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Magnetic entropy change and large refrigerant capacity of $Ce_6Ni_2Si_3$-type GdCoSiGe compound*

Shen Jun(沈 俊)[a)†], Zhang Hu(张 虎)[b)], and Wu Jian-Feng(吴剑峰)[a)]

a) *Key Laboratory of Cryogenics, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing* 100190, *China*

b) *State Key Laboratory for Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing* 100190, *China*

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Magnetic entropy change ($\Delta S_{\rm M}$) and refrigerant capacity (RC) of $Ce_6Ni_2Si_3$-type $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ compounds have been investigated. The $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ undergoes a reversible second-order phase transition at the Curie temperature $T_{\rm C} = 296$ K. The high saturation magnetization leads to a large $\Delta S_{\rm M}$ and the maximal value of $\Delta S_{\rm M}$ is found to be 5.9 J/kg·K around $T_{\rm C}$ for a field change of 0–5 T. A broad distribution of the $\Delta S_{\rm M}$ peak is observed and the full width at half maximum of the $\Delta S_{\rm M}$ peak is about 101 K under a magnetic field of 5 T. The large RC is found around $T_{\rm C}$ and its value is 424 J/kg.

Keywords: $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ compound, magnetocaloric effect, refrigerant capacity

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1. Introduction

In recent years, much attention has been paid to magnetic materials with the giant magnetocaloric effect (MCE) due to their potential application as magnetic refrigerants.[1−3] Large MCE around the transition temperatures has been found in many materials with a first-order phase transition, such as $Gd_5Si_2Ge_2$, La(Fe, Si)$_{13}$, $MnAs_{1-x}Sb_x$, $MnFeP_{1-x}As_x$, NiMnGa, etc.[4−10] Although, these materials have usually large magnetic entropy change ($\Delta S_{\rm M}$), magnetic hysteresis loss happens inevitably, which greatly reduce the actual refrigerant capacity (RC). Therefore, it is important to explore advanced magnetic refrigerant materials which possess not only large reversible $\Delta S_{\rm M}$ but also considerable RC. Recently, there has been a great deal of interest in the study of MCE of ferromagnetic materials that experience a second-order phase transition because of their high RC. Generally, heavy rare earth elements and their compounds are considered to be the best candidate materials for finding a large MCE due to their high magnetic moments. Gd metal has the highest MCE among the second-order phase transition materials and it shows a maximum $\Delta S_{\rm M}$ of 9.7 J/kg·K at $T_{\rm C} = 293$ K under a field change 0–5 T.[11,12] Recently, a ferromagnetic silicide $Gd_6Co_{1.67}Si_3$ derived from the $Ce_6Ni_2Si_3$-type structure was reported.[13,14] The compound exhibits a good MCE and a reversible second-order magnetic transition at room temperature.[15−17] In this paper, we study the magnetic properties and magnetocaloric effects of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ compound. Room-temperature maximum $\Delta S_{\rm M}$ of 5.9 J/kg·K and large RC of 424 J/kg are observed.

2. Experiments

Polycrystalline $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ was prepared by arc melting in a high-purity argon atmosphere. The purities of starting materials were better than 99.9%. The sample was turned over and remelted several times to ensure its homogeneity. Ingot obtained by arc melting was subsequently wrapped by molybdenum foil, sealed in a quartz tube of high vacuum, annealed at 1073 K for 30 days and then quenched to room temperature. The crystal structure of the samples was characterized using power x-ray diffraction (XRD) with Cu Kα radiation. Magnetizations were measured as functions of both temperature and

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†Corresponding author. E-mail: jshen@mail.ipc.ac.cn

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

3. Results and discussion

Figure 1 displays the room-temperature powder XRD pattern of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$. All the diffraction peaks can be indexed in a hexagonal $Ce_6Ni_2Si_3$-type crystal structure (space group $P6_3/m$) except some smaller peaks (centred at about 23.98°, 25.02° and 36.40°) that indicate the existence of a minor phase other than the $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ compound. The lattice parameters are determined to be a = 1.1761(9) nm and c = 0.4161(3) nm by using the Rietveld refinement method, which are slightly larger than those of $Gd_6Co_{1.67}Si_3$[15] because of the atomic radius of Ge is larger than that of Si.

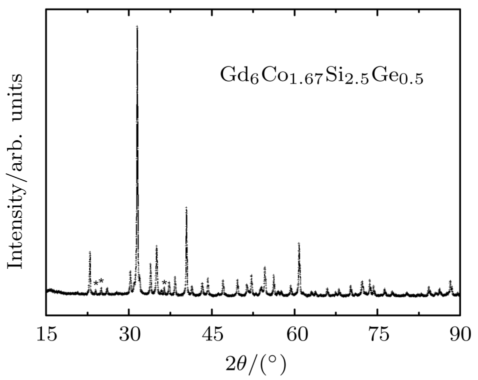

Fig. 1. Room-temperature powder XRD pattern of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$.

