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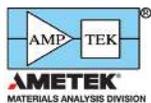
Citation: *Journal of Applied Physics* **99**, 08P301 (2006); doi: 10.1063/1.2167052

View online: <https://doi.org/10.1063/1.2167052>

View Table of Contents: <http://aip.scitation.org/toc/jap/99/8>

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(Presented on 2 November 2005; published online 20 April 2006)

The effect of Al on the structural and magnetic properties of $\text{Pr}_3(\text{Fe}_{1-x}\text{Al}_x)_{27.5}\text{Ti}_{1.5}$ ($x=0.1, 0.2,$ and 0.3) compounds has been investigated by x-ray-diffraction, magnetization, and Curie temperature measurements. All these compounds have formed in monoclinic symmetry with $A2/m$ space group with $\text{Pr}(\text{Fe}, \text{Ti})_{12}$ as secondary phase and traces of α -Fe. The monotonic decreases in M_S both at 300 and 80 K are discussed on the basis of electron transfer from the $3p$ band of Al to the $3d$ band of Fe near E_F . The variations in T_C are explained using the Friedel approach. In all the compounds, the easy magnetization direction is away from the b axis. © 2006 American Institute of Physics. [DOI: 10.1063/1.2167052]

INTRODUCTION

The findings of $\text{Nd}_2(\text{Fe}, \text{Ti})_{29}$ by Collocott *et al.* in 1992 (Ref. 1) recognized as having $\text{Nd}_3(\text{Fe}, \text{Ti})_{29}$ (3:29) stoichiometry with monoclinic symmetry²⁻⁵ and $A2/m$ space group (with 11 inequivalent sites for Fe and 2 inequivalent sites for R) have led to the addition of 3:29 compounds to several of the R - TM intermetallics, viz., RCO_5 (hexagonal), $\text{R}_2(\text{Fe}, \text{TM})_{17}$ (2:17 hexagonal or rhombohedral), $\text{R}(\text{Fe}, \text{TM})_{12}$ (1:12 tetragonal), and $\text{Nd}_2\text{Fe}_{14}\text{B}$ (tetragonal) for permanent magnet applications. The 3:29 compounds are reported to be stable at high temperatures (>1000 °C) (Ref. 6) and the formation of this phase strongly depends on the composition of the stabilizing element(s) and the heat treatment parameters. Yang *et al.* reported⁷ that from the compound $\text{Sm}_{10}\text{Fe}_{85}\text{Ti}_5$, 3:29 phase could be obtained after annealing at 1000 °C followed by water quenching, the 2:17 phase could be formed as major phase when heat treated at 1100 °C followed by air quenching, and the hexagonal TbCu_7 phase could be realized when heat treated at 1200 °C followed by water quenching. The enhancement of magnetic properties of $\text{Sm}_3(\text{Fe}, \text{Ti})_{29}$ by interstitial modifications by nitrogen⁸ has resulted in considerable investigations on the magnetic properties of the 3:29 compounds with $R = \text{Y}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Tb}, \text{Dy},$ and Er and a stabilizing element $\text{TM} = \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{W}, \text{Ta},$ and Si for permanent magnet applications.²⁻⁵ Shah *et al.*⁹ have observed a first-order magnetization process (FOMP) in $(\text{Sm}_{0.2}\text{Pr}_{0.8})_3\text{Fe}_{27.5}\text{Ti}_{1.5}$ compound and uniaxial anisotropy in $(\text{Sm}_{0.5}\text{Pr}_{0.5})_3\text{Fe}_{27.5}\text{Ti}_{1.5}\text{N}_5$ compound. The substitution of Al

has been reported to cause the anisotropy to become uniaxial in $(\text{Sm}_{0.9}\text{Pr}_{0.1})_3(\text{Fe}_{1-x}\text{Al}_x)_{27.5}\text{Ti}_{1.5}$ compounds.¹⁰ However, the magnetization and Curie temperature have been seen to decrease with Al substitution. The effect of Co substitution on the magnetic properties of $\text{Pr}_3(\text{Fe}_{1-x}\text{Co}_x)_{27.5}\text{Ti}_{1.5}$ (Refs. 11 and 12) compounds has been reported to increase the Curie temperature (T_C), anisotropy, and magnetization. In this paper, the effect of Al substitution for Fe on the magnetic properties of $\text{Pr}_3\text{Fe}_{27.5}\text{Ti}_{1.5}$ is reported.

