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On Ferromagnetism and Related Problems of the Theory of Electrons*

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In this paper is presented a study of those electrons which hold together a chemically elementary crystal and are responsible for the homoeopolar bonds between neighboring atoms. The starting point of the theory is Slater's form of the secular equations for first order perturbations arising from the interactions of identical atoms composing a system. A rigorous solution of these equations is given in section 4. The investigation is carried through in a unified way for magnetic and non-magnetic materials, with respect to internal energies and to magnetic properties. As anticipated by Heisenberg, the deciding factor is the sign of the Heitler and London interchange integral J_1. Substances with large negative J_1 are non-magnetic, those with large positive J_1, potentially ferromagnetic. For non-magnetic bodies, the theory gives a confirmation of Bloch's conclusions with slight differences of interpretation. On the other hand, the results for magnetic materials are new and entirely different from Bloch's. As to specific heats, it is found that at very low temperatures they have the expression $c=0.208\ sR(T/\theta)^{3/2}$, where R is the gas constant, s the number of valency electrons per atom, and θ has a close relation to the Curie point. With respect to ferromagnetism, the result is that a crystal satisfying Slater's equations is spontaneously magnetized almost to saturation but that the polarity of this magnetization changes its sense at irregular intervals. This fact suggests that ferromagnetic crystals must have a block structure and that they are coherent, in the sense of the validity of Slater s equations, only within the blocks (compare sections 10 and 11). With this hypothesis the theory accounts for the fundamental facts of ferromagnetism.

1. Introduction

The discoveries of quantum dynamics, especially Pauli's exclusion principle and Fermi's statistics based on it, gave a new stimulus to the theory of electrons in metals. While Sommerfeld[1] treated in an exhaustive way the subject of free electrons, it was pointed out by Heisenberg[2] that the exclusion principle must exercise a powerful influence on the orientation of the spins of valency electrons and that it may play the role of the *molecular field* postulated by Weiss for ferromagnetic materials. The theory of the more tightly bound electrons was investigated by Bloch in a series of important papers. While his work is fundamental in many respects, it treats the non-magnetic properties[3] and the magnetic[4] separately and by different methods. Moreover, we believe that his results relating to ferromagnetism are open to objection.

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* An abridgment of this paper was read before the *National Academy of Sciences* on April 26, 1932 at Washington, D. C.

[1] A. Sommerfeld, Zeits. f. Physik **47,** 1, 43 (1928).

[2] W. Heisenberg, Zeits. f. Physik **49,** 619 (1928).

[3] F. Bloch, Zeits. f. Physik **52,** 555 (1928); **59,** 208 (1930).

[4] F. Bloch, Zeits. f. Physik **57,** 545 (1929); **61,** 206 (1930); **74,** 295 (1932).

[5] This assumption is made for simplicity but is not necessary. We shall see in section 5 that our theory applies, almost without change, to more general cases.

2. FORMULATION OF THE MATHEMATICAL PROBLEM

We consider with Heisenberg and Bloch a system of N electrons each pertaining, in the unperturbed state, to a different atom of a crystal.[5] Let the orbital motion of the electron be that corresponding to the lowest quantum state. Besides, with every electron there is associated a spin the projection of which on a given axis can be either positive or negative. Let r electrons have negative spins and $N-r$ positive. The projection of the total spin moment is then equal to $mh/2\pi$,where $2m=N-2r$. If all the atoms are successively labeled by the numbers 1, 2, $\cdots$ N, let the positions of those containing an electron with a negative spin be $f_1, f_2, \cdots f_r$ $(f_1<f_2<\cdots<f_r)$. We denote the antisymmetric wave function for such a distribution by $\psi(f_1, f_2, \cdots f_r)$. As the magnetic interactions are neglected, all the functions with the same number r, correspond to the same energy and the total wave function pertaining to the magnetic moment m can be written as the linear expression

$$\psi(r) = \sum_{f_1,\cdots f_r} a(f_1, \cdots f_r)\psi(f_1, \cdots f_r). \tag{1}$$

The coefficients $a(f_1, \cdots f_r)$ are determined, in the usual way, by a secular system of equations when we introduce the mutual influence of the electrons and protons as a perturbation. The form of the secular equations was explicitly derived by Slater:[6]

$$\epsilon a(f_1, \cdots f_r) + \sum J_{ff'}[a(f_1', \cdots f_r') - a(f_1, \cdots f_r)] = 0. \tag{2}$$

The summation is extended over all pairs of electrons having opposite spins and $f_1', \cdots f_r'$ and $f_1, \cdots f_r$ differ only in that this pair of spins is interchanged. The coefficient $J_{ff'}$ denotes the London and Heitler interchange integral for the pair and ϵ is the energy measured from an arbitrary zero point. Usually, it is permissible to neglect the mutual influence of the more distant atoms and to take into consideration only the interactions between contiguous electrons. In this case the Eq. (2) is for most crystals reduced to

$$\epsilon a(f_1, \cdots f_r) + J_1 \sum [a(f_1', \cdots f_r') - a(f_1, \cdots f_r)] = 0. \tag{3}$$

The sum includes now all pairs of contiguous electrons having opposite spins. J_1 represents the interchange integral for two adjacent atoms.

The main problem is to find a solution of the Eqs. (2) or (3), satisfying the conditions at the surface of the crystal and other subsidiary conditions which we shall state in the next section. Bloch has given a very elegant method of transforming these equations. However, we shall not use it because the solution can be derived directly from the form given here.

3. SOLUTION IN A SPECIAL CASE

In order to show how the solution is arrived at, it is best to start from an example. We take, therefore, the case of a linear chain of atoms with $r=2$. The form which Eq. (3) takes in this case is

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[6] J. C. Slater, Phys. Rev. **34**, 1293 (1929); **35**, 509 (1930).

$$\begin{aligned}\epsilon a(f_1, f_2) + J_1[a(f_1 - 1, f_2) - a(f_1, f_2) + a(f_1 + 1, f_2) - a(f_1, f_2) \\ + a(f_1, f_2 - 1) - a(f_1, f_2) + a(f_1, f_2 + 1) - a(f_1, f_2)] = 0,\end{aligned} \tag{4a}$$

which holds for $f_2 > f_1 + 1$. In the case $f_2 = f_1 + 1$ two of the interchanges are precluded and the equation becomes

$$\epsilon a(f_1, f_2) + J_1[a(f_1 - 1, f_2) - a(f_1, f_2) + a(f_1, f_2 + 1) - a(f_1, f_2)] = 0. \tag{4b}$$

