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Specific heat in magnetic field and magnetocaloric effects of α-R_2S_3 (R = Tb, Dy) single crystals

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ABSTRACT

The magnetocaloric effects (MCE) of α-Tb_2S_3 and α-Dy_2S_3 single crystals exhibiting successive antiferromagnetic (AFM) transitions have been investigated by analyzing specific heat measured in magnetic field. The temperature dependence of specific heat in the vicinity of the successive transitions shows obvious distinction depending on the orientations of the applied magnetic field for both α-Tb_2S_3 and α-Dy_2S_3 that having orthorhombic crystal structures. When the magnetic field is increased, the specific heat is as follows: For α-Tb_2S_3 in $\boldsymbol{H}\|\boldsymbol{b}$, the peak around T_{N2} shifts to lower temperature but the other one peak around T_{N1} barely moves; In $\boldsymbol{H}\perp\boldsymbol{b}$, the peak around T_{N2} has no shift almost within 3 T but suddenly moves to lower temperature in 4 T and the other one peak around T_{N1} shifts to lower temperature in specific heat versus temperature. In the case of α-Dy_2S_3, the two peaks around T_{N2} and T_{N1} shift to lower temperatures in $\boldsymbol{H}\|\boldsymbol{b}$ but move to higher temperatures when the magnetic field is increased up to 5 T by $\boldsymbol{H}\perp\boldsymbol{b}$ in spite of antiferromagnetic transitions. Therefore, the maximum value and corresponding temperature of both isothermal magnetic entropy change (ΔS_m) and adiabatic temperature change (ΔT_{ad}) in the magnetic field $\boldsymbol{H}\perp\boldsymbol{b}$ are extremely different in low temperature range from that in the field of $\boldsymbol{H}\|\boldsymbol{b}$. The results propone that the MCE of α-Tb_2S_3 and α-Dy_2S_3 could be controlled at low temperature by the magnitude and orientation of magnetic field. It also indicates that the refrigerating capacity and thermal absorption capacity will be controlled by changing magnitude and orientation of magnetic field on the α-Tb_2S_3 and α-Dy_2S_3 single crystals.

1. Introduction

Since the magnetic refrigeration technology based on the magnetocaloric effects (MCE) have thrived in the last decade and many magnetic materials with the giant MCE have been investigated for better cooling efficiency and environmental friendliness. For example, $Gd_5(Ge_{1-x}Si_x)_4$ compounds with $0.3 \le x \le 0.5$ display giant MCE due to their first-order structural and magnetic phase transitions [1]. The $MnFeP_{0.45}As_{0.55}$ compound with Fe_2P-type structure also shows the giant MCE due to a first-order magnetic phase transition and the maximal magnetic entropy change is 14.5 J K^{-1} kg^{-1} and 18 J K^{-1} kg^{-1} for magnetic field change of 2 T and 5 T at 300 K [2]. The $LaFe_{13-x}Si_x$ compounds ($1.2 \le x \le 1.6$) undergo a first-order field induced itinerant-electron metamagnetic transition, so the compounds possess large MCE [3]. The RCo_2 (R = Er, Ho, Dy) alloys exhibit first-order magnetic transition and large MCE. The effects of element substitutions and pressure on RCo_2-based compounds for MCE are also reported [4]. The MCE of RAl_2 (R = Nd and Tm) single crystals with PM-FM transition are reported and the maximal magnetic entropy change in field change of 0–7 T is 35.9 and 8.9 J K^{-1} kg^{-1} at their Curie temperatures 6.0 and 76.5 K for $TmAl_2$ and $NdAl_2$, respectively [5].

