Growth anisotropy in the Nd-Y and Pr-Y iron garnets

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The magnetic phase of Nd-Y and Pr-Y iron garnets was investigated by Mössbauer spectroscopy and by an easy-axis monitor, both in flux-grown single crystals and in polycrystalline samples made by solid-state reaction. Contrary to a previous report, it was found that the cubic magnetic anisotropy properties of both systems do not differ from those of most iron garnets, namely, the easy magnetic axis is $\langle 111 \rangle$ from room temperature down to at least 77 K. However, peculiar features have been observed in the growth-induced anisotropy of these materials: besides a "normal" term, occurring in flux-grown crystals, that anneals away at temperatures $T \simeq 1200\,°C$, an "anomalous" term was found, clearly related to powder recrystallization at $T \simeq 1400\,°C$. The latter term, not previously reported for any iron garnets, can be eliminated from the Nd-Y (but not from the Pr-Y) iron garnet by substantially prolonging the higher-temperature annealing.

Reorientational magnetic transitions of several iron garnets have been discovered and studied in recent years.[1] Among these, Nd-Y and Pr-Y iron garnets (Nd-YIG and Pr-YIG) were reported to show very peculiar reorientational features. Specifically, an investigation of the $Nd_x Y_{3-x} Fe_5 O_{12}$ system made by Al'mukhametov, Belov, and Volkova[2] by ferromagnetic resonance on single crystals indicated that at room temperature the easy axis of magnetization was not coincident with any of the principal crystallographic axes, for samples having nominally[3] $x = 0.5$, 1.0, and 2.0; it was also shown that the easy axis at liquid-nitrogen temperature for all samples was along a $\langle 111 \rangle$ direction.[2] Furthermore, some preliminary Mössbauer measurements[1] have shown that in polycrystalline samples of $Nd_{1.5} Y_{1.5} Fe_5 O_{12}$ and $Pr Y_2 Fe_5 O_{12}$ made by solid-state reaction, the easy axis at room temperature was, in both cases, not along a $\langle 111 \rangle$ direction, although at liquid-nitrogen temperature it was along a $\langle 111 \rangle$ direction.

The above results are in contrast with the behavior of most iron garnets:[1] The Fe^{3+} sublattices tend indeed to keep their magnetic moments aligned with the $\langle 111 \rangle$ axes at any temperature, and, in a few cases, the anisotropy of the magnetic rare-earth metal prevails in changing the easy axis at low temperature. To investigate these phenomena more carefully, we have studied by Mössbauer spectroscopy, both powder samples and flux-grown single crystals of Nd-YIG and Pr-YIG. Moreover, measurements with the "easy-axis monitor" described elsewhere[4] were performed, from 77 K to room temperature, on single-crystal disks cut from the bulk samples.

In the Mössbauer spectra of iron garnets the width of the tetrahedral peaks is a sensitive probe of the direction of magnetization. In fact, when the magnetization is along a $\langle 111 \rangle$ crystallographic direction the structure is rhombohedral and all the tetrahedral sites have their symmetry (really pseudosymmetry) axes at an angle of 55° from the direction of magnetization. They are, therefore, all

equivalent, and there is only one sextet of tetrahedral lines with a strictly Lorentzian shape. When the magnetization **M** moves away from the $\langle 111 \rangle$ directions, the angle between the symmetry axes of the tetrahedral sites and **M** no longer has a unique value, and the single line of the tetrahedral sites splits (see, e.g., Ref. 5). This property of the Mössbauer spectra has been used to investigate a large number of magnetic phase transitions in the garnet system; the method is described in detail in Ref. 1. A Mössbauer spectrum of pure polycrystalline YIG is shown for purposes of comparison in Fig. 1(a). This spectrum is typical of an $\langle 111 \rangle$ easy axis and shows only one set of tetrahedral lines and two sets of octahedral lines with relative intensity 3:1.

