



# Giant magnetic refrigerant capacity in $\text{Ho}_3\text{Al}_2$ compound

H. Zhang<sup>a,\*</sup>, Z.Y. Xu<sup>a</sup>, X.Q. Zheng<sup>a</sup>, J. Shen<sup>b</sup>, F.X. Hua<sup>a,b</sup>, J.R. Sun<sup>a</sup>, B.G. Shen<sup>a,\*</sup>

<sup>a</sup> State Key Laboratory for Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, PR China

<sup>b</sup> Key laboratory of Cryogenics, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China

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## ABSTRACT

Magnetic properties and magnetocaloric effects (MCEs) of the intermetallic  $\text{Ho}_3\text{Al}_2$  compound are investigated by magnetization and heat capacity measurements. Two successive magnetic transitions, a spin-reorientation (SR) transition at  $T_{\text{SR}}=31$  K followed by a ferromagnetic (FM) to paramagnetic (PM) transition at  $T_{\text{C}}=40$  K, are observed. Both magnetic transitions contribute to the MCE and result in a large magnetic entropy change ( $\Delta S_{\text{M}}$ ) in a wide temperature range. The maximum values of  $-\Delta S_{\text{M}}$  and adiabatic temperature change ( $\Delta T_{\text{ad}}$ ) reach 18.7 J/kg K and 4.8 K for the field changes of 0–5 T, respectively. In particular, a giant value of refrigerant capacity (RC) is estimated to be 704 J/kg for a field change of 5 T, which is much higher than those of many potential refrigerant materials with similar transition temperatures.

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## 1. Introduction

Magnetocaloric effect (MCE) is a magneto-thermodynamic phenomenon, which is usually characterized by the magnetic entropy change ( $\Delta S_{\text{M}}$ ) and/or adiabatic temperature change ( $\Delta T_{\text{ad}}$ ) upon the variation of the magnetic field. In recent years, magnetic materials with large MCEs have attracted considerable attention due to their potentialities for magnetic refrigeration [1–3]. So far, numerous rare earth (R)-based compounds, exhibiting first-order magnetic or structural phase transition, have been found to exhibit large values of  $\Delta S_{\text{M}}$  and  $\Delta T_{\text{ad}}$  around their transition temperatures [4–7]. However, it is known that the  $\Delta S_{\text{M}}$  and/or  $\Delta T_{\text{ad}}$  are not the only parameters to identify the potentiality of a magnetic refrigerant. The refrigerant capacity (RC) is considered as another important measure of how much heat is transferred between the hot and cold sides in an ideal refrigeration cycle. Unfortunately, the first-order phase transition is usually accompanied with remarkable thermal and magnetic hystereses, which always reduce the effective RC value of magnetic materials [8,9]. On the contrary, materials with second-order magnetic transition generally show a good reversible behavior of the magnetization in response to the temperature and magnetic field. Therefore, it is desirable to search magnetocaloric materials with large reversible MCEs as well as high RC values based on the second-order magnetic transition. Very recently, some Ho-based intermetallic compounds, such as  $\text{HoNiIn}$  [10],  $\text{Ho}_2\text{In}$  [11],  $\text{HoGa}$  [12], have

been reported to exhibit several reversible magnetic transitions, and thus resulting in multiple  $\Delta S_{\text{M}}$  peaks and large RC values in a broad temperature region. The results on these materials stimulate us to explore new magnetic refrigerants in other Ho-based systems, which may show multiple reversible magnetic transitions. In the present paper, we carry out a systematic study on the magnetic properties and MCE of  $\text{Ho}_3\text{Al}_2$  compound. It is found that  $\text{Ho}_3\text{Al}_2$  undergoes two successive magnetic transitions with increasing temperature. The combined contribution of both transitions gives rise to a large MCE and giant RC without hysteresis loss in a wide temperature range.

## 2. Experiments

The polycrystalline  $\text{Ho}_3\text{Al}_2$  sample was synthesized by arc-melting appropriate proportion of constituent components with the purity better than 99.9 wt% in a water-cooled copper hearth under purified argon atmosphere. The ingot was melted several times with the button being turned over after each melting to ensure the homogeneity. The as-cast sample was then annealed in a high-vacuum quartz tube at 1073 K for 7 days. Powder X-ray diffraction (XRD) measurement was performed at room temperature by using  $\text{Cu K}\alpha$  radiation to identify the crystal structure and the lattice parameters. Magnetizations were measured as functions of temperature and magnetic field by employing a commercial superconducting quantum interference device (SQUID) magnetometer, model MPMS-7 from Quantum Design Inc. The specific heat was measured by using a physical property measurement system (PPMS) from Quantum Design.

