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Low-field induced giant magnetocaloric effect in TmCuAl compound

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A giant low field reversible magnetocaloric effect has been observed in TmCuAl compound around 4 K, which is the boiling point of helium. The maximum value of magnetic entropy change ($-\Delta S_M{}^{max}$) and adiabatic temperature change ($\Delta T_{ad}{}^{max}$) is 17.2 J/Kg K and 4.6 K without thermal and field hysteresis loss, for field changes of 0–2 T, respectively. Especially, the giant value of $-\Delta S_M{}^{max}$ (12.2 J/Kg K) is obtained for a field change of 0-1 T. The results indicate that the TmCuAl compound could be considered as a good candidate material for low-temperature and low-field magnetic refrigerant. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4804576]

Magnetic refrigeration based on the magnetocaloric effect (MCE) of materials is expected to be the future cooling technology, which has prominent advantages: energy efficiency and friendly environment.[1–6] Numerous ferromagnetic materials exhibiting giant $-\Delta S_M$ around their transition temperatures have been found, such as $LaFe_{13-x}Si_x$,[7,8] $MnAs_{1-x}Sb_x$,[9] $MnFeP_{0.45}As_{0.55}$,[10] and $Gd_5Si_2Ge_2$.[11] However, most of them are associated with the first-order magnetic or structural phase transition. The first-order transition is usually accompanied by a considerable thermal or magnetic hysteresis, which is disadvantageous for a magnetic refrigeration cycle and can also greatly reduce the actual refrigerant capacity (RC) of the materials.[12] RC is another important parameter, which is a measure of how much heat can be transferred between the cold and the hot sinks in one ideal refrigeration cycle. Additionally, if a sufficient MCE of material can only be achieved upon application of high magnetic fields (e.g., more than 2 T), it is not feasible to design a refrigeration cycle using permanent magnets. In practical application, some materials with large MCE may be limited by this factor. Therefore, it is desirable to search for materials that have giant MCE and large RC with zero or inappreciable thermal and field hysteresis loss under low field ($\Delta H \leq 2$ T).

Recently, many studies have been focused on rare-earth based intermetallic compounds, which exhibit low field giant MCEs and large RC together with small or zero hysteresis loss, such as $ErMn_2Si_2$,[13] HoCoAl,[14] and HoNiAl.[15] Much effort has been devoted for the study of the intermetallic ternary compounds of the RTX 1:1:1 type (R = rare-earth, T = transition metal, X = p-metal). Among the RTX compounds, the RCuAl compounds crystallize in the ZrNiAl-type hexagonal structure with complex magnetic structures.[16] The magnetic structures, phase transitions, and magnetic properties for RCuAl (R = Gd-Tm) compounds have been investigated in detail by neutron diffraction, specific heat, and magnetic measurements.[17–21] Uniaxial magnetic anisotropy in GdCuAl, DyCuAl, and ErCuAl and a basal-plane type of magnetic anisotropy in HoCuAl have been revealed. For TmCuAl compound, the magnetic sublattice of Tm^{3+} is a longitudinal spin wave along the *c*-axis with a propagation vector k = (1/2, 0, q) at 1.9 K, and an antiferromagnetic (AFM) transition within the basal plane with k = (1/2, 0, 1/2) develops below the magnetic phase transition at 1.2 K.[22] Their magnetocaloric properties should also be particularity investigated, yet rare earth can always contribute large magnetic moment. Dong *et al.*[23] has reported the magnetic properties and magnetocaloric effects of HoCuAl (14 J/kg K) and ErCuAl (14.7 J/kg K) for field changes of 2 T. In the present paper, we investigate the magnetic property and magnetocaloric effect in TmCuAl compound. The giant reversible MCE is observed with $-\Delta S_M{}^{max} = 17.2$ and 12.2 J/Kg K for a low field change of 2 and 1 T, respectively. Moreover, the large value of ΔT_{ad} (4.6 K) is obtained for a field change of 2 T. Our results suggest TmCuAl compound could be expected to have effective applications in low temperature magnetic refrigeration.

