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## Magnetization, magnetic interactions and spin structure in ultrafine rare-earth iron garnets

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**Abstract.** The study involves the investigation of basic magnetic properties of ultrafine rare-earth iron garnets in the size range 1.0–35 nm, prepared by a citrate precursor method. The crystallites of 10–35 nm size are monolithic ferrimagnetic particles which have saturation magnetization and magnetic interactions (as shown by the Curie temperature) comparable with those of bulk crystalline garnets. The small reduction in saturation magnetization in the 10–20 nm crystallites is attributed to spin canting and non-collinearity at the surface of the crystallites, and a model based on surface spin canting is proposed for the spin structure of these crystallites. The magnetization and magnetic interactions of smaller crystallites of 1.0–1.5 nm which exist as x-ray amorphous magnetic clusters are different from those in the bulk crystalline garnets. Reduction in the rare-earth sublattice contribution due to a weakening of the  $R^{3+}-O^{2-}-Fe^{3+}$  super-exchange interaction in the disordered state accounts for the difference in saturation magnetization in these magnetic clusters, whereas the enhanced Curie temperatures are attributed to an increase in the number of effective magnetic interactions in the disordered state. A model based on bulk spin non-collinearity is proposed for the spin structure of the magnetic clusters consisting of 1.0–1.5 nm crystallites.

### 1. Introduction

In the past, pure, mixed and substituted rare-earth iron garnets (RIGs) have been extensively studied in the form of single crystals, polycrystalline and thin-film materials [1, 2]. However, there are few reports in the literature on amorphous and ultrafine RIGs. Amorphous RIGs prepared by roller quenching, sputtering and chemical methods show remarkably different properties [3–5]. The roller quenching and sputtering give rise to amorphous RIGs which are antiferromagnetic with a Néel temperature below 100 K, a substantial deviation from the behaviour of crystalline RIGs which are ferrimagnetic with a Curie temperature  $T_C$  around 550 K. The ultrafine non-crystalline YIGs prepared by pyrolysis of a citrate precursor, in contrast, show a  $T_C$  of around 900 K. The well known dependence of microstructural polymorphism on the preparation conditions in non-crystalline networks is often reflected in their interesting magnetic properties. It is particularly evident in the non-crystalline non-metallic materials where superexchange coupling dominates. Differences in the details of packing of oxygen and metal ions leads to large variations in magnetic behaviour.

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In the studies on ultrafine magnetic materials, certain extraordinary phenomena have recently been recognized as arising from the effects of finite dimensions [6–9]. The specific saturation magnetization and magnetic hyperfine fields which are often thought of as being intrinsic magnetic properties of ferromagnetic and ferrimagnetic materials have been found to vary between bulk and fine particles. Non-collinear magnetic spin structures have been found to exist in ultrafine particles particularly at the surface. Particles of the smallest size range of the order of 1.0–1.5 nm would thus be effectively all surface and would exhibit extraordinary magnetic properties. Therefore, in the present study we have undertaken an investigation of saturation magnetization, magnetic transition temperature and spin structure in ultrafine nanometre-sized RIGs prepared by a citrate method.

## 2. Experimental procedure

Ultrafine RIGs were prepared by thermal decomposition of citrate precursors,  $R_3Fe_5(\text{cit})_{25} \cdot (36 + n)H_2O$ , where  $R \equiv \text{Sm, Tb, Dy, Ho, Er, Yb, (YNd) and (YGd)}$ . The preparation and decomposition studies of the citrate precursors have been reported elsewhere [10]. Decomposition of the precursor in air yields x-ray amorphous ultrafine particles at 450 °C and crystalline particles above 600 °C. On heat treatment at temperatures between 450 and 1000 °C, the amorphous RIG materials yield crystallites in the size range 10–35 nm. The powder XRD patterns of the materials were recorded on a Rich Seifert Isodebyflex 2002 diffractometer with Ni-filtered  $\text{Cu K}\alpha$  radiation. The magnetization measurements were carried out on a PAR 150 vibrating-sample magnetometer in conjunction with a V-7200 electromagnet assembly that provides a magnetic field of up to 10 kG. A furnace assembly (model 151) which can provide temperatures up to 1000 K, associated with the magnetometer was used for temperature variation studies of magnetization.

## 3. Characteristics of ultrafine rare-earth iron garnets

Ultrafine RIGs were characterized in detail by XRD, TEM and BET surface area measurements as described elsewhere [11]. In the heat treatment temperature range 450–600 °C, the ultrafine garnets exhibit only a broad hump in the XRD pattern corresponding to reflection in the  $d$ -value range  $d_{420} = 0.2\text{--}0.35$  nm. It indicates the absence of crystalline periodicity and the existence of a highly strained disordered state having a crystallite size of 1.0–1.5 nm. Above 600 °C, the crystallites grow to 10–35 nm monoliths with  $d_{420} = 0.275\text{--}0.285$  nm, owing to crystallization with negligible lattice strain. The larger  $d_{420}$  spacing for crystallites of 1.0–1.5 nm size compared with 10–35 nm corresponds to a relative increase in the specific volume of the RIG lattice. The larger-size-induced strain is proposed to be responsible for the distortion and instability of the garnet lattice. Such a lattice expansion with decreasing particle size has been reported for various metallic and non-metallic fine-particle systems [12–14].