EXPERIMENTAL DETAILS

All the compounds were prepared by arc furnace under argon atmosphere starting with highly pure elements (Pr with 99.9%, Fe and Al with 99.95%, and Ti with 99.99%). The ingots were melted several times to ensure homogeneity. The weight loss after the melting was ensured to be less than 0.5%. The ingots were wrapped in a tantalum foil and sealed in a quartz tube under vacuum (10^{-6} mbar), homogenized at 1050 °C for five days, and was then subsequently quenched in water. Phase identification and structural characterization were carried out by powder x-ray-diffraction patterns employing $\text{Fe } K_\alpha$ radiation and microstructural analyses by scanning electron microscope (SEM) (using LEO 440i scanning electron microscope) and energy dispersive x ray (EDX) (Oxford ISIS300 ultracool energy dispersive x-ray SiLi detector). Magnetization measurements were carried out using a PAR model 155 vibrating-sample magnetometer (VSM) up to an applied field of 12 kOe. In order to determine the easy direction of magnetization (EMD) and the nature of anisotropy, the powder of samples were mixed with a 5 min epoxy resin and arresting the moments by keeping the sample holder geometry parallel and perpendicular to an external magnetic field of 2.4 T. X-ray-diffraction (XRD)

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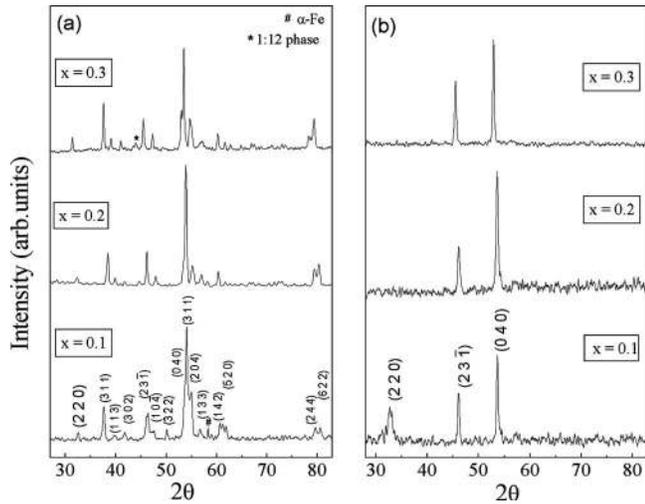


FIG. 1. XRD patterns of (a) random and (b) aligned powders of $\text{Pr}_3(\text{Fe}_{1-x}\text{Al}_x)_{27.5}\text{Ti}_{1.5}$.

patterns on the magnetically oriented sample (keeping the sample holder perpendicular to the field) were taken to identify the EMD.

RESULTS AND DISCUSSION

Figure 1(a) shows the powder XRD patterns of $\text{Pr}_3(\text{Fe}_{1-x}\text{Al}_x)\text{Ti}_{1.5}$ ($x=0.1, 0.2,$ and 0.3) compounds. It is observed that all the compounds have formed with 3:29 phase as the major phase with monoclinic structure and 1:12 phase as the secondary phase and traces of $\alpha\text{-Fe}$. The patterns were indexed according to $A2/m$ space group. Several attempts to stabilize the 3:29 phase in this series of compounds with $x=0.4$ and 0.5 failed. The lattice parameters are listed in Table I.

It is seen that there is an increase in the lattice parameters and thus the cell volume on increasing the Al concentration. This is due to the larger atomic size of Al replacing a smaller Fe atom. Figure 2 shows a typical backscattered electron image (BSE) of the $\text{Pr}_3(\text{Fe}_{0.8}\text{Al}_{0.2})_{27.5}\text{Ti}_{1.5}$ by SEM, which shows the presence of impurity phases (as dark spots) in addition to the main 3:29 phase. The energy dispersive x-ray

TABLE I. Lattice parameters and magnetic parameters of $\text{Pr}_3(\text{Fe}_{1-x}\text{Al}_x)_{27.5}\text{Ti}_{1.5}$ compounds.

