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Growth-Induced Magnetic Anisotropy of Epitaxial Films of Mixed Garnets Containing Europium

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We have measured the ferromagnetic resonance of three garnet films with the approximate composition $R_2EuFe_4O_{12}$, where R = Y or Lu and M = Al or Ga, grown by liquid-phase epitaxy on 001 and {111} gadolinium gallium garnet substrates. The anisotropy has a growth-induced component which anneals out at 1250 °C. Measurements from $0.04T_C$ to $0.92T_C$ on a {111} film with T_C=404 °K show that this component is proportional to the calculated uniaxial anisotropy of a Eu^{3+} ion in garnet, up to $0.75T_C$. This proportionality is predicted by the site-preference theory of the growth-induced anisotropy. The calculation is based on the Wolf–Van Vleck model of europium iron garnet, extended to include spin-correlation effects on the d sublattice in a heuristic manner. Anisotropic exchange is found to be the dominant source of the anisotropy. We find site preferences of about 20% in all three films. The calculation also accounts reasonably well for the temperature dependence of the magnetostriction of europium iron garnet.

I. INTRODUCTION

Mixed rare-earth–iron garnets grown from solution often show a noncubic magnetocrystalline anisotropy related to the growth direction. This anisotropy is believed to be due to the differential incorporation of rare-earth ions into sites which, while crystallographically equivalent, are inequivalent during the growth process.[1] It has proved difficult to make quantitative predictions of this effect. The size and form of the anisotropy depends not only on the site preferences but also on the anisotropy of the magnetic energy surface of the individual rare-earth ions.

Only Gd^{3+}, Eu^{3+}, and perhaps Yb^{3+} have ground levels in garnet which are sufficiently simple and well understood to permit a meaningful calculation of the anisotropy of the magnetic energy surface for a single rare-earth ion. In Gd^{3+} this anisotropy is almost entirely dipolar in origin. While it can be calculated with reasonable accuracy,[2] it is quite small and is liable to be obscured by other contributions to the bulk noncubic anisotropy, which we do not (at present) know how to calculate. For this reason only partial agreement with the data on mixed-YGd garnets has so far been obtained.[3] Ytterbium has not been found to give an appreciable growth-induced anisotropy. Europium, on the other hand, gives a large anisotropy, and many of the garnets of technical interest for bubble-domain devices contain europium as their main anisotropy-producing constituent.

The magnetic anisotropy of the Eu^{3+} ion arises from two causes: anisotropic exchange interaction with the nearest-neighbor Fe^{3+} ions, and the noncubic crystal field splitting of the excited states. The anisotropic exchange and the crystal field splittings are known from NMR,[4] Mössbauer effect,[5] and optical spectroscopy.[6] Since we also know the d-sublattice magnetization from NMR[7] and Mössbauer[8] data on yttrium iron garnet (YIG), we have all the information needed for a molecular-field calculation of the anisotropy as a function of temperature. This calculation will follow the lines of the Wolf–Van Vleck calculation of the magnetization of europium iron garnet (EuIG).[9] We can attempt to go beyond the molecular field approximation by taking spin correlations on the d sublattice into account in a heuristic, but reasonably successful, manner.

The growth-induced anisotropy is predominantly due to the nonrandom occupancy of sites on the c (dodecahedral) sublattice, this being the sublattice occupied by rare-earth ions. The contribution of the iron on the a (octahedral) and d (tetrahedral) sublattices is relatively small.[1] These site occupancies can only be altered by annealing at temperatures above 1200 °C. It follows that the experimental noncubic anisotropy should be proportional to the magnetic anisotropy of the Eu^{3+} ion as a function of temperature. The constant of proportionality should give us the magnitude of the site preference.

The liquid-phase-epitaxy (LPE) growth method enables us to obtain films of high quality in virtually any crystallographic orientation.[10] In particular, $\{001\}$ and $\{111\}$ films are desirable since their growth-induced anisotropy is uniaxial. The anisotropy of such films can readily be obtained by ferromagnetic resonance. We correct for the contribution of magnetostriction and cubic anisotropy to the observed anisotropy field by measuring its change on annealing at a sufficiently high temperature to randomize the site occupancies. Concurrent measurements of the magnetization enable us to obtain the anisotropy energy from the corrected anisotropy field.

II. EXPERIMENTAL

Measurements were made on single-crystal garnet films of the composition $\{\mathrm{Eu}_x R_{3-x}\}$ $(\mathrm{Fe}_y M_{3-y})$ $[\mathrm{Fe}_z M_{2-z}]\mathrm{O}_{12}$, where R = Y or Lu, M = Al or Ga, and the brackets indicate the site according to Geller's notation: $\{c\}$, (d), $[a]$.[11] The two nearest neighbors of the c site are d (tetrahedral iron) sites, all other cation sites being too far away to interact appreciably.[12] These films were grown by the "dipping" technique, in which an oriented substrate is dipped for a few minutes into a supercooled flux containing the constituent oxides in the required proportions.[10] The starting material contained less than 10 ppm of unwanted impurity.

The parameters x, y, and z were obtained from the lattice constant of the film a_0, the Curie point T_C, and the saturation magnetization extrapolated to 0 °K, $M(0)$. T_C is a function primarily of $(y+z)$,[13] a_0 of x and $(y+z)$,[11] and $M(0)$ of x and $(y-z)$.[9,14]

Resonance measurements were made at 13 150 MHz by standard methods. The resonance is quite sharp and the field for resonance can be determined within a few gauss. If the fields for resonance perpendicular and parallel to a $\{111\}$ film are $H_\perp$ and $H_\parallel$, respectively, we have

$$\omega/\gamma = H_\perp + H_u - 4\pi M + \tfrac{4}{3}H_1 \ , \tag{1a}$$

$$(\omega/\gamma)^2 = H_\parallel(H_\parallel - H_u + 4\pi M + H_1) \ . \tag{1b}$$

Here $\omega/2\pi$ is the resonant frequency, γ is the gyromagnetic ratio, M is the magnetization, $H_u = 2K_u^t/M$ is the total uniaxial anisotropy field (including the magnetostrictive contribution), and $H_1 = -K_1/M$ is the cubic anisotropy field. Equation (1b) is only accurate to first order in $H_1/H_\parallel$.

