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The Magnetic Properties of Rare Earth Ions in Garnets

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Susceptibility measurements in the range 20° to 1.5°K are reported for the eight paramagnetic garnets with the composition $R_3X_5O_{12}$, where $R=Gd^{3+}$, Tb^{3+}, Ho^{3+} or Tm^{3+} and $X=Al^{3+}$ or Ga^{3+}, together with microwave resonance determinations of the principal g-values of the ions Nd^{3+}, Dy^{3+}, Er^{3+} and Yb^{3+} substituted into diamagnetic $Lu_3Al_5O_{12}$ and $Lu_3Ga_5O_{12}$. The results are interpreted qualitatively as indicating highly anisotropic and relatively large local crystalline electric fields, and the effect of these on the properties of ferrimagnetic rare earth iron garnets is considered. It is shown that in the ferrimagnetic garnets the rare earth ions will almost always divide into 6 non-collinear sublattices, whose magnetic moments make quite large angles with the two antiparallel iron sublattices. For one case, YbIG, it has been possible to make a numerical estimate of the angles of canting.

Introduction

Continuing our survey of the properties of paramagnetic garnets with the general formula $R_3X_5O_{12}$, where X=Al or Ga[1,2,3] we have measured the low temperature susceptibilities of crystals with $R=Gd^{3+}$, Tb^{3+}, Ho^{3+} and Tm^{3+}, and we have made paramagnetic resonance determinations of the principal g-values of Nd^{3+}, Dy^{3+}, Er^{3+} and Yb^{3+} substituted in small amounts ($<1\%$) into LuAl and LuGa garnets. Measurements of this kind can immediately be interpreted in a qualitative way to give information on the strength and symmetry of the crystalline electric field acting on the rare earth ions, an important factor in the theory of the ferrimagnetic rare earth iron garnets. A detailed analysis of the results in terms of crystal fields with various symmetries is not possible from these data alone, both on account of the general complexity of the problem (nine independent parameters), and also because the results reveal considerable variations depending on the particular diamagnetic host lattice in which the rare earth ions are situated. However, even the general conclusions are sufficiently striking to draw attention to some powerful anisotropy effects generally omitted from the theory of ferrimagnetism.

The Susceptibility Measurements

The susceptibility measurements were made on single crystals grown by the standard PbO/PbF$_2$ flux method[4], except for the GdAl garnet for which a slightly modified composition was used[5]. An a.c. inductance method[6] was used to obtain high precision ($<0.1\%$) for the temperature dependence,

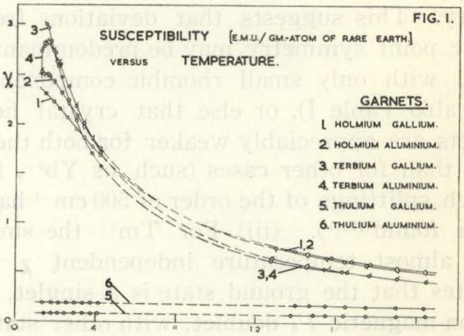

Fig. 1. Susceptibility versus temperature for six 'non-Kramers' rare earth gallium and aluminium garnets.

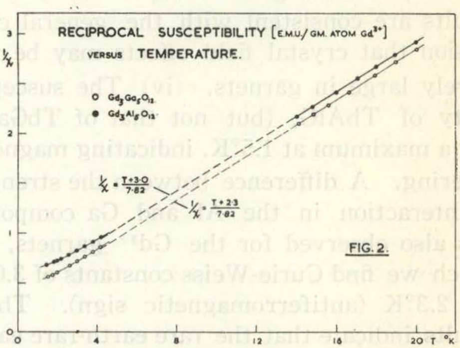

Fig. 2. Reciprocal susceptibility versus temperature for two Gd garnets. The Curie constant of 7.82 in each case corresponds to $g=1.992$, $S=7/2$, as expected for the Gd^{3+} ion.

which was investigated in the ranges 20° to 14°K and 4.2° to 1.5°K. The results are shown in figures 1 and 2.

