Magnetic Susceptibility of Pressed Powders of Some Rare-Earth Iron Garnets

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The molar magnetic susceptibilities (χ_M) of spherical balls of rare-earth iron garnets REIG's, with RE = Y, Gd, Dy, Ho, Er and Yb, prepared from pellets pressed at pressures ranging from 2 to 8×10^7 kg m^{-2}, have been measured in the temperature range 300–900 K. It is found that $\chi_M \propto \exp(-f)$, where f is the pore fraction of the pressed balls. It has also been observed that χ_M for a particular garnet at a fixed temperature increases from powder through pressed material to single crystal. REIG's reveal typical ferrimagnetic behaviour with the ferrimagnetic Curie temperature (T_c) lying in the range 550–570 K for single crystals. In general, for pressed material T_c increases linearly with density. The χ_M^{-1} vs, T variation has been analysed using molecular field theory. It has been found that for $T \gg T_c$ the magnetic ions behave as if they were almost free and yield a magneton number very close to their free ion value.

1. Introduction

The name rare-earth iron garnets (REIG) is given to a series of compounds with the general chemical formula $RE_3Fe_5O_{12}$, where RE stands for a rare-earth. REIG's as a class of ferrimagnetic oxides were first established by Bertaut and Forrat [1] and independently by Geller and Gilleo [2]. These garnets have high initial permeabilities, a narrow hysteresis, low dielectric losses and high resistivities [3–5]. In technical applications they are used in the form of thin films, poly- or single crystals, powder and pressed pellets. Their structure [1, 2, 6], magnetic [7–9], optical [10, 11], electrical transport [12–14] and other properties have been reported. For the last several years we have been trying to understand the electrical transport and magnetic properties of lanthanide compounds, particularly their oxides [15–17], tungstates [18–24], molybdates [25–28] and orthochromites [29, 30]. Recently we have studied the transport properties of Gadolinium and Dysprosium iron garnets [31, 32] and the magnetic susceptibility of Yttrium iron garnets doped with heavy lanthanides [33]. In this paper we report on the magnetic susceptibility of some rare-earth iron garnets REIG, where RE = Y, Gd, Dy, Ho, Er and Yb, in the form of powder and pressed balls. The garnets in general are cubic ionic compounds. The REIG structure is characterised by three types of sites, usually referred to as sites "a", "d" and "c". Three Fe^{3+} ions occupy site "d" with tetrahedral oxygen surrounding, the other two Fe^{3+} ions are located at site "a" with octahedral oxygen surrounding. The three RE^{3+} ions occupy site "c" with dodecahedral oxygen surrounding. The lattice parameters together with the X-ray densities of different REIG are given in Table 1.

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2. Material and Experimental Technique

All REIG powders have been prepared in the usual way [4] from RE_2O_3 (M/S Rare-Earth Product Ltd., England) with stated purity of 99.99 percent and Fe_2O_3 (M/s Bonds, India) with stated purity of 99.99 percent. The compounds were thoroughly

Table 1. The lattice parameters and measured and X-ray densities of the studied REIG's.

Garnets	Lattice constant * a_0 (Å)	Density d_0 (kg/m^3) $\times 10^{-3}$	Density of** pressed balls d_p (kg/m^3) $\times 10^{-3}$	Pore fraction (f)
YIG	12.376	5.17	3.20	0.38
GdIG	12.471	6.44	3.90	0.39
DyIG	12.405	6.61	3.92	0.40
HoIG	12.375	6.77	4.05	0.40
ErIG	12.347	6.87	4.07	0.40
YbIG	12.302	7.06	4.16	0.41

* From G. P. Epinosa, J. Chem. Phys. **37**, 2344 (1962).
** Made out of pellets pressed at a pressure of 8×10^7 kg/m^2.

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mixed, pelletized and heated at 1400 °C for five hours in a platinum crucible in air. The material was crushed, reground into powder, made into pellets again and refired under the same conditions for about ten hours. X-ray diffraction checks did show that single phase garnets have been obtained. The magnetic susceptibilities have been measured by Faraday's method on samples prepared separately for each garnet in each form. The measurement on each sample has been repeated once or twice. $Gd_2(WO_4)_3$ has been used as standard substance. A correction for the container has been taken into account. The overall error in these measurements is about two percent around 300 K and becomes about five percent at 900 K. The details are described elsewhere [34].

3. Results and Discussion

The REIG powders were pressed to form small cylinders. Spherical samples of about 4 mm diameter were prepared from these cylinders. The densities (d_p) of the cylinders have been measured by the usual method and are given in Table 1 together with the pore fractions (f).