Since $H_\parallel$ is usually large relative to the other terms inside the parentheses, we can linearize Eqs. (1) to obtain

$$H_u = \tfrac{2}{3}(H_\parallel - H_\perp) + 4\pi M - \tfrac{5}{9}H_1 \ . \tag{2}$$

To eliminate H_1 and the contribution of magnetostriction to H_u from Eq. (2), we annealed the films for 30 h at 1250 °C in an O_2 atmosphere. This removes the growth-induced contribution without affecting the others appreciably.[15] The growth-induced anisotropy is then

$$K_u = \tfrac{1}{3}M[\,(H_\parallel - H_\perp)_{\mathrm{before}} - (H_\parallel - H_\perp)_{\mathrm{after}}\,] \ . \tag{3}$$

This procedure not only eliminates H_1 and the magnetostrictive contribution, but also, to a very good approximation, cancels out the error due to the linearization, by which Eq. (2) was obtained from Eqs. (1). For the largest observed K_u, with any reasonable values of K_1, the residual error is less than 2%. Dispersion corrections to K_u are small, since the relaxation time is quite isotropic.[16]

Equation (3), though not Eqs. (1), applies equally to a $\{001\}$ film. However, whereas $H_\parallel$ is independent of azimuth for a $\{111\}$ film (since K_2 is very small), this is not the case for a $\{001\}$ film. The value of $H_\parallel$ to be used in Eq. (3) is that corresponding to the [100] and [010] directions; since K_1 is negative, this is the maximum $H_\parallel$, found by rotating the field in the plane of the film.

To obtain K_u from H_u we need the magnetization. This was obtained with a vibrating-sample magnetometer. Great care had to be taken to extrapolate the data to zero field because of the very large paramagnetic susceptibility of the gadolinium gallium garnet substrate. Its magnetic moment is as large as that of the film at low temperatures and moderate fields.

Measurements were made from 16 to 368 °K on a $\{111\}$ film with R = Lu, M = Ga, T_C = 403 °K, x = 1.47, y = 2.02, and z = 1.73. Its magnetization

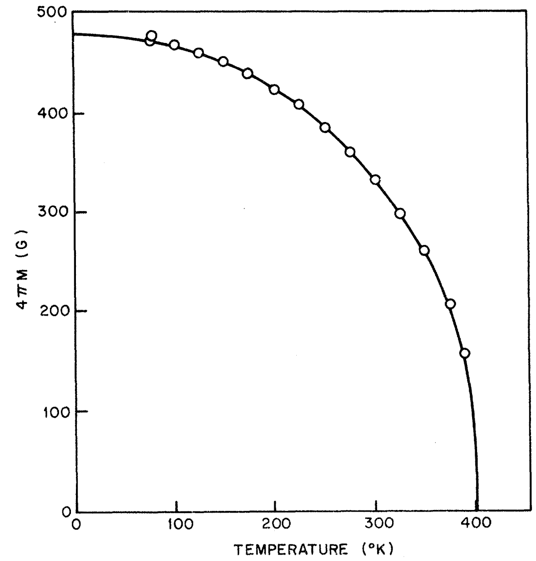

FIG. 1. Magnetization curve of a $\{111\}$ garnet film with the composition $\{\mathrm{Lu}_{1.53}\mathrm{Eu}_{1.47}\}$ $(\mathrm{Fe}_{2.02}\mathrm{Ga}_{0.98})$ $[\mathrm{Fe}_{1.73}\mathrm{Ga}_{0.27}]\,\mathrm{O}_{12}$.

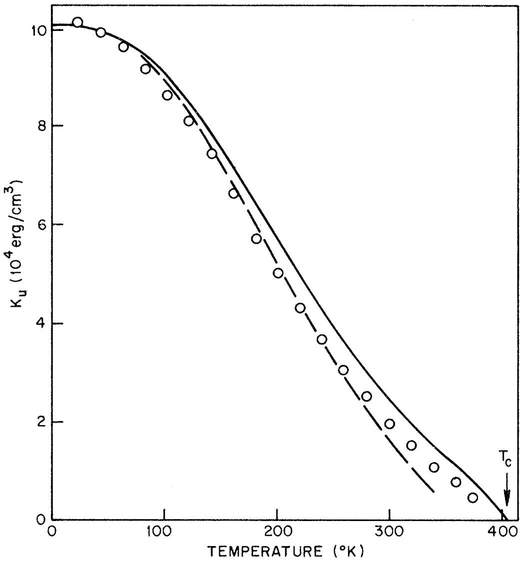

FIG. 2. Circles: K_u for the {111} film of Fig. 1 deduced from ferromagnetic-resonance data with the aid of Eq. (3). Solid line: molecular-field calculation of the [Eqs. (6), (9), and (10)], normalized to K_u at 16 °K. Dashed line: corrected theoretical curve, in which the effect of spin correlations on the d sublattice is taken into account [Eq. (15)]. This theory is not valid for $T > 0.8 T_C$.

is shown in Fig. 1. The corresponding K_u, deduced from Eq. (3), is shown by the circles in Fig. 2

Two films with the approximate composition $Y_2EuFe_{4.2}Al_{0.8}O_{12}$ were grown successively from a single melt on {111} and {001} substrates. They were measured at 300 °K only. K_u for the {001} film became too large to measure as the temperature was lowered. Their composition corresponds to $T_C = 440$ °K. These both had $4\pi M = 700$ G at 300 °K, and the values of K_u obtained from Eq. (3) were $+2.8 \times 10^4$ erg/cm^3 for the {111} film and -7.1×10^4 erg/cm^3 for the {001} film.

