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Crystal Structures of the Metal Diborides ReB_2, RuB_2, and OsB_2 from Neutron Powder Diffraction

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Dedicated to Professor Bernd Harbrecht on the Occasion of His 60th Birthday

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Abstract. Because of the very small scattering power of the light element, the crystal structures of metal borides that contain heavy metal atoms are difficult to determine unambiguously from X-ray diffraction data only. Using neutron diffraction methods and applying them to isotopically enriched ^{11}B boride powders, the crystal structures of ReB_2, RuB_2, and OsB_2 were re-determined and analysed with respect to the boron atom arrangement. In accordance with the findings from X-ray diffraction experiments, the structures exhibit corrugated boron atom layers of conjugated six-rings, either seat-like (ReB_2) or boat-like (RuB_2, OsB_2). ReB_2 crystallises in the hexagonal crystal system, space group $P6_3/mmc$ (no. 194, a = 290.05(1) pm, c = 747.72(1) pm); OsB_2 and RuB_2 are isostructural and crystallise orthorhombically, space group $Pmmn$ (no. 59, a = 464.479(5) pm, b = 286.515(3) pm, c = 404.560(6) pm (RuB_2); a = 468.408(5) pm, b = 287.255(3) pm, c = 407.693(6) pm (OsB_2)). Boron–boron distances vary between 181.7 and 189.9 pm. For RuB_2 and OsB_2, shortest metal-boron distances range from 217.2 to 217.3 pm, indicating a covalent interaction between metal and boron, compared to 222.7 pm for ReB_2. Metal–metal distances are between 286.5 pm and 302.2 pm. All three compounds have been described as very hard or incompressible materials.

Introduction

The structures of ruthenium, osmium and rhenium diboride have been known since 1962, when *Aronsson* et al. [1] and *Roof* and *Kempter* [2] described RuB_2 and OsB_2, whereas *La Placa* and *Post* published the structure of ReB_2 [3], which had formerly been falsely assigned ("ReB_3") [4]. The MB_2 (M = Re, Ru, Os) structures were determined by single-crystal X-ray diffraction. It was not until very recently that these compounds raised fresh interest and were described as super-hard or ultra-incompressible [5–14]. RuB_2 and OsB_2 are known to become superconducting at T_C = 1.7 K [15] (Ru) and 2.1 K [16] (Os). Several first principle studies were undertaken to analyse the anisotropic hardness of OsB_2, RuB_2, and ReB_2 [17–26]. However, no up-to-date structural data and especially no accurate boron atom positions became available. Only very recently did *Zogal* et al. publish new single-crystal X-ray data on one of the three compounds under discussion, ReB_2 [27]. Boride structures that consist of heavy metal atoms next to light boron atoms are difficult to be solved unambiguously from X-ray diffraction data. Neutron diffraction methods have now been applied to isotopically enriched ^{11}B boride powders to re-determine the crystal structures of ReB_2, RuB_2, and OsB_2, special attention being paid to the boron atom arrangement. To the best of our knowledge, this is the first time neutron diffraction has been applied to these metal diborides. We will discuss the different layer structures of diborides in the light of the new findings.

Results and Discussion

Mono-phase samples of ReB_2, RuB_2 and OsB_2 were obtained from melting the elements at 2500–2600 K (1 h) under argon in an induction furnace. After ball-milling, the powders were subjected to laboratory X-ray data collection (Co-$K_{\alpha 1}$ radiation) and neutron powder diffractometry at the SPODI beamline of the FRM2 reactor (Garching, Germany). Rietveld refinements (Programme GSAS [28] were performed by using data from the literature [1, 3] as starting models. Both X-ray and neutron data sets for all three samples were refined separately. The refinement results are comprised in Table 1, Table 2, Table 3, and Table 4. The structures proved to be essentially identical to earlier published models, with small deviations in the boron atom arrangement.

ReB_2 (Figure 1) is characterised by alternating layers of metal atoms and boron atoms, the latter forming condensed six-rings in chair-like conformation. Each boron atom has three boron neighbours at distances of 182.10(5) (182(2) pm in [27]). Rhenium has eight boron neighbours, all of them at distances between 222 pm and 226 pm. The coordination polyhe-

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Table 1. Structure determination and crystallographic data for ReB_2.

