

## MAGNETIC PROPERTIES OF Eu–Sc–Fe GARNETS STUDIED WITH THE MÖSSBAUER EFFECT

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Magnetic properties of the garnet system  $\text{Eu}_{3-y}\text{Sc}_{2+y}\text{Fe}_3\text{O}_{12}$  for  $0 \leq y \leq 0.5$  have been studied with  $^{57}\text{Fe}$  and  $^{151}\text{Eu}$  Mössbauer spectroscopy. The system is shown to have a ferrimagnetic structure. Both, the ordering temperatures and the hyperfine magnetic fields at the  $^{57}\text{Fe}$  nuclei are found to increase with an increase in  $y$ . The iron magnetic moments at the octahedral and the tetrahedral sites are non-collinear. The average canting angles at these sites are determined and used for the calculation of the magnetic moments. Good agreement is obtained between the calculated and the experimental moment for the  $y = 0.0$  sample. The determined magnetic properties are consistent with the recently proposed cation distribution in this system.

### 1. Introduction

The investigated series  $\text{Eu}_{3-y}\text{Sc}_{2+y}\text{Fe}_3\text{O}_{12}$  ( $0 \leq y \leq 0.5$ ) belongs to garnets which are cubic compounds with a space group  $\text{Ia}\bar{3}\text{d}(\text{O}_h^{10})$ . The general formula of garnets is  $\langle \text{X}_3 \rangle [\text{Y}_2] (\text{Z}_3) \text{O}_{12}$ , where X, Y and Z denote cations at the dodecahedral (c), octahedral (a) and tetrahedral (d) sites, respectively [1]. X-ray studies of the  $\text{Eu}_{3-y}\text{Sc}_{2+y}\text{Fe}_3\text{O}_{12}$  system [2] showed that it is possible to produce single phase compounds for the composition range  $0 \leq y \leq 0.7$ . From the conformance of the lattice constant with Vegard's law, the authors concluded that only the c-site composition varies over the single phase range. They postulated the cation distribution

$$\langle \text{Eu}_{3-y}\text{Sc}_y \rangle [\text{Sc}_2] (\text{Fe}_3) \text{O}_{12}. \quad (1)$$

For the  $y = 0.0$  composition, magnetization measurements were performed by Mondegarian and Suchow [3]. They found a slope change in the temperature dependence of the molar susceptibil-

ity,  $\chi_M$ , at about 80 K. This temperature was supposed to be the ordering temperature,  $T_N$ . They also measured a spontaneous magnetization of  $0.1\mu_B$  at 1.5 K and suggested a ferrimagnetic ordering with possible canting of the  $\text{Eu}^{3+}$  ions at the c-sites and the  $\text{Fe}^{3+}$  ions at the d-sites.

In our previous study of the  $\text{Eu}_{3-y}\text{Sc}_{2+y}\text{Fe}_3\text{O}_{12}$  system [4] we showed that the cation distribution (1) is not correct, by using Mössbauer measurements at temperatures above  $T_N$  and the composition dependence of the lattice constant. The most probable cation distribution of the  $y = 0.0, 0.2$  and  $0.5$  samples were shown to be

$$\langle \text{Eu}_3 \rangle [\text{Sc}_{1.764}\text{Fe}_{0.236}] (\text{Sc}_{0.236}\text{Fe}_{2.764}) \text{O}_{12}, \quad (2)$$

$$\langle \text{Eu}_{2.997}\text{Sc}_{0.003} \rangle [\text{Sc}_{1.685}\text{Fe}_{0.315}] (\text{Sc}_{0.315}\text{Fe}_{2.685}) \text{O}_{12}, \quad (3)$$

and

$$\langle \text{Eu}_{2.937}\text{Sc}_{0.063} \rangle [\text{Sc}_{1.525}\text{Fe}_{0.475}] (\text{Sc}_{0.475}\text{Fe}_{2.525}) \text{O}_{12}, \quad (4)$$

respectively.

In this paper the results of  $^{57}\text{Fe}$  and  $^{151}\text{Eu}$  Mössbauer measurements at low temperatures are presented. The ordering temperatures of all the samples are determined accurately. The samples

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are shown to be ferrimagnets, with non-collinear alignment of the  $\text{Fe}^{3+}$  spins at the a- and d-sites. The canting angles of the  $\text{Fe}^{3+}$  spins at these sites are determined and used for the calculation of the magnetic moments of the samples. Good agreement is obtained between the calculated and measured moments for the  $y = 0.0$  sample. All magnetic properties of the investigated garnets which are derived from the Mössbauer spectra are shown to be consistent with the cation distributions (2)–(4).

