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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 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 are obtained. Contributions to the electric field gradients and anisotropic hyperfine fields are discussed and compared with theory.

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, however, have been restricted to "zero fields" where the magnetization is along the easy, ⟨111⟩, direction. From Mössbauer data in this direction only, it turns out to be impossible to evaluate independently all three hyperfine-field parameters associated with the orthorhombic symmetry at the rare-earth site. We have studied[7] the NMR of $Eu^{151}$ and $Eu^{153}$ in a single crystal of EuIG with external fields sufficient to align the magnetization along the orthorhombic axes of the rare-earth sites and have determined the hyperfine fields and quadrupole splittings.

The studies were made at 4.2°K using spin-echo equipment by plotting the spin-echo amplitudes as a function of frequency. The crystal, which was roughly spherical and about 1 cm in diameter, was mounted so that it could be rotated about the ⟨110⟩ axis which was parallel to the rf field and perpendicular to the dc field $H_0$. Studies were made with a value of $H_0$ of about 8 kG, sufficient to overcome the anisotropy field of EuIG which is about 5 kG at 4.2°K.[8] The $Eu^{151}$ spectra for the case of $H_0$ along the ⟨110⟩ and ⟨100⟩ directions are shown in Figs. 1(a) and 1(b). Corresponding $Eu^{153}$ spectra are shown in Figs. 2(a) and 2(b). The spin-echo signals at each fre-

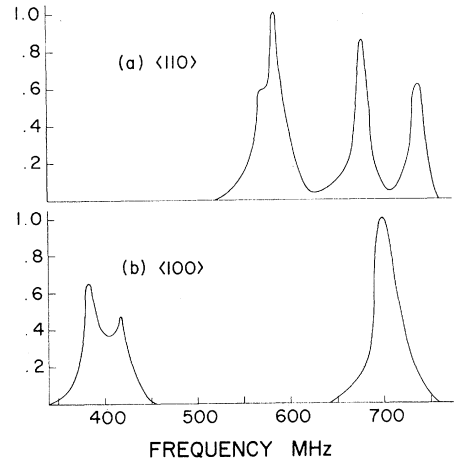


FIG. 1. (a) Corrected (see text) spin-echo spectrum of $Eu^{151}$ at 4.2°K for $H_0$ along the ⟨110⟩ direction; (b) spectrum for $H_0$ along the ⟨100⟩ direction.

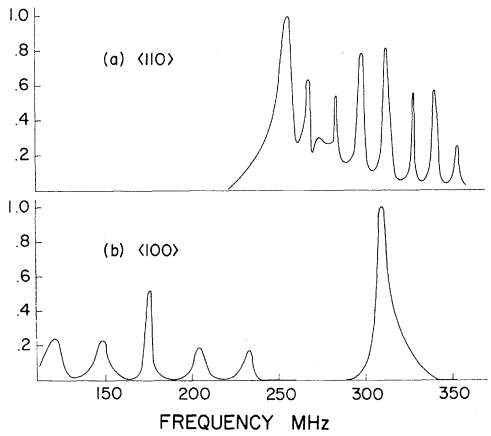


FIG. 2. (a) Spectrum of $Eu^{153}$ at 4.2°K for $H_0$ along the ⟨110⟩ direction; (b) spectrum for $H_0$ along the ⟨100⟩ direction.

quency have been divided by a factor of $\nu^2$ ($\nu$ being the frequency) in order to take into account the frequency dependence of the signal amplitude. The spectra have also been corrected for the differences in the relaxation times, $T_2$, of the various lines.

The hyperfine fields at the $Eu^{+3}$ ions for each of the six magnetically inequivalent rare-earth sites can be written as

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

Here $H_x$, $H_y$, and $H_z$ are the principal values of $H_{\mathrm{eff}}$ along the orthorhombic axes of the rare-earth sites and $n_x$, $n_y$, and $n_z$ are the direction cosines of the magnetization $\vec{M}$ with respect to these local axes. We take the $z$ axis to lie along a cubic $\langle 100\rangle$ direction and $x$ and $y$ as the axes which lie along $\langle 110\rangle$ directions.

