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Temperature Dependence of Ferromagnetic Anisotropy in Cubic Crystals*

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Two theories of the temperature dependence of ferromagnetic anisotropy in cubic crystals, the nearest-neighbor quadrupole-quadrupole coupling theory of Van Vleck, and the more recent classical theory of Zener, seem to be contradictory. It is shown that these theories are, respectively, high- and low-temperature approximations to the same physical picture: namely, an anisotropy which decreases with rising temperature due to statistical fluctuations from alignment of anisotropically-coupled neighbor spins. Zener's low-temperature approximation shows that the anisotropy decreases as the tenth power of the magnetization, Van Vleck's high-temperature approximation yields a lower power law. It is argued that most of the anisotropy has vanished before sufficiently high temperatures are reached for Van Vleck's approximation to be appropriate. Van Vleck's nearest-neighbor dipole-dipole coupling theory, which has no classical analog and cannot be compared with Zener's theory, is discussed from a spin-wave picture.

I. INTRODUCTION

THE standard theoretical study of the temperature dependence of ferromagnetic anisotropy in cubic crystals has been given by Van Vleck.[1] Recently Zener[2] has proposed a very simple classical theory which, at first sight, seems to be at variance with Van Vleck, both as to method and as to results. It is the purpose of this paper to show that the methods of Van Vleck and of Zener are different limiting approximations of the same physical picture. We shall attempt to arrive at the true state of affairs by taking a judicious middle path between these two limiting approximations.

Van Vleck considers the anisotropy to originate from an indirect coupling between nearest-neighbor spins i and j produced by the series of interactions: spin i—orbit i—crystalline field—orbit j—spin j. The effective coupling energy is then expanded into a dipole-dipole term

$$\mathcal{H}_D=\sum_{(i,j)} C_{ij}[\mathbf{S}_i\cdot\mathbf{S}_j-3r_{ij}^{-2}(\mathbf{S}_i\cdot\mathbf{r}_{ij})(\mathbf{S}_j\cdot\mathbf{r}_{ij})], \quad (1)$$

plus a quadrupole-quadrupole term

$$\mathcal{H}_Q=\sum_{(i,j)} \gamma_{ij}r_{ij}^{-4}(\mathbf{S}_i\cdot\mathbf{r}_{ij})^2(\mathbf{S}_j\cdot\mathbf{r}_{ij})^2. \quad (2)$$

Here r_{ij} connects nearest neighbors, and C_{ij} and γ_{ij} are coupling constants, considered temperature-independent and acting only between nearest neighbors. The temperature dependence of the resultant anisotropy is caused by statistical deviations of $\mathbf{S}_i$ and $\mathbf{S}_j$ from maximum alignment.

In a cubic crystal whose bulk magnetization vector makes direction cosines α_1, α_2, α_3 with the three cubic axes, symmetry restrictions require the anisotropy to be an expression of the form

$$E_A=K_1(\alpha_1^2\alpha_2^2+\alpha_2^2\alpha_3^2+\alpha_3^2\alpha_1^2)+K_2\alpha_1^2\alpha_2^2\alpha_3^2+\cdots. \quad (3)$$

Van Vleck's calculations are numerical, and he gives his results in tabular form. For convenience we express the temperature dependence of the anisotropy as a power of the temperature dependence of the magnetization:

$$K_1(T)/K_1(0)=[M(T)/M(0)]^n. \quad (4)$$

In Fig. 1 we present Van Vleck's results in terms of the exponent n.

The anisotropy coming from $\mathcal{H}_Q$, as evaluated in the molecular-field approximation, behaves with an exponent n dropping slowly from 6 to 5 as the temperature decreases. Van Vleck also gives an improved calculation, in which part of the exchange energy is taken explicitly into account; in this calculation the exponent n drops from 10 to 5. For the anisotropy from $\mathcal{H}_D$ the exponent rises slowly from 2 to 4 as the temperature increases. In Fig. 1 the values of the magnetization are determined in the same theoretical approximation as are the values of K_1.

Van Vleck makes no attempt to evaluate the temperature dependence of K_2.

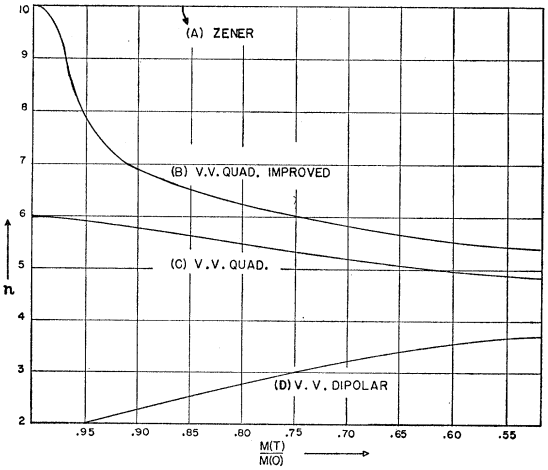

FIG. 1. The exponent n in Eq. (4) plotted against $M(T)/M(0)$. Curve (A), Zener's tenth-power law; curves (B) and (C), Van Vleck's quadrupolar results; and curve (D), Van Vleck's dipolar result. In all cases $M(T)/M(0)$ is evaluated in the same theory as is the anisotropy.