ReB_2	X-ray	Neutron
Temperature /K	293(2)	
Crystal system	hexagonal	
Space group	$P6_3/mmc$ (No. 194)	
Lattice parameters		
a, b /pm	290.059(2)	290.05(1)
c /pm	747.745(6)	747.72(1)
V /Å^3	54.482(0)	54.48(1)
Calculated density /g·cm^{-3}	12.669	12.671
2θ range /°	25 < 2θ < 110	20 < 2θ < 152
No. reflections	17 measured	35 measured
Structure parameters	5 refined	6 refined
$\rho_{min./max.}$ [a)]	–1.72/1.17	–
Residuals	R_p: 0.0502; R_{wp}: 0.0583; χ^2: 1.651	R_p: 0.0439; R_{wp}: 0.0566; χ^2: 3.836

a) Maximum residual electron density is found at the origin of the cell, but residual neutron scattering is very low at that position.

Table 2. Structure determination and crystallographic data for RuB_2.

RuB_2	X-ray	Neutron
Temperature /K	293(2)	
Crystal system	orthorhombic	
Space group	Pmmn (No. 59)	
Lattice parameters		
a /pm	464.569(5)	464.479(5)
b /pm	286.559(3)	286.515(3)
c /pm	404.605(6)	404.560(6)
V /Å^3	53.863(1)	53.839(1)
Calculated density /g·cm^{-3}	7.565	7.565
2θ range /°	15 < 2θ < 110	15 < 2θ < 150
No. reflections	34 measured	77 measured
Structure parameters	10 refined	10 refined
$\rho_{min./max.}$	–0.70/1.07	–
Residuals	R_p: 0.0559; R_{wp}: 0.0704; χ^2: 1.518	R_p: 0.0621; R_{wp}: 0.0843; χ^2: 14.90

Table 3. Structure determination and crystallographic data for OsB_2.

OsB_2	X-ray	Neutron
Temperature /K	293(2)	
Crystal system	orthorhombic	
Space group	*Pmmn* (No. 59)	
Lattice parameters		
a /pm	468.450(6)	468.408(5)
b /pm	287.372(4)	287.255(3)
c /pm	407.742(6)	407.693(6)
V /Å^3	54.890(1)	54.856(1)
Calculated density /g·cm^{-3}	12.816	12.826
2θ range /°	15 < 2θ < 110	15 < 2θ < 152
No. reflections	34 measured	77 measured
Structure parameters	9 refined	10 refined
$\rho_{min./max.}$	–2.18/2.28	–
Residuals	R_p: 0.0616; R_{wp}: 0.0737; χ^2: 1.857	R_p: 0.0411; R_{wp}: 0.0551; χ^2: 11.95

dron of rhenium could be described as a trigonal prism of boron atoms with both triangular faces capped with additional boron atoms. The shortest Re–B distances are 222.70(6) pm (2x) (vs. 222(2) pm in [27]). The metal atom arrangement can be de derived from a hexagonal close packing, with each rhenium atom coordinated by six rhenium neighbours within the planar layer (Re–Re distances are 290.058(1) pm vs. 289.82 pm in [27]) and an AB stacking sequence of these metal atom layers perpendicular to the *c* axis.

The ReB_2 structure is similar to that of AlB_2 with its planar six-ring sheets of boron atoms and planar metal atom layers, although the latter exhibits a metal atom arrangement that has a stacking sequence of AA. The AlB_2 structure type is known for diborides of magnesium, aluminium, yttrium, molybdenum, tungsten and many others. There are further modifications of MoB_2 and WB_2, better known as W_2B_4 and Mo_2B_4 [29], which are even more similar to ReB_2. Their crystal structures again consist of alternating layers of metal and boron atoms; hence the boron atom layers are alternating planar (as in AlB_2) or corrugated (as in ReB_2).

OsB_2 and RuB_2 are isostructural to each other (Figure 2). Here, both the layers of metal atoms and those of the boron atoms are undulated. The boron-atom sheets consist of boat-like six-rings, again conjugated. The metal atom arrangement is that of corrugated hexagonal sheets, stacking sequence AA perpendicular to the *c* axis. Each metal atom has two plus four metal atom neighbours within the layer.

For OsB_2, short Os–B distances have been described to be essential for the mechanical properties. Here, we observed values between 217.2(2) pm and 229.3(3) pm, compared to a range of 215.6–231.8 pm according to [1]. Again, like in ReB_2, each metal atom has eight boron neighbours, but the coordination polyhedron formed is different from that in the rhenium compound. Each osmium atom is surrounded by 2+4+2 boron atoms, forming an irregular polyhedron which resembles to a distorted trigonal trapezohedron. Within the corrugated boron atom layer, we found the two B–B distances larger than previously described. For OsB_2 they are 182.0(2) pm and 189.9 (2) pm (2x) vs. 179.9 pm and 187.8 pm according to [1]. For RuB_2, they had been described as 177.4 and 190.2 pm; neutron diffraction data now led to values of 181.7(2) pm and 188.8(2) pm (2x).

