Magnetic properties of praseodymium iron garnet and neodymium iron garnet

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(Received 30 May 1986)

We have measured saturation magnetization, ferromagnetic resonance linewidth, effective g factor, and magnetocrystalline anisotropy coefficients on single-crystal samples of praseodymium iron garnet (PrIG) and neodymium iron garnet (NdIG). Saturation magnetizations were measured from 77 to 550 K. The other properties were measured from 150 to 350 K in PrIG and from 200 to 450 K in NdIG. PrIG has a positive first-order magnetocrystalline anisotropy coefficient in contrast with all the other single rare-earth iron garnets. Our results support the idea that the contributions to linewidth and anisotropy of praseodymium and neodymium ions in an iron garnet lattice vary with lattice parameter.

I. INTRODUCTION

At the time that the magnetic properties of most of the single rare-earth iron garnets were measured,[1] neither praseodymium iron garnet (PrIG) nor neodymium iron garnet (NdIG) had been grown. Studies on the formation of garnets by solid-state reaction had led both Geller *et al.*[2] and Espinosa[3] to conclude that the maximum lattice constant for any iron garnet (that is, a garnet with only iron on its tetrahedral and octahedral sites) is 12.540 Å. Extrapolations from their data led these investigators to predict lattice constants greater than 12.540 Å for both PrIG [12.646 Å (Ref. 3)] and NdIG [12.596 Å (Ref. 2) and 12.600 Å (Ref. 3)]. Therefore, it was generally believed that NdIG and PrIG could not be grown. Conclusions about the properties of these large rare-earth ions in the garnet structure were drawn from measurements of garnets with small amounts of praseodymium and neodymium (Pr:YIG and Nd:YIG) (Refs. 4 and 5) or garnets with large ions on octahedral sites to enlarge the lattice ($Pr_3Fe_4ScO_{12}$).[6] However, it now appears that the instability of these large garnets was dictated by the high temperatures at which their formation was attempted. The recent successful growth of both PrIG and NdIG by liquid-phase epitaxy at low temperature[7] has enabled us to determine magnetic properties of these materials and thus fill in gaps in the understanding of rare earths in garnets. The reader is referred to Ref. 7 for further discussion of the technique and the reasoning that led to its development. In this paper we present measurements of the saturation magnetization, the ferromagnetic resonance linewidth, the effective g factor, and the magnetocrystalline anisotropy coefficients for these two materials. The saturation magnetization was measured at temperatures from 77 to 550 K. The other properties were measured from 150 to 350 K for PrIG and from 200 to 450 K for NdIG.

II. EXPERIMENT

All measurements were performed on single-crystal material grown as described in Ref. 7. Note that the use of the liquid-phase-epitaxy technique implies Pt and Pb impurities in the crystals from the crucible and flux, respectively. Chunks of this material were milled to spheres using the pneumatic method described by Bond[8] many years ago. Because of the wide resonance lines encountered, we deemed it unnecessary to polish the spheres. The spheres used for the measurements ranged from 0.7 to 1.0 mm in diameter. The ferromagnetic resonance linewidths ΔH, the effective g factors, and the ratios of magnetocrystalline anisotropy coefficients to saturation magnetization K_1/M and K_2/M were measured in a ferromagnetic resonance (FMR) apparatus with provision for resistance heating and cooling by boil off from liquid nitrogen. The resonance frequency of the cavity of the FMR apparatus ranges from 10.93 to 10.97 GHz depending on temperature. The spheres were oriented along a [110] axis using the Buerger precession technique.[9] They were then coated with epoxy and affixed to sapphire rods with the [110] axis pointing along the rod. The rod and sphere combination was then mounted in the cavity such that the magnetic field was always applied perpendicular to the [110] axis. Measurements were made approximately every 10° as the field was swept around the (110) plane. The locations of the [111] and [100] axes, as well as g and K_1/M and K_2/M, were determined by least-squares fits of the resonance field versus orientation measurements to the expected functions. Then, using that fitted orientation, the FMR linewidth was measured with the magnetic field applied along the [111], [100], and [110] axes. The linewidths reported are full width at half maximum (FWHM). The FMR field for resonance and linewidth were also examined at orientations 2° and 4° on either side of the three principal directions at the lowest temperature attained for each material. This was done to determine whether sharp peaks in linewidth or field for resonance, analogous to those reported by Dillon and Nielsen[4,10] for both Nd:YIG and Pr:YIG, could be discovered. We determined that, in these materials and at these temperatures, the linewidth and field for resonance do not show such peaks.

