

Thus we feel at present that the energy band description can account for some reduction in the number of d electrons but it seems rather unlikely that this reduction can amount to more than one or two electrons.

ACKNOWLEDGMENTS

The writer thanks Professor J. C. Slater who suggested this problem. He is also indebted to members of

the Solid-State and Molecular Theory Group at the Massachusetts Institute of Technology for many discussions. In particular, he would like to thank Dr. M. M. Saffren for the use of the computer programs for the augmented plane wave method without which the work would have been impossible, and for many discussions.

PHYSICAL REVIEW

VOLUME 117, NUMBER 3

FEBRUARY 1, 1960

Ferromagnetic Anisotropy in Cubic Crystals*

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(Received August 21, 1959)

A re-evaluation has been made of Van Vleck's second-order perturbation theory of dipolar-type anisotropy in cubic ferromagnets. In the low-temperature limit of strong correlation between the direction of neighbor spins, the first anisotropy constant K_1 varies as the 10th power of the magnetization. The theory is somewhat analogous to a previous treatment of quadrupolar-type anisotropy in the strong-correlation limit. In both cases, the results are in agreement with the Akulov-Zener classical theory. For the dipolar case, complete agreement is also established between the Dyson-type spin-wave analysis of Charap and Weiss and the Holstein-Primakoff approach. Higher order terms in the latter are shown to lead to the Charap-Weiss correction from exchange interaction between spin waves, and this correction is extended to $S > \frac{1}{2}$. Essentially the same correction is obtained very easily from a simple modification of the Van Vleck formalism to take careful account of the average energy involved in simultaneous reversal of neighbor spins. It is shown that spin-wave theory, in agreement with classical theory, predicts identical values of dipolar-type anisotropy whether measured statically in a torque experiment or dynamically in a microwave resonance experiment.

I. INTRODUCTION

THE classical theory of ferromagnetic anisotropy in cubic crystals was formulated by Akulov.¹ He showed that if the anisotropy energy is expanded in powers of the direction cosines $\alpha_1, \alpha_2, \alpha_3$ between the bulk magnetization vector and the three cubic axes, then the lowest nonvanishing term must be of the form

$$F_1 = K_1(\alpha_1^2\alpha_2^2 + \alpha_2^2\alpha_3^2 + \alpha_3^2\alpha_1^2) \equiv K_1\Gamma. \quad (1)$$

A rough estimate of the temperature dependence of K_1 was also given by Akulov. He considered the crystal to be composed of a number of small regions, and within each region he assumed that the magnetization vector makes a random small angle θ with respect to the average over-all direction of bulk magnetization. The anisotropy energy of each region is assumed to take the form (1). As the temperature increases the angle θ between regional and average magnetization becomes larger and larger, and the total anisotropy energy drops precipitously. The reason for the very rapid drop is illustrated in Fig. 1. When the average

value of the angle θ is as shown in the figure, the total anisotropy energy will disappear; however, the sample magnetization $M(T)$, which is given by the average value of M_z , will be quite large. Akulov derived the expression

$$K_1(T)/K_1(0) \approx 1 - 10[M(0) - M(T)]/M(0). \quad (2)$$

Zener² has shown by a random-walk calculation of the average angle θ that a more precise formulation of (2) is a "10th power law."

$$K_1(T)/K_1(0) = [M(T)/M(0)]^{10}. \quad (3)$$

Furthermore, Zener has given a general expression for higher-order anisotropy. In particular, in the first term beyond (1),

$$F_2 = K_2\alpha_1^2\alpha_2^2\alpha_3^2, \quad (4)$$

the temperature dependence of K_2 is as the 21st power of $M(T)$. If the solid curve in Fig. 1 were redrawn to represent F_2 it would cross the dotted curve at smaller θ , which accounts for the higher power. Zener has also shown that if $K_2(0)$ is of comparable magnitude to $K_1(0)$, the temperature falloff of K_1 increases. This is clear from Fig. 1 since, if the solid curve were to include both F_1 and a large F_2 , it would have many wiggles and the total anisotropy would vanish as K_2 .

* This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command.

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¹ N. Akulov, *Z. Physik* **100**, 197 (1936).

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

The Akulov-Zener macroscopic classical theory is quite general, and seems to be a correct first approximation regardless of the type of microscopic quantum-mechanical source of the anisotropy. The standard quantum-mechanical theory has been given by Van Vleck.³ He has expanded the indirect anisotropic coupling between neighbor spins into a dipole-dipole term

$$\mathcal{H}_D = \sum_{i>j} D_{ij} [\mathbf{S}_i \cdot \mathbf{S}_j - 3\mathbf{r}_{ij}^{-2} (\mathbf{S}_i \cdot \mathbf{r}_{ij})(\mathbf{S}_j \cdot \mathbf{r}_{ij})], \quad (5)$$

plus a quadrupole-quadrupole term

$$\mathcal{H}_Q = \sum_{i>j} Q_{ij} \mathbf{r}_{ij}^{-4} (\mathbf{S}_i \cdot \mathbf{r}_{ij})^2 (\mathbf{S}_j \cdot \mathbf{r}_{ij})^2. \quad (6)$$

Here \mathbf{r}_{ij} connects nearest neighbors, and D_{ij} and Q_{ij} are coupling constants, considered temperature independent and acting only between nearest neighbors. The constant D_{ij} is frequently called a "pseudodipolar" constant to distinguish it from the much smaller (but long range) normal magnetic dipole constant $g^2\beta^2\mathbf{r}_{ij}^{-3}$. In what follows we shall neglect the magnetic dipole forces since they are too small to lead to observed magnitudes of ferromagnetic anisotropy. Their long-range nature does, however, produce important shape-dependent effects, which shall be ignored.

In the Van Vleck theory the temperature dependence of the macroscopic anisotropy is caused by statistical deviations of \mathbf{S}_i and \mathbf{S}_j from maximum alignment. Because he evaluated these deviations in a molecular field, that is, assuming complete lack of correlation in the alignment of neighbor spins, Van Vleck obtained too slow a temperature dependence of K_1 . It has been shown⁴ that if correlation is properly taken into account, Van Vleck's \mathcal{H}_Q leads to the 10th-power law, Eq. (3). This may be demonstrated in a general way, and also by means of a spin-wave analysis. Pal⁵ has independently made a spin-wave calculation leading to an equivalent result. In an excellent recent review article⁶ Van Vleck has exhibited a very powerful and completely general extension of our correlation concept. Thus the anisotropy arising from \mathcal{H}_Q behaves according to the Akulov-Zener theory, and the quadrupolar-coupling problem is now well-understood.

