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Sublattice Magnetization of $FeBO_3$ Single Crystals by Mössbauer Effect

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Mössbauer-effect (ME) measurements of the hyperfine interaction of the iron nuclei in single crystals of $FeBO_3$ have been used to study the temperature dependence of the sublattice magnetization. The results are found to be consistent with previously published nuclear-magnetic-resonance results and agree quantitatively with simple noninteracting-spin-wave theory for $T \leq T_N/3$, where T_N is the Néel temperature. The exchange integral calculated from fitting ME data to spin-wave theory, $J = 27.3 \pm 0.5$ °K, is in very good agreement with that calculated from the Rushbrooke and Wood T_N relation, indicating that $FeBO_3$ is very dominantly a nearest-neighbor-exchange system. We estimate that the upper spin-wave branch (out plane) has a gap of about 23 °K, which is primarily due to dipolar anisotropy but partly to the Dzyaloshinskii–Moriya field.

I. INTRODUCTION

Recently, there has been a great deal of interest in iron borate, $FeBO_3$, a transparent, green, weak ferromagnet, due to its possible application for magneto-optical devices.[1] The successful growth of single crystals of $FeBO_3$ has led to studies of crystal structure,[2] magnetic properties,[3,4] optical properties,[4] ferromagnetic resonance,[5] magnetic structure,[6] nuclear magnetic resonance,[7–9] acoustic resonance,[10] and Mössbauer effect.[11]

$FeBO_3$ was first prepared by Bernal *et al.*,[2] who found it to have the rhombohedral calcite structure, space group $R\bar{3}c$, with lattice constants $a = 5.496$ Å and $\alpha = 49°\ 38'$ (see Fig. 1). The compound is a typical weak ferromagnet[3] with a spontaneous magnetization[4] $4\pi M_s$ at 300 °K of 115 G and a Néel temperature $T_N = 348.35$ °K.[11]

Neutron diffraction[6] shows that the spins are perpendicular to the rhombohedral axis, in agreement with Mössbauer studies and symmetry considerations for the calcite structure. The Fe^{3+} magnetic moment at 77 °K is $4.7\mu_B$. The threefold [111] axis is the hard axis and the (111) plane is the easy plane of magnetization. The hard-axis anisotropy field (made up of dipolar and Dzyaloshinskii contributions) is 62 500 Oe at 300 °K, while the in-plane anisotropy field is less than 1 Oe, as measured by ferromagnetic resonance.[1,10] All of the iron spins are in the (111) plane with a small canting away from antiparallel configuration. Symmetry considerations show that the canting must also be in the easy plane.

The ferric ions in $FeBO_3$ are arranged essentially in two sublattices which are strongly coupled antiferromagnetically. The sublattice moments are slightly canted with respect to the antiferromagnetic axis so that a small net ferromagnetic moment results in a direction perpendicular to this axis. The angle between sublattice magnetization and the antiferromagnetic axis at zero external field is the canting angle. Petrov *et al.*,[8] from their ferromagnetic-moment and sublattice-moment measurements, deduced a canting angle $\varphi = 0.016$ rad, which is constant over a very large temperature range. This result indicates that antisymmetric exchange[12] is responsible for the canting and the weak ferromagnetism. The same conclusion has been obtained for other weak ferromagnets such as the orthoferrites.[13]

The sublattice magnetization is measured by Petrov *et al.*[7,8] in terms of the hyperfine field (hf) at the Fe^{57} nucleus from nuclear-magnetic-resonance (NMR) measurements. The measurements

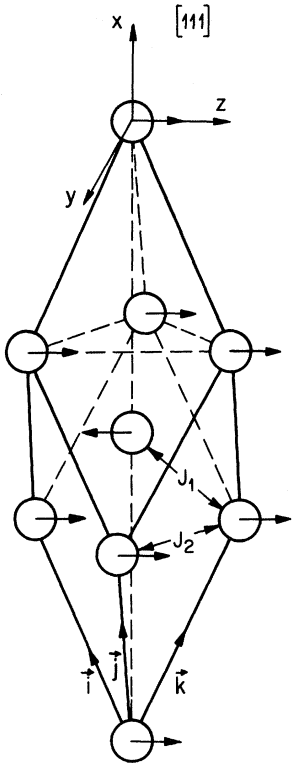

FIG. 1. Crystal structure of $FeBO_3$ showing rhombohedral sublattice cell with basis vectors $\vec{i}$, $\vec{j}$, and $\vec{k}$ and orthogonal axes x, y, and z, as used in the text.

were first claimed to follow a T^2 law, $f(T)/f(0) = 1 - A(T/T_N)^2$, with $A = 0.315$ over a range of temperature $0 < T < 100\,^\circ\mathrm{K}$.[7] Later results[8] were fitted to different quadratic laws in two separate temperature ranges: $0 < T < 40\,^\circ\mathrm{K}$, $A = 0.15$, and $70 < T < 100\,^\circ\mathrm{K}$, $A = 0.27$ to 0.32.[8,14] However, no quantitative spin-wave calculations were performed to test the theoretical soundness of such fitting procedures and we shall show in this paper that they are spurious.

