Magnetic property and magnetocaloric effect in TmCoAl compound

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A large reversible magnetocaloric effect accompanied by a second order magnetic phase transition from paramagnetic (PM) to ferromagnetic (FM) has been observed in TmCoAl intermetallic compound. For the magnetic field change of 5 T, the maximum value of magnetic entropy change (−ΔSM max) and the value of refrigerant capacity (RC) are evaluated to be 18.2 J/kg K and 211 J/kg, respectively. In particular, a large −ΔSM max (10.2 J/kg K) is achieved at 7.5 K under a low magnetic field change from 0 to 2 T with no thermal hysteresis and magnetic hysteresis loss. The large reversible magnetocaloric effect (both the large −ΔSM and the high RC) indicates that TmCoAl is one of a promising material for magnetic refrigeration in low temperature.

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1. Introduction

The magnetic refrigerator is based on magnetocaloric effect (MCE), which has attracted much attention due to its higher energy-efficiency and lower environmental impact than the conventional gas compression refrigeration [1,2,3]. It is necessary to go on exploring advanced magnetic refrigerant materials with a large magnitude of isothermal magnetic entropy change (ΔSM) and/or adiabatic temperature change (ΔTad) for the purpose of magnetic refrigerant application [4]. Up to now, many magnetic materials with large −ΔSM have been found, such as ErCo 5 [5], LaFe 13−xSi x [6], MnAs 1−xSbx [7], MnFe 0.45As 0.555 [8] and Gd 2S 1.7Ge 2 [9,10] etc. However, most of them are associated with a first-order magnetic or structural phase transition. The first-order phase transition is usually accompanied by a considerable thermal and magnetic hysteresis, which can greatly reduce the actual RC [11,12,13,14]. RC is a crucial parameter for evaluating the technological significance in a refrigerant material. However, materials with a second-order phase transition (SOPT) may have a lower peak value of −ΔSM, whereas this could be compensated by their large RC due to its thermal and magnetic reversibility. In addition, the permanent magnets in present market can only provide a maximum field of ~2T, and this indicates that a large MCE under low magnetic field change is desirable for the fulfillment of a magnetic refrigerator simply using permanent magnets. Therefore, it is desirable to search new magnetocaloric materials exhibiting a large MCE under low field (ΔH ≤ 2T) with a second-order phase transition, such as ErMnSi 2 [15], GdNi 3M (M = Al, Si) [16], PrMn 1.4Fe 0.6Ge 2 [17] and TbCo 3B 2 [18].

The intermetallic ternary compounds of the RTX 1:1:1 type (R = rare-earth, T = transition metal, X = p-metal) have been devoted much effort to study. The RTX exhibit a very rich variety of crystallographic structures. Among the RTX compounds, the RCoAl were found to crystallize in the more densely packed hexagonal Laves phase MgZn 2-type structure [19]. RCoAl compounds have been reported to show anisotropic lattice expansion/contraction as a function of temperature which could affect their magnetic and transport properties [20]. Magnetic and magnetocaloric properties of RCoAl (R = Gd, Tb, Dy and Ho) have been studied. Under a magnetic field change of 5 T from zero field, the values of −ΔSM max are 10.4, 12.5, 16.3, and 21.5 J/kg K for the RCoAl (R = Gd, Tb, Dy, and Ho) alloys, respectively [21]. In the present paper, we report a study on the magnetic and magnetocaloric properties of TmCoAl alloy. The large reversible −ΔSM max (10.2 J/kg K) with zero thermal hysteresis and magnetic hysteresis is achieved for a low magnetic field change of 2 T. The RC value of the TmCoAl is increased with the increasing field changes and reached to 72 and 211 J/kg for the field...
changes of 2 and 5 T, respectively. The results imply TmCoAl compound is expected to have effective applications in low temperature magnetic refrigeration.

2. Experiments

The polycrystalline sample of TmCoAl compound was synthesized by arc melting of stoichiometric amounts of the elements Tm, Co and Al (99.9%) under a purified argon atmosphere on a water-cooled copper hearth using a titanium zirconium alloy as a getter. The sample was annealed at 1123 K for 10 days, and a subsequent quenching to room temperature was performed to obtain crystalline samples. Powder X-ray diffraction (XRD) measurements were performed at room temperature by using Cu Kα radiation to identify the crystal structure and the lattice parameters. Magnetizations were measured by employing a commercial superconducting quantum interference device (SQUID) magnetometer, model MPMS-7 from Quantum Design Inc.

