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Magnetic Properties and Structural Transitions of Fluorite-Related

Rare Earth Osmates $Ln_3OsO_7$ ($Ln = Pr, Tb$)

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Abstract

Ternary rare-earth osmates $Ln_3\text{OsO}_7$ ($Ln = \text{Pr, Tb}$) have been prepared. They crystallize in an orthorhombic superstructure of cubic fluorite with space group $Cmcm$. Both of these compounds undergo a structural phase transition at 130 K ($Ln = \text{Pr}$) and 580 K ($Ln = \text{Tb}$). These compounds show complex magnetic behavior at low temperatures. $\text{Pr}_3\text{OsO}_7$ exhibits magnetic transitions at 8 and 73 K, and $\text{Tb}_3\text{OsO}_7$ magnetically orders at 8 and 60 K. The Os moments become one-dimensionally ordered, and when the temperature is furthermore decreased, provokes the ordering in the Ln$^{3+}$ sublattice that simultaneously becomes three-dimensionally ordered with the Os sublattice.
1. Introduction

Ternary metal oxides of general formula $Ln_3MO_7$ ($Ln$ is a rare earth element; $M$ is a pentavalent transition element such as Nb, Mo, Ru, Sb, Ta, Re, Os, or Ir) have been intensively studied, because of their one-dimensional structural features and possible magnetic properties. They have an ordered, defect-fluorite structure. 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 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. 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. One-third of Ln ions are coordinated by eight oxygen ions and the distorted LnO$_8$ cubes also form a one-dimensional chain through edge-sharing. Many studies have been performed [1-28], especially for the magnetic properties of compounds containing Ru$^{5+}$ ion at the $M$-site because of its largest possible spin ($S = 3/2$) [5-12].

Another topic for $Ln_3MO_7$ compounds is that detailed magnetic and thermal investigations on the ruthenium-, iridium- and osmium-containing members of the $Ln_3MO_7$ family show low-temperature structural phase transitions [8-10, 12, 13, 18, 22, 25, 26, 29-34].

We have paid our attention on the $M = Os$ compounds. IJdo et al. first reported the preparation, structures and magnetic properties of polycrystalline samples of $Ln_3OsO_7$ ($Ln$ = Pr, Nd, Sm) [17]. These compounds crystallized in an orthorhombic phase with space group $Cnma$ from their powder X-ray diffraction measurements, and $Ln = Nd$ and Sm compounds exhibited complex magnetic behavior at
low temperatures. Later, Greedan et al. prepared La₃OsO₇ and reported the presence of the evidence for long-range antiferromagnetic ordering at 45 K [11]. Recently zur Loye’s research group prepared single crystals of Ln₃OsO₇ (Ln = Sm, Eu, Gd) and performed their X-ray diffraction measurements [18]. They observed that these compounds undergo a structural phase transition from space group Cmcm to P2₁nb and exhibit complex magnetic behavior below 50 K.

In this study, we prepared Ln₃OsO₇ (Ln = Pr, Tb) without using oxygen donor reactants. Through their magnetic susceptibility, specific heat and differential scanning calorimetry (DSC) measurements, we observed an antiferromagnetic transition at 73 K (Ln = Pr) and 60 K (Ln = Tb), and a phase transition at 130 K (Ln = Pr) and 580 K (Ln = Tb). In this paper, the preparation, structures, and magnetic properties of these compounds will be presented.

2. Experimental

2.1. Sample preparation

Rare earth oxides Pr₆O₁₁ (99.99 %, Shin-etsu Chemical) and Tb₄O₇ (99.9 %, Shin-etsu Chemical) and an osmium oxide OsO₂ (99.99 %, Premion from Alfa Aesar) were used as starting materials. Pr₃OsO₇ and Tb₃OsO₇ were prepared in a closed system:

\[
\frac{3}{4} \text{Pr}_2\text{O}_3 + \frac{1}{4} \text{Pr}_6\text{O}_{11} + \text{OsO}_2 \rightarrow \text{Pr}_3\text{OsO}_7,
\]

\[
\frac{1}{2} \text{Tb}_2\text{O}_3 + \frac{1}{2} \text{Tb}_4\text{O}_7 + \text{OsO}_2 \rightarrow \text{Tb}_3\text{OsO}_7.
\]

For the preparation of sesquioxides Pr₂O₃ and Tb₂O₃, the Pr₆O₁₁ and Tb₄O₇ were reduced in a flowing H₂ atmosphere at 900 °C for a day. These starting materials were weighed in an appropriate metal ratio and were ground in an agate mortar. The mixtures were pressed into pellets and then sealed in an
evacuated quartz tube. They were heated at 950 °C for 5 h, and then cooled down to room temperature.