The difference equation (4a) has constant coefficients and its particular solutions can be written in the form exp $i\alpha(k_1 f_1 + k_2 f_2)$. The corresponding energy level is

$$\epsilon_{k_1, k_2} = 4J_1(\sin^2 \tfrac{1}{2}\alpha k_1 + \sin^2 \tfrac{1}{2}\alpha k_2). \tag{5}$$

This expression is symmetrical in k_1 and k_2 so that the solution exp $i\alpha(k_2 f_1 + k_1 f_2)$ belongs to the same energy. We can, therefore, build up the slightly more general solution $a(k_1, k_2) = c_1 \exp i\alpha(k_1 f_1 + k_2 f_2) + c_2 \exp i\alpha(k_2 f_1 + k_1 f_2)$ and try to choose the coefficients c_1 and c_2 in such a way as to satisfy the subsidiary condition (4b). It is important to note that while (4a) is supposed to apply only in the case $f_2 > f_1 + 1$, our solution is of such a type that it satisfies the Eq. (4a) for all values of f_1 and f_2, including $f_2 = f_1 + 1$. In this last case, both Eqs. (4a) and (4b) are true and we can replace the subsidiary condition by the difference

$$\begin{aligned}a(f_1 + 1, f_2) + a(f_1, f_2 - 1) - 2a(f_1, f_2) = 0, \\ f_2 = f_1 + 1.\end{aligned} \tag{6}$$

It is easy to see that this condition is satisfied if we put

$$c_1 : c_2 = -\exp i[\alpha(k_1 - k_2) + 2\phi(k_1, k_2)],$$

where

$$\phi(k_1, k_2) = \operatorname{arctg} \frac{\sin \alpha k_1 - \sin \alpha k_2}{2 - \cos \alpha k_1 - \cos \alpha k_2}. \tag{7}$$

The solution itself can then be written in the form

$$\begin{aligned}a(k_1, k_2) = \exp i[\alpha(k_1 f_1 + k_2 f_2) + \alpha k_1 + \phi(k_1, k_2)] \\ - \exp i[\alpha(k_2 f_1 + k_1 f_2) + \alpha k_2 + \phi(k_2, k_1)].\end{aligned} \tag{8}$$

If we substitute for the surface conditions the periodicity requirement of Bloch's, all we have to do is to define k_1, k_2 as integers and $\alpha = 2\pi/N$. The Eqs. (8) and (5) will then represent a rigorous solution of the problem. It differs from Bloch's result only inasmuch as $a(k_1, k_2)$ vanishes for $k_1 = k_2$. This means that the case of two equal quantic numbers does not occur and must be excluded.

To obviate possible objections, we prefer, however, to show how a solution satisfying the actual border conditions can be found. These conditions result from the fact that when an electron is at one of the ends of the chain ($f_1 = 1$ or $f_2 = N$) a further decrease (or increase) of the number f labelling its position is no longer possible. The corresponding transitions must be, therefore, excluded from the conditions (4a) and (4b). This means

$$a(f_1 - 1, f_2) - a(f_1, f_2) = O, \qquad \text{when } f_1 = 1, \tag{9a}$$

$$a(f_1, f_2 + 1) - a(f_1, f_2) = O, \qquad \text{when } f_2 = N. \tag{9b}$$

It is easy to see that in addition to $a(k_1,k_2)$ the expressions $a(-k_1, k_2)$, $a(k_1, -k_2)$, $a(-k_1, -k_2)$ are also solutions of the system (4a), (4b) pertaining to the same energy (5), because this energy does not change if we reverse the sign of k_1 or k_2. Combining these four expressions with suitable coefficients we can build up a solution satisfying the condition (9a). In fact, the Eq. (9a) is fulfilled if the expression is arranged as a sum of terms each containing the factor $\cos\alpha k_j(f_1 - \frac{1}{2})$, where j is 1 or 2. Such an arrangement is possible for any value of the parameters αk_j. On the other hand, the border condition (9b) can be satisfied by the same expression only for definite and discreet values of these parameters. It is obvious from the symmetry with respect to the two ends of the chain that α must be taken as

$$\alpha = \frac{\pi}{N}. \tag{10}$$

The condition (9b) is equivalent to the requirement that the solution can be arranged as a sum of terms each containing the factor $\cos\alpha k_j(f_2 - N - \frac{1}{2})$. The arguments of the cos functions can be reduced to this form only if we impose upon the numbers k_j the conditions

$$\left.\begin{aligned} (1 - 1/N)k_1 - (1/\pi)[\phi(k_1, k_2) + \phi(k_1, -k_2)] &= k_1', \\ (1 - 1/N)k_2 - (1/\pi)[\phi(k_2, k_1) + \phi(k_2, -k_1)] &= k_2'. \end{aligned}\right\} \tag{11}$$

Where the numbers k_1', k_2' are integers $(1, 2, \cdots N)$ and represent the quantic numbers of the problem. The rigorous border conditions lead, therefore, to a different result from Bloch's periodicity relation: The numbers k_j are no longer quantic numbers but non-integral auxiliary parameters.

The coefficients of the secular problem acquire in this case the simple form

$$\begin{aligned} a(f_1, f_2) = {} & \cos \alpha k_1(f_1 - \tfrac{1}{2}) \cos \alpha k_2(f_2 - N - \tfrac{1}{2}) \\ & \mp \cos \alpha k_2(f_1 - \tfrac{1}{2}) \cos \alpha k_1(f_2 - N - \tfrac{1}{2}). \end{aligned}$$

4. General Solution

The results of the preceding section apply with slight changes to the general case. For a system with $r = \frac{1}{2}N - m$ negative spins the energy expression is quite generally

$$\epsilon_m = \sum_{j=1}^{\frac{1}{2}N - |m|} \epsilon_j. \tag{12}$$

In the case of a linear chain, we have

$$\epsilon_j = 4J_1 \sin^2 \frac{\alpha k_j}{2N}, \tag{13}$$

where the parameters k_j are determined in relation to the quantic numbers $k_j'(=1, 2, \cdots N)$ by the equations

$$\left(1 - \frac{1}{N}\right) k_j - \frac{1}{\pi} \sum_{i\neq j}^{i} [\phi(k_j, k_i) + \phi(k_j, -k_i)] = k_j', \qquad i, j = 1, 2, \cdots, \tfrac{1}{2}N - | m | . \tag{14}$$

The expression for $a(f_1, \cdots f_r)$ becomes rather cumbersome. It is built up of terms derived from the product

$$\cos \alpha k_1(f_1 - \tfrac{1}{2}) \cdot \cos [\alpha k_2(f_2 - 3/2) - \phi(k_2, k_1) - \phi(k_2, -k_1)]$$
$$\cdot \cos [\alpha k_3(f_3 - 3/2) - \phi(k_3, k_1) - \phi(k_3, -k_1) - \phi(k_3, k_2) - \phi(k_3, -k_2)] \cdots$$

by all possible permutations of $k_1, k_2, \cdots k_r$.