Recently, the series compounds of α-R_2S_3 (R = rare earth elements) become attractive for their novel physical properties related to magnetic transitions [6–17]. The α-R_2S_3 (R = La-Dy, except Pm and Eu) have an orthorhombic crystal structure (space group *Pnma*), as shown in Fig. 1: there are two crystallographically inequivalent R sites labeled $R1$ and $R2$ in this structure; atoms on $R1$ with buckling in *ab* plane, where $R2$ atoms are connected to this plane [6,7,12,15]. Ebisu et al., discovered that α-R_2S_3 single crystal showed a novel antiferromagnetic transition at 10 K with anisotropic behavior in the temperature dependence of magnetic susceptibility [6]. Neutron Diffraction data [18] of α-Gd_2S_3 demonstrated that the magnetic unit cell was the same as the chemical unit cell. The heat capacity versus temperature of α-Gd_2S_3 single crystal shows a sharp anomaly at about 10 K, which also means magnetic moments of both Gd1 and Gd2 site order the same temperature [7]. The specific heat of α-Gd_2S_3 is high, so the α-Gd_2S_3 is likely to be used as regenerator material [16]. Then, the magnetic entropy change is also large and the α-Gd_2S_3 can be a candidate of refrigerant

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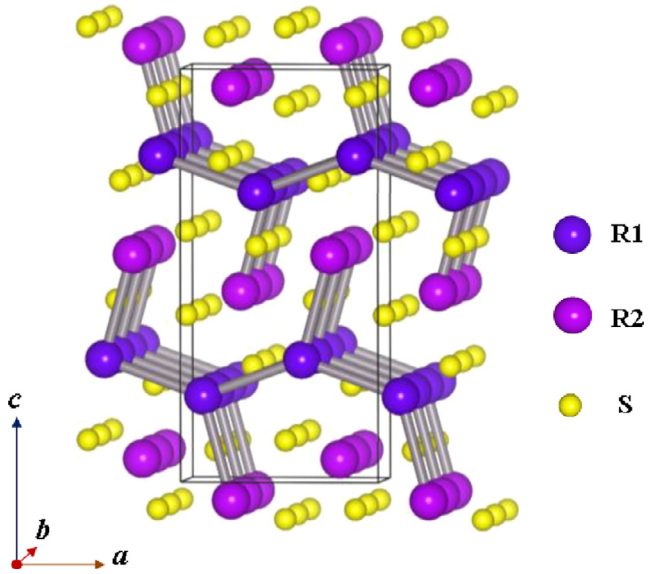

Fig. 1. The crystal structure of α-R_2S_3 compound: rare earth atoms are connected by banding and sulfurs atoms are free.

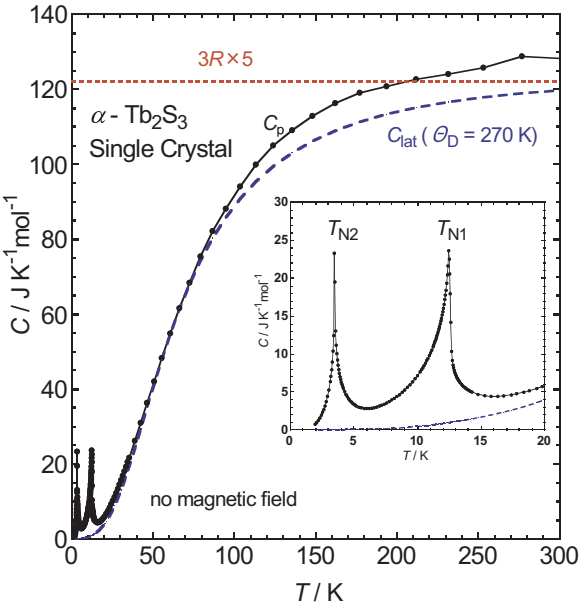

Fig. 2. Temperature dependence of the molar specific heat of α-Tb_2S_3.

materials. In contrast with α-Gd_2S_3, the α-Tb_2S_3 single crystal exhibits successive antiferromagnetic (AFM) transitions at T_{N1} = 12.5 K and T_{N2} = 3.5 K [14]. The two transitions occur in Tb1 and Tb2 sites, respectively [19]. For α-Dy_2S_3 single crystal, the successive AFM transitions occur at their Neèl temperatures 11.4 and 6.4 K and that the two peaks shifted to different directions depending on the applied magnetic field [14]. When the magnetic field (up to 2 T) was applied parallel with the *b*-axis those shifted toward lower temperature side, while those shifted to higher temperature side in the magnetic field perpendicular to the *b*-axis.