\* Corresponding author. Tel.: +86 10 82648085; fax: +86 10 82649485.

E-mail addresses: zhanghuxt@aphy.iphy.ac.cn (H. Zhang), shenbg@aphy.iphy.ac.cn (B.G. Shen).

### 3. Results and discussion

Fig. 1 shows the observed and refined powder X-ray diffraction (XRD) patterns of  $\text{Ho}_3\text{Al}_2$  compound. The Rietveld refinement confirms that  $\text{Ho}_3\text{Al}_2$  crystallizes in a single tetragonal  $\text{Zr}_3\text{Al}_2$ -type structure with space group  $P4_2nm$ . The Ho atoms occupy three crystallographic positions: two 4c and one 4b, while the Al atoms are distributed over two 4c positions. The lattice parameters  $a$  and  $c$  are determined to be 8.1656(5) and 7.5223(6) Å, respectively, which are in accord with the data in the previous report [13].

Fig. 2 shows the specific heat ( $C_p$ ) curve of  $\text{Ho}_3\text{Al}_2$  in the fields of 0, 2, and 5 T, respectively, and the temperature ( $T$ ) dependence of zero-field-cooling (ZFC) and field-cooling (FC) magnetizations ( $M$ ) under a magnetic field of 0.01 T. It is clearly seen that there are two successive magnetic transitions in the specific heat curve under zero field (Fig. 2(a)). The peak at higher temperature corresponds to a change from ferromagnetic (FM) to paramagnetic (PM) state with increasing temperature, and the Curie temperature  $T_C$  is determined to be 40 K. The transition at lower temperature of 31 K may be associated with a spin-reorientation (SR) transition, which is often observed in Ho-based intermetallic compounds [10,14,15]. With the application of magnetic field, the peak of SR transition vanishes while the  $T_C$  peak becomes a broad anomaly with a lower magnitude. On the other hand, it is interesting to note that the change of magnetization around  $T_C$  is indistinct in  $M$ - $T$  curve (see Fig. 2(b)). This is likely due to the fact that the SR transition is followed closely by the FM-PM transition, and therefore both transitions occur in the almost same temperature range, leading to a slow change of magnetization in a relatively wide temperature region. In addition, one can see that there is another anomaly around  $T_{sf} = 14$  K in the ZFC curve and an obvious discrepancy between ZFC and FC curves appears below this temperature. However, specific heat measurement does not exhibit a peak of transition around 14 K. Similar phenomenon was also observed in the study of  $\text{Ho}_3\text{Ni}$  compound, and it is reported that this behavior is attributed to the spin-freezing effect [16]. Therefore, we also suppose that a spin-freezing behavior occurs below  $T_{sf}$ , and thus leading to a large difference between ZFC and FC curves. The temperature dependence of the reciprocal magnetic susceptibility  $\chi_m^{-1}$  measured in a field of 1 T is shown in the inset of Fig. 2(b). The magnetic