If the number N is large, the difference between k_j and k_j' does not materially affect the energy expressions for smaller values of r, i.e., in the neighborhood of magnetic saturation. As to the opposite case $r = N/2$, $m = 0$, the terms of the energy expression in which k_j is small and those in which it is large (near to N) remain practically unchanged. But the middle range of values of k_j, about $N/2$, is considerably influenced in the sense of an increase of this number. In the more important of our applications the states of small magnetic moment will play but a negligible role. Therefore, we shall be satisfied with the approximation which is obtained by identifying k with k', as it is amply sufficient for our purpose.

For a two dimensional quadratic lattice

$$\epsilon_j = 4J_1\left(\sin^2 \frac{\pi k_j}{2G} + \sin^2 \frac{\pi l_j}{2G}\right), \qquad G^2 = N. \tag{15}$$

In the case of a three-dimensional cubical crystal

$$\epsilon_j = 4J_1\left(\sin^2 \frac{\pi k_j}{2G} + \sin^2 \frac{\pi l_j}{2G} + \sin^2 \frac{\pi n_j}{2G}\right), \qquad G^3 = N. \tag{16}$$

The parameters k_j, l_j, n_j are in both cases connected with a set of quantic numbers $k_j', l_j', n_j' = 1, 2, \cdots G$ by the relations (14) (with G in place of N) and by two similar sets of equations which are obtained from (14) by substituting l or n instead of k.

In all cases, the Eq. (13) can be divided into a main condition, analogous to (4a), which holds when no two negative spins are in contiguous atoms, and into subsidiary conditions like (4b) which are true in the opposite case. The main condition is satisfied by an exponential function (analogous to $\exp\alpha(k_1f_1 + k_2f_2)$ of the preceding section) and by a large number of other exponentials derived from this. The form of the energy terms in the sum (12) is here also completely defined by the main condition and by the exponential function satisfying it. The subsidiary conditions are satisfied by a proper combination of the exponentials and do not affect the form of the energy expressions. Finally, the border conditions serve to define the parameters entering into the energy terms. Bloch succeeded in solving the main condition, therefore, his energy expressions are formally identical with ours, although the symbols have a somewhat different meaning. To this extent his results for other types of two and three dimensional lattices can also be used. However, if we inquire into the substance instead of the form, there is a profound difference in two other respects which are far more important than the changed definition of the parameters.

(1) In the first place, *no two terms of the energy sum* (12) *may be equal.* In the example of section (3) we see from the formula (8) that $a(f_1, f_2)$ vanishes when $k_1 = k_2$. This means that the corresponding energy level does not exist. The conditions are the same in the general case. Whenever two triples of numbers k_j, l_j, n_j are equal the function $a(f_1, \cdots f_r)$ vanishes identically. This is by no means surprising because the exclusion principle is contained in the formulation of Slater's Eqs. (2) or (3) and makes itself manifest in all the conclusions drawn from it.

(2). In the second place, the number of terms in the sum (12) depends only on the absolute value of the magnetic moment. It is equal to $\frac{1}{2}N - |m|$, and not to $\frac{1}{2}N - m$ as Bloch has it. The mathematical reason for this is that the case of no two negative spins being in contiguous atoms can be realized only as long as the number of these negative spins is smaller than (or equal to) half the number of atoms ($r = \frac{1}{2}N - m \leqq \frac{1}{2}N$, or $m \geqq 0$). If this requirement is not satisfied, we have no main condition but only subsidiary conditions, which completely changes the aspect of the problem. However, we can reduce the new problem to the old one by reversing the direction of our system of coordinates, and by counting as negative those spins which were considered as positive. *To positive and negative magnetic moments of the same absolute magnitude correspond the same energy levels.* This fact is an immediate consequence of the fundamental assumptions of this theory (section 2) which neglects magnetic interactions. Both directions in space are equivalent and the energy cannot depend on sense of the magnetic moment.

These two features of our energy expressions have an important influence on the results and lead to conclusions which are considerably different from Bloch's. Before closing this section, we should like to point out that the theory can be carried through also in the case of Slater's general Eq. (2) which takes into account interactions between non-contiguous atoms. For instance, in the case of a cubical crystal the energy expressions become

$$\epsilon_j = 4 \sum_{g_1 g_2 g_3} J_{g_1 g_2 g_3}[\sin^2 \tfrac{1}{2}\alpha g_1 k_j + \sin^2 \tfrac{1}{2}\alpha g_2 l_j + \sin^2 \tfrac{1}{2}\alpha g_3 n_j]. \qquad (18)$$

where $J_{g_1 g_2 g_3}$ is the interchange integral for two atoms with a distance between them having the projections $g_1 d$, $g_2 d$, $g_3 d$ if d denotes the lattice constant.

5. THE SUM OF STATES

To the energy expressions (12) there must be added the magnetic energy of the crystal equal to $-2\mu m H$, where μ denotes the Bohr magneton and H the strength of the magnetic field. The total energy is, therefore,

$$\epsilon = \epsilon_m - 2\mu m H. \tag{19}$$

The part ϵ_m depends only on the absolute value of the moment so that $\epsilon_{-m} = \epsilon_m$. For every energy level (19) there exists, therefore, another of the form

$$\epsilon = \epsilon_m + 2\mu m H, \tag{19'}$$

which corresponds to the magnetic moment $-\mu m$.

Accordingly, the sum of states $Q = \Sigma \exp(-\epsilon/kT)$ can be divided into two parts

$$Q = Z(H) + Z(-H), \tag{20}$$

the first containing all the terms with exponents of the type (19), the second all those of the type (19′). The two halfs $Z(H)$ and $Z(-H)$ differ only in the sign of H so that the sum of states Q is an even function of this quantity. The average magnetic moment of the system

$$M = kT\frac{d \log Q}{dH} = kT\frac{Z'(H) - Z'(-H)}{Z(H) + Z(-H)} \tag{21}$$

becomes an odd function of H which vanishes for $H = 0$. This fact seems to make this theory inadequate for the explanation of permanent magnetization. We believe, however, that this average is obtained by a type of statistics which has a limited physical reality. In the case of ferromagnetic substances the averaging must be done in a different way. We shall return to this question in section 10 and shall first develop a few equations for the evaluation of the function $Z(H)$. With the help of the formula (12), we can represent each term of the sum of states as $\prod_{j=1}^{r} \exp(-\epsilon_j/kT + 2m\mu H/kT)$, where $2m = N - 2r$. But according to (13) or (16), ϵ_j is a function of the parameters k_j, l_j, n_j and, for a given m, there will be as many different terms as there are possible choices of these numbers. The totality of them is $\exp(2m\mu H/kT)Z_r$,

$$Z_r = \sum_{k_j} \prod_{j=1}^{r} \exp(-\epsilon_{k_j}/kT). \tag{22}$$

We use here the subscript k_j as an abbreviation for the triple of parameters k_j, l_j, n_j. As we found in the preceding section, all the ϵ_{k_j} in the sum (12), or all those in our product, must be different. In other words, our problem is subject to Fermi statistics. Our formula can, therefore, be treated in the usual way: If we consider the expression

$$R = \prod_{k_j} [1 + z \exp(-\epsilon_{k_j}/kT)], \tag{23}$$

then, Z_r is obviously the coefficient of the term of the degree r of the expansion of R in powers of z:

$$Z_r = \frac{1}{2\pi i}\int \frac{R}{z^{r+1}}\, dz, \tag{24}$$

the path of integration being a circuit round the point $z = 0$.