Table I lists the samples used and the results obtained in the present set of experiments. Figure 1(b) shows the Mössbauer spectrum of an as-grown single crystal (named sample 1) of composition $Nd_{1.38} Y_{1.62} Fe_5 O_{12}$, as determined from the lattice parameter (in this case small fragments of the crystals were crushed and finely ground to obtain Mössbauer absorbers); a large broadening of the tetrahedral peaks relative to Fig. 1(a) is observed. From another crystal of the same batch, a small disk (named sample 2) was cut in a (110) plane parallel to a growth facet, and measured with the easy-axis monitor. A single easy axis was detected in the disk plane, not coincident with any principal crystallographic direction, and unchanged from room temperature to 77 K.

Both the above results clearly indicate the presence of a strong growth-induced anisotropy, which is attributed[6] to the large difference[7] in the ionic radii of Nd^{3+} ions with respect to Y^{3+} ions. Because the growth facets of garnet crystals are (110) or (211) planes, the easy axes in an as-grown bulk crystal can be either along the $\langle 110 \rangle$ or $\langle 211 \rangle$ directions or in the (110) and (211) planes, depending on the sign of the uniaxial anisotropy constant K_u. In general, the samples for the Mössbauer measurements are
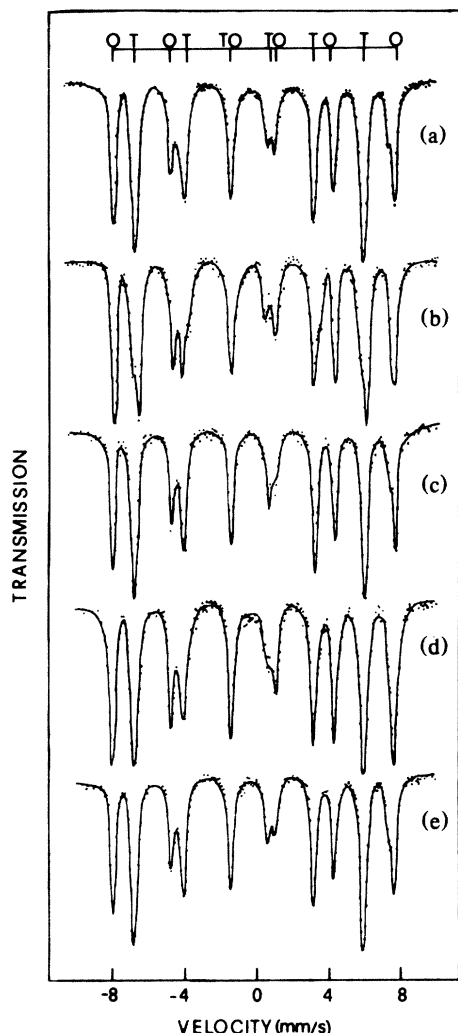
FIG. 1. Mössbauer spectra of sample 1 [a single crystal of composition $Nd_{1.38}Y_{1.62}Fe_5O_{12}$ after successive annealing treatments: (a) Mössbauer spectrum of pure YIG, shown for comparison], (b) as grown, (c) after annealing at 1200 °C in air for 72 h, (d) after a further annealing in air at 1400 °C for 2 h, (e) after a further annealing in air at 1400 °C for 72 h.

made of fine powders obtained by crushing several small pieces of the bulk crystal. It is then clear that the Mössbauer spectra will not show a well-defined easy axis of magnetization, but rather they will correspond to a superposition of different directions. Therefore, we would expect to see only a broadening of the tetrahedral peaks. Of course in this case the fitting of the tetrahedral lines with a single Lorentzian is not formally correct; however, the linewidth resulting from such fitting still gives a phenomenological measurement of the growth-induced anisotropy.