The temperature-dependent magnetization was measured in both zero field-cooled (ZFC) and field-cooled (FC) processes in order to determine the thermal hysteresis and the magnetic transition temperature. Figure 2(a) shows the thermomagnetic curves M–T of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ measured under an external magnetic field of 0.05 T. The sample was cooled down to 5 K in a zero field, the heating curve from 5 K to 300 K was measured first in a magnetic field of 0.05 T, then the cooling curve from 300 K to 5 K was measured in the same field. It is found that the M–T curves show a reversible behaviour in heating and cooling processes at the Curie temperature T_C, but without being accompanied by thermal hysteresis, indicating a nature of the second-order phase transition. It can be seen from Fig. 2(a) that $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ undergoes a magnetic transition from ferromagnetic (FM) to paramagnetic (PM) state, and its T_C is determined to be 296 K by evaluating the minimum value of the dM/dT on the ZFC M–T curve under a field of 0.05 T, which is nearly as large as that of pure Gd.[11,12] Figure 2(b) shows the temperature dependences of magnetization of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ in different magnetic fields. The magnetization exhibits a continuous change around T_C in different magnetic fields and T_C significantly increases with increasing magnetic field. The temperature dependence of the magnetization exhibits a rapid decrease at T_C, even at higher magnetic fields, therefore, a large ΔS_M may be expected of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$.

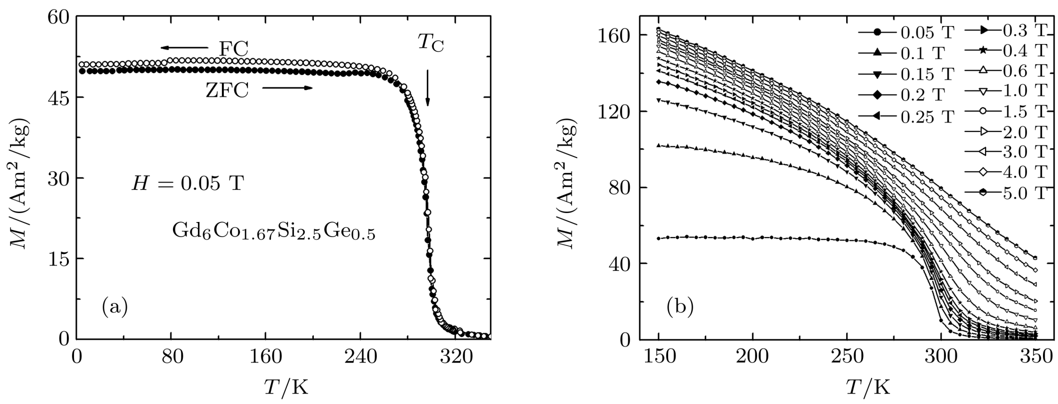

Fig. 2. Temperature-dependent magnetization of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ in both zero field-cooled (ZFC) and field-cooled (FC) processes under a magnetic field of 0.05 T (a), and thermomagnetic curves in different magnetic fields (b).

Figure 3(a) shows the magnetic hysteresis loop at 5 K. One can see from the figure that the hysteresis loop of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ exhibits a soft magnetic behaviour, because Gd has no orbital momentum with relatively small magnetocrystalline anisotropy. Figure 3(b) shows the field dependence of magnetization of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ at 5 K. The magnetic moment per f.u. in an external field of 13 T is found to be 42.3 μ_B. Thus, the magnetic moment of Gd atom is 7.06 μ_B, which is very close to the value of a free Gd^{3+} ion (7 μ_B).

These results mean that the Co atoms are non-magnetic in the $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ compound as observed in $R_6Co_{1.67}Si_3$ (R = Nd and Tb).[14]

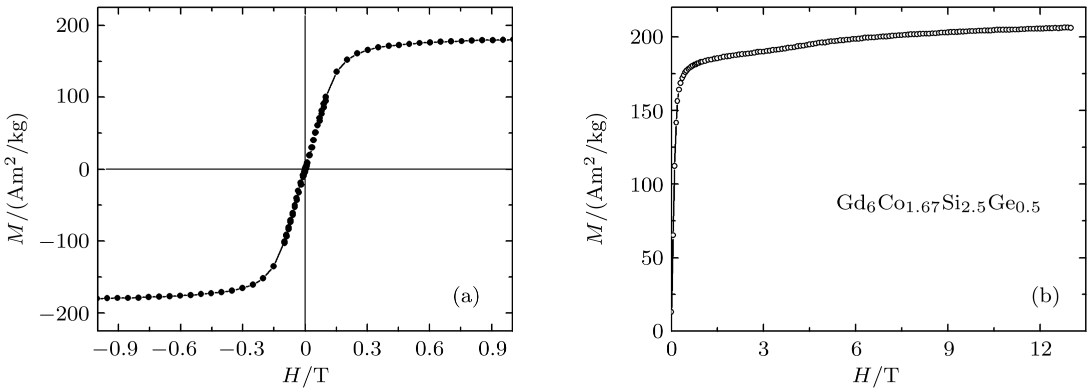

Fig. 3. Magnetic hysteresis loop (a), and field dependence of magnetization (b) of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ at 5 K.

