Magnetic Ordering of Divalent Europium in Double Perovskites Eu$_2$LnTaO$_6$ (Ln = Rare Earths)

-Magnetic Interactions of Eu$^{2+}$ ions Determined by Magnetic Susceptibility, Specific Heat, and $^{151}$Eu Mössbauer Spectrum Measurements-

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ABSTRACT

Structures and magnetic properties of double perovskite-type oxides Eu$_2$LnTaO$_6$ (Ln = Eu, Dy ~ Lu) were investigated. These compounds adopt a distorted double perovskite structure with space group $P2_1/n$. Magnetic susceptibility, specific heat, and $^{151}$Eu Mössbauer spectrum measurements show that the Eu$^{2+}$ ions at the 12-coordinate sites of the perovskite structure are antiferromagnetically ordered at $\sim$ 4 K, and that Ln$^{3+}$ ions at the 6-coordinate site are in the paramagnetic state down to 1.8 K.

Keywords: magnetic properties; perovskite; europium; magnetic susceptibility; specific heat; Mössbauer spectrum.
1. Introduction

It is well known that the magnetism of perovskite-type oxides ABO₃ is due to the B-site cations because the three-dimensional network of BO₆ octahedra gives the linear superexchange B–O–B pathway. On the other hand, the magnetic interaction between A-site cations is too weak, and we can seldom observe it down to 4.2 K.

It is reported that divalent europium perovskites Eu²⁺M⁴⁺O₃ (M = Ti, Zr; diamagnetic) show an antiferromagnetic ordering at 4 ~ 6 K [1, 2]. In addition, when paramagnetic ions such as Nb⁵⁺ ions are introduced at the B-site of the perovskites, those compounds sometimes show ferromagnetic behavior at low temperatures [3].

We focused our attention on the Eu²⁺-bearing double perovskites Eu₂LnTaO₆. Since the trivalent Ln ions are located at the B-site of the perovskites, not only the magnetic interactions of the Eu²⁺ ions at the A sites, but also the interactions of the Eu-Ln ions are expected for Eu₂LnTaO₆. Previously, Sato et al. prepared a series of Eu₂LnTaO₆ (Ln = Nd-Yb, Y) compounds, and measured magnetic susceptibilities for Ln = Eu and Gd compounds. However, no magnetic ordering was observed down to 1.6 K [4] In this study, we performed magnetic susceptibility, specific heat, and ¹⁵¹Eu Mössbauer spectrum measurements for Eu₂LnTaO₆ (Ln = La ~ Lu). Since the total number of electrons of Ta⁵⁺ ion is comparable to that of Ln³⁺ ions, the arrangement of the B-site cations is not perfectly determined by the X-ray diffraction
measurements. To ascertain the B-site cation ordering in the Eu\(^{2+}\)-bearing double perovskites Eu\(_2\)LnTaO\(_6\), we also prepared niobium-substituted perovskite compounds Eu\(_2\)LnNbO\(_6\) and measured their X-ray diffraction profiles and magnetic properties.

2. Experimental

2.1. Sample preparation

Polycrystalline samples of Eu\(^{2+}\)-bearing double perovskites Eu\(_2\)LnMO\(_6\) (Ln = La ~ Lu; M = Ta, Nb) were prepared by the standard solid-state reaction. Rare earth oxides (Ln\(_2\)O\(_3\), EuO), Ta\(_2\)O\(_5\), Ta, Nb\(_2\)O\(_5\), and Nb were used as starting materials. The EuO was prepared by heating mixtures of Eu metal (50 % excess) and Eu\(_2\)O\(_3\) in an evacuated quartz tube at 1073 K for 5 h and then at 1323 K for 1 h. These starting materials were well mixed in an agate mortar. The mixtures were pressed into pellets and enwrapped with molybdenum foils, and they were sealed in evacuated silica tubes. They were fired at 1523 K for 12–24 h.

