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Magnetic Properties and Structural Transitions of Orthorhombic Fluorite-Related Compounds  $Ln_3MO_7$

( $Ln$  = Rare Earths,  $M$  = Transition Metals)

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## Abstract

Magnetic properties and structural transitions of ternary rare-earth transition-metal oxides  $Ln_3MO_7$  ( $Ln$  = rare earths,  $M$  = transition metals) were investigated. In this study, we prepared a series of molybdates  $Ln_3MoO_7$  ( $Ln$  = La ~ Gd). They crystallize in an orthorhombic superstructure of cubic fluorite with space group  $P2_12_12_1$ , in which  $Ln^{3+}$  ions occupy two different crystallographic sites (the 8-coordinated and 7-coordinated sites). All of these compounds show a phase transition from the space group  $P2_12_12_1$  to  $Pnma$  in the temperature range between 370 and 710 K. Their magnetic properties were characterized by magnetic susceptibility measurements from 1.8 to 400 K and specific heat measurements from 0.4 K to 400 K.  $Gd_3MoO_7$  shows an antiferromagnetic transition at 1.9 K. Measurements of the specific heat for  $Sm_3MoO_7$  and the analysis of the magnetic specific heat indicate a “two-step” antiferromagnetic transition due to the ordering of Sm magnetic moments in different crystallographic sites, i.e., with decreasing temperature, the antiferromagnetic ordering of the 7-coordinated Sm ions occur at 2.5 K, and then the 8-coordinated Sm ions order at 0.8 K. The results of  $Ln_3MoO_7$  were compared with the magnetic properties and structural transitions of  $Ln_3MO_7$  ( $M$  = Nb, Ru, Sb, Ta, Re, Os, or Ir).

## 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. 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. In 1979, Rossell first determined the crystal structure of an orthorhombic  $La_3NbO_7$  [1]. 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. A variety of the space groups such as  $Pnma$ ,  $Cmcm$ ,  $P2_12_12_1$ ,  $C222_1$ , and  $P2_1nb$  has been proposed for the  $Ln_3MO_7$ . Due to this unique crystal structures and possible related magnetic properties, many studies have been performed [2-41], especially for the magnetic properties of compounds containing  $Ru^{5+}$  ion at the  $M$ -site because of its largest possible spin ( $S = 3/2$ ) [5-13]. However, there was scant evidence for the expected one-dimensionality in the magnetic susceptibility.

Another topic for  $Ln_3MO_7$  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 [9-11, 13, 14, 19, 26, 30, 31, 35-38, 40, 41]. However, the low temperature structures are, in most cases, not known, or different structures were presented for the same compounds.

We have paid our attention on the  $M = Mo$  compounds. Prevost-Czeskleba first reported that  $Ln_3MoO_7$  ( $Ln = La, Pr, Nd, Sm, Eu$ ) crystallized in an orthorhombic phase with space group  $Cmcm$

from their powder X-ray diffraction measurements [27]. Later, Greedan and Gougeon prepared single crystals of  $Ln_3MoO_7$  ( $Ln = La, Pr$ ) and performed their X-ray diffraction measurements [28, 29]. These compounds crystallize in the orthorhombic space group  $P2_12_12_1$ . They studied the electronic and thermal properties of  $La_3MoO_7$  by magnetic susceptibility, electric resistivity, and neutron diffraction measurements as a function of temperature. The magnetic susceptibility was quite complex. The main feature was a broad maximum at 655 K which was interpreted as due to intra-chain spin corrections of the  $Mo^{5+}$  ions. Several other anomalies were observed at 483, 140, and 100 K. Then, we prepared a series of  $LnMoO_7$  compounds ( $Ln = La, Pr, Nd, Sm, \text{ and } Eu$ ) and reported their crystal structures and magnetic properties [30]. The structures at room temperature were analyzed with the space group  $P2_12_12_1$ . The differential scanning calorimetry (DSC) measurements indicated that the phase-transition occurs for any  $Ln_3MO_7$  compound in the temperature range between 370 and 710 K. However, we could not determine the crystal structure above the phase-transition temperature. Very recently, Gougeon et al. determined the crystal structures of  $Ce_3MoO_7$  and  $Sm_3MoO_7$  by using their single crystals [33, 39].

In this study, we extended the preparation of  $Ln_3MoO_7$  compounds from  $Ln = La$  to  $Gd$ . Through high-temperature X-ray diffraction measurements, their crystal structures above the phase-transition were determined. In order to elucidate magnetic properties of these  $Ln_3MoO_7$  compounds, the magnetic susceptibility measurements from 1.8 to 400 K and the specific heat measurements from 0.4 to 400 K were performed. The results of the magnetic properties and structural transitions for  $Ln_3MoO_7$  were compared with those for  $Ln_3MO_7$  ( $M = Nb, Ru, Sb, Ta, Re, Os, \text{ or } Ir$ ).

## 2. Experimental

### 2.1. Sample preparation

As starting materials, rare earth oxides  $Ln_2O_3$  ( $Ln = La, Nd, Sm-Gd$ ),  $MoO_2$ , and  $MoO_3$  were used. For the preparation of  $Ln = Pr$  compound,  $Pr_6O_{11}$  was used as the starting material. To obtain sesquioxide  $Pr_2O_3$ , the  $Pr_6O_{11}$  was reduced in a flowing  $H_2$  atmosphere at  $900\text{ }^\circ\text{C}$  for a day. For  $La_2O_3$  and  $Nd_2O_3$ , they absorb moisture in air and easily form rare earth hydroxides  $Ln(OH)_3$ . Therefore, they were dried at  $1173\text{ K}$  for 24 h before use. 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 platinum tube. They were heated at  $1200\text{ }^\circ\text{C}$  for 12 h, and then cooled down to room temperature. After regrinding and repelleting, the same heating procedure was repeated again. For the preparation of  $Ln = Gd$  compound, the pelletized starting materials were sealed in a platinum tube, and were heated at  $1350\text{ }^\circ\text{C}$  for  $3\text{ h} \times 2$ . In the first stage of sample preparations, very small amounts of impurities remained in the desired compound because of the evaporation of Mo oxides; they were unreacted starting materials  $Gd_2O_3$ . In order to remove these impurities, the sample was washed with diluted hydrochloric acid. After this treatment, a single-phase  $Gd_3MoO_7$  compound could be obtained.

### 2.2. X-ray diffraction analysis

Powder X-ray diffraction profiles were measured using a Rigaku Multi-Flex diffractometer with  $Cu-K\alpha$  radiation ( $\lambda = 1.5406\text{ \AA}$ ) equipped with a curved graphite monochromator. The data were collected by step-scanning in the angle range of  $10^\circ \leq 2\theta \leq 120^\circ$  at a  $2\theta$  step-size of  $0.02^\circ$ . The X-ray diffraction data were analyzed by the Rietveld technique, using the programs RIETAN2000 [42].

### *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  $1.8 \text{ K} \leq T \leq 400 \text{ K}$ , 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.

### *2.5. Differential scanning calorimetry measurements*

The DSC measurements were carried out under flowing Ar gas atmosphere over the temperature range 300-800 K using DSC 200 (Seiko, Japan). The heating rate was 5 K/min.

### 3. Results and discussion

#### 3.1. Preparation and crystal structure

In this study, we could obtain a new compound  $\text{Gd}_3\text{MoO}_7$  as a single phase. Figure 1 shows the powder X-ray diffraction profile for  $\text{Gd}_3\text{MoO}_7$  measured at room temperature. The diffraction pattern is quite similar to those for  $Ln = \text{La} \sim \text{Eu}$  compounds. Their crystal structures have been elucidated and they are orthorhombic with space group  $P2_12_12_1$  [28-30, 33]. We have performed refinement of the crystal structure with the same space group. The results of the Rietveld analysis show that  $\text{Gd}_3\text{MoO}_7$  are isomorphous with  $Ln_3\text{MoO}_7$  ( $Ln = \text{La} \sim \text{Eu}$ ). Table 1 lists the crystallographic data for  $\text{Gd}_3\text{MoO}_7$ , and Figure 2 (a) shows its crystal structure. The structural feature of  $\text{Gd}_3\text{MoO}_7$  is the occurrence of infinite single chains of tilted corner-linked  $\text{MoO}_6$  octahedra running parallel to the b axis. These  $\text{MoO}_6$  chains alternate with rows of edge-shared  $\text{Gd}(1)\text{O}_8$  pseudo-cubes to form slabs parallel to the  $ab$ -plane. The slabs are separated by the  $\text{Gd}(2)$  and  $\text{Gd}(3)$  cations, which are seven-coordinated by O atoms forming highly distorted pentagonal bipyramids. Gall and Gougeon found that the average value of Mo-O distances within the  $\text{MoO}_6$  octahedra decreases from 1.981 to 1.966 Å when the  $Ln^{3+}$  ionic radius decreases from La to Sm [39]. The average Mo-O distance determined for  $\text{Gd}_3\text{MoO}_7$  is 1.953 Å, which follows the above-mentioned relationship. They also pointed out that a slight decrease in the Mo-O(5)-Mo angle was observed when the  $Ln^{3+}$  ionic radius decreases, and it changes from  $149.1^\circ$  ( $Ln = \text{La}$ ) to  $146.6^\circ$  ( $Ln = \text{Sm}$ ). The value of  $\text{Gd}_3\text{MoO}_7$  is  $146.2^\circ$ , which also follows the above-mentioned relationship. The  $\text{MoO}_6$  octahedra and  $\text{Gd}(1)\text{O}_8$  cubes in this  $P2_12_12_1$  structure are obviously not so much regular. The Mo-O distances change from 1.81(2) to 2.04(3) Å. The  $\text{Gd}(1)$  cation has seven

oxygen atoms as its nearest neighbors at distances ranging between 2.29(3) and 2.71(2) Å and an eighth at 3.34(2) Å (Gd(1)-O(3)) which form a highly distorted cube. This distortion results from the rotation of the MoO<sub>6</sub> octahedra around the b-axis.

