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Nuclear-Magnetic-Resonance Studies of Eu^{151} and Eu^{153} in Europium Iron Garnet Single Crystals

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The nuclear magnetic resonances of Eu^{151} and Eu^{153} have been studied at 4.2 °K in single crystals of europium iron garnet with externally applied fields of sufficient magnitude to align the magnetization along various crystallographic directions. Hyperfine field and quadrupole splitting parameters of the Eu^{+3} ions are obtained. Hyperfine fields along the principal orthorhombic axes (x, y, and z) of the rare-earth sites are found to be 649, 706, and 382 kG, respectively, where the z axis corresponds to the orthorhombic axis which lies along the cubic [100] direction. The anisotropy of the hyperfine field is shown to be due in part to the crystal field distortion and in part to the anisotropy of the exchange fields arising from the iron ions. From the Eu^{153} quadrupole splittings, contributions to the electric field gradient arising from the crystal fields and the exchange fields are obtained. Values of the crystal field parameters and anisotropic exchange fields are obtained and discussed in relation to those in other rare-earth iron garnets.

I. INTRODUCTION

In recent years a number of experimental studies[1-4] using the Mössbauer effect as well as theoretical studies[2-6] have been carried out to determine the hyperfine fields and quadrupole interactions of the Eu^{+3} ions in europium iron garnet (EuIG). The Mössbauer studies of pure EuIG, however, have been restricted to "zero fields" where the magnetization is along the easy $\langle 111 \rangle$ direction. From studies in this direction only, one cannot obtain independently all three hyperfine field parameters associated with the orthorhombic symmetry at the rare-earth site. We have studied the nuclear magnetic resonance (NMR) of Eu^{151} and Eu^{153} in a single crystal of EuIG with external fields of sufficient magnitude to align the magnetization along the orthorhombic axes of the rare-earth sites and have determined the hyperfine fields and quadrupole splittings. A preliminary account of this study and an account of a zero-field study of the Eu^{151} and Eu^{153} NMR in polycrystalline EuIG were reported previously.[7,8] In the present paper we present results of more extended experimental studies and a more extended discussion of the findings.

As a result of the exchange and crystal fields acting on the Eu^{+3} ion, the $^7F_0$ ground state is mixed with the excited ionic states $^7F_1$ and $^7F_2$. The hyperfine field anisotropy arises from both the anisotropy of the exchange field and from the orthorhombic crystal fields. The hyperfine field parameters and electric field gradients associated with the

Eu^{+3} ions in EuIG were originally discussed by Gilat and Nowik,[6] but the anisotropy of the hyperfine field was neglected. In a subsequent paper Eicher[5] took into account the effect of the crystal fields on the hyperfine field parameters and quadrupole interactions, but neglected the anisotropy of the exchange field. More recently, closed-form expressions for the hyperfine field parameters in terms of the exchange fields and crystal field parameters have been derived by Atzmony and co-workers.[2] In Sec. III, we review the theory. Contributions to the electric field gradients have been obtained by various authors[3,6,9,10] and are also discussed in Sec. II.

In Sec. III, the experimental techniques are discussed and the results are given. In Sec. IV, values for the hyperfine field parameters, quadrupole interaction parameters, crystal field parameters, and exchange field parameters are obtained. In Sec. V, a discussion of the crystal field parameters and exchange field parameters is presented and comparisons with the results of other studies are made.

II. THEORY

A. Anisotropic Hyperfine Field and Exchange Field

As has been discussed by various authors, the rare-earth ions in the iron garnets reside at sites which are known to possess a local orthorhombic symmetry. The local orthorhombic axes of these sites take on six orientations with respect to the cubic crystal axes, resulting in general in six magnetically inequivalent rare-earth sites. As a consequence of the orthorhombic symmetry, the effective hyperfine field for Eu^{+3} ions at these sites can be written as

$$|H_{\text{eff}}| = (H_x^2 n_x^2 + H_y^2 n_y^2 + H_z^2 n_z^2)^{1/2} . \tag{1}$$

Here H_x, H_y, and H_z are the principal values of $\vec{H}_{\text{eff}}$ along the orthorhombic axes of the rare-earth sites, and n_x, n_y, and n_z are the direction cosines of the iron magnetization $\vec{M}$ with respect to these local axes. For one of the sites, the orthorhombic z axis lies along the cubic [001] direction while the x and y axes lie along the [110] and [1$\bar{1}$0] directions. The other orthorhombic sites can be obtained by taking the orthorhombic axes to be along equivalent directions.