Conclusions

For the first time, the crystal structures of ReB_2, RuB_2 and OsB_2 were investigated using neutron diffraction, resulting in an accurate localisation of the boron atoms.

Experimental Section

Synthesis

Pure crystalline boron powder (Chemotrade, > 99 % ^{11}B-enriched for neutron diffraction) was mixed with rhenium (Degussa, 99.9 %), osmium (American Elements, 99.99 %), or ruthenium (W.C. Heraeus) powder in stoichiometric ratios and pressed into pellets using a hydraulic press. All samples were prepared in an induction furnace using a

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Table 4. Positional and displacement parameters of atoms in ReB_2, RuB_2, OsB_2. U_{iso} values (pm^2) are defined as one third of track of the orthogonalised tensor U_{ij}. Figures in brackets are standard deviations that refer to the last digit.

Atom	Wyckoff site	x	y	z	U_{iso} or U_{11}, U_{22}, U_{33}, U_{12}, U_{13}, U_{23}
ReB_2					
Re	2*c*	1/3	2/3	1/4	0.0039(2), 0.0039(2), 0.0038(3), 0.0019(1), 0, 0
B	4*f*	1/3	2/3	0.54783(8)	0.0005(2)
RuB_2					
Ru	2*a*	1/4	1/4	0.1505(5)	0.0185(4), 0.0243(5), 0.0392(7), 0, 0, 0
B	4*f*	0.0544(2)	1/4	0.6385(3)	0.0161(2)
OsB_2					
Os	2*a*	1/4	1/4	0.1545(3)	0.0251(4), 0.0326(5), 0.0296(5), 0, 0, 0
B	4*f*	0.0557(2)	1/4	0.6325(4)	0.016(2)

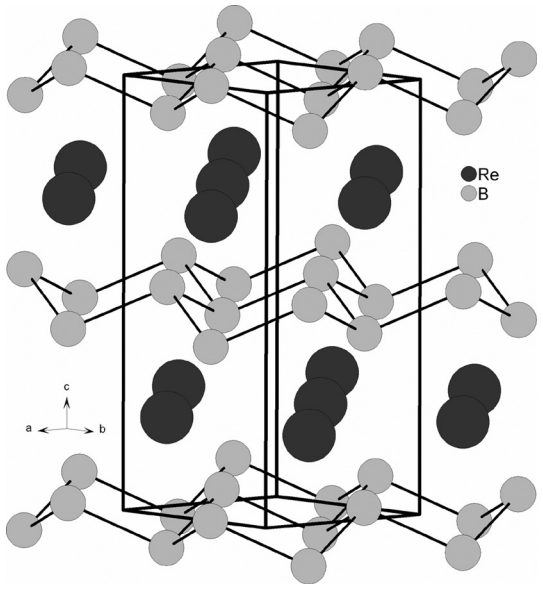

Figure 1. Crystal structure of ReB_2 (light grey: boron atoms, dark grey: metal atoms, Programme DIAMOND [30]).

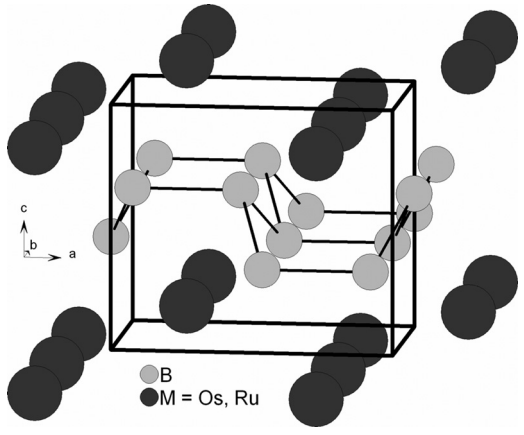

Figure 2. Crystal structures of OsB_2 and RuB_2 (light grey: boron atoms, dark grey: metal atoms, Programme DIAMOND [30]).

combination of an inner reaction crucible (hexagonal boron nitride) and an outer inductive coupling crucible (glassy carbon) under purified argon by melting the starting materials at temperatures of T = 2600 K

