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Structural inhomogeneity on length scales comparable to magnetic interaction lengths can produce complex magnetic behavior. Crystalline $GdAl_2$ is a ferromagnet with a Curie temperature of 170 K, while amorphous $GdAl_2$ thin films exhibit classic spin-glass behavior with a freezing temperature of 16 K. Nanostructured $GdAl_2$, made by mechanically milling initially crystalline $GdAl_2$, exhibits ferromagnetic and spin-glass-like transitions; however, the spin-glass-like transition occurs at a higher temperature than the freezing temperature of amorphous $GdAl_2$ thin films. Curie–Weiss analysis suggests that the paramagnetic-to-ferromagnetic transition is due to the ferromagnetic ordering of small $GdAl_2$ clusters and that the glassy transition is most likely due to spin-glass-like ordering of a surface/interface phase. © *2003 American Institute of Physics.*
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I. INTRODUCTION

Structural inhomogeneity on length scales comparable to magnetic interaction lengths can produce complex magnetic behavior as different parts of the system order at different temperatures. Crystalline $GdAl_2$ is a ferromagnet with a Curie temperature T_C of 170 K,[1] and a small magnetocrystalline anisotropy.[2] Amorphous $GdAl_2$ thin films exhibit classic spin-glass behavior—a peak in the zero-field-cooled (ZFC) susceptibility and irreversibility between the ZFC and field-cooled (FC) susceptibilities—with peak temperature $T_p = 16$ K.[3] Curie–Weiss (CW) behavior is observed in crystalline bulk and amorphous films above their respective transition temperatures.[4] Nanostructured $GdAl_2$ exhibits ferromagnetic and spin-glass-like (SGL) transitions. CW analysis provides valuable information about the mechanisms responsible for the magnetic behavior in this and in other complex magnetic systems.

II. SAMPLE FABRICATION

Gadolinium chips (99.9% pure) and aluminum pellets (99.99% pure) were arc melted under an argon atmosphere. The procedure was repeated several times to insure homogeneous mixing. The alloy was crushed, milled for 2 h in a tungsten carbide vial under an argon atmosphere to produce a fine powder, then annealed for 24 h at 800 °C under vacuum to remove milling-induced stress in the powder. X-ray diffraction confirmed that the sample was a crystalline, highly ordered alloy, and showed no tungsten carbide contamination or oxide peaks.

Nanostructured $GdAl_2$ was produced by milling the crystalline powder using a ball-to-powder ratio of 1:1.75 and a total sample mass of 18.9 g. Milling periods 15 min long were alternated with 15 min rest periods to reduce heating. The vial was turned every 2 h to reduce clumping, and a small amount of sample was removed at various intervals for x-ray diffraction and magnetic measurements. An amount of unmilled powder was reserved as a reference.

The grain size was calculated from x-ray diffraction peaks using an integral-breadth technique after the $K\alpha_2$ contributions were removed. The grain size decreases to 15 nm after 3 h of milling. A terminal grain size of ~8 nm was obtained after 20 h of milling.

III. MAGNETIC DATA

Samples for measurement in a superconducting quantum interference device (SQUID) magnetometer were prepared in an argon atmosphere and sealed in paraffin-filled polyethylene bags to protect the samples from oxidation and prevent the particles from rotating during measurement. The magnetization as a function of temperature $M(T)$ was measured from 310 to 5 K in FC and ZFC configurations. Figure 1 shows the ZFC $M(T)$ measured in 100 Oe for several milling times. The unmilled sample shows the expected sharp paramagnetic–ferromagnetic (PM–FM) transition at 170 K, which is consistent with bulk T_C.[1] This transition shifts to-

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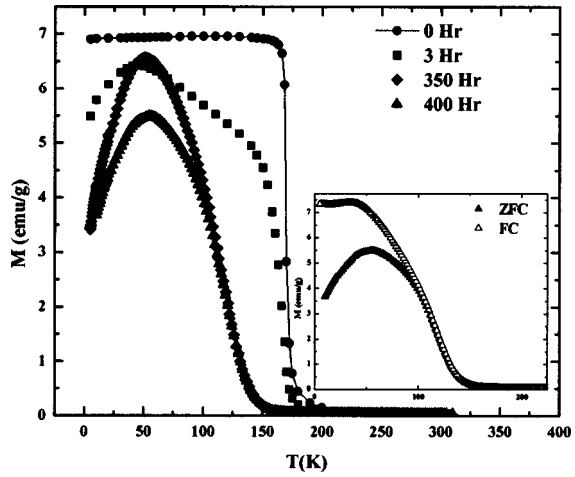

FIG. 1. Zero-field-cooled magnetization for several milling times, measured in 100 Oe. The inset shows the FC (closed symbols) and ZFC (open symbols) $M(T)$ for the 400 h milled sample.