3. Results and discussion

Fig. 1 shows the Rietveld refined powder XRD patterns of TmCoAl compound at room temperature. The refinement shows that the prepared sample is of single phase. The compound TmCoAl crystallizes in the hexagonal MgZn2-type crystal structure (space group P63/mmc, No. 194). In this structure, the Tm has an unique crystallographic site (4f); the Co and Al atoms statistically occupy the sites of 2a and 6h, respectively. The lattice parameters are determined to be \(a = 5.2714 (2) \text{Å}\) and \(c = 8.4593 (7) \text{Å}\) with \(R_{wp} = 4.5\%\) by the Rietveld technique using GSAS program.

Fig. 2 shows the typical temperature dependences of the magnetization \(M(T)\) curves for TmCoAl compounds under an applied magnetic field of \(H = 0.01\text{T}\). The TmCoAl compound exhibits a magnetic transition from ferromagnetic (FM) to paramagnetic (PM), and the Curie temperature \(T_C\) is determined to be 6 K, defined as the maximum slope of \(M(T)\) curve. It can be seen that there is almost no thermal hysteresis between the ZFC and FC curves as observed usually in SOPT, when the temperature increases above \(T_C\). However, a significant thermal irreversibility is clearly observed below \(T_C\). The thermomagnetic irreversibility can be observed in many cases, such as, spin-glass systems, materials with competing magnetic interactions, and materials with high anisotropy and low ordering temperature \([22]\), where the domain wall width could be comparable to that of lattice spacing, thus resulting in a large pinning effect \([21]\).

Considering the magnetic anisotropy due to the large orbital angular momentum in Tm atoms (or ions) and low \(T_C\) for TmCoAl, the thermomagnetic irreversibility is likely arising from the narrow domain wall pinning effect. The inset of Fig. 1 shows the reciprocal magnetic susceptibility \(\chi^{-1}\) versus temperature for TmCoAl. The magnetic susceptibility of the TmCoAl compound at temperatures above 10 K follows the Curie–Weiss law \(\chi = \frac{C}{T} - \theta\), where \(\theta\) is the Curie–Weiss constant. The value of \(\theta\) for TmCoAl is 4 K, which is lower than \(T_C\) in spite of the ferromagnetic ordering at low temperature. It indicates that the indirect RKKY-type exchange interaction is mainly responsible for magnetic order in these materials \([23]\).

Previous studies have shown that the magnetic contribution of the Co atoms could be neglected because of the filling of the \(d\) band by aluminum electrons in the hexagonal MgZn2 structure, which is a close-packed Laves phase \([24]\). The effective magnetic moment \(\mu_{eff}\) per Tm atom (5.93 \(\mu_B\)) is obtained based on the value of \(c_m\). This value is smaller than the free-ion value for Tm\(^{3+}\) (7.1 \(\mu_B\)) due to the crystal field effects and magnetic anisotropy.

Fig. 3(a) shows the isothermal magnetization curves as a function of magnetic field, which were measured in applied fields of up to 5 T in a temperature range from 2 to 26 K. It can be seen from Fig. 3(a) that there is a considerable difference in the \(M(H)\) curves for TmCoAl compound in different temperature ranges. In the 18–26 K temperature ranges, the field dependence of the magnetization shows a linear relation, whereas the isothermal curves for \(T_C < T < 18 \text{ K}\) shows an appreciable nonlinearity. The curvatures in the \(M(H)\) curves above \(T_C\) probably indicate the existence of short-range FM correlations in the PM state, which is in agreement with the result of positive \(\theta\) for TmCoAl compound (see Fig. 2). It should be noticed that although the isothermal magnetization curves are gradually saturated with increasing magnetic fields at considerably lower fields below \(T_C\), the complete saturation is not observed at 5 T. The lack of complete saturation in TmCoAl compound is likely attributed to the strong anisotropy and the crystalline electric field. The magnetic moment value per Tm atom at 2 K and 5 T reaches about 4.0 \(\mu_B\), which is close to that reported in Ref. \([25]\) and this is much smaller than the theoretical ordered state magnetic moment (7.1 \(\mu_B\)) of Tm\(^{3+}\) ion. This reduction in ordered state moment might...
The magnetic order transition temperature \( T \), \(-\Delta S_M \) and RC with the field change of 2 T for TmCoAl and other MCE materials around 10 K.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>( T ) (K)</th>
<th>Order of transition</th>
<th>(-\Delta S_M ) (J/kg K)</th>
<th>RC (J/kg)</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ErRu2Si2</td>
<td>5.5</td>
<td>First</td>
<td>11</td>
<td>55</td>
<td>[29]</td>
</tr>
<tr>
<td>HoNi2B2C</td>
<td>6.5</td>
<td>First</td>
<td>5.7</td>
<td>62</td>
<td>[30]</td>
</tr>
<tr>
<td>DyCo2B2</td>
<td>10</td>
<td>Second</td>
<td>4.5</td>
<td>0.9 ( J/cm^3 )</td>
<td>[31]</td>
</tr>
<tr>
<td>DyCuSi</td>
<td>10</td>
<td>First</td>
<td>-10.5</td>
<td>-160</td>
<td>[32]</td>
</tr>
<tr>
<td>Eu4Ga14Ge40</td>
<td>10</td>
<td>Second</td>
<td>8.0</td>
<td>80</td>
<td>[11]</td>
</tr>
<tr>
<td>HoCoAl</td>
<td>10</td>
<td>-</td>
<td>12.5</td>
<td>-</td>
<td>[21]</td>
</tr>
<tr>
<td>Dy0.9Tm0.1Ni2B2C</td>
<td>9.2</td>
<td>First</td>
<td>4.05</td>
<td>52</td>
<td>[33]</td>
</tr>
<tr>
<td>TmCoAl</td>
<td>7.5</td>
<td>Second</td>
<td>10.2</td>
<td>-72</td>
<td>Present</td>
</tr>
</tbody>
</table>