III. THEORY

In this section we will calculate the second-rank tensor which, to a good approximation, represents the magnetic energy surface of a Eu^{3+} ion in a c (dodecahedral) site of an iron garnet. The anisotropic part of this tensor is defined by two parameters, w' and w'', where the magnetic free energy per ion is[17]

$$F_i = w'(\alpha_z^2 - \tfrac{1}{3}) + w''(\alpha_x^2 - \alpha_y^2) + \text{const} . \qquad (4)$$

Here $\vec{\alpha}$ is the direction of magnetization referred to the local principal axes of the site. Only w' enters K_u for a {001} film; only w'' for a {111} film.

The calculation is based on the Wolf–Van Vleck theory of the magnetism of the isolated Eu^{3+} ion. The lowest level of Eu^{3+} is $^7F_0$, and there would be no magnetism at low temperatures if it were not for the admixture of the $^7F_1$ level (350 cm^{-1} above $^7F_0$) into the ground level by a magnetic field. In EuIG an effective field is provided by the strong antiferromagnetic exchange coupling between the Eu^{3+} ion and its two nearest-neighbor Fe^{3+} ions, which are on the d (tetrahedral) sublattice.

Anisotropy in this system has two main causes. The exchange field itself may be anisotropic, that is, it depends on $\vec{\alpha}$, the direction of the magnetization relative to the local axes; and also, the crystalline field splits the $J = 1$ and higher levels so that the degree of admixture of these states into the ground state (and into each other) depends on $\vec{\alpha}$. This contribution is of third order in the exchange and crystalline fields, regarded as perturbations on the dominant (isotropic) spin-orbit coupling, but is nevertheless found to be quite substantial. There is a third contribution, from the dipolar interaction of the induced Eu^{3+} moment with the Fe^{3+} moments; however, this is very weak because of the small Eu^{3+} moment. To a good approximation it is included in our calculation of the effect of anisotropic exchange, since we use empirical data on this anisotropy in EuIG, and these data include a dipolar contribution.

A. Anisotropic Exchange

In the molecular field approximation, exchange is represented in the single-ion Hamiltonian by a term

$$\mathcal{H}_{\text{ex}} = 2\mu_B \vec{H} \cdot \vec{S}_E , \quad \mu_B \vec{H} = -\overleftrightarrow{\lambda} \cdot \vec{S}_F . \qquad (5)$$

Here $\vec{S}_E$ is the spin operator for the Eu^{3+} ion, $\vec{H}$ is the effective exchange field, $\vec{S}_F$ is the spin of an Fe^{3+} ion on the d sublattice ($S_F = \frac{5}{2}$), and $\overleftrightarrow{\lambda}$ is a second-order tensor. Equation (5) has been found to give a good description of the angular dependence of NMR frequencies in EuIG.[4] The principal values of $\overleftrightarrow{\lambda}$ at 4 °K were found in Ref. 4 to be $\lambda_x = 0.97\lambda_0$, $\lambda_y = 1.22\lambda_0$, and $\lambda_z = 0.81\lambda_0$, where $\frac{5}{2}\lambda_0$ is the mean molecular field at 0 °K (16 cm^{-1} [14]) and $\vec{z}$ is the local ⟨001⟩-type axis. The contributions of anisotropic exchange to ω' and ω'' are, respectively,

$$w_a' = w_a(T)(2\lambda_z - \lambda_x - \lambda_y)/\lambda_0 ,$$

$$w_a'' = w_a(T)(\lambda_x - \lambda_y)/\lambda_0 ,$$

where

$$w_a(T) = \frac{-16(\mu_B H_0)^2\{1 - u[1 - (\Delta_1/16kT) - (15\Delta_1/8\Delta_2)]\}}{\Delta_1(1 + 3u)} \qquad (6)$$

and $u = e^{-\Delta_1/kT}$. Here Δ_1 and Δ_2 are the energy intervals between successive J levels (Δ_1 from $J = 0$ to 1, Δ_2 from $J = 1$ to 2), and $\mu_B H_0$ is the effective molecular field. At 0 °K, $\mu_B H_0 = \frac{5}{2}\lambda_0$; its temperature dependence will be discussed later.

Equation (6) is only accurate to first order in the anisotropy. The contribution of the Curie susceptibility of the $J=1$ level is $(\Delta_1/16kT)e^{-\Delta_1/kT}$ (relative to the 0 °K anisotropy). This is always a small number, which is fortunate, since there is really no justification for assuming that the effective anisotropy of $\overleftrightarrow{\lambda}$ is the same for this diagonal term as it is for the off-diagonal terms.

If we substitute for the Δ's and λ's in Eq. (6) we find, at 0 °K,

$$w_a'(0) = 6.6\ \text{cm}^{-1}/\text{ion}\ ,$$

$$|\, w_a''(0)\,| = 2.9\ \text{cm}^{-1}/\text{ion}\ .$$

The sign of w_a'' is ambiguous because the assignment of x and y axes to the NMR spectra of Ref. 4 is arbitrary.

B. Crystal Field Effects

We only consider the second-order orthorhombic crystal field, which can be written

$$\mathcal{H}_c = 2V_2^0 C_2^0 + (\tfrac{2}{3})^{1/2}\, V_2^2 (C_2^2 + C_2^{-2})\ , \qquad (7)$$

where the C_l^m are Racah's tensor operators and the numerical coefficients are chosen to make the crystal field parameters V_2^0 and V_2^2 agree with those used in Ref. 4. Fourth-order contributions to $\mathcal{H}_c$, while vital to the understanding of the cubic anisotropy of EuIG,[18] do not contribute appreciably to the growth-induced noncubic anisotropy.

