Effects of Co substitution on magnetic properties of $Pr_3(Fe_{1-x}Co_x)_{27.5}Ti_{1.5}$ ($x=0-0.3$)

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X-ray diffraction carried out on random and oriented samples of $Pr_3(Fe_{1-x}Co_x)_{27.5}Ti_{1.5}$ ($x=0$, 0.1, 0.2, 0.3) showed that the easy magnetization direction is near the b axis for $x=0$, 0.2, and 0.3 and is almost along the b axis for $x=0.1$. Magnetic hysteresis data taken on oriented samples showed that the anisotropy field (H_A) varies from 12 kOe for $x=0$ to 25 kOe for $x=0.3$ at 300 K. At 10 K, H_A increases from 55 kOe for $x=0.1$ to 70 kOe for $x=0.3$. An indication of spin reorientation transition has been observed at ~250 K in $x=0.3$. © *1999 American Institute of Physics.* [S0021-8979(99)56708-X]

I. INTRODUCTION

The new class of intermetallic compounds, $R_3(Fe,TM)_{29}$ (3:29 compounds) which are structurally related to both the 2:17 and the 1:12 phase have attracted special attention because of their potential for permanent magnet applications.[1] Kalogirou *et al.*[2] using powder x-ray diffraction (XRD) reported the structure of this new ternary compound to be monoclinic, having a space group $A2/m$. Recently, we reported the substitution of Co for Fe in Pr containing 3:29 compounds.[3] The alloys, $Pr_3(Fe_{1-x}Co_x)_{27.5}Ti_{1.5}$ ($x=0$, 0.1, 0.2, 0.3) were synthesized and characterized by XRD. From the detailed structural analysis by Rietveld refinement of the XRD patterns, it was estimated that the weight percentage of the 3:29 phase ranged from 93 to 97 with the rest being α-Fe for the $x=0$, 0.1, and 0.2 compounds. Neither the 1:12 phase nor the 2:17 phase, which has the normal impurities observed in the 3:29 phase, was confirmed by XRD for $x=0$, 0.1, and 0.2 compounds. However, in the case of $x=0.3$, traces of a (Co/Fe)–Ti(1:12) (~1–2 wt %) phase is seen in addition to the α-Fe phase.

Magnetization studies carried out in the temperature range of 5–1027 K up to a field of 5 T revealed very interesting results. The increase in saturation magnetization at 5 and 300 K with increasing Co content has been explained based on a rigid band model. It was found that the Curie temperature increases by 185° for $x=0.1$ and by approximately 110° for each of the next two Co concentrations. Such a large increase may be because of the strengthening of the exchange by preferential occupation of Co in some of the sites where there is an antiparallel coupling between the Fe moments. In order to determine the potential applications of these novel compounds, $Pr_3(Fe_{1-x}Co_x)_{27.5}Ti_{1.5}$ ($x=0$, 0.1, 0.2, 0.3) we have carried out detailed magnetization measurements on the oriented samples to find the nature of the anisotropy fields present and we report these results in this article.

II. EXPERIMENTAL DETAILS

The preparation of $Pr_3(Fe_{1-x}Co_x)_{27.5}Ti_{1.5}$ ($x=0.0$, 0.1, 0.2, 0.3) compounds was reported earlier.[3] The oriented samples were prepared in the following way. Initially, ingots were pulverized to approximately a 20 μm size. This powder was mixed with a binder spread on a plastic substrate and subjected to a field of 1.2 T until the binder dried. Following the same procedure, the particles were oriented both in the plane of the substrate as well as perpendicular to the plane of the substrate. X-ray diffraction data were obtained using Fe $K\alpha$ radiation. The hysteresis loops were measured up to a field of 5 T using a superconducting quantum interference device (SQUID) magnetometer at 10 and 300 K. Low field magnetization measurements were carried out to find possible spin reorientations occurring in the system. The compounds were initially saturated at 5 T at 10 K and then the field was reduced to 5 kOe. At this field, the magnetization studies were carried out in the temperature range of 10–300 K.