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[1] J. H. Van Vleck, Phys. Rev. **52**, 1178 (1937).

[2] C. Zener, Phys. Rev. **96**, 1335 (1954).

Zener's method, on the other hand, is both classical and macroscopic. He considers the crystal to be composed of many small regions of unspecified dimensions, and in each region the magnetization vector is taken as constant in length but subject to random fluctuations in direction. The anisotropy energy of each region is a function of the direction of magnetization in that region, the functional form being taken as Eq. (3). Local fluctuations in the directions of magnetization then give rise to a temperature dependence of the total anisotropy energy of the crystal. Zener then evaluates the net effect of the fluctuations by a random-walk calculation. He finds the exponent in Eq. (4) to be 10 for K_1 and 21 for K_2, independent of temperature.

Both Van Vleck and Zener obtain their temperature effects from statistical deviations from maximum alignment. Van Vleck's calculation is somewhat cumbersome, but his interactions are quite explicit and his approach, except for the use of the molecular field, is quantum-mechanical. Zener's approach, although giving a classical fuzz to the nature of the interactions, is very direct and simple, and his mathematical methods are extremely powerful. For example, he is able to evaluate the temperature dependence of K_2 [and indeed of all the other constants in the expansion (3)] in a quite general manner.

As pointed out by Van Vleck, an interaction of the form $\mathcal{H}_D$ is incapable of yielding the anisotropy of Eq. (3) in a classical approximation. This is because in $\mathcal{H}_D$ the direction cosines of $\mathbf{r}_{ij}$ appear at most in the square, whereas Eq. (3) is at least quartic in the direction cosines of the resultant bulk magnetization. Quantum-mechanically, however, because of terms nondiagonal in $\sum_j S_j^z$, the dipole-dipole interaction in a cubic crystal does give rise to anisotropy. This anisotropy is calculated by Van Vleck by means of second-order perturbation theory, and the temperature dependence is evaluated in the molecular-field approximation. In Sec. VII of this paper we discuss this temperature dependence and conclude that Van Vleck's molecular-field method gives too high a value of the exponent in Eq. (4).

However, we are concerned here principally with the interaction $\mathcal{H}_Q$, which classically is capable of yielding an anisotropy of quartic form. Only for this interaction can the Van Vleck and Zener theories be compared, since only for this interaction do the two theories represent the same physical reality.

II. VAN VLECK'S APPROACH TO $\mathcal{H}_Q$

In the quadrupole-quadrupole Hamiltonian (2), the spins are quantized with respect to the axis of magnetization. To exhibit the anisotropy it is necessary to transform Eq. (2) into an expression involving α_{ij}, β_{ij}, γ_{ij} (the direction cosines of $\mathbf{r}_{ij}$ with respect to the crystal axes) times an expression involving α_1, α_2, α_3 (the direction cosines of the crystal axes with respect to the axis of magnetization). This transformation is given in detail in Sec. 11 of Van Vleck's paper,[1] and we shall not reproduce it here. (We shall present a similar transformation in the next section.) When account is taken of cubic symmetry, the result may be written

$$\mathcal{H}_Q=H_0+\tfrac{1}{3}\Omega_5[f_1+f_2][\alpha_1^2\alpha_2^2+\alpha_2^2\alpha_3^2+\alpha_3^2\alpha_1^2]. \quad (5)$$

Here H_0 is isotropic. The quantity Ω_5 is a lattice sum which is temperature independent:

$$\Omega_5=-N\sum_j \gamma_{ij}[1-5(\alpha_{ij}^2\beta_{ij}^2+\beta_{ij}^2\gamma_{ij}^2+\gamma_{ij}^2\alpha_{ij}^2)]. \quad (6)$$

The factor $\frac{1}{3}$ before Ω_5 is a correction as noted in a subsequent paper by Van Vleck.[3]

The temperature dependence of the anisotropy is contained in the factor

$$[f_1+f_2]=\sum_{\mu,\nu=x,y,z}\{(S_i^\mu)^2[(S_j^\mu)^2-\tfrac{1}{2}(S_j^\nu)^2] -\tfrac{1}{2}S_i^\mu S_i^\nu(S_j^\mu S_j^\nu+S_j^\nu S_j^\mu)\}. \quad (7)$$

