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Large reversible magnetocaloric effect in $TbCoC_2$ in low magnetic field

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A large reversible negative magnetic-entropy change ΔS_M has been observed in $TbCoC_2$, accompanied by a second-order phase transition at 28 K. The maximum value of $-\Delta S_M$ is 15.3 J kg^{-1} K^{-1} at 30 K for a magnetic-field change from 0 to 5 T, with the refrigerant capacity of 354 J kg^{-1}. In particular, also the large $-\Delta S_M^{max}$ of 7.8 J kg^{-1} K^{-1}, is obtained for a small field change from 0 to 2 T. The large reversible ΔS_M and the high reversible refrigerant capacity in low magnetic field indicate that $TbCoC_2$ may be a promising candidate for magnetic refrigeration at low temperatures. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2948900]

It is well known that conventional vapor-cycle refrigeration achieves cooling efficiencies only approaching 40% of the theoretical (Carnot) limit and meanwhile it usually employs hazardous substances.[1–6] Consequently, efficient and environment-friendly refrigerant technology will be demanded.[1–6] Magnetic refrigeration based on the magnetocaloric effect (MCE) of magnetic materials can well satisfy this demand because it has been proven that the cooling efficiency of 60% of the theoretical limit can be achieved without any toxic matter involved.[1–6] However, this high efficiency is only realized in a high magnetic-field change (usually from 0 to 5 T), using currently available magnetic refrigerant materials.[6] In this regard, it is important to extract advanced magnetic refrigerant materials with a large isothermal magnetic-entropy change ΔS_M and/or adiabatic temperature change ΔT_{ad} in low magnetic field that can be realized by permanent magnets. Typically, the giant MCE is closely related to a field-induced first-order phase transition such as a magnetostructural coupled phase transition or a metamagnetic transition.[4] However, the first-order phase transition is usually accompanied by considerable thermal and magnetic hysteresis, reducing the refrigerant capacity (RC) of magnetic refrigerant materials.[7–16] It has been reported that itinerant electron metamagnetism (IEM) is responsible for the metamagnetic transition associated with a volume change as usual,[17] which may bring serious stress accumulations accelerating fatigue of the material in use. The application of the giant MCE materials may be limited by such disadvantages. Recently, attention has been paid on searching advanced magnetic refrigerant materials with a large reversible ΔS_M based on a second-order phase transition.[4,18] In the present work, we report a large reversible MCE in $TbCoC_2$, which results from a second-order magnetic phase transition. The maximum value of $-\Delta S_M$ is 15.3 J kg^{-1} K^{-1} at 30 K for a magnetic-field change from 0 to 5 T, with the RC value of 354 J kg^{-1}. In particular, a large $-\Delta S_M^{max}$ (7.8 J kg^{-1} K^{-1}) is achieved for a small magnetic-field change from 0 to 2 T, which is very important for application.

Polycrystalline $TbCoC_2$ was prepared by melting the constituent elements with a purity of 99.9% under argon atmosphere. The ingot was annealed in an evacuated and sealed silica tube at 900 °C for 7 days for achieving homogeneousness. X-ray diffraction showed the material to be single phase, crystallized in the orthorhombic $CeNiC_2$-type structure (space group *Amm*2). By using Rietveld refinement, the lattice parameters *a*, *b*, and *c* were determined to be 3.57, 4.52, and 6.05 Å, respectively, consistent with values reported in literature.[19] The $CeNiC_2$-type structure is a kind of layered structure, in which the Ce atoms occupy 2*a* sites in the *a* plane while the Ni and C atoms are located at 2*b* and 4*e* sites in the $\frac{1}{2}$ *a* plane.[19] The magnetic properties were measured by using a superconducting quantum inference device magnetometer (Quantum Design) from 2 to 60 K in applied magnetic field up to 7 T.

