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Magnetic hysteresis and crytallization studies are reported for several $(Pr_{80}Ga_{20})_{100-x}Fe_x$ metallic glasses, where $30 \leq x \leq 80$. Thermomagnetic data show the presence of two magnetic phases which are probably responsible for the relatively high coercive fields observed at cryogenic temperatures. As the iron content of the sample is increased, the magnetic moment increases substantially but the coercivity is drastically reduced. In $(Pr_{80}Ga_{20})_{70}Fe_{30}$ the observed coercive fields are strongly temperature dependent indicating strong thermal activation effects which are consistent with the magnetic viscosity measurements. The hard magnetic properties disappear after crystallization and the samples appear to be paramagnetic at room temperature.

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INTRODUCTION

Amorphous rare-earth alloys have attracted considerable attention in recent years because of their unusual magnetic properties [1, 2, 3, 4, 5]. Below the ordering temperature, the non S-state ion alloys develop a high magnetic anisotropy which leads to lack of saturation and high coercive fields at cryogenic temperatures. These magnetic properties are explained by the local random anisotropy model of Harris et al [6], in which the local random anisotropy which exists in each magnetic site competes with the exchange forces leading to non-collinear magnetic structures. The magnetic properties of $(Pr_{80}Ga_{20})_{100-x}Fe_x$, where $0 \leq x \leq 30$, have been reported previously [7]. Field cooling effects and displaced hysteresis loops have been observed in $(Pr_{80}Ga_{20})_{70}Fe_{30}$ at very low temperature. The coercivity shows a maximum ($\sim$50 kOe) at about 100 K and then decreases to the small value of 2 kOe at room temperature. The relatively high coercivity makes this material a good candidate for permanent magnets but its very small magnetic moment at room temperature limits the energy product $(BH)_m$ to relatively low values.

In the present study the magnetic properties of $(Pr_{80}Ga_{20})_{100-x}Fe_x$, where $30 \leq x \leq 80$, are examined above room temperature. The range of chemical compositions is broadened to include the Fe-richer alloys in order to increase the room temperature magnetic moment and therefore achieve higher energy products. Attempts are also made to further improve the hard magnetic properties by crystallization.

EXPERIMENTAL

Thin foils of amorphous PrGaFe alloys were prepared by the splat-cooling technique using the piston and anvil method. The amorphous samples did not have a uniform thickness and were extremely brittle. Partially crystallized samples were made using slower quenching rates by varying the pressure of the piston. The higher Fe-content samples ($x > 60$) were always partially crystallized in the as quenched form.

The crystallization of the samples was examined with differential scanning calorimetry using a Dupont 900 system with a maximum operating temperature of 870 K and with a heating rate of 10–20 K/min. The microstructure of the amorphous and crystallized samples was examined with a Philips 400 transmission electron microscope equipped with an energy dispersive x-ray analysis unit.

Magnetic measurements were made with a vibrating sample magnetometer (VSM) in fields up to 80 kOe and in the temperature range of 4.2–1000 K. Thermomagnetic data M(T) were obtained by monitoring the change of magnetization under a constant magnetic field of 50–100 Oe while the temperature was rising at a rate of 10–15 K/min. Magnetic susceptibility was measured with an a.c technique in a rms field of 0.01 Oe and a frequency of 280 Hz.

RESULTS

In all the PrGaFe alloys, except $(Pr_{80}Ga_{20})_{20}Fe_{80}$, the thermomagnetic data above room temperature indicate a transition around 470 K (Fig. 1). This is in addition to another peak which has been observed [7] at liquid helium temperatures ($\sim$8 K). In the $(Pr_{80}Ga_{20})_{20}Fe_{80}$ sample magnetic transitions are observed around 780 and 1050 K respectively. This behavior indicates that these alloys are examples of a two magnetic phase system. This is further suggested by the constricted hysteresis loops which are observed at cryogenic temperatures (Fig. 2). The presence of the two magnetic phases might be responsible for the high coercivities which have been observed in these materials.