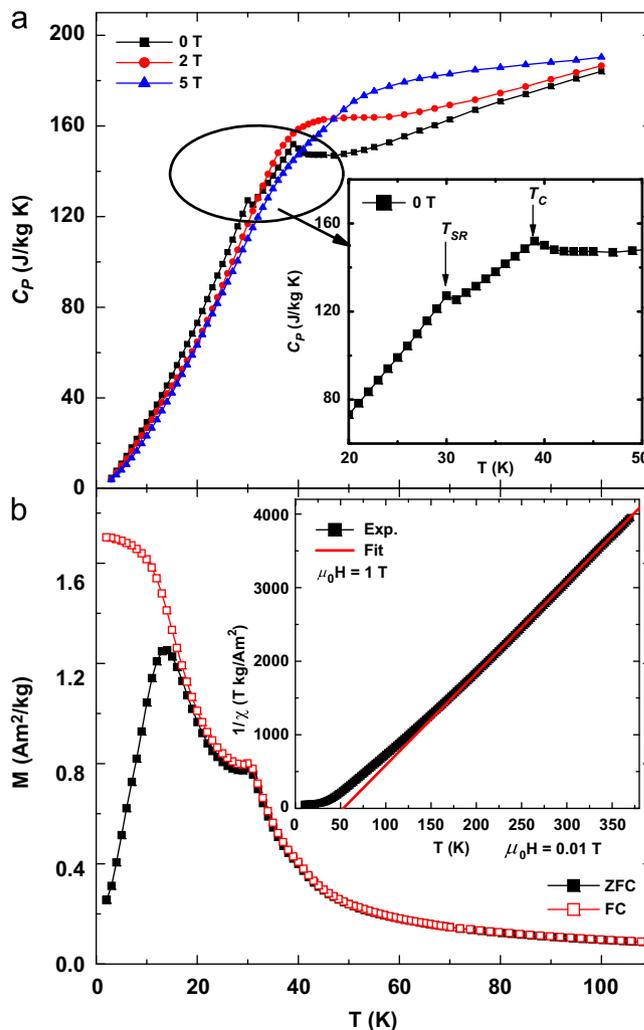


Fig. 2. (Color online) (a) The specific heat ( $C_p$ ) of  $\text{Ho}_3\text{Al}_2$  measured in the fields of 0, 2, and 5 T, respectively. (b) Temperature dependencies of the ZFC and FC magnetizations for  $\text{Ho}_3\text{Al}_2$  compound under a magnetic field of 0.01 T. The inset shows the temperature variation of inverse dc magnetic susceptibility fitted to the Curie-Weiss law under 1 T.

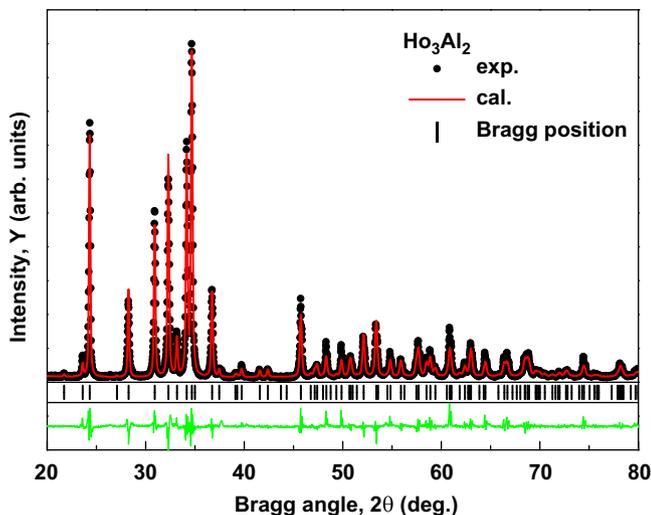


Fig. 1. (Color online) The observed (dots) and calculated intensities (line drawn through the data points) of the fully refined powder diffraction pattern of  $\text{Ho}_3\text{Al}_2$  compound. The short vertical lines indicate the calculated Bragg peak positions of the tetragonal  $\text{Zr}_3\text{Al}_2$ -type crystal structure. The curve at the bottom of plot shows the difference between the observed and calculated intensities.

susceptibility follows the Curie-Weiss law in PM region with an effective moment  $\mu_{\text{eff}}$  of  $10.82 \mu_B/\text{Ho}^{3+}$  and a PM Curie temperature of 53 K. The  $\mu_{\text{eff}}$  determined from the fit is in a good agreement with the value reported in Ref. [17].

The magnetization isotherms of  $\text{Ho}_3\text{Al}_2$  were measured under applied fields up to 5 T in a temperature range of 11–80 K with different temperature steps as shown in Fig. 3. It is found that the magnetization below  $T_C$  increases rapidly at low fields and shows a tendency to saturate with the increase of field, indicating the typical FM characteristic. However, the magnetization does not fully saturate even at the highest field of 5 T, and this fact implies the existence of large anisotropy caused by the spin-freezing effect [16]. In addition, it is noted that no magnetic hysteresis is observed in each magnetization isotherm in field increasing and decreasing modes, suggesting the perfect reversibility of the magnetic transitions. Moreover, the Arrott plots of  $\text{Ho}_3\text{Al}_2$  compound, derived from  $M$ - $H$  curves, are shown in Fig. 4. According to Banerjee criterion [18], a magnetic transition is expected to be of first-order when the slope of Arrott plot is negative; otherwise it is considered as second-order when the slope is positive. Therefore, the positive slopes near  $T_{SR}$  and  $T_C$  confirm that the associated magnetic transitions in  $\text{Ho}_3\text{Al}_2$  compound are of second-order in nature.