In contrast, the dipolar-coupling problem, until very recently, had the aspects of an involved comedy of errors. The temperature dependence of that part of K_1 arising from \mathcal{H}_D , as originally calculated by Van Vleck, varied as the second or third power of the magnetization. In some remarks about \mathcal{H}_D which were included in the paper⁴ devoted mainly to \mathcal{H}_Q , we compounded Van Vleck's error and claimed that the spin-wave theory gave an even lower power of the magnetization. The first step in the right direction was taken by Kasuya,⁷ who showed that interactions between spin waves must

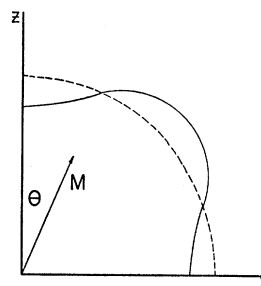


FIG. 1. Cross section of energy surface of a cubic ferromagnet, taken in the (010) plane. The dotted curve represents the isotropic magnetic energy, the solid curve the isotropic plus (exaggerated) anisotropic energy F_1 , with K_1 positive. According to the Akulov-Zener theory, the angle θ increases with temperature, and when on the average it is the size shown above, the anisotropy energy will be negligible. However, the magnetization M_z will still be appreciable. (This is a low-temperature approximation.)

be taken into account. He obtained a 16th-power law, but he made an error of a factor of 2, as was discovered by Charap and Weiss.⁸ The latter authors claimed an 8th-power law until we located some terms missing in their analysis which just account for two extra powers. Thus, after all these corrections, it now appears that the anisotropy arising from \mathcal{H}_D also behaves according to the classical Akulov-Zener theory.

This classical temperature behavior is not entirely obvious. In his original paper Van Vleck pointed out that \mathcal{H}_D is incapable of yielding cubic anisotropy in a classical approximation. This is because \mathcal{H}_D is only quadratic in the direction cosines of \mathbf{r}_{ij} , whereas F_1 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 interaction \mathcal{H}_D does give rise to cubic anisotropy. This has been calculated by Van Vleck by means of second-order perturbation theory. We discuss this calculation in Sec. V.

A physical picture of the origin of dipolar-type anisotropy is as follows. As noted above, the energy of a cubic array of classical dipoles which all point in the same direction is independent of that direction. Quantum dipoles, however, are not rigidly aligned; the spin vectors can be pictured as precessing about the axis of quantization. Thus the energy may depend upon the direction that axis takes with respect to the crystal axes. As Tessman⁹ has shown, the anisotropy energy at 0°K can be expressed as a zero-point energy of ferromagnetic spin waves. Tessman's results for $K_1(0)$ are identical to Van Vleck's; both authors use a molecular field approximation. By another method not involving this approximation Van Peype¹⁰ arrived at a slightly different result for $K_1(0)$, and Van Peype's ground state has recently been confirmed by Charap and Weiss.⁸

³ J. H. Van Vleck, Phys. Rev. **52**, 1178 (1937).

⁴ F. Keffer, Phys. Rev. **100**, 1692 (1955).

⁵ L. Pal, Acta. Phys. Acad. Hung. Sci. **3**, 287 (1954).

⁶ J. H. Van Vleck, J. phys. radium **20**, 124 (1959).

⁷ T. Kasuya, J. Phys. Soc. Japan **11**, 944 (1956).

⁸ S. H. Charap and P. R. Weiss, Phys. Rev. **116**, 1372 (1959).

⁹ J. R. Tessman, Phys. Rev. **96**, 1192 (1954).

¹⁰ W. F. Van Peype, Physica **5**, 465 (1938).

Thus the calculation of $K_1(0)$ arising from \mathcal{H}_D is definitely a quantum-mechanical problem, and it is at first sight puzzling that the temperature dependence of this K_1 should follow the classical Akulov-Zener theory. What seems to happen is that as the temperature increases and spin waves are excited, these spin waves—which at low T are of long wavelength—cause the local magnetization to vary in direction throughout the ferromagnet, just as in Akulov's model. This may be thought of as a variation of the axis of quantization with respect to which the zero-point spin-wave energy arises. The classical result will be correct up to temperatures at which the excited spin waves begin to have wavelengths comparable to the lattice spacing. However, $K_1(T)$ becomes negligible before this temperature is reached.

The above picture seems to be the interpretation of the very beautiful calculation of Charap and Weiss. These authors use the powerful new spin-wave techniques introduced by Dyson,¹¹ whereas Kasuya used the more familiar Holstein-Primakoff¹² formalism. Elsewhere¹³ we have shown that the results of Dyson, for the exchange Hamiltonian only, can be achieved in a simple fashion by a careful expansion of the Holstein-Primakoff operators. In Sec. II we extend this expansion to Kasuya's calculation. The results are in complete agreement with Charap and Weiss. In particular, they have discovered that exchange interaction between spin waves increases the value of K_1 by $\sim 15\%$. This is for individual spin quantum number $S = \frac{1}{2}$, the only case they considered. In Sec. III the interaction is calculated for all S ; the percentage increase in K_1 is found to be proportional to $1/S$. The same correction can be obtained most easily from a simple improvement of Van Vleck's method, as is shown in Sec. V. It comes from simultaneous reversal of neighbor spins.

It is clear that the above considerations apply to ferromagnetic anisotropy as measured in a static torque experiment or as inferred from magnetization curves. But anisotropy may also be measured in a ferromagnetic resonance experiment; we shall call this the dynamic anisotropy. Several years ago¹⁴ we pointed out that the static and dynamic anisotropy are not necessarily the same. This is because the static anisotropy involves the zero-point energy of all the spin waves, whereas the dynamic anisotropy involves the energy of only the spin waves of very long wavelength which are excited by a microwave field. These spin waves, representing as they do a classical in-phase motion of all the spins, carry very little anisotropy. Indeed, the bulk of the static K_1 arises from the zero-point energy of the very short wavelength spin waves.

