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Magnetic and structural properties of $PrCo_{3-x}Si_x$ compounds

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We have systematically investigated the magnetic properties of the rare-earth compounds $PrCo_8Si$ and $PrCo_{3-x}Si_x$, the crystal structures of which are hexagonal $CeNi_3$-type and rhombohedral Be_3Nb-type, respectively. Sharp cusps were observed in the real and imaginary parts of the ac susceptibility at temperatures between 282 ($x=0.08$) and 209 K ($x=0.23$). Also observed were bifurcations of the zero-field-cooled and field-cooled magnetization curves at the same temperatures, showing that the magnetization was irreversible below these temperatures. The effect of Si substitution for Co in this system is to decrease the average ferromagnetic exchange interaction, thus decreasing the Curie temperature, without introducing significant random magnetism effects due to exchange fluctuations or random magnetic anisotropy. [S0021-8979(98)46211-X]

I. INTRODUCTION

Considerable effort has been devoted to understanding disordered magnetic systems which can result from exchange fluctuations or random anisotropy.[1–3] Letting $\mathbf{S}_i$ be the spin vector at site i and n_i be a random unit vector whose direction varies independently from site to site, the Hamiltonian describing the system can be written

$$H=-\Sigma(J_0+\Delta J_{ij})\mathbf{S}_i\cdot\mathbf{S}_j-D\Sigma(\mathbf{n}_i\cdot\mathbf{S}_i)^2, \tag{1}$$

where J_0 is an average exchange interaction, ΔJ_{ij} is the fluctuations in the exchange interactions, and D is a measure of the strength of the random anisotropy.[4] For real materials, both exchange fluctuations and random anisotropy should be taken into consideration. In the case of $D\approx 0$, for example materials containing isotropic rare-earth elements, there is a possibility for a spin-glass phase (SG) or a re-entrant spin glass phase (RSG) as a disordered state. However, if ΔJ_{ij} is negligible compared to D, a random magnetic anisotropy (RMA) glass phase may appear. In such a case the above equation becomes the Harris–Plischke–Zuckermann Hamiltonian on which much of the theory of the RMA problem is based.[5] Almost all of the materials studied previously can be classified as either SG or RMA, which avoids difficulties in separating an exchange-fluctuation effect and a random-anisotropy effect.

In this study we have sought to investigate the above effects in an intermetallic compound system, $PrCo_{3-x}Si_x$, in which one expects strong single-ion anisotropy from the Pr, and a weakening average exchange (J_0) from the Si doping. The presence of any randomness is anisotropy or significant exchange fluctuation was also a subject for study.

II. EXPERIMENTAL PROCEDURE

Bulk samples of $PrCo_{3-x}Si_x$ ($x=0.0$–0.23) were prepared by arc melting in purified argon gas. The starting elements all had purity higher than 99.9%. The compositions of the samples were determined from the initial weights of the component elements and checked by weighing after melting. The alloys were subsequently homogenized for 100 h at 800 °C in vacuum. The crystal structures were determined by x-ray diffraction using Cu $K\alpha$ radiation and a graphite monochromator. The magnetization was measured by a Faraday balance and a superconducting quantum interference device (SQUID) magnetometer over the temperature range from 5 to 500 K. Powdered samples were used for SQUID measurements so that individual grains could rotate freely along the direction of the applied magnetic field. The ac susceptibility measurements for the bulk samples were performed with a driving frequency between 10 and 1600 Hz and a driving field of 1 Oe.

III. RESULTS AND DISCUSSION

Figure 1 shows the x-ray diffraction scans for the $PrCo_{3-x}Si_x$ samples with various x values. It is found that the pattern for the $x=0.0$ sample was almost entirely single phase $PrCo_3$. Upon adding silicon up to $x=0.23$ the diffraction patterns did not change basically except for that a very small peak around $2\theta=44.5°$ (indicated by lower triangle) appeared in some of the alloys. This peak is likely due to ferromagnetic Pr_2Co_7. However, the effect of this small amount of Pr_2Co_7 on the magnetic properties discussed here could be accounted for easily.

