Letter

# Magnetocaloric effect in $Pr_6Co_{1.67}Si_3$ compound

Jun Shen [a,b,*], Fang Wang [a], Yang-Xian Li [b], Ji-Rong Sun [a], Bao-Gen Shen [a]

[a] *State Key Laboratory for Magnetism, Beijing National Laboratory for Condensed Matter Physics and Institute of Physics,*
*Chinese Academy of Sciences, Beijing 100080, People's Republic of China*
[b] *School of Material Science and Engineering, Hebei University of Technology, Tianjin 300130, People's Republic of China*

## Abstract

Magnetic properties and magnetocaloric effects of $Pr_6Co_{1.67}Si_3$ compound have been investigated by magnetization measurements. The saturation moment at 5 K is found to be $10.7\mu_B$. The compound undergoes two magnetic transitions below Curie temperature $T_C = 48$ K and shows a reversible second-order magnetic transition around $T_C$. A magnetic entropy change $\Delta S = 6.9$ J/(kg K) is observed for a magnetic field change from 0 to 5 T. The full width at half maximum of the $\Delta S$ peak is found to be about 38 K.
© 2008 Elsevier B.V. All rights reserved.

*Keywords:* $Pr_6Co_{1.67}Si_3$ compounds; Magnetocaloric effect; Magnetic properties

## 1. Introduction

Magnetic refrigeration is based on the magnetocaloric effect (MCE), which means that the isothermal entropy or the adiabatic temperature of the magnetic material may be varied by applying or deapplying a magnetic field. Compared with the conventional gas refrigeration, magnetic refrigeration has several advantages, such as environmental safety and high efficiency [1,2]. Many investigations have been made to search for new magnetic materials with a large MCE [2–10]. In the last few years, in order to achieve a larger MCE, much attention has been paid to the materials with the first-order phase transition [3–9]. Different from a second-order transition, the first-order transition tends to concentrate $\Delta S$ to a narrow temperature range around the Curie temperature, which implies that a large $\Delta S$ is much easier to obtain in the vicinity of transition temperature. The first-order phase-transition materials, such as $Gd_5Si_2Ge_2$ [3], $LaFe_{13-x}Si_x$ [4,5], $MnAs_{1-x}Sb_x$ [6], $MnFeP_{1-x}As_x$ [7], etc., have been found to have large values of $\Delta S$. Although the second-order phase-transition materials usually have a lower $\Delta S$ than the first-order phase-transition materials, their magnetiza-

tion exhibits excellent reversibility for the temperature/magnetic field cycling, which is highly desired in the practical application of the magnetic refrigeration technique. It is therefore necessary to search for the materials with a strong MCE around the second-order transition.

Recently, Gaudin et al. [11] have discovered a new ferromagnetic silicide $Gd_6Co_{1.67}Si_3$ with a Curie temperature of 294 K. They subsequently extended the study to other rare earth silicides $R_6Co_{1.67}Si_3$ (R = Ce, Nd, Tb and Dy) [12], which are of single phase except $Dy_6Co_{1.67}Si_3$. Synthesis, crystal structure and magnetic properties of these compounds have been systematically studied. In the present paper, we report the magnetocaloric effects of the compound $Pr_6Co_{1.67}Si_3$. A magnetic entropy change of 6.9 J/(kg K) at $T_C$ and a reversible dependence of the magnetization on temperature and magnetic field are obtained.

## 2. Experimental

The sample with the nominal composition $Pr_6Co_{1.67}Si_3$ was prepared by arc melting in a high-purity argon atmosphere. The purities of starting materials are 99% for Pr, 99.9% for Co, and 99.999% for Si. The sample was turned over and remelted several times to ensure homogeneity. The as-prepared ingots were wrapped up in a molybdenum foil, sealed in a quartz tube with a high vacuum, annealed at 1073 K for 50 days and then quenched to room temperature. The ingots were then ground into powders. X-ray diffraction (XRD) measurements on powder samples were performed using Cu Kα radiation to identify the phase purity and the crystal structure. Magnetization was measured as a function of

* Corresponding author at: State Key Laboratory for Magnetism, Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China.
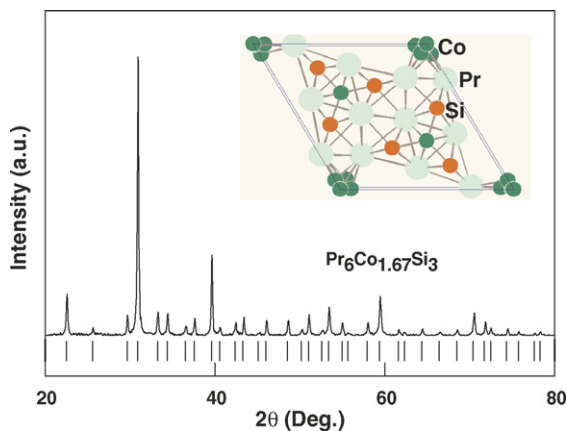*E-mail address:* sj@g203.iphy.ac.cn (J. Shen).