The polycrystalline TmCuAl sample was synthesized by arc-melting in a water-cooled copper hearth under a purified argon atmosphere using Tm, Cu, and Al of 99.9% purity (3% excess Tm was included in the starting materials). The ingot was melted three times with the button being turned over after each melting to ensure the homogeneity. The sample was wrapped by molybdenum foil, sealed in a quartz tube of high vacuum, annealed at 1123 K for 10 days, and subsequently quenched to room temperature to obtain crystalline samples. Powder X-ray diffraction (XRD) measurement was performed at room temperature by using Cu Kα radiation to identify the crystal structure and the lattice parameters. It indicates that sample is of single phase with a hexagonal ZrNiAl-type structure (space group P62 *m*). The lattice parameters *a* and *c* were determined to be 6.921(5) and 3.980(9) Å with $R_{wp} = 7.1\%$ by the Rietveld technique using GSAS program. Magnetizations were measured by employing a commercial superconducting quantum interference device (SQUID) magnetometer, model MPMS-7 (Quantum Design). Heat capacity was measured by using a physical property measurement system (Quantum Design).

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Fig. 1 shows the typical temperature dependences of the magnetization M (T) curves for TmCuAl compound under an applied magnetic field of 0.01 T. According to the powder neutron diffraction investigation,[22] TmCuAl undergoes two magnetic structures: a longitudinal spin wave magnetic structure (the Tm magnetic moments align along the c-axis) below Curie temperature ($T_C = 1.9$ K) and an AFM basal-plane component at 1.2 K. As displayed in Fig. 1, the M-T curve of TmCuAl compound exhibits a transition from paramagnetic (PM) to ferromagnetic (FM) and $T_C = 2.8$ K, corresponding to the maximum slope of M-T curve, which is slightly higher than the reported transition temperature.[22] However, the transition from FM to AFM at lower temperature could not be detected in M-T curve since the temperature of our MPMS cannot achieve lower temperature than 2 K by using liquid He.[4] We also notice that the zero-field-cooling (ZFC) and field-cooling (FC) curves for TmCuAl are reversible, indicating no thermal hysteresis as shown usually in magnetic materials with a second-order magnetic transition. The inset shows that the reciprocal magnetic susceptibility χ_m^{-1} of the TmCuAl compound follows the Curie-Weiss law above 10 K. The effective magnetic moment $\mu_{eff} = 7.45\mu_B$ is slightly smaller than theoretical value ($7.56\,\mu_B$) for the Tm^{3+} ion, which can be attributed to crystal-field effect.[24] The positive value of $\theta_p \approx 9$ K implies a ferromagnetic ground state.

The magnetization isotherms of TmCuAl are measured under magnetic fields up to 5 T in a temperature range around the transition temperature. Fig. 2(a) shows the field dependences of magnetization data collected during both increasing (black line) and decreasing (red line) fields at 2 K. No magnetic hysteresis can be observed, implying that TmCuAl compound is a soft ferromagnet. The M (H) data show a rapid increase at considerably low fields, and in strong magnetic fields, the magnetization isotherm tends to saturate, which exhibits typical FM nature. The magnetic moment calculated at 5 T is about $6.38\,\mu_B$. This value is smaller than the expected value for Tm^{3+} ion. Similar reduction in isostructural thulium intermetallics TmAgGe has been reported.[25] It is likely related to the crystal field felt by Tm^{3+}. The selected M-H curves (in the temperature range of 2–30 K) are displayed in the inset of Fig. 2(a). The isothermal curves for $T_C < T < 18$ K show an appreciable nonlinearity, which indicate the existence of short-range FM correlations in the PM state. Fig. 2(b) shows the Arrott plot of the TmCuAl compound. Based on the Banerjee criterion,[26] a magnetic transition is expected to be of the first order when the slope of Arrott plot is negative, whereas it will be of second order when the slope is positive. It is very obvious that the Arrott plot for TmCuAl is positive and confirms the second-order magnetic transition from FM to PM.

