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Magnetic and ¹⁵¹Eu Mössbauer spectroscopic studies on rare earth bismuth sulfides, $EuLnBiS_4$ (Ln = Eu, Gd)



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ABSTRACT

Keywords: ¹⁵¹Eu Mössbauer spectrum Rare earth Sulfide Magnetic properties Ternary and quaternary rare earth bismuth sulfides $EuLnBiS_4$ (Ln = Eu, Gd) have been investigated by X-ray diffraction, ¹⁵¹Eu Mössbauer spectroscopy, and magnetic susceptibility measurements. Both compounds have the orthorhombic CaFe₂O₄-type structure with space group *Pnma*. In Eu_2BiS_4 , Eu^{2+} and Eu^{3+} ions occupy two crystallographically independent sites. The ¹⁵¹Eu Mössbauer spectra for Eu_2BiS_4 indicate that the Eu^{2+} and Eu^{3+} ions exist in the molar ratio of 1:1, and the Debye temperatures of Eu^{2+} and Eu^{3+} are 175 and 230 K, respectively. Magnetic susceptibility measurements for Eu_2BiS_4 and $EuGdBiS_4$ reveal that an antiferromagnetic transition occurs at 2.8 and 6.5 K, respectively.

1. Introduction

It is well known that mixed-valence europium sulfides show an interesting electronic and magnetic behavior. For example, Eu_3S_4 has the Verwey transition at 186 K [1] and the ferromagnetic transition at 3.1 K [2]. $EuPd_3S_4$ shows an electron hopping between Eu^{2+} and Eu^{3+} , and has the antiferromagnetic transition at 3 K [3]. Similar electron hopping between Eu^{2+} and Eu^{3+} has been observed in $Eu_5Zr_3S_{12}$ [4], $Na_{1.515}EuGeS_4$ [5], and $(EuS)_{1.173}NbS_2$ [6]. $Eu_5Sn_3S_{12}$ is metamagnetic and has two field-dependent antiferromagnetic phases at low temperatures [7–9].

In these compounds, the europium ions have two oxidation states. In general, the divalent state of Eu is stable in sulfides, but some compounds contain trivalent europium. Flahaut noted that they are classified into two types [10]. In the case of compounds containing only Eu^{3+} ions, there is necessarily a strongly electronegative anion, or a second weakly electronegative cation. For compounds containing both Eu^{2+} and Eu^{3+} , such as Eu_3S_4 and $EuPd_3S_4$, ¹⁵¹Eu Mössbauer spectroscopic measurements were performed to investigate the mixed-valence state of Eu [3,11]. These compounds show the occurrence of the electron transfer and/or the electron hopping between Eu^{2+} and Eu^{3+} , which may stabilize the Eu^{3+} ions.

Ternary europium bismuth sulfide Eu_2BiS_4 has been reported to crystallize in the orthorhombic $CaFe_2O_4$ -type structure with space group *Pnma* [12]. The schematic structure of Eu_2BiS_4 is illustrated in Fig. 1. This compound has the formal oxidation state of $Eu^{2+}Eu^{3+}Bi^{3+}S^{2-}_4$, and the Eu^{2+} and Eu^{3+} ions occupy crystallographically different sites. The situation for Eu_2BiS_4 is different from the case

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of the above-mentioned sulfides and is similar to that for Eu_2CuS_3 [13], i.e., Eu_2BiS_4 has two crystallographically distinguishable sites for Eu^{2+} and Eu^{3+} ions. However, none of the studies on the electronic and magnetic properties for this mixed valence compound has been carried out.

In this study, two polycrystalline samples of $EuLnBiS_4$ (Ln = Eu, Gd) were prepared. Their magnetic susceptibilities were measured in the temperature range from 1.8 to 300 K and ¹⁵¹Eu Mössbauer spectrum measurements were performed from 20 to 300 K.