The results of the X-ray diffraction measurements show that any of the Ln<sub>3</sub>MoO<sub>7</sub> compounds crystallizes in the orthorhombic space group *P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>* at room temperature. The DSC measurements indicate that the phase transition occurs for all Ln<sub>3</sub>MoO<sub>7</sub> (Ln = La ~ Sm) compounds in the temperature range between 370 and 710 K and that the phase-transition temperature increases from La<sub>3</sub>MoO<sub>7</sub> to Sm<sub>3</sub>MoO<sub>7</sub>. We performed high-temperature XRD measurements for La<sub>3</sub>MoO<sub>7</sub> in the temperature range between 300 and 500 K. Figure 3 (a) shows the XRD profiles measured at 300 and 460 K, and Fig. 3 (b) depicts its low 2θ region. When the temperature was increased above 370 K, some weak diffraction lines (for example, the peaks at 2θ ~ 20° and 39° corresponding to the 1 0 2 (0 1 2) and 3 0 2 reflections, respectively) disappeared and the XRD profile was successfully refined with the space group *Pnma*. This space group is a supergroup of *P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>*, and has been applied also for Ln<sub>3</sub>NbO<sub>7</sub> (Ln = La, Pr, Nd) [2, 38]. Table 2 lists the structural parameters for La<sub>3</sub>MoO<sub>7</sub>. The high-temperature structure of La<sub>3</sub>MoO<sub>7</sub> is illustrated in Fig. 2 (b). Two kinds of infinite chains are formed by corner-sharing MoO<sub>6</sub> octahedra and edge-sharing La(1)O<sub>8</sub> cubes, and the slabs consist of alternate chains, and 7-coordinated La(2) ions exist between the slabs. The MoO<sub>6</sub> octahedra and La(1)O<sub>8</sub> cubes in the *Pnma* structure are obviously much more regular than those in the *P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>* structure. In the former, the tilting of the MoO<sub>6</sub> chain is along the 001 direction with the tilting angle (Mo-O-Mo) of 152.6°, and in the latter, it is along the 100 direction with the tilting angles of 149.1° for La<sub>3</sub>MoO<sub>7</sub> and 146.2° for Gd<sub>3</sub>MoO<sub>7</sub>.

Table 3 lists the room-temperature crystal structures for Ln<sub>3</sub>MoO<sub>7</sub> and other Ln<sub>3</sub>MO<sub>7</sub> compounds

( $M = \text{Nb, Ta, Sb, Re, Os, Ir, Ru}$ ). Structural studies on  $\text{Ln}_3\text{TaO}_7$  compounds show that with decreasing the size of  $\text{Ln}^{3+}$  ion, the space group of the  $\text{Ln}_3\text{TaO}_7$  compounds changes from  $Cmcm$  to  $C222_1$  to  $Fm-3m$  [24]. For  $\text{Ln} = \text{Nd}$  and  $\text{Ho}$  compounds, two-phases coexist at room temperature. With increasing temperature, they changed to a single-phase compound with the space group  $Cmcm$  (for  $\text{Ln} = \text{Nd}$ ) and  $C2_12_12_1$  (for  $\text{Ln} = \text{Ho}$ ). Similar change of the structure with increasing temperature and with decreasing the size of  $\text{Ln}^{3+}$  ions has been observed for diamagnetic  $M$  ions, i.e.,  $M^{5+} = \text{Nb}^{5+}, \text{Sb}^{5+}$  [38, 40].

Figure 4 shows the variation of the structural phase transition temperatures of  $\text{Ln}_3\text{MoO}_7$  against the ionic radius of  $\text{Ln}^{3+}$  in eight-coordination. The data for a series of  $\text{Ln}_3\text{MO}_7$  ( $M = \text{Re, Os, Ir, Ru}$ ) compounds are also shown in the same figure. These  $M^{5+}$  ions have a  $d$ -electron configuration ranging from  $d^1$  to  $d^4$ , indicating that the  $\text{Ln}_3\text{MO}_7$  compounds are magnetically active. For each of the five series of  $\text{Ln}_3\text{MO}_7$  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 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 trend of the transition temperature against  $\text{Ln}^{3+}$  radius for  $\text{Ln}_3\text{MoO}_7$  is different from those for  $\text{Ln}_3\text{MO}_7$  ( $M = \text{Ru, Re, Os, Ir}$ ). The reason for this may be related to the difference in their high-temperature structures, that is, the  $\text{Ln}_3\text{MoO}_7$  exists in the  $Pnma$  structure, whereas the other  $\text{Ln}_3\text{MO}_7$  ( $M = \text{Ru, Re, Os, Ir}$ ) exists in the  $Cmcm$  structure.

### 3.2. Magnetic properties

### 3.2.1. General magnetic properties of $Ln_3MoO_7$

In the preceding paper, we briefly reported magnetic properties of  $Ln_3MoO_7$  compounds [30]. In this study, we performed measurements of magnetic susceptibilities and specific heat for  $Gd_3MoO_7$  and re-measured magnetic susceptibilities and specific heat of  $Sm_3MoO_7$ . Table 4 summarizes their results with the data reported by Greedan et al. [28] and Gall and Gougeon [39]. The  $La_3MoO_7$  shows complex magnetic behavior at 150 and 380 K. Below these temperatures, there is a large difference in the temperature-dependence of the magnetic susceptibility measured under zero-field-cooled condition and under field-cooled condition [28, 30]. The magnitude of the susceptibility of  $La_3MoO_7$  is much smaller than that expected by about a factor of  $10^{-2}$  for a simple  $S = 1/2$  paramagnet, and there is no Curie-Weiss regime in the experimental temperature range. Therefore, magnetic properties of  $Ln_3MoO_7$  are mainly due to the magnetic behavior of  $Ln^{3+}$  ions in the compounds. The  $Nd_3MoO_7$  and  $Gd_3MoO_7$  show a clear antiferromagnetic transition at 2.5 and 1.9 K, respectively. From the susceptibility measurements, both  $Pr_3MoO_7$  and  $Sm_3MoO_7$  show the existence of magnetic anomaly at 8.0 and 2.5 K, respectively. Other compounds ( $Ln = Ce, Eu$ ) are paramagnetic down to 1.8 K [30, 39]. The effective magnetic moments and the Weiss constants were determined in the Curie-Weiss law temperature region. For  $Sm_3MoO_7$  and  $Eu_3MoO_7$ , the susceptibility does not obey the Curie-Weiss law because  $Sm^{3+}$  and  $Eu^{3+}$  ions show the well-known van Vleck paramagnetism [43].

### 3.2.2. Magnetic properties of $Gd_3MoO_7$

Figure 5 shows the temperature dependence of the magnetic susceptibility for  $Gd_3MoO_7$  in the low temperature region. An antiferromagnetic transition has been observed at 1.9 K. There is no divergence between the ZFC and FC susceptibilities. The inset of Fig. 5 shows the reciprocal

susceptibility versus temperature curve and the Curie-Weiss fitting in the temperature range of 10 to 400 K. The effective magnetic moment of  $\text{Gd}_3\text{MoO}_7$  is determined to be  $14.06 (2) \mu_B$ . From this value, the magnetic moment of each  $\text{Gd}^{3+}$  ion is calculated to be  $8.12 (1) \mu_B$ , which is a little larger than the moment of free  $\text{Gd}^{3+}$  ion ( $7.94 \mu_B$ ), indicating the magnetic contribution of  $\text{Mo}^{5+}$  ion.

In order to obtain the information on the low-temperature magnetic behavior, specific heat measurements were performed down to 0.4 K. Figure 6 (a) shows the temperature dependence of the specific heat divided by temperature ( $C_p/T$ ) for  $\text{Gd}_3\text{MoO}_7$ . A clear  $\lambda$ -type specific heat anomaly has been observed at 1.9 K, which corresponds to the results by magnetic susceptibility measurements. 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  $\text{La}_3\text{MoO}_7$  (the solid line of Fig. 6 (a)). From the temperature dependence of the magnetic specific heat, the magnetic entropy change for  $\text{Gd}_3\text{MoO}_7$  ( $S_{\text{mag}}$ ) is calculated by the relation  $S_{\text{mag}} = \int (C_{\text{mag}}/T) dT$ . Temperature dependences of the magnetic specific heat divided by temperature ( $C_{\text{mag}}/T$ ) and the magnetic entropy change ( $S_{\text{mag}}$ ) for  $\text{Gd}_3\text{MoO}_7$  are shown in Fig. 6 (b). The total magnetic entropy change is  $\sim 34$  J/mol K, and this value is a little smaller than the value of  $3R \ln 8 = 51.9$  J/mol K ( $R$ : gas constant). One reason for this is that we do not include the magnetic specific heat below 0.4 K in the estimation of the magnetic entropy change. Anyway, the results indicate that all the  $\text{Gd}^{3+}$  ions contribute to the antiferromagnetic transition and that the ground state of the  $\text{Gd}^{3+}$  ions is still eight-degenerate ( ${}^8S_{7/2}$ ) without crystal field splitting.

