PHYSICAL REVIEW VOLUME 148, NUMBER 1 5 AUGUST 1966

Determination of Eu^{3+}–Fe^{3+} and Eu^{3+}–Gd^{3+} Exchange Interactions from Electron Paramagnetic Resonance Shifts in Europium Gallium Garnet*†

M. T. Hutchings,‡ C. G. Windsor,§ and W. P. Wolf
Hammond Laboratory, Yale University, New Haven, Connecticut

(Received 26 January 1966)

The paramagnetic resonance from Fe^{3+} and Gd^{3+} ions substituted into weakly paramagnetic europium gallium garnet has been investigated at 77°K and 26 Gc/sec. The spectra have been fitted to conventional spin Hamiltonians for Fe^{3+} occupying the $[a]$ site and Gd^{3+} occupying the $\{c\}$ site. No resonance was observed from (d)-site Fe^{3+}, indicating a strong preferential population of the $[a]$ site in these garnets. By comparing the spin-Hamiltonian parameters found with those for other *diamagnetic* garnets, shifts due to the interaction of the substituted ions with the Eu^{3+} host lattice have been determined. A general theory for shifts of S-state ion resonances in europium compounds is developed and used to give *quantitative* estimates of the interactions in the garnet. From the shift in the Fe^{3+} g values, the isotropic part of $Eu^{3+}\{c\}$-$Fe^{3+}[a]$ interaction is found to be small and ferromagnetic in sign, $J_{is}\sim -0.016$ cm^{-1} (where $\mathcal{H}=+J_{is}\mathbf{S}^1\cdot\mathbf{S}^2$), and comparable anisotropic interactions are indicated. Moreover, a large apparent shift observed in the parameter D suggests a dominant antisymmetric (Moriya) interaction of at least $\sim$1 cm^{-1} between these ions, which is unobservable in the ordered concentrated iron garnet. The shifts in the Gd^{3+} g values are well explained by an isotropic exchange of the magnitude expected, $J_{is}\sim +0.07$ cm^{-1}, together with the calculated magnetic dipole interaction.

I. INTRODUCTION

There are six types of interactions between the magnetic ions on different crystal sites of the rare-earth garnets which are all potentially important for the understanding of the bulk properties. The large interactions between the Fe^{3+} spins have been studied extensively by analyses of measurements on yttrium-iron-garnet (YIG)[1–7] but there has been relatively little quantitative information on the rather smaller interactions involving the rare-earth ions. Such analyses as have been reported almost all give information on the *average* effect of the spins on different sites (generally in terms of a single molecular field coefficient), and only recently has there been any indication that some of the rare-earth–Fe^{3+} interactions are much weaker than others.[8–10] One of the most interesting, and from a theoretical point of view, one of the simplest, rare-earth ions is Eu^{3+}, and we have therefore carried out some detailed measurements on doped europium gallium garnet (EuGaG) which can be interpreted in terms of specific interaction Hamiltonians between Eu^{3+} and Fe^{3+} and Eu^{3+} and Gd^{3+} in this lattice.

The method used was to measure the ESR exchange shift as described recently by Hutchings and Wolf[11] and Rimai and Bierig.[12] The shift in the ESR spectrum of a particular paramagnetic ion, the A spin, arises from interactions with neighboring magnetic ions, the B spins, and is observable if the interactions do not at the same time broaden the A-ion resonance. This situation arises at low temperatures when the B spins have a nondegenerate ground state. To first order such a singlet ground state is nonmagnetic, but off-diagonal matrix elements to excited states can produce admixtures which give the B spins a weak but *time-independent* magnetic moment. The interaction of this moment with the A spins does then not produce any line broadening. Theoretical expressions for the increase in line broadening as the temperature is raised and excited states of the B spins are populated have been given by Moriya and Obata,[13] who also discuss the formal theory for the exchange shift.

In order to identify a shift due to magnetic interactions it is first necessary to estimate the spectrum in the absence of the interactions, i.e., for the ion in an otherwise similar but diamagnetic environment. In general, this may be quite difficult, as paramagnetic-resonance spectra tend to be quite sensitive to small changes in environment, especially in the garnets,[14] but it may still be possible to interpolate parameters from measurements on a number of structurally similar diamagnetic host lattices.[11] A specially simple situation

---

* This work was supported in part by the U. S. Atomic Energy Commission.

† A preliminary account of the results was presented at the Kansas meeting of the APS: Bull Am. Phys. Soc. **10**, 329 (1964).

‡ Present address: Clarendon Laboratory, Oxford, England.

§ Present address: Atomic Energy Research Establishment, Harwell, England.

[1] R. Pauthenet, Ann. Phys. **3**, 424 (1958).

[2] P. J. Wojtowicz, J. Appl. Phys. **33**, 1257 (1962), and Phys. Letters **11**, 18 (1964).

[3] A. B. Harris, Phys. Rev. **132**, 2398 (1963).

[4] E. E. Anderson, Phys. Rev. **134**, A1581 (1964).

[5] S. Geller, H. J. Williams, G. P. Espinosa, and R. C. Sherwood, Bell System Tech. J. **43**, 565 (1964). (This paper also contains a number of other references.)

[6] B. Lüthi and T. Henningsen, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (The Institute of Physics and The Physical Society, London, 1965), p. 668.

[7] E. Prince, J. Appl. Phys. **36**, 1845 (1965).

[8] R. C. LeCraw, J. P. Remeika, and H. Matthews, Phys. Letters **12**, 9 (1964); J. Appl. Phys. **36**, 901 (1965).

[9] E. E. Anderson, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (The Institute of Physics and The Physical Society, London, 1965), p. 660.

[10] S. Geller, H. J. Williams, R. C. Sherwood, and G. P. Espinosa, J. Appl. Phys. **36**, 88 (1965).

[11] M. T. Hutchings and W. P. Wolf, Phys. Rev. Letters **11**, 187 (1963).

[12] L. Rimai and R. W. Bierig, Phys. Rev. Letters **12**, 284 (1964).

[13] T. Moriya and Y. Obata, J. Phys. Soc. Japan **13**, 1333 (1958).

[14] W. P. Wolf, M. Ball, M. T. Hutchings, M. J. M. Leask, and A. F. G. Wyatt, J. Phys. Soc. Japan Suppl. B-I, **17**, 443 (1962).

arises when the A spins are in S states, since the g values are then very close to 2 and almost completely independent of any diamagnetic environment. This is the case for the both Fe^{3+} and Gd^{3+}, the two ions we have studied, for which even small g shifts can be identified quite unambiguously. Other parameters in the spin Hamiltonian of S-state ions are not quite so insensitive to changes in the environment, but a large shift such as we have observed in the case of the Fe^{3+} spectrum may be interpreted with reasonable confidence.

In the only previous measurements of exchange shifts which have been reported[11,12] the B spins used were Tm^{3+}, for which the electronic states are the result of a relatively complex and unknown crystal field, so that no quantitative estimates of exchange interactions could be made. For Eu^{3+} the situation is very much more favorable since the ground state, even in a solid, is well described by the simple term $^7F_0$ with three excited states $^7F_1$ about 350 cm^{-1} higher. The excited state is split by the crystal field and these splittings have recently been investigated by Koningstein[15] for our particular case of EuGaG. Since Koningstein's measurements were made in zero magnetic field the three states cannot be identified individually, but the measurements show that the splittings are relatively small so that it is a good approximation to take the levels to be degenerate close to their mean energy. This enables one to make quantitative estimates of the matrix elements involved in the exchange shifts and to predict the shifts to be expected from various forms of interactions.

The general theory for interaction shifts is discussed in Sec. VII in a form which makes it readily applicable to a wide range of situations. The applications to the special cases of the Fe^{3+} and Gd^{3+} spectra in EuGaG are discussed in Secs. VIII and IX. The experimental measurements and their analysis in terms of suitable spin Hamiltonians are first described in Secs. II, III, IV, and V, and the shifts in the parameters due to the magnetic interactions in Sec. VI. Some possible implications of the results on the interpretation of the properties of europium iron garnet (EuIG) are discussed in Sec. X. The conclusions are summarized in Sec. XI.

II. EXPERIMENTAL METHOD

Crystals of EuGaG were grown from a PbO-PbF_2 flux in the usual manner[16] by S. Mroczkowski of this laboratory. The melts were doped with a wide range of Fe^{3+} concentrations (0.01% to 3%) in an attempt to produce crystals with Fe^{3+} ions on both the $[a]$ and (d) sites (see below). No analysis of the samples was made, but judging from the color there was a strong correlation between the composition of the melt and the crystals. Several different batches of Eu_2O_3 were used (Lindsay Code 1014, 99.99%; and Code 1014.92, 99.999%) in an attempt to eliminate the Gd^{3+} spectrum which was found in all samples, but even in the best crystals the Gd^{3+} lines were clearly visible and had to be identified before the Fe^{3+} spectrum could be investigated.

No attempt was made to shape the samples, but all the crystals used were roughly spherical. An order-of-magnitude estimate showed that the effect of any uncertainty in sample shape was negligible. The crystals were aligned with x rays (±1°), final adjustments being made with the sample in the spectrometer while observing the resonance from the Gd^{3+} impurities. Since these lines were narrow any splitting due to misorientation could easily be observed. The magnetic field **H** was parallel to a $\{110\}$ plane during all the experiments described here.

Experiments were carried out at 4.2, 20.4, 77, and 300°K in a conventional transmission spectrometer operating at about 26 Gc/sec, with 115 kc/sec modulation and lock-in detection.[17] The magnetic field was supplied by a 12-in. Varian magnet with *Field-dial* stabilization, and was measured with proton and lithium NMR. The microwave frequency was measured with a calibrated wavemeter, accurate to 1 part in 5000, which was checked against the known g value of the free radical diphenyl picryl hydrazyl.

III. CRYSTAL STRUCTURE

The crystal structure of the garnets has been discussed extensively by several authors[18–20] and we shall here summarize only those features necessary for the interpretation of our measurements. The rare-earth ions occupy the 24 pseudo-cubic $\{c\}$ sites with D_2 symmetry, while the Fe^{3+} and Ga^{3+} ions generally occupy the 16 octahedral $[a]$ sites with C_{3i} point symmetry and the 24 tetrahedral (d) sites with S_4 point symmetry. In pure garnets both the $[a]$ and (d) sites are completely filled with either Fe^{3+} or Ga^{3+}, but in a mixed garnet there is a marked preference for the Ga^{3+} ions to occupy the (d) sites and the Fe^{3+} ions the $[a]$ sites. Thus in Fe-doped YGaG, Geschwind[20] found only about 10% of all Fe ions on (d) sites, and we might have expected a similar distribution in EuGaG. However in spite of an intensive search we have been unable to find any resonances due to Fe^{3+} on (d) sites and we must tentatively conclude that in this lattice the site preference for the $[a]$ site is greater than 50:1. It is just possible that the (d) site resonance was not observed for other reasons and these are discussed in Sec. IX, but from a practical point of

---

[15] J. A. Koningstein, J. Chem. Phys. 42, 3195 (1965).

[16] J. W. Nielsen, J. Appl. Phys. 31, 51S (1960).

[17] M. T. Hutchings, D. Phil. thesis, Oxford, 1963 (unpublished).