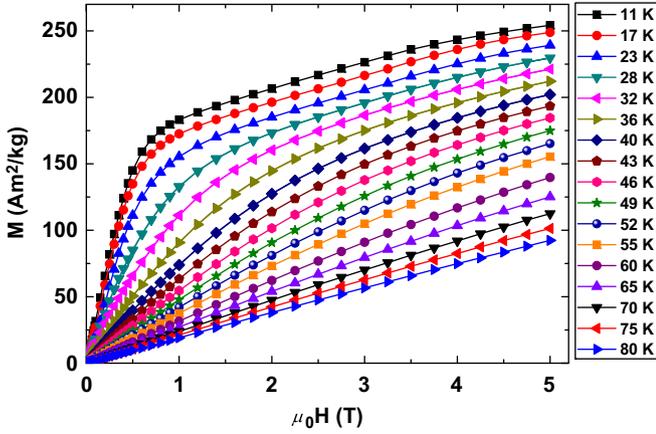


Fig. 3. (Color online) Isothermal magnetization curves of  $\text{Ho}_3\text{Al}_2$  in a temperature range from 11 to 80 K.

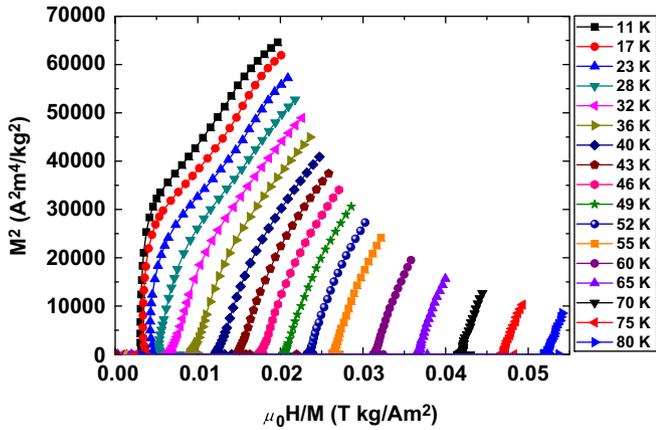


Fig. 4. (Color online) The Arrott plots of  $\text{Ho}_3\text{Al}_2$  compound at different temperatures near  $T_{SR}$  and  $T_C$ .

The magnetic entropy change  $\Delta S_M$  of  $\text{Ho}_3\text{Al}_2$  was calculated from the isothermal magnetization curves by using the Maxwell relation  $\Delta S(T, H) = \int_0^H (\partial M / \partial T)_H dH$ . Fig. 5(a) displays the  $\Delta S_M$  of  $\text{Ho}_3\text{Al}_2$  as a function of temperature for different magnetic field changes up to 5 T. Unlike other systems with successive transitions which usually exhibit multiple  $\Delta S_M$  peaks [11,12],  $\text{Ho}_3\text{Al}_2$  only shows a single peak of  $\Delta S_M$  in a wide temperature range. As mentioned above, both SR and FM–PM transitions take place closely, thus two  $\Delta S_M$  peaks may overlap with each other and lead to a large  $\Delta S_M$  in a broad temperature region. The maximum values of  $-\Delta S_M$  are found to be 9.6 and 18.7 J/kg K for the field changes of 0–2 T and 0–5 T, respectively. For comparison, the  $\Delta S_M$  values were also calculated from the heat capacity by  $\Delta S(T) = \int_0^T [C_H(T) - C_0(T)] / T dT$  and are shown in Fig. 5(a). It is clearly seen that the results obtained from both methods are consistent with each other. In addition, the adiabatic temperature change  $\Delta T_{ad}$ , which is defined as the temperature change in the adiabatic demagnetization process, was calculated from heat capacity data by using the formula  $\Delta T_{ad} = [T \times \Delta S_M(T, H)] / C_p(T, H)$ , where  $C_p$  is the specific heat. Fig. 5(b) shows the temperature dependence of  $\Delta T_{ad}$  for magnetic field changes of 0–2 T and 0–5 T, respectively. It can be seen that the behavior of  $\Delta T_{ad}$  as a function of temperature is similar to that of  $\Delta S_M$  vs.  $T$  curves. The maximum values of  $\Delta T_{ad}$  are estimated to be 2.1 and 4.8 K under the field changes of 0–2 T and 0–5 T, respectively, which are comparable with those of  $\text{Gd}_3\text{Al}_2$  compound [19].