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°. For Tb₃OsO₇, the temperature dependence of the X-ray diffraction profiles (15° ≤ 2θ ≤ 120°) was obtained in the temperature range from 373 to 723 K.

The X-ray diffraction data were analyzed by the Rietveld technique, using the programs RIETAN-FP [35], and the crystal structure was drawn by using the VESTA program [36].

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 ≤ 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. For Tb₃OsO₇, the temperature dependence of its susceptibility was measured under the applied magnetic field of 0.01 T.

The remnant magnetization measurements were also performed. The samples were cooled to 1.8 K in a zero magnetic field. The magnetic field was applied up to 5 T and then reduced to zero. The magnetization measurements were performed in the temperature range from 1.8 K to room temperature.

The field dependence of the magnetization was measured for Tb₃OsO₇ at several temperatures (5,
20, 50 K) by changing the magnetic field strength in the range between -5 T and 5 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 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.

2.5. ac magnetic susceptibility measurements

The ac magnetic susceptibility measurements were performed for Tb$_3$OsO$_7$ with the same measurement system (Quantum Design, PPMS) in the temperature range between 1.8 and 100 K. The temperature dependence of the ac susceptibilities was measured at 10, 100, 1,000, and 10,000 Hz. The samples were first cooled in a zero magnetic field and then an ac field was applied up to 0.0005 T.

2.6. Differential scanning calorimetry (DSC) measurements

The DSC measurements were carried out under flowing Ar gas atmosphere over the temperature range 350-700 K using DSC 200 (Seiko, Japan). The heating rate was 5 K/min.

3. Results and discussion

3.1. Preparation and crystal structure

Two rare earth osmates Pr$_3$OsO$_7$ and Tb$_3$OsO$_7$ were isolated from the reaction of a mixture of Pr$_2$O$_3$ (Tb$_2$O$_3$), Pr$_6$O$_{11}$ (Tb$_4$O$_7$) and OsO$_2$ in a closed system, without using oxygen donor reactants. Concerning the preparation of osmium-containing oxides, Plaisier and IJdo reported that it is difficult to control the oxidation state of osmium in oxides by using oxygen donor reactants [17]. In the present
study, we used OsO₂ instead of Os metal as a starting material, which considerably reduces the formation of volatile osmium tetroxide OsO₄. In addition, for the case of preparing Pr₃OsO₇ and Tb₃OsO₇, we need not use oxygen donors such as Ag₂O and KClO₃, because Pr₆O₁₁ and Tb₂O₇ are available.

Figure 1 (a) shows the powder X-ray diffraction profile for Pr₃OsO₇ at room temperature. This diffraction pattern is similar to that for the fluorite structure and all reflections appear to be consistent with the C-centered condition, \( h + k = 2n \). A variety of space groups such as \( Pnma, Cmcm, P2_12_12_1 \), \( C222_1 \), \( P2/n \) and \( P2_{1}nb \) have been proposed for the \( \text{Ln}_3\text{MO}_7 \). The C-centering extinction condition ruled out space groups such as \( Pnma, P2_12_12_1, P2/n \) and \( P2_{1}nb \). Some extra reflection peaks which should be observed with space group \( C222_1 \) (for example, the peak at \( 2\theta \sim 20.5^\circ \) corresponding to the 2 0 1 reflection) were not observed in the X-ray diffraction profile. This fact shows that the \( C222_1 \) was also ruled out from the space group for Pr₃OsO₇. We performed refinements of the crystal structure with the space group \( Cmcm \). All the reflections observed could be successfully indexed. Table 1 lists the crystallographic data for Pr₃OsO₇, and Fig. 2 illustrates the crystal structure of Pr₃OsO₇. The OsO₆ octahedra are corner-linked through the O(3) atoms, and they form one-dimensional chains along the \( c \)-axis. One-third of the Pr atoms are in eight-fold oxygen coordination, forming distorted cubes Pr(1)O₈. These Pr(1)O₈ cubes are aligned one-dimensionally by edge sharing along the \( c \)-axis, which alternate with the parallel zigzag chains of Os octahedra, forming slabs parallel to the b-c plane. The remaining two-thirds of Pr(2) ions are in seven coordination and lie between the slabs of the Pr(1)O₈ and the OsO₆ polyhedra.