The molar magnetic susceptibility (χ_M) of the powder and balls (pressed at 4×10^7 and $8 \times 10^7\,\text{kg m}^{-2}$) have been measured in the temperature range 300 to 900 K at a field strength of

$$8.36 \times 10^5\,\text{A-m}^{-1} \quad (\sim 11\,\text{kOe}).$$

No hysteresis in the susceptibility has been observed during the heating and cooling cycles. The results for all the garnets are shown in Figure 1. Obviously different curves are obtained for powders and pressed balls. The susceptibility increases from powder to pressed material to single crystals. This result is not altogether unexpected. In Fig. 2, the molar magnetic susceptibility has been plotted against the density for different REIG's at a fixed temperature. The densities of the powders have been obtained by extrapolation of the d vs. p curves to $p = 0$. The variation of the molar magnetic susceptibility with density can be represented by the equation

$$(\chi_M)_p = (\chi_M)_c \exp(-f), \tag{1}$$

where $(\chi_M)_p$ and $(\chi_M)_c$ are the molar magnetic susceptibilities of pressed material and single crystals, respectively, and f is the pore fraction given by

$$f = (d_0 - d_p)/d_0, \tag{2}$$

Table 2. Some magnetic parameters of REIG's.

Garnets	State	Parametric temperatures θ_a(K)	θ(K)	θ_b(K)	Curie temperature T_c(K)	$\bar{C}_M$ (K m³/mole) $\times 10^4$
YIG	P_0	−1250	520	133.4	530	2.567
	P_4	−1210	525	132.1	535	2.657
	P_8	−1170	530	130.8	540	2.587
GdIG	P_0	− 260	470	60.6	475	5.639
	P_4	− 212	485	59.3	490	5.643
	P_8	− 175	495	58.1	500	5.645
DyIG	P_0	− 240	505	61.2	510	7.917
	P_4	− 163	515	58.5	520	7.917
	P_8	− 102	525	56.2	530	7.917
HoIG	P_0	− 232	485	60.1	490	7.964
	P_4	− 128	505	56.5	510	7.967
	P_8	− 49	510	53.1	515	7.969
ErIG	P_0	− 120	495	55.7	500	7.046
	P_4	− 37	500	52.1	505	7.046
	P_8	− 4	505	50.7	510	7.046
YbIG	P_0	− 630	470	74.3	475	3.667
	P_4	− 545	475	71.6	480	3.667
	P_8	− 445	480	63.6	485	3.667

P_0 — powder, P_4 and P_8 stands for material pressed at 4.3×10^7 kg m^{-2} and 8.7×10^7 kg m^{2-}, respectively.

where d_p is the density of the pressed material and d_0 is the X-ray density.

The χ_M^{-1} vs. T curves (Fig. 1) are of the ferrimagnetic type. For $T > T_c$ can be expressed by the relation

$$\chi_M^{-1} = \frac{T - \theta_a}{\bar{C}_M} - \frac{\theta_b^2}{\bar{C}_M (T - \theta)}, \tag{3}$$

where θ_a, θ_b and θ are empirical parameters, the physical significance of which is not assigned here. The values of θ_a, θ_b and $\bar{C}_M$ are shown in Table 2. The ferrimagnetic ordering temperature (T_c) is defined as the temperature at which $\chi_M^{-1} \to 0$. Using this definition one gets the following relation for evaluating T_c:

$$(T_c - \theta_a)(T_c - \theta) = \theta_b^2. \tag{4}$$

Only real and positive values of T_c are physically meaningful. The evaluated values of T_c for powder and pressed material of different garnets are also given in Table 2. It is seen that T_c increases with pelletizing pressure. For a particular garnet it is highest for single crystals.

The variation of T_c with d, as shown in Fig. 3, can be represented by the relation

$$T_c = m d + q. \tag{5}$$

The values of m and q are given in Table 3.

