Magnetocaloric effect in Ho2In over a wide temperature range

Q. Zhang,1,a) J. H. Cho,2 B. Li,1 W. J. Hu,1 and Z. D. Zhang1
1Shenyang National Laboratory for Materials Science, Institute of Metal Research, and International Centre for Materials Physics, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, People’s Republic of China
2Research Center for Dielectric and Advanced Matter Physics and Department of Physics, Pusan National University, Busan 609-735, Korea

(Received 22 March 2009; accepted 14 April 2009; published online 4 May 2009)

The compound Ho2In exhibits two successive magnetic phase transitions: a spin-reorientation transition at \( T_{SR}=32 \) K and a magnetic-ordering transition at \( T_C=85 \) K. The maximum reversible \( -\Delta S_M \) values are 6.3 and 11.2 J/kg K at \( T_{SR} \) and \( T_C \), respectively, for a field change of 5 T. These two \( -\Delta S_M \) peaks with the same sign are partly overlapping, which results in a wide temperature interval with appreciable magnetocaloric effect. The results on Ho2In indicate that materials with successive SR and magnetic-ordering transitions may constitute an important new class of magnetic refrigerants since they work in a wider temperature range than the conventional refrigerant materials. © 2009 American Institute of Physics. [DOI: 10.1063/1.3130090]

Recently, magnetic refrigeration based on the magnetocaloric effect (MCE) has attracted much interest because it offers an energy-efficient and environment-friendly alternative for the usual vapor-cycle refrigeration technology.1–4 In general, investigation of the MCE has been focused on ferromagnets, such as Gd, (Mn,Fe)2Ge,5 etc.,6–8 and antiferromagnets9,10 because a large MCE may happen in the vicinity of the ferromagnetic (FM) to paramagnetic (PM) transition or the antiferromagnetic (AF) to PM transition. Recently, Isnard et al.11 have reported a small \( -\Delta S_M \) of not more than 1.8 J/kg K for a field change of 4.5 T at the spin-reorientation (SR) temperature at \( T_{SR} \) in ThFe1.7C0.3 compounds. This effect is so small that not much attention has been focused yet on this kind of MCE materials, but it would be interesting to search for systems with a SR that exhibits a larger MCE. Moreover, since the MCE generally shows a maximum at temperatures at which a magnetic phase transition occurs, the temperature range with a large MCE is relatively limited, which is a practical limitation. From the viewpoint of application, it is highly desirable that large MCE spans over a wide temperature range. Therefore it is a challenging topic to enlarge the working-temperature range of magnetic refrigeration materials.12–14 Recently, two magnetic-entropy changes have been found in some magnetic materials with two successive AF-FM and FM-PM magnetic transitions, like in Ce(Fe,Ru)2,15 \( \text{Tb}_2\text{NiSn} \)16 or successive structurally and magnetic transitions in Ni–Mn–In-based Heusler alloys.17–19 It is worthwhile noting that the signs of the two entropy changes in all these materials are opposite, which may not fully enlarge the working-temperature range since the MCE cannot be avoided to be zero in the transitional temperature range between the conventional and inverse MCE. In order to enlarge the temperature span efficiently, SR materials that exhibit two transitions at \( T_{SR} \) and \( T_C \) close to each other with the same sign of the magnetic-entropy changes would be extremely interesting. In the present paper, two magnetic-entropy changes with the same negative sign are reported in Ho2In at \( T_{SR} \) and \( T_C \) based on a different type of phase transition. Combined together, these two magnetic-entropy changes efficiently enlarge the working-temperature range for magnetic refrigeration and provide a significant refrigerant capacity (RC).

The preparation and measurement methods of polycrystalline Ho2In are the same as those described in Ref. 20. The measurements of x-ray diffraction (XRD) and magnetic properties of Ho2In are also described in Ref. 20. XRD indicates that as-cast material is single phase and has crystallized in the hexagonal NiIn-type structure with space group \( P6_3/mmc \). In both ZFC and FC curves (Fig. 1), there are two temperature ranges with rapid decrease in the magnetization, indicative of two phase magnetic transitions. The first decrease in magnetization at 32 K is due to a SR transition, corresponding to the low-temperature peak of the first derivative of the ZFC magnetization (\( dM/dT \)) (see inset of Fig. 1). Previous studies21,22 have pointed out that higher order axial-anisotropy terms favor tilting of the magnetic moments resulting in an angle with the crystallographic c-axis below \( T_{SR} \), while above \( T_{SR} \), the dominating second-order anisotropy makes the moments rotate toward the c-axis. Furthermore, the c-axis component of moments has a reduced value. So this SR transition leads to the rapid decrease in magnetization. The second distinct decrease in the magnetization oc-

FIG. 1. (Color online) Temperature dependences of the ZFC and FC magnetization of Ho2In in a field of 0.1 T. The inset shows the first-order derivative of the ZFC magnetization as a function of temperature.

