Magnetic Properties of Orthorhombic Fluorite-related Oxides

$Ln_3SbO_7$ ($Ln =$ Rare Earths)

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Abstract

Ternary rare earth antimonates $Ln_3SbO_7$ ($Ln =$ rare earths) were prepared and their structures were determined by x-ray diffraction measurements. They crystallize in an orthorhombic superstructure of cubic fluorite (space group $Cmcm$ for $Ln =$ La, Pr, Nd; $C222_1$ for $Ln =$ Nd - Lu), in which $Ln^{3+}$ ions occupy two different crystallographic sites (the 8-coordinated and 7-coordinated sites). Their magnetic properties were characterized by magnetic susceptibility and specific heat measurements from 1.8 to 400 K. The $Ln_3SbO_7$ ($Ln =$ Nd, Gd - Ho) compounds show an antiferromagnetic transition at 2.2 ~ 3.2 K. Sm$_3$SbO$_7$ and Eu$_3$SbO$_7$ show van Vleck paramagnetism. Measurements of the specific heat down to 0.4 K for Gd$_3$SbO$_7$ and the analysis of the magnetic specific heat indicate that the antiferromagnetic ordering of the 8-coordinated Gd ions occur at 2.6 K, and the 7-coordinated Gd ions order at a furthermore low temperature.
1. Introduction

Compounds of the general composition $Ln_3MO_7$ ($Ln$ = rare earths, $M$ = Nb, Ru, Ta, Re, etc.) have been attracting interest. They have an ordered, defect-fluorite superstructure. The relationship to the fluorite structure is as follows. The fluorite unit cell for oxides has the composition $M^{4+}_4O_8$. If the four tetravalent metal ions are replaced by three trivalent ions ($Ln$) and one pentavalent ion ($M$), one oxide vacancy is formed per fluorite cell. Due to the significant differences in radii between the $Ln^{3+}$ and $M^{5+}$ ions, cation ordering occurs on the metal sites and the oxide-vacancy orders on the anion sites. Rossell first determined the crystal structure of La$_3$NbO$_7$ [1]. It was well described in the orthorhombic space group $Cmcm$: The $M^{5+}$ ion is coordinated with six oxygen ions, forming a $MO_6$ octahedron. These octahedra share corners forming one-dimensional chains which are oriented along the c-axis. Although the space group for the La$_3$NbO$_7$ now turned out to be $Pnma$ [2], the space group $Cmcm$ has been applied for many Ln$_3$MO$_7$ compounds [3-26]. For some compounds such as Ln$_3$TaO$_7$ ($Ln$ = Y, Sm - Ho) [20-22, 24] and Ln$_3$MoO$_7$ ($Ln$ = La - Nd, Sm, Eu) [27-30], the space groups $C222_1$ and $P2_12_12_1$ have been applied, respectively.

Due to this unique crystal structures and possible related magnetic properties, many studies have been performed, especially for the magnetic properties of compounds containing Ru$^{5+}$ ion at the M-site because of its largest possible spin ($S = 3/2$) [3-13].

Another topic for Ln$_3$MO$_7$ is that detailed magnetic and thermal investigations on the ruthenium-, iridium- and osmium-containing members of the Ln$_3$MO$_7$ family show low-temperature structural phase transitions [9-11, 13, 14, 19, 26, 29, 31].

As for $M$ = Sb compounds, a series of Ln$_3$SbO$_7$ with Ln = Nd, Sm – Yb, and Y was reported to
have the pyrochlore structure [32]. However, Faurie et al. pointed out that the random distribution of 
Y$^{3+}$ and Sb$^{5+}$ required for the pyrochlore structure was unlikely on grounds of the different size and 
charge of the ions [33]. Rossell determined the crystal structure of Y$_2$GdSbO$_7$ with the space group 
C222$_1$ [1]. Later, IJdo et al. determined the structure for Pr$_3$SbO$_7$ with the space group Cmcm [23]. 
Fennell et al. investigated the structure and magnetic properties of Ho$_3$SbO$_7$ and Dy$_3$SbO$_7$ [34]. They 
adopted the space group C222$_1$ for the two compounds. However, no atomic coordinates were presented 
for any of the compounds. A possibility of magnetically frustrated system was noted for Ho$_3$SbO$_7$ and 
Dy$_3$SbO$_7$ through magnetic susceptibility measurements. However, no systematic study on the crystal 
structure and magnetic properties of Ln$_3$SbO$_7$ has been carried out.

