Structural Phase Transition and Antiferromagnetic Transition of \( \text{Tb}_3\text{RuO}_7 \)

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Abstract

Magnetic properties and structural phase transition of terbium ruthenate Tb$_3$RuO$_7$ are investigated through magnetic susceptibility, specific heat, high-temperature x-ray diffraction and differential scanning calorimetry measurements. The structural phase transition from space group $P2_1/nb$ to $Cmcm$ has been observed at 402 K. Tb$_3$RuO$_7$ shows an antiferromagnetic transition at 17 K. In addition, another magnetic anomaly has been found at 10 K. Analysis of the magnetic specific heat for Tb$_3$RuO$_7$ indicates that the magnetic transitions at 10 and 17 K are due to the magnetic ordering of Tb$^{3+}$ and Ru$^{5+}$ ions, respectively.
1. Introduction

In the last decades, compounds of the general formula $\text{Ln}_3\text{MO}_7$ ($\text{Ln} = \text{lanthanides, } M = \text{Nb, Ru, Ta, etc.}$) have been attracting interest, because of their one-dimensional structural features. They have a defect-fluorite structure. The relationship to the fluorite structure is as follows. The fluorite unit cell for oxides has the composition $\text{M}^{4+}_4\text{O}_8$. If the four tetravalent metal ions are replaced by three trivalent ions ($\text{Ln}$) and one pentavalent ion ($M$), one oxide vacancy is formed per fluorite cell. Due to the significant differences in radii between the $\text{Ln}^{3+}$ and $\text{M}^{5+}$ ions, cation ordering occurs on the metal sites and the oxide-vacancy orders on the anion sites. Rossell determined first the parent structure of this family of compounds, $\text{La}_3\text{NbO}_7$ [1]. It is well described in the orthorhombic space group \textit{Cmcm}: The $\text{M}^{5+}$ ion is coordinated with six oxygen ions, forming an $\text{MO}_6$ octahedron. These octahedra share corners forming one-dimensional chains which are oriented along the $c$-axis. The same space group \textit{Cmcm} has been applied for $\text{Ln}_3\text{RuO}_7$ ($\text{Ln} = \text{La} \sim \text{Gd}$) [2-13], $\text{Ln}_3\text{ReO}_7$ ($\text{Ln} = \text{Pr, Nd, Sm} \sim \text{Tb}$) [14-17], $\text{Ln}_3\text{OsO}_7$ ($\text{Ln} = \text{Pr, Nd, Sm} \sim \text{Gd}$) [11, 18-20], $\text{Ln}_3\text{IrO}_7$ ($\text{Ln} = \text{Pr, Nd, Sm, Eu}$) [26-29], $\text{Pr}_3\text{NbO}_7$ [24] and $\text{Pr}_3\text{SbO}_7$ [24].

Many studies have been performed, due to this unique crystal structure and possible related magnetic properties, especially for the magnetic properties of compounds containing $\text{Ru}^{5+}$ ion at the $M$-site because of its largest possible spin ($S = 3/2$) [2-12]. However, there was scant evidence for the expected one-dimensionality in the magnetic susceptibility.

Another topic for $\text{Ln}_3\text{MO}_7$ is that ruthenium-, iridium- and osmium-containing members of the $\text{Ln}_3\text{MO}_7$ family show low-temperature structural phase transitions by detailed magnetic and thermal investigations [8-10, 12, 13, 19, 20, 27, 30]. The transition temperature is a function of the specific rare
earth ion in the $Ln_3MO_7$. For Gd$_3$RuO$_7$, we performed neutron diffraction measurements and reported that its low-temperature structure is described with space group $P2/n$ [9]. Gemmill et al. claimed that the observed structural phase transition of $Ln_3MO_7 (M = $Ru, Os) is the one from space group $Cmcm$ to $P2_1/nb$ [12], and Ishizawa et al. presented the detailed structural description [13]. For Ir-containing $Ln_3IrO_7$ compounds, we showed that the observed structural phase transition is well described from space group $Cmcm$ to $P2_1/n$ [28].

In this study, we extended the magnetic and structural studies on $Ln_3RuO_7$ to $Ln = $Tb. After checking the existence of the phase transition in Tb$_3$RuO$_7$ by Differential Scanning Calorimetry (DSC) measurements, we performed high-temperature X-ray diffraction measurements in order to obtain information on the structures above and below the phase transition temperature. Through magnetic susceptibility and specific heat measurements, we observed an antiferromagnetic transition at 17 K. Their results will be discussed in this paper.