Mössbauer-effect (ME) measurements of the hf interaction in single crystals of $FeBO_3$ are the subject of the experimental part of this paper. The critical behavior of the sublattice magnetization near the Néel temperature T_N has already been reported.[11] The temperature dependence of sublattice magnetization is measured in terms of the ME hf field to compare the results with NMR and with the computed results of a quantitative spin-wave theory. In the next section we discuss the experimental details and present and analyze the results of our measurements. In Sec. III, we develop the simple spin-wave theory for the temperature dependence of sublattice magnetization and compute numerical results which are compared, in turn, with the ME and NMR experimental measurements. The exchange interaction calculated from the fit of theory with experiment is compared with that resulting from the Néel temperature, using the series expansion formalism. We demonstrate that $FeBO_3$ is quite accurately a nearest-neighbor-only-exchange system. Finally, a semi-quantitative estimate is made of the spin-wave gap, and the range of validity of a true T^2 law for sublattice magnetization is discussed in detail.

II. EXPERIMENTAL PROCEDURE AND RESULTS

High-quality single crystals of $FeBO_3$, prepared by a flux method[4,11] by Nielsen, have been used in the ME measurements. The crystals obtained from several runs have usually been (111) platelets with maximum planar dimensions of 4 mm and thickness of ~ 0.05 mm.

A Mössbauer absorber was made by gluing the crystal platelets on a Vespel plastic holder with a soft pressure-sensitive adhesive. The ME spectra were taken between 4.2 and 300 °K. Temperatures of 4.2, 20.3, and 77.3 °K were obtained with sample immersed in a cryogenic liquid. Other temperatures were obtained with the sample mounted in the Dewar vacuum space on a "cold finger" connected to the liquid reservoir by a variable thermal resistance. In the latter case, temperature was measured by a platinum resistance thermometer[15] mounted near the sample. A germanium resistance thermometer[16] was a sensor up to 100 °K for an automatic temperature controller which controlled the current to a heater on the cold finger. Above 100 °K, the platinum resistance thermometer was used as the sensor. Fluctuations in the temperature of the platinum resistor during runs of 24 h were always under 0.05 °K. We estimate a gradient of 0.2 °K across the sample and that the platinum resistor provided a measure of the average sample temperature accurate to ±0.5 °K.

The ME absorption spectra were obtained in a standard transmission geometry using a conventional constant-acceleration spectrometer.[17] The source used was ^{57}Co in Pd. The ground-state splitting of the Fe foil, as recently measured by Violet and Pipkorn,[18] was used for calibration.

The ME spectra displayed a well-resolved six-line[19] pattern in agreement with the existence of only one type of crystallographic site for the ferric ions. A characteristic ME spectrum is shown in Fig. 2. The relative intensities of the ME spectral lines are close to 3:4:1:1:4:3, indicating that the propagation direction of the γ rays is perpendicular to the plane of the internal fields. This shows that the two nearly antiferromagnetic sublattice moments lie within the easy (111) plane of the platelets, in agreement with neutron-diffraction results and symmetry considerations for a canted antiferromagnet with this structure.[20]

The spectra were analyzed by fitting to a sum of six Lorentzian curves of independent position, width, and dip. From these, two independent values for the ground-state splitting were obtained.

These are, in general, consistent to four parts in 10^4, which is about the uncertainty of the line positions indicated by the least-squares procedure. The hf field acting on the ^{57}Fe nucleus was obtained from the average value of the ground-state splittings. The results are given in Table I. The hf-field values are in very good agreement with those measured by the NMR technique.[7-9] This value of hf field was then introduced with the quadrupole coupling and the known g factors into a computer program which simulated the ME spectrum in each case. Best fits were obtained using an almost constant quadrupole coupling of 0.38 mm/sec.

TABLE I. Mössbauer measurements of hf field H_{in} in $FeBO_3$ at various temperatures.

T (°K)	H_{in} (kOe)[a]
4.2	555.0
20.3	554.9
29.88	554.7
44.77	553.0
54.87	551.4
65.12	549.6
74.94	548.2
77.30	548.0
84.22	545.4
94.45	541.9
105.48	537.7
125.08	527.7
149.94	513.1
174.99	494.9
200.00	473.5
225.15	448.3
248.96	419.4
271.11	388.5
297.7	332.2

[a]Estimated uncertainty is ±1.5 kOe.

III. DISCUSSION OF EXPERIMENTAL RESULTS

We assume that the hf field at the Fe^{3+} nucleus as a function of temperature is proportional to the sublattice magnetization.[21] The relatively large range in temperature covered in this work and its accuracy make it possible to compare the experimental results with spin-wave theory and to get some indication of the range of validity of the theory.

A. Spin-Wave Theory

We have constructed a simple noninteracting-spin-wave theory for the $FeBO_3$ system and computed from it the deviation (as a function of temperature) of sublattice magnetization from its value at absolute zero. At low temperatures, this deviation depends significantly on the magnitude and symmetry of anisotropy. For $FeBO_3$, the dominant anisotropy is that which constrains the spins to the (111) plane. This we term the "out-of-plane" anisotropy and it is comprised for the most part of dipolar and Dzyaloshinskii components. The "in-plane" anisotropy pins down the spins to certain preferred orientations within the (111) planes. In iron borate it is very small indeed[1,5,10] and can safely be set equal to zero for all statistical calculations of sublattice magnetization above 1 °K. By this we mean that 1 °K is already large compared with the spin-wave gap for the in-plane magnon mode.

