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Microscopic Model for Reorientation of the Easy Axis of Magnetization*

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We present a microscopic model to describe the reorientation of the easy axis of magnetization from one symmetry axis of the crystal to another, which is known to occur in a number of magnetic insulators. We find that the easy axis either rotates continuously with temperature, beginning at T_1 and ending at a higher temperature T_2, or jumps discontinuously with associated hysteresis effects. In the former case, we have calculated the temperature dependence of the easy direction of magnetization, and the behavior of the specific heat and correlation lengths in the vicinity of T_1 and T_2. Measurement of T_1 and T_2 allows the evaluation of the ratios K_1/K_4 and K_2/K_4, where K_1, K_2, and K_4 give the strength of the pseudodipolar spin interaction, and the second- and fourth-order single-ion anisotropy terms in the spin Hamiltonian, respectively.

I. INTRODUCTION

A NUMBER of magnetic insulators exhibit a displacive-type[1] phase transition, in which the easy axis of magnetization reorients itself from one symmetry axis of the crystal to another upon changing the temperature.[2–10] Well-known examples of such transitions include the Morin transition in α-$\mathrm{Fe_2O_3}$ (hematite)[2] and the reorientation of the net magnetic moment from the *a*- to the *c*-symmetry axis, which occurs on heating in a number of the orthorhombic rare-earth orthoferrites[3] (formula $R\mathrm{FeO_3}$, where R is a rare earth). The behavior of $D_y\mathrm{FeO_3}$, which exhibits a spin reorientation from the G_y- to the G_x-spin structures[9] at about 30°K with no detectable specific-heat anomaly,[10] is also noteworthy. Indeed, a very large quantity of often contradictory experimental data is at present available regarding this effect in hematite and the orthoferrites. We list some recent studies[11–27] of the easy axis reorientation in these materials which have employed torque, magnetic moment, and susceptibility measurements, as well as microwave absorption, neutron diffraction, and the Mössbauer technique. Among other materials evidencing easy-axis–reorientation phase tran-

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[1] By displacive phase transition we shall intend a phase transition of the $\mathrm{BaTiO_3}$ type (as opposed to order-disorder transitions), which is characterized by a specific-heat anomaly small compared to Boltzmann's constant k_B at the transition temperature. A similar definition has been employed by Tisza [L. Tisza, *Phase Transformations in Solids* (Wiley-Interscience, Inc., New York, 1951), pp. 18–28].

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sitions are the ferromagnet[7] $NdCO_5$ and the ferrimagnets[4,8] Mn_2Sb and $Ba_2Co_2Fe_{12}O_{22}$.

Analyses of the above wealth of data have generally followed phenomenological lines, with the thermodynamic free energy controlling the easy-axis reorientation usually introduced on a somewhat *ad hoc* basis.[28] Horner and Varma[29] have given a phenomenological treatment of the reorientation occurring in materials which undergo easy-axis rotation, beginning at some temperature T_1 and ending at T_2. They employ the Landau theory of second-order phase transitions to describe the easy-axis rotation, assuming that the macroscopic second-order anisotropy energy varies linearly with temperature in the interval T_1–T_2.

Since the preferred direction of the magnetic moment is determined by the magnetic-anisotropy energy, it is clear that the easy-axis–reorientation process is governed by the temperature variation of the anisotropy energy K acting upon the spin system. The spin-spin couplings, on the other hand, are of the order of the exchange integral J. As will become apparent in the following, the small ratio K/J ($\simeq 10^{-4}$ in many cases) makes this problem readily amenable to perturbation-theory treatment.

We shall demonstrate that our model Hamiltonian *does* predict that the easy axis of magnetization passes from one crystal symmetry axis to another as the temperature is altered. The reorientation occurs by one of two possible processes:

(a) The easy axis *jumps* suddenly from one crystal symmetry axis to the other at the transition temperature, the phase transition being of first order. The transition is characterized by hysteresis effects, whereby the spin reorientation occurs at different temperatures depending on whether the transition region is approached from the high- or low-temperature side.

(b) The easy axis *rotates* continuously from one crystal symmetry axis to another, the transition beginning at some temperature T_1 and ending at a higher temperature T_2. For temperatures in the immediate vicinity of both T_1 and T_2, the usual Landau theory for second-order phase transitions is applicable provided that the perturbation series in powers of K/J converges.

When case (b) is relevant, the calculated free-energy function displays the general features characteristic of second-order phase transitions.[30–32] As for other displacive-type phase transitions,[33–36] we find specific-heat anomalies at the transition temperatures, which are small compared to Boltzmann's constant. This reflects the absence of major changes in the short-range order throughout the reorientation region. Our explicit calculation for small K/J serves to verify the assumptions of Horner and Varma[29] for temperatures in the immediate neighborhood of T_1 and T_2.

In Sec. II A of this article we present the model Hamiltonian of our system and solve for the free energy as a function of the formal "order parameter" θ (θ = angle between spin easy axis and z axis) in the approximation $K/J \ll 1$. In order to obtain expressions for the temperature dependence of the relevant anisotropy constants in terms of tabulated functions, we evaluate our results in the classical molecular-field approximation in Sec. II B.

In Sec. III, we briefly consider the available experimental data for the spin reorientation in hematite and in the rare-earth orthoferrites in the light of our results. Finally, we discuss the applicability of the Landau theory of phase transitions to our model in the case where the reorientation transition is of the second order.

