Vol 16 No 12, December 2007
1009-1963/2007/16(12)/3853-05

Chinese Physics

Magnetic properties and magnetocaloric effects in $Tb_6Co_{1.67}Si_3$ compound*

Shen Jun(沈 俊)[a)b)†], Wang Fang(王 芳)[a)],
Li Yang-Xian(李养贤)[b)], Sun Ji-Rong(孙继荣)[a)], and Shen Bao-Gen(沈保根)[a)]

[a)] *State Key Laboratory for Magnetism, Institute of physics, Chinese Academy of Sciences, Beijing* 100080, *China*
[b)] *School of Material Science and Engineering, Hebei University of Technology, Tianjin* 300130, *China*

(Received 1 August 2007; revised manuscript received 22 October 2007)

Magnetic properties and magnetocaloric effects of $Tb_6Co_{1.67}Si_3$ have been investigated by magnetization measurement. This compound is of a hexagonal $Ce_6Ni_2Si_3$-type structure with a saturation magnetization of 187 emu/g at 5 K and a reversible second-order magnetic transition at Curie temperature $T_C = 186$ K. A magnetic entropy change $\Delta S = 7\,J \cdot kg^{-1} \cdot K^{-1}$ is observed for a magnetic field change from 0 to 5 T. A large value of refrigerant capacity (RC) is found to be 330 J/kg for fields ranging from 0 to 5 T. The large RC, the reversible magnetization around T_C and the easy fabrication make the $Tb_6Co_{1.67}Si_3$ compound a suitable candidate for magnetic refrigerants in a corresponding temperature range.

Keywords: $Tb_6Co_{1.67}Si_3$ compound, magnetocaloric effect, magnetic properties
PACC: 7530S, 7550C

1. Introduction

Recently, there has been a great deal of interest in the study of magnetocaloric effect (MCE) of ferromagnetic materials because of their potential applications as magnetic refrigerants.[1,2] In order to serve as a magnetic refrigerant near an ambient temperature, it is necessary to search for suitable materials with a large magnetic entropy change (ΔS). A large ΔS has been observed in material systems involving the first-order phase transition, such as $Gd_5Si_2Ge_2$,[3] $Gd_5Si_2Ge_{1.9}Fe_{0.1}$,[4] La(Fe, Si)$_{13}$,[5,6] $MnAs_{1-x}Sb_x$,[7] $MnFeP_{1-x}As_x$,[8] polycrystalline perovskite manganese oxides,[9] shape memory alloys,[10,11] etc. It has been found that the first-order transition tends to restrict ΔS to a narrow temperature range around the Curie temperature, which implies that large ΔS is much easy to achieve in the vicinity of transition temperature. However, the large irreversibility and the obvious hysteresis loss in the first-order transition materials[4,12] make magnetic refrigeration less efficient and thereby restrict their practical applications. Although the second-order transition materials generally show a lower ΔS than the first-order ones, they usually exhibit a good reversible behaviour in magnetization as a function of temperature and magnetic field and a large refrigerant capacity (RC), which is very important for a material to be efficiently used as a magnetic refrigerant. It should be realistic to search for materials with remarkable magnetocaloric response around the second-order transition. Recently, a new ferromagnetic compound system $R_6Co_{1.67}Si_3$ (R = Ce, Nd, Gd, Tb and Dy) has been reported by Gaudin *et al*[13] and Chevalier *et al.*[14] They have obtained a single phase except for $Dy_6Co_{1.67}Si_3$ and studied systematically their crystal structures and magnetic properties. In this paper, we report on the magnetic properties and magnetocaloric effects of compound $Tb_6Co_{1.67}Si_3$. A reversible second-order magnetic transition around Curie temperature and a large refrigerant capacity are obtained in $Tb_6Co_{1.67}Si_3$.

2. Experimental

Sample of $Tb_6Co_{1.67}Si_3$ was prepared by arc melting an appropriate mixture of Tb (99% in purity), Co (99.9%), and Si (99.999%) in a high-purity argon atmosphere. The ingots obtained by arc melting were

*Project supported by 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 Chinese Academy of Sciences (Grant No KJCX2-YW-W02).
†E-mail: sj@g203.iphy.ac.cn

wrapped in Mo foil, sealed in an evacuated quartz tube, annealed at 1073 K for 30 d and then quenched to room temperature. X-ray diffraction (XRD) measurement on powder sample was performed by using Cu $K\alpha$ radiation to identify the phase purity and the crystal structure. Magnetization was measured as a function of temperature and magnetic field by using a physical property measurement system (PPMS) purchased from Quantum Design. The isothermal magnetic entropy change was calculated from the magnetization data by using the Maxwell relation.

