# Substituting Al for Fe in $Pr(Al_xFe_{1-x})_{1.9}$ alloys: Effects on magnetic and magnetostrictive properties*

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The magnetostrictive effects of substituting Al for Fe in $Pr(Al_xFe_{1-x})_{1.9}$ ($x = 0.0$, 0.02, 0.05, 0.10) alloys between 5 K and 300 K were investigated. The substitution decreases the Curie temperature and the value of $\lambda_{111}$. Fortunately, the substitution slightly increases the magnetostriction in a low magnetic field, which imbues these materials with potential advantages for applications. Rotation of the easy magnetization direction (EMD) from [111] to [100] in the $Pr(Al_{0.02}Fe_{0.98})_{1.9}$ alloy as temperature decreases was detected by step scanned XRD reflections.

**Keywords:** magnetostriction, magnetizations, easy magnetization direction

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## 1. Introduction

In applications of magnetostrictive materials, low magnetocrystalline anisotropy and large magnetostriction are needed. Clark proposed to prepare pseudobinary $RR'Fe_2$ compounds by using the effects of different $R^{3+}$ ions on the anisotropy to lower their anisotropies (one example is the well known Terfenol-D ($Tb_{0.27}Dy_{0.73}Fe_{1.92}$)).[1] Since then, much attention has been paid to preparing $RR'Fe_2$ alloys with low magnetocrystalline anisotropy and large magnetostriction.[2–4] As Ren *et al.* reported, $Tb_{0.2}Dy_{0.58}Pr_{0.22}(Fe_{0.9}B_{0.1})_{1.93}$ exhibits a minimum of magnetocrystalline anisotropy and a maximum value of magnetostriction among the $Tb_{0.2}Dy_{0.8-x}Pr_x(Fe_{0.9}B_{0.1})_{1.93}$ alloys.[4] Furthermore, another method to achieve high magnetostriction and low magnetocrystalline anisotropy in a magnetostrictive material is replacing some Fe with another transition metal, such as Al, Mn, Ga, Co, Ni, and Ti.[5–15] Among these elements, Al is regarded as ideal. Wang *et al.* reported that the substitutions of Al for Fe in $Dy_{0.65}Tb_{0.25}Pr_{0.1}(Fe_{l-x}Al_x)_{1.8}$ and $Dy_{0.65}Tb_{0.25}Pr_{0.1}(Fe_{l-x}Al_x)_2$ alloys are beneficial to increase the magnetostriction in a low magnetic field.[5,7] In addition, Zheng *et al.*[8] and Gao *et al.*[13] found that substituting a small amount of Al for Fe decreases the magnetocrystalline anisotropy of the alloys. However, little experimental work has been done on the $PrFe_{1.9}$ alloy because it is synthesized only under high pressure.[16,17] Recent study on $PrFe_{1.9}$ alloys indicated that the alloys exhibit a remarkable giant intrinsic magnetostriction $\lambda_{111}$; however, it also shows high magnetocrystalline anisotropy at low temperature.[18] Therefore, it might be meaningful to investigate the effect of substituting Al for Fe in $PrFe_{1.9}$ alloy to develop new magnetostrictive materials for low temperature applications.

In this manuscript, the magnetic and magnetostrictive effects of substituting Al for Fe in $Pr(Al_xFe_{1-x})_{1.9}$ alloys, as well as the reorientation of the easy magnetization direction (EMD), were investigated.