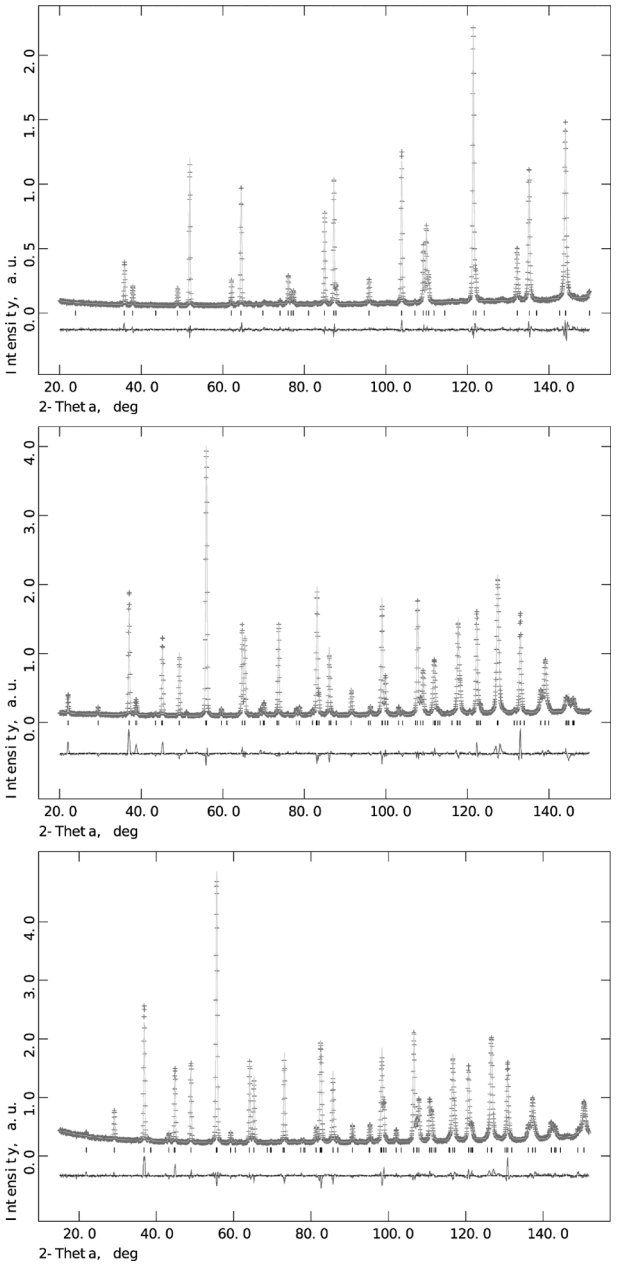

Figure 3. Traces of the neutron powder patterns of ReB_2, RuB_2, and OsB_2 (+: observed, –: calculated, bottom: difference curve). Intensities (y axis) are given in arbitrary units.

(ReB_2) and T = 2500 K (OsB_2, RuB_2) for one hour. Samples were then ground down in an electric ball mill using tungsten carbide grinding cups and balls.

X-ray and Neutron Powder Diffraction

Powder diffraction data were collected at room temperature, first with a powder diffractometer (STOE Stadi P, linear PSD) with Co-$K_{\alpha 1}$ radiation (Ge monochromator, λ = 178.89 pm, flat plate sample holder, transmission geometry), afterwards at a neutron source (FRM-II Garching, SPODI beamline, Ge(551) monochromator, ^{3}He counter, λ = 154.81 pm (ReB_2) or 154.82 pm (OsB_2/RuB_2), cylindrical vanadium container, diameter 8 mm). For Rietveld refinements of the neutron data, zero point, scale factor and background of the neutron patterns were refined using a shifted Chebyshev function with twelve parameters for the background. The pseudovoigt function with four parameters was used to fit the profile (Figure 3). The positions of all atoms and their displacement parameters were refined simultaneously together with the lattice parameters and without constraints. The displacement parameters of the metal atoms were refined anisotropically, those of the boron atoms were refined isotropically. The absorption coefficient was set to 2.5379 cm^{-1} (1 % ^{11}B). It is important to note, that the χ^2 values are too high. We believe that the reason for this is a non-perfect absorption correction. Le Bail fits (without structure information) of the data did not result in better residuals, indicating that the structure determination is correct, despite the unsatisfying χ^2 values.

Further details of the structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldhafen, Germany (Fax: +49-7247-808-666, E-Mail: crysdata@fiz-karlsruhe.de; http://www.fiz-karlsruhe.de/obtaining_ crystal_structure_ data.html) on quoting the depository numbers CSD-421522 (ReB_2), CSD-421524 (RuB_2) and CSD-421523 (OsB_2).