randomness associated with the statistical occupancy of 6h site. Fig. 3(b) shows the Arrott plot of the TmCoAl compound in the temperature range of 2–26 K. As is well known, according to the Banwejee criterion [27], a magnetic transition is expected to be of the first order when the slope of \( M^2 \) versus \( H/M \) plot is negative, whereas it will be of the second order when the slope is positive. Neither negative slope nor inflection point is observed in the Arrott plots of TmCoAl, indicating a characteristic of second-order FM-PM magnetic transition.

The MCE in terms of isothermal magnetic entropy change has been determined by utilizing Maxwell’s relationship

\[
\Delta S(T,H) = \int_0^H \frac{\partial M}{\partial T} dH
\]

in which \( T \) is the absolute temperature and \( H \) is the applied field. The values of \(-\Delta S_M\) for different magnetic field changes as a function of temperature are showed in Fig. 4. The value of \(-\Delta S_M^{\text{max}}\) is found to increase monotonically with the increase of applied magnetic field. For the magnetic field change of 5 T, the value of \(-\Delta S_M^{\text{max}}\) is 18.2 J/kg K at 7.5 K, which is just above the boiling point of helium. Particularly, the value of \(-\Delta S_M^{\text{max}}\) is found to be 10.2 J/kg K under a low magnetic change of 2 T, this value is larger than 4.9 J/kg K for GdCoAl, 5.3 J/kg K for TbCoAl and 9.2 J/kg K for DyCoAl. Although the values of \(-\Delta S_M^{\text{max}}\) are 12.5 J/kg K and 21.5 J/kg K around 20 K for HoCoAl under the field change 2 and 5T, respectively. The temperature is near the boiling point of hydrogen (20.4 K). The TmCoAl compound has confirmed a characteristic of second-order FM-PM magnetic transition, no thermal hysteresis and zero field hysteresis. The low field MCE parameters of TmCoAl are comparable or larger than those of most potential magnetic refrigerant materials in a similar magnetic transition temperature which are listed in Table 1. Moreover, the \(-\Delta S_M\) does not die out even at temperatures well above \( T_c \), possibly due to the presence of spin fluctuations [28]. The RC is considered to be another important requirement of a potential magnetic refrigerant, which is a measure of how much heat can be transferred between the cold and hot sinks in one ideal refrigerant cycle [34]. The value of \( RC \) is defined as:

\[
RC = \int_{T_1}^{T_2} |\Delta S_M|dT,
\]

where \( T_1 \) and \( T_2 \) are the temperatures corresponding to both sides of the half-maximum value of \(-\Delta S_M\) peak, respectively. One can find that the RC value of the TmCoAl increases with the increasing field changes and reaches to 72 and 211 J/kg, for the field changes of 0–2 and 0–5T, respectively. This RC value is higher than that (55 J/kg) of ErRu2Si2, which is 55 J/kg calculated for a field change of 0–2T in Ref. [29]. Our results suggest the TmCoAl compound could be a very attractive candidate material by using in a magnetic refrigerator working at low temperature.

4. Conclusion

In summary, the polycrystalline TmCoAl intermetallic compound with a single phase has been synthesized. The magnetic
property and MCE are investigated. A large reversible MCE without thermal and magnetic hysteresis loss has been observed in TmCoAl compound, which originates from the second order magnetic phase transition from PM to FM. With the magnetic field change of 0—5 T, the values of $-\Delta S^\text{max}$ is evaluated to be 18.2 J/kg K and the maximum value of RC is 211 J/kg. In particular, a large $-\Delta S^\text{max}$ and RC values are 10.2 J/kg K and 72 J/kg at 7.5 K under a magnetic field change from 0 to 2 T, respectively, which is important for the practical application of the TmCoAl compound in low-temperatures. The present results indicate that TmCoAl is one of a promising candidate for magnetic refrigeration in low temperature, particularly for helium liquefaction.

Acknowledgments

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