| x | 0 ^a | 0.1 | 0.2 | 0.3 |
|-------------------------------|----------------|--------|--------|--------|
| $a(\text{\AA}) \pm 0.002$ | 10.640 | 10.614 | 10.631 | 10.753 |
| $b(\text{\AA}) \pm 0.002$ | 8.600 | 8.699 | 8.611 | 8.658 |
| $c(\text{\AA}) \pm 0.002$ | 9.755 | 9.797 | 9.923 | 10.077 |
| $\beta(\text{deg}) \pm 0.002$ | 96.910 | 96.729 | 97.744 | 96.799 |
| $V(\text{\AA})^3$ | 887 | 897 | 907 | 937 |
| $M_S(\text{emu/g})$ | 124 | 108 | 84 | 59 |
| 300 K | | | | |
| $M_S(\text{emu/g})$ | ... | 119 | 105 | 103 |
| 80 K | | | | |
| $T_C(\text{K})$ | 393 | 396 | 408 | 326 |
| $H_A(\text{kOe})$ | | 24 | 18 | 14 |

^aData from Ref. 9.

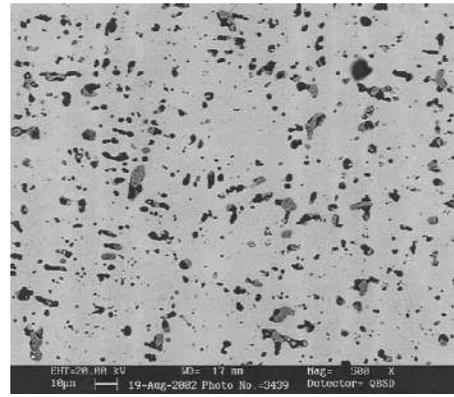


FIG. 2. BSE image of $\text{Pr}_3(\text{Fe}_{0.8}\text{Al}_{0.2})_{27.5}\text{Ti}_{1.5}$ using SEM.

spectrum for the same reveals that the matrix, dark, and grey phases are $\text{Pr}_3(\text{Fe}_{1-x}\text{Al}_x)\text{Ti}_{1.5}$ (88%), $\alpha\text{-Fe}$ (5%), and $\text{Pr}(\text{Fe}, \text{Ti})_{12}$ (7%), respectively.

Figure 3 shows the magnetization curves out at 300 K (open symbols) and 80 K (solid symbols). The magnetization at 300 K is seen to nearly saturate in all the compounds whereas, at 80 K, the magnetizations of the $x=0.2$ and 0.3 compounds are seen not to saturate, indicative of an increase in the anisotropy. The saturation magnetization values (M_S) were therefore determined by Honda plots and are listed in Table I. The values of M_S are seen to decrease with increasing Al concentration. Similar decreases in M_S have been reported in Al-substituted 2:17 compounds.^{13–15} Ming-Zhu and Ching¹⁶ have attributed the decrease in the average Fe moment and hence the magnetization upon Al substitution in $\text{Nd}_2\text{Fe}_{17}$ compounds to the transfer of charges from the $3p$ band of Al lying at the bottom of the $3d$ band of Fe, to the $3d$ band. In the present case too, a similar charge transfer may be responsible for the decrease of magnetization with Al content. The spin-up subband could be almost completely filled near the Fermi level (E_F) and consequently any additional transfer of electrons could start filling the spin-down subband thereby decreasing the difference between the density of states (DOS) of spin-up and spin-down subbands and hence decrease in magnetization.

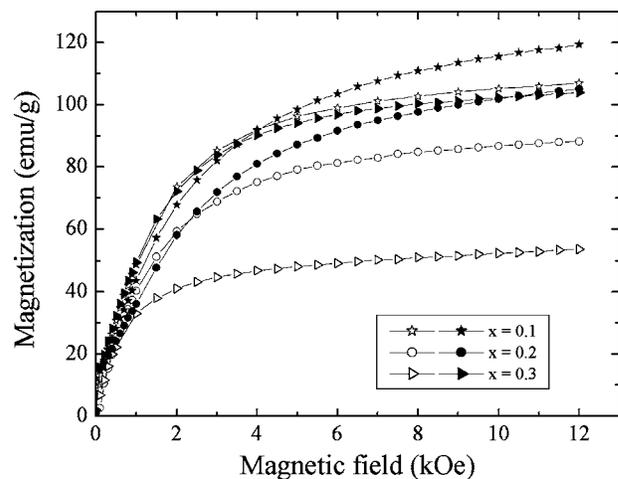


FIG. 3. Magnetization curves of $\text{Pr}_3(\text{Fe}_{1-x}\text{Al}_x)_{27.5}\text{Ti}_{1.5}$ compounds at 300 K (open symbols) and at 80 K (solid symbols).