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References

[1] a) B. Aronsson, E. Stenberg, J. Aselius, *Nature* **1962**, *195*, 377; b) B. Aronsson, *Acta Chem. Scand.* **1963**, *17*, 2036.
[2] R. B. Roof, C. P. Kempter, *J. Chem. Phys.* **1962**, *37*, 1473.
[3] S. La Placa, B. Post, *Acta Crystallogr.* **1962**, *15*, 97.
[4] B. Aronsson, E. Stenberg, J. Aselius, *Acta Chem. Scand.* **1960**, *14*, 733.
[5] H.-Y. Chung, M. B. Weinberger, J. B. Levine, A. Kavner, J.-M. Yang, S. H. Tolbert, R. B. Kaner, *Science* **2007**, *316*, 436.
[6] H.-Y. Chung, M. B. Weinberger, J.-M. Yang, S. H. Tolbert, R. B. Kaner, *Appl. Phys. Lett.* **2008**, *92*, 261904.
[7] R. W. Cumberland, M. B. Weinberger, J. J. Gilman, S. M. Clark, S. H. Tolbert, R. B. Kaner, *J. Am. Chem. Soc.* **2005**, *127*, 7264.
[8] M. B. Weinberger, J. B. Levine, H.-Y. Chung, R. W. Cumberland, H. I. Rasool, J.-M. Yang, R. B. Kaner, S. H. Tolbert, *Chem. Mater.* **2009**, *21*, 1915.
[9] J. B. Levine, S. H. Tolbert, R. B. Kaner, *Adv. Funct. Mater.* **2009**, *19*, 3519.
[10] J. B. Levine, S. L. Nguyen, H. I. Rasool, J. A. Wright, S. E. Brown, R. B. Kaner, *J. Am. Chem. Soc.* **2008**, *130*, 16953.
[11] J. V. Rau, A. Latini, A. Generosi, V. Rossi Albertini, D. Ferro, R. Teghil, S. M. Barinov, *Acta Material.* **2009**, *57*, 637.
[12] M. Koehler, V. Keppens, B. C. Sales, R. Jin, D. Mandrus, *J. Phys. D: Appl. Phys.* **2009**, *42*, 095414.
[13] R. H. Wentorf, R. C. DeVries, F. P. Bundy, *Science* **1980**, *208*, 873.
[14] Q. Gu, G. Krauss, W. Steurer, *Adv. Mater.* **2008**, *20*, 3620.
[15] J. M. Vandenberg, B. T. Matthias, E. Corenzwit, H. Barz, *Mater. Res. Bull.* **1975**, *10*, 889.
[16] Y. Singh, A. Niazi, M. D. Vannette, R. Prozorov, D. C. Johnston, *Phys. Rev. B* **2007**, *76*, 214510.
[17] M. Hebbache, L. Stuparevic, D. Zivkovic, *Solid State Commun.* **2006**, *139*, 227.
[18] J. Yang, H. Sun, C. Chen, *J. Am. Chem. Soc.* **2008**, *130*, 7200.
[19] S. Chiodo, H. J. Gotsis, N. Russo, E. Silicia, *Chem. Phys. Lett.* **2006**, *425*, 311.
[20] J. Wang, Y.-J. Wang, *J. Appl. Phys.* **2009**, *105*, 083539.
[21] P. Lazar, X.-Q. Chen, R. Podloucky, *Phys. Rev. B* **2009**, *80*, 012103.
[22] A. Simunek, *Phys. Rev. B* **2009**, *80*, 060103.
[23] S. Aydin, M. Simsek, *Phys. Rev. B* **2009**, *80*, 134107.
[24] W. Zhou, H. Wu, T. Yildirim, *Phys. Rev. B* **2007**, *76*, 184113.
[25] F. Peng, Q. Liu, H. Fu, X. Yang, *Solid State Commun.* **2009**, *149*, 56.
[26] Y.-Q. Wang, L.-F. Yuan, J.-L. Yang, *Chin. Phys. Lett.* **2008**, *25*, 3036.
[27] O. Zogal, Z. Fojud, P. Herzig, A. Pietraszko, A. B. Lyashchenko, S. Jurga, V. N. Paderno, *J. Appl. Phys.* **2009**, *106*, 033514.
[28] a) A. C. Larson, R. B. von Dreele, "*General Structure Analysis System* (GSAS)", Los Alamos National Laboratory Report LAUR 86–748, **1994**; b) B. H. Toby, *J. Appl. Crystallogr.* **2001**, *34*, 210.
[29] M. Frotscher, W. Klein, J. Bauer, C.-M. Fang, J.-F. Halet, A. Senyshyn, C. Baehtz, B. Albert, *Z. Anorg. Allg. Chem.* **2007**, *633*, 2626.
[30] K. Brandenburg, H. Putz, *DIAMOND* v.2.1e, Crystal Impact GbR., **2001**.

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