## 2. Experimental

The polycrystalline samples of the series  $\text{Eu}_{3-y}\text{Sc}_{2+y}\text{Fe}_3\text{O}_{12}$  were the same as those used by Mondegarian et al. [2,3]. They had nominal compositions  $y = 0.0, 0.2$  and  $0.5$ . According to X-ray diffraction studies [2] the samples are single phase. Mössbauer absorbers with thickness of about  $20 \text{ mg/cm}^2$  were prepared by mixing the samples with boron nitride and pressing the mixture into lucite containers, which were covered with iron-free aluminium foils.

The Mössbauer measurements were carried out in the temperature range  $1.4\text{--}66 \text{ K}$  using the  $14.41 \text{ keV}$  transition in  $^{57}\text{Fe}$  and the  $21.53 \text{ keV}$  transition in  $^{151}\text{Eu}$ . The Mössbauer spectra were recorded with a standard spectrometer in which a source of gamma rays moved with a constant acceleration and the multichannel analyzer was operated in the time mode. The spectrometer was calibrated with a Michelson interferometer using a He/Ne laser. A symmetric sawtooth reference signal was used, producing two mirror Mössbauer spectra which were folded with a computer program [5]. The sources  $^{57}\text{Co}(\text{Rh})$  and  $^{151}\text{Sm}(\text{SmF}_3)$  were kept at  $4.2 \text{ K}$ . The stability of the absorber temperature was  $0.1 \text{ K}$ . For measuring spectra in an external magnetic field,  $H_{\text{ext}}$ , a superconducting solenoid was used with the  $H_{\text{ext}}$  direction parallel to the direction of propagation of the gamma rays. The spectra were measured in transmission geometry. The gamma rays were detected with a Xe– $\text{CO}_2$  filled proportional counter or with an intrinsic germanium solid state detector.

## 3. Results and discussion

It is generally accepted that in magnetically ordered materials the hyperfine magnetic field,  $H_{\text{hf}}$ , as measured with the Mössbauer effect, is proportional to the magnetization. Thus, the ordering temperature is defined as the temperature at which the magnetically split Mössbauer spectrum disappears. By measuring  $^{57}\text{Fe}$  Mössbauer spectra at different temperatures (fig. 1) we found that the magnetically split spectra disappear at  $T_{\text{N}}$  equal to  $19.5(0.5)$ ,  $20.5(0.5)$  and  $32.5(0.5) \text{ K}$  for the  $y = 0.0, 0.2$  and  $0.5$  samples, respectively. In order to check these  $T_{\text{N}}$  values, two other techniques were used for measuring  $T_{\text{N}}$ . In the first one, the thermal scanning technique [6], the number of counts at a given temperature, with a transducer set at a fixed velocity near the centroid of the spectrum, is recorded for a short time interval. At the onset of magnetic ordering, the number of counts is expected to show a rapid increase. With this technique we found for the  $y = 0.0$  sample (fig. 2)  $T_{\text{N}} = 20.0(0.5) \text{ K}$ , which compares well with the value of  $19.5(0.5) \text{ K}$  determined from the collapse of the magnetically split spectrum. The second technique makes use of the fact that in rare-earth iron garnets, apart from the dominant superexchange interaction between the  $\text{Fe}^{3+}$  ions at the a- and d-sites, also the superexchange interaction between the rare-earth ions at the c-sites and the  $\text{Fe}^{3+}$  ions at the d-sites is an important one [1]. Thus, the disappearance of  $H_{\text{hf}}$  corresponding to the  $\text{Fe}^{3+}$  ions at the a- and d-sites at  $T = T_{\text{N}}$  is accompanied with a simultaneous disappearance of  $H_{\text{hf}}$  corresponding to the  $\text{Eu}^{3+}$  ions at the c-sites (such a situation does not occur, for example, in rare-earth orthoferrites [7]). The  $^{151}\text{Eu}$  Mössbauer spectra of the investigated samples at temperatures close to  $4.2 \text{ K}$  are very complex (fig. 3). At higher temperatures, but still below  $T_{\text{N}}$ , they are broad single lines. It is possible to detect the disappearance of  $H_{\text{hf}}$  at the  $^{151}\text{Eu}$  nuclei by measuring the temperature dependence of the full width at half maximum,  $\Gamma_{\text{exp}}$ , of these lines (fig. 4). In this dependence three different temperature regions can be distinguished. In the first one,  $\Gamma_{\text{exp}}$  decreases very rapidly as the temperature approaches  $T_{\text{N}}$ , due to the sharp decrease of  $H_{\text{hf}}$ . In