[18] S. Geller and M. A. Gilleo, J. Phys. Chem. Solids 3, 30 (1957).

[19] M. A. Gilleo and S. Geller, J. Phys. Chem. Solids 10, 187 (1959).

[20] S. Geschwind, Phys. Rev. 121, 363 (1961).

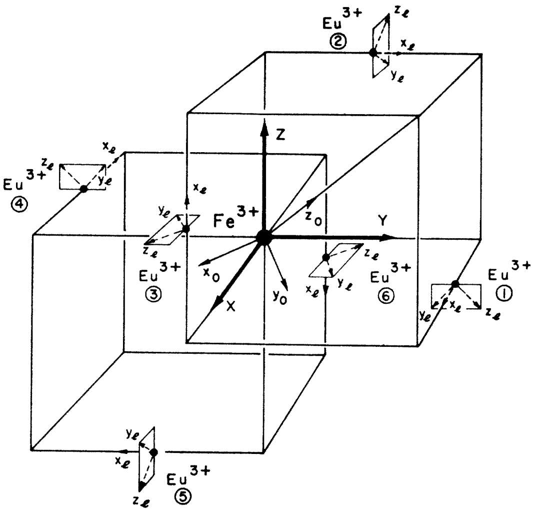

FIG. 1. Location of six nearest $Eu^{3+}\{c\}$ site neighbors to a given $Fe^{3+}[a]$ site. (X,Y,Z) are the axes of the cubic unit cell; local axes (x_0,y_0,z_0) are defined at the Fe^{3+} site, such that z_0 lies along the [111] direction and x_0 lies in the [1̄10] direction. Local axes (x_l,y_l,z_l) are defined at the $Eu^{3+}\{c\}$ sites to lie along the D_2 symmetry axes, such that x_l lies along a ⟨001⟩ direction and z_l lies along the pseudofourfold direction.

view we need from here on consider only the resonance of Fe^{3+} spins on $[a]$ sites.

There are eight inequivalently oriented $[a]$ sites, as described by Geschwind,[20] which produce four different spectra with a field applied in a {110} plane. These will be labeled A, B, C, and D. There are six inequivalently oriented $\{c\}$ sites which also produce four different spectra with a field in a {110} plane.[14] These will be labeled A', B', C', and D'.

In addition to the point symmetry we must consider the number and position of the magnetic neighbors to a given Fe^{3+} or Gd^{3+} spin. These are indicated in Figs. 1 and 2. It may be seen that any Fe^{3+} spin on a given $[a]$ site has six equidistant Eu^{3+} neighbors which are related to one another by 120° rotations about the threefold (z_0) axis and inversion through the center, while each Gd^{3+} has four nearest Eu^{3+} neighbors related by 180° rotations. The local (D_2) symmetry axes (x_l,y_l,z_l) at the various Eu^{3+} sites are thus not all parallel and this must be taken into account in summing the effect of the several neighbors. The simplest procedure in practice is to evaluate all the effects due to one given Eu^{3+} neighbor (we shall use the neighbors labeled 1 and 1′ in Figs. 1 and 2), and to find the effects of the others by direct transformation of the different tensor elements using appropriate rotation matrices. This procedure will be described in Sec. VIII.

IV. SPIN HAMILTONIANS

The terms occurring in the spin Hamiltonian of any given ion depend only on the point symmetry, and we can therefore use the previous analyses of the spectra of Fe^{3+} and Gd^{3+} in various diamagnetic garnets. Following Geschwind,[20] we take for the spin Hamiltonian of an Fe^{3+} spin on an $[a]$ site:

$$\begin{aligned}\mathcal{H}=&\,g_{\shortparallel}\mu_BH(\cos\theta)S_z+\tfrac{1}{2}g_\perp\mu_BH(\sin\theta)(S_++S_-)\\&+D[S_z^2-\tfrac{1}{3}S(S+1)]-(1/180)(a-F)\{35S_z^4\\&-30S(S+1)S_z^2+25S_z^2-6S(S+1)+3S^2(S+1)^2\}\\&+(a\sqrt{2}/36)[S_z(S_+^3e^{i3(\phi\mp\alpha)}+S_-^3e^{-i3(\phi\mp\alpha)})\\&\qquad+(S_+^3e^{i3(\phi\mp\alpha)}+S_-^3e^{-i3(\phi\mp\alpha)})S_z],\end{aligned}\tag{1}$$

where θ, α, and ϕ specify the orientation of **H** relative to the local symmetry axes.[20]

ESR spectra of Gd^{3+} in garnets have previously been observed and analyzed by Rimai and deMars[21] and by Overmeyer *et al.*[22] The spin Hamiltonian, referred to the local D_2 symmetry axes, may be written as

$$\begin{aligned}\mathcal{H}=&\,\mu_B(g_xH_xS_x+g_{yy}HS_y+g_zH_zS_z)+B_2^0O_2^0+B_2^2O_2^2\\&+B_4^0O_4^0+B_4^2O_4^2+B_4^4O_4^4+B_6^0O_6^0\\&+B_6^2O_6^2+B_6^4O_6^4+B_6^6O_6^6,\end{aligned}\tag{2}$$

where the $O_n{}^m$ are the standard spin operators.[23] The form of this spin Hamiltonian, though not of course its coefficients, is the same for all the six possible identifications of x, y, and z with the local x_0, y_0, z_0 axes. Following the now generally accepted convention[24] we choose x to lie along the local D_2 axis parallel to a crystallographic ⟨001⟩ axis,[25] but there is some ambiguity in defining the z axis. This is because the sites occur in inequivalent pairs which are related by a 90° rotation about the local x axis and whose spectra therefore have the same general form.[24] However, if we assume, as seems reasonable, that the symmetry of the spectrum reflects the pseudofourfold symmetry of the eight nearest O^{2-} neighbors about one of the axes perpendicular to Ox we may identify Oz as that D_2 axis which leads to a more nearly tetragonal form for the final spin Hamiltanian and we shall follow this choice. The ambiguity between Oy and Oz can only be resolved with complete certainty by further experiments, such as a measurement of the ENDOR spectrum due to the O^{2-} neighbors.

As mentioned above, there are in general four superimposed spectra due to each of the $Fe^{3+}[a]$ sites and the $Gd^{3+}\{c\}$ sites when **H** is applied in a {110} plane. For **H** along ⟨001⟩ these spectra coalesce to, respectively, 5 and 14 lines, while for **H** along ⟨110⟩ the spectra expand to 10 and 21 lines. The coincidences in the Gd^{3+}

---

[21] L. Rimai and G. A. deMars, J. Appl. Phys. 33, 1254 (1962).

[22] J. Overmeyer, E. A. Giess, M. J. Freiser, and B. A. Calhoun, in *Proceeding of the First International Conference on Paramagnetic Resonance, Jerusalem* (Academic Press Inc., New York, 1963), Vol. I, p. 224; B. A. Calhoun and M. J. Freiser, J. Appl. Phys. 34, 1140 (1963).

[23] D. A. Jones, J. M. Baker, and D. F. D. Pope, Proc. Phys. Soc. (London) 74, 249 (1959). See also M. H. Weiler and D. W. Wylie, Proc. Phys. Soc. (London) 85, 608 (1965).

[24] See, for example, M. T. Hutchings and W. P. Wolf, J. Chem. Phys. 41, 617 (1964).

[25] This convention is not the same as that used in some of our earlier papers, see, for example, Ref. 14.

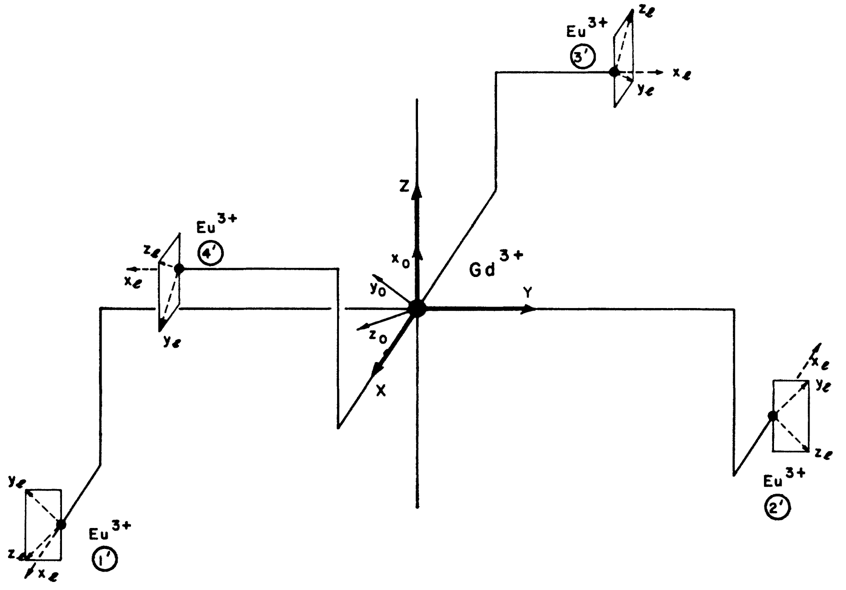

FIG. 2. Location of four nearest Eu$^{3+}\{c\}$ site neighbors to a given Gd$^{3+}\{c\}$ site. (X,Y,Z) are the axes of the cubic unit cell. (x_0,y_0,z_0) and (x_l,y_l,z_l) are axes defined at each $\{c\}$ site such that Ox_l is along a $\langle 001 \rangle$ direction and Oz_l is the pseudofourfold direction.

spectrum provided a convenient and accurate means of checking and adjusting the alignment of the sample relative to the plane of the magnetic field.

V. EXPERIMENTAL RESULTS

At room temperature only one broad resonance centered on $g=2$ was observed, but on cooling to 77°K a spectrum of about 40 well-resolved lines developed. Linewidths were generally similar to those found for dilute impurities in diamagnetic garnet host lattices ($\sim$20 G). All the major lines were identified from their number and angular variation as arising from either Fe^{3+} occupying $[a]$ sites or Gd^{3+} occupying $\{c\}$ sites. The Gd^{3+} lines were generally smaller than those from Fe^{3+} and became considerably less intense when high-purity Eu$_2$O$_3$ was used in the preparation of the samples. A very careful search at temperatures between 77 and 4.2°K was made for resonances from Fe^{3+} ions occupying the (d) sites, but none could be positively identified. In order to carry out this search it was found to be necessary to identify all the Gd^{3+} impurity lines, and it was mainly for this reason that the Gd^{3+} spectrum was investigated in detail. However, the resulting spin Hamiltonian parameters do enable us to estimate the size and nature of the Eu^{3+}-Gd^{3+} interactions as well as the more important Eu^{3+}-Fe^{3+} interaction found from the Fe^{3+} spectrum. Very many weak lines, of the order of magnitude expected for pair transitions were observed in some of the more concentrated samples, and we were able to make an estimate of the preference of Fe^{3+} ions for the $[a]$ site over the (d) site as at least 50:1.

The details of the experimental results, the method of fitting the spin Hamiltonian, and the final parameters will be discussed for each ion separately in the next two subsections.