II. THEORY

A. Model Hamiltonian

For the sake of clarity we will consider a magnetic insulator having its spins on equivalent sites. This assumption simplifies the problem and will not materially affect the qualitative features of our results. We expect that such a model will also, in some approximation, describe the easy-axis reorientation occurring in antiferromagnets. We adopt the spin Hamiltonian $\mathcal{H}$ given by

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_a \,, \tag{1}$$

where

$$\mathcal{H}_0 = -\sum_{\substack{i,j\\ i\neq j}} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \tag{2}$$

is the isotropic Heisenberg Hamiltonian, and where

$$\mathcal{H}_a = \sum_i \kappa_2 (S_i^z)^2 + \sum_i \kappa_4 (S_i^z)^4 + \sum_{\substack{i,j\\ i\neq j}} \kappa_{1,ij} S_i^z S_j^z \tag{3}$$

describes the spin anisotropy. In (2) and (3) the quantity $\mathbf{S}_i$ is the spin operator at site i divided by its magnitude S. The first and second term on the right-hand side of (3) represent the second- and fourth-order single-ion anisotropy contributions, respectively. The third term on the right-hand side of (3) describes the effect of the dipolar and pseudodipolar spin interactions, and is of the same order of magnitude as the

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[28] It should be noted that J. O. Artman *et al.* [Phys. Rev. **138**, A912 (1965)] have treated the Morin transition in hematite on a microscopic basis, using spin operators up to second order in the spin Hamiltonian. Their model predicts the occurrence of a first-order phase transition without hysteresis effects. The presence of fourth-order terms in the spin Hamiltonian is crucial to our treatment.

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second-order single-ion anisotropy term.[37] If J denotes the sum

$$\sum_j J_{ij},$$

which measures the strength of the isotropic exchange coupling of a spin to its neighbors, then[37] $\kappa_2/J \simeq 10^{-4}$ for ions having the $^6S_{5/2}$-$3d^5$ configuration of Fe^{3+}, which is our main interest. The ratio κ_4/J is probably at least an order of magnitude smaller. The anisotropic part of the Hamiltonian has been assumed to depend only on S^z. This simplification serves to restrict the easy-axis reorientation to a single plane, say the x-z plane.

It is useful to express $\mathcal{H}_a$ in terms of operator equivalents of the spherical harmonics.[38] Thus, neglecting a constant, we find that

$$\mathcal{H}_a = \sum_i \left[K_2 Y_2^0(\mathbf{S}_i) + K_4 Y_4^0(\mathbf{S}_i)\right] + \sum_{\substack{i,j \\ i\neq j}} K_{1,ij} Y_1^0(\mathbf{S}_i) Y_1^0(\mathbf{S}_j). \quad (4)$$

The constants K in (4) are simple linear combinations of the constants κ in (3).

The free energy F of the system, to first order in K/J is given by[39]

$$F = -kT \ln \mathrm{Tr}(e^{-\beta\mathcal{H}_0}) + \langle\mathcal{H}_a\rangle \quad (5)$$

$$\equiv F_0 + \langle\mathcal{H}_a\rangle, \quad (6)$$

where angular brackets denote the thermal average taken with respect to the *unperturbed* density matrix $\rho_0 = e^{-\beta\mathcal{H}_0}/\mathrm{Tr}e^{-\beta\mathcal{H}_0}$. It is evident that the angular dependence of the free energy arises solely from $\langle\mathcal{H}_a\rangle$ in (5). We shall evaluate this angular dependence using a method due to Callen and Callen,[40] and will briefly repeat parts of their derivation for the sake of continuity. Let us suppose that at temperature T the mean magnetic moment $\langle\mathbf{S}\rangle$ points along $\mathbf{n}$, where $\mathbf{n}$ is a unit vector. The spherical harmonics $Y_l^0(\mathbf{S})$ in (4) are defined with respect to the coordinate axes Oxyz fixed relative to the crystal. We transform $Y_l^0(\mathbf{S})$ to a new set of spherical harmonics $Y_l^m(\mathbf{S}')$ having $\mathbf{n}$ as polar axis, to obtain

$$Y_l^0(\mathbf{S}) = \sum_{m=-l}^{l} a_l^m Y_l^m(\mathbf{S}'). \quad (7)$$

Since $\mathcal{H}_0$ is cylindrically symmetric about $\mathbf{n}$, it follows that

$$\langle Y_l^0(\mathbf{S})\rangle = a_l^0 \langle Y_l^0(\mathbf{S}')\rangle. \quad (8)$$

From the properties of spherical harmonics[40,41] we obtain $a_l^0 = Y_l^0(\mathbf{n})$, aside from a possible normalization factor, which, in any event, we will absorb into the anisotropy constants.

From (4)–(8) we obtain[42]

$$\langle\mathcal{H}_a\rangle = \sum_i \left[K_2 Y_2^0(\mathbf{n})\langle Y_2^0(\mathbf{S}_i')\rangle + K_4 Y_4^0(\mathbf{n})\langle Y_4^0(\mathbf{S}_i')\rangle\right] + \sum_{\substack{i,j \\ i\neq j}} K_{1,ij}[Y_1^0(\mathbf{n})]^2 \langle Y_1^0(\mathbf{S}_i') Y_1^0(\mathbf{S}_j')\rangle. \quad (9)$$

Equation (9) explicitly displays the angular dependence of the anisotropy energy $\langle\mathcal{H}_a\rangle$, and represents the fundamental expression for the temperature variation of the anisotropy coefficients.