2.2. X-ray diffraction analysis

Powder X-ray diffraction profiles were measured using a Rigaku Multi-Flex diffractometer with Cu-K\(\alpha\) radiation equipped with a curved graphite monochromator. The data were collected by step-scanning in the angle range of 10° ≤ 2\(\theta\) ≤ 120° at a 2\(\theta\) step-size of 0.02°. The X-ray diffraction data were analyzed by the Rietveld technique, using the program RIETAN-FP [5] and the crystal structure was drawn by VESTA program [6].
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 100 to 1.8 K in the applied field of 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 1.8–300 K. The sintered sample in the form of a pellet was mounted on a thin alumina plate with Apiezon grease for better thermal contact.

2.5. $^{151}$Eu Mössbauer spectroscopy measurements

The $^{151}$Eu Mössbauer spectra were measured with a Mössbauer spectrometer VT-6000 (Laboratory Equipment Co.) in the constant acceleration mode using a radiation source $^{151}$SmF$_3$ (1.85 GBq). The spectrometer was calibrated with a spectrum of $\alpha$-Fe at room temperature. The $\gamma$-rays were detected with a NaI scintillation counter. Europium trifluoride (EuF$_3$) was used as a
reference standard for the chemical isomer shift. The sample was wrapped in an aluminum foil so as to have its average surface density of 10 mg (Eu) cm\(^{-2}\).

3. Results and discussion

3.1. Preparation and crystal structure

The Eu\(_2\)LnTaO\(_6\) compounds with Ln = Eu, Dy ~ Lu were successfully prepared, although a small amount (1 ~ 5 \%) of Ln\(_2\)O\(_3\) was contained as an impurity phase. A representative powder X-ray diffraction profile is shown in Fig. 1 (a) for Eu\(_2\)HoTaO\(_6\). The results indicate that these compounds adopt the perovskite-type structure with a much lower symmetry than the cubic perovskite structure reported previously [4], and finally the observed diffraction peaks were indexed on a monoclinic cell. This unit cell is related to the primitive perovskite unit cell (\(a_p\)) by \(a \approx \sqrt{2} a_p\), \(b \approx \sqrt{2} a_p\), \(c \approx 2a_p\). Figure 2 shows the variation of lattice parameters of Eu\(_2\)LnTaO\(_6\) with the ionic radius of Ln\(^{3+}\) ion in the six-coordination. The lattice parameters (\(a\), \(b\), and \(c\)) increase with the ionic radius of Ln\(^{3+}\) ion.

The Eu\(_2\)LnTaO\(_6\) have two kinds of B-site cations; however, its order/disorder arrangement is not perfectly determined by the X-ray diffraction measurements because the total number of electrons of Ta\(^{5+}\) ion is comparable to that of Ln\(^{3+}\) ions. To ascertain the B-site cation ordering in the Eu\(^{2+}\)-bearing double perovskites Eu\(_2\)LnTaO\(_6\), we prepared a europium niobate Eu\(_3\)NbO\(_6\). The
result of the Rietveld analysis for the X-ray diffraction measurements of this niobate is shown in Fig. 1 (b). It is found that this compound has a monoclinic double-perovskite structure with space group $P2_1/n$ and Eu and Nb atoms are structurally ordered at the B-site with rock-salt sublattice. Structural parameters for Eu$_3$NbO$_7$ (atomic positional parameters and isotropic thermal parameters) are listed in Table 1. Since the ionic radius of Ta$^{5+}$ (0.64 Å) is almost the same as that of Nb$^{5+}$ (0.64 Å) [7], we have performed the Rietveld analysis of the X-ray diffraction data for Eu$_2$LnTaO$_6$ by assuming the same structural model as Eu$_3$NbO$_7$. The calculated profiles gave good fittings for all the Eu$_2$LnTaO$_6$ compounds. The refined lattice parameters and reliability factors for Eu$_2$LnTaO$_6$ are summarized in Table 2. Its crystal structure is schematically shown in Fig. 3. Table 3 lists the atomic positional parameters and isotropic thermal parameters for Eu$_2$HoTaO$_6$.

