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# Magnetic Studies on $\text{Eu}_3\text{MO}_7$ ( $M = \text{Nb}, \text{Ta}, \text{Ir}$ ) with Fluorite-related Structure by $^{151}\text{Eu}$ Mössbauer Spectroscopy and Magnetic Susceptibility Measurements



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## ABSTRACT

Magnetic properties of europium-containing compounds  $\text{Eu}_3\text{MO}_7$  ( $M = \text{Nb}, \text{Ta}, \text{Ir}$ ) with fluorite-related structure have been investigated. Magnetic susceptibility measurements show that all these compounds are paramagnetic and have no magnetic ordering down to 1.8 K. At very low temperatures ( $T < 50$  K), the susceptibilities of each compound attain constant values, which is characteristic of the ground state for  $\text{Eu}^{3+}$  ions. The results of  $^{151}\text{Eu}$  Mössbauer spectroscopic measurements show that the asymmetric parameter for  $\text{Eu}(2)$  in seven-coordination is much larger than that for  $\text{Eu}(1)$  in cubic environment, which in accordance with the crystallographic result.

## 1. Introduction

Recently, the rare-earth transition metal oxides with general composition  $\text{Ln}_3\text{MO}_7$  ( $\text{Ln} =$  rare earths;  $M =$  transition metals such as Nb, Ru, Ta et al.) have been widely investigated from the viewpoint of their one-dimensional nature. They have a defect-fluorite structure. The relationship to the fluorite structure is as follows. The fluorite unit cell for oxides has the composition  $M^{4+}_2\text{O}_8$ . If the four tetravalent metal ions are replaced by three trivalent ions ( $\text{Ln}$ ) and one pentavalent ion ( $M$ ), one oxide vacancy is formed per fluorite cell. Due to the significant differences in radii between the  $\text{Ln}^{3+}$  and  $M^{5+}$  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 an  $\text{MO}_6$  octahedron. These octahedra share corners forming one-dimensional chains which are oriented along the  $c$ -axis [1–7].

Many studies have been performed [8–37], due to this unique crystal structure and possible related magnetic properties for  $\text{Ln}_3\text{MO}_7$  compounds ( $M = \text{Mo}, \text{Ru}, \text{Re}, \text{Os}, \text{Ir}$ ), especially for the magnetic properties of compounds containing  $\text{Ru}^{5+}$  ion at the  $M$ -site because of its largest possible spin ( $S = 3/2$ ) among the  $4d$  and  $5d$  transition metals. However, there was scant evidence for the expected one-dimensionality in the magnetic susceptibility.

This type of compound  $\text{Ln}_3\text{MO}_7$  is also attractive because it exhibits dielectric properties [38,39] as well as photocatalytic activity [40,41].

In the case that  $M$  ions are diamagnetic, magnetic properties of  $\text{Ln}_3\text{MO}_7$  are due to magnetic interactions between  $\text{Ln}$  ions. There are two kinds of oxygen-coordination environment around  $\text{Ln}$  ions. One-third of the  $\text{Ln}$  ions are coordinated by eight oxygen ions and the remaining two-third of the  $\text{Ln}$  ions are seven-coordinated. Previous

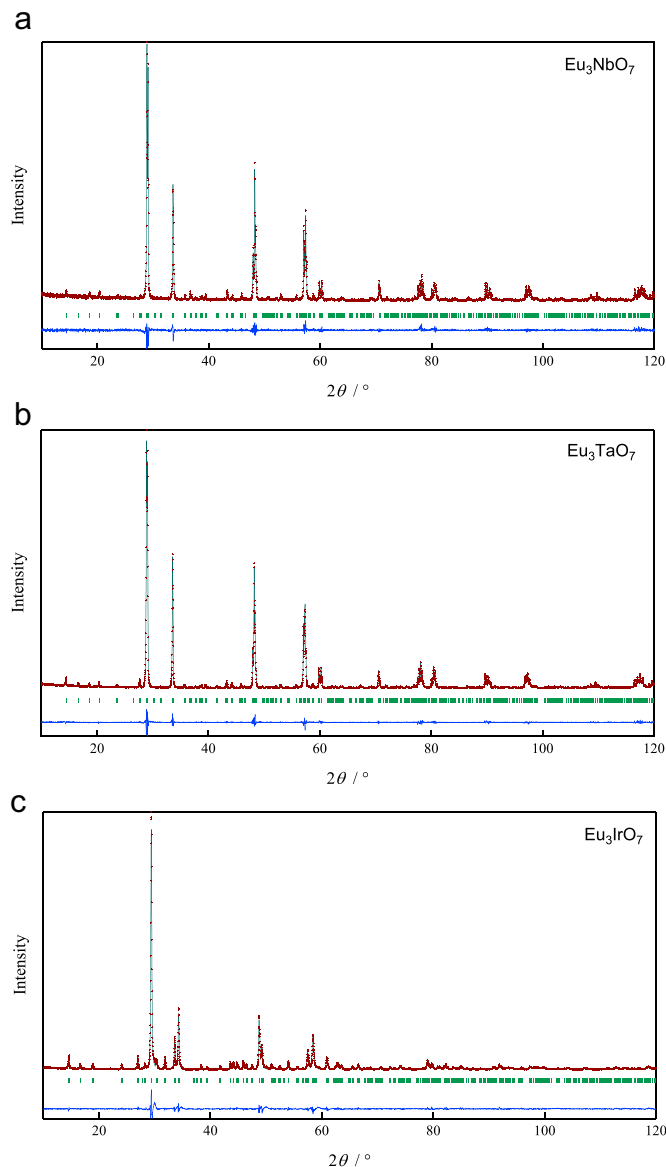
magnetic susceptibility and specific heat measurements on  $\text{Ln}_3\text{MO}_7$  ( $\text{Ln} = \text{Nd}, \text{Tb}; M = \text{Nb}, \text{Sb}, \text{Ta}$ ) showed “two-step” magnetic transition [30,42–44]. It is discussed that the eight-coordinate  $\text{Ln}(1)$  and seven-coordinate  $\text{Ln}(2)$  ions individually order at different temperatures.

