Specific-heat study on successive magnetic transitions in α-Dy2S3 single crystals under magnetic fields

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Specific heat measurements in magnetic fields have been performed on α-Dy_2S_3 single crystal that shows successive magnetic transitions at T_{N_1} = 11.4 K and T_{N_2} = 6.4 K. The specific heat in no magnetic field exhibits sharp peaks at both temperatures of T_{N_1} and T_{N_2}. The change of magnetic entropy across each transition is estimated as Rln2/2 per mol-Dy, which suggests magnetic moments on only one Dy site between two crystallographically inequivalent Dy sites order at each transition temperature. When the magnetic field is applied along the *b*-axis of the orthorhombic system, two peaks of the specific heat shift toward lower temperatures. On the other hand, the magnetic field perpendicular to the *b*-axis shifts the peaks toward higher temperatures. The T_{N1} shifts to 9.6 K ($\boldsymbol{H} /\!/ \boldsymbol{b}$) and 12.5 K ($\boldsymbol{H} \perp \boldsymbol{b}$) under the magnetic field of 2 T. The peak of T_{N_2} broadens gradually with increasing magnetic field for each direction, and the peak is consequently obscure under the field of 2 T.

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I. INTRODUCTION

The isostructural compounds of α-R_2S_3 (R = Sm, Gd, Tb and Dy) are fascinating because of their novel physical properties related to magnetic transitions [1-10]. Their crystal structure with an orthorhombic symmetry that belongs to the space group *Pnma* [1, 11, 12] is shown for α-Dy_2S_3 in Fig. 1. There are two crystallographically inequivalent Dy sites labeled Dy1 and Dy2 in this structure. The Dy1 atoms form planes with buckling in the *ab*-plane. The Dy2 atoms are connected to these planes. The decorated planes are stacked along the *c*-axis. The α-Dy_2S_3 shows successive magnetic transitions at T_{N_1} = 11.5 K and T_{N_2} = 6.4 K [7]. The behavior of the magnetization in the vicinities of T_{N_1} and T_{N_2} is extremely anisotropic [7] and the electrical resistivity shows anomalous enlargement between T_{N_1} and T_{N_2} [8]. It has been considered that the antiferromagnetic (AFM) ordering of the magnetic moments on Dy1 site with collinearity along the *b*-axis occurs at T_{N_1}. On the other hand, non-collinear AFM ordering of the Dy2 site moments takes place at T_{N_2}. Moreover, it has been proposed that a weak ferromagnetic (WFM) ordering of the canted moments on Dy2 site occurs at T_{N_1}, because ferromagnetic-like properties are observed at the temperature range of $T_{N_2} < T < T_{N_1}$ [7]. The temperature dependence of the magnetization $M(T)$ under the magnetic field applied along the *c*-axis becomes steeper just below T_{N_1}, and the magnetization curve $M(H)$ is concave down below T_{N_1}. However, the magnitude of $M(H)$ is not so large as about 1 μ_B/(Dy atom) at the magnetic field of 0.2 T, and remanent magnetization is not observed in $M(H)$. In this paper, we present the results of the specific-heat measurements in magnetic fields (0, 1 and 2 T), and discuss the effects of the magnetic field on the successive magnetic transitions in α-Dy_2S_3.

II. EXPERIMENTAL

The single crystals of α-Dy_2S_3 were grown by a chemical transport reaction method from the powder sample prepared by sulfurizing method with iodine as a carrier [1]. Identification of the powder sample and determination of the crystal orientation were made by X-ray (Cu K_α-radiation)

diffraction measurements. The specific heat was measured by a relaxation method using PPMS (Quantum Design). The measurements were made at the temperature range of 2-300 K without magnetic field and 2-20 K under magnetic fields. The magnetic fields of 1 or 2 T were applied along to the *b*-axis and perpendicular to the *b*-axis. The magnetic field of the latter case was applied in the intermediate direction between the *a*- and the *c*-axis to ensure thermal contact between the sample and platform of sample holder.

