Magnetocaloric effect in Ho_2In over a wide temperature range

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The compound Ho_2In 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 Ho_2In 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, $(Mn,Fe)_5Ge_3$,[5] etc.,[6–8] and antiferromagnets[9,10] 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 T_{SR} in $ThFe_{11}C_x$ 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] Tb_2Ni_2Sn,[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 Ho_2In 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 Ho_2In are the same as those described in Ref. 20. The measurements of x-ray diffraction (XRD) and magnetic properties of Ho_2In are also described in Ref. 20. XRD indicates that as-cast material is single phase and has crystallized in the hexagonal Ni_2In-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 studies[21,22] 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-

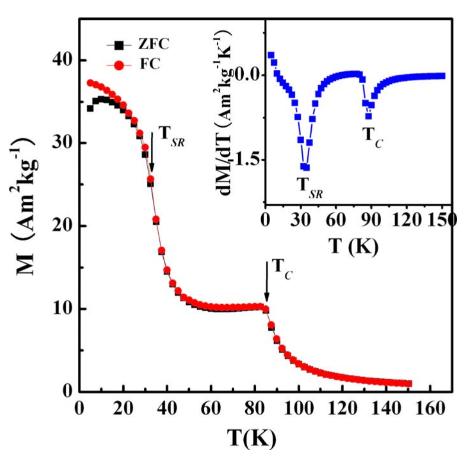

FIG. 1. (Color online) Temperature dependences of the ZFC and FC magnetization of Ho_2In in a field of 0.1 T. The inset shows the first-order derivative of the ZFC magnetization as a function of temperature.

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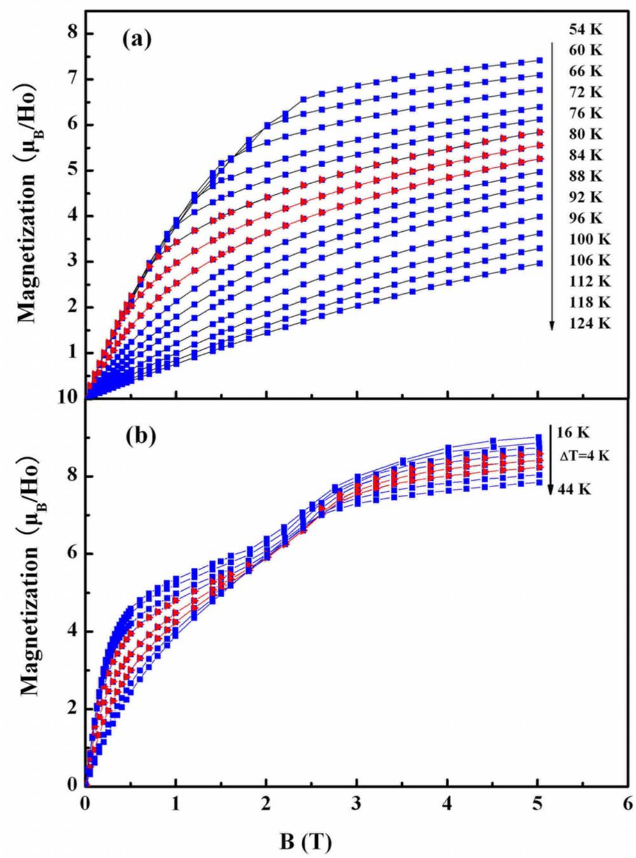

FIG. 2. (Color online) Magnetic isotherms of Ho_2In in the temperature range (a) from 54 to 124 K and (b) from 16 to 44 K, measured with increasing field (solid squares) and decreasing field (solid triangles).

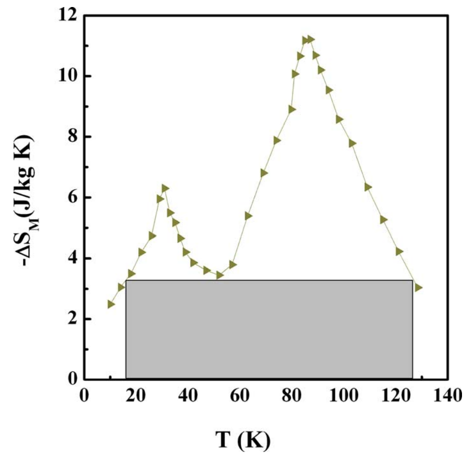

FIG. 3. (Color online) Temperature dependence of the magnetic-entropy changes in Ho_2In for a magnetic-field change from 0 to 5 T.

curs at $T_C=85$ K due to FM-PM transition, corresponding to the second peak at the higher temperature of dM/dT (see inset of Fig. 1). Our results accord well with results reported by Anh *et al.*[21] In addition, it is evident from Fig. 1 that there is negligible thermal hysteresis in ZFC and FC curves above 20 K. At low temperatures below 20 K, the small difference between the ZFC and FC curves may be a result of larger magnetization due to domain-wall pinning upon cooling in a field in the FC process.