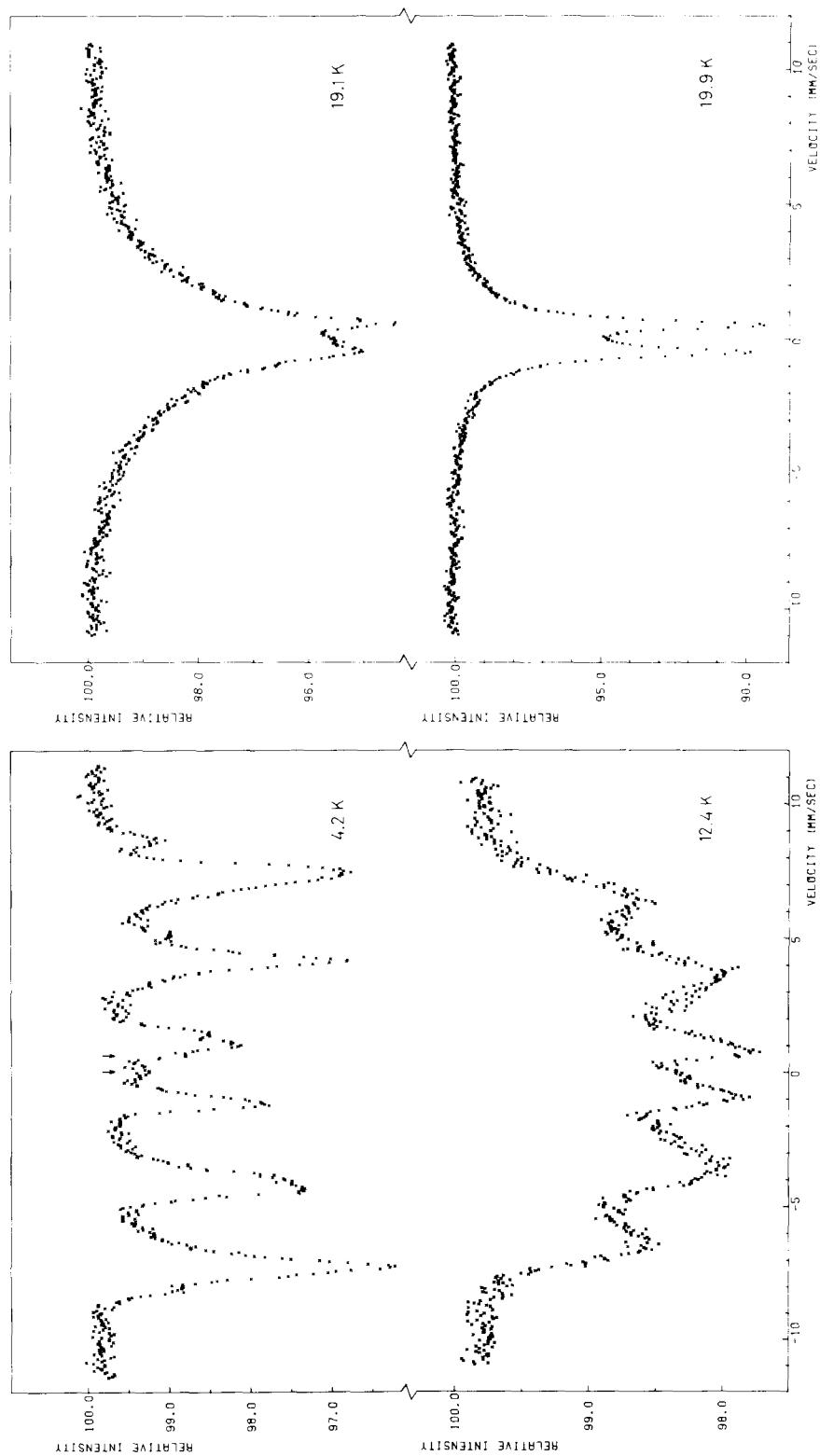


Fig. 1.  $^{57}\text{Fe}$  Mössbauer spectra of the  $y = 0.2$  sample at a few selected temperatures below  $T_N$ . The arrows in the 4.2 K spectrum indicate the positions of two impurity lines.