Saturation magnetization measurements were performed in an EG&G Princeton Applied Research

vibrating-sample magnetometer (VSM). The magnetometer is equipped with a Dewar attachment and a resistance heater. Thus, the sample can be immersed in liquid nitrogen and heated to provide for measurement from 77 to 600 K. The samples used were small single crystals. The volume of the samples (necessary to convert the response of the magnetometer to a saturation magnetization) was derived from their weight and their density, since the density of the material was calculable from x-ray diffraction measurements of the lattice parameters. A field of 5 kOe was applied to saturate the samples at and above room temperature; a field of 10 kOe below room temperature. At room temperature we assured ourselves that we had indeed saturated the sample by checking that the results were the same whether a 5- or 10-kOe field was applied. We also found the same results for thin-film samples at room temperature, which are much easier to saturate. At all temperatures, the signals showed a significant part of the curve as a distinctly straight line, again assuring us that we had reached saturation. At 77 K we are however clearly approaching the temperature at which 10 kOe will no longer saturate the material.

III. RESULTS

A. Linewidth

The FMR linewidth (FWHM) of PrIG as measured along the three principal crystalline directions is shown plotted versus temperature in Fig. 1. The linewidths in the [100] and [111] directions were indistinguishable within the expected experimental uncertainty. Therefore, Fig. 1 shows the average of the linewidths measured in the [100] and the [111] directions. In Pr-doped YIG, Dillon[4] reported the [110] linewidth to be the largest, which is what we see in PrIG. However his measurements showed the [100] linewidth to be distinctly larger than the [111] linewidth.

The FMR linewidth (FWHM) of NdIG as measured along the three principal crystalline directions is shown plotted versus temperature in Fig. 2. Dillon[4] reported the same ordering of the magnitudes of linewidths in Nd-doped YIG that we see in NdIG. The [111] linewidth is the largest and the [100] the smallest.

Both Seiden[5] and Dillon[4] reported linewidths in Pr-doped YIG of about 100 Oe per %Pr at 150 K. Seiden,[5] who measured only in the [111] direction, reported linear dependence of linewidth on Pr content in the 0.2 to 4.6 % range of doping. These results extrapolate to a linewidth of 10 kOe for PrIG at 150 K if the linewidth continued to depend linearly on Pr content; this is clearly not the case. We find a [111] linewidth of less than 2 kOe at 150 K. Seiden[5] and Dillon[4] also report linewidths of about 40 Oe per % Nd in doped YIG at 200 K. A linear dependence on Nd content would then imply a linewidth of 4 kOe in NdIG at 200 K. We measure less than 3 kOe in the [111] direction. These results indicate that FMR linewidth does not depend linearly on Pr or Nd content throughout the entire concentration range.

Similarly, Gyorgy *et al.*[6] demonstrated the nonlinear dependence of linewidth on Pr and Nd content in measurements on $(YPr)_3(FeSc)_5O_{12}$ and $(YNd)_3(FeSc)_5O_{12}$ at 80 K. They presented data to show that the linewidth contribution from Nd and Pr ions depends on the lattice parameter. Our data support their general conclusion as to nonlinearity although we cannot match our data to their lattice-parameter dependence because of the differ-

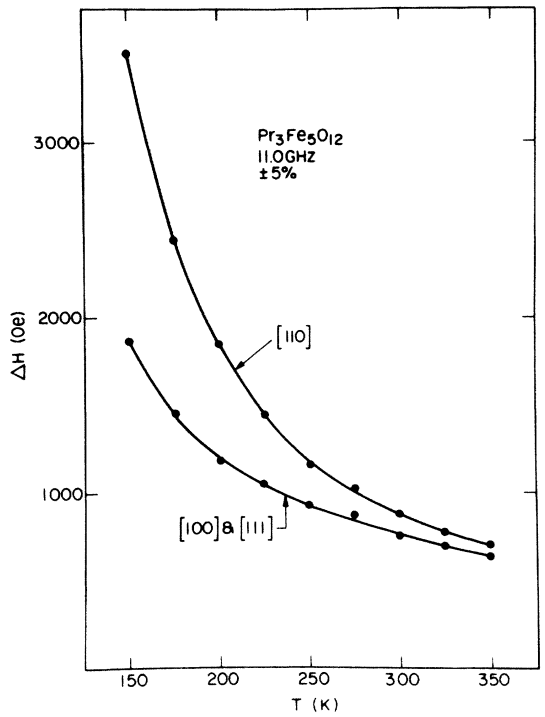

FIG. 1. Ferromagnetic resonance linewidth in praseodymium iron garnet from 150 to 350 K as measured with field applied in the three different principal directions. Because the measurements in the [100] and [111] directions were indistinguishable within experimental error, we plotted the average of the linewidths measured in those two directions. The lines connecting the data points are included only to guide the eye.