2. Experimental

2.1. Sample preparation

Two europium bismuth sulfides, Eu_2BiS_4 and $EuGdBiS_4$, were prepared by the solid-state reaction. As starting materials, rare earth sesquioxides (Eu_2O_3 , Gd_2O_3), powder sulfur (S), and powered Bi metals were used. Europium monosulfide EuS was prepared by heating europium sesquioxide (Eu_2O_3) on a graphite boat at 1073 K for 10 h in a flowing gaseous CS_2 by bubbling the nitrogen gas through liquid CS_2 . Eu_3S_4 was prepared by heating stoichiometric mixtures of EuS and S powders in a quartz ampoule at 1073 K for 24 h. Gadolinium sesquisulfide (Gd_2S_3) was obtained by heating Gd_2O_3 in a flowing atmosphere of CS_2 gas at 1473 K for 2 h. Bismuth sesquisulfide (Bi_2S_3) was prepared by heating stoichiometric amounts of Bi and S powders at 823 K for 6 h. Then, stoichiometric mixtures of Eu_3S_4 , Gd_2S_3 , and Bi_2S_3 were intimately ground and pressed into pellets. They were heated in a quartz ampoule at 1223 K for 12 h.

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Fig. 1. Crystal structure of Eu₂BiS₄.

2.2. Powder X-ray diffraction

Powder X-ray diffraction profiles were measured using a Rigaku Multi-Flex diffractometer with Cu-K α radiation equipped with a curved graphite monochromator. The data were collected by step-scanning in the angle range of $10^{\circ} \le 2\theta \le 120^{\circ}$ at a 2θ step-size of 0.02° . The X-ray diffraction data were analyzed by the Rietveld technique, using the program RIETAN-FP [14] and the crystal structure was drawn by VESTA program [15].

2.3. ¹⁵¹Eu Mössbauer spectra

The ¹⁵¹Eu Mössbauer spectra were measured in the temperature range between 20 and 300 K with a Mössbauer spectrometer VT-6000 (Laboratory Equipment Co.) in the constant acceleration mode using a radiation source ¹⁵¹SmF₃ (1.85 GBq). The spectrometer was calibrated with a spectrum of α -Fe at room temperature. The γ -rays were detected with a NaI scintillation counter. Europium trifluoride (EuF₃) 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.

2.4. Magnetic susceptibility

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 \leq T \leq 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 in the applied field of 0.1 T.



Fig. 2. Powder x-ray diffraction patterns and Rietveld refinements for (a) Eu_2BiS_4 and (b) $EuGdBiS_4$. The bottom trace is a plot of the difference between observed + (cross makers) and calculated (solid line) intensities. All allowed Bragg reflections are shown by vertical lines.

3. Results and discussion

3.1. Structures of Eu₂BiS₄ and EuGdBiS₄

Both the Eu₂BiS₄ and EuGdBiS₄ compounds were obtained as a single phase. The X-ray diffraction profiles were indexed on an orthorhombic cell with the space group Pnma, and their crystallographic parameters were refined by the RIETAN-FP program. Fig. 2(a) and (b) show the X-ray diffraction profiles of Eu₂BiS₄ and EuGdBiS₄, respectively. The calculated profiles are in good agreements with the observed ones (Eu₂BiS₄: $R_{wp} = 8.49\%$, $R_I = 2.08\%$; EuGdBiS₄: $R_{\rm wp}$ = 7.13%, R_I = 1.84%). The refined lattice parameters and positional parameters for Eu2BiS4 and EuGdBiS4 are listed in Table 1. From the X-ray diffraction profile for EuGdBiS₄, the crystallographic site of Gd³⁺ cannot be distinguished from that of Eu²⁺ because these ions have the same number of electrons. However, on the assumption that the divalent Eu and trivalent Gd sites in the EuGdBiS₄ correspond to the the Eu(1) and Eu(2) sites in the Eu₂BiS₄, respectively, the positional parameters for EuGdBiS₄ should be well refined, as will be discussed later. Some selected interatomic distances for Eu₂BiS₄ and EuGdBiS₄ are listed in Table 2.