We may note the following general features: (i) For both Tb^{3+} and Ho^{3+} the results are very similar in the Al and Ga compounds, in contrast to Tm^{3+} and the previously observed results for Dy^{3+} and Er^{3+}[3]. In a qualitative sense, this gives one some confidence that any deductions about crystal fields for these garnets can also be applied to the ferrimagnetic iron garnets, though it must be borne in mind that the average susceptibility is not very sensitive to small changes in the crystal field. (ii) The absolute magnitudes of χ for both Tb^{3+} and Ho^{3+} are very large and strongly temperature dependent down to the lowest temperatures. This indicates small splittings ($<5\,\mathrm{cm}^{-1}$) between the lowest energy levels, a result which may be considered *a priori* surprising, since both these ions have an even number of electrons and are situated in sites of rhombic symmetry. This suggests that deviations from cubic point symmetry may be predominantly axial with only small rhombic components, (see also Table I), or else that crystal field effects are appreciably weaker for both these ions than for other cases (such as Yb^{3+}, for which splittings of the order of $500\,\mathrm{cm}^{-1}$ have been found[7,2,9]). (iii) For Tm^{3+} the small and almost temperature independent χ indicates that the ground state is a singlet, or a non-magnetic Γ_3 doublet, with other states considerably higher ($>50\,\mathrm{cm}^{-1}$) in energy. In this case, the splittings in the Al and Ga compounds seem to be appreciably different. As in the unambiguous case of Yb^{3+}, these results are consistent with the general conclusion that crystal field effects may be relatively large in garnets. (iv) The susceptibility of TbAlG, (but not that of TbGaG), has a maximum at 1.5°K, indicating magnetic ordering. A difference between the strength of interaction in the Al and Ga componds was also observed for the Gd^{3+} garnets, for which we find Curie-Weiss constants of 3.0°K and 2.3°K (antiferromagnetic sign). These results indicate that the rare earth-rare earth interactions in garnets are in part due to exchange forces, rather than magnetic dipole coupling alone. The order of magnitude of the implied interactions is consistent with previous results for paramagnetic Yb^{3+}[2], Dy^{3+} and Er^{3+}[3] garnets, but it is considerably smaller than the values deduced by Pauthenet[10] from measurements on ferrimagnetic rare earth garnets. Reasons for this discrepancy have been discussed elsewhere[11].

The Paramagnetic Resonance Measurements

The paramagnetic resonance experiments were carried out and analysed as described previously[1,3]. The measurements were made at frequencies near 9 KMc/s, and except for the case of Yb^{3+} all were made at 4.2°K, to reduce relaxation broadening. The Yb^{3+} spectra were clearly resolved at 20°K and did not change with decreasing temperature. A striking feature in some of the observations was a large variation of the signal intensity with the orientation of the applied d.c. field. This was a result of the highly anisotropic *g*-values, and in some cases it led to difficulties in following certain lines over all angles. However all observed lines could be fitted very closely to the calculated curves based on three adjustable *g*-values and there was no ambiguity in the identification of the spectra. A typical set of results is shown in Fig. 3, in which the variation of effective *g*-value is plotted as a function of the direction of the d.c. field in a (110) plane.

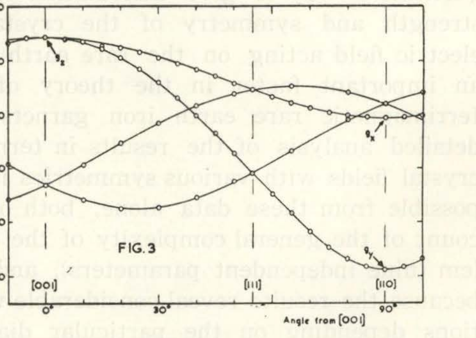

Fig. 3. Angular variation of the effective *g*-values for Er^{3+} in LGG, for the four resonances observed when a magnetic field is applied in a (110) plane.

The four curves correspond to the four types of ions which are inequivalently oriented with respect to a magnetic field in that plane. The points represent experimental measurements, and the solid lines the variation calculated from the three principal *g*-values chosen to give the best fit. Fig. 3

also illustrates graphically the very marked anisotropy found in these compounds. The results for all the ions are summarized in Table I, which includes for comparision previously published results for the same ions in YAl and YGa garnets.

The qualitative significance of these results to the theory of ferrimagnetism is that they emphasize again that the properties of most of the rare earth ions are extremely anisotropic and sensitive to the precise nature of their environment in the garnet structure. For Nd^{3+} and Yb^{3+} there are systematic trends in the *g*-values, and one can extrapolate from the paramagnetic to the ferrimagnetic iron garnets with some confidence. For Dy^{3+} and Er^{3+} these are big and seemingly random differences and quantitative extrapolation is rather more uncertain. Even so, we can quite definitely draw the general conclusion that all rare earth ions in garnets are individually very anisotropic, and this has important consequences for various bulk properties in the ferrimagnetic state. We shall examine here some of the resulting sublattice arrangements.