### 3.2.3. Low-temperature magnetic properties of $\text{Sm}_3\text{MoO}_7$

Measurements of the specific heat down to 0.4 K for  $\text{Sm}_3\text{MoO}_7$  and the analysis of the magnetic

specific heat indicate a “two-step” antiferromagnetic transition due to the ordering of Mo magnetic moments in different crystallographic sites.

Figure 7 shows the temperature dependence of the magnetic susceptibility for  $\text{Sm}_3\text{MoO}_7$  in the low temperature region. Small magnetic anomaly has been observed at 2.5 K, but the susceptibility increases with decreasing temperature below this temperature. There is no divergence between the ZFC and FC susceptibilities, even below this temperature. Figure 8 (a) shows the temperature dependence of the specific heat ( $C_p$ ) for  $\text{Sm}_3\text{MoO}_7$ . A  $\lambda$ -type specific heat anomaly has been observed at 2.5 K, which corresponds to the results by magnetic susceptibility measurements. In addition, another  $\lambda$ -type specific heat anomaly has been found at 0.8 K, indicating the existence of another magnetic ordering at this temperature. The magnetic specific heat of  $\text{Sm}_3\text{MoO}_7$  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  $\text{Gd}_3\text{MoO}_7$ . The temperature dependences of the magnetic specific heat divided by temperature ( $C_{\text{mag}}/T$ ) and the magnetic entropy change ( $S_{\text{mag}}$ ) for  $\text{Sm}_3\text{MoO}_7$  are shown in Fig. 8 (b). 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 [44] (the dotted line of Fig. 8 (b)). The magnetic entropy change associated with the sum of the two magnetic anomalies (at 0.8 and 2.5 K) is determined to be 15.3 J/mol K. The  $\text{Sm}^{3+}$  ions in the  $\text{Sm}_3\text{MoO}_7$  occupy two crystallographic sites, the 8-coordinated Sm(1) site and 7-coordinated Sm(2) site, with the ratio 1:2. In both sites, the ground multiplet  $^4I_{9/2}$  of the  $\text{Sm}^{3+}$  ion should be split into five Kramers doublets by the crystal field in the orthorhombic symmetry. At sufficiently low temperatures, only the lowest doublet of each  $\text{Sm}^{3+}$  ions needs to be considered. The observed value of magnetic entropy is close to  $3R \ln 2 = 17.3$  J/mol K, which indicates that the ground doublets for three  $\text{Sm}^{3+}$  ions cause the

antiferromagnetic ordering.

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 higher temperature (2.5 K) is larger than that at a lower temperature (0.8 K), and the magnetic entropy seems to show a step-wise increase ( $R\ln 2 + 2R\ln 2$ ) corresponding to two specific heat anomalies at 0.8 and 2.5 K, respectively. This experimental result suggests that the anomalies observed at 0.8 and 2.5 K are due to the antiferromagnetic ordering of  $\text{Sm}^{3+}$  ions independently in the 8-coordinated Sm(1) and 7-coordinated Sm(2) sites, respectively. Similar “two-step” antiferromagnetic transitions have been found in  $\text{Ln}_3\text{TaO}_7$  ( $\text{Ln} = \text{Nd}, \text{Tb}$ ) [24],  $\text{Ln}_3\text{NbO}_7$  ( $\text{Ln} = \text{Nd}, \text{Tb}$ ) [38], and  $\text{Gd}_3\text{SbO}_7$  [40].

#### 3.2.4. Comparison of the magnetic properties of $\text{Ln}_3\text{MoO}_7$ with those of $\text{Ln}_3\text{MO}_7$ ( $M = \text{Nb}, \text{Ta}, \text{Sb}, \text{Re}, \text{Os}, \text{Ir}, \text{Ru}$ )

Table 5 lists the magnetic properties of  $\text{Ln}_3\text{MoO}_7$  with those of  $\text{Ln}_3\text{MO}_7$  compounds ( $M = \text{Nb}, \text{Ta}, \text{Sb}, \text{Re}, \text{Os}, \text{Ir}, \text{Ru}$ ). Since the pentavalent Nb, Ta, and Sb ions are diamagnetic, only the trivalent Ln ions contribute to the magnetic properties of  $\text{Ln}_3\text{MO}_7$  compounds. Their magnetic properties are very similar. For example, any of the  $\text{Ln} = \text{Nd}$  compounds shows “two-step” antiferromagnetic transitions at 0.6 ~ 3.0 K. All  $\text{Ln} = \text{Tb}$  compounds order at 2.2 ~ 3.9 K. Other compounds such as  $\text{Ln} = \text{Pr}, \text{Sm}, \text{Eu}, \text{Er}, \text{Tm},$  and  $\text{Yb}$  are paramagnetic. Although  $\text{Ir}^{5+}$  ions have  $5d^2$  unpaired electrons, magnetic properties of  $\text{Ln}_3\text{IrO}_7$  compounds are close to those of  $\text{Ln}_3\text{MO}_7$  ( $M = \text{Nb}, \text{Ta}, \text{Sb}$ ) compounds, that is, a  $\text{Ln} = \text{Nd}$  compound shows an antiferromagnetic ordering at almost the same temperature, 2.6 K, and other  $\text{Ln}_3\text{IrO}_7$  ( $\text{Ln} = \text{Pr}, \text{Sm}, \text{Eu}$ ) compounds are paramagnetic down to 1.8 K. It seems that  $\text{Ir}^{5+}$  ions do not contribute to the magnetic properties of  $\text{Ln}_3\text{IrO}_7$  compounds. On the other hand, both  $\text{Os}^{5+}$  and  $\text{Ru}^{5+}$  ions

have the largest possible spin ( $S = 3/2$ ) and any of the  $Ln_3MO_7$  compounds containing these  $M^{5+}$  ions shows a variety of magnetic transitions at relatively high temperatures. Their magnetic properties are due to both  $Ln^{3+}$  and  $M^{5+}$  ions, and therefore could be modulated as a function of the electronic configuration of the  $Ln^{3+}$  ions. Magnetic properties of  $Ln_3MoO_7$  compounds are not classified into any of the above mentioned two categories, and are unique, as described in this paper.

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## Figure captions

Fig. 1 Powder X-ray diffraction profiles for  $Gd_3MoO_7$ . 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  $Ln_3MoO_7$ . (a): Structure at room temperature (space group:  $P2_12_12_1$ ); (b): Structure of  $La_3MoO_7$  at 460 K (space group:  $Pnma$ ).

Fig. 3. (a) Powder X-ray diffraction profiles of  $La_3MoO_7$  at 300 and 460 K. (b) The profiles in the low  $2\theta$  range ( $15^\circ \leq 2\theta \leq 40^\circ$ ).

Fig. 4. 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. 5. Temperature dependence of magnetic susceptibility for  $Gd_3MoO_7$  at low temperatures. The inset shows the reciprocal susceptibility vs. temperature curve. The solid line is the Curie-Weiss fitting.

Fig. 6. (a) Temperature dependence of the specific heat divided by temperature ( $C_p/T$ ) for  $Gd_3MoO_7$ . (b) Temperature dependences of the magnetic specific heat divided by temperature ( $C_{mag}/T$ ) and the magnetic entropy change ( $S_{mag}$ ) for  $Gd_3MoO_7$ .

Fig. 7. Temperature dependence of the magnetic susceptibility for  $Sm_3MoO_7$  below 15 K.

Fig. 8. (a) Temperature dependence of the specific heat ( $C_p$ ) for  $Sm_3MoO_7$ . (b) Temperature dependences of the magnetic specific heat divided by temperature ( $C_{mag}/T$ ) and the magnetic entropy change ( $S_{mag}$ ) for  $Sm_3MoO_7$ .