## 2. Experimental

Ingots with $Pr(Al_xFe_{1-x})_{1.9}$ stoichiometry were prepared by melting the high purity metals in a magneto-controlled arc furnace in an argon atmosphere. The purity of the constituents is 99.9% for Pr, 99.8% for Fe, and 99.8% for Al. The ingots (about 1 g for each samples) were pressed into disks and wrapped in tantalum foils, and then were loaded into a cylinder-shaped graphite pipe heater. The assembly was pressed to 6 GPa by a hexahedral anvil press and heated to 900 °C for 30 min.[16,17] Conventional X-ray diffraction (XRD) analysis was carried out using Cu $K\alpha$ radiation with a Rigaku D/Max-ga diffractometer. The samples for XRD were ground into powders to reduce the preferred orientation effect. $Pr(Al_xFe_{1-x})_{1.9}$ alloy exhibits almost a single $MgCu_2$ cubic Laves phase structure when $x < 0.10$, which could be ascribed to the high-pressure annealing.[16,17] A small amount of impurity hcp-(Pr) phase was found when $x = 0.10$. High precision step scanning for $40.5° \leq 2\theta \leq 43°$ and $70.5° \leq 2\theta \leq 72.5°$ enabled the spontaneous magnetostriction-induced splitting of the {222} and {440} lines to be investigated, respectively.[2] The XRD peaks were fitted by Jade 6.5 XRD analytical software, and $K\alpha_2$ was deducted from the profiles of the {440} and {222} lines by a standard method.[2] A physical property

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measurement system (PPMS) was used to measure the magnetization of the samples (a grain close to an ellipsoid with the aspect ratio $k \geq 2$ for each sample).[19] The temperature dependencies of magnetization were also measured using PPMS to determine the spin reorientation temperature $T_{sr}$.[20] The magnetostriction was also measured by the standard strain-gauge technique, both parallel ($\lambda_{||}$) and perpendicular ($\lambda_{\perp}$) to the magnetic field for each sample (a rectangular block about 6 mm × 4 mm × 1 mm for each sample). The magnetic field was supplied by the Quantum Design PPMS.

## 3. Results and discussion

The lattice constant and the Curie temperature $T_c$ of the alloys are listed in Table 1. In general, the lattice constant of the compounds increases linearly with an increase of the Al content because the atom radius of Al is larger than that of Fe.[5,7,9] Whereas, the gradual replacement of Fe by Al leads to a progressive decrease in $T_c$, which decreases continually from 513 K to 439 K with increasing $x$. This result can be explained by the fact that when Fe is partially replaced by Al, partial Fe–Fe, and Pr–Fe interactions are replaced by the weaker Al–Fe, Al–Al, Pr–Al ones, resulting in a decrease in the exchange energy, and hence the $T_c$ decreases.[5,7,9]

**Table 1.** Lattice constant $a$ and Curie temperature $T_c$ for $Pr(Al_xFe_{1-x})_{1.9}$ compounds.

| $x$ | $a$/nm | $T_c$/K |
|---|---|---|
| $x = 0.0$ | 0.7464 | 513 |
| $x = 0.02$ | 0.7487 | 499 |
| $x = 0.05$ | 0.7490 | 478 |
| $x = 0.10$ | 0.7502 | 439 |

The applied magnetic field dependencies of the magnetostriction $\lambda = (\lambda_{||} - \lambda_{\perp})$ and magnetization ($M$) at 5 K were measured, and are shown in Figs. 1 and 2, respectively. The magnetostriction in high magnetic field decreases with increasing $x$ (Fig. 1), and the most valuable property for applications is that the low-field magnetostriction increases at 5 K due to the Al substitution. As seen in the inset of Fig. 1, the maximum value of magnetostriction occurs at $x = 0.02$ in the magnetic fields of $0 \leq H \leq 8$ kOe, indicating that the $Pr(Al_{0.02}Fe_{0.98})_{1.9}$ alloy exhibits the largest magnetostriction of all of these alloys. Meanwhile, the minimum value of magnetostriction occurs at $x = 0.0$ in the low-magnetic field of $0 \leq H \leq 2$ kOe, implying that Al substitution in this magnetic field range improves the low-magnetic field magnetostriction of the $PrFe_{1.9}$ alloys. This result is similar to that of Al substitution for Fe in other intermetallic compounds such as $Tb_{0.3}DY_{0.7}Fe_{1.95}$ alloys.[5,8,21]

