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Magnetic structure and modification of hyperfine field in $Er_xY_{3-x}Fe_5O_{12}$ garnets: a nuclear magnetic resonance study

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Abstract. The NMR on ^{57}Fe nuclei located at octahedral and tetrahedral sites of $Y_{3-x}Er_xFe_5O_{12}$ garnets was measured at liquid-helium temperature. By analysing the results on polycrystalline samples with $x = 0.2$ and 2.8, obtained in a zero external field (magnetization along the $\langle 100 \rangle$ direction), we determined the non-collinear umbrella-like arrangement of the magnetic moments of Er^{3+} ions and modification of the hyperfine field on ^{57}Fe nuclei caused by Er ↔ Y substitution. The umbrella angle is $23(\pm 3)°$. These results were then used in the analysis of NMR of the single crystal with $x = 0.12$ in an external magnetic field parallel to the [111] direction. In this case there are two angles characterizing the magnetic umbrella, their values being $12(\pm 10)°$ and $48(\pm 9)°$.

1. Introduction

The subject of recent studies (Englich *et al* 1985, 1990, Brabenec *et al* 1987a, b) in which one of us participated was the NMR of ^{57}Fe in several rare-earth(RE)-substituted ferrimagnetic garnets $RE_xY_{3-x}Fe_5O_{12}$. It was shown that in these systems it is possible to determine from the NMR spectra the non-collinear 'umbrella' magnetic structure of the RE^{3+} moments. The underlying idea is very simple; for low concentrations of RE (typically $x \simeq 0.2$) the Fe^{3+} ions, in the vicinity of which one Y^{3+} ion is replaced by RE^{3+}, give rise to distinct 'satellite' lines. The splittings between the satellites and main lines are directly connected with the RE^{3+} moments m_{RE}. Under favourable conditions (well resolved satellites, and a small change in the transferred hyperfine fields) the determination of m_{RE} is then simple and straightforward. For the Ho^{3+} ion the corresponding analysis (Englich *et al* 1985) yielded results which agreed both with the crystal field analysis and with the experimental value of total magnetization. At the same time it indicated on possible misinterpretation (Guillot *et al* 1984) of the neutron diffraction data.

In the present paper the above-described method is applied to garnets containing Er^{3+}. Although these systems have been the subject of numerous studies, the umbrella structure of Er^{3+} moments is still not known (the analysis of the neutron diffraction data by Tchéou *et al* (1980) was based on a false assumption that [111] is the easy direction of magnetization). Recently we have studied the NMR of ^{167}Er nuclei in $Er_3Fe_5O_{12}$ and obtained the magnitudes of Er^{3+} magnetic moments (Savosta *et al* 1989). However, the

Table 1. Local coordinate systems of c sites and magnetic moments of RE^{3+} for the total magnetization M along [001] and [111] directions.

| | | | | Magnetic moments | |
| | | | | | |
c site	ξ	η	ζ	$M\|[001]$	$M\|[111]$
1	0$\bar{1}$1	0$\bar{1}$1	100	$m'(0\,a\,c)$	$\mu(\beta\,\alpha\,\alpha)$
2	101	10$\bar{1}$	010	$m'(a\,0\,c)$	$\mu(\alpha\,\beta\,\alpha)$
3	110	$\bar{1}$10	001	$m(0\,0\,1)$	$\mu(\alpha\,\alpha\,\beta)$
4	01$\bar{1}$	011	$\bar{1}$00	$m'(0\,\bar{a}\,c)$	$\mu'(\beta'\,\alpha'\,\alpha')$
5	$\bar{1}$01	101	010	$m'(\bar{a}\,0\,c)$	$\mu'(\alpha'\,\beta'\,\alpha')$
6	1$\bar{1}$0	110	001	$m(0\,0\,1)$	$\mu'(\alpha'\,\alpha'\,\beta')$

Table 2. Crystal structure data of YIG and ErIG.

| Garnet | a_0 (nm) | Oxygen parameters | | | Distances (nm) | | |
		x	y	z	RE–O	Fe(a)–O	Fe(d)–O
YIG	1.2367	-0.0271	0.0567	0.1504	0.2357	0.2017	0.1865
					0.2436		
ErIG	1.2347	-0.0267	0.0579	0.1506	0.2351	0.2019	0.1868
					0.2415		

uncertainty in the value of the total magnetic moment did not allow us to determine the umbrella angle with sufficient precision. On comparison with the paper of Englich *et al* (1985) the present study has two novel features. First, the system $Er_xY_{3-x}Fe_5O_{12}$ is studied for both small ($x = 0.2$) and large ($x = 2.8$) concentrations of Er. Second, the measurements on single crystals in an external magnetic field allowed NMR to be measured with the magnetization along other than the easy direction.

