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Giant coercivities and chemical short-range order in Pr-Ga-Fe metallic glasses*

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Results of magnetic, Mössbauer, and structural studies are presented for $(Pr_{80}Ga_{20})_{100-x}Fe_x$ metallic glasses, where $0 \leq x \leq 30$. For $x \geq 20$ two magnetic transitions are observed and the structural studies indicate the presence of a phase separation into at least two glassy phases, one being Fe-rich and the other Fe-deficient. Coercivities above 60 kOe are observed and the results are discussed in terms of a model involving the magnetic properties of the two phases.

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INTRODUCTION

Recently there has been considerable interest in the magnetic properties of rare-earth-rich metallic glasses. (1-4) Unlike transition-metal-based metallic glasses such as the Metglas alloys which are often very soft ferromagnets, anisotropic rare-earth-rich metallic glasses often exhibit large curvature in the high-field magnetization as well as very large coercive forces. The local-random-anisotropy theory of Harris et al. (5) was developed to explain these effects by assuming the presence at each magnetic site of a randomly-directed uniaxial anisotropy which could compete with exchange forces to determine the direction of the local magnetic moment.

We recently have reported some unusual magnetic properties of rare-earth-based metallic glasses of composition $(R_{80}Ga_{20})_{100-x}T_x$ (6) where R is a rare-earth and T is a transition metal. In the heavy rare-earth glasses, $(Tb_{80}Ga_{20})_{100-x}Fe_x$, we found a scattered spin structure in the Tb subnetwork but with antiparallel coupling to the Fe atoms. Also there was large low temperature coercivity which monotonically decreased as the temperature increased. The Pr-based glasses displayed a more complex behavior in which a relatively small magnetization was observed at high fields, and the coercive force in the 30% Fe glass increased from less than 1 kOe at 4.2 K to over 60 kOe at 90 K. Apparently two or more amorphous magnetic phases are present in these alloys which give rise to the observed effects. In this paper we report results of further magnetic and structural studies of the Pr-Ga-Fe glasses.

EXPERIMENTAL

Samples were prepared from pure materials by rapidly cooling from the melt using a splat-cooling technique. Each sample was examined by MoKα x-ray diffraction utilizing a high resolution Si:Li detector in conjunction with a pulse height analyzer and discriminators. Smooth, well-defined liquid-like diffraction patterns were observed for all the alloys. Susceptibility data were taken from 4.2 K to room temp in a field of 700 Oe with a Faraday balance system. Fe^{57} Mössbauer data were taken with a sinusoidal Mössbauer spectrometer between 4.2 K and 300 K. High-field magnetization data were taken from 2 K to 300 K in fields up to 80 kOe in a vibrating sample magnetometer [VSM]. Faraday, VSM, and Mössbauer data were taken utilizing microprocessor-based data-acquisition systems.

RESULTS

Figure 1 shows a typical x-ray diffractogram for $(Pr_{80}Ga_{20})_{80}Fe_{20}$ and a reduced radial-distribution function. There is no obvious division of the large first peak into two components in the diffractogram which might indicate the gross precipitation into a second amorphous phase, nor is there any indication of crystalline precipitates. Evidence for a phase separation in $(Pr_{80}Ga_{20})_{80}Fe_{20}$ has been obtained from selected-area-electron diffraction and fluorescence measurements (7). The results indicate that there are at least two amorphous phases present, one of which is rich in Fe and the other deficient in Fe. The spatial resolution of the measurements is about 400 Å, so this represents a lower limit on the dimensions of the amorphous phases.

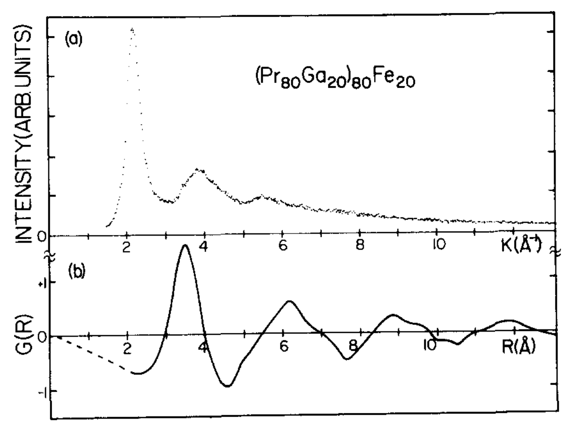

Fig. 1. (a) X-ray diffractogram of $(Pr_{80}Ga_{20})_{80}Fe_{20}$. (b) Reduced RDF of data in (a).