III. RESULTS AND DISCUSSION

The temperature dependence of the molar specific heat; C, and the magnetic entropy change per mol-Dy; ΔS_m, in no magnetic field for α-Dy_2S_3 is shown in Fig. 2. The molar specific heat C shows two peaks at T_{N1} = 11.4 K and T_{N2} = 6.4 K which values are consistent with the results of the magnetic experiment [7] within a difference of 0.1 K. Lattice specific heat C_{lat} evaluated by using the Debye model is also shown as dashed curve in Fig. 2. The Debye temperature Θ_D was estimated as 370 K by fitting the data of higher temperatures than 150 K to the Debye's equation. This Θ_D is somewhat higher than the value of 317 K for non-magnetic α-La_2S_3 reported by Gschneidner, Jr. et al. [13]. We assume the specific heat C consists of the lattice contribution C_{lat} and the magnetic one C_m; $C = C_{lat} + C_m$, because the electrical properties are not metallic in lower temperature range [8]. The difference between the C_m and the experimental value of C is less than 0.9 % below T_{N1}. Even if we assume the value of Θ_D as 317 K [13], it is less than 1.6 %. The $\Delta S_m(T)$ means the magnetic entropy change from the lowest temperature of the measurement T_0 per mol-Dy, and it is estimated from the C_m using the equation

$$\Delta S_m(T) = \int_{T_0}^{T} \frac{C_m}{2T} dT . \qquad (1)$$

Here, the C_m is divided by 2 because α-Dy_2S_3 has two Dy-atoms in a molecule. As shown in Fig. 2, both values of the magnetic entropy change across the magnetic transitions are estimated as $R\ln 2/2$,

where R is the gas constant. This fact means that the magnetic moments on only one Dy site order at each transition temperature and the ground term of Dy^{3+} on each Dy site is doublet. It looks valid that one of Kramers doublet is ground term of Dy^{3+} in the present crystal structure having low symmetry because Dy^{3+} has 9, odd number, electrons in 4*f* orbital. It has been found out that the model of spontaneous WFM ordering of the Dy2 moments at T_{N_1} proposed previously [7] is incorrect. Only AFM ordering of the Dy1 moments occurs at T_{N_1}, and spontaneous magnetization due to the Dy2 moments does not exist below T_{N_1}. We consider the AFM ordering of the Dy1 moments eases the Dy2 moments to align along the magnetic field, and it is a reason of the ferromagnetic-like properties observed in magnetic measurements. The C at the lowest temperature 1.9 K has a finite value of about 2 J K^{-1} mol^{-1}. Although the origin of the remaining specific heat is unidentified at the present stage, a certain freedom might remain on Dy2 site.

Figure 3(a) shows the specific heat in the magnetic field applied along the *b*-axis. The magnetic field shifts both transition temperatures toward lower temperatures. The magnetic field of 1 T shifts T_{N_1} to 11.1 K from 11.4 K and T_{N_2} to 5.1 K from 6.4 K. Since the magnetic entropy changes across the transitions are almost the same between the field of 0 and 1 T as shown in Fig. 3(b), the same-type magnetic alignment is formed with decreasing temperature across the transitions in both cases. However, it seems that the transition of lower temperature occurs over a wide temperature range because of the broad peak of $C(T)$ around T_{N_2} and the linear increase of $\Delta S_m(T)$ in the field of 1 T. On the other hand, the peak of $C(T)$ at T_{N_1} keeps sharpness. Furthermore, the field of 2 T shifts T_{N_1} to 9.6 K with keeping the sharpness of the peak in $C(T)$. The $C(T)$ peak of lower temperature is obscure in the field of 2 T, although an abrupt increase exists at 5.4 K. At the present stage, it is unclear that this increase is owing to a magnetic transition or an experimental error.

The specific heat in the magnetic field perpendicular to the *b*-axis is shown in Fig. 4(a). The magnetic field shifts T_{N_1} to 11.8 K (1 T) or 12.4 K (2 T) from 11.4 K (no field) with keeping the sharpness of the peak in $C(T)$. Such effect, the shift of transition temperature toward higher temperatures by applying magnetic field, has not been observed in α-R_2S_3 (R = Sm, Gd and Tb). An

AFM transition temperature of α-Gd_2S_3 shifts lower temperatures [2], and two AFM transition temperatures of α-Tb_2S_3 also shift lower temperatures by applying magnetic field regardless of its orientation [14]. In the case for α-Sm_2S_3, two WFM transition temperatures do not affected so much by magnetic field regardless of its orientation [14]. Although the peaks around T_{N_2} are vague in the field of 1 and 2 T, they seem to be in higher temperature range above 6.4 K. The magnetic entropy change $\Delta S_m(T)$ for $\boldsymbol{H} \perp \boldsymbol{b}$ is shown in Fig. 4(b). The $\Delta S_m(T)$ for 1 T increases monotonically with increasing temperature around T_{N_1} = 6.4 K for 0 T (no field); however, it rises to almost the same value as the one for 0 T at T_{N_1}. Larger value of $\Delta S_m(T)$ at T_{N_2} = 12.4 K for 2 T might originate from excited states of Dy^{3+} on Dy2 site.