Since $\mathcal{H}_Q$ is small compared to the exchange part of the ferromagnetic Hamiltonian, we may evaluate the anisotropy energy by taking the expectation value of (7) with respect to the exchange (first-order perturbation). To facilitate calculation we now introduce the operators $S^\pm=S^x\pm iS^y$. Dropping all terms in (7) nondiagonal in S^+S^-, we then obtain

$$\begin{aligned}\langle f_1+f_2\rangle=\langle&[\tfrac{3}{2}(S_i^z)^2-\tfrac{1}{2}S(S+1)][\tfrac{3}{2}(S_j^z)^2-\tfrac{1}{2}S(S+1)]\\&+\tfrac{1}{16}[(S_i^+)^2(S_j^-)^2+(S_i^-)^2(S_j^+)^2]\\&-\tfrac{1}{4}(2S_i^z-1)S_i^+S_j^-(2S_j^z-1)\\&-\tfrac{1}{4}S_i^-(2S_i^z-1)(2S_j^z-1)S_j^+\rangle. \quad (8)\end{aligned}$$

The problem of the temperature dependence of the anisotropy constant K_1 is now reduced to the evaluation of (8). The rapidity with which (8) goes to zero as the temperature increases will depend upon the correlation assumed between the directions of neighbor spins, $\mathbf{S}_i$ and $\mathbf{S}_j$. Unfortunately, we have no exact way of taking into account this correlation. However, the several approximations considered below put well-defined limits on the temperature dependence.

III. LIMIT OF NO CORRELATION—THE SIXTH POWER LAW FOR $\mathcal{H}_Q$

The limit of no correlation between neighbor spins has been considered in detail by Van Vleck.[1] Each spin is independently quantized in a molecular field, and Eq. (8) reduces to

$$\langle f_1+f_2\rangle=[\tfrac{3}{2}\langle m^2\rangle-\tfrac{1}{2}S(S+1)]^2. \quad (9)$$

Here $\langle m^2\rangle$ is the expectation value of $(S_i^z)^2$ in the molecular field. Van Vleck evaluates (9) as a function of temperature for $S=1$. His numerical results indicate a temperature dependence going as $\langle m\rangle^6$ for $T/T_c\lesssim 0.5$ and dropping to approximately $\langle m\rangle^5$ at higher temperatures. Here $\langle m\rangle$ is the calculated Brillouin function for $S=1$, and not the experimental ratio $M(T)/M(0)$. We show Van Vleck's numerical results in Fig. 1.

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[3] J. H. Van Vleck, Phys. Rev. 78, 266 (1950), footnote 13.

A simple physical picture of the effect of temperature on the anisotropy energy may be achieved as follows: We apply the molecular-field approximation directly to the Hamiltonian (2). Since $\mathbf{S}_i$ and $\mathbf{S}_j$ are independently quantized, we may expand $\langle r_{ij}^{-2}(\mathbf{S}_i\cdot\mathbf{r}_{ij})^2\rangle$ in a series of Legendre polynomials $P_n(\Theta_{ij})$ where Θ_{ij} is the angle between $\mathbf{r}_{ij}$ and the axis of quantization. Reversing the direction of $\mathbf{r}_{ij}$ cannot change the sign of $(\mathbf{S}_i\cdot\mathbf{r}_{ij})^2$; hence the odd Legendre polynomials cannot appear in the expansion. Furthermore, since the direction cosine between $\mathbf{S}_i$ and $\mathbf{r}_{ij}$ is present only in the square, no polynomials beyond $P_2(\Theta_{ij})$ can appear. Thus

$$\langle r_{ij}^{-2}(\mathbf{S}_i\cdot\mathbf{r}_{ij})^2\rangle = aP_0(\Theta_{ij})+bP_2(\Theta_{ij}). \tag{10}$$

The coefficient a is determined by averaging over all directions Θ_{ij}. In this average $P_2(\Theta_{ij})\to 0$ and the left side of (10), regardless of the "direction" of S_i, goes to the unweighted average of all possible values of m^2. Hence

$$a=\frac{1}{2S+1}\sum_{m=-S}^{S} m^2=\tfrac{1}{3}S(S+1). \tag{11}$$

To determine the coefficient b we let $\Theta_{ij}=0$. Then (10) reduces to

$$\langle m^2\rangle = a+b. \tag{12}$$

When (11) and (12) are inserted into (10), we have

$$\langle r_{ij}^{-2}(\mathbf{S}_i\cdot\mathbf{r}_{ij})^2\rangle=\tfrac{1}{3}S(S+1)+[\langle m^2\rangle-\tfrac{1}{3}S(S+1)]P_2(\Theta_{ij}),$$

and hence,

$$\langle \mathcal{H}_Q\rangle = E_1+[\langle m^2\rangle-\tfrac{1}{3}S(S+1)]^2\textstyle\sum_{(i,j)}\gamma_{ij} \times[\tfrac{3}{2}\cos^2(\Theta_{ij})]^2. \tag{13}$$

In the above equation we have lumped some of the isotropic terms into E_1. As we have noted, the angles Θ_{ij} are defined with respect to the axis of quantization. We now let this axis make the direction cosines α_1, α_2, α_3 with the crystal axes. On taking account of the cubic symmetry we find

$$\textstyle\sum_{(i,j)}\gamma_{ij}[\tfrac{3}{2}\cos^2(\Theta_{ij})]^2 =E_2+\tfrac{3}{4}\Omega_5(\alpha_1^2\alpha_2^2+\alpha_2^2\alpha_3^2+\alpha_3^2\alpha_1^2), \tag{14}$$

where E_2 is isotropic and Ω_5 is given by Eq. (6). We are thus led to Van Vleck's expression Eq. (5) above, with $\langle f_1+f_2\rangle$ as given by Eq. (9).