As for the magnetization curves in Fig. 2, a decrease in the magnetization with increasing $x$ is found in high magnetic fields, indicating a decrease in the saturation magnetization due to Al substitution. According to Clark, the resultant 4f magnetic moment, due to the Pr sublattice, lies parallel to the net 3d moment,[1,9] and assuming the Al moments are small enough to be neglected, the decrease of $M_S$ with increasing $x$ in $Pr(Al_xFe_{1-x})_{1.9}$ alloys might be ascribed to the gradually decreasing concentration of Fe moments in the (Fe, Al) sublattice.[9] Magnetic anisotropy is a crucial property for a magnetostrictive material.[22] The magnetic field dependence of the normalized magnetization $M/M$ (70 kOe) at 5 K of $Pr(Al_xFe_{1-x})_{1.9}$ alloys, presented in Fig. 3, shows the influence of Al substitution on the magnetic anisotropy. It is found that in a magnetic field larger than 10 kOe, M/M (70 kOe) increases with increasing Al content, with $Pr(Al_{0.1}Fe_{0.9})_{1.9}$ possessing the maximum $M/M$ (70 kOe) values. This phenomenon might indicate that Al substitution in $PrFe_{1.9}$ is indeed a successful method to reduce its magnetic anisotropy at 5 K.[8,21] Therefore, the fast increase of the magnetostriction in a low magnetic field in the Al-contained alloys, shown in the inset of Fig. 1, can be explained by the decrease of the magnetocrystalline anisotropy in the alloys due to the Al substitution.

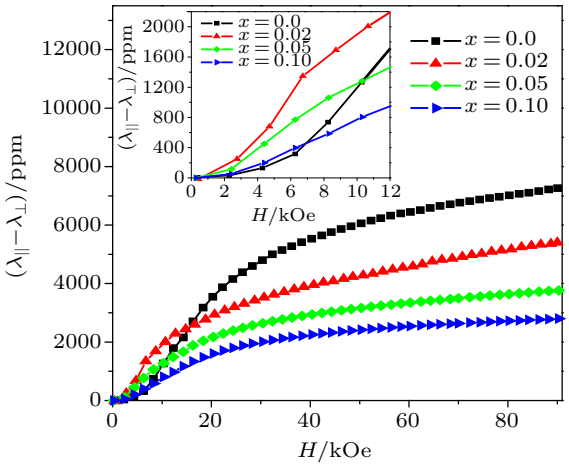



**Fig. 1.** (color online) Magnetic field dependence of the magnetostriction ($\lambda = \lambda_{||} - \lambda_{\perp}$) of polycrystalline $Pr(Al_xFe_{1-x})_{1.9}$ alloys. The inset shows the composition dependence of the magnetostriction of the alloys in the low magnetic field ($0 \leq H \leq 12$ kOe).

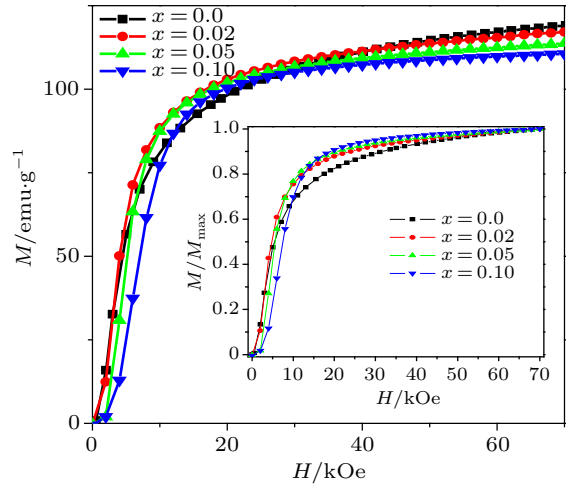



**Fig. 2.** (color online) Magnetic field dependence of the magnetizations ($M$) of polycrystalline $Pr(Al_xFe_{1-x})_{1.9}$ alloys. The inset shows the normalized magnetizations ($M/M_{max}$) as a function of the applied field.