Equation (1) can be rewritten in the form

$$|H_{\text{eff}}| = \overline{H}_{\text{eff}} (\mu_x^2 n_x^2 + \mu_y^2 n_y^2 + \mu_z^2 n_z^2)^{1/2}, \tag{2a}$$

where

$$\overline{H}_{\text{eff}} = \tfrac{1}{3}(H_x + H_y + H_z) \tag{2b}$$

and

$$\mu_x = H_x / \overline{H}_{\text{eff}} , \quad \text{etc.} \tag{2c}$$

Because of the anisotropy, $\vec{H}_{\text{eff}}$ does not in general lie along $\vec{M}$. If we take h_x, h_y, and h_z to be the direction cosines of $\vec{H}_{\text{eff}}$ with respect to the local axes, it then follows that

$$h_x^2 = n_x^2 (H_x / H_{\text{eff}})^2 . \tag{2d}$$

Taking $H_{\text{ex}}(x)$, $H_{\text{ex}}(y)$, and $H_{\text{ex}}(z)$ to be the principal values of the exchange fields acting on the Eu^{+3} ions, we can write similarly to Eq. (1)

$$|H_{\text{ex}}| = [H_{\text{ex}}(x)^2 n_x^2 + H_{\text{ex}}(y)^2 n_y^2 + H_{\text{ex}}(z)^2 n_z^2]^{1/2} \tag{3a}$$

and

$$\overline{H}_{\text{ex}} = \tfrac{1}{3}[H_{\text{ex}}(x) + H_{\text{ex}}(y) + H_{\text{ex}}(z)] . \tag{3b}$$

B. Eu^{+3} Ground State

As a consequence of the exchange and crystal fields, the excited ionic levels $|J, M\rangle$ $(J = 1, 2)$ are mixed into the ground state $|0, 0\rangle$. Considering the case of H_{ex} along z and treating the exchange energy[11] $+2\mu_B H_{\text{ex}}(z) \langle S_z \rangle$ and the orthorhombic crystal field[12] as perturbations on the spin-orbit levels, the ground state can be written as

$$|\psi_0(z)\rangle = b_{00}|0,0\rangle + b_{10}|1,0\rangle + b_{20}|2,0\rangle + b_{22}(|2,2\rangle + |2,-2\rangle)/\sqrt{2} , \tag{4}$$

where

$$b_{00} = 1 - 8\left(\frac{\mu_B H_{\text{ex}}(z)}{E_1}\right)^2 ,$$

$$b_{10} = \left(\frac{-4\mu_B H_{\text{ex}}(z)}{E_1}\right)\left(1 - \frac{2}{5}\frac{V_2^0}{E_1} - \frac{2}{5}\frac{V_2^0}{E_2}\right) ,$$

$$b_{20} = \frac{-4V_2^0}{5\sqrt{3}\,E_2} + \frac{8\sqrt{3}\,\mu_B^2 H_{\text{ex}}(z)^2}{E_1 E_2} , \quad b_{22} = \frac{-4V_2^2}{15E_2} .$$

Here V_2^0 and V_2^2 are the crystal field parameters and E_1 and E_2 are the energies of the unperturbed states. Equation (4) has been carried to second order in the ground-state wave function except that we have omitted terms involving $(1/E_2)^2$, which are small and which do not enter into the hyperfine field corrections if they are carried only to first order in V_2^0 and V_2^2.

The crystal field parameters V_2^0 and V_2^2 can be expressed in terms of the crystal field splittings of the $J = 1$ level. We can write[12]

$$\Delta_x \equiv -\tfrac{1}{5}(V_2^0 - V_2^2) , \quad \Delta_y \equiv -\tfrac{1}{5}(V_2^0 + V_2^2) , \quad \Delta_z \equiv \tfrac{2}{5} V_2^0 , \tag{5}$$

where Δ_x, Δ_y, and Δ_z are the energy shifts of the multiplets of the $J = 1$ level, relative to the center of gravity of the level, arising from the orthorhombic distortion.

C. Hyperfine Field

The hyperfine field for the case of $\vec{H}_{\text{ex}}$ along z can be written

$$H_z = +2\mu_B \langle r^{-3} \rangle \langle \psi_0(z) | N_z | \psi_0(z) \rangle . \tag{6}$$

Here N_z is the operator defined by Elliott and Stevens.[13] For Eu^{+3}, N_z can be written[5] as

$$N_z = L_z - \tfrac{4}{45} S_z + \tfrac{1}{90}[(\vec{L} \cdot \vec{S}) L_z + L_z (\vec{L} \cdot \vec{S})] .$$

One can show that $\langle 0, 0|N_z|1, 0\rangle = -\frac{5}{3}$ and $\langle 1, 0|N_z|2, 0\rangle = -13\sqrt{3}/15$. Using these relations, we can evaluate (6) as follows[14]:

$$H_z = \frac{80\mu_B^2}{3E_1}\langle r^{-3}\rangle H_{ex}(z)\left[1 - \frac{\Delta_z}{E_1} - \frac{51}{25}\frac{\Delta_z}{E_2}\right]. \tag{7}$$

A similar relation applies for H_x and H_y. From (7) we can obtain [after writing $H_{ex}(z)$ as $\overline{H}_{ex} + \Delta H_{ex}(z)$ and expanding]

$$\frac{|H_z|}{|\overline{H}_{eff}|} = 1 + \frac{\Delta H_{ex}(z)}{\overline{H}_{ex}} - \frac{\Delta_z}{E_1} - \frac{51}{25}\frac{\Delta_z}{E_2}\ . \tag{8}$$