For $\vec{M}$ along the $\langle 100\rangle$ 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 $\vec{M}$ along the $\langle 110\rangle$ direction we expect 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. Referring to the $Eu^{151}$ data, and taking $\nu_z = 400$ MHz, $\nu_x = 680$ MHz, and $\nu_y = 740$ MHz, we also expect from Eq. (1) lines at 710 MHz (for the $\langle 100\rangle$ orientation) and at 576 MHz (for the $\langle 110\rangle$ orientation) in agreement with the observed lines. The line at 576 MHz was observed to require a somewhat higher rf pulse level than did the lines at 680 and 470 MHz and we were unable to optimize the echo signal. This is probably the reason the intensity of this line is less than expected.

From the $Eu^{151}$ frequencies we can obtain $|H_x| = 649$ kG, $|H_y| = 706$ kG, and $|H_z| = 382$ kG. Using these values in Eq. (1), we can calculate values of 617 and 573 kG for the hyperfine fields at the two types of sites arising when $M$ is along a $\langle 111\rangle$ direction. These values are in good agreement with the Mössbauer values[1] of $629 \pm 10$ and $571 \pm 10$ kG. (We have neglected the effects of the external field $H_0$ which represents only about 8 MHz in the $Eu^{151}$ frequency.)

Our values of $H_x$, $H_y$, and $H_z$ are considerably different from the values obtained by Atzmony and co-workers from Mössbauer studies of $Eu^{151}$ in the mixed europium-samarium iron garnets. They obtained (assuming $M$ to be approximately along a $\langle 110\rangle$ direction) typical values for $H_x$, $H_y$, and $H_z$ of 490, 472, and 766 kG, respectively.

Consider now the quadrupole splittings. The electric field gradients at the Eu nuclei have been discussed in Ref. 3. Defining a parameter $\nu \equiv e^2qQ/h$, the values of $\nu'$ along the principal axes can be written

$$\nu_{zz}' = \alpha[H_{\mathrm{ex}}(z)/\bar{H}_{\mathrm{ex}}]^2 + \nu_{zz}'', \quad (2)$$

with similar equations for $x$ and $y$. Here the first term is the part of $\nu'$ which arises from the polarization of the $4f$ orbitals by the exchange field (which is axial with respect to the direction of $M$), while the second term is the part of $\nu'$ due to the crystal lattice. Assuming that to a first approximation the exchange fields $H_{\mathrm{ex}}$ are proportional to $H_{\mathrm{eff}}$, we can use the experimental values of $\nu_{zz}'$, etc., to evaluate $\alpha$ and the parameters $\nu''$.

Consider the $Eu^{153}$ splittings of Fig. 2. From the splitting 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. Bauminger, Nowik, and Ofer[3] have, from $Eu^{153}$ Mössbauer studies, obtained values of $\nu'$ for the two types of $\langle 111\rangle$ sites of $-57$ and $+38$ MHz, where the negative value corresponds to the site with the higher hyperfine field. The signs of the parameters $\nu'$ must be chosen so as to give agreement with the Mössbauer values and a reasonable value for the parameter $\alpha$. Taking $\nu_{xx}'$, $\nu_{yy}'$, and $\nu_{zz}'$ to be $+100$, $-87$, and $-186$ MHz, respectively, and using Eq. (2) and the relation

$$\nu_{zz}'' + \nu_{xx}'' + \nu_{yy}'' = 0,$$

we obtain for $\nu_{xx}''$, $\nu_{yy}''$, $\nu_{zz}''$ values of $+168$, $-6$, and $-162$ MHz, while for $\alpha$ we obtain a value of $-54$ MHz. From these parameters the quadrupole fields for a general direction of $H_{\mathrm{eff}}$ can be calculated [see, for example, Eq. (4) of Ref. 3]. For the two types of $\langle 111\rangle$ sites we obtain values of $\nu'$ of $-87$ and $+65$ MHz which are in fairly good agreement with the Mössbauer values.