In the classical limit (large values of S), we note from Eq. (9):

$$\langle f_1+f_2\rangle=[P_2(\Theta)]^2, \tag{15}$$

where Θ is the angle between the direction of the classical spin and the axis of magnetization. We could have obtained this temperature dependence of the anisotropy of a classical spin directly from the Hamiltonian (2) on using the addition theorem for Legendre polynomials. Thus we see in a very direct way how the temperature effect arises from statistical fluctuations.

It is interesting to calculate the temperature dependence in the classical limit. We have

$$\langle P_n(x)\rangle=\int_{-1}^{1}P_n(x)e^{\epsilon x}dx\bigg/\int_{-1}^{1}P_0(x)e^{\epsilon x}dx, \tag{16}$$

where

$$\epsilon=g\beta H/kT.$$

Here H is the molecular field. In terms of the Bessel functions of imaginary argument,[4]

$$\langle P_n(x)\rangle=I_{n+\frac{1}{2}}(\epsilon)/I_{\frac{1}{2}}(\epsilon). \tag{17}$$

For $n=1$, the right-hand side of (17) reduces to the familiar Langevin function.

In the limit of large ϵ (low T), Eq. (17) yields

$$\langle P_n(x)\rangle\sim\langle P_1(x)\rangle^{\frac{1}{2}n(n+1)}. \tag{18}$$

Thus the classical limit, as well as Van Vleck's case $S=1$, starts out with a sixth-power law. In fact, for the entire temperature range there seems to be no significant difference between the classical and quantum-mechanical averages when expressed as functions of $\langle m\rangle$.

IV. LIMIT OF COMPLETE CORRELATION—THE TENTH-POWER LAW FOR $\mathcal{H}_Q$

The limit of complete correlation has been considered by Zener.[2] In this limit a region of spins may be thought of as pointing in the same direction and moving together as a unit. Zener considers the total spin of this region to behave in a classical way. The anisotropy energy of the region depends on the direction cosines of the total spin in a manner described by Eq. (3). As the temperature rises the various correlated regions of spins will point in different directions, and the total anisotropy will be a statistical average of expressions of the form of Eq. (3).

We may derive Zener's result from Van Vleck's approach. We let the direction of S_i coincide with the direction of its neighbor S_j. From Eq. (8) we then obtain

$$\langle f_1+f_2\rangle=\tfrac{1}{8}\{35\langle m^4\rangle-5[6S(S+1)-5]\langle m^2\rangle +3S(S+1)[S(S+1)-2]\}, \tag{19}$$

where S is now the quantum number of the system of two spins. We note that (19) yields zero for any value of S less than 2. This is because we are considering spins $\mathbf{S}_i$ and $\mathbf{S}_j$ "locked" together as a unit, and in order for this unit to exhibit anisotropy in a cubic field it must behave as a 2^4 pole.

We have obtained (19) from Van Vleck's calculation, but it may also be obtained from the quantum-mechanical analog of Zener's method. As in the steps leading to Eq. (10), we now assume

$$\langle r_{ij}^{-4}(\mathbf{S}_i\cdot\mathbf{r}_{ij})^4\rangle=cP_0(\Theta_{ij})+dP_2(\Theta_{ij})+eP_4(\Theta_{ij}).$$

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[4] Numerical values are given in C. W. Jones, *A Short Table for the Bessel Functions $I_{n+\frac{1}{2}}(x)$, $(2/\pi)K_{n+\frac{1}{2}}(x)$* (Cambridge University Press, Cambridge, 1952).

The constant c is evaluated by averaging over all directions Θ_{ij}:

$$c=\frac{1}{2S+1}\sum_{m=-S}^{S} m^4=\frac{1}{15}S(S+1)(3S^2+3S-1).$$

We may determine d and e from the equations obtained when $\Theta_{ij}=0$:

$$\langle m^4\rangle=c+d+e,$$

and when $\Theta_{ij}=\pi/2$:

$$\langle (S_i^x)^4\rangle=c-\tfrac{1}{2}d+\tfrac{3}{8}e.$$

Equation (19) then follows when we invoke cubic symmetry, and when we use the general relation

$$\langle (S_i^x)^4\rangle=\tfrac{3}{8}\langle (S^2+S-m^2)\rangle+\tfrac{5}{8}\langle m^2\rangle-\tfrac{1}{4}(S^2+S).$$