In addition to the orbital and spin-dipolar contribution to H_{eff} combined in the operator N_z, one must take into account the core polarization contribution which can be taken to be roughly − 90 kG/unpaired spin.[6] Taking $\langle S_z\rangle = 16\mu_B H_{ex}/E_1$ or about 0.8, yields a core polarization hyperfine field of about − 72 kG, which is not negligible compared with the orbital and spin-dipolar fields of about 600 kG. It can be shown, however, that aside from the coefficient of the term involving $1/E_2$, S_z exhibits the same anisotropy with respect to H_{ex} and the crystal fields as does H_{eff}. Consequently, Eq. (8) applies to a good approximation even when the effect of the core polarization hyperfine field is considered.

D. Electric Field Gradient

The electric field gradient $eq_{zz}(4f)$ arising from the $4f$ electrons (for the case of $\vec{H}_{ex}$ along z) can be written

$$eq_{zz} = -e(1-R)\langle r^{-3}\rangle\langle\psi_0(z)\,|\,3\cos^2\theta - 1\,|\,\psi_0(z)\rangle\ , \tag{9}$$

where R is the Steinheimer shielding factor.

From evaluation of (9) one finds[3,6,9] terms proportional to V_2^0 which arise from the polarization of $4f$ orbitals by the crystal field and terms proportional to H_{ex}^2 which arise from the polarization of $4f$ orbitals by the exchange fields. In addition one must consider the effects of the external charges.[10]

Defining

$$\nu'_{zz} \equiv e^2 Q q_{zz}/h \tag{10a}$$

as a measure of the quadrupole interaction, we can write

$$\nu'_{zz} = \alpha[H_{ex}(z)/\overline{H}_{ex}]^2 + \nu''_{zz}\ , \tag{10b}$$

with similar equations applying for x and y. The quantity α in (10b) can be written as

$$\alpha = -\tfrac{32}{5}\, e^2(1-R)Q\mu_B^2\,\overline{H}_{ex}^2\langle r^{-3}\rangle\,(2E_1 + E_2)/(E_1)^2 E_2 h\ . \tag{10c}$$

The first term in (10b) arises from the field gradient produced by the exchange field polarization of $4f$ orbitals and is axial with respect to the exchange field. The second term is the contribution from the crystal fields and is the sum of two contributions, a contribution from the $4f$ electrons which can be written as[9]

$$\nu''_{zz}(1) = \tfrac{16}{15}\Delta_z\langle r^{-3}\rangle\, e^2 Q(1-R)/E_2 h\ , \tag{10d}$$

and a contribution from the external charges which can be written as[10]

$$\nu''_{zz}(2) = -10\Delta_z Q(1-\gamma_\infty)/(1-\sigma_2)\langle r^2\rangle h\ , \tag{10e}$$

where γ_∞ and σ_2 are shielding factors.

For a general direction of H_{eff}, one can write

$$\nu' = \alpha\left(\frac{H_{ex}}{\overline{H}_{ex}}\right)^2\left(\frac{3\cos^2\delta - 1}{2}\right) + \left(\frac{\nu''_{zz}}{2}\right)[3h_z^2 - 1 + \eta(h_x^2 - h_y^2)]\ , \tag{10f}$$

where δ is the angle between H_{eff} and H_{ex}.

The asymmetry parameter η is defined by the relation

$$\eta = (\nu''_{xx} - \nu''_{yy})/\nu''_{zz}\ . \tag{10g}$$

III. EXPERIMENTAL

A. Equipment and Measuring Technique

The spin-echo equipment employed high-power pulsed oscillators, receivers, and calibration oscillators to cover the required frequency range. The resonant element was a tank circuit at the lower frequencies and a capacitor-tuned rectangular quarter-wave coaxial cavity at the higher frequencies, with double-stub tuners at both input and output. The cavity was similar to that described by Kubo *et al.*[15]

The sample was a roughly spherical single crystal about 1 cm in diameter. It was mounted so that it could be rotated about a ⟨110⟩ axis, which was parallel to the rf field and perpendicular to the dc field $\vec{H}_0$. All measurements were carried out at 4.2 °K with an exposed-tip Dewar vessel, the tip of which fitted inside the coil or cavity.

The effective anisotropy field of EuIG for the ⟨111⟩ direction has been determined by ferromagnetic resonance studies[16] to be about 5 kG. All studies were made with a field strength H_0 of about 8 kG, which was sufficient to saturate the magnetization in the principal directions.

The studies were made for various orientations of $\vec{H}_0$ with respect to the crystal axes by plotting the spin-echo amplitude as a function of frequency.

In addition to the spectral measurement of spin-echo intensity, the relaxation times were determined when necessary to correct for differing signal decay at the various Eu sites.