Preliminary results which mainly concerned the modification of the hyperfine field in substituted Er–Y iron garnets were recently reported by Novák *et al* (1990).

2. $Er_xY_{3-x}Fe_5O_{12}$ crystal and magnetic data

The system in question crystallizes in the cubic O_h^{10} group with 160 atoms in the unit cell. Fe^{3+} ions occupy tetrahedral (d) and octahedral (a) positions, while Y^{3+} and Er^{3+} ions enter the dodecahedral (c) sublattice. d sites are tetragonally distorted with the S_4 axis parallel to $\langle 100\rangle$, while a sites are distorted trigonally (C_3 axis$\|\langle 111\rangle$). The c sites have a rhombic symmetry; there are six c sites with differently oriented local coordinate systems (table 1). The oxygen atoms are situated in general positions characterized by three oxygen parameters x, y, z. The crystal data taken from Winkler (1981) of both yttrium iron garnet (YIG) $Y_3Fe_5O_{12}$ and erbium iron garnet (ErIG) $Er_3Fe_5O_{12}$ are given in table 2.

YIG belongs to the group of most thoroughly studied ferrimagnets. The moments $m(a)$ and $m(d)$ of the a and d site Fe^{3+} ions are antiparallel and the following equation holds:

$$3m(d) - 2m(a) = 5\mu_B \qquad \text{at 4.2 K.} \tag{1}$$

In REIG the magnetic moments of individual RE^{3+} ions make an angle with the total magnetization, forming a so-called umbrella structure. For the general direction of M there are six different moments $m(RE^{3+})$ corresponding to six c sites in table 1. If M is along the symmetry axis, the number of magnetically inequivalent RE^{3+} ions is reduced; for $M \| [001]$ or $M \| [111]$, only two remain (table 1).

According to our recent results (Savosta *et al* 1990) the magnitudes of Er^{3+} magnetic moments and the umbrella angle for M along $\langle 001 \rangle$ are

$$m = 6.59(7)\mu_B \qquad m' = 4.29(9)\mu_B \qquad 0° < \varphi < 26° \tag{2}$$

where the angle $\varphi = \cos^{-1}(c)$.

The magnetic properties of ErIG have been studied experimentally by many workers (see Guillot *et al* (1981) and Veltruský (1987) for references). Guillot *et al* (1981) performed an extensive study of the field and temperature dependences of the magnetization. For our work the most pertinent results are the values of the magnetization at 4.2 K with the magnetic field along the [100] (easy direction) and [111] directions:

$$M_{100} = 19.7(6)\mu_B \qquad M_{111} = 17.9(6)\mu_B \text{ per 2 } Er_3Fe_5O_{12}. \tag{3}$$

3. Hyperfine field on ^{57}Fe nuclei

We write the hyperfine field as a sum of three terms

$$B_{HF} = B_0 + B_{dip} + B_c \tag{4}$$

where B_0 is the field on the nuclei of a free Fe^{3+} ion, B_{dip} is the dipolar field due to all other magnetic ions present in the crystal and B_c is the change in B_0 due to the ligand field effects.

In stoichiometric YIG B_{HF} is parallel to the spin $\langle S \rangle$ of the Fe^{3+} ion. In substituted systems the dipolar field generally makes an angle with $\langle S \rangle$ but, as $|B_{dip}| \ll |B_0|$, only the projection of B_{dip} on $\langle S \rangle$ plays a role when calculating the hyperfine splitting. In what follows we therefore by B_{dip} mean the projection of B_{dip} on the direction of $\langle S \rangle$.

B_{dip} is the sum of individual moment contributions:

$$B_{dip} = \sum_i B_{dip}^{(i)} \qquad B_{dip}^{(i)} = \frac{\mu_0}{4\pi r_i^5} [3(m_i r_i)(r_i n) - (m_i n)r_i^2] \tag{5}$$

where the ith moment m_i is at the point r_i; $n = \langle S \rangle / |\langle S \rangle|$. B_c consists of two parts:

$$B_c = B_{cf} + B_{tr}$$

B_{cf} and B_{tr} being the crystal field and transferred contributions, respectively. The ground electronic state ^6S of the free Fe^{3+} ion has a zero orbital moment. As a consequence, B_{cf} arises only through a small admixture of the excited states into the ^6S state (see, e.g., Karnatchev *et al* (1980) for a more detailed discussion). It is generally believed that a more important role is played by B_{tr}, i.e. by the transfer of Fe^{3+} valence electrons to and

from the surrounding ions. Here, of course the transfer involving O^{2-} ligands (covalency) dominates, but the effect of the nearest cations may also be important.

When the Y^{3+} ion is replaced by Er^{3+}, both B_{dip} and B_c are modified. If we neglect the effect of small distortion, the change ΔB_{dip} in B_{dip} is readily expressed in terms of the Er^{3+} moment using (5). The change ΔB_c in B_c is much more difficult to estimate, but use can be made of the results obtained by Englich *et al* (1990) and Brabenec *et al* (1987a, b). These may be summarized as follows.