The average bond lengths (Eu–O, Ln–O and Ta–O) of Eu$_2$LnTaO$_6$ were calculated using the refined structural parameters. The oxidation state of the ions in these compounds is estimated by the bond valence sums (BVS) [8, 9]. The BVS values for Eu, Ln, and Ta ions were calculated using the bond lengths, and they are listed in Table 4. The values for the Ln and Ta ions are almost constant (~3.3 and ~5.0, respectively) and they are reasonable for trivalent and pentavalent ions, respectively. The BVS values for the Eu ions are almost 2.0 for any of the Eu$_2$LnTaO$_6$ compounds, indicating that the Eu ions are in the divalent state. The following $^{151}$Eu
Mössbauer spectrum measurements clearly show the oxidation state of the Eu ions in the compounds.

3.2. $^{151}$Eu Mössbauer spectrum

Figure 4 shows the $^{151}$Eu Mössbauer spectra of Eu$_3$TaO$_6$ measured at room temperature. Two absorption peaks appeared at $\delta = -12.3$ and 1.51 mm/sec, indicating that the Eu ions are in both the divalent and the trivalent states. Because of the low symmetry of the Eu sites in Eu$_3$TaO$_6$, the electric field gradient tensor should exist and the nonzero quadrupole interaction is expected at the Eu sites. The quadrupole Hamiltonian is given by

$$H_Q = \frac{e^2 qQ}{4I(2I-1)} \left( 3I_z^2 - I(I+1) + \eta(I_x^2 + I_y^2) \right)$$

(1)

where $I$ is the nuclear spin, $Q$ is the quadrupole moment, $eq = V_{zz}$, and the asymmetric parameter $\eta = (V_{xx} - V_{yy}) / V_{zz}$ ($V_{ii}$ is the electric field gradient tensor). Actually, the spectra exhibited a slightly asymmetric line ($\eta \neq 0$). It is impossible to fit such a spectrum with a single Lorentzian line because of the distortion due to the quadrupole interaction. The 12 possible transitions (eight allowed transitions and four forbidden transitions) due to a quadrupole interaction were taken into account; the observed data were fitted with the sum of these Lorentzian lines (see Fig. 4). In order to derive these Lorentzian equations, the results by Shenoy and Dunlap were used [10] and the ratio of the excited and ground state quadrupole
moments \((R_Q = Q_e/Q_g)\) was taken as 1.312 \([11]\). The fitting parameters, the isomer shift \((\delta)\), the quadrupole coupling constant \((eV_{zz}Q_g)\) and the asymmetry parameter \((\eta)\) are determined for Eu₃TaO₆, and they are listed in Table 5.

Fig. 5 shows the temperature dependence of the absorption area of the intensity curves of Eu²⁺ and Eu³⁺ ions for Eu₃TaO₆. At room temperature, the ratio is Eu²⁺: Eu³⁺ = 2: 1. Both intensities increase monotonously with decreasing temperature, and the increase for Eu²⁺ is larger than that for Eu³⁺. This difference may be due to a small difference in the Debye-Waller factors between Eu²⁺ and Eu³⁺. The area of the intensity curve is proportional to the recoil-free fraction. Therefore, the Debye temperatures for Eu²⁺ and Eu³⁺ are estimated from the recoil-free fraction. The recoil-free fraction is represented by the following equation \([12]\):

\[
f' = \exp \left[ -\frac{6E_R}{k\Theta_D} \left( \frac{1}{4} + \left( \frac{T}{\Theta_D} \right)^2 \right) \int_{0}^{T/\Theta_D} \frac{xdx}{(e^x - 1)} \right]
\]

where \(k\) is the Boltzmann’s constant, \(\Theta_D\) is the Debye temperature, and \(E_R\) is the free-atom recoil energy. By using this equation, the Debye temperatures for Eu²⁺ and Eu³⁺ ions are obtained to be 205 and 270 K, respectively. This result indicates that compared to the Eu²⁺ ions, Eu³⁺ ions are more tightly coordinated to the six oxygen ions.