On the other hand, classical considerations clearly require the static anisotropy to appear in the dynamic

experiment.¹⁵ In Sec. IV this discrepancy is resolved in favor of the classical picture. It is shown that the dynamic anisotropy arises from spin wave interactions. The excitation by microwaves of a long wavelength spin wave produces a change in the zero-point energy of all spin waves, and this in effect shifts the energy of the long spin wave. The effect is very similar to the shift of zero-point energy with temperature.

To return to the temperature problem, it is tempting to apply the results to a real ferromagnet. Certainly that part of the temperature behavior of K_1 arising from statistical fluctuations should obey the 10th-power law. However, a number of other temperature effects may tend to overbalance this simple law. Carr¹⁶ has shown how change of lattice spacing with temperature can make the coupling constants D_{ij} and Q_{ij} temperature dependent. In metals any band-like properties of ferromagnetism may cause other variations in $K_1(T)$.

Furthermore, there are numerous conflicting experimental results. Iron was once thought to obey the 10th-power law with amazing fidelity,² but recent measurements by Graham¹⁷ indicate a much lower power. It is possible that shape-dependent demagnetizing effects may cause some of the differences. Nickel is perhaps the most interesting case since its $K_1(T)$ falls off very roughly as the 50th power¹⁸ of $M(T)$. It is now clear, however, that any more involved theory of a real ferromagnet must take into account the universal statistical 10th-power law.

II. SPIN-WAVE ANALYSIS

The exchange Hamiltonian is

$$\mathcal{H}_E = - \sum_{i \neq j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (7)$$

and the perturbing pseudodipolar Hamiltonian (5) may be written in the form

$$\mathcal{H}_D = \mathcal{H}^0 + \mathcal{H}^{++} + \mathcal{H}^{--} + \mathcal{H}^{+-} + \mathcal{H}^{-+}, \quad (8)$$

with

$$\begin{aligned} \mathcal{H}^0 &= \sum_{i \neq j} E_{ij} (\mathbf{S}_i \cdot \mathbf{S}_j - 3S_i^z S_j^z), \\ \mathcal{H}^{++} &= \sum_{i \neq j} B_{ij} S_i^+ S_j^+, \quad \mathcal{H}^{--} = \sum_{i \neq j} B_{ij}^* S_i^- S_j^-, \\ \mathcal{H}^{+-} &= \sum_{i \neq j} F_{ij} S_i^+ S_j^z, \quad \mathcal{H}^{-+} = \sum_{i \neq j} F_{ij}^* S_i^- S_j^z, \end{aligned} \quad (9)$$

in which

$$\begin{aligned} E_{ij} &= -\frac{1}{4} D_{ij} (1 - 3\gamma_{ij}^2), \\ B_{ij} &= -\frac{3}{8} D_{ij} (\alpha_{ij} - i\beta_{ij})^2, \\ F_{ij} &= -\frac{3}{2} D_{ij} \gamma_{ij} (\alpha_{ij} - i\beta_{ij}). \end{aligned} \quad (10)$$

¹¹ C. Kittel, Phys. Rev. **73**, 155 (1948).

¹² W. J. Carr, Jr., Phys. Rev. **109**, 1971 (1958).

¹³ C. D. Graham, Phys. Rev. **112**, 1117 (1958).

¹⁴ The measured values of $K_1(T)$ of nickel only approximately match a simple power law; however a rough fit can be made and it appears that the statement of a 20th power law in references 2 and 4 is a gross underestimate, except possibly at very low temperatures. We are indebted to Mr. Victor Rehn for a careful analysis of available data.

¹¹ F. J. Dyson, Phys. Rev. **102**, 1217 (1956).

¹² T. Holstein and H. Primakoff, Phys. Rev. **58**, 1098 (1940).

¹³ T. Oguchi, Phys. Rev. **117**, 117 (1960).

¹⁴ F. Keffer, Phys. Rev. **91**, 206A (1953).

In the above equations α_{ij} , β_{ij} , γ_{ij} are direction cosines of \mathbf{r}_{ij} with respect to the axes of quantization. The exchange integral J_{ij} will be taken to equal J for nearest neighbors, zero otherwise; and the pseudodipolar constant D_{ij} will be taken to equal D for nearest neighbors, zero otherwise.

It will prove of use to introduce

$$\begin{aligned} A_k &= 2S \sum_h J [1 - \exp(i\mathbf{k} \cdot \mathbf{r}_h)], \\ E_k &= 2S \sum_h E_h \exp(i\mathbf{k} \cdot \mathbf{r}_h), \\ B_k &= 4S \sum_h B_h \exp(i\mathbf{k} \cdot \mathbf{r}_h), \\ F_k &= (2S)^{\frac{1}{2}} \sum_h F_h \exp(i\mathbf{k} \cdot \mathbf{r}_h), \end{aligned} \quad (11)$$

where \mathbf{r}_h stands for \mathbf{r}_{ij} between nearest neighbors.

The Holstein-Primakoff¹² formalism will be used, which introduces creation and annihilation operators a_i^* and a_i .

$$\begin{aligned} S_i^+ &= (2S)^{\frac{1}{2}} f_i a_i; \quad S_i^- = (2S)^{\frac{1}{2}} a_i^* f_i; \\ S_i^z &= S - a_i^* a_i, \end{aligned} \quad (12)$$

with

$$f_i = [1 - (a_i^* a_i / 2S)]^{\frac{1}{2}}. \quad (13)$$

As we have shown elsewhere,¹³ higher-order terms may correctly be taken into account (except for Dyson's very small "kinematical interaction" between spin waves) by the simple expansion

$$f_i = 1 - (4S)^{-1} a_i^* a_i + \dots \quad (14)$$

Spin waves are introduced by the following Fourier expansions in terms of wave vectors \mathbf{k} within a Brillouin zone of the reciprocal lattice:

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

Here $n_{\mathbf{k}}$ is the number of spin waves of wave vector \mathbf{k} , and N is the total number of spins in the sample.