B. Experimental Results

Since the magnetic moments of Eu^{151} and Eu^{153} are 3.46 and 1.56 nm, respectively (and the spins are both $\frac{5}{2}$), it is easy to identify the spectra of the

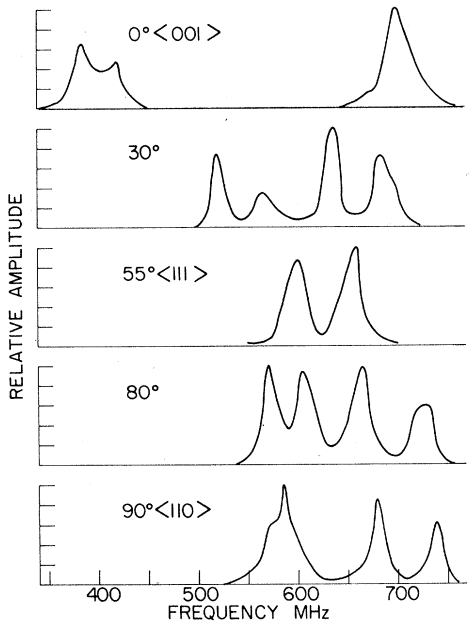

FIG. 1. Eu^{151} spectra at five different values of θ where θ is the angle in the $(1\bar{1}0)$ plane between $\vec{\mathrm{H}}_0$ and the [001] axis.

two isotopes. Figure 1 shows the Eu^{151} spectra at five different positions of the crystal where θ is the angle in the $(1\bar{1}0)$ plane between $\vec{\mathrm{H}}_0$ and the [001] axis. Four spectra of Eu^{153} are shown in Fig. 2.

The spin-echo amplitudes were observed to be a strong function of the orientation of $\vec{\mathrm{H}}_0$ with respect to the crystal axes, being strongest when $\vec{\mathrm{H}}_0$ was along the hard [001] direction. The origin of the effect lies in the dependence of the rf enhancement on magnetocrystalline anisotropy energy and has been discussed in Ref. 15 in connection with studies of $\mathrm{MnFe_2O_4}$.

IV. INTERPRETATION

A. Hyperfine Fields

The hyperfine field given by Eq. (1) is different at each of the six sites for a general orientation of the magnetization. However, at certain symmetrical positions of $\vec{\mathrm{M}}$ the number of distinct hyperfine fields is reduced. For example, when $\vec{\mathrm{M}}$ is along the [100] direction, we expect two lines corresponding to direction cosines $(0, 0, 1)$ and $(1/\sqrt{2}, 1/\sqrt{2}, 0)$ with relative site populations of 2:4, while for $\vec{\mathrm{M}}$ along [110], there should be three lines with direction cosines $(1, 0, 0)$, $(0, 1, 0)$, and $(\frac{1}{2}, \frac{1}{2}, 1/\sqrt{2})$ with relative site populations of 1:1:4. The Eu^{151} resonances observed for these two orientations can be fitted to these predictions if we take $\nu_x = 680$ MHz, $\nu_y = 740$ MHz, and $\nu_z = 400$ MHz, corresponding to $|H_x| = 649$ kG, $|H_y| = 706$ kG, and $|H_z| = 382$ kG. For the case of $\vec{\mathrm{M}}$ along a $\langle 111 \rangle$ direction, we expect two lines of equal intensity corresponding to direction cosines of $(\sqrt{\frac{2}{3}}, 0, \sqrt{\frac{1}{3}})$ and $(0, \sqrt{\frac{2}{3}}, \sqrt{\frac{1}{3}})$ with values of $|H_{\mathrm{eff}}|$ of 617 and 573 kG. These values are in good agreement with the observed lines and are also in agreement with the fields of 629 ± 10 and 571 ± 10 kG observed in zero-field Mössbauer studies[1] of EuIG where the magnetization lies along a $\langle 111 \rangle$ direction.

Now we consider the hyperfine fields when $\vec{\mathrm{M}}$ is along other directions in the $(1\bar{1}0)$ plane. From Eq. (1) the theoretical H_{eff} can be plotted for all angles, and the symmetry of this plane does not allow for more than four resonances at any orientation. Figures 3 and 4 show the calculated curves together with the experimental points. Figure 3 was calculated by taking ν_x, ν_y, and ν_z to be 680, 740, and 400 MHz, respectively. Figure 4 was plotted by multiplying the Eu^{151} frequencies by a factor of 0.444 which is approximately the ratio of γ for the two isotopes.

In dealing with orientations other than special cubic directions, the direction of $\vec{\mathrm{M}}$ will not coincide with $\vec{\mathrm{H}}_0$, unless the latter is infinitely strong. The magnetocrystalline energy causes the magnetization to lie between the applied and the nearest easy direction. In our case the easy direction is $\langle 111 \rangle$ and the equation relating the angle θ from [001] to $\vec{\mathrm{H}}_0$ and the angle θ_0 from [001] to $\vec{\mathrm{M}}$ in the $(1\bar{1}0)$ plane is

$$\frac{I_s H_0}{K_1} = \frac{\sin\theta_0 \cos\theta_0 (3\sin^2\theta_0 - 2)}{\cos\theta \sin\theta_0 - \sin\theta \cos\theta_0} .$$