Table 1. Lattice and positional parameters for Gd<sub>3</sub>MoO<sub>7</sub>

Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> / Å <sup>2</sup>	
Space Group: <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> <i>a</i> = 7.4459(1) Å, <i>b</i> = 7.4840(1) Å, <i>c</i> = 10.5620(2) Å					
<i>R</i> <sub>I</sub> = 2.26 %, <i>R</i> <sub>wp</sub> = 9.91 %					
Gd(1)	4 <i>a</i>	0.9801(2)	0.0100(5)	0.7573(6)	0.45(2)
Gd(2)	4 <i>a</i>	0.7145(1)	0.7536(8)	0.5334(2)	0.45
Gd(3)	4 <i>a</i>	0.6970(5)	0.7479(8)	0.9843(2)	0.45
Mo	4 <i>a</i>	0.4955(5)	0.0020(8)	0.7518(8)	0.10(4)
O(1)	4 <i>a</i>	0.574(2)	0.742(4)	0.763(2)	0.50(30)
O(2)	4 <i>a</i>	0.782(3)	0.969(4)	0.143(2)	0.50
O(3)	4 <i>a</i>	0.128(3)	0.048(4)	0.109(2)	0.50
O(4)	4 <i>a</i>	0.832(3)	0.962(4)	0.388(2)	0.50
O(5)	4 <i>a</i>	0.216(3)	0.034(4)	0.368(2)	0.50
O(6)	4 <i>a</i>	0.960(3)	0.740(6)	0.879(3)	0.50
O(7)	4 <i>a</i>	0.011(3)	0.771(5)	0.606(3)	0.50

Note:  $R_{wp} = \left[ \frac{\sum w(|F(o)| - |F(c)|)^2}{\sum w|F(o)|^2} \right]^{1/2}$  and

$$R_I = \frac{\sum |I_k(o) - I_k(c)|}{\sum I_k(o)}.$$

Table 2. Lattice and positional parameters for La<sub>3</sub>MoO<sub>7</sub>

	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> / Å <sup>2</sup>
300 K					
Space Group: <i>P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub></i> <i>a</i> = 7.6043(3) Å, <i>b</i> = 7.7225(4) Å, <i>c</i> = 11.1090(7) Å					
<i>R<sub>I</sub></i> = 1.83 %, <i>R<sub>wp</sub></i> = 9.18 %					
La(1)	4 <i>a</i>	0.9801(2)	0.0078(5)	0.7555(6)	0.34(2)
La(2)	4 <i>a</i>	0.6935(1)	0.7522(8)	0.5352(2)	0.34
La(3)	4 <i>a</i>	0.6923(5)	0.7487(8)	0.9795(2)	0.34
Mo	4 <i>a</i>	0.4960(5)	0.0018(8)	0.7496(8)	0.19(4)
O(1)	4 <i>a</i>	0.571(2)	0.746(4)	0.760(2)	0.21(15)
O(2)	4 <i>a</i>	0.799(3)	0.962(4)	0.132(2)	0.21
O(3)	4 <i>a</i>	0.139(3)	0.049(4)	0.114(2)	0.21
O(4)	4 <i>a</i>	0.825(3)	0.952(4)	0.382(2)	0.21
O(5)	4 <i>a</i>	0.197(3)	0.048(4)	0.375(2)	0.21
O(6)	4 <i>a</i>	0.970(3)	0.765(6)	0.885(3)	0.21
O(7)	4 <i>a</i>	0.984(3)	0.770(5)	0.624(3)	0.21
460 K					
Space Group: <i>Pnma</i> <i>a</i> = 7.7273(2) Å, <i>b</i> = 11.1406(3) Å, <i>c</i> = 7.5881(2) Å					
<i>R<sub>I</sub></i> = 2.31 %, <i>R<sub>wp</sub></i> = 12.06 %					
La(1)	4 <i>c</i>	0.0030(9)	1/4	0.7590(6)	0.76(3)
La(2)	8 <i>d</i>	0.2498(7)	0.4720(1)	0.4422(2)	0.76
Mo	4 <i>c</i>	0.9965(13)	1/4	0.2486(9)	0.24(6)
O(1)	8 <i>d</i>	0.974(4)	0.370(3)	0.433(4)	0.72(20)
O(2)	8 <i>d</i>	0.945(4)	0.880(3)	0.922(4)	0.72
O(3)	8 <i>d</i>	0.232(4)	0.384(1)	0.724(2)	0.72
O(4)	4 <i>c</i>	0.263(7)	1/4	0.312(2)	0.72

Note:  $R_{wp} = \left[ \frac{\sum w(|F(o)| - |F(c)|)^2}{\sum w|F(o)|^2} \right]^{1/2}$  and

$$R_I = \frac{\sum |I_k(o) - I_k(c)|}{\sum I_k(o)}.$$

Table 3 Crystal structures of  $Ln_3MO_7$  at room temperature

$Ln$	$Ln_3MoO_7$	$Ln_3NbO_7$	$Ln_3TaO_7$	$Ln_3SbO_7$	$Ln_3ReO_7$	$Ln_3OsO_7$	$Ln_3IrO_7$	$Ln_3RuO_7$
La	$P2_12_12_1$	$Pnma$	$Cmcm$	$Cmcm$		$Cmcm$		$Cmcm$
Pr	↓	↓	↓	↓	$Cmcm$	↓	$Cmcm$	↓
Nd	↓	↓	↓ } $C222_1$	↓ } $C222_1$	↓	↓	↓	↓
Sm	↓	$C222_1$	↓	↓	↓	↓	↓	↓
Eu	↓	↓	↓	↓	↓	↓	↓	↓
Gd	↓	↓	↓	↓	↓	↓		$P2_1nb$
Tb	↓	↓	↓	↓	↓ } $C222_1$	↓		↓
Dy	↓	$Fm-3m$	↓	↓	↓	↓		↓
Ho	↓	↓	↓ } $Fm-3m$	↓	↓	↓		↓
Er	↓	↓	↓	↓	↓	↓		↓
Tm	↓	↓	↓	↓	↓	↓		↓
Yb	↓	↓	↓	↓	↓	↓		↓
Lu	↓	↓	↓	↓	↓	↓		↓

Note: A symbol } denotes that two phases coexist.

Table 4 Magnetic data for  $Ln_3MoO_7$ 

	magnetic properties	$\mu_{\text{eff}}$ ( $\mu_B$ )	$\theta$ (K)	Ref.
$La_3MoO_7$	magnetic anomaly at 150, 380 K			[28,30]
$Ce_3MoO_7$	paramagnetic	2.49	-155	[39]
$Pr_3MoO_7$	magnetic anomaly at 8.0 K	6.42	-79(1)	[30]
$Nd_3MoO_7$	antiferromagnetic, $T_N = 2.5$ K	6.46	-57.4(8)	[30]
$Sm_3MoO_7$	magnetic anomaly at 0.8, 2.5 K	*	*	this study
$Eu_3MoO_7$	paramagnetic	*	*	[30]
$Gd_3MoO_7$	antiferromagnetic, $T_N = 1.9$ K	14.06(2)	-7.4(1)	this study

\*  $Sm^{3+}$  and  $Eu^{3+}$  ions show the van Vleck paramagnetism.

Table 5 Magnetic Properties of  $Ln_3MO_7$ 

$Ln$	$Ln_3MoO_7$	$Ln_3NbO_7$	$Ln_3TaO_7$	$Ln_3SbO_7$	$Ln_3ReO_7$	$Ln_3OsO_7$	$Ln_3IrO_7$	$Ln_3RuO_7$
La	$T_N = 150$ K	–	dia	dia		$T_N = 45$ K		$T_N = 18$ K
Pr	anomaly at 8.0 K	para	para	para	spin-glass like at 10 K	-	para	$T_N = 55$ K
Nd	$T_N = 2.5$ K	$T_N = 0.6,$ 2.6 K	$T_N = 2.1,$ 2.6 K	$T_N = 2.5,$ 3.0 K	long-range magnetic order at 9 K	$T_C = 75$ K	$T_N = 2.6$ K	$T_N = 19$ K
Sm	anomaly at 0.8, 2.5 K	para	para	para	$T_N = 1.9$ K	weak ferro $T_C = 48$ K	para	$T_N = 10.5,$ 22.5 K
Eu	para	para	para	para	anomaly at 12 K	complex behavior at 50 K	para	$T_N = 22.5$ K
Gd	$T_N = 1.9$ K	para	para	$T_N = 2.6$ K	$T_N = 7.0$ K	ferro $T_C = 34$ K		$T_N = 9.5, 15$ K
Tb		$T_N = 2.2,$ 3.9 K	$T_N = 2.9,$ 3.6 K	$T_N = 3.0$ K	$T_N = 14.0$ K			
Dy		para	$T_N = 2.3$ K	$T_N = 3.2$ K	$T_N = 2.8$ K			
Ho		para	weak ferro $T_N = 2.6$ K	$T_N = 2.2$ K	para			
Er		para	para	para				
Tm		para	para	para				
Yb		para	para	para				
Lu		–	dia	dia				

