Magnetic properties and magnetocaloric effect of $HoCo_3B_2$ compound

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Magnetic properties and magnetocaloric effect of $HoCo_3B_2$ compound

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A sample of $HoCo_3B_2$ compound was synthesized, and the magnetic and MCE properties were investigated. Compound shows a change corresponding to R-R (R = rare earth) sublattice magnetic order transition and the transition temperature is determined to be 11.8 K (T_C). The characteristic of Arrott plots with positive slope around T_C was observed, indicating a second-order phase transition. Based on isothermal magnetization data, together with Maxwell's relationship, the magnetic entropy change ($-\Delta S_M$) was calculated. The maximum $-\Delta S_M$ reaches 7.8, 12.7 and 14.4 J/kg K for field range of 0-2 T, 0-5 T and 0-7 T, respectively. Accordingly, the value of RC (refrigerant capacity) is 99, 289 and 432 J/kg for above field ranges. The large MCE of $HoCo_3B_2$ compound indicates its potential application for magnetic refrigeration in low temperature range. https://doi.org/10.1063/1.5006505

I. INTRODUCTION

Compared with traditional gas compression/expansion technology, the magnetic refrigeration technology based on magnetocaloric effect (MCE) has the advantages of environmental friendliness and high energy efficiency.[1–4] MCE is an intrinsic property of magnetic materials and it is usually evaluated by the isothermal magnetic entropy change ($-\Delta S_M$), adiabatic temperature change (ΔT_{ad}) and refrigerant capacity (RC). In the subject of magnetic refrigeration technology, it is of great importance to explore materials with large MCEs. So far, numerous magnetic materials, such as $La(Fe,Si)_{13}$-series,[5–7] $Gd_5(Si,Ge)_4$-series,[4,8] MnAs-series,[1,9] MnFe-series[10–13] and NiMn-series,[14–16] have been studied for the large MCE based on first order magnetic transitions in room temperature range. In recent years, MCE materials with low magnetic transition temperatures are becoming a research hotspot because they are expected to be used in liquid nitrogen and liquid helium liquefaction.[17–20] $ErCo_2$ compound is a kind of representative low temperature MCE material because of its giant MCE, and it has been considered as a referenced material in low temperature range.[21,22] However, it is accompanied by magnetic hysteresis and thermal hysteresis due to the first-order magnetic transition. Therefore, it is necessary to search for magnetic materials with large and reversible MCE based on the second-order magnetic transition.

The $R_{n+1}Co_{3n+5}B_{2n}$ (R=Rare earth, n=0, 1, 2, 3 and ∞) family of magnetic compounds shows several forms such as RCo_5, RCo_4B, $R_3Co_{11}B_4$ and $R_2Co_7B_3$.[23–26] The RCo_3B_2 compounds

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are the extreme case for n= infinite and they crystallize in the hexagonal (P6/mmm) $CaCu_5$-type structure.[23–31] It can also be imagined as being built up by ordered substitutions of B atoms into the Co sites in an RCo_5-type structure.[24–29,31] Recently, the system of RCo_3B_2 (R=Gd, Sm, Tb, Dy, Ho) has been studied for electronic and magnetic properties.[24–31] Some of RCo_3B_2 series are paramagnetic and some are ferromagnetically ordered at low temperatures.[28] Especially, $GdCo_3B_2$ compound has been proved to undergo two magnetic transitions at 54 K and 160 K respectively while increasing the temperature.[32] $TbCo_3B_2$ compound was also described to experience two magnetic transitions according to Dubman[26] *et al.*, but only one transition temperature was observed by Li[33] *et al.* Large MCE has also been found in $GdCo_3B_2$, $TbCo_3B_2$ and $DyHo_3B_2$ compounds.[32–35] The magnetic and crystallographic properties of $HoCo_3B_2$ compound[30] have been investigated before, however, no research work on MCE has been reported. In this work, the magnetic and MCE properties of $HoCo_3B_2$ compound is studied in detail.

II. EXPERIMENTAL DETAILS

A polycrystalline sample of $HoCo_3B_2$ was synthesized by arc-melting method in argon atmosphere. The starting substances are elementary Ho, Co and CoB alloy (wt% Co-83.864 wt. % B-14.78 wt. %). The elementary metal Ho, Co with a purity more than 99.9 wt. % and the alloy metal CoB with a purity more than 98.5 wt. % were melted several times for homogeneity on a water-cooled copper hearth. Then the sample was wrapped with a molybdenum foil and annealed at 1023 K for 7 days in an evacuated quartz tube. Finally, the quartz tube was quenched in liquid nitrogen and smashed. The crystal structure and purity of the sample were confirmed by powder X-ray diffraction (XRD) experiment using the Cu Kα radiation. The magnetic measurements were performed by employing a vibrating sample magnetometer (VSM) in the temperature range from 2 K to 50 K.