The room temperature magnetic properties of all the samples are summarized in Table I. The sample $(Pr_{80}Ga_{20})_{70}Fe_{30}$ has the highest coercivity, H_c=2400 Oe, but its magnetic moment is relatively weak ($M_S \simeq 25.0$ emu/g). $(Pr_{80}Ga_{20})_{70}Fe_{30}$ samples with different quenching rates have coercivities between 500 and 3000 Oe. As the iron content is increased, the magnetic moment increases but the coercivity

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is substantially reduced to very small values (200 Oe). In $(Pr_{80}Ga_{20})_{70}Fe_{30}$ the room temperature coercivity (2400 Oe) decreases rather rapidly at higher temperatures and it is negligible at around 420 K (Fig. 3) indicating a strong thermal activation effect. This is consistent with the measured magnetic viscosity which is due to thermal activation of domain walls over the energy barriers and shows a logarithmic time dependence of the magnetization,

$$M = \text{const.} - S \ln t \qquad (1)$$

with a magnetic viscosity coefficient, $S = 1 \times 10^{-3}$ emu/g, (Fig. 4) at the coercivity H_c.

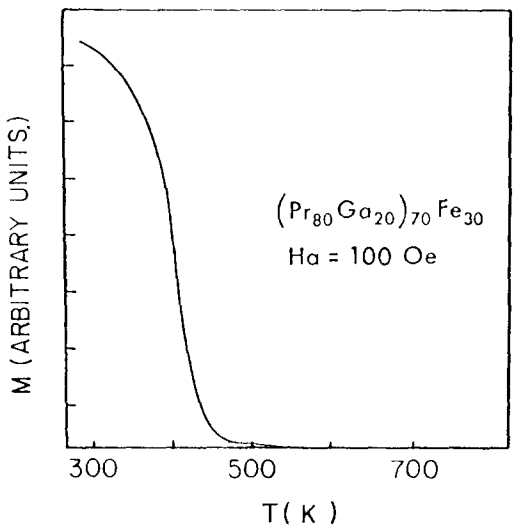

Fig. 1. Thermomagnetic data in $(Pr_{80}Ga_{20})_{70}Fe_{30}$ showing a magnetic transition around 470 K.

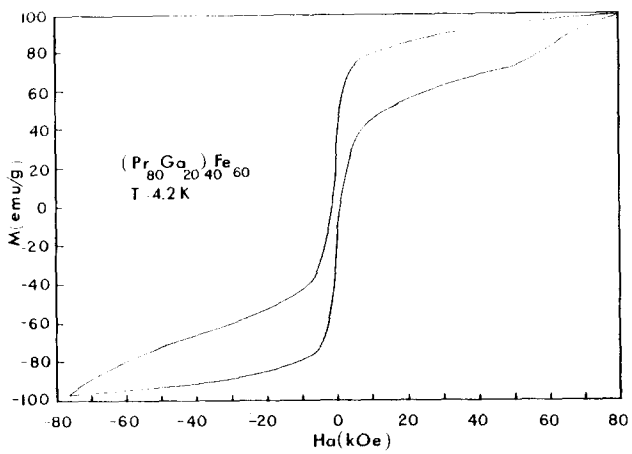

Fig. 2. Constricted hysteresis loop in $(Pr_{80}Ga_{20})_{40}Fe_{60}$ at 4.2 K.

TABLE I
Magnetic Properties of $(Pr_{80}Ga_{20})_{100-x}Fe_x$ Alloys

Sample (x)	H (Oe)	M(20 kOe) (emu/g)	M_r (emu/g)	T_c (K)
30	2400*	22.5	9.0	475
40	1300	22.7	8.8	460
60	220	75.15	5.4	455
80	300	153.22	-	783; 1053

*Displaced hysteresis loops (600 Oe).

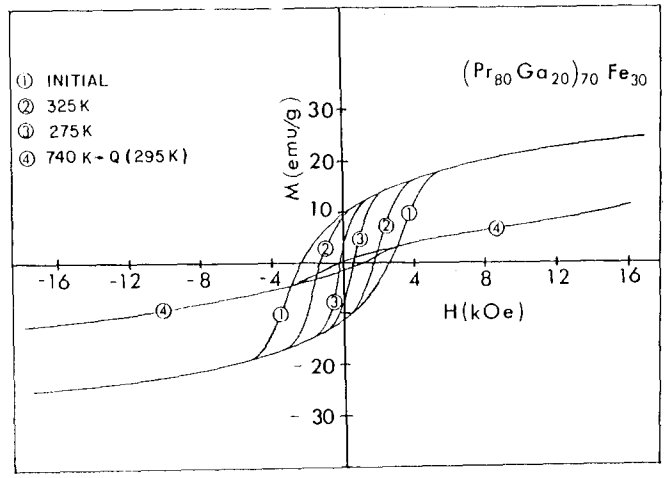

Fig. 3. Temperature dependence of hysteresis loops in $(Pr_{80}Ga_{20})_{70}Fe_{30}$.

