

## Broad magnetic transitions in cobalt-substituted yttrium iron garnet

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Mössbauer spectra of polycrystalline specimens of yttrium iron garnet containing small amounts of divalent cobalt ions, compensated by  $\text{Ge}^{4+}$  ions ( $\text{Y}_3\text{Fe}_{5-2x}\text{Co}_x\text{Ge}_x\text{O}_{12}$ ) indicate that in zero applied magnetic field, they have very broad magnetic transition regions. However, there is clear evidence that two magnetic phases exist in these regions, one with  $\langle 111 \rangle$ , the other with  $\langle 100 \rangle$  easy directions. The broad transition region is attributed to the low  $\text{Co}^{2+}$  concentration and statistical fluctuation thereof, small particle size, and inhomogeneous internal stresses in the particles.

### I. INTRODUCTION

Substitution of divalent cobalt with charge-compensating tetravalent ions,  $\text{Ge}^{4+}$  or  $\text{Si}^{4+}$  in yttrium iron garnet was first reported about 20 years ago.<sup>1,2</sup> In these papers, the main interest was in the effects of such substitutions on the behavior of the spontaneous magnetization as a function of temperature and external magnetic field. From the 0-K results and results on other substituted yttrium iron garnets,<sup>3,4</sup> it was concluded that approximately 20% of the  $\text{Co}^{2+}$  ions entered tetrahedral sites.<sup>2</sup> (This was later qualitatively confirmed.<sup>5</sup>) Also found was the first ferrimagnetic garnet which has a compensation point resulting from a difference in the thermomagnetic behavior of only the  $a$  and  $d$  sublattices. In the high-cobalt-content garnets, there appeared to be low-temperature transitions which have still not been elucidated. The garnet containing no  $\text{Fe}^{3+}$  ions,  $\text{Y}_3\text{Co}_{2.5}\text{Ge}_{2.5}\text{O}_{12}$ , was shown to have a magnetic transition at 8 K.

Okada *et al.*<sup>6</sup> and Hansen *et al.*<sup>7</sup> have made ferromagnetic resonance measurements on single crystals containing small amounts of  $\text{Co}^{2+}$  compensated by  $\text{Ge}^{4+}$  ion. Anisotropy constants were determined as a function of temperature and concentration, and from these data one can, in principle, deduce the  $\langle 111 \rangle \rightleftharpoons \langle 100 \rangle$  magnetic-easy-axis transition tem-

peratures as a function of composition. The ferromagnetic resonance measurements require that the crystal be in an external magnetic field, of course; thus it is possible for zero external field measurements to give different results.

There are two spectroscopic methods that are particularly suited to studies of the reorientation of the magnetization of a magnetically ordered crystal in zero magnetic field; these are Mössbauer effect (MES) and nuclear magnetic resonance (NMR) spectroscopy. Overall, the latter is probably the stronger technique because of its higher resolution of magnetic hyperfine fields at the  $\text{Fe}^{3+}$  ion nuclei.

Recently, we have followed spin reorientation, at zero field, in silicon-substituted yttrium ion garnet (YIG) (Si) (Refs. 8 and 9) and in samarium iron garnet<sup>10</sup> (SmIG) by MES from liquid He (in some cases) to room temperature by taking series of spectra at various temperatures. It was concluded that in the YIG(Si) there are broad spin reorientations, the temperature range depending on composition, that are mainly a consequence of the persistence of a nonuniform distribution of  $\text{Fe}^{2+}$  ions over the octahedral sites. The spin-reorientation temperature region is bounded by second-order transitions, although it is possible that the easy directions never really reach  $[111]$  at the high-temperature end or  $[100]$  at the low-temperature end, even when the  $\text{Si}^{4+}$  ion con-

tent is large enough. Below  $x=0.18$ , as in  $Y_3Fe_{5-x}Si_xO_{12}$ , there are no transitions. For  $0.3 \leq x \leq 0.4$ , the temperature of onset of the transition is the same,  $\sim 260$  K. A model was obtained which accounted, semiquantitatively, for the observations.

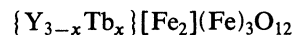
In the SmIG case, a new magnetic phase was found to exist below  $\sim 10$  K, namely, with [100] easy direction; the transition from the  $\langle 111 \rangle$  to the  $\langle 110 \rangle$  easy directions had been found earlier,<sup>11</sup> although the actual transition temperature itself had not been established. The MES of SmIG indicated that the spin reorientations might not be first order, but the temperature ranges of the spin reorientations were *much* narrower than those of YIG(Si). By the same method used by us, a more recent paper<sup>12</sup> indicates that the  $\langle 100 \rangle \rightleftharpoons \langle 111 \rangle$  spin reorientation in ErIG occurs over the region 74 to 95 K.