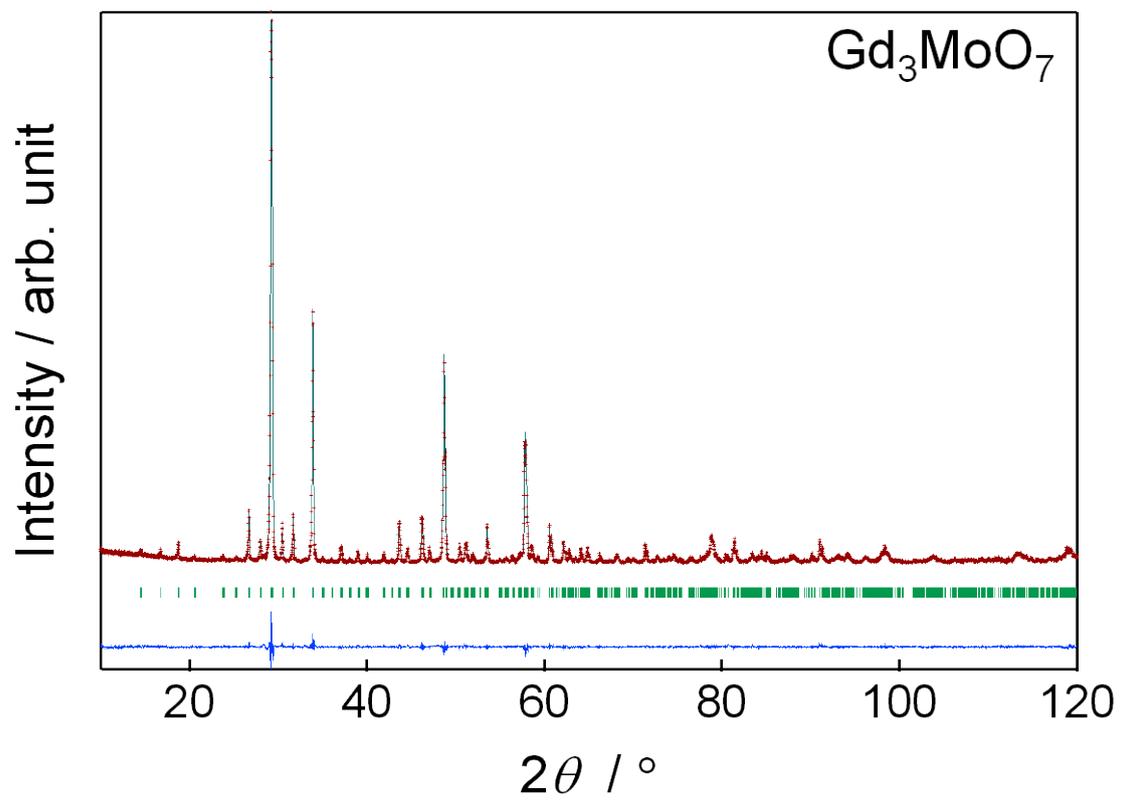
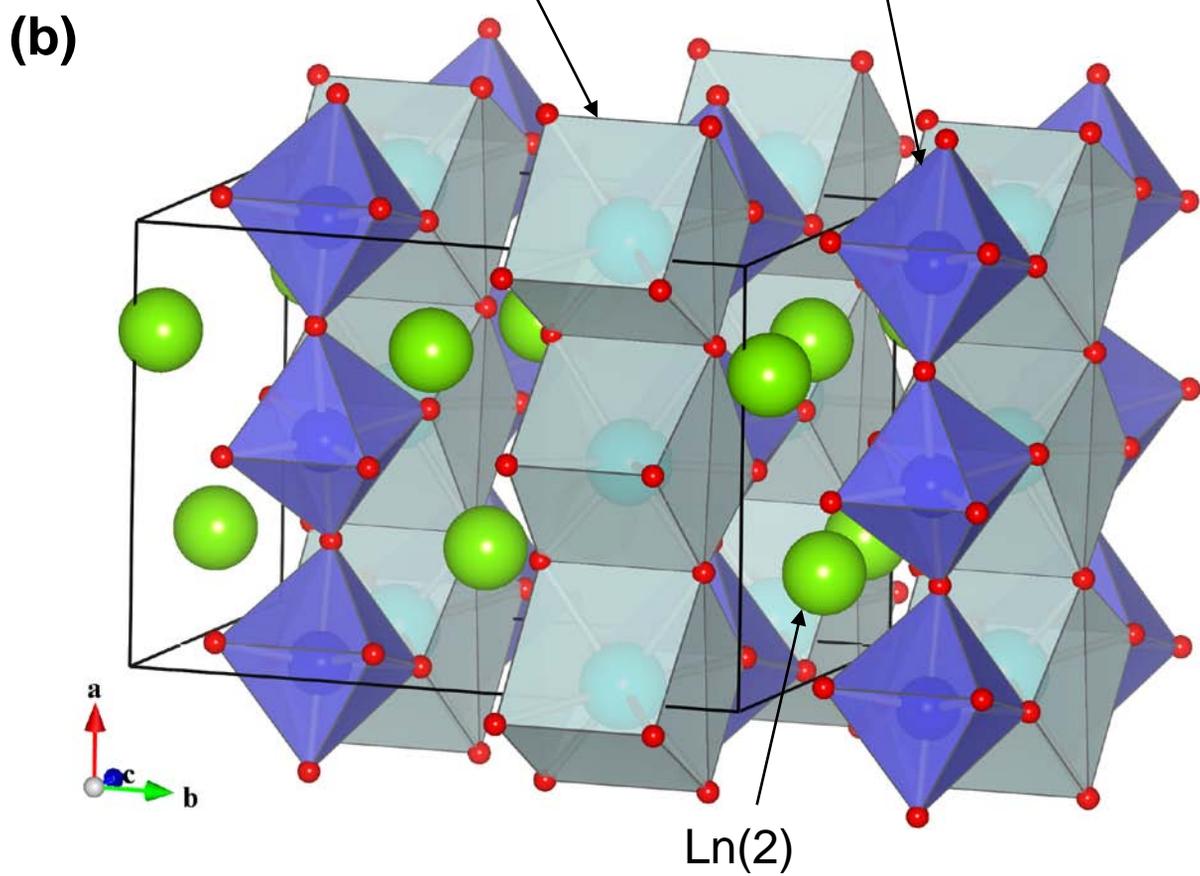
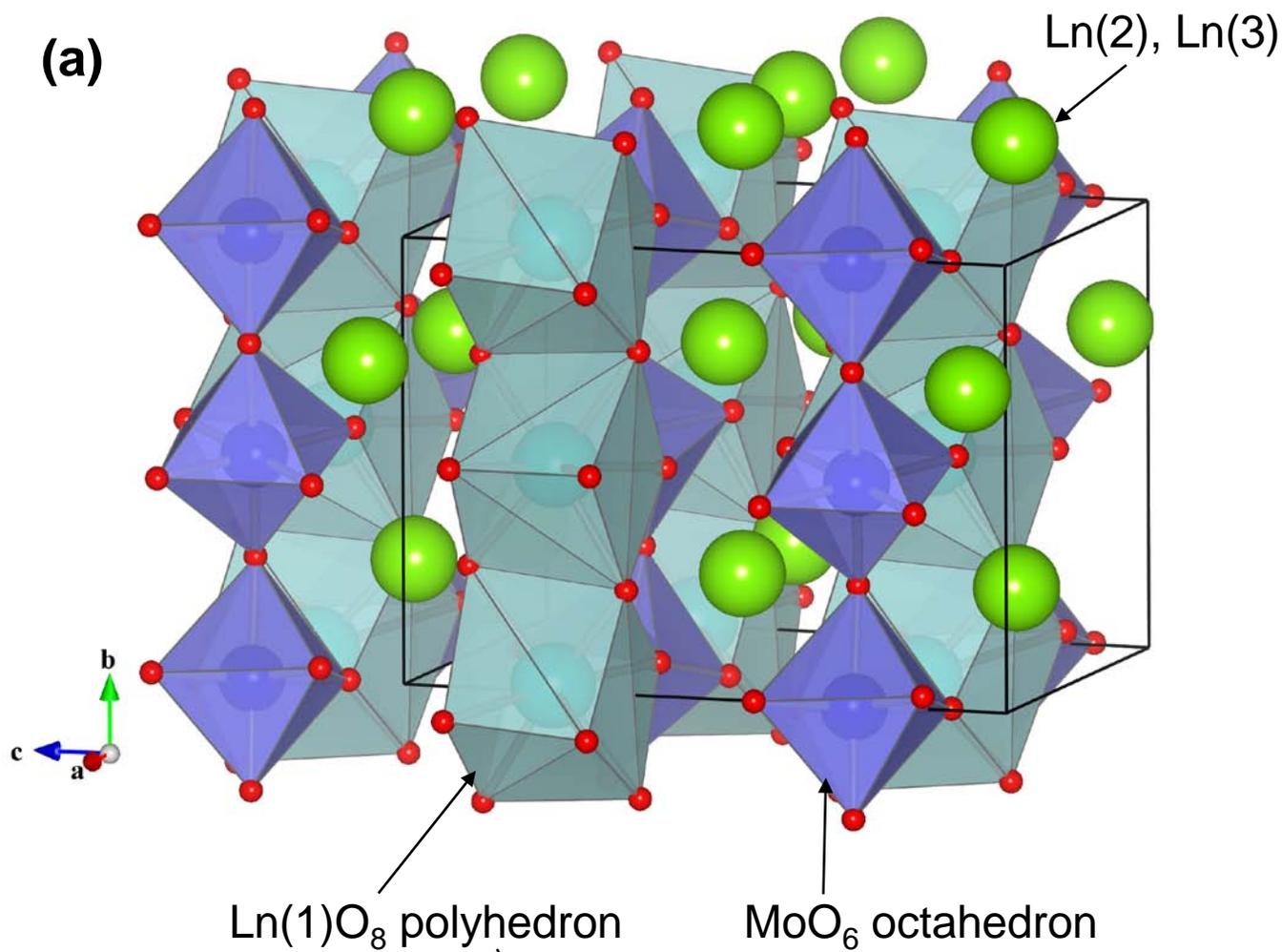


