Magnetic properties and large magnetocaloric effect in Laves phase metallic compound

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Abstract. We investigated the magnetic properties and magnetocaloric effect of C15 Laves phase TbMn$_{1.6}$Fe$_{0.4}$ by magnetization and heat capacity measurements. A sharp second-order magnetic Tb-Tb ordering transition at Curie temperature $T_C \approx 120$ K and a short-range Fe-Fe ordering transition at $\sim 230$ K are observed. Around $T_C$, the compound shows a large magnetocaloric effect with no obvious thermal and magnetic hysteresis loss. The maximum value of magnetic entropy change reaches 8.72 J kg$^{-1}$ K$^{-1}$ for a magnetic field change $\Delta H = 7$ T over a wide temperature range. The obtained relative cooling power reaches 184, 560, and 803 J kg$^{-1}$ for $\Delta H = 2$, 5 and 7 T, respectively. Large reversible magnetocaloric effect and the wide operating temperature range indicate that TbMn$_{1.6}$Fe$_{0.4}$ could be a promising candidate for magnetic refrigeration.

1. Introduction
The RT$_2$ binary compounds (where R = Y, Gd, Tb, Dy and T = Mn, Fe) crystallize in the C15 Laves phase type cubic crystal structure and exhibit distinct complex magnetic behaviors. In TbMn$_2$, the interaction between Tb and Mn ion is unstable below the Neel temperature $T_N \approx 40$ K and not all the Mn ions carry localized magnetic moments,[1] while TbFe$_2$ shows ferromagnetic (FM) ordering at Curie temperature $T_C \approx 697$ K with an effective Fe magnetic moment of 2.10 $\mu_B$.[2] The magnetic properties in intermetallic compound TbMn$_{1.6}$Fe$_{0.4}$ are mainly determined by the 4f-4f interactions of Tb and 3d-3d interactions of Fe and Mn atoms. The substitution of Fe for Mn induces a smaller interatomic spacing and a rapid decay of the Mn magnetism, and therefore increase both the Curie temperature and the magnetic moment compensation of Tb,[3] which would induce a large magnetocaloric effect (MCE).

Compared with conventional gas compression refrigeration, magnetic refrigeration methods based on the MCE is considered to be advantageous for both their potential energy savings and reduced environmental impact. The MCE presents a promising environmentally friendly refrigeration method as an alternative to conventional refrigeration, which can be observed by changing the magnetic entropy of a material. Many efforts have been made to find out advanced MCE materials for improving the application of this cooling technology. For FM materials, the largest MCE is often obtained in the vicinity of a magnetic phase transition. However, the narrow temperature region and the less efficient in fast cycling refrigerators because of the considerable thermal and magnetic hysteresis accompanied by the first-order phase transition will consume the relative cooling power (RCP) of magnetic refrigerants. In contrast to a first-order phase transition, the materials showing a...
second-order phase transition are suitable for practical applications because of the reversible MCE with negligible thermal and magnetic loss.[4,5]

In this paper, the MCE of metallic compound TbMn$_{1.6}$Fe$_{0.4}$ under a modest magnetic field has been investigated. A large isothermal magnetic entropy change (8.72 J kg$^{-1}$ K$^{-1}$ for 0-7 T) centered at $T_C \sim 120$ K are observed, accompanied by a second-order phase transition with no thermal and magnetic hysteresis over a wide temperature span. The full width at half maximum $\delta T_{\text{fwhm}}$ reaches 92 K at 7 T, and the corresponding RCP reaches 803 J kg$^{-1}$. These values, especially the huge $\delta T_{\text{fwhm}}$ and RCP, which implies a larger operating temperature range, make the applicability of TbMn$_{1.6}$Fe$_{0.4}$ as an ideal candidate for magnetic refrigerant.

2. Experimental

The TbMn$_{1.6}$Fe$_{0.4}$ polycrystal was prepared by an arc-melting method using a tungsten electrode in an argon atmosphere. Firstly, stoichiometric amounts of high purity Tb, Mn, and Fe were turned over and remelted six times to ensure homogeneity in a water-cooled copper hearth. Then the obtained ingot was wrapped in a molybdenum foil, sealed in a high-vacuum quartz tube, annealed at 700 °C for one week and then quenched into cold water. The x-ray powder diffraction pattern shows a single phase of the cubic C15 Laves MgCu$_2$-type structure (space group Fd3m) in the final sample. The lattice parameter was evaluated to be 7.564 Å. The magnetization measurements were carried out by using a superconducting quantum interference device magnetometer, MPMS-7 of Quantum Design Company of America. The specific heat measurement was performed in a physical property measurement system, PPMS-9 of Quantum Design Company.