The magnetic entropy change $-\Delta S_M$ for TmCuAl is calculated from isothermal magnetization data shown in Fig. 2 by using the Maxwell relation $\Delta S(T,H) = \int_0^H (\partial M/\partial T)_H dH$. Fig. 3(a) shows the values of $-\Delta S_M$ for different magnetic field changes as a function of temperature. The value of $-\Delta S_M{}^{max}$ is found to increase monotonically with the increase of applied magnetic field. The $-\Delta S_M{}^{max}$ reaches a value of 24.3 J/kg K at 7.5 K for a magnetic field change from 0 to 5 T. For a field change of 2 T, a giant $-\Delta S_M{}^{max}$ value of 17.2 J/kg K is achieved at 4.5 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 HoCuSi (16.7 J/kg K),[27] $ErRu_2Si_2$ (11 J/kg K),[28] and DyCuSi (10.5 J/kg K).[29] Particularly, the value of $-\Delta S_M{}^{max}$ is evaluated to be 12.2 J/kg K for the magnetic field changes of 1 T at 3.5 K, which can be realized by a permanent magnet. Moreover, the temperature with $-\Delta S_M{}^{max}$ value corresponding to the FM-PM transition is also increased linearly with the increasing magnetic field, indicating the FM ground state nature above 2 K. Fig. 3(b) shows magnetic field dependences of magnetic entropy change for different temperature changes.

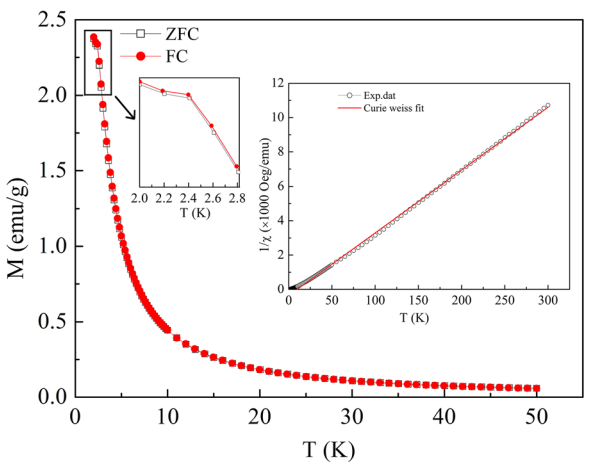

FIG. 1. Temperature dependences of ZFC and FC magnetizations of TmCuAl under the magnetic field of 0.01 T. Inset: the temperature variation of the ZFC inverse susceptibility fitted to the Curie-Weiss law.