Fe$^{3+}[a]$ Site Spectrum

The angular variation of the resonance field for the lines attributed to Fe^{3+} in $[a]$ sites is shown in Fig. 3. It may be seen that the over-all splittings are relatively small, a factor of 5 smaller than for the corresponding spectrum in several diamagnetic garnets,[12,20] and many of the inner lines were therefore unresolved over at least part of the angular variation. It was thus necessary to deduce the spin Hamiltonian parameters from a combination of measurements on several lines, rather than the variation of some single lines as had been possible in earlier cases.[20]

To find the spin Hamiltonian parameters, careful measurements were made of all the well-resolved resonance lines when the magnetic field was along the crystallographic [001], [111], and [110] axes, and these were fitted to general expressions for the theoretical line positions using an IBM 709 computer. The iterative fitting procedure used for finding the best values for the six unknowns from the measurements was that due to Powell.[26] The theoretical line position could be calculated to sufficient accuracy by second-order perturbation theory, using the computer to transform the crystal-field terms into a representation in which the Zeeman energy was diagonal. The accuracy of the perturbation theory was checked by comparison with an exact diagonalization with **H** parallel to the three crystallographic axes, using the final set of parameters. The agreement in **H** was better than 2 G. A comparison between the observed and calculated line positions for **H** along the three principal crystallographic directions is shown in Table I. The discrepancies are all within the estimated experimental errors, the main uncertainty arising from the incomplete resolution of some of the

---

[26] M. J. D. Powell, Computer J. **7**, 155 (1964).

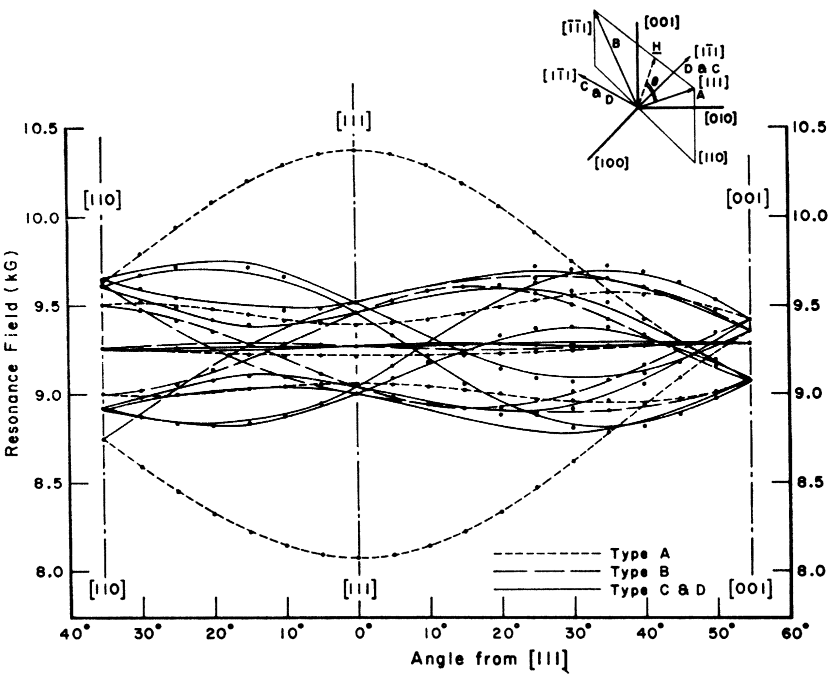

FIG. 3. Angular variation of $Fe^{3+}[a]$ site spectrum at 77°K and 25 981 Mc/sec when the magnetic field is rotated in a {110} plane. The dots represent the experimental points, and the lines the theoretical angular variation calculated from the parameters given in Table II. *A*, *B*, *C*, and *D* refer to the spectra from the four inequivalently oriented sites shown.

TABLE I. Experimental resonance fields, in gauss and difference between calculated and experimental fields (ΔH), for $Fe^{3+}[a]$ site spectrum at 77°K and 25 981 Mc/sec.

Transition[a]	[111] Turning (*A*)		[111] Crossing (*B*,*C*,*D*)		[001] Crossing (*A*,*B*,*C*,*D*)		[110] Crossing (*A*,*B*)		[110] Crossing (*C*,*D*)	
	H_{expt}	ΔH	H_{expt}	ΔH	H_{expt}	ΔH	H_{expt}	ΔH	H_{expt}	ΔH
$\frac{3}{2}\rightarrow\frac{5}{2}$	10376	−3	9004	0	9081[b]	8	9649[b]	−17	8923[b]	−10
$\frac{1}{2}\rightarrow\frac{3}{2}$	9397	+1	9048	−2	9419	3	9506	+1	8923[b]	+6
$-\frac{1}{2}\rightarrow\frac{1}{2}$	9217	+5	9279	−1	9293	−3	9263[b]	+2	9263[b]	−7
$-\frac{3}{2}\rightarrow-\frac{1}{2}$	9063	+1	9465	−3	9081[b]	−7	9005	−4	9615[b]	−9
$-\frac{5}{2}\rightarrow-\frac{3}{2}$	8079	−2	9519	−5	9360	−1	8744	−1	9649[b]	+8

[a] Lines labeled by main component of wave function when **H**∥[111].
[b] Not fully resolved.

TABLE II. Experimental spin Hamiltonian parameters for $Fe^{3+}[a]$ in EuGaG, measured at 77°K and 25 981 Mc/sec and corresponding values for diamagnetic lattices.

Host lattice Lattice constant (Å)[a]	EuGaG (77°K[b]) 12.407	YGaG[c] (4.2°K) 12.280	LuGaG[d] 12.188	YAlG[d] 12.000	LuAlG[d] 11.906
$g_{\parallel}$	2.012 (±0.001)	2.003 (±0.001)	2.001	2.0015	2.001
$g_{\perp}$	2.001 (±0.001)	2.003 (±0.001)	2.001	2.0015	2.001
D cm^{-1}	−0.0215 (±0.0001)	−0.1320 (±0.0004)	−0.1290	−0.1053	−0.0935
a cm^{-1}	+0.018[e] (±0.002)	+0.0189 (±0.0007)	+0.0174[e]	+0.0205[e]	+0.0292[e]
F cm^{-1}	+0.0019 (±0.0008)	+0.0034 (±0.0007)	−0.0043	+0.0027	+0.0064
α (deg)	26.8[e] (±1.0)	28	28[e]	27.5[e]	27.5[e]

[a] E. Euler (private communication).
[b] Values determined at 20°K lie within the error quoted.
[c] Reference 20.
[d] Reference 12.
[e] We assume here that for these lattices *a* has the sign of that in YGaG.

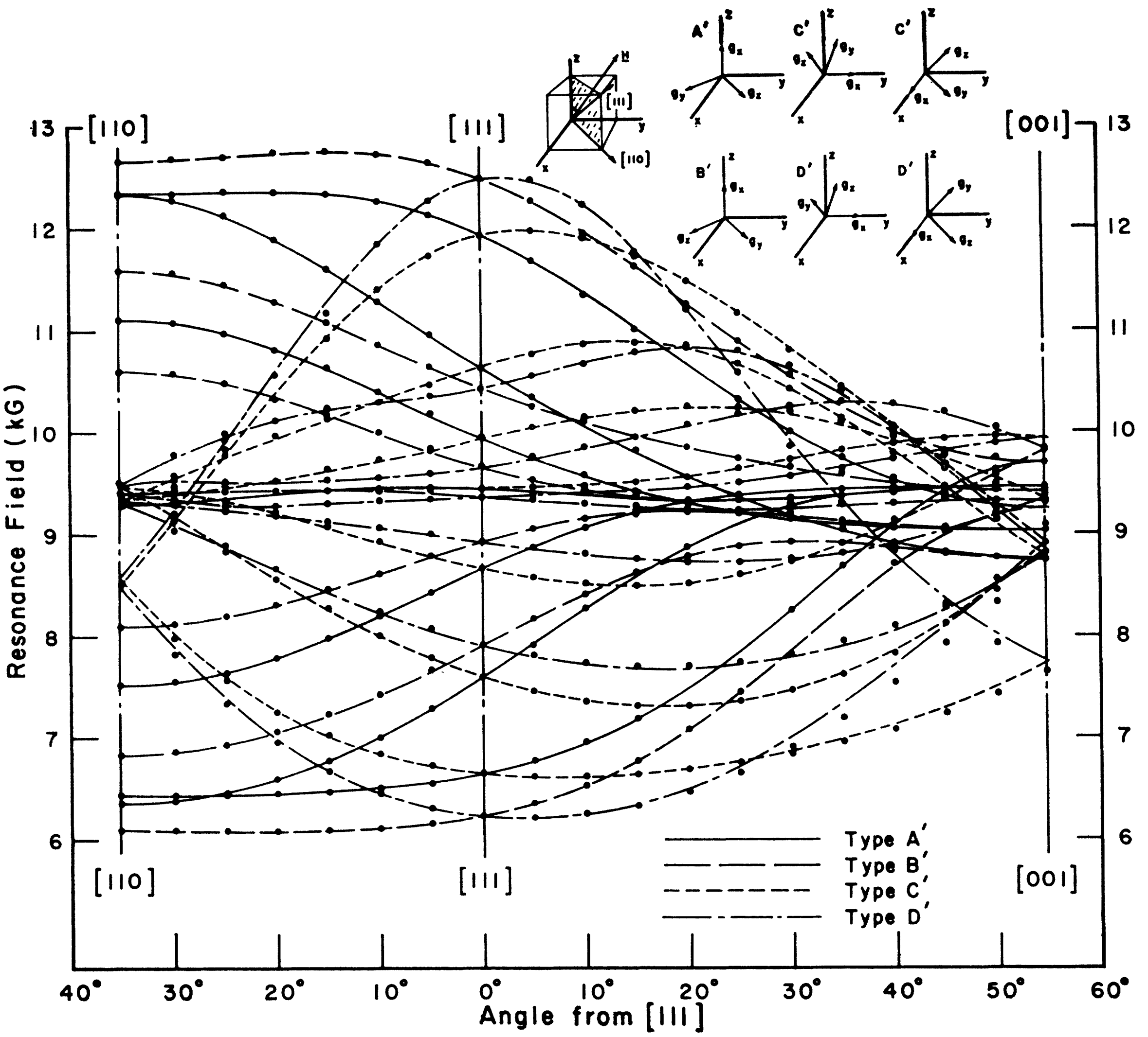

FIG. 4. Angular variation of $Gd^{3+}\{c\}$ site spectrum at 77°K and 25 995 Mc/sec when the magnetic field is rotated in a {110} plane. The dots represent the experimental points, and the lines the theoretical angular variation calculated from the parameters given in Table IV. *A′*, *B′*, *C′*, and *D′* refer to the spectra from the four inequivalently oriented sites shown.

lines. The final parameters are shown in Table II. The errors were estimated from the small spread of values obtained by fitting different combinations of experimental lines to the spin Hamiltonian. The sign of D was obtained from the increase in intensity of the low-field line at low temperatures.

The final parameters were used to calculate the theoretical angular variation of the spectrum as shown by the solid and broken lines in Fig. 3. This calculation was performed on the computer as described above using second-order perturbation theory and it can be seen that the agreement was generally very satisfactory. The small discrepancy of some of the C and D site lines is not due to inaccuracy in the perturbation theory, but probably reflects the relatively large errors in a and α which are least well determined by the fitting procedure used. The three parameters $g_{\parallel}$, $g_{\perp}$, and D, which are of interest for the exchange shift calculations are, on the other hand, well determined by this analysis.