(i) $|\Delta B_c(d_{nn})| > |\Delta B_c(a)| > |\Delta B_c(d_{nnn})|$ as a rule, i.e. the change in $|B_c|$ for the nearest $Fe^{3+}(d)$ neighbour of the Er^{3+} is larger than the change in $|B_c|$ of the nearest $Fe^{3+}(a)$ ion and this in turn is larger than $|\Delta B_c|$ for the next-nearest $Fe^{3+}(d)$ ion.

(ii) $|\Delta B_c|$ increases with increasing difference between the ionic radii:

$$\Delta R_{ion} = |R_{ion}(RE^{3+}) - R_{ion}(Y^{3+})|.$$

(iii) ΔB_c is anisotropic, i.e. it depends on the direction of magnetization relative to the local coordinate system of the Fe^{3+} ion in question.

The analysis of B_c may be considerably simplified by using the semiempirical 'independent bond' (or 'superposition') model (Englich *et al* 1990). This model is based on assumptions that the contributions of individual ligands to B_c are additive and independent of each other, and that each contribution has a cylindrical symmetry. B_c may then be written as

$$B_c = \sum_{i=1}^{N} (b_0^{(i)} + b^{(i)} \cos^2 \vartheta_i) \tag{6}$$

where the sum is over the N ligands of given Fe^{3+} ion, $b_0^{(i)}$ and $b^{(i)}$ are called the isotropic and anisotropic 'intrinsic fields' (in analogy with the nomenclature of superposition model for the crystal field (Newman 1971)) and ϑ_i is the angle which the magnetization makes with the bond of Fe^{3+} to ith O^{2-}. The intrinsic fields $b_0^{(i)}$ and $b^{(i)}$ depend only on the nature of the ligand and on the ligand–Fe^{3+} ion distance. In stoichiometric garnets the distances of six O^{2-} ligands of $Fe^{3+}(a)$ (four ligands of $Fe^{3+}(d)$) are the same and therefore $b_0^{(i)}$ and $b^{(i)}$ are independent of i; equation (6) then reduces to

$$B_c = Nb_0 + b \sum_{i=1}^{N} \cos^2 \vartheta_i \tag{7}$$

where $N = 4$ (6) for a d (a) site.

As ϑ_i are readily calculated from the known geometry of the garnet structure, B_c is—for each site—determined by the two parameters b_0 and b. However, this represents no simplification in the stoichiometric garnet; because of the high symmetry of a and d sites, the hyperfine coupling is in any case characterized by two parameters only. In the substituted systems the situation is different. If, for a particular Fe^{3+} ion in YIG, one nearest Y^{3+} ion is replaced by Er^{3+}, the symmetry of Fe^{3+} site is lowered and, without the use of the independent bond model, four and six parameters are necessary to characterize the hyperfine coupling of Fe^{3+} (d) and Fe^{3+} (a), respectively (for the d site the C_2 symmetry axis remains). The same applies of course to the satellite splittings. Turning now to the use of the independent bond model, we first note that the effect of the distortion around the substituted ion may be neglected as the ionic radii of Y^{3+} and Er^{3+} differ only slightly (see Brabenec *et al* (1987a, b) for a discussion of this). What is changed, however, is the electron structure of the O^{2-} ion in the triad Er^{3+}–O^{2-}–Fe^{3+}.
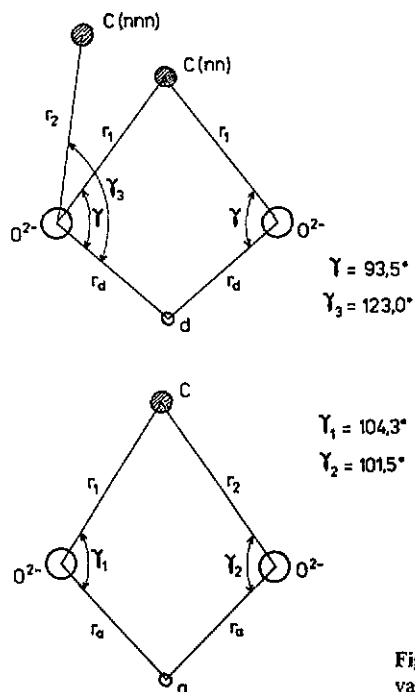
Figure 1. *a—c* and *d—c* bonds in garnets. The values of r_1, r_2, r_a and r_d are given in table 2.

As a consequence the values of the intrinsic fields are also modified. For the change ΔB_c we may write therefore

$$\Delta B_c = \Delta b_0 + \Delta b \cos^2 \vartheta_k \tag{8}$$

where k is the index of the oxygen in the triad, and Δb_0 and Δb are the changes in intrinsic fields. Only two parameters are therefore needed in order to characterize ΔB_c.