We have derived (19) by this alternate method because it is now clear that if an entire region R of spins may be thought of as correlated, and not just the neighbors $\mathbf{S}_i$ and $\mathbf{S}_j$, we may expand

$$\langle \textstyle\sum_R r_{ij}^{-4}(\mathbf{S}_i\cdot\mathbf{r}_{ij})^2(\mathbf{S}_j\cdot\mathbf{r}_{ij})^2\rangle =cP_0(\Theta_{ij})+dP_2(\Theta_{ij})+eP_4(\Theta_{ij}).$$

Again we are led to Eq. (19), with S now the quantum number of the total spin of the region. If this spin is large enough we may make a classical approximation, and Eq. (19) becomes

$$\langle f_1+f_2\rangle=\langle P_4(\Theta)\rangle. \tag{20}$$

This is precisely Zener's result. We note that in the limit of complete correlation it makes no difference whether we use a Hamiltonian involving the interaction between neighbor spins, such as Eq. (2), or a Hamiltonian involving single spins in some sort of an anisotropic crystalline field. In either case the temperature dependence of K_1 will go as $\langle P_4(\Theta)\rangle$.

It now remains to evaluate $\langle P_4(\Theta)\rangle$ in terms of the magnetization. Zener does this by imagining the directions of magnetization of the various regions as points on the surface of a unit sphere. At 0°K all these points are at the pole of the sphere, and as the temperature is increased the points are to be envisioned as undergoing a random walk (diffusing) on the surface of the sphere. On solving the resultant diffusion equation, Zener finds

$$\langle P_n(\Theta)\rangle_{RW}=\langle P_1(\Theta)\rangle_{RW}{}^{\frac{1}{2}n(n+1)}. \tag{21}$$

This is the same as Eq. (18), except that it holds for all temperatures, and not just in the low-temperature limit. The reason for the high-temperature disagreement between (17) and (21) may be traced to the omission of any molecular field in Zener's random walk. That is, Zener assumes it just as probable that a point on the sphere of diffusion moves away from the pole as it is that the point moves towards the pole; on the other hand a Boltzmann average in a molecular field may be thought of as a random walk in which the probability of returning to the pole is greater (random walk in a field of force).

Now if nearest neighbors are to be thought of as correlated, the ordering effect generally thought to take place in ferromagnetism has been completely taken into account. Thus, in the limit of complete correlation, we believe Zener's method of averaging to be correct. It will break down at temperatures at which neighbor spins move appreciably out of alignment, that is, at the same temperatures at which the general method of this section also breaks down.

V. VAN VLECK'S APPROXIMATION OF PARTIAL CORRELATION IN $\mathcal{H}_Q$

The two approximations of complete correlation and of no correlation are extremes, representing respectively low- and high-temperature limits. We now examine a calculation also given by Van Vleck[1] in which the correlation is partially taken into account.

Van Vleck focuses attention on the spins $\mathbf{S}_i$ and $\mathbf{S}_j$ for which he is calculating the interaction energy of Eq. (2). He takes the exchange interaction between these two spins rigorously into account, representing only the interaction between these spins and the rest of the neighbors by the molecular field. The justification for this method is that the quadrupole-quadrupole interaction energy between two spins is most sensitive to the relative alignment of those two spins. However, since all neighbor spins are coupled together, the form of the total quadrupole-quadrupole energy will not be identical to the sum of Van Vleck's partially-correlated terms. Nevertheless, we should expect the results of this calculation to lie between those of Secs. III and IV, i.e., between the sixth- and tenth-power laws.

The results are given in Fig. 1 under the label "Van Vleck Improved." It can be shown that in the low-temperature limit the anisotropy goes as $\langle m\rangle^{10}$. It drops very quickly to approximately $\langle m\rangle^6$.

VI. THE SPIN-WAVE APPROXIMATION TO $\mathcal{H}_Q$

By means of the spin-wave approximation we gain some appreciation of the manner in which the limit of complete correlation fades into the limit of no correlation as the temperature rises.

Following Holstein and Primakoff[5] we define:

$$\begin{aligned} S_i^z&=S-n_i,\\ S_i^+&=(2S)^{\frac{1}{2}}f_ia_i,\\ S_i^-&=(2S)^{\frac{1}{2}}a_i^*f_i,\\ f_i^2&=1-(n_i/2S).\end{aligned} \tag{22}$$

Here n_i is the "spin-deviation" and equals $a_i^*a_i$ where a_i^* and a_i are creation and destruction operators. We insert the operators (22) into Eq. (8) and make the following low-temperature approximations:

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[5] T. Holstein and H. Primakoff, Phys. Rev. **58**, 1098 (1940).

(1) We drop all terms involving two creation or two destruction operators on the same spin;

(2) We assume n_i is 0 or 1. Thus we set $n_i^2 = n_i$;

(3) We assume $f_i = 1$.