It is helpful to rewrite (9) to clarify its relation to the usual phenomenological expressions for $\langle\mathcal{H}_a\rangle$. We denote the angle between $\langle\mathbf{S}\rangle$ and the z axis by θ. Then, using explicit formulas for the spherical harmonics, we may reexpress (9) as a polynomial in $\sin^2\theta$:

$$\langle\mathcal{H}_a\rangle = A_0(T) + A_2(T)\sin^2\theta + A_4(T)\sin^4\theta, \quad (10)$$

where

$$A_0(T) = \left(\frac{5}{4\pi}\right)^{1/2} \sum_i K_2\langle Y_2^0(\mathbf{S}_i')\rangle + \left(\frac{9}{4\pi}\right)^{1/2} \sum_i K_4\langle Y_4^0(\mathbf{S}_i')\rangle + \frac{3}{4\pi} \sum_{\substack{i,j \\ i\neq j}} K_{1,ij} \times \langle Y_1^0(\mathbf{S}_i') Y_1^0(\mathbf{S}_j')\rangle, \quad (11)$$

$$A_2(T) = -\tfrac{3}{2}\left(\frac{5}{4\pi}\right)^{1/2} \sum_i K_2\langle Y_2^0(\mathbf{S}_i')\rangle - 5\left(\frac{9}{4\pi}\right)^{1/2} \sum_i K_4\langle Y_4^0(\mathbf{S}_i')\rangle - \frac{3}{4\pi} \sum_{\substack{i,j \\ i\neq j}} K_{1,ij} \times \langle Y_1^0(\mathbf{S}_i') Y_1^0(\mathbf{S}_j')\rangle, \quad (12)$$

and

$$A_4(T) = -\frac{35}{8}\left(\frac{9}{4\pi}\right)^{1/2} \sum_i K_4\langle Y_4^0(\mathbf{S}_i')\rangle. \quad (13)$$

Thus, we have

$$F = F_0 + A_0(T) + A_2(T)\sin^2\theta + A_4(T)\sin^4\theta. \quad (14)$$

It is helpful to consider the rather trivial properties of $F(\theta)$. To assist the reader we have plotted in Fig. 1 the simple function $(F - F_0 - A_0)/|A_4| = \alpha\sin^2\theta \pm \sin^4\theta$ versus θ for various values of the parameter $\alpha \equiv A_2/|A_4|$. It is convenient to consider the case $A_4 < 0$ [Fig. 1(a)] and $A_4 > 0$ [Fig. 1(b)] separately.

When $A_4 < 0$ [Fig. 1(a)], it is apparent that the only values of θ for which the free energy is minimized

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[37] T. Moriya, in *Magnetism*, edited by G. T. Rado and S. Suhl (Academic Press Inc., New York, 1963), Vol. I, p. 86.

[38] E. R. Callen and H. B. Callen, Phys. Rev. **129**, 578 (1963).

[39] It is clear that this approximation is better, the smaller K/J. Its validity is discussed in Sec. III.

[40] H. B. Callen and E. R. Callen, J. Phys. Chem. Solids **27**, 1271 (1966).

[41] E. R. Callen and H. B. Callen, J. Phys. Chem. Solids **16**, 310 (1960), Appendix C.

[42] In the derivation of (9) we have put pseudodipolar terms of the form $\langle Y_1^1(\mathbf{S}_i') Y_1^{-1}(\mathbf{S}_j')\rangle \simeq \langle Y_1^1(\mathbf{S}_i')\rangle\langle Y_1^{-1}(\mathbf{S}_j')\rangle = 0$. This is equivalent to neglecting correlations between different spin components of spins belonging to different sites, when evaluating the pseudodipolar contribution. This simplification allows us to easily put Eq. (9) in the form of Eq. (10).

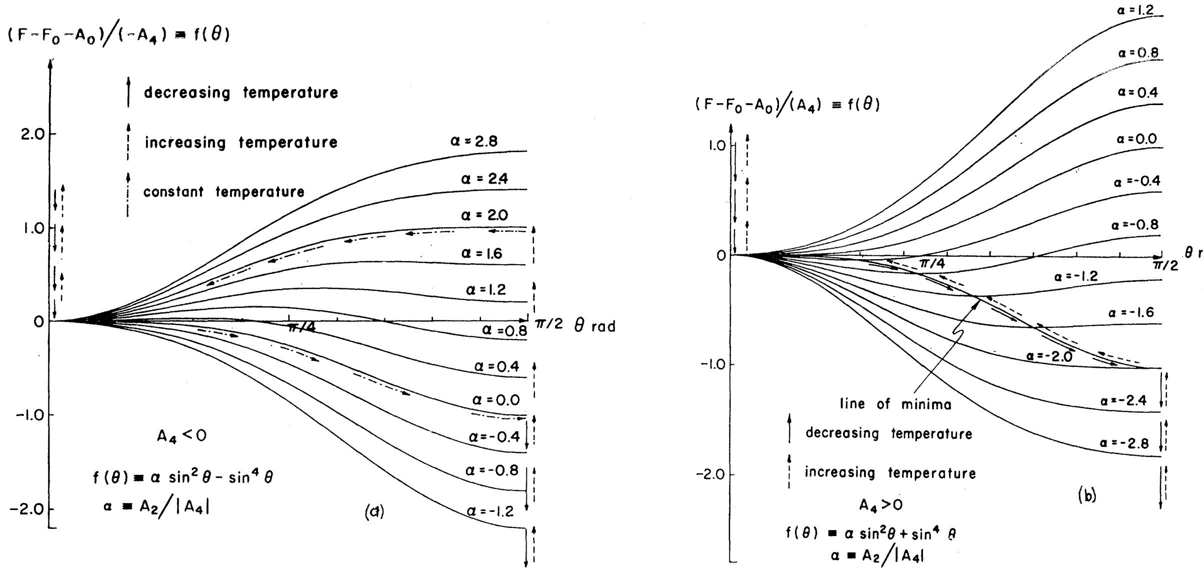

FIG. 1. (a) Angular variation of the reduced free energy $(F-F_0-A_0)/|A_4|$ for varying values of the parameter $\alpha\equiv A_2/|A_4|$. The fourth-order anisotropy term A_4 is negative. We have taken the easy axis to lie along the z axis at low temperatures. Expressions for F, A_0, A_2, and A_4 are given in Eqs. (11)–(14). The cyclic path indicated by the arrows is discussed in Sec. II A. (b) As for (a), but with A_4 positive.

are $\theta=0$ and $\theta=\frac{1}{2}\pi$. For values of α such that $0<\alpha<2$ the free-energy function has a local maximum, $(=\frac{1}{4}\alpha^2)$ corresponding to unstable equilibrium, at values of θ given by $\sin^2\theta=\frac{1}{2}\alpha$. It is also worth noting that for $0<\alpha<1$, the choice $\theta=0$ corresponds to metastable local equilibrium of the free energy, and that $\theta=\frac{1}{2}\pi$ is similarly metastable for $1<\alpha<2$.