The specific volume change in ultrafine RIG materials of 1.0–1.5 nm crystallite size is attributed to the modifications of various oxygen polyhedra in the ultrafine state, deduced from the spectrochemical studies as follows [15]. Ultrafine RIGs exhibit IR absorptions corresponding to an expanded dodecahedra and garnet lattice, which support the observed increase in the specific volume shown in the XRD studies. The parameters calculated from the optical spectra, namely the Racah parameter  $B$ , the ligand-field parameter  $\Delta$ , and the isomer shift in the Mössbauer spectra give a direct

indication of the cation-anion distances in the oxygen tetrahedra and octahedra in the structure. The ultrafine RIGs comprising 1.0–1.5 nm crystallites show larger  $B(\text{tet})$  and smaller isomer shifts compared with the bulk crystalline garnets, indicating an increase in  $\text{Fe}_d\text{-O}$  bond distances. The ligand field parameters  $\Delta(\text{tet})$  are smaller than in bulk garnets, which again indicates an enhanced  $\text{Fe}_d\text{-O}$  bond distance. In contrast, in the case of  $\text{FeO}_6$  octahedra, smaller  $B(\text{oct})$ , larger isomer shifts and larger  $\Delta(\text{oct})$  are observed which indicate a decrease in  $\text{Fe}_a\text{-O}$  bond distances. Therefore, the overall increase in specific volume observed in 1.0–1.5 nm crystallites is associated with a relative expansion of tetrahedra and dodecahedra, leading to an increase in  $\text{Fe}_d\text{-O}$  and  $\text{R}_c\text{-O}$  bond distances, and a relative contraction of octahedra, leading to the decrease in  $\text{Fe}_a\text{-O}$  bond distances. In addition, interestingly, the  $g$ -factors and linewidths in the FMR spectra of 1.0–1.5 nm crystallites of RIGs clearly show substantially reduced rare-earth contributions. It has been attributed to the increase in  $\text{R}_c\text{-O-Fe}_2$  bond distances and the resultant weakening of the  $\text{R-O-Fe}$  superexchange [16].

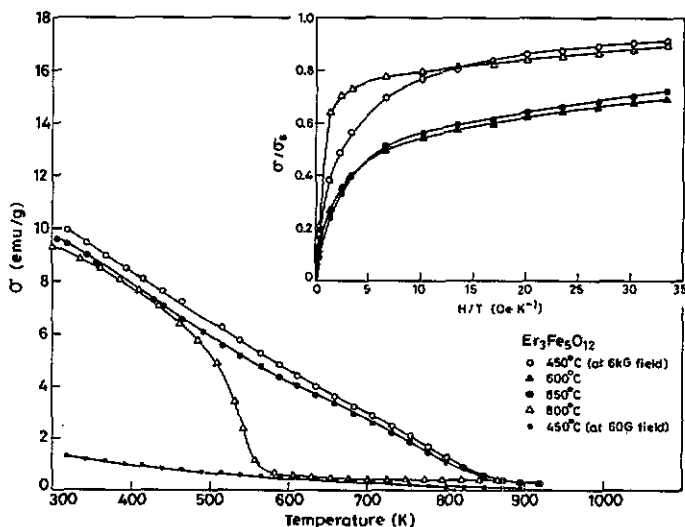


Figure 1. Magnetization as a function of temperature for  $\text{Er}_3\text{Fe}_5\text{O}_{12}$  materials heat treated at different temperatures. The inset shows relative magnetization as a function of field-temperature quotient.

The above-mentioned increase in the specific volume, the polyhedral rearrangements and their effect on superexchange interactions are indeed expected to affect the magnetic properties of ultrafine RIGs. It is in this context that the magnetization, magnetic interactions and spin structure of ultrafine RIGs are investigated and the results are presented.

## 4. Results and discussion

### 4.1. Magnetization curves

The temperature dependence of magnetization at a field of 6 kG for a typical ultrafine RIG is shown in figure 1. The inset represents the relative magnetization  $\sigma/\sigma_s$

as a function of field-temperature quotient  $H/T$ . The 10–35 nm crystallites, i.e. heat treated above 650 °C, show magnetization curves and Curie temperatures  $T_C$  as reported for bulk crystalline garnets [17]. In the case of 1.0–1.5 nm crystallites having an amorphous nature, however, the magnetization gradually decreases with increasing temperature and approaches zero at around 900 K, which is much higher than the  $T_C$  for crystalline garnets. These fine crystallites show nearly superimposed  $\sigma/\sigma_s$  versus  $H/T$  curves and do not show any hysteresis. The magnetization does not saturate even at an applied field of 10 kG and the curves resemble Langevin curves. The observations are characteristic of the superparamagnetic behaviour of ultrafine particles which has been confirmed in the Mössbauer studies [18, 19]. The room-temperature saturation magnetizations, i.e. the  $\sigma_s$ -values, for these ultrafine RIGs are obtained by extrapolation of the  $\sigma$  versus  $1/H$  curves to the limit  $1/H \rightarrow 0$ , following reports in the literature for  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> fine particles [20] and are presented in table 1.

Table 1. Saturation magnetization  $\sigma_s$  at room temperature for ultrafine amorphous and crystalline RIG materials heat treated at various temperatures.

