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Low field induced giant magnetocaloric effect in TmGa compound

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The magnetic properties and magnetocaloric effect in TmGa compound are investigated. TmGa exhibits two successive magnetic transitions: ferromagnetic-antiferromagnetic at $T_{FA} = 12$ K and antiferromagnetic-paramagnetic transition at $T_N = 15$ K. Under field changes of 1 and 2 T, giant reversible values of magnetic entropy change (12.9 and 20.6 J/kg K) and large values of refrigerant capacity (69 and 149 J/kg) are observed, respectively. Additionally, the maximal values of adiabatic temperature change are 3.2 and 5 K for field changes of 1 and 2 T, respectively. The TmGa compound with excellent magnetocaloric effect is expected to have effective applications in low temperature magnetic refrigeration. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4816729]

Magnetic refrigerator has attracted much attention due to its higher energy-efficiency and lower environmental influence than conventional gas compression refrigeration.[1–3] The feasibility of applying this technology highly depends on the design and synthesis of suitable magnetic cooling materials. In 1997, Pecharsky *et al.* reported on a giant magnetocaloric effect (MCE) of $Gd_5Si_2Ge_2$ near room temperature ($T_C = 276$ K), which was attributed to a field induced first-order magnetic and structural transition.[4] Since then, much attention has been paid to search for magnetic refrigerants in industrial applications near room temperature.[5–9] On the other hand, the study of system with large MCE at low temperature is also important for their potential applications in special technological areas such as space science and liquefaction of hydrogen in fuel industry.[1] Hydrogen is considered as one of the most important clean energy sources because of its high energy density and friendly environment. In general, hydrogen gas needs to be cooled down to liquid form gas for its storage and transportation. It has been reported that the Carnot magnetic refrigerator (CMR) achieved an efficiency of 90% in the liquefaction stage.[10] Therefore, it is significant to develop advanced magnetic refrigerants that show large MCEs around the liquid hydrogen temperature and are suitable for applications in CMR.

Paramagnetic salts such as $Gd_3Gd_5O_{12}$, $GdLiF_4$, and GdF_3[11,12] have been applied to magnetic refrigeration devices in order to achieve low temperature. However, the MCEs of the paramagnetic salts are small and strongly depend on the temperature. In contrast, rare-earth based compounds with large isothermal magnetic entropy change (ΔS_M) can be expected to have effective commercial applications in technology of magnetic refrigeration at low temperature. Additionally, a large MCE under low magnetic field change is desirable for the achieving a magnetic refrigerator simply by using permanent magnets. So far, only magnetic field less than 2 T can be well designed by permanent magnets. Therefore, much attention has been paid to search for materials that have giant MCE under low field ($\Delta H \leq 2$ T) working at low temperature. Recently, low field induced giant MCEs has been observed in some rare-earth based intermetallic compounds, such as $ErMn_2Si_2$,[13] $ErCr_2Si_2$,[14] $ErRu_2Si_2$,[15] HoCuSi,[16] etc. Binary RGa (R = rare-earth) intermetallic compound is crystallized in orthorhombic CrB type structure (Cmcm space group) and generally undergoes two successive magnetic transitions.[17] Recently, the magnetic and magnetocaloric properties of RGa (R = Tb, Dy, Ho, Er, and Tm) have been studied.[18–21] In the present paper, we report on the magnetic properties and giant reversible ΔS_M, large refrigerant capacity (RC) and adiabatic temperature change (ΔT_{ad}) under a low field with negligible thermal and field hysteresis loss in TmGa compound. The giant reversible MCE is attributed to the two successive magnetic transitions. The results indicate that the TmGa is a promising candidate for magnetic refrigeration in special technological applications such as space science and liquefaction of hydrogen in fuel industry.

The polycrystalline sample of TmGa compound was synthesized by arc melting of stoichiometric amounts of the elements Tm (99.9%) and Ga (99.9%) under a purified argon atmosphere. In order to compensate for the loss, the content of Tm was 3% more than the theoretical value. The ingot was melted three times with the button being turned over after each melting to ensure the homogeneity. The sample was annealed at 1123 K for 10 days, and a subsequent quenching to room temperature was performed to obtain crystalline sample. The x-ray powder diffraction pattern confirmed the single-phase nature of the compound, and crystallizing in the orthorhombic CrB-type structure (space group Cmcm). The lattice parameters were determined to be $a = 4.2309$ (2) Å, $b = 10.6497$ (3) Å, and $c = 4.0084$ (9) Å with $R_{wp} = 7.6\%$ by the Rietveld technique using GSAS program shown in Fig. 1. Magnetizations were measured by employing a commercial superconducting quantum interference device (SQUID) magnetometer, model MPMS-7 from Quantum Design Inc. Heat capacity was measured by using a physical property measurement system (Quantum Design).