A. Exchange Term

By means of the expansion (14) the exchange can be written (with $C_0 = \text{constant}$):

$$\begin{aligned} \mathcal{H}_E &= \mathcal{H}_{E1} + \mathcal{H}_{E2} + \dots, \\ \mathcal{H}_{E1} &= C_0 + \sum_{\mathbf{k}} A_{\mathbf{k}} (n_{\mathbf{k}} + \tfrac{1}{2}), \\ \mathcal{H}_{E2} &= (4NS)^{-1} \sum_{\mathbf{k} \dots \mathbf{k}'''} \delta(\mathbf{k} + \mathbf{k}' - \mathbf{k}'' - \mathbf{k}''') \\ &\quad \times (2A_{\mathbf{k}' - \mathbf{k}'''} - A_{\mathbf{k}} - A_{\mathbf{k}'''}) a_{\mathbf{k}}^* a_{\mathbf{k}'}^* a_{\mathbf{k}''} a_{\mathbf{k}'''}. \end{aligned} \quad (15)$$

The expression \mathcal{H}_{E2} takes account of "exchange interaction" between spin waves, and we have shown elsewhere¹³ that it leads to Dyson's¹¹ corrections of order T^4 to the temperature dependence of the magnetization. In Sec. III it will be shown that \mathcal{H}_{E2} leads to the Charap-Weiss⁸ anisotropy corrections.

B. \mathcal{H}^0 Term

The dipolar term \mathcal{H}^0 can be written

$$\mathcal{H}^0 = \mathcal{H}_1^0 + \mathcal{H}_2^0 + \dots, \quad \mathcal{H}_1^0 = \sum_{\mathbf{k}} E_{\mathbf{k}} n_{\mathbf{k}},$$

and with \mathcal{H}_2^0 similar to (15). Here we have used the relations valid for cubic symmetry

$$\sum_i E_{ij} = 0; \quad \sum_{\mathbf{k}} E_{\mathbf{k}} = 0. \quad (16)$$

Similarly, if $n_{\mathbf{k}}$ is isotropic in \mathbf{k} , \mathcal{H}_1^0 will vanish. Furthermore, the corrections introduced by \mathcal{H}_2^0 are very minor. Thus \mathcal{H}^0 makes no significant contribution to anisotropy in cubic ferromagnets.

C. $\mathcal{H}^{++} + \mathcal{H}^{--}$ Term

This term, as Tessman has shown, gives rise to the anisotropic zero-point spin-wave energy. It also contains a small temperature dependence which was originally missed both by Kasuya and by Charap and Weiss. With the aid of the expansion (14) the term can be written

$$\begin{aligned} \mathcal{H}^{++} &= \mathcal{H}_1^{++} + \mathcal{H}_2^{++} + \dots, \\ \mathcal{H}_1^{++} &= \tfrac{1}{2} \sum_{\mathbf{k}} B_{\mathbf{k}} a_{\mathbf{k}} a_{-\mathbf{k}}, \\ \mathcal{H}_2^{++} &= -(4NS)^{-1} \sum_{\mathbf{k} \dots \mathbf{k}'''} \delta(\mathbf{k} - \mathbf{k}' - \mathbf{k}'' - \mathbf{k}''') B_{\mathbf{k}'''} \\ &\quad \times a_{\mathbf{k}}^* a_{\mathbf{k}'} a_{\mathbf{k}''} a_{\mathbf{k}'''}, \end{aligned} \quad (17)$$

with \mathcal{H}^{--} expressed as the complex conjugate of the above.

Second-order perturbation, with \mathcal{H}_{E1} taken as the unperturbed Hamiltonian, gives rise to three important terms. The first is of the form

$$E_1 = \sum_{\nu} (g |\mathcal{H}_1^{++} | \nu) (\nu | \mathcal{H}_1^{--} | g) / (E_g - E_{\nu}) + \text{c.c.} \quad (18)$$

where g is the ground state (no spin waves). The other two terms, both of order N^{-1} , are

$$\begin{aligned} E_2 &= \sum_{\nu} (g |\mathcal{H}_1^{++} | \nu) (\nu | \mathcal{H}_2^{--} | g) / (E_g - E_{\nu}) + \text{c.c.}, \\ E_3 &= \sum_{\nu} (g |\mathcal{H}_2^{++} | \nu) (\nu | \mathcal{H}_1^{--} | g) / (E_g - E_{\nu}) + \text{c.c.} \end{aligned} \quad (19)$$

A further term involving $\mathcal{H}_2^{++} + \mathcal{H}_2^{--} + \text{c.c.}$ is of order N^{-2} and may be neglected. By use of the spin-wave operators the important terms can be expressed as follows (note that $A_{\mathbf{k}} = A_{-\mathbf{k}}$)

$$E_1 = -\tfrac{1}{2} \sum_{\mathbf{k}} (|B_{\mathbf{k}}|^2 / A_{\mathbf{k}}) (n_{\mathbf{k}} + \tfrac{1}{2}), \quad (20)$$

$$E_2 = E_3 = (4NS)^{-1} \sum_{\mathbf{k}} (|B_{\mathbf{k}}|^2 / A_{\mathbf{k}}) \sum_{\mathbf{k}'} n_{\mathbf{k}'}. \quad (21)$$

It should be remarked that Holstein and Primakoff were able to diagonalize the Hamiltonian

$$\mathcal{H}_{HP} = \mathcal{H}_{E1} + \mathcal{H}_1^{++} + \mathcal{H}_1^{--},$$

obtaining

$$E_{HP} = C_0 + \sum_{\mathbf{k}} (A_{\mathbf{k}}^2 - |B_{\mathbf{k}}|^2)^{\frac{1}{2}} (n_{\mathbf{k}} + \tfrac{1}{2}). \quad (22)$$

If the square-root in (22) is expanded in a Taylor series, the first two terms are our $\mathcal{H}_{E1} + E_1$.

As noted by Charap and Weiss, Kasuya's expression corresponding to E_1 is too small by a factor of 2. This

mistake, plus omission of E_2 and E_3 , led Kasuya to an incorrect 16th-power law.