The temperature dependence of magnetization for the $x=0.17$ sample is shown in Fig. 2. After initial zero-field cooling, the magnetization was measured in a 50 Oe applied field as the temperature was raised to 300 K [solid circles in Fig. 2(a)]. A peak at a temperature around 225 K was found. In subsequent cooling in the same applied field, the magnetization followed the same curve until it reached the peak. Below that temperature, it followed another path, showing a thermal hysteresis. The temperature at which the bifurcation of the zero-field-cooled (ZFC) and the field-cooled (FC) magnetization curves appears, decreases with an increasing applied magnetic field, as shown for the case of $H=1000$ Oe in Fig. 2(b).

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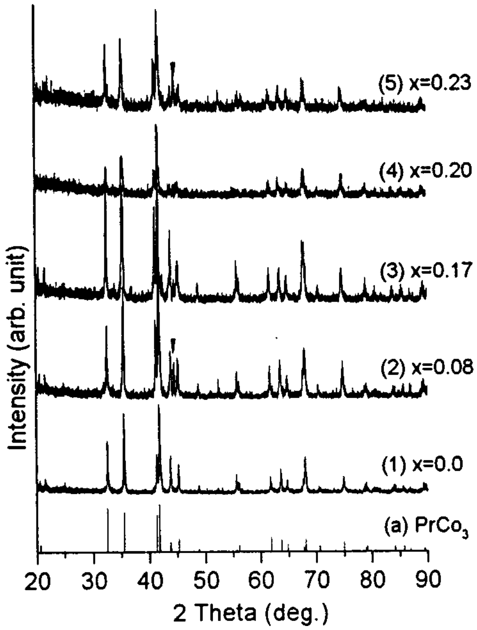

FIG. 1. X-ray diffraction scans for the $PrCo_{3-x}Si_x$ samples: (1) $x=0.08$, (2) 0.17, (3) 0.20, and (4) 0.23, and (a) peak intensities for $PrCo_3$ from (JCPDS) database.

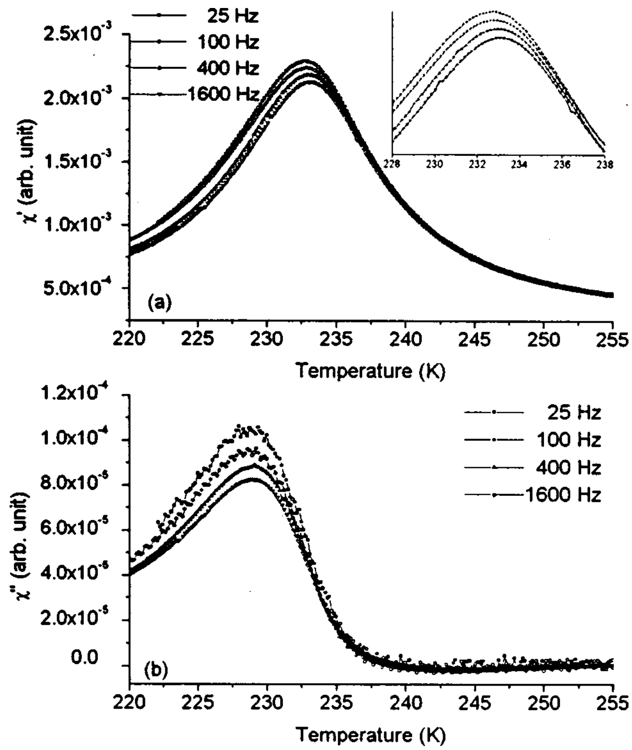

FIG. 3. Frequency dependence of in-phase (a) and out-of-phase (b) ac susceptibility of $PrCo_{3-x}Si_x$ for $x=0.17$ and $\nu=25$, 100, 400, and 1600 Hz. The inset shows the cusps in more detail.

Figure 3 shows the in-phase (χ') and out-of-phase (χ'') components of the ac susceptibility for the $x=0.17$ sample. Sharp cusps are found in both the χ' and χ'' curves in the same temperature region where the bifurcation appears on the FC and ZFC magnetization curves. It should be noticed that the peak in χ' shifts towards a higher temperature with increasing frequency, suggesting that thermally activated processes are significant. In addition, the peak in $\chi'(T)$ corresponds to the maximum slope in $\chi''(T)$, $(d\chi''/dT)_{\max}$.