The Effect of Crystal Fields on the Sublattice Structure of the Ferrimagnetic Rare Earth Iron Garnets

In the ferrimagnetic iron garnets the rare earth ions are subject to exchange forces from two Fe^{3+} sublattices, which below room temperature are strongly alined by their own mutual interactions[10]. Were it not for the crystal field, the induced rare earth moment would be parallel (or antiparallel) to the resultant magnetization, but at low temperatures when only some of the states of the rare earth ions are populated, the situation is more complicated. The simplest case to consider arises when the crystal field is very large compared with both kT and the exchange interactions, and each ion has an odd number of electrons. It is then only necessary to take account of the exchange effects on the lowest Kramers doublet of each of the rare earth ions, which can then be represented by fictitious spins $s'=1/2$. The first order change of energy produced by the interactions can be represented by the splittings produced by an isotropic exchange field $-\boldsymbol{H}_e$ in the direction of the iron sublattice magnetization, acting on the fictitious spins through an anisotropic exchange *G*-tensor which has the same axes as the magnetic *g*-tensor[8,14]. If we assume that the form of anisotropy of G is similar to that of g, we can very simply specify the type of sublattice arrangement from the sequence in order of magnitude of the measured g_x, g_y and g_z[15].

Table I.

		g_x	g_y	g_z	ref.
Nd^{3+}	LuGaG	2.083±0.007	1.323±0.007	3.550±0.007	*
	YGaG	2.027±0.008	1.251±0.008	3.667±0.018	3
	LuAlG	1.789±0.005	1.237±0.006	3.834±0.005	*
	YAlG	1.733±0.002	1.179±0.002	3.915±0.026	3
Dy^{3+}	LuGaG	13.45 ±0.10	0.57 ±0.10	3.41 ±0.03	*
	YGaG	11.07 ±0.2	1.07 ±0.14	7.85 ±0.10	3
	LuAlG	2.29±0.03	0.91 ±0.05	16.6 ±0.3	*
	YAlG	No resonance detected**			3
Er^{3+}	LuGaG	3.183±0.015	3.183±0.015	12.62 ±0.10	*
	YGaG	4.69 ±0.03	4.03 ±0.02	10.73 ±0.05	3
	LuAlG	6.93 ±0.02	4.12 ±0.03	8.43 ±0.04	*
	YAlG	7.75 ±0.09	3.71 ±0.02	7.35 ±0.08	3
Yb^{3+}	LuGaG	3.653±0.013	3.559±0.013	2.994±0.011	*
	YGaG	3.73 ±0.02	3.60 ±0.02	2.85 ±0.02	1,12
	LuAlG	3.842±0.005	3.738±0.007	2.594±0.004	*
	YAlG	3.87	3.78	2.47	12

* This work.

** From preliminary measurements we find a weak resonance with $g_z \sim 18$, g_x and $g_y < 0.7$.

To calculate the magnetic moment $\boldsymbol{M}$ of a particular rare earth sublattice we derive an expression for the total free energy F of the individual ions subject to the exchange effects of the iron sublattices together with a small, arbitrarily oriented magnetic field $\boldsymbol{H}_0$. The component of $\boldsymbol{M}$ along one of the principal directions (α) of the g-tensor is then given by $-(\partial F/\partial H_{0\alpha})$, provided that the exchange energy is independent of $\boldsymbol{H}_0$, (as it will be in the garnets for small fields and low temperatures). The calculation of $\boldsymbol{M}$ is particularly simple at $T=0°\mathrm{K}$. The free energy is then identical with the spectroscopically measured internal energy, and to first order F (per ion) becomes equal to the lowest eigenvalue of the Hamiltonian[13]

$$\mathscr{H}=\boldsymbol{H}_e\cdot G\cdot s'+\mu_B\boldsymbol{H}_0\cdot g\cdot s'\,, \tag{1}$$

which is

$$E_-=-\frac{1}{2}\Big[\sum_{\alpha=x,y,z}(H_{e\alpha}G_\alpha+\mu_BH_{0\alpha}g_\alpha)^2\Big]^{1/2} \tag{2}$$