In 1969, it was shown<sup>13</sup> unequivocally that the spin reorientation in erbium orthoferrite  $ErFeO_3$  is a continuous coherent rotation of the  $Fe^{3+}$  ion spin system. The technique<sup>14</sup> whereby this was done employed linearly polarized  $\gamma$  rays. The spin reorientation region is bounded by second-order transitions; it was hypothesized<sup>13</sup> that in the direction of increasing temperature the magnetic space groups were  $Pbn'm' \rightarrow P2'_1/n' \rightarrow Pb'm'$  (where the primes indicate antisymmetry operations). In the two orthorhombic groups, the  $Fe^{3+}$  ions are crystallographically equivalent; on the assumption that there is no change in the size of the unit cell, there should be two crystallographically nonequivalent sets of sites for the  $Fe^{3+}$  ions in  $P2'_1/n'$ . However, Mössbauer spectra obtained with unpolarized  $\gamma$  rays did not resolve the two sets of lines in the spin reorientation region.<sup>13</sup>

Several years later, an NMR study<sup>15,16</sup> of the spin reorientation in  $ErFeO_3$  confirmed the prediction of Ref. 13 by clearly resolving the resonance frequencies of the two sets of  $Fe^{57}$  nuclei. This appeared to

be the first application of NMR to such a study, that is, to the following of the continuous spin reorientation.

Subsequently, there were several papers in which magnetic transitions in some rare-earth iron garnets were followed by means of the NMR technique in zero field. In particular, it was shown that the  $\langle 111 \rangle \rightleftharpoons \langle 110 \rangle$  transition in SMIG (Ref. 17) and the  $\langle 111 \rangle \rightleftharpoons \langle 100 \rangle$  transition in the



(Ref. 18) system are first order. Some NMR work has been done on single crystals containing very small amounts of  $Co^{2+}$  compensated by  $Si^{4+}$  ions.<sup>19</sup>

In this paper we give the results of the MES spectroscopy of the  $Y_3Fe_{5-2x}Co_xGe_xO_{12}$  system, mainly for small  $x$ .

## II. EXPERIMENTAL DETAILS

### A. Material preparation

Polycrystalline specimens were prepared by solid-state reaction as described in Ref. 3, with only minor modifications to take into account the lower substituent levels of  $Co^{2+}$  and  $Ge^{4+}$ . Most important of the modifications was the preparation of larger samples and the use of larger platinum vessels for the firings. Firing conditions for the new specimens are listed in Table I. In some of the experiments, specimens originally prepared in the investigation of Ref. 2 were used.

X-ray powder diffraction photographs were taken with 114.6-mm-diameter cameras and CrK radiation. Lattice constants are given in Table I; the values of the new specimens agree within 0.001 Å with the plot reported earlier.<sup>2</sup>

TABLE I. Lattice constants and preparation conditions of the polycrystalline specimens  $Y_3Fe_{5-2x}Co_xGe_xO_{12}$  prepared in this study.

$x$	$a$ (Å)	Firing conditions [°C(h)] <sup>a</sup>
0.01	12.376	800( $\frac{1}{2}$ ),1380(2),1380(2),1380(2),1380(15)
0.02	12.376	800( $\frac{1}{2}$ ),1380(2),1380(2),1380(2),1380(15)
0.06	12.377	900( $\frac{1}{2}$ ),1380(1),1380(2),1380(2),1380(6),1400(8)
0.10	12.379	1000(1),1410(3),1425(2),1410(6)
0.20	12.377	1180(2),1390(2),1420(2),1415(3),1380(18)
0.80	12.376	900( $\frac{1}{2}$ ),1370(2),1380(2),1380(2),1380(7)
1.00	12.375	1000(2),1350(1),1350(2),1350(2),1350(10)

<sup>a</sup>Specimens were reground and recompact between firings.

### B. Mössbauer spectroscopy

The Mössbauer spectra in both Rome and Boulder were taken with constant acceleration spectrometers. (In Rome, the equipment is by Elscint.) The velocity scales were calibrated by means of spectra taken of pure iron foil. The resonant radiation was the 14.4 keV  $\gamma$  transition in  $^{57}\text{Fe}$ ; the sources were  $^{57}\text{Co}$  in Pd at temperatures  $25 \pm 3^\circ\text{C}$ . Specimens were ground to fine powders in agate mortars; material passing through a 400-mesh nylon sieve was used to make the absorber. Absorber thicknesses were 20  $\text{mg}/\text{cm}^2$  (Rome), and 25  $\text{mg}/\text{cm}^2$  (Boulder). In all Rome and most Boulder cases the absorber was the pure powdered specimen held between two Be disks. In a few runs at ambient temperature (Boulder), the absorber was held between lucite discs. Thickness uniformity was attained by rotating the disks with respect to each other before clamping at the perimeter.

