

Giant reversible magnetocaloric effect in metamagnetic HoCuSi compound

J. Chen, B. G. Shen,^{a)} Q. Y. Dong, F. X. Hu, and J. R. Sun

State Key Laboratory for Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

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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 [$\Delta S_M = \int_0^H (\partial M / \partial T)_H dH$], which is expected to achieve its maximal value at the magnetic transition temperature. Numerous materials, such as $Gd_5(Si,Ge)_4$,⁵ Ni–Mn–Ga,⁶ La(Fe, Si)₁₃,^{7,8} RCO_2 ($R=Ho,Er$),^{9–12} etc. have been found to exhibit giant ΔS_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 ΔS_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 $RCuSi$. It has been reported that $RCuSi$ 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 $P6/mmm$),²⁰ whereas the low-temperature phase is of the Ni_2In -type structure (space group $P6_3/mmc$).²¹ On the basis of neutron diffraction measurements, HoCuSi compound with the Ni_2In -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_2In -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 $K\alpha$ 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_2In -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 (χ) measured under a field of 0.01 T. Both the ZFC and FC χ -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 χ -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-

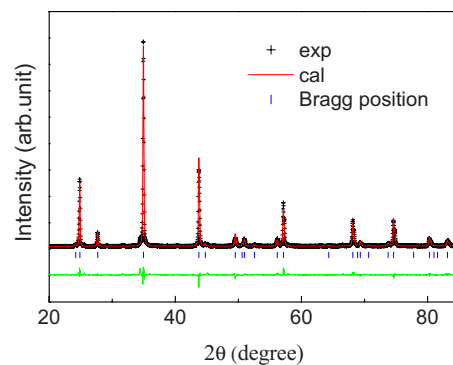


FIG. 1. (Color online) Rietveld refined powder XRD pattern of HoCuSi at room temperature. The observed data are indicated by crosses, and the calculated profile is the continuous line overlying them. The short vertical lines indicate the angular positions of the Bragg peaks of HoCuSi. The lower curve shows the difference between the observed and calculated intensity.

^{a)} Author to whom correspondence should be addressed. Electronic mail: shenbg@g203.iphy.ac.cn.

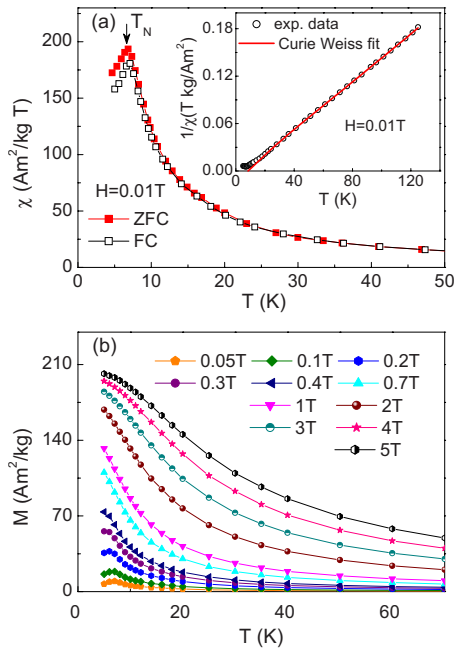


FIG. 2. (Color online) (a) Temperature dependences of the ZFC and FC susceptibility (χ) for HoCuSi under a magnetic field of 0.01 T. The inset shows the inverse of the ZFC susceptibility ($1/\chi$) as a function of temperature. (b) Temperature dependences of the magnetization under different magnetic fields.

mined by the peak position of χ -T curve is ~ 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 (μ_{eff}), evaluated from the slope of $1/\chi$ in the paramagnetic region, is equal to $10.62 \mu_B/\text{Ho}^{3+}$, 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 ~ 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 meta-

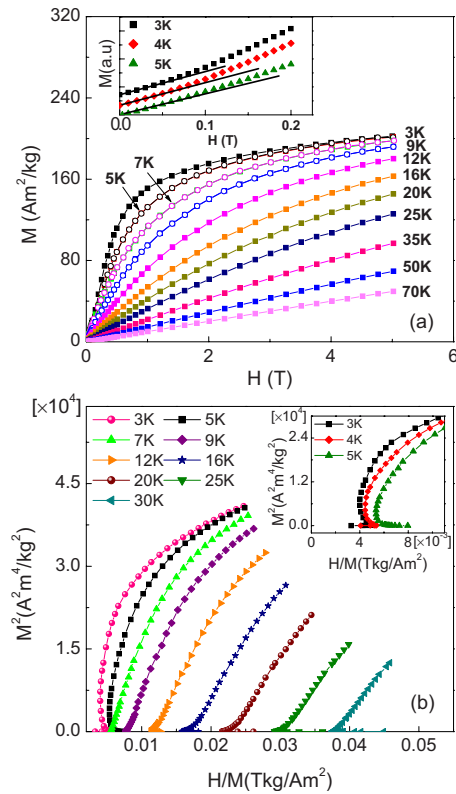


FIG. 3. (Color online) (a) Magnetization isotherms of HoCuSi measured on increasing (solid squares) and decreasing field (open circles). The inset shows the magnetization isotherms at 3, 4, and 5 K in low field range. (b) Arrott plots of HoCuSi. The inset displays the Arrott plots at temperatures of 3 K, 4 K, and 5 K, respectively.

magnetic transition.²⁵ 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 $\Delta S_M = \int_0^H (\partial M / \partial T)_H dH$. 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/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_2Si_2 (17.6 J/kg K),¹³ HoNiAl (23.6 J/kg K),¹⁴ ErNi_5 (15 J/kg K),¹⁵ and DySb (15.8 J/kg K),¹⁶ and also comparable to that of ErCo_2 (32–36 J/kg K).^{4,11,12} Particularly, a large $-\Delta S_M$ value of 16.7 J/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

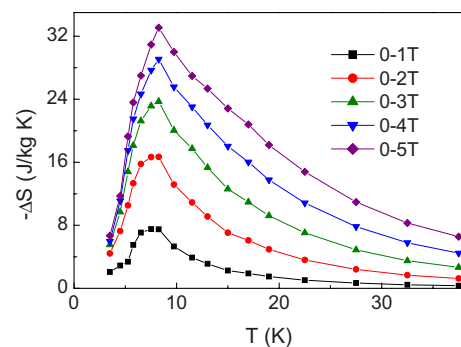


FIG. 4. (Color online) Temperature dependences of magnetic entropy change in HoCuSi for different magnetic field changes.