Sample 1 was then annealed at 1200 °C in air for 72 h. After this treatment the easy axis was definitely along a $\langle 111 \rangle$ direction, as shown in Fig. 1(c). This spectrum is similar to that of pure YIG [see Fig. 1(a)]; in particular, the average linewidth of the tetrahedral lines, calculated from the Lorentzian fitting of the tetrahedral lines 1 and 6 $[(m_I = -\frac{3}{2}) \rightarrow (m_I = -\frac{1}{2})$ and $(m_I = +\frac{3}{2}) \rightarrow (m_I = +\frac{1}{2})]$ was equal to that of pure YIG (see Table II). Similarly, sample 2 was annealed at 1250 °C in oxygen for 120 h; after this annealing, by the easy-axis monitor two easy axes were detected in the (110) plane, coincident with the $\langle 111 \rangle$ axes. Both these results indicated that the initial shift of the easy axis from the $\langle 111 \rangle$ directions was merely a consequence of the uniaxial growth-induced anisotropy (removable, as usual,[8] by annealings at 1200 °C), and that the easy axis is along a $\langle 111 \rangle$ direction as far as the magnetic cubic anisotropy is concerned. However, this appeared to be in contradiction to the results from the polycrystalline sample [named sample 3; see Fig. 2(a)] obtained by solid-state reaction, for which the Mössbauer spectra at room temperature also show a broadening of the tetrahedral peaks (see Table I), whereas no growth-induced anisotropy is expected in this case.

To clarify this point, sample 1, already annealed at 1200 °C, was annealed again at 1400 °C in air for about 2 h (identical to the last firing in the preparation process of the polycrystalline sample 3). After this treatment, the powders had undergone some recrystallization, and very small crystallites could even be seen by the eye. The consequent Mössbauer spectrum is shown in Fig. 1(d); the tetrahedral lines are now broadened, and look similar to

TABLE I. List of samples and summary of the experiments. The easy magnetic axes were determined with the "easy-axis monitor" (see Ref. 4) for samples 2 and 5, and by Mössbauer spectroscopy (see text) for other samples. Successive annealings (numbers not in parentheses are temperatures, numbers in parentheses are times) and easy magnetic axis at room temperature (NPCA means "no principal crystal axis").

Sample No.	Composition					
1	$Nd_{1.38}Y_{1.62}Fe_5O_{12}$ (ground single crystal)	As grown NPCA	1200 (72) $\langle 111 \rangle$	1400 (2) NPCA	1200 (72) NPCA	1400 (72) $\langle 111 \rangle$
2	$Nd_{1.38}Y_{1.62}Fe_5O_{12}$ [single crystal (110) disk]	As grown NPCA	1250 (120) $\langle 111 \rangle$	1400 (2) $\langle 111 \rangle$		
3	$Nd_{1.5}Y_{1.5}Fe_5O_{12}$ (polycrystalline)	As prepared NPCA	1400 (72) $\langle 111 \rangle$			
4	$Pr_{0.63}Y_{2.37}Fe_5O_{12}$ (ground single crystal)	As grown NPCA	1250 (120) $\langle 111 \rangle$	1400 (16) NPCA		
5	$Pr_{0.63}Y_{2.37}Fe_5O_{12}$ [single crystal (110) disk]	As grown NPCA	1250 (120) $\langle 111 \rangle$			
6	$PrY_2Fe_5O_{12}$ (polycrystalline)	As prepared NPCA	1450 (120) NPCA			

TABLE II. Full width at half maximum $\bar{\Gamma}$ averaged over the tetrahedral lines 1 and 6 for the Mössbauer spectra shown in Figs. 1 and 2. The experimental error is ± 0.5 channels in all cases. $\bar{\Gamma}$ for the Mössbauer spectrum Fig. 1(b) is not given here because in this case the tetrahedral lines 1 and 6 are too different from Lorentzian.

	1(a)	1(c)	1(d)	1(e)	2(a)	2(b)
$\bar{\Gamma}$ (channels)	10.5	9.7	12.3	10.2	12.6	10.8

those observed for sample 3 as prepared (see also, Table II). When sample 2 was subjected to the same anneal, it did not show any change in easy axis. These experiments indicate that during the annealing treatment at 1400 °C the small powder grains act as nuclei for the growth of very small crystallites, which acquire a growth-induced anisotropy.