Absorber temperatures were obtained in a cryogenic Dewar (Boulder) and flux cryogenic Dewar (Rome).

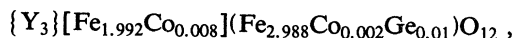
In Boulder, the sample temperature was measured with a Au (0.03 at. % Fe)-Chromel thermocouple; temperature was held constant ( $\pm 0.5^\circ$ ) with an Oxford Instruments temperature controller which supplied power to a resistance heater to maintain the preset temperature. In Rome, temperature was held constant ( $\pm 0.5^\circ$ ) by electronically controlling the cryogenic flux.

All the least-square fits were made, without any constraint, by the computer equipment (software and hardware) associated with the Elscint spectrometer (Rome).

Absorber temperatures above room temperature were obtained (Boulder) with a small vacuum oven (kindly lent to us by R. M. Housley and R. W. Grant of the Rockwell International Science Center), Chromel-Alumel thermocouple and an Oxford Instruments temperature controller in conjunction with a Eurotherm thyristor (931) and driver (024).

### III. RESULTS AND DISCUSSION

Spectra were taken of a specimen with formula  $\{\text{Y}_3\}\text{Fe}_{4.98}\text{Co}_{0.01}\text{Ge}_{0.01}\text{O}_{12}$  at temperatures as shown in Fig. 1. (If the conclusion that 80% of the  $\text{Co}^{2+}$  ions are in octahedral sites and 20% in tetrahedral sites is correct, the structural formula would be written



but we shall write the formulas in the simpler fashion here.) Examination of the spectra (Fig. 1) indicates that a transition takes place over a wide

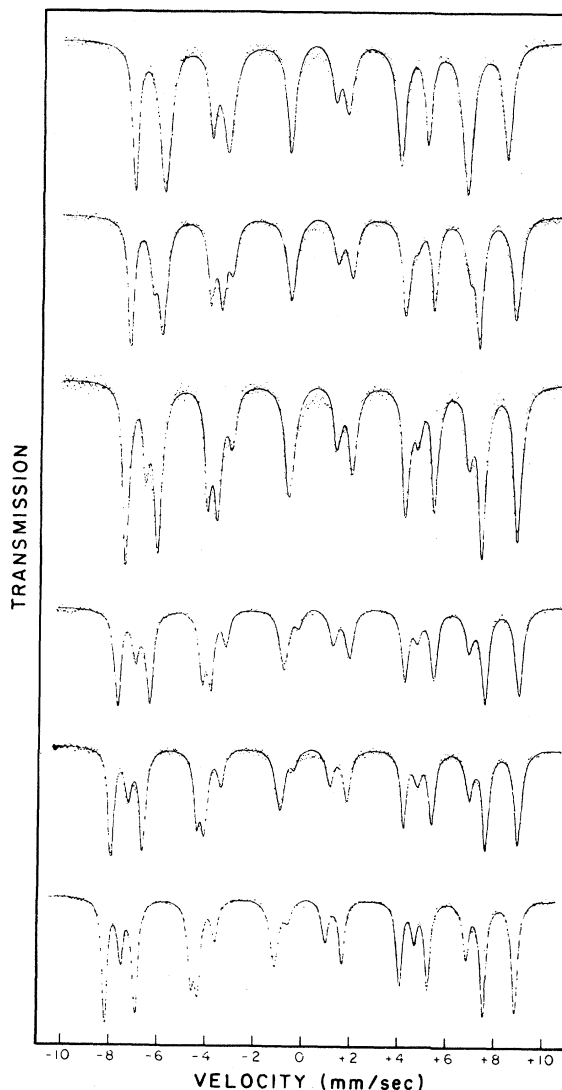


FIG. 1. Mössbauer spectra of the specimen  $\text{Y}_3\text{Fe}_{4.98}\text{Co}_{0.01}\text{Ge}_{0.01}\text{O}_{12}$  at temperatures, reading from top to bottom, 295, 260, 230, 200, 170, and 150 K, as listed in Table II.

temperature range.