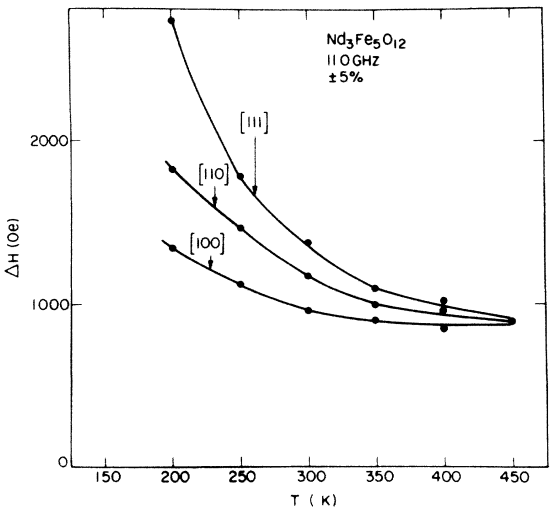

FIG. 2. Ferromagnetic resonance linewidth in neodymium iron garnet from 200 to 450 K measured with the field applied in the three different principal directions. The lines are included only to guide the eye.

TABLE I. $\Delta H[111]$ fit to $aT^{-2}+b$.

	a (kOe K^2)	b (kOe)	χ^2
PrIG	$(3.3\pm0.4)\times10^4$	0.38 ± 0.06	0.46
NdIG	$(8.8\pm0.7)\times10^4$	0.41 ± 0.06	1.01

ence in the temperatures at which the two sets of data were taken.

Seiden's[5] measurements of the FMR linewidths on YIG with rare-earth doping taken as a function of temperature from 4 K to room temperature and above showed linewidths rising to a single broad peak then falling at higher temperatures. He reported a T^{-2} dependence of linewidth at temperatures higher than the peak in all his samples. Our measurements on PrIG and NdIG did not extend to temperatures low enough to see peaks in linewidth. However, the [111] linewidth data for both PrIG and NdIG fit well to the form $aT^{-2}+b$. The best value for a and b, as established by a least-squares fit criterion, are shown in Table I.

B. Magnetization

Saturation magnetizations of PrIG and NdIG are shown plotted versus temperature in Figs. 3 and 4, respectively. The magnitudes of the saturation magnetizations of the two materials are about equal above room temperature. The saturation magnetization of NdIG becomes somewhat larger than that of PrIG at low temperature. The Curie temperatures of PrIG and NdIG are 569 ± 2 K and 567 ± 2 K.

In Table II, we compare our PrIG saturation magnetization data to data published by Aharoni and Schieber[11] and by Geller *et al.*[12] on $PrY_2Fe_5O_{12}$. (It must be noted that Geller *et al.*[12] state that their magnetization data is taken with the sample unsaturated; the Aharoni and Schieber[11] data may also be unsaturated as they give no value for their applied field. Note that failure to saturate would lead to largest errors at low temperatures.) In order to compare our results to theirs, we have converted our results to units of Bohr magnetons and used the formula

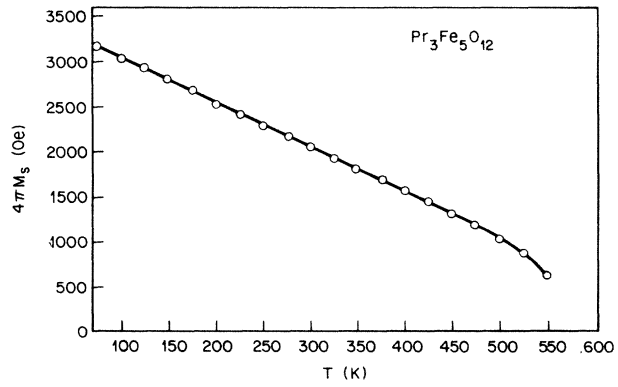

FIG. 3. Saturation magnetization in praseodymium iron garnet from 77 to 550 K. The line connecting the data points is included only to guide the eye.