III. RESULTS AND DISCUSSION

X-ray diffraction data taken for random, aligned (perpendicular and parallel) $Pr_3(Fe_{1-x}Co_x)_{27.5}Ti_{1.5}$ ($x=0.0$, 0.1, 0.2, 0.3) samples are shown in Figs. 1(a)–1(c), respectively. The XRD data for the randomly oriented samples [Fig. 1(a)] shows all reflections corresponding to the monoclinic $A2/m$ space group. The perpendicularly oriented samples [Fig. 1(b)] showed interesting results. In the case of $x=0$, a strong reflection corresponding to (040) and weak reflections corresponding to (311), (23−1), (322), (13−3), (204), (142), and (520) are seen. This implies that the easy magnetization direction (EMD) is near the b axis. However in the case of $x=0.1$, the reflection corresponding to (040) is very strong the rest being weak suggesting that the EMD is almost along the
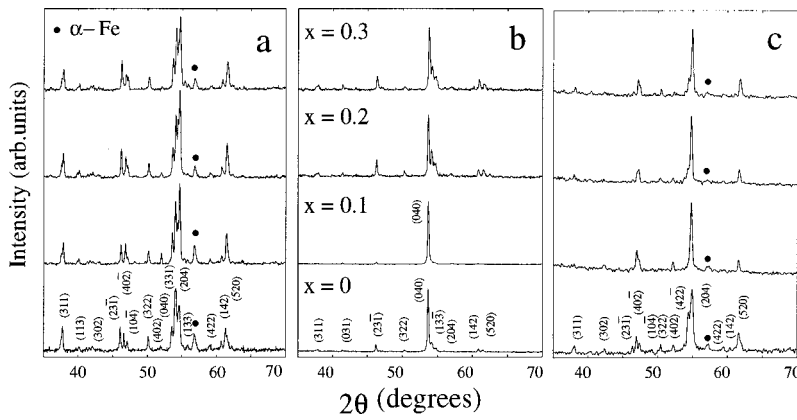
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FIG. 1. XRD spectra of $Pr_3(Fe_{1-x}Co_x)_{27.5}Ti_{1.5}$ compounds (a) randomly oriented, (b) magnetically aligned with the magnetic field perpendicular to the substrate, and (c) magnetically aligned with the magnetic field parallel to the substrate.

b axis. In the case of $x=0.2$ and 0.3, the patterns are similar to that observed in $x=0$. In parallel oriented samples, except for $x=0$, in all other compounds, the $(h01)$ reflections are prominent with (520) reflection present, suggesting that the hard direction of magnetization is almost in the *ac* plane.

Magnetic hysteresis data taken on parallel and perpendicularly oriented samples (at 10 and 300 K) are shown in Figs. 2(a) and 2(b), respectively. Anisotropy fields (H_A) evaluated using the method of Velge and Buschow[4] are shown in Table I. H_A increased from 12 kOe for $x=0.1$ to 25 kOe for $x=0.3$ at 300 K. When the temperature was lowered to 10 K, there was a dramatic increase in the values of H_A to 55 kOe for $x=0.1$ and to 70 kOe for $x=0.3$. The saturation magnetization (M_s) and Curie temperature (T_C) reported earlier are given in Table I.[3] The M_s is nearly constant at both 5 and 300 K with increasing Co substitution. Since $H_A=2K_1/M_s$, it can be inferred that there is an increase in

the first order magnetocrystalline anisotropy constant (K_1) with increasing Co concentration. The K_1 for the R sublattice can be written as[5]

$$K_1 = -(3/2)\alpha_j \langle r_{4f}^2 \rangle \langle 3J_z^2 - J(J+1) \rangle A_2^0,$$

where α_j is the second order Stevens coefficient, $\langle r_{4f}^2 \rangle$ is the average of r^2 over the radial wave function of $4f$ electrons, J and J_z are the total and z component of the total angular momentum, and A_2^0 is the second order crystal field parameter. As a consequence of Co substitution for Fe, there will be an influence on the second order crystal field parameter, thereby increasing the total anisotropy. Sometimes domain wall pinning which is associated with the smaller domain wall width $\sim [(T_C/K_1)^{1/2}]$ can be observed in materials possessing a large anisotropy field, particularly at low temperatures where K_1 has a very large value.[6] In $Pr_3(Fe_{1-x}Co_x)_{27.5}Ti_{1.5}$ ($x=0$, 0.1, 0.2, 0.3) compounds, both K_1 and T_C increase with an increase of the Co content, and domain wall pinning is not observed.