In order to elucidate the role of each  $\text{Ln}(1)$  and  $\text{Ln}(2)$  ions on the magnetic properties of  $\text{Ln}_3\text{MO}_7$  compounds, we prepared europium containing compounds  $\text{Eu}_3\text{MO}_7$  ( $M = \text{Nb}, \text{Ta}, \text{Ir}$ ). Through X-ray diffraction measurements, their structures were determined, and magnetic susceptibility and  $^{151}\text{Eu}$  Mössbauer Spectroscopy measurements were performed to study their magnetic properties.

## 2. Experimental

## 2.1. Sample preparation

Polycrystalline samples of  $\text{Eu}_3\text{MO}_7$  ( $M = \text{Nb}, \text{Ta}, \text{Ir}$ ) were prepared by the standard solid-state reaction. Europium sesqui-oxides  $\text{Eu}_2\text{O}_3$ , niobium oxides  $\text{Nb}_2\text{O}_5$ , tantalum oxides  $\text{Ta}_2\text{O}_5$ , and Ir metals were used as starting materials. These starting materials were well mixed in an agate mortar. The mixtures were pressed into pellets, and heated in the following conditions. For preparing  $\text{Eu}_3\text{NbO}_7$  and  $\text{Eu}_3\text{TaO}_7$ , the pellets were heated in air at 1300 and 1500 °C, respectively for 12 h.  $\text{Eu}_3\text{IrO}_7$  were prepared in flowing oxygen atmosphere at 1200 °C for 12 h. These heating procedure were repeated twice. In the first stage of sample preparations, very small amounts of impurities remained in the desired compounds; they were unreacted starting materials  $\text{Eu}_2\text{O}_3$ . In order to remove these impurities, the samples were washed with diluted hydrochloric acid. After this treatment, single-phase  $\text{Eu}_3\text{MO}_7$  ( $M = \text{Nb}, \text{Ta}, \text{Ir}$ ) compounds could be obtained.



**Fig. 1.** Powder x-ray diffraction patterns and Rietveld refinements for (a)  $\text{Eu}_3\text{NbO}_7$ , (b)  $\text{Eu}_3\text{TaO}_7$ , and (c)  $\text{Eu}_3\text{IrO}_7$ . The bottom trace is a plot of the difference between observed + (cross markers) and calculated (solid line) intensities. All allowed Bragg reflections are shown by vertical lines.

## 2.2. X-ray diffraction measurements

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  $10^\circ \leq 2\theta \leq 120^\circ$  at a  $2\theta$  step-size of  $0.02^\circ$ . The X-ray diffraction data were analyzed by the Rietveld technique, using the program RIETAN-FP [45] and the crystal structure was drawn by VESTA program [46].

## 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 in the applied field of 0.1 T.

**Table 1**  
Structural parameters for  $\text{Eu}_3\text{MO}_7$  ( $M = \text{Nb, Ta, Ir}$ ).

$\text{Eu}_3\text{NbO}_7$					
Atom	Site	$x$	$y$	$z$	$B / \text{\AA}^2$ <sup>a</sup>
Eu(1)	4b	0	0.4954(9)	1/4	0.49(3)
Eu(2)	8c	0.2338(2)	0.2349(2)	0.0002(1)	0.49
Nb	4b	0	0.9992(9)	1/4	0.51(8)
O(1)	8c	0.129(4)	0.177(4)	0.273(4)	0.69(7)
O(2)	8c	0.116(3)	0.794(4)	0.279(4)	0.69
O(3)	4a	0.138(1)	1/2	0	0.69
O(4)	4a	0.145(2)	1/2	1/2	0.69
O(5)	4a	0.057(3)	0	0	0.69

