0{,}91$
μH
0
1
2
3
4
5
6
100
200
300
400
500
600
700
Oe
Hm
Hк
cm
1·10⁻⁵
1·10⁻⁴
2·10⁻⁴

Fig. 4

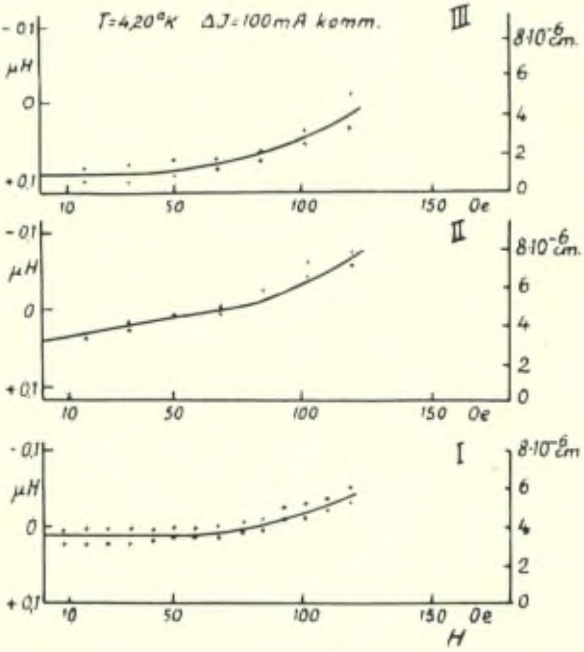
T = 4,20 °K ΔJ = 100 mA komm.
III
II
I
μH
- 0,1
0
+ 0,1
10
50
100
150
Oe
H
0
2
4
6
8·10⁻⁶ cm

Fig. 5

Fig. 5 III. — Entmagnetisierung mit 50-periodischem Wechselstrom mit von H_t stetig abnehmender Amplitude. Sodann Aufnahme 5 III, die fast 5 I gleicht.

Weiter wurde der Einfluss der Grösse des mit Kommutator K von ΔH auf $-\Delta H$ kommutierten Messfeldes untersucht. Ergebnis Fig. 6, Abscisse ΔH, Ordinate δ (Änderung der Eindringtiefe).

Fig. 6 I. — H stets null. ΔH wächst von 0 an. Nur bis $\Delta H = 15$ Oe konstante Eindringtiefe.

Fig. 6 II. — Vor Beginn der Messung H einmal grösser als H_t, dann $H = 0$. Eindringtiefe δ stark angewachsen und mit ΔH stark steigend.

Fig. 6 III. — Zunächst 60-maliges Kommutieren von H mit abnehmenden Wert von H_t auf null. Dann Messung, Eindringtiefe erheblich kleiner als in 6 II.

Fig. 6 IV. — Zuerst « Entmagnetisierung » mit 50 periodischem Wechselstrom. Dann Aufnahme von 6 IV, besser als 6 I.

Die ballistrische Methode is danach unzweckmässig. Die Eindringtiefe ist sehr stark von der Vorgeschichte abhängig. Offenbar sprechen die noch vorhandenen kleinen Unregelmässigkeiten an der Oberfläche (Abweichungen von völliger Ebenheit) eine Rolle. Das Feld wird durch kleine Krümmungsradien verzerrt und dringt dort ein.

Die Messungen wurden nun weiter ohne Verwendung des Messstromes als fluxmetrische Messungen fortgesetzt, wobei das Panzergalvanometer mit starker Dämpfung als Fluxmeter benutzt wurde. Die Änderung seines Ausschlages bei Änderung von H ist ein Mass für die Änderung des Flusses. Auf die Ergebnisse bei kleinen Feldänderungen sei hier nicht eingegangen, sondern nur noch auf die Aufnahme der Übergangskurve. Ergebnisse Fig. 7 und Fig. 8.

Fig. 7. — Abscisse Zeit. Ordinate Magnetfluss $\varnothing$ durch Bleitoroid. Photographische Registrierungen. Jede Teilfigur entspricht einem Einschalten und Ausschalten von H, angefangen mit $H > H_t$. Die Zahlen geben die Feldstärken an der inneren und äusseren Oberfläche des Hohlzylinders. Bei den mittleren unterstrichenen Zahlen ist nur an der inneren Oberfläche $H > H_t$, nicht an der äusseren. Bei den folgenden Teilfiguren $H < H_t$. Einstellzeit des Galvano-

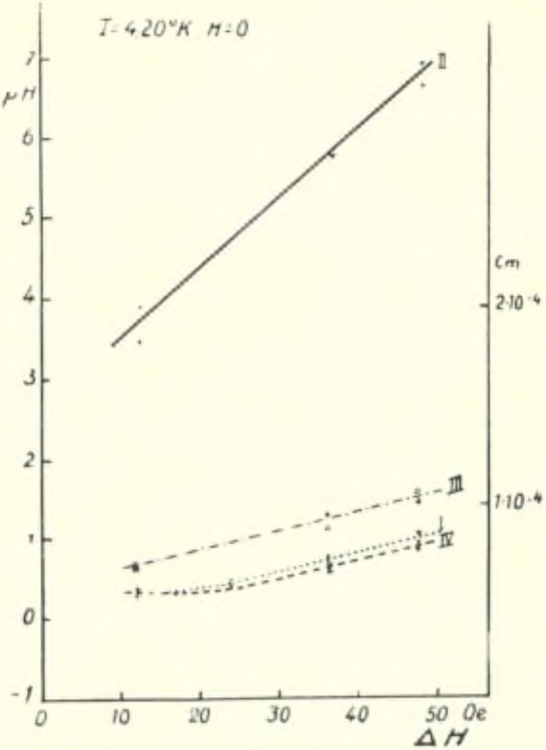
T=4.20°K H=0
μH
7
6
5
4
3
2
1
0
-1
0
10
20
30
40
50 Oe
ΔH
cm
2·10⁻⁴
1·10⁻⁴
II
III
I
IV

Fig. 6

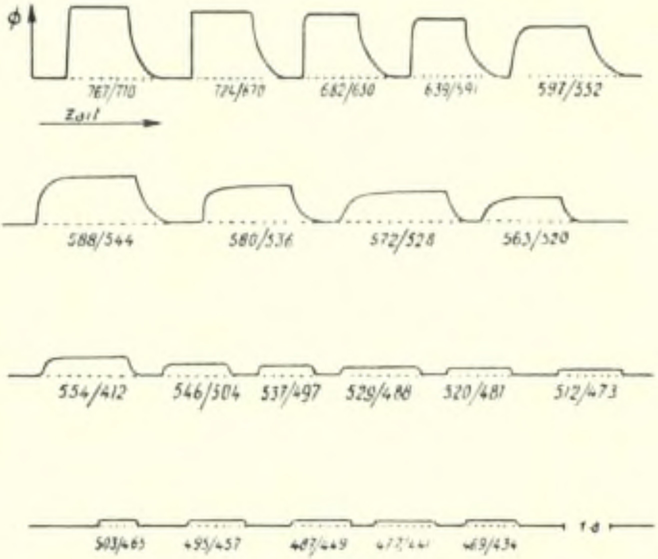
ϕ
767/710
724/670
682/630
639/591
597/552
Zeit
588/544
580/536
572/528
563/520
554/412
546/504
537/497
529/488
520/481
512/473
503/465
495/457
487/449
477/441
469/434
1 s

Fig. 7

meters so klein, dass man genau das Eindringen und Austreten von H zeitlich verfolgen kann. Man kann auf Grund dieser Messungen die Rechnungen von Pippard und Beck prüfen. Je mehr das eingeschaltete Feld das kritische überschreitet, um so schneller dringt das Feld ein. Die Zeit für den Austritt scheint ziemlich unabhängig von der Flussgrösse zu sein. Aus den einzelnen Teilbildern von Fig. 7 erhält man die Übergangskurve Fig. 8.

Fig. 8. — Ordinate Magnetfluss $\varnothing$ (proportional Ausschlag α). Abscisse zu einander gehörige Werte von H_i an der inneren Oberfläche und H_a an der äusseren Oberfläche des Hohlzylinders. Obere Gerade = Fluss im normalleitenden Zustand. Untere Gerade = Fluss durch Spalt zwischen Blei und Messspule. Jeder Kurvenpunkt entspricht einem Teilbild von Fig. 7, angefangen mit dem höchsten Punkt. Mittlerer Teil der Übergangskurve eine Gerade. Verlängerung nach oben und unten ergibt genau gleichen Wert von H_i innen und aussen am Hohlzylinder : *Die Phasengrenzfläche wandert offenbar ohne komplizierten Zwischenzustand von innen nach aussen! Die kleinen unerwarteten Kurvenübergänge oben und unten entsprechen offenbar den Unregelmässigkeiten an der Oberfläche, die wir vorhin behandelten.*

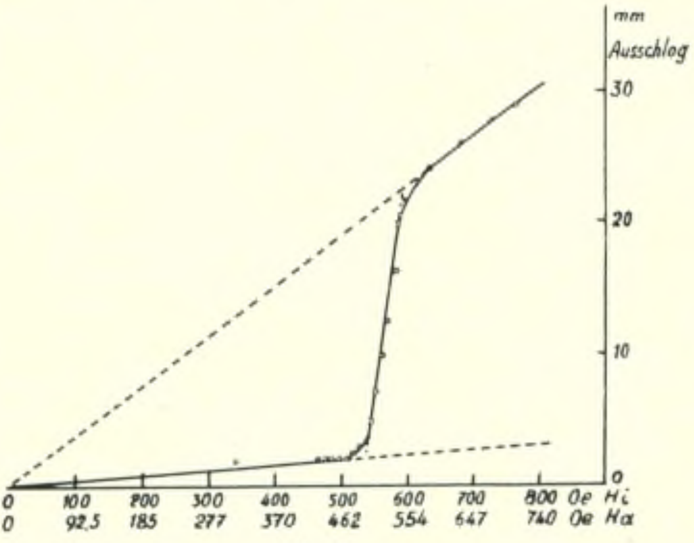

Fig. 8

Als Gegenstück zu dem idealen Fall des in sich geschlossenen Magnetfeldes im Toroid möchte ich Ihnen noch fluxmetrische Aufnahmen an einem Indium-Einkristall zeigen, die direkt photographisch registriert wurden. Dabei wurde auch der Widerstandsverlauf registriert. Das konnte nur indirekt gemacht werden, da der Restwiderstand des Indiumkristalls nur $10^{-7}\ \Omega$ war. Die benutzte Versuchsunordnung zeigt Fig. 9. Parallel zum Indiumkristall mit Widerstand R_1 ist in Serie gelegt ein stets konstant bleibender Kupferwiderstand R_2 und eine Pb-Bi-Spule L_2. Sinkt R_1, so sinkt T_2 in L_2 und in L_3 wird eine elektromotorische Kraft induciert, die einen Ausschlag des Flussmeters F erzeugt. Eine Auswahl aus den photographisch aufgenommenen Registrierkurven geben Fig. 10 bis Fig. 16. In allen Fällentritt der komplizierte Zwischenzustand zu Tage:

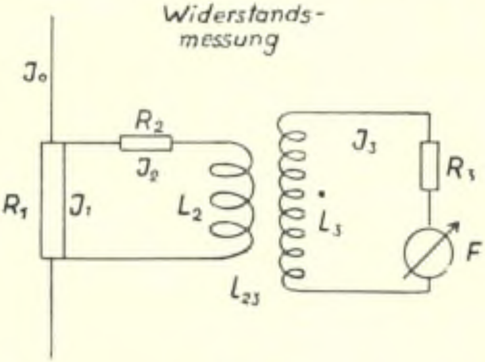

Fig. 9

Fig. 10. — Widerstand R allein registriert. Anstieg (links) mit I ziemlich regelmässig. Abfall mit sinkendem I (rechts) in einzelnen

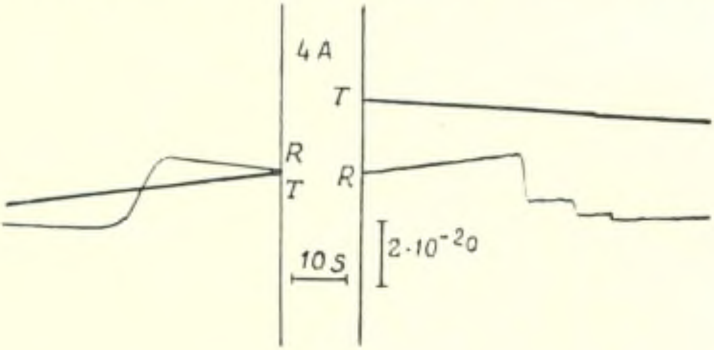

Fig. 10

Sprüngen. Beides is reproduzierbar, wie nächste Aufnahme nach einiger Zeit zeigt :

Fig. 11. — Wiederholung der Messung Fig. 10. Etwas schnellerer Anstieg und Abfall von I. Trotzdem Ergebnis genau das gleiche.

Fig. 12. — Fluss ∅ allein registriert. Wieder wie bei R Anstieg mit I regelmässig, Abfall (rechts) unregelmässig in Sprüngen.

Fig. 13. — Widerstand R und Fluss ∅ gleichzeitig registriert (1 Oe; 4A). Bei Anstieg und Abfall von I Maximum von ∅ (sogen. paramagnetischer Effekt). Beim Anstieg Beginn und Ende der Änderung von R und ∅ etwa in gleicher Zeit. Beim Abfall Ende des Abfalls von ∅ viel später als Ende des Abfalls von R. Beim Abfall wieder Sprünge von R und ∅.

Fig. 14. — Dasselbe wie in Fig. 13, jedoch 7A statt 4A. Stärkere Sprünge. Auch beim Anstieg etwas Sprünge. Beim Abfall wieder ∅ viel später null als R. Sprünge von R und ∅ laufen völlig synchron ineinander.

Fig. 15. — Langsamerer I-Abfall. 10-. Sehr steiler Abfall von R. Langsamer Abfall von ∅ in Wellen. Dass die R -und ∅-Linien bei Normalleitung und völliger Supraleitung nicht parallel der Zeitachse verlaufen, liegt überall an der Null-Punktswanderung des empflindlichen Fluxmeters.

Wie das Maximum des Flusses grundsätzlich zustande kommt, haben wir ja schon publiziert. Um es kurz zu wiederholen : Das äussere longitudinale Magnetfeld und das zirkulare Feld des Stroms bilden zusammen ein schraubenförmiges Magnetfeld. Die entstehenden kleinen supraleitenden Bereiche richten mit ihrer grössten Achse in die Richtung des schraubenförmigen Magnetfeldes ein. Daher ist für den Strom nun auch die Vorzugsrichtung mit kleinstem Widerstand eine Schraubenlinie. Dieser schraubenförmige Strom hat ein Magnetfeld mit longitudinaler Komponente. Diese gibt immer eine Vergrösserung des longitudinalen äusseren Feldes unabhängig von der Stromrichtung. — Noch nicht geklärt aber ist die von uns gefundene Beziehung für den Minimalstrom J_0 der zur Fluxverstärkung nötig ist : $J_0 = J_9 + \gamma HD$ (J_9 = konstanter Grenzwert, γ = Konstante, D = Durchmesser des Zylinders, H = Stärke des äusseren Magnetfeldes).

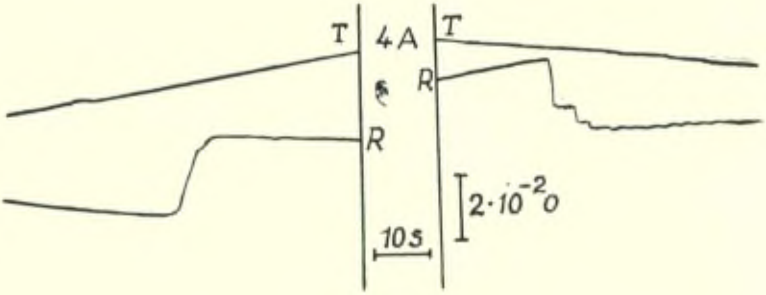

Fig. 11

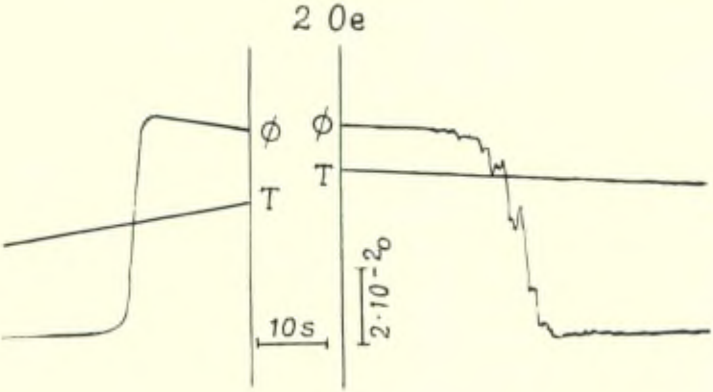

Fig. 12

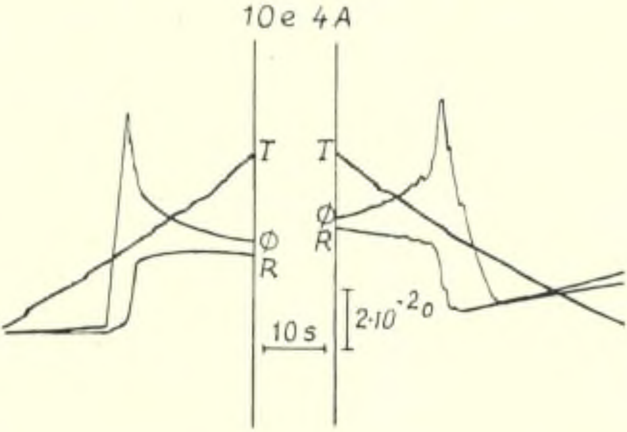

Fig. 13

Ich glaube, dass weitere Versuche zu ihrer Aufklärung lohnend sind, weil diese einfache Beziehung auf noch nicht bekannte einfache Gesetzmässigkeiten betreffs der Supraleitung hindeutet.

Dass die Erklärung für die Fluxverstärkung richtig ist, zeigt z.B., dass sie ausbleibt, wenn der Vollzylinder durch einen ebenen Achsenschnitt geteilt wird und beide Hälften gegeneinander isoliert werden. Nun ist kein schraubenförmiger Strom möglich. Eine derartige Messung zeigt Fig. 16 für 1 Oe und 5A. Es sei noch erwähnt, dass bei allen Messungen das Erdfeld kompensiert war und dass das flüssige Helium stets kräftig gerührt wurde.

Mr Mendelssohn. — Die Heisenbergsche Theorie fordert natürlich ein Ansteigen der Eindringstiefe mit dem Magnetfeld. In den vorliegenden Messungen ist die Eindringstiefe aber von einer Hysteresis begleitet und scheint ausserdem mit den kleinen Abweichungen der fluxmetrischen Messungen vom Idealfall verbunden zu sein.