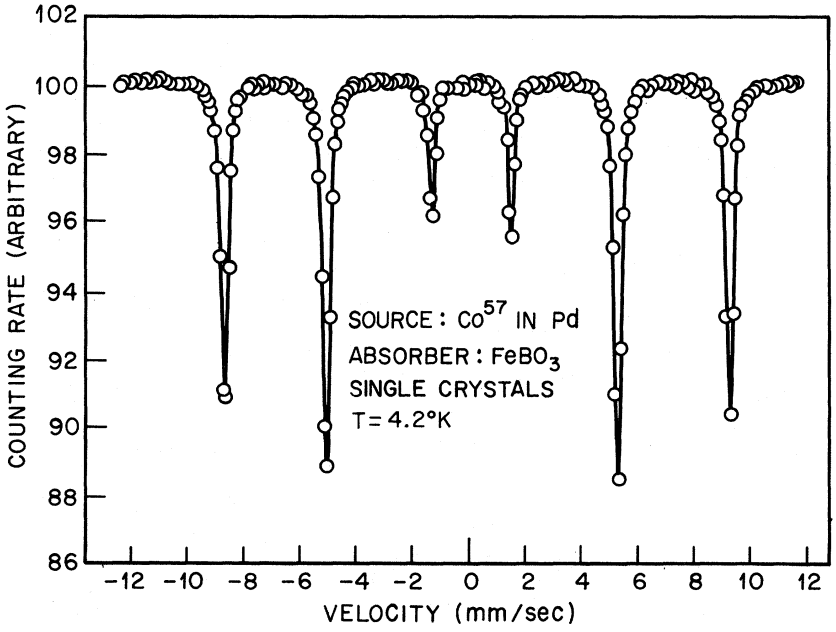

FIG. 2. Typical Mössbauer absorption spectra of $FeBO_3$ single crystals. The [111] direction of the crystal is parallel to the direction of the γ rays.

We assume for the calculation of sublattice magnetization that canting effects are negligible and that exchange is dominated by nearest-neighbor (nn) contributions, as is the case in isomorphic $FeCO_3$.[22] Both assumptions will be fully justified later in the paper. Thus, we write a spin Hamiltonian for $FeBO_3$ in the form

$$\mathcal{H}=\sum_{nn} J\vec{S}_i\cdot\vec{S}_j+\sum_n D_1 S_{ix}^2+\sum_n D_2 S_{iy}^2 , \tag{1}$$

where $\sum_{nn}$ runs over all pairs of nn, $\sum_n$ runs over all spins in the lattice, z is the direction of ordered sublattice spin, x is the [111] direction, y is chosen to make up a right-handed orthogonal set, and D_1 and D_2 are "out-of-plane" and "in-plane" anisotropy parameters, respectively. Thus, we have set $J_1=J$, $J_2=0$ from Fig. 1 and have retained an in-plane anisotropy for completeness of the formalism. Anisotropy has been assumed to be of single-ion form, which is, in fact, incorrect for $FeBO_3$. This approximation amounts to a neglect of wave-vector dependence of anisotropy and is more than adequate in the present context since the statistical calculations for $T\ll T_N$ are dominated by the contributions of long-wavelength magnons.

The average sublattice spin per magnetic site can be written, following Lines and Jones,[23] as $\overline{S}=S+\frac{1}{2}-\frac{1}{2}x$, where

$$x=\left\langle\frac{\frac{1}{2}(\beta_1+\beta_2)}{[(\beta_1+\gamma_K)(\beta_2-\gamma_K)]^{1/2}}\times\coth\frac{S[(\beta_1+\gamma_K)(\beta_2-\gamma_K)]^{1/2}}{2kT}\right\rangle_K , \tag{2}$$

and

$$\beta_1=zJ+2D_1 , \tag{3a}$$

$$\beta_2=zJ+2D_2 , \tag{3b}$$

$$\gamma_K=\sum_{nn} J e^{i\vec{K}\cdot(\vec{r}-\vec{r}_0)} , \tag{3c}$$

where $\langle\cdots\rangle_K$ is an average over the first Brillouin zone of the reciprocal sublattice (K space), $z=6$ is the number of nearest neighbors, and the sum $\sum_{nn}$ in (3c) runs over the z nearest neighbors r of r_0. The two nondegenerate spin-wave branches are

$$\hbar\omega_{1K}=S[(\beta_1+\gamma_K)(\beta_2-\gamma_K)]^{1/2} , \tag{4a}$$

$$\hbar\omega_{2K}=S[(\beta_1-\gamma_K)(\beta_2+\gamma_K)]^{1/2} , \tag{4b}$$

where ω_{1K} and ω_{2K} are the respective spin-wave frequencies with wave vector $\vec{K}$. In the long-wavelength limit $K\to 0$ we find the two antiferromagnetic-resonance modes (afmr)

$$\hbar\omega_1=S[(12J+2D_1)2D_2]^{1/2} , \tag{5a}$$

$$\hbar\omega_2=S[(12J+2D_2)2D_1]^{1/2} . \tag{5b}$$

Putting $D_2=0$, as appropriate for our calculations, the afmr modes are

$$\hbar\omega_1=0, \tag{6a}$$

$$\hbar\omega_2=S(24JD_1)^{1/2}=g\mu_B(2H_EH_A)^{1/2} , \tag{6b}$$

where

$$g\mu_BH_E=6JS \tag{7}$$

defines an "exchange field" H_E, and

$$g\mu_BH_A=2D_1S \tag{8}$$

defines an out-of-plane anisotropy field H_A.

