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ABSTRACT

The coupled system of multi-degrees of freedom, such as charge, spin, orbital and lattice, has recently received much attention due to its potential to improve the magnetocaloric effect (MCE). The exotic inverse MCE was observed in rare-earth tetraborides of $Ho_{1-x}Dy_xB_4$ (x = 0.0, 0.5, and 1.0), associated with a strong coupling between magnetic dipoles and orbital quadrupoles in the strong spin-orbit coupling and geometric frustration. Here, the magnetism and magnetocaloric effects of ErB_4 and TmB_4 are investigated. It shows the maximum entropy changes of 11.4 J/kgK, and 12.6 J/kgK with the field of $\Delta H \approx 40$ kOe ($H \| c$) in ErB_4 and TmB_4, respectively. The field- and temperature-dependence of the entropy change is found to be quite different from those of the conventional MCE. And the entropy change is also found to have strong correlation with the field induced meta-magnetic transition. Because the field induced transition is due to magnetic moment reorientation, which is strongly coupled with quadrupole moment, the abnormal MCE of ErB_4 and TmB_4 is attributed to the dipole-quadrupole interaction and magnetic frustration. Thus, it supports the fact that the strong coupling between quadrupole and magnetic dipole moments plays important role in the exotic inverse MCE in rare-earth tetraboride system.

I. INTRODUCTION

The magnetocaloric cooling technology has been widely studied for the high-efficiency and environmental-friendly refrigeration system.[1] For the discovery of new materials, which exhibit a large magnetocaloric effect, an interesting scenario have been proposed that large entropy change is expected in a system with an enormous ground state degeneracy such as geometric frustration.[2,3] Rare-earth tetraborides, RB_4 (R = rare-earth elements) has been known as compounds of geometrically frustrated magnetic system. The sub-lattice of rare-earth ions in the c-plane forms the Shastry-Sutherland lattice. It has been known that the coexistence of strong spin-orbit coupling and geometrical frustration is led to the interesting magnetic states in the rare-earth tetraborides.[4–6] The frustration in DyB_4 and HoB_4 are caused not only by pure magnetic interactions but also by the quadrupole interactions. These compounds show common features of two successive magnetic transitions, exhibiting magnetic dipole ordering at $T = T_{N1}$ and quadrupole ordering at $T = T_{N2}$ ($T_{N1} \approx 20.5$ K, and 7 K and $T_{N2} \approx 13.0$ K, and 5.7 K for DyB_4 and HoB_4, respectively). The maximum value of positive entropy change is observed near $T = T_{N2}$ with the values of 19.6 J/kg·K and 22.7 J/kg·K at the critical fields of $\Delta H \approx 50$ kOe and 25 kOe for DyB_4 and HoB_4, respectively. It is found that the exotic inverse MCE is due to the interplay of strong spin-orbit coupling and geometric frustration.[7] To continue the study of series compounds of RB_4 (R = rare-earth elements), we further investigate the magnetic and magnetocaloric properties of ErB_4 and TmB_4, which show fractional magnetization plateaus in isotherm and anisotropic antiferromagnetic ground state in Shastry-Sutherland lattice. In addition, the rotating magnetocaloric effect was recently reported, involving the interesting feature of the angular dependence of magnetic properties.[8,9]

Herein, we investigated the magnetocaloric effects of RB_4 (R = Er and Tm) single crystals. The entropy change exhibits the maximum values of 11.4 J/kgK and 12.6 J/kgK with field of $\Delta H = 40$ kOe for $H \| c$ in ErB_4 and TmB_4, respectively. It is found that the temperature- and field-dependence of the entropy change is quite different from those of conventional magnetocaloric effects.

II. EXPERIMENTAL DETAILS

Single crystals of RB_4 (R = Er and Tm) are prepared with a high-temperature metal flux method. A stoichiometric mixture of rare earth metals (≥ 99.9%, China Rare Metal Material Co., LTD.) and boron pieces (99.9%, RND Korea) are placed in an alumina crucible (99.8%, Samhwa Ceramic Company) together with the Al pellets (99.999%, RND Korea) with a mass ratio of samples to Al = 1:60. The samples are placed in a heated tube furnace with an $MoSi_2$ heating element. The heat treatment is followed by heating up to 1650 °C under a high-purity argon atmosphere after dehydration and cooled slowly at a rate of 4.8 °C per hour to 650 °C. The single crystals are separated from the flux by dissolving the excess Al in NaOH.