This type of free-energy function leads to hysteresis effects. For example, if high temperatures correspond to large values of $\alpha(T)$, then on cooling, $\theta=0$ will remain the locally stable direction of the easy axis until a temperature T_1, where α has decreased to zero. For $T<T_1$, the easy axis jumps to $\theta=\frac{1}{2}\pi$. On subsequent heating, to return the easy axis to its original direction, it will be necessary to heat the system to a higher temperature T_2, $(T_2>T_1)$ such that $\alpha(T_2)=2$, before θ jumps from $\theta=\frac{1}{2}\pi$ to 0.

In Fig. 1(b) we present plots of the reduced free energy $(F-F_0-A_0)/A_4$ for $A_4>0$. In the range -2 $2<\alpha<0$, the free energy has a minimum at values of θ given by $\sin^2\theta=-\frac{1}{2}\alpha$. For $\alpha>0$, $\theta=0$ is the only stable solution, and for $\alpha<-2$, $\theta=\frac{1}{2}\pi$ alone is stable. In contrast to the case $A_4<0$, no hysteresis effects occur, the easy-axis equilibrium value $\theta=0$ for high α passing smoothly to the $\theta=\frac{1}{2}\pi$ equilibrium position as $\alpha(T)$ decreases. In this case the easy axis rotates continuously between the crystal-symmetry axes.

In the temperature region where $\alpha\simeq0$ (easy axis about to begin rotation), the plot of F versus θ is similar to that of the standard Landau theory of second-order phase transitions.[43] This similarity has been pointed out by Horner and Varma,[29] who, on phenomenological grounds, assume a free-energy function of the form (14).

A second, analogous, Landau-type phase transition occurs in the region $\alpha\simeq-2$. In this region the appropriate order parameter is $\frac{1}{2}\pi-\theta$, as distinct from the order parameter θ for the region where $\alpha\simeq0$. Defining T_1 and T_2 by $\alpha(T_1)=0$, $\alpha(T_2)=-2$, respectively, then for $T_1<T<T_2$ (assuming $T_1<T_2$) the spin system is stable in a phase of lowered symmetry. It is, moreover, noteworthy that the easy-axis rotation is characterized by both an upper- and a lower-transition temperature. Such behavior is not uncommon for second-order displacive phase transitions.[36,44]

It is instructive to consider the easy-axis reorientation pictorially, using the graphic portrayal of the anisotropy energy due to Callen and Callen.[45] Consider a surface whose distance from the origin in every direction is proportional to the $T=0$°K anisotropy energy in that direction. Let us assume that the spins then lie along the z axis. The anisotropy-energy surface will thus have a valley centered about the point where the surface is cut by the z axis. Upon heating, the spins are agitated by thermal energy, and spend part of their time away from the z direction, and thus sample regions of the anisotropy-energy surface corresponding to higher energies. The thermal sampling therefore serves to smooth out the effective anisotropy felt by the spins as the temperature is raised, and leads to the well-known[40] decrease in the anisotropy coefficients with increasing temperature.

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[43] L. D. Landau and E. M. Lifshits, *Statistical Physics* (Pergamon Press, Inc., New York, 1959).

[44] Reference 42, p. 433.

[45] Reference 39, Fig. 1.

In the particular case when easy-axis reorientation arises, the anisotropy-energy surface is such, that upon the spins sampling larger regions of the energy surface, a temperature is reached which makes it energetically favorable for the mean spin direction to rotate. Thus, upon heating to temperature T_1, the spins begin to sample different regions of the anisotropy-energy surface due to the movement of the mean spin direction, and not merely as a result of the increasing available thermal energy spreading the instantaneous spin directions over a wider area. The initiation of this process signals the onset of the phase transition.

It is worth emphasizing the significance of Eq. (10) in the context of the theory of phase transitions. By employing thermal perturbation theory, we have obtained a Landau-type expansion in powers of the order parameter for our model. In the following paragraph we present a plausibility argument to the effect that $A_2(T)$ and $A_4(T)$ can be expanded in Taylor series about the transition temperature.

The temperature dependence of $A_2(T)$ and $A_4(T)$ is determined by terms which typically have the form $\mathrm{Tr}[\rho_0(S_z')^m]$, where m is an integer. At the temperatures T_1 and T_2 nothing unusual is occurring as regards the *zero-order* density matrix ρ_0. Indeed, T_1 and T_2 have no connection whatever with the behavior of the isotropic Heisenberg Hamiltonian ρ_0. Thus, while we have no rigorous proof of this point, the mathematical regularity of $A_2(T)$ and $A_4(T)$ at T_1 and T_2 appears to be very plausible.

In the following we specialize to the classical molecular-field approximation for ρ_0 so as to facilitate the calculation of $A_2(T)$ and $A_4(T)$ in terms of tabulated functions.

B. Classical Molecular-Field Approximation

We shall employ the molecular-field approximation to calculate $A_2(T)$ and $A_4(T)$. We thus approximate our zero-order Hamiltonian $\mathcal{H}_0$ and density matrix ρ_0 by

$$\mathcal{H}_0^{MF} = -J\langle \mathbf{S}'\rangle \cdot \mathbf{S}'$$

and

$$\rho_0^{MF} = e^{-\beta\mathcal{H}_0^{MF}} / \mathrm{Tr}\, e^{-\beta\mathcal{H}_0^{MF}}.$$

Throughout this section, angular brackets denote the thermal average with respect to ρ_0^{MF}.