The matrix elements of $\mathcal{H}_c$ are calculated from the following formula, readily derived from Eqs. (1.15), (1.25), and (2.20) of Ref. 19:

$$\langle LSJ'M' \mid C_l^m \mid LSJM\rangle$$
$$= (-1)^{J'+J+L+S+l-M'}\,[(2J'+1)(2J+1)]^{1/2} \times \begin{pmatrix} J' & l & J \\ -M' & m & M \end{pmatrix} \begin{Bmatrix} J' & J & l \\ L & L & S \end{Bmatrix} \langle L \| C_l \| L\rangle\ .$$

For a single hole in the half-filled f shell, the reduced matrix element is given by[19,20]

$$\langle L \| C_l \| L\rangle = (-1)^{L+1}(2L+1) \begin{Bmatrix} L & l & L \\ 0 & 0 & 0 \end{Bmatrix}\ ,$$

and $L=S=3$. The corresponding formula for the matrix elements of S_z, used here and in Sec. IIIA, is

$$\langle LSJ'M \mid S_z \mid LSJM\rangle = (-1)^{J'+J+S+L+1-M} \times [(2J'+1)(2J+1)S(S+1)]^{1/2} \times \begin{pmatrix} J' & 1 & J \\ -M & 0 & M \end{pmatrix} \begin{Bmatrix} J' & J & 1 \\ S & S & L \end{Bmatrix}\ .$$

Since $\mathcal{H}_c$ connects levels with $\Delta J \leq 2$, and the $J=1$ level is partially occupied over the temperature range of interest, we have to include all levels up to $J=3$ in our third-order perturbation calculation. The matrices of $\mathcal{H} = \mathcal{H}_{ex} + \mathcal{H}_c$ for these levels are given in Table I. Only matrix elements which contribute to the anisotropy in third order are included. The matrices are given for the case $\vec{H} \parallel \vec{z}$. The corresponding matrices for $\vec{H} \parallel \vec{x}$ or $\vec{y}$ are obtained by simply substituting $-\frac{1}{2}(V_2^0 \pm V_2^2)$ for V_2^0 and $-\frac{1}{2}(V_2^2 \mp 3V_2^0)$ for V_2^2.

To third order, the crystal field contributions to

TABLE I. Matrix elements of $\mathcal{H}_{ex} + \mathcal{H}_c$ in a $|J\,M\rangle$ basis.

(a)	$\|0\ 0\rangle$	$\|1\ 0\rangle$	$\|2\ 0\rangle$	$\|2\ 2\rangle$	$\|2\ -2\rangle$	$\|3\ 0\rangle$
$\langle 0\ 0\|$	0	$4H$	$4V_2^0/5\sqrt{3}$	$\frac{2}{15}\sqrt{2}\,V_2^2$	$\frac{2}{15}\sqrt{2}\,V_2^2$	0
$\langle 1\ 0\|$		$\frac{2}{5}V_2^0$	$2\sqrt{3}\,H$	N. C.[a]	N. C.	$2\sqrt{6}\,V_2^0/5\sqrt{7}$
$\langle 2\ 0\|$			$\frac{22}{105}V_2^0$	N. C.	N. C.	$6\sqrt{2}H/\sqrt{7}$
$\langle 2\ 2\|$				$2H - \frac{22}{105}V_2^0$	0	N. C.
$\langle 2\ -2\|$					$-2H - \frac{22}{105}V_2^0$	N. C.
$\langle 3\ 0\|$						N. C.

(b)	$\|1\ 1\rangle$	$\|1\ -1\rangle$	$\|2\ 1\rangle$	$\|2\ -1\rangle$	$\|3\ 1\rangle$	$\|3\ -1\rangle$
$\langle 1\ 1\|$	$H - \frac{1}{5}V_2^0$	$-\frac{1}{5}V_2^2$	$3H + \frac{1}{5}V_2^0$	$\frac{1}{15}V_2^2$	$4V_2^0/5\sqrt{7}$	$2V_2^2/15\sqrt{7}$
$\langle 1\ -1\|$		$-H - \frac{1}{5}V_2^0$	$-\frac{1}{15}V_2^0$	$3H - \frac{1}{5}V_2^0$	$2V_2^2/15\sqrt{7}$	$4V_2^0/5\sqrt{7}$
$\langle 2\ 1\|$			$H + \frac{11}{105}V_2^0$	$-\frac{11}{105}V_2^2$	$8H/\sqrt{7}$	N. C.
$\langle 2\ -1\|$				$-H + \frac{11}{105}V_2^0$	N. C.	$8H/\sqrt{7}$
$\langle 3\ 1\|$					N. C.	
$\langle 3\ -1\|$						N. C.

[a] N. C., not calculated.

w' and w'' are, respectively,

$$w_c' = w_c(T)(3V_2^0/2\Delta_1)\ ,\qquad w_c'' = w_c(T)(V_2^2/2\Delta_1)\ , \tag{8}$$

where

$$w_c(T) = \frac{32(\mu_B H_0)^2(A - Bu)}{5\Delta_1(1+3u)}\ .$$

Here,

$$u = e^{-\Delta_1/kT}\ ,$$

$$A = 1 + 2\Delta_1/(\Delta_1 + \Delta_2)\ ,$$

$$B = 1 + 2\Delta_1/\Delta_2 - \Delta_1^2/2\Delta_2^2 - 30\,\Delta_1^2/14\,\Delta_2(\Delta_2 + \Delta_3)\ ,$$

and Δ_3 is the $J=2$ to $J=3$ interval. Substituting for the Δ's[6] we find $A = 1.75$ and $B = 1.75$ (the equality is coincidental) so that

$$w_c(T) = \frac{11.2(\mu_B H_0)^2(1-u)}{\Delta_1(1+3u)}\ . \tag{9}$$

Reference 4 gives $V_2^0 = 77\ \mathrm{cm}^{-1}$, $V_2^2 = -82\ \mathrm{cm}^{-1}$, whence $w_c'(0) = 2.8\ \mathrm{cm}^{-1}$/ion and $|w_c''| = 1.0\ \mathrm{cm}^{-1}$/ion.