RIG materials	Saturation magnetization $\sigma_s$ (emu g <sup>-1</sup> ) at the following heat treatment temperatures					RT saturation magnetization $\sigma_s$ (emu g <sup>-1</sup> ) for polycrystalline garnets [17]
	450 °C	600 °C	650 °C	700 °C	900 °C	
Sm <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub>	18.3	12.6	8.4	14.4	19.0	21.5
Tb <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub>	12.6	11.3	11.1	5.1	—	2.4
Dy <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub>	7.9	6.8	4.5	4.7	4.5	4.58
Ho <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub>	17.0	15.0	14.6	11.6	10.0	10.34
Er <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub>	11.0	10.9	7.3	9.7	11.0	14.36
Yb <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub>	12.4	11.6	8.8	17.4	17.5	17.64
Y <sub>2</sub> NdFe <sub>5</sub> O <sub>12</sub>	20.4	19.0	18.8	19.0	19.9	28.0
Y <sub>2</sub> GdFe <sub>5</sub> O <sub>12</sub>	14.3	—	10.9	—	17.1	18.5

The magnetization curves of 1.0–1.5 nm crystallites resemble Langevin curves. Therefore, the magnetic moment per particle and the magnetic particle size of RIG materials were determined from the low-field slopes of the magnetization curves, by using the limit to the Langevin function as reported earlier [11]. The magnetic particle size is greater than the crystallite size obtained from XRD. The difference between magnetic particle size and crystallite size suggests magnetic interaction among crystallites in the crystallite aggregates (or magnetic clusters) wherein intercrystallite bonds exist. Such aggregates are identified as responsible for higher magnetizations accompanied by an increase in  $T_C$ -values in ultrafine garnets.

#### 4.2. Saturation magnetization

As shown by the saturation magnetization  $\sigma_s$  versus ionic radii plots in figure 2,  $\sigma_s$ -values of ultrafine RIG materials of 10–35 nm crystallite size prepared at 700 °C are 20–25% lower than their polycrystalline counterparts. This reduction can be attributed to the spin non-collinearity and canting on the surface of the 10–25 nm ultrafine particles. In addition, there is a small reduction due to the fraction of superparamagnetic fine crystallites as observed in the magnetization curves for these samples. The samples annealed at 900 °C have  $\sigma_s$ -values comparable with the polycrystalline garnets

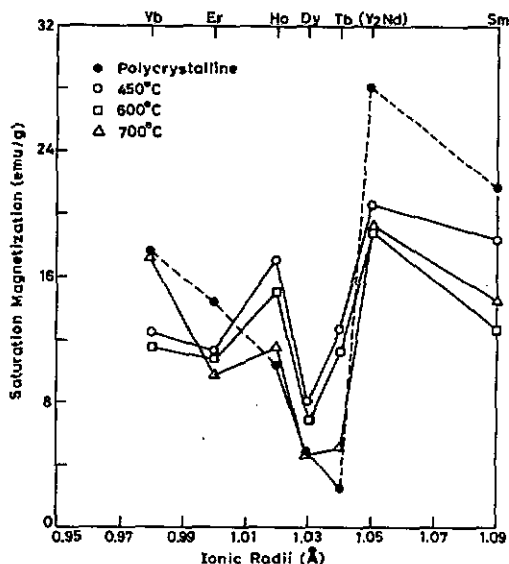


Figure 2. Dependence of saturation magnetization on ionic radii of the rare-earth ions in ultrafine RIG materials.

(table 1), indicating the approach to collinearity in the larger particles of 25–35 nm size.

Ultrafine RIG materials of 1.0–1.5 nm crystallite size, except  $R \equiv \text{Tb}$ , Dy and Ho, show  $\sigma_s$ -values which are 25–30% lower than the polycrystalline garnets, as shown in figure 2. The reduction can again be ascribed to the non-collinearity of spins and the superparamagnetic nature of ultrafine particles. Interestingly, the 1.0–1.5 nm crystallites of RIG materials where  $R \equiv \text{Tb}$ , Dy and Ho behave at variance. They show larger  $\sigma_s$ -values than do the polycrystalline garnets (table 1). The larger  $\sigma_s$ -values of these amorphous RIG materials are related to the smaller  $\sigma_s$ -values (less than  $10 \text{ emu g}^{-1}$ ) at RT in the respective bulk polycrystalline garnets in the following way. These polycrystalline garnets have smaller  $\sigma_s$ -values due to the greater  $R^{3+}$  ( $c$  sublattice) contribution at RT in these garnets which neutralize the Fe-sublattice ( $a$ - $d$ ) magnetization due to the antiparallel nature of the coupling between these two sublattices. Therefore, a reduction in  $c$ -sublattice magnetization in amorphous RIG materials would allow the Fe magnetization to dominate, and then the  $\sigma_s$ -values would understandably show an increase. Indeed such a reduction in  $R^{3+}$  contribution has been indicated by both  $g$ -values and linewidth in the FMR spectral studies [16]. Moreover the  $R^{3+}-O^{2-}-Fe^{3+}$  coupling ( $2 \times 10^5$  Oe molecular field) in polycrystalline garnets is weaker and anisotropic compared with the  $Fe_a^{3+}-O^{2-}-Fe_d^{3+}$  coupling ( $2 \times 10^6$  Oe molecular field). Therefore, a weakening of  $R^{3+}-O^{2-}-Fe^{3+}$  coupling can be expected in ultrafine RIG materials in view of the increase in bond distances in tetrahedra and dodecahedra observed in spectrochemical studies. Thus, a weakening of the  $c$ -sublattice contribution explains the increase in  $\sigma_s$ -values at RT, in the TbIG, DyIG and HoIG materials, compared with polycrystalline garnets. However, a weakening of the  $c$ -sublattice contribution should also be applicable to other ultrafine amorphous RIG materials of 1.0–1.5 nm crystallite size, as is evident in the FMR results of all RIGs and therefore an increase in  $\sigma_s$ -values should have been observed. However, owing to the lower magnetization of  $R^{3+}$  ions in these garnets at RT, an increase in  $\sigma_s$ -values is not observed. In any case the increase in  $\sigma_s$ -value would be