The situation is in fact slightly more complex as both a and d sites are bonded to a particular c site through two oxygen atoms (figure 1). This brings little complication for $Fe^{3+}(d)$ where both bonds are equivalent and the sum of the two contributions (8) may be written as

$$\Delta B_c(d) = 2 \Delta b_0 + \Delta b (\cos^2 \vartheta_k + \cos^2 \vartheta_l). \tag{9}$$

For $Fe^{3+}(a)$ the two bonds are non-equivalent and the sum is

$$\Delta B_c(a) = \Delta b_0^{(i)} + \Delta b_0^{(j)} + \Delta b^{(i)} \cos^2 \vartheta_i + \Delta b^{(j)} \cos^2 \vartheta_j. \tag{10}$$

To emphasize the different importance of the two bonds we rewrite (10) as

$$\Delta B_c(a) = 2 \Delta b_0^{(a)} + \Delta b^{(a)} [(1 - \tau) \cos^2 \vartheta_i + \tau \cos^2 \vartheta_j] \tag{11}$$

where $0 < \tau < 1$. The index i (j) denotes the oxygen in the triad Er^{3+}–O^{2-}–Fe^{3+} with shorter (longer) Er^{3+}–O^{2-} distance.

4. Experimental details

Single crystals of the mixed $Er_xY_{3-x}Fe_5O_{12}$ garnets ($x = 0.12, 0.52, 2.55$ and 3) were grown by the method of spontaneous crystallization from the melt (for details see
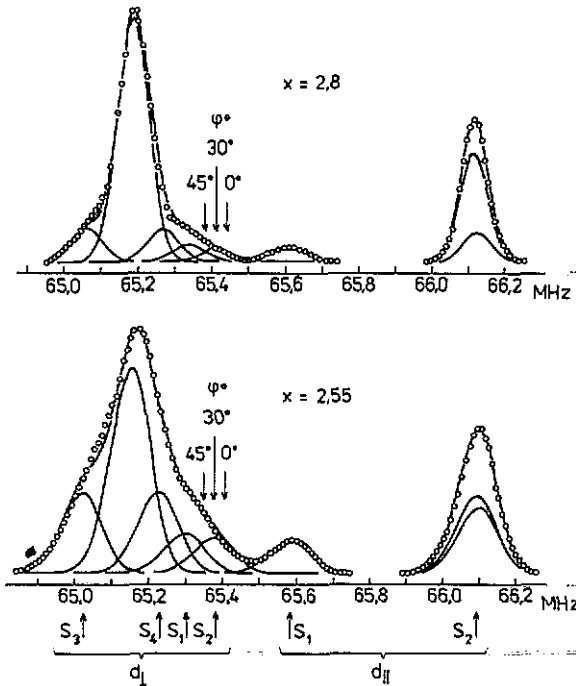
Figure 2. Comparison of the experimental (O) and calculated (——) NMR spectra of Fe^{3+} (*d*) ions (*T* = 4.2 K; *M* along [001] direction).

Gapeev *et al* (1974)). The crystal composition was checked using x-rays, by measuring the unit-cell parameter. The magnetocrystalline anisotropy of the single crystals used in the present study, as well as the temperature of the first-order spin-reorientation transitions $\langle 111 \rangle \leftrightarrow \langle 100 \rangle$, were studied earlier (Kolatchev *et al* 1977, Kolatcheva *et al* 1979, Borodin *et al* 1980). Polycrystalline samples (*x* = 0.2 and 2.8) were prepared by ceramic technology (sintering temperature, 1400 °C).

NMR spectra of ^{57}Fe at liquid-helium temperature were recorded using the two-pulse-spin-echo method with $\tau_2 = 2\tau_1$. NMR spectra represent an average over the spin echo signals as a function of the frequency of excitation pulse. A semiautomatic non-coherent NMR spectrometer with a quarter-wavelength coaxial cavity and with varying of the frequency was used. Measurement of the amplitude of the spin echo signal was made using a boxcar detector, which markedly improved the signal-to-noise ratio. The error in the frequency measurement was less than 5 kHz. To exclude the instrument-induced broadening of NMR lines the length of the pulses was chosen to be sufficiently long (10–30 μs) and the amplitude of the radio-frequency field H_1 was chosen to be close to its optimal value, corresponding to the maximum of the spin echo magnitude. The parameters of the pulses were selected so that only the nuclei in the domains were excited.

The analysis given below is based on the results obtained on polycrystalline samples and on a single crystal with *x* = 0.12. The NMR lines in systems with *x* = 0.52 and *x* = 2.55 were broader (see figure 2 for an example) and the structure of the spectrum was not well resolved.