It has been reported that $TbCoC_2$ is a collinear ferromagnetic (FM) compound with a spontaneous magnetization of $8.4\mu_B$/f.u. at 4.2 K.[20] The magnetic ordering is driven by the rare earth sublattice with moments along the crystallographic *a* axis, while the Co atoms carry no moment.[20] Figure 1 shows the temperature dependences of the zero-field-cooled (ZFC) and the field-cooled (FC) magnetization in a magnetic field of 0.01 T. With increasing temperature, the magnetization of $TbCoC_2$ starts to decrease sharply at about 25 K. The compound undergoes a second-order FM to paramagnetic (PM) phase transition at T_c=28 K, corresponding to the maximum slope in the *M*-*T* curve. For a second-order magnetic phase transition from FM to PM state, such abrupt change in *M*-*T* curve has been also found in RCoAl system.[21] The very small thermal hysteresis of the magneti-

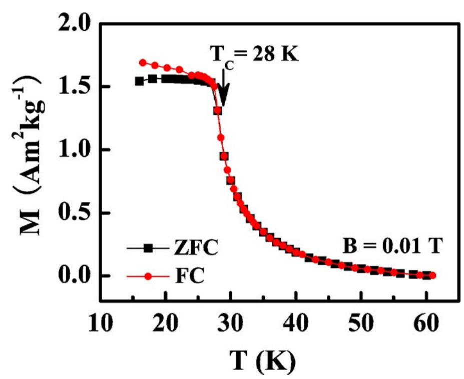

FIG. 1. (Color online) Temperature dependences of the ZFC and the FC magnetization of $TbCoC_2$ at a magnetic field of 0.01 T.

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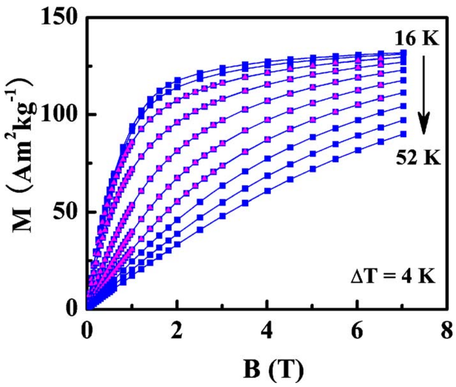

FIG. 2. (Color online) Magnetic isotherms of $TbCoC_2$ measured in increasing (solid squares) and decreasing field (solid triangles), in the temperature range of 16–52 K with temperature steps of 4 K.

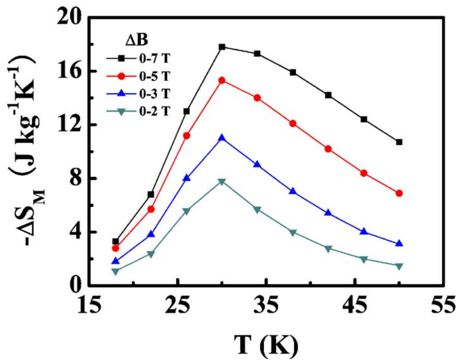

FIG. 4. (Color online) Temperature dependences of the magnetic-entropy change ΔS_M of $TbCoC_2$ for magnetic-field changes ΔB from 0 to 2, 3, 5, and 7 T.

zation (and also the M^2 versus B/M plots discussed below) confirms the second-order nature of the magnetic phase transition. A series of selected isothermal magnetization curves between 16 and 54 K is shown in Fig. 2 for $TbCoC_2$. In Fig. 2, the temperature steps are 4 K and solid squares denote the field increasing process while solid triangles denote the field decreasing one. The magnetization rapidly increases at low field and shows a tendency to saturate with increasing field, as is typical behaviors of FM materials. The saturation magnetization is about 125 A m^2 kg^{-1} at 16 K. Figure 2 displays that M-B isotherms (from 24 to 40 K), measured on increasing and decreasing field, nearly coincide, i.e., there is no magnetic hysteresis around the transition temperature.

The Inoue–Shimizu model, which involves a Landau expansion of the magnetic free energy up to the sixth power of the total magnetization M, can be used to determine the transition type,[22]

$$F(M,T) = \frac{c_1(T)}{2}M^2 + \frac{c_2(T)}{4}M^4 + \frac{c_3(T)}{6}M^6 + \cdot \cdot \cdot - BM. \tag{1}$$

It has been reported that the order of a magnetic transition is related to the sign of the Landau coefficient $c_2(T)$.[23] A transition is expected to be first order when $c_2(T_c)$ is negative, whereas it will be second-order for a positive $c_2(T_c)$. The sign of $c_2(T_c)$ can be determined by means of Arrott plots.[24] If the Arrott plot is S-shaped near T_c, $c_2(T_c)$ is negative, otherwise, positive. The Arrott plots of $TbCoC_2$ from 16 to 54 K (shown in Fig. 3) reveal the occurrence of a second-order phase transition because there is no S-shaped curve near T_c, which is consistent with Fig. 1.