IV. CONCLUSION

We have measured specific heat of α-Dy_2S_3 that shows successive magnetic transitions. It has been found out by evaluating the magnetic entropy change across the transitions that the WFM ordering model of the Dy2 moments at T_{N_1} is incorrect. The WFM alignment of the Dy2 moments does not occur spontaneously but was made by applied magnetic field. The magnetic entropy changes across the transitions suggest the ground states of Dy^{3+} on both Dy sites are doublet. The measurements are performed also in magnetic fields to investigated magnetic field effect on the successive magnetic transitions. The higher transition temperature T_{N_1} shifts toward lower temperatures by applying the magnetic field along the *b*-axis, while it shifts toward higher temperatures by the field perpendicular to the *b*-axis, with keeping sharpness of the peak in $C(T)$. Therefore, the present compound has a magnetocaloric effect in only the case of the magnetic field perpendicular to the *b*-axis, although the value of the magnetic entropy change is not so large. The lower transition temperature T_{N_2} also shows the same tendency of the shift by magnetic field as T_{N_1}; however, the shape of peak in $C(T)$ is broaden and collapsed by the field of 1 T. Consequently, the peak is obscure in stronger field of 2 T. We conclude the ordered state of the Dy2 moments below

T_{N_2} is not stable, and it is easily influenced by magnetic field. The alignment of the Dy2 moments above T_{N_2} is also affected by magnetic field. We consider that the alignment of the Dy2 moments by magnetic field might assist the shift of T_{N_1} toward higher temperatures.

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Figure Captions.

Fig. 1. Crystal structure of α-Dy_2S_3, in which S atoms are omitted for clarity. The orthorhombic unit cell is shown by a box. Two crystallographically inequivalent Dy sites are shown as Dy1 (filled circles) and Dy2 (open circles). Thin lines are drawn between the neighbor atoms on the same *ac*-plane.

Fig. 2. The temperature dependence of the molar specific heat; C, and the magnetic entropy change per mol-Dy; ΔS_m, in no magnetic field for α-Dy_2S_3. The lattice specific heat C_{lat} is also shown as dashed curve. The $\Delta S_m(T)$ means entropy change between T and T_0, where T_0 is the lowest temperature of the measurement. The values of the magnetic entropy change across the transitions are also shown.

Fig. 3. (a) The temperature dependence of the molar specific heat C in the magnetic field along the *b*-axis. (b) The magnetic entropy change per mol-Dy in the magnetic field along the *b*-axis.

Fig. 4. (a) The temperature dependence of the molar specific heat C in the magnetic field perpendicular to the *b*-axis. (b) The magnetic entropy change per mol-Dy in the magnetic field perpendicular to the *b*-axis.