Fig. 1. Room-temperature powder XRD patterns of $Pr_6Co_{1.67}Si_3$ compound, where the short vertical lines show the Bragg reflections. The inset presents the crystal structure of $Pr_6Co_{1.67}Si_3$.

temperature and magnetic field by using a superconducting quantum interference device (SQUID) magnetometer.

## 3. Results and discussion

Fig. 1 shows the room-temperature powder XRD patterns of $Pr_6Co_{1.67}Si_3$ compound. The sample is found to have a single phase with a hexagonal $Gd_6Co_{1.67}Si_3$-type structure (space group $P6_3/m$) [11]. The lattice parameters are found to be $a = 12.034(6)$ Å and $c = 4.258(4)$ Å. Fig. 2 shows the thermomagnetic M–T curves of $Pr_6Co_{1.67}Si_3$ recorded under a field of 0.01 T. One can find that the compound undergoes two magnetic transitions at about 20 and 48 K, which results probably from two different kinds of environments in which rare earth atoms lie [12]. The transition at higher temperatures is a change from ferromagnetic to paramagnetic state with a Curie temperature of 48 K. The heating and cooling magnetization curves are reversible around $T_C$, which is a characteristic of the second-order transition. However, the magnetization at low temperatures is significantly thermal history dependent,
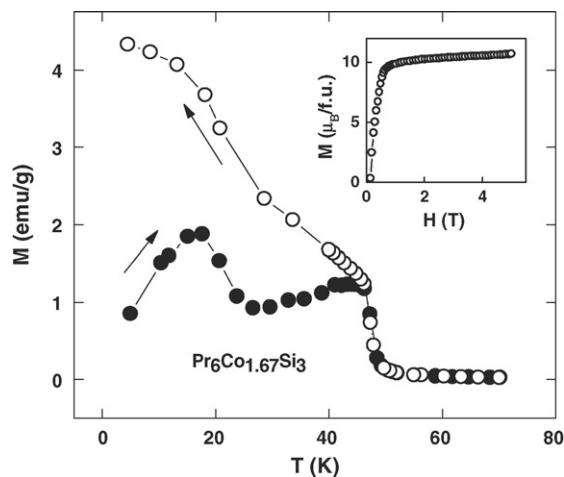
and a strong irreversibility appears below $T_C$ for the M–T curves obtained in the heating and cooling processes, as has been observed in $Nd_6Co_{1.67}Si_3$ [12]. The saturation moment $\mu_s = 10.7\mu_B$ per $Pr_6Co_{1.67}Si_3$ molecule is obtained from the magnetization curves measured at 5 K (see the inset of Fig. 2). According to the experimental results by Chevalier et al. [12], the Co atoms are non-magnetic in the $R_6Co_{1.67}Si_3$ ternary silicide. Thus, the average magnetic moment per Pr atom is $1.79\mu_B$, which is obviously smaller than that of its corresponding free ion ($3.56\mu_B$). This may be due to the crystalline field effects, which quench the angular momentum [12].

Fig. 3(a) shows the isothermal magnetization curves measured in a temperature range of 20–73 K under the magnetic fields up to 5 T. In the vicinity of the Curie temperature, from 35 to 53 K, the temperature step is 3 K, and in far regions of 20–35 K and 53–73 K the step was chosen to be 5 K. The sweep rate of field was slow enough to ensure that M–H curves were recorded in an isothermal process. Fig. 3(b) shows Arrott plots of $Pr_6Co_{1.67}Si_3$ in which no inflection or negative slope is observed as a signature of metamagnetic transition above the $T_C$, indicating a nature of the second-order phase transition. It is observed that the isothermal magnetization curves of $Pr_6Co_{1.67}Si_3$ show a reversible behavior for the field increasing/decreasing cycling, and there appears no hysteresis in the magnetization as a function of both the temperature and the magnetic field, which is highly desired in the magnetic refrigeration application [2,10].