different for different garnets, because the  $R^{3+}$  contribution is different in different garnets at RT.

In order to assess the extent of rare-earth contributions, let us assume that the percentage reduction in  $c$ -sublattice contribution in various ultrafine amorphous RIG materials are identical. The  $c$ -sublattice magnetization in different crystalline RIG materials at RT can be calculated using the RT  $\sigma_s$ -values of YIG as follows. The  $\sigma_s$ -value of YIG at RT is due to the Fe-sublattice contribution alone because  $Y^{3+}$  is non-magnetic. The reduction in  $\sigma_s$ -values of crystalline RIGs compared with YIG values is the result of the antiparallel  $c$ -sublattice contribution. Therefore, by subtraction of  $\sigma_s$ -values of crystalline RIGs from the  $\sigma_s$ -values of YIG, the  $c$ -sublattice magnetization of various RIGs at RT are arrived at. The expected  $\sigma_s$ -values of ultrafine amorphous RIG materials of 1.0–1.5 nm crystallite size are then calculated for different percentage reductions in  $c$ -sublattice contribution and are given in table 2. The difference between the experimentally observed and the above-calculated  $\sigma_s$ -values would reflect the reduction in  $\sigma_s$ -values due to the factors including superparamagnetic nature and the non-collinearity of spins. Since the reduction in  $\sigma_s$ -values due to the above factors is expected in all ultrafine amorphous RIG materials, the observed  $\sigma_s$ -values have to be smaller than the calculated values. It can be noticed from table 2 that the observed  $\sigma_s$ -values for all amorphous RIG materials are less than the calculated values only when the percentage reduction is assumed to be greater than 70%. Hence, apparently, there is a sizable reduction in the  $c$ -sublattice contribution to  $\sigma_s$ -values in ultrafine amorphous RIG materials. It should be remembered that none of the amorphous RIG materials shows a sharp increase in FMR linewidths at or below LNT, which is an indication of a complete or substantial weakening of  $R^{3+}$  contribution in garnets [16]. The  $g$ -values also do not show the characteristics of  $R^{3+}$  contribution. The amorphous GdIG reported in the literature did not show a compensation temperature (which is a manifestation of rare-earth magnetization) down to LNT [21]. Thus, the substantial reduction of 70% in the  $c$ -sublattice contribution is understandable, which is also supported by the above-mentioned experimental evidence.

The differences between the observed  $\sigma_s$ -values and the above-calculated values for various ultrafine amorphous RIG materials represent the reduction due to superparamagnetism and non-collinearity. These values differ markedly for various RIG materials as depicted in table 2. The reductions due to non-collinearity and superparamagnetism for various RIG materials are not comparable and probably indicate the following.

(i) The percentage reduction in  $R^{3+}$  contribution in different RIG materials differs (contrary to the assumption made in the calculation) because of the strong temperature dependence due to varying orbital and spin contributions to the magnetization in different  $R^{3+}$  ions.

(ii) The magnitude of the reduction in magnetization due to superparamagnetic nature in different RIG materials varies owing to particle size and its distributions.

Therefore, it is not possible to separate out quantitatively the contribution of various inherent factors such as superparamagnetism and non-collinearity in ultrafine particles from the difference in observed and calculated  $\sigma_s$ -values.

### 4.3. Superexchange interaction energy and the magnetic transition temperature

As already mentioned, the magnetic ordering temperature  $T_C$  of ultrafine garnets comprising 1.0–1.5 nm crystallites falls in the temperature range 850–950 K and, for

Table 2. Saturation magnetization  $\sigma_s$ -values of ultrafine amorphous RIGs and c-sublattice contributions  $\sigma_c$ .

RIG	$\sigma_s$ for RIG prepared at 450 °C		$\sigma_P$	$\sigma_R$ at RT	Values for 70% reduction in $\sigma_R$			Values for 80% reduction in $\sigma_R$		
	$\sigma_A$	$\sigma_s$			$0.7\sigma_R$	$\sigma_C = \sigma_P + 0.7\sigma_R$	$\sigma_C - \sigma_A$	$0.8\sigma_R$	$\sigma_C = \sigma_P + 0.8\sigma_R$	$\sigma_C - \sigma_A$
Sm <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub>	18.30	22.50	—	—	—	4.19	—	—	4.19	
Tb <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub>	12.60	2.40	18.90	13.23	15.63	3.03	15.12	17.52	4.93	
Dy <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub>	7.81	4.57	16.54	11.58	16.15	8.26	13.20	17.77	9.91	
Ho <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub>	17.0	10.34	10.27	7.20	17.54	0.54	8.20	18.54	1.56	
Er <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub>	10.99	14.40	5.91	4.13	18.53	7.55	4.72	19.12	8.14	
Yb <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub>	12.40	17.59	2.17	1.52	19.11	6.72	1.73	19.32	6.93	
Y <sub>2</sub> NdFe <sub>5</sub> O <sub>12</sub>	20.40	27.99	2.39	1.66	26.33	5.92	1.90	26.09	5.69	
Y <sub>2</sub> GdFe <sub>5</sub> O <sub>12</sub>	14.29	18.50	6.42	4.49	24.92	4.48	5.13	23.63	7.80	