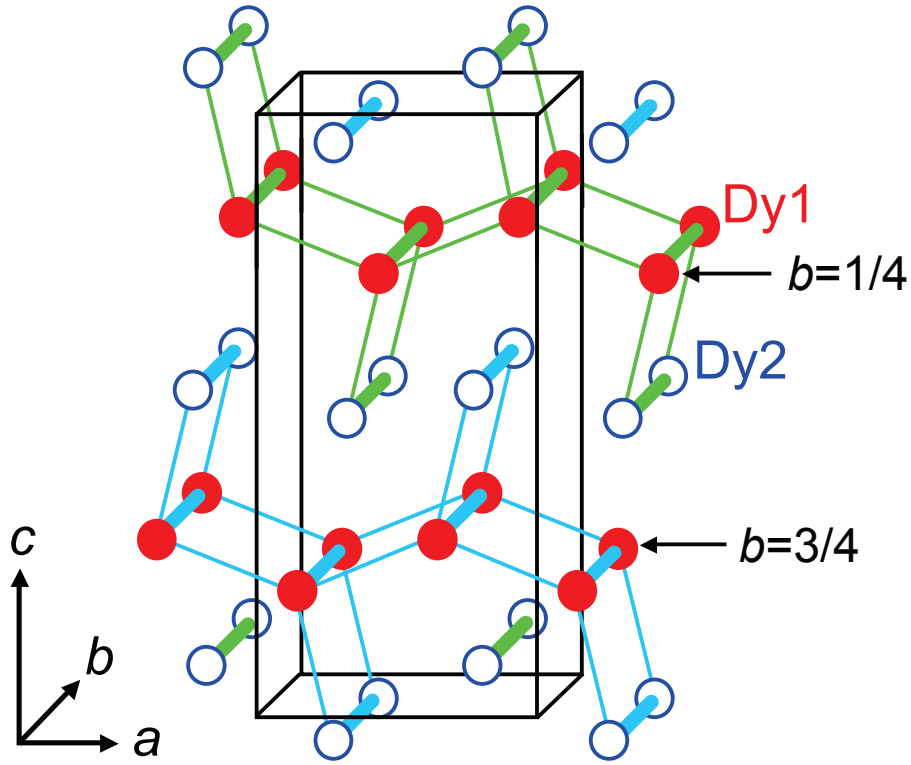

Fig. 1.

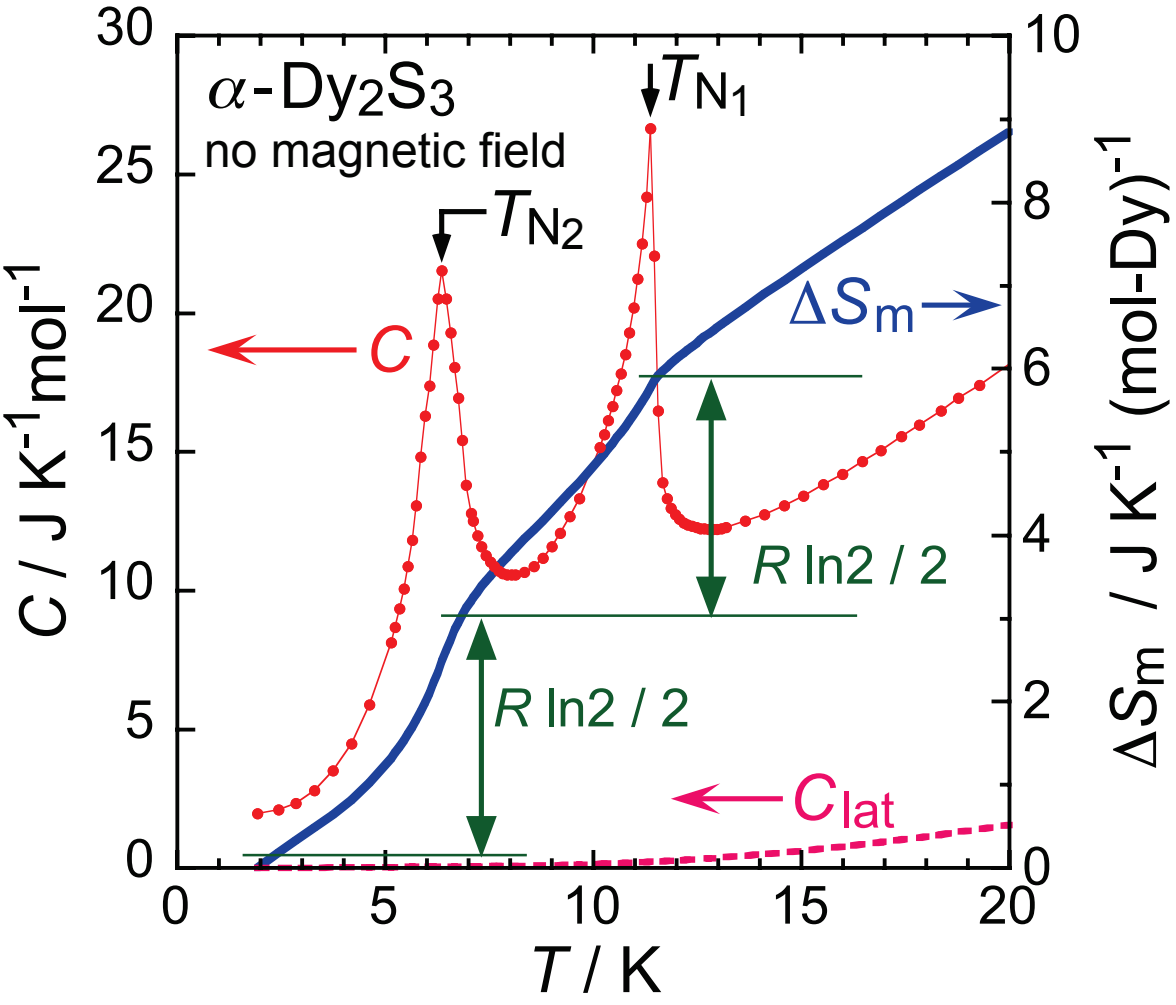
α-Dy2S3
no magnetic field
TN1
TN2
C
ΔSm
R ln2 / 2
R ln2 / 2
Clat
C / J K-1mol-1
ΔSm / J K-1 (mol-Dy)-1
T / K
0
5
10
15
20
25
30
0
2
4
6
8
10

Fig. 2.

