

^{151}Eu and ^{121}Sb Mössbauer spectroscopy of EuSbSe_3 and EuBiSe_3

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Abstract

^{151}Eu and ^{121}Sb Mössbauer spectroscopy of EuSbSe_3 and EuBiSe_3 were measured at different temperatures. The presence of divalent europium and trivalent antimony were confirmed. The largely negative values of the isomer shift in ^{151}Eu spectrum show highly ionic bonding within these two compounds. Both of them show magnetic hyperfine field splitting at 4.2 K, which indicates a change in the orientation of the EFG principal axis with respect to the magnetic hyperfine field direction. EuSbSe_3 has slightly smaller electron density at the antimony nuclei, compared to Sb_2Se_3 .

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1. Introduction

Sb/Bi chalcogenide compounds have been extensively studied not only because of their potential applications as thermoelectric materials, but also because of the stereochemical activity of their ns^2 lone pair electrons, which influence the crystallographic and electronic structures. The inclusion of lanthanides usually results in a more complex structure than the parent binary pnictogen chalcogenide phases and consequently adds interesting physical properties. Europium is especially intriguing due to the divalent or mixed-valent character of the Eu ions. Many ternary europium pnictogen chalcogenide compounds have been reported including EuPn_2Q_4 ($Pn = \text{Sb, Bi}$; $Q = \text{S, Se, Te}$) [1,2], EuSb_4S_7 [2], $\text{Eu}_3\text{Sb}_4\text{S}_9$ [3], $\text{Eu}_{1.1}\text{Bi}_2\text{S}_4$ [4], Eu_2BiS_4 [5], EuPn_4Q_7 ($Pn = \text{Sb, Bi}$; $Q = \text{S, Se}$) [6], $\text{Eu}_3\text{Pn}_4\text{Q}_9$ ($Pn = \text{Sb, Bi}$; $Q = \text{S, Se, Te}$) [6], $\text{Eu}_6\text{Sb}_6\text{S}_{17}$ [7], and the metal-rich phase $\text{Eu}_4\text{Bi}_2\text{Te}$ [8].

Recently, we detailed the syntheses and characterization of EuPnSe_3 ($Pn = \text{Sb, Bi}$) [9]. Both compounds are isotypic with SrPnSe_3 ($Pn = \text{Sb, Bi}$), which has an intricate three-

dimensional structure with four crystallographically unique sites for both Sr and Pn. Magnetic susceptibility measurements showed that these compounds have divalent europium ions, and undergo antiferromagnetic ordering below 5 K. In order to further investigate EuSbSe_3 and EuBiSe_3 , ^{151}Eu and ^{121}Sb Mössbauer spectroscopy studies were undertaken, which is a powerful tool to investigate the valence state, electronic structure, and coordination environment of the Mössbauer active nuclides.

2. Experimental

2.1. Starting materials

Eu (99.9%, Alfa-Aesar) and Se (99.5%, Alfa-Aesar) were used as received. Sb_2Se_3 and Bi_2Se_3 were prepared from the direct reaction of the elements at 850 °C.

2.2. Syntheses of EuPnSe_3 ($Pn = \text{Sb, Bi}$)

Two grams of Eu, Pn_2Se_3 , and Se, in molar ratio of 1:0.5:1.5 were mixed into fused-silica ampoules in an argon-filled glovebox. Then the ampoules were sealed under vacuum and heated in a programmable tube furnace using the following heating profiles: EuSbSe_3 : 2 °C/min to

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200 °C for 1 h, 0.5 °C/min to 850 °C for 10 day, 0.05 °C/min to 450 °C for 2 day, and 0.5 °C/min to 24 °C; EuBiSe₃: 2 °C/min to 200 °C for 1 h, 0.5 °C/min to 900 °C for 10 day, 0.05 °C/min to 500 °C for 2 day, and 0.5 °C/min to 24 °C. Large black polycrystalline slabs were isolated manually and ground into powder in both cases. PXRD measurements confirmed phase purity by comparison with powder patterns calculated from the single crystal X-ray structures.

2.3. Powder X-ray diffraction

Powder X-ray diffraction patterns were collected with a Rigaku Miniflex powder X-ray diffractometer using CuK α ₁ ($\lambda = 1.54056 \text{ \AA}$) radiation.