3. Results and discussion

The powder XRD pattern of $Tb_6Co_{1.67}Si_3$ collected at room-temperature is shown in Fig.1. All the diffraction peaks can be indexed in a hexagonal $Ce_6Ni_2Si_3$-type structure (space group $P6_3/m$)[13] except some smaller pecks (centred at about 24.4°, 25.5° and 37°), which indicates the existence of a minor phase other than the $Tb_6Co_{1.67}Si_3$ compound. The crystal lattice parameters obtained from the XRD pattern are found to be $a = 1.1673(6)$ nm and $c = 0.4129(8)$ nm, which are almost in agreement with those reported by Chevalier *et al.*[14]

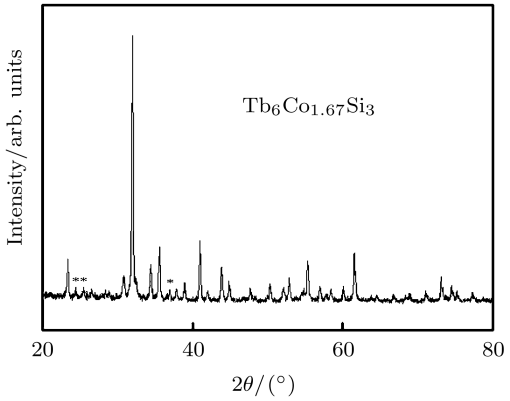

Fig.1. Room-temperature powder XRD patterns of $Tb_6Co_{1.67}Si_3$ compound. The diffraction peak from impurity phase is indicated by '∗'.

Figure 2 shows the thermomagnetic M-T curves of $Tb_6Co_{1.67}Si_3$ measured in the zero field- cooled (ZFC) and the field-cooled (FC) processes under a field of $H = 0.01$ T. One can find from the ZFC and FC curves that the compound undergoes two magnetic transitions at 168 and 186 K separately. The transition at a lower temperature corresponds probably to a spin reorientation. The transition at a higher temperature indicates a state changing from ferromagnetic to paramagnetic (FM-PM) with a Curie temperature $T_C = 186$ K, where the T_C is defined as the temperature corresponding to the maximum M-T slope. The ZFC and FC curves for $Tb_6Co_{1.67}Si_3$ are completely reversible around T_C, which is a characteristic of the second-order transition. However, an irreversibility between the ZFC and FC curves appears below T_C, indicating that the magnetization at low temperatures has a significantly thermal history dependence.

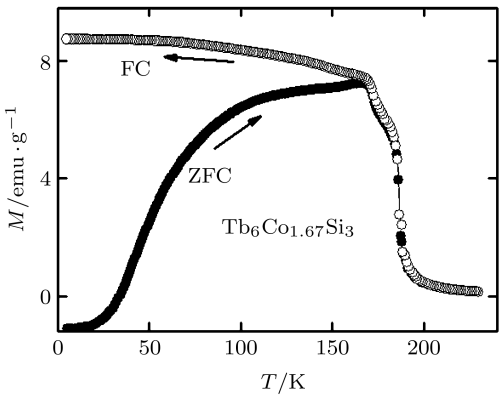

Fig.2. Temperature-dependent magnetization of $Tb_6Co_{1.67}Si_3$ in zero field- cooled (ZFC) and field-cooled (FC) processes under a field of $H = 0.01$ T.