Fig. 3(a) and (b) illustrate the polyhedral representation of the Eu_2BiS_4 structure. The Eu ions occupy two crystallographically independent sites. The Eu(1) and Eu(2) ions are coordinated by eight and seven sulfide ions, respectively. The Eu(1)S₈ and Eu(2)S₇ polyhedra are connected to each other by face sharing as shown in Fig. 3(a). The Bi ions are coordinated by six sulfide ions and the BiS₆ octahedra share edges, forming double chains along the *b*-axis as shown in Fig. 3(b).

The valences of the cations are calculated by the bond valence sum (V_i) [16]:

$$v_{ij} = \exp\left(\frac{R_0 - d_{ij}}{b}\right),\tag{1}$$
$$V = \sum v_{i}$$

$$v_i = \sum_j v_{ij}, \tag{2}$$

where R_0 and b are known as the bond valence parameters of various cations and a constant value (0.37 Å), respectively, and d_{ij} means the

Table 1

Lattice and positional parameters for Eu2BiS4 and EuGdBiS4.

Eu₂BiS4

 Eu_2BIS_4

Space Group: Pnma (No. 62)

a = 11.5132(8) Å, b = 4.0775(3) Å, c = 14.4501(8) Å R_{I} = 2.08 %, $R_{\rm wp}$ = 8.49 %, S = 1.31

-	·				
	Site	x	у	Z	B / ${\rm \AA^2}$
Eu(1)	4c	0.2698(2)	1/4	0.6537(1)	0.9(2)
Eu(2)	4c	0.1126(1)	1/4	0.9050(1)	0.6(3)
Bi	4c	0.0650(1)	1/4	0.3905(1)	0.8(1)
S(1)	4c	0.0121(6)	1/4	0.7169(4)	1.1(3)
S(2)	4c	0.2628(6)	1/4	0.3050(5)	1.1
S(3)	4c	0.0495(6)	1/4	0.0898(4)	1.1
S(4)	4c	0.3235(6)	1/4	0.0121(5)	1.1

EuGdBiS₄

Space Group: Pnma (No. 62)

a = 11.4842(8) Å, b = 4.0730(3) Å, c = 14.4383(8) Å R_I = 1.84 %, $R_{\rm wp}$ = 7.13 %, S = 1.21

	Site	x	y	Ζ	B / ${\rm \AA}^2$
Eu	4c	0.2707(2)	1/4	0.6539(1)	0.8(2)
Gd	4c	0.1114(1)	1/4	0.9040(1)	0.4(2)
Bi	4c	0.0642(1)	1/4	0.3901(1)	0.6(1)
S(1)	4c	0.0127(6)	1/4	0.7164(4)	1.0(3)
S(2)	4c	0.2665(6)	1/4	0.3048(5)	1.0^{*}
S(3)	4c	0.0502(6)	1/4	0.0906(4)	1.0^{*}
S(4)	4c	0.3262(6)	1/4	0.0117(5)	1.0

* The atomic displacement parameters of S(2), S(3), and S(4) are fixed to be that of S(1).

Table 2

Selected interatomic distances (Å) for Eu2BiS4 and EuGdBiS4.