Zur ersten Frage : Der anormale Verlauf der Übergangskurve nach Heisenberg ist erst bei $J < 1/2J_t$ zu erwarten.

Dies bezügliche Versuche sind von uns beabsichtigt, aber noch nicht durchgeführt.

Zur zweiten Frage : Die Abrandungen am oberen und unteren Ende der Übergangskurve sollen nicht durch die einleitend behandelten Änderungen der Eindringstiefe direkt erklärt werden. Aber, analog zu diesen werden sich vielleicht die Unebenheiten und die damit verbundenen Krümmungsradien auch am Beginn und Ende der Übergangskurve bemerkbar machen und eine Abweichung von der theoretisch zu erwartenden Geraden ergeben.

Mr. Matthias. — By finding a great number of superconducting compounds, it has been possible to deduce an empirical correlation between the transition temperatures and the average number of valence electrons per atom (*). Until now, no superconductors have been found, that have less than two or more than 8 valence electrons per atom. For the intervening range the temperature varies with the number of valence electrons per atom roughly as shown in the diagram.

(*) The valence electrons are considered to be all those outside closed shells.

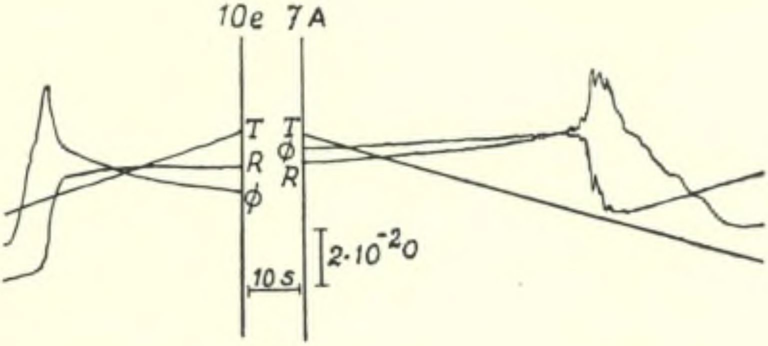

Fig. 14

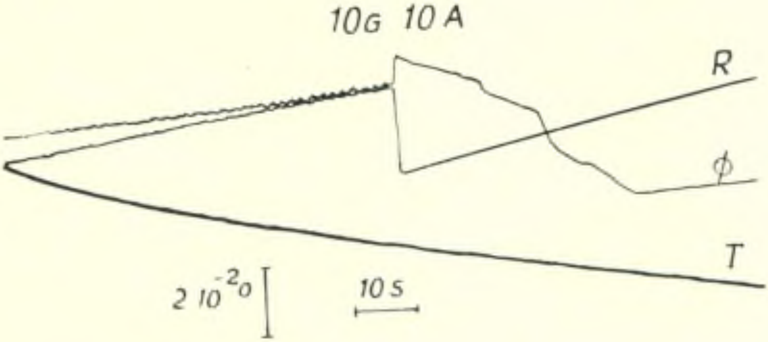

Fig 15

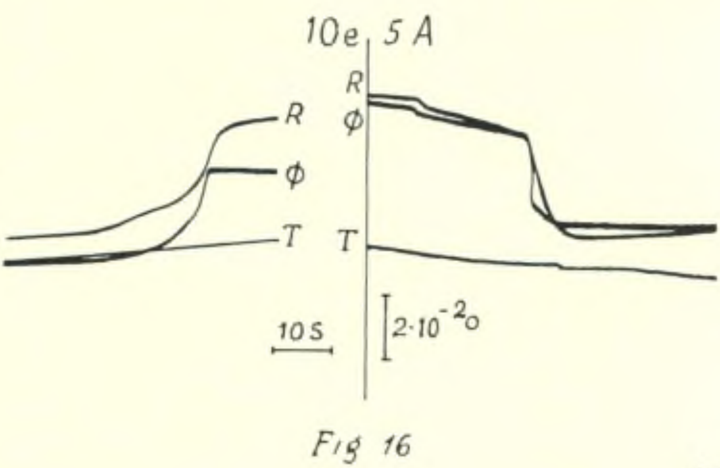

Fig 16

This curve shows qualitatively a behaviour similar to the electronic term of the specific heat for elements in this region. For alloys obeying these conditions, the peaks in transition temperature can be traced continuously and an attempt will now be made to correlate these transition temperatures with the electronic specific heat.

The most suitable metal here for this purpose is probably zirconium which dissolves rhodium. Small amounts (less than 5 atomic percent) of rhodium raise the transition temperature of zirconium from 0.7° K to above 8° K.

Neither the crystal structure nor the lattice constant change, however, and the masses of zirconium and rhodium are not very different, so that the density of electronic levels is probably the only quantity which changes significantly. Its influence on the superconducting properties can, therefore, be observed by the proposed measurements.

Mr. Van Vleck. — One of the most striking properties of superconductors is their enormously large diamagnetic susceptibility whereby they repel all flux. Since most of my research has been concerned with magnetism in one form or another, the explanation of this as yet unsolved puzzle is the aspect of the superconductivity problem which interests me the most. As Fröhlich has pointed out to me, it is not sufficient to obtain merely a susceptibility — $1/4\pi$; instead much larger negative susceptibilities are necessary in order to counteract the effect of demagnetizing corrections. To calculate the susceptibility χ, it suffices to compute the partition function Z since :

$$\chi = \frac{\mathrm{N}k'\mathrm{T}}{\mathrm{H}} \frac{\delta \log \mathrm{Z}\,.}{\delta \mathrm{H}}$$

One would like to show that somehow the vibrational motions of the nuclei give Z an abnormally large dependence on the field strength H. The problem is thus in principle to compute the partition function with a Hamiltonian of the form :

$$\begin{aligned} \mathscr{H} = {} & \frac{1}{2m}\,\Sigma_i({p_{x_i}}^2 + {p_{y_i}}^2 + {p_{z_i}}^2) + \frac{\mathrm{H}e}{4\pi mc}\,\Sigma_i(x_i p_{y_i} - y_i p_{x_i}) \\ & + \frac{\mathrm{H}^2 e^2}{8mc^2}\,\Sigma_i({x_i}^2 + {y_i}^2) + \mathrm{V}(x_1\,, \ldots\, z_n) + \Sigma_j\left(\frac{1}{2\,\mathrm{M}_j}{\mathrm{P}_j}^2 + \frac{1}{2}a_j\,\mathrm{Q}_j^2\right) \\ & + \lambda\Sigma_j \mathrm{Q}_j \mathrm{F}_j(x_1\,, \ldots, z_n)\,, \end{aligned} \tag{1}$$

where x_1 , ... y_n are electronic coordinates and the Q_j are the displacements of the nuclei from their equilibrium positions. λ is a perturbation parameter which can be taken equal to unity. We have not here included spin terms since they are presumably not necessary to explain the *modus operandi* of superconductivity. Also the Coulomb interactions have been omitted, as Pines' paper seems to indicate that they are rather unimportant for problems of the present sort. The magnetic orbit-orbit terms omitted in (1) are not necessary according to presently accepted views, but they played a vital role in some of the older theories of superconductivity. The question is, of course, to find just what terms are really essential.

An exact computation with a partition function of this sort is, naturally, prohibitively difficult. One might, however, resort to a series development of the partition function, say in powers of λ , and from the standpoint of the magnetic theorist, no theory of superconductivity can be regarded as convincing until some indication is obtained from the type of convergence of the development, or perhaps lack thereof, as to why the magnetic properties of superconductors obtain. I do not mean to imply that such series developments lead to really definitive results, but some trace of singularities should be manifest if there is a really correct theory. The situation may be likened, say, to that in the theory of ferromagnetism if one did not use a molecular field model, but instead simply computed the first few terms of a series development in the exchange integral J, i.e. :

$$\chi = \frac{C}{T}\left(1 + \frac{azJ}{T} + \frac{(bz^2+cz)J^2}{T^2} + \frac{(dz^3+ \dots)J^3}{T^3} + \dots\right)$$

Here the fact that the powers of z, the number of neighbors, increase as more terms are included indicates the presence of some sort of a cooperative phenomenon. An effect of this sort would, by contrast, be absent in a one-atom model in a magnetic field. A badly converging series calculation of this sort is, of course, no real theory of ferromagnetism, but does give an inkling that there may be some sort of a cooperative exchange effect which greatly amplifies χ. It should be possible to do something analogous with the Hamiltonian function (1), that would indicate why a large negative χ should be expected, presumably because of the vibrational terms. I would like to stress particularly that it is dangerous to try to compute magnetic properties from the study of individual states.

Near the beginning of the century there were published, for example, several calculations that purported to give a non-vanishing diamagnetic susceptibility for free electrons is classical theory. These erroneous results were obtained because the partition function was not systematically computed, and it is important not to make similar errors in theories of the magnetic properties of superconductors. The great advantage of the partition function method is that it gets rid of the nearly zero denominators which are found when an individual state is strongly perturbed, but which almost cancel out when one sums over all states. Since a purely classical model gives vanishing susceptibility, some of the peculiar non-commuting properties of quantum algebra must somehow be responsible for generating an enormously large negative χ when the partition function is developed for a superconductor. Presumably these non-commuting terms must involve the vibrational coordinates in view of the empirical dependence of superconductivity on isotope species. So far, alas, the germ of the idea of how the needed properties work out in this approach seems to be wanting.

Mr. Onsager. — As long as we have no adequate theory of superconductivity we may ask whether the fault lies with the mathematical methods, or with the physical principles which constitute the premises of the theory. A simple consideration leads me to suspect the premises. In substance, I accept London's discussion of a superconducting ring. If the ring encloses a magnetic flux, the wave-function for the electron system is modified thereby even though the flux be trapped in an iron core so that there is no magnetic field at the surface of the superconductor. The wave-function then contains a gauge-factor, so that the phase gains an increment proportional to the contained flux whenever an electron encircles the ring. Since the wave-function must be single-valued, the phase increment must be a multiple of 2π, and this in turn requires that the flux must be an integral multiple of :

$$hc/e = 4.135 \times 10^{-7} \text{ gauss cm}^2.$$

This fundamental unit equals the flux from one of Dirac's hypothetical magnetic poles; Dirac's reason for this particular choice is closely related to London's analysis.

When we want to enclose a magnetic flux in a superconducting ring, we can trap the flux first in an iron core and close the superconducting ring afterwards. How can the superconductor know that the flux is integral? It seems natural to assume that the flux trapped by the core is integral in the first place. In that case, however, the phenomenon of superconductivity is related to a general principle which governs the measurement of magnetic flux. It would appear that no general theory of electrodynamics containing this principle has been formulated as yet.

Mr. Fröhlich. — Professor Onsager's quantization of flux is normally accounted for by the quantization of electronic motion in a ring, and this in fact is the condition from which F. London derived it, using the equations of F. & H. London. It must be noticed in this connection that the quantity which is quantized is not the magnetic flux $\int_s \underline{h} \cdot d\underline{\sigma}$ ($\underline{h}$ = magnetic field, the integration extending over a surface S, bounded by a curve C) but what London denotes as fluxoid $\varnothing$, namely :

$$\varnothing = \int_s \underline{h} \cdot d\underline{\sigma} + c\int_c \Lambda \underline{j} \cdot d\underline{s}$$

where $\underline{j}$ is the current in C, and Λ is a parameter in the London equations introduced by $\partial(\Lambda \underline{j})/\partial t = \underline{e}$, $\underline{e}$ being the electric field. Thus there may always be a contribution to $\varnothing$ due to the electronic motion in the ring.

I think that this consideration of F. London's does not take into account the possibility considered by Prof. Onsager, namely that the entire flux be trapped in an iron core. To postulate that even then $\varnothing$ be quantized is a step which does not necessarily follow from any semi-empirical description of the properties of superconductors. This in my opinion forms an independent hypothesis.

Mr. Matthias. — A. L. Schawlow, H.W. Lewis and I have studied the distribution of a superconducting (and therefore diamagnetic) niobium powder on the surface of a tin sample in the intermediate state. It was found that the powder distributed itself in a rather distinct pattern, which we believe is characteristic of the underlying structure of the superconducting and normal regions. Similar patterns had previously been observed by the Russian workers, using the bismuth microprobe technique.

This method lends itself to graphic portrayal of the intermediate state structure, and we are beginning a program of studies in this direction. The photographs shown are typical of our early results.

The Empirical Relation between Superconductivity and the Number of Valence Electrons per Atom

by **B. T. Matthias**

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It has been found empirically that superconductors with highest transition temperatures are those which have an average valence electron/atom ratio near 5 or 7. Furthermore, the superconducting transition temperatures in the horizontal rows of the periodic system seem to be more or less symmetrical with respect to the sixth column; see Table I.

TABLE I

Superconducting transition temperatures for elements of the IVth to the VIIIth column.

IV	V	VI	VII	VIII
Zr 0.7°	Nb 8.6°	Mo *	Tc 11°	Ru 0.47°
Hf 0.35°	Ta 4.4°	W *	Re 1.7°	Os 0.71°

* Not superconducting above 0.05° K.

Our data now suggest tentatively that the qualitative dependence of the transition temperature on the valence electron/atom ratio is as indicated in Figure 1.

In the next four paragraphs, we could like to give four examples of how this curve was traced experimentally.

a) Superconducting compounds with the beta-W structure.

As it was not possible in this type structure to vary the electron density continuously, we were limited to a number of discrete points corresponding to the available compounds. In order not to confuse the issue too much by variation of mass and volume, we restricted

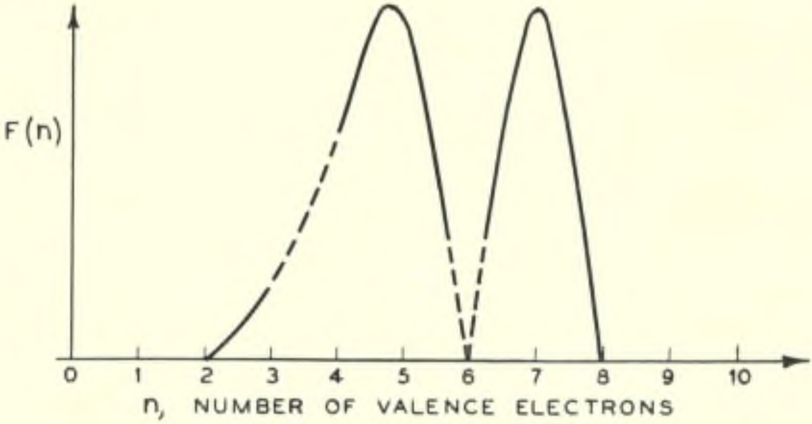

Fig. 1

ourselves to compounds of two elements, niobium and molybdenum, which are next to one another in the periodic system. Figure 2 shows the variation of the superconducting transition temperature with the electron density. It shows high values for the transition temperature near 5 and 7 and a minimum near 6.

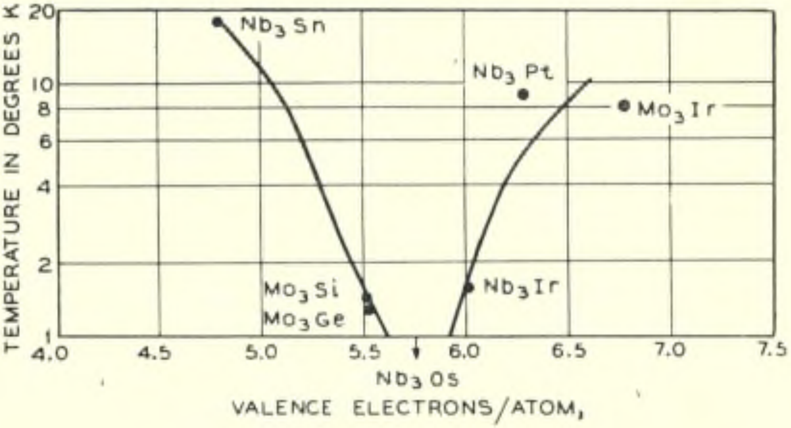

Fig. 2

b) **The rhodium-selenium and rhodium-tellurium systems.**

Rhodium-selenide crystallizes in the pyrite structure over a wide homogeneity range from about $RhSe_{1.5}$ to $RhSe_{2.5}$. Superconductivity occurs only inside this range. The cell size decreases with increasing Se content, but considering that the transition temperature appears proportional to not more than the tenth power of the volume this change is negligible. The maximum transition temperature at 6° K was observed for $RhSe_{1.75}$ corresponding to an average electron/atom ratio near 7.1. The structure of $RhTe_2$, at which composition the transition temperature reaches the maximum at 1.51° K is unknown but may be related to that of $RhSe_2$. Its electron/atom ratio at the maximum is 7.

c) The molybdenum and tungsten alloys.

These alloys serve to illustrate that the maximum transition temperature occurs near electron/atom ratios of 7. Table 2 and figure 3 compare the observed values of transition temperature with the corresponding electron/atom ratios.

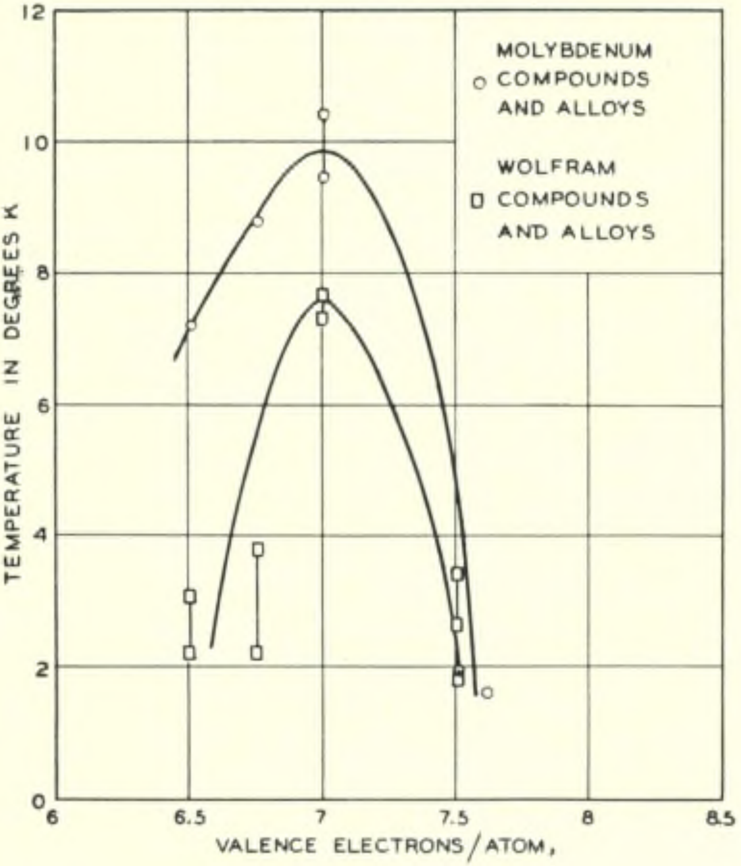

Fig. 3

It was discovered (*) that alloys of the body centered cubic Mo and W with the face centered cubic Rh, Ir and Pt form a hexagonal closed packed phase. This seems to be an averaging which produces behavior like that in the elements which are intermediate in the periodic table. The large solubility of Mo in Ru enables us to simulate technetium quite closely both in crystal structure and superconducting transition temperature, thus strengthening our faith in the validity of this point of view.

d) **Solutions of rhodium in zirconium.**

We have found that up to approximately 15 % Rh can be dissolved in Zr without appreciably (**) changing the size of the lattice constant. Above 15 % Rh, additional lines in the X-ray powder photograph indicate that either a superlattice or a new crystal structure closely related to that of Zr exists. Whereas results obtained for Zr-Rh alloys with more than 15 % Rh have therefore to be considered with caution, it becomes obvious for smaller Rh amounts how strongly the superconducting transition temperature is affected by the electron concentration. See figure 2.