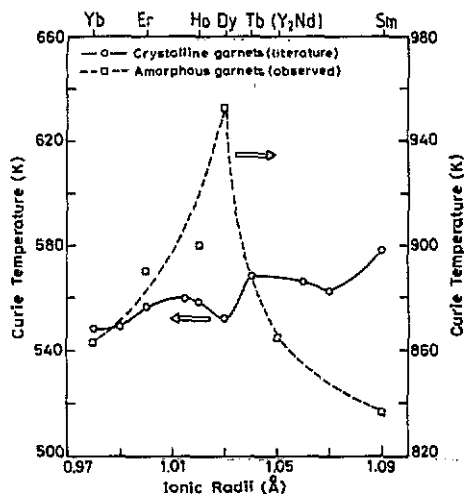


Figure 3. Curie temperatures of ultrafine RIGs as a function of ionic radii of the rare-earth ions.

10–35 nm crystallites  $T_C$  falls in the temperature range 550–580 °C (table 3).  $T_C$  appears to be a function of ionic size of rare-earth ion as shown in figure 3 for both well crystallized and 1.0–1.5 nm crystallites. Apparently, the dependence of  $T_C$ -values on ionic radii is different in the above two cases. In the well crystallized materials,  $T_C$  increases with increasing ionic radii of the rare earths. In the case of ultrafine crystallites, however, an intermediate ionic size (e.g.  $Dy^{3+}$  with  $r = 1.03 \text{ \AA}$ , or  $Ho^{3+}$  with  $r = 1.02 \text{ \AA}$ ) gives rise to higher  $T_C$ -values of 950 K and 900 K, respectively. An increase or decrease in ionic radii from the intermediate values lead to lower  $T_C$ -values. Also, non-crystalline YIG with a  $Y^{3+}$  ionic radius of 1.015 Å, which is closer to the  $Ho^{3+}$  radius, has been reported to have a  $T_C$  of 900 K [5]. Therefore it is possible that, in ultrafine RIG materials of 1.0–1.5 nm crystallite size, ionic radii of the order of  $Dy^{3+}$  give rise to the optimum bond angles and bond distances for stronger superexchange interactions and thus higher  $T_C$ -values, since it is known that  $T_C$  is a measure of the strength of the superexchange interaction [22].

Table 3. Magnetic ordering temperatures  $T_C$  of ultrafine, amorphous and crystalline RIG materials and their relation with ionic radii of  $R^{3+}$

RIG material	Ionic radii of $R^{3+}$ (Å)	$T_C$ (K) of amorphous RIG material at the following heat treatment temperatures		$T_C$ of crystalline RIG material observed (K)	$T_C$ of crystalline RIG from the literature [17] (K)
		450 °C	600 °C		
$Sm_3Fe_5O_{12}$	1.09 ( $Sm^{3+}$ )	837	840	583	578, 563
$Dy_3Fe_5O_{12}$	1.03 ( $Dy^{3+}$ )	953	948	553	552
$Ho_3Fe_5O_{12}$	1.02 ( $Ho^{3+}$ )	900	895	555	558
$Er_3Fe_5O_{12}$	1.00 ( $Er^{3+}$ )	890	890	554	556
$Yb_3Fe_5O_{12}$	0.98 ( $Yb^{3+}$ )	863	860	547	548
$Y_2NdFe_5O_{12}$	1.015 ( $Y^{3+}$ );	865	865	554	552
	1.12 ( $Nd^{3+}$ )				

The ultrafine amorphous RIG materials comprising 1.0–1.5 nm crystallites have a magnetic transition temperature  $T_C$  in the temperature range 850–950 K, which is

substantially higher than the  $T_C$ -values of their crystalline counterparts, for which  $T_C \simeq 550$  K. The Curie temperature  $T_C$  of a material is considered to be a direct measure of the interaction energy between magnetic ions. Therefore, a higher Curie temperature would mean stronger magnetic interactions. The transition temperature  $T_C$  in garnets is determined by the  $\text{Fe}_a^{3+}-\text{O}^{2-}-\text{Fe}_d^{3+}$  interaction. In view of the relative increase in  $\text{Fe}_d-\text{O}$  and decrease in  $\text{Fe}_a-\text{O}$  bond distances observed in reflectance spectra and the relative increase in isomer shift values for tetrahedral  $\text{Fe}^{3+}$  compared with bulk crystalline garnets, a change in the magnetic interactions can be expected.