Figure 1 (b) shows the powder X-ray diffraction profile for Tb₃OsO₇ measured at room
temperature. If we assume the same space group with that for Pr$_3$OsO$_7$, some reflection peaks (for example at $2\theta = 28.9^\circ$, $33.3^\circ$, $48.2^\circ$, and $56.9^\circ$) cannot be explained from the extinction condition. As will be described later, Pr$_3$OsO$_7$ and Tb$_3$OsO$_7$ undergo a crystallographic phase transition at 130 and 580 K, respectively. Therefore, the structure of Tb$_3$OsO$_7$ at room temperature should be the one at low temperature phase.

Figure 3 shows the X-ray diffraction profiles of Tb$_3$OsO$_7$ measured at various temperatures. We performed the Rietveld analysis for the X-ray diffraction data above 580 K with space group Cmcm. The results show that the refinement for the diffraction data was successful with the space group Cmcm and that a very small amount of the pyrochlore Tb$_2$Os$_2$O$_7$ was contained in the product. Figure 4 shows the X-ray diffraction profiles of Tb$_3$OsO$_7$ measured at 673 K. The crystallographic data for Tb$_3$OsO$_7$ at 673 K are also listed in Table 1. The Os-O(3)-Os angle is $157.0^\circ$ for Pr$_3$OsO$_7$ and $149.3^\circ$ for Tb$_3$OsO$_7$. This increased buckling of the Os-O(3)-Os angle with decreasing the size of the Ln ion is due to the shortening of the c-axis, which is observed for other Ln$_3$MO$_7$ compounds.

With decreasing temperature, some additional diffraction lines which cannot be fitted with Cmcm appear (for example at $2\theta = 28.9^\circ$, $33.3^\circ$, $48.2^\circ$, and $56.9^\circ$, see Fig. 3). We consider that these extra diffraction lines originate from a low-temperature phase.

Gemmill et al. reported that Ln$_3$OsO$_7$ (Ln = Sm, Eu, Gd) compounds undergo a structural phase transition from space group Cmcm to P2$_1$nb with decreasing temperature [18]. We tried to analyze the X-ray diffraction data measured at room temperature with the P2$_1$nb model. All the reflections observed could be indexed, as shown in Fig. 5. Figure 6 illustrates the crystal structure of Tb$_3$OsO$_7$ at room temperature. The lattice parameters determined for Tb$_3$OsO$_7$ are $a = 10.5514(22)$ Å, $b = 14.7424(38)$ Å,
$c = 7.3771(18)$ Å, and $V = 1145.19(47)$ Å$^3$. These values are smaller than those for Gd$_3$OsO$_7$ [18]. The structure transitions from $Cmcm$ to $P2_1/nb$ involves a distortion in the trans vertex-sharing OsO$_6$ chains that causes a doubling of the orthorhombic b-axis and a concomitant reduction in the coordination environment of the Tb cations from 8 to 7. On the other hand, the Os-O distances are not much affected by the structural distortion, and the average Os-O distances is 1.947 Å. In the low-temperature structure of $Ln_3$OsO$_7$, the average value of Os-O distance within the OsO$_6$ octahedra decreases from 1.959 to 1.947 Å when the $Ln^{3+}$ ionic radius decreases from Sm to Tb. Similar trends have been reported for the structures of $Ln_3$MoO$_7$ ($Ln =$ La ~ Gd) compounds [45].

In order to determine the structural phase transition temperature of Tb$_3$OsO$_7$, we performed its DSC measurements in the temperature range between 350 and 700 K. Figure 7 depicts the DSC profile of Tb$_3$OsO$_7$ during heating. The endothermic reaction begins at ~ 580 K, showing that the structural phase transition occurs at this temperature.

Figure 8 shows the temperature dependence of the lattice parameters and volume for Tb$_3$OsO$_7$ in the temperature range of 373 K $\leq T \leq$ 723 K. The lattice parameters were refined with space group $Cmcm$ for any temperature. With increasing temperature, the lattice parameter $b$ increases monotonically, while clear changes have been observed between 573 and 598 K for the parameters $a$, $c$ and volume. These changes correspond to the results by the DSC measurements, i.e., the structural phase transition has occurred at ~ 580 K.

