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Magnetocaloric effect in $Gd_6Co_{1.67}Si_3$ compound with a second-order phase transition*

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The magnetic properties and the magnetic entropy change ΔS have been investigated for $Gd_6Co_{1.67}Si_3$ compounds with a second-order phase transition. The saturation moment at 5 K and the Curie temperature T_C are 38.1 μ_B and 298 K, respectively. The ΔS originates from a reversible second-order magnetic transition around T_C and its value reaches 5.2 J/kg·K for a magnetic field change from 0 to 5 T. The refrigerant capacity (RC) of $Gd_6Co_{1.67}Si_3$ are calculated by using the methods given in Refs.[12] and [21], respectively, for a field change of 0–5 T and its values are 310 and 440 J/kg, which is larger than those of some magnetocaloric materials with a first-order phase transition.

Keywords: $Gd_6Co_{1.67}Si_3$ compound, magnetic properties, magnetic entropy change
PACC: 7530S, 7550C

1. Introduction

The magnetic materials involving first-order and second-order magnetic transitions have been extensively investigated in an attempt to achieve a large magnetocaloric effect (MCE).[1−11] The materials with first-order phase transitions, such as $Gd_5Si_2Ge_2$,[4] $LaFe_{13-x}Si_x$,[5,6] $MnAs_{1-x}Sb_x$,[7] $MnFeP_{1-x}As_x$,[8] $Ni_{0.5}Mn_{0.5-x}Sn_x$,[9] $ErCo_2$,[10] and $La_{1-x}Ca_xMnO_3$,[11] etc have been revealed to have a large value of magnetic entropy change ΔS. However, the first-order phase transition materials exhibit generally considerable hysteresis loss, which makes magnetic refrigeration less efficient. Refrigerant capacity (RC) is a measure of the performance of magnetocaloric material.[12−16] Moreover, it is necessary to take into account the hysteresis loss for evaluating the refrigerant material by subtracting it from the corresponding RC.[15] To improve the efficiency of magnetic refrigeration, it is important to depress the hysteresis loss and enhance the RC. Although the second-order phase transition materials usually show a lower value of ΔS than the first-order ones, their magnetization exhibits an excellent reversibility in the temperature/magnetic field cycling and no magnetic hysteresis loss is observed.[17] Moreover, they usually exhibit a larger RC, which is highly desired in the practical applications of the magnetic refrigeration technique. It is therefore necessary to search for materials with a remarkable magnetocaloric response at temperatures close to 300 K and around the second-order phase transition. Recently, a ferromagnetic silicide $Gd_6Co_{1.67}Si_3$ has been reported by Gaudin *et al.*[18] This compound exhibits a high saturation magnetization and a good reversible second-order magnetic transition at a Curie temperature T_C of 294 K.[19] Therefore, both the RC and the MCE could be expected to be large at room temperature in the $Gd_6Co_{1.67}Si_3$ compound. In this paper, we report the magnetic entropy change and the enhanced magnetic refrigeration in the compound $Gd_6Co_{1.67}Si_3$. A large RC at room temperature and a reversible dependence of the magnetization on temperature and magnetic field are obtained.

2. Experiments

The $Gd_6Co_{1.67}Si_3$ sample was prepared by using arc melting appropriate mixture of the raw materials of Gd (99.9% in purity), Co (99.9%), and Si (99.999%) in an atmosphere of high-purity argon. The sample

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was turned over and remelted several times to ensure homogeneity. Ingots obtained by arc melting were wrapped by a molybdenum foil, sealed in a quartz tube with high vacuum, annealed at 1073 K for 30 days and then quenched to room temperature. Then ingots were ground into powders. x-ray diffraction (XRD) measurements on powder samples were performed by 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 physical property measurement system (PPMS) purchased from Quantum Design. By using the Maxwell relation, the magnetic entropy change was calculated based on the isothermal magnetization around the Curie temperature.

3. Results and discussion

Figure 1 displays the room-temperature powder XRD pattern of $Gd_6Co_{1.67}Si_3$. All the diffraction peaks can be indexed to a hexagonal "$Ce_6Ni_2Si_3$"-type structure (space group $P6_3/m$)[18] except some smaller pecks (centred at about 27.2° and 33.1°) that indicate the existence of a minor phase other than the $Gd_6Co_{1.67}Si_3$ compound. The lattice parameters are found to be $a = 1.1760(1)$ nm and $c = 0.4160(3)$ nm, which are almost in agreement with the experimental results reported by Chevalier *et al.*[19]

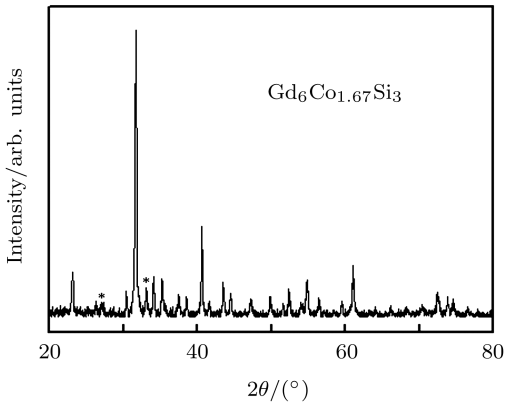


Fig.1. Room-temperature powder XRD pattern of $Gd_6Co_{1.67}Si_3$, in which the diffraction peaks from impurity phase are asterisked.

