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Magnetic Effects of Indium and Gallium Substitutions in Yttrium Iron Garnet

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This paper is a report on the magnetic properties of polycrystalline garnets of the form $3Y_2O_3\cdot(5\text{-}x)Fe_2O_3\cdot xM_2O_3$, where M=Ga or In and $0\leq x\leq 1$. Gallium and indium both produce a monotonic decrease in the Curie temperature as x increases. The magnetic moment at all temperatures is progressively lowered by gallium substitution. On the other hand, indium substitution up to $x=0.6$ results in a nearly constant room temperature magnetic moment. At very low temperatures, indium substitution gradually increases the moment; this increase reaches a maximum of nearly 40% at $x=0.6$. The initial permeability at room temperature decreases with x for gallium but increases with x (for $x\leq 0.6$) for indium. Ferrimagnetic resonance line widths at room temperature vary from about 25 for YIG to 90 for 1.0 Ga_2O_3. The indium samples show approximately the same dependence up to $x=0.6$; beyond this point broadening due to the presence of a perovskite phase completely masks all intrinsic effects of the indium.

Introduction

Comprehensive studies of the distribution of indium and gallium ions in substituted YIG have shown that In^{3+} prefers the octahedral 16a sites whereas Ga^{3+} enters both the octahedral and tetrahedral sites.1),2) Complete substitution of gallium for iron is possible but there is a limit to the extent that indium can replace iron. The effects of these diamagnetic substituents on the static and low frequency magnetic properties of YIG have been discussed by several authors.2)-8) Ferrimagnetic resonance data have been reported for In-YIG by Japanese researchers8),9) and for Ga-YIG by several groups in the United States.10)-12) The present paper resulted from an attempt to reconcile some of the existing data in the literature.

Sample preparation, x-ray diffraction and permeability measurements are described elsewhere.5),7) Magnetic moments vs. temperature were measured in a field of 12.5 kilogauss on a vibrating sample magnetometer built by W. M. Hubbard of this laboratory.

Ferrimagnetic resonance was performed at X-band in a transmission cavity operating in a TE_{102} mode. The klystron frequency was stabilized at the resonant frequency of the cavity. Point by point plots of the absorption vs. field were used for determining the width of the resonance at the half power points. An FM method was used for obtaining g values. The magnetic field was monitored with an NMR probe whose frequency was determined accurately by means of a counter. The estimated experimental error is ±0.001 for g values and is less than 10% for line widths. The samples were polished spheres about 0.020″ in diameter which were ground from the same high density toroids used in the permeability studies.

Experimental results

Lattice constants decrease linearly with Ga^{3+} substitution but increase linearly with In^{3+} content; this is consistent with differences in respective ionic radii.1) Lattice constants for indium-YIG are shown in Fig. 1. The limiting value of x for In^{3+} is not precisely known but we have been unsuccessful thus far in our attempts to eliminate a perovskite phase for x greater than 0.65. Shichijo and Miyadai have reported8) only the garnet phase for $0\leq x\leq 1.0$ but their lattice constant data do not agree with that shown in Fig 1. It is probable that their samples do indeed contain an undetected perovskite phase.

The saturation magnetization (in Bohr magnetons per O_{12} unit) extrapolated to 0°K and the Curie temperatures for the indium series are plotted in Fig. 2. These values are in excellent agreement with the second order interaction theory of Gilleo.13) This agreement was previously shown for Zr, Sn, Sc and for one value of In.[1] The results of applying the theory to gallium are given in the Table I but are of limited value because the theory used assumes that gallium enters only the tetrahedral sites.

The room temperature initial (relative) permeability at low frequencies is shown in the last column of the Table I. Note that a four-fold increase over the YIG value occurs due to In^{3+} substitution in contrast with the decrease caused by Ga^{3+} substitution. The maximum attainable permeability (i.e., the value just below the Curie temperature) for the indium-YIG series is of the order of 2000. The permeability vs. frequency curves for these materials are quite flat below 1 Mc/sec but begin to relax rapidly above 10 Mc/sec.