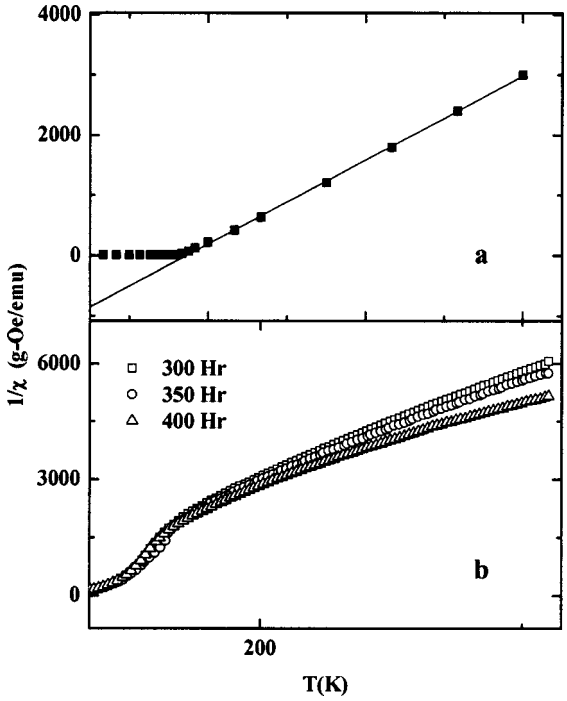

FIG. 2. Inverse susceptibility of (a) unmilled crystalline $GdAl_2$ and (b) $GdAl_2$ milled for 300, 350 and 400 h, all measured in 100 Oe.

ward lower temperatures and becomes broader with the milling time, but is still present after 400 h of milling. A broad peak near 45 K is observed after 3 h of milling and it shifts toward slightly higher temperatures with additional milling time. Bifurcation between the FC and ZFC magnetization is shown in the inset of Fig. 1 for a sample milled for 400 h.

A plot of the inverse susceptibility as a function of the temperature [Fig. 2(a)], shows that unmilled $GdAl_2$ obeys a Curie–Weiss law ($H=100$ Oe), with an effective moment of $8.60(\pm 0.04)\mu_B$ and a Curie–Weiss temperature of 171 (± 1) K. The moment is higher than the value of $7.9\mu_B$ expected from Gd^{3+} ions; however, this has been observed previously in $GdAl_2$ and attributed to conduction-electron enhancement effects.[5]

Figure 2(b) shows the inverse susceptibility of $GdAl_2$ milled for 300, 350 and 400 h. The magnetic behavior of the milled samples cannot be described by a single Curie–Weiss expression, but is instead consistent with the existence of two distinct magnetic components. The downturn at lower T signals the dominance of the component that undergoes a FM transition at a temperature slightly depressed from the bulk T_C of $GdAl_2$. The second component remains paramagnetic until the freezing process at the peak temperature in the ZFC $M(T)$.

The best fit in the region above the ferromagnetic transition is given by either the sum of a Curie–Weiss and a term proportional to $1/T$: $\chi=(c_1/T-\theta_1)+c_2/T$, or two Curie–Weiss terms: $\chi=(c_1/T-\theta_1)+(c_2/T-\theta_2)$. Values for the fits are shown in Table I. The onset of the glassy transition introduces significant uncertainties in the values of θ_2. No fit for the 400 h data was possible using a nonzero value of θ_2.

From the CW expression, $N_i\mu_{\mathrm{eff},i}^2=3c_iMk_B$, where M is the molecular weight of $GdAl_2$, k_B is the Boltzmann constant, and N_i is the number of atoms in the ith component. We find $c_1<c_2$, (i.e., $N_1\mu_{\mathrm{eff},1}^2<N_2\mu_{\mathrm{eff},2}^2$). If we assume that the values of μ_{eff} are comparable in both components, then $N_1<N_2$, i.e., the component that gives rise to the FM transition is the minority component. The relative heights of the shoulder indicating the FM transition and the low-temperature peak in $M(T)$ support this interpretation. c_1+c_2 is approximately equal to the value of C obtained from the single CW fit to the unmilled material.

The PM–FM transition near 170 K is attributable to FM ordering within $GdAl_2$ grains. The CW fits indicate effective moments consistent with those of the unmilled material, and the paramagnetic CW temperature is close to that of the FM transition. Possible origins of the peak in the ZFC $M(T)$ include surface-spin-glass freezing, cooperative freezing of

TABLE I. Parameters from fitting the inverse susceptibility. The top set of numbers for each sample is the fit to $\chi=(c_1/T-\theta_1)+c_2/T$; the second set is a fit to $\chi=(c_1/T-\theta_1)+(c_2/T-\theta_2)$; (NA=nonapplicable).