D. $\mathcal{H}^+ + \mathcal{H}^-$ Term

This term was first evaluated by Kasuya. It can be written

$$\mathcal{H}^+ \approx N^{-\frac{1}{2}} \sum_{\mathbf{k}, \mathbf{k}', \mathbf{k}''} \delta(\mathbf{k}' - \mathbf{k} - \mathbf{k}'') F_{\mathbf{k}} a_{\mathbf{k}} a_{\mathbf{k}'}^* a_{\mathbf{k}''}, \quad (23)$$

with \mathcal{H}^- expressed as the complex conjugate of the above. Further terms are much smaller and may be neglected at low temperatures. Second-order perturbation yields

$$\begin{aligned} E_4 &= \sum_{\nu} (g|\mathcal{H}^+|\nu)(\nu|\mathcal{H}^-|g)/(E_g - E_{\nu}) + \text{c.c.} \\ &\approx (2N)^{-1} \sum_{\mathbf{k}, \mathbf{k}', \mathbf{k}''} \delta(\mathbf{k}' - \mathbf{k} - \mathbf{k}'') |F_{\mathbf{k}} + F_{\mathbf{k}'}|^2 n_{\mathbf{k}'} \\ &\quad \times (A_{\mathbf{k}'} - A_{\mathbf{k}} - A_{\mathbf{k}''})^{-1}. \end{aligned} \quad (24)$$

This expression includes only terms of first order in $n_{\mathbf{k}}$ (low-temperature approximation—few spin-waves excited). Kasuya evaluated (24) by a further assumption that since $n_{\mathbf{k}'}$ involves only long wavelength spin waves at low temperatures, one may approximate $A_{\mathbf{k}'} \approx A_0 = 0$. This gives

$$E_4 \approx -N^{-1} \sum_{\mathbf{k}} (|F_{\mathbf{k}}|^2/A_{\mathbf{k}}) \sum_{\mathbf{k}'} n_{\mathbf{k}'}. \quad (25)$$

This approximation of Kasuya's is that of a temperature independent perturbation denominator and is related to the approximation of a temperature independent molecular field H_E in Van Vleck's method (see Sec. V).

E. Total Anisotropy Energy

Because the coupling constant D is much smaller than J , the entropy contribution to the dipolar free energy is negligible, as shown in detail by Kasuya. This free energy is therefore

$$F_D = E_1 + E_2 + E_3 + E_4, \quad (26)$$

neglecting higher-order corrections considered in Sec. III. For a rough evaluation of (26) one can approximate all denominators $A_{\mathbf{k}}$ by

$$A_{\mathbf{k}} \approx 2S \sum_{\mathbf{h}} J = 2S z J, \quad (27)$$

where z is the number of nearest-neighbors. This approximation was used by Tessman, and is equivalent to replacing the exchange Hamiltonian by a molecular field Hamiltonian. In a detailed analysis, which we discuss in Sec. III, Charap and Weiss have shown that this approximation is remarkably good. The dipole sums are then evaluated as follows:

$$\begin{aligned} \sum_{\mathbf{k}} |B_{\mathbf{k}}|^2 &= 16S^2 N \sum_{\mathbf{h}} |B_{\mathbf{h}}|^2 \\ &= (9NS^2/4) D^2 \sum_{\mathbf{h}} (1 - \gamma_{\mathbf{h}}^2)^2, \\ \sum_{\mathbf{k}} |F_{\mathbf{k}}|^2 &= 2SN \sum_{\mathbf{h}} F_{\mathbf{h}}^2 \\ &= (9NS/2) D^2 \sum_{\mathbf{h}} \gamma_{\mathbf{h}}^2 (1 - \gamma_{\mathbf{h}}^2). \end{aligned} \quad (28)$$

Thus by use of (27) and (28) one obtains for the dipolar

free energy

$$F_D = - (9NS/32zJ) D^2 \sum_{\mathbf{h}} [(1 - \gamma_{\mathbf{h}}^2)^2 - (2/NS) \sum_{\mathbf{k}} n_{\mathbf{k}} (1 - 6\gamma_{\mathbf{h}}^2 + 5\gamma_{\mathbf{h}}^4)]. \quad (29)$$

As defined above, the direction cosine $\gamma_{\mathbf{h}}$ is with respect to the axis of quantization. It may be expressed as

$$\gamma_{\mathbf{h}} = \alpha_1 \bar{\alpha}_{\mathbf{h}} + \alpha_2 \bar{\beta}_{\mathbf{h}} + \alpha_3 \bar{\gamma}_{\mathbf{h}}, \quad (30)$$

where $\alpha_1, \alpha_2, \alpha_3$ are direction cosines of the axis of quantization, and $\bar{\alpha}_{\mathbf{h}}, \bar{\beta}_{\mathbf{h}}, \bar{\gamma}_{\mathbf{h}}$ are direction cosines of $\mathbf{r}_{\mathbf{h}}$, all taken with respect to the cubic crystal axes. On invoking cubic symmetry one can express the sums in (29) in terms of Γ , as defined by Eq. (1), and of a lattice sum introduced by Van Vleck²:

$$\Omega_4 \equiv 3D^2 \sum_{\mathbf{h}} [1 - 5(\bar{\alpha}_{\mathbf{h}}^2 \bar{\beta}_{\mathbf{h}}^2 + \bar{\beta}_{\mathbf{h}}^2 \bar{\gamma}_{\mathbf{h}}^2 + \bar{\gamma}_{\mathbf{h}}^2 \bar{\alpha}_{\mathbf{h}}^2)]. \quad (31)$$

The result is

$$F_D = C_1 + K_1(0) [\Gamma - (10/NS) (\Gamma - \frac{1}{5}) \sum_{\mathbf{k}} n_{\mathbf{k}}], \quad (32)$$

where

$$K_1(0) = (NS/16zJ) \Omega_4, \quad (33)$$

and C_1 is isotropic.

The temperature independent anisotropy $K_1(0)\Gamma$ was first obtained from spin waves by Tessman, and is in agreement with the early results of Van Vleck. Since the magnetization is given by

$$[M(0) - M(T)]/M(0) = \sum_{\mathbf{k}} n_{\mathbf{k}}/NS, \quad (34)$$

the result (32) may be written in the form

$$F_D = C_2 + K_1(T)\Gamma, \quad (35)$$

with C_2 isotropic and $K_1(T)$ given by the Akulov expression, Eq. (2). Thus classical and quantum theory are in agreement.