2.4. ¹⁵¹Eu and ¹²¹Sb Mössbauer spectroscopy

The 21.53 keV transition of ¹⁵¹Eu with an activity of 130 MBq (2% of the total activity of a ¹⁵¹Sm:EuF₃ source) and a Ba^{121m}SnO₃ source were used for the Mössbauer spectroscopic experiments, which were conducted in the usual transmission geometry. The measurements were performed with a commercial helium bath cryostat. The temperature of the absorber was varied between 4.2 K and room temperature, while the source was kept at room temperature. The temperature was controlled by a resistance thermometer ($\pm 0.5 \text{ K}$ accuracy). The samples were placed within a thin-walled PVC container at a thickness corresponding to about 10 Eu/cm², respectively.

3. Results and discussion

3.1. ¹⁵¹Eu Mössbauer spectroscopy

The ¹⁵¹Eu Mössbauer spectra of EuSbSe₃ and EuBiSe₃ at 298, 77, and 4.2 K are presented in Figs. 1 and 2 together with transmission integral fits. The corresponding fitting parameters are listed in Table 1. Both samples show significant absorption, leading to medium signal-to-noise ratios. To give an example, the 4.2 K data of EuBiSe₃ were collected over a period of 5 days.

At room temperature, EuBiSe₃ (Fig. 2) shows a single signal at an isomer shift of $-12.18(2) \text{ mm/s}$, indicating purely divalent europium, in full agreement with the magnetic data [9]. The largely negative value of the isomer shift is indicative for highly ionic bonding within EuBiSe₃. Similar data have been observed at 7 K, slightly above the Néel temperature. The slightly higher line width (in comparison to the room temperature data) indicates already the onset of magnetic ordering.

The room temperature spectrum of EuSbSe₃ clearly shows two spectral contributions, a main signal at -12.10 mm/s and a second one around 0 mm/s with an area ratio of 90/10. The minority contribution corresponds to a Eu^{III} impurity, most likely due to a surface oxidation of the powdered sample.

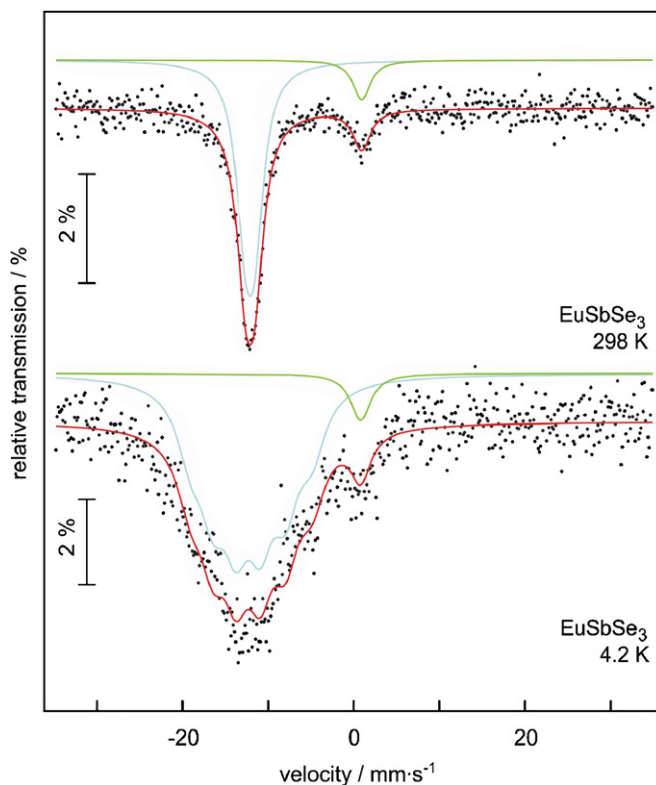


Fig. 1. Experimental and simulated ¹⁵¹Eu Mössbauer spectra of EuSbSe₃ at various temperatures.