$Gd^{3+}\{c\}$ Site Spectrum

The weaker resonances due to the Gd^{3+} trace impurities in the crystals varied in intensity according to the purity of the Eu_2O_3 used in preparation. However a large number of small lines, about 15 G wide due to Gd^{3+}, were always present and had to be identified in order to distinguish them from possible resonances due to Fe^{3+} in the tetrahedral (d) sites.

The observed angular variation of the Gd^{3+} spectrum with **H** in a {110} plane is shown in Figs. 4 and 5. The lines can be identified as four separate spectra of seven

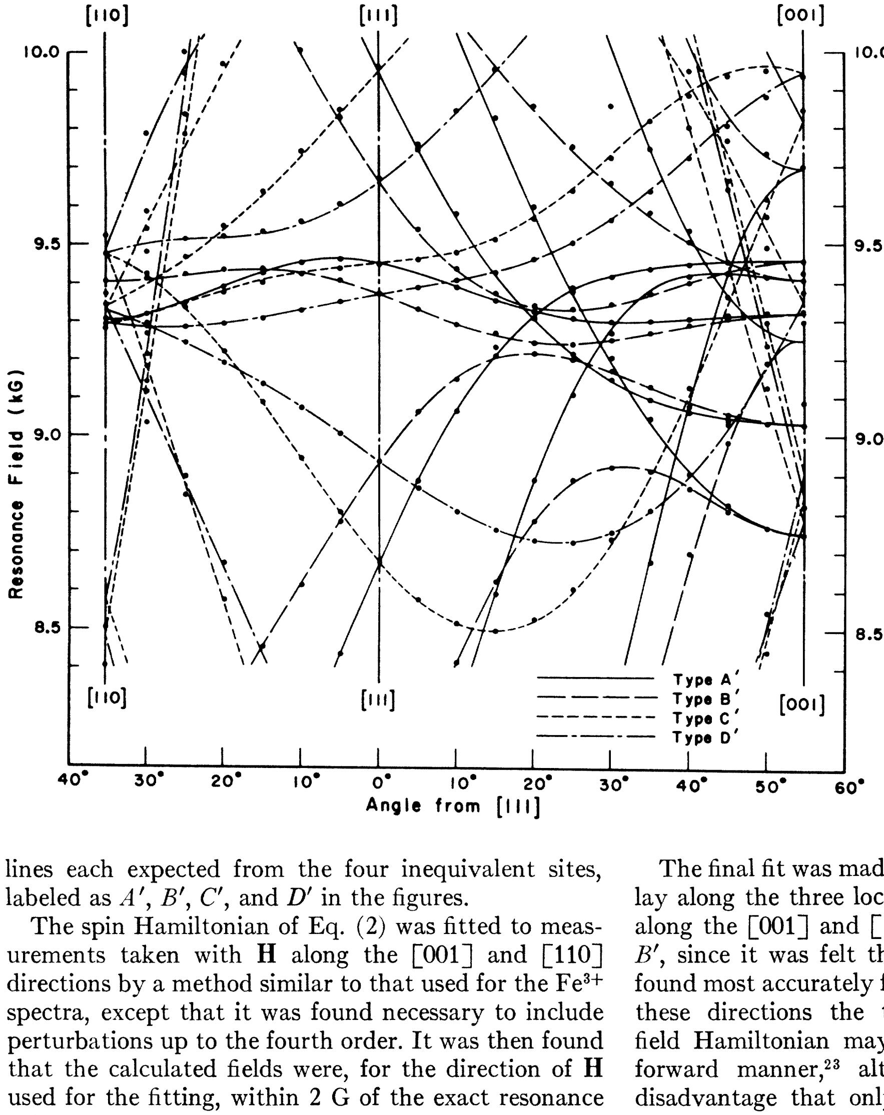

FIG. 5. Central portion of the angular variation shown in Fig. 4.

lines each expected from the four inequivalent sites, labeled as A', B', C', and D' in the figures.

The spin Hamiltonian of Eq. (2) was fitted to measurements taken with **H** along the [001] and [110] directions by a method similar to that used for the Fe^{3+} spectra, except that it was found necessary to include perturbations up to the fourth order. It was then found that the calculated fields were, for the direction of **H** used for the fitting, within 2 G of the exact resonance fields from direct diagonalization of the Hamiltonian, compared with errors of the order of 10 G if only second-order perturbation was used. In certain regions of the angular spectrum even fourth-order theory was noticeably inaccurate (see Figs. 4 and 5).

The final fit was made to the resonance fields when **H** lay along the three local axes, Ox, Oy, and Oz, that is along the [001] and [110] directions for sites A' and B', since it was felt that the three g values could be found most accurately from these spectra. Moreover for these directions the transformations of the crystal field Hamiltonian may be found in a very straightforward manner,[23] although there is also a minor disadvantage that only the combination of $B_6^2+B_6^6$ can be determined. Both of these, however, are very small in our case.

A comparison between the line positions observed and calculated from the fitted parameters is shown in Table III. It may be seen that the agreement is excel-

TABLE III. Experimental resonance fields, in gauss, and differences between calculated and experimental fields (ΔH), for $Gd^{3+}\{c\}$ site spectrum at 77°K and 25 995 Mc/sec.

Transition[a]	[110] Turning (A') H_{expt}	ΔH	[110] Turning (B') H_{expt}	ΔH	[001] Turning ($A'B'$) H_{expt}	ΔH	[111] Crossing ($A'C'$) H_{expt}	ΔH	[111] Crossing ($B'D'$) H_{expt}	ΔH
$\frac{5}{2}\rightarrow\frac{7}{2}$	6 432.7	+1.5	12 671.3	−0.8	9 696.2	−3.3	6 657.5	−5.4	12 491.5	+0.7
$\frac{3}{2}\rightarrow\frac{5}{2}$	6 355.4	−4.3	11 594.6	0.0	9 409.2	+1.0	7 596.8	+2.8	10 445.8	−1.3
$\frac{1}{2}\rightarrow\frac{3}{2}$	7 519.1	−2.4	10 608.9	−0.1	9 456.1	+2.5	8 673.3	+0.5	9 668.5	−8.0
$-\frac{1}{2}\rightarrow+\frac{1}{2}$	9 305.8	+0.1	9 405.5	−2.1	9 323.8	−6.2	9 448.1	+3.6	9 370.8	−1.1
$-\frac{3}{2}\rightarrow-\frac{1}{2}$	11 114.3	+1.7	8 100.3	−0.6	9 027.5	+4.5	9 960.5	−13.7	8 934.9	+3.4
$-\frac{5}{2}\rightarrow-\frac{3}{2}$	12 333.6	+1.4	6 831.3	+2.4	8 747.1	+0.4	10 644.7	+2.4	7 923.3	−4.5
$-\frac{7}{2}\rightarrow-\frac{5}{2}$	12 343.3	−1.5	6 081.9	+0.6	···	···	11 935.2	+3.5	6 232.3	−1.8

[a] Lines labeled by the main component of the wave function for site A', when H was parallel to [110].

TABLE IV. Experimental spin Hamiltonian parameters for $Gd^{3+}\{c\}$ in EuGaG measured at 77°K and 25 995 Mc/sec, and corresponding values for diamagnetic lattices.

Lattice	EuGaG (77°K[b])	YGaG[c] (300°K)	LuGaG[c] (4.2°K)	YAlG[d] (4.2°K)	LuAlG[c] (300°K)
Lattice constant Å[a]	12.407	12.280	12.188	12.000	11.906
g_x	1.984(±0.001)	1.991	1.99	1.990	1.989
g_y	1.984(±0.001)	1.991	1.99	1.990	1.989
g_z	1.987(±0.001)	1.991	1.99	1.990	1.989
$B_2^0\times10^4$ cm^{-1}	198.3(±0.3)	146.9	93	258.8	190.5
$B_2^2\times10^4$ cm^{-1}	159.5(±0.6)	216.1	238	96.9	112.4
$B_4^0\times10^4$ cm^{-1}	−0.687(±0.003)	−0.720	−0.788	−0.81	−0.84
$B_4^2\times10^4$ cm^{-1}	0.039(±0.020)	0.05	...	...	...
$B_4^4\times10^4$ cm^{-1}	3.03(±0.02)	3.01	3.61	3.92	3.37
$B_6^0\times10^4$ cm^{-1}	0.0000(±0.0001)	0.0002	...	...	...
$B_6^2\times10^4$ cm^{-1}	...	0.0007	...	...	...
$B_6^4\times10^4$ cm^{-1}	−0.0017(±0.0020)	−0.012	...	...	...
$B_6^6\times10^4$ cm^{-1}	...	0.011	...	...	...
$B_6^6+B_6^2\times10^4$ cm^{-1}	0.0004(±0.0020)				

[a] E. Euler (private communication).
[b] Values of **g**, and second- and fourth-degree terms determined at 20°K lie within the experimental error.
[c] Reference 22.
[d] Reference 21.

lent, both for the lines used to fit the parameters as well as for the two spectra with **H** in the [111] direction, which thus provides an independent check.

The final set of parameters with their estimated maximum errors is given in Table IV, which also includes for comparison previous results for Gd^{3+} in four diamagnetic garnets. The signs of the parameters were again determined from intensities at low temperatures. The lines in Figs. 4 and 5 show the theoretical angular variation of the spectra calculated from the final parameters using fourth-order perturbation theory. The agreement for spectra A' and B' is seen to be excellent. The small discrepancies for some of the C' and D' lines are due to the inaccuracy of the perturbation theory, as mentioned above.

VI. ESTIMATES OF THE INTERACTION SHIFTS

In order to find the effects of the magnetic and exchange interactions on the various spin Hamiltonian parameters, we now examine the corresponding values for the same ions in four similar diamagnetic garnet lattices, YGaG, LuGaG, YAlG, and LuAlG. The available results are collected in Tables II and IV.

It may be seen that the g values of both Fe^{3+} and Gd^{3+} are indeed very insensitive to changes of environment, as would be expected, while most of the crystal-field parameters show variations up to a factor of about two from lattice to lattice. From the trends with lattice constant, a_0, we may conclude that the appropriate values for EuGaG will be quite close to those of YGaG and we can estimate reasonable values and errors by inspection, as shown in Tables V and VI. The errors in the estimated g values are primarily due to uncertainties in the original experimental data, while those for D, $(a-F)$, (Fe^{3+}), and B_2^0, B_2^2, B_4^0, and B_4^4 (Gd^{3+}) are based on the reasonable assumption that there are no major unexpected changes in the electrostatic crystal field for EuGaG compared with the other garnets.

Comparison between these estimated parameters and those actually observed for EuGaG shows that there are significant differences in the case of the g values for both Gd^{3+} and Fe^{3+} and D for Fe^{3+}. These may be ascribed to the magnetic interactions. The large extrapolation uncertainty in B_2^0 and B_2^2 for Gd^{3+} precludes any accurate estimate of exchange shifts for these parameters, but it is clear that they are much smaller than the very large D shift for Fe^{3+}. For the fourth-degree parameters no large exchange shifts would be expected (since they would involve fourth-order perturbations) and it is gratifying to note that the observed value of a is essentially the same as the extrapolated one. The large experimental uncertainties in F preclude any comparison for this parameter. Tables V and VI summarize the significant shifts, which will be analyzed in the next two sections.