At the lowest temperature, the spectrum actually contains eighteen lines, some overlapped, and is typical of  $\langle 100 \rangle$  easy directions; that is, in this case, the magnetic structure is tetragonal, most probable space group  $I4_1/ac'd'$ . If the transition were one involving a continuous rotation of the spin system with bounding second-order transitions, the intermediate phase, i.e., in the spin reorientation region, would be monoclinic ( $F2'/d'$ ) and there would be three crystallographically nonequivalent sets of tetrahedral sites of equal number per set and four nonequivalent sets of equal number of octahedral sites. Because the arrangement of the ions remains

essentially cubic, there would be accidental degeneracy overlap of peaks. Thus there would be two tetrahedral peaks with exactly 1:2 intensity ratio and three octahedral peaks with 1:2:1 ratio. In each of these sets there would also be overlap, the amount

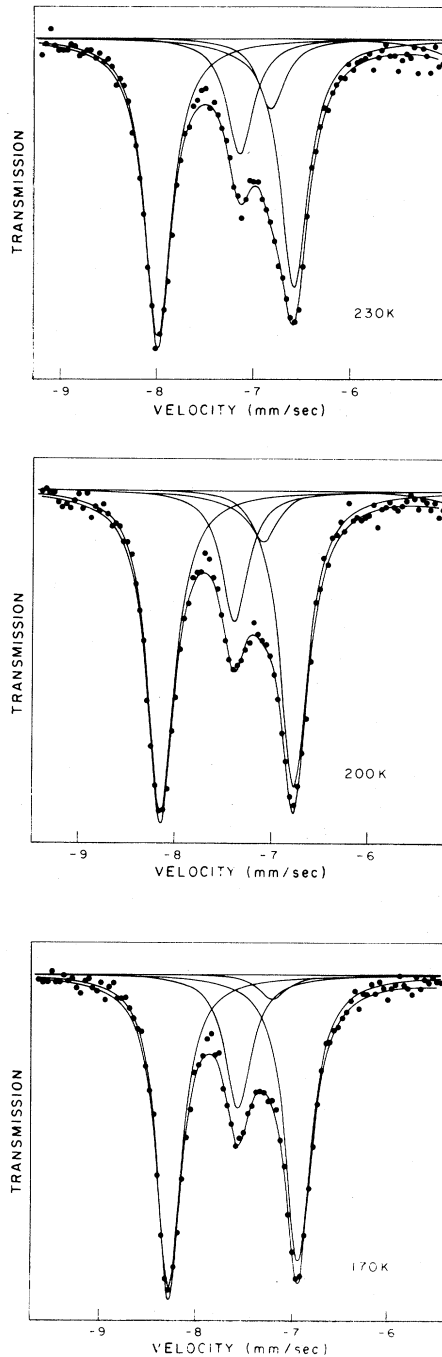


FIG. 2. Examples of four-line fits of the ( $I = \frac{1}{2}$ ,  $m_I = -\frac{1}{2} \rightarrow I = \frac{3}{2}$ ,  $m_I = -\frac{3}{2}$ ) lines of the specimen  $Y_3Fe_{4.98}Co_{0.01}Ge_{0.01}O_{12}$ .

depending on the angle that the magnetization makes with the  $\langle 100 \rangle$  directions, say.

Actually, one should not expect to discern easily the splitting of the octahedral peaks in a spectrum of a powder absorber. (This is true for the case of powdered yttrium iron garnet itself, although the splitting was readily seen in a spectrum of single-crystal YIG taken in a field of 55 kOe along the  $[111]$  direction and also the  $\gamma$ -ray direction.<sup>20</sup>) However, such splitting was observed in some of the YIG(Si) spectra; for example, it is noticeable as a shoulder on the right of the first peak in the 260-K spectrum of Fig. 1 of Ref. 8. It has been observed in several spectra of the YIG(Si) system near the  $\langle 111 \rangle$  end of the transition. The angular factors  $(3 \cos^2 \theta - 1)/2$  indicate that if the hyperfine fields at the nuclei did not change markedly with  $\theta$ , the largest splitting would occur when the magnetization made an angle of  $19.5^\circ$  with the original threefold axis. No similar splitting is observed in any of the spectra of the  $Y_3Fe_{5-2x}Co_xGe_xO_{12}$  system.

As to the splitting of the tetrahedral peak, one should expect a constant 1:2 ratio throughout the spin reorientation region. On the contrary, the coexistence of two phases, one with  $\langle 111 \rangle$ , the other with  $\langle 100 \rangle$  easy directions of magnetization is indicated by the variation of the ratio of intensities of these two peaks from zero, when the only phase present is rhombohedral ( $\langle 111 \rangle$  easy) to 1:2, when the only phase present is tetragonal ( $\langle 100 \rangle$  easy). This is proved by the fitting of the spectra of  $Y_3Fe_{4.98}Co_{0.01}Ge_{0.01}O_{12}$  with Lorentzians (Figs. 1 and 2).

The lines for the 16-fold tetrahedral sites of the tetragonal phase and that for the tetrahedral sites of the rhombohedral phase do not overlap exactly. Therefore, for the outermost sets of lines, the fitting was made with four lines, one for the octahedral sites and three for the tetrahedral sites in the two phases. The results are shown for a few temperatures for the ( $I = \frac{1}{2}$ ,  $m_I = -\frac{1}{2} \rightarrow I = \frac{3}{2}$ ,  $m_I = -\frac{3}{2}$ ) lines in Fig. 2.