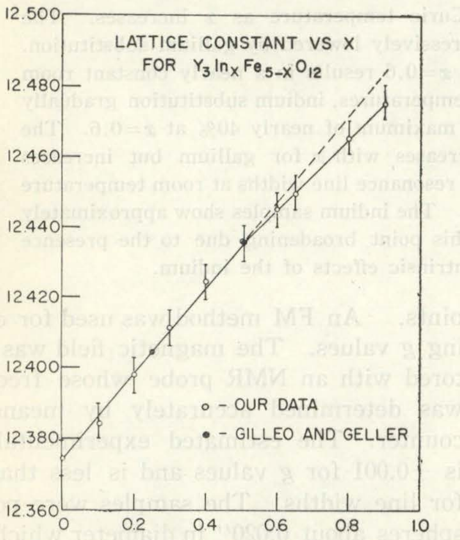

Fig. 1. Lattice constants of indium substituted YIG.

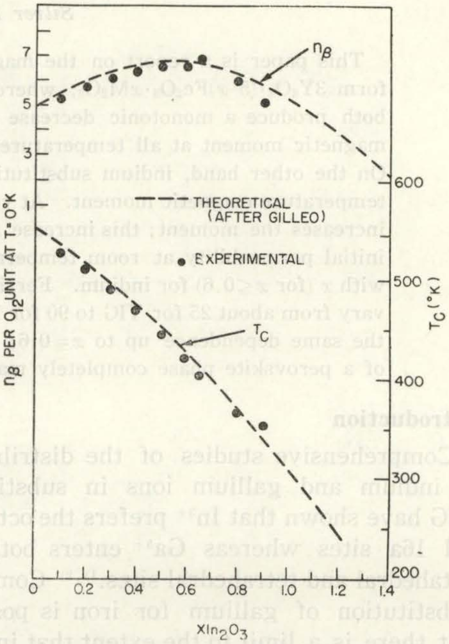

Fig. 2. The effects of indium substitution on the Curie temperature and the saturation magnetization (in Bohr magnetons) of YIG.

Table I.

xM_2O_3	n_B(0°K)		Room temperature data			
	Calc.[13]	Exp.	n_B(exp.)	$4\pi M_s$	ΔH	μ_0'
0	5.0	4.9	3.7	1830	25	130
0.1 In_2O_3	5.5	5.3	3.7	1810		
0.2	5.9	5.8	3.7	1830	44	220
0.3	6.3	6.1	3.6	1750	58	280
0.4	6.6	6.5	3.7	1820	58	350
0.5	6.8	6.7	3.8	1850	50	460
0.6	6.8	6.6	3.5	1710	68	520
0.65	6.7	6.8	3.3	1590	86	
0.8	6.3	6.1	2.8		100	
0.9	5.9	5.2	2.3		290	
0.2 Ga_2O_3	4.0	4.0	2.8	1430	32*	120
0.4	3.0	3.5	2.2		66	
0.6	2.0	2.5	1.7	890	71	40
0.8	1.1	1.7	1.1		60	
1.0	0.3	1.0	0.7	350*	90	15

* Data taken from reference 10.

Room temperature line widths (full width at half power) and effective *g* values measured at *X*-band are given in the Table I and are shown in Fig. 3. The gallium data are in good agreement with that of Harrison and Hodges.[10] The indium line-width data closely parallels the gallium data for *x* less than about 0.6; for $x>0.6$ the line width increases rapidly. For example, for 0.9 In_2O_3 we obtained a line width of 290 gauss. Such an increase in line width is expected when a second phase is present and is consistent with the existence of a perovskite phase in the x-ray diffraction spectrum. As mentioned above, we detected a very slight amount of perovskite in the indium samples for $x=0.65$; the amount of perovskite phase became increasingly greater for $x=0.8$ and 0.9.

An interesting anisotropy effect was discovered in one of our narrow line width polycrystalline YIG spheres. Careful plots of the field for resonance vs. angular orientation of the sphere resulted in a curve analogous to the single crystal data reported by Dillon and Nielsen.[15] Such an effect can only be accounted for on the grounds that the sphere is essentially a single grain. Van Uitert's study[14] of grain growth as a function of firing temperature indicates that grains as large as ten times the diameter of this sphere are quite likely at the firing temperature used for this sphere (1460°C).

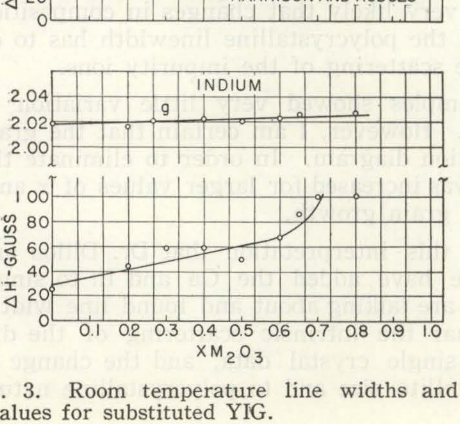

Fig. 3. Room temperature line widths and *g* values for substituted YIG.