The half $Z(H)$ of the sum of states is now

$$Z(H) = \sum_{r=0}^{N/2} \exp\,[(N - 2r)\mu H/kT]Z_r. \tag{25}$$

Strictly speaking, the expressions R are not the same in the different functions Z_r. But within the approximation of putting k_j equal to k_j', etc. (section 4) we can regard them as identical. Substituting (24) in (25) and summing under the sign of the integral, we find

$$Z(H) = \frac{1}{2\pi i}\int \frac{R}{z^{\frac{1}{2}N+1}}\cdot\frac{(ze^{\tau})^{\frac{1}{2}N+1} - 1}{ze^{\tau} - 1}\,dz, \tag{26}$$

where τ is an abbreviation for

$$\tau = 2\mu H/kT. \tag{27}$$

Although we spoke of one electron in every atom our equations apply as well to the case of several valency electrons of different energy. In fact, each of them will be in resonance only with its own kind in the other atoms and will satisfy a separate secular system. The total sum of states is then the product of the sums of state (26). If there are in an atom two or more electrons in nearly equivalent orbital states and with unlinked or weakly linked spins, the conditions are somewhat different; they are being now investigated by Mr. D. Weinstein. It is probable that our expressions will continue to be true, also in this case, with a change of the physical meaning of the symbol J_1 which will now include both the external and the inner interchange energies.

6. Partial Evaluation of the Sum of States

We consider the case that ϵ_j/kT is, in the average, large in absolute value compared with the quantity τ. In fact the characteristic feature of our theory is Heisenberg's assumption that there is a strong inner directing force due to the energies ϵ_j. The case of small ϵ_j is that when this assumption is not justified; it is, therefore, uninteresting in this connection. We have two terms under the integral (26), let us focus our attention on the second and evaluate it by the method of the steepest descents. In the usual way, we put the integrand equal to e^{ϕ} and obtain the position of the saddle point $z=A$ from the condition $d\phi/dz=0$:

$$\sum_{k_j}\frac{A\exp\,(-\,\epsilon_j/kT)}{1 + A\exp\,(-\,\epsilon_j/kT)} - (\tfrac{1}{2}N + 1) - \frac{A}{A - e^{-\tau}} = O. \tag{28}$$

The second derivative we denote by

$$q = -\sum_{k_j}\left[\frac{\exp\,(-\,\epsilon_j/kT)}{1 + A\exp\,(-\,\epsilon_j/kT)}\right]^2 + \frac{\frac{1}{2}N + 1}{A^2} + \frac{1}{(A - e^{-\tau})^2}\cdot \tag{29}$$

The position of the saddle point depends on the sign of the energy ϵ_j or of the interchange integral J_1. If the sign is *negative*, A is small compared with exp $(-\tau)$: In fact, the left side of the Eq. (28) is negative when $A=0$, but since the exponentials are large, most terms of the sum are, practically, equal to one already for moderate values of A. The sum becomes equal to N and the expression positive. There is a root in between, which does not lie close to the point $z=e^{-\tau}$. Therefore, the last term in (28) is negligible compared with the first two and must be omitted. Neglecting, at the same time, 1 beside $\frac{1}{2}N$, we write it in the form

$$\sum_{kj}\frac{A\exp(-\epsilon_j/kT)}{1+A(-\epsilon_j/kT)}=\frac{N}{2}\,. \tag{28'}$$

Turning to the first term of the integrand of (26), we see that it is regular within the path of integration. It has no pole in $z=0$ and the point $z=e^{-\tau}$ lies outside the circuit of integration. The second term represents, therefore, the whole integral which takes the form

$$Z(H)=\frac{1}{(2\pi q)^{1/2}}\prod_{k_j}[1+A\exp(-\epsilon_j/kT)]A^{-N/2}\cdot(1-Ae^{\tau})^{-1}. \tag{30}$$

It must be noted that A does not depend on the magnetic field because the term containing τ is neglected in the Eq. (28′) $Z(H)$ depends on H, only inasmuch as it enters into the last factor of the expression.

The results are quite different in the case of a *positive* energy ϵ_j. A becomes now much larger than $e^{-\tau}$. In fact, for $A=\infty$ the left side of the Eq. (28′) is positive. But for comparatively large values of A the terms of the sum become negligible so that the other terms dominate and make the expression negative. The integral retains exactly the same form (30) but it does not represent now the whole function $Z(H)$. The circuit of integration is widened to pass through the distant point $z=A$ and the point $z=e^{-\tau}$ is now within this circuit. Consequently, the first term of the integrand (26) has now a pole in this point and the integral does not vanish but has the value $Z^{(1)}(H)$:

$$Z(H)=Z^{(1)}(H)+Z^{(2)}(H),$$

where

$$Z^{(1)}(H)=\exp\frac{N\tau}{2}\cdot\prod_{kj}[1+\exp(-\tau-\epsilon_j/kT)] \tag{31}$$

and $Z^{(2)}$ is identical with the expression (30). It is obvious , for physical and for mathematical reasons, that at low temperatures $Z^{(2)}$ is negligible compared with $Z^{(1)}$. In fact, apart from the unimportant factor $(1-Ae^{\tau})^{-1}$, $Z^{(2)}(H)$ is identical with the expression $Z_{N/e}$ of the last section which represents the totality of all terms of the sum of states corresponding to $m=0$. It follows from our expression of the energy (12) that the exponents of these terms are very large, because all the terms of the sum (12) must be different and, consequently, only few of them can have very small values. For this reason $Z_{N/2}$ is negligible, if J_1/T is sufficiently large.

