Magnetism in $\alpha$-$R_2S_3$ ($R = $ Pr and Nd) single crystals

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Abstract. Magnetic susceptibility, $\chi$, and specific heat, $C$, of the isostructural rare-earth sesquisulfides $\alpha$-$R_2S_3$ ($R = $ Pr and Nd) have been investigated on single crystals. The $\chi(T)$ of $\alpha$-Nd$_2S_3$ shows a broad peak around 3.5 K when a magnetic field of 100 Oe is applied along the $b$-axis of the orthorhombic crystal structure. A Neel temperature $T_N$ above 2 K has been determined as 2.75 K by an inflection point in the $\chi(T)$ and a sharp peak in the $C(T)$. Furthermore, the $C(T)$ indicates another peak at around 0.65 K. The ground states of Nd$^{3+}$ on both the two Nd sites are concluded as Kramers doublets. The $\chi(T)$ of $\alpha$-Pr$_2S_3$ shows a broad peak around 3.8 K only in the case of $H//b$. The $\chi$ for $H//b$ is almost constant below 5 K, which suggests existence of Van Vleck paramagnetic contribution. An inflection point in the $\chi(T)$ ($H//b$) exists at $T_N = 2.95$ K which is consistent with the temperature of a sharp peak observed in the $C(T)$. A Schottky-type anomaly around 8 K in the $C(T)$ has also been found.

The ground states of Pr$^{3+}$ on two Pr sites are considered as a pseudo-doublet and a singlet.

1. Introduction

Rare-earth sesquisulfides $\alpha$-$R_2S_3$ ($R = $ Pr and Nd) possess an orthorhombic crystal structure having the $Pnma$ symmetry [1, 2]. The crystal structure is shown in figure 1, where S atoms are omitted for clarity. There are two crystallographically inequivalent $R$ sites labeled R1 and R2 in this structure. We have reported fascinating physical properties in the isostructural compounds of $\alpha$-$R_2S_3$ ($R = $ Sm, Gd, Tb and Dy) related to their magnetic transitions [2-13]. The $\alpha$-Gd$_2S_3$ shows an antiferromagnetic transition at $T_N = 9.9$ K with large anisotropy [2-5]. The compounds of $\alpha$-Tb$_2S_3$ and $\alpha$-Dy$_2S_3$ demonstrate successive antiferromagnetic transitions at $T_{N1} = 12.5$ and 11.4 K, $T_{N2} = 3.5$ and 6.4 K, respectively [6, 8]. A neutron scattering measurement for $\alpha$-Tb$_2S_3$ has clarified the Tb1 site moments order at $T_{N1}$ and Tb2 moments do at $T_{N2}$ [7]. In the case of $\alpha$-Sm$_2S_3$, weak ferromagnetic transition occurs at around 4.5 K [11]. Recent our study on the specific heat of $\alpha$-Sm$_2S_3$ has clarified that successive weak ferromagnetic transitions occur at $T_{C1} = 3.8$ K and $T_{C2} = 1.9$ K, which will be reported elsewhere. Anomalies in the temperature dependence of the electrical resistivity $\rho(T)$ for $\alpha$-$R_2S_3$ ($R = $ Sm, Gd, Tb and Dy) have also been found at the temperatures near magnetic transition temperatures [2, 6, 9, 11], especially the extremely large changes of the resistivity in narrow temperature ranges for $\alpha$-Dy$_2S_3$ and $\alpha$-Sm$_2S_3$ are noticeable. These features appear as sharp peaks in the $\rho(T)$ [9, 11]. Furthermore, extremely broad hysteresis in magnetization process of $\alpha$-Dy$_2S_3$ after cooling in magnetic field of 18 T has also been reported [12].
On the other hand, detail of the low temperature physics in $\alpha$-R$_2$S$_3$ ($R = \text{Pr}$ and Nd) has not been reported. We have successfully grown single crystals of these compounds. In this paper, we present the experimental results for magnetic susceptibility and specific heat in $\alpha$-Pr$_2$S$_3$ and $\alpha$-Nd$_2$S$_3$, and discuss the ground states of the $R^{3+}$ ions on the two $R$ sites in each compound.