Figure 2 shows the temperature dependence of the magnetization of $Gd_6Co_{1.67}Si_3$ under an external magnetic field of 0.01 T. The value of T_C, defined as the temperature corresponding to the maximum slope of the thermal magnetization curve, is found to be 298 K. The heating and cooling magnetization cycles are reversible, indicating a characteristic of second-order transition. The magnetic field dependence of the magnetization measured at 5 K for $Gd_6Co_{1.67}Si_3$ is shown in the inset of Fig.2. The saturation magnetization is 188.9 emu/g, that is, the saturation moment per $Gd_6Co_{1.67}Si_3$ molecule is 38.1 μ_B.

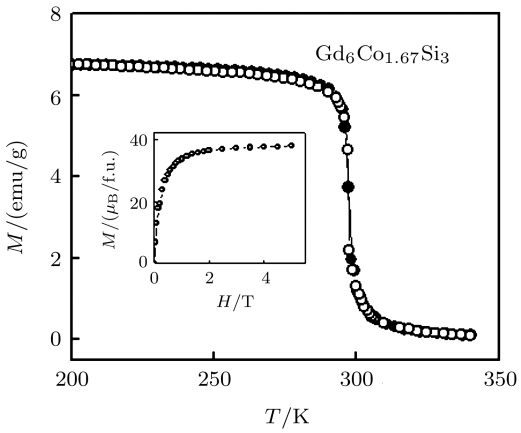


Fig.2. Temperature dependence of magnetization of $Gd_6Co_{1.67}Si_3$ under a magnetic field of 0.01 T, in which the inset shows the magnetic field dependence of magnetization at 5 K.

Figure 3(a) shows the isothermal magnetization curves for $Gd_6Co_{1.67}Si_3$ in a temperature range of 211–342 K at different temperature steps in magnetic fields up to 5.0 T. The temperature steps are chosen to be 2 K in the vicinity of T_C and 10 K for the regions far away from T_C. The sweep rate of field is slow enough to ensure that M–H curves are recorded in an isothermal process. It can be observed from Fig.3(a) that the isothermal magnetization curves around T_C show a reversible behaviour for the field increasing/decreasing cycling, and there is 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.[2,3,17] The magnetic entropy change as a function of temperature for the $Gd_6Co_{1.67}Si_3$ compound is shown in Fig.4. The maximum values of ΔS at T_C are found to be 2.6 and 5.2 J/kg·K for the field changes of 0–2 and 0–5 T, respectively. No change in peak temperature of ΔS has been observed up to the field of 5 T, and the ΔS shape shows a symmetrical broadening with a field applied, indicating that the large magnetic entropy change originates from a reversible second-order magnetic transition at T_C.[17,20] The Arrott plot of $Gd_6Co_{1.67}Si_3$ is shown in Fig.3(b), in which neither inflection nor negative slope is observed as a signature of metamagnetic transition above the T_C.

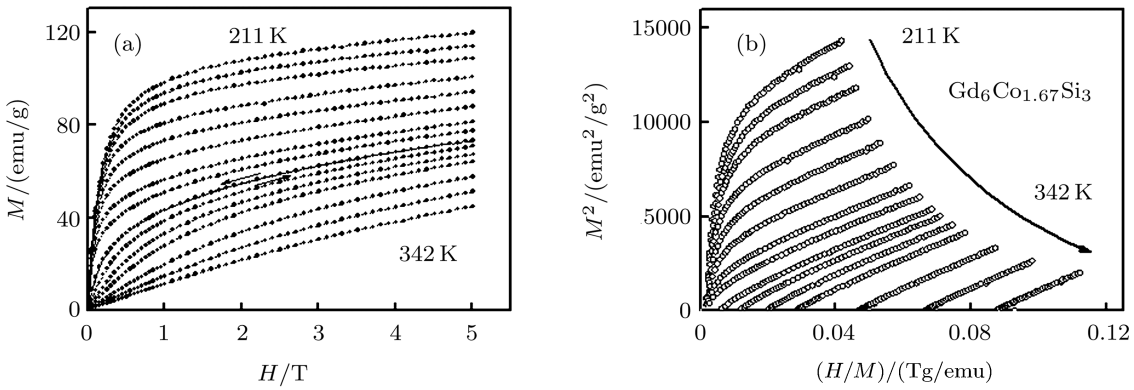


Fig.3. Magnetization of $Gd_6Co_{1.67}Si_3$ as a function of applied field measured near the Curie temperature (a) and the Arrott plots of $Gd_6Co_{1.67}Si_3$ (b).