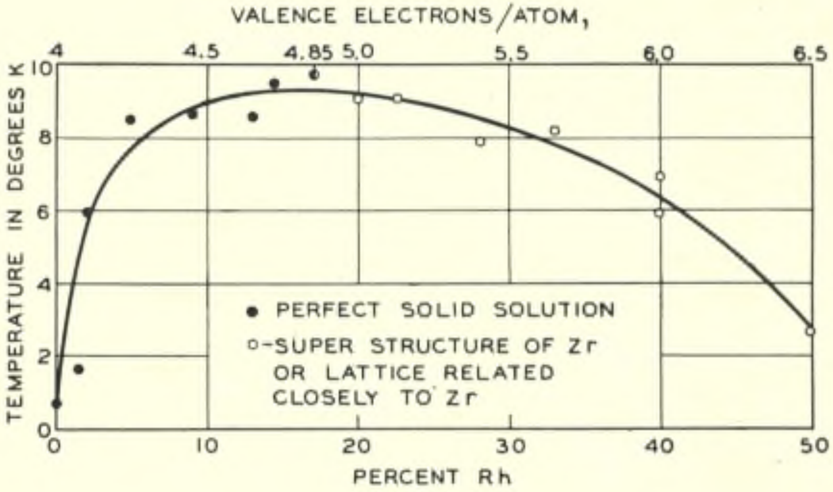

Fig. 4

(*) E. Raub and P. Walter, *Festschrift Heraeus 75 Jahre*, Seite 124; E. Raub, *Zschr. F. Metallkunde*, 23 (1954).

(**) By « appreciably » we mean to an extent which would effect the transition temperature assuming $T_c \sim (\text{Volume})^{10}$.

These data on the Zr-Rh system should be considered only of preliminary nature outside the range of 0.2 % to 20 % Rh. For Rh percentages below 1 % the purity of our Zr (99 %) was not good enough, and above 20 % Rh we seem to have a two-phase system (*). All we wished to show here is how the maximum transition temperature occurs for an electron density slightly below 5 as observed so often before (**).

Whereas all alloys indicated a close connection between superconductivity and the number of valence electron/atom, it appears that the Zr-Rh system is the most interesting. Here the electron density alone seems to determine the transition temperature and the attempts will therefore be made to obtain a relation between the electronic term of the specific heat and the transition temperature by a continuous variation of the electron density as was suggested by Flöhlich.

(*) We were not able to find any literature on the Zr-Rh system.

(**) B.T. Matthias, *Phys. Rev.*, **92**, 874 (1953).

Hall Effect in Ferromagnetics

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1. INTRODUCTION — EXPERIMENTAL STATUS

The Hall effect in ferromagnetics is not direct proportional to the applied magnetic field, but an extra term connected with the spontaneous magnetization has to be added, so that we get, if the sample is saturated in the z direction :

$$E_y/i_x = R_0B + R_1 M_s \text{ ....} \qquad (1)$$

with R_0 the normal Hall coefficient, and R_1 the extraordinary Hall coefficient. We have used B in stead of H, since B is the mean field inside the specimen. This is because the magnetic dipoles are not dumbbell dipoles, but have to be regarded as being caused by circular currents. If we say that the mean field B acts on a conduction electron, then we have to allow for the penetration of this electron into the interior of the circular current of the dipole. This has peculiar consequences if one recognizes that these magnetic moments are mainly those of the spins of the 3d electrons. The 4*s* conduction electron has then to penetrate the 3d electrons. These difficulties are of course formally explained in the Dirac theory of the electron, and we can sail round them by bearing in mind that the electrons are smeared out, and with them their spin currents, which have then the dimensions of the electronic orbits.

The normal Hall coefficient R_0 has the same order of magnitude as for the non ferromagnetic metals, and permits the application of free electron theory for finding the number of free electrons. This has been done by Pugh (1) a.o. and they find it to be of the order of one electron per atom, or somewath less. Iron shows a positive Hall coefficient (electron holes).

The most striking property of the spontaneous Hall effect is, besides its great value, its strong temperature dependence, as has been found for nickel by Smith in 1910 and recently by Jan and Gijsman (2) at low temperatures. In these samples R_1/R_0 was about 120 at room temperature, but at the lowest temperatures it decreased to 20 whereas it increased to about 1 000 near the Curie temperature. Especially the change in R_1 below room temperature is very remarkable, since there the magnetization does not vary appreciably. The only property of the material whose magnitude increases in a comparable way is its electrical resistance. If a correlation does exist indeed, one should expect a much smaller variation of R_1 for an alloy below room temperature than for a pure metal.

These considerations were the starting point of some measurements by Dr. Volger and myself (3) on the Hall effect together with the resistivity of several Ni alloys and of some Ni specimens of different purity at temperatures of liquid H_2 and N_2 and at room temperature.

It was found that the purest Ni sample has no extraordinary Hall effect (R_1) near $T = 0° K$, whereas R_1 for the alloys was still finite there. In general R_1 varied about in the same way as the resistivity ρ; in some cases a power law $R_1 \sim \rho^n$ with $n \gtrsim 1.5$ is satisfied.

It appeared that R_1 and also R_0 is extremely sensitive to the chemical composition as was found for several Ni samples with different impurity content. Ni has a negative R_0 and R_1. Addition of Co or Fe lowers $|R_1|$, and for 30 % Co or 16 % Fe R_1 is positive, just as for pure iron. R_1 is extremely large for Ni alloys with non magnetic metals, like Si, Al or Sn. At the same time these additions increase the resistivity, so that it may be assumed that R_1 is closely related to the resistivity of the material.

2. THEORETICAL DISCUSSION

We shall show that for a periodic lattice (pure metal at $T = 0° K$) R_1 is zero. This is most easily seen by writing down the total Hamiltonian of the lattice, thus including spin-orbit interaction and other magnetic interactions. A resultant current exists in the x direction. The total Hamiltan H can then be split up in three parts, i.e. :

$$H = H_p + H_B + H_i .$$

The part H_B is simply due to the action of the mean magnetic induction B and gives the term R_0B in the expression for the Hall effect. The part H_f is caused by the action of the inhomogeneous field induced by the mean primary current. We postpone the discussion of the influence of this part of the Hamiltonian and are left with the remaining part H_p, which is then purely periodic. Its electronic eigenfunctions will be of the Bloch type, both the one-electron eigenfunctions and the wave function for the total electronic system. The electrons can have a resultant velocity in these states in the x direction, and therefore these wave functions can belong to steady states in which a current is flowing, without the presence of an external voltage. That is to say, ρ and R_1 are zero. This is merely Houston's proof that a periodic lattice has no resistance. The zero point vibrations of the lattice do not change this conclusion.

We have still to discuss the influence of H_f. The mean value of the component of the inhomogeneous magnetic field in the direction of B is zero, so the mean Lorentz force vanishes, giving no external Hall voltage. Another effect might be caused by the spontaneous magnetization of the specimen, i.e. electrons which carry the current may have polarized their spin moments, so that they feel a force in an inhomogeneous magnetic field.

Due to the fact that the magnetic moments have to be regarded as being caused by circular currents, the force on an electron with magnetic moment $\overleftarrow{\mu}$ is given by $\overleftarrow{f} = \overleftarrow{\nabla}\ (\overleftarrow{\mu}\overleftarrow{H})$, where $\overleftarrow{H}$ is the magnetic field. This is a gradient field, so if we determine the resulting e.m.f. in the Hall circuit, we get no contribution.

The action of the inhomogeneous field has also been discussed in the literature (1), but then the force equation :

$$\overleftarrow{f} = (\overleftarrow{\mu}\overleftarrow{\nabla})\ \overleftarrow{H}$$

has been used.

This gives in particular :

$$f_y = \mu_z \frac{\delta H_y}{\delta z} = \mu_z \left(\frac{\delta H_y}{\delta z} - \frac{\delta H_z}{\delta y} \right) + \mu_z \frac{\delta h_z}{\delta y} = \mu_z \cdot \frac{4\pi i_x}{c} + \mu_z \frac{\delta H_z}{\delta y}$$

The term with $\frac{\delta H_z}{\delta y}$ gives no contribution, but the remaining term with i_x does, and its action is equivalent to that of a homogeneous field $4\pi M$, where it is assumed that the conduction electrons also give the magnetic moment, this being not the case in real ferromagnetic metals.

Since we know that the circular current model applies we may conclude that in a periodic lattice the spontaneous Hall effect vanishes, or that the effective field is equal to B ($R_1 = O$), in agreement with our experimental results on the purest nickel. It may be noted that the idealized dumbbell model gives the same result.

One is now left with the problem to explain the occurrence of a finite R_1 in non-periodic lattices. If a resultant current is flowing in such a lattice, the steady state is maintained by the opposite action of the applied field and the collisions of the electrons against the imperfections. The wavefunctions will be changed by these two effects and possibly the magnetic interactions can then give a transverse effect. Recently Karplus and Luttinger (4) have considered the influence of the applied field and found R_1 to be proportional to ρ^2, and of the right order of magnitude. Professor Kittel will speak about this theory.

We have overlooked this effect of the applied field completely, and sticked to the influence of the collisions on the wavefunctions. It will be shown that these collisions also give rise to a transversal effect, but that it is too small by a factor of the order of ten to explain the experimental values. The magnetic interaction can be of two kinds :

a) There can be a change in magnetic dipole moment of the scattering centre;

b) If the colliding electron has in the mean a net magnetic moment in the z direction, the electrostatic perturbing potential gives also a change in spin-orbit interaction according to :

$$U = (\vec{\mu} \times \vec{\nabla} V)\vec{p}/2\,mec$$

where V is the electrostatic perturbing potential, $\vec{\mu}$ the magnetic moment, and $\vec{p}$ the momentum operator of the electron.

It is mostly believed that the electrons which carry the current in ferromagnetic metals, and in particular in nickel, have predominantly 4 *s* character, whereas the magnetic moment is practically only due to the 3d electrons. In that case one should expect that mechanisme *b*) cannot be active. Mott (5), however, has shown that the resistance-temperature curve of nickel can be explained very well by assuming that at low temperatures practically only 4s electrons with parallel spin moment carry the current. This is due to the fact that they cannot make transitions under conservation of their spin direction, to holes in the 3d band. The 4 s electrons with antiparallel spins can do so, and are heavily scattered, and do not therefore participate appreciable in the conduction process. Neglecting these antiparallel electrons for a moment, we can say that in effect the conduction electrons are magnetized, so mechanism *b*) can also apply to *s* electrons.

It looks plausible to attack to problem by calculating the scattering of a beam of free electrons by a square well potential. We calculate first the wavefunction without magnetic effects, which has the asymptotic form :

$$\chi_o = e^{ikx} + \frac{e^{ikr}}{r} f_o(\theta) ,$$

if the polar axis is in the *x* direction. The magnetic interaction can be regarded as a small perturbation, and the total asymptotic wavefunction is of the form :

$$\chi = e^{ikx} + \frac{e^{ikr}}{r} \{ f_o(\theta) + \sin \varphi f_1(\theta) \} .$$

The resistance in the *x* direction is proportional to :

$$A_x \sim 2\pi \int_o^{\pi} | f_o(\theta) |^2 (1 - \cos \theta) \sin \theta \, d \theta ,$$

whereas that in the *y* direction is in first approximation given by :

$$A_y \sim \int_o^{\pi} \int_o^{2\pi} \left\{ f_o(\theta) f_1{}^*(\theta) + f_o{}^* (\theta) f_1 (\theta) \right\} \sin^2 \theta \sin^2 \varphi d\theta d\varphi .$$

From this the spontaneous Hall angle $\varphi_t - A_y/A_x$ is found. The two mechanisms *a*) and *b*) give answers of the same order of magnitude, being, however, for reasonable values of V, far too small (about 10^{-4} to 10^{-3}, as to be compared with the experimental value of 10^{-2}).

Eindhoven, October 5th, 1954.

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Discussion of Dr. SMIT's report

Mr. Kittel. — Karplus and Luttinger [*Phys. Rev.*, 95, 1154 (1954)] have given a theory of the anomalous part of the Hall effect in pure ferromagnetic and paramagnetic metals. They account successfully both for the large magnitude of the effect and for the astonishing temperature dependence. They first proposed that the anomalous part of the Hall effect in fact should have nothing in common with the ordinary conductivity Hall effect, but should represent a resistanceless property of the Bloch functions in the presence of net magnetization, spin-orbit interaction, and an applied electric field. They show that the fundamental physics of the problem gives rise to a transverse current density :

$$\mathrm{J}_t = r\mathrm{M}\mathrm{E}_l \,,$$

where r is a constant which is not highly temperature dependent; M is the magnetization; E_l is the longitudinal electric field. If we express this as a relation between E_t and J_l, as is usual in Hall effect work, we have directly :

$$\mathrm{E}_t = \rho^2 r\mathrm{M}\mathrm{J}_l \,,$$

where ρ is the electrical resistivity. The apparent temperature dependence of the anomalous Hall effect is explained by Karplus and Luttinger as caused in large part by the temperature dependence of the conductivity. Measurements on pure iron at Leiden by Jan and Gijsman and on silicon iron at Berkeley by Kooi are in satisfactory agreement with the theory.

It remains to explain the origin of the transverse current J_t. The effective perturbation is first order in the electric field and first order in the spin-orbit interaction, so that the mean transverse current is of the order of :

$$\mathrm{J}_t = \mathrm{N}ev_t \approxeq \mathrm{N}ev_{\mathrm{F}} \cdot \frac{\lambda}{\Delta\mathrm{W}} \cdot \frac{e\mathrm{E}_l\bar{x}}{\Delta\mathrm{W}} \,,$$

where v_{F} is the velocity at the Fermi surface; λ is the spin-orbit interaction; N is the concentration of magnetized electrons; $\Delta\mathrm{W}$ is an interband energy separation; $\bar{x}$ is an electric dipole matrix element. We note that $(\lambda/\Delta W)$ is of the order of the g-shift, Δg. The current predicted by the above relation is of the correct order of magnitude.

Mr. Pines. — We have had considerable discussion concerning the measurement of specific heat in the alkali metals. I should like to suggest that to the extent that we are interested in obtaining the density of states at the top of the Fermi distribution, nuclear magnetic resonance offers a more promising approach.

For the nuclear spin-lattice relaxation time due to the hyperfine interaction may be written as :

$$\frac{1}{T_1} \cong A\rho^2(E_o)|\Psi_k(o)|^4$$

where the quantity A is well-known, and $|\Psi_k(o)|^2$ may be calculated rather well for the alkalis, or alternately obtained from the Knight shift combined with experimental or theoretical knowledge of the spin susceptibility.

The present experimental situation is as follows : Norberg and Holcomb have measured T_1 for Li, Na and Rb. Their results may be interpreted in terms of a substantial contribution to the relaxation mechanism from the above process, plus a smaller frequency-dependent term which is not yet understood. Taking the longest time they observe for each metal, and combining this with the effective mass values of Brooks, we find the following values for the state density in terms of the free electron value :

	$\rho\,^{act}/\rho\,_{free}$
Li	1.20
Na	1.03
Rb	1.10

These results are probably accurate to within $\sim 20\ \%$. The experiments of Norberg and Holcomb have been carried out in the region of room temperature. To the extent that the hyperfine interaction dominates the relaxation process, such experiments are in principle capable of giving the state density at helium temperatures. Experiments at low temperatures could be quite valuable for a determination of the state density in this region, and hence a verification of Prof. Fröhlich's conjecture concerning its behaviour. For I don't believe the Knight shift experiment is in itself conclusive, since as mentioned earlier, the spin susceptibility does not depend simply on the density of states when correlations are taken into account.

Thus, Knight shift experiments must be combined with T_g measurements before an unambiguous determination of the state density may be made.

Zur Elektronentheorie der Übergangsmetalle

von **ALFRED SEEGER**

Max-Planck-Institut für Metallforschung, Stuttgart, und Institut für theoretische und angewandte Physik der Technischen Hochschule Stuttgart.

ZUSAMMENFASSUNG

Die vorliegende Arbeit enthält eine Diskussion der Elektronenbänder und der Kristallstrukturen der Uebergangsmetalle. Dabei wird ein Modell zugrunde gelegt, das eine Unterteilung des gesamten *d*-Bandes nach Massgabe der Kristallsymmetrie sowie in bindende und lockernde Funktionen berücksichtigt. Man wird auf diese Weise zu der Vorstellung geführt, dass gewisse Untergruppen der *d*-Elektronen vorwiegend van der Waals'sche, andere dagegen homöopolare Bindung ergeben. Man kann daraus Aussagen über das bei einer bestimmten Konfiguration $d^n s^m$ der Aussenelectronen zu erwartende Auftreten der drei einfachen metallischen Strukturen (kubische und hexagonale dichteste Kugelpackung, kubisch-raumzentriertes Gitter) ableiten, die durch die Erfahrung im wesentlichen bestätigt werden. Auch die Folgerungen hinsichtlich des Gangs der spezifischen Elektronenwärme und der magnetischen Suszeptibilität innerhalb der nicht ferromagnetischen Übergangselemente stimmen gut mit der Erfahrung überein. Hinsichtlich der Eigenschaften der ferromagnetischen Übergangsmetalle wird vor allem die Bedeutung der Resultate einiger neuerer Experimente (Neutroneninterferenzen) und Rechnungen (Plasma-Methode und Konfigurationswechselwirkung) für die Elektronentheorie des Ferromagnetismus diskutiert. Über eine derartige Rechnung (Vierelektronenproblem mit Konfigurationswechselwirkung) wird in einem Anhang berichtet.