The most striking features of these results are the relatively small and anisotropic g shifts for Fe^{3+} and

TABLE V. Estimated shifts in the spin Hamiltonian parameters for $Fe^{3+}[a]$ in EuGaG. Shifts are defined as $\Delta X=X_{\mathrm{EuGaG}}-X_{\mathrm{extrap}}$, where X_{extrap} is the value estimated from several diamagnetic lattices.

	EuGaG (expt)	Extrapolated	Shift
$g_{\parallel}$	2.012(±0.001)	2.0025(±0.0010)	+0.0095(±0.0020)
$g_{\perp}$	2.001(±0.001)	2.0025(±0.0010)	−0.0015(±0.0020)
D cm^{-1}	−0.0215(±0.0001)	−0.137(±0.010)	+0.115(±0.010)
a cm^{-1}	0.018(±0.002)	0.020(±0.003)	−0.002(±0.005)

TABLE VI. Estimated shifts in the spin Hamiltonian parameters for $\mathrm{Gd}^{3+}\{c\}$ in EuGaG. Shifts are defined as $\Delta X = X_{\mathrm{EuGaG}} - X_{\mathrm{extrap}}$, where X_{extrap} is the value estimated from several diamagnetic lattices.

	EuGaG (expt)	Extrapolated	Shift
g_x	$1.984(\pm 0.001)$	$1.991(\pm 0.001)$	$-0.007(\pm 0.002)$
g_y	$1.984(\pm 0.001)$	$1.991(\pm 0.001)$	$-0.007(\pm 0.002)$
g_z	$1.987(\pm 0.001)$	$1.991(\pm 0.001)$	$-0.004(\pm 0.002)$
$B_2^0 \times 10^4\ \mathrm{cm}^{-1}$	$198.3(\pm 0.3)$	$220(\pm 80)$	$-20(\pm 80)$
$B_2^2 \times 10^4\ \mathrm{cm}^{-1}$	$159.5(\pm 0.6)$	$200(\pm 60)$	$-40(\pm 60)$
$B_4^0 \times 10^4\ \mathrm{cm}^{-1}$	$-0.687(\pm 0.003)$	$-0.7(\pm 0.2)$	$0(\pm 0.2)$
$B_4^4 \times 10^4\ \mathrm{cm}^{-1}$	$3.03(\pm 0.02)$	$3.3(\pm 0.5)$	$-0.3(\pm 0.5)$

the relatively huge shift in D. It might be argued that the change in D is largely due to an unexpected change in the crystal field effect due to the slightly different lattice structure of EuGaG. While this possibility cannot be ruled out for certain, it does seem most unlikely for a number of reasons:

(i) From Table II it may be seen that for the other lattices, the general trend is for D to increase with lattice constant, which would make it larger and not six times smaller, as observed.

(ii) The value of a is not significantly shifted, indicating no drastic change in the actual crystal field potential.

(iii) No similar large change in D was found by Rimai and Bierig in their measurements on Fe^{3+} in TmAlG and TmGaG,[12] suggesting that this effect is particular to the Eu^{3+} environment.

For Gd^{3+} there are no comparable shifts in the second-degree parameters B_2^0 and B_2^2, but the g values are shifted significantly. We shall see that this is in fact what might be expected and that the Fe^{3+} behavior is anomalous and interesting. It may be noted that the Gd^{3+} spectrum shows approximately tetragonal symmetry, and this fact was used to distinguish between the local z and y axes, as discussed in Sec. IV.

VII. THEORY OF THE INTERACTION SHIFTS

The elements of the theory have previously been described for the case of isotropic interactions with equivalent neighbors[11] and we shall here generalize the discussion to include anisotropic interactions with a number of inequivalent neighbors.

Let us consider first a pair of ions A and B, where A is the probe whose resonance is observed and B is one of the host lattice ions with nondegenerate ground state $|0\rangle$ and excited states $|n\rangle$. We consider the case of temperatures low enough so that only the ground state is appreciably populated, when B shows only a temperature independent (Van Vleck) paramagnetism.

We write the Hamiltonian for the pair in the form

$$\mathcal{H} = \mathcal{H}_0(A) + \mathcal{H}_{\mathrm{mag}}(A) + \mathcal{H}_0(B) + \mathcal{H}_{\mathrm{mag}}(B) + \mathcal{H}_{\mathrm{int}}(A-B),$$

where $\mathcal{H}_0(A)$ and $\mathcal{H}_0(B)$ represent the effects of crystal fields, spin-orbit coupling, etc., of the individual ions in zero mangetic field, $\mathcal{H}_{\mathrm{mag}}(A) + \mathcal{H}_{\mathrm{mag}}(B)$ the effect of a magnetic field and $\mathcal{H}_{\mathrm{int}}(A-B)$ the interactions between the ions. When the interaction term is missing and the temperature is sufficiently low, so that only the ground state of B is populated, the paramagnetic resonance spectrum will be completely described by $\mathcal{H}(A) = \mathcal{H}_0(A) + \mathcal{H}_{\mathrm{mag}}(A)$. This is in effect the spin Hamiltonian of an A spin in a similar but diamagnetic lattice, whose terms may be estimated as described in the previous section. The interaction shift arises from second- and higher-order cross terms involving $\mathcal{H}_{\mathrm{mag}}(B)$ and $\mathcal{H}_{\mathrm{int}}(A-B)$. For $\mathcal{H}_{\mathrm{mag}}(B)$ we can take quite generally

$$\mathcal{H}_{\mathrm{mag}}(B) = \mu_B \mathbf{H} \cdot (\mathbf{L}^B + 2\mathbf{S}^B), \tag{3}$$

but for $\mathcal{H}_{\mathrm{int}}(A-B)$ we must make some specific assumption about the form of the interaction. We shall here restrict ourselves to the most general bilinear interaction between the *spins* of ions A and B:

$$\mathcal{H}_{\mathrm{int}}(A-B) = \mathbf{S}^A \cdot \mathbf{K} \cdot \mathbf{S}^B, \tag{4}$$

since this includes all the terms which we may reasonably expect in our case, and also for a wide variety of other situations. The exclusion of orbital angular momentum operators for the A ion should be a very good approximation for all S-state ions. The representation of the B ion by its spin operator, on the other hand, is not such a generally applicable approximation, since exchange interactions may depend on orbital as well as spin variables[27–29] especially for rare-earth ions. However for the special case of the Eu^{3+}, whose level structure is particularly simple, all possible matrix elements from the ground state to the three excited states can be written formally in terms of those of a single spin vector, and the form [Eq. (4)] becomes completely general. To this extent our results here are immediately applicable only to exchange shifts in Eu^{3+} compounds, though the tensor interaction between spins is often also taken as the best tractable approximation in cases where it is not strictly applicable.

To find the effective spin Hamiltonian due to the cross terms involving $\mathcal{H}_{\mathrm{mag}}(B)$ and $\mathcal{H}_{\mathrm{int}}(A-B)$ we employ the usual procedure[30] of evaluating the matrix elements of all B-spin variables while leaving the components of $\mathbf{S}^A$ in operator form. The first-order terms $\langle 0|\mathcal{H}_{\mathrm{mag}}(B) + \mathcal{H}_{\mathrm{int}}(A-B)|0\rangle$ vanish and we must

---

[27] W. P. Wolf, Proc. Phys. Soc. (London) **74**, 665 (1959).

[28] P. Levy, Phys. Rev. **135**, A155 (1964).

[29] J. H. Van Vleck, Mat. y Fis. Teor. **14**, 189 (1962).

[30] M. H. L. Pryce, Proc. Phys. Soc. (London) **A63**, 25 (1960).

calculate the second-order terms

$$\delta\mathcal{H}^{(2)}=\sum_{n}\frac{\langle 0|\mathcal{H}_{\mathrm{mag}}(B)+\mathcal{H}_{\mathrm{int}}(A-B)|n\rangle\langle n|\mathcal{H}_{\mathrm{mag}}(B)+\mathcal{H}_{\mathrm{int}}(A-B)|0\rangle}{E(0)-E(n)}. \tag{5}$$

If there are j B-type neighbors we may sum their contributions, and write for the second-order part of the spin Hamiltonian of the central A ion

$$\delta\mathcal{H}^{(2)}=\sum_{j}\sum_{n}\frac{\langle 0_j|\mathcal{H}_{\mathrm{mag}}(B_j)+\mathcal{H}_{\mathrm{int}}(A-B_j)|n_j\rangle\langle n_j|\mathcal{H}_{\mathrm{mag}}(B_j)+\mathcal{H}_{\mathrm{int}}(A-B_j)|0_j\rangle}{E(0_j)-E(n_j)}. \tag{6}$$

We must note that all wave functions and spin components in this expression must be referred to one common set of axes, and that we have also neglected possible interactions between the B spins themselves.

Expanding now the products of the matrix elements, and substituting for $\mathcal{H}_{\mathrm{mag}}(B_j)$ and $\mathcal{H}_{\mathrm{int}}(A-B_j)$, we find

$$\delta\mathcal{H}^{(2)}=\delta\mathcal{H}(g)+\delta\mathcal{H}(D)+\delta\mathcal{H}(\mathrm{V.V.}), \tag{7}$$

where

$$\delta\mathcal{H}(g)=\sum_{j}\sum_{n}\mu_B\frac{[\langle 0_j|(\mathbf{L}^{B_j}+2\mathbf{S}^{B_j})\cdot\mathbf{H}|n_j\rangle\langle n_j|\mathbf{S}^{A}\cdot\mathbf{K}(j)\cdot\mathbf{S}^{B_j}|0_j\rangle]}{E(0_j)-E(n_j)}+\text{complex conjugate},$$

$$\delta\mathcal{H}(D)=\sum_{j}\sum_{n}\frac{\langle 0_j|\mathbf{S}^{A}\cdot\mathbf{K}(j)\cdot\mathbf{S}^{B_j}|n_j\rangle\langle n_j|\mathbf{S}^{A}\cdot\mathbf{K}(j)\cdot\mathbf{S}^{B_j}|0_j\rangle}{E(0_j)-E(n_j)},$$

$$\delta\mathcal{H}(\mathrm{V.V.})=\sum_{j}\sum_{n}\mu_B^2\frac{\langle 0_j|(\mathbf{L}^{B_j}+2\mathbf{S}^{B_j})\cdot\mathbf{H}|n_j\rangle\langle n_j|(\mathbf{L}^{B_j}+2\mathbf{S}^{B_j})\cdot\mathbf{H}|0_j\rangle}{E(0_j)-E(n_j)}.$$

Evaluating the matrix elements of $\mathbf{L}^{B_j}$ and $\mathbf{S}^{B_j}$ and preserving the components of $\mathbf{S}^A$ as noncommuting operators, we see that $\delta\mathcal{H}(g)$ can be written in the form $\mu_B\mathbf{H}\cdot\Delta\mathbf{g}\cdot\mathbf{S}^A$, where $\Delta\mathbf{g}$ is a second-rank tensor (not necessarily symmetric—see the Appendix), and that $\delta\mathcal{H}(D)$ can likewise be written as $\mathbf{S}^A\cdot\Delta\mathbf{D}\cdot\mathbf{S}^A$. The term $\delta\mathcal{H}(\mathrm{V.V.})=\mu_B^2\mathbf{H}\cdot\mathbf{v}\cdot\mathbf{H}$ is independent of $\mathbf{S}^A$ and therefore does not affect the ESR spectrum, but its effect may be observed as the Van Vleck temperature independent susceptibility, $\chi(\mathrm{V.V.})=2\mathrm{v}\mu_B^2/\mathrm{spin}$. We may note that the orders of magnitude of Δg, ΔD, and v are roughly related by $\Delta D\sim(\Delta g)^2/v$.