We do not know the sign of w_a'' or w_c'', since the assignment of x and y axes to the data of Ref. 4 is arbitrary, but we do know that they have opposite signs. The crystal field contribution is less than that of the anisotropic exchange, but is quite appreciable.

C. Temperature Dependence of Anisotropy

To calculate $w_a(T)$ and $w_c(T)$ at finite temperatures we need the mean-square value of the effective field. We cannot simply replace $\mu_B H_0$ by $\lambda_0 M_F(T)$, where $M_F(T)$ is the d-sublattice magnetization, because of spin fluctuations. The magnetization is proportional to $\langle S_Z \rangle$, the average projection of the Fe^{3+} spin on the direction of magnetization. The anisotropy, on the other hand, depends on the anisotropy of the mean-square projected spin, which we call $\langle S_A^2 \rangle$. For a single Fe^{3+} ion,

$$\langle S_A^2 \rangle = \langle S_Z^2 \rangle - \tfrac{1}{2}\langle S_X^2 \rangle - \tfrac{1}{2}\langle S_Y^2 \rangle = \tfrac{1}{2}\langle 3S_Z^2 - S(S+1) \rangle\ , \tag{10}$$

where $\vec{S}$ now refers to the Fe^{3+} ion ($S = \frac{5}{2}$).

The temperature dependence of this quantity is well known; it varies as M_F^3 at low temperatures and as M_F^2 near T_C. The exact dependence is a function of S and is given in Fig. 2 of Callen and Callen.[21] If we substitute $\langle S_A^2(T) \rangle / \langle S_A^2(0) \rangle$ for $(\mu_B H)^2$ in Eqs. (6) and (9), we obtain $w_a(T)/w_a(0)$ and $w_c(T)/w_c(0)$, shown by the full and dashed lines in Fig. 3. In this calculation, T_C is taken as 560 °K, corresponding to the composition $\mathrm{Y}_{3-x}\mathrm{Eu}_x\mathrm{Fe}_5\mathrm{O}_{12}$. The temperature dependence is not a universal function of T/T_C since the parameter (Δ_1/kT) also enters.

Since w_a and w_c vary somewhat differently with temperature, and their contributions add in w' and subtract in w'', w' varies somewhat faster than w''. However, the difference is not great, and at temperatures below about $0.8T_C$ it is quite a good approximation to take

$$w' \propto w'' \propto M_F^2 M_E\ ,$$

where M_F is the d-sublattice magnetization and M_E that of the Eu^{3+} sublattice [given by Eq. (1) of Ref. 9].

D. Effect of Spin Correlations in d Sublattice

So far we have made the assumption that the Eu^{3+} ion only interacts with one Fe^{3+} ion. In fact we know that this is incorrect; there are two nearest-neighbor Fe^{3+} ions which contribute equally to the effective exchange field $\vec{H}$ at the Eu^{3+} ion. Since the anisotropy is proportional to $\langle H^2 \rangle$, we have to take into account correlations between the spins on the two Fe^{3+} ions.

Let us label the ions 1 and 2, and assume for the moment that their instantaneous contributions to $\vec{H}$ are strictly additive. Then we should replace Eq. (10) by

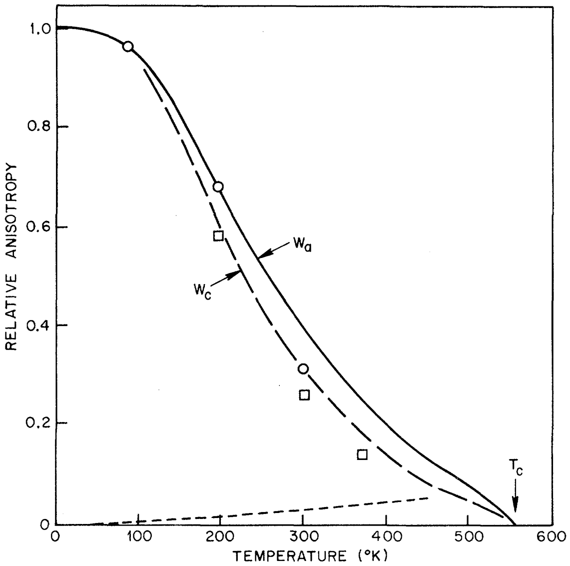

FIG. 3. Solid line: molecular-field calculation of w'' anisotropy of Eu^{3+} due to anisotropic exchange, normalized to unity at 0 °K [Eq. (6)]. Dashed line: the same for the crystal field anisotropy [(Eq. (9)]. Dotted line: correction term for spin-correlation effects on the d sublattice [Eq. (15)]. This correction is to be subtracted from the solid and dashed lines. The points are the magnetostriction data of Iida (Ref. 39) on EuIG, corrected for the Fe^{3+} contribution and normalized to theory at 77 °K; □, λ_{100}; ○, λ_{111}.

$$\begin{aligned}\langle S_A^2\rangle &= \tfrac{1}{2}\langle (S_{Z1}+S_{Z2})^2\rangle - \tfrac{1}{4}\langle (S_{X1}+S_{X2})^2\rangle \\ &\qquad - \tfrac{1}{4}\langle (S_{Y1}+S_{Y2})^2\rangle \\ &= \tfrac{1}{2}\langle 3S_Z^2 - S(S+1)\rangle \\ &\quad - [(\langle S_Z^2\rangle - \langle S_{Z1}S_{Z2}\rangle) - \tfrac{1}{2}(\langle S_X^2\rangle - \langle S_{X1}S_{X2}\rangle) \\ &\qquad - \tfrac{1}{2}(\langle S_Y^2\rangle - \langle S_{Y1}S_{Y2}\rangle)]\,, \qquad (11)\end{aligned}$$

where the index labeling the Fe^{3+} ion has been dropped where irrelevant. The first term is simply the right-hand side of Eq. (10); the term in the square brackets represents the effect of spin correlations.

