Magnetic properties and magnetocaloric effect in compound $PrFe_{12}B_6$*

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(Received 12 October 2009; revised manuscript received 12 December 2009)

Magnetic properties and magnetocaloric effect of compound $PrFe_{12}B_6$ are investigated. The coexistence of hard phase $PrFe_{12}B_6$ and soft phase α–Fe causes interesting phenomena on the curves for the temperature dependence of magnetization. $PrFe_{12}B_6$ experiences a first order phase transition at the Curie temperature 200 K, accompanied by an obvious lattice contraction, which in turn results in a large magnetic entropy change. The Maxwell relation fails to give the correct information about magnetic entropy change due to the first order phase transition nature. The large magnetic entropy changes of $PrFe_{12.3}B_{4.7}$ obtained from heat capacity method are 11.7 and 16.2 J/kg.K for magnetic field changes of 0–2 T and 0–5 T respectively.

Keywords: magnetic properties, magnetic entropy change, first order phase transition

PACC: 7530S, 6540

Magnetic refrigeration, which is based on magnetocaloric effect (MCE), has attracted considerable attention due to its eco-friendliness and high efficiency.[1−5] The current trend in material research related to this field is to enhance material performance and reduce cost. Many rare earth and transition metal-based alloys including the alloys such as $Gd_5(Si,Ge)_4$,[1,3] $MnAs_{1-x}Sb$,[6] $MnFeP_{1-x}As_x$,[7] $La(Fe,Si)_{13}$[8] and its hydrides[9] have been found to show promising results.

Very recently, a giant magnetic entropy change (ΔS_M) was observed in the compound $NdFe_{12}B_6$, which has not been found in classical melting, but crystallizes in the melt-spun amorphous alloy on annealing, and is thus considered to be a metastable phase.[10] The compound $NdFe_{12}B_6$ has a hexagonal $SrNi_{12}B_6$ structure, with a Curie temperature (T_C) of about 230 K and a high magnetization of about 19.7 μ_B/f.u. at 4.2 K.[11−13] The maximum values of ΔS_M, which is ascribed to the abrupt change in magnetization around T_C , are 8.4 and 5.4 J/kg·K for the applied field changes of 0–10 and 0–7 kOe (1 Oe=79.5775 A/m), respectively. Therefore, as a magnetic refrigerant, compound $NdFe_{12}B_6$ is advantageous due to its low cost and its large magnetic entropy change in relatively low magnetic field change, which can be easily supplied by a permanent magnet.[10]

According to some relevant reports, the hexagonal $SrNi_{12}B_6$ structure can also be obtained in other rare earth R–Fe–B systems.[13] Here we present an investigation of magnetic properties of $PrFe_{12}B_6$ as well as its large magnetic entropy change by combining x-ray diffraction, magnetic measurements and heat capacity.

An alloy of composition $PrFe_{12.3}B_{4.7}$ was prepared by vacuum induction melting from elements with a purity better than 99.9%. Then, ribbons were obtained from the ingot by means of standard melt spinning in a purified argon atmosphere with a wheel speed of 40 m/s. Selected ribbons were annealed at 630 °C for 60 h to optimize crystallization.

Powder x-ray diffraction (XRD) data was measured by using Philips X'PERT MPD. Data was collected over a 2θ range of 20°–90°, in steps of 0.02° for the 2θ-scan and the temperature range varied from 77 K to 300 K in steps of 1 K around T_C and 5 K far

*Project supported by the Scientific Research Foundation for Bringing Talents of Tianjin University of Science and Technology, China (Grant No. 20090426), the National Natural Science Foundation of China (Grant Nos. 50571112 and 50731007), the National Basic Research Program of China (Grant No. 2006CB601101), and the Basic Research Program of the Chinese Academy of Sciences (Grant No. KJCX2-YW-W02s).

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from T_C.

In addition to hexagonal $SrNi_{12}B_6$-structure $PrFe_{12}B_6$, peaks from α–Fe are present, which indicates a mixture of $PrFe_{12}B_6$ and α–Fe. The single phase of hexagonal $PrFe_{12}B_6$ is very hard to obtain.

The magnetization and the heat capacity were measured by using a magnetic property measurement system (MPMS) and a physical property measurement system (PPMS).