In order to get an insight into the effect of the Si substitution on the interaction parameters of Eq. (1), the Si content

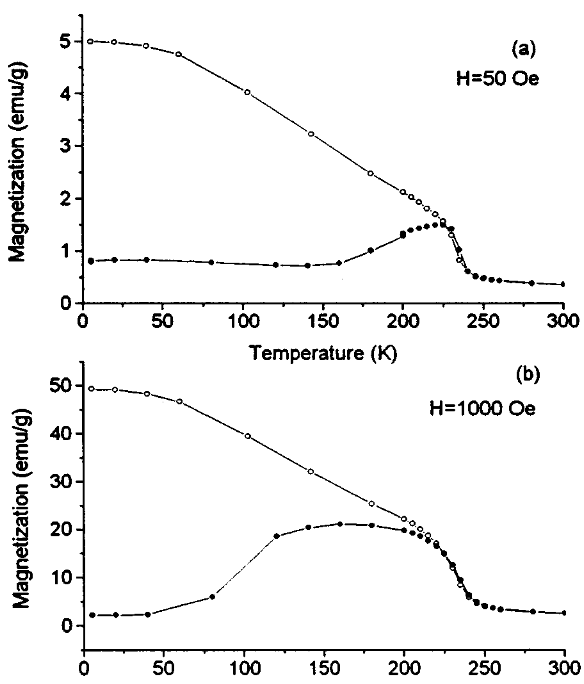

FIG. 2. Zero-field-cooled (solid) and field-cooled (open) magnetization vs temperature of $PrCo_{3-x}Si_x$ for $x=0.17$, measured at applied field of 50 Oe (a) and 1000 Oe (b).

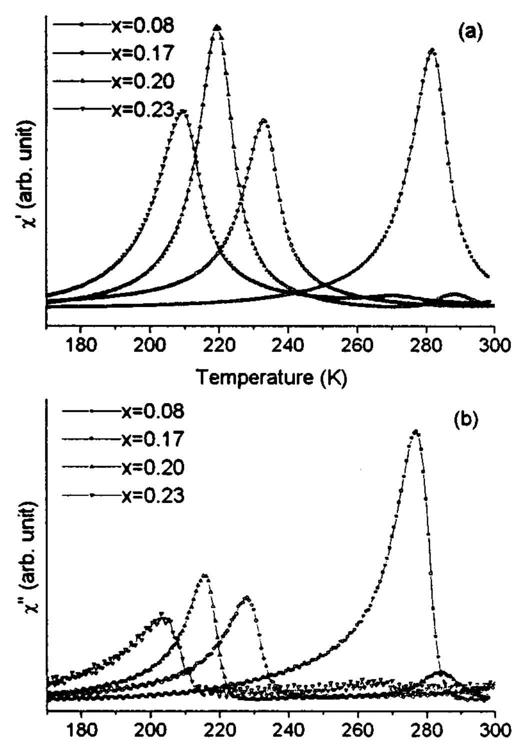

FIG. 4. In-phase (a) and out-of-phase (b) ac susceptibility vs temperature of $PrCo_{3-x}Si_x$ for $x=0.08$, 0.17, 0.20, and 0.23.