The question of the range of spin correlations is discussed in a review by Marshall and Lowde[22] and in more detail by Mori and Kawasaki.[23] Although the two Fe^{3+} ions which are nearest neighbors to the Eu^{3+} ion are only 6 Å apart, they are well separated magnetically; there are two intervening a-site (and one d-site) Fe^{3+} ions in the shortest exchange pathway connecting them (assuming that exchange only connects nearest neighbors). Except near T_C, longitudinal correlations have a very short range; we can therefore replace $\langle S_{Z1}S_{Z2}\rangle$ by its value at infinity $\langle S_Z\rangle^2$.

Transverse correlations, on the other hand, have a very long range in a Heisenberg (low-anisotropy) system such as this.[22] Hence $\langle S_{X1}S_{X2}\rangle \sim \langle S_X^2\rangle$, and except near T_C the transverse terms in the square brackets are small relative to the longitudinal terms. Thus for temperatures not too close to T_C we have

$$\langle S_A^2\rangle = \tfrac{1}{2}\langle 3S_Z^2 - S(S+1)\rangle - \langle S_Z^2\rangle + \langle S_Z\rangle^2\,. \qquad (12)$$

Since the range of the longitudinal correlations is short, the bulk longitudinal susceptibility per Fe^{3+} ion is given approximately by[22]

$$\chi^Z = g^2\mu_B^2(\langle S_Z^2\rangle - \langle S_Z\rangle^2)/kT\,. \qquad (13)$$

This is in principle a measurable quantity, though in practice it is difficult to measure in a ferrimagnet. In MnF_2, which is an almost ideal Heisenberg antiferromagnet, the observed longitudinal susceptibility[24] can be approximated by the following empirical expression, valid for $0.5 < m < 1$:

$$\chi^Z = 0.13\, g^2\mu_B^2\, S(S+1)(1-m^{1.67})/kT\,, \qquad (14)$$

where m is the reduced sublattice magnetization.[25] Thus we have, in MnF_2 well below the Néel temperature,

$$\langle S_Z^2\rangle - \langle S_Z\rangle^2 \approx 0.13(1-m^{1.67})S(S+1)\,,$$

or, for $S=\frac{5}{2}$,

$$\frac{\langle S_Z^2\rangle - \langle S_Z\rangle^2}{\langle S_A^2(0)\rangle} \approx 0.2(1-m^{1.67})\,, \qquad (15)$$

since $\langle S_A^2(0)\rangle = \frac{1}{2}[3S^2 - S(S+1)] = S(S-\frac{1}{2})$. If we assume that Eq. (15) holds for the d sublattice in YIG, we obtain the dotted curve in Fig. 3. Equation (15) should hold so long as the longitudinal correlation length is much less than the smallest Fe^{3+}–Fe^{3+} distance; this is true for $T/T_C \lesssim 0.85$ according to a molecular field calculation.[22] It is obvious from Fig. 3 that we will get absurd results if we use Eq. (15) for $T/T_C \gtrsim 0.8$. For T/T_C greater than this, not only does Eq. (13) fail, but transverse correlations must be taken into account.

Even at very low temperatures the exact validity of Eq. (10) is not assured. Since we are dealing with a ferrimagnet, we should take zero-point spin deviations into account. However, the correction appears to be very small; at most a few percent in the exponent of m.[21]

Another problem in using Eqs. (12) and (15) arises from the fact that the assumption that the effective fields of the two Fe^{3+} ions are simply additive is not justified. So long as Eq. (10) holds there is no problem, but when spin flucutations become important we cannot assume that the anisotropy remains the same. This leads to an uncertainty of the coefficient in Eq. (15); it should not affect the temperature dependence.

IV. COMPARISON OF EXPERIMENT WITH THEORY

A. Temperature Dependence

The uniaxial anisotropy energy K_u for a {111} film should be proportional to $w'' = w_a'' + w_c''$. This function is calculated (neglecting spin-correlation effects) from Eqs. (6), (9), and (10) and compared with experiment in Fig. 2 (full curve). The parameters are $w_c''(0)/w_a''(0) = -0.43$ and $T_C = 403\,°K$. The theoretical curve is normalized to the data at 16 °K. The data fall consistently below the theory as the temperature is raised. If instead of Eq. (10) for $\langle S_A^2\rangle$ we use Eq. (12), with the spin-fluctuation term given by Eq. (15), we obtain the dashed line in Fig. 2. Over its range of validity ($T \lesssim 320\,°K$) this curve agrees with the data within experimental error, which tends to increase at the lowest temperatures.

In this comparison of experiment and theory we have ignored the contribution of the Fe^{3+} ions to K_u. It is known that iron garnets with no magnetic ions whatever on the c sites can still show growth-induced anisotropy, with $|K_u| \sim 5\times10^3$ erg/cm^3 at 300 °K.[26,27] This might affect the absolute magnitude of K_u by up to 25%. However, it is unlikely to make much difference to the temperature dependence, since it depends on the same function of temperature, $\langle S_A^2\rangle$, which is the dominant term in the temperature dependence of the Eu^{3+} contribution.

We conclude that there is no significant deviation of the data from the theoretical temperature dependence. Furthermore, we tentatively conclude that the data provide at least qualitative evidence for the validity of our heuristic approach to spin correlations (Sec. III D).