2. Experimental

2.1. Sample preparation

Polycrystalline samples of Tb$_3$RuO$_7$ were prepared by the standard solid state reaction. Reagent grade powders of Tb$_4$O$_7$ and RuO$_2$ were used as starting materials. They were well mixed in an agate mortar. These mixtures were pressed into pellets and heated at 1473 K for 30 h with two interval re-grinding and re-pelletizing. In the first stage of sample preparations, very small amounts of impurities remained in the desired compounds; they were un-reacted starting materials Tb$_4$O$_7$. In order to remove these impurities, the samples were washed with diluted hydrochloric acid. After this
treatment, single-phase Tb$_3$RuO$_7$ 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 (λ = 1.5406 Å) equipped with a curved graphite monochromator. The data were collected by step-scanning in the angle range of 10° ≤ 2θ ≤ 120° at a 2θ step-size of 0.02°. The temperature dependence of the X-ray diffraction profiles (15° ≤ 2θ ≤ 120°) was obtained in the temperature range from 323 to 1248 K.

The X-ray diffraction data were analyzed by the Rietveld technique, using the programs RIETAN-FP [31], and the crystal structure was drawn by using the VESTA program [32].

2.3. Differential scanning calorimetry (DSC) measurements

The DSC measurements were carried out under flowing Ar gas atmosphere over the temperature range 250-700 K using DSC 200 (Seiko, Japan). The heating and cooling rate was 5 K/min.

2.4. Magnetic susceptibility measurements

The temperature-dependence of the magnetic susceptibility for Tb$_3$RuO$_7$ was measured in an applied field of 0.1 T over the temperature range of 1.8 K ≤ T ≤ 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.

2.5. 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 1.8-400 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

Figure 1 shows the powder X-ray diffraction profile for Tb$_3$RuO$_7$ measured at room temperature.
Following report by Ishizawa et al. [33], we performed Rietveld analysis for our X-ray diffraction data
and found that the structure of Tb$_3$RuO$_7$ is well described with the orthorhombic space group $P2_1nb$.
Figure 2 shows the schematic crystal structure of Tb$_3$RuO$_7$ and the structural parameters are listed in
supplementary Table 1.

Previous studies on $Ln_3$RuO$_7$ ($Ln$ = Sm, Eu, and Gd) showed that these compounds undergo a
structural phase transitions at 190, 280, and 382 K, respectively between the $P2_1nb$ and $Cmcm$ [12, 34].
So, we performed measurements on the temperature dependence of the X-ray diffraction profiles and
differential scanning calorimetry (DSC) measurements for Tb$_3$RuO$_7$. Figure 3 depicts the DSC profile
for Tb$_3$RuO$_7$ during heating and cooling, which shows that the structural phase transition temperature
for Tb$_3$RuO$_7$ is 402 K.

Above the phase transition temperature, some reflection peaks (for example at $2\theta = 21.58^\circ$, $23.47^\circ$,
and $40.81^\circ$ in Fig. 2) disappeared. Gemmill et al. reported that $Ln_3$OsO$_7$ ($Ln$ = Pr, Sm-Tb) compounds
undergo a structural phase transition from space group $P2_1nb$ to $Cmcm$ with increasing temperature [19,
20]. For $Ln_3$RuO$_7$, the same structural phase transition has been reported for $Ln$ = Sm, Eu, and Gd [12,
We tried to analyze the X-ray diffraction data above the phase transition with the *Cmcm* model. Figure 4 shows the X-ray diffraction profiles of Tb$_3$RuO$_7$ at 473 K. All the reflection observed could be successfully indexed. Table 1 lists the crystallographic data for Tb$_3$RuO$_7$ at 473 K, and Fig. 5 illustrates its crystal structure. The main features of the crystal structure of Tb$_3$RuO$_7$ are the same between below and above the phase transition temperature. The RuO$_6$ octahedra are corner-linked through the O atoms, and they form one-dimensional chains along the *c*-axis. One-third of the Tb-O polyhedra are aligned one-dimensionally by edge sharing along the *c*-axis, which alternate with the parallel zigzag chains of RuO$_6$ octahedra, forming slabs parallel to the *bc* plane. The remaining two-thirds of Tb ions are in seven-coordination and lie between the slabs. The two independent Ru(1)O$_6$ and Ru(2)O$_6$ octahedra in the *P*$_{21}$*nb* modification (Fig. 2) become crystallographically identical in the *Cmcm* modification (Fig. 5). The RuO$_6$ octahedron in the high-temperature form tilts in the *bc* plane. On the other hand, Ru(1)O$_6$ and Ru(2)O$_6$ octahedra in the *P*$_{21}$*nb* modification tilt in the *ab* plane, in addition to the tilt in the *bc* plane, which causes a doubling of the orthorhombic *b*-axis and a concomitant reduction in the coordination environment of the Tb cations from 8 to 7 (see Tb(1,2)O$_7$ in Fig. 2).