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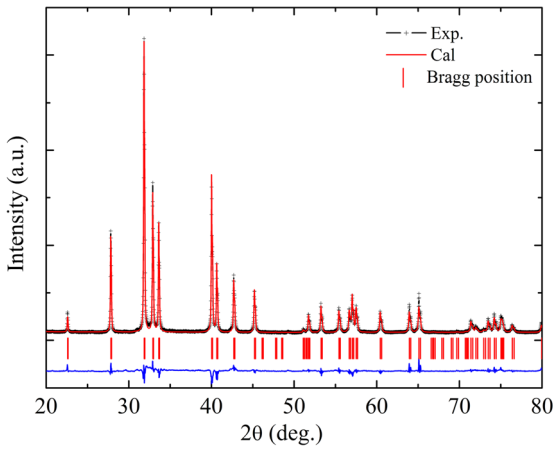

FIG. 1. Rietveld refined powder XRD patterns of TmGa compound at room temperature. The observed data are indicated by crosses, and the calculated profile is the continuous line overlying them. The short vertical lines indicate the angular positions of the Bragg peaks of TmGa. The lower curve shows the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

The zero-field-cooling (ZFC) and field-cooling (FC) temperature dependence of magnetization for TmGa compound under an applied magnetic field of 0.04 T are shown in Fig. 2. It exhibits two successive magnetic transitions: ferromagnetic (FM)-antiferromagnetic (AFM) at $T_{FA} = 12$ K and AFM-paramagnetic (PM) at $T_N = 15$ K. The ZFC and FC curves are well overlapped above T_C, indicating that there is no thermal hysteresis as usually observed in magnetic materials with a second-order magnetic transition. However, there is an obvious bifurcation at temperatures below T_{FA} as reported in Ref. 21 and it is likely due to a domain wall pinning effect. Whereas, with increasing magnetic field, the thermomagnetic irreversibility becomes smaller and vanishes completely when field is higher than 0.5 T, as shown in the inset of Fig. 2. This indicates that higher magnetic field would provide more energy for domain walls to conquer the barriers of pinning effect, thus reducing the irreversibility. The magnetization in AFM region, namely in the temperature range between T_{FA} and T_N, increases greatly with increasing field,

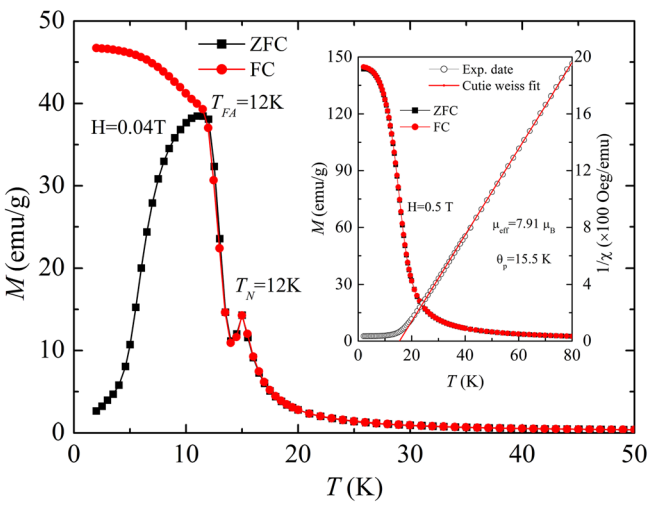

FIG. 2. Temperature dependences of ZFC and FC magnetizations under the magnetic fields of 0.04 T; Inset: Temperature dependences of ZFC and FC magnetizations under the magnetic field of 0.5 T and the temperature variation of the ZFC inverse susceptibility fitted to the Curie-Weiss law.

indicating a field-induced AFM-FM transition. Therefore, the *M-T* curve above T_N under high fields corresponds to a FM-PM transition. On the other hand, we also notice that the reciprocal magnetic susceptibility (χ_m^{-1}) of the TmGa compound follows the Curie-Weiss law $\chi_m^{-1} = (T-\theta_p)/C_m$ above 20 K. Here θ_p is the PM Curie temperature and C_m is the Curie-Weiss constant. The effective magnetic moment $\mu_{eff} = 7.91\ \mu_B$ is obtained based on the value of C_m, which is similar to the theoretical value ($7.56\ \mu_B$) for the Tm^{3+} ion.[22] The PM Curie temperature is found to be $\theta_p = 15.5$ K, which implies a FM ground state of the TmGa compound.

