Giant reversible magnetocaloric effect in metamagnetic HoCuSi compound

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The magnetic properties and magnetocaloric effect (MCE) of antiferromagnetic HoCuSi compound have been studied. It is found that HoCuSi undergoes a field-induced first order metamagnetic transition from antiferromagnetic (AFM) to ferromagnetic (FM) states below the Néel temperature ($T_N$). A giant MCE without hysteresis loss is observed in HoCuSi around $T_N$. The maximal magnetic entropy change ($-\Delta S_M$) and refrigerant capacity are 33.1 J/kgK and 385 J/kg, respectively, for a field change of 0–5 T. The excellent magnetocaloric properties can result from the field-induced AFM-FM transition below $T_N$ and the increase in magnetization change caused by the change in lattice volume at $T_N$. © 2010 American Institute of Physics. [doi:10.1063/1.3386536]

In recent years, magnetic refrigeration based on magnetocaloric effect (MCE) has attracted much attention due to its higher energy efficiency and friendly environment than the conventional gas compression refrigeration.1–4 To improve the application of this cooling technology, many efforts have been made to explore advanced magnetic materials that are applicable to magnetic refrigeration in different temperature regimes. One of the most important parameters for evaluating the potentiality of a magnetic refrigerant material is the isothermal magnetic entropy change ($\Delta S_M = \int_0^H (\partial M / \partial T) dH$), which is expected to achieve its maximal value at the magnetic transition temperature. Numerous materials, such as Gd$_4$(Si,Ge)$_4$, Ni–Mn–Ga, La(Fe,Si)$_2$, RCo$_2$ (R=Ho,Er), etc. have been found to exhibit giant $\Delta S_M$ around their transition temperatures due to the large magnetic moment and the sharp change in magnetization, which is usually associated with the metamagnetic transition or structure/volume change.

The ErCo$_2$ was found to have the tremendous $\Delta S_M$ among the magnetocaloric materials and show a low-temperature phase transition.11,12 This arouses the interest in exploring for materials with excellent magnetocaloric properties at low temperatures. Some rare-earth (R) based compounds with a ferromagnetic (FM) or an antiferromagnetic (AFM) phase transition have been found to possess not only large magnetic entropy change but also a small hysteresis loss.13–19 One of the most typical rare-earth based compounds is RCoSi. It has been reported that RCoSi compounds exhibit interesting physical properties.20–23 Their crystal structure was found to be dependent on the annealing temperature. The high-temperature phase has the AlB$_2$-type structure (space group P6$_3/mmm$),20 whereas the low-temperature phase is of the Ni$_3$In-type structure (space group P6$_2$3/mmc).21 On the basis of neutron diffraction measurements, HoCoSi compound with the Ni$_3$In-type structure was originally reported by Bažela et al.22 to not to order down to 4.2 K. Later on it is found that Ni$_3$In-type HoCuSi undergoes a magnetic transition from AFM to paramagnetic (PM) states at $T_N=9$ K,23,24 accompanied by a small change in lattice constants.24 In the present paper, we carry out a study on the magnetic and MCE properties of HoCuSi. It is found that HoCuSi undergoes a field-induced AFM-FM metamagnetic transition below $T_N$, accompanied by a giant MCE without hysteresis loss.

The polycrystalline HoCuSi compound was prepared by arc melting the constituent elements with the purity better than 99.9% in argon atmosphere. For homogeneity, the ingot was annealed in an evacuated sealed quartz tube at 850 °C for one week. Powder x-ray diffraction (XRD) measurements were performed at room temperature by using Cu Kα radiation to identify the crystal structure and the lattice parameters. The Rietveld refined XRD pattern of HoCuSi is shown in Fig. 1. It shows that the sample is clean single phase with a hexagonal Ni$_3$In-type structure. The lattice parameters are $a=4.140(5)$ and $c=7.366(6)$ Å.

The magnetization was measured by employing a physical property measurement system. Figure 2(a) displays the zero-field-cooling (ZFC) and field-cooling (FC) susceptibility ($\chi$) measured under a field of 0.01 T. Both the ZFC and FC $\chi$–T curves exhibit maxima around $T_N$, which is characteristic of a magnetic transition from AFM to PM states. One can see that there is a tiny difference between ZFC and FC $\chi$–T curves above $T_N$, which is associated with the thermal hysteresis. The difference between them below $T_N$ may be due to domain-wall pinning. The Néel temperature $T_N$ deter-

FIG. 1. (Color online) Rietveld refined powder XRD pattern of HoCuSi at room temperature. The observed data are indicated by crosses, and the calculated profile is the continuous line overlaying them. The short vertical lines indicate the angular positions of the Bragg peaks of HoCuSi. The lower curve shows the difference between the observed and calculated intensity.
minded by the peak position of $\chi$-$T$ curve is $\sim 7$ K, close to the value reported in Ref. 24. The inverse ZFC susceptibility $(1/\chi)$ as a function of temperature at 0.01 T magnetic field is plotted in the inset of Fig. 2(a). One can see that in the PM region, the susceptibility obeys the Curie–Weiss law. The effective magnetic moment ($\mu_{\text{eff}}$), evaluated from the slope of $1/\chi$ in the paramagnetic region, is equal to 10.62 $\mu_B$/Ho$^{3+}$, which is in good agreement with the free ion moment of Ho$^{3+}$ (10.60 $\mu_B$), and the PM Curie temperature is found to be $\sim 8$ K. Figure 2(b) shows the temperature dependences of the magnetization of HoCuSi in various magnetic fields. It is clearly seen that the magnetization at low temperatures increases greatly with increasing field, indicating a field-induced AFM-FM transition. The stepwise behavior of the $M$-$T$ curves above $T_N$ under high fields corresponds to a FM-to-PM transition.