In this study, we successfully prepared a series of Ln$_3$SbO$_7$ from Ln = La to Lu. Through X-ray 
diffraction measurements, their crystal structures were determined. In order to elucidate magnetic 
properties and to check the existence of the phase transition in the Ln$_3$SbO$_7$ series, their magnetic 
susceptibility measurements from 1.8 to 400 K and the specific heat measurements from 0.4 to 400 K 
were performed.

2. Experimental

2.1. Sample preparation

As starting materials, rare earth oxides Ln$_2$O$_3$ (Ln = La, Nd, Sm-Gd, Dy-Lu), Pr$_6$O$_{11}$, Tb$_4$O$_{17}$, and 
Sb$_2$O$_3$ were used. For La$_2$O$_3$ and Nd$_2$O$_3$, they absorb moisture in air and easily form rare earth 
hydroxides Ln(OH)$_3$. Therefore, they were dried at 1173 K for 24 h before use. For better reactivity, 
mixtures of the rare earth oxides and Sb$_2$O$_3$ were dissolved in the conc. nitric acid, and were heated first
at 150 °C for one night and then at 600 °C for 6 h. These mixtures were pressed into pellets and heated at 1200 °C for 12 h. In the first stage of sample preparations, very small amounts of impurities remained in the desired compounds; they were unreacted starting materials $Ln_2O_3$. In order to remove these impurities, the samples were washed with diluted hydrochloric acid. After this treatment, single-phase $Ln_3SbO_7$ compounds could be obtained.

2.2. X-ray diffraction analysis

Powder X-ray diffraction profiles were measured using a Rigaku Multi-Flex diffractometer with Cu-Kα radiation equipped with a curved graphite monochromator. The data were collected by step-scanning in the angle range of $10° \leq 2\theta \leq 120°$ at a $2\theta$ step-size of 0.02°. The X-ray diffraction data were analyzed by the Rietveld technique, using the programs RIETAN2000 [35].

2.3. Magnetic susceptibility measurements

The temperature-dependence of the magnetic susceptibility was measured in an applied field of 0.1 T over the temperature range of $1.8 \, K \leq T \leq 400 \, K$, using a SQUID magnetometer (Quantum Design, MPMS5S). The susceptibility measurements were performed under both zero-field-cooled (ZFC) and field-cooled (FC) conditions. The former was measured upon heating the sample to 400 K under the applied magnetic field of 0.1 T after zero-field cooling to 1.8 K. The latter was measured upon cooling the sample from 400 to 1.8 K at 0.1 T.

2.4. Specific heat measurements

Specific heat measurements were performed using a relaxation technique by a commercial heat capacity measuring system (Quantum Design, PPMS) in the temperature range of 0.4-400 K. The
sintered sample in the form of a pellet was mounted on a thin alumina plate with Apiezon for better thermal contact.

3. Results and discussion

3.1. Preparation and crystal structure

Except for Ln = Nd, all the Ln₃SbO₇ compounds (Ln = La, Pr, Sm-Lu) were obtained as a single phase. Figure 1 shows the powder X-ray diffraction profiles for La₃SbO₇ and Sm₃SbO₇. Any of these diffraction patterns are similar to that for the fluorite structure and all reflections appeared to be consistent with the C-centered condition, h + k = 2n.

As described in the Introduction section, many space groups have been applied for the structure of Ln₃MO₇ compounds. Following earlier work on Pr₃SbO₇ and Y₂GdSbO₇ [1, 23], we tried to analyze the crystal structures of Ln₃SbO₇ prepared in this study. The structure for La₃SbO₇ was well refined with the space group $Cmcm$. Table 1 lists the lattice parameters and atomic coordinates for La₃SbO₇. The structure of La₃NbO₇ is reported to be better described with the space group Pnma than with Cmcm [2]. However, some extra reflection peaks which should be observed with the Pnma were not observed in the X-ray diffraction profile of La₃SbO₇. For the X-ray diffraction profiles of Ln₃SbO₇ (Ln = Sm ~ Lu), there exist many very weak $h0l$ reflections with odd $l$ (see Fig. 1 (b)), which could not be indexed based on the $Cmcm$. In addition to this, the C-centering extinction condition ruled out other space groups such as $Pnma$ (for La₃NbO₇) [2] and $P2_12_12_1$ (for Ln₃MoO₇) [27-30]. This fact indicates that they have a different symmetry. We analyzed the X-ray diffraction profiles for Ln₃SbO₇ (Ln = Sm ~ Lu) with the space group $C22_1$. All the reflections observed could be successfully indexed. The refinement by using
the structural model with the space group $C22_1$ converged rapidly, and yielded low residual factors and acceptably low values for the calculated standard deviations of refined parameters. Table 2 lists the lattice parameters and atomic coordinates for Sm$_3$SbO$_7$.