The isothermal magnetization curves as a function of magnetic field were measured in applied fields of up to 5 T in a temperature range from 4 to 46 K, as shown in Fig. 3. The magnetic moment calculated at 5 T is $6.57\ \mu_B$ per Tm atom at 4 K, which is slightly smaller than the expected value of 7.56 for Tm^{3+} ion. This discrepancy can be partly due to the crystal-field effect.[23] It is noteworthy that there exists considerable difference in the *M-H* characteristics for TmGa compound at different temperatures. The isothermal curves for $T<T_N$ show a rapid increase at considerably low fields, and tend to be saturated in strong magnetic fields, which indicate the FM ground state nature. It indicates the occurrence of a field-induced AFM-FM transition between T_{FA} and T_N. The isothermal curves for $T_N < T < 30$ K show strong curvatures, indicating the existence of short-range FM correlations in the PM state. In the temperature range of 30–46 K, the field dependence of the magnetization shows a linear relation (typical PM nature). Furthermore, the isothermal curves under field increasing and decreasing modes at different temperatures (4 and 10 K) were measured for investigating the reversibility of the magnetic transitions for TmGa. A tiny magnetic hysteresis about 0.1 T is observed at 4 K under low field range, but no magnetic hysteresis is observed at 10 K. it indicates that the magnetic transition in TmGa around T_{FA} is reversible.

Figure 4 displays the heat capacity (C_P) curves for TmGa under the fields of 0, 1, 2, and 5 T, respectively. It clearly shows two successive magnetic transitions at $T_C = 12$ K and at $T_N = 15$ K, which is fully consistent with the magnetic measurements. With the increase of magnetic field, the two peaks are not only turn a broader and lower, but also shifts toward higher temperature, which is the typical characteristic of

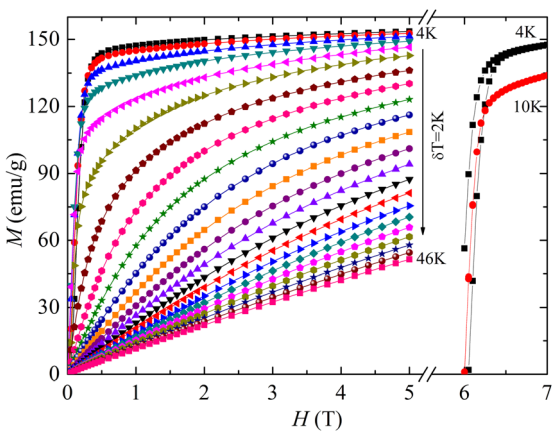

FIG. 3. Magnetization isotherms of TmGa collected in the temperature range of 4-40 K and the mold increasing and decreasing field at 4 and 10 K.

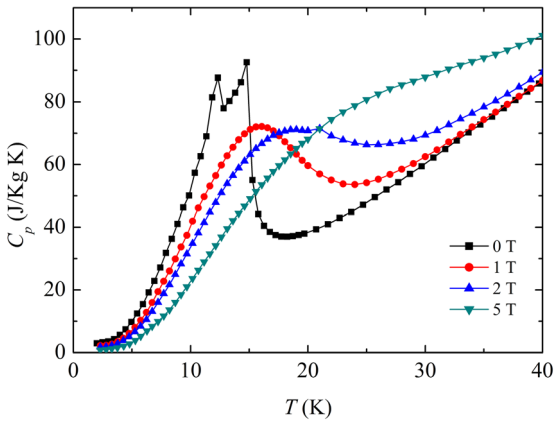

FIG. 4. Temperature dependence of heat capacity (C_P) for TmGa measuredin the fields of 0, 1, 2, and 5 T, respectively.

ferromagnet.[2] It implies FM-to-PM instead of AFM-to-PM transition. It is known that the heat capacity peak is caused by the absorption of heat which is utilized in randomization of magnetic moments around transition temperature. With the application of field, the randomization of moments would spread out over a wide temperature region, and the maximum peak moves towards higher temperature.[4,24]