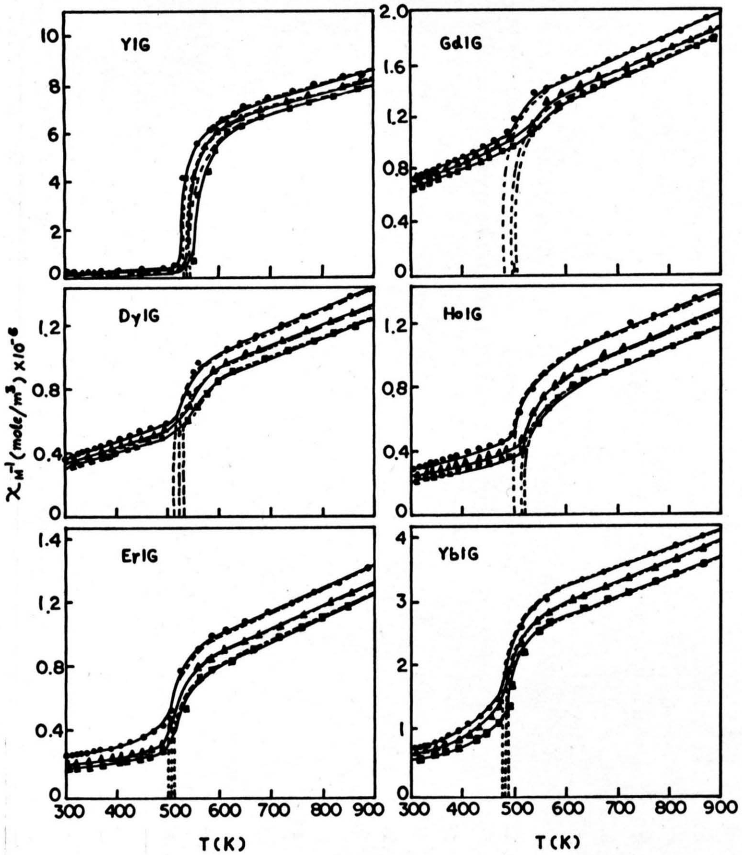

Fig. 1. Inverse of molar magnetic susceptibility (χ_M^{-1}) vs. temperature (T) for powder (●) and pressed balls (▲, ■) of REIG (RE = Y, Gd, Dy, Ho, Er and Yb) at an applied magnetic field of 8.36×10^5 A-m^{-1}. ▲ pressed at 4.3×10^7 kg-m^{-2}, ■ pressed at 8.7×10^7 kg-m^{-2}. --- theoretical curves.

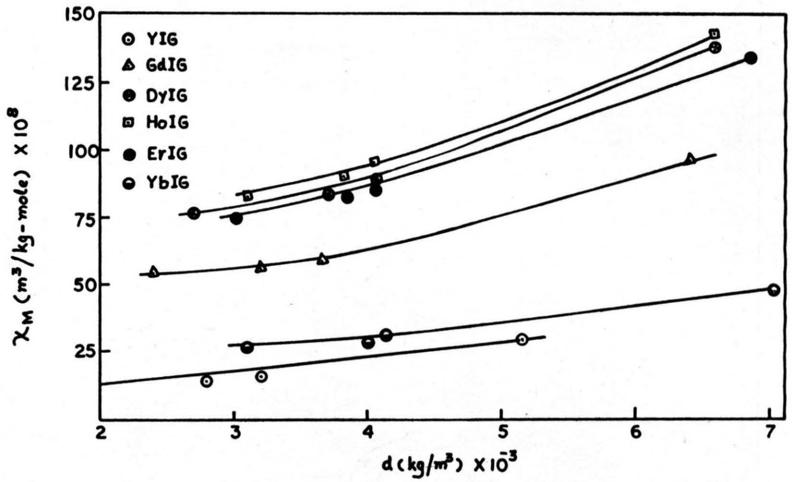

Fig. 2. Inverse of molar magnetic susceptibility (χ_M^{-1}) vs. (d) density for REIG at $T = 800$K.

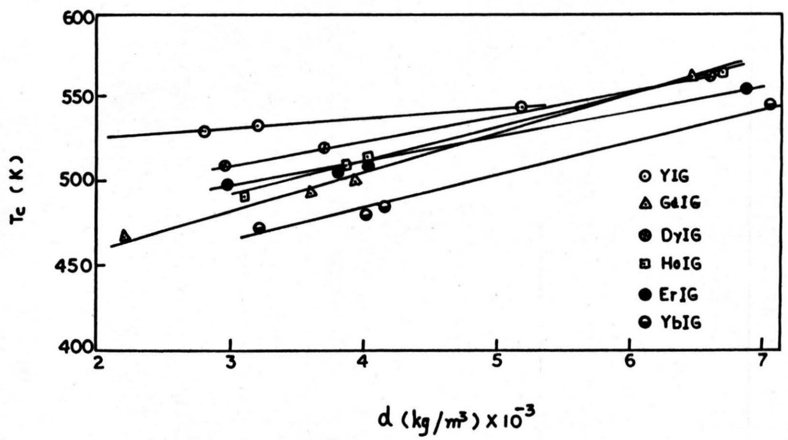

Fig. 3. Ferrimagnetic Curie temperature (T_c) vs. density (d) for REIG.