As noted by Van Vleck, since D appears squared in Ω_4 , the sign of $K_1(0)$ is independent of the sign of D . The sign is determined by the sign of the lattice sum Ω_4 . Van Vleck gives the following values of Ω_4 for simple cube, body-centered cube, and face-centered cube, respectively: $+18D^2$, $-16D^2$, $-9D^2$.

III. HIGHER APPROXIMATIONS

Charap and Weiss have made two rather involved corrections to the dipolar energy as given by Eq. (32). The first correction removes the approximation (27) and evaluates (20), (21), and (25) by complicated integration over \mathbf{k} space. The result is that $K_1(0)$ gets multiplied by the factor

$$\eta = 1.26, 1.072, 0.974, \quad (36)$$

for s.c., bcc, and fcc, respectively. It is seen that the correction is small for bcc and fcc.

Similar complicated integrals were involved in Van Peyppe's work,¹⁰ and Charap and Weiss establish an equivalence between their zero-point result and Van

Peyppe's ground state. It might be mentioned that for the case of dipolar ferromagnetism (no exchange, only long range magnetic dipole forces), the evaluation of the zero-point anisotropy cannot be well-approximated by any simple expansion. Instead the expression (22) must be numerically integrated. It is found that a large anisotropy constant K_2 is also present.¹⁹

The second Charap-Weiss correction is much more interesting and important. It comes from exchange interactions between spin waves and has been evaluated according to the Dyson formalism. It can also be obtained in the Holstein-Primakoff formalism by use of (14). The term in question appears in third-order perturbation:

$$\begin{aligned} E_5 &= \sum_{\mu, \nu} \frac{(g|\mathcal{H}_1^{++}|\mu)(\mu|\mathcal{H}_{E2}|\nu)(\nu|\mathcal{H}_1^{--}|g)}{(E_\mu - E_0)(E_\nu - E_0)} + \text{c.c.} \\ &= (4NS)^{-1} \sum_{\mathbf{k}, \mathbf{k}'} (2A_{\mathbf{k}-\mathbf{k}'} - A_{\mathbf{k}} - A_{\mathbf{k}'}) B_{\mathbf{k}} B_{\mathbf{k}'}^* \\ &\quad \times (1+n_{\mathbf{k}})(1+n_{-\mathbf{k}})(1+n_{\mathbf{k}'})(1+n_{-\mathbf{k}'}) \\ &\quad \times (A_{\mathbf{k}} + A_{-\mathbf{k}})^{-1} (A_{\mathbf{k}'} + A_{-\mathbf{k}'})^{-1}. \quad (37) \end{aligned}$$

The constant-denominator approximation (27) is now introduced. The only part of the numerator contributing to zero-point anisotropy involves $A_{\mathbf{k}-\mathbf{k}'}$. This anisotropy reduces to

$$E_{50} \approx (2Sz)^{-1} K_1(0) \rightarrow [\eta/2Sz] K_1(0). \quad (38)$$

The bracketted relation comes from improving the constant denominator approximation by (36).

For $S = \frac{1}{2}$, the only case considered by Charap and Weiss, our bracket $[\eta/z]$ equals their ν_j . They then derive a series of corrections, corresponding to perturbations beyond (37). The final result, extended to general S , is to replace the bracket of (38) by a simple power series in $[\eta/2Sz]$. When this result is added to Tessman's zero-point energy, as corrected by (36), the anisotropy constant becomes

$$[K_1(0)]_{\text{corrected}} = (\eta NS/16zJ) \xi \Omega_4, \quad (39)$$

with

$$\begin{aligned} \xi &= 1 + (\eta/2Sz) + (\eta/2Sz)^2 + \dots \\ &= \frac{(2Sz/\eta)}{(2Sz/\eta) - 1}. \quad (40) \end{aligned}$$

It is to be noted that the correction factor ξ approaches unity for large S . In Sec. V it is shown that the factor ξ , in the constant-denominator approximation $\eta=1$, can be obtained very easily from Van Vleck's method.

The above corrections have been made in the zero-point anisotropy only. Charap and Weiss² have applied similar corrections to the temperature-dependent part. To obtain this we would have to consider terms of order $n_{\mathbf{k}}$ in (37) and also carry (23) out to higher order. The 10th-power law is not affected by these higher

terms. For details the reader is referred to the Charap and Weiss paper.

IV. STATIC VS DYNAMIC ANISOTROPY

As discussed in the introduction, the dynamic anisotropy measured by ferromagnetic resonance should agree with the static anisotropy measured in a torque experiment. This agreement will now be derived.

Consider the uncorrected zero-point anisotropy obtained in Sec. II. (The Charap-Weiss corrections will simply multiply all our results by a common factor.)

$$F_D(0) = C_1 + K_1(0)\Gamma. \quad (41)$$

This may be considered as a macroscopic anisotropy energy leading to an effective anisotropy "field" in a resonance experiment performed near 0°K.

For simplicity we assume zero external static applied field. For a simple cubic (Ω_4 and hence K_1 positive) an easy direction will be (001). Let θ be a small angle away from this axis. Then it is easy to show that

$$\partial F_D(0)/\partial \theta \approx 2K_1(0)\theta. \quad (42)$$

By definition, the anisotropy field H_A is given by

$$\partial F_D(0)/\partial \theta = M \sin \theta H_A \approx M \theta H_A. \quad (43)$$

Thus

$$H_A \approx 2K_1(0)/M = 2K_1(0)/Ng\beta S. \quad (44)$$

The resonance energy in this field will be given by

$$E_R(001) = g\beta H_A \approx 2K_1(0)/NS. \quad (45)$$

Now let us see if this energy is contained in the $\mathbf{k}=0$ spin wave excited by the microwaves. From (32) the additional spin-wave energy to be added to $A_{\mathbf{k}}$ is

$$E_{\mathbf{k}} = K_1(0)(10/NS)(\frac{1}{2} - \Gamma). \quad (46)$$

For the easy direction (001), $\Gamma=0$, and hence

$$E_{\mathbf{k}}(001) = E_R(001) = 2K_1(0)/NS. \quad (47a)$$

Thus the equivalence of static and dynamic anisotropy is established. Similarly for K_1 negative as in fcc and bcc, with (111) as an easy direction, one can show that

$$E_{\mathbf{k}}(111) = E_R(111) = -\frac{4}{3}K_1(0)/NS. \quad (47b)$$

The result has been derived for simple cases with no applied field and near 0°K. But it is clear that there is a general equivalence between the spin wave and classical theories of dipolar-type anisotropy.