The curves for temperature-dependent magnetization (M–T) of $PrFe_{12.3}B_{4.7}$ under various magnetic fields were measured, and the M–T curves in warming (solid) and cooling (hollow) modes are both shown in Fig. 1. The magnetic transition shows a clear thermal hysteresis around 200 K as the evidence of a first-order transition. And an obvious separation appears below T_C between the warming mode and the cooling mode. When the applied field is 0.005 T, the magnetization increases almost linearly with temperature increasing and jumps upward significantly near T_C with an obvious thermal hysteresis between the warming mode and the cooling mode. When the applied field is 0.1 T, similar phenomena occur in the warming mode, on the contrary the magnetization decreases abruptly around T_C in the cooling mode. With further increasing applied field to 2 T, the magnetizations in both modes decrease drastically around T_C with thermal hysteresis strengthening and an obvious difference between the curves of warming-mode and the cooling-mode is found, and this difference disappears in a larger applied field of 5 T.

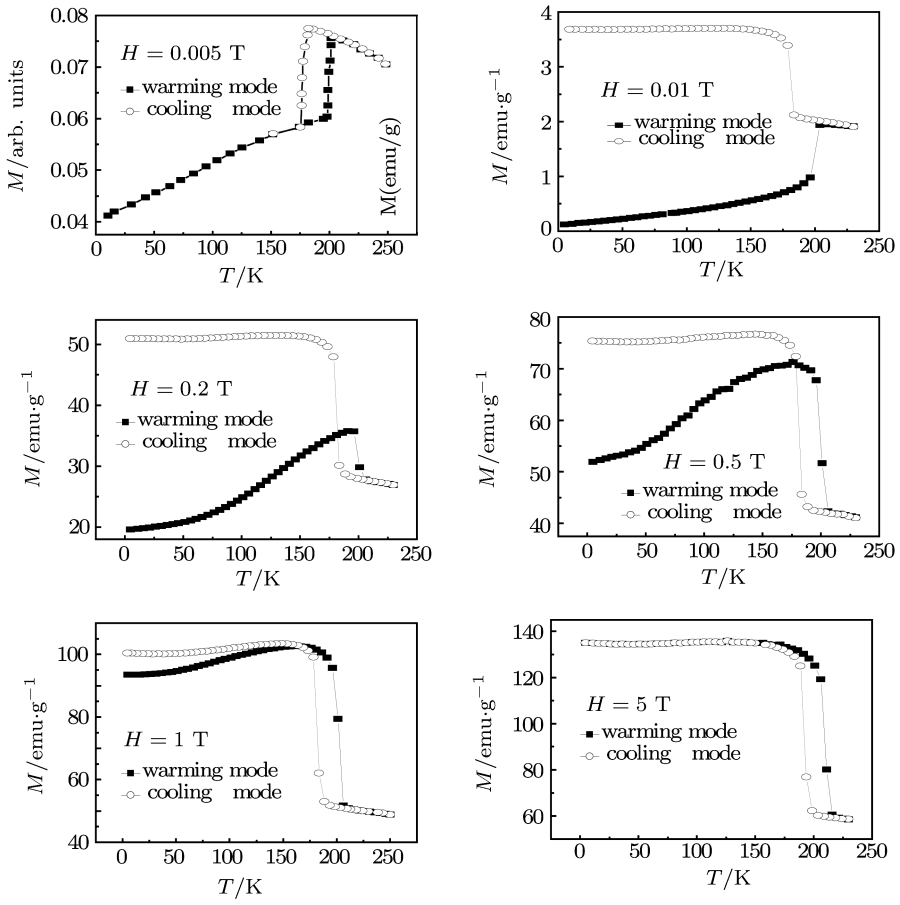


Fig. 1. Temperature-dependent magnetization of $PrFe_{12.3}B_{4.7}$ under various magnetic fields in warming (solid symbols) and cooling (open symbols) modes (1 emu·g^{-1}=1 A·m^2·kg^{-1}).