One of the possible ways of explaining the increase in  $T_C$ -values in the amorphous state could be the increase in the number  $n$  of effective interactions as calculated by Gilileo [22] for various iron-containing oxides, given in table 4. The superexchange energy can be estimated from the value of  $T_C/n$  where  $T_C$  is the Curie temperature and  $n$  is the number of  $\text{Fe}^{3+}-\text{O}^{2-}-\text{Fe}^{3+}$  interactions (with an  $\text{Fe}-\text{O}$  distance of about 2 Å and a bond angle greater than 125°) per  $\text{Fe}^{3+}$  ion per formula unit. It may be remembered that the superexchange interaction increases in strength as the  $\text{Fe}^{3+}-\text{O}^{2-}$  distance decreases and the  $\text{Fe}^{3+}-\text{O}^{2-}-\text{Fe}^{3+}$  bond angle approaches 180° [23]. An average value of  $T_C/n = 115$  K is calculated for various Fe oxides [22]. Using this average value of 115 K, and  $T_C$  values of 850–950 K for ultrafine amorphous RIG materials, the number  $n$  of effective interactions equal to 7.4–8.25 per  $\text{Fe}^{3+}$  ion is obtained and adjusted to a whole number  $n \simeq 8$ . Then the number of interactions per formula unit is  $8 \times 5 = 40$ . This number is 24 for well crystallized RIGs as given in table 4. Therefore, the number of interactions increases from 24 to 40 during the change from well crystallized garnets to 1.0–1.5 nm crystallites of RIGs. Is it possible to have such an increase in number of interactions in materials, where  $\text{Fe}^{3+}$  is present in tetrahedral and octahedral sites?

From table 4 it can be seen that 24 Fe sites (16 octahedral and eight tetrahedral) in  $\text{Fe}_3\text{O}_4$  give rise to 24 effective interactions. On the other hand, in bulk crystalline garnets, it is evident that 40 Fe sites give rise to only 24 interactions per formula unit. The example of  $\text{Fe}_3\text{O}_4$  shows that in Fe oxides it is possible to have 24 interactions for 24 Fe sites or 40 interactions for 40 Fe sites for a suitable arrangement of lattice sites. Therefore it appears that theoretically it is possible to have 40 interactions for 40  $\text{Fe}^{3+}$  sites in Fe oxides. Such an increase in the number of interactions per formula unit from 24 to 40 accounts for the  $T_C$ -value of 900 K in ultrafine amorphous RIG materials comprising 1.0–1.5 nm crystallites. Since little is known about the interactions and ionic arrangements in the amorphous state, such an increase in the number of interactions is proposed to lead to an increase in  $T_C$ -values in amorphous RIG materials. In view of the increase in specific volume observed in the ultrafine crystallites of 1.0–1.5 nm size, an ionic rearrangement leading to the increase in the number of interactions may be taking place, which explains the higher  $T_C$  in these materials. A change in magnetic interaction has been reported when larger ions such as  $\text{Gd}^{3+}$  are substituted in crystalline YIG lattice which leads to an expansion of the lattice [24]. Also, recently, large increases in  $T_C$ -values of the order of 300–400 K have been observed in  $\text{R}_2\text{Fe}_{17}\text{X}$  compounds (where  $\text{X} \equiv \text{H}, \text{C}$  and  $\text{N}$ ), owing to an increase in specific volume of the lattice caused by the presence of X atoms [25, 26]. The higher  $T_C$  is therefore not due to any phase separation such as iron oxides, as has been suggested before [21]. Had the higher  $T_C$  been due to separation of any iron oxide phase, all amorphous RIG materials would have shown identical  $T_C$ -values. The very fact that the  $T_C$ -values of various ultrafine amorphous RIG materials are as far apart as 850–950 K strongly negates such possibilities of iron oxide phase separation.

Table 4. Relationship between the Curie temperature, number of interactions and other bonding parameters in various  $\text{Fe}^{3+}$ -containing oxides.

Compound	$\text{Fe}^{3+}$ position	$\text{Fe}^{3+}-\text{O}^{2-}$ distance ( $\text{\AA}$ )	Included angle (deg)	$\text{Fe}^{3+}-\text{O}^{2-}$ distance ( $\text{\AA}$ )	$\text{Fe}^{3+}$ position	Number of interactions per $\text{Fe}^{3+}$ ion	$T_c$ (K)	Number of interactions per $\text{Fe}^{3+}$ ion	$T_c/n$ (K)
$\text{Fe}_3\text{O}_4$	16d	2.07	124.0	1.88	8a	24	848	8	106
	16d	2.07	91.9	2.07	16d	24	—	—	—
$\text{Y}_3\text{Fe}_5\text{O}_{12}$	16a	2.00	126.6	1.88	24d	24	545	4-4/5	114
	16d	2.00	126.6	1.88	24d	24	549	4-4/5	114
$\text{Lu}_3\text{Fe}_5\text{O}_{12}$	4b	1.92	163.8	1.92	4b	2	648	6	108
	4b	2.02	153.2	1.94	4b	4	—	—	—
Amorphous RIG materials	16a	<2.00	?	>1.88	24d	40	850-950	~8	115

Moreover, the magnetic anisotropy constants and saturation magnetization values are substantially different from those of different iron oxide phases [17, 18]. There is no phase separation observed in XRD after crystallization. The formation of well crystallized garnets at temperatures just above 600 °C directly from the amorphous state rules out the possibility of formations of RIGs via solid state reactions between oxide phases which require much higher temperatures (above 1000 °C) because of the high activation energy involved.