The $^{151}$Eu Mössbauer spectra of Eu₃NbO₆ measured at room temperature are shown in Fig. 6, which is quite similar to those of Eu₃TaO₆. Two absorption peaks appeared at \(\delta = -12.0\) and 1.56 mm/sec are corresponding to the Eu²⁺ and Eu³⁺ ions, respectively. The absorption areas of
the intensity curves of Eu$^{2+}$ and Eu$^{3+}$ ions are obtained and the ratio is Eu$^{2+}$: Eu$^{3+}$ = 2: 1, showing that the Eu$^{2+}$ ions are located at the A-site of the perovskite-type structure and the Eu$^{3+}$ ions are situated at the B-site.

3.3. Magnetic properties

Temperature dependences of the magnetic susceptibility of Eu$_2$DyTaO$_6$, Eu$_2$HoTaO$_6$, and Eu$_2$LuTaO$_6$ are shown in Figs. 7 (a), (b), and (c), respectively. Any of the compounds prepared in this study showed magnetic anomaly at ca. 4 K, and no divergence between the ZFC and FC susceptibilities was observed in the whole temperature range.

The effective magnetic moments and Weiss constants determined from the Curie-Weiss law are listed in Table 6. The effective magnetic moments for Eu$_2$LnTaO$_6$ should be given by the following equation:

$$\mu_{\text{eff}}^2 = 2\mu_{\text{Eu}^{2+}}^2 + \mu_{\text{Ln}^{3+}}^2. \quad (3)$$

The moments experimentally obtained are almost consistent with the moment calculated by this equation with using the free ion values of Eu$^{2+}$ and Ln$^{3+}$ ions. The Weiss constant for any compound is negative, which corresponds to the occurrence of the antiferromagnetic interactions at ca. 4 K.

To ascertain the magnetic interaction between the Eu$^{2+}$ moments, we performed the
specific heat measurements in the temperature range of 1.8 and 300 K. Figs. 8 (a), (b), and (c) show the temperature dependence of the specific heat $C_p$ for Eu$_2$LnTaO$_6$ (Ln = Dy, Ho, and Lu) at low temperatures, respectively. The specific heat data show a $\lambda$-type anomaly at the temperature at which each magnetic susceptibility shows the antiferromagnetic behavior. To calculate the magnetic contribution to the specific heat ($C_{\text{mag}}$), we have to subtract the contribution of lattice specific heat ($C_{\text{lattice}}$) from the total specific heat ($C_p$), i.e., $C_{\text{mag}} = C_p - C_{\text{lattice}}$. For Eu$_2$LuTaO$_6$, the lattice specific heat was estimated by using a polynomial function of the temperature, $f(T) = aT^3 + bT^5 + cT^7$ [13] (see Fig. 8 (c)), in which the constants $a$, $b$, and $c$ were determined by fitting this function to the observed specific heat data above 30 K. A dashed line in the $C_p - T$ curve below 1.8 K represents the extrapolated specific heat by the relation $C_p \propto T^3$ from the spin-wave model for an antiferromagnet [14]. For the lattice specific heat of Eu$_2$DyTaO$_6$ and Eu$_2$HoTaO$_6$ compounds, the data of Eu$_2$LuTaO$_6$ (the above-mentioned fitting results) were used. From the temperature dependence of the magnetic specific heat ($C_{\text{mag}}$), the magnetic entropy change of Eu$_2$LnTaO$_6$ is calculated by the relation $S_{\text{mag}} = \int \left( C_{\text{mag}} / T \right) dT$. It is shown in Fig. 9. The magnetic entropy change due to the antiferromagnetic ordering is about 30 J mol$^{-1}$ K$^{-1}$ for any of the Eu$_2$LnTaO$_6$ compounds. Magnetic entropy change due to the magnetic ordering of Eu$^{2+}$ ions is expected to be $R \ln(2S+1) = R \ln 8 = 34.5$ J mol$^{-1}$ K$^{-1}$, where $R$ and $S$ are the molar gas constant and the total spin quantum number, respectively. Although the
magnetic entropy change experimentally observed is a little smaller than the theoretically expected value, this result clearly indicates that the magnetic ordering observed at 4~5 K is due to the magnetic interactions between Eu\(^{2+}\) ions at the A-site, and that the Ln\(^{3+}\) ions do not contribute to it. We consider that the difference in the magnetic entropy values found for Ln = Ho and Lu compounds is not due to the magnetic contribution of Ho\(^{3+}\) ions to the magnetic ordering, but due to poor estimation of the lattice specific heat for the Ho compound (see Fig. 8 (b)).