Considering the fact that there are two phases in our sample: $PrFe_{12}B_6$ and soft magnetic phase α–Fe, we believe that the above phenomena on the temperature-dependent magnetization curves are probably caused by the coexistence of hard and soft magnetic phases. The initial magnetizations and the

hysteresis loops at different temperatures were measured. From the initial magnetization curve as shown in Fig. 2(a), one can see that the magnetization is hard to saturate even at the applied field of 5 T, suggesting a large coercive force of $PrFe_{12}B_6$. The average coercive force is 0.35 T at 5 K, decreases almost linearly with increasing temperature, and has a sharp drop at T_C as shown in Fig. 2(b). Therefore, our sample shows hard phase $PrFe_{12}B_6$ and soft phase α–Fe co-existing inside. At a low applied field, the magnetic moments of hard phase $PrFe_{12}B_6$ remain in the easy orientation and hardly turn to the applied field direction due to its large coercive force, at the same time the magnetic moments of soft phase α–Fe, pinned by the hard phase, also align to the easy orientation of $PrFe_{12}B_6$,

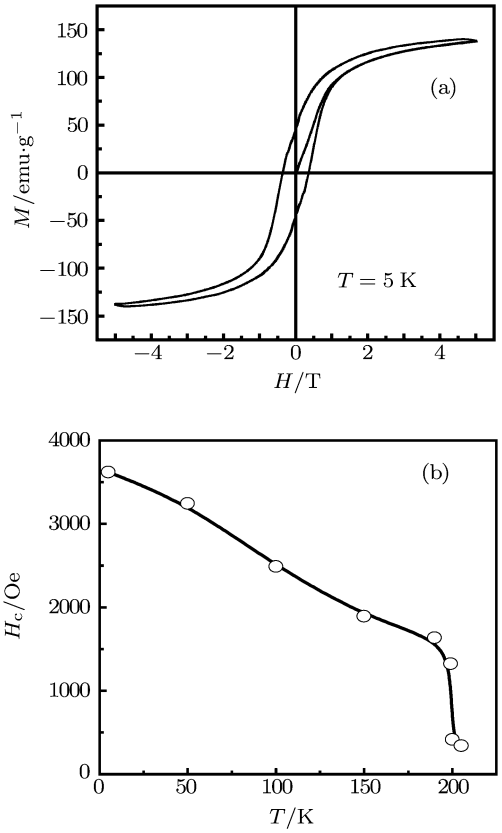


Fig. 2. Initial magnetization and hysteresis loop at 5 K of $PrFe_{12.3}B_{4.7}$ (a), and temperature dependence of average coercive force of $PrFe_{12.3}B_{4.7}$ (b).

which results in a relatively small net magnetization below T_C. Due to the H_C decreasing with temperature increasing, more and more magnetic moments turn to the applied field direction and the magnetization increases with temperature increasing. Above T_C, the magnetic moments of soft phase α–Fe are released and turn to the applied field direction, resulting in a nonzero magnetization.

Figure 3 shows the observed XRD patterns collected at 198 K and 201 K for $PrFe_{12.3}B_{4.7}$. The temperature dependences of lattice constants a, b and c are shown in Fig. 4. The values of a, b and c decrease with increasing temperature and are discontinuous around T_C. The lattice constants change from $a = b = 9.604(2)$ Å (1 Å=0.1 nm) and $c = 7.557(8)$ Å to $a = b = 9.602(0)$ Å, and $c = 7.554(6)$ Å as the temperature increases from 200 K to 201 K. a (b) and c contract by about 0.02% and 0.04%, respectively, thus the lattice volume decreases by about 0.1%. Combining the thermal and the magnetic hystereses before and after magnetic phase transition, we conclude that compound $PrFe_{12}B_6$ experiences a first order phase transition at T_C, accompanied with a lattice contraction.

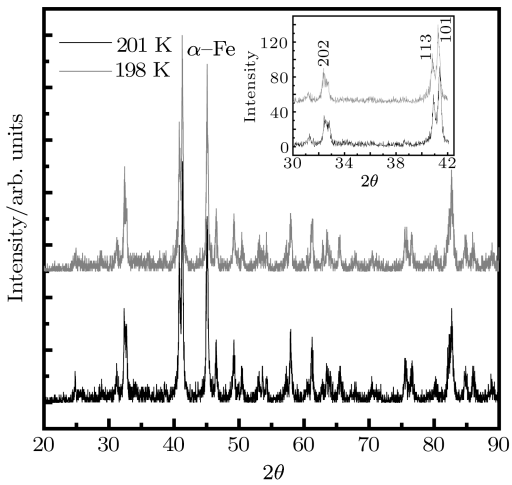


Fig. 3. Powder x-ray diffraction patterns at 198 K and 201 K.