V. VAN VLECK'S METHOD

Van Vleck³ expresses the unperturbed exchange Hamiltonian in the molecular field approximation

$$\mathcal{H}_E = -g\beta H_E \sum_i S_i^z, \quad (48)$$

where the exchange field H_E is taken as temperature independent [see the remarks below Eq. (25)]. The partition function is then expanded in powers of the

¹⁹ M. H. Cohen and F. Keffer, Phys. Rev. **99**, 1135 (1955).

dipolar perturbation.²⁰

$$\begin{aligned} Z &= \sum_{\mu} \exp(-E_{\mu}/k_B T) [1 - (k_B T)^{-1}(a+b+c+d)], \\ a &= \langle \mu | \mathcal{H}^0 | \mu \rangle, \\ b &= -(2k_B T)^{-1} \sum_{\nu} \langle \mu | \mathcal{H}^0 | \nu \rangle \langle \nu | \mathcal{H}^0 | \mu \rangle, \\ c &= \sum_{\nu} \langle \mu | \mathcal{H}^{++} | \nu \rangle \langle \nu | \mathcal{H}^{--} | \mu \rangle / (E_{\mu} - E_{\nu}) + \text{c.c.}, \\ d &= \sum_{\nu} \langle \mu | \mathcal{H}^{+-} | \nu \rangle \langle \nu | \mathcal{H}^{-+} | \mu \rangle / (E_{\mu} - E_{\nu}) + \text{c.c.} \end{aligned} \quad (49)$$

Here E_{μ} are eigenvalues of (48). Since Z is given by a spur, any system of representation may be chosen, and for convenience Van Vleck picks that system in which each spin is separately space-quantized. Terms which would ordinarily have vanishing energy denominators in second order perturbation appear in Z in the form b above, that is, the degeneracy problem can be handled in a simple fashion if one is interested only in the partition function. For details the reader is referred to a very interesting discussion in Van Vleck's paper.³ The matrix expansion (49) is equivalent to an operator expansion of Z which is frequently used in current papers.²¹

Let

$$Z = Z_0(1 + \epsilon),$$

then

$$F = -k_B T \ln Z \approx -k_B T \ln Z_0 - k_B T \epsilon,$$

to a first approximation. Thus the dipolar portion of the free energy is given by

$$F_D = \langle a + b + c + d \rangle. \quad (50)$$

where

$$\langle x \rangle \equiv Z_0^{-1} \sum_{\mu} x \exp(-E_{\mu}/k_B T) \quad (51)$$

is the temperature dependent statistical average of x in the molecular field.

It is obvious that $\langle a \rangle$ cannot exhibit cubic anisotropy. The term $\langle b \rangle$ is evaluated as follows:

$$\begin{aligned} \langle b \rangle &= -(2k_B T)^{-1} \sum_{i \neq j} \sum_{i' \neq j'} E_{ij} E_{i'j'} \\ &\quad \times \langle (\mathbf{S}_i \cdot \mathbf{S}_j - 3S_i^z S_j^z)(\mathbf{S}_{i'} \cdot \mathbf{S}_{j'} - 3S_{i'}^z S_{j'}^z) \rangle. \end{aligned} \quad (52)$$

The value of (52) depends upon the correlation assumed between neighbor spins. Van Vleck assumes complete lack of correlation, i.e., each spin is free to fluctuate in the molecular field without regard to the direction of its neighbor spin. Thus, for example

$$\langle S_i^z S_{i'}^z - (S_i^z)^2 \rangle = \langle m^2 \rangle - \langle m^2 \rangle, \quad (53)$$

$$\langle S_i^+ S_{i'}^- \rangle = [S^2 + S - \langle m^2 \rangle + \langle m \rangle] \delta_{ii'}, \quad (54)$$

where $\langle m^n \rangle$ is the statistical average, in the molecular field, of the eigenvalue of the n th power of the operator S_i^z . With this assumption, and with use of (16), Van Vleck finds

$$\begin{aligned} \langle b \rangle_{VV} &= -(2k_B T)^{-1} N \sum_h (E_h)^2 [(S^2 + S - \langle m^2 \rangle)^2 \\ &\quad - \langle m^2 \rangle^2 + 8\langle m^2 \rangle^2 - 16\langle m^2 \rangle \langle m \rangle^2 + 8\langle m \rangle^4]. \end{aligned} \quad (55)$$

²⁰ R. Serber, Phys. Rev. 43, 1011 (1933); J. H. Van Vleck, J. Chem. Phys. 5, 320 (1937).

²¹ M. L. Goldberger and E. N. Adams, J. Chem. Phys. 20, 240 (1952).

A quite different value is obtained for (52), however, with the assumption of strong correlation between neighbor spins. In the limit of complete correlation (which corresponds to the approximation of Sec. II that only $\mathbf{k}=0$ spin waves are excited) we must take (53) as zero. Furthermore, for neighbor spins, $\mathbf{S}_i \cdot \mathbf{S}_j \approx S^2$. With the aid of (16), the correlated approximation yields

$$\langle a \rangle_{\text{cor}} = \langle b \rangle_{\text{cor}} = 0, \quad (56)$$

corresponding to the results of Sec. II B. The remaining terms of (49) are expressed as follows:

$$\begin{aligned} \langle c \rangle &= -[(2g\beta H_E)^{-1} \sum_{i \neq j} \sum_{i' \neq j'} B_{ij} B_{i'j'}^* \\ &\quad \times \langle S_i^+ S_j^+ S_{i'}^- S_{j'}^- \rangle - \text{c.c.}], \\ \langle d \rangle &= -[(g\beta H_E)^{-1} \sum_{i \neq j} \sum_{i' \neq j'} F_{ij} F_{i'j'}^* \\ &\quad \times \langle S_i^+ S_j^z S_{i'}^- S_{j'}^z \rangle - \text{c.c.}]. \end{aligned} \quad (57)$$