Fig. 1



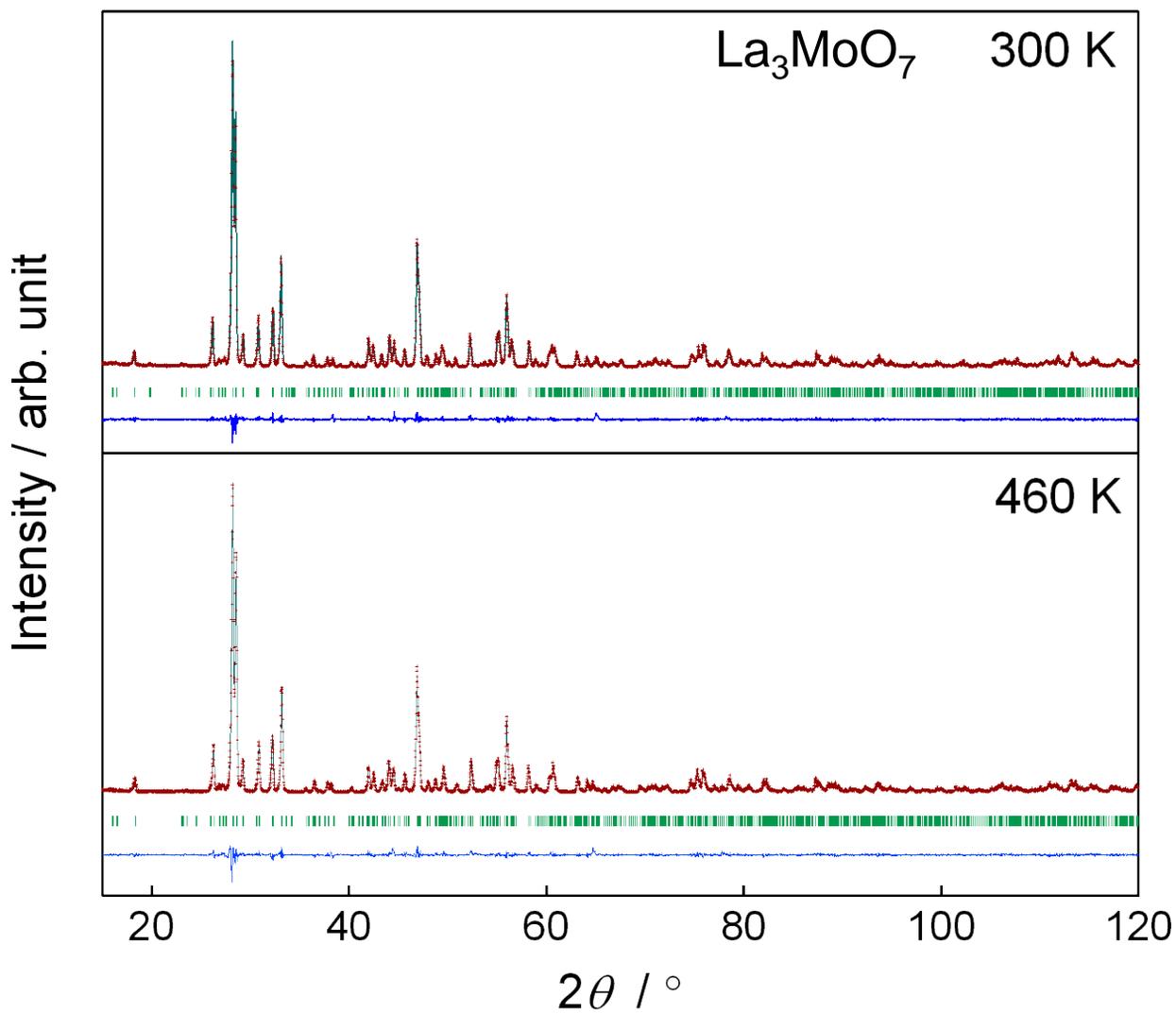


Fig. 3 (a)

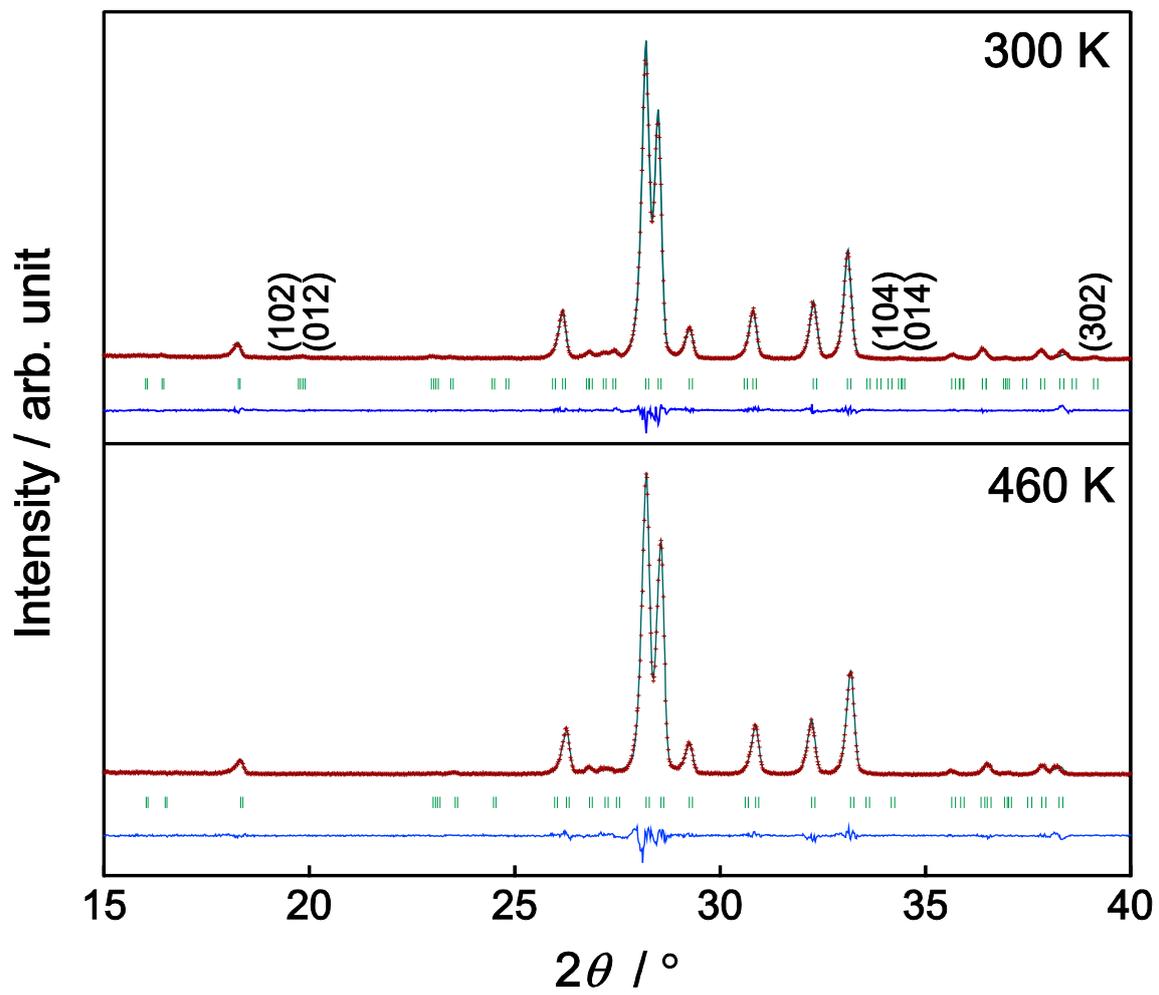


Fig. 3(b)