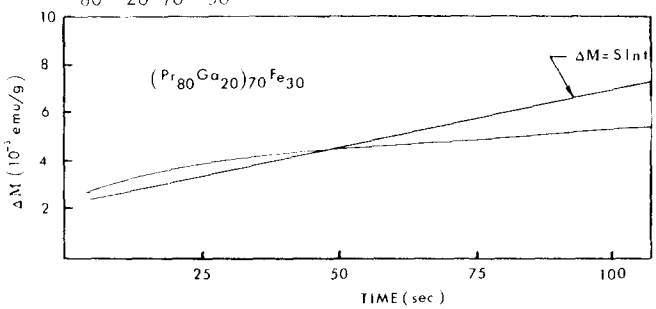

Fig. 4. Magnetic viscosity data in $(Pr_{80}Ga_{20})_{70}Fe_{30}$ at 300 K.

The thermal analysis measurements show a number of exothermic and endothermic peaks in all the samples (Table II). This is shown in Fig. 5 for $(Pr_{80}Ga_{20})_{70}Fe_{30}$. The irreversible exothermic peak is attributed to the crystallization of the amorphous material. The reversible endothermic peak is probably due to partial melting of the sample during heating or to a phase transition of the crystalline phase which is formed after crystallization. Crystallization temperatures vary from 620 K at x=40 to 780 K at x=80 (Table II). Comparison of the thermal peaks with the observed Curie temperatures indicates that calorimetry is not very sensitive to magnetic phase transitions (Fig. 1). The thermal data are used as benchmarks to determine possible annealing temperatures to produce crystal nucleation within the amorphous material.

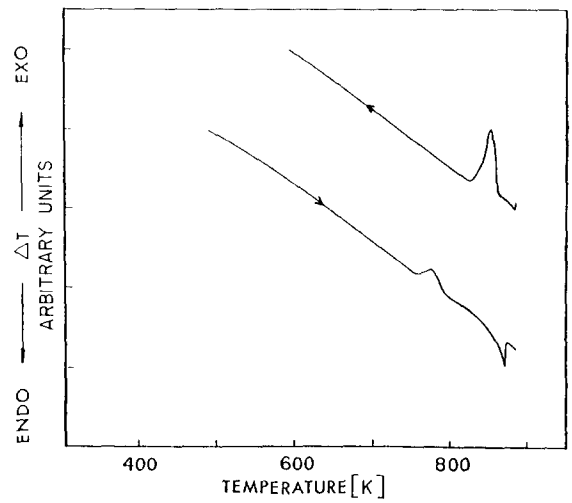

Fig. 5. Differential scanning calorimetry data in $(Pr_{80}Ga_{20})_{70}Fe_{30}$.

TABLE II
Differential Scanning Calorimetry in $(Pr_{80}Ga_{20})_{100-x}Fe_x$ Amorphous Materials

Sample (x)	Peak Temperature (K)	Comments
30	755	Exothermic, irreversible
	845	Endothermic, reversible
40	625	Exothermic, irreversible, broad
60	500	Exothermic, irreversible
	723	Exothermic, irreversible
80	780	Exothermic, irreversible possible artifact
	955	Endothermic, reversible
	1104	Endothermic, irreversible

The hard magnetic properties of all the alloys deteriorate rapidly after crystallization and the samples appear to be paramagnetic at room temperature. Figure 3 (curve 4) shows the loop of $(Pr_{80}Ga_{20})_{70}Fe_{30}$ in the very early stages of crystallization. The hysteresis loops of the completely crystallized $(Pr_{80}Ga_{20})_{70}Fe_{30}$ samples at cryogenic temperatures are shown in Figure 7. The large coercive fields observed in the amorphous state[7] disappear and the samples are basically paramagnetic above 19.5 K. A.C. susceptibility measurements on a crystallized $(Pr_{80}Ga_{20})_{70}Fe_{30}$ sample show a reduction in the magnitude of the higher temperature peak ($\sim$470 K) and a drastic increase in the magnitude of the lower temperature peak ($\sim$8 K), indicating that the high T_c phase regions have transformed to the lower T_c phase after crystallization (Figure 6).