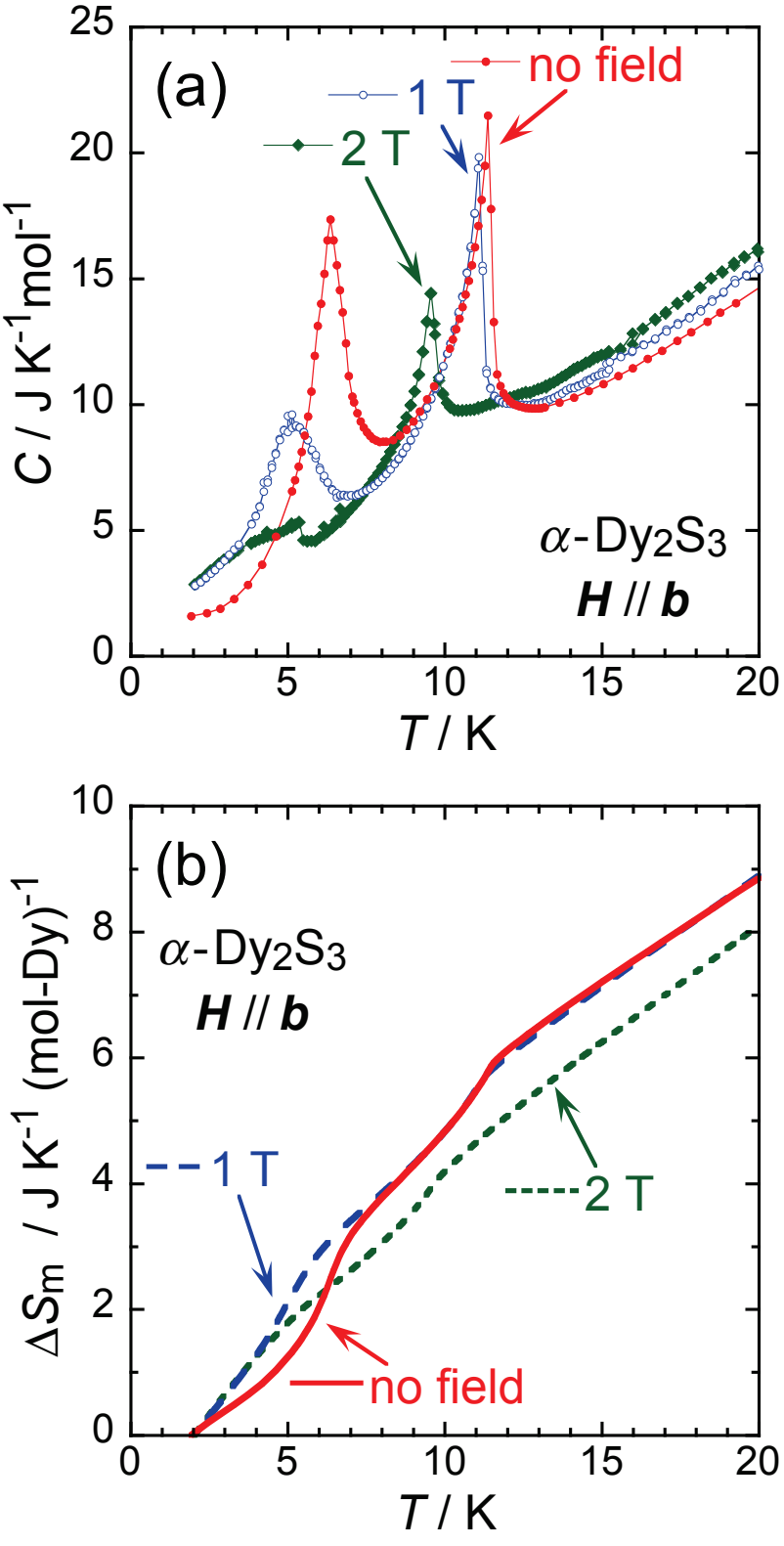
(a)
no field
1 T
2 T
α-Dy2S3
H // b
C / J K-1mol-1
T / K
(b)
α-Dy2S3
H // b
1 T
2 T
no field
ΔSm / J K-1 (mol-Dy)-1
T / K

Fig. 3.