#### 4.4. Magnetic spin structure in ultrafine RIG materials

Ultrafine amorphous RIG materials show plate-like structures in electron micrographs. These are aggregates and clusters of crystallites of 1.0–1.5 nm size. The crystallite aggregate is a non-porous particle and it appears in an amorphous state. The clustering or aggregation occurs as a result of the highly energetic nature of the crystallites which have unsaturated bonds at their extended surface. Therefore, the crystallites are bound together by primary bonds in the aggregates. The particle size of about 30 nm obtained from BET surface area measurements indicates aggregation of crystallites in the amorphous state [11]. The magnetic particle size obtained from magnetization curves points to the presence of intercrystallite bonds and magnetic ordering within aggregates. Thus, the smallest ultrafine magnetically ordered particle in the ultrafine amorphous RIG materials is a tiny cluster, called a magnetic cluster, comprising a countable number of crystallites of 1.0–1.5 nm size. Upon crystallization, the crystallite aggregates become destabilized and the individual crystallites grow to 10–35 nm size as is evident from BET studies, selected-area diffraction (SAD) patterns and electron micrographs [11].

The magnetization behaviour of fine particles shows extraordinary phenomena which arise from the effects of finite dimension and (or) surfaces or interfaces. The specific saturation magnetization  $\sigma_s$  is considered to be an intrinsic property of ferrimagnetic RIG materials. The  $\sigma_s$ -values measured in bulk RIG materials may be expected to apply to very small particles independent of their particle size or morphology. The variation in saturation magnetization  $\sigma_s$  in various ultrafine RIG materials with specific surface area is shown in figure 4. The curves are divided into two regions AB and BC. The specific surface area decreases from A to B to C in all the ultrafine RIG materials. The AB region of the curve corresponds to the ultrafine amorphous and the BC region corresponds to ultrafine crystalline RIG materials. In the amorphous state,  $\sigma_s$ -values decrease with decrease in surface area and, in contrast,  $\sigma_s$ -values increase with decrease in surface area in the ultrafine crystalline state. The  $\sigma_s$ -values for ultrafine amorphous and crystalline materials is less than those for polycrystalline materials (bulk  $\sigma_s$ -values), which indicates that some change in magnetic structure has occurred although this deduction is not definite because some of the particles may remain superparamagnetic if the temperature is high. The decrease in  $\sigma_s$ -values with increasing surface area in the case of particles composed of smaller (50–700 Å) crystallites in  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> was explained by assuming that the crystallites were separated by a non-magnetic grain boundary of the order of 6 Å wide [27]. It may be remembered that the smallest particle in the ultrafine amorphous RIG materials is a magnetic cluster of crystallites whereas ultrafine crystalline materials have larger individual crystallites as the magnetic particle. Therefore, a difference in spin structure can be expected in these two cases from the difference in  $\sigma_s$  behaviour observed as a function of surface area.

Ultrafine particles of magnetic materials usually have a non-collinear or canted spin structure [7]. In the crystalline RIG, the tetrahedral  $\text{Fe}^{3+}$  magnetization and octahedral  $\text{Fe}^{3+}$  magnetization are coupled antiparallel to each other and the  $\text{R}^{3+}$  magnetization antiparallel to the resultant  $\text{Fe}^{3+}$  magnetization i.e., in effect, a collinear magnetic structure. The ultrafine RIG materials in the present study, particularly amorphous RIGs, are expected to have substantial non-collinearity or spin canting due to the ultrafine nature of the particles. An increase in non-collinearity of spins would be reflected in a decrease in saturation magnetization  $\sigma_s$  in ultrafine magnetic materials. The ultrafine amorphous RIG materials are superparamagnetic, which would also lead to a decrease in  $\sigma_s$ -values. However, the ultrafine particles of the various magnetic oxides studied invariably are reported to show non-collinearity and canting of spins [7, 28, 29]. Therefore, non-collinearity is expected to be present in ultrafine RIG materials from the magnetization measurements. Because of the lack of Mössbauer studies in the presence of an applied field at low temperatures, additional quantitative evidence for non-collinearity is not presented in this study. Two alternative interpretations are possible. First the degree of non-collinearity throughout the particle may increase as the volume decreases, i.e. a uniform size effect and, second, the non-collinearity may be large near the surface of the particle and appears to increase for smaller particles because of the greater specific surface area.

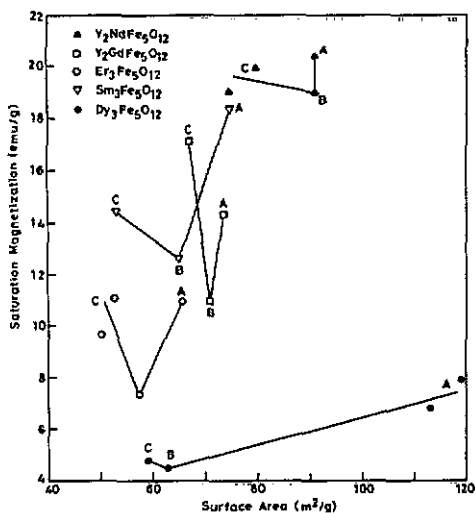


Figure 4. Variation in saturation magnetization with surface area in ultrafine RIG materials.

