Properties of non-crystalline EuIG and DyIG obtained from Mössbauer and magnetization data[a]

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Non-crystalline (nc) EuIG and DyIG have been prepared by dc-sputtering. Mössbauer data on ^{57}Fe, ^{151}Eu and ^{161}Dy reveal sharp magnetic transitions at 62 K and 70 K for nc EuIG and DyIg, respectively. The ^{57}Fe hyperfine (hf) spectra consist of three superpositioned patterns for Fe^{3+} in tetrahedral and octahedral and for Fe^{2+} in tetrahedral oxygen coordination. The saturation hf fields at 4.2 K are reduced compared to the values of the corresponding crystalline materials. The induced hf field at ^{151}Eu is only 1/8 of that for crystalline EuIG.

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1. INTRODUCTION

The well-known dependence on preparation conditions of the microstructural polymorphism in nc networks is often also reflected in their magnetic properties. This is particularly evident for non-metallic nc materials where superexchange coupling dominates. The latter is very sensitive to slight variations in bond lengths and angles. For example, this counterplay of local structural and magnetic properties has successfully been investigated by Mössbauer spectroscopy on nc ferrous halides[1-3]. Here we report about the characterization of nc EuIG and DyIG with the help of Mössbauer and macroscopic magnetization measurements.

2. EXPERIMENTAL

Nc EuIG and DyIG have been prepared by slow dc-sputtering (8kVAr+) from crystalline garnet targets. The argon pressure was 10^{-5}Torr. Both, the target and the mylar substrate were kept at ∼80 K. Samples of thicknesses between some 10^3 up to 10^5Å were obtained with deposition times ranging from 10 to 100 hours. Mössbauer absorption studies on ^{57}Fe and ^{151}Eu were carried out in the temperature range between 4.2 and 300 K. Additional measurements with ^{161}Dy are presently limited to the range above 70 K. Macroscopic magnetization data between 4.2 and 200 K were obtained with a vibrating sample magnetometer. X-ray characterization of the samples was done at room temperature.

3. RESULTS

The sputtered garnet samples are X-ray amorphous. Crystallization can be achieved by heating in air to 800-1000 K. ^{57}Fe Mössbauer spectra of nc EuIG and DyIG taken at 300 K in the paramagnetic regime are shown in Fig.1. In Fig.2 we show spectra in the magnetically ordered state at 4.2 K. The high temperature spectra can be interpreted by a superposition of three quadrupole patterns reflecting differ-
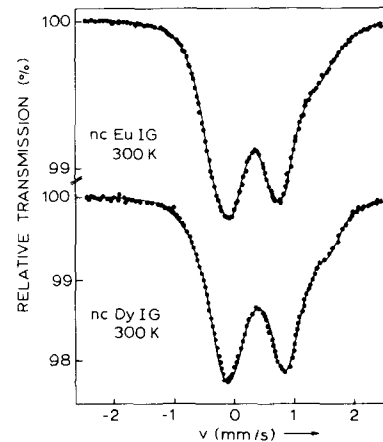
Fig.1: ^{57}Fe absorption spectra of nc EuIG and DyIG at 300 K. (source 30mCi $^{57}CoRh$, eff. absorber thickness 0.10 and $0.\overline{15}$mg $^{57}Fe/cm^2$)

ent Fe sites. The values of their spectral parameters are given in Table I. One can tentatively identify tetrahedral and octahedral Fe^{3+} sites. The hf parameters of the third site are close to those known for tetrahedral Fe^{2+} (e.g. in silica garnets[6]). The relative intensities of the three subspectra were corrected for different Lamb-Mössbauer factors (as estimated from their temperature dependence between 80 and 300 K) in order to obtain the occupancy of the three sites (Table I).

