^{151}Eu Mössbauer Spectroscopic Characterization of $EuRu_4B_4$ and the New Boride $EuRuB_4$

Thomas Harmening and Rainer Pöttgen

Institut für Anorganische und Analytische Chemie and
NRW Graduate School of Chemistry, Westfälische
Wilhelms-Universität Münster, Corrensstraße 30,
48149 Münster, Germany

Reprint requests to R. Pöttgen.
E-mail: pottgen@uni-muenster.de

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Samples of $EuRu_4B_4$ 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. $EuRu_4B_4$ crystallizes with the $LuRu_4B_4$ 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, $wR2$ = 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}Eu Mössbauer spectra show stable trivalent europium for $EuRu_4B_4$ and $EuRuB_4$.

Key words: Europium, Borides, Mössbauer Spectroscopy

Introduction

The rare earth elements (*RE*) form the series of boron-rich borides $RERu_4B_4$ (*RE* = Sc, Y, La–Nd, Sm, Eu–Lu) [1 – 6] with $LuRu_4B_4$ [1] or $NdCo_4B_4$ [7] type structure, and $RERuB_4$ (*RE* = Y, Gd–Lu) [8 – 10] with $YCrB_4$ [11] type structure. Especially the series of $RERu_4B_4$ borides has intensively been investigated with respect to superconductivity. The highest transition temperature of 7.2 K was observed for $ScRu_4B_4$ [2]. An inspection of the lattice parameters of the $RERu_4B_4$ series has shown that the lattice parameters a and c of $EuRu_4B_4$ smoothly fit between those of the samarium and gadolinium compound, a clear crystal chemical hint for trivalent europium. This is different to $EuOs_4B_4$ and $EuIr_4B_4$ [12] which contain stable divalent europium. In the course of our systematic ^{151}Eu Mössbauer spectroscopic studies of intermetallic europium compounds [13 – 15, and refs. therein] we became interested in the valence behavior of $EuRu_4B_4$. During the preparation of $EuRu_4B_4$ 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}Eu Mössbauer spectroscopic study of $EuRuB_4$ and $EuRu_4B_4$.

Experimental Section

Synthesis

Starting materials for the preparation of the $EuRu_4B_4$ 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 $EuRu_4B_4$ 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 $EuRu_4B_4$ were characterized by Guinier patterns (imaging plate de-

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Table 1. Crystallographic data and structure refinement of $EuRuB_4$.

Structure type	$YCrB_4$
Space group	*Pbam*
Lattice parameters (Guinier powder data)	
a, pm	599.7(1)
b, pm	1160.7(3)
c, pm	358.06(7)
Cell volume V, nm^3	0.2492
Molar mass, g mol^{-1}	296.27
Formula units per cell, Z	4
Crystal size, μm^3	20 × 50 × 50
Calculated density, g cm^{-3}	7.90
Transmission (max / min)	2.21
Radiation; λ, pm	MoK_α; 71.073
μ, mm^{-1}	30.6
$F(000)$, e	508
θ range, deg	3 – 32
Range in *hkl*	±8, ±17, ±5
Total reflections	2180
Independent reflections / R_{int}	474 / 0.0396
Reflections with $I \geq 2\sigma(I)$ / R_{sigma}	451 / 0.0215
Data / parameters	474 / 38
Final $R1$ / $wR2$ indices [$I \geq 2\sigma(I)$]	0.0302 / 0.0678
$R1$ / $wR2$ indices (all data)	0.0320 / 0.0691
Goodness-of-fit	1.204
Extinction coefficient	0.056(3)
Largest diff. peak / hole, e Å^{-3}	3.28 / −3.14

Table 3. Interatomic distances (pm) in the structure of $EuRuB_4$. Standard deviations are all equal or less than 0.6 pm.