The magnetic entropy change is calculated from magnetization data by using the Maxwell relation $\Delta S(T, H) =$
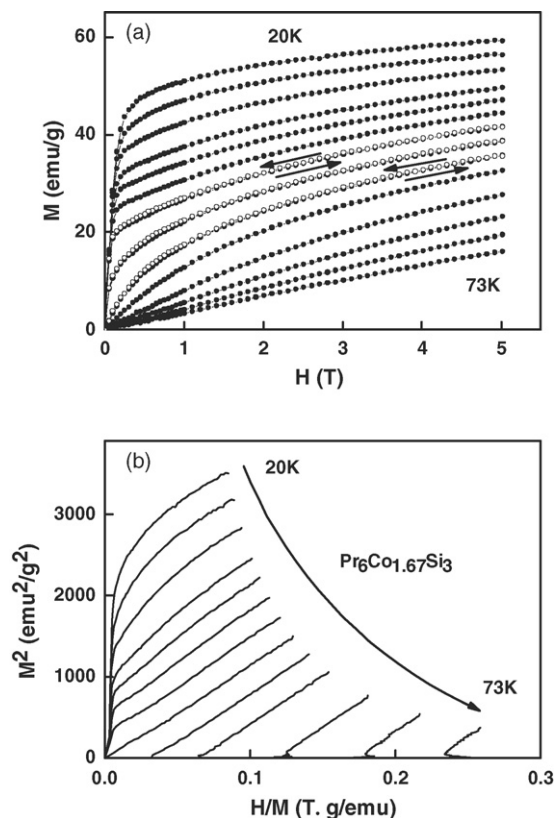


Fig. 2. Temperature dependence of magnetization of $Pr_6Co_{1.67}Si_3$ under a magnetic field of 0.01 T. The inset shows the magnetic field dependence of magnetization at 5 K for $Pr_6Co_{1.67}Si_3$.



Fig. 3. Magnetization of $Pr_6Co_{1.67}Si_3$ as a function of applied field measured near the Curie temperature (a) and the Arrott plot of $Pr_6Co_{1.67}Si_3$ (b).
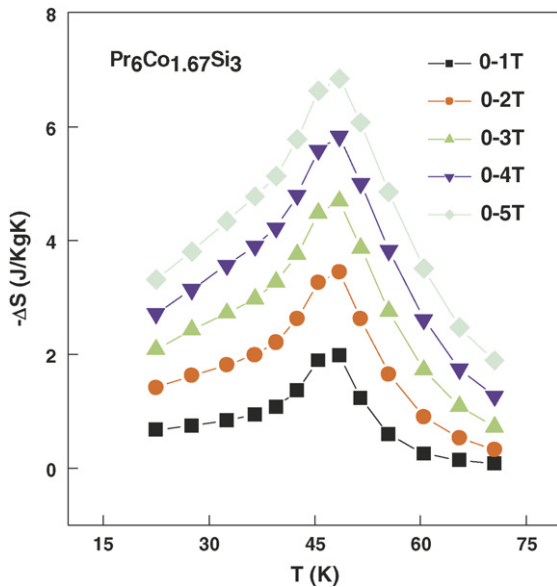
Fig. 4. Magnetic entropy changes of $Pr_6Co_{1.67}Si_3$ extracted from magnetization measurements with the magnetic field changes from 0 to 1.0, 2.0, 3.0, 4.0 and 5.0 T.

$\int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH$. Fig. 4 shows the magnetic entropy change as a function of temperature for the $Pr_6Co_{1.67}Si_3$ compound. The maximum values of $\Delta S$ at $T_C$ are found to be 3.5 and 6.9 J/(kg K) for the field change of 0–2 T and 0–5 T, respectively. No change in peak temperature of $\Delta S$ is observed up to a field of 5 T, and the $\Delta S$ shape shows a symmetrical broadening with the applied field increasing, which indicates that the large magnetic entropy change originates from a reversible second-order magnetic transition [13]. Although the maximum $\Delta S$ of $Pr_6Co_{1.67}Si_3$ is smaller than that of the most conspicuous magnetocaloric material [3–9], the full width at half maximum of the $\Delta S$–$T$ curves, $\delta T$, defined as the temperature interval corresponding to the half maximum of $\Delta S$, approaches to about 38 K for the magnetic field change from 0 to 5 T. According to the mean field
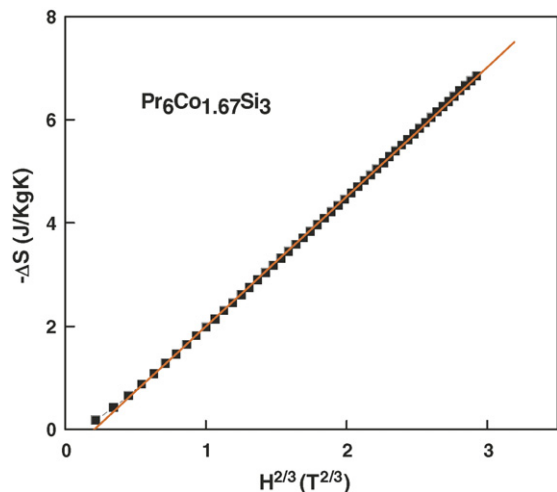