Magnetic ions in the Eu\(_2\)LuTaO\(_6\) are only Eu\(^{2+}\). This compound shows a simple antiferromagnetic behavior, i.e., its magnetic susceptibility decreases with decreasing temperature below the antiferromagnetic temperature (Fig. 7 (c)). On the other hand, for the Eu\(_2\)LnTaO\(_6\) compounds with paramagnetic Ln ions, their magnetic susceptibilities increase with decreasing temperature below the ordering temperature (Fig. 7 (a), (b)). The magnetic ordering temperature of Eu\(_2\)LnTaO\(_6\) does not change with Ln, and the temperature dependence of the magnetic entropy does not change between paramagnetic Ln ions and diamagnetic Ln ions (Fig. 9). These experimental results indicate that Ln\(^{3+}\) ions at the B-sites are in the paramagnetic state and that long-range magnetic ordering is due to the magnetic interactions between Eu\(^{2+}\) ions at the A-sites.
ACKNOWLEDGEMENTS

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REFERENCES


FIGURE CAPTIONS

Fig. 1. (a) Powder X-ray diffraction profile of Eu₂HoTaO₆. The calculated and observed profiles are shown on the top solid line and cross markers, respectively. The second vertical marks in the middle show positions calculated for Bragg reflections. The first vertical marks show positions for an impurity of Ho₂O₃ (the content is 1 mol %). The lower trace is a plot of the difference between calculated and observed intensities.

(b) Powder X-ray diffraction profile of Eu₁NbO₆.

Fig. 2. Variation of lattice parameters for Eu₂LnTaO₆ with the ionic radius of Ln³⁺ ion in six-coordination.

Fig. 3. The schematic crystal structure of Eu₂LnTaO₆.

Fig. 4. ¹⁵¹Eu Mössbauer spectrum of Eu₃TaO₆ measured at room temperature. The red solid line is a calculated line with Lorentzians. Blue and green solid lines are 12 Lorentzians for Eu²⁺ and Eu³⁺ ions, respectively.

Fig. 5. Temperature dependence of absorption area of intensity curves (A) for Eu₃TaO₆. The red solid line is the theoretical curve of the recoil free fraction (Eq. (2), Θ₀ = 205 K) normalized to A (Eu²⁺) at 25 K. The black solid line is the theoretical curve of the recoil free fraction (Eq. (2), Θ₀ = 270 K) normalized to A (Eu³⁺) at 25 K.

Fig. 6. ¹⁵¹Eu Mössbauer spectrum of Eu₃NbO₆ measured at room temperature. The red solid
line is a calculated line with Lorentzians. Blue and green solid lines are 12 Lorentzians for Eu$^{2+}$ and Eu$^{3+}$ ions, respectively.

Fig. 7. Temperature dependences of the magnetic susceptibility of Eu$_2$LnTaO$_6$ (Ln = Dy, Ho, Lu). The insets show the susceptibility in the lower temperature region.

Fig. 8. Temperature dependence of the specific heat $C_p$ for Eu$_2$LnTaO$_6$ (Ln = Dy, Ho, Lu) at low temperatures ($T \leq 30$ K). A red solid line is the lattice specific heat calculated from fitting (see text). A dashed line below 1.8 K represents the extrapolated specific heat.