Figure 2 shows the magnetic susceptibility for $(Pr_{80}Ga_{20})_{80}Fe_{20}$ from 4.2 K to 500 K. (8) The higher-temperature peak occurs at about 375 K and the low-temperature peak is at about 8 K which is very close to the peak observed in amorphous $Pr_{80}Ga_{20}$. Measurements on similar light-rare-earth based glasses showed two transitions while heavy-rare-earth based glasses have only one transition. Figure 3b shows Fe^{57} Mössbauer data on enriched $(Pr_{80}Ga_{20})_{80}Fe_{20}$ at 300 K where the solid line is the fit to the data (below). Figure 3a shows Fourier deconvolution (9) of the 300 K Mössbauer spectrum into an internal field distribution function, P(H). The first peak in the deconvolution spectrum represents 'non-magnetic' or paramagnetic iron contributions to the spectrum since it is a fit to the central two peaks of the six-line spectrum. Its position on the H axis is an artifact of the fitting procedure

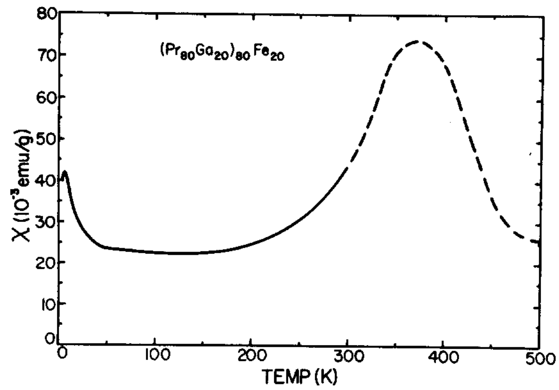

Fig. 2. Magnetic susceptibility from 4.2 K to 500 K for $(Pr_{80}Ga_{20})_{80}Fe_{20}$.

but its intensity should be representative of the number of Fe atoms experiencing little or no hyperfine-field splitting. The large peak at 250 kOe represents the magnetic iron contribution to the spectrum and is 67% of the total intensity. Assuming 330 kOe corresponds to 2.2 μ_B/Fe we obtain 1.66 μ_B/Fe in this glass at 300 K. Thus the total Fe moment is about 10 emu/g at 300K in this alloy assuming complete ferromagnetic coupling. As the temperature is lowered to 4.2 K the peak position moves to 295 kOe but the relative intensities of the peaks stay about the same. Work on related Fe-rich Nd and Pr amorphous alloys by Buschow et al. (10) and Croat et al. (11) indicated a loss of the Fe moment as the Fe concentration went below 30%. Thus it is likely that the Fe atoms represented by the lower peak in our P(H) distribution actually are those whose environments are rich enough in Pr that their moments are destabilized.

Magnetization data from 4.2 K to 300 K were obtained on all the samples in fields up to 80 kOe. Figure 4 shows magnetization loops for $(Pr_{80}Ga_{20})_{70}Fe_{30}$ taken at different temperatures after the sample had been cooled in an 80 kOe field from 215 K to 4.2 K.

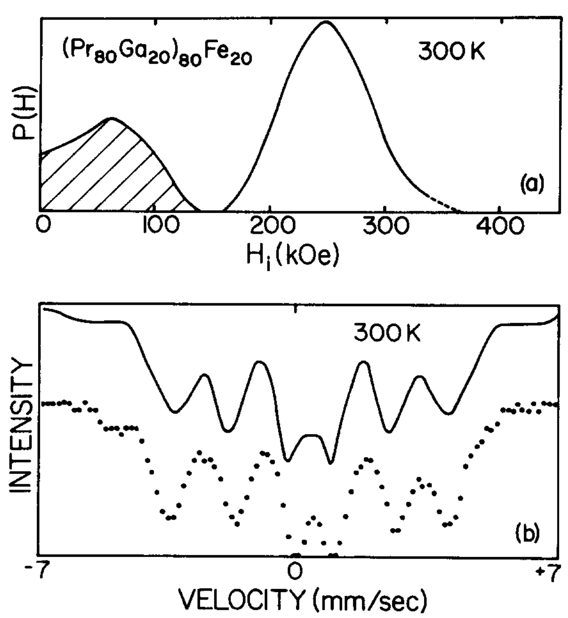

Fig. 3. (a) P(H) curve for $(Pr_{80}Ga_{20})_{80}Fe_{20}$ at 300 K. Spurious data above H ≈ 330 kOe are excluded. (b) Fe^{57} Mössbauer data (points) and fit (solid curve) for P(H) curve in (a).

