Magnetocaloric effect in Pr₆Co₁.₆⁷Si₃ compound

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Abstract

Magnetic properties and magnetocaloric effects of Pr₆Co₁.₆⁷Si₃ compound have been investigated by magnetization measurements. The saturation moment at 5 K is found to be 10.7μB. 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 ΔS = 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 ΔS peak is found to be about 38 K.

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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 ΔS to a narrow temperature range around the Curie temperature, which implies that a large ΔS is much easier to obtain in the vicinity of transition temperature. The first-order phase-transition materials, such as Gd₅Si₂Ge₂ [3], LaFe₁₃₋ₓSiₓ [4,5], MnAs₁₋ₓSbx [6], MnFeP₁₋ₓAsₓ [7], etc., have been found to have large values of ΔS. Although the second-order phase-transition materials usually have a lower ΔS than the first-order phase-transition materials, their magnetization 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 Gd₆Co₁.₆⁷Si₃ with a Curie temperature of 294 K. They subsequently extended the study to other rare earth silicides R₆Co₁.₆⁷Si₃ (R = Ce, Nd, Tb and Dy) [12], which are of single phase except Dy₆Co₁.₆⁷Si₃. 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 Pr₆Co₁.₆⁷Si₃. 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 Pr₆Co₁.₆⁷Si₃ 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
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\textsubscript{6}Co\textsubscript{1.67}Si\textsubscript{3} compound. The sample is found to have a single phase with a hexagonal Gd\textsubscript{6}Co\textsubscript{1.67}Si\textsubscript{3}-type structure (space group \textit{P}6\textsubscript{3}/\textit{m}) \cite{11}. The lattice parameters are found to be \(a = 12.034(6)\ \text{Å}\) and \(c = 4.258(4)\ \text{Å}\). Fig. 2 shows the thermomagnetic M–T curves of Pr\textsubscript{6}Co\textsubscript{1.67}Si\textsubscript{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 \cite{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\textsubscript{6}Co\textsubscript{1.67}Si\textsubscript{3} \cite{12}. The saturation moment \(\mu_s = 10.7\mu_B\) per Pr\textsubscript{6}Co\textsubscript{1.67}Si\textsubscript{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. \cite{12}, the Co atoms are non-magnetic in the R\textsubscript{6}Co\textsubscript{1.67}Si\textsubscript{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 \cite{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\textsubscript{6}Co\textsubscript{1.67}Si\textsubscript{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\textsubscript{6}Co\textsubscript{1.67}Si\textsubscript{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 \cite{2,10}.

The magnetic entropy change is calculated from magnetization data by using the Maxwell relation \(\Delta S(T, H) =\)
Fig. 4. Magnetic entropy changes of Pr$_6$Co$_{1.67}$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$_6$Co$_{1.67}$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$_6$Co$_{1.67}$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 theory, the relation between the magnetic entropy change and the magnetic field near the Curie temperature is described as [14]

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

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$_6$Co$_{1.67}$Si$_3$ [15]. The value of isothermal magnetic entropy change will rise with the increase of magnetic field. Pr$_6$Co$_{1.67}$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$_6$Co$_{1.67}$Si$_3$. XRD patterns show that the compound is of a single phase with a hexagonal Gd$_6$Co$_{1.67}$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.

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References