III. RESULTS AND DISCUSSION

Powder X-ray diffraction pattern was measured at room temperature and the pattern was shown in the inset of Fig. 1. The XRD pattern was fitted by using Rietveld method and both observed and calculated patterns are shown in the plots. It can be found that almost all the peaks can be indexed in the Bragg positions of $CeCo_3B_2$-type[36] hexagonal crystal structure with space group of P6/mmm. Although there are tiny peaks which cannot be indexed in the crystal structure of hexagonal crystal structure, it doesn't affect the discussions of the nearly single phase of $HoCo_3B_2$ sample.

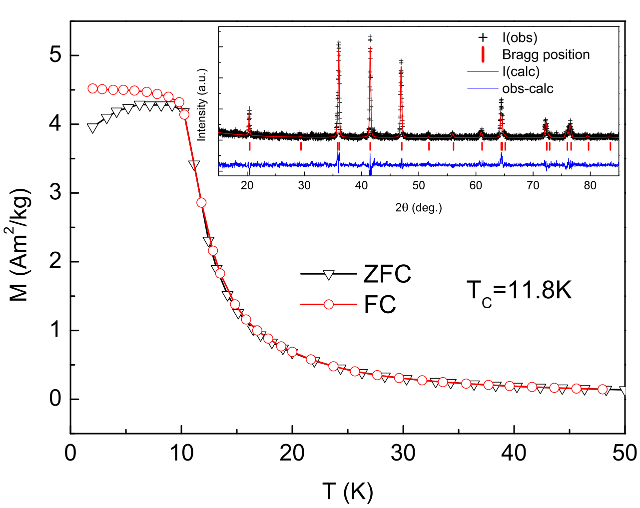

FIG. 1. Temperature dependences of zero-field-cooling and field-cooling magnetizations for $HoCo_3B_2$ compound at a magnetic field of 0.01 T. Inset: XRD pattern at room temperature and fitted curves.

The results of refinement show that the lattice parameters of main phase, a and c, are 5.0156(5) Å and 3.0380(4) Å, respectively with χ^2 of 1.451. The results are in good agreement with previous report.[30,36] Both zero-field-cooling and field-cooling thermal magnetization curves were measured at a field of 0.01 T and they are shown in Fig. 1. The relationship between magnetization and temperature obeys the Curie-Weiss law from 20 K to 300 K, which means $HoCo_3B_2$ compound is paramagnetic (PM) in this temperature range. As temperature decreases, magnetization goes up gradually and finally arrives at a stable high value indicating ferromagnetic (FM) order is established. The Curie temperature is determined to be 11.8 K by evaluating the minimum value of the dM/dT on the ZFC curve at 0.01 T. Separation of ZFC and FC exists below T_C, but no heat hysteresis has been observed in the temperature range above T_C. The misalignment of ZFC and FC has always been observed in FM materials resulting from domain wall pinning.[37] Though a small anomaly was observed around 150 K in $HoCo_3B_2$ compound from AC susceptibility measurement by Caspi *et al.*, no long range magnetic order was detected above 10 K according to the results of neutron diffraction experiment in the same work.[30] In this work, no obvious changes are observed around 150 K according to the thermal magnetization data, as is observed in $TbCo_3B_2$ and $DyCo_3B_2$ compounds.[33,34]

Isothermal magnetization curves of $HoCo_3B_2$ at different temperatures were measured under a magnetic field up to 7 T and they are all plotted in Fig. 2(a). For temperatures below T_C, $HoCo_3B_2$ compound show the typical characteristic of FM order. Magnetization increases quickly with increasing of magnetic field, and then arrives at a saturation value of 8.3 μ_B. Compared with the theoretical saturation value of 10 μ_B, it indicates that it is difficult for Ho atoms to saturate completely with a field of 7 T in $HoCo_3B_2$ compound. As a matter of fact, similar situations have been observed in $TbCo_3B_2$ and $DyCo_3B_2$ compounds.[33,34] It should be noted that the isothermal magnetization curves still keep a sharp curvature even though the temperature has exceeded T_C. This kind of M-H curves has been observed in many magnetic materials such as ErGa compound,[37] which results from the short range FM order in the compounds. As for $HoCo_3B_2$ compound, though no long range FM order was detected above T_C, short range FM order actually exists according to the above results. The short range FM order exists in a large temperature range and it is not disappeared

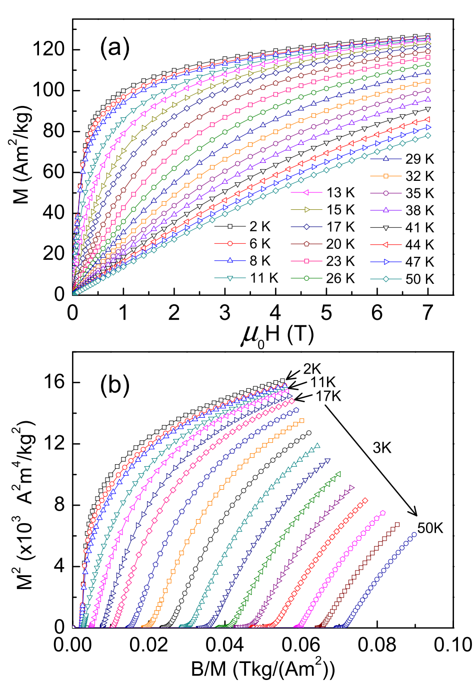

FIG. 2. (a) Isothermal magnetization curves of $HoCo_3B_2$ compound in a wide temperature range with applied fields up to 7 T. (b) The Arrott plots of $HoCo_3B_2$ compound.