Van Vleck's evaluations are

$$\begin{aligned} \langle c \rangle_{VV} &= -(2g\beta H_E)^{-1} N \sum_h |B_h|^2 \\ &\quad \times 8(S^2 + S - \langle m^2 \rangle) \langle m \rangle; \end{aligned} \quad (58)$$

$$\langle d \rangle_{VV} = -(g\beta H_E)^{-1} N \sum_h |F_h|^2 \langle m \rangle (\langle m^2 \rangle - \langle m \rangle^2);$$

whereas the correlated approximation yields

$$\langle c \rangle_{\text{cor}} = -(2g\beta H_E)^{-1} N \sum_h |B_h|^2 8\langle m^2 \rangle; \quad (59a)$$

$$\langle d \rangle_{\text{cor}} = -(g\beta H_E)^{-1} N \sum_h |F_h|^2 [S^2 - \langle m^2 \rangle]. \quad (59b)$$

To obtain (59) most simply one carries out the commutation of spin operators in (57) and rearranges the results so that S^+ operators are to the right. Sums containing $S_i^- S_{i'}^z S_j^+ \delta_{i'j'}$, etc., are then taken to be zero, as can most easily be seen from spin-wave considerations (these sums are quadratic in n_k).

It is to be noted that (59) is quite different from (58) for $T > 0$. On using the relations (10) one obtains for the dipolar free energy

$$\begin{aligned} F_D &= \langle c \rangle_{\text{cor}} + \langle d \rangle_{\text{cor}} \\ &= -(9NS^2/16g\beta H_E) D^2 \sum_h [(1 - \gamma_h^2)^2 S^{-2} \langle m^2 \rangle \\ &\quad + 4\gamma_h^2 (1 - \gamma_h^2) (1 - S^{-2} \langle m^2 \rangle)]. \end{aligned} \quad (60)$$

The anisotropic portion of the above is the coefficient of γ_h^4 . With the approximation

$$\langle m^2 \rangle = S^2 (1 - \epsilon)^2 \approx S^2 (1 - 2\epsilon), \quad (61)$$

where

$$\epsilon = [M(0) - M(T)]/M(0),$$

this portion contains

$$1 - 2\epsilon - 8\epsilon = 1 - 10\epsilon, \quad (62)$$

in agreement with the Akulov expression (2).

Equation (60) is to be compared to the spin-wave result (29). They are equivalent if

$$g\beta H_E = 2JSz. \quad (63)$$

It is possible to improve this simple relation, at least insofar as it enters into (59a), which equation gives the zero-point anisotropy. The denominator of (59a) is

the energy involved in reversing in succession two neighbor spins. From (7) the average energy to reverse the first spin is

$$\Delta E_1 = 2JSz. \quad (64)$$

The average energy to reverse the second spin, in the presence of the reversed first spin, is

$$\Delta E_2 = 2J(Sz - 1). \quad (65)$$

Thus in (59a) we replace

$$\begin{aligned} 2g\beta H_E &= \Delta E_1 + \Delta E_2 \\ &= 2J(2Sz - 1), \end{aligned} \quad (66)$$

and now the result differs from (29) by the factor

$$\xi_0 = \frac{2Sz}{2Sz - 1}. \quad (67)$$

This is equivalent to the exchange-interaction correction of Sec. III, Eq. (40), in the constant-denominator approximation $\eta = 1$.

The η correction cannot be obtained easily from Van Vleck's method. This is because the state with a spin reversed is not an eigenstate of the entire exchange Hamiltonian, but only of the $S_i^z S_j^z$ portion. Therefore the improvement embodied in (66) replaces the molecular-field approximation by an Ising model. The correct energy denominator, as exhibited by the spin-wave calculation, has an additional fluctuating term.

ACKNOWLEDGMENT

We wish to thank Professor P. R. Weiss and Dr. S. H. Charap for sending us a preprint of their paper, which stimulated this investigation.

Time-Dependent Internal Friction in Aluminum and Magnesium Single Crystals*†

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(Received August 3, 1959)

Magnesium and aluminum single crystals subjected to varying amounts of oscillatory strain of audio frequency have been investigated by measuring the strain amplitude-dependent complex dynamical-mechanical modulus at audio frequencies as a function of temperature and time. If the amplitude of the applied excitation exceeds a critical breakaway strain, an excited mechanical state is manifested in a modification of the amplitude dependence of the complex modulus. Upon cessation of the excitation, the excited state decays. The decay following short excitation times obeys a $t^{1/2}$ law, becoming a t^1 law as excitation approaches saturation. The short excitation decay rate is found to be governed by an activation energy in the range of 7–10 kcal per mole.

The time dependence is considered to be caused by the dispersal and condensation of a pinning atmosphere which has high diffusivity and is easily dispersed by a dislocation segment undergoing pinning interactions with the atmosphere.

INTRODUCTION

THE literature relating to nonlinear mechanical behavior of metal single crystals has increased steadily ever since Read's^{1–3} early experiments and his interpretation of the amplitude dependence of internal friction and Young's modulus in terms of the motion of dislocations. It was early recognized that amplitude dependent internal friction measurements also showed

marked time dependence.^{1–6} At temperatures well below the recrystallization temperature, rapid recovery of internal friction occurs following deformation of metal single crystals (Koester effect, after Nowick⁷) and is attributed to the redistribution of dislocation lines.

The following is a study made of a time-dependent phenomenon in amplitude-dependent internal friction and modulus measurements of aluminum and magnesium single crystals resulting from controlled oscillatory deformations.

EXPERIMENTAL TECHNIQUE

A resonant bar technique is used to measure the decrement and effective Young's modulus of 16 cm long

* Work supported in part by the U. S. Atomic Energy Commission.

† Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology.

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⁴ I. H. Swift and J. E. Richardson, *J. Appl. Phys.* **18**, 417 (1947).

⁵ A. S. Nowick, *Symposium on Plastic Deformation of Crystalline Solids*, Office of Naval Research, 1950 (unpublished).

⁶ T. A. Read (quoted in discussion to reference 5).

⁷ A. S. Nowick, *J. Appl. Phys.* **25**, 1129 (1954).