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 ErRu₂Si₂ (Ref. 13) and GdCo₂B₂,¹⁷ and the change in lattice volume around T_N .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.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.*,²⁷ namely $RC = \int_{T_1}^{T_2} |\Delta S_M| dT$, where T_1 and T_2 are the temperatures corresponding to both sides of the half-maximum value of $-\Delta S_M$ peak, 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 ErCo₂ 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 ErCo₂ is ~ 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 applica-

bility of HoCuSi to the magnetic refrigeration in the low temperature range.

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- ¹C. Zimm, A. Jastrab, A. Sternberg, V. Pecharsky, K. Gschneidner, Jr., M. Osborne, and I. Anderson, *Adv. Cryog. Eng.* **43**, 1759 (1998).
- ²A. M. Tishin and Y. I. Spichkin, in *The Magnetocaloric Effect and its Applications*, edited by J. M. D. Coey, D. R. Tilley, and D. R. Vij (Institute of Physics, London, 2003).
- ³V. K. Pecharsky and K. A. Gschneidner, Jr., *J. Magn. Magn. Mater.* **200**, 44 (1999).
- ⁴K. A. Gschneidner, Jr., V. K. Pecharsky, and A. O. Tsokol, *Rep. Prog. Phys.* **68**, 1479 (2005).
- ⁵V. K. Pecharsky and K. A. Gschneidner, Jr., *Phys. Rev. Lett.* **78**, 4494 (1997).
- ⁶F. X. Hu, B. G. Shen, and J. R. Sun, *Appl. Phys. Lett.* **76**, 3460 (2000).
- ⁷F. X. Hu, B. G. Shen, J. R. Sun, Z. H. Cheng, G. H. Rao, and X. X. Zhang, *Appl. Phys. Lett.* **78**, 3675 (2001).
- ⁸B. G. Shen, J. R. Sun, F. X. Hu, H. W. Zhang, and Z. H. Chen, *Adv. Mater.* **21**, 4545 (2009).
- ⁹N. A. de Oliveira, P. J. von Ranke, M. V. Tovar Costa, and A. Troper, *Phys. Rev. B* **66**, 094402 (2002).
- ¹⁰N. H. Duc, D. T. Kim Anh, and P. E. Brommer, *Physica B* **319**, 1 (2002).
- ¹¹N. K. Singh, P. Kumar, K. G. Suresh, A. K. Nigam, A. A. Coelho, and S. Gama, *J. Phys.: Condens. Matter* **19**, 036213 (2007).
- ¹²H. Wada, Y. Tanabe, M. Shiga, H. Sugawara, and H. Sato, *J. Alloys Compd.* **316**, 245 (2001).
- ¹³T. Samanta, I. Das, and S. Banerjee, *Appl. Phys. Lett.* **91**, 152506 (2007).
- ¹⁴N. K. Singh, K. G. Suresh, R. Nirmala, A. K. Nigam, and S. K. Malik, *J. Appl. Phys.* **101**, 093904 (2007).
- ¹⁵P. J. von Ranke, M. A. Mota, D. F. Grangeia, A. M. G. Carvalho, F. C. G. Gandra, A. A. Coelho, A. Caldas, N. A. de Oliveira, and S. Gama, *Phys. Rev. B* **70**, 134428 (2004).
- ¹⁶W. J. Hu, J. Du, B. Li, Q. Zhang, and Z. D. Zhang, *Appl. Phys. Lett.* **92**, 192505 (2008).
- ¹⁷L. W. Li, K. Nishimura, and H. Yamane, *Appl. Phys. Lett.* **94**, 102509 (2009).
- ¹⁸P. J. von Ranke, V. K. Pecharsky, and K. A. Gschneidner, Jr., *Phys. Rev. B* **58**, 12110 (1998).
- ¹⁹T. Samanta, I. Das, and S. Banerjee, *Appl. Phys. Lett.* **91**, 082511 (2007).
- ²⁰W. Rieger and E. Parthé, *Monatsch. Chem.* **100**, 439 (1969).
- ²¹A. Iandelli, *J. Less-Common Met.* **90**, 121 (1983).
- ²²W. Bažela, A. Szytuła, and J. Leciejewicz, *Solid State Commun.* **56**, 1043 (1985).
- ²³A. Oleś, R. Duraj, M. Kolenda, B. Penc, and A. Szytuła, *J. Alloys Compd.* **363**, 63 (2004).
- ²⁴P. Schobinger-Papamantellos, K. H. J. Buschow, and C. Ritter, *J. Alloys Compd.* **384**, 12 (2004).
- ²⁵S. K. Banerjee, *Phys. Lett.* **12**, 16 (1964).
- ²⁶H. T. Wang, X. W. Zhou, L. B. Sun, J. L. Dong, and S. Y. Yu, *Nucl. Eng. Des.* **239**, 484 (2009).
- ²⁷K. A. Gschneidner, Jr., V. K. Pecharsky, A. O. Pecharsky, and C. B. Zimm, *Mater. Sci. Forum* **315-317**, 69 (1999).