The crystal structures of the samples are characterized using X-ray diffraction measurements (XRD; Rigaku D/MAX-2500 with a Cu target) at room temperature. The lattice parameters are determined from LeBail refinements using FULLPROF software. The XRD patterns show a single phase of ErB_4 and TmB_4 without any observable impurity phases. The crystal structures are in good agreement with the tetragonal symmetry of the ThB_4-type structure and space group $P4/mbm$ (No. 127). The refined lattice parameters are a = 7.0647(6) Å and c = 3.9936(6) Å for ErB_4 and a = 7.067(5) Å and c = 3.9820(0) Å for TmB_4. The refinement values are in a good agreement with previous reports.[10] The temperature- and field-dependent magnetizations are measured using a superconducting quantum interference device magnetometer (SQUID; Quantum Design MPMS XL).

III. RESULTS AND DISCUSSION

The temperature-dependence of magnetization of ErB_4 under magnetic field of H = 10 kOe for $H\|c$ and $H\perp c$ is plotted in Fig. 1. It shows the strongly anisotropic behaviour of magnetization. Whereas the broad maximum is observed around T = 30 K for $H\perp c$ due to the Schottky anomaly associated with crystalline electric-field (CEF) level split,[11] the antiferromagnetic transition is observed at T_N = 15.5 K for $H\|c$. The inset shows that the paramagnetic phase for both $H\|c$ and $H\perp c$ follows the Curies-Weiss law, $\frac{M(T)}{H} = \frac{C}{T-\theta}$, where $C = N_0\mu_{eff}^2/3k_B$, N_0 is Avogadro's number, k_B is the Boltzmann constant, and μ_{eff} is the effective magnetic moment. The effective magnetic moments are determined to be $9.27\mu_B$, and $9.50\mu_B$, where μ_B is the Bohr magneton, and the Weiss temperatures, θ, are also found to be +11.24 K and -23.26 K for $H\|c$ and $H\perp c$, respectively. The μ_{eff} values are close to the theoretical value of Hund's rule for the ground state of the isolated Er^{3+} ions (μ_{eff} = 9.59 μ_B).

Figure 2 shows the isothermal magnetization data of ErB_4 at various temperatures for both $H\|c$ and $H\perp c$. The field-induced meta-magnetic transition and magnetization plateau are noticeably observed at T = 5 K in a range of 20 kOe ≤ H ≤ 40 kOe for $H\|c$ and there is no magnetic hysteresis in the magnetization at T = 2 K, as shown in the inset of Fig. 2(a). The magnetic moment of Er^{3+} ion at H = 50 kOe is found to be ≈ 5.1 μ_B. On the other hand, the isothermal magnetizations for $H\perp c$ at various temperatures show the typical antiferromagnetic behaviour and the inset shows the data at T = 2 K.

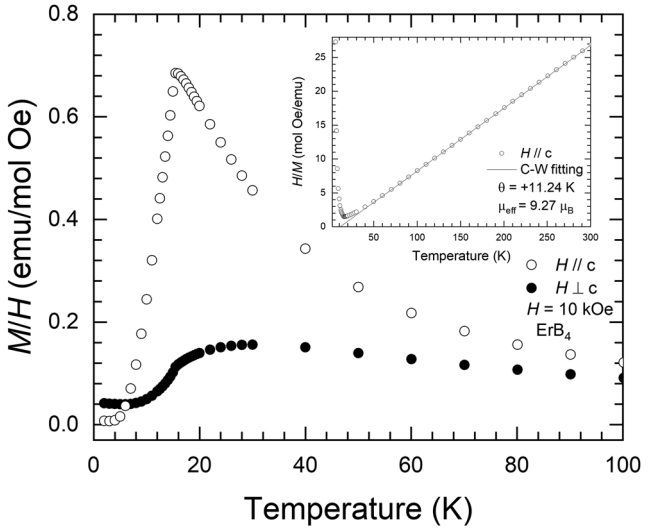

FIG. 1. Temperature-dependence of magnetization with an applied magnetic field, H = 10 kOe, for $H\|c$ and $H\perp c$ of ErB_4.