3.2. Magnetic properties

3.2.1. Magnetic properties of Pr$_3$OsO$_7$
Figure 9 shows the temperature dependence of the magnetic susceptibility for Pr$_3$OsO$_7$. A clear divergence between the ZFC and FC susceptibilities has been observed below 73 K. Below this temperature, the FC susceptibility rapidly increases with decreasing temperature, and reaches a maximum at 28 K. Below 4.7 K, the FC susceptibility turns to increase with decreasing temperature. The ZFC susceptibility also increases with decreasing temperature, but the increment of the ZFC susceptibility against temperature drastically changes at 73 and 22 K. It seems that another magnetic anomaly is observed at 8 K. The inset of Fig. 9 shows the temperature dependence of the $d(\chi_M T)/dT$. A great change has been found at 8 K for both the ZFC and FC susceptibility data.

Figure 10 shows the temperature dependence of the specific heat divided by temperature ($C_p/T$) for Pr$_3$OsO$_7$. Specific heat anomalies have been observed at 130, 73, and 8 K. The anomaly at 130 K indicates the existence of the phase transition at this temperature. The anomaly at 73 K is in accordance with the results by the magnetic susceptibility, i.e., a magnetic transition has occurred at this temperature. The $\lambda$-type specific heat anomaly observed at 8 K seems to correspond to the anomaly found in the ZFC and FC susceptibilities at the same temperature, indicating the occurrence of another magnetic transition at this temperature. We consider that the Os moments become one-dimensionally ordered at 73 K, and when the temperature is furthermore decreased, provokes the ordering in the Ln$^{3+}$ sublattice that simultaneously becomes three-dimensionally ordered with the Os sublattice at 8 K. Similar magnetic behavior has been reported for Nd$_3$OsO$_7$, i.e., two magnetic anomalies are observed at ~10 and 75 K [17].

Figure 11 depicts the temperature dependence of the reciprocal susceptibility of Pr$_3$OsO$_7$, and the Curie-Weiss fitting in the temperature range of 100 and 400 K. The effective magnetic moment of
Pr$_3$OsO$_7$ is determined to be 6.37 $\mu_B$. It is generally known that the moment of Pr$^{3+}$ is 3.58 $\mu_B$. Assuming the effective moment of 3.58 $\mu_B$ per Pr$^{3+}$, the effective magnetic moment of Os$^{5+}$ is found to be 1.46 $\mu_B$. Since the spin-orbit coupling cannot be ignored for the 5d$^3$ ions, the expected moment of Os$^{5+}$ should be lower than the spin-only value of 3.87 $\mu_B$. Comparable lower effective magnetic moment of Os$^{5+}$ is reported for Nd$_3$OsO$_7$ [17]. That is, the contribution of the Os$^{5+}$ ions to the effective magnetic moment of Pr$_3$OsO$_7$ is small, which has been observed in some Os-containing compounds [17, 37-42].

The negative Weiss constant of Pr$_3$OsO$_7$ ($\theta = -39.9$ K) indicates that the magnetic interaction observed at low temperatures is antiferromagnetic.

3.2.2. Magnetic properties of Tb$_3$OsO$_7$

Figure 12 shows the magnetic susceptibility vs temperature curve of Tb$_3$OsO$_7$ in the temperature range between 1.8 and 300 K. The ZFC and FC susceptibilities begin to diverse when the temperature is decreased through ca 60 K. At 26 K, the temperature dependence of the ZFC susceptibility shows a steep maximum. On the contrary, the FC susceptibility shows a clear click at the same temperature. When the temperature is furthermore decreased, a clear antiferromagnetic behavior has been observed for both the ZFC and FC susceptibilities at 8 K. A very small anomaly found at 2.4 K in the ZFC susceptibility-temperature curve is due to the antiferromagnetic ordering of an impurity Tb$_2$O$_3$ (a starting material) with the C-type structure [43, 44].

Figure 13 shows the temperature dependence of the in-phase and out-of-phase magnetic susceptibility for Tb$_3$OsO$_7$ in the temperature range of 1.8-100 K. When the temperature is decreased below 60 K, both the in-phase and the out-of-phase susceptibilities change with the frequency. There
appear two maxima at 8 and 28 K in the in-phase susceptibility vs. temperature curve. The temperature of the maximum ac susceptibilities for Tb₃OsO₇ appears to be independent of the frequency, indicating that the transition is not a transition to a spin-glass state.