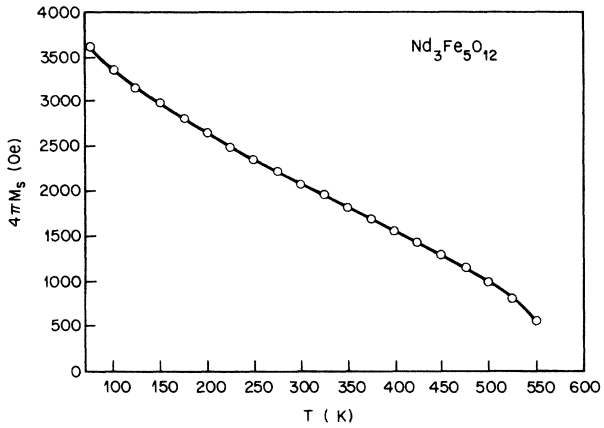

FIG. 4. Saturation magnetization in neodymium iron garnet from 77 to 550 K. The line connecting the data points is included only to guide the eye.

$$n_B(R_1Y_2Fe_5O_{12})=[n_B(RIG)-n_B(YIG)]/3+n_B(YIG)$$

with n_B(YIG) values taken from Ref. 13. Our data agrees closely with that of Geller *et al.*[12] and Aharoni and Schieber[11] at 298 K. At 100 K, our data agrees with that of Geller *et al.*[12] The Aharoni and Scheiber data gives a larger value.

Table II also compares our NdIG saturation magnetization data to data published by Aharoni and Schieber[11] and Geller *et al.*[2] on $NdY_2Fe_5O_{12}$. A similar warning as to the saturated state of the samples applies to these papers. The result of the comparison again shows agreement among this paper and the other two at 298 K. At 100 K we see agreement between this paper and the Geller *et al.*[2] paper with the Aharoni and Schieber paper showing a larger value.

The gentle upward concavity of the NdIG magnetization at low temperature is presumably attributable to the contribution of the neodymium. We note quite generally that the rare-earth magnetization in the rare-earth iron garnets falls off much more rapidly with temperature than the iron magnetization.

C. Anisotropy

The first-order magnetocrystalline anisotropy coefficient K_1 for PrIG is shown plotted versus temperature in Fig. 5. The coefficient K_1 was obtained by multiplying the value of K_1/M (obtained using FMR) times the value of M (obtained at the same temperature by VSM). Note that the K_1 of PrIG is positive, in contrast to the negative K_1 measured in all the other pure rare-earth iron garnets. This is not entirely unexpected, in that Gyorgy *et al.*[6] reported a K_1 per formula unit of Pr that depended on lattice parameter (unlike most of the rare-earth metals) and that became positive at lattice parameters larger than 12.6 Å. They based these conclusions on measurements on $(YPr)_3(FeSc)_5O_{12}$ with varying concentrations of Pr at 80 K. The lattice parameter of our PrIG sample is 12.646 Å. At this lattice parameter, Gyorgy *et al.*[6] show a K_1 per formula unit of Pr equal to 3×10^3 erg/cm^3 at 80 K. We

TABLE II. Comparison of saturation magnetization data (in Bohr magnetons) to literature values for $R_1Y_2Fe_5O_{12}$ (R = Nd, Pr).

	100 K		298 K	
	NdIG	PrIG	NdIG	PrIG
$n_B(R\text{IG})$ this work	7.16	6.59	4.46	4.48
n_B(YIG) Geller (Ref. 13)	4.88		3.66	
$n_B(R_1Y_2Fe_5O_{12})$ interpolated	5.64	5.45	3.93	3.93
$n_B(R_1Y_2Fe_5O_{12})$ Geller *et al.* (Refs. 2 and 12)	5.7	5.4	4.0	3.9
$n_B(R_1Y_2Fe_5O_{12})$ Aharoni and Schieber (Ref. 11)	6.1	5.6	4.0	3.9

