Journal of Solid State Chemistry **154,** 232–237 (2000)
doi:10.1006/jssc.2000.8841, available online at http://www.idealibrary.com on IDEAL®

$MgOs_3B_4$ and $ScOs_3B_4$, Ternary Borides with a New Channel Structure

Joachim Schiffer and Walter Jung[1]

Institut für Anorganische Chemie, Universität Köln, Greinstrasse 6, 50939 Köln, Germany

Received September 9, 1999; in revised form December 28, 1999; accepted January 2, 2000

The new ternary osmium borides $MgOs_3B_4$ and $ScOs_3B_4$ were prepared by reaction of the elements. They crystallize orthorhombically with $Z = 4$ in the space group *Cmcm*. The crystal structures were determined from single crystal X-ray diffraction intensity data. $MgOs_3B_4$ ($a = 291.28(2)$ pm, $b = 1185.9(1)$ pm, $c = 975.8(1)$ pm, 621 reflections, $R_1 = 0.054$) and $ScOs_3B_4$ ($a = 295.03(4)$ pm, $b = 1179.7(2)$ pm, $c = 981.9(1)$ pm, 516 reflections, $R_1 = 0.054$) are isotypic. The structure contains isolated boron atoms coordinated by six osmium atoms at the corners of a trigonal prism and in addition boron atoms forming a new one-dimensional building element composed of corner sharing, slightly distorted squares with B–B distances of 200(1) pm in the Mg compound and 203(2) pm in the Sc compound. The Mg and Sc atoms, respectively, fill channels in the Os/B-framework running along the *a* axis. © 2000 Academic Press

Key Words: **ternary osmium borides; preparation; crystal structure.**

1. INTRODUCTION

Intermetallic compounds of scandium and magnesium frequently crystallize with isotypic structures. Looking for new examples of this observation we investigated the boron-rich regions of the systems Sc–Os–B and Mg–Os–B. While in the Sc system the ternary compound $ScOsB_2$ has been reported by Shelton *et al.* (1), no reference is made to the Mg–Os–B system in the literature. Our studies resulted in the preparation of two pairs of isotypic compounds, $MgOs_3B_4$/$ScOs_3B_4$ and Mg_2OsB_6/Sc_2OsB_6. The latter one crystallizes with the Y_2ReB_6 structure (2) and will be discussed in a forthcoming paper. Here we report on $MgOs_3B_4$ and $ScOs_3B_4$ which form a new structure type with an unusual aggregation of boron atoms.

2. SAMPLE PREPARATION AND PROPERTIES

$MgOs_3B_4$ and $ScOs_3B_4$ were prepared by reaction of the elemental components (Mg: 99.8%, rod, Ventron; Sc: 99.9%, pieces, Johnson Matthey; Os: 99.9%, powder, Degussa; B: 99.9%, pieces, Aldrich). $ScOs_3B_4$ was obtained by arc-melting stoichiometric mixtures of the elements compressed into pellets on a water-cooled copper plate in an argon atmosphere using a tungsten tip as a second electrode. In order to get a single phase product, arc-melting was repeated twice after turning over the pellet. In the case of $MgOs_3B_4$ a large excess of Mg had to be applied (molar ratio Mg:Os:B = 6:3:4), and the mixture of the elements was heated to 1100°C for 20 h in a boron nitride crucible placed in a sealed molybdenum tube under an atmosphere of argon. After homogenization in a boron carbide mortar the product was again heated to 1100°C for 2 days. The excess of Mg was leached by treatment with diluted hydrochloric acid. Thus the compound was obtained single phase as a dark gray powder.

$ScOs_3B_4$ obviously is a high-temperature phase, because it decomposes when annealed at 1100°C for about 4 h and is rebuilt after remelting in the electric arc. Only $OsB_{1.1}$ could be identified as a decomposition product by X-ray powder methods. Attempts to synthesize the compound at 1500°C failed. So it is supposed that it is stable only above this temperature.

Both compounds are stable to air and moisture and do not show any reaction when treated with half-concentration hydrochloric acid for several days. They are, however, dissolved by aqua regia.

Analyses were carried out by the following methods: Mg, Sc, complexometrically with Titriplex III after removing Os as OsO_4 by distillation; Os, gravimetrically as osmium metal after OsO_4 distillation, precipitation of osmium sulfide, and reduction with H_2; B, decomposition with Na_2O_2, distillation of $B(OCH_3)_3$, titration by the mannit method. The results are listed in Table 1 together with the pycnometrically determined densities.

The electrical resistivity of $MgOs_3B_4$ was measured in the range 300 to 5 K applying a four-probe d.c. method (powder

---

Paper presented at the 13th International Symposium on Boron, Borides and Related Compounds, Dinard, France, September 5–10, 1999.