7. Evaluation Continued

We now substitute into our general expressions the formula (16) for the energy term. It will be sufficient to treat the case of the three dimensional lattice as the other cases have no physical interest. We use the approximation $k_j, l_j, n_j = 1, 2, \cdots G$ which is good enough as was shown in section 4. If we define

$$\xi = \frac{\pi k_j}{2G}, \qquad \eta = \frac{\pi l_j}{2G}, \qquad \zeta = \frac{\pi n_j}{2G}, \tag{32}$$

the summation can be replaced by an integration with respect to ξ, η, ζ between the limits 0 and $\pi/2$. Moreover, we use the abbreviations

$$\beta = 2J_1/kT, \qquad \cos 2\xi + \cos 2\eta + \cos 2\zeta = \rho. \tag{33}$$

The terms of the formula (16) become then

$$\epsilon_j = 2\beta kT(\sin^2 \xi + \sin^2 \eta + \sin^2 \zeta) = \beta kT(3 - \rho). \tag{34}$$

Turning to the condition (29′) we can include the first term $3\beta kT$ into the parameter A writing $A' = A \exp(-3\beta)$. We obtain, then,

$$\frac{8}{\pi^3}\int\int_0^{\pi/2}\int \frac{A' \exp \beta\rho}{1 + A' \exp \beta\rho}\, d\xi d\eta d\zeta = \tfrac{1}{2}. \tag{35}$$

The constant A' can be determined from this relation in the following way. Let us subtract both sides of the equation from 1: The right side remains equal to $\frac{1}{2}$ while the left side has an integrand with the same denominator as (35) but with the numerator 1. The equation can, therefore, be represented as

$$\frac{8}{\pi^3}\int\int_0^{\pi/2}\int \frac{(1/A') \exp(-\beta\rho)}{1 + (1/A') \exp(-\beta\rho)}\, d\xi d\eta d\zeta = \tfrac{1}{2}.$$

We substitute now $\xi = \frac{1}{2}\pi - \xi'$ and similarly for η, ζ, so that $\rho = -(\cos 2\xi' + \cos 2\eta' + \cos 2\zeta') = -\rho'$, obtaining an equation which has quite the same form as (35) except that A' is replaced by $1/A'$. We conclude from this that $A' = 1/A'$ or

$$A' = 1, \qquad A = \exp 3\beta. \tag{36}$$

If we omit in (30) the unimportant factor $1/(2\pi q)^{\frac{1}{2}}$, $Z(H)$ takes in the case of negative interchange integrals $J_1 < 0$ the form

$$\begin{aligned} \log Z(H) = &- (3/2)\beta N + \frac{8N}{\pi^3} \\ &\cdot \int\int_0^{\pi/2}\int \log\left[1 + \exp \beta (\cos 2\xi + \cos 2\eta + \cos 2\zeta)\right] d\xi d\eta d\zeta \\ &- \log\left[1 - \exp(3\beta/2 + \tau)\right]. \end{aligned} \tag{37}$$

Equally simple are the expressions in the case of a positive interchange integral ($J_1 > 0$). Substituting the notations (32) into the expression (31) we find

$$\log Z^{(1)}(H) = \tfrac{1}{2}N\tau + \frac{8N}{\pi^2} \cdot \int\!\!\int_0^{\pi/2}\!\!\int \log\left[1 + \exp\left(-\tau - 2\beta(\sin^2\xi + \sin^2\eta + \sin^2\zeta)\right)\right]d\xi d\eta d\zeta, \tag{38}$$

to this must be added negative term $Z^{(2)}$ of the form (37) which is negligible for low temperatures.

8. Electronic Specific Heats

If the crystal is not subject to magnetic forces ($H=\tau=0$), the two halfs of the sum of state Q become identical and $Q=2Z(0)$. As the free energy is connected with Q by the relation $\psi=-kT\log Q$, it is easy to find the expressions for the internal energy and the specific heat.

We shall see in the next section that the case $J_1<0$ is that of non-magnetic (diamagnetic) bodies. It we denote, in the usual way, $kN=R$ and, moreover,

$$\beta = -\theta/T, \qquad \theta = -2J_1/k, \tag{39}$$

and the number of valency electrons in an atom by s, we find for such materials the temperature dependent part of the internal energy

$$U = sR\theta\frac{8}{\pi^3}\int\!\!\int_0^{\pi/2}\!\!\int\frac{\rho d\xi d\eta d\zeta}{1+\exp(-\beta\rho)}\cdot \tag{40}$$

This expression is but slightly different from Bloch's and agrees with it in every important respect giving results analogous to those obtained by Sommerfeld for free electrons. For high temperatures we can expand with respect to $\beta\rho$ taking only terms of zero and first order. This gives

$$\log Z(0) = Ns(\log 2 - 3\beta/2 + 3\beta^2/16), \tag{41}$$

the temperature dependent part of the internal energy

$$U = -3sR\theta^2/8T,$$

and the specific heat

$$c = dU/dT = 3sR(\theta/T)^2/8. \tag{42}$$

The evaluation for low temperatures can be carried out in a similar way as with the integrals of Fermi and Sommerfeld. The zero order approximation is obtained by taking the integral $\int\int\int\rho d\xi d\eta d\zeta$ over the part of the cube $0\leqq\xi\leqq\pi/2$, etc., limited by the surface $\rho=\theta$. This term which, in every case, constant and of little interest happens to vanish. For the next approximation it is well to remember that the normal distance between neighboring surfaces $\rho=\cos 2\xi+\cos 2\eta+\cos 2\zeta=\text{const.}$ is equal to $[(\partial\rho/\partial\xi)^2+(\partial\rho/\partial\eta)^2+(\partial\rho/\partial\zeta)^2]^{-\frac{1}{2}}\Delta\rho=\frac{1}{2}[\sin^2 2\xi+\sin^2 2\eta+\sin^2 2\zeta]^{-\frac{1}{2}}\Delta\rho$. Near $\rho=0$ it can be expressed by $\frac{1}{2}[3-2(\cos 2\eta+\cos 2\zeta)^2+2\cos 2\eta\cos 2\zeta]^{-\frac{1}{2}}\Delta\rho$. The factor of $\Delta\rho$ varies between a minimum of $1/2\cdot 3^{\frac{1}{2}}$ and a maximum of $\frac{1}{2}$. As the lower values have a larger weight, we take as a rough average $\frac{2}{3}$ of the minimum plus $\frac{1}{3}$ of the maximum which is very close to $\frac{1}{4}$. On the other hand, we must know the area of that part of the surface $\rho = 0$ which lies inside the fundamental cube. This surface goes through the middle of six edges of the cube which lie at the corners of a plane regular hexagon and also through the center of the hexagon. The surface itself is not quite plane and its area is, therefore, slightly larger than that of the hexagon. We take as its rough approximation the area of the circle circumscribed about the hexagon which is equal to $\pi^3/8$. Multiplying the area by the thickness we find that in the neighborhood of the element of volume element takes the form $d\tau = \pi^3 d\rho/32$ and the correction of the integral becomes

$$\tfrac{1}{2}\int_0^\infty \frac{\rho\, d\rho}{1 + e^{-\beta\rho}} = \frac{\pi^2}{24\beta^2}\,\cdot \tag{43}$$