### 2. Experimental

The single crystals of $\alpha$-Pr$_2$S$_3$ and $\alpha$-Nd$_2$S$_3$ were grown by using a chemical transport reaction method with iodine for carrier gas [2]. Identification of the powder sample and determination of the crystal orientation were performed by using X-ray (Cu $K_{\alpha}$ radiation) diffraction measurements. The magnetization measurements were made in the temperature range of 1.8-300 K using an rf-SQUID magnetometer with Magnetic Property Measurement System (MPMS, Quantum Design). The specific heat was measured at the temperatures of 0.4-300 K without applying magnetic field by using a relaxation method with Physical Property Measurement System (PPMS, Quantum Design).

### 3. Results and discussion

#### 3.1. Magnetic susceptibility

The temperature dependence of molar magnetic susceptibility $\chi$, magnetization $M$ divided by a constant magnetic field $H$, of $\alpha$-Nd$_2$S$_3$ is shown in figure 2. Magnetic field of 100 Oe was applied along the three crystal axes of orthorhombic system after cooling the sample to 1.8 K. The inset is an enlargement of the temperature region below 20 K. The $\chi(T)$ shows a broad peak around 3.5 K for $H//b$, while it increases monotonically with decreasing temperature for $H//b$. An inflection point is clearly observed at 2.7 K below the peak temperature in $\chi(T)$ for $H//b$. The $\chi$ values at temperatures higher than 100 K are well fitted to the Curie-Weiss law,

$$ \chi = C \left( \frac{1}{T-\theta} \right), $$

where $C$ is the molar Curie constant and $\theta$ is the Weiss constant. The fitting in the case of $H//b$ gives...
C = 3.69 emu K mol⁻¹ and θ = −19.9 K. The effective magnetic moment \( \mu_{\text{eff}} \) is estimated as 3.84 \( \mu_B \) per one Nd atom. This value is almost the same in the case of \( \mathbf{H} \perp \mathbf{b} \) and close to the theoretical value of 3.62 \( \mu_B \) for free Nd³⁺. The \( \chi'(T) \) curves for \( \mathbf{H} \perp \mathbf{b} \) below 10 K are convex, which is consistent that Nd³⁺ ion has electronic configuration of \( 4f^3 \). The Kramers double degeneracy in the system having odd number electrons cannot be lifted by crystalline electric field (CEF).

The magnetic susceptibility of \( \alpha\text{-Pr}_2\text{S}_3 \) is plotted as a function of temperature in figure 3. The \( \chi'(T) \) indicates a broad peak around 3.5 K with an inflection point at 2.7 K in the case of \( \mathbf{H} \parallel \mathbf{b} \). On the other hand, the increase of the \( \chi \) for \( \mathbf{H} \perp \mathbf{b} \) becomes dull at temperatures below 20 K. It is marked under \( \mathbf{H} \parallel \mathbf{c} \), namely the susceptibility is almost constant below 5 K. This feature suggests existence of Van Vleck paramagnetic contribution. The Curie-Weiss fitting of the \( \chi \) data at higher temperatures than 100 K gives the \( \mu_{\text{eff}} \) of 3.03 \( \mu_B \) per one Pr atom. This value is somewhat smaller than the value of 3.58 \( \mu_B \) calculated for free Pr³⁺. Furthermore, the linearity of the \( \chi^{-1} \) to \( T \) at the fitting range is not so good. These facts also support the existence of Van Vleck paramagnetic contribution.

### 3.2. Specific heat

Figure 4 shows the specific heat \( C \) of \( \alpha\text{-Nd}_2\text{S}_3 \) for mole of formula-unit as a function of temperature. Although the data at higher temperatures are somewhat scattered, the \( C \) approaches the value of \( 3R \times 5 = 125 \) J K⁻¹ mol⁻¹ asymptotically with increasing temperature. Here, \( R \) is gas constant and 5 means the number of atoms in formula-unit of \( \alpha\text{-Nd}_2\text{S}_3 \). The lattice contribution \( C_{\text{lat}} \) evaluated by using the Debye model is shown as dashed curve in figure 4. The Debye temperature \( \Theta_D \) was estimated as 387 K by fitting the data at temperatures higher than 150 K to the Debye equation,

\[
C_{\text{lat}} = 9N_A \frac{k_B}{\Theta_D^2} \int_0^{\Theta_D/\Theta_B} \frac{z^4 e^z}{(e^z - 1)^2} dz
\]

where \( r \) is the number of atoms per formula-unit, which is 5 for \( \text{Nd}_2\text{S}_3 \), \( N_A \) is the Avogadro constant, and \( k_B \) is the Boltzmann’s constant. The \( \Theta_D \) of 387 K is close to the value of 370 K estimated for \( \alpha\text{-Dy}_2\text{S}_3 \) [13]. The magnetic specific heat \( C_m \) derived by subtracting \( C_{\text{lat}} \) from \( C \) is plotted in figure 5. The \( C_m \) demonstrates a sharp peak at 2.75 K, which is consistent to the temperature of the inflection point in the \( \chi(T) \) for \( \mathbf{H} \parallel \mathbf{b} \). Therefore we conclude antiferromagnetic ordering of Nd³⁺ moments occurs.