For an accurate determination of the magnetic ordering temperature T_m we performed thermal scanning[7] for the resonances of ^{57}Fe, ^{151}Eu resp. ^{161}Dy. We found $T_m=62.\pm0.5$ K for nc EuIG and 70.±0.5 K for nc DyIG. The ^{57}Fe magnetic hf patterns below T_m were fitted by a superposition of three sets for 6-line effective field patterns. Their isomer shifts and the relative intensities were fixed to the

Fig.2: ^{57}Fe absorption spectra of nc EuIG and DyIG at 4.2 K, the inserts give the probability distribution of B^{hf}.

values valid above T_m (Table I). No variation in spectral shape was found by changing the angle between the direction of the γ-rays and the plane of the absorber substrate. This indicates the absence of a preferred orientation of the Fe moments. The distribution of the magnetic hf fields can be satisfactorily described by a sum of three Lorentzians. The effective hf fields B^{hf} for the three Fe sites and the relative widths of the distributions at 4.2 K are also summarized in Table I. In Fig.3 the variation of B^{hf} with temperature is plotted for nc DyIG. The shape of the distribution function of B^{hf} (as shown in the inserts in Fig.2 for 4.2 K) is qualitatively maintained up to T_m.

The Eu^{3+} ions experience only an induced hf magnetic field. A value of 8T was found at 4.2 K which is about 1/8 of the value for crystalline EuIG[8]. The quadrupole interaction above T_m corresponds to $e^2qQ_{gd}\approx130$MHz for

^{151}Eu^{3+} in nc EuIG and ≈1600MHz for ^{161}Dy^{3+} in nc DyIG.

From macroscopic magnetization measurements we find roughly a Curie-Weiss behaviour above 90 K. The extrapolated Curie-Weiss temperatures are -220 K and -120 K for nc EuIG and DyIG, resp. The magnetic moments are $(24\pm2)\mu_B$ per ficitive formula unit Eu$_3$Fe$_5$O$_{12}$ and $(45\pm2)\mu_B$ for Dy$_3$Fe$_5$O$_{12}$. The increase of moment below 90 K indicates ferrimagnetic order. No remanence is found down to 30 K. Even at 4.2 K a large amount of spins is unblocked. The magnetization in a field of 5T is about half the value estimated for any collinear ferrimagnetic arrangement of the Fe^{3+}, Fe^{2+} and Eu^{3+} resp. Dy^{3+} moments. The compensation temperature of nc DyIG is about (35 ± 2)K but is strongly masked by the unblocked contribution to the magnetization.

4. DISCUSSION

The appearance of different valence states in sputter-deposited materials is well-known[9]. Here we can trace it to a preferential oxygen sputtering from the target: surface probes also contain Fe^{2+}. During evaporation total molecular units may be conserved thus allowing a close structural relationship between target and sputtered sample. We assume that the nc structure and its stoichiometry are stabilized by an oxygen deficiency δ. Per formula unit RE$_3$Fe$_5$O$_{12-\delta}$ we estimated $\delta\approx0.4$ for nc EuIG and DyIG. These values compare with $\delta\approx0.5$ reported for melt quenched nc GdIG[10].

The large efg for octahedral Fe^{3+} together with the increased isomer shift can be connected to a widening of the lattice with a corresponding distortion of the O^{2-} octahedra[6]. The isomer shift of tetrahedral Fe^{3+} is enhanced in a similar way. The major part of the reduction of the saturation hf magnetic fields for Fe^{3+} can be explained by a distribution of the molecular field due to the dis-

Table I: ^{57}Fe hf parameters for non-crystalline (nc) and crystalline[4,5] (cr) EuIG and DyIG: isomer shift IS rel. α Fe(300 K), quadrupole interaction $\frac{1}{2}e^2qQ$(300 K), magnetic hf field B^{hf}(4.2 K), width $\Delta B^{hf}/B^{hf}$ of the Lorentzian hf field distributions, rel. occupation I for the different Fe sites, magnetic transition temperatures T_m.