The temperature dependence of the cell dimensions for Tb$_3$RuO$_7$ in the temperature range between 323 and 1248 K is shown in Fig. 6. Although the increase of *a*-length with temperature is monotonous, the change of *c*-length and *b*-length against temperature is not simple, i.e., it is noticeable. Discontinuous increase of the *c*-length was observed between 398 and 423 K. It seemed that the expansion of the *b*-length with increasing temperature once stopped in the same temperature range. As described above, DSC measurements showed that the structural phase transition of Tb$_3$RuO$_7$ occurred in this temperature range. Therefore, the observed change of cell dimensions against temperature is
associated with the structural phase transition of Tb$_3$RuO$_7$.

### 3.2. Magnetic properties

Figure 7 shows the temperature dependence of the magnetic susceptibility for Tb$_3$RuO$_7$. A clear antiferromagnetic transition has been observed at 10 K, and there is no divergence between the ZFC and FC susceptibilities below this temperature, indicating that this antiferromagnetic transition is the one without any ferromagnetic properties. In addition to the susceptibility peak at 11 K, a cusp has been observed at ~17 K in the susceptibility vs. temperature curve (see an arrow in Fig. 7). Following the method by Fisher [35], temperature dependence of $\partial (\chi T)/\partial T$ is shown in the inset of Fig. 7, indicating that there exists another magnetic ordering at 17 K, in addition to that at 10 K. This result accords with the specific heat data, as will be described later. Figure 8 shows the reciprocal susceptibility versus temperature curve for Tb$_3$RuO$_7$ and the Curie-Weiss fitting in the temperature range between 30 and 400 K. The effective magnetic moment of Tb$_3$RuO$_7$ is determined to be 17.21 $\mu_B$. Since the theoretical effective magnetic moment of Tb$^{3+}$ is 9.72 $\mu_B$, the effective magnetic moment of Ru$^{5+}$ in this compound is calculated to be 3.58 $\mu_B$, which is the appropriate moment for Ru$^{5+}$ ion with [Kr]$4d^5$ electronic configuration ([Kr] : krypton electronic core). The negative Weiss constant of Tb$_3$RuO$_7$ ($\theta = -10.5$ K) indicates that the magnetic interaction observed at low temperatures is antiferromagnetic.

In order to obtain the information about the low-temperature magnetic behavior, specific heat measurements were performed down to 1.8 K. Figure 9 shows the temperature dependence of the specific heat ($C_p$) for Tb$_3$RuO$_7$. A clear $\lambda$-type specific heat anomaly has been observed at ca 17 K,
which corresponds to the results by magnetic susceptibility measurements. It seems that there exists another specific heat anomaly around 10 K. So, the specific heat data divided by temperature \((C_p/T)\) were plotted against temperature in the inset of Fig. 9. At 10 K, another specific heat anomaly has been observed, which is in accordance with the magnetic susceptibility data.