Defining dimensionless quantities $D=H_A/H_E=D_1/3J$ and $\gamma_K'=\gamma_K/6J$, and putting $D_2=0$, Eq. (2) reduces to

$$x=\left\langle\frac{1+\frac{1}{2}D}{[(1+D+\gamma_K')(1-\gamma_K')]^{1/2}}\times\coth\left(\frac{3JS}{kT}[(1+D+\gamma_K')(1-\gamma_K')]^{1/2}\right)\right\rangle_K . \tag{9}$$

Equation (9) now leads directly to $\overline{S}$ as a function of kT/J and D, once the relevant form γ_K' is calculated for the $FeBO_3$ structure. We shall find that D is small in the context of its effects on sublattice magnetization, although its presence is readily deduced from the fit to NMR data. In spite of this, it will not prove possible to obtain a very precise value for D from the following statistical fit; a more accurate assessment of out-of-plane anisotropy can be obtained from an analysis of existing related data.

B. Evaluation of Magnetic Parameters

The out-of-plane anisotropy field H_A for $MnCO_3$ has been calculated by Kotyuzhanskii,[24] who assumed it to be of dipolar origin. His theoretical value of 2.9 kOe agrees well with the experimental value of 3.0 kOe obtained from afmr measurements by Richards.[25] This value must also be close to the dipolar contribution to H_A in $FeBO_3$, since the systems are crystallographically and magnetically isomorphic, have the same spin quantum number $S=\frac{5}{2}$, and possess similar unit-cell dimensions (for $MnCO_3$, $a=5.84$ Å, $\alpha=47°20'$).[26] We shall therefore assume a value $H_A\sim 3$ kOe as appropriate for $FeBO_3$.

Since our computed sublattice magnetization curves are quite insensitive to moderate variations in H_A about this value, we are not immediately concerned with our lack of precise knowledge of the latter. Indeed, in Sec. III D we shall also assess the role played by the Dzyaloshinskii–Moriya field H_{DM} and sublattice canting on the afmr frequencies and spin-wave theory, and confirm the extent to which the crude assessment of anisotropy and neglect of canting in the basic theory are inconsequential for our

purposes.

The magnetic sublattice in $FeBO_3$ is a rhombohedron with unit basis vectors $\vec{i}$, $\vec{j}$, and $\vec{k}$, as shown in Fig. 1. Wave vector $\vec{K}$ is now

$$\vec{K} = (2\pi/L)(n_1\vec{b}_1 + n_2\vec{b}_2 + n_3\vec{b}_3), \tag{10}$$

where $\vec{b}_i$ ($i = 1, 2, 3$) is the reciprocal triad of $\vec{i}$, $\vec{j}$, $\vec{k}$, integers n_i run between $-\frac{1}{2}L$ and $\frac{1}{2}L$, and L^3 is the macroscopic crystal dimension measured in lattice spacings along the basis vectors. Using Eq. (3c) and the definition $\gamma'_K = \gamma_K/6J$, we easily establish the form

$$\gamma'_K = \tfrac{1}{3}[\cos\tfrac{1}{2}(K_1 - K_2 - K_3) + \cos\tfrac{1}{2}(K_2 - K_3 - K_1) + \cos\tfrac{1}{2}(K_3 - K_1 - K_2)], \tag{11}$$

where $K_i = 2\pi n_i/L$, and $-\pi < K_i < \pi$ covers the first Brillouin zone.

Jacobs's work[22] on $FeCO_3$ suggests that nearest-neighbor-exchange terms are dominant in the $FeBO_3$ structure. This finding will be fully confirmed by the present work. For such a case, the magnetic lattice in $FeBO_3$ becomes topologically equivalent to the simple cubic lattice. Using the Rushbrooke-Wood[27] equation for the simple cubic Néel temperature (as obtained from extrapolation of the high-temperature staggered susceptibility series) in the form

$$kT_N = \tfrac{5}{192}\, J(z-1)[11\,S(S+1) - 1]\{1 + 0.63[zS(S+1)]^{-1}\}, \tag{12}$$

and putting $z = 6$, $S = \frac{5}{2}$, we find

$$T_N = 12.55J/k. \tag{13}$$

For $FeBO_3$ we have from ME measurements[11] $T_N = 348.35\,^\circ\mathrm{K}$, from which, using (13), we assess $J \approx 28\,^\circ\mathrm{K}$. Using this value as at least semiquantitatively valid for $FeBO_3$, and combining the above value $H_A \sim 3$ kOe and $g = 2$, $S = \frac{5}{2}$, we find for the dimensionless anisotropy parameter D of Eq. (9) a value of ~ 0.0010.