As is well known, the ΔS_M value can be calculated either from the magnetization isotherms by using the Maxwell relation $\Delta S(T,H) = \int_0^H (\partial M/\partial T)_H \, dH$ or from the heat capacity by using the equation $\Delta S(T) = \int_0^T [C_H(T) - C_0(T)]/T dT$.[25] However, sometimes the values of ΔS_M calculated from heat capacity may be much lower than those obtained from magnetization isotherms, which is likely due to the poor contact between sample and measuring platform. For comparison, the ΔS_M values were determined from both methods as shown in Fig. 5(a), and it is clearly seen that the ΔS_M curves obtained from two methods match well with each other. The maximum value of $-\Delta S_M$ is found to increase monotonically with applied magnetic field increasing and reaches a value of 34.2 J/kgK for a magnetic field change from 0 to 5 T at 15.5 K. Particularly, under the magnetic field changes of 1 and 2 T, which can be realized by permanent magnet and advantageous to applications, the maximum values of $-\Delta S_M$ are evaluated to be 12.9 and 20.7 J/kg K at 14.5 K, respectively. 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, where T_1 and T_2 are the temperatures at half maximum of the peak taken as the integration limits.[26] By using this method, the RC values of the TmGa are evaluated to be 69, 149, and 364 J/kg for the magnetic field changes of 1, 2, and 5 T, respectively. As another important parameter to evaluate the MCE of magnetocaloric materials, the adiabatic temperature change ΔT_{ad} was calculated from the C_P *vs.* T curves by using the equation of $\Delta T_{ad}(\Delta H, T) = [T(S)_H - T(S)_0]_S$.[25] Figure 5(b) shows the maximum values of ΔT_{ad} are 3.2, 5, and 9.1 K for the field change of 1, 2, and 5 T, respectively. For comparison, the magnetocaloric properties of TmGa and some other refrigerant materials with a magnetic ordering temperature around 20.3 K are listed in Table I.[27–31] It can be seen that the MCE of TmGa, especially under the low magnetic field change, is comparable with or even larger than

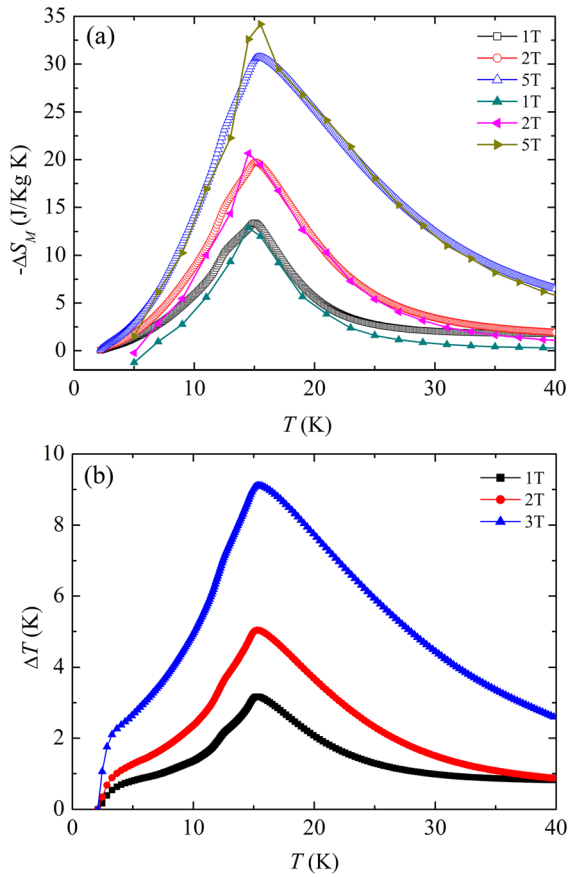

FIG. 5. (a) Temperature dependences of magnetic entropy change in TmGa for different magnetic field changes; (b) Temperature dependence of adiabatic temperature change ΔT_{ad}.

those of other magnetocaloric materials around the liquid hydrogen temperature. Therefore, TmGa compound appears to be a very attractive candidate material for use in a magnetic refrigerator working in low temperature.

In summary, a giant reversible MCE and large RC in TmGa compound were observed. With the magnetic field changes of 5 T, the maximum value of $-\Delta S_M$ is evaluated to be 34.2 J/kg K, and the maximum value of RC is 364 J/kg in TmGa compound. Especially, for the magnetic field changes of 1 and 2 T, the large values of $-\Delta S_M$ are 12.9 and 20.7 J/Kg K with considerable refrigerant capacity values of 69 and 149 J/kg are also obtained, respectively. Additional, the maximum values of ΔT_{ad} reach 3.2, 5, and 9.1 K for the field change of 1, 2, and 5 T. The low magnetic field can be realized by permanent magnet. Therefore, the giant reversible

TABLE I. The ordering temperature (T_{ord}), $-\Delta S_M$, ΔT_{ad}, and RC under the field changes of 2 T for TmGa and some other refrigerant materials with a magnetic ordering temperature around liquid hydrogen temperature (20.3 K).

Compounds	T_{ord} (K)	$-\Delta S_M$ (J/kg K)	ΔT_{ad}	RC (J/kg)	Refs.
Er_3Ni_2	17	11	3.3	407[a]	27
ErFeSi	22	14.2	3.4	130	28
$GdPb_2Si$	17	4.5	3.2	204[a]	[29]
$DyNi_2$	20	10.7	4.2	349[a]	30
PrNi	20	2.4	0.8	43	31
TmGa	11.5/15	20.6	5	149	This work

[a]Field change (ΔH) = 5 T.

MCE, large RC, and ΔT_{ad} make the TmGa a promising candidate for magnetic refrigeration.

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