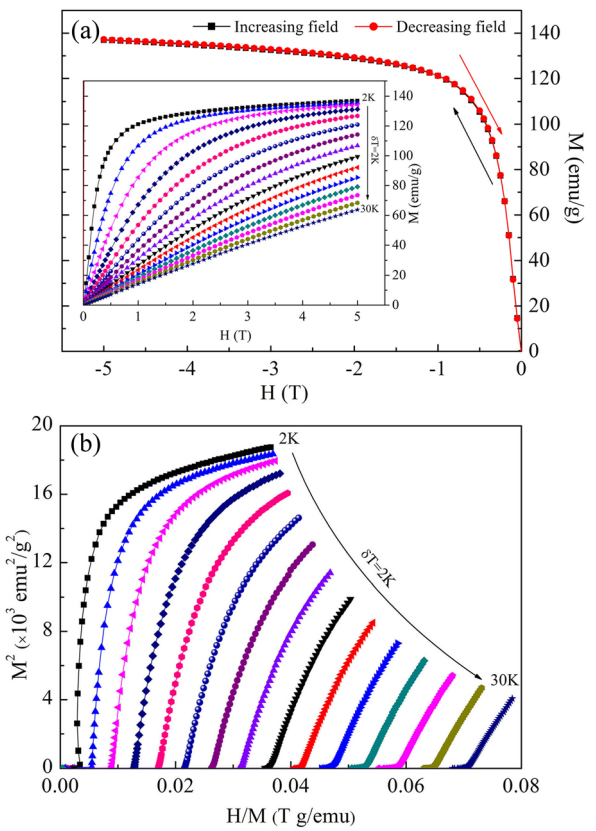

FIG. 2. (a) Magnetization isotherms of TmCuAl measured on increasing and decreasing field at 2 K. The inset shows the M (H) isotherms collected in the temperature range of 2–30 K; (b) the Arrott plot of the TmCuAl compound.

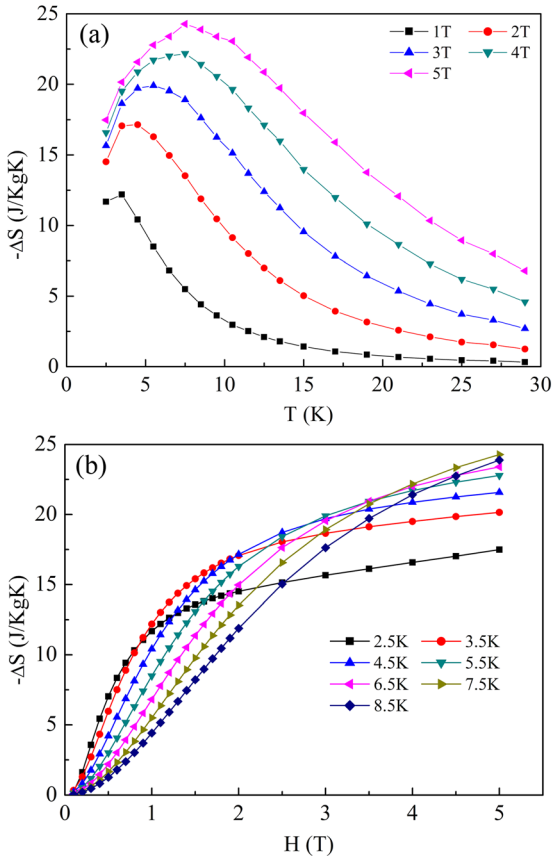

FIG. 3. (a) Temperature dependences of magnetic entropy change for TmCuAl; (b) magnetic field dependences of magnetic entropy change for TmCuAl.

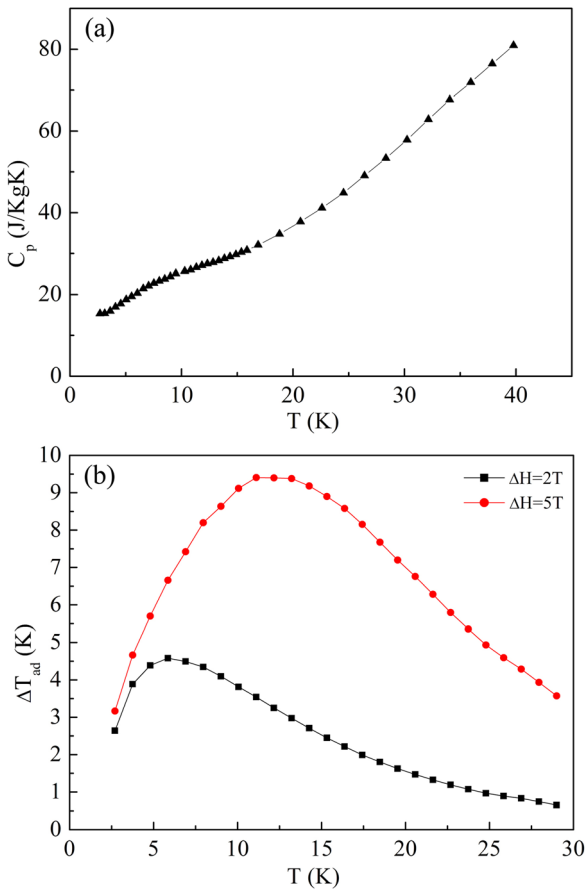

FIG. 4. (a)Temperature dependence of heat capacity C_p for TmCuAl under the magnetic fields of 0 T; (b) temperature dependences of the adiabatic temperature change for TmCuAl.