A further 72 h annealing at 1200 °C of sample 1 did not cause noticeable effects. Finally, both samples 1 and 3 were annealed for 72 h at 1400 °C in air. Mössbauer spectra taken after this last anneal [see Figs. 1(e) and 2(b)] look just like that of pure YIG, thus showing that the regrowth anisotropy has also been removed.

At variance with the results of Ref. 2 (results attributable to missing or incomplete removal of the growth-induced anisotropy from single crystals), we conclude that the cubic magnetic anisotropy properties of Nd-YIG are just the same as those of most iron garnets; i.e., the magnetic phase is rhombohedral with the easy axes along $\langle 111 \rangle$ crystallographic directions, from room temperature down to at least 77 K. However, just their *growth-induced* magnetic anisotropy may be considered unusual. Two contributions are clearly distinguished: a "normal" term, occurring in flux-grown crystals, that anneals away after several tens of hours at $T \simeq 1200$ °C, and an "anomalous" term, occurring in powder samples (either samples made by solid-state reaction or ground crystals) when subjected to a few hours anneal at 1400 °C, which can be eliminated by prolonging the anneal, at the same temperature, to several tens of hours. The latter contribution, not previously observed in garnets, and clearly related to grain recrystallization, has therefore an activation energy rather higher than the former and should be related to a different kind of ordering of Y and Nd ions.

Similar measurements have been made on the Pr-YIG system and are also summarized in Table I. Samples 4
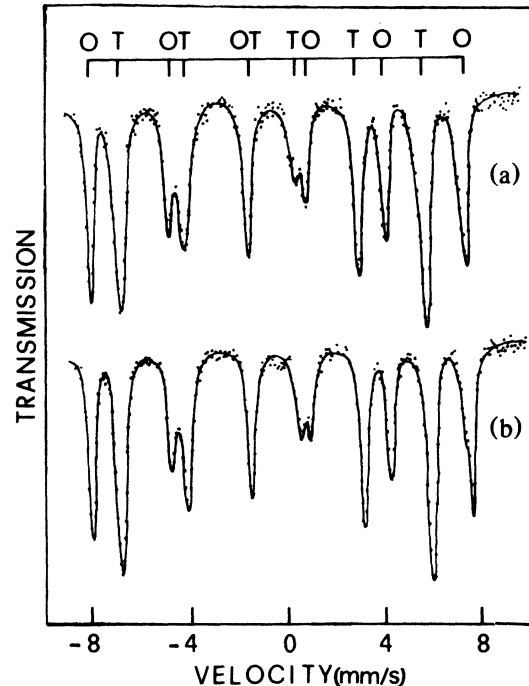

FIG. 2. Mössbauer spectra sample 2, a polycrystalline sample of $Nd_{1.5}Y_{1.5}Fe_5O_{12}$: (a) as prepared, (b) after an annealing treatment at 1400 °C for 72 h in air.

and 5 are single crystals with composition $Pr_{0.63}Y_{2.37}Fe_5O_{12}$ (as deduced from the lattice parameter) and sample 6 is a polycrystalline specimen of composition $PrY_2Fe_5O_{12}$ made by solid-state reaction. The results are similar to the Nd-YIG case, although the increase of $\bar{\Gamma}$ (full width at half maximum) of sample 4 after the 1400 °C anneal was less evident than that observed in sample 1. Moreover, the "anomalous" regrowth anisotropy could not be removed from sample 6, even after an anneal of 120 h at 1450 °C. This indicates that the regrowth-induced anisotropy in $PrY_2Fe_5O_{12}$ has an activation energy even higher than in $Nd_{1.5}Y_{1.5}Fe_5O_{12}$. Such an effect can be attributed to the larger difference in the ionic radii[7] of Pr-Y with respect to Nd-Y.

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