Figure 3 shows the field dependence of magnetization of $Tb_6Co_{1.67}Si_3$ at 5 K. Magnetization curve exhibits a different saturation state even though for an applied magnetic field reaching 5 T. The 'saturation magnetization' at 5 K and in a field of 5 T is 187 emu/g, i.e. the saturation moment per $Tb_6Co_{1.67}Si_3$ molecule is 38 μ_B. According to the experimental results by Chevalier *et al*,[14] the magnetic moment of Co atoms is zero in the $R_6Co_{1.67}Si_3$ ternary silicide. Thus, for $Tb_6Co_{1.67}Si_3$ the average

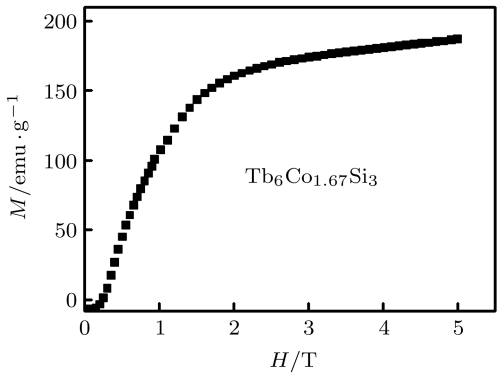

Fig.3. Magnetic field dependence of magnetization for $Tb_6Co_{1.67}Si_3$ at 5 K.

magnetic moment per Tb atom is $6.3\,\mu_B$, which is obviously smaller than that expected of Tb^{3+} free ion saturated moment ($9\,\mu_B$). This may be due to the crystalline field effects, which can quench the angular momentum.[14]

It can be seen from Fig.2 that for $Tb_6Co_{1.67}Si_3$ an obviously negative value of magnetization is observed from the ZFC curve at temperatures lower than 34 K. A similar behaviour has been also observed in $TbFe_{3.5}Al_{8.5}$ single crystal.[15] The negative magnetization is ascribed to the occurrence of a large coercivity at low temperatures in conjunction with an unbalance of magnetic domains.[14] The hysteresis loop of $Tb_6Co_{1.67}Si_3$ at 5 K is shown in Fig.4. The compound has a coercive field of 5.92×10^5 A/m.

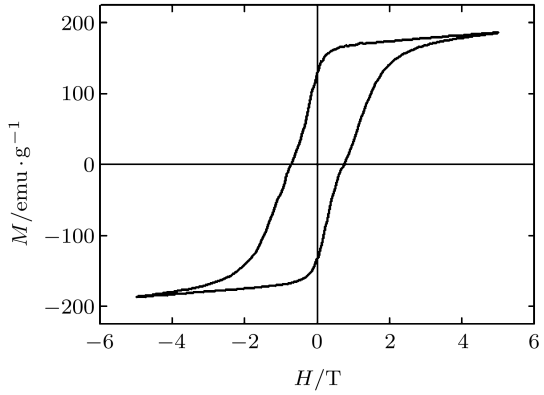

Fig.4. Magnetization curve for $Tb_6Co_{1.67}Si_3$ at 5 K.

Figure 5 shows the magnetization isotherms of $Tb_6Co_{1.67}Si_3$ measured under increasing and decreasing fields in a temperature range of 70—240 K. In the vicinity of the Curie temperature, from 162 to 194 K, the temperature step is 4 K; in the far regions of 70—160 K and 200—240 K a step is chosen to be 10 K. The sweep rate of field is slow enough to ensure that M-H curves are recorded in an isothermal process. It is observed that the isothermal magnetization curves of $Tb_6Co_{1.67}Si_3$ show a reversible behaviour for the field increasing/decreasing cycling around T_C, and there is no hysteresis in magnetization as a function of both the temperature and the magnetic field. In the Arrott plot of $Tb_6Co_{1.67}Si_3$ as shown in Fig.6, neither inflection nor negative slope is observed as a signature of metamagnetic transition above the T_C, indicating a nature of the second-order phase transition.

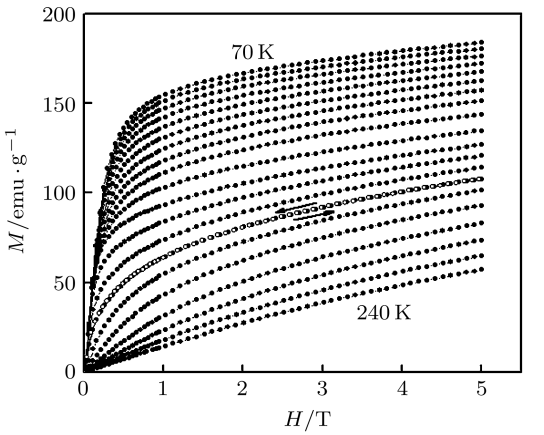

Fig.5. Magnetization isotherms of $Tb_6Co_{1.67}Si_3$, measured around the Curie temperature.