B. Determination of Site-Preference Parameters

It is convenient to write the site occupancies c_i in a form analogous to Eq. (3)[17]:

$$c_i = c_0 + c'(\beta_z^2 - \tfrac{1}{3}) + c''(\beta_x^2 - \beta_y^2) , \tag{16}$$

where $\vec{\beta}$ is the growth direction referred to the principal axes of the ith site, c_0 is the average concentration of the magnetic ion, and c' and c'' are parameters which may vary with growth direction and from one film to another.

It can be shown that for a $\{001\}$ film of garnet,[28] containing only one type of magnetic ion on the c sites,

$$K_u = F_{100} - F_{001} = -\tfrac{1}{3}N_0 c' w' , \tag{17a}$$

while for a $\{111\}$ film

$$K_u = F_{1\bar{1}0} - F_{111} = -\tfrac{2}{3}N_0 c'' w'' . \tag{17b}$$

Here F_{hkl} is the free energy when the magnetization lies along $[hkl]$; $N_0 = 1.25\times 10^{22}\ \mathrm{cm}^{-3}$, the density of c sites, and the parameters w' and w'' appear in Eq. (3). Thus, if we measure K_u for $\{001\}$ and $\{111\}$ films and can calculate w' and w'', we can deduce the site-preference parameters c' and c''.

The saturation magnetization of a garnet of composition $Y_{3-x}Eu_xFe_5O_{12}$ is too high for use as a bubble material, and it is customary to reduce the magnetization by substituting Al or Ga for Fe. The fraction of d sites occupied by Fe^{3+} ions is $\frac{1}{3}y$, and only a fraction $\frac{1}{9}y^2$ of the Eu^{3+} ions see the full exchange interaction. A further fraction $\frac{2}{9}y(3-y)$ has one nearest Fe^{3+} neighbor instead of two. Again assuming that the contributions of these two Fe^{3+} ions to the molecular field are additive, then $(\mu_B H_0)^2$ and, consequently, w_a and w_c, are reduced by a factor of $\frac{1}{4}$ for these sites.[29] We ignore the effect of spin correlations on this correction. Hence the average values of w_a and w_c are reduced by a factor $\frac{1}{18}y(3+y)$. This is typically 0.6 in our films. Including this factor, we have for the values of w' and w'' at 0 °K, from Sec. III,[30]

$$w'(0) = +5.6\ \mathrm{cm}^{-6} ,$$

$$|\, w''(0)\,| = 1.2\ \mathrm{cm}^{-1} .$$

The $\{111\}$ film of Lu_2Eu iron garnet measured to low temperature has $K_u(0) = 1.06\times 10^5\ \mathrm{erg/cm^3}$, when $|c''| = 0.06$. Since $c_0 = 0.49$, the relative site preference is $|c''|/c_0 = 0.12$. If we use the theoretical temperature dependence to obtain $K_u(0)$ from $K_u(300)$ for the $\{111\}$ film of Y_2Eu iron garnet, we obtain $c''/c_0 = 0.16$. With the same assumption, the $\{001\}$ film has $c'/c_0 = +0.2$.

Thus we find site preferences of the same order in $\{001\}$ and $\{111\}$ films and in films of different composition. If we extrapolate to zero concentration, using Callen's formula for the concentration dependence[31] we obtain $c'/c_0 \sim |c''|/c_0 \sim 0.25$ $(c_0 \to 0)$ for Eu^{3+} in YIG or LuIG. These numbers can be compared with the results of spin-resonance measurements on films of YAG (yttrium aluminum garnet) dilutely doped with Nd^{3+}.[32] There c'/c_0 is so large that Eq. (16) breaks down and must be replaced by an equation of the form

$$\ln(c_i/c_0) = (c'/c_0)(\beta_z^2 - \tfrac{1}{3}) + (c''/c_0)(\beta_x^2 - \beta_y^2) ,$$

with $c'/c_0 \sim 1.3$. On the other hand, c''/c_0 is small and uncertain: A typical value is 0.05. We are unable to account for this great difference, which suggests that the mechanism of site selectivity is different in the two systems.

The fact that c''/c_0 is much the same in the LuEu and YEu garnets is surprising. The ionic radii of Eu and Lu differ by 0.042 Å, those of Eu and Y by only 0.023 Å.[33] The data on growth-induced anisotropy in facetted bulk crystals[27] and direct measurements of site occupancies by spin resonance[34] have shown that c'/c_0 depends strongly on differences in ionic radii. It appears that this may not be true of c''/c_0.

C. Growth-Induced Anisotropy in Other Garnets Containing Europium

The growth-induced anisotropy of a $\{111\}$ film with the composition $Er_2EuGa_{0.7}Al_{0.7}Fe_{3.6}O_{12}$ between 98 °K and the Curie point of 370 °K was reported earlier.[35] If we normalize these data to our present data at 300 °K we find that the temperature dependence of K_u is the same for films with or without Er down to 160 °K, as shown in Fig. 4. Even at 100 °K there is only a 20% deviation. It appears that Er makes very little contribution to the anisotropy except at low temperatures. This agrees with the general result of Gyorgy *et al.*[27] that the rare-earth ions heavier than Tb do not give a large growth-induced anisotropy at room temperature.

Measurements of the bubble parameters of (111) LPE films of several garnets containing europium have been reported.[36] The measurements cover the range 0–100 °C. The relation between these parameters and K_u is indirect, but the data are in qualitative agreement with those reported here.