Fig. 9. The magnetic entropy change $S_{mag}$ for Eu$_2$LnTaO$_6$ (Ln = Dy, Ho, Lu) in the low temperature range ($T \leq 30$ K).
Fig. 1

(a) Eu$_2$HoTaO$_6$

(b) Eu$_3$NbO$_6$
Lattice parameters (Å)

Ionic radii of Ln$^{3+}$ (Å)

Fig. 2
Fig. 3
Fig. 4

Intensity (arb. unit) vs. Velocity (mm·s⁻¹) for Eu₃TaO₆ at room temperature.
Eu$^{2+}$
$\Theta_D = 205$ K

Eu$^{3+}$
$\Theta_D = 270$ K

Fig. 5
Fig. 6

Eu$_3$NbO$_6$
Room temperature

Intensity (arb. unit)

Velocity (mm·s$^{-1}$)
Fig. 7 (a)(b)

(a) $\chi_M / \text{emu} \cdot \text{mol}^{-1}$ vs. $T / \text{K}$ for $\text{Eu}_2\text{DyTaO}_6$

(b) $\chi_M / \text{emu} \cdot \text{mol}^{-1}$ vs. $T / \text{K}$ for $\text{Eu}_2\text{HoTaO}_6$
Fig. 7 (c)

[Graph showing magnetic susceptibility ($\chi_M$) vs. temperature ($T$) for Eu$_2$LuTaO$_6$.]

$\chi_M$ / emu·mol$^{-1}$

$T / K$

- ZFC
- FC
The figure displays the specific heat capacity ($C_p$) against temperature ($T$) for two different compounds: Eu$_2$DyTaO$_6$ and Eu$_2$HoTaO$_6$. The graphs show the variation of $C_p$ with temperature for each compound. The specific heat capacity is given in J mol$^{-1}$ K$^{-1}$.
Fig. 8 (c)

$C_p$ (J·mol$^{-1}$·K$^{-1}$) vs $T$ (K) for $\text{Eu}_2\text{LuTaO}_6$. The graph shows a sharp peak at low temperatures, followed by a gradual increase as the temperature rises.
Fig. 9

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

\[ T (\text{K}) \]

\[ 2R \ln 8 \]

\[ \text{Eu}_2\text{LnTaO}_6 \]

- Ho
- Dy
- Lu
Table 1. Structural parameters for Eu$_3$NbO$_6$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$B$ / Å$^2$</th>
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<tr>
<td>Eu</td>
<td>4e</td>
<td>0.0096(3)</td>
<td>0.0388(1)</td>
<td>1/4</td>
<td>0.52(2)</td>
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<tr>
<td>Eu</td>
<td>2d</td>
<td>1/2</td>
<td>0</td>
<td>0</td>
<td>0.13(3)</td>
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<tr>
<td>Nb</td>
<td>2c</td>
<td>1/2</td>
<td>0</td>
<td>1/2</td>
<td>0.06(4)</td>
</tr>
<tr>
<td>O1</td>
<td>4e</td>
<td>–0.091(2)</td>
<td>0.477(2)</td>
<td>0.232(2)</td>
<td>1.1(1)</td>
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<tr>
<td>O2</td>
<td>4e</td>
<td>0.275(2)</td>
<td>0.314(2)</td>
<td>0.036(2)</td>
<td>1.1</td>
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<tr>
<td>O3</td>
<td>4e</td>
<td>0.313(2)</td>
<td>0.268(2)</td>
<td>0.448(2)</td>
<td>1.1</td>
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Space group $P2_1/n$; $a = 5.8345(2)$ Å, $b = 5.9188(2)$ Å, $c = 8.2926(3)$ Å, $\beta = 90.280(2)^\circ$; $R_{wp} = 7.88\%$, $R_I = 1.59\%$. 
Table 2. Lattice parameters and reliability factors for Eu$_2$LnTaO$_6$.