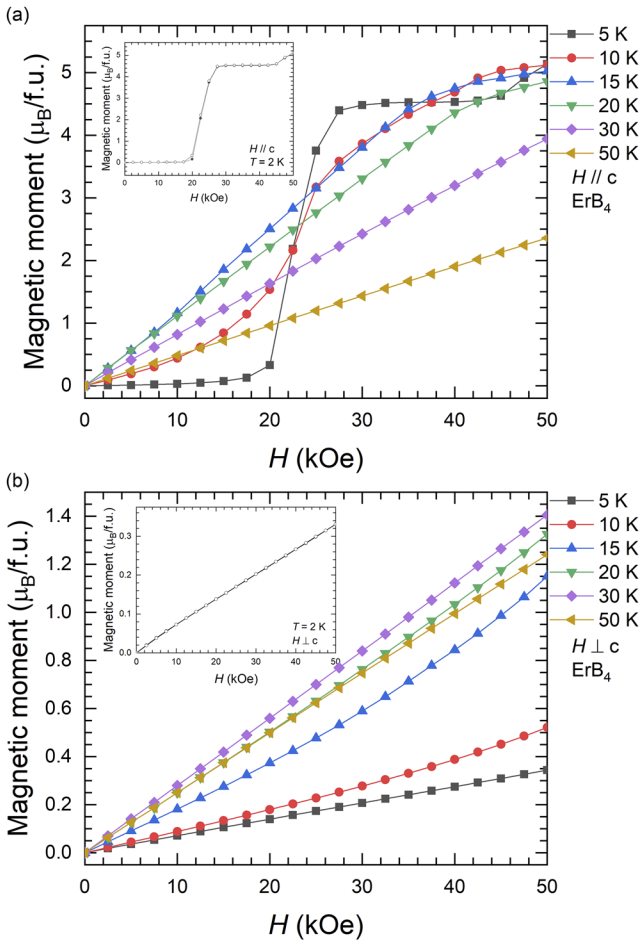

FIG. 2. Field-dependence of the isothermal magnetization at various temperatures in a range of 2 K ≤ T ≤ 50 K for (a) $H\|c$ and (b) $H\perp c$ of ErB_4.

The magnetic moment at T = 2 K and H = 50 kOe is found to be 0.3 μ_B, indicating that the orientation of Er^{3+} ion moment is aligned along the c-axis.

The magnetic entropy change, ΔS_M, can be estimated from the Maxwell equation in the approximated form

$$\Delta S_M(T,H) = \sum_i \frac{M_{i+1}(T_{i+1},H) - M_i(T_i,H)}{T_{i+1} - T_i}\Delta H_i$$

where M_{i+1} and M_i are the experimentally measured values at temperatures T_{i+1} and T_i under applied magnetic field, H, respectively, in the interval of magnetic field, ΔH_i. Figure 3 shows the temperature-dependence of the magnetic entropy change of ErB_4, which is calculated from isothermal magnetization data for $H\|c$ and $H\perp c$. The positive entropy change, ΔS_M, is observed for $H\|c$ at $T \approx 13$ K, which is significantly lower than T_N (= 15.5 K), as shown in Fig. 3(a). The maximum value of entropy change is observed to be +11.4 J/kgK and almost constant with the fields of ΔH = 30, 40, and 50 kOe. The negative entropy change at higher temperatures is likely due to the crystal field degeneracy and follows field-dependence of typical magneto-caloric effect. Figure 3(b) shows also a positive entropy change for $H\perp c$ with the maximum value of +11.13 J/kgK at $T = T_N$ with ΔH=50 kOe.

Figure 4 shows the temperature-dependence of magnetization of TmB_4 under magnetic field of H = 10 kOe for $H\|c$ and $H\perp c$. It also shows the strongly anisotropic behaviour of magnetization as like ErB_4. Whereas the broad maximum is found near T = 90 K for $H\perp c$ due to the influence of crystal electric field,[12] there are two successive magnetic transition at T_{N1} = 11.9 K and T_{N2} = 9.2 K for $H\|c$. It is already known that there is incommensurate-incommensurate magnetic transition with magnetic fluctuation below $T = T_{N1}$ and that the fluctuation disappears and the commensurate magnetic structure is developed below $T = T_{N2}$.[13] The inset of Fig. 4 shows that the paramagnetic phase for both $H\|c$ and $H\perp c$ follows the Curies-Weiss law. The effective magnetic moment is determined to be 7.49μ_B and 7.70μ_B and the Weiss temperature to be + 40.7 K and - 63.5 K for $H\|c$ and $H\perp c$, respectively. The μ_{eff} values are close to the theoretical value of Hund's rule for the ground state of the isolated Tm^{3+} ions (μ_{eff} = 7.55 μ_B).