3. Results and discussion

The temperature dependence of magnetization ($M$) and its inverse ($1/M$) for TbMn$_{1.6}$Fe$_{0.4}$ in an external magnetic field $H = 0.1$ T are plotted in Fig. 1. The compound undergoes a clear FM transition at $T_C \sim 120$ K. At temperatures above ~230 K, it shows the Curie-Weiss behavior with a PM Curie temperature $\theta_P \sim 156$ K, which is much higher than $T_C$. A visible anomaly of $1/M$ at $T \sim 230$ K is indicated by arrow, which may be induced by the short-range 3d-3d ordering of Fe atoms.[6] It is considered that the observed sharp FM transition at ~120 K and the anomaly of $1/M$ at ~230 K in TbMn$_{1.6}$Fe$_{0.4}$ compound is corresponding to the 4f-4f ordering of Tb and the 3d-3d ordering of Fe, respectively. The effective magnetic moment is evaluated to be 9.08 $\mu_B$/f.u., which is slightly smaller than the theoretical PM moment of free Tb$^{3+}$ (9.72 $\mu_B$). Below $T_C$, the sample shows strong FM properties, and the magnetization increases with temperature down to the lowest temperature reached.

![Figure 1. The temperature dependence of magnetization and its inverse in an external field $H = 0.1$ T. The solid line is the best fit for the Curie-Weiss law.](image1)

![Figure 2. The specific heat $C(T)$ results for TbMn$_{1.6}$Fe$_{0.4}$ under zero-field. The inset shows the temperature dependence of zero-field magnetic entropy.](image2)
The temperature dependence of zero field specific heat $C(T)$ for TbMn$_{1.6}$Fe$_{0.4}$ is displayed in Fig. 2. The clear transition at $T_C \sim 120$ K indicates the magnetic transition of Tb-Tb sublattice ordering. Similar to those transitions induced by Co-Co interactions in TbCo$_3$B$_2$[7] and DyCo$_3$B$_2$[8] compounds, no obvious anomaly is observed around $\sim 230$ K. In the inset of Fig. 2, the temperature dependence of zero field magnetic entropy $S(T)$ for TbMn$_{1.6}$Fe$_{0.4}$ has been displayed. $S$ increases with temperature and changes the slope at $T_C$.

Fig. 3 shows the behavior of the magnetization isotherms as a function of magnetic field. Below $T_C \sim 120$ K, it exhibits typical FM characteristics. At high temperatures far above $T_C$, it shows the characteristics of a paramagnet. One can find that the isothermal magnetization curves obtained well above $T_C$ show strong curvatures at a low magnetic field. Similar results have been observed in some other intermetallic compounds,[9] which indicates the short-range Fe-Fe correlations below $\sim 230$ K. We extrapolate the high field data to zero field and get the saturation moment is $\sim 7.56 \mu_B$/f.u. at 30 K, much less than the theoretical FM moment of the free ion Tb$^{3+}$ (9.0 $\mu_B$). It is considered that the short-range Fe-Fe ordering and the unstable 3d-3d interaction of Mn partly compensate the long-range ordered magnetic moment of Tb, in the forms of (canted) antiferromagnetism and magnetocrystalline anisotropy.[6,10]

To illustrate the magnetic inhomogeneity at low temperatures, magnetic hysteresis loops of the TbMn$_{1.6}$Fe$_{0.4}$ compound at 30 K and 120 K are measured (not shown here). At 30 K, the compound exhibits a typical FM characteristic. The coercive field is $\sim 0.08$ T, and the remanent magnetization is $\sim 16$ emu/g. Both the coercivity and remanence may be caused by the magnetocrystalline anisotropy for the integral anisotropy of 3d atoms in transition elements.[3] At 120 K, the coercive field and the remanent magnetization cannot be detected. The $M^2$ versus $H/M$ curves, i.e., Arrott plots (not shown here), shows positive slopes around $T_C$, which suggests that the magnetic Tb-Tb ordering transition at $\sim 120$ K is of second order and declares the absence of both thermal and magnetic hysteresis loss.

A large value of MCE is expected in TbMn$_{1.6}$Fe$_{0.4}$ from the magnetization curves, which often appears at the magnetic transition temperature and is considered to be an important requirement for application of magnetic refrigeration. The approximate temperature dependence of isothermal magnetic entropy change $\Delta S_M$, corresponding to a magnetic field change $\Delta H$ starting from zero field, can be numerically calculated from the discrete magnetization data by means of the following expression that can be obtained from the Maxwell relationship,