The exchange polarization contribution to $\nu'$ has been calculated theoretically[3,6] and corresponds to a value of $\alpha$ of about $-87$ MHz which is in reasonably good agreement with our experimental value.[9] Our values of $\nu''$ along the principal axes, however, are quite different from the values obtained in Ref. 3, since the values obtained there depended on the assumption that the hyperfine fields and exchange fields in EuIG and the europium-samarium iron garnets were the same.

The field gradients $\nu_{zz}''$, etc., are a sum of two

terms: (1) A contribution arising from the polarization of the $4f$ orbitals by the crystal fields which can be written[10]

$$(\nu_{zz}'')_1 = (16/15)\Delta_z\langle r^{-3}\rangle e^2Q(1-R)/E_2h, \qquad (3)$$

where $\Delta_z$ is the energy of the $z$ singlet of the $J=1$ level relative to the center of gravity of the level, and $E_2$ is the energy of the $J=2$ level.[11] The quantity $R$ is a shielding correction. (2) A contribution arising from the lattice charges which can be written[12]

$$(\nu_{zz}'')_2 = -10\Delta_z Q(1-\gamma_\infty)/(1-\sigma_2)\langle r^2\rangle, \qquad (4)$$

where $\gamma_\infty$ and $\sigma_2$ are shielding factors.

Taking for the shielding factor $R$ a value[13] of 0.2, taking $(1-\gamma_\infty)$ to be[12] about 70, using for $\sigma_2$ a value[14] of 0.73, taking $Q(\mathrm{Eu}^{153}) = 2.9$ b, and using for the other quantities values appropriate to $\mathrm{Eu}^{+3}$, we obtain from the two contributions

$$\nu_{zz}''/\Delta_z = +3.2-8.6 = -5.4\ \mathrm{MHz/cm}^{-1}. \qquad (5)$$

Using our values of $\nu_{zz}''$, etc., in Eq. (5) and similar equations for $x$ and $y$, we obtain, finally, for $\Delta_x$, $\Delta_y$, and $\Delta_z$, values of $-31$, $+1$, and $+30$ $\mathrm{cm}^{-1}$, respectively.

These values can be compared with values of $-34$, $-4$, and $+38$ $\mathrm{cm}^{-1}$ obtained from optical studies by Koningstein.[15] Apart from the fact that there is some ambiguity associated with which of his levels go with which axes,[16] we see that there is reasonably good agreement with our values.

Finally we will discuss the values of the hyperfine-field parameters. The contributions of the anisotropic exchange fields and of the crystal fields to the hyperfine-field anisotropy can be calculated by using the equations in Ref. 2. The total hyperfine field anisotropy can be written

$$\frac{|H_z|}{|\bar{H}|} = \left(\frac{H_{ex}(z)}{\bar{H}_{ex}}\right) - \frac{\Delta_z}{E_1} - \left(\frac{51}{50}\right)\frac{\Delta_z}{E_2}. \qquad (6)$$

Here $E_1$ and $E_2$ are the energies of the $J=1$ and $J=2$ levels. Similar equations apply for $x$ and $y$. We now define $G_z = H_{ex}(z)/\bar{H}_{ex}$, etc. Using the experimental hyperfine-field parameters to evaluate $|H_z|/|\bar{H}|$, and using the measured[15] energy splittings, we can obtain the anisotropic exchange parameters $G_z$, etc. We find $G_x = 1.00$, $G_y = 1.20$, and $G_z = 0.80$.

Our values of $G_x$, etc., can be compared with the anisotropy of the exchange fields obtained from optical studies by Wickersheim for YbIG.[17] He found principal values of $(H_{ex}/\bar{H}_{ex})$ to be about 1.12, 1.24, and 0.64, where the lowest value corresponds to the orthorhombic axis lying along the crystal $\langle 100\rangle$ direction. We see that there is a considerable degree of correspondence with our values.