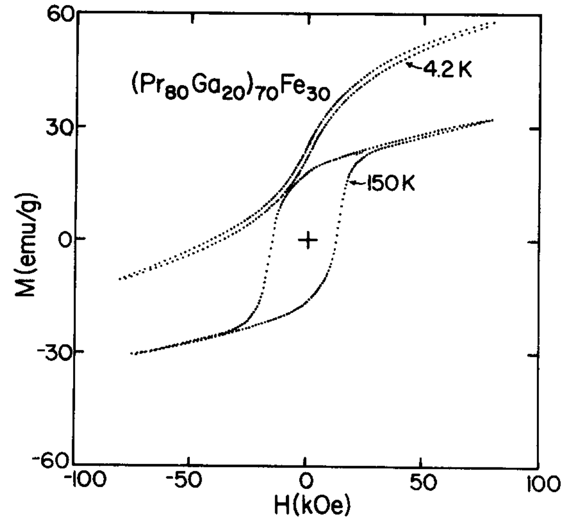

Fig. 4. Field-cooled magnetization data (80 kOe) for $(Pr_{80}Ga_{20})_{70}Fe_{30}$ at 4.2 K and 150 K.

The loop is clearly shifted upward along the magnetization axis but the reversible magnetization is symmetric about H=0. Figure 5 shows the typical temperature dependence of the 'spontaneous' magnetization μ_0 as extrapolated from high field to H=0, and the thermoremanent magnetization μ_{shift}. Above about 100 K the spontaneous moment is very close to what is expected from the Mössbauer measurements for aligned Fe spins in this alloy. In each anisotropic-light-rare-earth alloy with 20% or more Fe similar shifts can be observed and the shift disappears at about 90 K in each case. Figure 6 shows the intrinsic coercive force H_c as a function of temperature for the 10 and 20 percent Pr alloys. For the 30% alloy the maximum value of H_c is 62 kOe at 75 K.

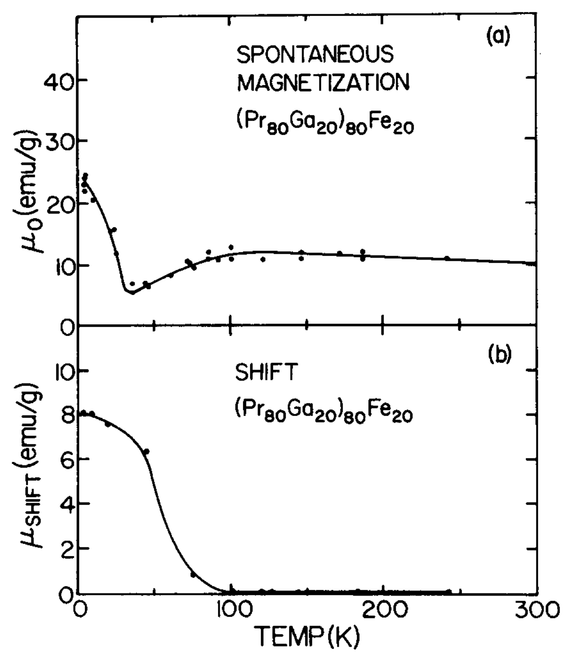

Fig. 5. (a) Spontaneous magnetization for $(Pr_{80}Ga_{20})_{80}Fe_{20}$. (b) Shift along the magnetization axis for a $(Pr_{80}Ga_{20})_{80}Fe_{20}$ specimen cooled from 215 K in an 80 kOe field.