![Figure 4. Temperature dependence of the molar specific heat of \( \alpha\text{-Nd}_2\text{S}_3 \).](image)

![Figure 5. The magnetic specific heat and the magnetic entropy change of \( \alpha\text{-Nd}_2\text{S}_3 \).](image)
at the Neel temperature $T_N$ of 2.75 K. Another peak with roundness is also observed at around 0.65 K. Magnetic entropy change $\Delta S_m$ per mol-Nd from the lowest temperature in the present measurement is also shown as a solid curve in figure 5. It is evaluated using the equation,

$$\Delta S_m = \int_{T_0}^{T} \frac{C_m}{2T} dT,$$

where $T_0$ is the lowest temperature of about 0.4 K, and $N$ is number of Nd atoms in the formula-unit of Nd$_2$S$_3$. The magnitude of the magnetic entropy change across the transition at $T_N = 2.75$ K is about $(\ln 2)/2$ as shown in figure 5. This fact means that only the magnetic moments on one Nd site order at $T_N$ and the ground state of Nd$^{3+}$ on this site is (Kramers) doublet. It seems that extrapolation of the $\Delta S_m$ curve to 0 K gives the entropy change with the magnitude of $(\ln 2)/2$ across another transition at around 0.65 K. It is speculated the magnetic moments on another Nd site having ground state of Kramers doublet order at around 0.65 K.

The $C_m$ per mol-(formula unit) and the $\Delta S_m$ per mol-Pr for $\alpha$-Pr$_2$S$_3$ are shown as a function of temperature in figure 6. Here the lattice contribution $C_{lat}$ calculated by the Debye model with $\Theta_D = 440$ K is also shown as a dashed curve. The value of $\Theta_D$ is rather larger than the value for $\alpha$-Nd$_2$S$_3$, which shows difficulty of estimation of the lattice contribution by the present method. However, the lattice contribution is smaller than the magnetic one sufficiently near the magnetic transition temperature. The $C_m$ exhibits a sharp peak at 2.95 K. Since this temperature agrees with the temperature of the inflection point in $\chi(T)$ for $H//b$, it is inferred that antiferromagnetic ordering of Pr$^{3+}$ takes place at $T_N = 2.95$ K. At temperature below $T_N$, the $C_m$ starts rising again at about 1 K with decreasing temperature. It suggests some degrees of freedom remains in this system in the temperature region below 1 K. The magnitude of the magnetic entropy change across the transition at $T_N = 2.95$ K is about $(\ln 2)/4$. If complete magnetic ordering occurs on one Pr site of which ground state is doublet, the expected entropy change is $(\ln 2)/2$. It is speculated that the ordering of Pr$^{3+}$ moments on one site is not perfect but leaves some degrees of freedom. The upturn of $C_m$ below $T_N$ mentioned above supports this speculation. At higher temperature than $T_N$ a hump is observed around 8 K, which is considered to be the Schottky anomaly. The Schottky specific heat $C_S$ for mol-(magnetic atom) under taking account of only two lowest levels is expressed as

$$C_S = R \left( \frac{\Delta}{T} \right)^2 \frac{g_0}{g_1} \left[ 1 + \left( \frac{g_0}{g_1} \right) \exp \left( \frac{\Delta}{T} \right) \right]^2,$$

where $\Delta$ is energy separation measured in K between the lowest and the first excited state, and the degeneracy for each state is denoted as $g_0$ and $g_1$. Two convenient equations about $T_{max}$ and $C_{S, max}$ representing the values of $T$ and $C_S$ at the maximum point of the hump in $C_S(T)$ deduced from equation (4) are as follows:

$$\frac{g_0}{g_1} \exp \left( \frac{\Delta}{T_{max}} \right) = \left( \frac{\Delta}{T_{max}} \right)^2 + 2 \left( \frac{\Delta}{T_{max}} \right) - 2,$$

$$C_{S, max} = \frac{R}{4} \left[ \left( \frac{\Delta}{T_{max}} \right)^2 - 4 \right].$$

