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Magnetic entropy change and large refrigerant capacity of Ce$_6$Ni$_2$Si$_3$-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 (Δ$S_M$), and refrigerant capacity (RC) of Ce$_6$Ni$_2$Si$_3$-type Gd$_5$Co$_{1.6}$Si$_{2.5}$Ge$_{0.5}$ compounds have been investigated. The Gd$_5$Co$_{1.6}$Si$_{2.5}$Ge$_{0.5}$ undergoes a reversible second-order phase transition at the Curie temperature $T_C$ = 296 K. The high saturation magnetization leads to a large Δ$S_M$ and the maximal value of Δ$S_M$ is found to be 5.9 J/kg·K around $T_C$ for a field change of 0–5 T. A broad distribution of the Δ$S_M$ peak is observed and the full width at half maximum of the Δ$S_M$ peak is about 101 K under a magnetic field of 5 T. The large RC is found around $T_C$ and its value is 424 J/kg.

Keywords: Gd$_5$Co$_{1.6}$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$_5$Si$_2$Ge$_2$, 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 (Δ$S_M$), 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 Δ$S_M$ 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 Δ$S_M$ of 9.7 J/kg·K at $T_C$ = 293 K under a field change 0–5 T.$^{[11,12]}$ Recently, a ferromagnetic silicide Gd$_5$Co$_{1.6}$Si$_3$ derived from the Ce$_6$Ni$_2$Si$_3$-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$_5$Co$_{1.6}$Si$_{2.5}$Ge$_{0.5}$ compound. Room-temperature maximum Δ$S_M$ of 5.9 J/kg·K and large RC of 424 J/kg are observed.

2. Experiments

Polycrystalline Gd$_5$Co$_{1.6}$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 field.
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$_{6}$Co$_{1.67}$Si$_{2.5}$Ge$_{0.5}$. All the diffraction peaks can be indexed in a hexagonal Ce$_{6}$Ni$_{2}$Si$_{3}$-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$_{6}$Co$_{1.67}$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$_{6}$Co$_{1.67}$Si$_{3}$[15] because of the atomic radius of Ge is larger than that of Si.

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$_{6}$Co$_{1.67}$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$_{6}$Co$_{1.67}$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$_{6}$Co$_{1.67}$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 $\Delta S_M$ may be expected of Gd$_{6}$Co$_{1.67}$Si$_{2.5}$Ge$_{0.5}$.

Figure 3(a) shows the magnetic hysteresis loop at 5 K. One can see from the figure that the hysteresis loop of Gd$_{6}$Co$_{1.67}$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$_{6}$Co$_{1.67}$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 $\mu_B$. Thus, the magnetic moment of Gd atom is 7.06 $\mu_B$, which is very close to the value of a free Gd$^{3+}$ ion (7 $\mu_B$).
These results mean that the Co atoms are non-magnetic in the Gd$_{6}$Co$_{1.67}$Si$_{2.5}$Ge$_{0.5}$ compound as observed in $R_6$Co$_{1.67}$Si$_3$ ($R$ = Nd and Tb).\cite{14}

The isothermal magnetization curves of Gd$_6$Co$_{1.67}$Si$_{2.5}$Ge$_{0.5}$ were measured from 0 T up to 5 T around $T_C$ in order to determine the $\Delta S_M$. 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$_6$Co$_{1.67}$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$_6$Co$_{1.67}$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.\cite{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$_6$Co$_{1.67}$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$_6$Co$_{1.67}$Si$_{2.5}$Ge$_{0.5}$.

The $\Delta S_M$ of Gd$_6$Co$_{1.67}$Si$_{2.5}$Ge$_{0.5}$ has been calculated from isothermal magnetization data by using the Maxwell relation $\Delta S_M = \int_{0}^{H} (\partial M/\partial T)_H dH$. Figure 5 shows the $\Delta S_M$ as a function of temperature and magnetic field. One can see from Fig. 5 that both the peak and the width of $\Delta S_M$ depend on the applied
magnetic field, and increase obviously with increasing field. No change in peak temperature of $\Delta S_M$ is observed and the $\Delta S_M$ shape shows a “$\lambda$”-type one as is usually seen in magnetic materials with a second-order magnetic transition. The maximal values of $\Delta S_M$ for Gd$_6$Co$_{1.67}$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$_6$Co$_{1.67}$Si$_3$$^{[15–17]}$, Gd$_6$Ni$_{1.67}$Si$_3$$^{[16]}$, Gd$_7$Pd$_3$$^{[21]}$, Gd$_5$Si$_2$Ge$_2$ compound prepared with low purity (99%) commercial Gd metal$^{[22]}$ and Mn$_5$Ge$_2$Gd$_{0.9}$.$^{[23]}$ The large value of $\Delta S_M$ is due to the high saturation magnetization in Gd$_6$Co$_{1.67}$Si$_{2.5}$Ge$_{0.5}$.