Table 3. Values of m and q for different REIG's.

Garnets	$m(\mathrm{K/kg \cdot m^{-3}}) \times 10^3$	q(K)
YIG	6.0	522
GdIG	23.0	436
DyIG	14.5	480
HoIG	20.0	456
ErIG	16.0	466
YbIG	19.5	420

The magnetically simplest garnet is YIG. It contains only Fe^{3+} as magnetic ion at sites "a" and "d" and can be pictured by a two sublattice model with three types of magnetic interactions, which are customarily represented by the constants α, β and n [35]. These constants are related with the parametric temperatures θ_a, θ_b and θ and the Curie constants of the sublattices, namely C_a and C_d, by the relations given elsewhere [35]. From these relations α, β and n for powder and pressed balls of YIG have been obtained and are given in Table 4. Both α and β are small compared to unity, which indicates that the a—d magnetic interaction dominates over the others, as expected. Further α, β and n for powder and pressed pellets are nearly the same, indicating that the internal fields on various sites remain unchanged. Thus the increase in χ_M from powder to pressed pellets to single crystal is not a microscopic effect but related to the grains. The interaction between these magnetized granules affects the value of χ_M. Obviously, the interaction will be larger in more dense packed granules. The case of single crystals seems to be entirely different. Here the highest value is obtained because there are no grain boundaries and long range ordering extends over the whole crystal. Such results have also been observed by other workers for other materials [36, 37]. The size of the grains may also affect the χ_M values. However, we did not observe such effects. The dependence of χ_M on density may be important in applications.

In the other REIG's we have an additional magnetic ion RE^{3+} situated at site "c". Thus we have three sublattices and six magnetic interactions.

Table 4. Molecular field parameters for YIG.

State	α	β	n
P_0	− 0.38	− 0.43	2.7×10^4
P_4	− 0.38	− 0.43	1.6×10^4
P_8	− 0.34	− 0.40	1.3×10^4

These interactions are nearly same for a garnet in either form, and have been evaluated for single crystals elsewhere [7].

At temperatures $T \gg T_c$ the magnetic interactions become weak compared to the thermal energy kT and hence χ_M can be expressed by the relation

$$\chi_M = \frac{N \mu_\beta^2 \mu_0}{3k} \left[\frac{5p^2}{(T-\theta_a)} + \frac{3p'^2}{(T-\theta_a')} \right], \tag{6}$$

where μ_β Bohr's magneton, μ_0 is the permeability of free space, $5N$ and $3N$ are the number of Fe^{3+} and RE^{3+} ions per gram-mole of REIG (N being Avogadro's number), p is the magneton number of Fe^{3+} ion, p' is the magneton number of RE^{3+} ion, and θ_a and θ_a' are the paramagnetic Curie temperatures which take into account the effect of various interactions on Fe^{3+} and RE^{3+} ions respectively. At higher temperature the ratio $(T-\theta_a)/(T-\theta_a')$ tends to unity and (6) reduces to

$$\chi_M^{-1} = \frac{3k}{8N\mu_\beta^2\mu_0} \left[\frac{T-\theta_a}{\bar{p}^2} \right], \tag{7}$$

where

$$\bar{p} = \left[\frac{5p^2 + 3p'^2}{8} \right]^{1/2} \tag{8}$$

is the average magneton number per magnetic ion of the REIG. It has already been pointed out that the χ_M of all studied garnets can be expressed by (3). For $T \to \infty$ this relation reduces to

$$\chi_M^{-1} = (T-\theta_a)/\bar{C}_M . \tag{9}$$

This is the equation of the asymptotic line to curve expressed by (3). From the slope of the asymptotic line $\bar{C}_M$ can be obtained. Comparing (7) and (9) one gets

$$\bar{C}_M = \frac{8N\mu_\beta^2\mu_0\bar{p}^2}{3k}$$

or

$$\bar{p} = \left[\frac{3k\bar{C}_M}{8N\mu_\beta^2\mu_0} \right]^{1/2}. \tag{10}$$

Experimental values of $\bar{p}$ have been evaluated from the values of $\bar{C}_M$ and are given in Table 5. Theoretical values of p and p' are known, and hence one can evaluate theoretical values of $\bar{p}$ using (8). It is seen from Table 5 that there is fair agreement between the theoretical and experimental values of $\bar{p}$. The agreement becomes closer for dense balls. However, the experimental $\bar{p}$ values are somewhat

Table 5. Experimental and theoretical values of magneton numbers for different REIG's.