Table 3. Satellites for $M\|[001]$. I is the intensity ratio of the satellites to corresponding main lines. $r = c/(1-c)$, where c is the concentration of the substitution. Δb corresponds to $Y^{3+} \leftrightarrow Er^{3+}$ substitution in the second coordination sphere of the Fe^{3+} ion. All other Δb correspond to substitution in the first coordination sphere.

Main line	Satellite	ΔB_{dip}	ΔB_c	I	ΔB_{exp} (MHz)	
					$x = 0.2$	$x = 2.8$
$d_\|$	s_1	$2c_1 m$	$\Delta b_0^{(d)} + 2g_1\,\Delta b^{(d)}$	$2r$	0.495(15)	$-0.506(5)$
$d_\|$	s_2	$c_1 m'(a - \frac{1}{2}c)$	$\Delta b_0^{(d)} + g_1\,\Delta b^{(d)}$	$4r$	<0.04	0.00(20)
$d_\perp$	s_1	$-c_1 m'c$	$\Delta b_0^{(d)} + 2g_2\,\Delta b^{(d)}$	r	—	<0.230
$d_\perp$	s_2	$-c_1 m'c$	$\Delta b_0^{(d)} + 2g_3\,\Delta b^{(d)}$	r		<0.230
$d_\perp$	s_3	$c_2 m'(a + c)$	$\Delta \bar{b}_0^{(d)} + g_2\,\Delta \bar{b}^{(d)}$	$2r$	0.132(10)	$-0.135(20)$
$d_\perp$	s_4	$-\frac{1}{2}c_2 m$	$\Delta \bar{b}_0^{(d)} + g_3\,\Delta \bar{b}^{(d)}$	$2r$		>-0.20
a	s_1	$-\frac{5}{8}c_3 m'c$	$\Delta b_0^{(a)} + \Delta b^{(a)}[(1-\tau)g_4 + \tau g_5]$	$2r$	$-0.191(5)$	0.193(9)
a	s_2	$c_3 m'c$	$\Delta b_0^{(a)} + \Delta b^{(a)}[(1-\tau)g_5 + \tau g_6]$	$2r$	0.110(15)	$-0.11(3)$
a	s_3	$\frac{5}{8}c_3 m$	$\Delta b_0^{(a)} + \Delta b^{(a)}[(1-\tau)g_6 + \tau g_4]$	$2r$	<0.1	>-0.12

Table 4. Values of constants in table 3 for YIG and ErIG.

	c_1 (MHz)	c_2 (MHz)	c_3 (MHz)	g_1	g_2	g_3	g_4	g_5	g_6
YIG	0.0433	0.0236	0.0310	0.4219	0.1415	0.4366	0.8514	0.1210	0.0276
ErIG	-0.0436	-0.0237	-0.0312	-0.4220	-0.1464	-0.4315	-0.8480	-0.1253	-0.0267

5. Results and their analysis

5.1. M along the [001] direction, with a zero external field

If $M\|[001]$, then in stoichiometric YIG all $Fe^{3+}(a)$ ions are magnetically equivalent, while there are two inequivalent tetrahedral Fe^{3+} ions: those with the S_4 axis along M (denoted as $d_\|$ in what follows) and those with $S_4 \perp M$ (denoted as $d_\perp$). The relative intensities of the corresponding three main lines $d_\| : d_\perp : a$ are in the ratio $1 : 2 : 2$.

If one of the nearest Y^{3+} neighbours of the Fe^{3+} ion is replaced by Er^{3+}, satellite lines appear. The corresponding splittings are determined by (5), (9) and (11). On the assumption of a random distribution of Er^{3+} substitutions, the relative intensities of the satellites are given by the simple binomial rule. These quantities are summarized in table 3, together with the experimentally determined splittings (see the discussion below).

There is a simple relation between the two opposite limits of YIG:Er and ErIG:Y; the expressions for the absolute values of splittings given in table 3 are the same in the two limits, but the signs are opposite. Note that it is the independent bond model which makes such a relation possible. Minor differences in B_{dip} arise from the different lattice constants of ErIG and YIG. Differences in the oxygen parameters slightly modify the parameters in front of b (table 4).