Fig. 5. Relation between maximum $\Delta S$ and $H^{2/3}$ near Curie temperature for $Pr_6Co_{1.67}Si_3$. The straight line shows the linear fitting to data.

theory, the relation between the magnetic entropy change and the magnetic field near the Curie temperature is described as [14]

$$\Delta S \approx -1.07 qR \left(\frac{g\mu_B JH}{kT_c}\right)^{2/3},$$

where $q$ is the number of magnetic ions, $R$ is the gas constant and $g$ is the Landé g-factor. Fig. 5 shows that the $\Delta S$ depends well linearly on the $H^{2/3}$ near the Curie temperature, implying the strong localization of electrons and the second-order character of magnetic transition for $Pr_6Co_{1.67}Si_3$ [15]. The value of isothermal magnetic entropy change will rise with the increase of magnetic field. $Pr_6Co_{1.67}Si_3$ shows a higher magnetization and a sharp change in magnetization as the temperature passes through $T_C$, which results in a larger magnetic entropy change.

## 4. Conclusion

We have prepared a new compound $Pr_6Co_{1.67}Si_3$. XRD patterns show that the compound is of a single phase with a hexagonal $Gd_6Co_{1.67}Si_3$-type structure (space group $P6_3/m$) [11]. The saturation moment at 5 K and the Curie temperature are found to be $10.7\mu_B$ and 48 K, respectively. A magnetic entropy change of 6.9 J/(kg K), which originates from a reversible second-order magnetic transition around $T_C$, has been obtained for a magnetic field change from 0 to 5 T.

## Acknowledgements

## References

[1] A.M. Tishin, in: K.H.J. Buschow (Ed.), Handbook of Magnetic Materials, vol. 12, Elsevier, Amsterdam, 1999, p. 395.
[2] A.M. Tishin, Y.I. Spichkin, in: J.M.D. Coey, et al. (Eds.), The Magnetocaloric Effect and its Applications, Institute of Physics Publishing, 2003.
[3] V.K. Pecharsky, K.A. Gschneidner Jr., Phys. Rev. Lett. 78 (1997) 4494.
[4] F.X. Hu, B.G. Shen, J.R. Sun, X.X. Zhang, Chin. Phys. 9 (2000) 550.
[5] F.X. Hu, B.G. Shen, J.R. Sun, Z.H. Chen, G.H. Rao, X.X. Zhang, Appl. Phys. Lett. 78 (2001) 3675.
[6] H. Wada, Y. Tanabe, Appl. Phys. Lett. 79 (2001) 3302.
[7] O. Tegus, E. Brück, K.H.J. Buschow, F.R. de Boer, Nature (London) 415 (2002) 150.
[8] A. Giguere, M. Foldeaki, W. Shcnelle, E. Gmelin, J. Phys.: Condens. Matter 11 (1999) 6969.
[9] Z.B. Guo, Y.W. Du, J.S. Zhu, H. Huang, W.P. Ding, D. Feng, Phys. Rev. Lett. 78 (1997) 1142.
[10] K.A. Gschneidner Jr., V.K. Pecharsky, A.O. Tsokol, Rep. Prog. Phys. 68 (2005) 1479.
[11] E. Gaudin, F. Weill, B. Chevalier, Z. Naturforsch. 61b (2006) 825.
[12] B. Chevalier, E. Gaudin, F. Weill, J. Alloys Compd. 442 (2007) 149.
[13] G.V. Brown, J. Appl. Phys. 47 (1976) 3673.
[14] H. Oesterriecher, F.T. Parker, J. Appl. Phys. 55 (1984) 4334.
[15] Q.Y. Dong, H.W. Zhang, J.L. Shen, J.R. Sun, B.G. Shen, J. Magn. Magn. Mater. 319 (2007) 56.