The X-ray diffraction profile for Nd$_3$SbO$_7$ indicated that the phase with the space group $Cmcm$ and that with $C22_1$ coexist in this compound at room temperature. We determined the ratio of the $Cmcm$ phase and the $C22_1$ phase to be 44% : 56% by the Rietveld analysis.

Figures 2 (a) and (b) illustrate the crystal structures determined for La$_3$SbO$_7$ and Sm$_3$SbO$_7$, respectively. The orthorhombic structures have features in common for both the compounds. The SbO$_6$ octahedra share the O(3) for La$_3$SbO$_7$ and O(5) for Sm$_3$SbO$_7$ ions, forming an infinite one-dimensional zig-zag chain parallel to the [001] direction. The Ln(1) ions are coordinated by eight oxygen ions and the distorted Ln(1)O$_8$ cubes also form a one-dimensional chain through edge-sharing. The SbO$_6$ and Ln(1)O$_8$ chains lie alternately parallel to the (100) plane, and the Ln(2) ions are seven-coordinated by oxygen ions between slabs consisting of these chains. The SbO$_6$ octahedron and Ln(1)O$_8$ cube in the La$_3$SbO$_7$ structure are more regular than those in the Sm$_3$SbO$_7$ structure. The SbO$_6$ octahedra in the La$_3$SbO$_7$ and Sm$_3$SbO$_7$ structures are tilted along the [100] and [010] directions, respectively.

Figure 3 shows the variation of lattice parameters for Ln$_3$SbO$_7$ (Ln = La ~ Lu) against the ionic radius of the eight-coordinated Ln$^{3+}$ ion. The lattice parameters increase with the ionic radius of Ln$^{3+}$ and the differences among the $a/\sqrt{2}$, $b$, and $c$ values become wide. For the $C22_1$ phase, the $b$ values are almost equal to the $c$ values between Ln = Gd and Lu, and the $b$ values become smaller than the $c$ values from Ln = Eu to Nd. The differences among $a/\sqrt{2}$, $b$, and $c$ for the $Cmcm$ phase are larger than those for the $C22_1$ phase.
Figure 4 shows the variation of the average Ln-O and Sb-O bond lengths with the ionic radius of eight-coordinated Ln$^{3+}$ ion. The average bond lengths Ln(1)-O and Ln(2)-O both increase with the ionic radius of Ln$^{3+}$. On the other hand, the average Sb-O bond lengths are nearly constant (~2.00 Å). This value is equal to the bond length calculated from the Shannon’s ionic radii [36].

3.2. Paramagnetic behavior

Figure 5 shows the temperature dependence of magnetic susceptibility of Pr$_3$SbO$_7$. Paramagnetic behavior was observed down to 1.8 K, i.e., no magnetic interaction was found in the experimental temperature range. In the inset, the reciprocal magnetic susceptibility was plotted against temperature. The susceptibility follows the Curie-Weiss law in the temperature range between 200 and 400 K. Magnetic susceptibility measurements for other Ln$_3$SbO$_7$ compounds also show that Ln = Sm, Eu, Er, Tm, and Yb compounds exhibit paramagnetic behavior down to 1.8 K. The effective magnetic moments ($\mu_{\text{eff}}$) and Weiss constants ($\Theta$) are determined in the temperature range between 200 and 400 K, and they are listed in Table 3. The effective magnetic moments are very close to the moments calculated for free Ln$^{3+}$ ions. The negative Weiss constants indicate that the predominant magnetic interaction between Ln$^{3+}$ ions is antiferromagnetic. If the magnetic susceptibility measurements were carried out furthermore below 1.8 K, these compounds should show an antiferromagnetic transition.