The result is

$$\langle f_1 + f_2 \rangle = (S-\tfrac{1}{2})^2 S[S - 6\langle n_i \rangle - 4\langle a_i^* a_j \rangle]. \tag{23}$$

Introducing spin-wave operators $a_{\mathbf{k}}^*$ and $a_{\mathbf{k}}$:

$$\begin{aligned} a_i &= N^{-\frac{1}{2}} \textstyle\sum_{\mathbf{k}} \exp(-i\mathbf{k}\cdot\mathbf{r}_i) a_{\mathbf{k}}; \\ a_i^* &= N^{-\frac{1}{2}} \textstyle\sum_{\mathbf{k}} \exp(i\mathbf{k}\cdot\mathbf{r}_i) a_{\mathbf{k}}^*; \end{aligned} \tag{24}$$

we obtain:

$$\langle f_1 + f_2 \rangle = (S-\tfrac{1}{2})^2 S[S - N^{-1} \textstyle\sum_{\mathbf{k}} n_{\mathbf{k}} (6 + 4\gamma_{\mathbf{k}})]. \tag{25}$$

Here

$$\gamma_{\mathbf{k}} = z^{-1} \textstyle\sum_h \exp(i\mathbf{k}\cdot\mathbf{r}_h), \tag{26}$$

where $\mathbf{r}_h = \mathbf{r}_i - \mathbf{r}_j$, and the sum is over the z nearest neighbors j to any spin i.

We have obtained (25) with the aid of Van Vleck's transformation (Sec. II); the same result can be obtained, but with more trouble, directly from the Hamiltonian (2).

Equation (25) points out the correlation problem in a very illuminating way. If we assume the power law (4) and introduce

$$\Delta K_1 = K_1(0) - K_1(T),$$
$$\Delta M = M(0) - M(T),$$

then, at low temperatures,

$$1 - \frac{\Delta K_1}{K_1(0)} \approx 1 - n\frac{\Delta M}{M(0)},$$

or

$$\frac{\Delta K_1}{K_1(0)} \approx n\frac{\Delta M}{M(0)}. \tag{27}$$

Now according to the spin-wave picture,

$$\Delta M / M(0) = N^{-1} \textstyle\sum_{\mathbf{k}} n_{\mathbf{k}}. \tag{28}$$

Comparison of (25), (27), and (28) shows that:

(1) In the approximation of no correlation, since $\langle a_i^* a_j \rangle = 0$, we have only the term in (25) with the multiplicative factor 6. Thus we get a sixth-power law in agreement with Sec. III.

(2) In the approximation of complete correlation, only spin waves of very long wavelength are excited. Thus, in effect, $\mathbf{k} = 0$, and we have the tenth-power law of Sec. IV.

Now standard spin-wave theory[5] gives as the energy of a spin wave of wave number $\mathbf{k}$:

$$E_{\mathbf{k}} = 2SJz(1 - \gamma_{\mathbf{k}}),$$

where J is the exchange integral. Hence

$$\begin{aligned} \textstyle\sum_{\mathbf{k}} n_{\mathbf{k}} \gamma_{\mathbf{k}} &= \textstyle\sum_{\mathbf{k}} n_{\mathbf{k}} [1 - (E_{\mathbf{k}}/2SJz)] \\ &= N\left(\frac{\Delta M}{M(0)} - \frac{E}{2SJz}\right), \end{aligned} \tag{29}$$

where E is the density of spin-wave energy. We may now write (25) in the form

$$\langle f_1 + f_2 \rangle = (S-\tfrac{1}{2})^2 S \left\{ S - \frac{10\Delta M}{M(0)} + \frac{2E}{SJz} \right\}. \tag{30}$$

To relate E to ΔM, we note that for spin waves of small k,

$$\frac{\Delta M}{M(0)} \approx \text{const} \int_0^\infty \frac{E^{\frac{1}{2}} dE}{\exp(E/kT) - 1};$$

$$E \approx \text{const} \int_0^\infty \frac{E^{\frac{3}{2}} dE}{\exp(E/kT) - 1};$$

where the constants are the same. Carrying out the integration, we have

$$E \approx \frac{\Delta M}{M(0)} \frac{1.782}{2.315} kT.$$

Thus,

$$\langle f_1 + f_2 \rangle \approx (S-\tfrac{1}{2})^2 S \left\{ S - \left(10 - \frac{(S+1)T}{ST_c}\right) \frac{\Delta M}{M(0)} \right\}. \tag{31}$$

We have approximated $2Jz$ by $[3kT_c/(S^2+S)]$, where T_c is the Curie temperature.

From Eq. (31) we note that the "tenth-power" gradually drops with increasing temperature. Long before the drop is important, however, Eq. (27) has ceased to hold, and furthermore the spin-wave approximation itself has broken down.

Nevertheless, the general picture of the way the anisotropy energy behaves with temperature is now clear.

VII. SOME REMARKS ABOUT $\mathcal{H}_D$

As we have seen in Sec. I, since the anisotropy arising from $\mathcal{H}_D$, for cubic crystals, appears only in second-order perturbation theory, it has no classical analog and cannot be approximated by Zener's theory.