1. CHEMISCHE BINDUNG DER ÜBERGANGSMETALLE

Die Natur der chemischen Bindungsenergien der einfachsten Elemente mit abgeschlossenen *d*-Schalen, der Edelmetalle Cu, Ag und Au, erscheint heute als zum mindesten qualitativ geklärt : die Kohäsionsenergie rührt in grössenordnungsmässig gleichen Teilen von der metallischen Bindung der *s*-Elektronen und von der van der Waalsschen Bindung der abgeschlossenen *d*-Schalen her. Genaue Berechnungen der Kohäsionsenergie ohne Verwendung empirischer Parameter liegen noch nicht vor, doch sind die Grössenordnungen der experimentellen Werte so, dass sie sich in der oben angegebenen Weise deuten lassen. Insbesondere rührt die gegenüber Au und Cu kleinere Kohäsionsenergie von Ag wohl daher, dass hier infolge der grösseren Stabilität des $4d^{10}$-Rumpfes (ein freies Pd-Atom hat den Grundzustand $4d^{10}$, während Ni $3d^8\,4s^2$ und Pt $5d^9\,6s$ als Grundzustand haben) die van der Waalssche Energie geringer ist. Damit hängt sicher auch das abweichende optische Verhalten von Ag und wohl auch die im Vergleich zu Au und Cu viel geringere Bereitwilligkeit des Silbers zur Legierungsbildung zusammen. Der Kompressionsmodul der Edelmetalle ist um ein Faktor von der Grössenordnung 20 grösser als derjenige der Alkali-Metalle. Dies wird dadurch erklärt, dass der Widerstand gegen Kompression bei den Edelmetallen nicht von der Fermiexpansion des *s*-Elektronengases, sondern von der Abstossung der sich berührenden *d*-Schalen benachbarter Atome im Gitter herrührt (1).

Bei den Übergangsmetallen sind die Verhältnisse in mancherlei Hinsicht komplizierter. Wir betrachten zunächst die empirischen Resultate. Abb. 1 gibt die bis jetzt bekannten Werte der Sublimationsenergien der Übergangsmetalle an. Besonders in der zweiten und dritten langen Periode des periodischen Systems liegt ein ausgeprägtes Maximum bei denjenigen Metallen vor, die gerade eine

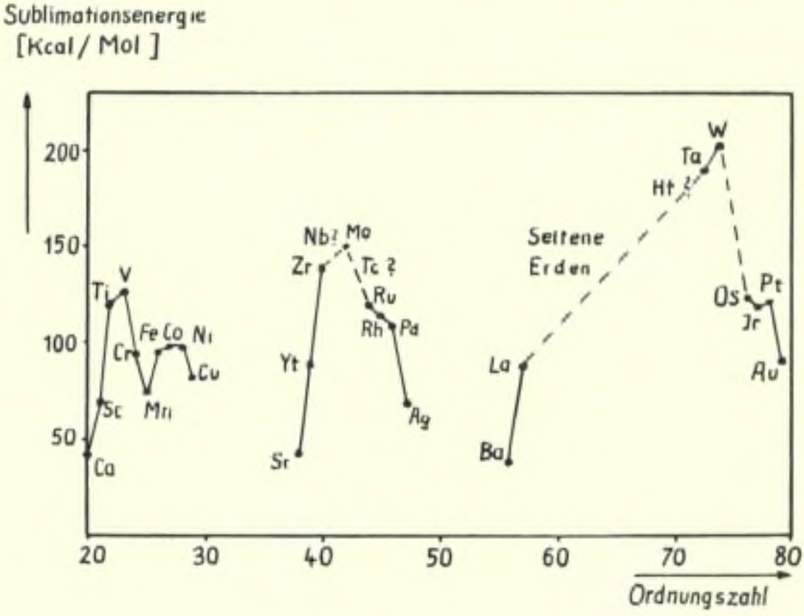

Abb. 1. — Sublimationsenergien der Uebergangsmetalle nach(20) sowie H. Staude, *Physikalisch-Chemisches Taschbuch*, Bd. II, Leipzig, 1949, und F. Seitz, *Modern Theory of Solids*, New York, 1940.

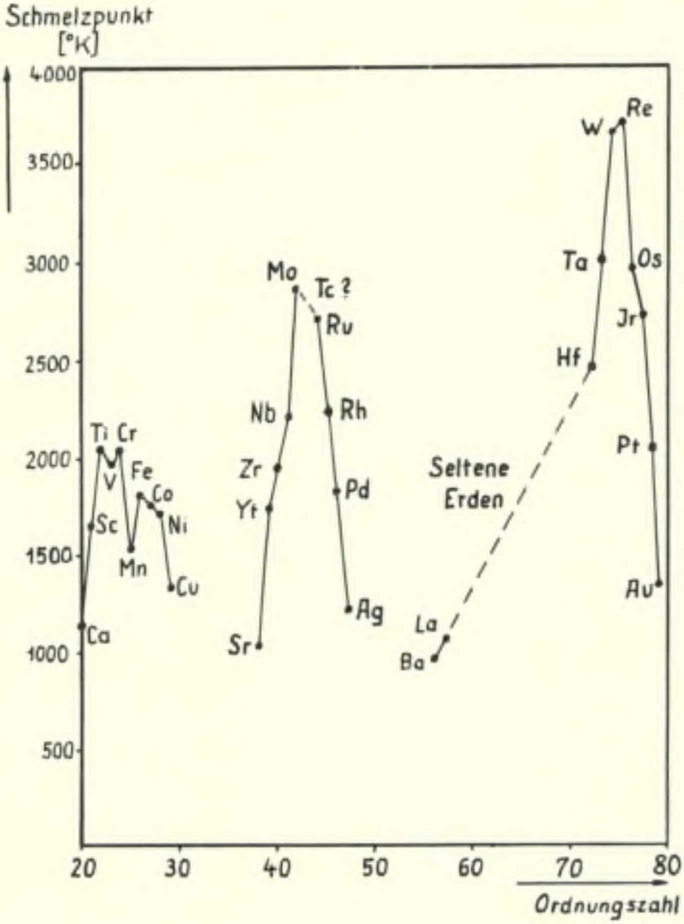

Abb. 2. — Schmelzpunkte der Uebergangsmetalle nach (39) und (20).

halb aufgefüllte *d*-Schale besitzen. Einen ähnlichen Verlauf zeigen die Schmelzpunkte der Übergangsmetalle (Abb. 2). Abb. 3 und Abb. 4 zeigen, dass Kompressibilität und Abstand nächster Nachbarn ein Minimum etwa in der Mitte der langen Periode des periodischen Systems aufweisen, was ebenfalls auf eine besonders starke Bindungsfestigkeit im Falle halbgefüllter *d*-Schalen hinweist.

Kann man diesen stetigen Anstieg der Bindungsfestigkeit von den Edelmetallen zu den Elementen mit halbgefüllter *d*-Schale anhand derselben Überlegungen verstehen, die wir oben bei den Edelmetallen angeführt haben? Dies ist nach unserer Meinung aus folgen den

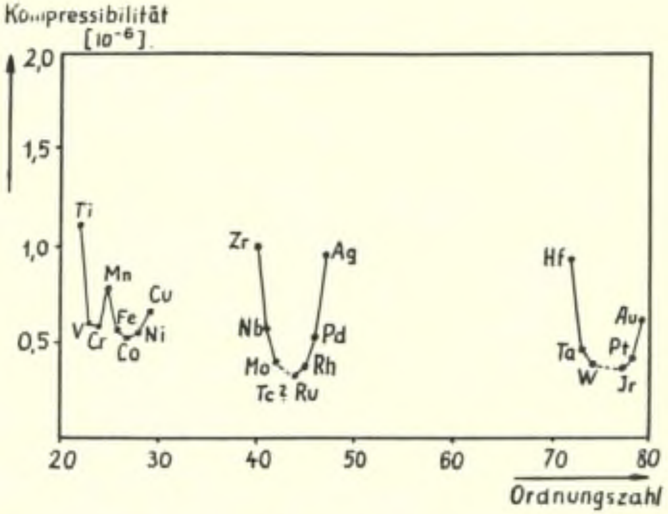

Abb. 3. — Kompressibilität der Uebergangsmetalle nach (20).

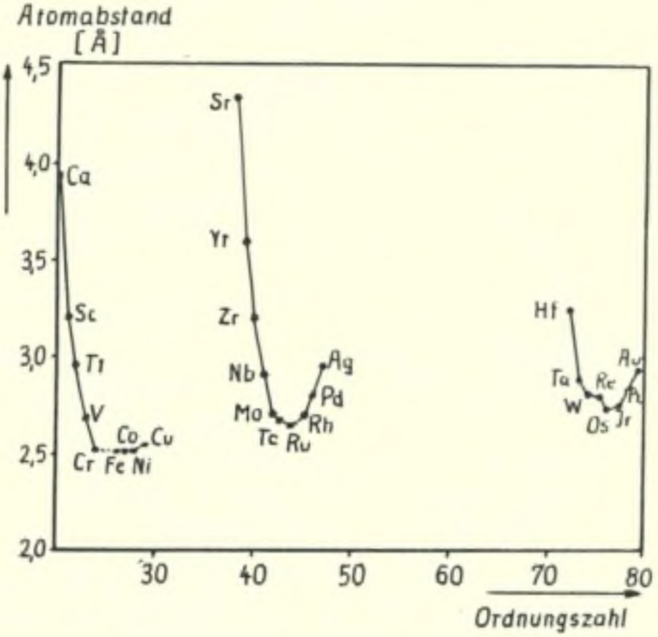

Abb. 4. — Atomabstände der Uebergangsmetalle.

Gründen zu verneinen : Die Zahl der *s*-Elektronen im festen Zustand sinkt von einem Elektron pro Atom auf etwa 0,6 Elektronen pro Atom in der Gruppe Ni, Pd, Pt ab, sodass sicherlich der Anteil der *s*-Elektronen an der chemischen Bindung zunächst vermindert wird. Die magnetischen Daten scheinen allerdings darauf hinzuweisen, dass mit weiterer Verringerung der Ordnungszahl zumindest in der ersten langen Periode die Zahl der *s*-Elektronen wieder etwas ansteigt(*).

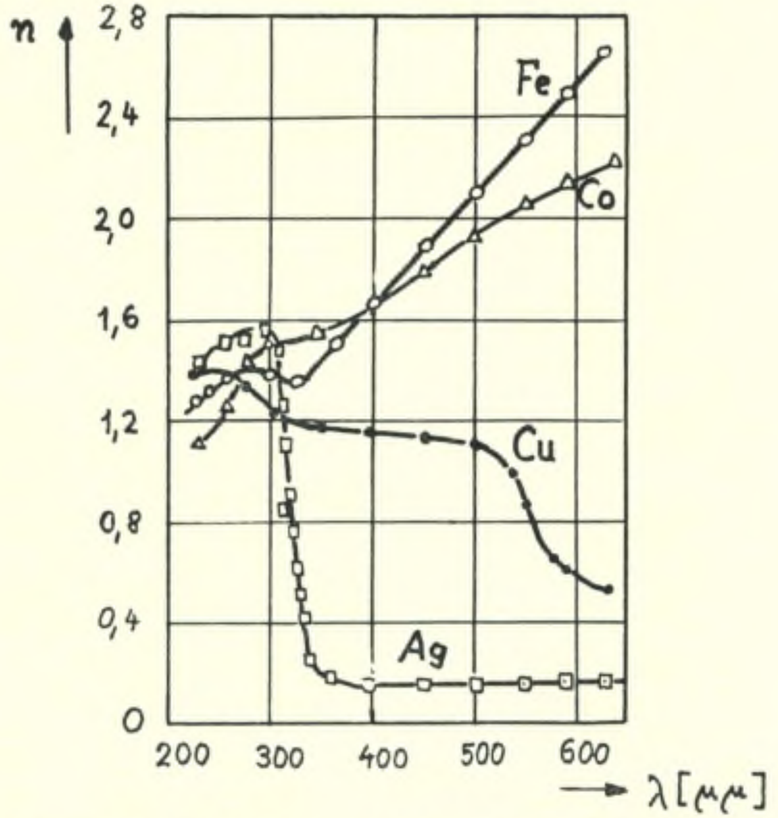

Abb. 5. — Brechzahln im sichtbaren Gebiet von Eisen (Stahl), Kobalt, Kupfer und Silber nach Messungen von R.S. Minor, *Ann. Physik*, Lpzg. [4], **10**, 581 (1903). Der Absorptionskoeffizient $n\kappa$ ist bei F. Seitz, *Modern Theory of Solids* (1940), p. 635, f. angegeben.

(*) Die Deutung der magnetischen Daten führt auf 0,7 bezw. 0,8 *s*-Electronen pro Atom für Co bezw. Fe. Der Antiferromagnetismus von Cr legt einen Wert von 1 *s*-Electron pro Atom nahe (s.u.).

Da mit abnehmender Ordnungszahl eine zunehmende Anzahl von Löchern in den *d*-Schalen der Übergangsmetalle auftreten, muss es als höchst zweifelhaft erscheinen, ob eine Beschreibung der bindenden Wirkung der *d*-Elektronen als van der Waalssche Wechselwirkung allein noch zulässig ist. Wie wir unten näher ausführen werden, werden vermutlich Teilschalen der *d*-Elektronen noch van der Waalssche Kräfte aufeinander ausüben, doch scheint es sicher zu sein, dass diese nicht die Abnahme des « metallischen » Bindungsanteils der *s*-Elektronen überkompensieren können. Die in Abb. 4 dargestellte Abnahme des Atomabstandes weist auf eine Durchdringung der *d*-Rümpfe benachbarter Atome in den Strukturen der Übergangsmetalle und auf eine Bindung durch die *d*-Elektronen hin, welche bei halbgefüllter *d*-Schale am wirkungsvollsten ist. Man wird auf diese Weise auf die Betrachtung einer homöopolaren chemischen Bindung der Übergangsmetalle geführt. Die hieraus sich ergebenden Folgerungen für die Bandstruktur der Übergangsmetalle werden wir im nächsten Abschnitt ausführlich betrachten.

In der Diskussion wies Prof. Fröhlich daraufhin, dass sich ein homöopolarer Bildungsanteil bei den Uebergangsmetallen in Analogie zur grossen Brechzahl *n* von Diamant, Silizium und Germanium ebenfalls in einer gegenüber den Edelmetallen vergrösserten Brechzahl äussern müsste. Die experimentellen Ergebnisse von R.S. Minor (Abb. 5) und W. Meier (Abb. 6) bestätigen diese Erwartung in der Tat : im roten Teil des Spektrums übertreffen die Brechzahlen von Platin und Stahl sogar diejenige von Diamant.

Wir erwähnen hier noch eine empirische Stütze für das Zurücktreten der van der Waalsschen Bindung bei den Übergangsmetallen. Das Ausnahmeverhalten von Ag war oben mit der grösseren Stabilität des $4d^{10}$-Rumpfes erklärt worden, die wohl auch für den Diamagnetismus der Legierungsreihe Ag-Pd bis zu 50 % Pd verantwortlich ist. Da Palladium selbst hinsichtlich der Bindungsenergie der Zahl der *s*-Elektronen etc., sich ganz dem Verhalten der übrigen Übergangsmetalle einordnet, darf man daraus schliessen, dass die spezifische Wirkung der abgeschlossenen *d*-Schale bei diesem Element nebensächlich geworden ist und dass die *d*-Elektronen noch durch eine andere Bindungsart als der van der Waalsschen zur Kohäsionsenergie beitragen.

2. DIE BANDSTRUKTUR DER ÜBERGANGSMETALLE

Über die Bandstruktur der Übergangsmetalle liegen verschiedene Berechnungen vor, die mit der Zellenmethode [Literatur siehe (2)] und mit der sog. Blochschen Näherung durchgeführt worden sind (3).

Keine dieser Rechnungen scheint der Bedeutung der Wechselwirkung zwischen übernächsten Nachbarn, auf die wir unten zurückkomen werden, gerecht zu werden. Da befriedigendere quantitative Untersuchungen bis jetzt noch nicht vorliegen, werden wir versuchen, wenigstens qualitativ einige Gesichtspunkte für die Bandstruktur der Übergangsmetalle anhand einer Diskussion der Eigenschaften lokalisierter *d*-Funktionen zu besprechen und diese dann mit dem Experiment zu vergleichen.

Die Erörterungen im ersten Teil des vorliegenden Abschnittes beziehen sich grossenteils darauf, dass eine korrekte Beschreibung der Elektronenstruktur der Übergangsmetalle auch die ferromagne-

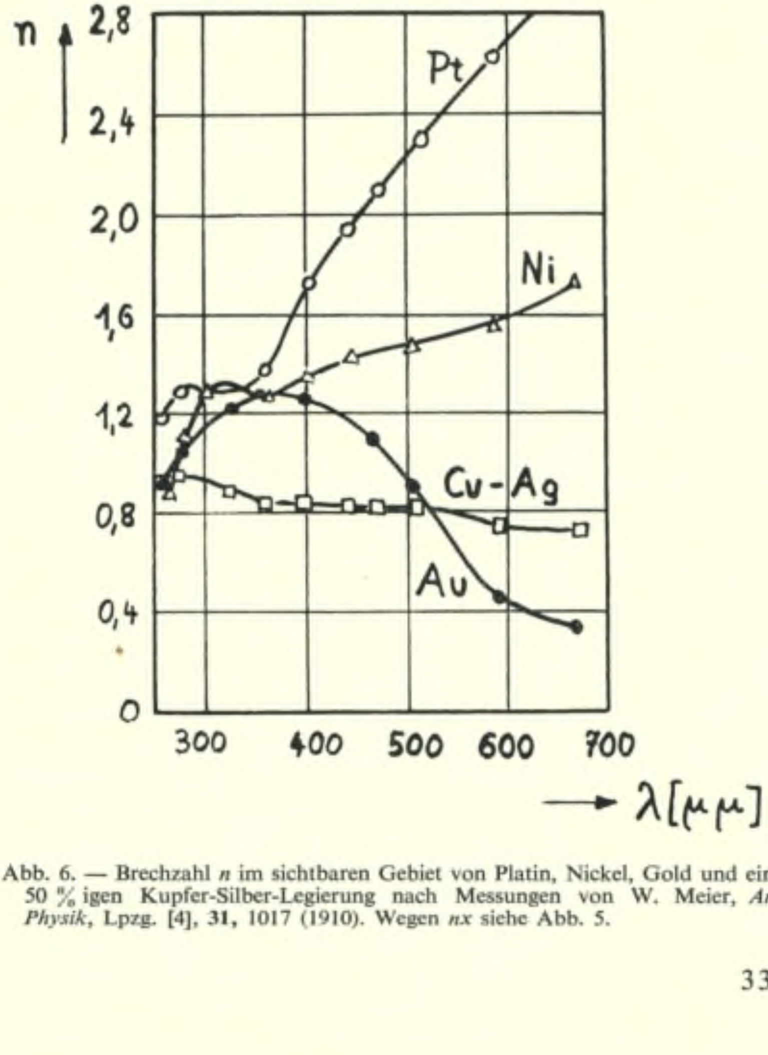

Abb. 6. — Brechzahl *n* im sichtbaren Gebiet von Platin, Nickel, Gold und einer 50 % igen Kupfer-Silber-Legierung nach Messungen von W. Meier, *Ann. Physik*, Lpzg. [4], **31**, 1017 (1910). Wegen *nx* siehe Abb. 5.

tischen Erscheinungen mit umfassen muss, und auf die Folgerungen, die sich hierauf für die Bändertheorie ergeben. Im zweiten Teil berichten wir über Überlegungen, die Aussagen über die möglichen stabilen Strukturen der Übergangsmetalle innerhalb der einzelnen Spalten des periodischen Systems — also auch zum Allotropieproblem — erlauben und die zu verhältnismässig definierten Ergebnissen über den allgemeinen Charakter der Bandstruktur der Übergangsmetalle führen werden.