The magnetization isotherms of HoCuSi were measured under applied fields up to 5 T in a wide temperature range around the transition temperature. The data were acquired in the processes of increasing and decreasing fields, respectively. Figure 3(a) displays the selected $M$-$H$ curves in the temperature range of $3$–$70$ K. A tiny magnetic hysteresis with coercive field $H_C \sim 0.01$ T is observed at 2 K. The value of $H_C$ decreases with increasing temperature and there is almost no magnetic hysteresis in the $M$-$H$ curves when the temperature is higher than 5 K. The linear increase in magnetization under low applied field, as shown in the inset in Fig. 3(a), reveals the AFM ordering of the compound below $T_N$. The magnetization curves deviate from this linear relationship and are gradually saturated under high applied field, indicating the field-induced metamagnetic transition from AFM to FM states. The negative slope of the Arrott plots below $T_N$, which is shown in Fig. 3(b) and the inset, further confirms the occurrence of the first order AFM-to-FM magnetic transition. The saturation magnetization derived from the $M$-$H$ curve at 3 K is $\sim 9.47$ $\mu_B$.

Based on magnetization data, the magnetic entropy change can be calculated by the Maxwell relation $\Delta S_M = \int_0^T \frac{\partial M}{\partial T} dH$. Figure 4 shows the temperature dependences of $\Delta S_M$ for different magnetic field changes. The maximal value of $\Delta S_M$ reaches 33.1 J/$\text{kg K}$ for a field change of 0–5 T, occurring at 8.3 K, which is much larger than those of most potential magnetic refrigerant materials in a similar magnetic transition temperature under the same field change, such as ErRu$_2$Si$_2$ (17.6 J/$\text{kg K}$), HoNiAl (23.6 J/$\text{kg K}$), ErNi$_5$ (15 J/$\text{kg K}$), and DySb (15.8 J/$\text{kg K}$), and also comparable to that of ErCO$_2$ (32–36 J/$\text{kg K}$). Particularly, a large $\Delta S_M$ value of 16.7 J/$\text{kg K}$ is achieved for a low field change of 0–2 T, which is advantageous to applications. In addition, one can see clearly from Fig. 4 that
the $-\Delta S_M$ peak broadens asymmetrically toward high temperatures with increasing field, resulting in a large MCE in the temperature regime above $T_N$. The giant MCE in HoCuSi is believed to be associated mainly with the field-induced metamagnetic transition from AFM to FM states, similar to those reported on ErRu$_2$Si$_2$ (Ref. 13) and GdCo$_2$B$_2$ (Ref. 17) and the change in lattice volume around $T_N$ (Ref. 23). To well comprehend the giant MCE of HoCuSi, we measured the thermal expansion data ($\Delta L/L_{(50 \text{ K})}$) under the fields of 0, 2, and 5 T by means of strain gauge method (Ref. 26). It is found that the value of $\Delta L/L_{(50 \text{ K})}$ almost decreases linearly with decreasing temperature above $T_N$ when the field is zero. However, it deviates from this linear relationship around $T_N$ and decreases abruptly with decreasing temperature, revealing the occurrence of the abrupt thermal expansion, i.e., great change in the lattice constants. Our result is in good agreement with that reported in Ref. 24. Similar phenomenon has been observed when a 2 T and 5 T field is applied, respectively. But it can be found that the abrupt thermal expansion around $T_N$ shifts to higher temperature with increasing field. This behavior is consistent with the asymmetrical broadening of the $-\Delta S_M$ peak.

As is known, it is not sufficient to identify the potentiality of a magnetic refrigerant material solely by the large magnetic entropy change ($-\Delta S_M$). Another important parameter is refrigerant capacity (RC), a measure of how much heat can be transferred between the cold and the hot sinks in one ideal refrigeration cycle. The RC of HoCuSi was estimated by using the approach suggested by Gschneidner et al. (Ref. 27) namely $RC=\frac{1}{T_1-T_2}\int_{T_1}^{T_2} -\Delta S_M\,dT$, where $T_1$ and $T_2$ are the temperatures corresponding to both sides of the half-maximum value of $-\Delta S_M$ peak, respectively. A large RC value of 385 J/kg is obtained in HoCuSi for a magnetic field change of 0–5 T. The RC of ErCo$_2$ is also calculated from the $-\Delta S_M$ versus $T$ curve in Ref. 12 by the same method without considering its hysteresis loss. The actual RC may be even smaller due to the magnetic hysteresis. The evaluated value of RC for ErCo$_2$ is $\sim 319$ J/kg for a field change of 0–5 T, which is less than that of HoCuSi, although the $-\Delta S_M$ value of the former is slightly larger than that of the latter.

In summary, antiferromagnetic HoCuSi undergoes a field-induced first order metamagnetic transition from AFM to FM states below $T_N$. A giant MCE without hysteresis loss is observed in HoCuSi, which is believed to be related to field-induced AFM-FM transition below $T_N$ and the volume change around $T_N$. The maximal $-\Delta S_M$ and RC value is $33.1$ J/kg K and 385 J/kg for a field change of 0–5 T, respectively. The excellent magnetocaloric properties indicate the applicability of HoCuSi to the magnetic refrigeration in the low temperature range.

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