Both compounds show magnetic hyperfine field splitting at 4.2 K. Since the Néel temperature of EuSbSe₃ is close to 4.2 K, we observe no full splitting. The detected hyperfine field at 4.2 K is 10.0 T. The area ratio of the Eu^{II} and Eu^{III} signals at 4.2 K is 94/6. For EuBiSe₃ with the higher Néel temperature of 6 K we observe the much higher hyperfine field of 21.2 T, a typical value for divalent europium compounds in the magnetically ordered state [10]. The magnetic hyperfine field splitting is associated with a reduction in the magnitude of the EFG parameter used to optimize the least-squares fits to the data (Table 1), indicating a change in the orientation of the EFG principal axis with respect to the magnetic hyperfine field direction. Similar behavior has recently been observed for EuPdIn [11] and Eu₂Si₅N₈ [12].

The isomer shifts of EuSbSe₃ and EuBiSe₃ are slightly smaller than for the selenogermanates(IV) Eu₂GeSe₄ ($\delta = -12.43 \text{ mm/s}$) and Eu₂Ge₂Se₅ ($\delta = -12.69 \text{ mm/s}$) [13], indicating slightly higher ionicity in the selenogermanates with respect to the group (V) compounds. Comparable values of $\delta = -12.2(5) \text{ mm/s}$ [14] and $\delta = -12.08(10) \text{ mm/s}$ [15] have been observed for binary EuSe.

3.2. ¹²¹Sb Mössbauer spectroscopy

The ¹²¹Sb resonance of EuSbSe₃ at 77 K is presented in Fig. 3 together with a transmission integral fit. Although the structure contains four crystallographically independent

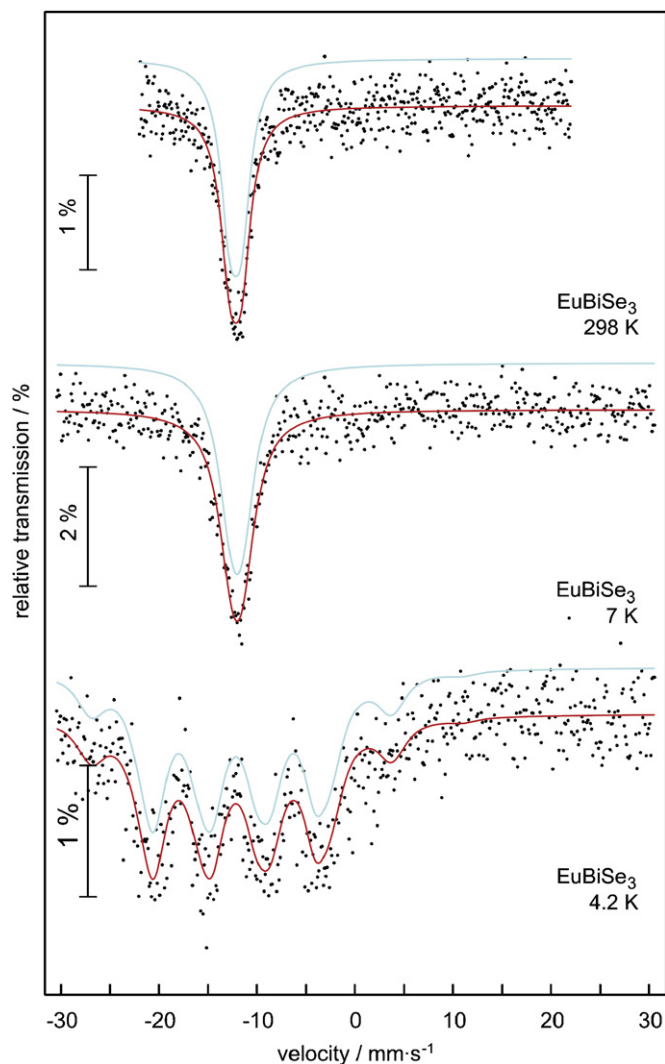


Fig. 2. Experimental and simulated ^{151}Eu Mössbauer spectra of EuBiSe_3 at various temperatures.