Here I_s is the saturation magnetization and K_1, the coefficient of magnetocrystalline energy, is negative. This equation can be plotted for a particular value of θ, and the corresponding value of θ_0 ob-

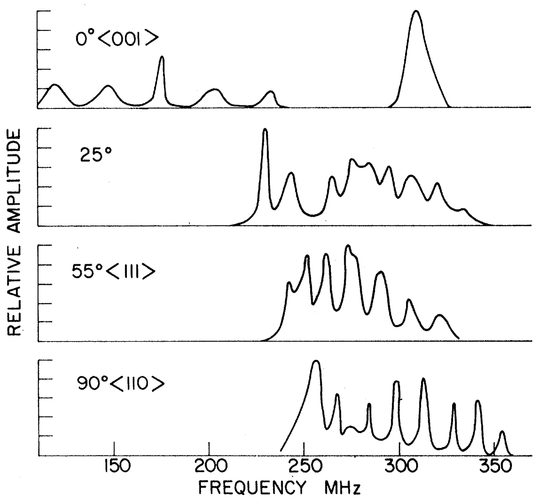

FIG. 2. Eu^{153} spectra at four different values of θ where θ is the angle in the $(1\bar{1}0)$ plane between $\vec{\mathrm{H}}_0$ and the [001] axis.

tained for the given applied field. Since a field of 8 kG was used and $|2K_1/I_s| = 5000$ G, the values of θ_0 for $I_sH_0/K_1 = 3.2$ were obtained as follows:

θ	0°	25°	30°	55°	80°	90°
θ_0	0°	34°	38°	55°	77°	90°

Thus when the magnet was oriented, for example, at 30° from [001], the results were plotted at 38° (see Fig. 3). The over-all results agree with the theoretical curves within the limits of experimental error involved in both the angular settings and the determination of the resonance peaks.

In some cases the intensity of the lines does not agree exactly with the intensity expected from the relative site populations. This is particularly true of the line at 576 MHz, which is about a factor of 2 weaker than one would expect. It should be noted, however, that this line had a shorter relaxation time than the lines at 680 and 740 MHz. Also the rf level needed to optimize the signal was greater than we could supply with our pulsed oscillator. This may be related to the fact that for this line the angle between $\vec{H}_{eff}$ and $\vec{M}$ is rather large [see Eq. (2d)].

Our values of $|H_x|$, $|H_y|$, and $|H_z|$ are considerably different from the values obtained by Atzmony and co-workers[2] from Mössbauer studies of Eu^{151} in mixed europium-samarium iron garnets. They obtained (assuming M to be approximately along a $\langle 110\rangle$ direction) a typical value for H_z of 760 kG and typical values for H_x and H_y of 490 and 472 kG. Whether the differences reflect some problem with their interpretation, an erroneous assumption concerning the direction of $\vec{M}$, or a real difference in the parameters remains unclear.

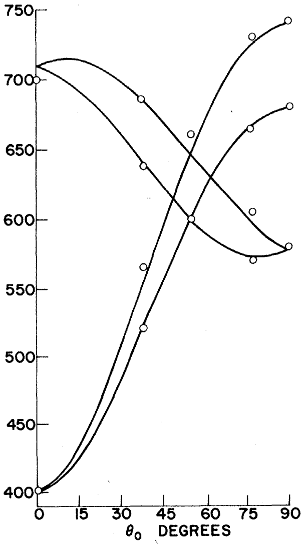

FIG. 3. Eu^{151} frequencies calculated from Eq. (1) as a function of the angle θ_0 in the (110) plane between $\vec{M}$ and the [001] axis, together with experimental points from Fig. 1.

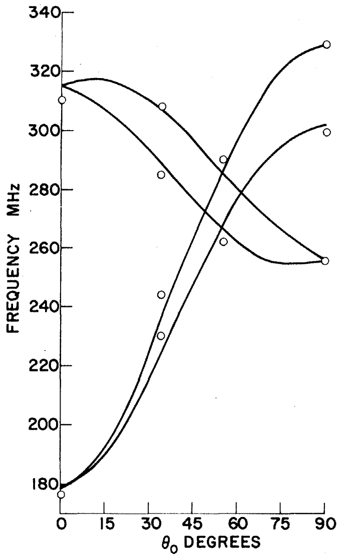

FIG. 4. Calculated Eu^{153} frequencies (obtained by multiplying the Eu^{151} frequencies by a factor of 0.444) together with experimental points from Fig. 2.

B. Quadrupole Effects

For a general direction of H_{eff}, the effective quadrupole interaction can be written

$$\mathcal{H}_Q = \frac{\nu'}{4I(2I-1)}\,[3I_z^2 - I(I+1)]\,, \tag{11}$$

where ν' was defined in (10f). Eu^{151} and Eu^{153} both have $I=\frac{5}{2}$ and quadrupole moments of about 1.16 and 2.92 b, respectively. For $I=\frac{5}{2}$, we expect the usual five-line splitting pattern with a separation between adjacent lines of $\frac{3}{20}|\nu'|$.