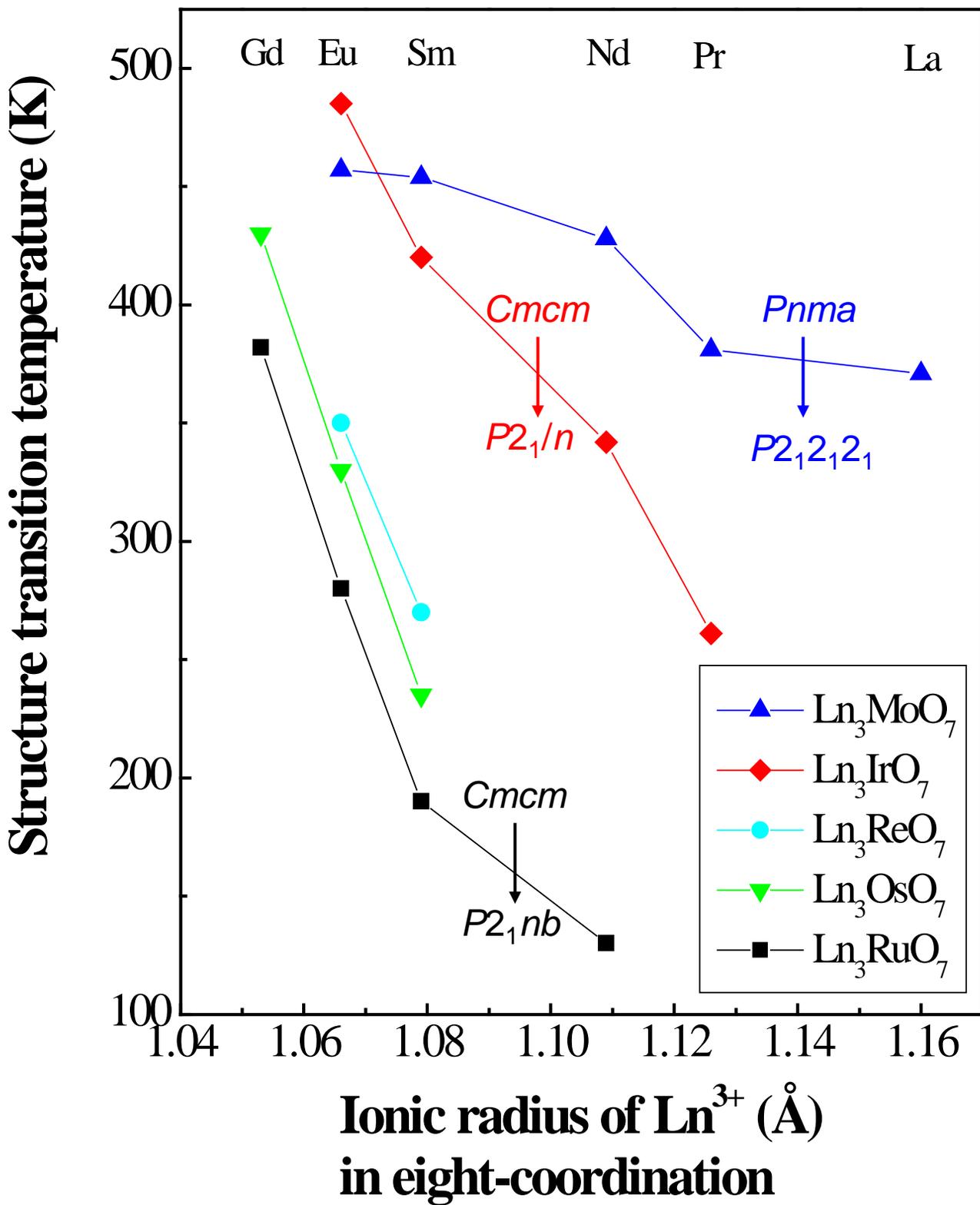


Fig. 4

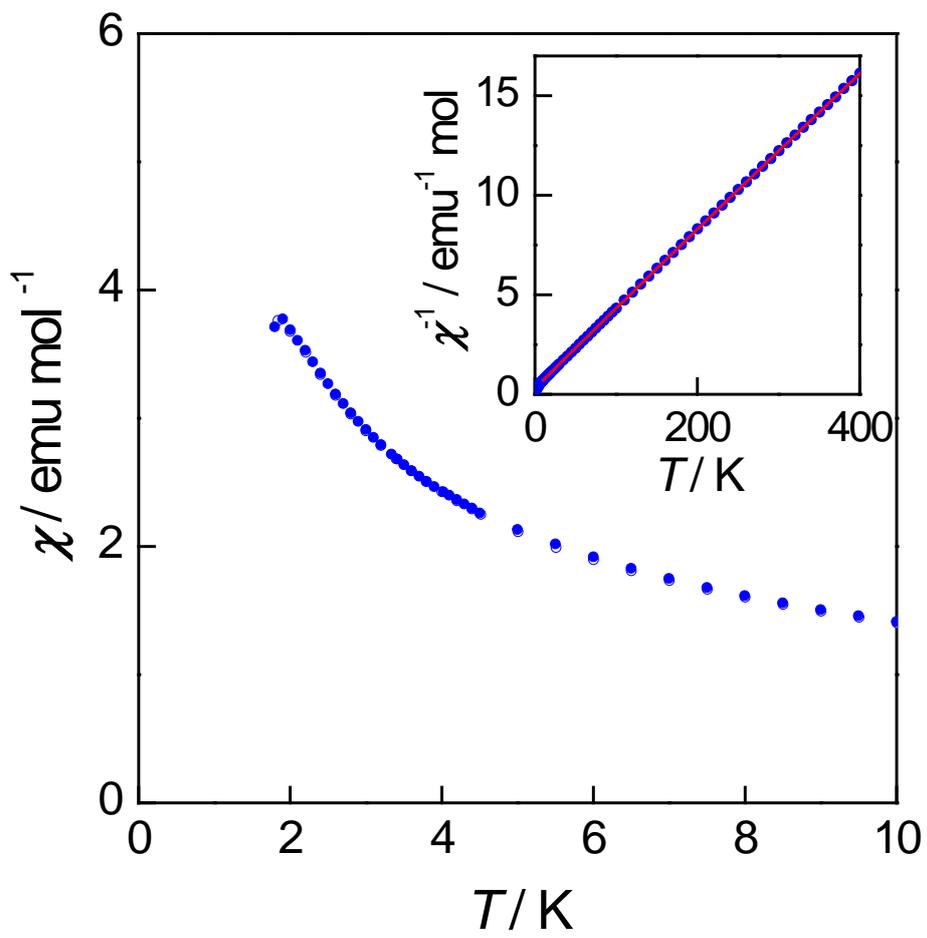
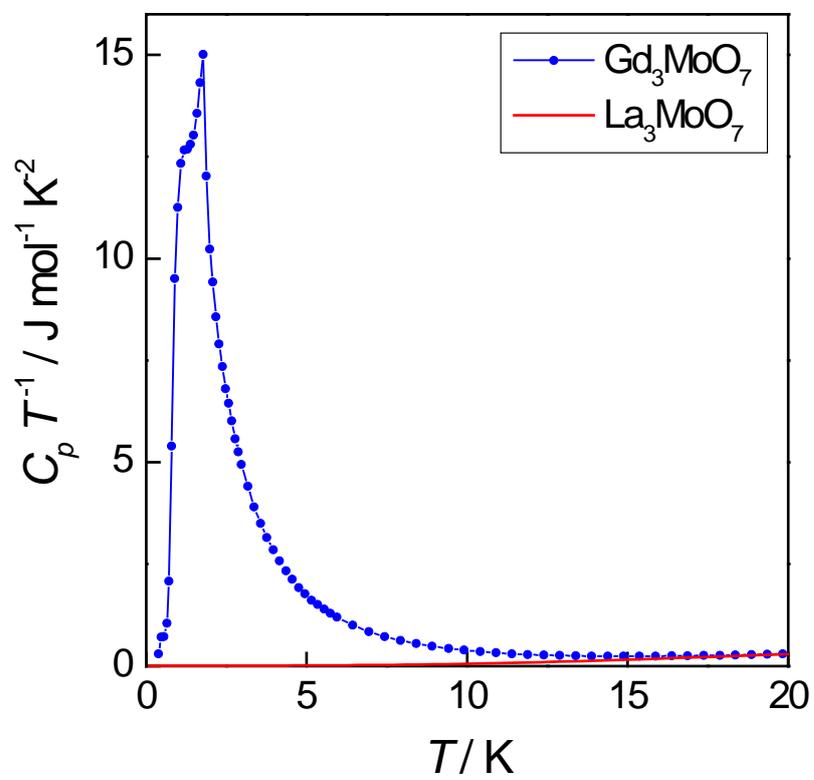


Fig. 5

(a)



(b)