[1] To whom correspondence should be addressed. Fax: + 49 221 470 5083. E-mail: walter.jung@uni-koeln.de.

0022-4596/00 $35.00

TABLE 1
Crystallographic and Analytical Data of $MgOs_3B_4$ and $ScOs_3B_4$

		$MgOs_3B_4$	$ScOs_3B_4$
Crystal system		Orthorhombic	Orthorhombic
Space group		*Cmcm*	*Cmcm*
Lattice constants (Guinier)	a (pm)	291.28(2)	295.03(4)
	b (pm)	1185.9(1)	1179.7(2)
	c (pm)	975.8(1)	981.9(1)
Formula units per cell		4	4
Chemical analysis, found (calc.)	Mg/Sc	3.87 (3.81)	6.70 (6.82)
weight %	Os	89.23 (89.41)	86.43 (86.61)
	B	6.69 (6.77)	6.37 (6.56)
$D_{X\text{-ray}}$. (g cm^{-3})		12.57	12.80
D_{pyc}. (g cm^{-3})		12.27	12.84
Crystal size (μm^3)		$120 \times 20 \times 15$	$120 \times 20 \times 15$
Scan range		$3 \leq \theta \leq 45°$	$3 \leq \theta \leq 45°$
Scan width ($\theta/2\theta$, + 25% background)		0.8°	0.8°
Measuring time per reflection(s)		120	120
Total number of reflections		3119	3118
Unique reflections		811	756
Unique reflections with $I > 2\sigma(I)$		621	516
Inner residual (on F^2 values)		$R_i = 0.132$	$R_i = 0.054$
R_1 ($I > 2\sigma(I)$)		0.054	0.054
wR_2		0.127	0.126
Number of variables		23	23
Refined extinction (17)		0.0054(6)	0.0026(4)
Highest residual density (e/Å^3)		20.1[a]	13.2[b]

[a] 61 pm from Os1.
[b] 73 pm from Os2.

specimen, pressed into a rod and sintered in a sealed tantalum tube at 900°C for 1 day). The values obtained are shown as a function of temperature in Fig. 1. They are likely to be somewhat too high, as only sintered material was used, but they indicate metallic behavior.

3. STRUCTURE DETERMINATION

A small, needle-shaped single crystal of $ScOs_3B_4$ could be isolated from an arc-melted pellet. To obtain single crystals of $MgOs_3B_4$ a mixture of the elements with molar composition Mg:Os:B = 40:3:4.5 was heated to 1100°C for 20 days. After treatment with diluted hydrochloric acid the specimen consisted of black, needle-shaped crystals suited for X-ray work.

Precession photographs revealed orthorhombic symmetry and the diffraction symbol *mmmC-c-* (corresponding space groups $Cmc2_1$, $C2cm$ and *Cmcm*) for both compounds. Guinier powder diagrams were recorded using Cu$K\alpha_1$ radiation and Si as an internal standard. They were completely indexed on the basis of the single-crystal data. The lattice constants obtained by least-square fits of the powder data are listed in Table 1.

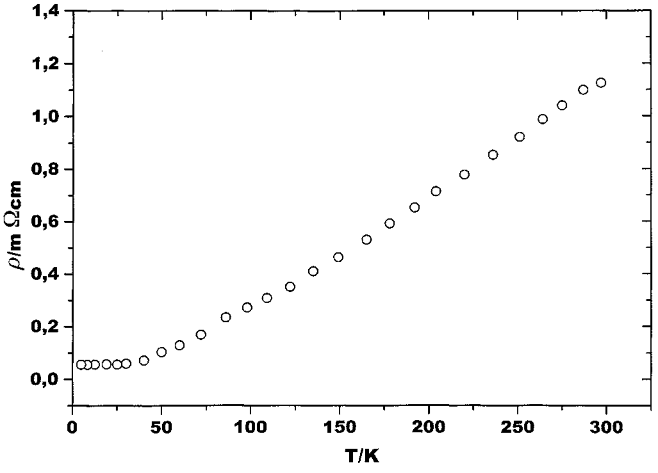

FIG. 1. Electrical resistivity of $MgOs_3B_4$ vs temperature (four-probe d.c. method, sintered powder specimen).

Single-crystal X-ray diffraction intensity data were collected with a four-circle diffractometer (CAD4, Enraf-Nonius, Delft, Netherlands) using graphite-monochromated Mo$K\alpha$ radiation. They were corrected for absorption according to the geometry of the crystals. Crystallographic data and details of the data collection are summarized in Table 1. The structure determinations with direct methods (3) in space group *Cmcm* showed that the two compounds are isotypic. The final parameters obtained from the full-matrix refinements (4) based on F^2 values are listed in Table 2. Interatomic distances up to 300 pm are given in Table 3. In the difference Fourier synthesis quite high residual densities occurred in the vicinity of the osmium positions (Table 1). As no superstructure reflections were observed in precession photographs exposed for very long times, they may be due to disorder or to the assignment of a wrong space group. However, no improvement was achieved by calculations in the lower symmetrical space groups $C2cm$ and $Cmc2_1$.