The α component of $\boldsymbol{M}$ at $T=0°\mathrm{K}$ is therefore given by

$$M_\alpha=\frac{N\mu_Bg_\alpha}{2}\,\frac{(H_{e\alpha}G_\alpha+\mu_BH_{0\alpha}g_\alpha)}{\Big[\sum_\alpha(H_{e\alpha}G_\alpha+\mu_BH_{0\alpha}g_\alpha)^2\Big]^{1/2}} \tag{3}$$

where N is the number of ions. The spontaneous moment produced by the exchange field alone can now be found by putting $H_0=0$. If $\boldsymbol{H}_e$ lies in one of the principal planes of the g's, the induced magnetization will also lie in that plane, and its components will be related by

$$\tan\Psi=\frac{M_\beta}{M_\alpha}=\frac{g_\beta G_\beta H_{e\beta}}{g_\alpha G_\alpha H_{e\alpha}}=\frac{g_\beta G_\beta}{g_\alpha G_\alpha}\tan\theta \tag{4}$$

where θ is the angle between $\boldsymbol{H}_e$ and the principal axis α, and Ψ the angle between $\boldsymbol{M}$ and α.

The orientation of the magnetic axes (of the six inequivalent ions in unit cell) relative to the cubic crystal axes (XYZ) is shown in Fig. 4A. If $\boldsymbol{H}_0$ is small, the iron sublattice magnetization, and hence also $\boldsymbol{H}_e$, will be parallel to one of the cubic [111] axes, (the 'easy' axis for most of the rare earth iron garnets), and we can identify $g_\alpha G_\alpha$ with g_zG_z for every ion, and $g_\beta G_\beta$ with either g_xG_x or g_yG_y: $\tan\theta=\sqrt{2}$ in each case. Values for G_β/G_α have so far only been determined for the case of Yb^{3+}[8], but we can make the reasonable guess that the anisotropy in the magnetic g will be strongly reflected in that of the exchange G[15]. In particular, if the magnetic g's are very different, it is most unlikely that the ratio $g_\beta G_\beta/g_\alpha G_\alpha$ will be close to one, so that Ψ and θ will be appreciably different. Three of the possible arrangements of the resulting rare earth polarization are shown in Figs. 4 (B, C and D). The ions indicated in parentheses represent speculative extrapolations based on Table I, assuming also that $g_\alpha>g_\beta$ implies $g_\alpha G_\alpha>g_\beta G_\beta$.

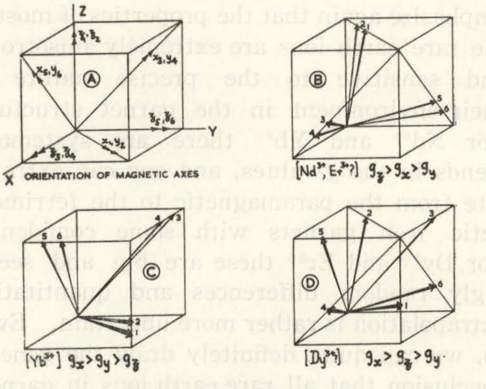

Fig. 4. (A) Orientation of the rare-earth ion magnetic axes relative to the cubic crystal axes (XYZ). Numbers 1 to 6 refer to the six inequivalent rare-earth ions in the unit cell.

(B), (C), (D) Three possible arrangements of the rare earth sublattice polarizations, for different relative strengths of the local distortions.

The precise extent to which the moments deviate from the [111] direction will depend on the anisotropy of both g and G, but from the values shown in Table I we can conclude with certainty that appreciably non-collinear arrangements will occur in most cases. Indeed, evidence for one such structure has already been reported[16], but unfortunately for a case (holmium) for which no paramagnetic resonance can be observed at ordinary microwave frequencies. For the one case (Yb^{3+}) for which both g and G are known, we can use equation (4) to estimate the angles made by the rare earth moments with the [111] axis. For three types of ions (1, 3 and 5 in Fig. 4C) we find 22.5°, and for the other three, 20°. These estimates should be only slightly affected by the second order terms, which we have neglected, and the uncertainty in extrapolating the g-values, and it would be very gratifying if they could be verified by neutron diffraction measurements.

From equation (3) we can also calculate the magnitudes of the moments on the six Yb sublattices and their resultant. By subtracting the Fe moment we can then predict the total spontaneous magnetization of pure YbIG at $T=0°\text{K}$. Using our values of g for LGG and Wickersheim's observed G, this leads to a calculated moment of $(5.01\text{-}5.00)=0.01\mu_B$[17], which may be compared with the value $7\mu_B$ predicted in the absence of crystal field anisotropy, and the observed value of $0.25\mu_B$[10]. The small residual discrepancy is almost certainly accounted for by second order Zeeman effects, whose contribution, estimated from the observed temperature independent susceptibility[2], will be of the order of $0.15\mu_B$.