Consider the Eu^{153} splittings of Fig. 2. From the splittings of the line centered at 176 MHz we obtain $|\nu'_{zz}| = 186$ MHz; while from the splittings of the lines centered at 300 and 330 MHz (which partially overlap), we obtain $|\nu'_{xx}| = 100$ MHz and $|\nu'_{yy}| = 87$ MHz. For the two types of $\langle 111\rangle$ sites, Bauminger and co-workers[3] obtained values of ν' of -57 MHz and $+38$ MHz, where the negative value corresponds to the site with the higher H_{eff}. To obtain approximate agreement with these values requires that we take $\nu'_{xx} = +100$, $\nu'_{yy} = -87$ MHz. To obtain a negative value of α [Eq. (11c)], we must take $\nu'_{zz} = -186$ MHz.

To obtain the principal values of ν'', we must know the principal values of $\vec{H}_{ex}$. Since, as we will show, most of the anisotropy of $\vec{H}_{eff}$ arises from the anisotropy of $\vec{H}_{ex}$, we can take, to a first approximation, H_{ex} to be proportional to H_{eff}. If we do this and use Eq. (10b) and the relation $\nu''_{xx} + \nu''_{yy} + \nu''_{zz} = 0$, we obtain for ν''_{xx}, ν''_{yy}, and ν''_{zz} values of

168, -6, and -162 MHz, respectively, while for α we obtain a value of -54 MHz.

For the case of Eu^{153}, we can evaluate (10c). Taking $1-R=0.8$,[17] $\mu_B H_{ex}=24\,^\circ\mathrm{K}$,[11] $E_1=352\ \mathrm{cm}^{-1}$,[18] $E_2=1030\ \mathrm{cm}^{-1}$,[19] and taking $\langle r^{-3}\rangle = 49\times 10^{24}\ \mathrm{cm}^{-3}$, we obtain for α a value of -108 MHz, which is somewhat larger than the experimental value.

From (10d) and (10e), we obtain using $1-\gamma_\infty = 70$,[10] $(1-\sigma_2)=0.25$,[20] and $\langle r^2\rangle = 0.26\times 10^{-16}\ \mathrm{cm}^2$,

$$\nu_{zz}''/\Delta_z = 4.1 - 9.4 = -5.3\ \mathrm{MHz/cm}^{-1}\ . \qquad (12)$$

From (12) and similar equations for x and y we finally obtain, for Δ_x, Δ_y, and Δ_z, values of -32, $+1$, and $+31\ \mathrm{cm}^{-1}$, respectively.

If we define $G(z)=H_{ex}(z)/\overline{H}_{ex}$, etc., and use our values of Δ_x, Δ_y, and Δ_z and $|H_x|$, $|H_y|$, and $|H_z|$ in (8), we obtain values of $G(x)$, $G(y)$, and $G(z)$ of about 0.97, 1.22, and 0.81, respectively. These values can be compared with the values obtained by Wickersheim[21] for YbIG of 1.12, 1.24, and 0.64, where the low value corresponds to an axis equivalent to our z axis. We see that the correspondence is quite good. Using these values in Eq. (10b) yields values for ν_{xx}'', ν_{yy}'', and ν_{zz}'' of 153, -4, and -149 MHz and for α a value of -56 MHz. These values are not very different from our previous values.

We have used these values in Eq. (10f) to calculate ν' as a function of θ_0, the angle in the (110) plane. Calculated values of ν' are plotted in Fig. 5 against θ_0. Also plotted are values of ν' obtained from the experimental splittings. We see there is quite good agreement with theory. In particular we obtain for the $\langle 111\rangle$ sites experimental values of ν' of -100 and $+65$ MHz, which are in good agreement with our calculated values. They are also in agreement with the signs of the Mössbauer values, although of a somewhat larger magnitude.

Finally in connection with the values of ν_{xx}'', ν_{yy}'', and ν_{zz}'', we might point out that our values are considerably different from those given in Ref. 3, which were obtained on the assumption that the exchange field parameters and hyperfine field parameters in EuIG and in the mixed Eu-Sm iron garnets were the same.

C. Interpretation of Zero-Field Studies

Although it is somewhat removed from the main trend of the present work, it is of interest to consider the interpretation of the Eu NMR studies in zero field where the signals are expected to arise from nuclei in domain walls. Since the easy magnetization direction in EuIG is the $\langle 111\rangle$ direction, we can consider a 180° wall with the moment at the wall center along a $[1\overline{1}0]$ direction.[22] Since the domain-wall signal might be expected to be largest for moments at the wall center, we might expect the zero-field spectra (Fig. 1 of Ref. 7) to be similar to the $\langle 110\rangle$ spectra. We see that this is in fact the case, which would seem to indicate that the zero-field excitation is largely through 180° domain-wall motion.