Higher order terms in the perturbation expansion will in our case be negligible giving contributions to a and F of the order of $v(\Delta D)^2$.

If we refer all wave functions and operators to a set of common axes (x_0,y_0,z_0) we may obtain expressions for the components of $\Delta\mathbf{g}$ and $\Delta\mathbf{D}$:

$$\Delta g_{\alpha\beta}=\mathrm{Re}\sum_{j}\sum_{n}\frac{2\langle 0_j|L_\alpha^{B_j}+2S_\alpha^{B_j}|n_j\rangle\langle n_j|\sum_p K_{\beta p}(j)S_p^{B_j}|0_j\rangle}{E(0_j)-E(n_j)}, \tag{8}$$

$$\Delta D_{\alpha\beta}=\sum_{j}\sum_{n}\frac{\langle 0_j|\sum_p K_{\alpha p}(j)S_p^{B_j}|n_j\rangle\langle n_j|\sum_q K_{\beta q}(j)S_q^{B_j}|0_j\rangle}{E(0_j)-E(n_j)}. \tag{9}$$

Here α, β, p and $q=x$, y, or z, and Re denotes the real part.

These expressions are quite general and subject only to a particular form used for $\mathcal{H}_{\mathrm{int}}(A-B_j)$, but they are cumbersome, and we shall now make an additional simplifying assumption and obtain expressions which can be applied more readily. We assume that the interaction of a given A spin is limited to N nearest neighbors, which are all similar except for their orientation relative to A. They are related to one another by the symmetry operations of the A-site point group and we can therefore find the effect of any one neighbor from that of another neighbor simply by using appropriate rotation or inversion matrices. At the same time it is convenient to refer all angular momentum operators to the local axes of symmetry of the ion to which they belong, so that their matrix elements can be evaluated most simply.

In practice this procedure is best carried out in three steps. First we choose one particular B-type neighbor (denoted by index 1) and write its interaction with A in our chosen form

$$\mathcal{H}_{\mathrm{int}}(A-B_1)=\mathbf{S}_1^A\cdot\mathbf{K}(1)\cdot\mathbf{S}_1^{B_1}, \tag{10}$$

referring all components to a common set of axes, which we may choose to be parallel to the A-site symmetry axes (x_0,y_0,z_0). These are generally not parallel to the B-site symmetry axes, in terms of which the B-site wave functions are usually expressed, and it is therefore necessary, as a second step, to transform the components of $\mathbf{S}_1^{B_1}$ to the local B-site axes. For this we define a rotation matrix $\mathbf{R}$ such that

$$\mathbf{S}_1^{B_1}=\mathbf{R}\cdot\mathbf{S}_l^{B_1}, \tag{11}$$

where the suffixes l and 1 denote components relative to local and A-site axes, respectively. Thirdly, to obtain the appropriate interaction Hamiltonians for the other $N-1$ neighbors we note that $\mathcal{H}_{\text{int}}$ for any other pair is identical to $\mathcal{H}_{\text{int}}(A-B_1)$ if all the spin components are expressed relative to new axes obtained from the original ones by one of the point group operations, $\mathbf{Q}(j)$. Thus

$$\mathcal{H}_{\text{int}}(A-B_j)=\mathbf{S}_j^{A}\cdot\mathbf{K}(1)\cdot\mathbf{S}_j^{B_j}, \tag{10a}$$

where

$$\mathbf{S}_j^{A}=\mathbf{Q}^{-1}(j)\mathbf{S}_1^{A},\quad\text{and}\quad \mathbf{S}_j^{B_j}=\mathbf{Q}^{-1}(j)\mathbf{S}_1^{B_j}. \tag{12}$$

Using the rotation matrix $\mathbf{R}$ to transform the components of $\mathbf{S}_j^{B_j}$ to those corresponding to local axes, we finally obtain

$$\mathcal{H}_{\text{int}}(A-B_j)=\mathbf{S}_1^{A}\cdot[\mathbf{Q}(j)\cdot\mathbf{K}(1)\cdot\mathbf{R}]\cdot\mathbf{S}_l^{B_j}, \tag{13}$$

where $\mathbf{S}_1^{A}$, $\mathbf{Q}(j)$, $\mathbf{K}(1)$, and $\mathbf{R}$ are now all referred to the A-site axes, while the components of $\mathbf{S}_l^{B_j}$ are taken relative to the local axes at the jth site. The matrices $\mathbf{Q}(j)$ and $\mathbf{R}$ are readily found from the structure, so that given any $\mathbf{K}(1)$ for one particular neighbor we can immediately find the corresponding interaction Hamiltonian for all the other neighbors. The advantage of expressing the B spin components relative to the appropriate local axes of symmetry for the particular site is that the matrix elements can be calculated most easily in this frame, and they will moreover be the same for all the neighbors.

The magnetic interaction between the B-site ions and $\mathbf{H}$ may likewise be transformed into a form in which each B-site operator is referred to the local axes of its particular site, while $\mathbf{H}$ is always referred to the A-site axes. Using the same matrices as above we find

$$\mathcal{H}_{\text{mag}}(B_j)=\mu_B\mathbf{H}\cdot[\mathbf{Q}(j)\cdot\mathbf{R}]\cdot(\mathbf{L}_l^{B_j}+2\mathbf{S}_l^{B_j}). \tag{14}$$

Substituting Eqs. (13) and (14) into Eqs. (8) and (9) we finally obtain

$$\Delta g_{\alpha\beta}=\mathrm{Re}\sum_j\sum_n\sum_\gamma\sum_\delta\frac{2[Q(j)R]_{\alpha\gamma}K_{\beta\delta}'(j)\langle 0|\,(L_\gamma^B+2S_\gamma^B)\,|n\rangle\langle n|S_\delta^B|0\rangle}{E(0)-E(n)} \tag{15}$$

and

$$\Delta D_{\alpha\beta}=\sum_j\sum_n\sum_\gamma\sum_\delta\frac{K_{\alpha\gamma}'(j)K_{\beta\delta}'(j)\langle 0|S_\gamma^B|n\rangle\langle n|S_\delta^B|0\rangle}{E(0)-E(n)}, \tag{16}$$

where we have written $\mathbf{K}'(j)$ for $[\mathbf{Q}(j)\cdot\mathbf{K}(1)\cdot\mathbf{R}]$ and the index j has been omitted in the specification of the states $|n\rangle$ and the angular momentum operators $\mathbf{L}^B$ and $\mathbf{S}^B$ to emphasize that they are all referred to the same local axes. The matrix elements are then the same for all N neighbors.

VIII. APPLICATION OF THE INTERACTION-SHIFT THEORY TO EuGaG

In order to apply the above expressions we must evaluate the matrix elements for the host lattice ions, find the rotation matrices $\mathbf{Q}(j)$ and $\mathbf{R}$ for the particular A-site from the structure, and finally specify symmetry restrictions (if any) on the form of the interaction tensor $\mathbf{K}(1)$.

The first of these steps can be carried out quite generally for all Eu^{3+} compounds in which the point symmetry at the Eu^{3+} site is C_2 or higher. For a free Eu^{3+} ion the low lying energy levels are well described by the terms ${}^7F_0$, ${}^7F_1$, ${}^7F_2$, $\cdots$, and the only matrix elements of $\mathbf{L}$ and $\mathbf{S}$ from the ground state are to the first excited state, $J=1$, which has an energy of about 350 cm^{-1}. In a crystal field of twofold or higher symmetry the $J=1$ splittings may be described in terms of states $|n_y\rangle$, $|n_x\rangle=(1/\sqrt{2})[|J=1,\ J_z=1\rangle\pm|J=1,\ J_z=-1\rangle]$ and $|n_z\rangle=|J=1, J_z=0\rangle$, with corresponding energies Δ_y, Δ_x, and Δ_z. The matrix elements of $\mathbf{L}$ and $\mathbf{S}$ from the ground state $|0\rangle=|J=0, J_z=0\rangle$ are very simple

$$\begin{aligned}\langle 0|S_z|n_z\rangle&=-\langle 0|L_z|n_z\rangle=2,\\ \langle 0|S_x|n_x\rangle&=-\langle 0|L_x|n_x\rangle=-2,\\ \langle 0|S_y|n_y\rangle&=-\langle 0|L_y|n_y\rangle=-2i,\end{aligned} \tag{17}$$

all others being zero. Substituting these in Eqs. (15) and (16) we find

$$\Delta g_{\alpha\beta}=-8\sum_j\sum_\gamma\frac{[Q(j)R]_{\alpha\gamma}K_{\beta\gamma}'(j)}{\Delta_\gamma}, \tag{18}$$

and

$$\Delta D_{\alpha\beta}=-4\sum_j\sum_\gamma\frac{K_{\alpha\gamma}'(j)K_{\beta\gamma}'(j)}{\Delta_\gamma}. \tag{19}$$

These expressions are generally applicable to most europium compounds, subject only to at least one twofold local symmetry axis. We now use them to obtain expressions for the $\mathbf{g}$ and $\mathbf{D}$ shift of Fe^{3+} in $[a]$ sites and Gd^{3+} in $\{c\}$ sites of EuGaG.

Fe^{3+} in $[a]$ Sites

The environment and axes of a particular $[a]$ site are shown in Fig. 1. The $\mathbf{Q}$ matrices for the six Eu^{3+} neighbors are given in Table VII. The $\mathbf{R}$ matrix to transform components between the axes (x_0, y_0, z_0) and the local axes (x_l, y_l, z_l) of site 1 (Fig. 1) is

$$\mathbf{R}=\begin{bmatrix} 1/\sqrt{2} & 1/2 & -1/2 \\ 1/\sqrt{6} & 1/\sqrt{12} & 3/\sqrt{12} \\ 1/\sqrt{3} & -2/\sqrt{6} & 0 \end{bmatrix}. \tag{20}$$

The splittings Δ_γ can in principle be found spectroscopically and Koningstein has given a set of values for EuGaG: 307, 345, and 388 cm^{-1}.[15] It is perhaps possible that the level at 307 cm^{-1} ascribed to Eu^{3+} is in fact a vibrational state of the crystal, since a level is found close to that energy in other garnets,[31] and that the third level was not resolved from one of the other two.[32] The uncertainty is, however, not very serious in our case since a bigger error results from the lack of information on the nature of eigenstates at the different energies. We are thus unable to relate our Δ_x, Δ_y, and Δ_z with any of the observed splittings, but since the splittings are not very different it is a good approximation to take them to be equal to their mean energy, Δ, which is close to the free ion spin-orbit splitting ≈ 350 cm^{-1}. The error from this approximation is of the order of 10%. This was verified by comparing exchange shifts obtained for various forms of interactions with different tentative identifications of the Δ's.