![Fig. 5. Temperature dependence of magnetic entropy change $-\Delta S_M$ for Gd$_6$Co$_{1.67}$Si$_{2.5}$Ge$_{0.5}$ compound for different magnetic field changes.](image)

To evaluate applicability of Gd$_6$Co$_{1.67}$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$_6$Co$_{1.67}$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$_{1.1}$ ($\sim 420$ J/kg at 274 K)$^{[25]}$, La(Fe$_{0.92}$Co$_{0.08}$)$_{11.83}$Al$_{1.17}$ ($\sim 415$ J/kg at 303 K)$^{[26]}$, LaFe$_{11.0}$Co$_{0.9}$Si$_{1.1}$ ($\sim 275$ J/kg at 294 K)$^{[27]}$ and LaFe$_{11.2}$Co$_{0.7}$Si$_{1.1}$Co$_{0.1}$ ($\sim 320$ J/kg at 290 K)$^{[28]}$ but their $\Delta S_M$ is larger than that of Gd$_6$Co$_{1.67}$Si$_{2.5}$Ge$_{0.5}$. Although some Gd- and Mn-based magnetocaloric materials with a first-order magnetic transition have a large $\Delta S_M$, but their $RC$ values are much smaller than that of Gd$_6$Co$_{1.67}$Si$_{2.5}$Ge$_{0.5}$ in a similar temperature range for a field change of 0–5 T, such as Gd$_5$Ge$_2$Si$_2$ (305 J/kg at 276 K)$^{[29]}$, Gd$_5$Ge$_{1.9}$Si$_{1.8}$Sn$_{0.4}$ (366 J/kg at 278 K)$^{[30]}$, MnFe$_{0.45}$As$_{0.55}$ ($\sim 359$ J/kg at 282 K)$^{[31]}$, MnFe$_{0.45}$As$_{0.55}$ ($\sim 356$ J/kg at 308 K)$^{[31]}$, where the $RC$ values are estimated from the temperature dependence of $\Delta S_M$ in the literature. It can also be observed that both the values of $\Delta S_M$ and $RC$ for Gd$_6$Co$_{1.67}$Si$_{2.5}$Ge$_{0.5}$ are comparable to those of Gd$_6$Co$_{1.67}$Si$_3$$^{[15,17]}$, and its $RC$ value is larger than those of Gd$_5$Ge$_{1.9}$Si$_2$Fe$_{0.1}$ and the melt-spun Gd$_5$Si$_{1.8}$Ge$_{1.8}$Sn$_{0.4}$ ribbons prepared at 30 m/s$^{[30]}$ and they have values of $\Delta S_M$ close to each other (see Table 1). The present study shows that large $RC$ and zero magnetic hysteresis are simultaneously achieved in Gd$_6$Co$_{1.67}$Si$_{2.5}$Ge$_{0.5}$ compound.

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<th>$RC$/(J/kg)</th>
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<td>[17]</td>
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<td>296</td>
<td>5.9</td>
<td>424</td>
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4. Conclusion

In conclusion, the Gd$_6$Co$_{1.67}$Si$_{2.5}$Ge$_{0.5}$ compound with a hexagonal Ce$_6$Ni$_2$Si$_3$-type structure undergoes a ferromagnetic ordering below the Curie temperature $T_C = 296$ K. A good magnetocaloric property is observed.
The maximal value of $\Delta S_M$ is $5.9 \text{ J/kg} \cdot \text{K}$ for a magnetic field change of $0$–$5 \text{ T}$, which originates from a reversible second-order magnetic transition. The peak of the $\Delta S_M$–$T$ curve shows a broad distribution and the full width at half maximum of the $\Delta S_M$ peak is about $101 \text{ K}$ under a magnetic field of $5 \text{ T}$. The value of $RC$ for a field change from $0$ to $5 \text{ T}$ is found to be $424 \text{ J/kg}$. Good magnetocaloric properties and especially considerable value of $RC$ indicate that the $\text{Gd}_{6.67}\text{Co}_{1.67}\text{Si}_{2.5}\text{Ge}_{0.5}$ compound is a suitable candidate as magnetic refrigerants in the room temperature range.

References