\textbf{151}\textsuperscript{Eu Mössbauer Spectroscopic Characterization of EuRu$_4$B$_4$ and the New Boride EuRuB$_4$}

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Samples of EuRu$_4$B$_4$ and of the new boride EuRuB$_4$ were prepared from europium, RuB, and RuB$_4$ precursor alloys, respectively, in sealed tantalum tubes in an induction furnace. EuRu$_4$B$_4$ crystallizes with the LuRu$_4$B$_4$ structure, $a = 748.1(1)$, $c = 1502.3(4)$ pm. The structure of EuRuB$_4$ was refined on the basis of X-ray diffractometer data: $Pbam$, $a = 599.7(1)$, $b = 1160.7(3)$, $c = 358.06(7)$ pm, $wR_2 = 0.0691$, 474 $F^2$ values, and 38 variables. The four crystallographically independent boron sites build up layers which consist of almost regular pentagons and heptagons which sandwich the ruthenium and europium atoms, respectively. Within the two-dimensional [B$_4$] networks each boron atom has a slightly distorted trigonal-planar boron coordination with B–B distances in the range 172 – 186 pm. Temperature-dependent 151\textsuperscript{Eu Mössbauer spectra show stable trivalent europium for EuRu$_4$B$_4$ and EuRuB$_4$.

Key words: Europium, Borides, Mössbauer Spectroscopy

Introduction

The rare earth elements (RE) form the series of boron-rich borides RERu$_4$B$_4$ (RE = Sc, Y, La–Nd, Sm, Eu–Lu) [1–6] with LuRu$_4$B$_4$ [1] or NdCo$_2$B$_4$ [7] type structure, and RERuB$_4$ (RE = Y, Gd–Lu) [8–10] with YCrB$_4$ [11] type structure. Especially the series of RERu$_4$B$_4$ borides has intensively been investigated with respect to superconductivity. The highest transition temperature of 7.2 K was observed for ScRu$_4$B$_4$ [2]. An inspection of the lattice parameters of the RERu$_4$B$_4$ series has shown that the lattice parameters $a$ and $c$ of EuRu$_4$B$_4$ smoothly fit between those of the samarium and gadolinium compound, a clear crystal chemical hint for trivalent europium. This is different to EuOs$_4$B$_4$ and EuIr$_4$B$_4$ [12] which contain stable divalent europium. In the course of our systematic 151\textsuperscript{Eu Mössbauer spectroscopic studies of intermetallic europium compounds [13–15, and refs. therein] we became interested in the valence behavior of EuRu$_4$B$_4$. During the preparation of EuRu$_4$B$_4$ samples we obtained crystals of the new boride EuRuB$_4$ with YCrB$_4$-type structure [11] which again contains trivalent europium. Herein we report on a structure refinement of EuRuB$_4$ and a 151\textsuperscript{Eu Mössbauer spectroscopic study of EuRuB$_4$ and EuRu$_4$B$_4$.

Experimental Section

Synthesis

Starting materials for the preparation of the EuRu$_4$B$_4$ and EuRuB$_4$ samples were sublimed ingots of europium (Johnson Matthey, > 99.9 %), ruthenium powder (Heraeus, ca. 200 mesh, > 99.9 %), and boron pieces (Alfa Aesar, > 99.5 %). For the synthesis of EuRu$_4$B$_4$ and EuRuB$_4$, ruthenium and boron were prereacted by arc melting [16] in 1:1 and 1:4 atomic ratio, respectively. The product buttons of compositions “RuB” and “RuB$_4$” were then finely ground and weighed with europium in the ideal 1:4 or 1:1 atomic ratio and sealed in tantalum ampoules under an argon pressure of 800 mbar in an arc-melting apparatus. The tantalum ampoules were subsequently placed in the water-cooled sample chamber [17] of an induction furnace (Hüttinger Elektronik, Freiburg, Germany, Typ TIG 2.5/300), heated to 1600 K and kept at that temperature for 30 min, followed by annealing at around 1000 K for another two hours. The polycrystalline products could then easily be separated from the tantalum tubes. No reaction with the container material was discernible. The compact light-gray pieces and the dark-gray powders were stable in air.

EDX data

The EuRuB$_4$ single crystal investigated on the diffractometer was analyzed using a LEICA 420 I scanning electron microscope with EuF$_3$ and Ru as standards. No impurity elements heavier than sodium (detection limit of the instrument) were observed. The Eu:Ru ratio determined semiquantitatively by EDX was in good agreement with the ideal composition. The presence of boron was clearly proven, but the boron content could not be determined reliably (limited resolution of the instrument).