TABLE VII. $\mathbf{Q}(j)$ matrices for the $\mathrm{Fe}^{3+}[a]$ site relative to axes (x_0, y_0, z_0) in Fig. 1. The $\mathbf{Q}(j)$ transform Eu^{3+} site 1 into sites j.

$$\mathbf{Q}(1)=-\mathbf{Q}(4)=\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix};$$

$$\mathbf{Q}(2)=-\mathbf{Q}(5)=\begin{bmatrix} -\frac{1}{2} & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix};$$

$$\mathbf{Q}(3)=-\mathbf{Q}(6)=\begin{bmatrix} -\frac{1}{2} & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

It is convenient to split the general interaction tensor $\mathbf{K}(1)$ into a symmetric and an antisymmetric part

$$\mathbf{K}(1)=\begin{bmatrix} K_{11}{}^s & K_{12}{}^s & K_{13}{}^s \\ K_{12}{}^s & K_{22}{}^s & K_{23}{}^s \\ K_{13}{}^s & K_{23}{}^s & K_{33}{}^s \end{bmatrix}+\begin{bmatrix} 0 & K_{12}{}^a & -K_{13}{}^a \\ -K_{12}{}^a & 0 & K_{23}{}^a \\ K_{13}{}^a & -K_{23}{}^a & 0 \end{bmatrix}. \tag{21}$$

Substituting for $\mathbf{K}(1)$, $\mathbf{R}$, and the $\mathbf{Q}(j)$ in Eqs. (18) and (19) and putting $\Delta_x=\Delta_y=\Delta_z=\Delta$, we find

$$\begin{aligned} \Delta g_{xx}=\Delta g_{yy}=\Delta g_{\perp}&=(-24/\Delta)(K_{11}{}^s+K_{22}{}^s)\,, \\ \Delta g_{zz}=\Delta g_{\parallel}&=(-48/\Delta)K_{33}{}^s\,, \end{aligned} \tag{22}$$

$$\Delta D=\Delta D_{zz}-\tfrac{1}{2}(\Delta D_{xx}+\Delta D_{yy})=(-12/\Delta)\begin{bmatrix} 2(K_{33}{}^s)^2-(K_{11}{}^s)^2-(K_{22}{}^s)^2-2(K_{12}{}^s)^2+(K_{13}{}^s)^2+(K_{23}{}^s)^2 \\ -2(K_{12}{}^a)^2+(K_{13}{}^a)^2+(K_{23}{}^a)^2 \end{bmatrix} \tag{23}$$

all other components of the $\Delta\mathbf{g}$ and $\Delta\mathbf{D}$ tensors being zero, in agreement with the C_{3i} point symmetry of the $[a]$ site. As has previously been noted by Rimai and Bierig[12] only the symmetric part of the interaction contributes to $\Delta\mathbf{g}$ as a consequence of the fact that the $[a]$ site has inversion symmetry. Both the symmetric and antisymmetric interactions contribute to ΔD. The mean g shift is given by

$$\langle\Delta g\rangle_{\mathrm{av}}=\frac{\Delta g_{\parallel}+2\Delta g_{\perp}}{3}=\frac{-16}{\Delta}\mathrm{Tr}\mathbf{K}. \tag{24}$$

It is clearly impossible to determine all nine parameters in the most general $\mathbf{K}$ tensor from the three experimentally observable shifts $\Delta g_{\parallel}$, $\Delta g_{\perp}$, and ΔD, and one can therefore only compare the observed shifts with those predicted by a specific form of interaction. We shall consider explicitly the three most usual interactions:

(i) *Isotropic exchange*:

$$\mathcal{H}=J_{\mathrm{is}}(\mathbf{S}^A\cdot\mathbf{S}^B) \tag{25}$$

for which $\mathbf{K}$ is simply J_{is} times the unit matrix.

(ii) *Dipolar interaction*:

$$\mathcal{H}_{\mathrm{dip}}=\frac{\mathbf{M}^A\cdot\mathbf{M}^B}{r^3}-\frac{3(\mathbf{M}^A\cdot\mathbf{r})(\mathbf{M}^B\cdot\mathbf{r})}{r^5}, \tag{26}$$

where $\mathbf{M}^A$ for the Fe^{3+} ion is given by $g\mu_B\mathbf{S}^A$ (taking g isotropic), while the operator $\mathbf{M}^B$ for the Eu^{3+} ion is $\mu_B(\mathbf{L}^B+2\mathbf{S}^B)$. However since we only require matrix elements of $\mathcal{H}_{\mathrm{int}}$ between the $J=0$ and $J=1$ states we may use the fact that $\mathbf{L}^B$ and $\mathbf{S}^B$ have equal and opposite matrix elements [Eq. (17)] so that $\mathbf{M}^B$ is effectively reduced to $\mu_B\mathbf{S}^B$. The effective dipolar Hamiltonian is therefore

$$\mathcal{H}_{\mathrm{dip}}'=-3g\mu_B{}^2/r^3[(\mathbf{S}^A\cdot\hat{\mathbf{r}})(\mathbf{S}^B\cdot\hat{\mathbf{r}})-\tfrac{1}{3}\mathbf{S}^A\cdot\mathbf{S}^B], \tag{27}$$

---

[31] D. L. Wood, J. Chem. Phys. 39, 1671 (1963).

[32] We are indebted to Professor J. H. Van Vleck for discussions on this point.

where r is the distance between the Fe^{3+} and Eu^{3+}sites, and $\hat{\mathbf{r}}$ is the corresponding unit vector. The angular terms in square parentheses may be evaluated from the known structure, and the result expressed as a symmetric $\mathbf{K}$ matrix for site 1 relative to axes (x_0,y_0,z_0):

$$K_{\mathrm{dip}}(1)=\frac{J_{\mathrm{d}}}{30}\begin{bmatrix} -7 & -3\sqrt{3} & -3\sqrt{6} \\ -3\sqrt{3} & -1 & +9\sqrt{2} \\ -3\sqrt{6} & +9\sqrt{2} & +8 \end{bmatrix}, \qquad (28)$$

where $J_d=-3g\mu_B^2/r^3$.

(iii) *Antisymmetric exchange*: The general antisymmetric interaction in Eq. (21) may be expressed most concisely in the form given by Moriya[33]

$$\mathcal{H}_{\mathrm{as}}=\mathbf{d}\cdot[\mathbf{S}^A\times\mathbf{S}^B], \qquad (29)$$

where $d_x=K_{23}^a$, $d_y=K_{13}^a$, and $d_z=K_{12}^a$. For the garnet lattice there are no symmetry restrictions on the allowed directions of $\mathbf{d}$.

Substituting Eqs. (25), (27), (28), and (29) in the expression (22) and (23) for $\Delta\mathbf{g}$ and $\Delta\mathbf{D}$ we find

$$\begin{aligned} \Delta g_{\parallel}&=-(48/\Delta)J_{\mathrm{is}}-(64/5\Delta)J_d \\ \Delta g_{\perp}&=-(48/\Delta)J_{\mathrm{is}}+(32/5\Delta)J_d \\ \Delta D&=-(96/5\Delta)J_{\mathrm{is}}J_d-(16/5\Delta)J_d^2 \\ &\quad+(12/\Delta)(2d_z^2-d_x^2-d_y^2). \end{aligned} \qquad (30)$$

Gd^{3+} in $\{c\}$ Sites

The theory for the shift of the $\{c\}$-site spectrum is very similar to that for the $[a]$ sites and only the essential results will be given here. The $\mathbf{Q}(j)$ matrices are listed in Table VIII and

$$\mathbf{R}=\begin{bmatrix} 0 & +(1/\sqrt{2}) & -(1/\sqrt{2}) \\ -(1/\sqrt{2}) & +(1/2) & +(1/2) \\ +(1/\sqrt{2}) & +(1/2) & +(1/2) \end{bmatrix}. \qquad (31)$$

The dipolar interaction corresponding to Eqs. (27) and (28) is given by

$$K_{\mathrm{dip}}(1')=J_d\begin{bmatrix} -1/6 & -1/6\sqrt{2} & -1/2\sqrt{2} \\ -1/6\sqrt{2} & -1/4 & +1/4 \\ -1/2\sqrt{2} & +1/4 & +5/12 \end{bmatrix}. \qquad (32)$$

The $\{c\}$ site has D_2 symmetry and different shifts may therefore be expected for g_x, g_y, and g_z and the two second degree parameters B_2^0 and B_2^2. However if we assume, as before, that all the Δ's are equal some of the anisotropy allowed by symmetry disappears, and we obtain the following simple expressions:

$$\begin{aligned} \Delta g_x&=-(32/\Delta)J_{\mathrm{is}}+(16/3\Delta)J_d, \\ \Delta g_y&=-(32/\Delta)J_{\mathrm{is}}+(24/3\Delta)J_d, \\ \Delta g_z&=-(32/\Delta)J_{\mathrm{is}}-(40/3\Delta)J_d, \\ \Delta B_2^0&=-(20/3\Delta)J_{\mathrm{is}}J_d-(10/9\Delta)J_d^2+a', \\ \Delta B_2^2&=-(4/3)\Delta J_{\mathrm{is}}J_d-(2/9)\Delta J_d^2+a''. \end{aligned} \qquad (33)$$

TABLE VIII. $\mathbf{Q}(j)$ matrices for $Gd^{3+}\{c\}$ site relative to axes (x_0, y_0, z_0) in Fig. 2.

$$\mathbf{Q}(1')=\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}; \qquad \mathbf{Q}(2')=\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix};$$

$$\mathbf{Q}(3')=\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}; \qquad \mathbf{Q}(4')=\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

Here a' and a'' denote contributions from the antisymmetric interactions, which we shall not consider in detail as there is no experimental indication that they are important in our case. The absence of antisymmetric terms in the Δg's is a result of putting the Δ's equal, as is the isotropic nature of the $\Delta\mathbf{g}$ shift produced by the isotropic exchange.

IX. INTERPRETATION OF THE OBSERVED SHIFTS

The observed shifts ascribed to interaction effects have been summarized in Tables V and VI and we shall now consider these in terms of Eq. (30) and (33) above.

$Fe^{3+}[a]$ Sites

We can estimate the isotropic exchange interaction from the mean g shift $\langle\Delta g\rangle_{\mathrm{av}}=-(48/\Delta)J_{\mathrm{is}}$. This gives $J_{\mathrm{is}}\approx-0.016$ cm^{-1}, a surprisingly small value and moreover ferromagnetic in sign. The anisotropy of Δg is partly accounted for by the magnetic dipole interactions which predict $\Delta g_{\parallel}=0.002$ and $\Delta g_{\perp}=-0.001$ for the calculated value $J_d=-0.062$ cm^{-1}. While these two interactions account reasonably well for the small shift in $\Delta g_{\perp}$ they leave a significant discrepancy for $\Delta g_{\parallel}$ indicating the importance of some other interactions not so far considered explicitly. Such anisotropic interactions are not at all unexpected as they have been found in other rare-earth iron garnets,[34,29] but there is at present no quantitative theory from which even the relative magnitudes of terms may be estimated.