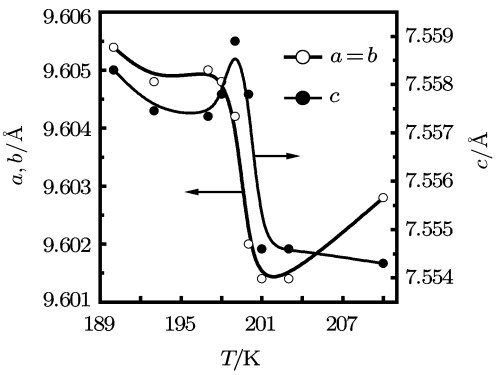


Fig. 4. Temperature dependences of lattice constants a, b and c (1 Å=0.1 nm).

From the above results, one can see a sharp change in the magnetization around T_C and a large saturated magnetization at 5 K (c.g. 150 emu/g), which are related to a large magnetocaloric effect. The field-dependent magnetizations of $PrFe_{12.3}B_{4.7}$

are shown in Fig. 5, around T_C both the field increasing and decreasing modes with a small hysteresis are measured. The M–H curves above T_C are not linear due to the existence of α–Fe. The above temperature-dependent lattice constants suggest that the first order phase transition in compound $PrFe_{12}B_6$ is completed in a very narrow temperature range. Therefore the M–H curves around T_C each have a large diverseness due to the sharp change of magnetization of hard phase $PrFe_{12}B_6$.

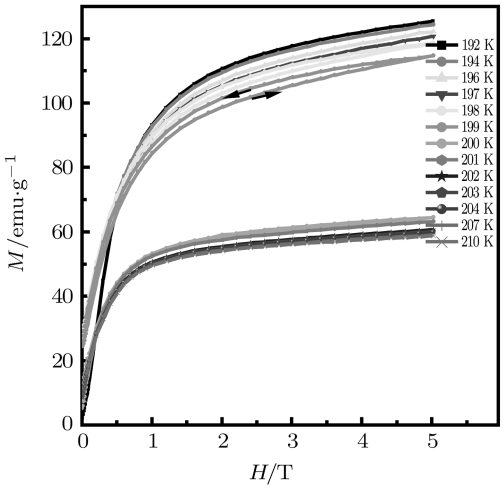


Fig. 5. Field-dependent magnetizations of $PrFe_{12.3}B_{4.7}$ around the Curie temperature.

Magnetic entropy change $|\Delta S|_M$ is calculated from Maxwell relation $\Delta S_M(T,H) = -\int (\partial M/\partial T)_H \mathrm{d}H$ by using the collected magnetization data. Figure 6 displays the temperature-dependent magnetic entropy change $|\Delta S|_M$ for the compound $PrFe_{12.3}B_{4.7}$. The calculated maximum value of $|\Delta S|_M$ for $PrFe_{12.3}B_{4.7}$ increases almost linearly from 12 J/kg·K to 102 J/kg·K for field changes varying from 1 T to 5 T, and its peak position is almost independent of field change. The Maxwell relation is based on the local equilibrium hypothesis. However, the hysteretic behaviour in compound $PrFe_{12}B_6$ and the lattice contraction around T_C suggest that compound $PrFe_{12}B_6$ is not in an equilibrium state during the phase transition. Combining the giant magnetic entropy change and its dependence on temperature step (the maximum values of $|\Delta S|_M$ in temperature steps of 1 K are almost twice those in temperature steps of 2 K), the applicability of the Maxwell relation in our sample needs to be proved. Liu *et al.*[14] have pointed out that the Maxwell relation is inapplicable for some first order phase transition systems in the vicinity of the Curie temperature because of the coexistence of paramagnetic and ferromagnetic phases. To obtain more accurate information about the magnetic entropy change, the calorimetric technique should be used. The specific heat capacities of $PrFe_{12.3}B_{4.7}$ as shown in Fig. 7, were measured over a temperature range of 2–295 K under the applied fields of 0, 2 and 5 T separately. Each heat capacity peak is very sharp, corresponding to the first order phase transition of hard phase from ferromagnetism to paramagnetism and the specific heat capacity has maximum values at 199, 201.5 and 208 K for applied fields of 0, 2 and 5 T, respectively, which suggests that the field can drive the phase transition to higher temperature.