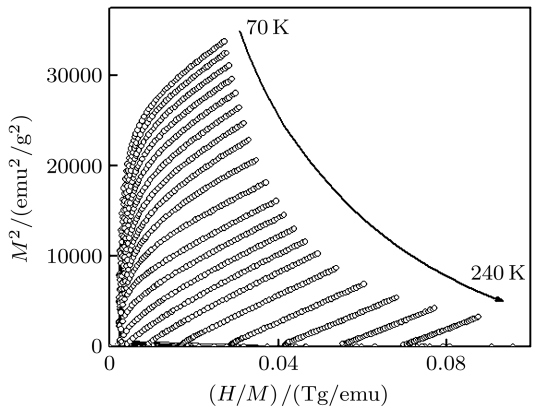

Fig.6. The Arrott plot of $Tb_6Co_{1.67}Si_3$.

The magnetic entropy change of $Tb_6Co_{1.67}Si_3$ compound is calculated from the isothermal magnetization curves, and the ΔS value as a function of temperature is shown in Fig.7. A negative peak around the Curie temperature can be observed from the curves, and the maximum value of ΔS for a magnetic field change of 0—5 T is found to be 7 J/kgK. Although the maximum ΔS of $Tb_6Co_{1.67}Si_3$ is smaller than those of most magnetocaloric materials with the first-order phase transition,[3−11] a broad distribution of the ΔS peak is observed, which is desired for the compound to be used in an Ericsson-cycle magnetic refrigerator. For $Tb_6Co_{1.67}Si_3$, the width of the ΔS peak, defined as the temperature interval corresponding to the half maximum of ΔS, approaches to about 80 K in magnetic fields changing from 0 to 5 T. No change in peak temperature of ΔS has been observed up to a field of 5 T, and the ΔS shape shows a symmetrical broadening due to an applied field, which indicates that the ΔS originates from a reversible second-order magnetic transition.

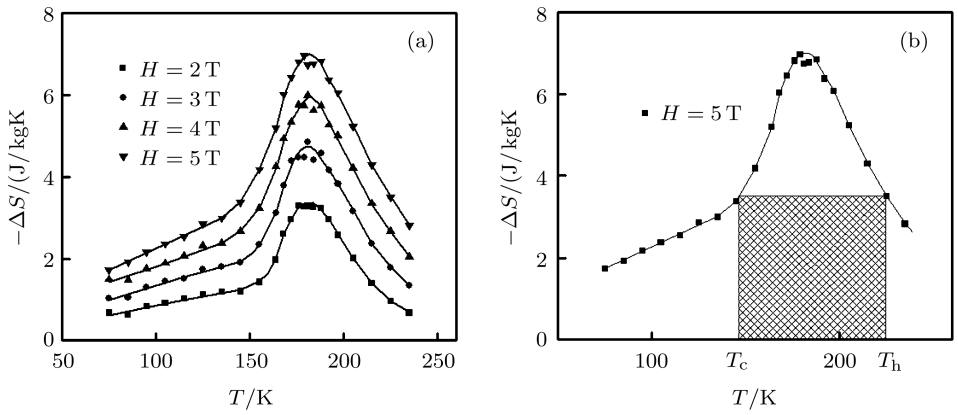

Fig.7. Magnetic entropy of $Tb_6Co_{1.67}Si_3$ varying with temperature under several different magnetic fields: 2, 3, 4 and 5 T (a), and refrigerant capacity (RC) shown as the shaded area (b).

The refrigerant capacity RC of $Tb_6Co_{1.67}Si_3$ is calculated by using the method suggested by Wood and Potter,[16] who defined the RC for a reversible refrigeration cycle operating between T_h (the temperature of the hot reservoir) and T_c (the temperature of the cold reservoir) as RC $= \Delta S \Delta T$, where ΔS is the magnetic entropy change at the hot and the cold ends of the cycle (defined as being equal) and a temperature span $\Delta T = T_\mathrm{h} - T_\mathrm{c}$. According to the definition, the value of RC is zero when T_c is equal to T_p (T_p is the temperature of ΔS peak). It is apparent that the value of RC of the material increases as T_c gradually deviates from T_p. An optimal refrigeration cycle can be found in an experimental temperature range, as evidenced by a maximum in RC.[4] Figure 8 shows the RC of $Tb_6Co_{1.67}Si_3$ as a function of T_c. The maximum value of RC is found to be about 330 J kg^{-1} for a magnetic field change from 0 to 5 T in a temperature range of 70—240 K. The RC value of $LaFe_{11.4}Si_{1.6}$ is also calculated from the ΔS versus T curve in Fig.4 of Ref.[6] for comparison to be about 250 J/kg for a field change of 0–5 T, which is much smaller than that of the $Tb_6Co_{1.67}Si_3$ despite its higher ΔS value (19.4 J/kgK for a magnetic field change from 0 to 5 T at T_C = 208 K).[6] The ΔS peak width of $Tb_6Co_{1.67}Si_3$ is considerably broader, which leads to a larger value of RC. Therefore, the $Tb_6Co_{1.67}Si_3$ compound is a magnetic refrigerant much better than the $LaFe_{11.4}Si_{1.6}$ compound.