Eu ₂ BiS ₄			EuGdBiS ₄				
Eu(1)	-S(1)	3.104(7)		Eu	-S(1)	3.098(8)	
	-S(1)	3.359(7)			-S(1)	3.351(8)	
	-S(2)	3.013(6)	×2		-S(2)	3.013(6)	×2
	-S(3)	3.056(5)	×2		-S(3)	3.035(6)	×2
	-S(4)	3.082(6)	×2		-S(4)	3.098(6)	×2
Eu(2)	-S(1)	2.955(7)		Gd	-S(1)	2.936(7)	
	-S(2)	2.882(5)	×2		-S(2)	2.858(5)	×2
	-S(3)	2.764(5)	×2		-S(3)	2.756(5)	×2
	-S(3)	2.767(7)			-S(3)	2.784(7)	
	-S(4)	2.879(7)			-S(4)	2.916(8)	
Bi	-S(1)	2.712(5)	×2	Bi	-S(1)	2.701(5)	×2
	-S(2)	2.591(7)			-S(2)	2.630(7)	
	-S(4)	2.981(6)	×2		-S(4)	2.969(6)	×2
	-S(4)	3.116(7)			-S(4)	3.079(8)	
	-S(4) -S(4)	2.981(6) 3.116(7)	×2		-S(4) -S(4)	2.969(6) 3.079(8)	×2

interatomic distance between cation *i* and anion *j*. For Eu₂BiS₄, the valences of the Eu(1), Eu(2), and Bi ions were determined to be +1.90, +3.55, and +3.19, respectively, which indicates that the divalent and trivalent europium ions occupy the Eu(1) and Eu(2) sites, respectively. The large value of $V(\text{Eu}^{3+})$ suggests that the site of Eu(2) is too small for Eu³⁺ ion. Due to this, the synthesis of Eu*Ln*BiS₄ containing a larger trivalent *Ln* ions than Eu³⁺ was unsuccessful. For EuGdBiS₄, the valences of the Eu(1), Gd, and Bi ions were calculated to be +1.92, +3.10, and +3.19, respectively.

3.2. ¹⁵¹Eu Mössbauer spectra

Fig. 4 shows the ¹⁵¹Eu Mössbauer spectrum of Eu₂BiS₄ measured at room temperature. Two absorption peaks appear at -12.2 mm s^{-1} and 0.7 mm s^{-1} , indicating the presence of the divalent and trivalent Eu ions in this compound. Since both the Eu sites in Eu₂BiS₄ have the low point symmetry (see Table 2), an electric field gradient (EFG) tensor exists. Due to the distortion by the quadrupole interaction, each



Fig. 3. Polyhedral representation of the Eu_2BiS_4 structure. (a) $Eu(1)S_8$ polyhedra and $Eu(2)S_7$ polyhedra. (b) The double chains composed of BiS_6 octahedra.



Fig. 4. $^{151}\mathrm{Eu}$ Mössbauer spectra of $\mathrm{Eu}_2\mathrm{BiS}_4$ at room temperature. The top trace is a plot of the difference between observed \bigcirc (circle makers) and calculated (solid line) transmissions.

absorption peak should be fitted with twelve Lorentzian lines. To simplify this analysis, each peak was fitted with a single Lorentzian. The isomer shifts (δ) relative to EuF₃ are obtained to be -12.23(2) mm s⁻¹ for Eu²⁺ and 0.74(2) mm s⁻¹ for Eu³⁺, and these values are nearly equal to those for Eu²⁺ and Eu³⁺ in other sulfides. The ratio of the absorption intensities for Eu²⁺ and Eu³⁺ is calculated to be 0.7: 1.0. On the other hand, the results of the X-ray diffraction measurements at room temperature showed that the ratio of Eu²⁺ and Eu³⁺ is 1: 1.

In order to elucidate the difference in the ratio of Eu²⁺ and Eu³⁺



Fig. 5. 151 Eu Mössbauer spectra of Eu₂BiS₄ measured at 20, 100, 200, and 300 K.