$$\Delta S_M(T,H) = S(T,H) - S(T,0) = \mu \int_0^H \left( \frac{\partial M}{\partial T} \right)_H dH$$
Fig. 4 gives the curves of $-\Delta S_M$ versus $T$ around $T_C$ for TbMn$_{1.6}$Fe$_{0.4}$ compound with $\Delta H$ up to 7 T. Here the sign of $-\Delta S_M$ is positive, which indicates the FM nature and a conventional magnetic cooling effect by adiabatic demagnetization in the present compound. No distinct temperature alteration of the peak position of $-\Delta S_M$ versus $T$ curves is observed under variable magnetic field. Around $T_C$, the maximum value of magnetic entropy change which goes up with increasing field, is calculated to be 3.16, 6.81 and 8.72 J kg$^{-1}$ K$^{-1}$ for a field change $\Delta H = 2$, 5 and 7 T, respectively. The large values of MCE are ascribed to the second-order Tb-Tb sublattice FM ordering. Accord well with the specific heat data in Fig. 2, no significant characteristic can be observed at $\sim$230 K, where the short-range FM ordering is formed. One may see the wide full width at half maximum ($\delta T_{fwhm}$) of $-\Delta S_M(T)$ plots, which implies a large operating temperature range. As displayed in Fig. 5, $\delta T_{fwhm}$ increases with magnetic field and reaches 58, 82 and 92 K for $\Delta H = 2$, 5 and 7 T, respectively. The values are even larger than those in TbMn$_{1.8}$Fe$_{0.2}$.[6] The large temperature span may be ascribe to the long-range Tb-Tb ordering at $T_C \sim 120$ K and the short-range Fe-Fe ordering at $T \sim 230$ K.

![Graph](image)

**Figure 5.** The full width at half maximum of the $-\Delta S_M(T)$ plots (left side) and the relative cooling power (right side) as a function of magnetic field for TbMn$_{1.6}$Fe$_{0.4}$ compound.

To further illustrate the MCE application of TbMn$_{1.6}$Fe$_{0.4}$, we have evaluated the total RCP, which is an important criterion for magnetic refrigeration materials and represents the amount of heat transferred in one thermodynamic cycle. The RCP of a reversible refrigeration cycle operating is defined as $\text{RCP} = \Delta S_M^{\text{max}} \times \delta T_{fwhm}$, where $\Delta S_M^{\text{max}}$ is the maximum value of magnetic entropy change at the hot and cold ends of the cycle and the full width at half maximum $\delta T_{fwhm}$ shows the operating temperature range in one thermodynamic cycle. For a given magnetic refrigerant, the optimum refrigeration cycle occurs when the quantity of RCP has a maximum value. In Fig. 5 for TbMn$_{1.6}$Fe$_{0.4}$, the RCP for $\Delta H = 2$, 5, 7 T are evaluated to be 184, 560 and 803 J kg$^{-1}$, respectively. The parameters RCP, $-\Delta S_M^{\text{max}}$, and $\delta T_{fwhm}$ have similar variation tendencies with the magnetic field. Although the present value of $-\Delta S_M^{\text{max}}$ for 5 T is smaller than those of CdCr$_2$S$_4$ (7.04 J kg$^{-1}$ K$^{-1}$),[11] TbCoAl (10.5 J kg$^{-1}$ K$^{-1}$),[12] Ho$_2$In (11.2 J kg$^{-1}$ K$^{-1}$),[13] HoGa (17.1 J kg$^{-1}$ K$^{-1}$),[14] HoCo$_2$ (22 J kg$^{-1}$ K$^{-1}$),[15] and Gd$_5$Sn$_4$ (~36 J kg$^{-1}$ K$^{-1}$),[16] at adjacent magnetic transition temperatures, the present RCP value for 5 T is larger than those of CdCr$_2$S$_4$ (~360 J kg$^{-1}$), TbCoAl (~420 J kg$^{-1}$), Ho$_2$In (360 J kg$^{-1}$), HoGa (455 J kg$^{-1}$), HoCo$_2$ (216 J kg$^{-1}$), and Gd$_5$Sn$_4$ (~400 J kg$^{-1}$) due to its large value of $\delta T_{fwhm}$. In addition, the RCP of TbMn$_{1.6}$Fe$_{0.4}$ Reaches 184 J kg$^{-1}$ at small $\Delta H = 2$ T with $\delta T_{fwhm} = 58$ K, both RCP and $\delta T_{fwhm}$ can reach higher values in higher magnetic fields.
4. Conclusions
To summarize, the polycrystalline TbMn$_{1.6}$Fe$_{0.4}$ compound exhibits a large MCE over a wide effective temperature range, related to a second-order Tb-Tb ordering transition. The observed values of $\Delta S_M$ is not so large in comparison with other potential magnetic refrigerant materials. However, the present material has a huge $\delta T_{(fwhm)}$ around $T_C \sim 120$ K, which results in a considerable RCP (803 J kg$^{-1}$ K$^{-1}$ for $\Delta H = 7$ T). The above parameters increase linearly with the field, i.e., the MCE could attain higher values in higher magnetic fields. In addition, there are several additional advantages, such as no hysteresis effect, easy synthesis procedure, and high chemical and physical stabilities, which suggest that the TbMn$_{1.6}$Fe$_{0.4}$ compound can be a promising candidate for the magnetic refrigeration application in 70 - 162 K.

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