Figure 6 depicts the temperature dependence of the magnetic susceptibility for Sm$_3$SbO$_7$ and Eu$_3$SbO$_7$. These compounds show the well-known van Vleck paramagnetism caused by the behavior of isolated Sm$^{3+}$ and Eu$^{3+}$ ions, respectively [37].

3.3. Magnetic ordering

Magnetic transitions have been observed for Ln = Nd, Gd-Ho compounds. Their transition
temperatures are also listed in Table 3.

3.3.1. Gd$_3$SbO$_7$

Figure 7 shows the temperature dependence of the magnetic susceptibility of Gd$_3$SbO$_7$. An antiferromagnetic transition has been observed at 2.6 K, and there is no divergence between the ZFC and FC susceptibilities below this temperature.

In order to obtain the information about the low-temperature magnetic behavior, specific heat measurements were performed down to 0.4 K. Figure 8 shows the temperature dependence of the specific heat ($C_p$) divided by temperature ($C_p/T$) for Gd$_3$SbO$_7$. A specific heat anomaly has been observed at 2.6 K, which corresponds to the results by magnetic susceptibility measurements. Below this temperature, the specific heat increases with decreasing temperature, indicating the existence of another magnetic anomaly below 0.4 K. To evaluate the magnetic contribution to the specific heat ($C_{\text{mag}}$), we have to subtract the contribution of lattice specific heat ($C_{\text{lat}}$) from the total specific heat ($C_{\text{mag}} = C_p - C_{\text{lat}}$). The lattice specific heat was estimated by using the data for a diamagnetic compound La$_3$NbO$_7$ (the solid line of Fig. 8). The magnetic specific heat below 0.4 K was extrapolated by the relation $C_{\text{mag}} \propto T^3$ from the spin-wave model for the antiferromagnet [38] (the dotted line of Fig. 8). From the temperature dependence of the magnetic specific heat, the magnetic entropy change for Gd$_3$SbO$_7$ ($S_{\text{mag}}$) is calculated by the relation $S_{\text{mag}} = \int \left( \frac{C_{\text{mag}}}{T} \right) dT$. Its temperature dependence is also shown in Fig. 8. The total magnetic entropy change is $\sim 50$ J/mol K, and this value is close to $3R \ln 8 = 51.9$ J/mol K. The results indicate that all the Gd$^{3+}$ ions contribute to the antiferromagnetic transition and that the ground state of the Gd$^{3+}$ ions is still eight-degenerate ($^8S_{7/2}$) without crystal field splitting.

As shown in Fig. 8, it is difficult to divide the magnetic entropy data into two anomalies.
However, it is clear that the magnetic entropy change due to the magnetic anomaly at a lower temperature is larger than that at a higher temperature (2.6 K). In the Gd$_3$SbO$_7$, the Gd$^{3+}$ ions occupy two crystallographic sites, the 8-coordinated Gd(1) site (4b) and 7-coordinated Gd(2) site (8c), with the 1:2 ratio. Therefore, we believe that the magnetic transition at 2.6 K is due to the antiferromagnetic ordering of the 8-coordinated Gd(1) ions and that the magnetic anomaly at the lower temperature (T < 0.4 K) is ascribable to the magnetic interactions of the 7-coordinated Gd(2) ions, i.e., Gd$^{3+}$ ions occupying the 4b and 8c sites individually order in the Gd$_3$SbO$_7$ compound. Similar “two-step” magnetic transitions have been found for Ln$_3$TaO$_7$ (Ln = Nd, Tb) [24] and Ln$_3$NbO$_7$ (Ln = Nd, Tb) [39].