The free energy per spin then becomes

$$f = f_0 + a_0(T) + a_2(T)\sin^2\theta + a_4(T)\sin^4\theta\,, \qquad (15)$$

where $a_0(T)$, $a_2(T)$, and $a_4(T)$ are given by

$$a_0(T) = (5/4\pi)^{1/2}K_2\langle Y_2^0(\mathbf{S}')\rangle + (9/4\pi)^{1/2}K_4\langle Y_4^0(\mathbf{S}')\rangle + (3/4\pi)K_1[\langle Y_1^0(\mathbf{S}')\rangle]^2, \qquad (16)$$

$$a_2(T) = -\tfrac{3}{2}(5/4\pi)^{1/2}K_2\langle Y_2^0(\mathbf{S}')\rangle - 5(9/4\pi)^{1/2}K_4\langle Y_4^0(\mathbf{S}')\rangle - (3/4\pi)K_1[\langle Y_1^0(\mathbf{S}')\rangle]^2, \qquad (17)$$

$$a_4(T) = -(35/8)(9/4\pi)^{1/2}K_4\langle Y_4^0(\mathbf{S}')\rangle. \qquad (18)$$

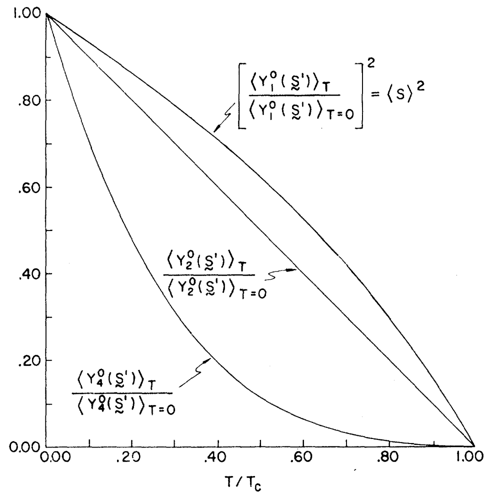

FIG. 2. Temperature dependence of $\langle Y_2^0(\mathbf{S}')\rangle_T/\langle Y_2^0(\mathbf{S}')\rangle_{T=0}$, $\langle Y_4^0(\mathbf{S}')\rangle_T/\langle Y_4^0(\mathbf{S})\rangle_{T=0}$, and $[\langle Y_1^0(\mathbf{S}')_T/Y_1^0(\mathbf{S}')\rangle_{T=0}]^2 = \langle S'\rangle^2$ in the classical molecular-field approximation. Explicit expressions for these function are given in Eqs. (19)–(21).

In (16) and (17) the quantity K_1 denotes $\sum_{i,j;\,i\neq j} K_{1,ij}/N$, where N is the number of spins.

Wolf[46] has provided numerical solutions for the thermal average of the spherical harmonics in (16)–(18) in the quantum case. We shall proceed to the classical limit to enable the evaluation of a_0, a_2, and a_4 in terms of tabulated functions. We then have

$$\langle Y_l^0(\mathbf{S}')\rangle = \int_{-1}^{1} Y_l^0(u)\exp[\beta J\langle S'\rangle u]du \Big/ \int_{-1}^{1}\exp[\beta J\langle S'\rangle u]du, \qquad (19)$$

where $u = \cos\theta$ and $\langle S'\rangle = |\langle \mathbf{S}'\rangle|$. Using the relation[40,41]

$$\int_{-1}^{1} Y_l^0(u)\exp[\beta J\langle S'\rangle u]du = I_{l+1/2}(\beta J\langle S'\rangle)\,, \qquad (20)$$

where I_ν is the Bessel function of imaginary argument of order ν, it follows that

$$\langle Y_l^0(\mathbf{S}')\rangle_T / \langle Y_l^0(\mathbf{S}')\rangle_{T=0} = I_{l+1/2}(\beta J\langle S'\rangle)/I_{1/2}(\beta J\langle S'\rangle) \equiv \hat{I}_{l+1/2}\,. \qquad (21)$$

For convenience we have adopted the notation of Callen and Callen.[40] In Fig. 2 we plot the quantities $\langle Y_2^0\rangle$, $\langle Y_4^0\rangle$, and $[\langle Y_1^0\rangle]^2$ versus T/T_c. It should be noted that

$$\langle Y_1^0(\mathbf{S}')\rangle_T / \langle Y_1^0(\mathbf{S}')\rangle_{T=0} = \langle S'\rangle = \hat{I}_{3/2}$$

gives the temperature dependence of the mean magnetization.

Differentiating (15) to obtain the equilibrium value

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[46] W. P. Wolf, Phys. Rev. **108**, 1152 (1957).

of θ between 0 and $\frac{1}{2}\pi$ when $a_4>0$, we have

$$\sin^2\theta = -a_2/2a_4. \tag{22}$$

From (17), (18), and (22), we then find

$$\sin^2\theta = -\frac{10K_2\hat{I}_{5/2}+60K_4\hat{I}_{9/2}+3K_1(\hat{I}_{3/2})^2/\pi}{105K_4\hat{I}_{9/2}}. \tag{23}$$

It is plausible that $|K_1|\gg|K_4|$ and $|K_2|\gg|K_4|$. Taking $|K_1/K_4|=10^3$, $|K_2/K_4|=10^2$, $K_1>0$, $K_2<0$, and $K_4<0$, then at $T=0$, the spin-easy-axis equilibrium position is stable at $\theta=0$. [$\alpha>0$, see Fig. 1(b).] Spin rotation begins at $T=T_1$, for which the numerator on the right-hand side of (23) equals zero. [$\alpha(T_1)=0$, Fig. 1(b).] On further increase of the temperature, the numerator becomes negative (see Fig. 2), and the ratio $-a_2/2a_4$ is positive and increases in magnitude due to the rapid decrease of $\hat{I}_{9/2}$ relative to $(\hat{I}_{3/2})^2$ and $\hat{I}_{5/2}$. The rotation process is completed[47] when the right-hand side of (22) equals unity [$\alpha=-2$, Fig. 1(b)]. In Fig. 3 we plot the temperature dependence of θ for the indicated choice of the anisotropy coefficients.

