Paramagnetic Resonance of Fe^{3+} in Yttrium Aluminum, Lutetium Aluminum, and Lutetium Gallium Garnets

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The spin-Hamiltonian parameters have been determined for the Fe^{3+} ion when present as substitutional impurity in the series of isomorphous diamagnetic garnets. Most of the parameters vary rather slowly from host to host. It is shown that the dependence of the cubic field splitting in the octahedral sites on lattice parameters as obtained from the present results is consistent with the dependence of the same parameters on hydrostatic pressure for substitutional Fe^{3+} in MgO. The fourth-order axial-field parameter F does show appreciable variation among the various hosts; this is discussed in terms of the extrapolation to yttrium iron garnet, and the calculation of the crystal-field-induced magnetic anisotropy in the latter.

I. INTRODUCTION

THE electron-paramagnetic-resonance spectrum of substitutional impurities of Fe^{3+} in yttrium gallium garnet (YGaG) has been studied previously in all detail.[1] There was twofold motivation for such a study. Fe^{3+} being present in both, octahedrally (a) and tetrahedrally (d) coordinated sites in the same hosts, made this system particularly attractive to test theoretical calculations of spin-Hamiltonian parameters for the ^6S ground state of Fe^{3+}, most particularly the cubic field parameter a.[2,3] The structure of this compound is very similar to that of the obviously important material, yttrium iron garnet (YIG). It is reasonable, therefore, to expect that crystalline-field-induced magnetic anisotropy energy of the Fe^{3+} ground state, as measured by its spin-Hamiltonian parameters in YGaG, would not be too different from its value in YIG. Thus, the corresponding contribution to the magnetic anisotropy of YIG could, perhaps approximately, be obtained from the EPR results. Many considerations were indicative that such a "single-ion mechanism" was the major contributor to the anisotropy energy of YIG.[4,5]

From the two preceding points, it seemed to be a useful enterprise to examine the EPR of Fe^{3+} in the whole series of isomorphous diamagnetic garnets. Variation of the spin-Hamiltonian parameters in a series of crystals with only slight variation in structure would be a more meaningful challenge for comparison with theoretical results than absolute values in widely differing structures. In addition, the variation of the parameters with structure might shed light on the relatively large discrepancies found by comparing the ani-

sotropy results in YIG[6] with predictions from the spin Hamiltonians of Fe^{3+} in YGaG.

More recently a third reason for these measurements has been found. It was possible to observe the EPR of Fe^{3+} in a number of rare-earth garnets for which the rare-earth ground states were singlets.[7-9] The corresponding spin-Hamiltonian parameters will contain contributions due to Fe^{3+} rare-earth interactions which may be isolated by comparison with parameters obtained by interpolation of measured values on the isomorphous diamagnetic compounds. A summary of some of the results discussed in this paper has been previously published in a note covering this third consideration.[8] A detailed discussion of these comparisons as well as of complete results on the resonance of Fe^{3+} in thulium garnets will be deferred to a later publication.

The experimental results on the EPR of Fe^{3+} in the three garnets are presented in Sec. II. A discussion covering their relationship to the two initial points is presented in Sec. III.

II. THE EXPERIMENTAL RESULTS

The single-crystal garnets were grown from lead-fluoride–lead-oxide fluxes.[10,11] The crystals were x-ray oriented and appropriately cut to permit determination of the angular dependence of the spectra with the magnetic field rotating either in a (110) or in a (100) plane. Usually, the Fe^{3+} resonances were observable even in crystals which were not purposely doped. Spectra were taken at a number of concentrations, up to 0.1 at. % without meaningful variations. Measurements were taken at liquid-helium temperatures, 77°K, and room temperature. The temperature dependence

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of the parameters was very small, less than the experimental-error limits for all except the axial-field parameter D, where a very small decrease was noted (in all cases less than 2%) when the temperature varied from 77°K to room temperature. There was no measurable variation below 77°K. The data quoted in what follows were obtained at 4.2°K.

The measurements were performed with a conventional spectrometer using audio frequency field modulation. The sample was at the center of a circular TE_{011} cavity which had an axis normal to the magnetic field. The microwave frequency was always near 35 Gc/sec as measured by a wave meter calibrated by a heterodyne-plus-counter system. The field was measured using a Varian NMR fluxmeter, with a frequency measured again by the same process.