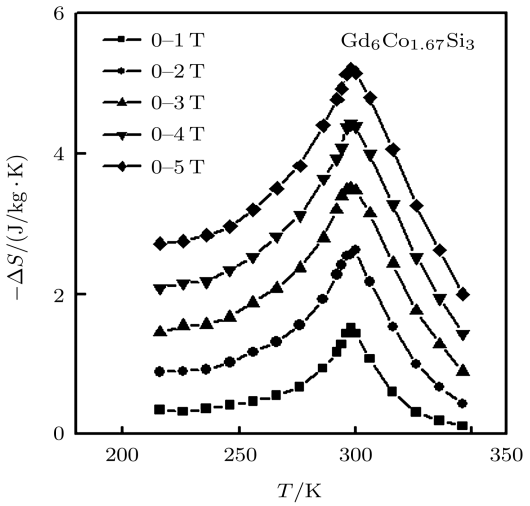


Fig.4. Magnetic entropy changes of $Gd_6Co_{1.67}Si_3$, extracted from magnetization measurements with magnetic fields changing from 0, respectively, to 1.0, 2.0, 3.0, 4.0 and 5.0 T.

Usually, a large RC value is advantageous to practical application of the materials. The RC value can give a comparison of the refrigerant capacities of different magnetocaloric materials and it is calculated by different methods in the literature.[12,21] Wood and Potter[12] have defined the RC for a reversible refrigeration cycle operating between the temperatures T_1 and T_2 of the hot and the cold reservoirs as RC = $\Delta S \Delta T$, where ΔS is the magnetic entropy change at the hot and the cold ends of the cycle and ΔT is the temperature span between the hot and the cold ends, respectively. An optimal refrigeration cycle can be found in the experimental temperature range, as evidenced by a maximum in RC. The other method[21] is to integrate numerically the area below the $\Delta S - T$ curve by using the temperatures at half maximum of the ΔS peak as the integration limits. According to the methods given in Refs.[12] and [21], the maximum values of RC for $Gd_6Co_{1.67}Si_3$ are found to be 310 and 440 J/kg for a magnetic field change from 0 to 5T, respectively. We have also measured the magnetic entropy change and the refrigerant capacity of the metal Gd for comparison. The maximum value of ΔS at T_C = 293 K is 9.7 J/kg K for the field change of 0–5 T. The RC values of Gd are calculated to be 378 and 556 J/kg by using the methods presented in Refs.[12] and [21], respectively, for a field change of 0–5 T. The RC value of $Gd_6Co_{1.67}Si_3$ is smaller than that of Gd, but it is larger than those of some magnetocaloric materials with a first-order phase transition, such as, $Gd_5Ge_{1.9}Si_2Fe_{0.1}$ (240 J/kg and 360 J/kg, obtained by using the methods in Refs.[12] and [21], respectively, for a field change of 0–5 T),[15] $MnFeP_{0.45}As_{0.55}$ ($\approx$250 J/kg and $\approx$ 400 J/kg for a field change of 0–5 T)[8] and $LaFe_{11.2}Co_{0.7}Si_{1.1}$ ($\approx$ 270 J/kg and $\approx$ 420 J/kg for a field change of 0–5 T),[22] where the RC values of $MnFeP_{0.45}As_{0.55}$ and $LaFe_{11.2}Co_{0.7}Si_{1.1}$ are calculated from the ΔS versus T curves in Fig.3 of Ref.[8] and Fig.2 of Ref.[22], respectively. Previous investigations have indicated that although some magnetocaloric materials with a first-order magnetic transition usually show higher values of ΔS,[2–11] the first-order transition tends to concentrate ΔS to a narrow temperature range around the Curie temperature, giving rise to a smaller value of RC. The ΔS peak width of $Gd_6Co_{1.67}Si_3$ is considerably broader, which leads to a larger value of RC. For the value of RC, it is necessary to take into account the hysteresis loss. The effective refrigeration capacity is the value obtained by subtracting the hysteretic loss from the value of RC. For the $Gd_6Co_{1.67}Si_3$ compound no hysteresis loss is observed as shown in Fig.3(a). Therefore, the $Gd_6Co_{1.67}Si_3$ compound can be a good working material for magnetic refrigeration

at room temperature.

In conclusion, we have found a remarkable magnetocaloric response in a $Gd_6Co_{1.67}Si_3$ compound. The compound has a high saturation magnetization ($M_s = 188.9\,\mathrm{emu/g}$, at 5 K), a Curie temperature at room temperature ($T_C = 298\,\mathrm{K}$), a magnetic entropy change ($\Delta S = 5.2\,\mathrm{J/kgK}$, for a field change of 0–5 T) originating from a reversible second-order magnetic transition around T_C. A broad distribution of the ΔS peak is observed in $Gd_6Co_{1.67}Si_3$. The values of refrigerant capacity (RC) of $Gd_6Co_{1.67}Si_3$ for a magnetic field change from 0 to 5T are obtained to be 310 J/kg and 440 J/kg by using the methods given in Refs.[12] and [21], respectively, which are larger than those of some magnetocaloric materials, such as $Gd_5Ge_{1.9}Si_2Fe_{0.1}$,[15] $MnFeP_{0.45}As_{0.55}$[8] and $LaFe_{11.2}Co_{0.7}Si_{1.1}$,[22] etc though it exhibits a lower ΔS value.

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