We may compute the rotational contribution to the specific heat by substituting the expression (23) for the equilibrium angle θ into (15), and using the relation

$$C=-T(\partial^2 f/\partial T^2).$$

The resulting expression is lengthy and is not given here; its derivation is quite straightforward. In Fig. 4 we plot C for the indicated choice of K_1, K_2, and K_4. We will, however, give expressions for the specific-heat jumps at the extremes of the rotation process. Employing (15), we obtain

$$C(T_2^-)-C(T_2^+)=\frac{1}{2}\frac{T_2}{a_4(T_2)}\left[\frac{d}{dT}(a_2+2a_4)_{T_2}\right]^2, \tag{24}$$

$$C(T_1^+)-C(T_1^-)=\frac{1}{2}\frac{T_1}{a_4(T_1)}\left[\left(\frac{da_2}{dT}\right)_{T_1}\right]^2. \tag{25}$$

The quantities on the right-hand side of (24) and (25) are always positive-definite. Explicit values for the a's and their derivatives follow at once using (17), (18), and (21).

Experimental observation of easy-axis rotation in a magnetic insulater will, in general, permit ready measurement of the temperatures T_1 and T_2, corresponding to the start and end of the easy-axis rotation, respectively. By inverting (23) for $\theta=0$ and $\theta=\frac{1}{2}\pi$, we can obtain the ratios K_1/K_4 and K_2/K_4, corresponding to the measured values of T_1 and T_2, thereby determining the relative importance of the various anisotropy terms in the spin Hamiltonian.

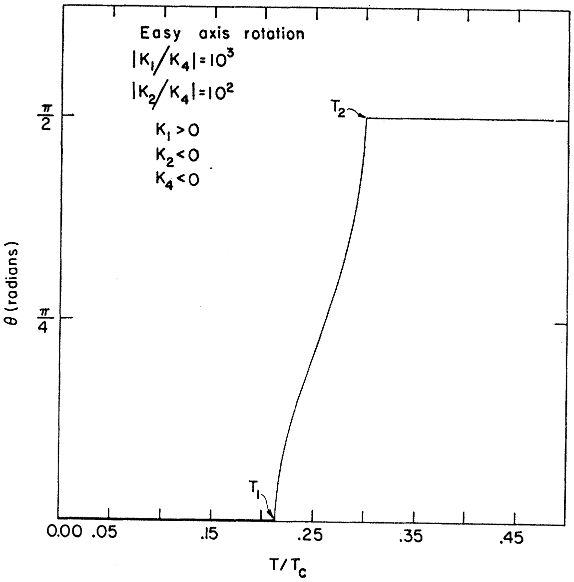

FIG. 3. Temperature dependence of the angle θ between the easy axis and the z axis, for the case of spin rotation ($A_4>0$, $K_4<0$). The temperatures T_1 and T_2 denote the end-point temperatures for the easy-axis rotation process, respectively. We have chosen the particular values indicated in the figure for K_1, K_2, and K_4.

In Figs. 5 and 6 we present contours of K_1/K_4 and K_2/K_4 for given T_1 and T_2. The values of K_1/K_4 and K_2/K_4 corresponding to easy-axis rotation lie in the region of the T_1-T_2 plane given by $T_2>T_1$. The line $T_1=T_2$ corresponds to $K_1/K_4=-\infty$ in Fig. 5, and to $K_2/K_4=\infty$ in Fig. 6.

As we mentioned at the beginning of this section, our numerical calculations have been specialized to the classical molecular-field approximation. However, we may also utilize Figs. 5 and 6 to evaluate K_1/K_4 and K_2/K_4 (for infinite spin) independent of the validity of the classical molecular-field approximation,[40,48] pro-

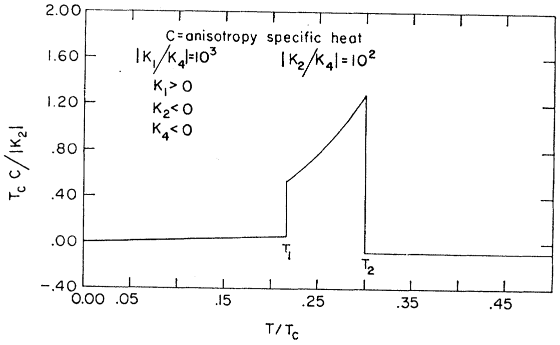

FIG. 4. Temperature dependence of the anisotropy contribution to the specific heat, in the case where spin rotation takes place ($A_4>0$, $K_4<0$). The quantities T_1 and T_2 denote the end-point temperatures for the easy-axis rotation process, respectively. We have chosen the particular values indicated in the figure for K_1, K_2, and K_4.

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[47] It is worth noting that the presence of the dipolar term is essential for the complete rotation from $\theta=0$ to $\frac{1}{2}\pi$ to take place. If there were no dipolar term, then putting $K_1=0$ in (23) and noting that $\hat{I}_{9/2}$ and $\hat{I}_{5/2}$ are positive-definite functions, it is easy to check that only a partial-rotation process can occur.

[48] H. B. Callen and S. Shtrikman, Solid State Commun. 2, 5 (1965).