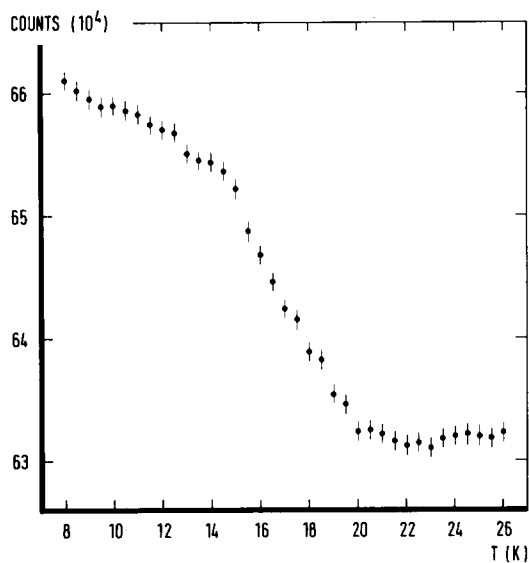


Fig. 2. Counts measured at zero Doppler velocity for 200 s each as a function of temperature for the  $y = 0.0$  sample.

the second region which is in the close vicinity of  $T_N$ , a slow decrease of  $\Gamma_{\text{exp}}$  is observed due to spin relaxation effects [8–10]. In the third region at temperatures well above  $T_N$ , a very slow decrease of  $\Gamma_{\text{exp}}$  is caused by the temperature dependence of the effective absorber thickness [11]. The ordering temperature of the  $y = 0.5$  sample determined from the intersection of straight lines which approximate well the  $\Gamma_{\text{exp}}(T)$  dependence in the first and the third region is equal to 32(1) K (fig. 4) and agrees well with the value of 32.5(0.5) K found from the collapse of the magnetically split  $^{57}\text{Fe}$  Mössbauer spectra.

The emphasis is put on the determination of the  $T_N$  values because the value of  $T_N$  for the  $y = 0.0$  sample as found from the  $\chi_M(T)$  dependence [3] differs significantly from our value: 80 vs. 19.5(0.5) K. A possible explanation of this discrepancy is that the  $y = 0.0$  sample contains a few per cent of an impurity, probably in a form of  $\text{Sc}_{2-x}\text{Fe}_x\text{O}_3$  with  $x > 1$  [4]. Up to 78 K we could detect a Zeeman pattern corresponding to this impurity. Thus, the impurity could be responsible for the observed change in the slope of the  $\chi_M(T)$  curve (fig. 2 in ref. [3]). On the other hand, one would expect that at 19.5 K a change would appear in the

$\chi_M(T)$  curve. Unfortunately, the appearance of this could not be assessed, since there are no experimental points between 14 and 28 K [3].

An increase in the values of  $T_N$  with an increase of the nominal composition  $y$  is consistent with the cation distributions (2)–(4). This can be shown qualitatively by using either the molecular field theory or the statistical theory of Gilleo [12]. If one assumes that the only important superexchange magnetic interaction in the investigated series is the one between the  $\text{Fe}^{3+}$  ions at the a- and d-sites, then it can be shown from the molecular field theory that  $T_N$  is proportional to  $[(1 - k_a)(1 - k_d)]^{1/2}$ , where  $k_i$  ( $i = a, d$ ) is the fraction of the  $\text{Sc}^{3+}$  ions at the  $i$ th site. With the cation distributions (2)–(4) one finds then that the  $T_N$  values of  $y = 0.0, 0.2$  and  $0.5$  samples should increase as 1 : 1.1 : 1.4. This reflects reasonably well the small increase in the  $T_N$  value upon going from the  $y = 0.0$  sample ( $T_N = 19.5$  K) to the  $y = 0.2$  sample ( $T_N = 20.5$  K) and the larger increase upon going from the  $y = 0.0$  sample to the  $y = 0.5$  one ( $T_N = 32.5$  K). With the same assumption one can show, using Gilleo's expression for an ordering temperature of a diamagnetically diluted ferrimagnet [12], that the  $T_N$  values corresponding to the  $y = 0.0, 0.2$  and  $0.5$  samples should increase as 1 : 1.5 : 2.5, which again agrees qualitatively with the experimental data.

Since the ordering temperature  $T_N$  of a sample reflects the strength of magnetic interaction in that sample, one should expect an increase in the values of the hyperfine magnetic field  $H_{\text{hf}}(0)$  at the  $^{57}\text{Fe}$  nuclei, measured in the absence of an external magnetic field  $H_{\text{ext}}$ , with an increase in  $y$ . This is, indeed, the case. The values of  $H_{\text{hf}}(0)$  at the a-sites for the samples  $y = 0.0, 0.2$  and  $0.5$  at 4.2 K are 521.3(1.1), 523.6(1.4) and 529.4(1.1) kOe. The corresponding values of  $H_{\text{hf}}(0)$  at the d-sites are 447.0(0.4), 450.6(0.4) and 462(0.4) kOe.