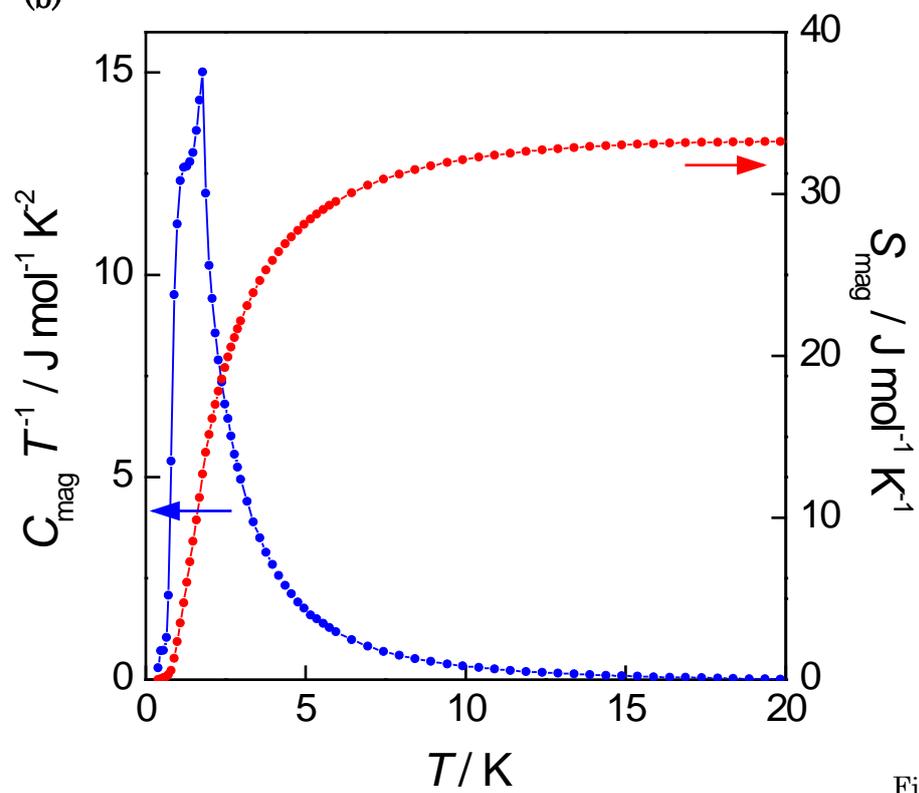


Fig. 6

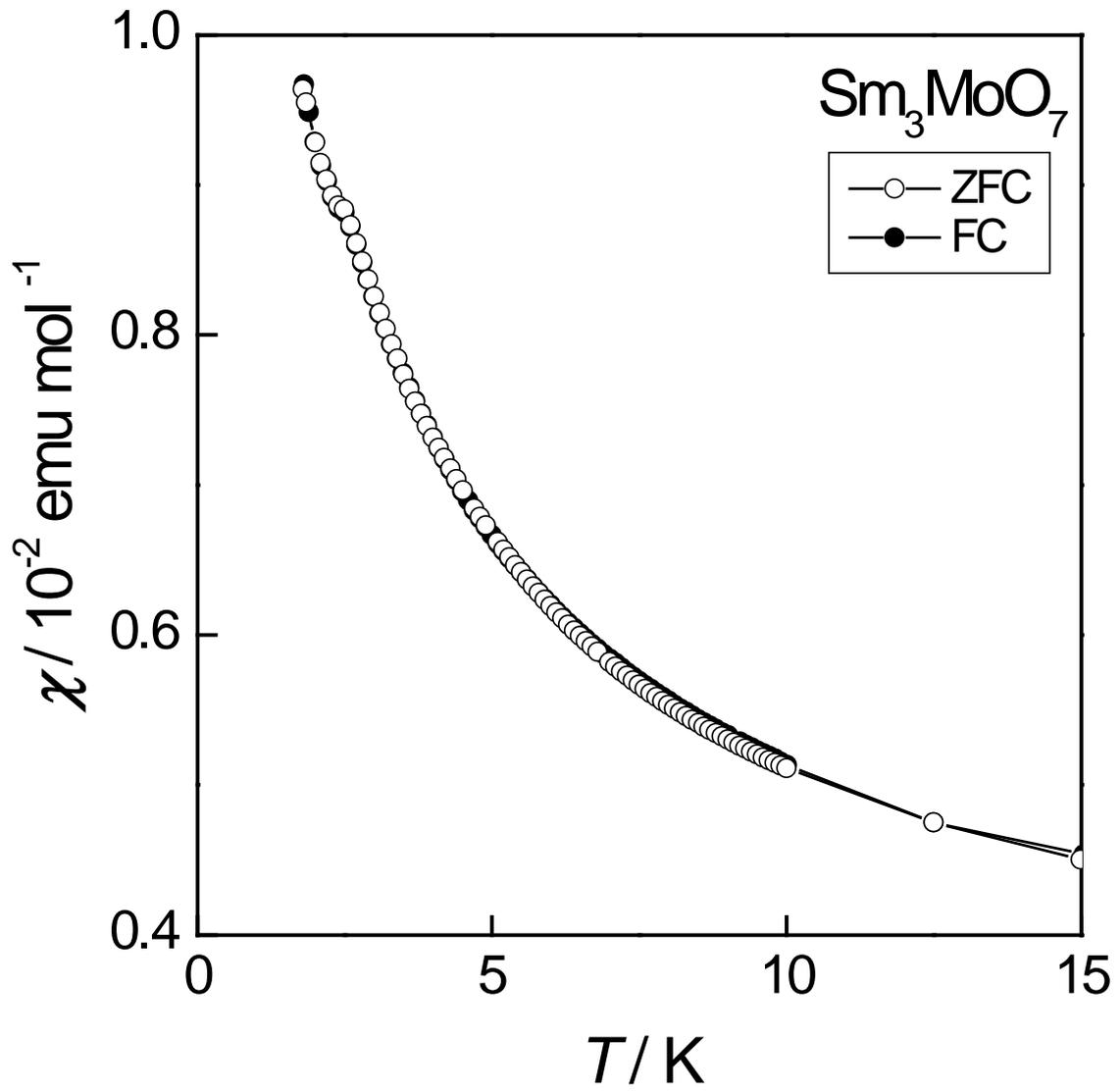
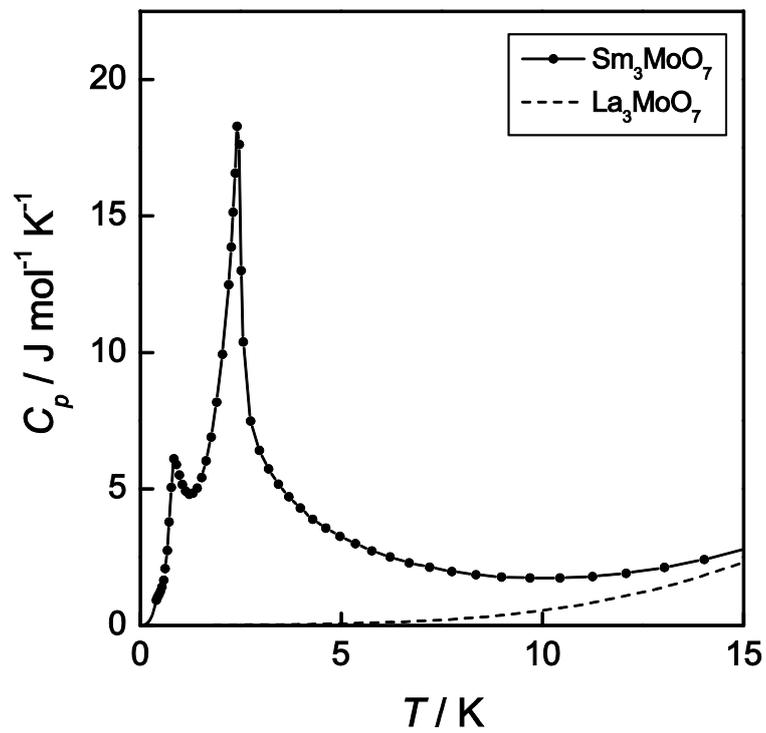


Fig. 7

(a)



(b)

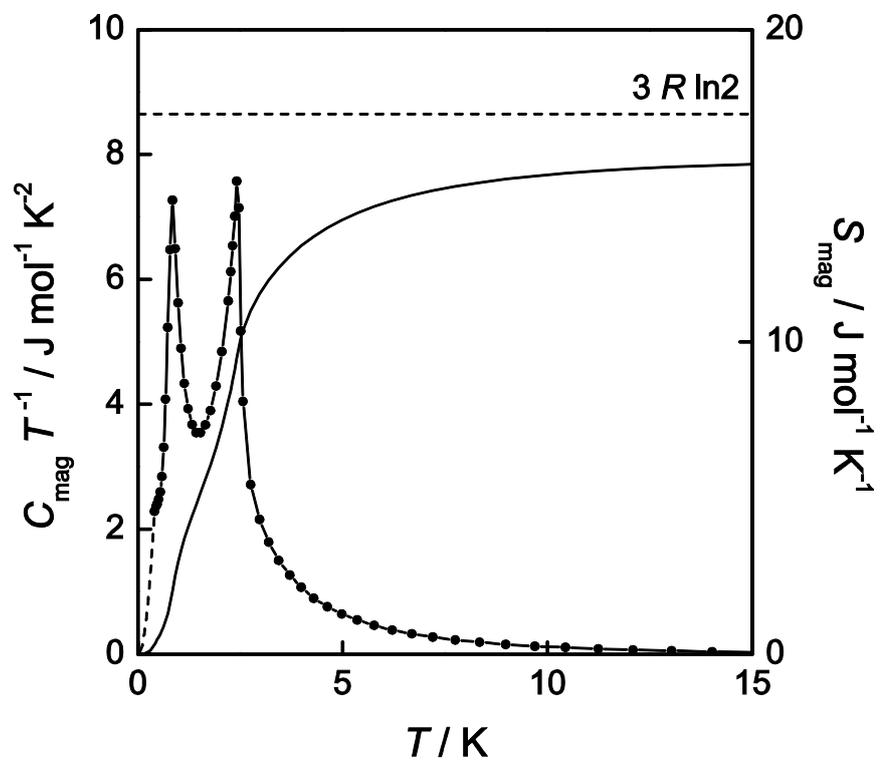


Fig.8