C. Comparison of Spin-Wave Theory and Experiment

We have computed $\bar{S}$ as a function of kT/J for $D = 0$, 0.001, and 0.003 from $\bar{S} = S + \frac{1}{2} - \frac{1}{2}x$ and from Eq. (9), the numerical calculation of the average $\langle \cdots \rangle_K$ being programmed for our GE-600 computer. Resulting curves have been fitted to ME and NMR[8] data.

For NMR (Fig. 3) the totally isotropic curve $D = 0$ is not in quantitative agreement with experiment for any value of J. A small out-of-plane anisotropy improves the fit and good quantitative agreement is obtained for $D = 0.001$, $J = 27.5 \pm 1.0\,^\circ\mathrm{K}$ (see the solid curve in Fig. 3). However, the value $D = 0.001$ is not uniquely determined by quality of fit and an equally good agreement can be obtained for $J = 26.5\,^\circ\mathrm{K}$ ($D = 0.003$); i.e., the fit is rather insensitive to $D > 0.001$. We note in particular from Fig. 3 that the theoretical curve corresponds to a quadratic deviation only for $T \lesssim 5\,^\circ\mathrm{K}$ (which is $T/T_N \lesssim 0.02$). The limiting low-temperature form of the deviation is

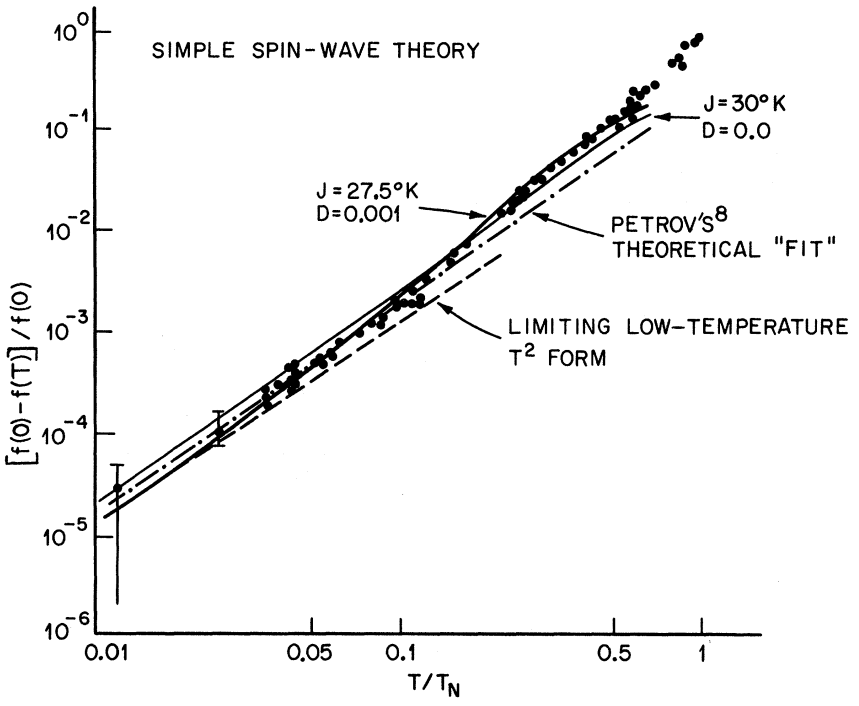

FIG. 3. Fractional decrease of NMR ^{57}Fe resonance frequency $[f(0) - f(T)]/f(0)$ in $FeBO_3$ vs reduced temperature T/T_N (from Petrov *et al.*[8]). Also shown are best-fit isotropic ($D = H_A/H_E = 0$) and anisotropic ($D = 0.001$) spin-wave curves and the limiting low-temperature asymptote.

$$\bar{S}(T)/\bar{S}(0) = 1 - 0.00385(kT/J)^2 , \qquad (14)$$

a result which can be obtained analytically and agrees with the direct numerical computation. This corresponds to $f(T)/f(0) = 1 - A(T/T_N)^2$ with $A \approx 0.12$, and is shown as a dashed line in Fig. 3. The "fit" obtained by Petrov *et al.*[8] with $A = 0.15$ is shown dot dashed in Fig. 3. Their claim that it represents the low-temperature behavior to $T \sim 35\,^\circ$K is clearly false, and results from large scatter of the data. In addition, the second T^2 region of Ref. 8, Eq. (3) (claimed by Petrov *et al.*[8] to occur for a temperature range 70–100 °K in $FeBO_3$), clearly does not exist.

For Mössbauer data (Fig. 4), the experimental accuracy at low temperatures is not sufficient to establish the existence of nonzero anisotropy, and equally good theoretical (spin-wave) fits to the data can be obtained for $D = 0$ and $D = 0.001$. The $D = 0.001$ curve, normalized at $T = 0$ to a hyperfine field of 555 kOe, is shown in Fig. 4 for a value of exchange $J = 27.8\,^\circ$K, and provides a quantitative fit to the data to $T = 110\,^\circ$K (or $T/T_N \approx \frac{1}{3}$). About the same range of validity for simple spin-wave theory was found by Lines[28] for the case of MnF_2. It is known that the region of quantitative fit to spin-wave theory can be (in general) extended to much higher temperatures by including spin-wave interactions to "renormalize" the energy spectrum of the excitations.[29,30]