The internal energy for low temperatures is, therefore,

$$U = (\pi^2/24)sRT^2/\theta, \tag{44}$$

and the specific heat

$$c = (\pi^2/12)sRT/\theta. \tag{45}$$

The expressions are different in the case of magnetic materials ($J_1 > 0$) and they are derived here for the first time. We have to use the expression (38) with $\tau = O$ and find

$$U = sRT\cdot\frac{8}{\pi^3}\int\int_0^{\pi/2}\int \frac{2\beta(\sin^2\xi + \sin^2\eta + \sin^2\zeta)d\xi d\eta d\zeta}{1 + \exp 2\beta(\sin^2\xi + \sin^2\eta + \sin^2\zeta)}\,\cdot \tag{46}$$

For high temperatures ($\beta \ll 1$) we can again expand with respect to the exponent and obtain

$$\log Z^{(1)}(0) = Ns\left(\log 2 - 3\beta/2 + \frac{21}{16}\beta^2\right), \tag{47}$$

while $-Z^{(2)}(0)$ is given by the expression (41). We see that for high temperatures $Z^{(2)}$ is not negligible compared with $Z^{(1)}$ but becomes of a similar order of magnitude, especially, as the factor $1/(2\pi q)^{\frac{1}{2}}$ is no longer small in this case. We introduce the slightly changed definitions

$$\beta = \theta/T, \qquad \theta = 2J_1/k, \tag{48}$$

If we determine U and c for $T \gg \theta$ from $Z^{(1)}$ alone,

$$U = -(21/8)sR\theta^2/T, \qquad c = (21/8)sR(\theta/T)^2, \tag{49}$$

we get the correct dependence on the temperature but coefficients which are slightly too large.

The evaluation for low temperatures $T \ll \theta$ is facilitated by the fact that the exponent retains its positive sign in the whole interval of integration. If β is large, the integrand is appreciable only for small values of the variables ξ, η, ζ. It is permissible to replace the signs by their arguments which lead to

$$U = \frac{3}{2}\frac{1}{(2\pi\beta)^{3/2}}\left[1 - \frac{1}{2^{5/2}} + \frac{1}{3^{5/2}} \cdots \right] sRT,$$

or

$$U = 0.0830 sRT^{5/2}/\theta^{3/2}, \tag{50}$$

and

$$c = 0.208 sR(T/\theta)^{3/2}. \tag{51}$$

The coefficient in this formula is rigorous and not approximate as in (45).

The measurements of Eucken and Werth[7] on the specific heats of iron and nickel show for temperatures between 16° and 22°K considerable deviations from the third power law in the sense of an increase of heat capacity. Eucken himself points out that his observations did not go to sufficiently deep temperatures to establish the law which this excess follows. All we can say is this: If the deviation is attributable to the cause discussed in the preceding paragraphs, its order of magnitude leads to a value of θ of a few hundred degrees and a value of J_1 of a few one hundredths of a volt. If the formula (51), for magnetic materials, were confirmed, it could give us very valuable information. The knowledge of the characteristic temperature θ would be very helpful in elucidating the mechanism of ferromagnetism (compare the next two sections).

It should be pointed out that our theory neglects the possible variability of J_1 and θ with temperature. This is not a rigorous procedure because J_1 must depend to some extent on the distance between the atoms. We presume, however, that this source of error is very small at low temperatures because of the insignificance of the thermal expansion in this region. Neither is the energy of magnetization contained in our expressions but this cause makes an appreciable contribution only in the vicinity of the Curie point.

9. MAGNETIZATION

We turn now to the behavior of our crystals in a magnetic field. The magnetic moment is obtained by differentiating the logarithm of the sum of states Q with respect to H

$$M = kT\frac{d \log Q}{dH} \cdot \tag{52}$$

Let us first discuss materials with negative interchange integrals ($J_1 < 0$, $\beta < 0$) for which we have to apply the expression (37). The dependence of $Z(H)$ on the strength of the field is all contained in the last factor $[1 - \exp(-3\beta/2 + \tau)]^{-1}$ which is very small compared with the other factors. In fact, it does not contain the number of atoms N and this makes its logarithm entirely negligible beside the logarithm of the rest of the expression. Substances with a negative J_1 are, therefore, magnetically inert as far as the electronic interchanges are concerned. We must remember, of course, that our formulas are valid only when β is considerably larger than τ, or $-J_1$ larger than $2\mu H$. For fields of about 10,000 gauss this would mean that $-J_1$ must

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[7] A. Eucken and H. Werth, Zeits. anorg. Chemie **188,** 152 (1930).

be larger than 10^{-4} volt. We have pointed out in section 6 that the assumption of very small values for J_1 has little interest as it corresponds to the case when Heisenberg's hypothesis does not apply and the older theory of paramagnetism enters into its rights. The fact that materials with negative interchange integrals of appreciable absolute value must be nonmagnetic is evident directly from the energy expressions (12), (16). The state of vanishing magnetic moment ($m=0$) is, then, that of the lowest energy which dominates, in an overwhelming way, over all other states. We arrive, in this way to the following classification of crystals with respect to their interchange integrals J_1. Materials with large negative values of J_1 are nonmagnetic as far as electronic interchanges are concerned. Materials with small values of J_1 (negative or positive) are paramagnetic. Those with large positive values of J_1 are, potentially, ferromagnetic (compare with next section).

In the next section we shall give reasons for the view that the formula (52) should be applied with restrictions to the case of magnetic materials ($J_1>0$). Here we wish only to investigate what sort of a magnetization curve would result if this equation were always valid. We know from formula (21) that this curve is antisymmetrical of the general character of those pertaining to paramagnetic bodies. What is its slope in the point $H=0$? It is easy to see that in this point the slope is given by the expression

$$\left(\frac{dM}{dH}\right)_0 = kT\left[\frac{d^2 \log Z(H)}{dH^2} + \left(\frac{d \log Z(H)}{dH}\right)^2\right]_{H=0} \cdot$$

We shall be satisfied with low temperatures when β becomes large. The Eq. (38) gives us then the approximation

$$\log Z(H) = \tfrac{1}{2}Ns\tau + Ns\left(\frac{T}{2\pi\theta}\right)^{3/2}\left[e^{-\tau} - \frac{e^{-2\tau}}{2^{5/2}} + \frac{e^{-3\tau}}{3^{5/2}} \cdots\right], \tag{53}$$

$$(dM/dH)_0 = (Ns\mu)^2/kT, \tag{54}$$

neglecting a term of the order N. If we refer M to one/cm³ of the material, the expression must be multiplied by n/N (n being the number of atoms per/cm³) and becomes $nNs^2\mu^2/kT$. The values of the constants are as follows $\mu=0.9\cdot 10^{-20}$, r is of the order 10^{23}, kT is about $4\cdot 10^{-14}$ for room temperature. $(dM/dH)_0$ is, therefore, of the order of magnitude $2s^2N\cdot 10^{-4}$. This represents a steep rise of the curve even for very small crystals.