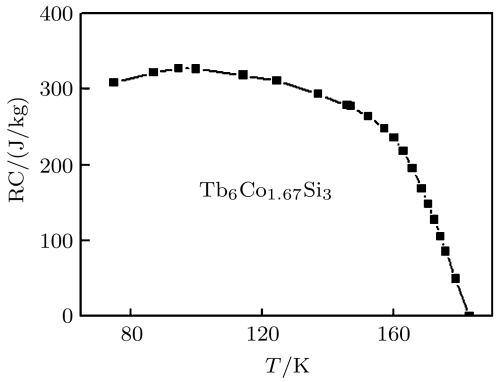

Fig.8. Temperature-dependent refrigerant capacity at the cold end of the refrigeration cycle for $Tb_6Co_{1.67}Si_3$ under a maximum applied field of 5 T.

4. Conclusion

We have reported on magnetocaloric effects of $Tb_6Co_{1.67}Si_3$. The compound presents a remarkable magnetocaloric response and its refrigerant capacity is found to be RC = 330 J/kg. $Tb_6Co_{1.67}Si_3$ has a high saturation magnetization, a reversible second-order magnetic transition, easily controlled Curie temperature from low temperature to room temperature by rare earth doping (Ref.[14]), a large RC, and easy fabrication as well. All these merits make the $Tb_6Co_{1.67}Si_3$ compound a very attractive candidate for magnetic refrigerants working in a corresponding temperature range.

References

[1] Tishin A M and Spichkin Y I 2003 *The Magnetocaloric Effect and its Applications*, edited by Coey J M D et al., Institute of Physics Publishing

[2] Jr Gschneidner K A, Pecharsky V K and Tsokol A O 2005 *Rep. Prog. Phys.* **68** 1479

[3] Pecharsky V K and Jr Gschneidner K A 1997 *Phys. Rev.*

Lett. **78** 4494

[4] Provenzano V, Shapiro A J and Shull R D 2004 *Nature* (London) **429** 853

[5] Hu F X, Shen B G, Sun J R and Zhang X X 2000 *Chin. Phys.* **9** 550

[6] Hu F X, Shen B G, Sun J R, Chen Z H, Rao G H and Zhang X X 2001 *Appl. Phys. Lett.* **78** 3675

[7] Wada H and Tanabe Y 2001 *Appl. Phys. Lett.* **79** 3302

[8] Tegus O, Brück E, Buschow K H J and de Boer F R 2002 *Nature* (London) **415** 150

[9] Guo Z B, Du Y W, Zhu J S, Huang H, Ding W P and Feng D 1997 *Phys. Rev. Lett.* **78** 1142

[10] Hu F X, Shen B G and Sun J R 2000 *Appl. Phys. Lett.* **76** 3460

[11] Krenke T, Duman E, Acet M, Wassermann E F, Moya X, Mañosa L and Planes A 2005 *Nature Materials* **4** 450

[12] Shen J, Gao B, Zhang H W, Hu F X, Li Y X, Sun J R and Shen B G 2007 *Appl. Phys. Lett.* **91** 142504

[13] Gaudin E, Weill F and Chevalier B 2006 *Z. Naturforsch* **61b** 825

[14] Chevalier B, Gaudin E and Weill F 2007 *J. Alloys Compd.* **442** 149

[15] Duong N P, Bruck E, Brommer P E, de Boer F R and Buschow K H J 2004 *J. Magn. Magn. Mater.* **268** 303

[16] Wood M E and Potter W H 1985 *Cryogenics* **25** 667