We have made no effort to go beyond a simple "noninteracting" spin-wave approximation in the detailed theory, but since, in the lowest order at low temperatures, the effect of magnon interactions[31] is just to scale J by a factor $1 + c/2zS$, where c is lattice dependent and equal to 0.582 for the simple cubic topology, we are easily able to include interaction effects to this order. We shall therefore refer to "Oguchi-corrected" exchange J_c,[30] related to simple spin wave J for our case by $J = 1.019 J_c$, as giving the most precise estimate for exchange obtainable by using the present theory. Thus, our final estimates for exchange from ME and NMR data are (with $D = 0.001$)

$$J(\text{Oguchi corrected}) = 27.0 \pm 1.0\,^\circ\text{K from NMR}$$

$$= 27.3 \pm 0.5\,^\circ\text{K from ME.}$$

These results are in good agreement with the value of $J = 27.6\,^\circ$K obtained by Meixner *et al.*[32] from two-magnon Raman scattering.

It is now necessary to discuss the neglect of next-nearest-neighbor exchange J_2 (Fig. 1) in the computations so far. It is true that the structure and earlier results on isomorphic $FeCO_3$ suggest that J_2 is small, but we can argue as follows: Since anisotropy is small in $FeBO_3$ ($D \ll 1$), the magnon dispersion curves dip to very low energies for long-wavelength excitations. These represent the relative motion of quasirigid spin sublattices against each other and therefore do not involve intrasublattice exchange. Since J_2 is an intrasublattice exchange, it is therefore not involved in long-wavelength excitations. But it is precisely the latter excitations which, by virtue of their low energies, dominate the statistical calculations at low temperatures. It follows that our spin-wave estimates for J_1 would still be closely valid even

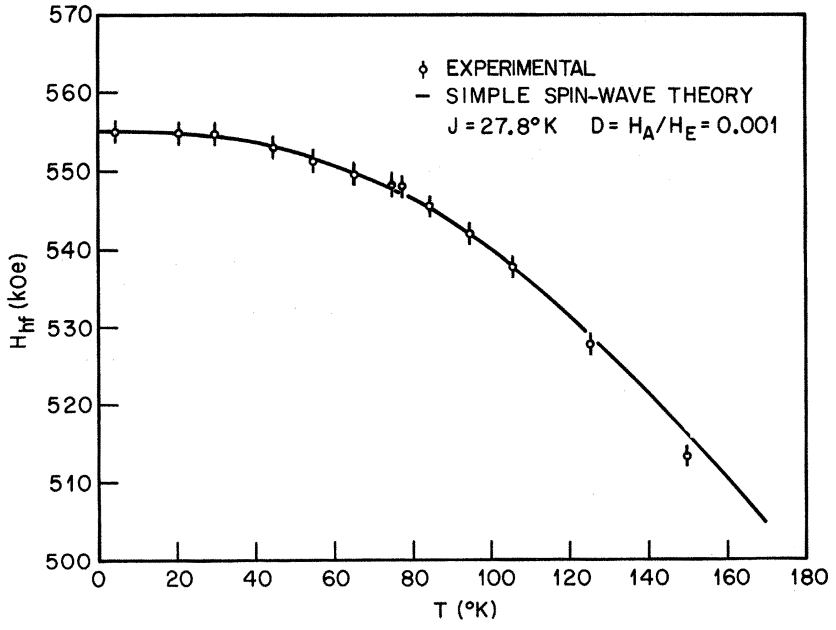

FIG. 4. Mössbauer hyperfine field H_{hf} at the ^{57}Fe nuclei in $FeBO_3$ as a function of temperature. The solid curve is computed from simple spin-wave theory.

if J_2 were markedly nonzero.

On the other hand, a nonzero J_2 would certainly influence the Néel temperature in lowest order, with T_N varying closely as $J_1 - J_2$ (i.e., as $z_1J_1 - z_2J_2$, $z_1 = z_2 = 6$). Putting $J_1 = J = 27.3 \pm 0.5$ °K in the Rushbrooke–Woods formula (13), we find a value $T_N = 343 \pm 6$ °K as being appropriate for $FeBO_3$, if $J_2 = 0$. Since experimentally $T_N = 348.35$ °K, we conclude that J_2 is indeed negligible and that iron borate is a good example of a nearest-neighbor-only magnetic system.

Finally, to demonstrate the existence of real and/or spurious quadratic-law behavior of spin deviation, we have plotted $[\bar{S}(0) - \bar{S}(T)]^{1/2}$ against temperature as computed from the simple spin-wave theory of this paper. Curves for $D = 0$, 0.001, and 0.01 are shown in Fig. 5. The limiting low-temperature behavior can be calculated analytically,[31] and in Fig. 5 is shown as one or the other of two (dashed) straight lines through the origin (corresponding to isotropic or anisotropic behavior) with relative slopes in the ratio $1:\sqrt{2}$. The approach of the computed curves to the limiting form as $T \to 0$ is clearly seen in Fig. 5 and a second "quasiquadratic" region is noted for all curves when $kT/J \sim 6$ to 8. This second region, however, has no simple physical interpretation and bears no simple relationship to the low-temperature limiting behavior.