The  $^{57}\text{Fe}$  Mössbauer spectra measured in external magnetic fields (fig. 5) could be fitted reasonably well with one Zeeman pattern corresponding to the  $\text{Fe}^{3+}$  ions at the a-sites (a-pattern) and at least three Zeeman patterns corresponding to the  $\text{Fe}^{3+}$  ions at the d-sites ( $d_1$ -,  $d_2$ - and  $d_3$ -patterns). Because the samples are in a powder form, the electric field gradient tensor is randomly oriented

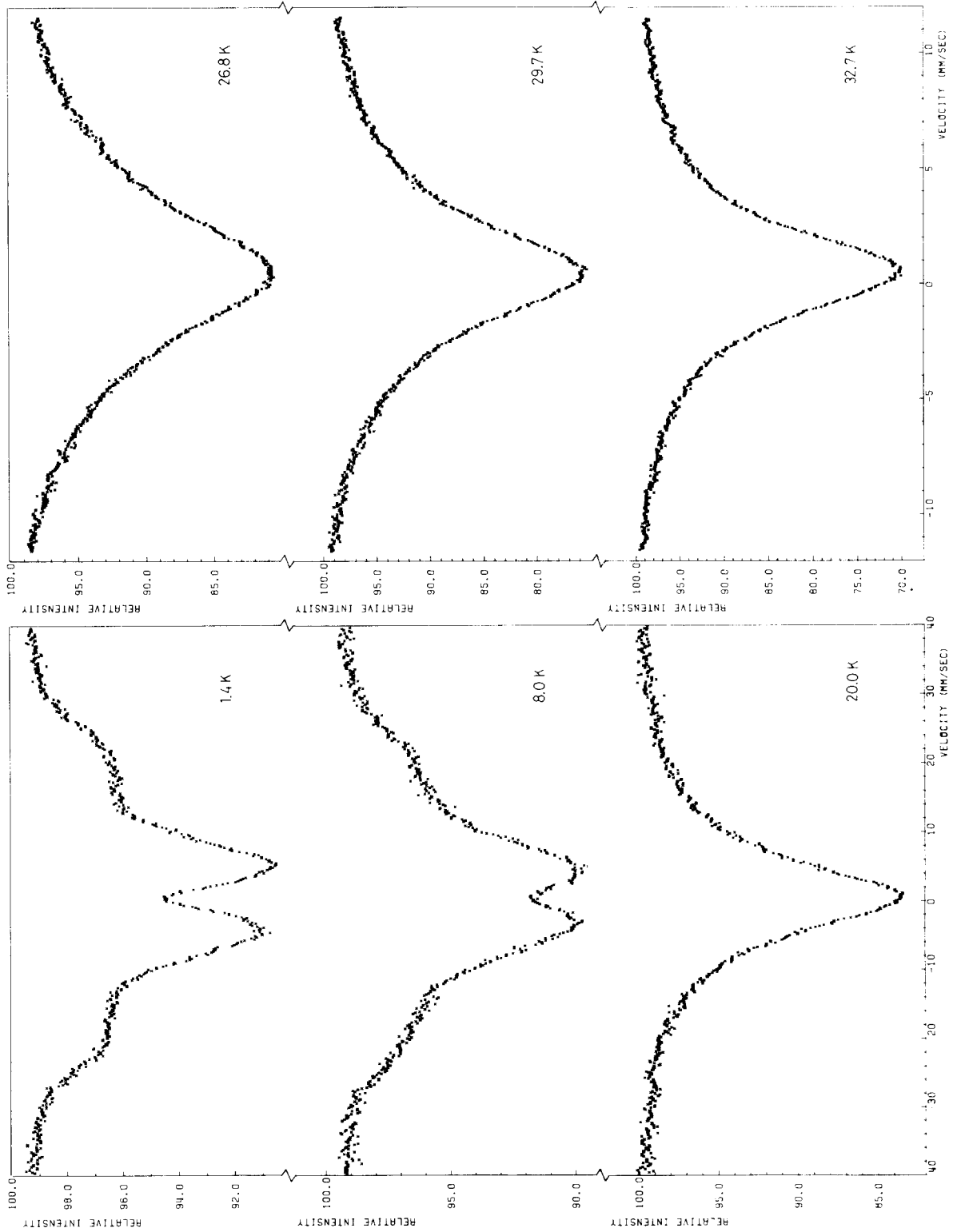


Fig. 3.  $^{151}\text{Eu}$  Mössbauer spectra of the  $y = 0.5$  sample at selected temperatures. Note the different velocity scales corresponding to the spectra at the left and right half sides of the figure.