At low temperature, the $-\Delta S_M$ shows a rapid increase and persuasive signs of domain saturation at considerably low fields, and in high magnetic fields, the $-\Delta S_M$ tends to saturate. It indicates that TmCuAl is a promising candidate for magnetic refrigeration at low temperature (around 3 K), such as helium liquefaction. However, the $-\Delta S_M$ increases linearly with the increase of the magnetic field at high temperature. It confirms that the MCE of TmCuAl is governed by the short range interactions and spin fluctuations at high temperature.

It is not sufficient to identify the potentiality of a magnetic refrigerant material solely by the large $-\Delta S_M$. The adiabatic temperature change (ΔT_{ad}) is also an effective parameter for evaluation. In order to get a better comparison of the application potential of this compound, we have calculated the MCE in terms of ΔT_{ad} by using $\Delta T_{ad} = -\Delta S_M (T_0, H) \times T_0 / C_P (T_0, H_0)$, where $C_P (T_0, H_0)$ is zero-field specific heat as shown in Fig. 4(a). For field changes of 2 and 5 T, the values of ΔT_{ad}^{max} are found to be 4.6 and 9.4 K, as shown in Fig. 4(b). It has been reported that in the case of DyCuAl, the values of ΔT_{ad}^{max} are 3.6 and 7.0 K for magnetic field changes of 2 and 5 T, respectively.[30] For the (Gd, Dy, Ho, Er)NiAl compounds,[31,32] the values of ΔT_{ad}^{max} vary in the range of 4–9 K for a field change of 5 T. The value of ΔT_{ad}^{max} also indicates the TmCuAl could be a good candidate as a low temperature magnetic refrigerant. The RC, defined as a cooling capacity of $RC = \int_{T_1}^{T_2} |\Delta S_M| dT$, is calculated by numerically integrating the area under the $-\Delta S_M$–T curve, with the temperatures at half maximum of the peak taken as the integration limits.[33] The RC values of TmCuAl are calculated to be 371.7, 129.2, and 50.5 J/kg for the magnetic field changes of 5, 2, and 1 T, respectively. The giant value of $-\Delta S_M$, the large ΔT_{ad}, and the considerable RC without thermal as well as magnetic hysteresis loss make TmCuAl compound become a promising candidate for its application in magnetic refrigeration, such as helium and hydrogen liquefaction.

A giant low field reversible MCE has been observed in TmCuAl compound, accompanied by a field-induced second order metamagnetic transition from FM to PM. Under a field change of 5 T, the value of $-\Delta S_M^{max}$ is 24.3 J/Kg K with no thermal and field hysteresis loss, and the corresponding value of ΔT_{ad}^{max} is 9.4 K. For field changes of 0–2 T, the values of $-\Delta S_M^{max}$ and ΔT_{ad}^{max} are 17.2 J/Kg K and 4.6 K, respectively. Especially, the giant values of $-\Delta S_M^{max}$ (12.2 J/Kg K) are obtained for a relatively low field change of 0–1 T. Additionally, the RC values of TmCuAl are 371.7, 129.2, and 50.5 J/kg for the magnetic field changes of 5, 2, and 1 T, respectively. The giant reversible $-\Delta S_M$, ΔT_{ad}, and large RC together with the absence of thermal and field hysteresis indicate that TmCuAl compound could be a promising candidate for magnetic refrigeration at low temperatures.

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