D. Evaluation of Spin-Wave Energy Gap

The justification for the neglect of J_2 in the spin-wave theory has been provided above. It remains to discuss the neglect of canting. The correct long-wavelength spin-wave (afmr) frequencies for the case of a Dzyaloshinskii–Moriya canted antiferromagnet have been given by Pincus.[33] In the absence of an applied field the low- and high-frequency modes are

$$\hbar\omega_1 = g\mu_B(2H_A'H_E)^{1/2} \quad \text{(in plane)}, \tag{15a}$$

$$\hbar\omega_2 = g\mu_B(2H_AH_E + H_{DM}^2)^{1/2} \quad \text{(out of plane)}, \tag{15b}$$

where H_E is the exchange field of Eq. (7), H_A is an out-of-plane anisotropy field as in Eq. (8), H_A' is an in-plane anisotropy field, and H_{DM} is the Dzyaloshinskii–Moriya field defined by

$$g\mu_B H_{DM} = zD'S\,, \tag{16}$$

where the antisymmetric energy term is $\vec{D}' \cdot \vec{S}_i \times \vec{S}_j$ between the pair of spins $\vec{S}_i$ and $\vec{S}_j$.

In $FeBO_3$, the value of in-plane anisotropy is so small that we have put $\omega_1 = 0$ throughout. We have also neglected H_{DM} and must now assess the significance of this approximation in the context of the spin-wave calculations. We find in the literature two estimates for H_{DM}: $H_{DM} = 1.1 \times 10^5$ Oe by LeCraw *et al.*[5] and $H_{DM} = 0.8 \times 10^5$ Oe by Petrov *et al.*[8] We are now in a position to make a third estimate using the equation for canting angle φ, which is

$$H_{DM} = 2\varphi H_E\,. \tag{17}$$

From our estimate of $J = 27.3$ °K we find $H_E = 3.0 \times 10^6$ Oe. Combined with the measured value $\varphi = 0.0155$ rad,[34] we find $H_{DM} = 0.93 \times 10^5$ Oe. The estimates are clearly consistent to the extent that $H_{DM} \sim 1 \times 10^5$ Oe. Using this value with $H_E = 3 \times 10^6$ Oe and $H_A = 3 \times 10^3$ Oe,[24] we find, from (15b), a spin-wave gap $\hbar\omega_2/g\mu_B = 1.7 \times 10^5$ Oe. In temperature units this corresponds to an energy $\Delta = 23$ °K. Putting $H_{DM} = 0$ results in a diminished gap $\Delta = 18$ °K. These two estimates (with and without canting) correspond to D values of Eq. (9) of 0.0013 and

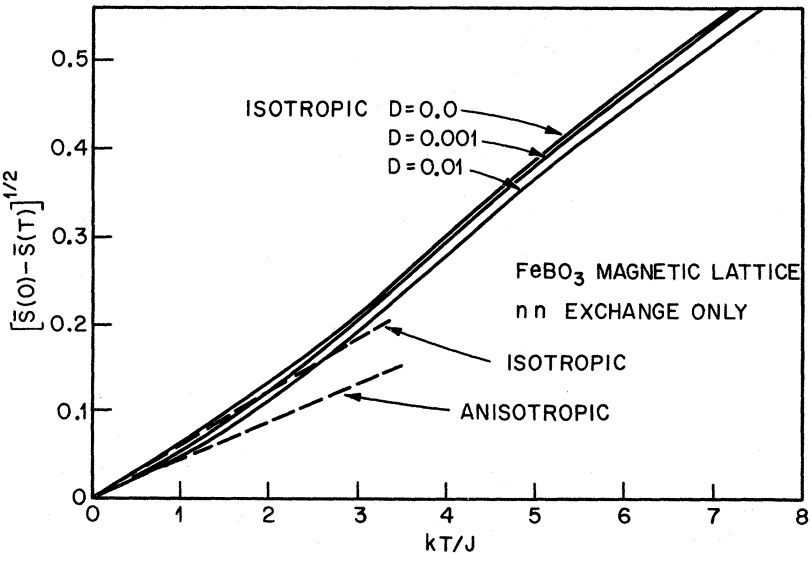

FIG. 5. Square root of spin deviation plotted against kT/J from the spin-wave theory, described in the text for anisotropy values $D = 0$, 0.001, and 0.01. Limiting low-temperature linear forms for the isotropic and (arbitrary $D \neq 0$) anisotropic situations are also shown (dashed curves, see text).

0.0010, respectively. Since the statistical calculations are dominated by the long-wavelength excitations, and a variation of D between 0.0010 and 0.0013 is completely inconsequential in interpreting the experimental sublattice magnetization data, we conclude that the neglect of canting is justified.

Our final estimate for spin-wave gap (viz., 23 °K) is in conflict with the conclusion of Petrov *et al.*[8] that $\Delta > 50$ °K. We believe that Petrov *et al.* are in error, since they appear to use an incorrect resonance formula.

IV. CONCLUSIONS

From the study of the sublattice magnetization in terms of hf field in $FeBO_3$ we have reached the following conclusions.

(a) The ME of ^{57}Fe in single crystals of (111) platelets from liquid-helium to room temperatures shows a characteristic six-line pattern, indicating that all the Fe^{3+} atoms are in equivalent sites, in agreement with the crystallographic structure of this material.