Figure 14 shows the temperature dependence of the specific heat (C_p) for Tb₃OsO₇. Two specific heat anomalies have been observed at 2.4 and 8 K. The anomaly at 8 K is in accordance with the results by the magnetic susceptibility, i.e., a magnetic transition has occurred at this temperature. Another anomaly observed at 2.4 K is due to the Tb₂O₃ as an impurity in the sample. From the results of magnetic susceptibility and specific heat measurements, we consider that the Os moments become one-dimensionally ordered at ca 60 K. When the temperature is furthermore decreased, provokes the ordering in the Ln³⁺ sublattice that simultaneously becomes three-dimensionally ordered with the Os sublattice at 8 K.

Figure 15 shows the field dependence of the magnetization of Tb₃OsO₇ measured at 5, 20, and 50 K. Even at 50 K, the magnetization vs the applied magnetic field curve is not linear. It is clear that at 5K, there exists an isothermal magnetization loop. From the large divergence between ZFC and FC magnetic susceptibilities, there exists a ferromagnetic component in the antiferromagnetic moments.

To check the existence of the ferromagnetic moment, the remnant magnetization measurements were performed. Figure 16 shows that the weak ferromagnetic moment of Tb₃OsO₇ completely disappears when the temperature is increased above ca 60 K. That is, the antiferromagnetic interactions at low temperatures have a weak ferromagnetic component.

Figure 17 depicts the temperature dependence of the reciprocal susceptibility of Tb₃OsO₇, and the Curie-Weiss fitting in the temperature range of 100 and 400 K. The effective magnetic moment of
Tb$_3$OsO$_7$ is determined to be 16.81 $\mu_B$. Since the moment of Tb$^{3+}$ is 9.7 $\mu_B$, the effective magnetic moment of Os$^{5+}$ is calculated to be 0.60 $\mu_B$. The contribution of the Os$^{5+}$ ions to the effective magnetic moment of Tb$_3$OsO$_7$ is small, which is found in some Os-containing compounds [17, 37-42].

The negative Weiss constant of Tb$_3$OsO$_7$ ($\theta = -12.4$ K) indicates that the magnetic interaction observed at low temperatures is antiferromagnetic.

Magnetic properties of Ln$_3$OsO$_7$ are summarized in Table 2.

3.3. Structural phase transition

The results of the specific heat measurements show that Pr$_3$OsO$_7$ undergoes a structural phase transition at 130 K (see Fig. 10). DSC measurements for Tb$_3$OsO$_7$ show that the structural phase transition occurs at 580 K (see Fig. 7).

Most of the Ln$_3$MO$_7$ compounds crystallize in the orthorhombic phase with space group Cmcm. M = Ru and Os compounds undergo a structural phase transition from space group Cmcm to $P2_1n nb$ with decreasing temperature [12, 18, 26, 31]. Iridium compounds Ln$_3$IrO$_7$ show a phase transition from the orthorhombic phase with space group Cmcm to a monoclinic phase with space group $P2_1/n$ [34]. On the other hand, Ln$_3$MoO$_7$ show a phase transition from space group Pnma to $P2_12_12_1$[25, 45]. A neodymium tantalate Nd$_3$TaO$_7$ undergoes a phase transition from space group Cmcm to $C22_2_1$ [20].

Figure 18 shows the variation of the structural phase transition temperatures for a series of Ln$_3$MO$_7$ compounds (M = Mo, Re, Os, Ir, Ru) against the ionic radius of Ln$^{3+}$ in eight-coordination. These M$^{5+}$ ions have a d-electron configuration ranging from $d^1$ to $d^4$, indicating that the Ln$_3$MO$_7$ compounds are magnetically active. For each of the five series of Ln$_3$MO$_7$ compounds, the structure transition
temperatures decrease with increasing the ionic radius of \( \text{Ln}^{3+} \), i.e., it is clear that the structure transition of \( \text{Ln}_3\text{MO}_7 \) is clearly influenced by the size of the \( \text{Ln}^{3+} \) cation. As the transition temperature increases with decreasing the ionic radius of \( \text{Ln}^{3+} \), 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 \( \text{Ln}_3\text{MoO}_7 \). The reason for this may be related to the difference in their high-temperature structures, that is, \( \text{Ln}_3\text{MO}_7 \) (\( M = \text{Ru, Re, Os, Ir} \)) compounds exist in the \textit{Cmcm} structure, whereas \( \text{Ln}_3\text{MoO}_7 \) exists in the \textit{Pnma} structure.