The following interesting qualitative feature was observed: Whereas, in lutetium gallium garnet (LuGaG), just as in YGaG,[1] the Fe^{3+} impurities have a strong preference for octahedral sites, in the Al garnets this effect, although present, is much less marked.

Initially a rotation pattern was taken with the external field H in the (110) plane. Thus it was possible to identify the 5 transitions when H was parallel to the local axis of symmetry for each particular type of site, without the additional splitting[1] due to the cubic field a. Such local axes are, a [111] for the a sites and a [100] for the d sites. The data are exemplified in Fig. 1, where the angular dependence in the (110) plane of some of the transitions of Fe^{3+} in lutetium
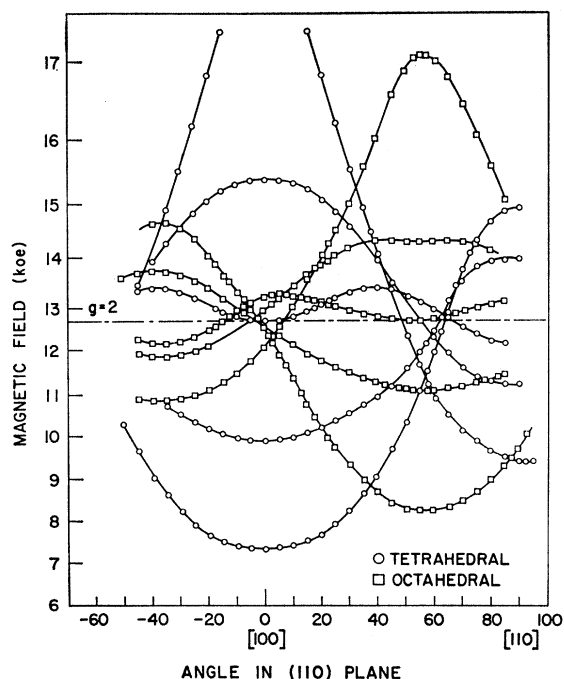

FIG. 1. Angular dependence of some of the transitions in the EPR of Fe^{3+} in LuAlG when the magnetic field is rotated in a (110) plane.
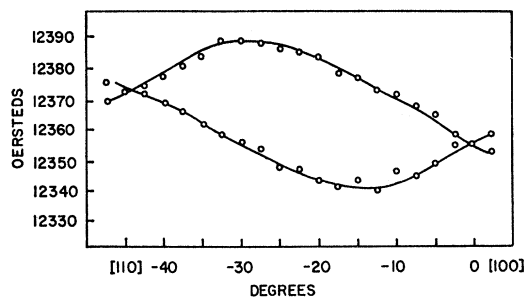

FIG. 2. The central transitions for tetrahedral sites in YAlG when the magnetic field is rotated in the (010) plane perpendicular to the local axis.

aluminum garnet (LuAlG) is displayed. Spin-Hamiltonian expressions for the two types of sites have been given in Ref. 1. The present data were analyzed in the same way as the (YGaG) results of Ref. 1, to which the reader is referred for notation and detail. Initially, for each site, the parameters g and D in the axial-crystal-field approximation were determined from the parallel spectrum (H||100 or 110 as the case might be). Next, following Geschwind[1] the angular dependence of the central transitions was investigated in the (001) plane. For d sites interest was in those transitions for which there was only a fourth-order angular variation present [i.e., those for which the (001) plane was perpendicular to the local axis]. There are two such transitions corresponding to the fact that, in this plane, the cubic axes are rotated by an angle β with respect to the edges of the unit cell.[1] The data are exemplified in the case of yttrium aluminum garnet (YAlG) in Fig. 2. Using the axial parameters determined before, the tetrahedral Hamiltonian was diagonalized for $\theta = 90°$, and for a few values of the magnetic field at which the transitions in Fig. 2 occur (near the position of largest splitting between the two branches). In first-order perturbation this splitting varies as $K_d = a[\cos4(\varphi+\beta) - \cos4(\varphi-\beta)]$. Using the wave functions obtained from the diagonalization, one can determine K_d, and therefore $|a|$ may be determined from the measured splitting. The two possible values of β determined from the extremes in the line positions would give opposite signs to a.