		IS_{300}(mm/s)	$\frac{1}{2}e^2qQ_{300}$(mm/s)	$-B^{hf}_{4.2}$(T)	$\Delta B^{hf}/B^{hf}$	I	T_m(K)
EuIG	Fe^{3+}(tetr)	0.35	0.89	43.6	±0.05	2.55	
	nc Fe^{3+}(oct)	0.56	0.84	35.2	±0.2	1.70	62.
	Fe^{2+}(tetr)	0.68	1.84	27.1	±0.2	0.75	$\pm$ 0.5
		±0.01	±0.02	$\pm$ 0.5		±0.05	
	cr Fe^{3+}(tetr)	0.21	0.85	47.5		3	566
	Fe^{3+}(oct)	0.46	0.45	54.5		2	
DyIG	Fe^{3+}(tetr)	0.38	0.90	45.1	±0.03	2.4	
	nc Fe^{3+}(oct)	0.56	0.84	39.0	±0.15	1.85	70.
	Fe^{2+}(tetr)	0.68	2.05	28.4	±0.4	0.75	$\pm$ 0.5
		±0.01	±0.02	$\pm$ 0.5		±0.05	
	cr Fe^{3+}(tetr)	0.20	0.90	48.0		3	563
	Fe^{3+}(oct)	0.42	0.49	55.1		2	

Fig.3: Variation of the ^{57}Fe magnetic hf fields B^{hf} with temperature for tetrahedral (×) and octahedral (●) Fe^{3+} and tetrahedral (△) Fe^{2+} in nc DyIG

torted bonds in the nc solid which are responsible for the superchange. This distribution leads also to the observed distribution of B^{hf}. From this we calculate[11] a reduction of 4-6% for the hf field of tetrahedral Fe^{3+} and 18-24% for octahedral Fe^{3+}. The larger distribution and thus the stronger reduction for octahedral Fe^{3+} are due to its higher number of bonds. The same arguments explain successfully the small saturation field of ~28T for tetrahedral Fe^{2+}. In view of the relatively narrow distribution ΔB^{hf} for tetrahedral Fe^{3+} it is not surprising that the variation of the hf dield with temperature for this site is close to the functional dependence of the sublattice magnetization in a crystal. Unfortunately the data for the two other, are too inaccurate for a more quantitative analysis near T_m where a less steep variation would be expected. The drastically reduced induced hf field at $^{151}Eu^{3+}$ and also the high efg indicate a severe distortion of the RE dodecahedral sites accompanied by a reduction of the exchange field.

Previously a strongly increased magnetic ordering temperature (~850 K) was reported for pyrolytic nc YIG[12]. In contrast to our results the Mössbauer data for this material are characterized by superparamagnetic effects. The agreement of the magnetic transition for nc EuIG and DyIG determined with ^{57}Fe, ^{151}Eu and ^{57}Fe, ^{161}Dy, resp., with their different nuclear Larmor precession periods and the variation of the ^{57}Fe hf fields near T_m prove T_m as true magnetic transition point, despite the fact that macroscopic magnetization is blocked at much lower temperatures. From the low magnetization at 4.2 K we propose a randomly canted spin arrangement although the overall order appears ferrimagnetic. Further Mössbauer epxeriments under an applied external magnetic field are needed to check whether the spin arrangement is really sperimagnetic[13].

The nearly tenfold reduction of T_m in comparison to the crystalline state cannot be explained by fluctuations of the $Fe^{3+}(tetr)$-O^{2-}-$Fe^{3+}(oct)$ superexchange alone. This would only result in a decrease of several percents. The hf field distribution gives no indication for the presence of nearly non-magnetic clusters. Thus percolation arguments[14] involving a simple non-magnetic dilution cannot be applied either. One possible mechanism is the unknown coupling of the tetrahedral Fe^{2+} to its neighbours. It could introduce some ferromagnetic Fe^{3+}-Fe^{2+} double exchange. However, we propose that the dominant reason for the reduction of T_m lies in the reduction of the mean molecular field due to the widening of the lattice and the accompanying distortion of the bonds.

5. CONCLUSION

The microchemical composition and structure of sputtered nc EuIG and DyIG can be satisfactorily explained by a small oxygen deficiency due to preferential oxygen sputtering. Macroscopic magnetization suggests ferrimagnetic order possibly of sperimagnetic type. The sharp magnetic transition and the distribution of hf fields preclude a wide distribution of magnetic clusters with varying order parameters. Although a part of the deviations of the magnetic hf parameters from the values for the corresponding crystalline materials can be explained by a distribution in the molecular field, the strong reduction of T_m must be attributed to a decrease of the average molecular field due to the distorted superexchange bonds. The present Mössbauer experiments will be completed by further ^{161}Dy studies below T_m on nc DyIG in order to determine the sublattice magnetization of the rare-earth sites.

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