In the following, the {440} and {222} XRD lines of the $Pr(Al_{0.02}Fe_{0.98})_{1.9}$ alloy were step-scanned to study the EMD and spontaneous magnetostriction.[2] The $K\alpha_2$ was deducted from the profiles of the {440} and {222} lines by a standard method,[2] as was shown in Fig. 3. A distinct change in the crystal distortion of the sample is plainly evident here, indicating the occurrence of a change in its EMD. As seen in Fig. 3(a), the sample demonstrates a prominent rhombohedral symmetry[2,17,23] between 125 K and 300 K, which is characterized by the intensity ratio of split peaks in the {440} and {222} reflections (about 1:1 and 1:3), respectively, with the lattice elongated along [111]($M_s$|| [111]). The split tends to vanish at 250 K and 300 K for {222} reflections, indicating that the distortion may be too small to detect in this temperature range. With further decreasing temperature, and unusual type of EMD appears,[4,24] as is shown in Fig. 3(b). The {440} reflection at 90 K and 115 K seems to split into two peaks with the intensity ratio about 1:2, while the {222} reflection splits into two peaks at 115 K and keeps a single peak at 90 K, indicating that a [uvw] or [uv0] type of EMD may exist over this temperature range.[24] The sample demonstrates a prominent tetragonal symmetry between 15 K and 40 K, as shown in Fig. 3(c), which is characterized by the non-splitting of the {222} reflections and the intensity ratio of split peaks in the{440} reflections (about 2:1), respectively, with the lattice elongated along [100] ($M_s$||[100]). The change of the EMD in $PrFe_{1.9}$ alloys has been reported in our previous study, found by means of step-scanned XRD.[18] The EMD lies along the [111] axis for temperature values greater than $T_{sr}$, while it lies along the [100] axis for temperatures below $T_{sr}$,[2,20] and it is found here that Al substitution increases the $T_{sr}$ value at which the [uvw] or [uv0] type of EMD exists, compared to the EMD change of $PrFe_{1.9}$.

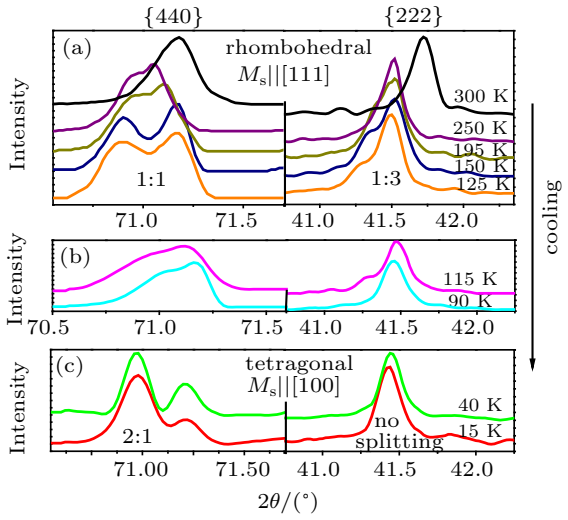



**Fig. 3.** (color online) Profiles of the step-scanned {440} and {222} XRD reflections of $Pr(Al_{0.02}Fe_{0.98})_{1.9}$. (a) Reflections between 125 K and 300 K. (b) Reflections between 90 K and 115 K. (c) Reflections between 15 K and 40 K.

To further study the effect of Al substitution on the EMD change, the magnetization temperature dependence at a magnetic field of 5 kOe between 15 K and 300 K was measured, as is shown in Fig. 4. Several anomalies were observed as can be seen from the figures.[20,25] These anomalies are similar to those observed in $Tb_{0.1}Ho_{0.9-x}Pr_x(Fe_{0.9}B_{0.1})_2$ alloys by Ren *et al.*, and they are mainly due to a spin reorientation.[20,25,26] For $PrFe_{1.9}$ alloy, the anomaly occurs between 30 K and 70 K, which is quite consistent with the step scanned XRD reflections in our previous report.[18] For $Pr(Al_{0.02}Fe_{0.98})_{1.9}$ alloy, the magnetization anomaly occurs between 40 K and 120 K (very consistent with the results in Fig. 3(b)), in the same temperature range where the [uvw] or [uv0] type of EMD exists. For the alloy with $x = 0.05$, the anomaly is probably between 45 K and 140 K. While for the alloy with $x = 0.10$, there may be a lower $T_{sr}$, which needs to be further investigated in a low magnetic field. This result suggests that the substitution of a small amount of Al increases the spin reorientation temperature.