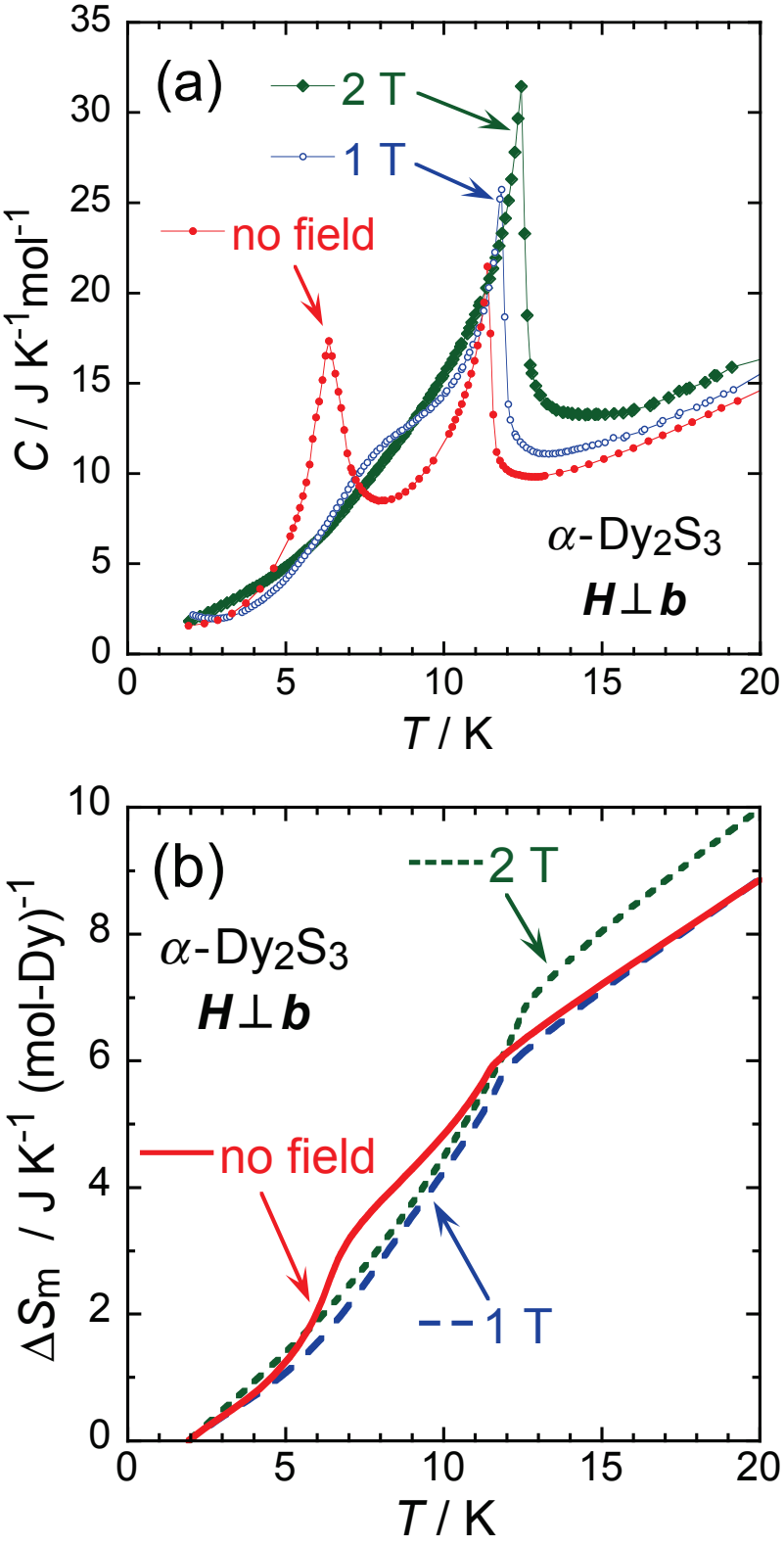
(a)
2 T
1 T
no field
α-Dy2S3
H⊥b
C / J K-1mol-1
T / K
(b)
2 T
α-Dy2S3
H⊥b
no field
1 T
ΔSm / J K-1 (mol-Dy)-1
T / K

Fig. 4.