For magnetic compounds, the total specific heat \((C_p)\) is the sum of the lattice specific heat \((C_{lat})\) and magnetic specific heat \((C_{mag})\). To evaluate the magnetic contribution to the specific heat, we have to subtract the contribution of lattice specific heat from the total specific heat, i.e., \(C_{mag} = C_p - C_{lat}\). The lattice specific heat was estimated by using the data for a diamagnetic compound \(La_3NbO_7\). Figure 10 shows the temperature dependence of the magnetic specific heat divided by temperature \((C_{mag}/T)\). The magnetic specific heat below 1.8 K was extrapolated by the relation \(C_{mag} \propto T^3\) from the spin-wave model for the antiferromagnet [36] (the dashed line of Fig. 10). From the temperature dependence of the magnetic specific heat, the magnetic entropy change for \(Tb_3RuO_7\) \((S_{mag})\) is calculated by the relation \(S_{mag} = \int \left( C_{mag}/T \right) dT\). Its temperature dependence is also shown in Fig. 10. The total magnetic entropy change is \(\sim 23\) J/mol K at 20 K, and this value is close to \(4R \ln 2 = 23.0\) J/mol K \((R:\) gas constant). In this \(Tb_3RuO_7\), \(Ru^{5+}\) and \(Tb^{3+}\) ions are magnetic, i.e., they both contribute to the magnetic transition. Although a total spin quantum number of the \(Ru^{4+}\) ion is calculated to be \(S = 3/2\), the four degenerating state splits into two doublets due to the orthorhombic symmetry, i.e., the ground state of the \(Ru^{4+}\) ion should be doublet, which means that the magnetic entropy change due to this ground doublet is \(R\ln 2\). Then, the rest of the magnetic entropy due to the magnetic ordering of \(Tb^{3+}\) ions is estimated to be \(4R\ln 2 - R\ln 2 = 3R\ln 2\). All the \(Tb^{3+}\) ions in the \(Tb_3RuO_7\) occupy in seven-coordinated sites. The ground multiplet \(^7F_6\) of the \(Tb^{3+}\) ion should split into many states due to the effect of the crystal field in low
symmetry. The estimated $S_{\text{mag}}$ value from specific heat measurements $3R\ln 2$ suggests that the degeneracy of the $\text{Tb}^{3+}$ ions is two. Similar results have been reported for $\text{Tb}_3\text{SbO}_7$ [37]. Therefore, it is considered that Kramers doublets of $\text{Ru}^{5+}$ ions and non-Kramers doublets of $\text{Tb}^{3+}$ ions cause the antiferromagnetic ordering found for $\text{Tb}_3\text{RuO}_7$. As shown in Fig. 10, it is difficult to divide the magnetic entropy data into two anomalies observed at 10 and 17 K. However, if we admit the $S_{\text{mag}}$ value for the magnetic ordering at 10 K is much larger than that at 17 K, the antiferromagnetic transition at 10 K should be due to the magnetic interactions of $\text{Tb}^{3+}$ and that at 17 K is ascribed to the magnetic ordering of $\text{Ru}^{5+}$ ions.

3.3. Structural phase transition

The structural phase transition temperatures of $Ln_3\text{RuO}_7$ ($Ln = \text{Nd}-\text{Tb}$) are plotted against the ionic radius of $Ln^{3+}$ in eight-coordination in Fig. 11. The data for other $Ln_3\text{MO}_7$ compounds ($M = \text{Mo, Re, Os, Ir}$) have been also included in this figure. For each of the five series of $Ln_3\text{MO}_7$ compounds, the structure transition temperatures decrease with increasing the ionic radius of $Ln^{3+}$, i.e., it is clear that the structure transition of $Ln_3\text{MO}_7$ is clearly influenced by the size of the $Ln^{3+}$ cation. As the transition temperature increases with decreasing the ionic radius of $Ln^{3+}$, the transition is stress-induced and it occurs with lattice contraction on cooling. Each transition temperature within a series is separated by approximately the same temperature interval except for the case of $Ln_3\text{MoO}_7$. The reason for this may be related to the difference in their high-temperature structures, that is, $Ln_3\text{MO}_7$ ($M = \text{Ru, Re, Os, Ir}$) compounds exist in the $Cmcm$ structure, whereas $Ln_3\text{MoO}_7$ exists in the $Pnma$ structure.
Summary

Terbium ruthenate $\text{Tb}_3\text{RuO}_7$ undergoes a structural phase transition from space group $P2_1nb$ to $Cmcm$ at 402 K. This compound shows two magnetic transitions at 10 and 17 K, which are due to the magnetic ordering of $\text{Tb}^{3+}$ and $\text{Ru}^{5+}$ ions, respectively.

References


Figure captions

Fig. 1 Powder X-ray diffraction profiles for Tb$_3$RuO$_7$ measured at room temperature. The calculated profiles based on the $P2_1nb$ model are shown on the top solid line. The vertical marks in the middle show positions calculated for Bragg reflections. The second and third marks in the middle show positions for impurities Tb$_4$O$_7$ (Tb$_7$O$_{12}$ and Tb$_{11}$O$_{20}$ phases, respectively). The lower trace is a plot of the difference between calculated and observed intensities.

Fig. 2 Schematic crystal structure of Tb$_3$RuO$_7$ at room temperature (space group: $P2_1nb$).

Fig. 3 DSC profiles of Tb$_3$RuO$_7$ in the temperature range between 350 and 600 K.

Fig. 4 Powder X-ray diffraction profiles for Tb$_3$RuO$_7$ measured at 473 K. The calculated profiles based on the $Cmcm$ model are shown on the top solid line. The vertical marks in the middle show positions calculated for Bragg reflections. The second and third marks in the middle show positions for impurities Tb$_4$O$_7$ (Tb$_7$O$_{12}$ and Tb$_{11}$O$_{20}$ phases, respectively). The lower trace is a plot of the difference between calculated and observed intensities.

Fig. 5 Schematic crystal structure of Tb$_3$RuO$_7$ at 473 K (space group: $Cmcm$).