In figure 3 the three main lines and their satellites of the $x = 0.2$ system are shown together with the mirror image of the spectrum of the $x = 2.8$ system. It is seen that
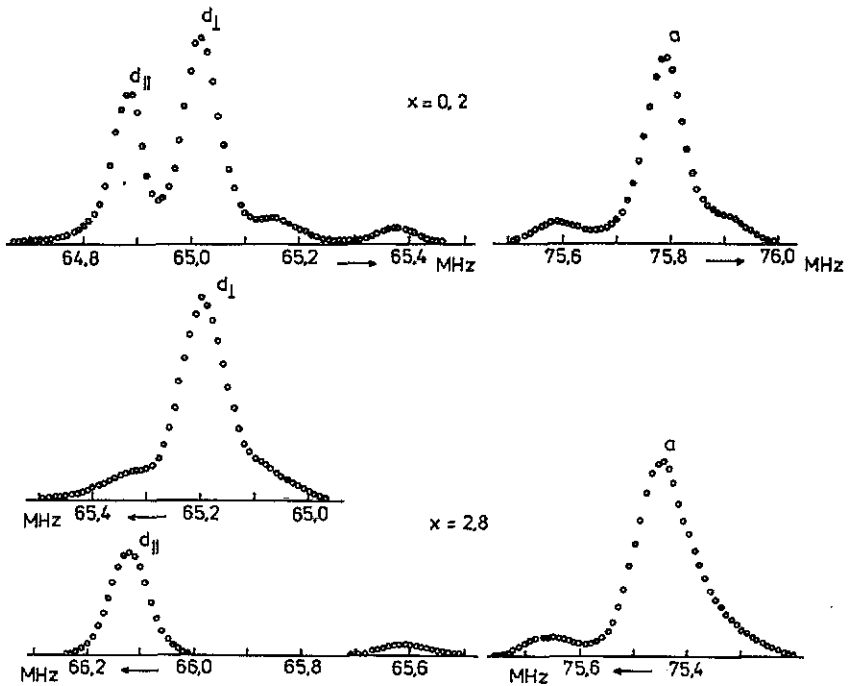
Figure 3. NMR spectra of ^{57}Fe in $Er_xY_{3-x}Fe_5O_{12}$ polycrystalline garnets ($x = 0.2$ and 2.8) for $T = 4.2$ K, and for zero external magnetic field. M along the [001] direction. Note that for $x = 2.8$ the mirror image of the spectrum is displayed.

within the experimental accuracy the positions of corresponding satellites, relative to the main lines, coincide in both systems. From this fact we may infer the following.

(i) The magnetic moments of Er^{3+} are almost identical in both systems.

(ii) ΔB_c either is very small or is well described by the independent bond model.

Besides the splittings between the satellites and the main lines, additional information is contained in the positions of the main lines. There is little reason to calculate their absolute positions, as nothing is known about the shape of the crystallites and consequently about the magnitude of the demagnetization field. The linear combinations

$$\Delta_{dd} = d_\parallel - d_\perp \qquad \Delta_{da} = d_\parallel + a \tag{12}$$

do not, however, depend on the demagnetization field. Δ_{dd} and Δ_{da} still depend on b_0 and b unlike the satellite splittings, in the expression for which only the changes Δb_0 and Δb appear (tables 3 and 5). For this reason we subtract the value of Δ_{dd} and Δ_{da} in the $x = 2.8$ and $x = 0.2$ systems. After rather cumbersome calculations we get the result (where the moments are in μ_B, and the splittings in megahertz)

$$\delta_{dd} = \Delta_{dd}(x = 2.8) - \Delta_{dd}(x = 0.2)$$

$$= 0.003m'a - 0.001m'c + 0.180m + 0.532(\Delta b^{(d)} + \Delta \tilde{b}^{(d)}) \tag{13}$$

$$\delta_{da} = \Delta_{ad}(x = 2.8) - \Delta_{ad}(x = 0.2)$$

$$= 0.067m'a - 0.023m'c + 0.142m + 1.688(\Delta b^{(d)} + \Delta \tilde{b}^{(d)})$$

$$+ 2\Delta b^{(a)} + 4(\Delta b_0^{(d)} + \Delta \tilde{b}_0^{(d)}) + 6\,\Delta b_0^{(a)}. \tag{14}$$

$\Delta \tilde{b}$ correspond to the substitution in the second coordination sphere, and all other Δb correspond to substitution in the first coordination sphere. Experiment gives $\delta_{dd} = 1.063(10)$ MHz and $\delta_{da} = 0.906(10)$ MHz.

One problem is to be noted; the correspondence between experimentally observed satellites and those predicted by theory is not unambiguous. We have removed all but one ambiguity by requiring that $0 < \mu$, $\mu' <$ free-ion values and $|\Delta b_0^{(d)}|$, $|\Delta b^{(d)}| < 0.3$ MHz.