### 3.3.2. Dy$_3$SbO$_7$

The temperature dependence of the magnetic susceptibility of Dy$_3$SbO$_7$ is shown in Fig. 9. A clear antiferromagnetic transition has been observed at 3.2 K. The inset of Fig. 9 shows the reciprocal susceptibility versus temperature curve and the Curie-Weiβ fitting. For this compound, specific heat measurements were also performed down to 0.4 K. The specific heat divided by temperature ($C_p/T$) is shown in Fig. 10. A clear $\lambda$-type specific heat anomaly has been observed at 3.2 K, at which the magnetic susceptibility shows antiferromagnetic behavior. The magnetic specific heat was estimated by subtracting the contribution of the lattice specific heat from the total specific heat in the same way as is the case for Gd$_3$SbO$_7$. The magnetic entropy change is calculated from the specific heat data by using the equation $S_{mag} = \int \left( C_{mag}/T \right) dT$, and it is obtained to be 17.1 J/mol K. This value is quite near to $3R \ln 2 = 17.3$ J/mol K. The ground multiplet of Dy$^{3+}$ ion, $^6H_{15/2}$ splits into eight Kramers’doublets due to the effect of the crystal field with low symmetry. The experimental results indicate that the ground Kramers’ doublets for three Dy$^{3+}$ ions cause the antiferromagnetic ordering.
For Tb$_3$SbO$_7$ and Ho$_3$SbO$_7$, a clear antiferromagnetic transition has been observed at 3.0 and 2.2 K, respectively. There is no divergence between ZFC and FC susceptibilities. Although Funnell et al. reported a possibility of magnetically frustrated system for Ho$_3$SbO$_7$ and Dy$_3$SbO$_7$ [34], there is no appearance of magnetic frustration. Figure 11 shows the temperature dependence of magnetic susceptibility of Nd$_3$SbO$_7$, indicating the antiferromagnetic transition at 3.0 K. In addition, another magnetic anomaly was observed at 2.5 K. No divergence between ZFC and FC susceptibilities was found below these transition temperatures. This is due to the fact that two phases of Nd$_3$SbO$_7$ possibly have different Neel temperatures.

4. Summary

Rare earth antimonates $Ln_3$SbO$_7$ ($Ln =$ Nd, Gd - Ho) show an antiferromagnetic transition at 2.2 ~ 3.2 K. Measurements of the specific heat down to 0.4 K for Gd$_3$SbO$_7$ indicate that the 8-coordinated Gd ions antiferromagnetically order at 2.6 K and with furthermore decreasing temperature, the 7-coordinated Gd ions show a magnetic anomaly, i.e., the magnetic moments at the two crystallographic sites order individually.

Acknowledgements

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References


In addition, the C-centering extinction condition ruled out the other space groups such as $Pnma$ (for $La_3NbO_7$) [2] and $P2_12_12_1$ (for $Ln_3MoO_7$) [27-30]. [27] J. E. Greedan, N. P. Raju, A. Wegner, P. Gougeon, and J. Padiou, J. Solid State Chem., 129, 320-327 (1997).


**Figure captions**

Fig. 1 Powder x-ray diffraction profiles for (a) La$_3$SbO$_7$ and (b) Sm$_3$SbO$_7$. The calculated and observed profiles are shown on the top solid line and cross markers, respectively. The vertical marks in the middle show positions calculated for Bragg reflections. The lower trace is a plot of the difference between calculated and observed intensities.

Fig. 2. Crystal structures of Ln$_3$SbO$_7$. (a): La$_3$SbO$_7$ (space group: $Cmcm$); (b): Sm$_3$SbO$_7$ (space group: $C222_1$).

Fig. 3. Variation of lattice parameters for Ln$_3$SbO$_7$ with the ionic radius of Ln$^{3+}$ in eight-coordination.

Fig. 4. Variation of Ln-O and Sb-O bond lengths with the ionic radius of Ln$^{3+}$ in eight-coordination.

Fig. 5. Temperature dependence of the magnetic susceptibility for Pr$_3$SbO$_7$. The inset shows the reciprocal susceptibility vs. temperature curve. The solid line is the Curie-Weiss fitting.

Fig. 6. Temperature dependences of the magnetic susceptibility for Sm$_3$SbO$_7$ and Eu$_3$SbO$_7$.

Fig. 7. Temperature dependence of the magnetic susceptibility for Gd$_3$SbO$_7$. The inset shows the detailed temperature dependence below 7 K.

Fig. 8. Temperature dependence of $C_p/T$ and $S_{mag}$ for Gd$_3$SbO$_7$.

Fig. 9. Temperature dependence of the magnetic susceptibility for Dy$_3$SbO$_7$. The inset shows the reciprocal susceptibility vs. temperature curve. The solid line is the Curie-Weiss fitting.

Fig. 10. Temperature dependence of $C_p/T$ and $S_{mag}$ for Dy$_3$SbO$_7$.

