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Structure and magnetic properties of $Pr_{0.1}Ce_xTb_{0.9-x}Fe_{1.9}$ alloys①

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Abstract: The structural and magnetic properties of $Pr_{0.1}Ce_xTb_{0.9-x}Fe_{1.9}$ alloys were investigated by using X-ray diffraction, AC susceptibility, VSM and standard strain gauge techniques. The lattice parameter exhibits positive deviation from Vegard's law with the increasing Ce content in the range of 0.4－0.6. Curie temperature decreases linearly with increasing Ce content. The saturation magnetization and magnetostriction decrease when $0.2 \leqslant x < 0.4$ and $x > 0.6$, while abnormally increase with Ce content increasing from 0.4 to 0.6. These abnormal changes of lattice parameter, saturation magnetization and magnetostriction can be attributed to the valence fluctuation of Ce ions.

Key words: magnetostriction; laves phase; $Pr_{0.1}Ce_xTb_{0.9-x}Fe_{1.9}$ alloy; valence fluctuation
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1 INTRODUCTION

Terfenol-D ($Tb_{0.27}Dy_{0.73}Fe_2$) exhibits large magentostriction and minimized magnetic anisotropy at room temperature[1], so it is widely used in actuators and transducers. But the main raw materials of Terfenol-D are expensive Tb and Dy. According to the single-ion model[2], $CeFe_2$ and $PrFe_2$ compounds have larger magnetostriction than $TbFe_2$ and $DyFe_2$ at 0 K. In addition, Ce and Pr are much cheaper than Tb and Dy. So Ce-based and Pr-based compounds may be candidate materials for applications. But the magnetostriction of $CeFe_2$ alloy only shows 6×10^{-5} at 4.2 K due to the mix-valence behaviors of Ce ions. The $PrFe_2$ compound cannot be fabricated at ambient pressure because of the bigger atomic radius of Pr. It is interesting that Ce has high atomic bonding energy and the substitution of Ce for Pr can enhance the formation of Laves phase compounds with high Pr content[3, 4]. So much effort has been done on the Pr-Fe and Ce-Fe compounds[5－10]. The investigations on Ce-based intermetallics show that there is valence fluctuation of Ce ions[11] and the Ce ions contribute a lot to magnetostriction when they fluctuate towards trivalence. It is also found that the Pr substitution for Tb can enhance the magnetostriction[12, 13].

In our previous work, the heavy rare earth Tb and Dy substitution for Ce in $Ce_xR_{1-x}Fe_2$ compounds result in the valence fluctuation of Ce ions towards localized state[14, 15], while light rare earth such as Pr results in the delocalized tendency of Ce ions[3]. In order to obtain light rare earth magnetostrictive materials with large magntostriction, and investigate the effect of valence fluctuation of Ce ions, the Pr content is chosen as 0.1, and the structure and magnetic properties of $Pr_{0.1}Ce_xTb_{0.9-x}Fe_{1.9}$ alloys are all studied.

2 EXPERIMENTAL

The $Pr_{0.1}Ce_xTb_{0.9-x}Fe_{1.9}$ ($x=0.2$－0.8) alloys were prepared by arc melting under a high purified-argon atmosphere. The purities of rare earth and Fe were 99.9% and 99.99%, respectively. The alloy buttons were melted four times and then wrapped in a stainless steel foil and vacuum annealed in a sealed quartz capsule at 850 ℃ for 72 h.

The structure analysis was performed by X-ray diffraction (Philips X'Pert MPD) using Cu K_α radiation at room temperature. The lattice parameters were determined by least-squares fitting to X-ray peaks, and the accuracy is estimated to be ±0.000 2 nm. Curie temperature was determined by measuring the temperature dependence of AC susceptibility. The magnetization was obtained with a VSM at room temperature. The anisotropic magnetostriction was measured using a standard strain gauge in directions of parallel ($\lambda_{/\!/}$) and perpendicular ($\lambda_\perp$) to the magnetic field up to 950 kA/m at room temperature.

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3 RESULTS AND DISCUSSION

The X-ray diffraction patterns of $Pr_{0.1}Ce_xTb_{0.9-x}Fe_{1.9}$ alloys are shown in Fig. 1. All the homogenized samples exhibit a perfect cubic Laves phase with $MgCu_2$-type structure.