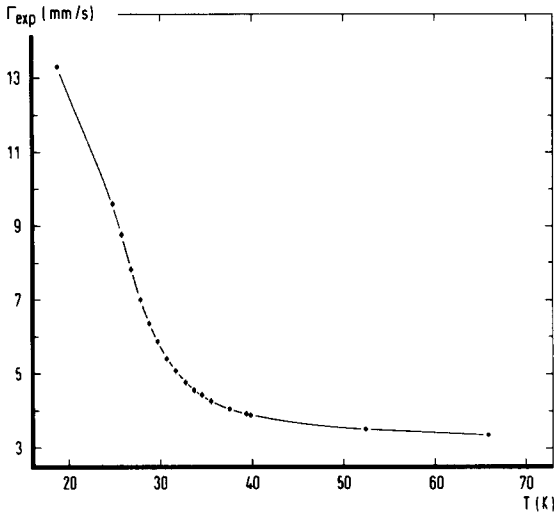


Fig. 4. Temperature dependence of the full width at half maximum,  $\Gamma_{\text{exp}}$ , for the  $y = 0.5$  sample.

with respect to the  $H_{\text{ext}}$  direction. Therefore, the shift of the Zeeman lines caused by the quadrupole interaction at the a- and d-sites was constrained to be zero. The presence of the second and fifth lines in the a- and  $d_1$ -,  $d_2$ -,  $d_3$ -patterns (fig. 5) shows that there is canting of the iron spins at both the octahedral and the tetrahedral sites. This is in accord with the localized canting model developed by Rosenzweig [13] which predicts the possibility of canting in both iron sublattices of a garnet system if diamagnetic substitution of the iron occurs at both the a- and the d-sites. Since according to the cation distributions (2)–(4) the  $\text{Sc}^{3+}$  ions do substitute the  $\text{Fe}^{3+}$  ions at the a- and d-sites one can, therefore, expect canting of the iron spins at both sites.

From the fits of the Mössbauer spectra measured in external magnetic fields (fig. 5) the hyperfine fields  $H_{\text{hf}}(H_{\text{ext}})$  at the a- and d-sites were determined, and the corresponding canting angles  $\theta$  (fig. 6) were calculated from the formula

$$\cos \theta = [H_{\text{hf}}^2(0) + H_{\text{ext}}^2 - H_{\text{hf}}^2(H_{\text{ext}})] / 2H_{\text{hf}}(0)H_{\text{ext}}. \quad (5)$$

The average canting angle at the d-site  $\bar{\theta}(d)$  was

calculated from the relation

$$\cos \bar{\theta}(d) = \sum_{n=1}^3 P(n) \cos \theta(d_n), \quad (6)$$

where  $P(n)$  is the probability of occurrence of the Zeeman pattern  $d_n$  with the local canting angle  $\theta(d_n)$ . One may try to assign the  $d_n$ -patterns ( $n = 1-3$ ) to configurations of the d-site  $\text{Fe}^{3+}$  ions with a different number of the nearest-neighbour  $\text{Sc}^{3+}$  ions at the a-site. Then the probability  $P(n)$  can be calculated from the binomial distribution formula, provided that there is a totally random distribution of ions within a given site [14]. The probabilities  $P(n)$  can also be calculated using the areas under the best resolved sixth lines of the  $d_n$ -patterns (fig. 5). It turned out that it was not possible to assign unambiguously the  $d_n$ -patterns to suitable nearest-neighbour configurations because there was a disagreement between the values of  $P(n)$  as calculated from the binomial distribution formula and those obtained from the areas under the sixth lines. This disagreement may be caused by a not complete randomness of the cation distributions (2)–(4) and also by the influence of the next-nearest-neighbours. For the calculation of  $\bar{\theta}(d)$  from eq. (6), the values of  $P(n)$  as obtained from the areas were used.

From the values of  $H_{\text{hf}}(H_{\text{ext}})$  and  $\theta$  in table 1, it is clear that the average canting angle at the d-site is much larger than the corresponding angle at the a-site. The degree of canting at the a-site depends on the concentration of diamagnetic ions at the d-sites, and vice versa [13]. Since the concentration of the  $\text{Sc}^{3+}$  ions at the a-site is much larger than at the d-site in the investigated system one can, therefore, expect the larger canting angle at the d-site.

It can be noticed from table 1 that within experimental error the value of  $\bar{\theta}(a)$  is independent of  $y$ , whereas  $\bar{\theta}(d)$  decreases with increasing  $y$ . Thus, the substitution of the d-site  $\text{Fe}^{3+}$  ions for the  $\text{Sc}^{3+}$  ions influences the values of  $\bar{\theta}(a)$  to a much lesser extent than the corresponding substitution at the a-site does to the values of  $\bar{\theta}(d)$ . This is in agreement with a general trend observed for many diamagnetically substituted iron garnets: the rate of decrease of the effective iron moment