The anisotropy of the exchange interactions makes a contribution to the magnetic anisotropy as has been discussed by Wolf.[18] Since the $\langle 100\rangle$ direction is a hard direction of magnetization, the low value of $H_{ex}$ in this direction is in the right direction to account for the anisotropy. Using an equation such as Eq. (5) of Ref. 18, the value of $K_1$ can be calculated in terms of the parameters $G$. Although the value of $K_1$ is quite sensitive to the parameters $G$, they appear to be of about the right magnitude to explain the experimental value of $K_1$, taking into account the other contributions[16] to the anisotropy.

In conclusion, the overall agreement of the hyperfine parameters with theory and the results of other studies appears to be reasonably good. We plan, however, to make more extended studies particularly of the quadrupole splittings and results of these studies will be published at a later date.

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## MAGNETIC HYPERFINE INTERACTION IN DILUTE HEMIN*

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Mössbauer spectra of magnetically dilute hemin solutions have been observed. These are found to be consistent with infrared measurements and with Mössbauer measurements of crystalline hemin. This confirms Blume's interpretation of the Mössbauer spectrum in terms of spin-spin relaxation.

The peculiar temperature dependence of the Mössbauer spectrum of high-spin ferric hemin (iron protoporphyrin IX chloride) was first reported by Shulman and Wertheim.[1] The spectrum at 4.2 K was a symmetric doublet, but with increasing temperature changed to a broad and asymmetric single line. This has been interpreted in terms of electron spin-spin relaxation which is fast at low temperature and which slows with increasing $T$ because of the thermal excitation of the system out of the fast-relaxing ground doublet.[2] Mössbauer measurements at large $H/T$ have confirmed that there is no fortuitous cancellation of the internal field in the ground doublet and, in fact, that a contact field near the usual value of 110 kG per unpaired electron is present.[3] The only puzzling feature has been the failure of attempts to reduce the relaxation rate by diluting the spins.[4] In this Letter we report a successful attempt at spin dilution and confirm that hemin is magnetically similar to high-spin heme proteins,[5,6] differing only in that crystalline hemin has fast spin relaxation and frozen hemin solutions have a range of relaxation rates, corresponding to the various interspin distances which occur.

Hemin chloride was enriched in $^{57}$Fe, diluted to about $10^{-3}M$ in tetrahydrofuran (THF), and examined by Mössbauer spectroscopy. The paramagnetic spectra which were observed are shown in Fig. 1(a) and Fig. 2.

The spectrum observed at 4.2 K in zero applied field is seen to consist of two parts. The first is a narrow component consisting of a quadrupole doublet with splitting $\Delta E = 0.8$ mm/sec, similar to the spectrum of crystalline hemin. This results from $^{57}$Fe sites on which the electron spins are relaxing rapidly. The second part of the zero-field spectrum is a broad component which clearly indicates the presence of a magnetic hyperfine interaction. Its diffuse appearance is characteristic of the $S_z = \pm\frac{1}{2}$ doublet of axially distorted high-spin complexes and probably results from the large number of hyperfine levels caused by transfer of electron spin to neighboring atoms and the resulting coupling of their nuclear spins to the iron-electron system.[7] The broad component is, in fact, very similar to the zero-field spectrum of acid methemoglobin, Fig. 1(b). This suggests that spin transfer to the four porphyrin nitrogens common to both is the dominant effect, and that the ligands above and below the iron,

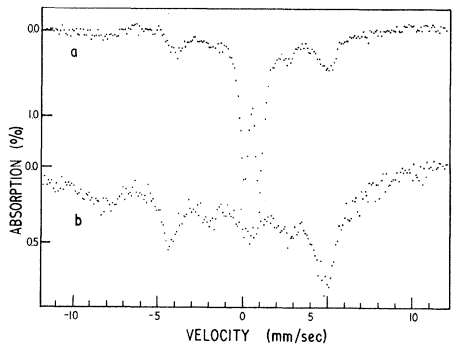


FIG. 1. Spectra observed at 4.2 K in zero applied field of (a) $10^{-3}M$ hemin dissolved in tetrahydrofuran, and (b) $10^{-3}M$ acid metamyoglobin, $p$H 6.