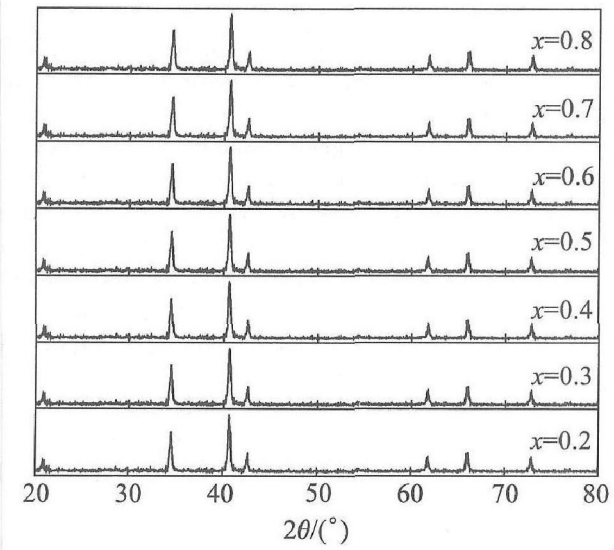

Fig. 1 XRD patterns of $Pr_{0.1}Ce_xTb_{0.9-x}Fe_{1.9}$ alloys

The dependence of lattice parameters on Ce content is shown in Fig. 2. The lattice parameters exhibit positive deviation from Vegard's law when $0.4 \leqslant x \leqslant 0.6$. It is well known that the volume of unit cell is related to the valence of elements in the compound. The positive deviation from Vegard's law is related to the valence fluctuation of Ce ions towards trivalence. In our previous work, with the increasing Ce content, the Ce 4f electrons in $Ce_xTb_{1-x}Fe_2$ compounds drift towards localized state[15], while drift towards delocalized state in $Pr_xCe_{1-x}Fe$ compounds[3]. In this work, the valence of Ce ions in $Pr_{0.1}Ce_xTb_{0.9-x}Fe_{1.9}$ alloys fluctuates towards localized state only in the range of 0.4 – 0.6. Anomalous behaviors can be also observed from magnetization and magnetostriction in this range.

The dependence of Curie temperature (T_C) on Ce content is shown in Fig. 3. It shows that Curie temperature decreases linearly with the increasing Ce content. This can be attributed to the fact that Curie temperature of $CeFe_2$ (235 K) is much lower than that of $TbFe_2$ (704 K).

The dependence of magnetization on the applied magnetic field is shown in Fig 4.

The saturation magnetization M_s was taken as the value of $Pr_{0.1}Ce_xTb_{0.9-x}Fe_{1.9}$ alloys at the largest available magnetic field of 800 kA/m. It can be clearly seen that M_s decreases with Ce content increasing from 0.2 to 0.4, but abruptly increases when $x = 0.6$. And then M_s drops again when $x >$

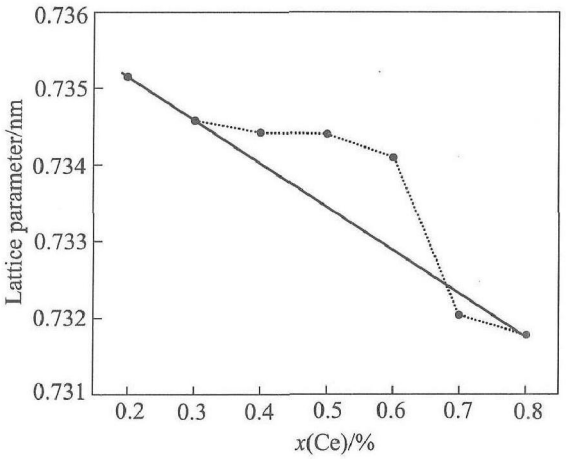

Fig. 2 Ce content dependence of lattice parameter for $Pr_{0.1}Ce_xTb_{0.9-x}Fe_{1.9}$ alloys
(Solid line represents Vegard's law behavior)

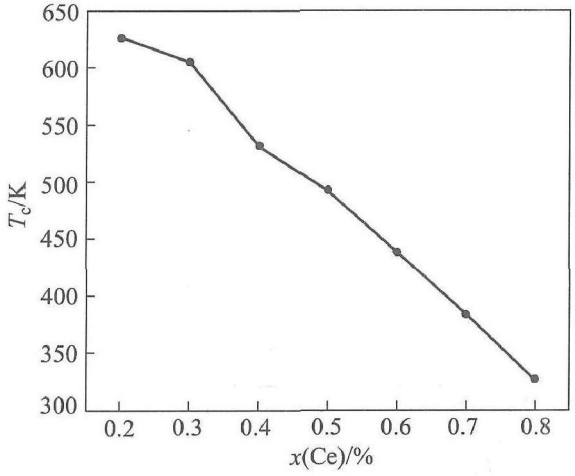

Fig. 3 Dependence of curie temperature (T_C) on Ce content for $Pr_{0.1}Ce_xTb_{0.9-x}Fe_{1.9}$ alloys