The remaining ambiguity concerns the two satellites of the $d_\perp$ line. We shall now show how this ambiguity may be removed and at the same time the umbrella angle determined by combining the results presented here with those obtained by us earlier (Savosta *et al* 1989). We first note that from tables 3 and 4 it follows that the changes ΔB_c for the satellites $s_1(d_\parallel)$ and $s_2(d_\perp)$ are almost identical, the difference being $0.02 \Delta b^{(d)}$. If we neglect this small quantity, using m, m' from (2) and experimental value for the splitting $s_1(d_\parallel)$ from table 3, the splitting $\Delta(s_2)$ between the line $d_\perp$ and its satellite $s_2(d_\perp)$ may be expressed as a function of the umbrella angle:

$$\Delta(s_2) = 0.254(12)c \text{ MHz} \qquad c = \cos \varphi. \tag{15}$$

We can now use the upper limit for the angle φ as given in (2), together with the limitation of $\Delta(s_2)$ (table 3) to obtain

$$0.222 \text{ MHz} < |\Delta(s_2)| < 0.230 \text{ MHz}$$

which leads to

$$\varphi = 23(\pm 3)^\circ. \tag{16}$$

We note that it is the strong dependence of the form of line $d_\perp$ on the position of $s_2(d_\perp)$ in the considered range of umbrella angles, which led to much more accurate value of φ compared with (2). To illustrate this point the positions of $s_2(d_\perp)$, as calculated from (15), are shown in figure 2 by arrows for several values of the angle φ.

The magnetic moments of the Er^{3+} ions are now known with sufficient accuracy. We may therefore calculate the dipolar part of the splitting for all satellite lines, as well as the dipolar contribution to δ_{dd} and δ_{da} in (13) and (14). There remains the dependence on the parameters of the superposition model. Using then the experimental results we were able to fix the values of most of these parameters:

$$\Delta b_0^{(d)} = 0.08(3) \text{ MHz} \qquad \Delta b^{(d)} = -0.18(4) \text{ MHz}$$
$$\Delta \tilde{b}_0^{(d)} = 0.003(15) \text{ MHz} \qquad \Delta \tilde{b}^{(d)} = -0.03(5) \text{ MHz} \tag{17}$$
$$\Delta b_0^{(a)} = -0.016(8) \text{ MHz}.$$

The quantity $\Delta b^{(a)}$ is small and its value is uncertain. No reliable value for the parameter τ can be deduced. We note that the values (17) agree with the qualitative discussion given in section 3.

5.2. *M along [111] direction*

With $M \| [111]$ in ideal garnets all d sites are magnetically equivalent and there are two inequivalent a sites: a_1 (C_3 axis parallel to [111]) and a_2 (C_3 axis along [$\bar{1}11$], [$1\bar{1}1$] or [$11\bar{1}$]). The ratio of intensities $d:a_1:a_2$ is $6:1:3$. The satellite splittings are summarized

Table 5. Satellites for $M\|[111]$. r has the same meaning as in table 3. The terms $\Delta\tilde{b}_0^{(d)}$, $\Delta\tilde{b}^{(d)}$ and $\Delta b^{(a)}$ are neglected. The values of constants c_k, g_k are given in table 6.

Main line	Satellite	ΔB_{dip}	ΔB_c	I	ΔB_{exp} (MHz)
a_1	s_1	$-c_4\mu(2\alpha+\beta)$	$\Delta b_0^{(a)}$	$6r$	-0.156
a_2	s_1	$-c_4\mu'(2\alpha'+\beta')$	$\Delta b_0^{(a)}$	$2r$	>-0.150
a_2	s_2	$c_4\mu(\alpha+2\beta)$	$\Delta b_0^{(a)}$	$2r$	$0.145(20)$
a_2	s_3	$c_4\mu'(\alpha'+2\beta')$	$\Delta b_0^{(a)}$	$2r$	$0.145(20)$
d	s_1	$c_5\mu(\beta-\alpha)$	$\Delta b_0^{(d)}+(g_7+g_8)\Delta b^{(d)}$	r	
d	s_2	$c_5\mu'(\beta'-\alpha')$	$\Delta b_0^{(d)}+(g_9+g_{10})\Delta b^{(d)}$	r	
d	s_3	$-c_6\mu'(2\alpha'+\beta')$		r	>-0.14
d	s_4	$-c_6\mu'\alpha'$		r	<0.26
d	s_5	$-c_6\mu(2\beta-\alpha)$		r	
d	s_6	$c_6\mu(4\alpha+\beta)$		r	

Table 6. Values of constants in table 5 calculated for YIG.