10. EXPLANATION OF PRIMARY FERROMAGNETISM

We shall see in the next section that, in a sense, our Eqs. (52) and (54) describe the magnetization curve of certain systems. However, their physical reality is derived in an indirect way: We believe that the method of the sum of states is inapplicable to a coherent crystal in the conditions which prevail at low temperatures. In fact, what is the physical meaning of the sum of states $Q=\Sigma \exp(-\epsilon/kT)$? It is derived from Gibbs' concept of the ensemble of systems which is equivalent to the succession, *in time*, of the different states of one given physical system. The mean value of any quantity derived by the use of the sum Q represents, therefore, the *time average* of this quantity. In the cases in which this method has been heretofore used this time average is what we really observe. In the theory of gases states which occur with an appreciable probability deviate but little from the mean state. The time average is very close to the most probable state of the system and very close to, or identical with, the readings of our instruments which always integrate over a finite, though sometimes small, time. The situation is entirely different in our theory of magnetization. It is true that positive and negative magnetic moments will occur equally often in the course of long periods and the time average will vanish. But this time average is not at all close to the most probable state. On the contrary, under the conditions mentioned, it coincides with one that is so improbable that it practically never occurs. To show this, let us compute the time average of the *absolute value* of the magnetic moment in the absence of a field.

$$\overline{|2\mu m|} = kT(d\log Z(H)/dH)_0 = Ns\mu[1 - 0.058(T/\theta)^{3/2}]. \qquad (55)$$

This means that, on the average, the crystal is in a state close to magnetic saturation. When we further compute the relative mean quadratic deviation from this time average

$$\overline{(|m| - \overline{|m)}|^{2}}/\overline{|m}|^{2} = (0.37/Ns)(T/\theta)^{3/2}, \qquad (56)$$

we find that the spread around the mean value is extremely small. These formulas show us that the crystal is, practically, always in a state approaching saturation. The time average zero is explained by the fact that the two senses of the magnetic moment are equally probable so that the crystal, at irregular intervals, spontaneously changes its magnetic polarity.

These results refer only to the case of low temperatures. When the temperature becomes sufficiently high, the state of vanishing magnetic moment is no longer one of low probability. This is apparent from our expression (41) valid for high temperatures. This expression is, practically, identical with the logarithm of $Z_{N/2}$ of section 6 representing the totality of all the terms of the sum of states pertaining to the magnetic moment $m=0$. The Eq. (41) shows us that this term has a negative exponent and is small as long as $3\beta/2 - 3\beta^2/16 > \log 2$. But when the temperature rises the inequality is reversed into $3\beta/2 - 3\beta^2/16 < \log 2$, the exponent becomes positive, and the term large. It is true that, in this form, the argument is not quite convincing: The formula is derived for small values of β and it is not certain that it still holds when $3\beta/2 - 3\beta^2/16$ becomes equal to log 2 or smaller. However, we get qualitatively the same result when we go back to the original definition $Z_{N/2} = \Sigma \exp(-\epsilon/kT)$ the summation being extended over all possible energy levels compatible with the condition $M=0$ or $r=N/2$. Now, let us look at our energy expressions (12) and (16). The number of terms in the sum (12) depends on the magnetic moment $2m$; it has its minimum 0 for saturation $(2m=N)$ and its maximum $N/2$ for the nonmagnetic state $(2m=0)$. As all the terms of the sum must be different, the mean energy also increases from

$\epsilon = 0$, for saturation, to a huge value, for the conditions of vanishing magnetic moment. It is easy to see that the energy excess of the state $2m = 0$ over the state $2m = N$ cannot be smaller than $1.45NJ_1$ (or $0.72kN\theta$) and not larger than $2.42NJ_1$ (or $1.21kN\theta$). On the other hand, the number of different energy levels pertaining to the state $2m = 0$ is $N!/(N/2)!(N/2)!$ or, within the accuracy of Stirling's formula 2^N. We find, therefore, for $Z_{N/2}$ the limits

$$N(\log 2 - 1.21\theta/T) < \log Z_{N/2} < N(\log 2 - 0.72\theta/T).$$

Owing to the large factor N, the change of $Z_{N/2}$ with T is very rapid. In the region $\log 2 > 1.21\theta/T$;(or $T > 1.8\theta$) it becomes a very large number; in the region $\log 2 < 0.72\theta/T$ (or $T < 1.04\theta$) it is a very small number. The transition from a high probability to a low probability of the unmagnetized state occurs somewhere between these two limits at a point which is roughly of the order

$$T_0 \approx 1.5\theta. \tag{57}$$

The conditions are the same for the other states of magnetization of our crystal ($2m = N - 2r$). As r increases from 0 to $N/2$ the individual terms of the groups Z_r defined by the Eq. (22) become smaller and smaller because their exponents grow in absolute value. On the other hand, the number of terms increases with r being equal to $N!/(N-r)!r!$ For high temperatures this second effect overweighs the first: The probability of a state increases with $r = \frac{1}{2}N - |m|$ and has its maximum for the unmagnetized state $m = 0$. The characteristic temperature above which such a distribution exists is, nearly, independent of r and approximately given by the Eq. (57). For temperatures $T > T_0$, the most probable state and the time average derived from the sum of states coincide and the sum of states has a good physical meaning. The crystal will be unmagnetized or very little magnetized. The opposite is true for low temperatures. The negative exponents are so large that all Z_1 are negligible but those pertaining to very small r. We have here the conditions analysed in the beginning of this section. *The point T_0 of Eq.* (57) *is, therefore, the primary Curie point of a coherent crystal*: Below it the crystal is a state of spontaneous magnetic saturation, above it, in a, practically, unmagnetic state.