Fig. 6. Temperature dependence of the absorption area of intensities for Eu^{2+} and Eu^{3+} in $Eu_2^{2}BiS_4$. The solid line is the theoretical curve ($\Theta_D = 230 \text{ K}$) normalized to $A(Eu^{3+})$ at 20 K and the broken line is the theoretical curve ($\Theta_D = 175 \text{ K}$) normalized to $A(Eu^{2+})$ at 20 K.

between the X-ray diffraction and the $^{151}\rm{Eu}$ Mössbauer spectrum measurements, low temperature $^{151}\rm{Eu}$ Mössbauer spectrum measurements were performed down to 20 K. Fig. 5 shows the $^{151}\rm{Eu}$ Mössbauer spectra of $\rm{Eu_2BiS_4}$ between 20 and 300 K. The absorptions of $\rm{Eu^{2+}}$ ($\delta \sim -12.2~\rm{mm~s^{-1}}$) and $\rm{Eu^{3+}}$ ($\delta \sim 0.8~\rm{mm~s^{-1}}$) are observed at all temperatures.

Fig. 6 shows the temperature dependences of the absorption area of the intensities for Eu^{2+} and Eu^{3+} in Eu_2BiS_4 . Both the intensities decrease monotonously with increasing temperature and the decrease for Eu^{2+} is larger than that for Eu^{3+} . At 20 K, the intensities for Eu^{2+} and Eu^{3+} are almost equal, but the ratio of the intensities for Eu^{2+} and Eu^{3+} is found to be 0.7: 1 at 300 K. This variation of the intensity with



Fig. 7. Temperature dependence of the isomer shifts (δ) for Eu²⁺ and Eu³⁺ in Eu₂BiS₄. The dotted line is the theoretical curve of the second-order Doppler (SOD) shift with Θ_D = 230 K and the broken line is that of the SOD shift with Θ_D = 175 K.



Fig. 8. Temperature dependence of the reciprocal magnetic susceptibility (χ^{-1}) of (a) Eu_2BiS_4 and (b) $EuGdBiS_4$ measured in the magnetic field of 0.1 T. A solid line is the fitting result by the Curie-Weiss law. The insets show the low-temperature dependence of susceptibility of (a) Eu_2BiS_4 and (b) $EuGdBiS_4$.

Table 3

The effective magnetic moments (μ_{eff} : experimental, μ_{calc} : calculated) per formula unit, Weiss constants, and Neel temperature for Eu₂BiS₄ and EuGdBiS₄.

	$\mu_{ m eff}$ / $\mu_{ m B}$	$\mu_{ m calc}$ / $\mu_{ m B}$	θ / K	$T_{\rm N}$ / K
Eu2BiS4	7.93(2)	7.94	2.7(1)	2.8
EuGdBiS4	11.13(1)	11.23	-0.9(1)	6.5

temperature may be due to a small difference in the Debye-Waller factors between Eu^{2+} and Eu^{3+} . The area of the intensity is proportional to the recoil-free fraction. On the assumption that the valence fluctuation does not occur below 300 K, the Debye temperatures (Θ_D) for Eu^{2+} and Eu^{3+} are estimated from the recoil-free fraction (*f*). The recoil-free fraction is represented by the following equation [17],

$$f = \exp\left[\frac{-6E_{\rm R}}{k_{\rm B}\Theta_{\rm D}}\left\{\frac{1}{4} + \left(\frac{T}{\Theta_{\rm D}}\right)^2 \int_0^{\Theta_{\rm D}/T} \frac{x \,\mathrm{d}x}{(e^x - 1)}\right\}\right],\tag{3}$$

where $k_{\rm B}$ is the Boltzmann's constant and $E_{\rm R}$ is the free-atom recoil energy. The theoretical curves with $\Theta_{\rm D} = 175$ K (broken line in Fig. 6) and $\Theta_{\rm D} = 230$ K (solid line in Fig. 6) using this equation are in good agreement with the experimental data for Eu²⁺ and Eu³⁺, respectively. The higher Debye temperature for the Eu³⁺ ion indicates that the Eu³⁺–S^{2–} bonds in the Eu(2)S₇ polyhedron are stronger than the Eu²⁺–S^{2–} bonds in the Eu(1)S₈ polyhedron.