The isothermal magnetization curves of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ were measured from 0 T up to 5 T around T_C in order to determine the ΔS_M. The sweep rate of the field was quite slow to ensure that the M–H curves could be recorded in an isothermal process. Figure 4(a) shows the magnetization isotherms of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ around T_C in a temperature range of 150–350 K with a temperature step of 5 K. It can be seen from Fig. 4(a) that the magnetization is smoothly saturated and its magnitude gradually decreases with the increase of temperature below T_C, exhibiting typical FM nature. For temperatures much higher than the T_C, the field dependence of the magnetization has a linear relation, indicating typical PM nature. Moreover, neither inflection nor negative slope in the Arrott plots of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ as shown in Fig. 4(b) indicates a characteristic of second-order FM-to-PM transition. It can also be seen from Fig. 4(a) that the isothermal magnetization curves obtained well above T_C show strong curvatures at low fields. Similar results have been observed in some other intermetallic compounds.[18–20] This may result from the existence of short-range ferromagnetic correlations in the PM state. To investigate the reversibility of the magnetic transitions in $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$, the M–H curves were measured respectively in field increasing and decreasing modes around T_C. There is no magnetic hysteresis in each curve shown, indicating the perfect magnetic reversibility of the magnetic transitions in $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$.

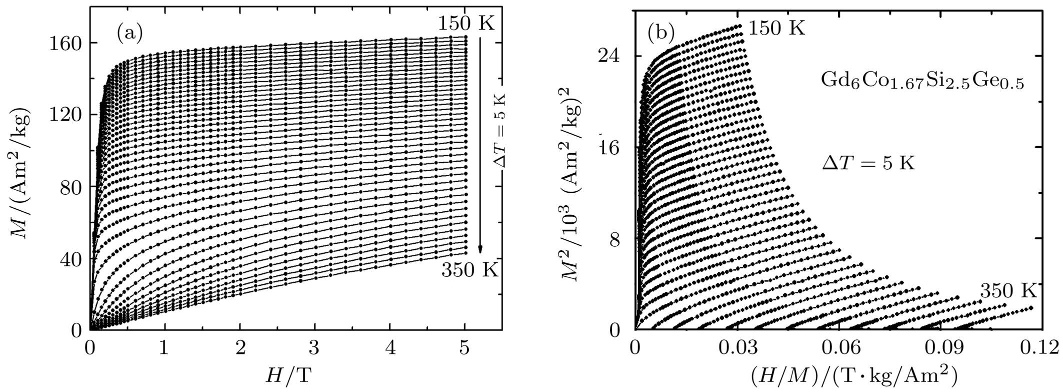

Fig. 4. Isothermal magnetization curves (a), and Arrott plot (b) of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ in a temperature range of 150–350 K with a temperature step of 5 K.

The ΔS_M of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ has been calculated from isothermal magnetization data by using the Maxwell relation $\Delta S_M = \int_0^H (\partial M/\partial T)_H \, \mathrm{d}H$. Figure 5 shows the ΔS_M as a function of temperature and magnetic field. One can see from Fig. 5 that both the peak and the width of ΔS_M depend on the applied magnetic field, and increase obviously with increasing field. No change in peak temperature of ΔS_M is observed and the ΔS_M shape shows a "λ"-type one as is usually seen in magnetic materials with a second-order magnetic transition. The maximal values of ΔS_M for $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ are found to be 3.1 J/kg·K and 5.9 J/kg·K at 297.5 K for a field change of 0–2 T and 0–5 T, respectively, which are smaller than those of pure Gd,[12] but are comparable with those of $Gd_6Co_{1.67}Si_3$,[15–17] $Gd_6Ni_{1.67}Si_3$,[16] Gd_7Pd_3,[21] $Gd_5Si_2Ge_2$ compound prepared with low purity (99%) commercial Gd metal,[22] and $Mn_5Ge_{2.1}Ga_{0.9}$.[23] The large value of ΔS_M is due to the high saturation magnetization in $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$.