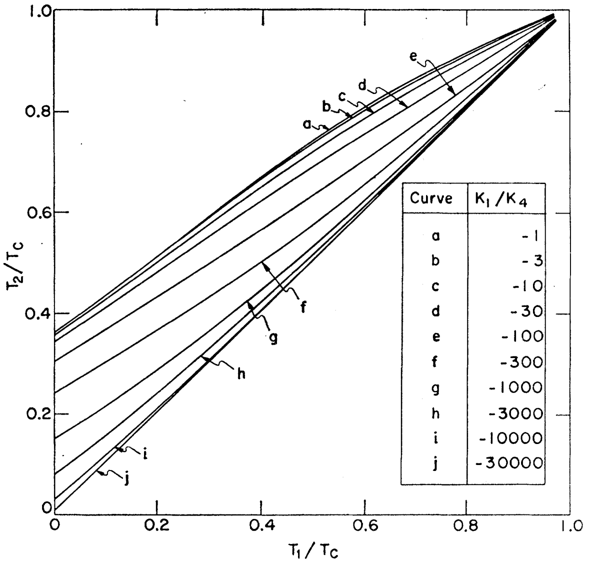

FIG. 5. Contours of K_1/K_4 as a function of T_1 and T_2. The temperatures T_1 and T_2 denote the end-point temperatures for the easy-axis rotation, respectively.

vided that we use the following prescription to obtain "proper" values for T_1 and T_2.

Let us assume the experimental relative magnetization $M^*(T_1)/M^*(0)$ at temperature T_1 has been measured. Using tables of the Langevin function L, we can obtain a corresponding x^* given by

$$M^*(T_1)/M^*(0)=L(x^*).$$

The proper value of T_1, which we denote by T_1^*, is then given by

$$3\bar{S}(T_1^*)T_c/T_1^*=x^*,$$

where $\bar{S}\equiv|\langle\mathbf{S}\rangle|$ is the classical molecular-field relative magnetization as a function of temperature. The function $\bar{S}(T)$ is available in the literature.[49] We plot $[\bar{S}(T)]^2$ in Fig. 2. A similar procedure gives T_2^*.

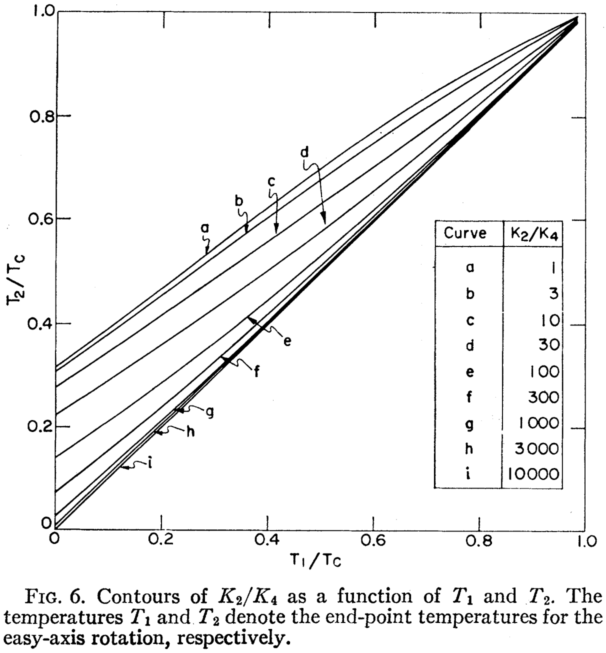

FIG. 6. Contours of K_2/K_4 as a function of T_1 and T_2. The temperatures T_1 and T_2 denote the end-point temperatures for the easy-axis rotation, respectively.

Finally, we note that the calculations of this section can be extended to the case of finite spin, provided appropriate account of quantum effects is taken in evaluating the thermal averages $\langle Y_l^0\rangle$. Figure 2 of Ref. 40 allows the importance of quantum effects to be estimated.

III. DISCUSSION

Our model Hamiltonian embodies the possibility of two distinct types of easy-axis-reorientation process. In practice, however, it is not easy to distinguish between the spin-jump and spin-rotation modes described in Sec. II A. The experimental difficulties arise from the extreme sensitivity of the easy-axis reorientation to slight deviations from ideal crystal structure. Thus, for example, Hagedorn *et al.*,[14,15] have presented striking evidence for the effect of slight crystalline inhomogeneities on microwave-resonance experiments in the spin-reorientation region of $TmFeO_3$. A further indication of the difficulties facing the investigators is given by the vastly differing temperature widths[25,27,50] for the Morin transition obtained in various studies of hematite. Similar, though less extreme, variations occur in the orthoferrites.[18]

The above experimental difficulties have complicated the clarification of the nature of the Morin transition. If our model is applicable and if the transition is of first order, then hysteresis effects should be present. This has not been observed. On the other hand, recent careful measurements[51] indicate that the order parameter $\theta(T)$ jumps discontinuously in the reorientation region. Thus, the situation as regards the Morin transition is unclear at present.

In the rare-earth orthoferrites, the experimental evidence available concerning the easy-axis reorientation tends to support the rotational mode. Microwave[13–15] and susceptibility[12] measurements at the extremes of the transition region are consistent with a second-order phase transition. The measurements of Gorodetsky and Levinson[18] also support a rotational mode in $SmFeO_3$. Moreover, a recent Mössbauer study[52] of $ErFeO_3$ provides clear-cut evidence for easy-axis rotation in this orthoferrite.

With regard to the experimental difficulties, it is encouraging to note that the extreme sensitivity of the spin reorientation to minor variations in crystalline perfection is readily understandable in terms of our

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[49] M. I. Darby, Brit. J. Appl. Phys. **18**, 1415 (1967).

[50] L. Neel and R. Pauthenet, Compt. Rend. Acad. Sci. Paris **234**, 2172 (1952).

[51] P. J. Flanders, J. Appl. Phys. **40**, 1247 (1969).

[52] G. Gorodetsky, L. M. Levinson, S. Shtrikman, D. Treves, and B. Wanklyn, this issue, Phys. Rev. **187**, 637 (1969).

model. The transition temperature is essentially determined by the mutual cancellation of the fine structure and the dipolar contributions to the second-order anisotropy in the spin Hamiltonian. Thus, the transition temperature will be sensitive to slight variations in either term. In particular, the dipolar term will be sensitive to strain inhomogeneity.