Ein grosser Teil der theoretischen Arbeiten über die Eigenschaften der Übergangsmetalle und den Ferromagnetismus benutzt die Näherung der Elektronenbänder und der Einelektronenfunktionen. Die Betrachtung zweier sich überlappender Bänder mit überwiegendem *d*- bezw. *s*-Charakter der in ihnen aufgegangenen Atomfunktionen geht auf N.F. Mott (4) zurück. Auf eigentliche ferromagnetische Probleme war die Bandtheorie zuerst von F. Bloch (5) und später von J.C. Slater (6) und von E.C. Stoner und Mitarbeitern [zusammenfassende Literatur siehe (7)] angewandt worden. Eine Reihe von Tatsachen spricht allerdings dafür, dass die übliche Elektronenbandmethode mit einem einzigen, undifferenzierten Band für die *d*-Elektronen ohne tiefgreifende Modifikationen zur quantitativen Diskussion des Ferromagnetismus und damit zumindest eines Teiles der Übergangsmetalle ungeeignet ist :

1) Die Elektronenbandmethode versagt bei sehr grossen Verdünnungen des Elektronengases, was man daran erkennt, dass sie auch noch im Grenzfall unendlicher Verdünnungen Ferromagnetismus liefert. Bei ihrer Anwendung wurde deshalb wohl immer die implizite Annahme gemacht, dass sie sinnvolle Ergebnisse wenigstens für die in Wirklichkeit vorkommenden inneratomaren Abstände geben würde.

2) Berücksichtigt man jedoch die in der Elektronenbandmethode vernachlässigte Coulomb-Korrelation, so erhält man nach Pines (8) für ein Elektronengas ohne Bahnentartung bei allen Dichten keinen Ferromagnetismus. Dieses Resultat gilt zwar zunächst nur für einen Vergleich des Singulett-Zustandes mit dem Zustand höchster Multiplizität, doch widerspricht bereits dieses Teilergebnis dem Bloch-Stoner'schen Resultat. Es besteht auch kein physikalischer Grund dafür, weshalb das Ergebnis für Zustände mittlerer Multiplizität und bei Überlagerung der infolge der Spinentartung hierbei auftretenden sehr zahlreichen Konfigurationen gleicher Multiplizität das

Ergebnis, sich zu Gunsten des Ferromagnetismus ändern sollte. Eine wesentliche Voraussetzung für das eben diskutierte Ergebnis über das Nichtauftreten von Ferromagnetismus ist jedoch, dass keine Bahnentartung vorliegt. Wir kommen so zu dem von J.C. Slater (9) auf anderem Wege erreichten Schluss, dass die für den Ferromagnetismus verantwortlichen Elektronen *p*-, *d*-, *f*-, ..., nicht aber *s*-Elektronen sein können (vergl. den Anhang).

3) Die Stonersche Theorie der magnetischen Erscheinungen in einem Elektronengas (7) lässt die Bahnentartung der ferromagnetischen Elektronen ausser Acht und sollte deshalb überhaupt keinen Ferromagnetismus ergeben. Durch die Einführung eines phänomenologischen Molekularfeldes lassen sich jedoch eine Reihe von Daten über magnetische und thermische Eigenschaften der Elemente und Legierungen mit fast gefüllten *d*-Schalen verhältnismässig gut wiedergeben. Dies gilt jedoch nicht für Fe und seine Legierungen. Offensichtlich spielen bei Fe die feineren Eigenschaften der *d*-Funktionen eine ganz wesentliche Rolle. Insbesondere scheint uns auch das verschiedenartige magnetische Verhalten von α- und γ-Eisen erst dann aufgeklärt werden zu können, wenn die Einzelheiten der chemischen Bindung durch die *d*-Elektronen im flächenzentriert-kubischen und raumzentriert-kubischen Gitter in Betracht gezogen werden.

4) Eine « reine » Bandtheorie des Ferromagnetismus lieferte das Ergebnis, dass das magnetische Moment oberhalb der Curie-Temperatur vollkommen zusammenbricht und ein vollständiger Ausgleich der Elektronen mit + und — Spinn stattfindet. Dem widerspricht die Erfahrung. Wie C.G. Shull (10) gezeigt hat, tritt bei Fe (und bei Ni) auch oberhalb der Curie-Temperatur eine paramagnetische Streuung der Elektronen auf, und zwar mit einem Moment pro streuendem Atom, das vergleichbar mit dem aus ferromagnetischen Daten ermittelten Moment ist. Diese Ergebnisse sprechen für die Interpretation des Curie-Punktes als derjenigen Temperatur, bei der zwar die magnetische Fernordnung verschwindet, oberhalb welcher jedoch immer noch eine ferromagnetische Nahordnung auftritt. Abschätzungen der Curie-Temperatur aufgrund der intraatomaren Austauschenergie (6) sind deshalb nur von zweifelhaften Wert. Diese ist zwar sicher numerisch grösser als die interatomare Austauschenergie, doch ist die Curie-Temperatur in erster Linie durch letztere bestimmt.

Die vorstehende Diskussion sollte auf eine Reihe von Schwierigkeiten hinweisen, denen sich die Elektronenbandtheorie des Ferromagnetismus gegenüber sieht. Versuchte man, diese Schwierigkeiten durch Rückkehr zur Heisenberg-Heitler-London'schen Behandlungsweise zu umgehen, so würden neue Schwierigkeiten, z.B. hinsichtlich der Interpretation des Beitrags der Elektronen zur spezifischen Wärme der paramagnetischen Suszeptibilität, etc., auftreten.

Die derzeitige Situation weist somit auf die Notwendigkeit einer Synthese der Heisenberg-Heitler-London'schen Behandlungsweise (Aufbau der Gesamtelektronenwellenfunktion aus Atomfunktionen) und der Bändertheorie (Verwendung von Bloch-Hund-Mullikan-Funktionen oder auch Wannier-Funktionen) hin. Eine derartige Synthese, die die Vorzüge der beiden genannten Näherungsmethoden vereinigt und im Prinzip bei Verwendung einer unendlichen Anzahl von Konfigarationen eine strenge Lösung des Vielelektronenproblems zu geben vermag, ist die sog. Überlagerung von Konfigurationen, auch Konfigurationswechselwirkung [configuration interaction — siehe ([11]), ([12])] genannt. Die Verwendung dieser Methode als der einzig richtigen für magnetische Probleme ist mit besonderem Nachdruk von J.C. Slater ([13]) vertreten worden. Die Schwierigkeit für ihre Anwendung liegt jedoch in ihrer Schwerfälligkeit. Das komplizierteste Problem aus der Kristallphysik, das bis jetzt mit dieser Methode rechnerisch gelöst wurde, ist ein von H. Stehle und A. Seeger ([14]) behandeltes Vierelektronenmodell eines zweidimensionalen Kristalls. Über das Ergebnis wird in einem Anhang kurz berichtet werden. Bei Verwendung elektronischer Rechenmaschinen können zwar noch etwas kompliziertere Probleme angegriffen werden, doch steigen die mathematischen Schwierigkeiten mit wachsendem Umfang des Problems so ungeheuer stark an, dass man nicht hoffen kann, auf diese Weise Lösungen wirklichkeitsnaher Probleme zu bekommen.

Die Weiterentwicklung der bisherigen Ansätze hängt somit in erster Linie davon ab, ob es gelingt solche Vereinfachungen an der Methode der Konfigurationsüberlagerung anzubringen, dass man handliche, aber zuverlässige Näherungslösungen für die praktisch interessierenden Probleme erhält. Für ferromagnetische Probleme, bei denen meist der widerstreitende Einfluss der Korrelationsenergie und der Austauschenergie wesentlich ist, erscheint für diesen Zweck eine Kombination der Bohm-Pines'schen Methode ([15]) mit der

Überlagerung von Konfigurationen als aussichtsreich. Bis jetzt sind allerdings noch keine Rechnungen in dieser Richtung veröffentlicht worden.

Ein Resultat von allgemeinerer Bedeutung vermag die Konfigarationswechselwirkung ohne weitere Rechnung zu geben. Wie A. Meckler (16) gezeigt hat, hängt das Endergebnis auch bei Verwendung einer endlichen Anzahl von Konfigurationen (statt der für eine strenge Lösung erforderlichen unendlich vielen, aus einem vollständigem Funktionensystem aufgebauten Konfigurationen) nicht davon ab, ob man statt einem Satz von Ausgangsfunktionen einen anderen, daraus durch Linearkombination hervorgehenden Satz linear unabhängiger Funktionen verwendet. Auf Kristallprobleme angewandt, besagt dieses Ergebnis, dass es gleichgültig ist, ob man von den auf die Umgebung einzelner Gitterplätze konzentrierten Wannier-Kunktionen oder den den ganzen Kristall durchziehenden Bloch-Funktionen ausgeht. Legt man Wannier-Funktionen zugrunde, so hat man darauf zu achten, dass das Pauliprinzip am Einzelatom gewahrt bleibt. Ferner ergibt sich die Möglichkeit, über den Spin am Einzelatom Aussagen zu machen, die Hundsche Regel für ein Atom anzuwenden, kurz gesagt, die von der Heitler-London'schen Theorie der chemischen Valenz her bekannten Begriffsbildungen auch auf Kristallprobleme zu übertragen. In diesem Sinne sind die unten gegebenen Diskussionen über lokalisierte Funktionen und die gleichzeitige Verwendung des Bänderschemas zu verstehen.

Nach diesen Erörterungen allgemeinerer Art wenden wir uns nunmehr den Eigenschaften der *d*-Funktionen in den Übergangsmetallen zu. Von H. Bethe (17) stammt die Erkenntnis, dass das im freien Atom 5-fach entartete *d*-Niveau in einem Feld kubischer Symmetrie in ein 2-fach und in ein 3-fach entartetes Niveau aufspaltet. K. Ganzhorn (18) hat als erster erkannt, dass die Vorzugsrichtungen der zu diesen beiden Niveaus gehörigen Eigenfunktionen bezw. geeigneter Linearkombinationen zu den nächsten bezw. übernächsten Nachbarn des kubisch-flächenzentrierten und des kubisch-raumzentrierten Gitters hinweist. Dieses Ergebnis lädt zu einer Anwendung des Überlappungsprinzips der Valenztheorie [siehe (19)] ein.

Wir geben zunächst die uns hier interessierenden Ergebnisse von Ganzhorn kurz wieder :

Da der Radialanteil der zu betrachtenden *d*-Funktionen (von einem Normierungsfaktor abgesehen) stets der gleiche ist, können wir uns auf die Diskussion der winkelabhängigen Anteile der d-Funktionen beschränken. Wir verwenden ein kartesisches x, y, z-Koordinatensystem mit :

$$r = (x^2 + y^2 + z^2)^{1/2} .$$

Im kubisch-flächenzentrierten Gitter umfasst die dreifach entartete Gruppe (im Folgenden kurz III-Gruppe genannt) die folgenden Funktionen :

$$\begin{aligned} \varphi_1 &\sim \frac{yz}{r^2} \\ \varphi_2 &\sim \frac{xz}{r^2} \\ \varphi_3 &\sim \frac{zx}{r^2} \end{aligned} \tag{1}$$

Die durch diese Funktionen dargestellten Aufenthaltswahrscheinlichkeiten haben Vorzugsrichtungen in den Flächendiagonalen eines kubischen Gitters und damit zu den nächsten Nachbarn des kubisch-flächenzentrierten Gitters hin, wie dies Abb. 7 zeigt.

Die zweifach-entartete Gruppe (II-Gruppe) umfasst die Funktionen :

$$\begin{aligned} \varphi^4 &\sim \frac{z^2 - y^2}{r^2} \\ \varphi_5 &\sim \frac{z^2 - x^2}{r^2} , \end{aligned} \tag{2}$$

von denen jede Vorzugsrichtungen entlang zweier Würfelkanten aufweist und

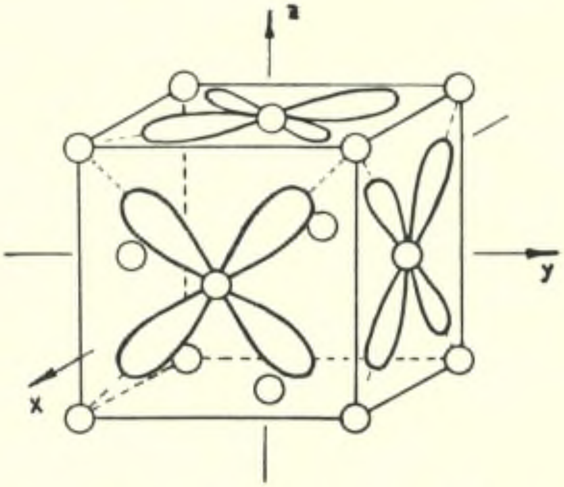

Abb. 7. — Konturen konstanter Aufenthaltswharscheinlichkeit für die Funktionen der III-Gruppe im kubisch-flächenzentrierten Gitter.

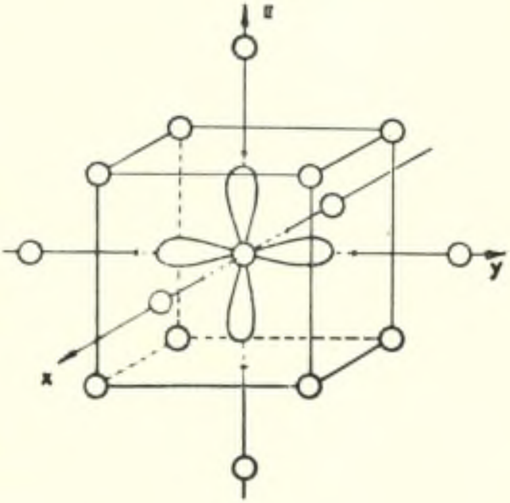

Abb. 8. — Kurve konstanter Aufenthaltswahrscheinlichkeit für eine der Funktionen der II-Gruppe. Gilt nicht nur wie angezeichnet für das kubisch-raumzentrierte Gitter, sondern auch für das kubisch-flächenzentrierte Gitter.

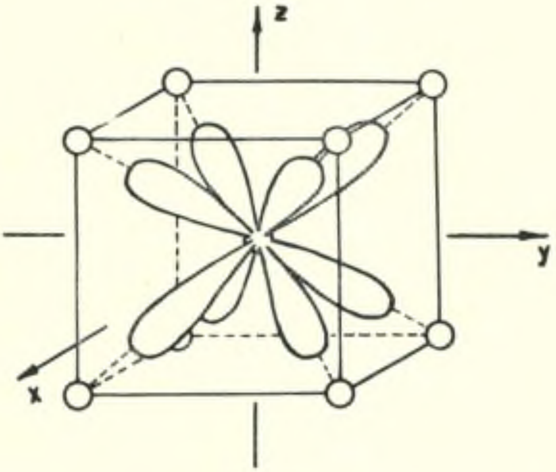

Abb. 9. — Konturen konstanter Aufenthaltswharscheinlichkeit für die Funktionen der III-Gruppe im kubisch-raumzentrierten Gitter.

somit auf die übernächsten Nachbarn sowohl im flächenzentriert-kubischen als auch im raumzentriert-kubischen Gitter hinzeigt, wie dies in Abb. 8 für die Funktion φ_4 dargestellt ist.

Will man das Ueberlappungsprinzip auch für die III-Gruppe im kubischraumzentrierten Gitter anwenden, so muss man von den Funktionen Gl. 1 zu den folgenden Linearkombinationen dieser Funktionen übergehen :

$$\begin{aligned} \varphi'_1 &\sim \frac{yz + xz + xy}{r^2} \\ \varphi'_2 &\sim \frac{yz - xz - xy}{r^2} \\ \varphi'_3 &\sim \frac{yz - xz + xy}{r^2} \,. \end{aligned} \tag{3}$$

Wie Abb. 9 zeigt, weisen diese Kunktionen Vorzugsrichtungen längs der Würfeldiagonalen und damit zu den nächsten Nachbarn im kubisch-raumzentrierten Gitter auf. Die Funktionen §§ Gl. 3 ergeben Maxima der Aufenthaltswahrscheinlichkeit zunächst nur in dreien der vier Würfeldiagonalen; die Summe der drei Funktionen besitzt jedoch in der vierten Diagonale eine vergrösserte Aufenthaltswahrscheinlichkeit.

Bekanntlich zeigen die Übergangsmetalle die komplizierteren Strukturen, nämlich α- und β-Mangan sowie die meisten Legierungsphasen können wir hier nicht behandeln, so dass wir nur noch die hexagonale dichteste Kugelpackung zu betrachten brauchen. Hier tritt eine Besonderheit gegenüber den kubischen Strukturen dadurch auf, dass die Gitterplätze in der hexagonalen dichtesten Kugelpackung nicht mehr Symmetriezentrum gegenüber Inversionen im Raum, sondern nur noch gegen Inversionen in der Ebene sind. Da die *d*-Funktionen (ebenso wie die *s*-Funktionen, welche für die Hybridbildung im Falle der Übergangsmetalle am ehesten in Frage kommen) zentrisch-symmetrisch sind, kann man zwar aus *d*- und *s*-Funktionen Linearkombinationen bilden, die Vorzugsrichtungen zu je zwei nächsten Nachbarn in der Basisebene haben, jedoch ist es nicht möglich, das Entsprechende für die Nachbaratome oberhalb oder unterhalb der Basisebene zu tun. Empirisch erscheint die Bindung in den hexagonalen Strukturen der Übergangsmetalle senkrecht zur Basisebene als besonders stark, da nur für Kobalt das Achsverhältnis c/a etwa der dichtesten Kugelpackung entspricht, während es für Titan, Zirkon, Rubidium und Osmium deutlich unternormal ist [20].

Welche der verschiedenen sich anbietenden Möglichkeiten zur Klärung dieses Sachverhalts (Bindung längs der hexagonalen Achse Überwiegen von metallischem oder van der Waals'schem Charakter, Hybridisierung mit p-Funktionen, starker Einfluss der zentrischsymmetrisch angeordneten übernächsten Nachbarn) die wahrscheinlichste ist, wurde vom Standpunkt der Theorie aus noch nicht untersucht. Wir kommen auf diese Frage weiter unten nochmals zurück und werden dabei unserer Diskussion die Ansicht zurgrundelegen, dass die Bindung parallel zur hexagonalen Achse im allgemeinen sowohl metallischen als auch van der Waals'schen Charakter hat.