**Summary**

Ternary rare-earth osmates \( \text{Ln}_3\text{OsO}_7 \) (\( \text{Ln} = \text{Pr, Tb} \)) have been prepared from the reaction of mixtures of \( \text{Pr}_2\text{O}_3 \) (\( \text{Tb}_2\text{O}_3 \)), \( \text{Pr}_6\text{O}_{11} \) (\( \text{Tb}_4\text{O}_7 \)) and \( \text{OsO}_2 \), without using oxygen donor reactants. We found a phase transition at 130 K (\( \text{Ln} = \text{Pr} \)) and 580 K (\( \text{Ln} = \text{Tb} \)). Magnetic ordering was observed at 8 and 73 K for \( \text{Pr}_3\text{OsO}_7 \), and 8 and 60 K for \( \text{Tb}_3\text{OsO}_7 \). These compounds \( \text{Pr}_3\text{OsO}_7 \) and \( \text{Tb}_3\text{OsO}_7 \) are candidates to behave as one-dimensional from the magnetic point of view, and 73 and 60 K correspond to the one-dimensional correlations temperatures of the antiferromagnetic interactions that take place along the Os-O-Os chains being in these \( \text{Pr} \) and \( \text{Tb} \) compounds that can be closely correlated with the decreasing of bond angle from 157° to 149° in going from \( \text{Pr} \) to \( \text{Tb} \) compounds.

**References**


Figure captions

Fig. 1 (a) Powder X-ray diffraction profile for Pr$_3$OsO$_7$ at room temperature. 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.

(b) Powder X-ray diffraction profile for Tb$_3$OsO$_7$ at room temperature. 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 lower trace is a plot of the difference between calculated and observed intensities. Arrows show the diffraction lines which cannot be indexed with Cmcm (see text).

Fig. 2 Crystal structure of Pr$_3$OsO$_7$ (space group: Cmcm).

Fig. 3 X-ray diffraction profiles of Tb$_3$OsO$_7$ at various temperatures. Arrows show the diffraction lines which cannot be indexed with Cmcm (see text).

Fig. 4 Powder X-ray diffraction profile for Tb$_3$OsO$_7$ measured at 673 K. 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 second vertical marks show positions for impurities Tb$_2$Os$_2$O$_7$. The lower trace is a plot of the difference between calculated and observed intensities.

Fig. 5 Powder X-ray diffraction profile for Tb$_3$OsO$_7$ at room temperature. 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 second vertical marks show
positions for impurities Tb$_2$Os$_2$O$_7$. The lower trace is a plot of the difference between calculated and observed intensities.

Fig. 6 Crystal structure of Tb$_3$OsO$_7$ at room temperature (space group: $P2_1/nb$).

Fig. 7 DSC profile of Tb$_3$OsO$_7$ during heating in the temperature range between 350 and 700 K. An arrow shows the temperature at which the endothermic reaction begins.

Fig. 8 Temperature dependence of lattice parameters and volume for Tb$_3$OsO$_7$ in the temperature range between 373 and 723 K.

Fig. 9 Temperature dependence of the magnetic susceptibility for Pr$_3$OsO$_7$ in the temperature range of 1.8 and 300 K. The inset shows the temperature dependence of the $d(\chi_M T)/dT$ at low temperatures.

Fig. 10 Temperature dependence of the specific heat divided by temperature $(C_p/T)$ for Pr$_3$OsO$_7$.

Fig. 11 Temperature dependence of the reciprocal magnetic susceptibility for Pr$_3$OsO$_7$. The solid line is the Curie-Weiss fitting.

Fig. 12 Temperature dependence of the magnetic susceptibility for Tb$_3$OsO$_7$.

Fig. 13 Temperature dependence of the in-phase and the out-of-phase ac magnetic susceptibility for Tb$_3$OsO$_7$ in the temperature range of 1.8 and 100 K. The applied magnetic field is 0.0005 T with frequencies of 10 ~ 10,000 Hz.

Fig. 14 Temperature dependence of the specific heat for Tb$_3$OsO$_7$ in the temperature range between 1.8 and 100 K. The inset shows the detailed temperature dependence of the specific heat below 30 K.

Fig. 15 Field dependence of the magnetization for Tb$_3$OsO$_7$ measured at 5, 20, and 50K.

Fig. 16 Temperature dependence of the remnant magnetization for Tb$_3$OsO$_7$. 