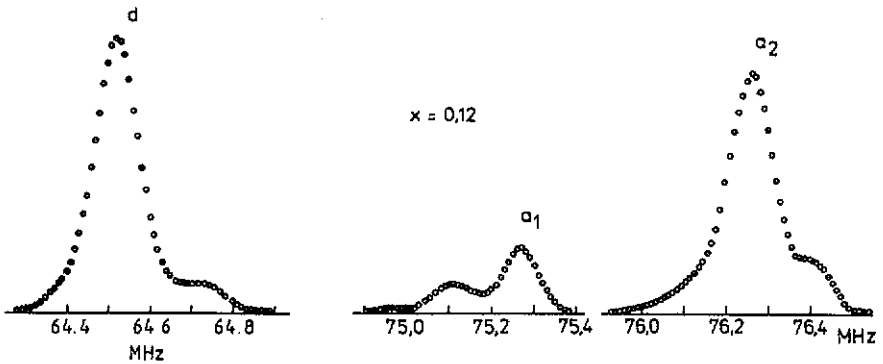| c_4 (MHz)	c_5 (MHz)	c_6 (MHz)	g_7	g_8	g_9	g_{10}
0.0143	0.050	0.014	0.045	0.029	0.050	0.949

Figure 4. NMR spectra of ^{57}Fe in an $Er_{0.12}Y_{2.88}Fe_5O_{12}$ single crystal for $T=4.2$ K and external magnetic induction along the [111] direction. The value of magnetic induction was 0.44 T when the spectrum of $Fe^{3+}(d)$ ions was measured while it was 0.27 T for $Fe^{3+}(a)$ ions.

in table 5. Experiments on only one single-crystal sample with $x=0.12$ were performed; the spectrum is shown in figure 4.

When determining the Er^{3+} magnetic moments we may use ErIG magnetization as additional information; after subtracting the contribution of Fe^{3+} moments from the value (3) and using table 1 we get

$$\mu(2\alpha+\beta)+\mu'(2\alpha'+\beta')=16.11(30)\mu_B. \tag{18}$$

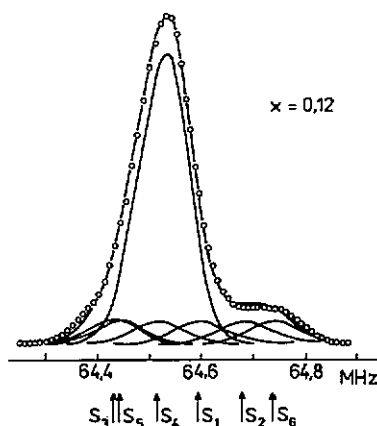x = 0,12

$s_3\|s_5$ s_4 s_1 s_2s_6

Figure 5. Comparison of the experimental (O) and calculated (——) NMR spectra of $Fe^{3+}(d)$ ions ($T = 4.2$ K; M along the [111] direction).

To calculate the four umbrella parameters $\mu\alpha$, $\mu\beta$, $\mu'\alpha'$ and $\mu'\beta'$ (α, β and α', β' are connected by $\beta^2 + 2\alpha^2 = 1$ and $\beta'^2 + 2\alpha'^2 = 1$) we used the change $\Delta b_0^{(a)}$ in the intrinsic field of $-0.016(8)$ MHz determined in section 5.1. The positions of three $Fe^{3+}(a)$ satellites $s_1(a_1)$, $s_2(a_2)$, $s_3(a_2)$ together with (18) constitute a convenient system of four linear equations for the four unknown parameters. After solving the equations, all six satellites of the $Fe^{3+}(d)$ line (with $\Delta b_0^{(d)}$ and $\Delta b^{(d)}$ again determined in section 5.1) were calculated and compared with experiment. As seen from figure 5, the model describes the experimentally obtained NMR spectrum adequately also in this case.

The values of the [111] umbrella parameters calculated in the way described above are (ψ and ψ' are the angles which the moments make with the [111] direction)

$$\mu = 5.80(30)\mu_B \qquad \mu' = 5.45(75)\mu_B \qquad \psi = 12(\pm10)° \qquad \psi' = 48(\pm9)°.$$

6. Conclusions

We have succeeded in the determination of the Er^{3+} magnetic structure in $Er_xY_{3-x}Fe_5O_{12}$ garnets for the total magnetization along the $\langle100\rangle$ and $\langle111\rangle$ directions. To obtain an unambiguous solution we had to combine the results obtained on systems with low and high concentrations of Er and moreover earlier information on Er^{3+} magnetic moments had to be considered. The superposition model was used to describe the modification of the hyperfine field by the crystal-field effects, so that the results obtained for the magnetic structure depends on the validity of this model.

It would be valuable to make the measurements on a single crystal with a high Er concentration and for $M\|[111]$ direction. We believe that a more precise solution for the [111] Er^{3+} umbrella will then be obtained.

Using the theory developed by Veltruský (1987) and Savosta *et al* (1989), the results obtained may be employed to get unequivocal values for the crystal-field parameters of the Er^{3+} ion. In this way a complete description of the behaviour of the Er^{3+} ion in iron garnets, within the framework of isotropic exchange model, will be achieved.

After this paper was submitted for publication, a neutron diffraction study of the crystal and magnetic structure of ErIG by Hock *et al* (1991) appeared. The value that

these workers obtained for the umbrella angle with M along the [001] direction is 25° at 5 K which is in excellent agreement with our value of $23(\pm 3)°$.

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