Fig. 11. Temperature dependence of the magnetic susceptibility for Nd$_3$SbO$_7$. The inset shows its detailed temperature dependence below 7 K.
Table 1  Structural parameters for La$_3$SbO$_7$.

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*Note. Space group Cmcm; $a = 11.1300(9)$ Å, $b = 7.6398(6)$ Å, $c = 7.7399(6)$ Å, $V = 658.13(9)$ Å$^3$, $R_{wp} = 11.65\%$, $R_I = 2.82\%$, and $R_e = 8.62\%$, where

\[
R_{wp} = \left[ \sum_i w_i (y_i - f_i(x))^2 / \sum_i w_i y_i^2 \right]^{1/2}, \quad R_J = \sum I_k(o) - I_k(c) / \sum I_k(o), \quad \text{and}
\]

\[
R_e = \left[ (N - P) / \sum_i w_i y_i^2 \right]^{1/2}.
\]
### Table 2  Structural parameters for Sm$_3$SbO$_7$.

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*Note. Space group $C22_{1}$; $a = 10.7280(4) \text{Å}$, $b = 7.5506(3) \text{Å}$, $c = 7.6048(3) \text{Å}$, $V = 615.60(4) \text{Å}^3$, $R_{wp} = 13.12 \%$, $R_I = 3.94 \%$, and $R_e = 9.81 \%$.***
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<tr>
<td>Ho</td>
<td>$C_{222_1}$</td>
<td>antiferromagnetic</td>
<td>10.6</td>
<td>10.58</td>
<td>-13.4</td>
<td>2.2</td>
</tr>
<tr>
<td>Er</td>
<td>$C_{222_1}$</td>
<td>paramagnetic</td>
<td>9.26</td>
<td>9.59</td>
<td>-9.7</td>
<td>—</td>
</tr>
<tr>
<td>Tm</td>
<td>$C_{222_1}$</td>
<td>paramagnetic</td>
<td>7.72</td>
<td>7.55</td>
<td>-4.6$c$</td>
<td>—</td>
</tr>
<tr>
<td>Yb</td>
<td>$C_{222_1}$</td>
<td>paramagnetic</td>
<td>4.72</td>
<td>4.54</td>
<td>-1.83$c$</td>
<td>—</td>
</tr>
<tr>
<td>Lu</td>
<td>$C_{222_1}$</td>
<td>diamagnetic</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>
La$_3$SbO$_7$ ($Cmcm$)

Sm$_3$SbO$_7$ ($C22_1$)

Intensity / arb. unit

$2\theta$/ degree
La(2)
SbO₆
La(1)O₈

(a) La₃SbO₇
(b) $\text{Sm}_3\text{SbO}_7$
Ionic radii of Ln$^{3+}$/ Å

- $a/\sqrt{2}$
- $b$
- $c$
Bond lengths / Å

Ionic radii of \( \text{Ln}^{3+} / \text{Å} \)

- • Ln(1)-O (8-coordinated)
- ○ Ln(2)-O (7-coordinated)
- ■ Sb-O

C222_1

Cmcm
$\chi_M / \text{emu\cdotmol}^{-1}$ vs $T / \text{K}$

Inset:

$\chi^{-1}_M / \text{emu}^{-1}\cdot\text{mol}$ vs $T / \text{K}$

- Pr$_3$SbO$_7$
- ZFC
- FC

Curie-Weiss fit
$\chi_m / \text{emu/mol}^{-1}$

$T / \text{K}$

$\text{Eu}_3\text{SbO}_7$
- ZFC

$\text{Sm}_3\text{SbO}_7$
- ZFC
- FC
\[ C_p T^{-1} \text{ / J\cdot mol}^{-1}\cdot \text{K}^{-2} \]

\[ S_{\text{mag}} \text{ / J\cdot mol}^{-1}\cdot \text{K}^{-1} \]

\[ T / \text{K} \]

\[ \text{Gd}_3\text{SbO}_7 \]

\[ 3R \ln 8 \]
\[ \chi_M / \text{emu} \cdot \text{mol}^{-1} \]

\[ T / \text{K} \]

**Dy₃SbO₇**

- ZFC
- FC

Curie-Weiss
\( C_p \) $/ \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$

\( T \) $/ \text{K}$

Dy\textsubscript{3}SbO\textsubscript{7}

La\textsubscript{3}NbO\textsubscript{7}

$3R \ln 2$