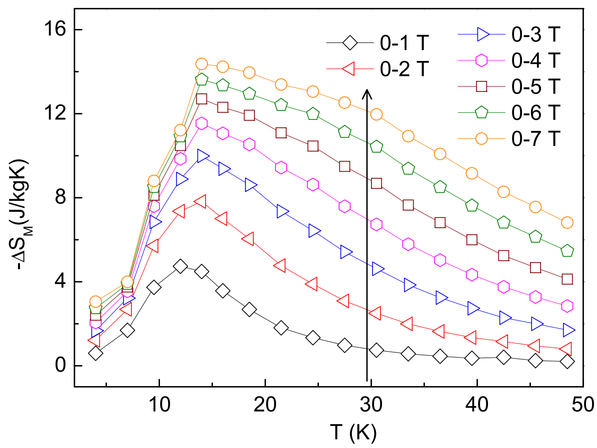

FIG. 3. Magnetic entropy change (ΔS_M) as a function of temperature for $HoCo_3B_2$ compound under field changes of 0-1 T, 0-2 T, 0-3 T, 0-4 T, 0-5 T, 0-6 T and 0-7 T, respectively.

until ~32 K. And the special feature has an important impact on the results of MCE, which will be discussed in the following section. The Arrott plots were obtained based on M-H data and are shown in Fig. 2(b). According to Banerjee's criterion,[38] the magnetic transition is of a second-order if all the Arrott plot curves have positive slope. According to Fig. 2(b), all curves are monotonically increasing with a positive slope, indicating a second-order magnetic transition in $HoCo_3B_2$ compound.

The magnetic entropy change (-ΔS_M) can be calculated from the isothermal magnetization curves using Maxwell's relation $\Delta S_M = \int_0^H (\partial M/\partial T)_H dH$. The temperature dependences of -ΔS_M curves for a field change from 0-1 T to 0-7 T are plotted in Fig. 3. It is clearly that only one peak can be observed on every -ΔS_M curve, and the peaks locate at the temperature around T_C. Our measurements indicate that FM-PM transition makes main contribution to the MCE of $HoCo_3B_2$ compound. The maximum values of -ΔS_M are determined to be 5.0, 7.8, 12.7 and 14.4 J/kg K for a field change of 0-1 T, 0-2 T, 0-5 T and 0-7 T, respectively. It should also be noted that small bulge can be observed on the -ΔS_M curves around 30 K for a field change of 0-5 T, 0-6 T and 0-7 T. The bulges are caused by the short range FM order at the temperatures above but not far from T_C. Magnetic refrigerant capacity (RC) is also an important parameter to measure the performance of MCE materials. The RC of $HoCo_3B_2$ compound was estimated based on the ΔS_M–T curves by using the approach suggested by Gschneidner[39] *et al.* The RC value is defined as $RC = \int_{T1}^{T2} |\Delta SM|\, dT$, where T_1 and T_2 are the temperatures corresponding to both sides of the half-maximum value of ΔS_M peak, respectively. The value of RC is calculated to be 99, 289 and 432 J/kg for a field change of 0-2 T, 0-5 T and 0- 7 T, respectively. Some MCE materials with a similar transition temperature to $HoCo_3B_2$ compound are listed for comparison in Table I. $HoCo_3B_2$ compound is not the best MCE materials at low temperatures, but it shows some competitiveness compared with other materials.

TABLE I. Magnetocaloric properties of $HoCo_3B_2$ compound and some other refrigerant materials with similar transition temperatures.

Materials	T_{ord} (K)	$-\Delta S_M$ (J/kg K)		RC (J/kg)		Refs.
		2T	5T	2T	5T	
TmCoAl	7.5	10.2	18.2	72	211	40
ErAgAl	14	4.2	10.5	50.1	261	41
$Ho_4Er_8Co_7$	15	9.6	18.0	122.6	342	42
HoCo3B2	11.8	7.8	12.7	99	289	this work

IV. CONCLUSIONS

In conclusion, $HoCo_3B_2$ compound crystallizes in the $CeCo_3B_2$-type hexagonal crystal structure, and it undergoes a second-order FM-PM transition at 11.8 K. Though no long range FM order is observed, short range FM order exists for temperatures above but not far from T_C. The maximum values of $-\Delta S_M$ are 7.8, 12.7 and 14.4 J/kg K and the values of RC are 99, 289 and 432 J/kg for the field change of 0-2 T, 0-5 T and 0-7 T, respectively. The $-\Delta S_M$ keeps a relative high value above T_C because of the short range FM order, indicating good MCE performance.

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