X-Ray powder and single-crystal diffraction

The polycrystalline samples of EuRuB$_4$ and EuRu$_4$B$_4$ were characterized by Guinier patterns (imaging plate de-
were collected with graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) in order to check their quality. Intensity data were obtained from the 1:4:4 sample (vide infra). They were investigated via Laue photographs on a Buerger camera (white Mo radiation) in order to check their quality. Intensity data were collected with graphite-monochromatized Mo Kα radiation on an IPDS-II diffractometer in oscillation mode. A numerical absorption correction was applied to the data set.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U_11</th>
<th>U_22</th>
<th>U_33</th>
<th>U_12</th>
<th>U_23</th>
</tr>
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<tbody>
<tr>
<td>Eu</td>
<td>4g</td>
<td>0.12767(4)</td>
<td>0.15007(2)</td>
<td>0.00000(0)</td>
<td>30(2)</td>
<td>33(2)</td>
<td>33(3)</td>
<td>2(1)</td>
<td>32(2)</td>
</tr>
<tr>
<td>Ru</td>
<td>4g</td>
<td>0.13833(6)</td>
<td>0.40819(4)</td>
<td>0.00000(0)</td>
<td>24(3)</td>
<td>23(3)</td>
<td>31(3)</td>
<td>1(1)</td>
<td>26(2)</td>
</tr>
<tr>
<td>B1</td>
<td>4h</td>
<td>0.286(1)</td>
<td>0.3148(6)</td>
<td>1/2</td>
<td>65(27)</td>
<td>57(26)</td>
<td>46(28)</td>
<td>9(20)</td>
<td>56(10)</td>
</tr>
<tr>
<td>B2</td>
<td>4h</td>
<td>0.360(9)</td>
<td>0.4699(7)</td>
<td>1/2</td>
<td>67(27)</td>
<td>64(28)</td>
<td>30(32)</td>
<td>9(18)</td>
<td>52(11)</td>
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<tr>
<td>B3</td>
<td>4h</td>
<td>0.389(1)</td>
<td>0.0463(6)</td>
<td>1/2</td>
<td>15(22)</td>
<td>44(26)</td>
<td>52(31)</td>
<td>0(18)</td>
<td>37(11)</td>
</tr>
<tr>
<td>B4</td>
<td>4h</td>
<td>0.476(1)</td>
<td>0.1908(6)</td>
<td>1/2</td>
<td>51(24)</td>
<td>47(27)</td>
<td>71(31)</td>
<td>-16(20)</td>
<td>56(11)</td>
</tr>
</tbody>
</table>

Table 2. Atomic coordinates and anisotropic displacement parameters (pm²) for EuRu₄B₄. Uₐq is defined as one third of the trace of the orthogonalized Uᵢᵢ tensor. U₁₃ = U₂₃ = 0.

All relevant crystallographic data for the data collection and evaluation are listed in Table 1.

Structure refinement

Examination of the data set revealed a primitive orthorhombic lattice, and the systematic extinctions were compatible with space group Pbam. This readily indicated the YCrB₄ type [11]. The atomic parameters of isotypic ScNiB₄ [19] were taken as starting values, and the structure was refined using SHELXL-97 [20] (full-matrix least-squares on F²) with anisotropic atomic displacement parameters for all atoms. As a check for the correct composition, the occupancy parameters were refined in separate series of least-squares cycles. All sites were fully occupied within two standard deviations, and in the final cycles the ideal occupancy parameters were assumed again. The final difference Fourier synthesis was flat (Table 1). The positional parameters and interatomic distances are listed in Tables 2 and 3.

Table 3. Interatomic distances (pm) in the structure of EuRu₄B₄. Standard deviations are all equal or less than 0.6 pm.

<table>
<thead>
<tr>
<th>Atom</th>
<th>B3</th>
<th>B1</th>
<th>B2</th>
<th>B4</th>
<th>Eu</th>
</tr>
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<tbody>
<tr>
<td>Eu</td>
<td>266.5</td>
<td>272.9</td>
<td>275.3</td>
<td>276.8</td>
<td>278.6</td>
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<td>272.9</td>
<td>275.2</td>
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<td>275.3</td>
<td>275.3</td>
<td>275.3</td>
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</tr>
<tr>
<td>B4</td>
<td>276.8</td>
<td>276.8</td>
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<td>276.8</td>
<td>276.8</td>
</tr>
<tr>
<td>Eu</td>
<td>278.6</td>
<td>278.6</td>
<td>278.6</td>
<td>278.6</td>
<td>278.6</td>
</tr>
</tbody>
</table>

Note
Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-420990.