Conclusions

1. Both gallium and indium reduce the Curie temperature of YIG but they have different effects on the saturation magnetization. Gallium produces a monotonic decrease in magnetic moment at all temperatures whereas indium results in an increase in the moment at 0°K with a maximum value occurring at $x\sim0.6$. At room temperature, the moment of the indium-YIG series is essentially constant up to about $x=0.6$.

2. The rise in the room temperature initial permeability with indium substitution may be explained by the depression of the Curie temperature. Since the permeability rises sharply just below the Curie temperature, the lowering of the latter effectively brings the room temperature point nearer that maximum. In the case of gallium, the increase in permeability due to the depression of the Curie temperature is more than compensated by a large drop in magnetic moment. Hence the permeability decreases as the amount of gallium is increased.

3. The ferrimagnetic resonance line width as a function of indium content is essentially the same as for gallium up to $x\sim0.65$. Beyond this point the indium line widths suffer from perovskite broadening and the indium curve departs from the gallium curve. It is our opinion that the large line widths reported for indium samples by Miyadai *et al.*[8),9)] are also indicative of perovskite broadening, in addition to the porosity broadening suggested by them. The theory of porosity broadening[16] which they use can hardly account for more than ~100 oe for samples having densities greater than 95% and saturation magnetizations as given in the Table. In the case of YIG, a porosity correction of ~100 oe does indeed bring the line width of references 8 and 9 into agreement with those shown in Fig. 3. But for all $x>0$, the line widths of those authors exceed ours by considerably more than 100 oe. Thus we conclude that the samples of Miyadai *et al.* must have a progressively increasing perovskite phase which first sets in at very low values of *x*. Other possible contributions to the broadening are the effects which result from deviations in stoichiometry and firing

temperature reported by Van Uitert *et al.*[14]

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DISCUSSION

K. HOSELITZ: Can the relatively large loss at about 1 Mc/sec in the substituted garnets be explained by the presence of Fe^{2+} ion and lack of perfect stoichiometry, which might also give rise to a relatively low resistivity?

E. E. ANDERSON: Although we did not measure the electrical resistivities of all of our samples, a few measurements were made. At room temperature our YIG samples had values $\sim 10^{13}$ ohm-cm. Gallium reduced the resistivity but the lowest value was still $\sim 10^{6}$ ohm-cm. Therefore I do not believe that electrical losses are responsible for the relaxation of the permeability.

E. W. GORTER: We have substituted Ti for Fe and Ca for Y in YIG up to $Y_{2.4}Ca_{0.6}Fe_{4.4}Ti_{0.6}O_4$. The majority of Ti ions enter octahedral sites as deduced from the saturation moments. We see the same rise of μ with Ti content, up to $\mu=450$, which supports your view on the cause of the effect of the In^{3+} substitution. On the other hand, in these polycrystalline samples the line width remains constant at ≈ 20. Can you account for the rise in linewidth you obtain for the In^{3+} substituted samples?

E. E. ANDERSON: The fact that our linewidths show the same rise as that obtained by Harrison and Hodges for Gallium led us to believe that the increase was an intrinsic scattering effect. However, we had planned to complete a study of single crystal sample before making any such statements.

J. F. DILLON: I am curious as to what examination you have made of the structure of the samples. Were the grain size and porosity, for instance, constant across the composition diagram? Offhand, it seems very likely that changes in composition are associated with changes in structure, and the polycrystalline linewidth has to do primarily with structure rather than with the scattering of the impurity ions.

E. E. ANDERSON: Examination of these samples showed very little variation of porosity; they are all of very high density. However, I am certain that the grain structure is not the same across the composition diagram. In order to eliminate the perovskite phase, the sintering temperature was increased for larger values of x and, as Van Uitert has shown, this will affect the grain growth.

R. C. LECRAW: I can almost assure that this interpretation that Dr. Dillon and others were suggesting is correct because we have added the Ga and In to single crystals up to percentages of about what you are talking about and found line widths still an oersted or two. One can conclude that the intrinsic scattering of the disordered Ga ions itself is negligible from the single crystal data, and the change in linewidth must be due to change of the crystallite size and to polycrystalline nature of this system.