As another important criterion to evaluate the refrigeration efficiency, the RC of  $\text{Ho}_3\text{Al}_2$  compound has been estimated by

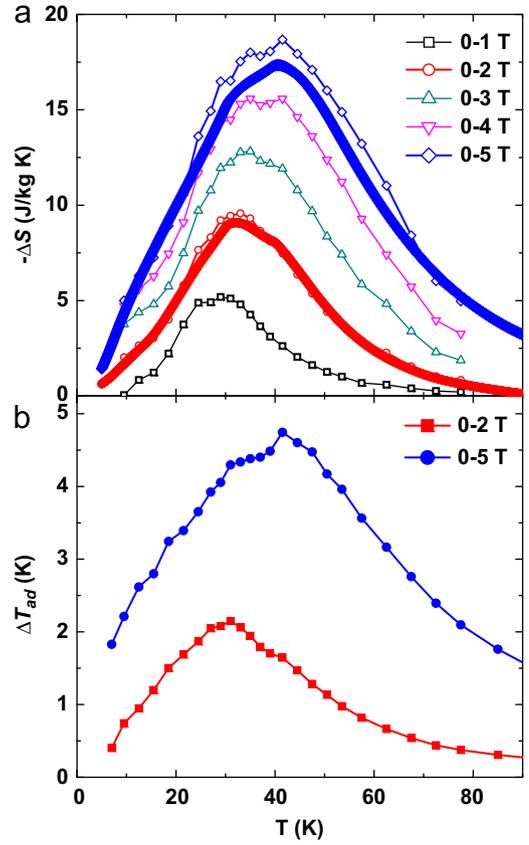


Fig. 5. (Color online) (a) Magnetic entropy changes of  $\text{Ho}_3\text{Al}_2$  calculated from magnetizations (open symbols) and heat capacity measurements (full symbols) as a function of temperature for different magnetic field changes. (b) Temperature dependence of  $\Delta T_{ad}$  for  $\text{Ho}_3\text{Al}_2$  compound under magnetic field changes of 0–2 T and 0–5 T, respectively.

Table 1.

Magnetocaloric properties of  $\text{Ho}_3\text{Al}_2$  and some representative refrigerant materials with magnetic transition temperatures around 40 K.

Materials	$T_{ord}$ (K)	$-\Delta S_M$ (0–5 T) (J/kg K)	RC (0–5 T) (J/kg)	Refs.
DyMn <sub>2</sub> Ge <sub>2</sub>	40	13.4	214 <sup>a</sup>	[21]
ErCo <sub>2</sub>	35	33.0	270 <sup>a</sup>	[22]
Gd <sub>2</sub> Al	44	7.2	290 <sup>a</sup>	[23]
DyCoAl	37	16.3	485 <sup>a</sup>	[24]
Dy <sub>3</sub> Co	44	13.9	498	[25]
GdNiAl	40	12	540 <sup>a</sup>	[26]
$\text{Ho}_3\text{Al}_2$	40	18.7	704	This work

<sup>a</sup> The RC values are estimated from the temperature dependences of  $\Delta S_M$  in the reference literatures.

numerically integrating the area under the  $\Delta S_M$  vs.  $T$  curve, using the temperatures at half maximum of the peak as the integration limits [20]. For a magnetic field change of 0–5 T,  $\text{Ho}_3\text{Al}_2$  exhibits a giant RC value of 704 J/kg with  $T_{cold} = 19$  K (temperature at the cold end) and  $T_{hot} = 66$  K (temperature at the hot end). Table 1 summarizes the magnetocaloric properties of  $\text{Ho}_3\text{Al}_2$  and some representative refrigerant materials with similar magnetic transition temperatures. It can be seen that  $\text{Ho}_3\text{Al}_2$  exhibits a considerably large MCE among these compounds. Especially, The RC value of  $\text{Ho}_3\text{Al}_2$  is significantly higher than those of other refrigerant materials. This giant RC value of  $\text{Ho}_3\text{Al}_2$  is due to the combined contribution of the successive SR and FM–PM transitions, which brings about a large  $\Delta S_M$  in a wide temperature span.

#### 4. Conclusions

In summary, the results of magnetization and specific heat measurements indicate that  $\text{Ho}_3\text{Al}_2$  undergoes successive SR and FM–PM transitions with the variation of temperature. For a magnetic field change of 0–5 T, the maximum value of  $-\Delta S_M$  is found to be 18.7 J/kg K and the RC value is as high as 704 J/kg without hysteresis loss. This quite high value of RC is due to the relatively broad distribution of  $\Delta S_M$  peak, which is caused by the overlap of the successive magnetic transitions. The present study suggests that  $\text{Ho}_3\text{Al}_2$  may be an appropriate magnetic refrigerant material for low temperature applications.

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