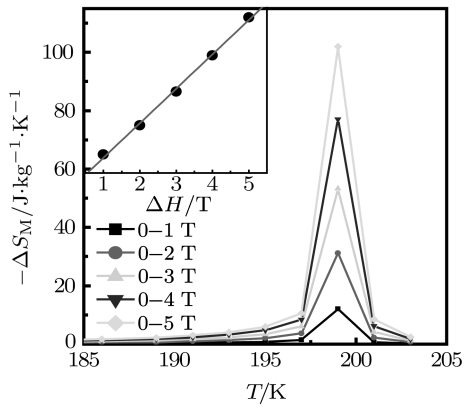


Fig. 6. Temperature dependences of magnetic entropy change, calculated from the Maxwell relation by using the collected magnetization data for the compound $PrFe_{12.3}B_{4.7}$.

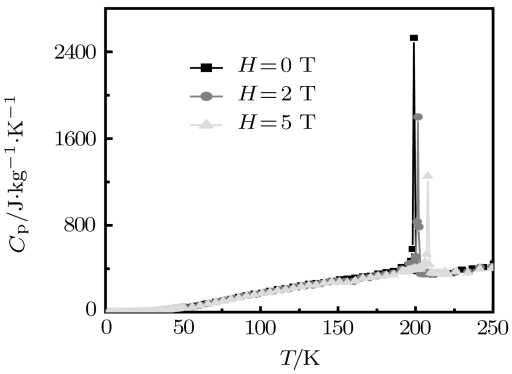


Fig. 7. Specific heat capacities of $PrFe_{12.3}B_{4.7}$ over a temperature range of 2–295 K under the applied fields of 0, 2 and 5 T.

The magnetic entropy change $|\Delta S|_M$ can be calculated based on the following equations

$$S(T) = \int_0^T \frac{C(T)_H}{T}\mathrm{d}T + S_{0,H},$$
$$\Delta S_M = \Delta S = S(H,T) - S(0,T).$$

Figure 8 shows the temperature dependences of magnetic entropy change, calculated from the heat capacity method with magnetic field increasing from

0 to 2 T and 0 to 5 T. The maximum values of $|\Delta S|_{\rm M}$ for magnetic field changes of 0–2 T and 0–5 T are 11.7 J/kg·K and 16.2 J/kg·K, respectively. The magnetic entropy change concentrates in a narrow temperature range of only about 2 K around $T_{\rm C}$ for the field change of 0–2 T, a broad distribution of about 10 K of the $|\Delta S|_{\rm M}$ peak is observed for a field change of 0–5 T and the peak temperature of $|\Delta S|_{\rm M}$ increases from 198 K to 208 K with field change varying from 0–2 T to 0–5 T.

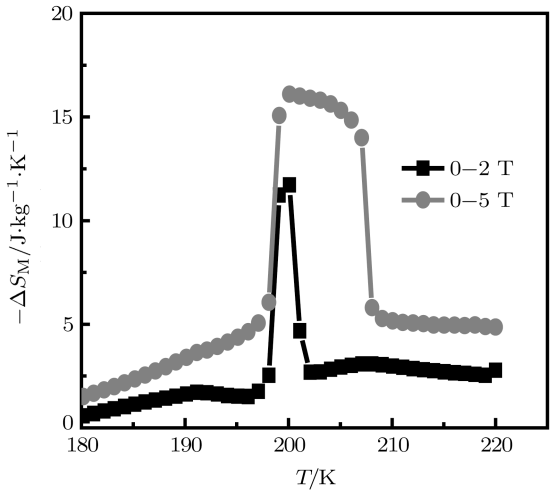


Fig. 8. Temperature dependences of magnetic entropy change, calculated from the heat capacity method with magnetic field increasing from 0 to 2 T and 0 to 5 T.

In conclusion, the magnetic properties and magnetocaloric effect of $PrFe_{12}B_6$ compound are investigated. Our sample is a mixture of hard phase $SrNi_{12}B_6$-structure $PrFe_{12}B_6$ and soft phase α–Fe, which results in the interesting phenomena on the curves for temperature dependence of magnetization. The results of magnetic entropy change, obtained from magnetic and heat capacity methods, are different due to the first order phase transition. A large magnetic entropy changes of $PrFe_{12.3}B_{4.7}$, obtained from heat capacity method, are 11.7 J/kg·K and 16.2 J/kg·K for magnetic field changes of 0–2 T and 0–5 T respectively, owing to the lattice contraction.

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