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Fig. 17 Temperature dependence of the reciprocal magnetic susceptibility for Tb$_3$OsO$_7$. The solid line is the Curie-Weiss fitting.

Fig. 18 Structural phase transition temperatures of Ln$_3$MO$_7$ ($M$ = Mo, Ru, Re, Os, Ir) against the ionic radius of Ln$^{3+}$ in eight-coordination.
Fig. 1(a)
Fig. 1(b)
Fig. 3

Intensity (arbitrary unit)

2θ (degree)

723 K
673 K
598 K
573 K
548 K
523 K
473 K
373 K
Fig. 5

Tb$_3$OsO$_7$

Room temperature

Intensity (arbitrary unit)

$2\theta$ (degree)
Fig. 6
Tb$_3$OsO$_7$

$\Delta E_{\text{endo}}$ vs $T$ (K)
Fig. 8

Lattice parameters (Å)

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</tbody>
</table>

Volume (Å³)

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>574</td>
</tr>
<tr>
<td>500</td>
<td>576</td>
</tr>
<tr>
<td>600</td>
<td>578</td>
</tr>
<tr>
<td>700</td>
<td>580</td>
</tr>
</tbody>
</table>
The graph shows the relationship between $C_p \cdot T^{-1}$ (in J·mol$^{-1}$·K$^{-2}$) and temperature $T$ (in K), for Pr$_3$OsO$_7$. The peak at approximately 150 K indicates a significant change in the heat capacity at this temperature.
\( \chi_M^{-1} \text{ (emu}^{-1}\text{mol)} \) vs. \( T \text{ (K)} \) for \( \text{Pr}_3\text{OsO}_7 \). The graph shows data for zero-field cooled (ZFC) and field cooled (FC) conditions.
Fig. 13

The graph shows the magnetic susceptibility ($\chi'$, $\chi''$) as a function of temperature ($T$) for $\text{Tb}_3\text{OsO}_7$. The data is presented for different frequencies: 10 Hz, 100 Hz, 1 kHz, and 10 kHz. The peaks in the $\chi'$ curve correspond to the glass transition temperature ($T_g$) and the Curie temperature ($T_C$). The $\chi''$ curve represents the imaginary part of the susceptibility, which is typically associated with the heat capacity.

$\chi'$, $\chi''$ (emu·mol$^{-1}$)
$T$ (K)

- $\chi'$
- $\chi''$

- 10 Hz
- 100 Hz
- 1 kHz
- 10 kHz

$\text{Tb}_3\text{OsO}_7$
Fig. 14

$C_p (J \cdot mol^{-1} \cdot K^{-1})$

$T (K)$

$Tb_3OsO_7$
$\text{Tb}_3\text{OsO}_7$
Remanent magnetization ($\mu_B \cdot \text{mol}^{-1}$) vs. $T$ (K)

$\text{Tb}_3\text{OsO}_7$
The graph shows the magnetic susceptibility $\chi_M^{-1}$ (emu$^{-1}$·mol) versus temperature $T$ (K) for the compound $\text{Tb}_3\text{OsO}_7$. The graph includes data points for zero-field-cooled (ZFC) and field-cooled (FC) conditions.
Fig. 18: Structural phase transition temperature (K) as a function of the ionic radius of Ln$^{3+}$ (Å) in eight-coordination for various Ln$_3$MO$_7$ compounds (MO = Mo, Ir, Re, Os, Ru). The graph shows a trend where the structural phase transition temperature decreases as the ionic radius increases.
Table 1 Structural parameters for $\text{Ln}_3\text{OsO}_7$ ($\text{Ln} = \text{Pr}, \text{Tb}$).

### $\text{Pr}_3\text{OsO}_7$ at room temperature

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$B$ / Å²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr(1)</td>
<td>4$a$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.89(7)</td>
</tr>
<tr>
<td>Pr(2)</td>
<td>8$g$</td>
<td>0.2259(1)</td>
<td>0.3054(2)</td>
<td>1/4</td>
<td>0.57(5)</td>
</tr>
<tr>
<td>Os</td>
<td>4$b$</td>
<td>0</td>
<td>1/2</td>
<td>0</td>
<td>0.41(6)</td>
</tr>
<tr>
<td>O(1)</td>
<td>16$h$</td>
<td>0.126(1)</td>
<td>0.314(1)</td>
<td>-0.042(1)</td>
<td>1.2(2)</td>
</tr>
<tr>
<td>O(2)</td>
<td>8$g$</td>
<td>0.135(1)</td>
<td>0.032(1)</td>
<td>1/4</td>
<td>1.2</td>
</tr>
<tr>
<td>O(3)</td>
<td>4$c$</td>
<td>0</td>
<td>0.448(2)</td>
<td>1/4</td>
<td>1.2</td>
</tr>
</tbody>
</table>