4. DISCUSSION

The isotypic compounds $MgOs_3B_4$ and $ScOs_3B_4$ crystallize with a new structure shown for $MgOs_3B_4$ as a projection along the short *a*-axis in Fig. 2 (5). The structure may be described as an Os/B framework containing channels filled by linear chains of magnesium atoms. The channels run along the *a*-axis, which is the direction of projection in Fig. 2. Building elements of the Os/B framework are trigonal Os_6B prisms connected by common triangular faces to form columns along [100] and boron ribbons consisting of corner sharing, slightly distorted squares. These two building elements are connected by Os–B bonds and alternate in the direction of the *b*-axis. This is depicted in Fig. 3,

TABLE 2
Atomic Parameters of $MgOs_3B_4$ and $ScOs_3B_4$, Space Group *Cmcm*, Anisotropic Displacement Factors (B: Isotropic) in pm^2, $U_{12} = U_{13} = 0$

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}
				(a) $MgOs_3B_4$				
Os1	8f	0	0.2002(1)	0.6073(1)	6(2)	27(2)	52(2)	0
Os2	4c	0	0.0149(1)	0.25	21(2)	21(3)	43(3)	0
Mg	4b	0	0.5	0	40(3)	30(3)	100(4)	4(38)
B1	8f	0	0.156(3)	0.109(3)	44(30)			
B2	4c	0	0.655(3)	0.25	61(23)			
B3	4c	0	0.377(5)	0.25	70(34)			
				(b) $ScOs_3B_4$				
Os1	8f	0	0.2014(1)	0.6082(1)	47(4)	29(3)	11(3)	0
Os2	4c	0	0.0106(1)	0.25	49(3)	32(3)	6(2)	0
Sc	4b	0	0.5	0	60(2)	50(2)	40(2)	5(19)
B1		0	0.153(3)	0.108(3)	113(46)			
B2	4c	0	0.646(3)	0.25	84(42)			
B3	4c	0	0.368(4)	0.25	135(34)			

which gives a perspective view of a selected area of the structure. From Fig. 2 it becomes obvious that the whole Os/B framework is made up by such patterns. Shifted and reflected according to the c glide plane of the space-group *Cmcm* and linked via Os–Os and Os–B bonds, they repeat in the direction of the *c*-axis. Thereby channels with hexagonal cross-sections are formed. The hexagons consist of four osmium atoms and two boron atoms.

TABLE 3
Interatomic Distances up to 300 pm

	$MgOs_3B_4$
Os1-	(Os1, 1 × 278.4(1), 2 × 280.97(9), 2 × 291.2(1); Os2, 1 × 290.20(8); Mg, 2 × 297.5(1); B1, 1 × 219(1), 2 × 224(3); B2, 1 × 221(1); B3, 2 × 220(1))
Os2-	(Os1, 2 × 290.20(8); Os2, 2 × 291.3(1); Mg, 4 × 284.6(1); B1, 2 × 216(1); B2, 2 × 222(1); B3, 2 × 219(2))
Mg-	(Os1, 4 × 297.5(1); Os2, 4 × 284.6(1); Mg, 2 × 291.2(3); B1, 4 × 258(1); B3, 2 × 284(1))
B1-	(Os1, 1 × 219(1), 2 × 224(3); Os2, 1 × 216(1); Mg, 2 × 258(1); B2, 2 × 200(1))
B2-	(Os1, 2 × 221(1); Os2, 2 × 222(1); Mg, 2 × 258(1); B1, 4 × 200(1))
B3-	(Os1, 4 × 220(1); Os2, 2 × 219(2); Mg, 2 × 284(1))
	$ScOs_3B_4$
Os1-	(Os1, 1 × 278.5(1), 2 × 282.9(1), 2 × 295.0(1); Os2, 1 × 286.3(2); Sc, 2 × 299.2(1); B1, 1 × 220(4), 2 × 227(2); B2, 1 × 228(3); B3, 2 × 219(2))
Os2-	(Os1, 2 × 278.5(1); Os2, 2 × 295.0(1); Sc, 4 × 286.7(1); B1, 2 × 218(3); B2, 2 × 217(3); B3, 2 × 223(4))
Sc-	(Os1, 4 × 299.2(1); Os2, 4 × 286.7(1); Sc, 2 × 295.0(1); B1, 4 × 258(1); B3, 2 × 290(3))
B1-	(Os1, 1 × 220(4), 2 × 227(2); Os2, 1 × 218(3); Sc, 2 × 258(1); B2, 2 × 203(2))
B2-	(Os1, 2 × 220(4); Os2, 2 × 218(3); Sc, 2 × 258(1); B1, 4 × 203(2))
B3-	(Os1, 4 × 219(2); Os2, 2 × 223(4); Sc, 2 × 290(3))