Benützt man für die Funtionen mit Vorzugsrichtungen zunächsten Nachbarn in der Basisebene nur Linearkombinationen von d-Funktionen, so erhält man nach K. Ganzhorn (18) die folgenden Funktionen :

$$\begin{aligned}
\varphi''_1 &\sim \frac{1}{\sqrt{3}}\,\frac{2z^2-(x^2+y^2)}{r^2}-\sqrt{2}\,\frac{x^2-y^2}{r^2} \qquad (4)\\
\varphi''_2 &\sim \frac{1}{\sqrt{3}}\,\frac{2z^2-(x^2+y^2)}{r^2}+\frac{1}{\sqrt{2}}\,\frac{x^2-y^2}{r^2}-\sqrt{\tfrac{3}{2}}\,\frac{2\,x\,y}{r^2}\\
\varphi''_3 &\sim \frac{1}{\sqrt{3}}\,\frac{2z^2-(x^2+y^2)}{r^2}+\frac{1}{\sqrt{2}}\,\frac{x^2-y^2}{r^2}+\sqrt{\tfrac{3}{2}}\,\frac{2\,x\,y}{r^2}
\end{aligned}$$

Eine Kurve $\varphi_1''^2 = \text{const}$ in der Basisebene ist in Abbildung 10 wiedergegeben. Die entsprechenden Kurven $\varphi_2''^2$ und $\varphi_3''^2$ sind dagegen um ± 120° verdreht.

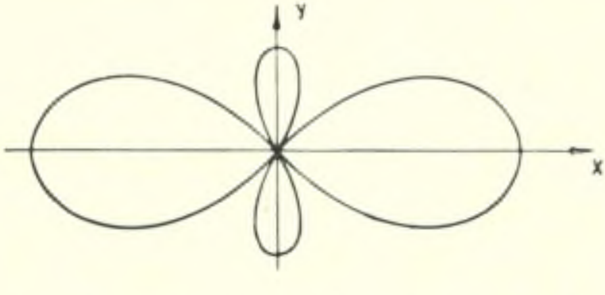

Abb. 10. — Konstante Aufenthaltswahrscheinlichkeit in der hexagonalen Basisebene für die Funktion φ_1'' Gl. 4. Die entsprechenden Kurven für die beiden andern Funktionen in Gl. 4 sind dagegen um ± 120° verdreht.

Wie man an der Form der Gl. 4 sieht, hängt eine der auftretenden d-Funktionen nicht von den Koordinaten x und y allein, sondern nur von der Kombination $x^2 + y^2$ ab. Hinsichtlich der Verhältnisse in der Basisebene spielt es somit keine Rolle, ob man bei der Bildung der der Anordnung nächster Nachbarn angepassten « symmetriegerechten » Funktionen die genannte d-Funktion ganz oder teilweise durch eine s-Funktion ersetzt. Man muss deshalb bei der Diskussion der hexagonalen dichtesten Kugelpackung die Möglichkeit im Auge behalten, dass je nach der Elektronenkonzentration eine mehr oder weniger starke Hybridisierung von s- und d-Funktionen stattgefunden hat.

Wir versuchen nunmehr, die vorstehenden Ergebnisse, die sich auf Atomeigenfunktionen beziehen, mit den allgemeinen Erkenntnissen der Theorie der chemischen Valenz zu kombinieren.

Sowohl die Hund-Mullikan'sche wie die Heitler-London'sche Näherung ergibt bei der homöopolaren Bindung eine Aufspaltung der Atomniveaus der Elektronen in bindende und lockernde Terme. Man darf wohl mit Recht annehmen, dass diese Unterteilung in einer allgemeineren, die beiden genannten Methoden als Spezialfälle enthaltenden Theorie ebenfalls ihren Platz haben wird. Bei Kristallen ist das entsprechende Auftreten von bindenden und lockernden Bändern von der Diamantstruktur her wohl bekannt. Da das Diamantgitter eine Struktur mit Basis ist, kann hier schon in der Einelektronennäherung eine endliche Energielücke zwischen bindendem und lockerndem Band auftreten. Das Gleiche gilt im Prinzip für die hexagonale dichteste Kugelpackung, obwohl hier nicht wie im Falle der Diamantstruktur bei den Elementen C, Si, Ge und Sn Strukturen bekannt sind, die tatsächlich eine solche Energielücke aufweisen. Bei Translationsgittern kann man ebenfalls von bindenden und lockernden Teilbändern sprechen, nur tritt hier natürlich bei der konventionellen Einelektronen-Bandtheorie keine Energielücke auf. Bei alternierenden Strukturen, wie z.B. dem kubisch-raumzentrierten Gitter, ist hierbei der Zusammenhang zwischen den Eigenfunktionen der beiden Teilbänder besonders einfach : Beim Aufbau der Blochfunktionen aus Atomfunktionen (bezw. Wannier-Funktionen) kehren sich die Vorzeichen der Beiträge von einem der beiden äquivalenten Teilgitter, aus denen man eine alternierende Struktur aufbauen kann, um. Beim kubisch flächenzentrierten Gitter ist der Zusammenhang komplizierter und noch nicht voll ausgearbeitet.

Energielücken zwischen bindendem und lockerndem Band können auch in Translationsgittern auftreten, wenn Wechselwirkungen, beispielsweise magnetischer Art, zwischen den Einelektronenfunktionen in Betracht gezogen werden. Ein Beispiel dafür ist der Antiferromagnetismus im Chrom. Die antiferromagnetische Überstruktur führt hier sicher dazu, dass in jeder Richtung des $\mathfrak{K}$-Raumes ein zusätzlicher Sprung der Energieeigenwerte als Funktion des Wellenzahlvektors $\mathfrak{K}$ auftritt. Ob jedoch die relative Lage dieser Sprünge zueinander so ist, dass sich eine Energielücke zwischen zwei Bändern ergibt, kann man nicht allgemein sagen. J.C. Slater und G.F. Koster (^{21}) haben gezeigt, dass im vorliegenden Falle dann eine wirkliche Energielücke auftritt, wenn Wechselwirkungen zwischen übernächsten Nachbarn vernachlässigt werden dürfen (*). Die Berechtigung einer solchen Vernachlässigung ist allerdings deswegen zweifelhaft, weil im kubisch-flächenzentrierten Gitter der Abstand übernächster Nachbarn nur um 16 % grösser als derjenige nächster Nachbarn ist. Nimmt man an, dass eine Energielücke vorhanden ist, so kann man aus dem Auftreten des Antiferromagnetismus schliessen, dass die Zahl der *s*-Elektronen pro Atom bei festem Chrom sehr nahe bei eins liegen muss (vergl. Seite 5, Fussnote *). Nur dann fällt die eben erwähnte Lücke mit der Lage der Fermienergie im *d*-Band etwa zusammen, so dass sich ein bedeutender Energiegewinn bei der Senkung der unteren und der Hebung der oberen Bandhälfte ergibt.

Für unsere Diskussion nehmen wir an, dass die Dichte der Energiezustände als Funktion der Energie zwar keine Lücke, aber ein ausgeprägtes Minimum aufweist. Fast alle bis jetzt durchgeführten Berechnungen der Eigenwertdichte von *d*-Bändern zeigen ein solches Minimum in der Nähe der Bandmitte, so dass es wohl auch in einer vollkommeren theoretischen Behandlung zu erwarten ist.

Die folgenden Überlegungen zur Bandstruktur sind sicher nur näherungsweise richtig, und zwar gelten sie in umso besserer Annäherung, je näher wir uns am Punkt $\mathfrak{R} = 0$ im Wellenzahlraum befinden. Für $\mathfrak{R} = 0$ muss sich nämlich die oben besprochene Aufspaltung in eine II-Gruppe und in eine III-Gruppe auch in der Bandstruktur wiederfinden (**). Wir nehmen an, dass man diese Unterteilung mit einiger Berechtigung für das ganze *d*-Band benützen darf. Die Rechtfertigung für dieses Vorgehen liegt darin, dass wegen der verschiedenartigen Vorzugsrichtungen und dem verschieden starken Überlappen der Wellenfunktionen benachbarter Atome in beiden Gruppen die Aufspaltung der entsprechenden Energieterme im Gitter sehr verschieden ist, und dass sich deswegen die betreffenden Zustände relativ wenig mischen. Wir erwarten somit in den Über-

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(*) Die ausführliche Fassung der zitierten Arbeit [*Phys. Rev.*, **94**, 1498 (1954)], die hinsichtlich der Rolle der *d*-Elektronen bei der chemischen Bindung der kubisch-raumzentrierten Uebergangsmetalle ganz ähnliche Ansichten wie die vorliegende Arbeit vertritt, stand bei der Abfassung dieser Mitteilung noch nicht zur Verfügung, so dass wir auf sie nicht näher eingehen konnten.

(**) Manche Rechnungen (z.B. diejenige von J.B. Greene und M.F. Manning (22) für γ—Fe) zeigen allerdings wegen der Verwendung eines kugelsymmetrischen Potentials (Zellenmethode) ohne zusätzliche Korrekturen diese Aufspaltung nicht.

gangsmetallen ein breites III-Band und ein schmäleres II-Band, welche beide ein Minimum der Zustandsdichte beim Übergang vom bindenden zum lockernden Teilband aufweisen. Als weitere Anwendung des Überlappungsprinzips können wir noch eine Aussage über die energetischen Schwerpunkte der Bänder machen. Da stärkere Überlappung stärkere Bindung bedeutet, muss der Schwerpunkt des bindenden III-Bandes tiefer als derjenige des bindenden II-Bandes liegen. Andererseits ist aber aus der Theorie der homöopolaren Bindung bekannt (19), dass die Summe der aus einem Atomniveau hervorgehenden bindenden und lockernden Energieterme umso höher liegt, je näher die bei der Bindung beteiligten Atome sich kommen. Auf unseren Fall angewandt bedeutet dies, dass der Gesamtschwerpunkt des III-Bandes höher als derjenige des II-Bandes liegen wird.

Zu der so erhaltenen Bandstruktur, die in Abb. 11 schematisch dargestellt ist, sind noch zwei Bemerkungen zu machen. Die erste

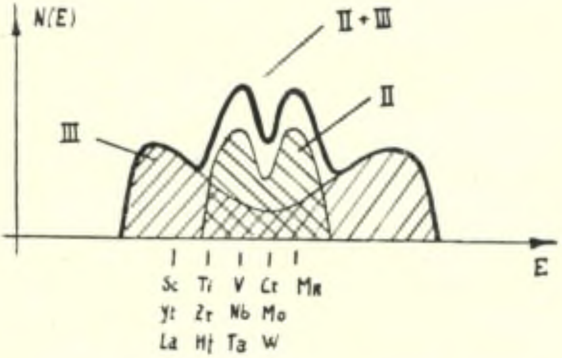

Abb. 11. — Dichte N(E) der Eigenwerte für das *d*-Band (II-Band und III-Band durch Schraffur unterschieden) mit Lage der Fermienergien einiger Uebergangselemente (schematisch).

bezieht sich auf die Tatsache, dass der Schwerpunkt zusammengehöriger bindender und lockernder Niveaus höher als das Atomniveau liegt. Sind so viele Elektronen vorhanden, dass auch bindende Niveaus besetzt werden müssen, so kann es energetisch günstiger sein, wenn die betreffenden Elektronen nicht an der homöopolaren Bindung teilnehmen, sondern nach Art der « lone pairs » (19) innerhalb der einzelnen Atome ihre Spins absättigen. In einem solchen

Fall treten Wellenfunktionen auf, die einer van der Waals'schen Bindung durch diese Elektronenpaare entsprechen. In extremem Masse ist dies bei den *d*-Elektronen der Edelmetalle der Fall. Hier sind gewissermassen nur noch « lone pairs » vorhanden, so dass der gesamte Beitrag der *d*-Elektronen zur Kohäsionsenergie der Edelmetalle van der Waals'sche Energie ist. Für die Theorie der Übergangsmetalle ist von Bedeutung, dass eine derartige Spin-Absättigung in guter Näherung innerhalb des II-Bandes allein erfolgen kann. Die II-Gruppe vermag somit in Form von van der Waals'scher Energie zur Bindung beizutragen, während gleichzeitig die III-Gruppe homöopolar bindet.

Die eben skizzierte Auffassung stellt also in gewissem Sinne einen Kompromiss dar zwischen der rein homöopolaren Auffassungen von K Ganzhorn (18) und C. Zener (25) [wegen einer Zusammenfassung der Zener'schen Arbeiten siehe (26)] und der Ansicht von N.F. Mott (27), wonach zumindest bei einigen Übergangsmetallen die Bindung ausschliesslich durch van der Waal'sche und metallische Kräfte erfolgen soll.

Versucht man die Dichteverteilung der Energieeigenwerte durch Röntgenemissionsmessungen experimentell zu bestimmen, so hat man zum Vergleich nicht die in Abb. 11 angedeutete, sondern eine durch Berücksichtigung der « lone pairs » verbesserte Eigenwertverteilung zu berücksichtigen. Leider ist die Röntgenspektroskopie der Valenzbänder der Uebergangsmetalle noch nicht so weit entwickelt, dass sie eindeutige und zuverlässige Resultate ergibt. Z.B. sollte nach der Theorie (23) die Uebergangswahrscheinlichkeit für die Emission aus dem 3*d*-Band in das 3*p*-Niveau drei- bis viermal grösser als für die Emission aus dem 4*s*-Band sein. Keine der gemessenen Emissionskurven (24) zeigt jedoch die erwähnte Einsattelung der Eigenwertdicht in der Mitte des Bandes. Da nach dem jetzigen Stand der experimentellen Ergebnisse ein Vergleich der Theorie mit den Röntgenemissionsdaten nicht lohnend erscheint, beschränken wir uns weiterhin auf die Diskussion der Bandform nach Abb. 11, welche, wie in Abschnitt 4 näher ausgeführt werden wird, einen Vergleich mit spezifischer Wärme der Elektronen und magnetischer Suszeptibilität erlaubt.

Die zweite Bemerkung bezieht sich auf eine Besonderheit der beiden dichtesten Kugelpackungen gegenüber dem kubisch-raumzentrierten Gitter. Wir hatten oben erwähnt, dass es bei der hexagonalen Kugelpackung nicht möglich ist, Linearkombinationen aus *d*- (und *s*-) Funktionen zu bilden, welche gleichzeitig Vorzugsrichtungen zu oberhalb und unterhalb der Basisebene gelegenen nächsten Nachbarn aufweisen. Wir werden für die weitere Diskussion annehmen, dass *d*-Elektronen, die aus diesem Grunde nicht senkrecht zur Basisebene homöopolar binden können, « lone pairs » bilden und dass somit die Kohäsion senkrecht zur Basisebene zum Teil von deren van der Waals'scher Wechselwirkung herrührt.

Ähnliche Überlegungen gelten, wie wir gleich sehen werden, auch für die kubische dichte Kugelpackung, wenn man die Spinverhältnisse bei homöopolarer Bindung in Betracht zieht, was für die bisherigen Überlegungen (von den « lone pairs » abgesehen) nicht erforderlich war. Wir nehmen an, dass, wie in der Molekültheorie, auch bei der homöopolaren Bindung in Kristallen zu einem bindenden Kunktionspaar entgegengesetzte Spins gehören. Dies führt auf die Betrachtung von geordneten Spinverteilungen in kubischen Gittern, oder was damit äquivalent ist — von Ionenkristallen und Ordnungsphasen der Zusammensetzung AB.

Beim kubisch-raumzentrierten Gitter liegen die Verhältnisse hinsichtlich der geordneten Spin-Verteilungen sehr einfach. Hier leistet der CsCl-Typ für das bindende III-Band das gewünschte : sämtliche Nachbaratome haben entgegengesetztes Ladungs- bezw. Spin-Vorzeichen (sog. Ordnung 1. Art). Beim II-Band erhält man das benötigte entgegengesetzte Vorzeichen übernächster Nachbarn, in dem man zwei NaCl-Teilgitter ineinander stellt (sog. Ordnung 2. Art). Beim kubisch-flächenzentrierten Gitter leistet für das II-Band die Ordnungsstruktur CuPt (sog. Ordnung 2. Art) das Gleiche : sämtliche übernächsten Nachbarn sind ungleiche Atome. Man kann jedoch nicht vermeiden, dass unter den nächsten Nachbarn im kubisch-flächenzentrierten Gitter gleichartige Atome sind. Die günstigsten Verhältnisse erreicht man mit der AuCu-Ordnungsstruktur (Ordnung 1. Art), bei welcher 8 Nachbarn von entgegengesetzter, 4 Nachbarn von gleicher Art sind (*). Das bedeutet aber, dass — wenn Spin-Absättigung Voraussetzung für die Ausbildung eines « Bindungsstriches » ist — von den drei Funktionen des III-Bandes im kubisch-flächenzentrierten Gitter eine nicht an der homöopolaren Bindung teilnehmen und allenfalls ein « lone pair » mit van der Waalsscher Bindung aufnehmen kann.

Die CuPt-Ordnungsphase weist trigonale, die AuCu-Ordnungsphase tetragonale Symmetrie auf, während die flächenzentrierten Übergangsmetalle innerhalb der Messgenauigkeit die volle kubische Symmetrie zeigen. Das quantenmechanische Problem, Lösungen der Schrödinger-Gleichung zu finden, die den oben diskutierten Gesichtspunkten Rechnung tragen und gleichzeitig die kubische Symmetrie wahren, ist bisher noch nicht gelöst worden. Vermutlich wird sich

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(*) Wegen einer Diskussion dieser geordneten Spin-Verteilungen und den zugehörigen Abbildungen siehe ([28]) und ([29]).

zur Behandlung dieser Frage die Löwdin'sche Methode (30) als sehr fruchtbar erweisen, die ja im Falle des raumzentrierten Gitters als einer alternierenden Struktur einen offenkundigen Zusammenhang mit unseren Vorstellungen aufweist.

Zur Anwendung und experimentellen Nachprüfung der theoretischen Vorstellungen bieten sich das Auftreten der drei einfachen metallischen Strukturen im periodischen System der Elemente sowie magnetische Suszeptibilität, spezifische Wärme der Elektronen und Hall-Effekt an (wegen der Röntgenspektroskopie der Valenz-Bänder vergl. die Bemerkung auf S. 14).

Das Problem der Strukturen wurde schon von K. Ganzhorn (18) angegriffen. In der in Abschnitt 3 zu gebenden Diskussion dieser Frage werden wir seine Grundgedanken verwenden, aber unsere Darlegungen auf das in diesem Abschnitt entworfene wesentlich detailliertere Bild stützen. Dementsprechend werden wir auch definiertere und mit der Erfahrung recht gut übereinstimmende Aussagen machen können.

Die übrigen drei Eigenschaften, die im wesentlichen eine Aussage über die Bandstruktur in der Nähe der Fermienergie erlauben, werden wir in Abschnitt 4 behandeln.