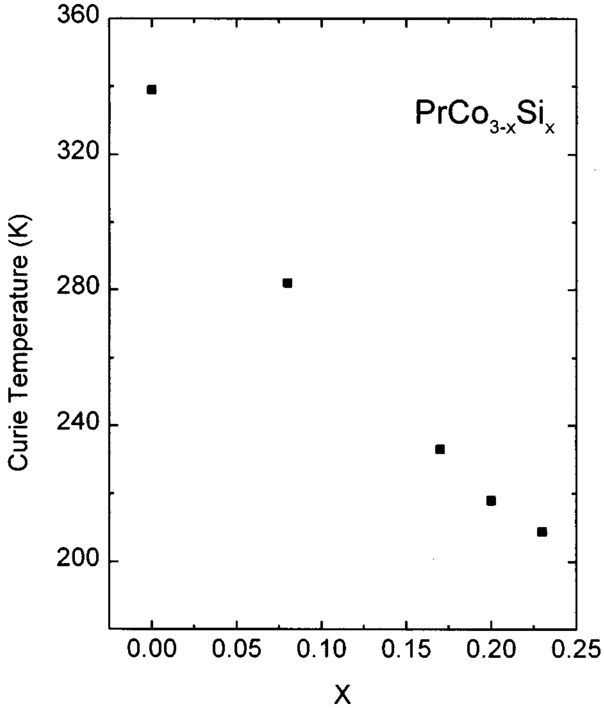

FIG. 5. Estimated Curie temperature of $PrCo_{3-x}Si_x$ as a function of x.

dependence of ac susceptibility was investigated. Figure 4 shows the χ' and χ'' versus temperature curves for the $x=0.08$, 0.17, 0.20, and 0.23 samples. Sharp cusps appear in both χ' and χ'' curves for all the samples at temperatures between 282 K ($x=0.08$) and 209 K ($x=0.23$). Although these measurements could not be extended above 300 K, χ' for the $x=0.0$ sample increases with temperature up to 300 K, suggesting that it will also exhibit a sharp cusp near the Curie temperature of 339 K. It was also found from the SQUID measurement that the magnetization becomes irreversible below each cusp temperature. The additional small peaks appearing on the high temperature side of the ac susceptibility peak for the $x=0.20$ and 0.23 samples may be due to the presence of a small amount of the Pr_2Co_7 phase. Magnetization measurements in the $x=0.0$ sample show an abrupt drop in the magnetization as the temperature increases above 339 K, suggesting the presence of a ferromagneticlike transition at that temperature.

The binary compound $PrCo_3$, was reported by Yakinthos *et al.*[6] and Buschow *et al.*[7] to be ferromagnetic with the easy direction along c axis below the Curie temperature of $T_c=349$ and 339.5 K, respectively, and our temperature dependent magnetization measurements are consistent with this.

Figure 5 shows the Si-concentration dependence of the Curie temperature as measured by the temperature of the peak in χ'. It can be seen that the decrease with x is clearly nonlinear in x. In a simple mean-field model $T_c \propto zJ_0$, where z is the number of nearest-neighbor magnetic ions and J_0 is the average exchange of Eq. (1). However, this model is not realistic for $PrCo_{3-x}Si_x$ alloys because the exchange interactions are quite sensitive to local environments. (It should be noted that YCo_2, for example, is not magnetic.[8]) A spin-fluctuation model for which $T_c \propto M_s^2/\chi_0$, where χ_0 is the exchange-enhanced susceptibility, is likely to be more appropriate.[9] For example, if χ_0 is assumed to be constant and M_s to vary linearly in x, then $T_c(x)$ would change in a nonlinear way as seen in Fig. 5.

The relatively sharp peaks in χ' and χ'' are of interest because they are reminiscent of spin-glasslike freezing due either to random anisotropy or exchange fluctuations. However, in this series of alloys, with relatively small Si doping levels, it seems likely that any such effects are small perturbations on a basically ferromagneticlike system whose positive exchange interactions are weakened by Si addition. The sharp susceptibility peaks can be understood in terms of a model developed by Buschow and Brouha[10] for rare earth-cobalt alloys based on RCo_5. In such compounds, where there is large single-ion anisotropy due to the rare earths, domain walls can be pinned by the lattice but thermal irreversibilities such as observed in Fig. 2, can be caused by thermally assisted domain-wall motion. This also could lead to the sharp cusps in susceptibility at T_c.

IV. CONCLUSIONS

In summary, $PrCo_{3-x}Si_x$ represents a diluted ferromagnetic system with a decreasing exchange and Curie temperature with an increasing Si concentration. The sharp ac susceptibility peaks and nonlinear variation of T_c can be rationalized on the basis of an itinerant spin-fluctuation model and thermally activated pinning of domain walls.

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