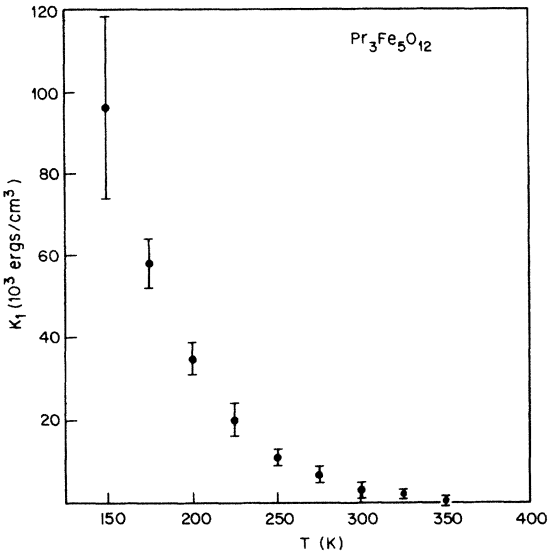

FIG. 5. First-order magnetocrystalline anisotropy coefficient in praseodymium iron garnet from 150 to 350 K.

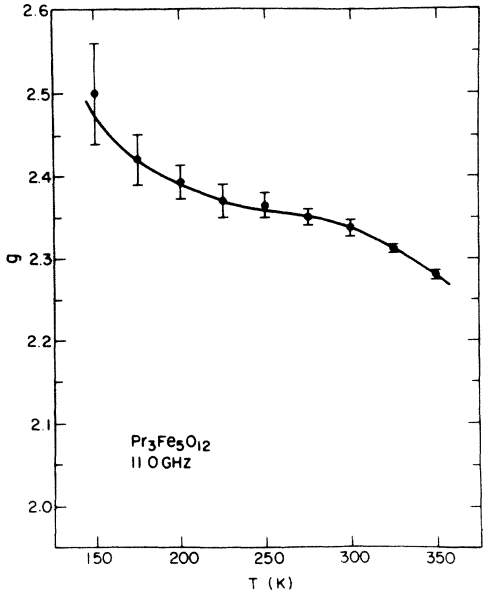

FIG. 7. Effective g factor in praseodymiun iron garnet from 150 to 350 K. The line connecting the data points is included only to guide the eye.

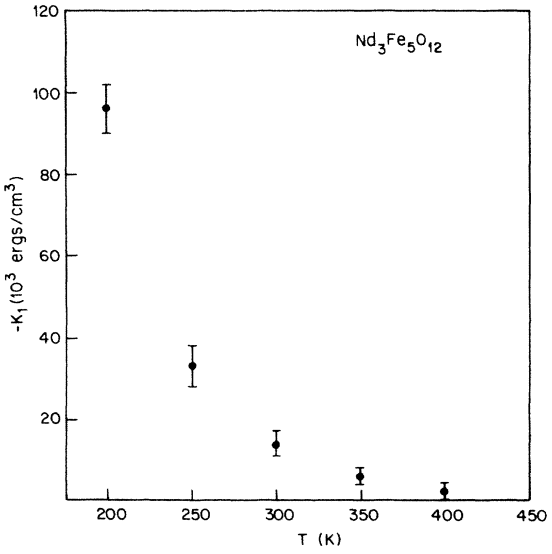

FIG. 6. First-order magnetocrystalline anisotropy coefficient in neodymium iron garnet from 200 to 400 K.

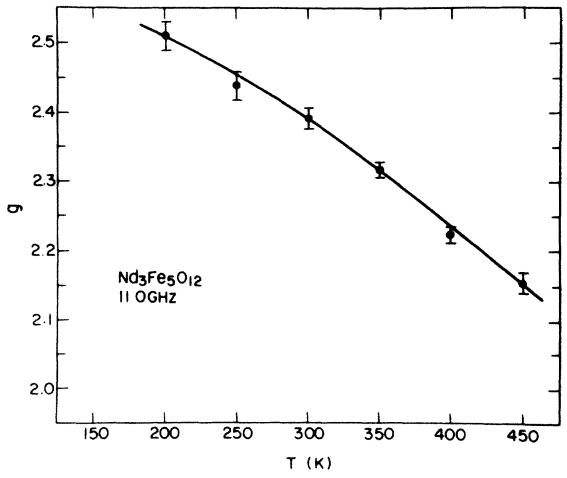

FIG. 8. Effective g factor in neodymium iron garnet from 200 to 450 K. The line connecting the data points is included only to guide the eye.

TABLE III. K_1 fit to $cT^{-3}+d$.

	c(K^{3}erg/cm^3)	d(erg/cm^3)	χ^2
PrIG	$(3.3\pm0.5)\times10^8$	-8 ± 2	0.46
NdIG	$(-8.1\pm0.8)\times10^8$	12 ± 3	1.94

TABLE IV. Significant K_2/M in Oe.