TABLE II. Fraction  $\rho_{\langle 100 \rangle}$  (symbol used is that of Ref. 19) of the phase with  $\langle 100 \rangle$  easy directions at different temperatures in  $Y_3Fe_{4.98}Co_{0.01}Ge_{0.01}O_{12}$  as deduced from line fitting of the Mössbauer spectra.

$T$ (K)	$\rho_{\langle 100 \rangle}$
295	0.42
260	0.62
230	0.84
200	0.88
170	0.94
150	1.00

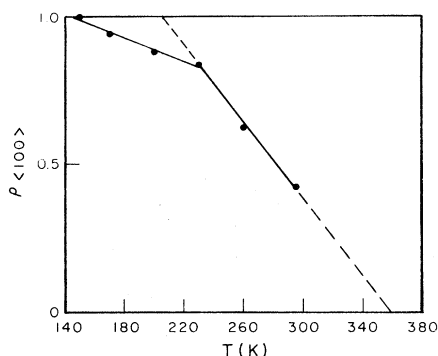


FIG. 3. Fractional volume of  $\langle 100 \rangle$  phase vs temperature.

From the tetrahedral-site line fits, one can obtain the volume fraction of one phase or the other in the specimen, at a given temperature. For example,

$$\begin{aligned} \rho_{\langle 100 \rangle} &= I_{\langle 100 \rangle} / (I_{\langle 100 \rangle} + I_{\langle 111 \rangle}) \\ &= V_{\langle 100 \rangle} / (V_{\langle 100 \rangle} + V_{\langle 111 \rangle}), \end{aligned} \quad (1)$$

where  $I_{\langle 100 \rangle}$  is the combined intensity of the two calculated tetrahedral-site lines from the phase with  $\langle 100 \rangle$  easy magnetic axes, and  $I_{\langle 111 \rangle}$  is the intensity of the single calculated tetrahedral-site line from the phase with  $\langle 111 \rangle$  easy magnetic axes. In Fig. 2, the latter is the smallest of the calculated lines and the former are, of course, the two calculated lines on either side of it. The values of  $\rho_{\langle 100 \rangle}$  at several temperatures are listed in Table II and plotted in Fig. 3. [The values are obtained by averaging the results for the lines ( $I = \frac{1}{2}$ ,  $m_I = -\frac{1}{2} \rightarrow I = \frac{3}{2}$ ,  $m_I = -\frac{3}{2}$ ) and ( $I = \frac{1}{2}$ ,  $m_I = \frac{1}{2} \rightarrow I = \frac{3}{2}$ ,  $m_I = \frac{3}{2}$ )].

Figure 3 indicates that there are at least two rates  $\rho_{\langle 100 \rangle}/K$  in the transformation process, which, it should be mentioned, do not have a noticeable hysteresis. With increasing temperature,  $\rho_{\langle 100 \rangle}/K$  is

TABLE III. Calculated values in  $\text{cm}^{-1}$  per formula unit, of  $(K_1/3) + (K_2/27) = F([111]) - F([100])$  for different values of  $x$  in  $\text{Y}_3\text{Fe}_{5-2x}\text{Co}_x\text{Ge}_x\text{O}_{12}$ , assuming all  $\text{Co}^{2+}$  ions to be in octahedral sites. (Values of single-ion anisotropies used are from Ref. 22.)

x	Temperature (K)		
	295	77	4.2
0.001	-0.0022	-0.0045	-0.0055
0.002	-0.0019	-0.0001	-0.0011
0.003	-0.0015	0.0042	0.0034
0.005	-0.0009	0.0130	0.0122
0.007	-0.0003	0.0217	0.0210
0.01	0.0006	0.0349	0.0343
0.02	0.0037	0.0785	0.0783
0.1	0.0288	0.4283	0.4310

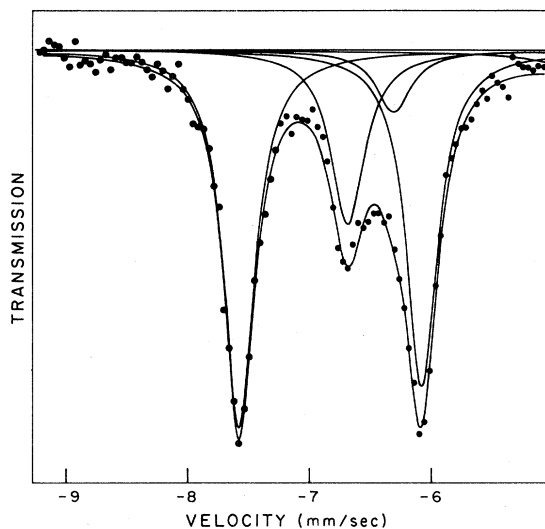


FIG. 4. Fitted ( $I = \frac{1}{2}$ ,  $m_I = -\frac{1}{2} \rightarrow I = \frac{3}{2}$ ,  $m_I = -\frac{3}{2}$ ) lines for specimen  $\text{Y}_3\text{Fe}_{4.96}\text{Co}_{0.02}\text{Ge}_{0.02}\text{O}_{12}$  at 295 K.