Figure 5 shows the isothermal magnetization data of TmB_4 at various temperatures for $H\|c$ and $H\perp c$. The meta-magnetic transitions and magnetization plateaus are observed at T = 5 K in a range of 15 kOe ≤ H ≤ 40 kOe for $H\|c$. The inset shows the similar isothermal magnetization at T = 2 K and the hysteresis at the transition near $H \approx$ 16 kOe, which is not found in ErB_4, may be an indication of lattice distortion due to electron-lattice coupling. The magnetic moment of the Tm^{3+} ion at T = 2 K and H = 50 kOe is 7.5 μ_B, which is close to the full saturation moment of Tm^{3+} ion (7.55 μ_B). The isothermal magnetization for $H\perp c$ in Fig. 5(b) shows

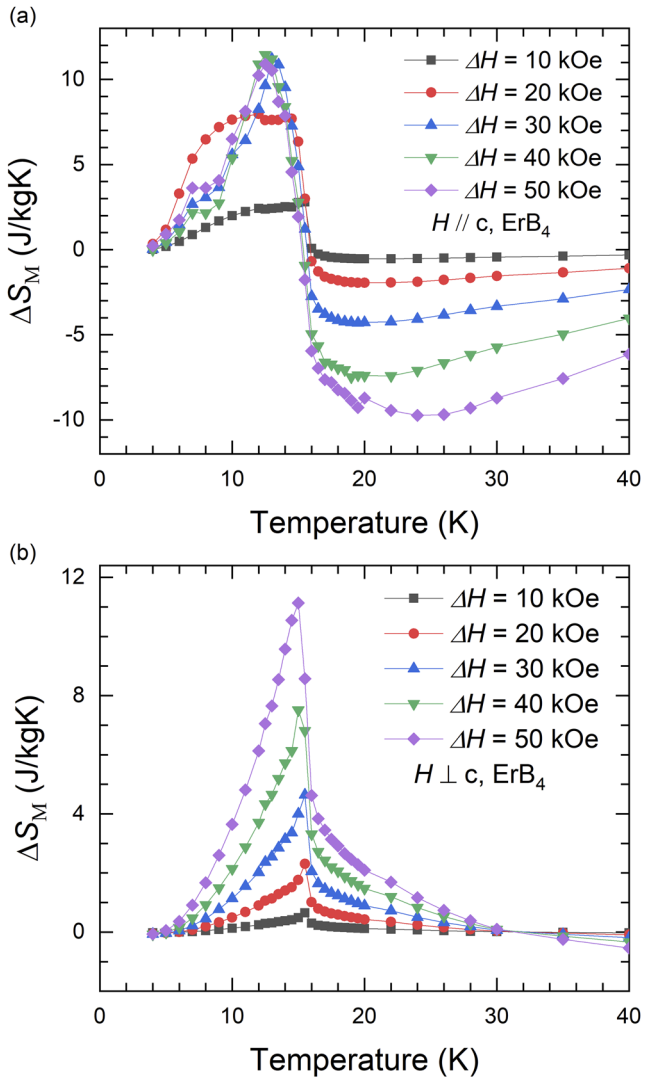

FIG. 3. The magnetic entropy change under various magnetic fields of ΔH = 10, 15, 20, 30, 40 and 50 kOe, for (a) $H\|c$ and (b) $H\perp c$ of ErB_4.

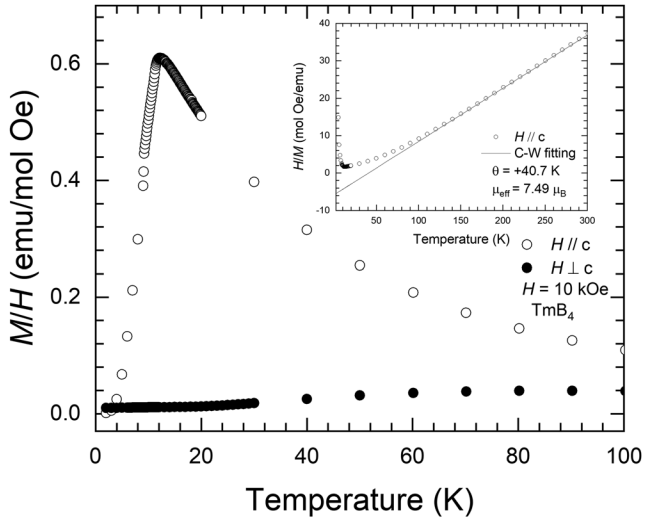

FIG. 4. Temperature-dependence of magnetization with an applied magnetic field, H = 10 kOe, for $H\|c$ and $H\perp c$ of TmB_4.