It is natural to consider the ground state of Pr$^{3+}$ on one Pr site is singlet and the ground state on the other is pseudo-multiplet, because both the magnetic ordering and the behavior of the Van Vleck paramagnetism are observed in the $\chi(T)$. If we assume one hump exists around $T_{max} = 8$ K with $C_{S, max} = 5$ J K$^{-1}$ mol$^{-1}$, the values of $\Delta = 20.2$ K and $g_0/g_1 = 0.68 \sim 2/3$ are deduced from equations (6) and (5). The calculated $C_S$ using these values ($g_0 = 2, g_1 = 3$) is drawn as the solid curve labeled by $C_S(a)$ with the $C_m$. Subsequently, we assume the lowest two states on the other site are the ground singlet and the first excited doublet separated by $\Delta = 71.6$ K. This contribution is shown as the curve labeled $C_S(b)$ in figure 7. The total of the Schottky contribution, namely $C_S(a) + C_S(b)$, is also drawn. This curve
reproduces the $C_m$ up to about 20 K. Large residual part of the $C_m$ above 20 K might be caused by the higher states. The analysis mentioned above is too rough to give precise energy level scheme; e.g. the $\Delta$ of 71.6 K might be too large. However, we consider the qualitative explanation of the ground states of Pr$^{3+}$ on each Pr site is valid.

4. Summary
The antiferromagnetic ordering of Nd$^{3+}$ moments on one Nd site at $T_N = 2.75$ K was confirmed in $\alpha$-Nd$_2$S$_3$. It was inferred the Nd$^{3+}$ moments on the other Nd site order near 3.5 K. The degeneracies of the ground states of Nd$^{3+}$ on both Nd sites were considered to be Kramers doublets. As for $\alpha$-Pr$_2$S$_3$, it was concluded the magnetic moments of Pr$^{3+}$ having pseudo-doublet ground state on one Pr site order at $T_N = 2.95$ K, however, the ordering at $T_N$ is not complete but leaves a certain degree of freedom. An indication of freezing of this degree of freedom below 1 K was observed as an upturn in the $C(T)$. It was considered the Pr$^{3+}$ on the other site has singlet ground state. Hence almost constant $\chi(T)$ at lower temperatures is due to the Van Vleck paramagnetism. The large $C_m(T)$ above $T_N$ was analyzed by superposition of two Schottky-type contributions of Pr$^{3+}$ on both Pr sites.

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References
[1] Picon M, Domange L, Flahaut J, Guittard M and Patrie M 1960 Bull. Soc. Chim. France 2 221-8.
[2] Ebisu S, Iijima Y, Iwasa T and Nagata S 2004 J. Phys. Chem. Solids 65 1113-20
[3] Kikkawa A, Katsumata K, Ebisu S and Nagata S 2004 J. Phys. Soc. Jpn. 73 2955-8
[4] Matsuda M, Kikkawa A, Katsumata K, Ebisu S and Nagata S 2005 J. Phys. Soc. Jpn. 74 1412-5
[5] Katsumata K, Kikkawa A, Tanaka Y, Shimomura S, Ebisu S and Nagata S 2005 J. Phys. Soc. Jpn. 74 1598-601
[6] Ebisu S, Gorai M, Maekawa K and Nagata S 2006 AIP Conf. Proc. 850 1237-8
[7] Matsuda M, Kakurai K, Ebisu S and Nagata S 2006 J. Phys. Soc. Jpn. 75 074710
[8] Ebisu S, Narumi M, Gorai M and Nagata S 2007 J. Magn. Magn. Mater. 310 1741-3
[9] Ebisu S, Narumi M and Nagata S 2006 J. Phys. Soc. Jpn. 75 085002
[10] Ebisu S, Koyama K, Omote H and Nagata S 2009 J. Phys.: Conf. Ser. 150 042027
[11] Ebisu S, Omote H and Nagata S 2010 J. Phys.: Conf. Ser. 200 092005
[12] Ebisu S, Koyama K, Horikoshi T, Kokita M and Nagata S 2012 J. Phys.: Conf. Ser. 400 032010
[13] Ebisu S, Ushiki Y and Takahashi S 2013 J. Kor. Phys. Soc. 63 571-574