$-2.0 \times 10^{-3} \text{ K}^{-1}$  between 144 K (for  $\rho_{\langle 100 \rangle} = 1.0$ , calculated from the straight-line fit of Fig. 3) and 230 K; between 230 and 359 K (for  $\rho_{\langle 100 \rangle} = 0$ , calculated from the straight-line fit), it is  $-6.4 \times 10^{-3} \text{ K}^{-1}$ . The line with this slope extrapolates to 204 K at  $\rho_{\langle 100 \rangle} = 1.0$ . It is likely, although not easily observable in the Mössbauer spectra, that there is a "tail-line" at the  $\langle 111 \rangle$ -easy-axis end of the transition region also. This could extend the region to about 415 K, making the overall range equal to 270 K. The width of the steeper-rate region, i.e., including extrapolations such that  $0 \leq \rho_{\langle 100 \rangle} \leq 1.0$ , is 165 K.

It has been shown<sup>21</sup> that the magnetic anisotropy free energies when the magnetizations are oriented along the [111] and [100] directions are related as follows:

$$F([111]) - F([100]) = K_1/3 + K_2/27. \quad (2)$$

It is a requirement also that  $K_1 \geq 0$  for the magnetization to be oriented along a [100] direction. Hansen<sup>22</sup> has compiled a list of single-ion anisotropies for a number of ions in the ferrimagnetic garnets for the different sites and for temperatures 295, 77, and 4.2 K. These values and Eq. (1) give a rough idea as to what the transition temperatures should be. A few examples for different values of  $x$ , assuming that all  $\text{Co}^{2+}$  are in octahedral sites, are given in Table III.

Table III shows that already for  $x = 0.003$ , a transition should occur at a temperature between 77 and 295 K. There could also be a transition for  $x = 0.002$  near 77 K, but there would be a transition

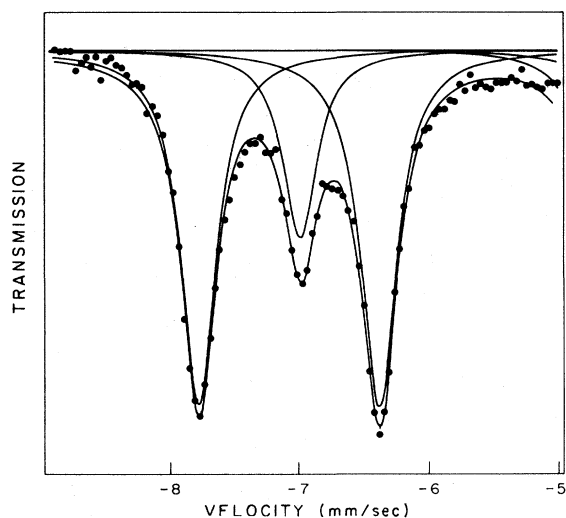


FIG. 5. Fitted ( $I = \frac{1}{2}$ ,  $m_I = -\frac{1}{2} \rightarrow I = \frac{3}{2}$ ,  $m_I = -\frac{3}{2}$ ) lines for specimens  $Y_3Fe_{4.88}Co_{0.06}Ge_{0.06}O_{12}$  at 295 K.

back to  $\langle 111 \rangle$  easy directions with decrease in temperature. For  $x = 0.01$ , the transition should occur at a temperature slightly above 295 K (i.e., if all  $Co^{2+}$  ions are in octahedral sites).

At a  $\langle 111 \rangle \rightleftharpoons \langle 100 \rangle$  easy-axis transition of a ferromagnetic garnet, in zero field, all the  $\langle 100 \rangle$  and  $\langle 111 \rangle$  easy directions should be equally probable. It therefore follows that at the true first-order transition temperature,  $\rho_{\langle 100 \rangle}$  should be  $\frac{3}{7}$  or 0.43. In the  $x = 0.01$  case, the temperature at which this occurs is 292 K (Fig. 3), in good agreement with the result deduced from Table III.