<table>
<thead>
<tr>
<th>Ln</th>
<th>$a$ / Å</th>
<th>$b$ / Å</th>
<th>$c$ / Å</th>
<th>$\beta$ /°</th>
<th>$R_{wp}$ / %</th>
<th>$R_I$ / %</th>
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<tr>
<td>Eu</td>
<td>5.8451(6)</td>
<td>5.9122(6)</td>
<td>8.2945(8)</td>
<td>90.208(4)</td>
<td>10.3</td>
<td>2.54</td>
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<tr>
<td>Dy</td>
<td>5.8209(5)</td>
<td>5.8743(4)</td>
<td>8.2531(6)</td>
<td>90.197(3)</td>
<td>8.35</td>
<td>1.54</td>
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<tr>
<td>Ho</td>
<td>5.8131(4)</td>
<td>5.8583(4)</td>
<td>8.2357(6)</td>
<td>90.177(3)</td>
<td>8.70</td>
<td>1.40</td>
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<tr>
<td>Er</td>
<td>5.8075(2)</td>
<td>5.8393(2)</td>
<td>8.2207(2)</td>
<td>90.170(3)</td>
<td>8.00</td>
<td>2.51</td>
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<tr>
<td>Tm</td>
<td>5.7974(4)</td>
<td>5.8305(3)</td>
<td>8.2090(5)</td>
<td>90.163(3)</td>
<td>6.00</td>
<td>1.98</td>
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<tr>
<td>Yb</td>
<td>5.7893(3)</td>
<td>5.8183(3)</td>
<td>8.1914(4)</td>
<td>90.154(3)</td>
<td>7.29</td>
<td>3.82</td>
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<tr>
<td>Lu</td>
<td>5.7820(6)</td>
<td>5.8063(8)</td>
<td>8.1857(6)</td>
<td>90.080(7)</td>
<td>9.05</td>
<td>2.88</td>
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Definitions of reliability factors $R_{wp}$ and $R_I$ are given as follows:

$$R_{wp} = \left[ \sum w|F_o| - |F_c| \right]^2 / \sum w|F_o|^2 \right]^{1/2} \text{ and } R_I = \sum |I_{o} - I_{c}| / \sum I_{o} .$$
Table 3. Structural parameters for Eu$_2$HoTaO$_6$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$B$ / Å$^2$</th>
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<tr>
<td>Eu</td>
<td>4e</td>
<td>0.0024(12)</td>
<td>−0.0295(2)</td>
<td>1/4</td>
<td>0.79(3)</td>
</tr>
<tr>
<td>Ho</td>
<td>2d</td>
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<td>0</td>
<td>0</td>
<td>0.28(4)</td>
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<tr>
<td>Ta</td>
<td>2c</td>
<td>1/2</td>
<td>0</td>
<td>1/2</td>
<td>0.10(3)</td>
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<tr>
<td>O1</td>
<td>4e</td>
<td>0.069(4)</td>
<td>0.525(2)</td>
<td>0.234(3)</td>
<td>1.0(1)</td>
</tr>
<tr>
<td>O2</td>
<td>4e</td>
<td>0.272(4)</td>
<td>0.302(4)</td>
<td>−0.042(5)</td>
<td>1.0</td>
</tr>
<tr>
<td>O3</td>
<td>4e</td>
<td>0.298(4)</td>
<td>0.266(4)</td>
<td>0.543(5)</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Table 4. The BVS values of Eu, Ln and Ta ions for Eu$_2$LnTaO$_6$ and Eu$_3$NbO$_6$.