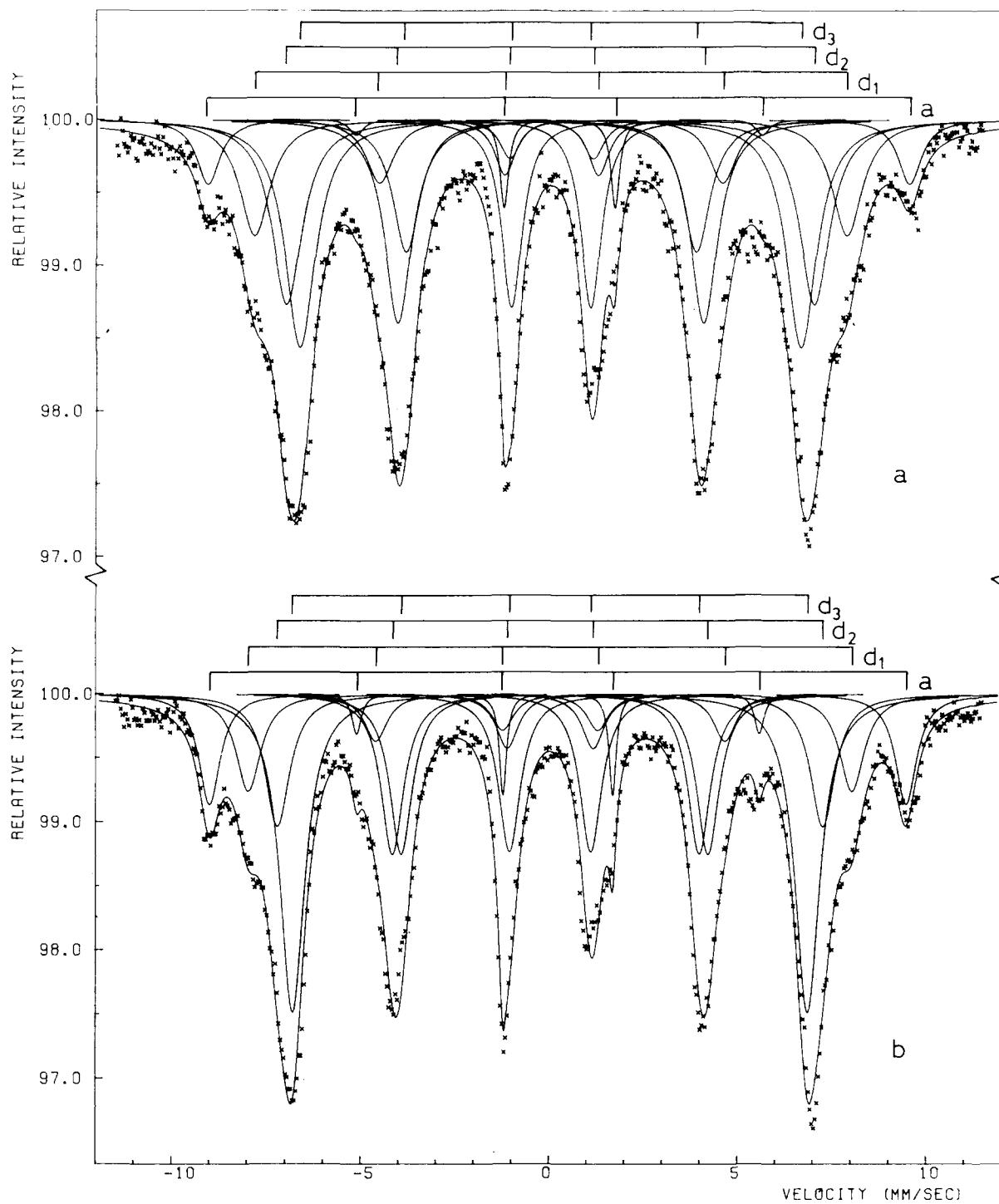


Fig. 5.  $^{57}\text{Fe}$  Mössbauer spectra at 4.2 K of (a) the  $y = 0.2$  sample in  $H_{\text{ext}} = 62.4$  kOe and (b) the  $y = 0.5$  sample in  $H_{\text{ext}} = 56.2$  kOe.

Table 1  
Experimental values of  $H_{hf}$  (kOe) and canting angles  $\theta$  (degrees) at the a- and d-sites as derived from the Mössbauer spectra measured at 4.2 K in an external magnetic field  $H_{ext}$  (kOe). Canting angles at the d-site are measured with respect to the direction of  $H_{ext}$ , and those at the a-site – with respect to the negative direction of  $H_{ext}$