Eu:	2	B3	266.5	B1:	1	B4	183.5
	2	B4	272.9		1	B2	185.9
	2	B1	275.2		1	B4	186.1
	2	B2	275.3		2	Ru	227.2
	2	B2	276.8		2	Eu	275.2
	2	B1	278.6		2	Eu	278.6
	2	B4	279.0	B2:	1	B3	175.0
	1	Ru	299.7		1	B2	178.5
	1	Ru	301.2		1	B1	185.9
	1	Ru	313.6		2	Ru	235.3
	1	Ru	313.9		2	Eu	275.3
	2	Eu	358.1		2	Eu	276.8
	2	Eu	379.1	B3:	1	B3	171.6
	1	Eu	380.6		1	B2	175.0
Ru:	2	B1	227.2		1	B4	175.7
	2	B4	234.1		2	Ru	239.4
	2	B2	235.3		2	Ru	240.8
	2	B3	239.4		2	Eu	266.5
	2	B3	240.8	B4:	1	B3	175.7
	1	Ru	270.1		1	B1	183.5
	1	Eu	299.7		1	B1	186.1
	1	Eu	301.2		2	Ru	234.1
	1	Eu	313.6		2	Eu	272.9
	1	Eu	313.9		2	Eu	279.0

tector, Fujifilm BAS-1800) with $CuK_{\alpha 1}$ radiation and α-quartz (a = 491.30, c = 540.46 pm) as an internal standard. Proper indexing of the patterns was ensured through intensity calculations [18]. The lattice parameters of both samples were refined by least-squares calculations. The data obtained for $EuRu_4B_4$ (a = 748.1(1), c = 1502.3(4) pm), are in good agreement with the ones reported in the literature (a = 747.7(5), c = 1504.5(10) pm) [1]. The 1:1:4 sample showed some EuB_6 as a secondary phase. The refined lattice parameter of a = 418.5(1) pm fits to the literature data.

Well shaped single crystals of $EuRuB_4$ were initially 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 MoK_α radiation on an IPDS-II diffractometer in oscillation mode. A numerical absorption correction was applied to the data set. 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 $YCrB_4$ type [11]. The atomic parameters of isotypic $ScNiB_4$ [19] were taken as starting values, and the structure was refined using SHELXL-97 [20] (full-matrix least-squares on F^2) 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 2. Atomic coordinates and anisotropic displacement parameters (pm^2) for $EuRuB_4$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. $U_{13} = U_{23} = 0$.

Atom	Wyckoff site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{eq}
Eu	4*g*	0.12767(4)	0.15007(2)	0	30(2)	33(2)	33(3)	2(1)	32(2)
Ru	4*g*	0.13833(6)	0.40819(4)	0	24(3)	23(3)	31(3)	1(1)	26(2)
B1	4*h*	0.286(1)	0.3148(6)	1/2	65(27)	57(26)	46(28)	9(20)	56(10)
B2	4*h*	0.3630(9)	0.4699(7)	1/2	61(27)	64(28)	30(32)	9(18)	52(11)
B3	4*h*	0.389(1)	0.0463(6)	1/2	15(22)	44(26)	52(31)	0(18)	37(11)
B4	4*h*	0.476(1)	0.1908(6)	1/2	51(24)	47(27)	71(31)	−16(20)	56(11)

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.

^{151}Eu Mössbauer spectroscopy

The 21.53 keV transition of ^{151}Eu with an activity of 130 MBq (2 % of the total activity of a ^{151}Sm:EuF$_3$ source) was used for the ^{151}Eu 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/cm^2.

Discussion

Crystal chemistry

The new boride EuRuB$_4$ crystallizes with the YCrB$_4$-type structure [7], space group *Pbam*. It is the first europium compound with this structure type. A projection of the EuRuB$_4$ 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.

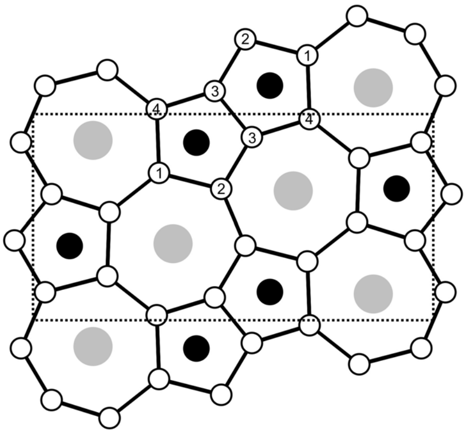

Fig. 1. Projection of the EuRuB$_4$ structure along the crystallographic *z* axis. Europium, ruthenium, and boron atoms are drawn as medium grey, black filled, and open circles, respectively. The pentagonal and heptagonal prismatic coordination of the metal atoms is emphasized.