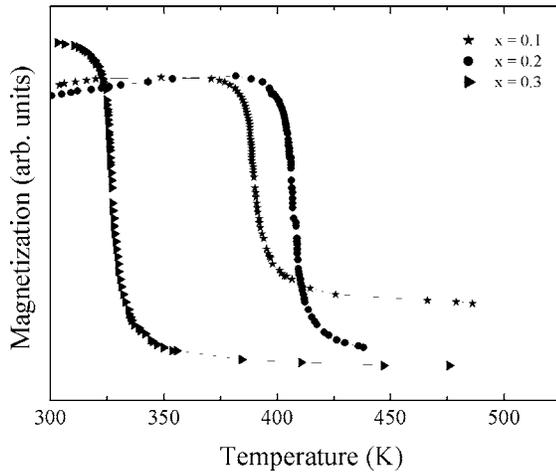


FIG. 4. Curie temperature variations in $\text{Pr}_3(\text{Fe}_{1-x}\text{Al}_x)_{27.5}\text{Ti}_{1.5}$.

The temperature variations of magnetization (in a constant field $H=50$ Oe) $\text{Pr}_3(\text{Fe}_{1-x}\text{Al}_x)\text{Ti}_{1.5}$ ($x=0.1, 0.2,$ and 0.3) compounds are shown in Fig. 4. The Curie temperatures (T_C) are shown in Table I. It is seen that T_C increases slightly from 393 K for the $x=0$ compound to 408 K for the $x=0.2$ compound and then decreases to 326 K for $x=0.3$. Such a variation could be explained on the basis of the model proposed by Friedel¹⁷ which was used to explain the variation of T_C upon substitution of Al in $(\text{Er}_{0.5}\text{Pr}_{0.5})_2\text{Fe}_{1-x}\text{Al}_x$ compounds.¹⁸ According to this model there is an empirical relation existing between the T_C and effective magnetic moment per atom μ_{eff} .

$$T_C = C\mu_{\text{eff}}^2 \left(\frac{\lambda}{d} \right), \quad (1)$$

where C is a constant in units of K/μ_B^2 , λ is the distance covered by the first peak of Friedel oscillations, and d is the interatomic distance. The interaction between the magnetic moments would be strong and ferromagnetic if the distance d between them is smaller than λ , i.e., if $(\lambda/d) > 1$. In the case of substitutionally modified (by Al or Ga) compounds, even though the μ_{eff} decreases with Al content, the increase in (λ/d) predominates initially, leading to an increase in T_C for initial concentrations. However, with further substitution of Al reduction in μ_{eff} dominates, leading to a decrease in T_C .

The x-ray-diffraction patterns on the magnetically oriented powders ($H \perp$ to the plane of the sample holder) of the samples are shown in Fig. 1(b). It is observed that for the compound with $x=0.1$, the $(2\ 2\ 0)$, $(0\ 4\ 0)$, and $(2\ 3\ -1)$ peaks are present whereas for the other two compounds only $(0\ 4\ 0)$ and $(2\ 3\ -1)$ are present, indicating a tendency for the EMD to be towards the monoclinic b axis with the increase in the Al content. Han *et al.*¹⁹ and Courtois *et al.*²⁰ have reported the relationship between the (h, k, l) values of

$3:29$, $1:12$, and $2:17$ and RTM_5 systems. According to this, $(0\ 4\ 0)$ corresponds to the monoclinic b axis and $(2\ 3\ -1)$ corresponds to $(3\ 0\ 0)$ of hexagonal $R_2(\text{Fe}, \text{TM})_{17}$ showing that the EMD is axial in the $2:17$ and $3:29$ settings. However, magnetization measurements carried out on magnetically oriented samples show a decrease in anisotropy field H_A with increasing Al concentration.

CONCLUSIONS

Al-substituted $\text{Pr}_3(\text{Fe}_{1-x}\text{Al}_x)_{27.5}\text{Ti}_{1.5}$ ($x=0.1, 0.2,$ and 0.3) compounds have been successfully prepared and the role of Al on the structure and magnetic properties is studied. The expansion of unit-cell volume is attributed to the atomic size of Al replacing a smaller Fe. The decrease in the magnetization with increasing Al is attributed to the modification in the DOS due to transfer of electrons from the $3p$ band of Al to the $3d$ band of Fe. The variation in T_C with Al content is explained on the basis of the Friedel model. The anisotropy is seen to decrease with increasing Al content.

ACKNOWLEDGMENT

The authors thank the Government of India for funding the project.

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