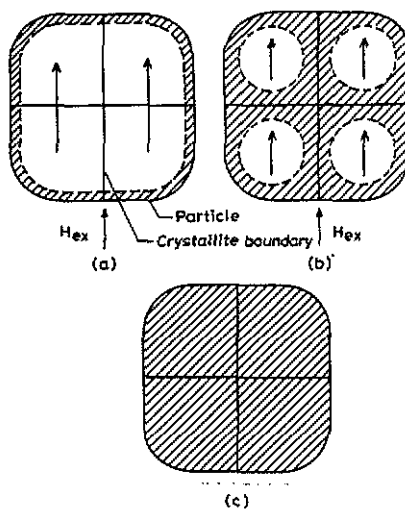


Figure 5. Schematic diagram showing magnetization together with spin canting and non-collinearity in (a) ultrafine crystalline materials, (b) other ultrafine materials and (c) magnetic clusters of 1.0–1.5 nm crystallites of RIGs. The shaded areas correspond to spin-canted regions.

The non-collinear spin structures of fine particles have been studied extensively by Haneda [7]. In the interior of the particle, the magnetic structure is similar and perhaps identical with the bulk material. In the outer shell, the spin canting is large. Fine particles are often composed of even smaller crystallites and hence it is pertinent to consider the effect of particle morphology on the non-collinear magnetic

structure. The thickness of surface layer contributing to canting is evaluated for two models shown in figure 5. One model assumes that spin canting is primarily on the surface layer of the particle and the other assumes that it is on the surface layer of each crystallite composing a particle. It is reasonable to assume that the thickness of surface layer in which spin canting occurs will be independent of size for a given material at a certain temperature. In both cases, a decrease in surface area would decrease the surface non-collinearity effect and thus increase  $\sigma_s$ -values. From figure 4 it can be seen that this is true for the BC part of the curve, i.e. for ultrafine crystalline RIG materials. This kind of dependence of  $\sigma_s$ -values on the surface area has been reported in the case of other fine particle magnetic materials [30]. However, the magnetic particle size in ultrafine crystalline materials (monolithic materials) is comparable with the x-ray crystallite size, which is an indication that particles do not comprise smaller crystallites. Therefore, the first model in figure 5(a) appears to represent the ultrafine crystalline RIG materials.

Ultrafine amorphous RIG materials comprise magnetic clusters. According to the second model (figure 5(b)), spin canting may be present in the surface layer of each crystallite composing a magnetic cluster particle. As mentioned above, it is reasonable to speculate that the thickness of surface layer in which spin canting occurs is independent of the size for a given material at a certain temperature. Since the individual crystallites of ultrafine amorphous RIGs are as small as 1.0–1.5 nm, a crystallite would be effectively all surface. Therefore, the surface canting on each crystallite results in uniform canting of spins throughout the interior of the particle as shown in figure 5(c). For this type of spin structure, even a decrease in surface area would not cause an increase in  $\sigma_s$ -values contrary to the case of surface canting as shown in figure 4 by the AB part of the curves. Since the crystallite size shows a negligible increase in the amorphous state, an increase in particle size (decrease in surface area) does not cause a reduction in non-collinearity and spin-canting effect and thus  $\sigma_s$ -values do not increase, but  $\sigma_s$ -values as seen in figure 4 show a decrease instead of remaining constant. The decrease in  $\sigma_s$ -values is the result of destabilization of crystallite aggregates and the increasing distortion (as shown by Mössbauer parameters) in the amorphous state as the particle size increases [11, 19]. A structure with spin canting as a uniform size effect (figure 5(c)) is therefore responsible for the decrease in  $\sigma_s$ -values in the amorphous state with decreasing surface area. It should be remembered that ultrafine amorphous RIG materials are superparamagnetic and most of the ultrafine crystalline RIG materials appear to comprise a particle size distribution and superparamagnetic fraction. Therefore the quantitative evaluation of the contribution of non-collinearity and surface thickness on the basis of decrease in  $\sigma_s$ -values is not possible without additional experimental data.

## 5. Conclusions

The nature of magnetic interactions and spin structure in ultrafine crystallites of RIG materials could be established by a detailed investigation of the basic magnetic properties such as saturation magnetization and Curie temperature. The ultrafine RIG materials comprising 10–35 nm crystallites show saturation magnetization and a Curie temperature comparable with those of bulk crystalline garnets. The 20–25% reduction in saturation magnetization in 10–25 nm crystallites is attributed to surface spin canting and a corresponding spin-canting model could be proposed.

The 1.0–1.5 nm crystallites of ultrafine RIGs, in contrast, exist as x-ray amorphous aggregates with a relative increase in specific volume and with magnetic interaction among crystallites—the magnetic clusters. The variation in saturation magnetization in these magnetic clusters compared with bulk crystalline garnets is attributed to a weakening of rare-earth sublattice contributions resulting from a weakening of the anisotropic  $R^{3+}-O^{2-}-Fe^{3+}$  interaction in the disordered state. A semiempirical calculation shows the above weakening to be greater than 70%, in agreement with the observation made earlier in the FMR studies. A calculation of  $T_C$  using the number of effective magnetic interactions, following Gilleo who calculated it earlier for different iron oxide systems, suggests that an increase in the number of  $Fe_a^{3+}-O^{2-}-Fe_d^{3+}$  interactions in the disordered state could account for the higher  $T_C$  in magnetic clusters. The decrease in saturation magnetization compared with that in bulk crystalline garnets is again attributed to spin canting. A model based on bulk spin non-collinearity is proposed to account for the spin structure.

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