For the octahedral sites a rotation of H in this same plane would, in the absence of a, give two inequivalent central transitions. Because of the a term the [111] axis is only threefold, and these two transitions will further split as a function of the orientation of the magnetic field. If a is treated in first order, it gives a contribution to the fields for resonance of the form $K(\theta)a \cos3(\varphi \pm \alpha)$, where φ is an azimuth in the plane perpendicular to the [111] axis. The origin for φ is the projection of the [100] onto this plane. The angular dependence of these four branches is shown in Fig. 3 for lutetium gallium garnet (LuGaG). In this case both φ and θ change as H is rotated in the (100) plane. Again one starts by diagonalizing the axial Hamiltonian

FIG. 3. The central transitions for octahedral sites in LuGaG.

plus Zeeman term for values of H and θ corresponding to line positions near points of large a splitting. From the wave functions one can determine $K(\theta)$, and from the splitting between branches, $|a|$ and $\pm a$ may again be determined, with the same ambiguity in sign as for the d sites. It is worth mentioning that this technique can be easily applied to determine other small perturbations on an initially approximate Hamiltonian. For instance an axial anisotropy in the g tensor could be determined by diagonalizing for $\theta = 90°$ and then using the state vectors thus obtained to calculate diagonal matrix elements of $(g_\perp - g_{11})\beta(S_x H_x + S_y H_y)$.

Since the largest parameter is always D, its absolute sign is determined by the changes in relative intensities of the symmetric transitions when the temperature is lowered to 4°K. The positive sign of a for all cases is determined with previously used assumptions,[1] i.e., the angles α, β are essentially those given by point charge calculations of the cubic crystal-field potential.

The results are summarized in Table I, where YGaG has also been included for the sake of completeness.

TABLE I. Spin-Hamiltonian parameters of Fe^{3+} in the diamagnetic garnets.[a]

Host	Site	g(iso-tropic)	D(cm^{-1})	a(cm^{-1})	F(cm^{-1})	α (deg)	β (deg)
YAlG	a	2.0015	−0.1053	0.0205	0.0027	27.5	
YAlG	d	2.004	−0.1028	0.0075	−0.0110		16
LuAlG	a	2.001	−0.0935	0.0292	0.0064	27.5	
LuAlG	d	2.004	−0.1249	0.0084	−0.0104		16.5
LuGaG	a	2.001	−0.1290	0.0174	−0.0033	28	
LuGaG	d	2.003	−0.1131	0.0065	−0.0047		16
YGaG[(1)]	a	2.003	−0.1320	0.0189	0.0047	28	
YGaG[(1)]	d	2.003	−0.0880	0.0062	−0.0040		16.5

[a] Experimental errors for g values are of the order of 0.0005, and for the other parameters, 0.0005 cm^{-1}.

III. DISCUSSION

When an impurity replaces a natural constituent, intuitively one expects the axial components of the crystal field to be much more sensitive to local distortions in the host structure than the cubic field. Therefore a discussion of the latter in terms of the structure of the host crystal seems somewhat more meaningful, especially for a series of crystals differing little in structure amongst themselves and with no

charge discrepancy in the substitution. An interesting question is that of the perturbation mechanism that affords a calculation of a from a knowledge of the cubic crystalline electrostatic potential V.[3] The latter, of course, depends on complicated effects of covalency and overlap of wave functions. It seems, however, that its variation with interatomic distance may be described with reasonable success by a point charge model.[12–14] Let us therefore see what such a model yields when combined with the present data. In Fig. 4 we have plotted the cubic field splitting of Fe^{3+} in various hosts in which it has O^{2-} anions as nearest neighbors. As independent variable, we have used a quantity V/q proportional to the point charge potential of the [$q = 6$ or 4 as the case may be] O^{2-} nearest neighbors: $V/q = kr^{-5}$ with $k = -35/9$ for tetrahedral coordination and $k = 35/4$ for octahedral sites. The crystallographic parameters for the garnets were taken from x-ray measurements.[15] Results in some other hosts are also illustrated. In the latter cases polarization corrections due to charge discrepancy in the substitution may, however, be important, which our independent variable does not take into account, and which may, for instance, bring the MgO and SrTiO$_3$ points closer in abscissa to the garnet results of the same value of a.

From this model one can derive the logarithmic derivative of a as a function of the cubic crystal potential, $n = (V/a)(\partial a/\partial V)$; one obtains $-n = 4 \pm 0.7$ for octahedral sites ($V > 0$, $0.018 < a < 0.03$ cm^{-1}) and $-n \simeq 1$ for tetrahedral sites ($V <$, $0.004 < a < 0.008$ cm^{-1}). The value thus obtained for octahedral sites seems to be in good agreement with the value of n obtained for MgO from pressure dependence of a using the same model.[12] Had we calculated n comparing octahedral to tetrahedral sites no such agreement would be obtained. Since the pressure measurements involve only small changes in the lattice constant, the present comparison

FIG. 4. The cubic field splitting parameter a for the ground state of Fe^{3+} in various hosts.