Milling time (h)	c_1 (emu K/g Oe)	θ_1 (K)	c_2 (emu K/g Oe)	θ_2 (K)	c_1+c_2 (emu K/g Oe)
Unmilled	0.0436±0.0004	171±1		NA	0.0436
300	0.0109±0.0020	136±6	0.0330±0.001	NA	0.0439
	0.0105±0.0020	136±6	0.0330±0.002	−0.4±18	0.0435
350	0.0090±0.0028	140±10	0.0370±0.008	NA	0.0460
	0.0080±0.0040	140±7	0.0370±0.002	−1.0±12	0.0450
400	0.0090±0.0030	140±10	0.0342±0.006	NA	0.0432

either Gd clusters or the now-ferromagnetic $GdAl_2$ grains, a reentrant spin-glass transition and superparamagnetic blocking.

Cluster-glass behavior due to strongly interacting 2–3 nm Fe nanoclusters has been observed in mechanically alloyed FeReCr and FeAlB.[6,7] Although 2–3 nm Gd nanoclusters have been observed in amorphous $GdAl_2$ thin films,[8] there is no evidence of a Gd PM-FM transition at 293 K. In contrast with our results, the ZFC/FC splitting in the Fe-based nanostructures occurs very close to the peak in low measuring fields and there is no splitting until temperatures well below the peak in high fields.

Similarly, the ZFC/FC magnetization bifurcation in most reentrant spin glasses occurs at temperatures significantly lower than T_C.[9,10] In contrast, nanostructured $GdAl_2$ shows ZFC/FC splitting very close to the FM transition in the lowest fields, indicating that irreversibility begins as soon as the FM grains have ordered. The low anisotropy[2] of $GdAl_2$ and ac-susceptibility measurements as a function of the frequency (which will be discussed elsewhere) suggest that the bifurcation is not a purely ferromagnetic phenomenon and instead suggest a glassy type of order.

$GdAl_2$ has very weak anisotropy,[2] so the superspins formed in each $GdAl_2$ grain by the FM–PM transition could act like superparamagnets, which either freeze into a correlated state or undergo superparamagnetic blocking. Although this appears inconsistent with the Curie–Weiss evidence of multiple magnetic components, glassy ordering often begins well above the freezing temperature, and the onset of that order could contribute to the non-Curie–Weiss behavior. The blocking temperature for 8 nm $GdAl_2$ grains (assuming bulk anisotropy values) should be significantly lower than the peak temperatures observed, so we do not believe the peak is due to superparamagnetic blocking.

Distinct magnetic behavior of surface or interface phases has been observed in many systems.[11–13] Aeppli *et al.*[14] analyzed a model consisting of two magnetic sublattices: one with FM order and one with spin-glass order. Although this model was originally intended for homogeneous samples, it is consistent with the physical nanostructure of FM grains separated by noncrystalline intergrain regions. The existence of ferromagnetic order does not prevent spin-glass freezing, but it does break the degeneracy in the spin-glass clusters and thus modify the nature of the freezing. Aeppli *et al.* argued that the decrease in ground-state entropy due to coupling between the FM and SG networks should produce an increase in the peak temperature compared to that expected in the absence of a FM-ordered network. The picture of a mixed FM-SG state above the peak temperature is supported by neutron scattering measurements, which indicate a phase having ferromagnetic order *and* paramagnetic-like disorder, which coexist on different length scales.[15]

As the fraction of sample involved in the FM transition decreases in our milled $GdAl_2$, the peak temperature *increases*, instead of the predicted decrease. A similar sample showing no evidence of a FM transition has an even higher peak temperature than our samples.[16] This discrepancy may be due to the need to take into account differences between homogeneous materials and inhomogeneous nanostructures. In nanostructures, the SGL intergrain phase is an interconnected structure, not the clusters of Aeppli's model. If the FM and glassy components are largely uncoupled, as suggested by the high-temperature behavior, the growth of the glassy part could lead to longer-range correlations and thus higher freezing temperatures. The combination of the high-temperature behavior and exclusion of other mechanisms suggests that surface/interphase SGL ordering is the most likely cause of the peak in the ZFC $M(T)$.

IV. CONCLUSIONS

Nanostructured $GdAl_2$ exhibits ferromagnetic and glassy transitions. Curie–Weiss analysis of the high-temperature inverse susceptibility shows the presence of two distinct magnetic components. The PM–FM transition is due to the FM ordering of small $GdAl_2$ clusters. As the milling time increases and the material becomes more disordered, a smaller fraction of the sample is involved in the FM transition, as evidenced by the Curie–Weiss fits, and by the relative sizes of the features in $M(T)$. The peak in the ZFC $M(T)$ is most likely due to spin-glass-like ordering of a surface/interface phase. Further studies of the magnetic properties as a function of the grain size and disorder are necessary to understand the role of the FM phase in determining the nature of the glassy transition.

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