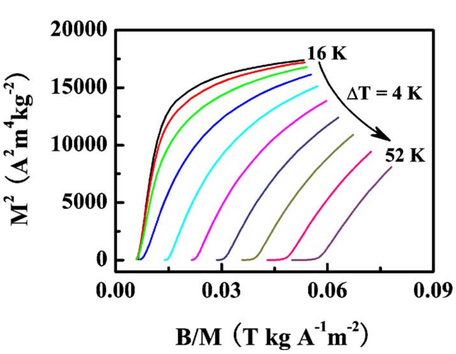

FIG. 3. (Color online) Arrott plots of $TbCoC_2$ from 16 to 52 K with temperature steps of 4 K.

Around T_c, where the magnetization changes rapidly with varying temperature, a large MCE is expected. The isothermal magnetic-entropy change $\Delta S_M(T,B)$ is obtained by integrating the Maxwell relation,[4]

$$\Delta S_M(T_{av},B) = \int_0^B \left(\frac{\partial M}{\partial T}\right)_B dB \approx \frac{1}{\Delta T}\int_0^B [M(T_{i+1},B) - M(T_i,B)]dB. \tag{2}$$

Here $T_{av}=(T_{i-1}-T_i)/2$ denotes the averaged temperature between T_{i+1} and T_i. ΔT is the temperature difference between two isotherms involved. The temperature dependence of $\Delta S_M(T,B)$ calculated for different magnetic-field changes by using Eq. (2) are presented in Fig. 4. The value of $-\Delta S_M^{\max}$ are 7.8, 11, 15.3, and 17.8 J kg^{-1} K^{-1} for the magnetic-field changes from 0 to 2, 3, 5, and 7 T, respectively. The large reversible $-\Delta S_M^{\max}$(7.8 J kg^{-1} K^{-1}) obtained for a small field change from 0 to 2 T, is beneficial to application. The maxima of $-\Delta S_M$ at 30 K for the different magnetic-field changes just correspond to the FM to PM phase transition.

RC is a measure of how much heat can be transferred between the cold and hot sinks in one ideal refrigerant cycle, which is of practical significance.[5] The RC value can be calculated as follows:[25]

$$\mathrm{RC} = \int_{T_1}^{T_2} |\Delta S_M(T)| dT. \tag{3}$$

Here, T_1 and T_2 are the temperatures corresponding to the half-maximum value of $-\Delta S_M$ peak, respectively. For $TbCoC_2$, RC value is 354 J kg^{-1} for a magnetic-field change from 0 to 5 T.

It is well known that $ErCo_2$ is an another material that has been reported to have interesting magnetocaloric property around 30 K.[26,27] The IEM of $ErCo_2$ leads to a first-order phase transition at its ordering temperature and to a giant MCE.[18] From the viewpoint of application, the true RC value of $ErCo_2$ will be much less than that calculated by Eq. (3) because the magnetic hysteresis loss should be subtracted.[17] Moreover, the volume change associated with the IEM may bring unexpected problems for application. Thus, the advantages of $ErCo_2$ for application would be weakened. In contrast, the MCE found in $TbCoC_2$ is magnetically and thermally reversible, which qualifies it as a suitable refrigerant for application to low temperature cooling.

To summarize, the magnetic and magnetocaloric properties of $TbCoC_2$ have been investigated. A large reversible MCE is observed at 30 K, accompanied by a second-order FM to PM transition, as revealed by the Arrott plots based on the Inoue–Shimizu model. In particular, the large ΔS_M^{max} is achieved for a small magnetic-field change from 0 to 2 T. The MCE in the title compound has been contrasted with the best-known magnetic refrigerant reported. The large reversible ΔS_M with the high reversible RC (especially for low magnetic-field change) indicates that $TbCoC_2$ may be a promising candidate for magnetic refrigeration at low temperatures.

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