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is obviously more meaningful, and seems to confirm the assumption of equality between local and bulk compressibility used in the analysis of the pressure dependence of a in MgO. In the one other host where the pressure dependence of a was measured, namely, $SrTiO_3$,[14] this simple model would yield n about twice as large, in spite of the fact that a is comparable to the values in MgO and in the garnets. There is good independent evidence, however, that in $SrTiO_3$ the local compressibility is much larger than the bulk value—the g shift of Cr^{3+}—which is inversely proportional to the cubic crystal potential, has a lattice constant dependence twice as fast as in MgO where it is consistent with that of a point charge model. In this sense the present results also supply additional evidence for the assumption that at the site occupied by the Fe^{3+} the local compressibility in $SrTiO_3$ is indeed about twice the bulk value.

Let us next examine the possibility of extrapolating the crystal field splittings of Fe^{3+} to a diamagnetic lattice otherwise equivalent to YIG.

We shall restrict ourselves to the consideration of the fourth-order parameters which are the ones of importance in connection with the magnetic anisotropy of YIG. In Fig. 4 we have indicated the abscissa corresponding to the structural parameter of YIG. In Figs. 5(a) and 5(b) we have also plotted, simply as a function of the cation-O^{2-} distance, the fourth-order axial parameter F. Reasonable extrapolated values can indeed be obtained for a of both sites and for F_d corresponding to the tetrahedral ions. For octahedral sites, on the other hand, one sees a very violent variation of F_a. Still, if we naively insist on obtaining a value, it will most probably be large and positive. As an educated guess we take F_a as given by a linear extrapolation from its values for LuGaG and YGaG. The parameters thus obtained are listed below:

$$A_a = 0.017 \times 10^{-4} \text{ cm}^{-1}, \quad F_a = 0.013,$$
$$d_d = 0.005, \quad F_d = -0.003.$$

The expression for the single-ion-anisotropy constant of YIG is[1,4]

$$K = K_a \gamma_a(T) + K_d \gamma_d(T),$$

with[1] the $\gamma(T)$ factors being temperature-dependent coefficients derived from molecular-field theory, and the K_a, K_d being linear combinations of the corresponding crystal-field parameters a and F, with the coefficient of a depending on α or β, respectively. For α and β as given by the YIG crystallography,

$$K_a = 5.01 a_a - 4.15 F_a,$$
$$K_d = 18.756 a_d + 9.3 F_d.$$

For illustration purposes we show in Table II the values of the above constants and also of the total anisotropy at $T=0$ ($\gamma_d = \gamma_a = -\frac{5}{2}$) obtained by the present extrapolation, and directly from the analysis
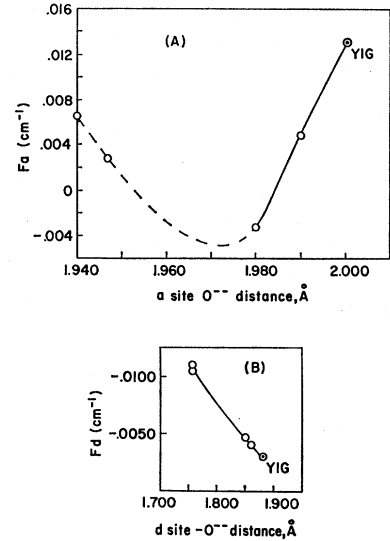

FIG. 5. Variation of the fourth-order axial-field parameter of Fe^{3+} with the iron oxygen separation in various garnet hosts —(A) octahedral sites, (B) tetrahedral sites.

of resonance and magnetization data of YIG.[6] The disagreement of the coefficients is not much improved from that obtained when YGaG parameters are used directly.[1] However, the theory leading to the temperature-dependent expressions[1] and the analysis of magnetic data used to separate K_a and K_d depend on the molecular-field approximation; spin-wave excitations are not considered. The expression of $K(0)$ at $T=0$, on the other hand, depends only on the assumption of full alignment of the sublattices, which should be reasonably good.[16] Here the agreement is, for what it is worth, much improved over that obtained using YGaG spin-Hamiltonian parameters.