T (K)	PrIG	NdIG
150	380±560	
175	310±190	
200	170±110	−200±110
225	110±110	

measure a much larger 32×10^3 erg/cm^3 per formula unit Pr at 150 K, which is unexpected. Typically, the absolute value of K_1 decreases monotonically with increasing temperature. However, Gyorgy *et al.*[6] speculate that the K_1 of Pr in iron garnets at 80 K arises from nearly equal contributions of opposite sign from anisotropic exchange and from crystal-field effects. Disparate dependences on temperature of these two effects might produce a nonmonotonically varying dependence of the total K_1 on temperature. This would resolve the apparent inconsistency between our measurements and those of Gyorgy *et al.*[6]

The first-order magnetocrystalline anisotropy coefficient K_1 for NdIG is shown plotted versus temperature in Fig. 6. Our results can be compared to measurements by Gyorgy *et al.*[6] at 80 K on samples of $(YNd)_3(FeSc)_5O_{12}$ with varying concentrations of Nd and to measurements by Al'mukametov *et al.*[14] at temperatures from 4 K to room temperature on $YNd_2Fe_5O_{12}$. Gyorgy *et al.*[6] show a K_1 per formula unit of Nd that depends on lattice parameter in much the same way as the K_1 per formula unit of Pr does. (Note that these two rare-earth metals are the only two for which this lattice parameter dependency has been seen.) They report the K_1 per formula unit of Nd to be -500×10^3 erg/cm^3 at 80 K and at the lattice parameter that we measure for NdIG, 12.596 Å. We measure -32×10^3 erg/cm^3 per formula unit of Nd at 200 K. One would expect the value of K_1 at 80 K to be much larger than that at 200 K. Al'mukhametov *et al.*[14] report a K_1 of -110×10^3 erg/cm^3 at 200 K. This implies a K_1 of -50×10^3 erg/cm^3 per formula unit Nd. Their sample had a lattice parameter of 12.46 Å. The data of Gyorgy *et al.*[6] imply that the K_1 per formula unit of Nd should be about 60% larger at that lattice parameter than at the one we measured. So one could infer a value of -30×10^3 erg/cm^3 per formula unit Nd at 200 K from the Al'mukhametov data and the Gyorgy dependence on lattice size. This value agrees closely with our measured value. However, it must be noted that the lattice constant reported by Al'mukhametov *et al.*[14] is so small as to cast doubt on their having actually grown material of the composition claimed.

We fit the K_1 values to the function $cT^{-3}+d$. The best values of c and d are shown in Table III. White[15] suggests that K_1 should be proportional to T^{-3} if the crystal field is strongly cubic. As can be seen from the values of χ^2 shown in Table III, the K_1 values of PrIG fit well to this form; the values of NdIG do not.

At temperatures above 225 K, we found K_2 to be less than our experimental error in both materials. Values of K_2 at and below 225 K are shown in Table IV. The sign of K_2 is the same as the sign of K_1 for each material.

D. Effective g factor

The effective g factors of PrIG and NdIG are shown plotted versus temperature in Figs. 7 and 8, respectively. For both materials g is larger than 2 at all the temperatures measured and g decreases with increasing temperature.

IV. CONCLUSIONS

We have measured magnetocrystalline anisotropy, saturation magnetization, effective g factor, and FMR linewidth in single-crystal NdIG and PrIG. The saturation magnetizations were measured from 77 to 550 K in each case. The other quantities were measured from 150 to 350 K in PrIG and from 200 to 450 K in NdIG. Our results support the proposition advanced by Gyorgy *et al.*[6] that the contributions to linewidth and anisotropy vary with lattice parameter for these ions in an iron garnet lattice. Our PrIG anisotropy results also suggest that the magnetocrystalline anisotropy in PrIG may result from two competing effects with relative magnitudes that change with temperature. Thus, although PrIG does have a positive magnetocrystalline anisotropy coefficient, in contrast with all the other rare-earth iron garnets, additions of praseodymium to other rare-earth iron garnet combinations would not be likely to achieve a reduction in the negative magnetocrystalline anisotropy coefficient in the way that cobalt additions do unless the garnet lattice parameter were greater than 12.6 Å.

ACKNOWLEDGMENTS

We thank G. P. Espinosa for a critical reading of the manuscript. This work was partially supported by Tri-Service/NASA Contract No. F33615-81-C-1404.

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