Selected magnetic isotherms of Ho_2In measured in increasing field and in decreasing field around T_C and T_{SR} are shown in Figs. 2(a) and 2(b), respectively. Around T_C, the magnetization increases rapidly at low fields and shows a tendency to saturate at higher field values, as is typical for FM materials. No magnetic hysteresis is found upon increasing or decreasing the field, indicating that the FM-PM transition at T_C is second-order. In sharp contrast, around T_{SR}, the magnetic isotherms [Fig. 2(b)] show a distinct saturating curvature at low fields, suggesting FM behavior. With increasing field, the magnetization starts to increase rapidly at an inflection point and exhibits upward curvature between 1 and 3 T, suggesting a rapid rotation of the moments toward the external field. When the field is further increased above 3 T, the magnetization almost saturates. Our results agree well with the results of Anh *et al.*[21] This crossover behavior at the inflection point is closely related to the SR behavior around T_{SR} and can be understood as a result of the competition between the Zeeman energy in the external field and the strong magnetocrystalline-anisotropy energy around T_{SR}. Moreover, there is no magnetic hysteresis losses, and all 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_2In, 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 (ΔB) 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_2In 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_2In shows two successive and conventional MCEs with cooling by adiabatic demagnetization. For $Ce(Fe,Ru)_2$ (Ref. 15) and Tb_2Ni_2Sn,[16] with increasing temperature, the magnetization first increases and then decreases due to successive AF-FM and FM-PM transitions, resulting in the opposite signs of $\partial M/\partial T$. Similarly, the first-order structural martensitic transition and the FM-PM 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 $\partial M/\partial T$. As shown in the above expression, the sign of ΔS_M is determined by the sign of $\partial M/\partial T$. In contrast to these systems that show the coexistence of inverse and conventional MCE, in Ho_2In, 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_2In 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_2In 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_2In partly overlap and that in the $-\Delta S_M$ versus T curve a minimum

TABLE I. Comparison of the main parameters of Ho_2In with corresponding data of the excellent refrigerant materials with working temperature around 85 K.

Material	$-\Delta S_M^{max}$ (5 T) (J/kg K)	T_{cold} (K)	T_{hot} (K)	ΔT_{cycl} (K)	RC (5 T) (J/kg)	T_C (K)	Evaluated from ref.
$CdCr_2S_4$	7.04	65	125	60	180	87	28
$HoCo_2$	22	76	94	18	216	78	29
TbCoAl	10.5	42	95	53	265	70	30
Gd_5Sn_4	36	82	98	16	56	86	31
Ho_2In	11.2	16	126	110	360	85	This work

$-\Delta S_M$ value of 3.4 J/kg K is still attained in the temperature ranges between the two peaks, which obviously enlarges the working-temperature range. One usually uses materials consisting of two or more phases with different transition temperatures to obtain such double peak MCE behavior.[23,24] So materials such as Ho_2In which exhibit a double peak MCE behavior may open an interesting possibility to achieve magnetic cooling in a wider temperature range than conventional refrigerant materials, although Ho_2In itself is not representative for application in magnetic refrigerant because of the expensive cost of Ho and the MCE results obtained in a high field change of 5 T.

To further illustrate this point, we have evaluated the total RC, which is an important criterion for magnetic-refrigeration materials and represents the amount of heat transferred in one thermodynamic cycle. According to the Wood and Potter method,[25] the RC of a reversible refrigeration cycle operating between T_{hot} and T_{cool} is defined as $RC=\Delta S_M \Delta T_{cycl}$, where ΔS_M is the magnetic-entropy change at the hot and cold ends of the cycle and ΔT_{cycl} $(=T_{hot}-T_{cold})$ is the operating-temperature range in one thermodynamic cycle.[25–27] For a given magnetic refrigerant, the optimum refrigeration cycle occurs when the quantity of $\Delta S_M \Delta T_{cycl}$ has a maximum value. For Ho_2In, a very large RC value of 360 J/kg, indicated by the shaded area in Fig. 3, is obtained for $T_{cold} \approx 16$ K and $T_{hot} \approx 126$ K. For clarity, we have compared the main parameters, such as $-\Delta S_M$, T_{cold}, T_{hot}, ΔT_{cycl}, and RC of Ho_2In with those of materials with excellent refrigerant properties around 85 K. As can be seen in Table I, Ho_2In works over a much wider temperature range, i.e., has a much higher ΔT_{cycl} value, than these excellent refrigerant materials, and therefore, a high RC value of 360 J/kg is obtained. Thus, compared with the conventional magnetic refrigeration materials with one phase transition only, the combined MCE due to successive SR and FM-PM transition in Ho_2In brings about a wider temperature span and, therefore, induces a high RC of the magnetic refrigeration cycle.

In conclusion, two magnetic-entropy changes with the same negative sign, due to different magnetic phase transitions, are reported to occur in Ho_2In. For $\Delta B=5$ T, two reversible $-\Delta S_M^{max}$ 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 Ho_2In leads to a wide-temperature range with an operating temperature region $\Delta T_{cycl} \approx 110$ K within one thermodynamic cycle with a very high RC value of 360 J/kg. This results on Ho_2In 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.

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