---

EDential: qzhangemail@gmail.com.
magnetization curves around $T_{SR}$ are also reversible. By using the Maxwell relation $(\partial S/\partial B)_T=(\partial M/\partial T)_B$, the $-\Delta S_M$ can be represented as

$$\Delta S_M(T,B) = S_M(T,B) - S_M(T,0) = \int_0^B \left( \frac{\partial S_M}{\partial B} \right)_T dB = \int_0^B \left( \frac{\partial M}{\partial T} \right)_B dB.$$  

From the magnetic isotherms of Ho$_2$In, we have derived values of $-\Delta S_M$ as a function of temperature. Figure 3 shows $-\Delta S_M(T)$ curves for the magnetic-field change ($\Delta B$) from 0 to 5 T. In contrast to the usual observation of a single MCE peak or two coexisting peaks of inverse and normal MCEs, the temperature dependence of the MCE in Ho$_2$In is quite different. A maximum $-\Delta S_M$ value of 11.2 J/kg K is found at the Curie temperature $T_C=85$ K. Interestingly, another appreciable $-\Delta S_M$ of 6.3 J/kg K is observed at 31 K, at the SR temperature $T_{SR}$. It should be noted that in this case the signs of the two magnetic entropies are both negative. That is, the present compound Ho$_2$In shows two successive and conventional MCEs with cooling by adiabatic demagnetization. For Ce(Fe,Ru)$_2$ (Ref. 15) and Tb$_2$Ni$_2$Sn, with increasing temperature, the magnetization first increases and then decreases due to successive AF-FM and FM-FM transitions, resulting in the opposite signs of $\partial M/\partial T$. Similarly, the first-order structural martensitic transition and the FM-FM transition in Ni–Mn–In based Heusler alloy$^{17-19}$ also first lead to an increase and then to a decrease in the magnetization, resulting in opposite signs of $\partial M/\partial T$. In contrast to these systems that show the coexistence of inverse and conventional MCE, in Ho$_2$In, the signs of $\partial M/\partial T$ around $T_{SR}$ and $T_C$ are both negative, leading to the same negative sign of the two magnetic entropies around $T_{SR}$ and $T_C$. In addition, the $-\Delta S_M$ around $T_{SR}$ in Ho$_2$In has an appreciable value of 6.3 J/kg K for $\Delta B=5$ T, which is associated with the considerable value of $\partial M/\partial T$ at $T_{SR}$ (see the inset of Fig. 1 and above formula). Note that thermal and magnetic hysteresis losses, which are detrimental for fast-cycling refrigerating, are not observed in Ho$_2$In around $T_{SR}$ and $T_C$.

A very important feature in Fig. 3 is that the two magnetic entropies with the same negative sign in Ho$_2$In partly overlap and that in the $-\Delta S_M$ versus T curve a minimum
The Magnetocaloric Effect and Its Application

In conclusion, two magnetic-entropy changes with the same negative sign, due to different magnetic phase transitions, are reported to occur in Ho2In. For ∆B=5 T, two reversible −∆SM max values of 11.2 and 6.3 J/kg K are found around second-order FM-PM transition and SR, respectively. This double peak MCE behavior in Ho2In leads to a wide-temperature range with an operating temperature region ∆T cycl = 110 K within one thermodynamic cycle with a very high RC value of 360 J/kg K. The results on Ho2In may be an important stimulus to search for suitable refrigerant materials in the category of materials that exhibit two or more successive magnetic phase transitions, particularly involving a SR. This work has been supported by the National Natural Science Foundation of China under Grant No. 50331030. The author Q. Zhang was partially supported by the Korea Research Foundation under Grant No. KRF-2006-005-J02801.

TABLE I. Comparison of the main parameters of Ho2In with corresponding data of the excellent refrigerant materials with working temperature around 85 K.

<table>
<thead>
<tr>
<th>Material</th>
<th>−∆SM max (5 T) (J/kg K)</th>
<th>Tcold (K)</th>
<th>Thot (K)</th>
<th>∆T cycl (K)</th>
<th>RC (5 T) (J/kg)</th>
<th>Tc (K)</th>
<th>Evaluated from ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdCr2S4</td>
<td>7.04</td>
<td>65</td>
<td>125</td>
<td>60</td>
<td>180</td>
<td>87</td>
<td>28</td>
</tr>
<tr>
<td>HoCo2</td>
<td>22</td>
<td>76</td>
<td>94</td>
<td>18</td>
<td>216</td>
<td>78</td>
<td>29</td>
</tr>
<tr>
<td>TbCoAl</td>
<td>10.5</td>
<td>42</td>
<td>95</td>
<td>53</td>
<td>265</td>
<td>76</td>
<td>30</td>
</tr>
<tr>
<td>Gd3S5</td>
<td>36</td>
<td>82</td>
<td>98</td>
<td>16</td>
<td>56</td>
<td>86</td>
<td>31</td>
</tr>
<tr>
<td>Ho2In</td>
<td>11.2</td>
<td>16</td>
<td>126</td>
<td>110</td>
<td>360</td>
<td>85</td>
<td>This work</td>
</tr>
</tbody>
</table>