Microstructure studies show that the unannealed $(Pr_{80}Ga_{20})_{70}Fe_{30}$ sample is basically amorphous with very few scattered microcrystalline regions present. Energy dispersive x-ray analysis reveals some fluctuations in chemical composition of the amorphous phase. Regions rich in PrGa and PrFe have been observed on a 400 Å scale indicating the existence of two amorphous phases corresponding to the high and low T_c magnetic phases.

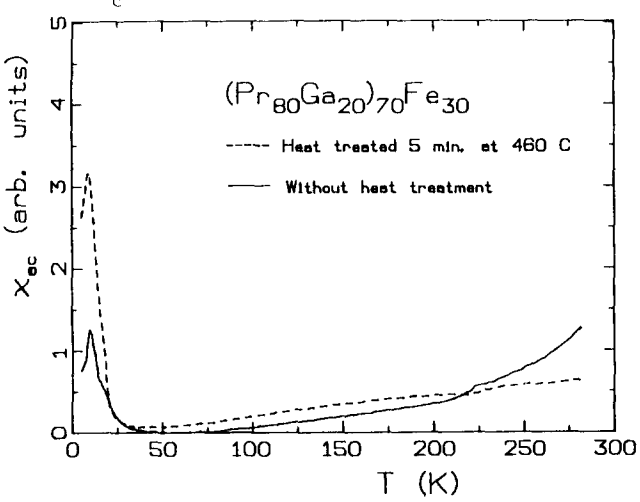

Fig. 6. A.C. susceptibility of an amorphous and a partially crystallized $(Pr_{80}Ga_{20})_{70}Fe_{30}$ sample.

DISCUSSION

The observed coercivities are found to be very sensitive to sample preparation. This, together with the thermomagnetic data and microstructure studies would indicate that the origin of the coercive fields is due either to the few scattered microcrystalline regions or to the local fluctuations in chemical composition which are produced during the rapid quenching. Magnetic viscosity measurements are used to differentiate between the two different pinning sites. According to Street and Wooley [8] the magnetic viscosity coefficient S is given by

$$S = -\chi kT / \left(\frac{\partial E}{\partial H}\right)_T \qquad (2)$$

where E is the activation energy and χ is the susceptibility at the field H where S is measured. The activation volume $V = 2Ax_o$, where $2x_o$ is the distance jumped due to thermal activation of an area A of the wall, can be deduced from $\left(\frac{\partial E}{\partial H}\right)_T$ using the relation [9],

$$\left(\frac{\partial E}{\partial H}\right)_T = -2MV \qquad (3)$$

where M is the magnetization per unit volume. Using the values of $S=1\times10^{-3}$ emu/g, $\chi=1.2\times10^{-3}$ emu/g. Oe and M=180 emu/cc, V is found to be 1.4×10^{8} Å^3 corresponding to a linear dimension of 520 Å. This is comparable to the size of the chemically differential amorphous regions while it is much smaller than the distance that would be swept as the domains move from one microcrystalline defect to another. Correlation with this model indicates that the amorphous phases give rise to the observed coercivities.

Crystallization does not improve the hard magnetic properties of the PrGaFe amorphous alloys because the crystallized phase formed is nonmagnetic at room temperature. It could be that the metastable phase which is responsible for the good magnetic properties observed in other rapidly quenched materials[10,11] cannot be induced by annealing but only by rapid quenching from the melt.

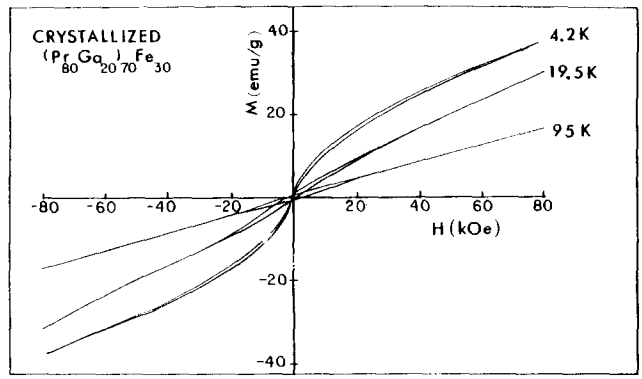

Fig. 7. Hysteresis loops of a partially crystallized $(Pr_{80}Ga_{20})_{70}Fe_{30}$ sample at cryogenic temperatures.

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