V. DISCUSSION

A. Crystal Field Parameters

From optical studies of EuIG, Koningstein[18] obtained energy splittings for the $J=1$ level (relative to the center of gravity of the level at $352\ \mathrm{cm}^{-1}$) of $-34\ \mathrm{cm}^{-1}$, $-4\ \mathrm{cm}^{-1}$, and $38\ \mathrm{cm}^{-1}$. Apart from the fact that there is some ambiguity associated with which of his levels go with which of the orthorhombic axes, there is reasonably good correspondence with our values of Δ. Our values of Δ correspond to $V_2^0 = 77\ \mathrm{cm}^{-1}$ and $V_2^2 = -82\ \mathrm{cm}^{-1}$ (taking the orthorhombic z axis as the quantization direction). These values are roughly consistent with those of Koningstein.

Actually, Koningstein's splittings would not be expected to agree exactly with our values of Δ because of the fact that his splittings reflect the combined effects of the crystal and exchange fields while our values of Δ reflect the crystal field splittings only (some of his levels appear to be deduced from studies at low temperatures where the exchange fields would be important). In order to estimate the effect of the exchange fields on the ${}^7F_1$ splittings, we have assumed an isotropic exchange field of magnitude $\mu_B H_{ex} = 24\,^\circ\mathrm{K}$ along the [111] direction and have calculated (Appendix) the splittings arising from the combined effects of crystal and exchange fields. For the two types of sites, the level splittings become -34, -1.8, and $35.8\ \mathrm{cm}^{-1}$ for the one site and -36.4, 3.3, and $33.1\ \mathrm{cm}^{-1}$ for the other site compared with splittings of -32, $+1$, and $+31\ \mathrm{cm}^{-1}$ from the crystal fields alone.

We see that the effects of the exchange field are not too great, which probably explains the similarity found by Koningstein between the spectra for EuIG

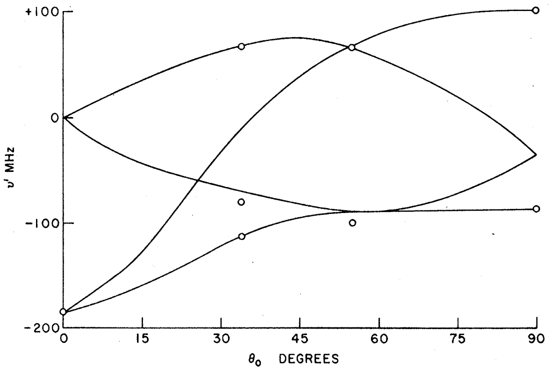

FIG. 5. Values of ν' calculated from Eq. (10f) as a function of θ_0 together with experimental values of ν' from Fig. 2.

and EuGaG.

It is customary in crystal field calculations of the iron garnets to refer the crystal field parameters to a set of local D_2 symmetry axes ξ, η, and ζ. The orientation of these axes with respect to the cubic crystal axes has been discussed by Hutchings and Wolf.[23] The ξ axis corresponds to our z axis, while the η and ζ axes correspond to our x and y axes. If we make the correspondence $z \rightarrow \xi$, $y \rightarrow \eta$, and $x \rightarrow \zeta$, then the new crystal field parameters referred to these axes become $V_2^0 = -80$ cm^{-1}, $V_2^2 = +75$ cm^{-1}. These values of V_2^0 and V_2^2 seem quite reasonable on the following grounds: The value of V_2^0 is in approximate agreement with the value of -70 cm^{-1} deduced from a complete crystal field analysis for Y(Yb)GaG.[24] Also a compilation[25] of the crystal field parameters of various rare-earth gallium garnets shows that V_2^0 for most of the garnets is negative. Furthermore, the ratio of -1.06 for V_2^0/V_2^2 would be consistent with the findings of Koningstein and with the point charge calculations of Hutchings and Wolf.

B. Anisotropic Exchange Interaction

As already discussed, our values of $G(x)$, $G(y)$, and $G(z)$ of 1.0, 1.2, and 0.8, respectively, are in rough agreement with the values of 1.12, 1.24, and 0.64 obtained by Wickersheim from optical studies of YbIG. The corresponding values obtained by Atzmony *et al.*, however, are 1.36 for $G(z)$ and 0.85 and 0.80 for $G(x)$ and $G(y)$. If we neglect crystal field effects, which are responsible for only about 10% of the hyperfine field anisotropy, the principal values of the exchange field are directly proportional to those of the hyperfine field. Consequently, the fact that the Atzmony values for the exchange fields differ from ours appears to be directly related to their different values for the hyperfine fields.

As discussed by Hutchings *et al.*,[26] the representation of the Eu^{+3} ion by its spin operator and the concept of an exchange field acting on the ionic spin should be particularly valid for the Eu^{+3} ion because of the simple level structure of the $J = 1$ level. For rare-earth ions in general, however, the expansion of the anisotropic exchange interaction in terms of exchange potential operators[27,28] appears to be a more valid approach.