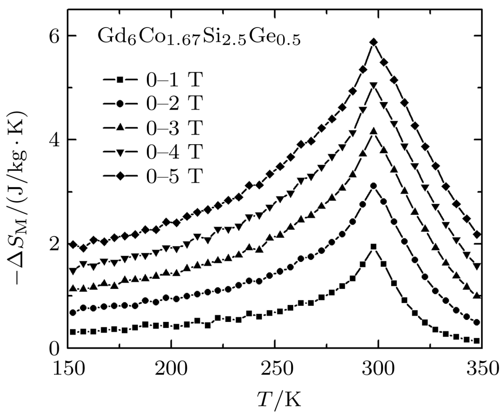

Fig. 5. Temperature dependence of magnetic entropy change $-\Delta S_M$ for $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ compound for different magnetic field changes.

To evaluate applicability of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ as a room-temperature magnetic refrigerant material, its RC values have been estimated by using the approach suggested by Gschneidner *et al.*[24] The refrigerant capacity is defined as $RC = \int_{T_1}^{T_2} |\Delta S_M| dT$, where T_1 and T_2 are the temperatures corresponding to both sides of the half-maximum value of $-\Delta S_M$ peak. Calculations show that the maximal value of RC for $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ is 424 J/kg for a field change of 0–5 T, which is comparable to or much larger than those of some magnetocaloric materials with a second-order magnetic transition, such as $LaFe_{11.2}Co_{0.7}Si_{1.1}$ (~420 J/kg at 274 K),[25] $La(Fe_{0.92}Co_{0.08})_{11.83}Al_{1.17}$ (~415 J/kg at 303 K),[26] $LaFe_{11.0}Co_{0.9}Si_{1.1}$ (~275 J/kg at 294 K),[27] and $LaFe_{11.2}Co_{0.7}Si_{1.1}C_{0.1}$ (~320 J/kg at 290 K),[28] but their ΔS_M is larger than that of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$. Although some Gd- and Mn-based magnetocaloric materials with a first-order magnetic transition have a large ΔS_M, but their RC values are much smaller than that of $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ in a similar temperature range for a field change of 0–5 T, such as $Gd_5Ge_2Si_2$ (305 J/kg at 276 K),[29] $Gd_5Ge_{18}Si_{18}Sn_{04}$ (366 J/kg at 278 K),[30] $MnFeP_{0.5}As_{0.5}$ (~359 J/kg at 282 K),[31] $MnFeP_{0.45}As_{0.55}$ (~356 J/kg at 308 K),[31] where the RC values are estimated from the temperature dependence of ΔS_M in the literature. It can also be observed that both the values of ΔS_M and RC for $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ are comparable to those of $Gd_6Co_{1.67}Si_3$,[15,17] and its RC value is larger than those of $Gd_5Ge_{1.9}Si_2Fe_{0.1}$[29] and the melt-spun $Gd_5Si_{18}Ge_{18}Sn_{04}$ ribbons prepared at 30 m/s,[30] and they have values of ΔS_M close to each other (see Table 1). The present study shows that large RC and zero magnetic hysteresis are simultaneously achieved in $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ compound.

Table 1. Curie temperature T_C, magnetic entropy change ΔS_M, and refrigerant capacity RC at T_C for a magnetic field change of 0–5 T for pure Gd and some Gd-based magnetocaloric materials.

materials	T_C/K	$-\Delta S_M/(J/kg\cdot K)$	$RC/(J/kg)$	Refs.
Gd	293	9.7	556	[12]
$Gd_6Co_2Si_3$	295	6.3	503	[12]
$Gd_6Co_{1.67}Si_3$	298	5.2	440	[15]
$Gd_6Co_{1.67}Si_3$	300	5.8	426	[17]
$Gd_5Ge_{1.9}Si_2Fe_{0.1}$	276	7.0	360	[29]
$Gd_5Si_{18}Ge_{18}Sn_{04}$	278	6.5	335	[30]
$Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$	296	5.9	424	this work

4. Conclusion

In conclusion, the $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ compound with a hexagonal $Ce_6Ni_2Si_3$-type structure undergoes a ferromagnetic ordering below the Curie temperature $T_C = 296$ K. A good magnetocaloric property is observed.

The maximal value of ΔS_M is 5.9 J/kg · K for a magnetic field change of 0–5 T, which originates from a reversible second-order magnetic transition. The peak of the ΔS_M–T curve shows a broad distribution and the full width at half maximum of the ΔS_M peak is about 101 K under a magnetic field of 5 T. The value of *RC* for a field change from 0 to 5 T is found to be 424 J/kg. Good magnetocaloric properties and especially considerable value of *RC* indicate that the $Gd_6Co_{1.67}Si_{2.5}Ge_{0.5}$ compound is a suitable candidate as magnetic refrigerants in the room temperature range.

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