Recently, an ingenious optical technique for obtaining the anisotropy of a bubble material directly has been devised.[37] This technique has been used to obtain K_1 and K_u, between room temperature and the Curie point, for (111) films of the following garnets: $Eu_1Er_2Ga_{0.7}Fe_{4.3}O_{12}$, $Eu_{1.85}Y_1Yb_{0.15}Al_{1.1}Fe_{3.9}O_{12}$, and $Eu_{1.7}Er_{1.3}Al_{0.7}Ga_{0.8}Fe_{3.5}O_{12}$.[38] The

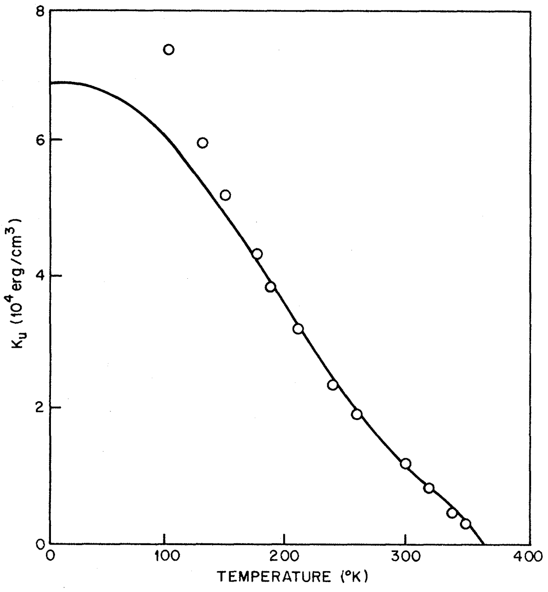

FIG. 4. Comparison of the molecular-field theory of the anisotropy of Eu^{3+} (solid line) with the data (circles) on a {111} garnet film of composition $Er_2EuFe_{3.6}Ga_{0.7}Al_{0.7}O_{12}$ (Ref. 35). The theory is normalized to the data at 300 °K.

data are in reasonable agreement with our theory, and the site-preference parameter c'' has the same order of magnitude as in our films. However, the theory does not claim to be accurate in this temperature range, and the fit cannot be regarded as particularly significant.

D. Magnetostriction in EuIG

If the magnetostriction is dominated by a single mechanism (crystal field or anisotropic exchange), it should vary with temperature according to $w_c(T)$ or $w_a(T)$ in Fig. 3 (appropriately corrected for spin correlation effects). We plot Iida's[39] results for λ_{100} and λ_{111} of EuIG, corrected for the Fe contribution by subtracting the values for YIG, and normalized at 77 °K, in Fig. 3. The 77 °K point is subject to a ± 15% experimental uncertainty. Within this uncertainty agreement with theory is good, although we cannot say for certain which curve, after correction for spin correlation effects, would give the better agreement.

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Magnetic Ordering of Dipolar Systems in the Molecular-Field Approximation

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A quantum-mechanical theory is given for the transition temperature and the nature of the ordered state for a system of spins interacting through general magnetic forces. The transition temperature and the ordered state below it are found to be, respectively, the lowest eigenvalue and the corresponding eigenvector of an Hermitian matrix derived quantum mechanically, within the framework of the molecular-field approximation. The method is then applied to the pure dipolar systems dysprosium ethyl sulphate and cerium magnesium nitrate.

I. INTRODUCTION

The low-temperature thermal and magnetic properties of some rare-earth salts, e.g., dysprosium ethyl sulphate (DES) and cerium magnesium nitrate (CMN) indicate the predominance of magnetic-dipole interactions between the rare-earth ions.[1,2] The ordered state of such crystals has been predicted[3,4] using the classical method of Luttinger and Tisza[5] for minimizing the dipole-dipole interaction energy. One hopes that the predicted configuration of minimum energy is a good approximation to the actual ground state. However, no direct estimate of the transition temperature T_C has been given.

The purpose of this paper is to present a quantum-mechanical estimate of T_C within the framework of the molecular-field approximation. The ordered state below T_C will also be given. A molecular-field theory on magnetic structures has already been published by Villain[6] who considered however only isotropic-exchange interactions. In the following we shall assume a general type of pairwise interaction. The results will then be applied to pure dipolar systems.

II. THEORY

We start with the Hamiltonian

$$\mathcal{H}=\frac{1}{2}\sum_{ij}\sum_{\mu\nu} v^{ij}_{\mu\nu} S^i_\mu S^j_\nu \,, \tag{1}$$

where S^i_μ is the μ component of an operator which is localized on the ith position in the lattice. This operator may have rather general properties, but for an easy understanding of the sequel it would best be regarded as a spin operator of the ith atom having $\vec{S}^2=S(S+1)$. Now μ, ν run over x, y, z and v^{ij} is a general interaction between i and j.

In the molecular-field approximation the Hamiltonian in Eq. (1) is approximated by

$$\mathcal{H}\cong\sum_{ij}\sum_{\mu\nu} v^{ij}_{\mu\nu}\langle S^j_\nu\rangle S^i_\mu-\frac{1}{2}\sum_{ij}\sum_{\mu\nu} v^{ij}_{\mu\nu}\langle S^i_\mu\rangle\langle S^j_\nu\rangle \,. \tag{2}$$

The Hamiltonian in Eq. (2) can further be written

$$\mathcal{H}=\sum_i H_i \,, \tag{3}$$

where

$$H_i=\sum_j\sum_{\mu\nu} v^{ij}_{\mu\nu}\langle S^j_\nu\rangle S^i_\mu-\frac{1}{2}\sum_j\sum_{\mu\nu} v^{ij}_{\mu\nu}\langle S^i_\mu\rangle\langle S^j_\nu\rangle \,. \tag{4}$$

Thus we have reduced the problem to that of independent noninteracting single particles, each of which is described by the Hamiltonian in Eq. (4). The partition function is a product of the partition functions

$$Z=\prod_i Z_i \,, \tag{5}$$

where

$$Z_i=\mathrm{Tr}\left[\exp\left(-\beta\sum_j\sum_{\mu\nu} v^{ij}_{\mu\nu}\langle S^j_\nu\rangle S^i_\mu\right)\right] \times\exp\left(\tfrac{1}{2}\beta\sum_j\sum_{\mu\nu} v^{ij}_{\mu\nu}\langle S^i_\mu\rangle\langle S^j_\nu\rangle\right) \tag{6}$$

and $\beta=1/kT$. The free energy of the system is