Table 4. Fitting parameters for ^{151}Eu Mössbauer spectroscopic measurements on EuRu$_4$B$_4$ and EuRuB$_4$: isomer shift (δ), electric quadrupole interaction (ΔE_Q) and experimental line width (Γ).

	T (K)	δ (mm s^{-1})	Γ (mm s^{-1})	ΔE_Q (mm s^{-1})
EuRu$_4$B$_4$	298	1.06(3)	2.5[a]	2.2(3)
	78	1.17(1)	2.5[a]	1.9(1)
EuRuB$_4$	78	0.64(1)	2.5[a]	2.56(5)

[a] Kept fixed during the fit.

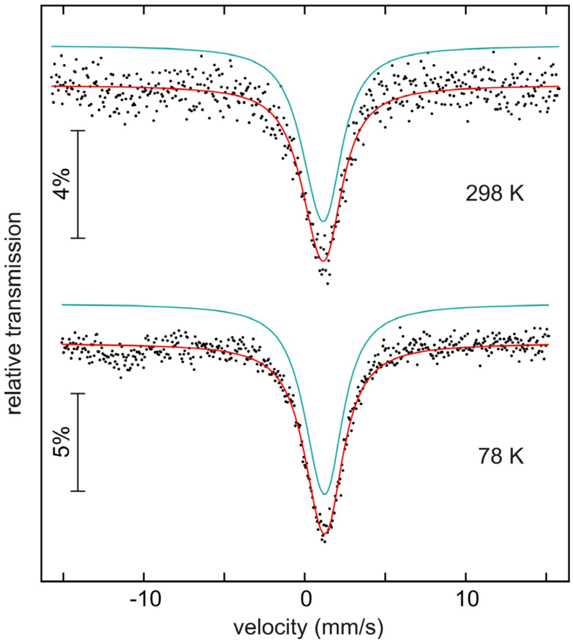

Fig. 2. Experimental and simulated ^{151}Eu Mössbauer spectra of EuRu$_4$B$_4$.

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 EuRu$_2$P$_2$ [23] or EuRu$_4$Sb$_{12}$ [24], the Eu–Ru distances of 336 and 402 pm are much longer. A similar trend is ob-

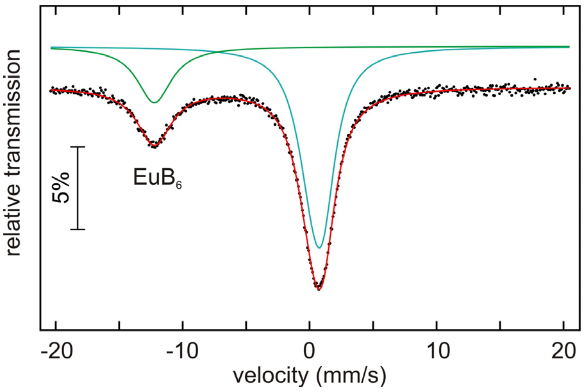

Fig. 3. Experimental and simulated ^{151}Eu Mössbauer spectrum of a $EuRuB_4$ sample at 78 K. For details see text.

served for the Eu–B distances (267 – 279 pm as compared to the sum of the covalent radii of 273 pm [21]). In $EuIr_4B_4$ [12] with divalent europium the shortest Eu–B distance of 290 pm is longer. The trivalent character of europium in $EuRuB_4$ is also evident from the course of the lattice parameters. The cell volume of $EuRuB_4$ is only slightly larger than the one of $GdRuB_4$ and thus smoothly follows the lanthanoid contraction.

Chemical bonding in $YCrB_4$-type borides has recently been studied exemplarily for $YRhB_4$. For further details we refer to that work [25].

Mössbauer spectroscopy

^{151}Eu Mössbauer spectra of $EuRu_4B_4$ 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 $EuRu_4B_4$ indicates a higher *s*-electron density at the europium nuclei with respect to $EuRuB_4$.

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