**151Eu 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) was used for the 151Eu Mössbauer spectroscopic measurements which were performed in the usual transmission geometry in a commercial helium bath cryostat. The temperature of the absorber could be varied from 78 to 300 K. The source was kept at room temperature in all experiments. The sample was placed within a thin-walled PVC container with a thickness corresponding to about 10 mg Eu/cm².

**Discussion**

**Crystal chemistry**

The new boride EuRuB4 crystallizes with the YCrB4-type structure [7], space group Pbam. It is the first europium compound with this structure type. A projection of the EuRuB4 structure along the short unit cell axis is presented in Fig. 1. The europium and ruthenium atoms are located in slightly distorted pentagonal and heptagonal prisms built up by the boron atoms. These prisms are condensed with each other via the rectangular faces. This leads to two-dimensional boron networks with B–B distances ranging from 172 to 186 pm. They compare well with twice the covalent radius of 176 pm [21], indicating single-bond character.

Between adjacent pentagonal prisms the ruthenium atoms have one ruthenium neighbor at 270 pm, close to the distances in hcp ruthenium (6 × 265 and 6 × 271 pm [22]). The Ru–B distances range from 227 to 241 pm, slightly longer than the sum of the covalent radii of 212 pm [21]. A remarkable feature are the Eu–Ru distances of 300 – 314 pm, which are close or even smaller than the sum of the covalent radii of 309 pm [21]. This is indicative of significant Eu–Ru bonding and is in agreement with the trivalent character of europium (vide infra). In crystal chemically related divalent europium intermetallics like EuRu2P2 [23] or EuRu4Sb12 [24], the Eu–Ru distances of 336 and 402 pm are much longer. A similar trend is ob-

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**Table 4. Fitting parameters for 151Eu Mössbauer spectroscopic measurements on EuRu4B4 and EuRuB4:** isomer shift ($\delta$), electric quadrupole interaction ($\Delta E_Q$) and experimental line width ($\Gamma$).

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$\delta$ (mm s$^{-1}$)</th>
<th>$\Gamma$ (mm s$^{-1}$)</th>
<th>$\Delta E_Q$ (mm s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EuRu4B4</td>
<td>78</td>
<td>0.64(1)</td>
<td>2.54(5)</td>
</tr>
<tr>
<td></td>
<td>78</td>
<td>0.64(1)</td>
<td>2.54(5)</td>
</tr>
</tbody>
</table>

- Kept fixed during the fit.

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**Fig. 1.** Projection of the EuRuB4 structure along the crystallographic z axis. Europium, ruthenium, and boron atoms are drawn as medium grey, black filled, and open circles, respectively. The pentagonal and heptagonal prismatic coordination of the metal atoms is emphasized.

**Fig. 2.** Experimental and simulated 151Eu Mössbauer spectra of EuRu4B4.
Mössbauer spectroscopy

$^{151}$Eu Mössbauer spectra of EuRu$_4$B$_4$ at 298 and 78 K are shown in Fig. 2, and the corresponding fitting parameters are listed in Table 4. As expected from the course of the unit cell volume (vide ultra), the nearly temperature-independent isomer shift values of 1.17(1) mm s$^{-1}$ at 78 K and 1.06(3) mm s$^{-1}$ at 298 K clearly reveal the trivalent nature of the europium atoms.

Fig. 3 shows the $^{151}$Eu Mössbauer spectrum of EuRuB$_4$ at 78 K. As already expected from the crystal structure the europium atoms appear in the trivalent state as suggested by the near zero velocity isomer shift. The 25% single line resonance at $-12.23(1)$ mm s$^{-1}$ is attributed to the EuB$_6$ impurity contribution. The experimentally observed isomer shift value (with respect to EuF$_3$) is very close to those observed by Steichele et al. of $-12.5$ mm s$^{-1}$ [27] and by Li et al. of $-12.1$ mm s$^{-1}$ [26].

The higher isomer shift observed for EuRu$_4$B$_4$ indicates a higher $s$-electron density at the europium nuclei with respect to EuRuB$_4$.

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