3. DIE KRISTALLSTRUKTUREN DER ÜBERGANGSELEMENTE

Da wir nicht in der Lage sind, die Beiträge der einzelnen, im Vorstehenden besprochenen Elektronenkonfigurationen zur Kohäsionsenergie zu berechnen, müssen wir uns mit einer mehr qualitativen Diskussion der möglichen stabilen Strukturen begnügen. Es ist jedoch in vielen Fällen ohne weiteres möglich, Angaben über die relative Wichtigkeit der verschiedenen Beiträge zu machen. Beispeilsweise ist eine homöopolare Bindung fester, wenn sie zwischen nächsten Nachbarn erfolgt als wenn sie zwischen übernächsten Nachbarn stattfindet. Ein weiterer allgemeiner Grundsatz ist, dass zwei zusammengehörende bindende und lockernde Zustände zusammen einen negativen Beitrag zur Bindungsenergie ergeben, sofern sie nicht einer abgeschlossenen Gruppe, welche van der Waals'sche Bindung gibt, angehören.

Dass die Besetzung eines sog. lockernden Termes tatsächlich zu einer Verminderung der Bindungsenergie führt, kann man durch viele Beispiele aus der Molekültheorie, z. B. durch einen Vergleich von O_2 mit O_2^+ belegen. Die Elektronenkonfiguration des Grundzustandes von O_2 ist in der Bezeichnungsweise der Valenztheorie :

$$(\sigma 1s)^2\,(\sigma^* 1s)^2\,(\sigma 2s)^2\,(\sigma^* 2s)^2\,(\sigma 2p)^2\,(\pi_y 2p)^2\,(\pi_z 2p)^2\,(\pi^*{}_y 2p)^1\,(\pi^*{}_z 2p)^1$$

(vergl. (19) — ein * bedeutet einen lockernden Zustand). Im Grundzustande sind die beiden (miteinander entarteten) lockernden Zustände $(\pi_y^* 2p)$ und $(\pi_z^* 2p)$ mit nur einem Elektron besetzt. Dementsprechend steigt die Bindungsenergie vom Wert 5,08 *e*V bei O_2 wegen des Wegfalls eines lockernden Elektrons auf 6,48 *e*V bei O_2^+ an. Beim Uebergang von N_2 zu N_2^+ fällt dagegen eines der bindenden Elektronen in den (ebenfalls mit einander entarteten) Zuständen $(\pi_y\, 2p)$ und $(\pi_z\, 2p)$ weg, so dass sich die Bindungsenergie von 7,38 *e*V (N_2) auf 6,35 *e*V (N_2^+) erniedrigt (19).

Zur Abzählung der verschiedenen Bindungsmöglichkeiten verwenden wir die folgenden Abkürzungen :

b bezw. *b′* : Zahl der Elektronen pro Atom in bindenden Funktionen, welche zwischen nächsten (*b*) bezw. übernächsten (*b′*) Nachbarn vermitteln.
1 bezw. 1′ : entsprechende Zahlen für die lockernden Funktionen.
s : Zahl der Elektronen pro Atom, welche metallische Bindung geben.
p : Zahl der am Atom hinsichtlich des Spins abgesättigten Elektronenpaare, welche van der Waalssche Bindung geben.

Für die folgende Abzählung nehmen wir bei den kubischen Strukturen durchweg an, dass die Zahl der *s*-Elektronen im festen Zustand der Übergangsmetalle gleich 1 ist. Zwar sind Abweichungen von dieser Zahl nach unten bekannt, doch ist dies auf unsere Diskussion (von den hexagonalen Strukturen abgesehen) ohne Einfluss. Bei der hexagonalen dichtesten Kugelpackung konnt die Frage nach der Zahl der *s*-Elektronen dadurch in unsere Diskussion herein, dass man, wie oben dargelegt, die gerichteten Funktionen in der Basisebene entweder aus *d*-Funktionen allein oder als Hybrid-Funktionen aus *s*- und *d*-Funktionen aufbauen kann. Für die beiden möglichen Grenzfälle (Verhältnis von *d*- und *s* Anteil wie 2 : 1 oder nur *d*-Funktionen) geben wir in den relevanten Fällen die Resultate in Tab. 1 an. In den beiden letzten Spalten erscheint die hexagonale dichteste Kugelpackung ohne Hybridisierung als gleichberechtigt mit dem kubisch-raumzentrierten Gitter und damit

TABELLE 1

Die Bindungsmöglichkeiten in den Uebergangsmetallen sowie die daraus folgenden möglichen stabilen Strukturen.

Elemente :	Sc Yt La	Ti Zr Hf	V Nb Ta	Cr Mo W	Mn Tc Re	Fe Ru Os	Co Rh Ir	Ni Pd Pt
Zugrunde gelegte Electronenstruktur :	d^2s	d^3s	d^4s	d^5s	d^6s	d^7s	d^8s	d^9s
Kubisch-raumzentriertes Gitter (K 8)	$b = 2$ $s = 1$	$b = 3$ $s = 1$	$b = 3$ $b' = 1$ $s = 1$	$b = 3$ $b' = 2$ $s = 1$	$b = 3$ $b' = 2$ $s = 1$ $l' = 1$	$b = 3$ $s = 1$ $p = 2$	$b = 3$ $s = 1$ $p = 2$ $l = 1$	$b = 3$ $s = 1$ $p = 2$ $l = 2$
Kubisch--flächenzentriertes Gitter (K12)	$b = 2$ $s = 1$	$b = 2$ $b' = 1$ $s = 1$	$b = 2$ $b' = 2$ $s = 1$	$b = 2$ $b' = 2$ $s = 1$	$b = 2$ $b' = 2$ $s = 1$ $p = 1$	$b = 2$ $s = 1$ $s = 1$ $p = 1$ $l' = 1$	$b = 2$ $s = 1$ $s = 1$ $p = 3$	$b = 2$ $s = 1$ $s = 1$ $p = 3$ $l = 1$
Hexagonale dichteste Kugelpackung (H12)	$b = 2$ $s = 1$	$b = 3$ $s = 1$	$b = 3$ $s = 1$	$b = 3$ $s = 1$	$b = 3$ $p = 2$	$b = 3$ $s = 1$ $p = 2$	$b = 3$ $b = 3$ $p = 3$ $s = 1$ $p = 2$ $l = 1$	$b = 3$ $b = 3$ $p = 3$ $s = 1$ $l = 1$ $p = 2$ $l = 2$
Mögliche stabile Strukturen :	K 8 K12 H12	K 8 H12	K 8	K 8	K 8 K12 H12	K 8 K12 H12	K12 H12 (?)	K12 H12 (?)

ungünstiger als das kubisch-flächenzentrierte Gitter. Mit Hybridisierung dagegen erscheint die Bindungsfestigkeit des hexagonalen Gitters derjenigen des kubischflächenzentrierten Gitters vergleichbar, doch hängt dies noch von der relativen Stärke von metallischer und homöopolarer Bindung ab. Das empirische Material legt folgende Deutung nahe : die Elektronenkonzentration, bei der das hexagonale Gitter in der zweiten und dritten langen Periode des Periodischen Systems günstiger oder ebenso günstig wie das kubisch-flächenzentrierte Gitter ist, endet bei einer Elektronenkonzentration pro Atom von etwa 7,5 *d*-Elektronen (unter der Annahme $s = 1$). Dies wird durch Messungen von Raub (31) über die Ausdehnung der hexagonalen dichtest gepackten Phase in den Systemen MoRh (bis 7,55), MoIr (bis 7,4) und MoPt (bis 7,2 *d*-Elektronen pro Atom) gestützt. Für höhere Elektronenkonzentrationen erscheint das flächenzentriert kubische Gitter als in sehr geringen Masse gegünstigt gegenüber der hexagonalen dichtesten Kugelpackung mit der alleinigen Ausnahme von Co und einigen seiner Legierungen. Es ist somit anzunehmen, dass in der Platin-Gruppe sowie in Nickel die Stapelfehlerenergie γ, die ein Mass für den energetischen Unterschied zwischen den beiden dichtesten Kugelpackungen ist, verhältnismässig niedrig liegt (32). Da ihre Grössenordnung bekannt ist, kann man die Energiedifferenz kubisch-hexagonal abschätzen. Es ergibt sich (mit $\gamma \sim 100$ erg/cm^2) eine Grössenordnung von 0,02 *e*V pro Atom, was in Anbetracht der hohen Curie-Temperatur von Co wesentlich kleiner als die magnetische Energie ist. Dieses Resultat legt die Vermutung nahe, dass die magnetische Energie bei der Stabilisierung der hexagonalen Modifikation von Co mitwirkt.

Beim Vergleich der Theorie mit der Erfahrung haben wir in Tab. 1 nur die drei einfachen Strukturen (K12 = kubisch-flächenzentriert, K8 = kubisch-raumzentriert, H12 = hexagonale dichteste Kugel-

TABELLE 2

Die stabilen Strukturen der Uebergangsmetalle.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni
	K8	K8	K8	K8	K8		
K12				K12	K12	K12	K12
H12	H12			β,α		H12	
Yt	Zr	Bb	Mo	Tc	Ru	Rh	Pd
	K8	K8	K8				
						K12	K12
H12	H12			H12	H12		
La	Hf	Ta	W	Re	Os	Ir	Pt
	K8(?)	K8	K8				
K12						K12	K12
H12	H12			H12	H12		

packung) berücksichtigt. Die Strukturen von α- und β-Mn sind zu kompliziert, um von einer so einfachen Theorie wie der unserigen erfasst zu werden. Die β-Wolfram Struktur tritt zwar in Legierungen zwischen Übergangsmetallen auf [z.B. $OsMo_3$, $IrMo_3$ — siehe (31)], ist jedoch beim elementaren Wolfram nicht stabil (*).

Wir geben in der letzten Zeile von Tab. 1 diejenigen Strukturen an, die man aufgrund der in Tab. 1 gegebenen Abzählung als die energetisch günstigsten anzunehmen hat. Wie ein Vergleich mit Tab. 2, die auf den Angaben von W. Hume-Rothery und B.R. Coles(20) basiert, zeigt, ist die Übereinstimmung mit der Erfahrung dort, wo die Theorie eindeutige Aussagen macht (d^4s und d^5s) sehr gut. Aber auch in allen anderen Fällen finden sich keine Strukturen, die aufgrund unserer Überlegungen unwahrscheinlich und deshalb nicht in Tab. 1 aufgeführt sind. Man gewinnt somit den Eindruck, dass unsere Überlegungen über Bandstruktur und Bindungscharacter der Übergangsmetalle in der Tat das Wesentliche treffen und dass ein Versuch zu ihrer quantitativen Erweiterung sich lohnen würde.

4. VERGLEICH DER BANDSTRUKTUR MIT DER ERFAHRUNG

Von den hier zu besprechenden experimentellen Daten geben der Koeffizient γ der spezifischen Wärme der Elektronen (experimentell : der der absoluten Temperatur proportionale Anteil der spezifischen Wärme bei tiefen Temperaturen) und die paramagnetische Suszeptibilität χ bei tiefen Temperaturen Aufschluss über die Zahl N(E) der Energiezustände der Elektronen bei der Energie $E = \mathcal{J}$ ($\mathcal{J}$ = Fermienergie). Gerade bei den Übergangsmetallen ist es jedoch um einen quantitativen Vergleich der Experimente mit den aus einer Bandtheorie errechneten Werten von N(E) schlecht bestellt. Man hat mit einer Vergrösserung der spezifischen Wärme der Elektronen durch die durch Schallquanten vermittelte Wechselwirkung zwischen den Elektronen zu rechnen (33). Bei der magnetischen Suszeptibilität wirkt sich der — ohne Kernspin-Resonanzexperimente nicht abzutrennende — Diamagnetismus abgeschlossener Schalen oder Teilschalen und natürlich der im allgemeinen unbekannte

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(*) Nach C. Zener (25) und G. Masing, *Lehrbuch der Metallkunde*, Berlin-Göttingen-Heidelberg, 1950, p. 477 kann β-Wolfram durch Elektrolyse erhalten werden.

Einfluss der Austausch- und Korrelationseffekte störend aus. Entsprechendes gilt für die Temperaturabhängigkeit der magnetischen Suszeptibilität, die im Prinzip Aufschlüsse über den Verlauf von N(E) in der Umgebung von $E = \mathcal{J}$ gibt.

Trotz dieser Schwierigkeiten haben sich in neuester Zeit eine ganze Reihe von Arbeiten mit diesen Fragen beschäftigt (34-39). Wir werden uns insbesondere auf die experimentellen Resultate in den beiden letztgenannten Arbeiten stützen (38) (39).

Die experimentellen Ergebnisse sind in Tab. 3 wiedergegeben. Die Zahlenangaben der magnetischen Suszeptibilitäten pro Gramm-

TABELLE 3

Koeffizient der Elektronenwärme nach (39), magnetische Suszeptibilität mit Temperaturgang nach (39) (*).

Element	Ti	V	Cr	Mn	Fe	Co	Ni
Kristallstruktur	H12	K8	K8	α-Mn	K8	H12	K12
$\gamma\left[10^4\frac{\text{Cal}}{\text{Mol.Grad}^2}\right]$	8,0	15	3,8	42	12,0	12,0	17,4
$\chi\left[10^6\frac{\text{el. magn. Einh.}}{\text{Mol}}\right]$	153	255	172	533	1600*	—	—
sgn $(d\chi/dT)$	+	—	+	—	—	—	—
Element	Zr	Nb	Mo	Tc	Ru	Rh	Pd
Kristallstruktur	H12	K8	K8	H12	H12	K12	K12
$\gamma\left[10^4\frac{\text{cal}}{\text{Mol.Grad}^2}\right]$	6,9	21	5,1	—	—	—	31
$\chi\left[10^6\frac{\text{el. magn. Einh.}}{\text{Mol}}\right]$	118	208	90,3	—	43,4	102	558
sgn $(d\chi/dT)$	+	—	+	—	+	+	—
Element	Hf	Ta	W	Re	Os	Ir	Pt
Kristallstruktur	H12	K8	K8	H12	H12	K12	K12
$\gamma\left[10^4\frac{\text{cal}}{\text{Mol.Grad}^2}\right]$	—	14,1	2	—	—	—	16,0
$\chi\left[10^6\frac{\text{el. magn. Einh.}}{\text{mol}}\right]$	73	152	55,0	69	95	34,7	190
sgn $(d\chi/dT)$	+	—	+	—	+	+	—

(*) Die Suszeptibilitätsangaben bei Fe gelten für γ-Fe und wurden auf Raumtemperatur extrapoliert.

atom beziehen sich auf Raumtemperatur; ferner geben wir noch das Vorzeichen der Temperaturabhängigkeit $d\chi/dT$ an. Dabei wurde nur der allgemeine Gang mit der Temperatur beachtet. Feinheiten, wie das Suszeptibilitätsmaximum von Palladium bei tiefen Temperaturen (40), sind dabei nicht berücksichtigt. Bei den Daten wurden die aus der Temperaturabhängigkeit des Schwellenwertes des Magnetfeldes bei der Supraleitung ermittelten Werte als zu unsicher ausgeschieden.

Zur Diskussion der experimentellen Ergebnisse benützen wir die von der Theorie eines freien Elektronengases ohne Austausch (Hartree-Theorie) gelieferten Formeln für sehr tiefe Tempetaturen :

$$\gamma = \frac{2}{3}\pi^2 k^2 N(\mathcal{J}) \tag{5}$$

$$\chi = 2\mu_B^2 N(\mathcal{J}) \ , \tag{6}$$

wobei $N(\mathcal{J})$ die Dichte der Zustände pro Mol für Elektronen einer Spinrichtung bei der Fermienergie $\mathcal{J}$ und μ_B das Bohrsche Magneton ist. Zwischen γ und χ besteht gemäss Gl. 5 und 6 der Zusammenhang :

$$\frac{\gamma}{\chi} = \frac{\pi^2}{3}\left(\frac{k}{\mu_B}\right)^2 = 17{,}42\left[\frac{\text{cal}}{\text{Grad}^2\ \text{el. magn. E.}}\right] \tag{7}$$

Ein Vergleich mit Tab. 3 zeigt, dass Gl. 7 bei den Übergangsmetallen nicht erfüllt ist. Die Abweichungen sind in dem Sinne, dass χ gegenüber dem theoretischen Wert um einen Faktor, der um den Wert 3 schwankt, zu gross ist. Diese Abweichung rührt wohl grössenteils von der Vernachlässigung der Austauschkräfte her. Soweit Messungen sowohl von γ als auch χ vorliegen, ist der Gang dieser Grössen innerhalb der einzelnen Periode derselbe, so dass es möglich ist, trotz der eben erwähnten Diskrepanz hieraus etwas über die Form der N(E)-Kurve abzuleiten.

Weitere Informationen über N(E) kann man aus der Temperaturabhängigkeit von χ erhalten. Eine elegante und einfache graphische Methode zur Bestimmung von $d\chi/dT$ bei gegebenem N(E) ist neeurdings angegeben worden (36). Wir beschränken uns auf eine qualitative Diskussion.

Die Temperaturabhängigkeit von χ rührt in der einfachen Bandvorstellung von zwei Ursachen her, nämlich erstens der Verbreiterung der Übergangszone der Fermiverteilung mit wachsender Temperatur, und zweitens der Verschiebung der Fermienergie mit der Temperatur. Der erste Beitrag ist proportional zu und seinem Vorzeichen nach gegeben durch $[d^2N(E)/dE^2]_{E=J}$. Der zweite Beitrag ist proportional zu :

$$\frac{dN(E)}{dE}_{\,E=J} \,.\, dJ/dT$$

und bei tiefen Temperaturen immer negativ. Befindet sich die Fermienergie J gerade in der Nähe eines Maximuns oder Minimums der N(E)-Kurve, so kann man den zweiten Anteil an $d\chi/dT$ vernachlässigen. In diesem Fall muss zu grossen Werten von γ, χ und $N(J)$ ein negativer Temperaturkoeffizient gehören und umgekehrt.

In Abb. 11 ist die ungefähre Lage der Fermienergie der Elemente zu Beginn der langen Periode sowie von Mn unter der Annahme eingetragen, dass die Zahl der *s*-Elektronen pro Atom $s = 1$ ist. Wie man durch Vergleich mit Tab. 3 sieht, entsprechen diese Lagen in Maximis und Minimis der N(E)-Kurve gerade den Erwartungen aufgrund der eben gegeben Diskussion. Dass sich zwar das kubische Mangan, nicht aber das in derselben Spalte stehende hexagonale Rhenium in Abb. 11 einordnet, ist leicht zu verstehen. Wie man aus Tab. 1 entnehmen kann, muss man annehmen, dass in Re eine Hybridbildung zwischen *s*- und *d*-Elektronen stattgefunden hat mit dem Resultat, dass sich alle diese Elektronen an der Bindung beteiligen. Die Fermienergie befindet sich gerade an der Übergangsstelle zum ersten (unbesetzten) lockernden Teilband, so dass man in der Tat ein kleines $N(J)$ zu erwarten hat.