In addition to the second-order perturbation approach of Van Vleck, this anisotropy may be evaluated in the spin-wave approximation. Holstein and Primakoff[5] have indicated the general spin-wave method of handling dipole-dipole interactions. The resultant anisotropy at 0°K has been calculated (a) in the presence of a strong applied field (or in a molecular field)[6]; and (b) in the absence of exchange interaction (dipolar ferromagnetism).[7]

It is clear from the above-mentioned calculations that the anisotropy at 0°K arises from the zero-point spin-wave energy. Furthermore, it is clear that the overwhelming part of this anisotropy comes from short-wave (high-energy) spin waves. This is readily seen

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[6] J. R. Tessman, Phys. Rev. **96**, 1192 (1954).

[7] M. H. Cohen and F. Keffer, Phys. Rev. **99**, 1135 (1955).

when one recalls that the long-wave spin waves merely cause changes in the direction of magnetization of large regions of spins; and the energy cannot be sensitive to these changes of direction, since there is no classical analog to dipolar anisotropy in cubic crystals. Anisotropy can only appear in a cubic array of dipoles when the dipoles near one another become significantly misaligned, and this misalignment can only be caused by short-wave spin waves.

Let us picture our cubic ferromagnetic crystal at 0°K with its zero-point anisotropy energy. As the temperature is raised, $\sum_{\mathbf{k}} n_{\mathbf{k}}$ spin waves will be excited, and their energy will add to the zero-point energy, so that

$$E=\sum_{\mathbf{k}} (n_{\mathbf{k}}+\tfrac{1}{2})E_{\mathbf{k}}. \qquad (32)$$

To a first approximation, $E_{\mathbf{k}}$ will be given by the exchange energy alone, and will be proportional to k^2. Thus the majority of excited spin waves are of low $\mathbf{k}$ and, in accordance with our above remarks, add a negligible amount to the anisotropy. A detailed calculation of the temperature dependence of the anisotropy would present a formidable numerical task, but it is clear that this temperature dependence cannot be very strong—at least not until quite high temperatures are reached and the occupation number of high-energy spin waves is significant compared to $\frac{1}{2}$.

It is seen from Fig. 1 that Van Vleck's results show that the dipolar anisotropy disappears much more slowly than does the quadrupolar. Furthermore, the value of the exponent n for the dipolar case *increases* as $M(T)$ drops. This general trend bears out what we have said above about high-temperature effects. Nevertheless, we think that the difference between the dipolar and quadrupolar must be even more pronounced than obtained by Van Vleck. His molecular-field method allows too many neighbor spins to take angles with respect to each other at low temperatures. In all likelihood the dipolar anisotropy energy does not change very much at all up to a large fraction of T_c.

VIII. CONCLUSIONS

In attempting any comparison of theory and experiment we must first bear in mind the following two points which have been emphasized by Van Vleck:

(1) Depending upon the sign of the coupling constant γ_{ij}, the interaction $\mathcal{H}_Q$ can lead to a positive or negative sign of K_1. On the other hand, since the coupling constant C_{ij} is squared in the second-order calculation, the interaction $\mathcal{H}_D$ can lead only to a negative sign of K_1.

(2) Unless the spin quantum-number of the individual atom is larger than $\frac{1}{2}$, the interaction $\mathcal{H}_Q$ is zero.

Since the average nickel atom has a spin of even less than $\frac{1}{2}$, it is probable that the only interaction present in nickel is of the type $\mathcal{H}_D$. This leads to the correct (negative) sign of K_1, but the temperature dependence is completely off. The anisotropy in nickel disappears with temperature as something like the twentieth power of the magnetization. We can only conclude that this anisotropy is of an entirely different nature than dealt with here.

On the other hand, there are both theoretical[8] and experimental[9] indications that the spin quantum-number of an iron atom is very nearly 1. The positive sign of K_1 in iron indicates an interaction $\mathcal{H}_Q$. As Zener has pointed out, experimentally the constant K_1 falls with temperature as the tenth power of the magnetization *at all temperatures*.

We have shown that this tenth-power law is to be expected only if the spins of neighbor atoms are very highly correlated. Now, as the spin directions of neighbors begin to misalign, the tenth-power law will give way to a law of lower power, eventually to a sixth- or fifth-power law. However, we make the following point: if at the temperature where the misalignment has become appreciable, the anisotropy has essentially disappeared, or has become so small as to defy accurate measurement, it may well appear that the tenth-power law is holding, as Zener maintains, at all temperatures. We believe this is the situation in iron.

There are several experimental confirmations of strong correlation in iron:

(1) The magnetization curve falls well above the Brillouin curve for $S=1$ at high temperatures.

(2) Neutron diffraction experiments[10] indicate that small but coherent domains are present in iron even through the Curie point.

(3) A sizeable fraction of the area of the curve of the specific-heat anomaly is above the Curie point.