Fig. 6 Temperature dependence of cell dimensions for Tb$_3$RuO$_7$ in the temperature range between 323 and 1248 K. The $b$-length of the $Cmcm$ modification above 402 K is doubled in the figure for comparison with the low-temperature $P2_1nb$ modification.

Fig. 7 Temperature dependence of the magnetic susceptibility for Tb$_3$RuO$_7$ between 1.8 and 300 K. The inset shows the temperature dependence of $\partial (\chi T)/\partial T$.

Fig. 8 Temperature dependence of the reciprocal magnetic susceptibility for Tb$_3$RuO$_7$ between 1.8 and 400 K. The solid line is the Curie-Weiss fitting.
Fig. 9 Temperature dependence of the specific heat ($C_p$) for Tb$_3$RuO$_7$ in the temperature range between 1.8 and 100 K. The inset shows the specific heat divided by temperature ($C_p/T$) for Tb$_3$RuO$_7$.

Fig.10 Temperature dependence of the magnetic specific heat divided by temperature ($C_{mag}/T$) and the magnetic entropy ($S_{mag}$) for Tb$_3$RuO$_7$.

Fig.11 Structural phase transition temperatures of $Ln_3MO_7$ ($M=$Mo, Ru, Re, Os, Ir) against the ionic radius of $Ln^{3+}$ in eight-coordination.
Fig. 1
Ru(1,2)O$_6$

Tb(3-6)

Tb(1,2)O$_7$

Fig. 2
Fig. 3

Temperature (K)

\[ \Delta E_{\text{endo}} \]

cooling

heating

Fig. 3
RuO$_6$

Tb(1)O$_8$

Tb(2)

Fig. 5
Fig. 6
Fig. 7
Figure 9

$c_p$ (J·mol$^{-1}$·K$^{-1}$) vs. Temperature (K)

Inset: $c_p T$ (J·mol$^{-1}$·K$^{-2}$) vs. Temperature (K)
Fig. 10

The graph shows the variation of magnetic specific heat ($C_{\text{mag}} \cdot T^{-1}$) and magnetic entropy ($S_{\text{mag}}$) with temperature ($T$). The data points and curves indicate a phase transition at a certain temperature.

Temperature (K) vs. $C_{\text{mag}} \cdot T^{-1}$ (J·mol$^{-1}$·K$^{-2}$) vs. $S_{\text{mag}}$ (J·mol$^{-1}$·K$^{-1}$)
1. Structural phase transition temperature (K)

2. Ionic radius of Ln$^{3+}$ (Å) in eight-coordination

Fig. 11
Table 1  Structural parameters for Tb$_3$RuO$_7$ at 473 K.

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<tr>
<th>Atom</th>
<th>Site</th>
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<th>$y$</th>
<th>$z$</th>
<th>$B / \text{Å}^2$ $^a$</th>
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<td>0</td>
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<td>0.413(4)</td>
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*Note. Space group Cmcm; $a = 10.57409(15)$ \text{Å}, $b = 7.30824(10)$ \text{Å}, $c = 7.36800(10)$ \text{Å}, $V = 569.3845(14)$ \text{Å}^3, $R_{wp} = 18.29$ \%, $R_B = 2.84$ \%, and $R_e = 13.41$ \%, where

\[
R_{wp} = \left[ \sum_i w_i (y_i - f_i(x))^2 / \sum_i w_i y_i^2 \right]^{1/2}, \quad R_B = \sum_K I\alpha(h_K) - I(h_K) / \sum_K I\alpha(h_K), \text{ and} \\
R_e = \left[ (N - P) / \sum_i w_i y_i^2 \right]^{1/2}.
\]
Supplementary Table 1. Structural parameters for Tb$_3$RuO$_7$ at room temperature.

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<td>O(13)</td>
<td>4$a$</td>
<td>0.312</td>
<td>0.144</td>
<td>0.236</td>
<td>1.0</td>
</tr>
<tr>
<td>O(14)</td>
<td>4$a$</td>
<td>0.546</td>
<td>0.393</td>
<td>0.262</td>
<td>1.0</td>
</tr>
</tbody>
</table>

*Note. Space group $P2_1/nb$; $a = 10.5603(10)$ Å, $b = 14.5879(15)$ Å, $c = 7.3453(7)$ Å, $V = 1131.56(19)$ Å$^3$, $R_{wp} = 12.36$ %, and $R_e = 8.91$ %, where

$$R_{wp} = \left[ \frac{\sum_i w_i(y_i - f_i(x))^2}{\sum_i w_i y_i^2} \right]^{1/2},$$

and

$$R_e = \left[ \frac{(N - P)}{\sum_i w_i y_i^2} \right]^{1/2}.$$