We have shown that our model Hamiltonian predicts the usual Landau expansion of the free energy in terms of the relevant order parameter. This observation bears comment in the light of the well-known inconsistencies[30,31] inherent in the Landau theory. The major approximation made in Sec. II A has been the neglect of terms of order $(K/J)^2$. If our perturbation series for F in powers of K/J converges [see Eq. (5)], our treatment becomes exact as $K \to 0$. In the following paragraph we shall attempt to estimate the temperature interval for given K, for which our treatment is valid.

As is well known,[30] the Landau theory is not valid if the correlation function $g(\mathbf{r}-\mathbf{r}') = \langle[\psi(\mathbf{r})-\langle\psi\rangle][\psi(\mathbf{r}')-\langle\psi\rangle]\rangle$ for the order parameter $\psi(\mathbf{r})$ is comparable to or larger than $\langle\psi\rangle^2$ for distances $|\mathbf{r}-\mathbf{r}'|>\xi$, where $\xi(T)$ is the coherence length. We shall attempt to estimate $\xi_r(T)$ for our model, where the subscript r refers to the rotational transition.

The free-energy coupling adjacent spins is proportional to the exchange energy. We adopt a classical continuum model for our system and consider the case of nearest-neighbor interactions. It then follows that the increase in energy due to inhomogeneities in θ can be written as $D[\nabla\theta(r)\cdot\nabla\theta(r)]$, where $D=a^2\epsilon J_{nn}S^2$. Here a is the lattice parameter, J_{nn} is the nearest-neighbor exchange coupling, and ϵ, a factor of the order of 1, depends on the type of lattice.

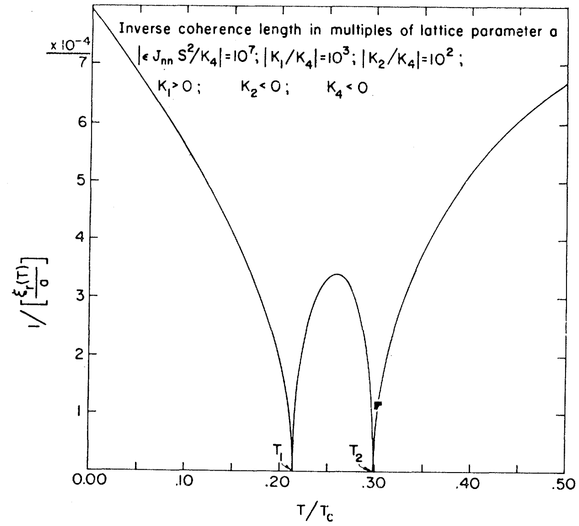

FIG. 7. Temperature dependence of the inverse correlation length $(\xi_r/a)^{-1}$. We have plotted $\xi_r(T)$ in units of the lattice parameter a. The symbols T_1 and T_2 denote the end-point temperatures for the easy-axis rotation, respectively.

The standard result[30] for the correlation length is

$$\xi_r(T) = (2D/\partial^2 f/\partial\theta^2)^{1/2}, \tag{26}$$

where $f(\theta)$ is given in (15) and represents the effect of the anisotropy energy. In Fig. 7 we plot $1/\xi_r$ for the indicated choice of $\epsilon J_{nn}S^2$, K_1, K_2, and K_4. It should be noted that even far from T_1 and T_2, ξ_r is a few hundred lattice parameters. This is essentially due to the large factor $(J_{nn}/K)^{1/2}$ which appears in (26) on substituting for D and $\partial^2 f/\partial\theta^2$. By comparison, far from the Curie temperature, ξ for the usual ferromagnetic-paramagnetic transition is a few angstroms.[30]

If, in the critical region,

$$\xi_r = \xi_{0r}(1-T/T_r)^{-1/2}, \tag{27}$$

(the subscript r refers to the rotational transition) and if ΔC_r is the specific-heat jump at T_r, the Landau theory is valid[30] for values $|T-T_r|/T_r$ satisfying

$$|T-T_r|/T_r > (1/32\pi^2)(k_B/\Delta C_r \xi_{0r}^3)^2. \tag{28}$$

Using the above values of J_{nn}, K_1, K_2, and K_4, we find from (24) and (26)–(28) that the Landau expansion will be valid for $|T-T_r|/T_r \gtrsim 10^{-8}$. For smaller values of $|T-T_r|/T_r$ our solution is possibly not valid. In this region it might be invalid to limit the expansion (5) to first order in K/J, though it is difficult (especially in the classical limit) to understand the origin of such a breakdown.

As $K \to 0$, the forces appropriate to the spin reorientation become infinitely long ranged, and the Landau theory is valid everywhere. In practice, since K/J is extremely small ($\simeq 10^{-4}$ for Fe^{3+}), any possible deviations from the classical critical exponents would be virtually undetectable. Experimental evidence on other displacive-type phase transitions[30,33,34,36] does, in fact, confirm the applicability of the classical Landau exponents.

In conclusion, we would like to mention that it should be possible to consider the easy-axis reorientation using a spin-wave approximation. Indeed, some easy-axis reorientations in the orthoferrites[3] occur at rather low temperatures, where the spin-wave formalism would be appropriate. The thermodynamic properties of displacive phase transitions are related to instabilities arising in collective modes of the system, and thus we would expect the frequency of a $k=0$ magnon mode to approach zero at the easy-axis transition temperature. In a similar manner the occurrence of ferroelectricity in perovskite-type crystals such as $\mathrm{BaTiO_3}$ has been correlated[53] with the existence of a zero-wave-number optical-phonon mode having an anomalously low frequency.

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[53] W. Cochran, Advan. Phys. 9, 387 (1960).