In Fig. 4, the fitted ( $I = \frac{1}{2}$ ,  $m_I = -\frac{1}{2} \rightarrow I = \frac{3}{2}$ ,  $m_I = -\frac{3}{2}$ ) lines are shown for a specimen with  $x = 0.02$  taken at room temperature. In this case  $\rho_{\langle 100 \rangle}$  is 0.88. Figure 5 shows a similar fitting for  $x = 0.06$ ; the easy direction for this specimen is  $\langle 100 \rangle$  at room temperature. The value of  $x$  at which  $\langle 100 \rangle$  just becomes the easy direction for the entire specimen at 298 K is estimated to be 0.023 for the powder specimens of this investigation.

At 298 K, for  $x = 0.06$ , the isomer shifts are  $0.20 \pm 0.01$  and  $-0.03 \pm 0.01$   $mm\ s^{-1}$  for the octahedral and tetrahedral sites, respectively,  $e^2qQ/4$  for the tetrahedral sites is  $0.44 \pm 0.02$   $mm\ s^{-1}$ , and the magnetic hyperfine fields are  $487 \pm 2$  and  $394 \pm 2$  kOe for the octahedral and tetrahedral sites, respectively. These were calculated from the total interaction Hamiltonian.<sup>23</sup>

The specimen with  $x = 0.02$  is estimated to be completely converted to  $\langle 100 \rangle$  easy directions at approximately 240 K. As a check on the results for the specimen with  $x = 0.01$ , a specimen of 50% by weight of each of pure yttrium iron garnet and of

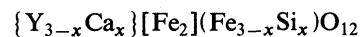
TABLE IV. Curie temperatures of specimens  $Y_3Fe_{5-2x}Co_xGe_xO_{12}$ .

$x$	Curie temperature (K)	
	This work	Ref. 2
0	556	
0.02	553	
0.04	547	
0.06	543	
0.10	531	
0.20	520	
0.50	452	
0.80	391	420 (high)
1.00		350
1.16	305	305

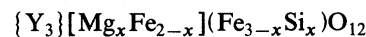
the specimen with  $x = 0.02$ , thoroughly ground and mixed was prepared and a spectrum taken at 240 K. This spectrum (except for difference in scale) fits very well between the spectra taken at 295 and 260 K for  $x = 0.01$ . The 300-K spectrum for this specimen also gives support to the distribution deduced from the line fits discussed earlier.

Spectra taken of various specimens with larger  $x$  at higher temperatures were increasingly noisy with increasing temperature as the Curie temperatures were approached. However, it is logical to presume that the temperature range of transition decreases with increasing  $x$ , if for no other reason than that the Curie temperature decreases as a result of the replacement of  $Fe^{3+}$  by  $Co^{2+}$  and  $Ge^{4+}$  ions.

In the original paper<sup>2</sup> on cobalt substitutions in yttrium iron garnet, Curie temperatures were not determined for specimens with  $x < 0.80$ . Therefore, these were determined by means of Mössbauer spectroscopy in the present investigation. The spectra sharpened considerably immediately at and above the Curie temperatures which were determined within  $\pm 1^\circ$ . The measurements were made on specimens with  $0 \leq x \leq 1.16$ . The specimens with  $x = 0.50$  and 1.16 were from the investigation of Ref. 2. The old determinations did not have the same accuracy. However, exactly the same value, 305 K, was obtained for the specimen with  $x = 1.16$ . The result for  $x = 0.80$  is substantially lower than that obtained earlier.<sup>2</sup> The new points (Table IV) and those for higher  $x$  obtained earlier are plotted in Fig. 6, as well as those for the systems



and



as in Fig. 9 of Ref. 2. This is to emphasize that the

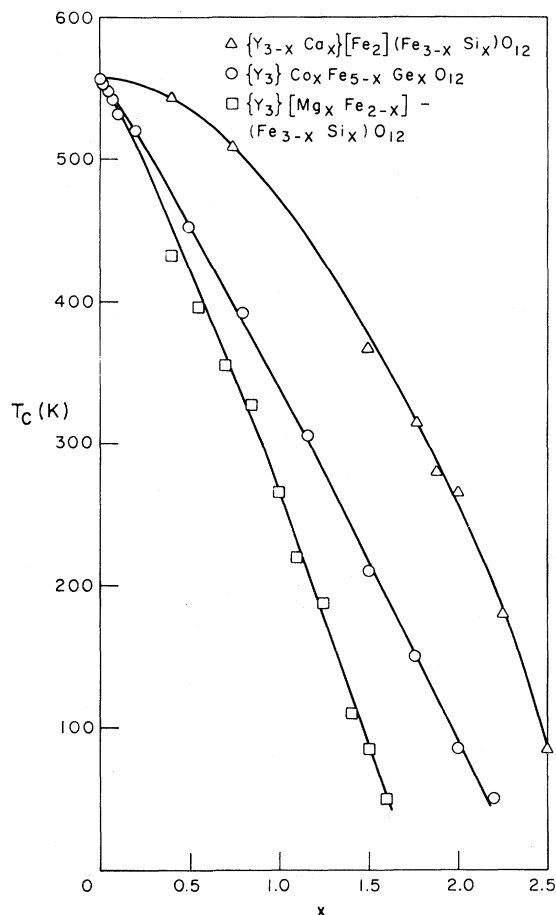


FIG. 6. Curie temperature vs.  $x$ .