The best possible procedure at present is therefore to fit the Δg's empirically to the appropriate coefficients of the $\mathbf{K}$ tensor. We thus find $K_{33}^s=-0.069$ cm^{-1} and $(K_{11}^s+K_{22}^s)=+0.022$ cm^{-1}. Using the present method, there is no possibility of separating K_{11}^s and K_{22}^s nor of estimating the other coefficients in $\mathbf{K}^s$. However it does not seem unreasonable to assume that all the components of $\mathbf{K}^s$ have much the same order of magnitude, i.e., $|K_{\alpha\beta}^s|\sim0.1$ cm^{-1}, and this enables us to make a rough estimate of the contribution of the symmetric interactions to the D shift. From Eq. (23) we then find $\Delta D\sim10^{-3}$ cm^{-1} compared with our observed shift $\Delta D\sim0.11$ cm^{-1}.

---

[33] T. Moriya, Phys. Rev. **120**, 91 (1960).

[34] K. A. Wichersheim and R. L. White, Phys. Rev. Letters **8**, 483 (1962).

This large discrepancy may be interpreted in one of two ways.[35] One possibility is a large and unexpected change in the actual crystal field, but as was discussed in Sec. VI this appears to be very unlikely. The only other reasonable explanation seems to be a large antisymmetric exchange interaction of the Moriya form which, as discussed in Sec. VIII, does not affect the g values. From Eq. (30) we see that this would produce a shift

$$\Delta D \sim (12/\Delta)|d|^2(3\cos^2\Theta - 1), \qquad (34)$$

where Θ is the angle between the d vector for site 1 and the z_0 axis. From Eq. (34) we can now estimate a *lower* limit for $|d|$ of 1.3 cm^{-1}. It is remarkable that this is about 20 times bigger than the isotropic part of the exchange interaction, and such a possibility was certainly not forseen in Moriya's original theory, which, however, was restricted to the case of orbitally nondegenerate states and small spin-orbit interaction.[33] If our observed D shift is, in fact, correctly ascribed to antisymmetric exchange, it would suggest that large antisymmetric interactions may also be found for other rare-earth compounds, most of which have some orbital degeneracy and large spin-orbit coupling. Large antisymmetric terms are not inconsistent with current ideas on anisotropic superexchange in rare-earth compounds.[36] On the other hand, Rimai and Bierig found appreciably smaller D shifts for Fe^{3+} on $[a]$ sites in TmAlG and TmGaG although their g shifts were larger than ours in EuGaG. It may therefore be that the large D shift is peculiar property of the Eu^{3+} ion, which does have a rather unique energy level structure, and it would be interesting to investigate exchange interactions in other europium compounds.

The possibility of a large antisymmetric interaction between the Eu^{3+} neighbors and any Fe^{3+} spins on (d) sites raises the question whether our inability to observe resonance lines due to spins on (d) sites might not have been due to large and possibly inhomogeneous shifts. We feel that the alternative explanation of a strong $[a]$ site preference for the Fe^{3+} spins is perhaps more reasonable but the other can certainly not be ruled out at the present time.

$\text{Gd}^{3+}\{c\}$ Sites

As may be seen from Table VI the only significant shifts observed for Gd^{3+} were those in the $\mathbf{g}$ tensor. The three shifts are well explained by Eq. (33) with an isotropic exchange interaction $J_{\text{is}} = +0.07$ cm^{-1} and the magnetic dipole interaction calculated from the structure, $J_d = -0.047$ cm^{-1}. Negligible shifts in B_2^0 and B_2^2 are predicted from these interactions and indeed no large shifts are observed, although the uncertainties due to the lattice extrapolation preclude any precise estimates of these shifts. There is no positive evidence for any antisymmetric interactions. The value of J_{is} may be compared with that found for the Gd^{3+}-Gd^{3+} interaction in GdGaG.[14] From the observed Curie-Weiss constant of +2.3°K we find $J_{\text{is}}(\text{Gd}-\text{Gd}) = +0.08$ cm^{-1} in reasonable agreement with our value for the Gd^{3+}-Eu^{3+} interaction.

APPLICATION OF THE RESULTS TO EuIG

It is tempting to use the above results to provide a quantitative explanation of the observed properties of EuIG and gallium substituted europium iron garnets. The lattice constants of these materials are slightly larger than those of the pure gallium garnet and it seems reasonable to assume, therefore, that the isotropic exchange interaction between the Eu^{3+} and Fe^{3+} spins on the $[a]$ sites will be as weak as, or even weaker than that deduced from our measurements. The antisymmetric interaction (if present) will likewise produce only a very small effect, since the Fe^{3+} $[a]$-site spins are held almost parallel by the strong ferrimagnetic interaction with the Fe^{3+} spins on (d) sites, so that their net coupling with any given Eu^{3+} spin through antisymmetric terms will vanish to first order. (If the $[a]$ spins were completely parallel their effect on any $\{c\}$ site would vanish by D_2 symmetry.) We might conclude therefore that our measurements predict a $\{c\}$-$[a]$ interaction which is very much smaller than the total observed interactions,[37] thus implying a dominant $\{c\}$-(d) interaction.

This is in fact in agreement with the conclusions drawn by LeCraw *et al.*[8] from measurements on a series of mixed EuFe-EuGa garnets, and also from analyses of various gadolinium garnets by Geller *et al.*,[10] and by Anderson.[9] However it must be cautioned that all these conclusions are to some extent based on an important assumption which is not easy to verify: namely, that the exchange interaction between any Eu^{3+}-Fe^{3+} pair is *independent* of the nature of the ions occupying other nearby sites. In the particular case of the $\{c\}$-$[a]$ exchange in the garnets this is not obvious, because each $[a]$ site shares a common O^{2-} neighbor with one $\{c\}$ site and one (d) site ion. When the (d) site is occupied by a magnetic ion, there is a strong superexchange interaction through this oxygen ion, and it does not seem impossible that this could affect the very much weaker interaction between the $\{c\}$ and $[a]$ sites, which simultaneously involves the same O^{2-} electrons. However all this conjecture probably will not alter the qualitative conclusion, that the $\{c\}$-$[a]$ interaction both in our gallium garnet and in the iron garnets is weak, and probably much weaker than the $\{c\}$-(d) interaction.

If this is so, we can now estimate the isotropic

---

[35] We reject as extremely unlikely a third possibility that some of the terms in $\mathbf{K}^s$ are in fact very much larger than K_{33}^s and $(K_{11}^s + K_{22}^s)$ since this would demand an extremely anisotropic form for $\mathbf{K}^s$.

[36] P. Levy (private communication).

[37] W. P. Wolf and J. H. Van Vleck, Phys. Rev. **118**, 1490 (1960).

exchange coefficient $J_{\text{is}}(c-d)$ for the Eu^{3+}-Fe^{3+} interaction, using Pauthenet's results[1] and the analysis of Wolf and Van Vleck.[37] Assuming interactions with only the two nearest neighbors we find $J_{\text{is}}(c-d)=+6.7$ cm^{-1}. We have no way of estimating any possible antisymmetric $\{c\}$-(d) interactions.

CONCLUSIONS

We have shown how the ESR shift method can give quantitative information on the interactions between an ordinary (Kramers) magnetic ion and an even electron ion with a singlet ground state. In order to detect a shift it is necessary to estimate the spectrum in the absence of interactions and the method is therefore particularly well suited to ions in an S state whose g values can be extrapolated with precision from measurements on the same ion in diamagnetic host lattices. The method has been applied to Fe^{3+} on $[a]$ sites and Gd^{3+} on $\{c\}$ sites of europium gallium garnet. This is a good host lattice both because the low lying levels of the Eu^{3+} ions are known and because interactions involving the rare-earth ions are of interest in connection with the properties of garnets in general.

The results for the Fe^{3+} spins indicate a very small isotropic exchange interaction ($J_{\text{is}}\approx-0.016$ cm^{-1}) and comparable anisotropic interactions. An apparently very large shift in the parameter D in the spin Hamiltonian was tentatively ascribed to a large antisymmetric interaction ($|d|>1.3$ cm^{-1}). It is possible, though rather unlikely, that part of this shift was produced by some other unknown effect, but it would seem worthwhile to investigate the possibility of large antisymmetric interactions in other cases involving rare-earth ions. No resonances which could be ascribed to Fe^{3+} on (d) sites were observed, indicating most probably a marked site preference (at least 50:1) for the substitutional Fe^{3+} ions.

Some dangers of applying these results directly to the concentrated europium iron garnets have been discussed but it was concluded that the properties of these are almost certainly dominated by an isotropic $\{c\}$-(d) interaction whose magnitude may be estimated from the magnetic moment of EuIG, $J_{\text{is}}(c-d)\sim6.7$ cm^{-1}, plus, of course, the usual Fe-Fe interactions.

The results for Gd^{3+} are well explained by an isotropic exchange interaction of the expected order of magnitude ($J_{\text{is}}\sim+0.07$ cm^{-1}), plus the calculated magnetic dipole interaction.

ACKNOWLEDGMENTS

We would like to thank S. Mroczkowski for preparing the crystals used in this investigation and for help with their orientation. We are grateful to Dr. P. Levy for helpful comments, and also to M. J. D. Powell for kindly giving us a copy of his computer program.

APPENDIX: ANTISYMMETRIC TERMS IN AN AXIALLY SYMMETRIC g TENSOR

Although it is rather hard to see from its general form, Eq. (18) for the g shift at the $[a]$ sites allows nonzero off-diagonal elements $g_{xy}=-g_{yx}$, and at first sight this seems contrary to one's expectation for a site with C_{3i} symmetry. However these components are not wrong and may be explained in terms of a different (implicit) choice of x axis for the spins operators and **H**. This is possible because **S** and **H** operate in different vector spaces which are not necessarily related (i.e., **g** is really a pseudotensor). If we rotate the x axis of either **S** (or **H**) through an angle Φ (or $-\Phi$) about the z axis, the spin Hamiltonian,

$$\mathcal{H}=\mu_B[g_\perp(H_xS_x+H_yS_y)+g_{xy}(H_xS_y-H_yS_x)],$$

is transformed to

$$\begin{aligned}\mathcal{H}=\mu_B[&(g_\perp\cos\Phi+g_{xy}\sin\Phi)(H_xS_{x'}+H_yS_{y'})\\&+(-g_\perp\sin\Phi+g_{xy}\cos\Phi)(H_xS_{y'}-H_yS_{x'}).\end{aligned}$$

If Φ is chosen such that $\tan\Phi=g_{xy}/g_\perp$ this reduces to $\mathcal{H}'=\mu_Bg_\perp'(H_xS_{x'}+H_yS_{y'})$, where $g_\perp'=\surd(g_\perp^2+g_{xy}^2)$, in agreement with the normal form used for axial symmetry. The choice of x axes thus has no effect on the form of the spectrum, but is of importance in comparing experimentally determined parameters ($g_\perp'$ in this case) with those calculated from a model, and it would be wrong to identify the calculated $g_{xx}=g_{yy}=g_\perp$ with $g_\perp'$.