<table>
<thead>
<tr>
<th></th>
<th>Eu$_3$TaO$_6$</th>
<th>Eu$_2$DyTaO$_6$</th>
<th>Eu$_2$HoTaO$_6$</th>
<th>Eu$_2$ErTaO$_6$</th>
<th>Eu$_2$TmTaO$_6$</th>
<th>Eu$_2$YbTaO$_6$</th>
<th>Eu$_2$LuTaO$_6$</th>
<th>Eu$_3$NbO$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu</td>
<td>1.86</td>
<td>1.90</td>
<td>1.89</td>
<td>1.84</td>
<td>1.91</td>
<td>1.92</td>
<td>1.95</td>
<td>1.96</td>
</tr>
<tr>
<td>Ln</td>
<td>3.37</td>
<td>2.98</td>
<td>3.38</td>
<td>3.27</td>
<td>3.31</td>
<td>3.28</td>
<td>3.20</td>
<td>3.22</td>
</tr>
<tr>
<td>Ta</td>
<td>5.24</td>
<td>5.18</td>
<td>5.10</td>
<td>5.40</td>
<td>5.17</td>
<td>5.15</td>
<td>5.16</td>
<td>5.00</td>
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Table 5. Mössbauer spectrum parameters for Eu$_3$TaO$_6$ at 25 ~ 300 K.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\delta$ (mm/s)</th>
<th>$eV_{zz}Q_g$ (mm/s)</th>
<th>$\eta$</th>
<th>$I_0$ (%)</th>
<th>$\Gamma$ (mm/s)</th>
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</thead>
<tbody>
<tr>
<td>300</td>
<td>Eu$^{2+}$ –12.3</td>
<td>12.9</td>
<td>0.668</td>
<td>6.18</td>
<td>2.85</td>
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<tr>
<td></td>
<td>Eu$^{3+}$ 1.51</td>
<td>5.63</td>
<td>0.481</td>
<td>4.19</td>
<td>2.04</td>
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<tr>
<td>250</td>
<td>Eu$^{2+}$ –12.2</td>
<td>13.4</td>
<td>0.815</td>
<td>5.54</td>
<td>3.70</td>
</tr>
<tr>
<td></td>
<td>Eu$^{3+}$ 1.55</td>
<td>9.10</td>
<td>0.971</td>
<td>3.50</td>
<td>2.78</td>
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<tr>
<td>200</td>
<td>Eu$^{2+}$ –12.2</td>
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<tr>
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<td>Eu$^{3+}$ 1.62</td>
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<td>0.996</td>
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</tr>
<tr>
<td>150</td>
<td>Eu$^{2+}$ –12.2</td>
<td>12.8</td>
<td>0.761</td>
<td>7.61</td>
<td>3.72</td>
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<tr>
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<td>8.88</td>
<td>0.849</td>
<td>4.47</td>
<td>2.57</td>
</tr>
<tr>
<td>100</td>
<td>Eu$^{2+}$ –12.1</td>
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<td>0.821</td>
<td>8.51</td>
<td>3.58</td>
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<td>Eu$^{3+}$ 1.57</td>
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<td>0.767</td>
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<td>2.69</td>
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<tr>
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<td>Eu$^{2+}$ –12.1</td>
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<td>0.741</td>
<td>11.1</td>
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<tr>
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<td>Eu$^{3+}$ 1.59</td>
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<td>0.822</td>
<td>5.26</td>
<td>2.41</td>
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<tr>
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<td>Eu$^{2+}$ –12.1</td>
<td>13.4</td>
<td>0.744</td>
<td>11.0</td>
<td>3.10</td>
</tr>
<tr>
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<td>Eu$^{3+}$ 1.54</td>
<td>6.37</td>
<td>0.349</td>
<td>5.94</td>
<td>2.19</td>
</tr>
</tbody>
</table>
Table 6. The effective magnetic moments ($\mu_{\text{eff}}$: experimental, $\mu_{\text{cal}}$: calculated) per formula unit and Weiss constants for Eu$_2$LnTaO$_6$.

<table>
<thead>
<tr>
<th>Ln</th>
<th>$\mu_{\text{eff}} / \mu_B$</th>
<th>$\mu_{\text{cal}} / \mu_B$</th>
<th>$\theta / \text{K}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu</td>
<td>11.5(2)</td>
<td>11.2</td>
<td>-5.4(3)</td>
</tr>
<tr>
<td>Dy</td>
<td>14.8(5)</td>
<td>15.4</td>
<td>-5.4(2)</td>
</tr>
<tr>
<td>Ho</td>
<td>14.8(3)</td>
<td>15.3</td>
<td>-6.7(6)</td>
</tr>
<tr>
<td>Er</td>
<td>14.3(2)</td>
<td>14.6</td>
<td>-5.5(4)</td>
</tr>
<tr>
<td>Tm</td>
<td>13.2(4)</td>
<td>13.3</td>
<td>-10.0(2)</td>
</tr>
<tr>
<td>Yb</td>
<td>11.4(3)</td>
<td>12.0</td>
<td>-4.0(2)</td>
</tr>
<tr>
<td>Lu</td>
<td>10.5(6)</td>
<td>11.2</td>
<td>-1.9(2)</td>
</tr>
</tbody>
</table>