$[\text{Co}^{2+}]\text{-O}^{2-}\text{-(Fe}^{3+})$  superexchange interaction is considerably weaker than the  $[\text{Fe}^{3+}]\text{-O}^{2-}\text{-(Fe}^{3+})$  interaction. In fact, the analogous  $[\text{M}^{2+}]\text{-O}^{2-}\text{-(Fe}^{3+})$  interactions of *all* divalent 3d magnetic ions have very nearly one-third the interaction strength of the latter interaction.<sup>3,4</sup>

The main problem in understanding these results is that of the width of the transition region. A good part of the key is given in papers by Belov *et al.*<sup>24</sup> and Borodin *et al.*<sup>18</sup> on the  $\langle 111 \rangle \rightleftharpoons \langle 100 \rangle$  easy-axis transitions in the system  $\{\text{Y}_{3-x}\text{Tb}_x\}[\text{Fe}_2](\text{Fe}_3)\text{O}_{12}$ . In the former, it is shown that in a polydomain crystal (in zero magnetic field), one phase grows continuously at the expense of the other from a domain wall which acts as a nucleus for the new phase, and under this condition both phases are thermodynamically stable. Thus such a transition occurs without hysteresis. However, the temperature ranges over which the transitions occur in single crystals of the  $\{\text{Y}_{3-x}\text{Tb}_x\}$ IG system are relatively *very* narrow, 5–6 K, for  $0.10 \leq x \leq 0.50$ .<sup>18</sup>

Borodin *et al.*<sup>19</sup> have made NMR measurements

on  $\{\text{Y}_3\}\text{Fe}_{5-2x}\text{Co}_x\text{Si}_x\text{O}_{12}$  for  $x=0.001$  and  $0.002$ , single crystals. For the first the transition range is 36 K, for the second 73 K. According to Table III, specimens with these compositions should not show the transition at all, so we would guess that the cobalt contents are somewhat higher. Second, it does seem strange that the specimen with less cobalt should have the narrower transition region. The authors argue that theoretically the transition width should not exceed 2–3 K for defect-free crystals and attribute their results to inhomogeneity of the crystals, for which they give some experimental evidence, and to other defects which could pin domain boundaries, and to inhomogeneous internal stresses which would affect the special changes in the domain structure which are required in these transitions at zero magnetic field.

While it is generally recognized that inhomogeneities in composition occur in single crystals of substituted garnets which are grown from fluxes, it is unlikely that our polycrystalline specimens are inhomogeneous in the same manner. (On a statistical basis, randomness still implies finite probabilities of microscopic inhomogeneities; see below.) However, other types of defects such as inhomogeneous internal stresses are likely.

There is another possible cause of broadening which may be magnified in polycrystals. For simplicity, consider that the  $\text{Co}^{2+}$  ions occupy only octahedral sites. In a crystal containing 0.01  $\text{Co}^{2+}$  per formula unit, there will be, on the average, only 0.08  $\text{Co}^{2+}$  ions per unit cell or two  $\text{Co}^{2+}$  ions in 25 unit cells. With respect to the magnetic interactions, the number of  $\text{Co}^{2+}$  ions in the octahedral sites is the important parameter. Thus in such a crystal, there will be, on the average, only one  $\text{Co}^{2+}$  ion in every 200 octahedral sites. Application of the Poisson distribution indicates that the probability that any group of 200 octahedral sites does not contain a  $\text{Co}^{2+}$  ion is 0.37. From the above, one infers that the effect of the cobalt ions must be long range but rather weak overall. At zero field, the small concentration of  $\text{Co}^{2+}$  ions must itself cause the spin system to flip to its new direction at the phase transition, i.e., without the aid of an external driving force. It would seem that on cooling, the nuclei of the new phase form first close to the  $\text{Co}^{2+}$ , then cause further  $\text{Fe}^{3+}$ -ion moments to flip. Thus even in a single crystal there will be transition broadening just as a result of the low concentration. However, in the single crystal the domain walls extend throughout, and thus, in a sense, act cooperatively in nucleating the new phase. It would seem therefore that the smaller particle size of the Mössbauer specimens magnifies the temperature range of the transition.

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