Fig. 7 shows the temperature dependence of isomer shifts (δ) for Eu²⁺ and Eu³⁺. Both the isomer shifts decrease with increasing temperature, which is attributable to the effects of the second-order Doppler shifts [17]. However, the difference in the isomer shifts between Eu²⁺ and Eu³⁺ is invariable against temperature. This result is contrastive to the result observed in the ¹⁵¹Eu Mössbauer spectra for some mixed-valence europium sulfides such as Eu₃S₄, EuPd₃S₄, Eu₅Zr₃S₁₂, Na_{1.515}EuGeS₄, and (EuS)_{1.173}NbS₂ [3–6,11]. In these compounds, the spectra consist of two absorption peaks for Eu²⁺ and Eu³⁺ at low temperatures. With increasing temperatures, the two peaks become wider and approach each other, and only one broad peak is observed at room temperature, which is due to the electron hopping between Eu²⁺ and Eu³⁺. Therefore, our experimental results show that such an electron hopping does not occur in the present sulfide Eu₂BiS₄.

3.3. Magnetic properties

Fig. 8(a) and (b) show the temperature dependence of reciprocal magnetic susceptibilities (χ^{-1}) for Eu₂BiS₄ and EuGdBiS₄, respectively. Both the magnetic susceptibilities follow the Curie-Weiss law in the temperature range between 50 and 300 K. Table 3 lists the effective magnetic moment (μ_{eff}) and the Weiss constant (Θ_W) for Eu₂BiS₄ and EuGdBiS₄. In the Eu₂BiS₄, both the europium ions, Eu²⁺ and Eu³⁺ contribute to its magnetic properties. The electron configuration of Eu²⁺ is [Xe]4f⁷ ([Xe]: core electron configuration of xenon) and the ground state of the Eu²⁺ ion is ${}^{8}S_{7/2}$. Therefore, the effective

magnetic moment is calculated to be 7.94 $\mu_{\rm B}$ from the relation $\mu_{\rm eff} = g_{\rm J} \sqrt{J(J+1)}$ ($g_{\rm J}$ is the Lande g-factor, and J is the total angular momentum). For the Eu³⁺ ion, the ground state is 7F_0 , which means that its contribution to the magnetic moment of Eu₂BiS₄ is negligible. Therefore, the effective magnetic moment for Eu₂BiS₄ should be 7.94 $\mu_{\rm B}$. The moment obtained from magnetic susceptibility measurements is in accordance with this value.

The values of $\mu_{\rm eff}$ and $\Theta_{\rm W}$ for EuGdBiS₄ have been determined to be 11.13 $\mu_{\rm B}$ and -0.92 K, respectively. Both the Eu²⁺ and Gd³⁺ contribute to the magnetic properties of EuGdBiS₄. These ions have the same electron configuration ([Xe]4f⁷) and the same ground state (⁸S_{7/2}). Therefore, the effective magnetic moment of EuGdBiS₄ is calculated to be $\mu_{\rm eff} = \sqrt{\mu_{\rm Eu^{2+}}^2 + \mu_{\rm Gd^{3+}}^2} = 11.23 \ \mu_{\rm B}$. The experimental magnetic moment is in good agreement with this theoretical moment.

The magnetic susceptibilities (χ) for Eu₂BiS₄ in the lower temperature region are shown in the inset of Fig. 8(a). It is found that Eu₂BiS₄ shows an antiferromagnetic transition at 2.8 K. No divergence between the ZFC and FC magnetic susceptibility is observed. For EuGdBiS₄, magnetic susceptibility measurements show the occurrence of an antiferromagnetic ordering without ferromagnetic component below 6.5 K (see the inset of Fig. 8(b)). It is considered that the substitution of the magnetic Gd³⁺ ion (⁸S_{7/2}) for the nonmagnetic Eu³⁺ ion (⁷F₀) causes the higher Néel temperature for EuGdBiS₄.

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