We wish to stress the point that the above agreement has only illustrative value. It shows that it is conceivable to explain most of the fourth-order anisotropy of YIG by a single-ion mechanism still with essentially full alignment of the sublattices at $T=0$. The very sensitive dependence of the fourth-order crystal-field parameters of Fe^{3+} on the host structure shows that the whole problem hinges on the lack of knowledge of the F parameter in YIG proper.

TABLE II. Comparison of estimates of magnetic anisotropy constants in YIG.

	K_a (cm⁻¹)	K_d	$K(0)$ (cm⁻¹)
Extrapolated	0.032	0.068	−0.25
YIG magnetic data	−0.006	0.101	−0.241

IV. CONCLUSION

We have presented the spin-Hamiltonian parameters of Fe^{3+} in a series of isomorphous host crystals differing

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only slightly in structure from each other and having no polarization effects in the substitution. These results are consistent with the dependence of the octahedral cubic field splitting on small variations of lattice spacing, as obtained from pressure data in MgO.[12] They also indicate that the variations of some of the parameters among different hosts are sufficiently large to explain discrepancies between the measured anisotropy constant in YIG and that obtained, assuming that the anisotropy originates in the crystalline field but using spin-Hamiltonian parameters obtained for YGaG. Such

results should, hopefully, motivate theoretical calculations of crystal field splitting for the Fe^{3+} ground state in order to elucidate the mechanisms responsible for their existence, thus permitting resonance results on such impurities to be used more efficiently in the study of their environment.

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Nuclear Magnetic Resonance of Indium Metal at 4.2°K*

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The nuclear magnetic resonance spectrum of indium metal power has been measured at twelve magnetic-field points in the range of 17.0 to 30.5 kG at 4.2°K. The analysis of this spectrum gives the isotropic Knight shift as $+0.80\pm0.02\%$, the anisotropic Knight shift as $-0.05\pm0.02\%$, and the nuclear quadrupole spliting parameter ν_q as 1.884 ± 0.002 Mc/sec. All three of these quantities were determined at each of the twelve field points, and no field dependence has been observed in this range.

INTRODUCTION

THE nuclear-magnetic-resonance (NMR) spectrum of indium metal powder has been measured at 4.2°K at magnetic fields ranging from 17 to 30.5 kG as an extension of the earlier measurements of D. R. Torgenson et al.[1] The possibility of observing magnetic breakdown and/or de Haas–van Alphen effects at these low temperatures combined with a faster convergence of the perturbation terms suggested the investigation of this higher field region. The availability of other electronic data[2,3] at 4.2°K made this temperature a good choice for comparisons. The isotropic Knight shift, anisotropic Knight shift, and the quadrupole coupling constant have been measured at 12 different field points in this region of 17 to 30.5 kG. The technique used for separating the isotropic Knight shift from the anisotropic Knight shift at a single field point along with the determination of the quadrupole coupling constant at each field point is based on powder pattern line-shape equations given by W. H. Jones et al.[4] The experimental determination of these parameters is particularly important in view of recent developments in techniques

for the theoretical calculation of energy bands[5] along with new methods for determining the shape and dimensions of the Fermi surface.[6]

THEORY

The NMR spectrum of a metal with $I>\frac{1}{2}$ will, in general, be affected by both the isotropic and the anisotropic Knight shifts and by the presence of quadrupolar interactions. The appropriate Hamiltonian is[7]

$$\mathfrak{IC}=H_0^{(e)}+H_0^{(n)}+\sum_{i=1}^{n} \beta H_0(L_z^{(i)}+2S_z^{(i)})$$

$$+\sum_{j=1}^{n} g\mu_0 H_0 I_z^{(j)}+\sum_{i=1}^{n}\sum_{j=1}^{n} \frac{16\pi}{3}g\mu_0\beta S^{(i)}\cdot I^{(j)}\delta(r_{ij})$$

$$-2g\mu_0\beta\left[\frac{S^{(i)}\cdot I^{(j)}}{r_{ij}^3}-3\frac{(S^{(i)}\cdot r_{ij})(I^{(j)}\cdot r_{ij})}{r_{ij}^5}\right] \qquad (1)$$

$$+\sum_{q=-2}^{2} (-1)^q Q_q(\nabla E)_{-q},$$

where $H_0^{(e)}$ is the Hamiltonian for the conduction electrons in the field of the ion cores and $H_0^{(n)}$ is the Hamiltonian for the ion cores. Q_q is the electric quad-

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