$\text{Eu}_3\text{TaO}_7$					
Atom	Site	$x$	$y$	$z$	$B / \text{\AA}^2$ <sup>a</sup>
Eu(1)	4b	0	0.4934(9)	1/4	1.15(5)
Eu(2)	8c	0.2345(2)	0.2354(2)	0.0000(1)	1.15
Ta	4b	0	0.9992(9)	1/4	0.69(7)
O(1)	8c	0.139(4)	0.184(4)	0.281(4)	0.7(1)
O(2)	8c	0.110(3)	0.782(4)	0.285(4)	0.7
O(3)	4a	0.130(1)	1/2	0	0.7
O(4)	4a	0.138(2)	1/2	1/2	0.7
O(5)	4a	0.065(3)	0	0	0.7

$\text{Eu}_3\text{IrO}_7$					
Atom	Site	$x$	$y$	$z$	$B / \text{\AA}^2$ <sup>a</sup>
Eu(1)	4a	0	0	0	0.52(4)
Eu(2)	8g	0.225(1)	0.299(2)	1/4	0.52
Ir	4b	0	1/2	0	0.30(4)
O(1)	16h	0.136(1)	0.309(1)	-0.033(1)	1.2(1)
O(2)	8g	0.126(2)	0.024(2)	1/4	1.2
O(3)	4c	0	0.411(2)	1/4	1.2

Note. For  $\text{Eu}_3\text{NbO}_7$ , space group  $C222_1$ ;  $a = 10.6480(4) \text{ \AA}$ ,  $b = 7.5064(3) \text{ \AA}$ ,  $c = 7.5829(3) \text{ \AA}$ ,  $V = 606.089(4) \text{ \AA}^3$ ,  $R_{\text{wp}} = 8.91\%$ ,  $R_1 = 2.56\%$ , and  $R_e = 6.69\%$ , where  $R_{\text{wp}} = [\sum_i w_i (y_i - f_i(x))^2 / \sum_i w_i y_i^2]^{1/2}$ ,  $R_1 = \sum |I_k(o) - I_k(c)| / \sum I_k(o)$ , and  $R_e = [(N - P) / \sum_i w_i y_i^2]^{1/2}$ .

a: For the same ions,  $B$  values were fixed to be equal.

Note. For  $\text{Eu}_3\text{TaO}_7$ , space group  $C222_1$ ;  $a = 10.6655(4) \text{ \AA}$ ,  $b = 7.5163(3) \text{ \AA}$ ,  $c = 7.5822(3) \text{ \AA}$ ,  $V = 607.828(4) \text{ \AA}^3$ ,  $R_{\text{wp}} = 8.06\%$ ,  $R_1 = 1.94\%$ , and  $R_e = 6.09\%$ .

Note. For  $\text{Eu}_3\text{IrO}_7$ , space group  $Cmcm$ ;  $a = 10.6807(10) \text{ \AA}$ ,  $b = 7.39238(6) \text{ \AA}$ ,  $c = 7.41024(6) \text{ \AA}$ ,  $V = 585.083(9) \text{ \AA}^3$ ,  $R_{\text{wp}} = 14.35\%$ ,  $R_1 = 3.84\%$ , and  $R_e = 10.34\%$ .

## 2.4. $^{151}\text{Eu}$ Mössbauer spectroscopy measurements

The  $^{151}\text{Eu}$  Mössbauer spectra were measured with a Mössbauer spectrometer VT-6000 (Laboratory Equipment Co.) in the constant acceleration mode using a radiation source  $^{151}\text{SmF}_3$  (1.85 GBq). The spectrometer was calibrated with a spectrum of  $\alpha\text{-Fe}$  at room temperature. The  $\gamma$ -rays were detected with a NaI scintillation counter. Europium trifluoride ( $\text{EuF}_3$ ) 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  $10 \text{ mg (Eu) cm}^{-2}$ .

## 3. Results and Discussion

### 3.1. Crystal structure

The X-ray diffraction patterns for  $\text{Eu}_3\text{MO}_7$  ( $M = \text{Nb, Ta, and Ir}$ ) are shown in Fig. 1(a), (b), and (c), respectively, and they are similar to that for the fluorite structure. All reflections appeared to be consistent with the C-centered conditions,  $h + k = 2n$ , and  $h0l$  reflections with odd  $l$  are absent.

We have analyzed the X-ray diffraction profiles  $\text{Eu}_3\text{IrO}_7$  with the space group  $Cmcm$ , which is the most found one for the  $\text{Ln}_3\text{MO}_7$  compounds, and all the reflections observed for  $\text{Eu}_3\text{IrO}_7$  could be successfully indexed.

For the X-ray diffraction profiles for  $\text{Eu}_3\text{NbO}_7$  and  $\text{Eu}_3\text{TaO}_7$ , there exist many very weak  $h0l$  reflections with odd  $l$ , which could not be

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