Garnets	Experimental value of $\bar{p}$			Theoretical $\bar{p}$	Fe^{3+} ion vacancies per mole
	P_0	P_4	P_8		
YIG	5.71	5.72	5.74	5.92	1.73×10^{23}
GdIG	6.70	6.70	6.70	6.75	4.75×10^{22}
DyIG	7.94	7.94	7.94	8.02	9.02×10^{22}
HoIG	7.96	7.96	7.96	8.00	4.51×10^{22}
ErIG	7.49	7.49	7.49	7.51	2.12×10^{22}
YbIG	5.40	5.40	5.40	5.4	3.06×10^{22}

smaller than the theoretical ones. The reason for this discrepancy is due to missing Fe^{3+} ions. It has been noticed from the study of the electrical properties [38] that all REIG's have native defects identified as Fe^{3+} ion vacancies and Fe^{4+} sites. The number of Fe^{4+} sites can be evaluated from the difference of the theoretical and experimental values of $\bar{p}$. To maintain charge neutrality, a single Fe^{3+} ion vacancy will create three Fe^{4+} sites. Let x be the number of Fe^{3+} ion vacant sites per mole of the garnet, then the number of Fe^{4+} sites per mole of the garnet will be $3x$. The corresponding decrease in the number of Fe^{3+} ions, which would have contributed to the molar susceptibility, will be $4x$. The molar susceptibility of garnets in the presence of these Fe^{3+} ion vacancies will be given by the relation (for $T \gg T_c$),

$$\chi_M = \frac{\mu_\beta^2 \mu_0}{3k(T-\theta_a)} \left\{ (5N-4x)p^2 + 3Np'^2 \cdot \left(\frac{T-\theta_a}{T-\theta_a{}'}\right) + 3xp''^2 \left(\frac{T-\theta_a}{T-\theta_a{}''}\right) \right\}, \quad (11)$$

where p'' is the magneton number for Fe^{4+} ions and $\theta_a{}''$ is the paramagnetic Curie temperature which takes account of various interactions involved. At very high temperatures ($T \to \infty$) the ratios $(T-\theta_a)/(T-\theta_a{}')$ and $(T-\theta_a)/(T-\theta_a{}'')$ will tend to unity and the above relation can be approximated by

$$\chi_M^{-1} = \frac{3k(T-\theta_a)}{8N\mu_\beta^2\mu_0} \cdot \frac{8}{5p^2 + 3p'^2 - (4x/N)p^2 + (3x/N)p''^2}$$

or

$$\chi_M^{-1} = \frac{3k(T-\theta_a)}{8N\mu_\beta^2\mu_0\bar{p}^2_{\text{exptl}}}, \quad (12)$$

where

$$\bar{p}^2_{\text{exptl}} = \left(\frac{5p^2 + 3p'^2}{8}\right) - \frac{1}{8}\left(\frac{4x}{N}p^2 - \frac{3x}{N}p''^2\right) \quad (13)$$

and $\frac{1}{8}(5p^2 + 3p'^2)$ is the square of the average magneton number of the magnetic ions in a mole of stoichiometric iron garnet. We can calculate $\bar{p}_{\text{theo}}$ and hence estimate the number of Fe^{3+} ion vacancies by the relation

$$x = 8N\frac{(\bar{p}^2_{\text{theo}} - \bar{p}^2_{\text{exptl}})}{4p^2 - 3p''^2}. \quad (14)$$

The estimated number of Fe^{3+} ion vacancies in the different garnets are given in Table 5.

4. Conclusions

1. The magnetic susceptibility of rare-earth iron garnets increases exponentially with pore fraction from powder to pressed material to single crystal.

2. Rare-earth iron garnets exhibit a typical ferrimagnetic characteristic. The magnetic ordering temperature lies in the range 550–570 K for single crystal. For pressed material and powder it is lowered.

3. T_c for a particular REIG is lowest for powder and highest for single crystal. It varies linearly with density.

4. At very high temperatures ($T \gg T_c$) the magnetic ions in REIG's behave as if they were almost free and the magnetic susceptibility varies inversely with the absolute temperature. There is fair agreement between the average magneton number per ion as obtained from χ_M^{-1} vs. T slopes and calculated values taking all ions as free.

5. Below T_c, the magnetic susceptibility becomes a complex function of the magnetic field and temperature. However, at a particular field it increases with decrease of temperature.

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