The relatively strong and highly anisotropic crystalline electric fields which our paramagnetic measurements have indicated, will similarly affect the overall magnetic anisotropy in the ferrimagnetic iron garnets, and also the field dependence of the saturation magnetization. A discussion of these effects will be presented elsewhere. The remarkable structure dependence of the g-values observed for the cases of Er^{3+} and Dy^{3+} suggests that these ions should also show anomalous magneto-elastic effects at low temperatures.

Conclusion

A number of measurements have been described which emphasize the importance of crystal field effects on the properties of rare earth ions in garnets. It is shown that these may be expected to dominate the rare earth sublattice structure in the ferrimagnetic rare earth-iron garnets, though from existing data detailed predictions are generally not possible on account of several complicating effects. In the one ideal case of Yb^{3+} our measurements combined with the spectroscopic data of Wickersheim[8] lead one to expect a relatively simple canted sublattice structure, involving angles of about 20° between the Yb^{3+} and Fe^{3+} magnetic moments.

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13 Throughout this discussion we omit terms arising from off-diagonal matrix elements to electronic states above the ground state Kramers' doublet, and these may not always be negligible. For ions in the second half of the rare earth series the effect of such terms will be to enhance the magnetic moment, and in general they will also change its direction. However, we ignore these complications here since we only aim at qualitative conclusions, which can be obtained by considering the first order Zeeman effect alone. For some cases, e.g. Yb^{3+}, even the quantitative error should be small.

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15 If the interaction were simply of the form $JS_{\mathrm{RE}}\cdot S_{\mathrm{Fe}}$, the component of G and g would be related through a single scalar factor. In general, however, J depends on the orbital state of the rare earth ion, and the two g-tensors are not simply related. Even so, the principal axes are in general still the same, and we might guess that corresponding principal values will be in the same sequence. (See also refs. 8 and 14).

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17 This result is somewhat lower than the value recently calculated by Henderson and White (Phys. Rev. **123** (1961) 1627), who used a simplified expression for M, ignoring the canting of the Yb moments.

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Theoretical Study of the Magnetic Properties of Rare Earth Ions in the Structure of Garnet[*]

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An attempt has been made to interpret for various rare earths in the structure of garnet the magnetic susceptibility curves (Cohen) as well as other data: magnetization curves (Pauthenet), paramagnetic resonance (Wolf, Oxford).

a) In the first approximation, the Hamiltonian is written by the assumption that the ions surrounding the magnetic ion form a perfect cube, and the magnetic properties are deduced by means of Van Vleck's calculation.

b) In the second approximation, the exact arrangement of the neighbours is taken into account. The Hamiltonian is written for one f electron by assuming that the crystalline field is purely electrostatic and that there are punctual charges $-2e$ on the sites occupied by the ions O^{--}. It is expanded in a series of spherical harmonics, but a multiplicative constant σ_l is introduced for each Y_m^l to take into account the departure from the reality of the hypothesis of punctual charges, the screening effect of the outer shell, and other interactions as covalence. The coefficient a_m^l of Y_m^l for the purely electrostatic field due to punctual charges is calculated from crystallographic data. Many a_m^l vanish because the arrangement of the neighbours has orthorhombic symmetry, and many others are without interest owing to selection rules. Among what remains, the ones which are not zero when the arrangement of the neighbours have the cubic symmetry are well determined from crystallographic data, but the others are found in the calculation to be the difference of nearly equal terms (these terms are exactly equal in cubic symmetry), so we must consider them as undetermined, the precision on the crystallographic data being too small. Among them $a_2^4=a_{-2}^4$ is negligible with respect to a_0^4 and a_4^4, and a_6^6 and a_2^6 with respect to a_0^6 and a_4^6, and only a_0^2 and $a_2^2=a_{-2}^2$ are to be taken into account because they are multiplied by $\langle r^2\rangle$ which is large with respect to $\langle r^4\rangle$. We can therefore write the Hamiltonian as a linear combination of

$$Y_0^2, Y_2^2+Y_{-2}^2, Y_0^4,\ Y_4^4+Y_{-4}^4,\ Y_0^6,\ Y_4^6+Y_{-4}^6\,.$$

For n electrons f it is considered that J is a "good quantum number", and the result of compounding the spherical harmonics for the n electrons is a new spherical tensor written in the space of J by the method of polynomicals (Y. Ayant and J. Rosset, Ann. Inst. Four. **10**, 1960, pp. 345-358). The Ham-

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[*] Comment to the paper by W.P. Wolf, *et al.*, read by Professor P. Brissonneau.