*Note. Space group Cmcm; $a = 10.9732(15)$ Å, $b = 7.4485(10)$ Å, $c = 7.5507(10)$ Å, $V = 617.15(14)$ Å³, $R_w = 11.59\%$, $R_B = 1.84\%$, and $R_e = 7.48\%$, where

$$R_w = \left[ \sum_i w_i (y_i - f_i(x))^2 / \sum_i w_i y_i^2 \right]^{1/2}, \quad R_B = \sum_k |I_o(h_k) - I(h_k)| / \sum_k I_o(h_k), \quad \text{and}$$

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

### $\text{Tb}_3\text{OsO}_7$ at 673 K

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$B$ / Å²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb(1)</td>
<td>4$a$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.15(9)</td>
</tr>
<tr>
<td>Tb(2)</td>
<td>8$g$</td>
<td>0.2351(1)</td>
<td>0.2796(2)</td>
<td>1/4</td>
<td>0.77(6)</td>
</tr>
<tr>
<td>Os</td>
<td>4$b$</td>
<td>0</td>
<td>1/2</td>
<td>0</td>
<td>0.21(6)</td>
</tr>
<tr>
<td>O(1)</td>
<td>16$h$</td>
<td>0.135(1)</td>
<td>0.295(1)</td>
<td>-0.033(2)</td>
<td>1.7(3)</td>
</tr>
<tr>
<td>O(2)</td>
<td>8$g$</td>
<td>0.137(3)</td>
<td>0.017(3)</td>
<td>1/4</td>
<td>1.7</td>
</tr>
<tr>
<td>O(3)</td>
<td>4$c$</td>
<td>0</td>
<td>0.431(4)</td>
<td>1/4</td>
<td>1.7</td>
</tr>
</tbody>
</table>

*Note. Space group Cmcm; $a = 10.5771(9)$ Å, $b = 7.3842(7)$ Å, $c = 7.4164(9)$ Å, $V = 579.28(10)$ Å³, $R_w = 11.54\%$, $R_B = 1.75\%$, and $R_e = 7.98\%$. 
Table 2  Magnetic data for \( \text{Ln}_3\text{OsO}_7 \)

<table>
<thead>
<tr>
<th>compounds</th>
<th>magnetic properties</th>
<th>( \mu_{\text{eff}} (\mu_B) )</th>
<th>( \theta ) (K)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{La}_3\text{OsO}_7 )</td>
<td>( T_N = 45\text{K}, 110\text{K}, ) non Curie-Weiss behavior up to 500 K</td>
<td>3.93</td>
<td>-278</td>
<td>[11]</td>
</tr>
<tr>
<td>( \text{Pr}_3\text{OsO}_7 )</td>
<td>( T_N = 8, 73 \text{K} )</td>
<td>6.37</td>
<td>-39.9</td>
<td>this study</td>
</tr>
<tr>
<td>( \text{Nd}_3\text{OsO}_7 )</td>
<td>( T_C = 75 \text{K} )</td>
<td>6.89</td>
<td>~0</td>
<td>[17]</td>
</tr>
<tr>
<td>( \text{Sm}_3\text{OsO}_7 )</td>
<td>Weak ferromagnetic, ( T_C = 48 \text{K} )</td>
<td>4.19</td>
<td>-8</td>
<td>[17]</td>
</tr>
<tr>
<td>( \text{Eu}_3\text{OsO}_7 )</td>
<td>Complex behavior below 50 K</td>
<td>*</td>
<td>*</td>
<td>[18]</td>
</tr>
<tr>
<td>( \text{Gd}_3\text{OsO}_7 )</td>
<td>Ferromagnetic, ( T_C = 34 \text{K} )</td>
<td>13.7</td>
<td>1.6</td>
<td>[18]</td>
</tr>
<tr>
<td>( \text{Tb}_3\text{OsO}_7 )</td>
<td>( T_N = 8, 60 \text{K} )</td>
<td>16.81</td>
<td>-12.4</td>
<td>this study</td>
</tr>
</tbody>
</table>

* These values are not shown in the reference.