Abb. 12 zeigt die bei flächenzentriert-kubischen und hexagonalen Metallen am Ende der lange Perioden zu erwartende Bandstruktur. Pt und Pd wurden unter Benützung des durch magnetische Untersuchungen nahegelegten Wertes $s = 0{,}6$ eingetragen. Bei Rh und Ir wurde $s = 1$ angenommen. Dass sich beim Fortschreiten von Pd zu Rh und Ru die Zahl der *s*-Elektronen erhöhen muss (evtl. sogar über $s = 1$ hinaus), sieht man an der Änderung des Vorzeichens des Hall-Effektes von Pd (—) zu Rh (+) und Ru (+)(41) (*). Da man bei Pd und Pt das negative Vorzeichen des Hall-Koeffizienten R nur verstehen kann (vergl. Gl. 8), wenn man den *d*-Elektronen

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(*) Auch bei Ti, V und Cr ist der Hall-Effekt positiv (42).

Beweglichkeiten zuschreibt, die klein gegen diejenigen der *s*-Elektronen sind, so muss man bei positivem R die Zahl der *s*-Elektronen soweit erhöhen, dass effektiv Löcherleitung eintritt, also mindestens bis zum Wert 1. Damit wird aber sofort das Verhalten von Rh und Ir nach Tab. 3 verständlich. Bei Pd und Pt hat man mit Komplikationen zu rechnen, da diese Elemente ja auf der Flanke der N(E)-Kurve liegen. Ihr Verhalten gemäss Tab. 3 ist mit Abb. 12 verträglich. Für Ru und Os hat man dieselbe Argumentation wie für Re, jedoch ohne Hybridisierung, anzuwenden, sodass die Angaben in Tab. 3 bei ihnen ebenfalls in Übereinstimmung mit unserem Bild sind.

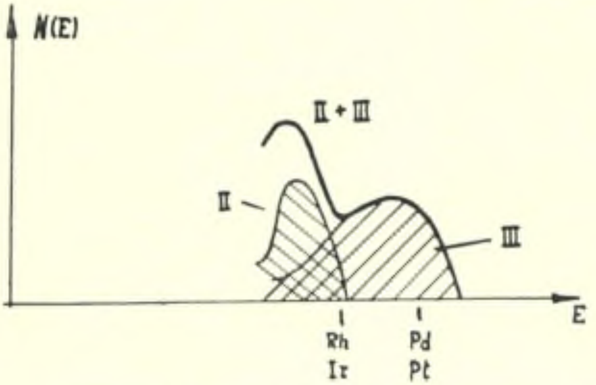

Abb. 12. — Eigenwertdichte N(E) für die nicht ferromagnetischen kubisch-flächenzentrierten Elemente mit fast gefülltem *d*-Band (schematisch).

Man kann somit sagen, dass die bis heute bekannten experimentellen Daten über die magnetische Suszeptibilität und die Elektronenwärme der nicht ferromagnetischen Übergangsmetalle das von uns entworfene Bild der Bandstruktur in vollem Umfange stützten. Da eine Betrachtung der ferromagnetischen Übergangsmetalle ohne eine ausführliche Diskussion des magnetischen Verhaltens ihrer Legierungen nicht lohnend erscheint, gehen wir auf sie hier nicht näher ein.

Als letzte experimentelle Grösse, die Schlüsse über die Bandstruktur zu ziehen erlaubt, bleibt noch der Hall-Koeffizient R zu diskutieren. Es scheint jedoch, als ob sich z.Zt. bei den Übergangsmetallen hieraus nur, wie oben geschehen, qualitative Ergebnisse folgern lassen. Der Grund dafür ist darin zu suchen, dass sich bei ihnen stets zwei nicht vollständig gefüllte Bänder überlappen, wodurch die einfache Bedeutung des Hall-Koeffizienten bei freien Elektronen in einem einzigen Band verloren geht.

Legt man die (unter der Voraussetzung freier Elektronen bezw. Löcher) abgeleitete Formel für den Hall-Effekt bei zwei sich überlappenden Bändern (43) :

$$R = R_1 \left(\frac{\sigma_1}{\sigma}\right)^2 + R_2 \left(\frac{\sigma_1}{\sigma}\right)^2 \tag{8}$$

zugrunde, so sieht man, dass der gemessene Hallkoeffizient R nicht nur von den Hallkoeffizienten der einzelnen Bänder

$$R_i = \frac{1}{e.c.\ N_i} \tag{9}$$

[Gausssche Einheiten; c = Lichtgeschwindigkeit, e = Betrag der Elementarladung, N_i = Zahl der Löcher (wenn $N_i > O$) bzw. Elektronen ($N_i < O$) im *i* ten Band] abhängt, sondern auch von den Beiträgen σ_i der einzelnen Bänder zur Gesamtleitfähigkeit :

$$\sigma = \sigma_1 + \sigma_2 \tag{10}$$

Bei den ferromagnetischen Metallen und Legierungen ist zwar über die Zahl N_s der *s*-Elektronen aus magnetischen Daten einiges bekannt, doch ist bis heute die Aufteilung der beobachteten Leitfähigkeit in σ_s und σ_d, besonders bei den Legierungen, recht unsicher. Wegen dieser Unsicherheit hinsichtlich der Leitfähigkeit ist es wohl auch nicht möglich, aus den Messungen des Koeffizienten R_0 des ordentlichen Halleffekts in der Reihe Fe-Co-Ni-Cu (44), die unter der Annahme σ_s/σ_d = const eine mit unserem Modell recht gut verträgliche Variation von N_d ergeben würde, gerechtfertigte Folgerungen über die Bandstruktur der Ferromagnetika zu ziehen. Es scheint jedoch, dass ein genaueres experimentelles und theoretisches Studium der elektrischen Leitfähigkeit der ferromagnetischen Elemente und Legierungen weiteren Aufschluss über deren Elektronenstruktur geben könnte.

Der Verfasser ist Herrn Prof. Dr. Dehlinger für die Anregung zur Beschäftigung mit dem behandelten Gebiet sowie für viele Diskussionen sehr dankbar.

ANHANG

ANWENDUNG DER KONFIGURATIONS-ÜBERLAGERUNG AUF EIN EINFACHES KRISTALLMODELL (*)

Anlass zu der Untersuchung (14), über deren Ergebnisse hier in aller Kürze berichtet werden soll, gab eine Arbeit von J.C. Slater, H. Statz und G.F. Koster (9). Diese Autoren untersuchten mit Hilfe der Konfigurationswechselwirkung einfache Kristallmodelle mit insgesamt zwei Elektronen oder Defektelektronen ausserhalb abgeschlossener Schalen. Ihr allgemeines Resultat, dass für das Zustandekommen des Ferromagnetismus Bahnentartung eine notwendige Bedingung ist, stimmt mit der von uns in § 2 aus den Rechnungen von Pines (8) gezogenen Folgerung überein. Dagegen glauben wir nicht, dass das Slater-Statz-Kostersche Zweielektronenmodell ein geeigneter Ausgangspunkt ist, um realistischere Probleme des Ferromagnetismus zu behandeln. Der Grund dafür ist, dass in wirklichen Metallen als Gegenkraft gegen die ferromagnetische Tendenz der Austauschkräfte in erster Linie die Fermienergie wirkt. Beim obigen Modell fällt jedoch diese Gegenkraft gerade weg, da sich ja infolge der Bahnentartung zwei Elektronen selbst im Triplettzustand stets im tiefstgelegenen Energieniveau befinden können. Man muss demnach erwarten, dass sich beim Übergang von zwei Elektronen oder Löchern zu einer Zahl, die grösser ist als der Entartungsgrad des Grundzustandes, wegen des Einflusses der Fermienergie die Verhältnisse hinsichtlich der Multiplizität des Grundzustandes wesentlich ändern.

Um diese Vermutung zu erhärten, wurde in derselben Näherung wie in (9) mit Hilfe der Konfigurationswechselwirkung ein Vierelektronenproblem behandelt (14). Das in (9) und ausführlicher in (45) betrachtete Kristallmodell besteht aus einem ebenen Gitter von 9 Atomen in quadratischer Anordnung. Die Elektronen können p_{x-y} oder p_y-Funktionen besetzen. Die Gesamtwellenfunktion wird periodischen Randbedingungen unterworfen.

Da die direkte Erweiterung dieses Modells auf 4 Elektronen zu einer unhandlich grossen Zahl von Konfigurationen Anlass geben würde, haben wir uns auf den Vergleich des Zwei- und Vierelektronen-

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(*) Für fruchtbare Diskussionen zu den hier behandelten Fragen danke ich Herrn Dipl. Phys. H. Stehle, Stuttgart.

problems bei einem quadratischen Gitter von 4 Atomen mit periodischen Randbedingungen beschränkt (Abb. 13). Durch Vergleich mit den Ergebnissen in (⁴⁵) wurde sichergestellt, dass alle wesentlichen

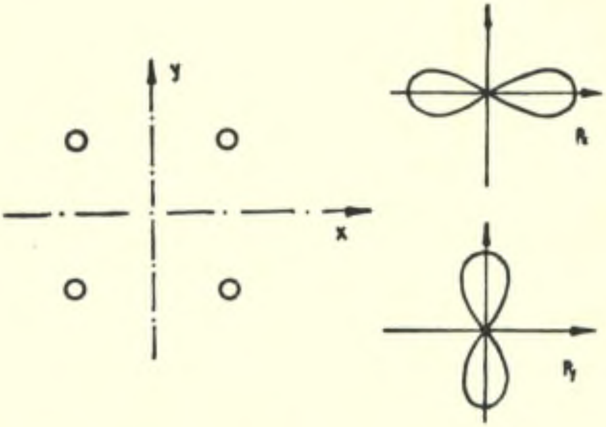

Abb. 13. — Vierelektronenmodell mit 4 Atomen und p_x, p_y-Funktionen.

Züge des Zweielektronenproblems unabhängig von dem Übergang von 9 zu 4 Atomen im Grundbereich erhalten bleiben. Für die numerische Behandlung wurden als p-Funktionen Slaterfunktionen benützt, so dass die Zahlenwerte für die auftretenden Integrale den Tafeln von H.J. Kopinek (⁴⁶) und C.C.J. Roothaan (⁴⁷) entnommen werden konnten.

J.C. Slater, H. Statz und G.F. Koster (⁹) besprechen besonders ausführlich ein eindimensionales Problem. In diesem Falle ist bei zwei Elektronen oder Löchern in einem sonst leeren oder vollen Band das von ihnen erhaltene Resultat zur Multiplizität des Grundzustandes ohne Rechnung einzusehen : Ist das tiefst gelegene Einelektronenniveau nicht entartet, so kann dies nur durch zwei Elektronen mit antiparalelen Spins besetzt werden. Der Grundzustand ist in diesem Falle ein Singulett. Ist das tiefst gelegene Niveau entartet, so kann es durch zwei Elektronen mit paralleln Spins besetzt werden. Nach der Hund'schen Regel liegt dieser Triplettzustand energetisch tiefer als der tiefste Singulettzustand, so dass in diesem Fall das System sich unabhängig vom interatomaren Abstand als ferromagnetisch ergibt.

Wie in (45) ausführlich dargelegt wurde, liegen die Verhältnisse im zweidimensionalen Fall mit je einem p_x- und p_y-Band komplizierter. Mit Hilfe der Hund'schen Regel kann man zwar folgern, dass das Triplett stets tiefer als das Singulett liegt, wenn die beiden Elektronen sich in verschiedenen Bändern befinden. Es ist jedoch möglich, dass das Singulett mit beiden Elektronen im gleichen Band noch tiefer liegt, und es hängt von den genauen Zahlenwerten der Austausch-, Übergangs- etc. Integrale und damit vom interatomaren Abstand ab, ob der Grundzustand ein Triplett oder ein Singulett ist, ob er also spontane Magnetisierung zeigt oder nicht.

In Abb. 14 sind nach den Ergebnissen von (14) der tiefste Tripletteigenwert und der tiefste Singuletteigenwert, die beide mit Hilfe der oben erwähnten Integrale unter Vernachlässigung der Nichtorthogonalitätsglieder berechnet wurden, als Funktion des Parameters :

$$\rho = \frac{Z}{2}\frac{R}{a_H}$$

aufgetragen. Hierbei bedeutet Z die effektive Kernladungszahl, R den Atomabstand und $c\ a_H$ den Bohr'schen Wasserstoffradius. Man sieht, dass nur über einen verhältnismässig engen Bereich interatomarer Abstände der Triplettzustand energetisch am tiefsten liegt. Die genaue Ausdehnung dieses « ferromagnetischen Bereiches » hängt natürlich von den zugrundegelegten Zahlenwerten für die auftretenden Integrale ab.

Für die Zwecke unserer Diskussion kommt es vor allem auf einen Vergleich mit dem in derselben Näherung und mit den gleichen Funktionen behandelten Vierelektronenproblem an. In Abb. 15 geben wir den tiefsten Quintettzustand und den tiefsten Singulettzustand als Funktion von ρ an. Man sieht, dass 1) für alle interatomaren Abstände der Singulettzustand energetisch günstiger ist und 2) dass gerade bei solchen Atomabständen, bei denen der Zustand höchster Multiplizität im Zweielektronenfall am günstigsten war, er im Vierelektronenfall besonders ungünstig ist.

Unsere Erwartung, dass das Hinzukommen der Fermienergie die Verhältnisse tiefgreifend ändern werde, hat sich somit bestätigt. Man kann demnach von den Verhältnissen bei extrem wenigen Löchern in einem sonst vollen Band nicht auf die bei Ferromagnetica wirklich vorkommenden Verhältnisse schliessen. Wesentlich schwie-

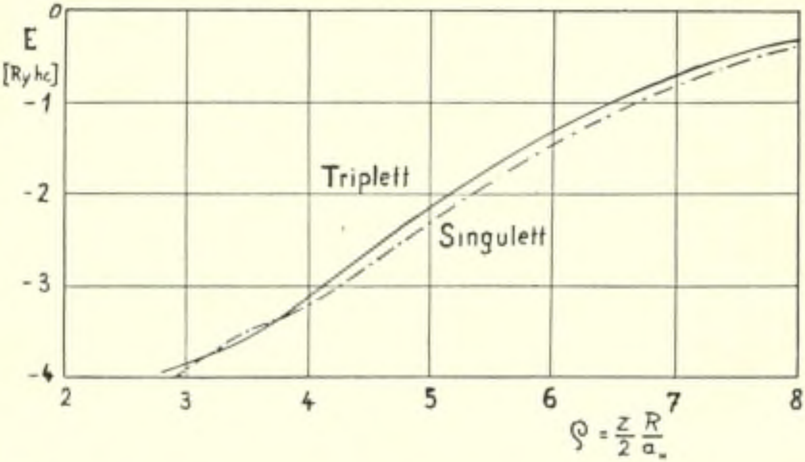

Abb. 14. — Energetische Lage von tiefstgelegenem Triplett- und tiefstgelegenem Singulett-Zustand im Zweielektronenfall. Wie in Abb. 15 ist ein für alle Zustände gleicher Anteil der Energie als Funktion des Atomabstandes weggelassen.

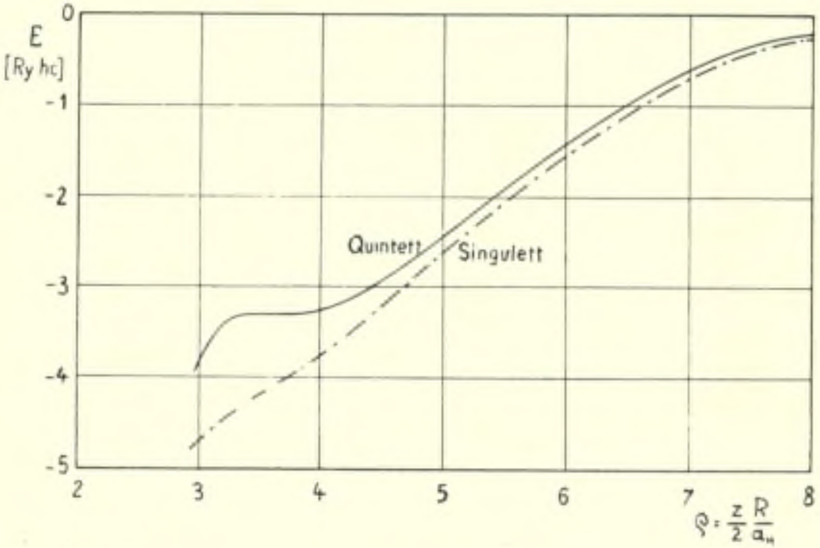

Abb. 15. — Energetische Lage von tiefstgelegenem Quintettzustand und tiefstgelegenem Singulettzustand im Viereelektronenfall als Funktion des Atomabstandes R.

riger ist es, aus unserem Ergebnis positive Folgerungen hinsichtlich des Auftretens einer spontanen Magnetisierung in Metallen zu ziehen. Es ist natürlich denkbar, dass ein zweidimensionales Gitter mit *p*-Funktionen überhaupt ungeeignet zum Studium ferromagnetischer Probleme ist und bei allen interatomaren Abständen die spontane Magnetisierung Null ergibt. In diesem Falle hätte man die entsprechenden Rechnungen für ein dreidimensionales Modell mit *d*-Funktionen zu wiederholen. Anderseits ist es aber auch möglich, dass die Vernachlässigung der Austauschintegrale zwischen Elektronen an benachbarten Atomen [wie in (9) wurden nur intraatomare Austauschintegrale berücksichtigt] der hauptsächlichst Mangel der vorliegenden Rechnung ist. Dies wird besonders durch unsere Diskussion in Abschnitt 2 über die Bedeutung des Austausches zwischen benachbarten Atomen für die Lage des Curiepunktes sowie den oft zu beobachtenden starken Einfluss des Ordnungsgrades von Legierungen auf deren ferromagnetische Eigenschaften gestützt. Dies würde bedeuten, dass das vielfach benutzte Modell für ferromagnetisches Nickel, bei dem der intraatomare Austausch allein für den Ferromagnetismus verantwortlich sein und die ferromagnetische Fernordnung durch die Bewegung von Löchern in der *d*-Schale mit einer Spinvorzugsrichtung von Gitterplatz zu Gitterplatz zustandekommen soll, nicht ausreichend ist. In der Tat hat dieses Modell einen offenkundigen Mangel : Während nach der einfachen Bandtheorie und nach dem empirischen Material ein möglichst schmales *d*-Band vorteilhaft für das Zustandekommen des Ferromagnetismus ist (um die Erhöhung der Fermienergie durch die Magnetisierung möglichst gering zu halten), benötigt man in dem eben erwähnten Modell ein hinreichend weites *d*-Band, um die Wahrscheinlichkeit für den Übergang eines Loches im *d*-Band zwischen zwei Nachbaratomen hinreichend gross zu halten. Bis jetzt ist noch nicht gezeigt worden, dass diese beiden Forderungen miteinander verträglich sind. Eine endgültige Entscheidung über die hier angeschnittenen Fragen kann wohl heute noch nicht gefällt werden, sondern muss noch ausführlichere und verbesserte Untersuchungen abwarten.

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