Atzmony *et al.*[2] expand the exchange integral in terms of spherical harmonic operators $G_n^m Y_n^m(L, L_z)$ (neglecting terms higher than $n = 2$) and relate the principal values of the exchange tensor to the parameters G_2^0 and G_2^2. From their Eq. (11) we can obtain values of G_2^0 and G_2^2 in terms of $G(x)$, $G(y)$, and $G(z)$. Our values of $G(x)$, $G(y)$, and $G(z)$ correspond to $G_2^0 = -0.02$ and $G_2^2 = -0.01$. Our values of G_2^0 and G_2^2 can be compared with the recalculated values of Wickershiem and White[29] for YbIG which are quoted in the paper by Atzmony: $G_2^0 = -0.03$ and $G_2^2 = 0.07$. We see that our values seem to be in fair agreement with their values, at least as far as the value of G_2^0 is concerned, while the Atzmony values ($G_2^0 = +0.021$ and $G_2^2 = -0.0055$) are not. It is reasonable to believe that the parameters G_2^0 and G_2^2 might be approximately the same in all rare-earth iron garnets. Although the preceding discussion suggests that a negative value of G_2^0 corresponding to a reduced value of $H_{ex}(z)$ relative to $H_{ex}(x)$ and $H_{ex}(y)$ might be a general feature of the rare-earth iron garnets, the approximation of retaining only two terms in the expansion of the exchange potential is probably not a generally valid approximation. A more detailed treatment as recently carried out by Orlich and Hüfner[30] for ErIG, in which all ten parameters of the exchange interaction are determined, is probably in order.

According to Nowik and Ofer,[31] 90% of the exchange field acting on the Eu ion in EuIG is produced by the two nearest-neighbor iron ions in tetrahedral sites. Since these two iron ions lie along the cubic ⟨100⟩ axis, one might expect some symmetry in the exchange fields about this direction. This symmetry is reflected to some extent in the values of the parameters G, but a detailed analysis is needed to arrive at the parameters from first principles.

VI. CONCLUSIONS

The over-all agreement between theory and experiment appears to be quite good with the exception of the calculated value of α, which is somewhat larger than that measured experimentally. This may be due in part to uncertainty in the value of $(1-R)$. Our values of the crystal field splittings and exchange fields appear to be in good agreement with the values obtained from other studies.

As discussed by Wolf,[32] the anisotropy of the exchange field makes a contribution to the magnetocrystalline anisotropy. Levy[33] has discussed the various contributions to the magnetic anisotropy of EuIG and finds the theoretical value of K_1 to be between 1 and 27×10^4 erg/cm^3 compared with an experimental value of -38×10^4 erg/cm^3. This discrepancy between theory and experiment probably lies in the fact that Levy neglected to take into account the anisotropy of the exchange fields, which we find to be quite large. As Levy states, with the anisotropic exchange it is necessary to go to fourth order in the ground-state energy to obtain a contribution to the magnetic anisotropy. Such a calculation would be of considerable interest, but is beyond the scope of the present study.

As we mentioned, the Eu^{+3} hyperfine field parameters which we obtain for EuIG are considerably different from those obtained by Atzmony and coworkers in the mixed Eu-Sm iron garnets. We plan to carry out studies of the Eu^{151} and Eu^{153} NMR in the mixed Eu-Sm iron garnets in order to try to resolve this apparent discrepancy.

APPENDIX

We wish to calculate the splitting of the $^7F_1$ free-ion level under the simultaneous perturbation of the orthorhombic crystal field and the exchange field. The crystal field matrix elements within a given J manifold can be calculated.[34,35]

The exchange field is along the $\langle 111 \rangle$ direction when there is no applied field, and we consider an Eu site with local orthorhombic x axis along [110] and z axis along [001]. In this case $\mathcal{H}_{ex} = 2\mu_B H_{ex} \times [(\sqrt{2})/3\, S_x + (\sqrt{1})/3\, S_z]$, the matrix elements of which are readily evaluated.[11,36] The resulting matrix is

$$\begin{array}{c|ccc|} M_J & 1 & 0 & -1 \\ 1 & J/\sqrt{3} - \frac{1}{5}V_2^0 - W & J/\sqrt{3} & -\frac{1}{5}V_2^2 \\ 0 & J/\sqrt{3} & \frac{2}{5}V_2^0 - W & J/\sqrt{3} \\ -1 & -\frac{1}{5}V_2^2 & J/\sqrt{3} & -J/\sqrt{3} - \frac{1}{5}V_2^0 - W \end{array},$$

where $J \equiv \mu_B H_{ex}$, $V_2^0 \approx 75\ \text{cm}^{-1}$, $V_2^2 \approx -80\ \text{cm}^{-1}$, and $J = 17\ \text{cm}^{-1}$. From the resulting cubic equation the splitting was evaluated as $W_1 = 35.8\ \text{cm}^{-1}$, $W_2 = -1.8\ \text{cm}^{-1}$, and $W_3 = -34\ \text{cm}^{-1}$.

If we consider the nonequivalent site where the exchange field has a y component but no x component, the results are $W_1 = 33.1\ \text{cm}^{-1}$, $W_2 = 3.3\ \text{cm}^{-1}$, and $W_3 = -36.4\ \text{cm}^{-1}$.

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