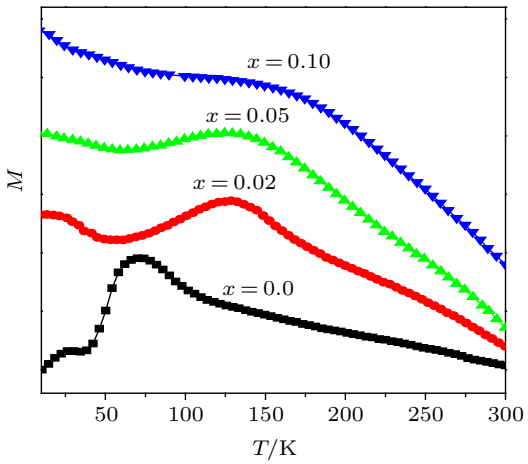



**Fig. 4.** (color online) Temperature dependence of the magnetization of the $Pr(Al_xFe_{1-x})_{1.9}$ alloys ($H = 5$ kOe).

The spontaneous magnetostrictions $\lambda_{111}$ of the alloys with $x = 0.0$ and $x = 0.02$ as functions of temperature are shown in Fig. 5, for which $\lambda_{111}$ was obtained from $\lambda_{111} = 2(d_{440} - d_{44\bar{0}})/(d_{440} + d_{44\bar{0}})$, where $d_{440}$ and $d_{44\bar{0}}$ denote the crystallographic plane distances of {440} and {44$\bar{0}$} in Fig. 3(a), respectively.[2,6,27–29] The value of $\lambda_{111}$ of $PrFe_{1.9}$ was obtained from reference 2. A sharp decrease of $\lambda_{111}$ in both of the two samples is observed with increasing temperature, which probably can be attributed to the rapid fall of the normalized rare earth sublattice moment with increasing temperature, as occurs in $TbFe_2$.[1] For $PrFe_{1.9}$, $\lambda_{111}$ decreases from 4790 ppm at 120 K to 1630 ppm at 250 K, and for $Pr(Al_{0.02}Fe_{0.98})_{1.9}$, $\lambda_{111}$ decreases from 3814 ppm at 125 K to 1345 ppm at 250 K. This fact indicates that Al substitution yields a rapid decrease of the spontaneous magnetostriction $\lambda_{111}$ at all temperatures investigated.

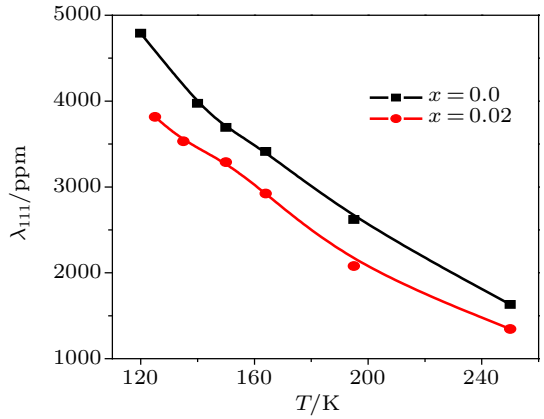



**Fig. 5.** (color online) Temperature dependence of $\lambda_{111}$ in $PrFe_{1.9}$ and $Pr(Al_{0.02}Fe_{0.98})_{1.9}$ alloys.

## 4. Conclusion

The substitution of Al for Fe decreases the Curie temperatures and the values of $\lambda_{111}$ of the $Pr(Al_xFe_{1-x})_{1.9}$ alloys. The easy magnetization direction changes as temperature decreases in $Pr(Al_{0.02}Fe_{0.98})_{1.9}$ alloy. Fortunately, in all these alloys, the substitution increases the magnetostriction slightly in a low magnetic field at 5 K ($0 \leq H \leq 8$ kOe). This makes the alloys good candidates for low temperature applications.

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