Table 1
Fitting parameters of ^{151}Eu Mössbauer measurements of EuBiSe_3 and EuSbSe_3

T (K)	δ (mm/s)	ΔE_{Q1} (mm/s)	B_{hf} (T)	Γ (mm/s)
EuBiSe₃				
298	-12.18(2)	1.18(4)	–	2.36(15)
7	-12.04(4)	1.1(3)	–	3.3(2)
4.2	-12.06(6)	-1.1	21.2(2)	3.12(16)
EuSbSe₃				
298	-12.10(2)	1.12(9)	–	2.56(15)
4.2	-12.40(9)	-1.1	10.0(3)	3.85

Numbers in parentheses represent the statistical errors in the last digit. Parameters without standard deviation were kept fixed during the fitting procedure; δ , isomer shift; Γ , experimental line width; B_{hf} , magnetic hyperfine field; ΔE_{Q} , electric quadrupole splitting parameter.

antimony sites, the spectrum is well reproduced by a single signal at $\delta = -14.04(2)$ mm/s, an experimental line width of $\Gamma = 3.00(9)$ mm/s and a quadrupole splitting parameter of

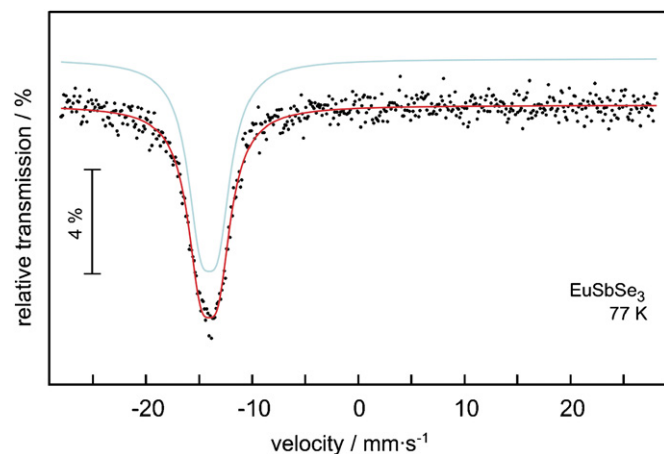


Fig. 3. Experimental and simulated ^{121}Sb Mössbauer spectrum of EuSbSe_3 at 77 K.

$\Delta E_{\text{Q}} = 1.66(6)$ mm/s. The latter is a consequence of the non-cubic site symmetry of the antimony sites. The four sub-spectra show superposition leading to a slightly enhanced line width.

The isomer shift is clearly indicative for trivalent antimony [16]. It is in between the values for the sesquioxide Sb_2O_3 ($\delta = -11.3$ mm/s) and the sesquiselenide Sb_2Se_3 ($\delta = -15.0$ mm/s) [16,17]. Similar isomer shifts have also been observed for $\text{Sb}_2\text{S}_2\text{O}$ (-12.64 mm/s) and $[\text{C}_6\text{H}_{21}\text{N}_4][\text{Sb}_9\text{S}_{14}\text{O}]$ (-12.66 mm/s) [18]. We therefore observe slightly smaller electron density at the antimony nuclei in EuSbSe_3 with respect to Sb_2Se_3 . For EuSbSe_3 , the Sb(1), Sb(2), and Sb(4) atoms are bonded to five Se atoms, and the Sb(3) position is six-coordinate, if we only consider the Sb...Se contacts with bond distances less than 3.4 Å [9]. Bond-valence calculations show that the valence sum of Sb for all four Sb positions is 2.63 on average. In the case of Sb_2Se_3 , the Sb(1) positions are six-coordinate and the Sb(2) sites are in five-coordinate environments [19]. The average bond-valence sum of Sb is 2.70. This finding is not consistent with the above result from ^{121}Sb Mössbauer spectroscopy. Longer Sb...Se contacts and the stereochemical activity of the lone electron pair on Sb^{3+} may affect the electron density at the antimony nuclei as well.

4. Conclusions

EuSbSe_3 and EuBiSe_3 have been examined using ^{151}Eu and ^{121}Sb Mössbauer spectroscopy. These measurements revealed the presence of divalent europium and trivalent antimony, which is consistent with previous results. Both of these compounds have highly ionic bonding and magnetic hyperfine field splitting in the ^{151}Eu spectrum at 4.2 K. EuSbSe_3 has slightly smaller electron density at the antimony nuclei than Sb_2Se_3 .

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