To examine spin reorientation in $Pr_3(Fe_{1-x}Co_x)_{27.5}Ti_{1.5}$ ($x=0$, 0.1, 0.2, 0.3) compounds, the temperature of the magnetization was varied from 10 to 300 K and the normalized $M(T)$ data are shown in Fig. 3. In the case of $x=0$, the usual behavior of monotonic decrease in the magnetic moment with an increase in temperature is observed. However, in the case of $x=0.1$, 0.2, and 0.3, it is observed that the magnetic moment increases initially with an increase in temperature, reaches a maximum of around 180 K, and then falls off rapidly. This is probably because, at low temperatures since the anisotropy field is very large in Co substituted compounds, the applied field of 5 kOe is not large enough to saturate the magnetization, leading to a lower value of magnetization. With increasing temperature, anisotropy de-
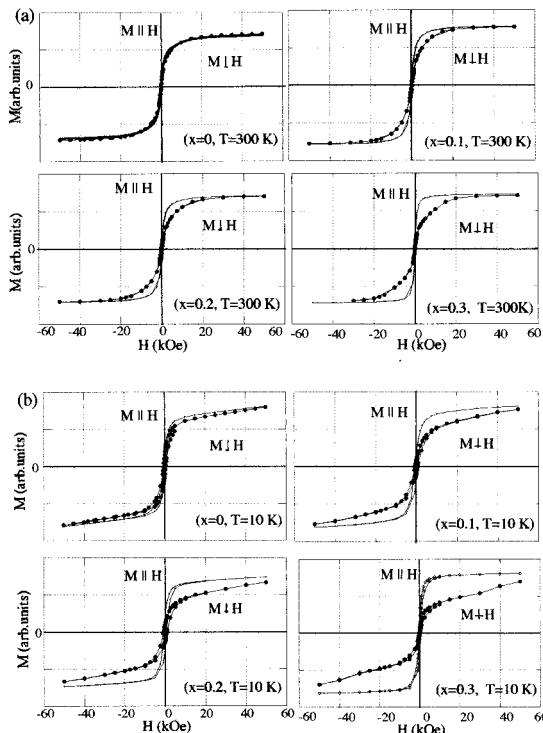

FIG. 2. Hysteresis curves for $Pr_3(Fe_{1-x}Co_x)_{27.5}Ti_{1.5}$ along and perpendicular to the direction of orientation at (a) 10 and (b) 300 K.

TABLE I. Saturation magnetization (M_s), anisotropy field (H_A) at 10 and 300 K, and Curie temperature (T_C) of $Pr_3(Fe_{1-x}Co_x)_{27.5}Ti_{1.5}$.

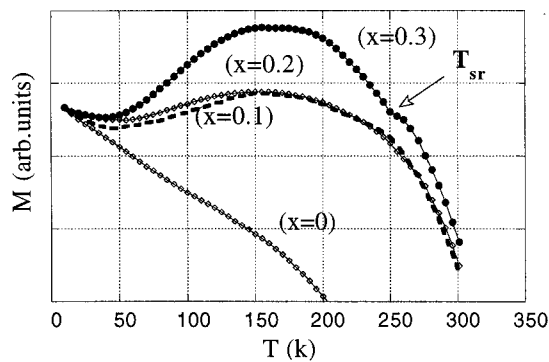|	M_s (emu/g)		H_A (kOe)		T_C (K)
X	300 K	5 K	300 K	10 K	(3-29 phase)
0	124.8	172.0			393
0.1	142.9	172.6	12	55	572
0.2	153.3	175.1	20	60	685
0.3	157.1	177.3	25	70	793

FIG. 3. Normalized plot of M vs T for $Pr_3(Fe_{1-x}Co_x)_{27.5}Ti_{1.5}$ with the magnetic fields perpendicular to the direction of orientation.

creases, leading to an increase in the magnetization. In the case of $x = 0.3$, an anomaly at about 250 K is observed, indicating a possible spin reorientation. Mössbauer, ac susceptibility and specific heat measurements are being carried out to confirm the possible spin reorientation transitions occurring in these compounds.

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