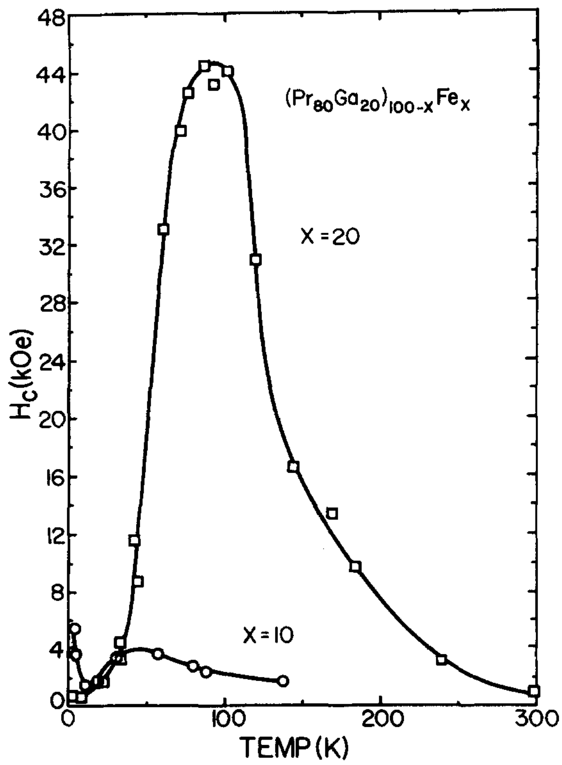

Fig. 6. Coercive force vs. temperature for Pr-based alloys.

DISCUSSION

The results presented above are clear evidence for the presence of at least two magnetic phases occurring because of a phase separation. Several theories have been proposed for high anisotropy materials in which a large value of H_c is predicted when the ratio of anisotropy to exchange exceeds a critical value (12,13). Friedberg and Paul (14) have proposed a domain-wall-pinning theory which considers ferromagnetics with planar defects and which can be applied to amorphous materials. It predicts

$$H_c = \frac{2}{\sqrt{27}} \frac{K_1 W}{M_1 \delta_1} \left(\frac{J_1}{J_2} - \frac{K_2}{K_1} \right) \quad (1)$$

where K_1, J_1 and δ_1 are the anisotropy, exchange and domain-wall-width parameters in the major portion of the sample and K_2, J_2 and W are analogous parameters for the defect region. In a relatively homogeneous single-phase amorphous material we might expect compositional fluctuations throughout the material to give rise to variations in the exchange and anisotropy coefficients between the two regions. Since δ_2 is small in high anisotropy materials, the large H_c observed at low temperatures would be expected. In a two-phase material such as ours, in which the Fe-deficient region is defined as region 2, it is likely that J_2 and K_2 are particularly small. In the limit of large fluctuations between the magnetic properties of the two regions, Eq. (1) becomes invalid. Paul (15) has recently extended the theory to treat this case, and in the limit in which the defect region becomes nonmagnetic, the coercivity approaches the coherent rotation limit

$$H_c = 2K_1/M_1 \quad . \quad (2)$$

If $(H_c)^{1/2}$ for the 20% alloy is plotted against T a straight line is obtained above about 100 K. Extrapolating these data to T=0 gives H_c = 90 kOe. A value of about 100 kOe is estimated from Eq. (2) if reasonable values of $K_1(10^7$ erg/cm$^3)$ and $M_1(200$ emu/cm$^3)$ are assumed. Thus this theory accounts in a natural way for the enhanced coercivity of this two-phase material.

The peak in the coercivity and the shift of the loops below the peak temperature may be explained as follows. At high temperatures it is the magnetic Fe atoms which participate in the reversible magnetization process (along with some paramagnetic contributions). Mössbauer data are consistent with this. The Pr atoms in the Fe-rich region may order speromagnetically and contribute no moment. As the temperature is lowered thermal activation processes weaken and H_c increases as expected. At a critical temperature ($\sim$ 90 K) some Fe atoms become pinned so strongly in some orientation that the available applied field (80 kOe) cannot reorient them along the field direction. Thus as the temperature is lowered, more and more Fe moments become 'frozen' and do not participate in the reversible magnetization process. Since this material has a paramagnetic contribution to the magnetization the observed loops show the sum of a linear magnetization curve and a ferromagnetic loop with $H_c > 80$ kOe. Thus as the temperature drops below 90 K the observed loops are open but relatively narrow; as more Fe moments freeze H_c drops and the loops become even narrower. The shift occurs if the field is applied during the spin-freezing process since the Fe moments tend to align themselves with the field at high temperatures and freeze, thus maintaining a preferred orientation.

In summary these materials appear to represent a class of multiphase amorphous alloys in which fluctuations of exchange and anisotropy are enhanced and thus H_c may be much larger at a given temperature than in a homogeneous, single-phase material. It is possible that inhomogeneities that may be present in multiphase metallic glasses offer a new path for the control of magnetic properties.

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