In the present study, we have investigated magnetic field effects on the specific heat of α-Tb_2S_3 and α-Dy_2S_3 single crystals in the vicinity of the successive magnetic transitions. Although the effect for α-Dy_2S_3 was reported previously [14], the range of applied magnetic field has been extended up to 5 T and the lowest temperature has been extended down to 0.4 K. The magnetocaloric effects (MCE) of α-Tb_2S_3 and α-Dy_2S_3 compounds were estimated from specific heat in magnetic field applied along the *b*-axis and perpendicular to the *b*-axis. The MCE, which expressed by magnetic entropy change and adiabatic temperature change, and the possibility of controlling the MCE in α-Tb_2S_3 and α-Dy_2S_3 single crystals in low temperature by the magnitude and orientation of magnetic field were discussed in this paper.

2. Experimental

Polycrystalline powder samples of α-Tb_2S_3 and α-Dy_2S_3 were synthesized by sulfurizing the powder materials of Tb_4O_7 and Dy_2O_3 (both 99.9%) on an alumina boat at a temperature in 1223–1273 K under the flow of the argon gas containing CS_2 [6]. The single crystals were grown from the powder sample by a chemical transport reaction method using iodine as a carrier [6]. The crystal structure and single crystal orientation were confirmed by X-ray diffraction measurements using Cu K_α-radiation. The specific heat was measured by using Physical Property Measurement System (PPMS, Quantum Design). The magnetic field in the specific heat measurements was applied to two directions of parallel and perpendicular to the *b*-axis ($\boldsymbol{H}\perp\boldsymbol{b}$ and $\boldsymbol{H}\|\boldsymbol{b}$). The specific heat of α-Tb_2S_3 was measured in the temperature range of 2.0–300 K in no magnetic field and in the temperature range of 2.0–20 K in the magnetic fields within 4 T. The specific heats of α-Dy_2S_3 were measured in the temperature range of 0.7–300 K in no magnetic field and in range of 0.4–20 K in the magnetic fields within 5 T. The isothermal magnetic entropy change and adiabatic temperature change were evaluated from the specific heat data in the magnetic field. Stick-shaped single crystals with hexangular cross sections were used for the specific heat measurements. The α-Tb_2S_3 sample had the mass of 2.2 mg and the length of 2.0 mm along the *b*-axis and the maximum length 0.8 mm in the cross section of the *ac*-plane. While the α-Dy_2S_3 sample had a weight of 2.5 mg, a 1.5 mm length along the *b*-axis and a 0.7 mm maximum-length in *ac*-plane.

3. Results and discussion

3.1. Confirmation of crystal structure and crystal plane

The X-ray diffraction patterns for powder samples of α-Tb_2S_3 and α-Dy_2S_3 were analyzed at the room temperature and the refinement showed that both of them were single phase having orthorhombic structure with the space group *Pnma*. The lattice parameters were a = 0.7303 nm, b = 0.3900 nm and c = 1.5202 nm for α-Tb_2S_3 and a = 0.7282 nm, b = 0.3878 nm and c = 1.5140 nm for α-Dy_2S_3. The crystal faces of six-side planes of the hexangular stick-shaped single crystals were determined by the X-ray diffraction method. Whenever these experiments are performed, one set of opposed planes is certainly (0 0 1) plane for both α-Tb_2S_3 and α-Dy_2S_3.

3.2. Specific heat

Fig. 2 shows temperature dependence of the molar specific heat for α-Tb_2S_3 under no magnetic field in the temperature range from 2 to 300 K. The solid curve represents the experimental specific heat C_p. It demonstrates two sharp peaks at the successive AFM transitions temperatures T_{N1} = 12.5 K and T_{N2} = 3.5 K [9] as clearly seen in the inset. The dashed straight line shows the Dulong-Petit law, thus it has a value of $C = 3R\times5 = 125\,\mathrm{J\,K^{-1}\,mol^{-1}}$, which R is the gas constant and five