These facts indicate considerable correlation even at temperatures above the point of "zero" anisotropy, $\sim 0.8T_c$. Thus it is quite reasonable that at $0.8T_c$, at which temperature $M(T)/M(0)\approx 0.8$, the correlation is nearly complete, or at least sufficient to maintain the tenth-power law.

The same arguments should hold, but with even more force, for Zener's twenty-first power law for K_2.

In this entire discussion we have been using the atomic model of ferromagnetism. A band model has been used by Brooks,[11] and more recently by Fletcher,[12] to yield in a very rough way the anisotropy of nickel at 0°K. Neither author attempts to explain the temperature dependence. We are well aware of the limitations of our atomic model. Still, we believe there is

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much truth in the picture of a change in anisotropy with statistical fluctuations, and we feel that any further synthesis of the band and atomic methods must take this picture into account.

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Interaction of Impurities and Mobile Carriers in Semiconductors*

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The interaction of mobile carriers in semiconductors with impurity atoms and ions tends to reduce the impurity activation energy. This effect is studied using the familiar model of the semiconductor as a uniform medium of dielectric constant K in which randomly distributed impurity ions appear as fixed unit charges and the mobile carriers as charges with opposite sign and effective mass m^*. The treatment is based on the solution of Hartree equations for nonlocalized orbitals ψ_i describing mobile carriers and localized orbitals φ_j describing electrons trapped in the neighborhood of impurity ions. Determination of the individual nonlocalized orbitals is made unnecessary by a method that expresses the fluctuation in mobile carrier density approximately as a linear functional of the fluctuations in electronic potential due to impurity atoms and ions. On use of this relation, Poisson's equation becomes a linear integro-differential equation for the electronic potential energy, which can be solved in terms of integrals involving the localized orbitals φ_j. All localized orbitals are taken to have the same form φ, satisfying an integro-differential equation obtained by averaging the potential energy for a trapped electron over all configurations of the other impurities; this is solved by a variational procedure. All orbitals in the theory depend on temperature T, the Fermi level ζ, and the impurity density N/V, since the distribution of qauntum numbers of the occupied orbitals depends on these quantities. The free energy F of the system, first expressed in terms of the orbitals, T, and ζ, is then reduced to a function of ζ, T, and N/V. For given T and N/V, the physically significant ζ is determined as that which minimizes F; the carrier density and the effective impurity activation energy are then computed as functions of T and N/V. The theory differs from all others in predicting a marked T-dependence of the activation energy, especially for high impurity concentrations. This appears because the polarizability of the mobile carrier distribution, which has an important effect on the interaction of impurities and mobile carriers, is temperature dependent in the present theory, and is completely ignored in earlier theories. For moderately high T the reduction in impurity activation energy predicted by the present theory is of the order of that predicted by Shifrin, and by Pearson and Bardeen; at low temperatures it is much less. Existing data on germanium and silicon suggest that the theory underestimates the reduction in activation energy at high impurity concentrations.

1. INTRODUCTION

THE first theoretical attempt to compute the ionization energy of impurity atoms in a semiconductor as a function of concentration was made by Shifrin.[1] Shifrin used the hydrogenic model of the impurities, which pictures the neutral atom as consisting of a single potential carrier (hole or electron) with appropriate effective mass m^*, moving about a fixed point charge (the atom core) in a medium of dielectric constant K. The ionization energy of an isolated impurity is then

$$E_0 = E_H m^*/mK^2, \tag{1.1}$$

where m is the true electronic mass and E_H the ionization energy of a hydrogen atom; the "radius" of the atom in the ground state is

$$a_0 = a_H Km/m^*, \tag{1.2}$$

where a_H is the Bohr radius. Shifrin assumes that in the impure semiconductor the impurity states with principal quantum number n merge with the continuum, and form its lower bound, when the "radius" n^2a_0 of the corresponding orbitals is the radius of a sphere of volume V/N, where N/V is the density of impurity atoms. He thus concludes that the activation energy of the impurity is given as a function of impurity density by

$$\Delta E_S = E_0\left[1-\left(\frac{4\pi}{3}a_0^3\right)^{\frac{1}{3}}\left(\frac{N}{V}\right)^{\frac{1}{3}}\right]. \tag{1.3}$$

A less schematic calculation has been made by Pearson and Bardeen[2] who note that the energy required to remove an electron from an impurity atom is reduced by the interaction of the resulting ion with the free carriers in the system. Treating the free carrier distribution as unaffected by the presence of the ions, and assuming that almost all impurities are ionized, they arrive at a formula resembling that of Shifrin:

$$\Delta E_{PB} = E_0\left[1-3.29\left(\frac{4\pi}{3}a_0^3\right)^{\frac{1}{3}}\left(\frac{N}{V}\right)^{\frac{1}{3}}\right]. \tag{1.4}$$

Like Shifrin, they thus conclude that the decrease in

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[*] Based in part on a thesis presented by G. W. Lehman in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Purdue University, January, 1954.

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