Nominal composition y	$H_{ext}$	$H_{hf}(a)$	$\bar{\theta}(a)$	$H_{hf}(d_1)$	$\theta(d_1)$	$H_{hf}(d_2)$	$\theta(d_2)$	$H_{hf}(d_3)$	$\theta(d_3)$	$\bar{\theta}(d)$
0.0	62.4	570.0(1.7)	40.8(4.3)	487.8(1.2)	127.9(2.1)	436.1(1.2)	76.0(1.5)	403.8(1.0)	43.2(1.7)	76.5(2.2)
0.2	62.4	575.9(1.5)	34.9(5.1)	486.2(1.4)	121.6(2.1)	433.0(2.7)	69.8(2.9)	411.3(2.1)	47.8(2.8)	72.8(3.4)
0.5	56.2	572.6(0.8)	41.6(3.1)	496.4(1.4)	124.3(2.4)	448.8(2.0)	72.4(2.5)	423.8(0.9)	43.7(1.8)	66.9(2.9)

[1], which is proportional to  $\cos \bar{\theta}$ , with a diamagnetic substitution is much smaller at the a-site than at the d-site.

In the above discussion it was assumed that the investigated magnetic properties are mainly determined by the superexchange interaction between the a-site and d-site iron spins. The superexchange interaction between the  $Eu^{3+}$  spins at the c-site is not expected to change significantly the discussed properties since almost the same amount of  $Eu^{3+}$  ions is present in all samples.

The investigated samples are canted ferrimagnets (fig. 6) since the application of an external magnetic field increases the value of the hyperfine magnetic field at the a-site and decreases the values of the hyperfine magnetic fields corresponding to the  $d_2$ - and  $d_3$ -patterns (table 1). The value of  $H_{hf}(H_{ext})$  corresponding to the  $d_1$ -pattern is actually larger than the value of  $H_{hf}(0)$  at the d-site. This gives direct evidence that some of the d-site  $Fe^{3+}$  spins are reversed ( $\theta(d_1) > 90^\circ$ ) with respect to the resultant iron spin of the d-sublattice, which is aligned parallel to  $H_{ext}$  (fig. 6). Such a reversal could be expected for those of the d-site iron ions

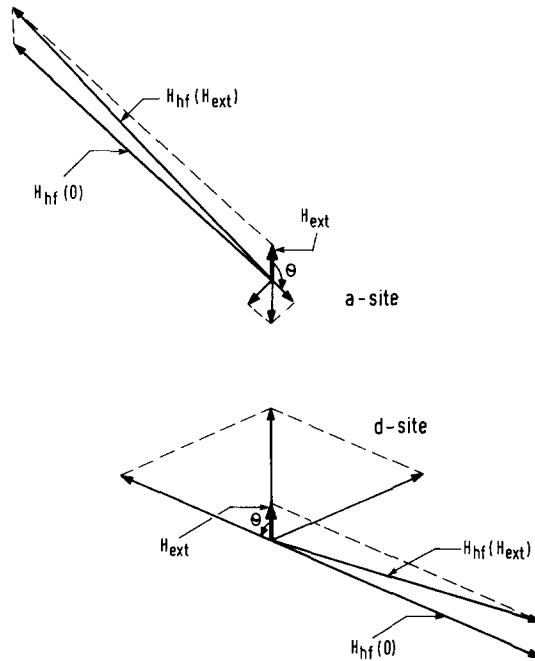


Fig. 6. Schematic diagram of the spin configuration at the a and d-sites. The spin is antiparallel to the direction of  $H_{hf}(0)$



which have a large number of diamagnetic scandium ions as nearest- and next-nearest-neighbours [15].

Using the values of  $\bar{\theta}(a)$  and  $\bar{\theta}(d)$  (table 1), one can calculate the magnetic moment per formula unit  $\mu$  (in units of  $\mu_B$ ) from the relation

$$\mu = 15(1 - k_d) \cos \bar{\theta}(d) - 10(1 - k_a) \cos \bar{\theta}(a) - 2.22(1 - k_c), \quad (7)$$

where  $k_i$  ( $i = a, d, c$ ) is the fraction of the  $\text{Sc}^{3+}$  ions at the  $i$ th site. It is assumed that  $\mu(\text{Fe}^{3+}) = 5\mu_B$  and  $\mu(\text{Eu}^{3+}) = 0.74\mu_B$  [1]. The values of  $\mu$  calculated from eq. (7) for the samples  $y = 0.0, 0.2$  and  $0.5$  are 0.11, 0.46 and  $1.00\mu_B$ , respectively. The experimental value of spontaneous magnetization at 1.5 K of the  $y = 0.0$  sample is  $0.1\mu_B$  [3]. Although the value of saturation, and not spontaneous magnetization should be compared with the calculated value, nevertheless the calculated value predicts the order of magnitude of the expected saturation magnetization. It is also to be noticed that the calculated values of  $\mu$  increase with  $y$ , as do the ordering temperatures  $T_N$  and the hyperfine magnetic fields  $H_{\text{hf}}(0)$ .

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