(b) The relative intensities (3:4:1:1:4:3) of ME spectra show that the two nearly antiferromagnetic sublattices lie within the easy plane, in agreement with symmetry considerations for weak ferromagnets with calcite structure and with neutron-diffraction results.

(c) The hf fields measured by ME are in good agreement with those measured by NMR.

(d) The hf field as a function of temperature is in quantitative agreement with simple spin-wave theory of sublattice magnetization up to $T \approx \frac{1}{3} T_N$.

(e) The exchange integral calculated from fitting ME data to spin-wave theory, $J = 27.3 \pm 0.5$ °K, is in very good agreement with that calculated from the Rushbrooke–Wood T_N relation, indicating that $FeBO_3$ is a nearest-neighbor-exchange system only.

(f) The quadratic law for low-temperature deviations of hf fields (or sublattice magnetization) from their zero-temperature values is strictly valid only below $T \sim 0.02\, T_N$ in $FeBO_3$.

(g) Canting, in-plane anisotropy, and next-nearest-neighbor-exchange effects are all negligible in the present context.

(h) The upper spin-wave branch (out plane) has a gap of order 23 °K which is primarily due to dipolar anisotropy and partly due to the Dzyaloshinskii–Moriya field.

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Stress-Induced Spin Flop in Cr_2O_3 †

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A complete phenomenological analysis of uniaxial stress-induced spin flop in Cr_2O_3 is given. The origins of the magnetic anisotropy and magnetoelastic interaction are discussed. The microscopic theory of the single-ion anisotropy and magnetoelastic interaction in ruby is reviewed, updated, and extended to Cr_2O_3.

I. INTRODUCTION

Recently, in a paper[1] to be referred to hereafter as I, optical data were presented and interpreted as strong evidence that uniaxial stress induces spin flop in the uniaxial antiferromagnet Cr_2O_3. The data consisted of the behavior of the $^4A_2 \rightarrow {}^2E$ optical-exciton absorption spectrum when either a magnetic field was applied along the c axis or uniaxial stress was applied along the a axis of a sample of Cr_2O_3. It was found that the changes induced in the spectrum as spin flop is forced by the applied magnetic field are nearly duplicated by the application of about 15 kbar of uniaxial stress. In a brief phenomenological discussion, based on a simple two-parameter magnetoelastic interaction, it was pointed out that very simple interrelations exist between the critical stresses required to induce spin flop and the magnetostrictive strains induced when spin flop is forced by a magnetic field. For Cr_2O_3 some of these strains have been measured by Dudko, Eremenko, and Semenenko[2] (DES). As pointed out in I, the interrelations predicted by the simple two-parameter magnetoelastic interaction discussed there are not satisfied by the data of DES and I. This discrepancy implies the need to consider the consequences of the most general magnetoelastic interaction allowed by crystal symmetry, and this is carried out in Sec. II of this paper. In I a brief discussion was also given of the origins of the magnetic anisotropy and magnetoelastic interaction in Cr_2O_3. Section III extends that discussion, and Sec. IV discusses the microscopic theory of the single-ion anisotropy and magnetoelastic interaction.

II. PHENOMENOLOGICAL ANALYSIS OF CRITICAL STRESSES AND MAGNETOELASTIC STRAINS

In this section phenomenological expressions for the critical stresses required to produce spin flop are obtained in terms of the elastic and magnetoelastic constants of the material. These expressions are then rewritten in terms of the magnetoelastic strains induced when spin flop is forced by an applied magnetic field, which provides the basis for a discussion of the relation of the results presented in I to the work of DES mentioned above. Such an analysis assumes small enough strains that magnetoelastic effects second order in the strains need not be considered and that Hook's law is obeyed. Although the analysis is straightforward, the portions dealing with stress-induced spin flop do not appear to have been given elsewhere before.[3]

In the absence of an applied stress, the magnetic anisotropy energy E_A can be written as $E_A = \sum_{ij} K_{ij} \times \alpha_i \alpha_j$, where K_{ij} is the anisotropy tensor and α_i is a direction cosine of the vector difference of the two sublattice magnetizations. The tensors K_{ij} and $\alpha_i \alpha_j$ are symmetric under interchange of i and j so it is convenient to employ the contracted indices notation of Voigt to write

$$E_A = \sum_j K_j \alpha_j . \tag{1}$$

The nonzero elements of K_j are restricted by the symmetry of the crystal. The presence of a strain ϵ_{ij} induces, through the magnetoelastic interaction, a further contribution to the anisotropy energy $\sum_{ijkl} \epsilon_{ij} F_{ijkl} \alpha_k \alpha_l$, as well as an elastic energy $\frac{1}{2} \sum_{ijkl} \epsilon_{ij} C_{ijkl} \epsilon_{kl}$, where F and C are the magnetoelastic and elastic tensors, respectively. These two energies may be written in Voigt's notation and added to (1) to give

$$E = \sum_j P_j \alpha_j + \frac{1}{2} \sum_{ij} \epsilon_i C_{ij} \epsilon_j , \tag{2}$$

where

$$P_j \equiv K_j + \sum_i \epsilon_i F_{ij} . \tag{3}$$

The nonzero elements of F_{ij} and C_{ij} are restricted