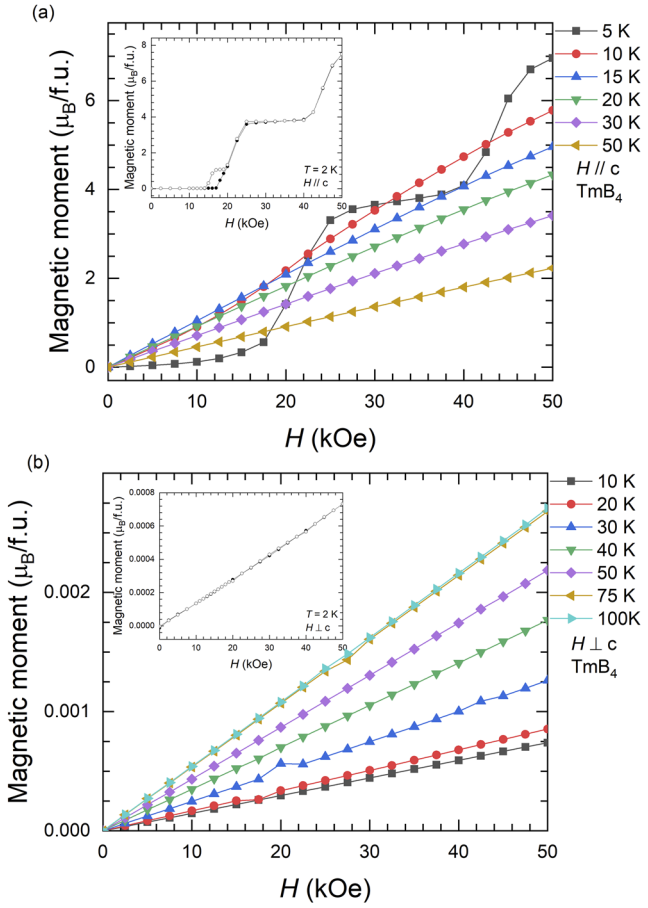

FIG. 5. Field-dependence of the isothermal magnetization at various temperatures in a range of 2 K ≤ T ≤ 100 K for (a) $H \| c$ and (b) $H \perp c$ of TmB_4.

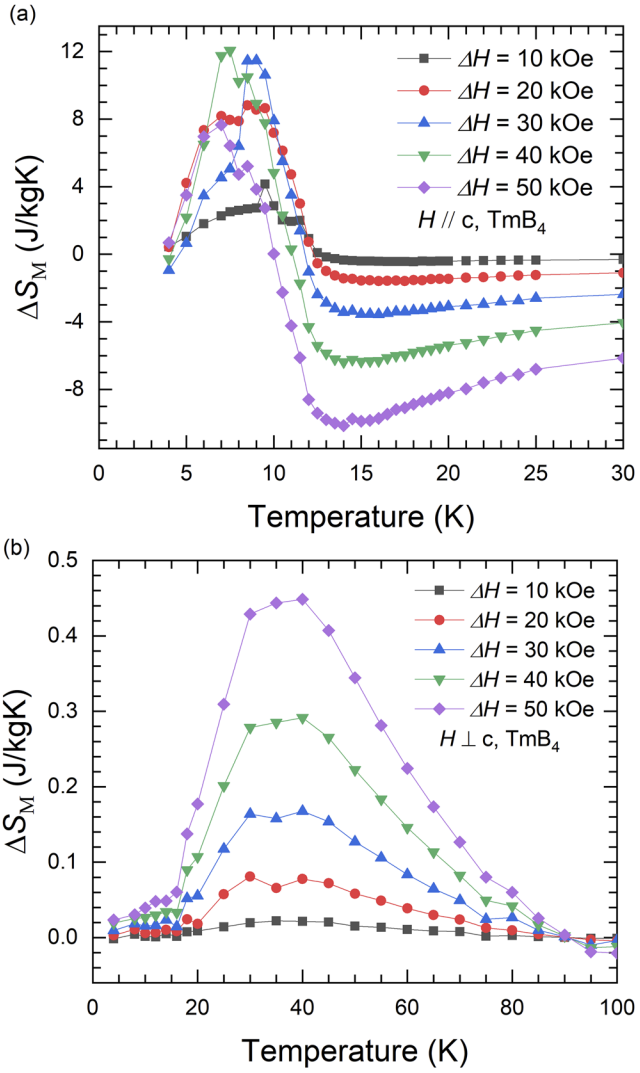

FIG. 6. The magnetic entropy change under various magnetic fields of ΔH = 10, 15, 20, 30, 40 and 50 kOe, for (a) $H \| c$ and (b) $H \perp c$ of TmB_4.

typical antiferromagnetic behaviour due to strongly anisotropy, as like ErB_4. Comparison of the isothermal data of ErB_4 and TmB_4 for $H \| c$ indicates that the meta-magnetic transition is a common feature for two compounds and that ErB_4 would have the second transition at higher fields of H > 50 kOe.