Let us now return to the discussion of conditions below the Curie point. As we have seen, a coherent crystal is, then, in a state very near to complete magnetic alignment but its magnetic polarity spontaneously reverses itself at irregular intervals. What is the length of these intervals? Any change of magnetization is due to perturbations coming from the irregular thermokinetic state of the medium around the crystal and of the crystal itself. If there were no mutual magnetic interactions between the electronic spins, every electron would respond to these perturbations independently. In order to change its polarity, the crystal would have to pass through the extremely improbable state of vanishing magnetic moment and such an event could occur only once in an eon. In reality, there exists some measure of magnetic linking between the spins and they can turn over in groups so that the crystal need not pass through the most improbable state. However, if the crystal is not small in size, the periods involved are still very long. The estimate can be made in a way analogous to that used by Bloch,[8] in a somewhat different case, from the magnetic linking of the spins and from the moment of momentum which the crystal has to pick up in order to reverse its magnetization. We call a crystal *coherent* if Slater's equation applies to it as to a unit, the numbers N and G determining its size. If there existed coherent crystals of a considerable size they would be always in a state of complete magnetization in some direction and a field could only change this direction but not demagnetize them. This is contrary to observation and we are compelled to conclude that the coherence extends only over microscopic elements. Even a well developed monocrystal must have a *block structure*. Slater's equation and all the consequences contained in it which we have developed in the preceding sections applies only to the separate blocks. It is unimportant for us whether these discontinuities of a crystal are irregular (in the sense of the *mosaic structure* surmized by Darwin and Smekal) or form a regular *secondary structure*, as advocated by Zwicky. The size of a few hundred atoms in each direction G, postulated by these authors, would insure a sufficiently frequent spontaneous change of magnetization.

We arrive, in this way, at the following picture of the constitution of ferromagnetic materials. They are built up of microscopical blocks which are in a state of permanent spontaneous magnetization. The polarity of this magnetization is subject to frequent spontaneous changes. As far as our simplified theory goes the electronic spins might have any direction and the magnetic axis could rotate freely within the block. In reality there must exist certain directions of preference related to the main crystallographic directions because of the interactions between spin and orbital momentum.[9] The magnetic polarity will alternate between these preferred directions. The permanent magnetization of these micro-crystalline blocks is what we designate as the *primary ferrogmagnetism*. The *secondary magnetization* of the bulk of a ferromagnetic substance is produced by the alignment of the magnetic axes of the primary elements. While this picture is, by no means, new we claim to have demonstrated, for the first time, that the permanent magnetization of the blocks is not a hypothesis but a necessary consequence of the exclusion principle.

11. Remarks on Secondary Magnetization

Already in Maxwell's *Treatise* we find the opinion that ferromagnetic materials are built up of permanently magnetized microcrystalline blocks. He believed that a magnetic field produces an alignment of the magnetic axes by rotating the whole block. Although this seemed little probable because of the enormous viscosity of these materials, I thought Maxwell's hypothesis sufficiently interesting to have it tested experimentally. A few years ago I caused Mr. Yensen[10] to look for a possible rotation using the Hull-Debye x-ray

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[8] F. Bloch, Zeits. f. Physik **74**, 295 (1932).

[9] Compare F. Bloch and G. Gentile, Zeits. f. Physik **70**, 395 (1931).

[10] T. D. Yensen, Phys. Rev. **32**, 114 (1928).

method. It was not very surprising that the result was negative. According to our results of the preceding sections, Maxwell's assumption is unnecessary because the magnetic polarity of a block alternates while the block itself remains in place. In modern times the idea of permanently magnetized microcrystals was used with great success by Weiss[11] in the case of polycrystalline materials. Recently, Bitter[12] gave a considerable amount of experimental evidence which tends to show that it applies also to monocrystals.

The objective of this paper and its main result is to establish the primary ferromagnetism of the microcrystalline blocks. There exists a considerable literature about secondary magnetization and we limit ourselves, in this connection, to a few remarks. The agglomeration of blocks represents a large number of similar systems side by side. We can interpret, therefore, the statistical averages of section 9 in a new way. They represent as well the time averages for a single block as the actual mean values for the agglomerate. The simplifying assumption is implied that the blocks are all equal and that the magnetization has one of two opposite directions. It would be easy to drop these restrictions but hardly worth our while. On the contrary, we simplify still further by dropping the small second term of (53), i.e., by assuming that our blocks are completely magnetized. Eq. (52) gives then for the magnetization (per unit volume of the agglomerate)

$$M = ns\mu \operatorname{tgh} \frac{Ns\mu H}{kT} \cdot$$

There are two effects left out of account in this formula, which can modify it sufficiently to produce a spontaneous and permanent secondary magnetization. The first is the field produced at a given point by the rest of the system. According to Lorentz,[13] this cause can be taken care of by substituting instead of the outer field H the actual strength of field $H' = H + \alpha M$. In Lorentz' cases α was of the order $\frac{1}{3}$ but it is hard to say what it is equal to in our case. The condition for secondary permanent magnetization would then be $(dM/dH)_0 < 0$ or $nNs^2\mu^2/kT > 1/\alpha$. The fact that monocrystals of iron and cobalt have little or no remanence indicates that this cause is not quite sufficient to produce permanent magnetization and points to a rather small size of the blocks or to a small value of α. The other effect which distorts the magnetization curve is the influence of mechanical stresses put forward by Akulov[14] and discussed in detail by Gans[15] and by Becker.[16] These two causes seem entirely sufficient to account for all the phenomena of secondary ferromagnetism. We wish, only, to point out that they may give rise to a secondary Curie point which would be observable by magnetic methods if it happened to be lower than the primary Curie point determined by the Eq.

[11] P. Weiss, Phys. Zeits. **9**, 361 (1908).

[12] F. Bitter, Phys. Rev. **38**, 528 (1931); **39**, 337 (1932).

[13] H. A. Lorentz, Enzyklopadie der math. Wiss. V 14, section 37.

[14] N. S. Akulov, Zeits. f. Physik **64**, 817 (1930).

[15] R. Gans, Schriften d. Königsberger gelehrten Gesellschaft **8**, 33 (1931).

[16] R. Becker, Zeits. f. Physik **62**, 256 (1930).

(57). The problem of relating these theoretical Curie points to those found by observation is not simple and we reserve it for another communication.

Note added in proof. It was overlooked by the writer that, in another paper (Leipziger Vortraege 1930, p. 67), Bloch gives the proportionality of the specific heat of ferromagnetic materials with $T^{3/2}$. However, the agreement with our results is more or less accidental, as Bloch's treatment is quite different and makes use of the two assumptions, pointed out at the end of our section 4, which we do not consider as permissible.—The experimental test of this law is complicated by the fact that the elements of the iron group contain two kinds of valency electrons, the first kind having, presumably, a negative interchange integral, the second a positive one. (Compare: Slater, note 6). The complete electronic specific heat is, then, to be represented by the sum of our formulas (45) and (51): $c=R[\alpha_1 s_1 T/\theta_1+\alpha_2 s_2 (T/\theta_2)^{3/2}]$, $\alpha_1=\pi^2/12$, $\alpha_2=0.208$. Only θ_2 is related to the primary Curie point.