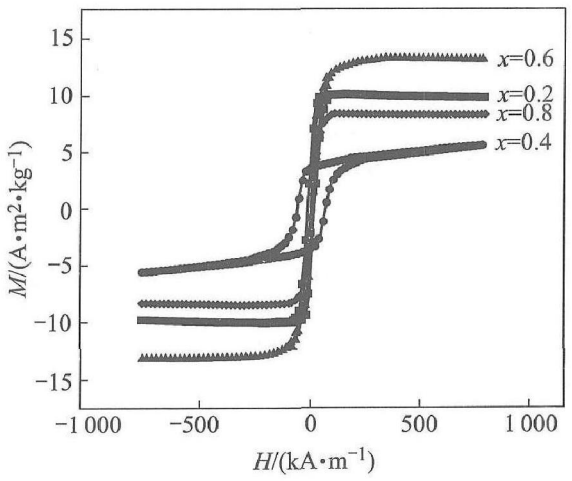

Fig. 4 Magnetization at room temperature of $Pr_{0.1}Ce_xTb_{0.9-x}Fe_{1.9}$ alloys

0.6. The fact may be related to the valence fluctuation of Ce ions. The moments of the Ce ion with + 3 valence and Fe in normal RFe_2 are 2.54 μ_B and

1.77 μ_B, respectively[11]. But the Ce and Fe moments in $CeFe_2$ alloy are − 0.14 μ_B and 1.17 μ_B, respectively from a polarized neutron study. The lattice parameter show the greatest deviation from Vegard's law at x= 0.6, and the moment of the Ce ion will increase a lot with the fluctuation tendency to + 3 valence, which may contribute to the M_s at room temperature. Table 1 shows the values of M_s, M_r, and H_c.

The dependence of magnetostriction on magnetic field is shown in Fig. 5.

Table 1 Saturation magnetization (M_s), remanent magnetization (M_r) and coercivity (H_c) of $Pr_{0.1}Ce_xTb_{0.9-x}Fe_{1.9}$ alloys

x	M_s/ ($A \cdot m^2 \cdot kg^{-1}$)	M_r/ ($A \cdot m^2 \cdot kg^{-1}$)	H_c/ ($kA \cdot A^{-1}$)
0.2	10.06	4.65	15.03
0.4	5.58	3.58	64.49
0.6	13.11	2.30	6.01
0.8	8.41	0.20	0.79

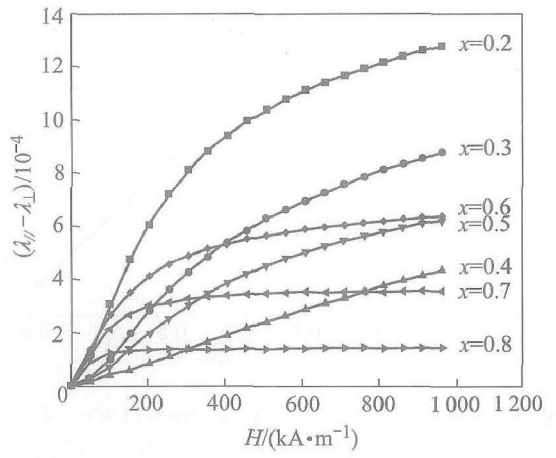

Fig. 5 Magnetostriction curves of $Pr_{0.1}Ce_xTb_{0.9-x}Fe_{1.9}$ alloys at room temperature

It can be seen that the magnetostriction decreases with the increasing Ce content when 0.2 ⩽ x < 0.4 and x > 0.6, but increases abnormally with Ce content increasing from 0.4 to 0.6. According to the single-ion model, the trivalent Ce ions have large magnetostriction, but the $CeFe_2$ compound shows 6.0×10^{-5} magnetostriction at 4.2 K and nearly 0 at the room temperature, which is ascribed to the mix valence (+ 3.29) of Ce ions and the low Curie temperature of $CeFe_2$. It is known from the dependence of the lattice parameter on Ce content that the valence of Ce ions in $Pr_{0.1}Ce_xTb_{0.9-x}Fe_{1.9}$ alloys is almost unchanged when x < 0.4 and x > 0.6. So the rapid decrease in magnetostriction when 0.2 ⩽ x < 0.4 and x > 0.6 is ascribed to the Ce substitution for Tb, that is the Ce ion dilutes the single-ion magnetostriction of Tb ion. The sudden increase of magnetostriction when 0.4 ⩽ x ⩽ 0.6 is ascribed to the valence fluctuation of Ce ions towards localized state, which has been confirmed from the change of lattice parameter. It is also found that when x < 0.5, the magnetostriction doesn't saturate at the magnetic field of 950 kA/m, while reaches saturation easily when x is larger than 0.6 even at low magnetic field.

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