Figure 6 shows the temperature-dependence of the magnetic entropy change for TmB_4, which is calculated from isothermal magnetization data for both $H \| c$ and $H \perp c$. The field-dependent entropy change is observed to be maximum with a value of + 12.6 J/kgK under the field of ΔH = 40 kOe at $T \approx 8$ K, which is close to $T = T_{N2}$. With further increase of magnetic field, the entropy change decreases to a value of + 7.7 J/kg·K with the field of ΔH = 50 kOe at $T \approx 7$ K. The negative entropy change is observed with the maximum value of ΔS_M = - 10.1 J/kg·K with ΔH = 50 kOe at $T \approx T_{N2}$, which shows the conventional magnetocaloric behaviour. On the other hand, the magnetic entropy change for $H \perp c$ is negligibly small, as shown in Fig. 6(b).

The entropy changes of ErB_4 and TmB_4 for $H \| c$ show common interesting peculiar features in terms of field-dependence and correlation with magnetic transition. The maximum entropy change occurs at significantly lower temperatures of $T \approx 12.5$ K for ErB_4, while T_N = 15.5 K, and $T \approx 8$ K for TmB_4, while T_N = 12 K. In addition, the maximum value of ErB_4 is found with the field of ΔH = 30 kOe and kept to be almost constant even with further increase of field. And that of TmB_4 is found with the field of ΔH = 40 kOe and decreases with the field of ΔH = 50 kOe. This abnormal field-dependence of entropy change is quite different from that of conventional magneto-caloric effect. So, the positive large entropy changes in ErB_4 (Fig. 3(a)) and TmB_4 (Fig. 6(a)) is not likely to be related with the antiferromagnetic transitions. Indeed, tetraboride compounds (RB_4; R = rare-earth elements) are known to have hidden quadrupole ordering and spin reorientation below $T = T_N$ due to strong spin-orbit coupling.[14–17] The meta-magnetic transitions in isothermal magnetization for $H \| c$ are the manifestation of the

magnetic coupling with quadrupole ordering. Thus, the abnormal entropy changes of ErB_4 and TmB_4 is likely the results of degeneracy release in the field-induced meta-magnetic transition. The peculiar field dependence of entropy change can be understood in terms of the strength of spin-orbit coupling. Similar entropy change in $Ho_{1-x}Dy_xB_4$ system and Landau free energy model for that are recently reported.[7]

Structural distortion in ErB_4 was found in the measurements of high resolution X-ray diffraction and specific heat.[18,19] Although the origin of the distortion is not fully understood at present time, it is conjectured that the contribution of the distortion to entropy change would be negligible because the temperature- and field-dependence of entropy change is of second-order nature. In addition, the distortion temperature is quite higher than the temperatures for maximum entropy change.

IV. CONCLUSIONS

In this study, the anisotropic and inverse magnetocaloric effects are investigated in rare-earth tetraboride system. ErB_4 and TmB_4 are successfully synthesized as the single crystals without any significant impurity phases. These compounds show common features of strongly anisotropic magnetism and field-dependent entropy change. The positive entropy change, i.e., inverse magnetocaloric effect, is observed for $H \| c$ with the maximum values of ΔS_m = +11.4 J/kgK, and +12.6 J/kgK at ΔH = 30 kOe and 40 kOe for ErB_4 and TmB_4, respectively. With further increase of field, no more increase of ΔS_M for ErB_4 and even decrease of ΔS_m for TmB_4 are observed. The abnormal entropy change is also found to come from magnetic degeneracy release in the field induced meta-magnetic transition. Because the meta-magnetic transition is influenced by competition between Zeeman effects and frustration in strong spin-orbit coupling regime, the peculiar characteristics of MCE in ErB_4 and TmB_4 is believed due to the multipolar degrees of freedom which is lain in a geometrically frustrated lattice.

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