Structures with hexagonal channels are frequently observed with ternary transition metal borides containing a larger nontransition metal atom. Examples are the numerous compounds with $CeCo_3B_2$-type or related structures (6–9). For smaller non-transition metal atoms like Mg or Sc, hexagonal channels are suitable if they are built by the smaller 3d-transition metal atoms Co or Ni ($ScCo_3B_2$ (10), $MgCo_3B_2$ (11), $MgNi_{3-x}B_2$ (12)). In compounds with the larger 4d-transition metal atoms, hexagonal channels seem to be too large for Mg and Sc. The channels in the structures of $Mg_2Ru_5B_4$ (13) and $Sc_2Ru_5B_4$ (14) have pentagonal cross sections. However, in all these cases, the channels are formed exclusively by transition metal atoms. Close contacts between boron atoms and the nontransition metal atoms inside of the channels are thus avoided. In the structure of $MgOs_3B_4$ the contribution of boron atoms to the cross section leads to smaller hexagonal channels well suited for the accommodation of magnesium atoms. At the same time quite short Mg–B contacts (259 pm) are formed. In Fig 4a the environment of the magnesium atoms is shown. It consists of eight osmium and four boron atoms at the corners of a distorted hexagonal prism and two magnesium atoms capping the hexagonal faces. The Mg–Mg distance (291 pm) is shorter than in magnesium metal (320 pm). This is possibly due to an electron transfer from magnesium to the Os/B framework decreasing the atomic radius of the magnesium atoms. Mg–Os– and Mg–B– distances are close to the sums of the metallic radii for CN 12.

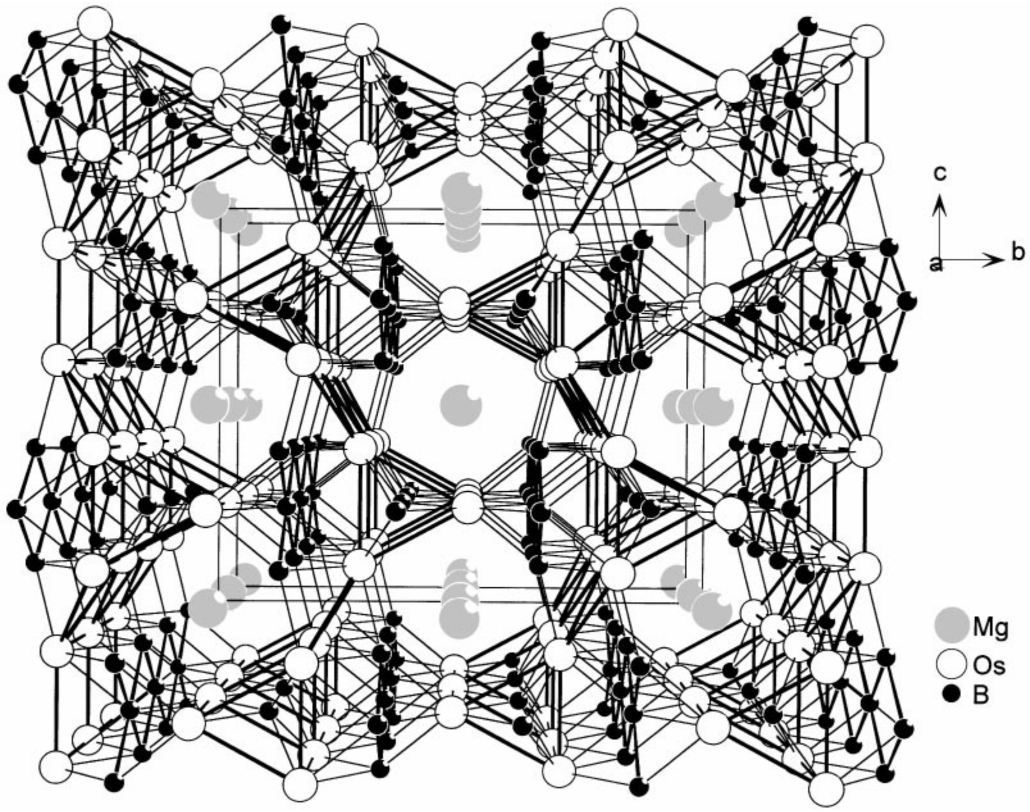

FIG. 2. Projection of the $MgOs_3B_4$ structure along the *a*-axis showing the Os/B framework with channels containing linear chains of magnesium atoms.

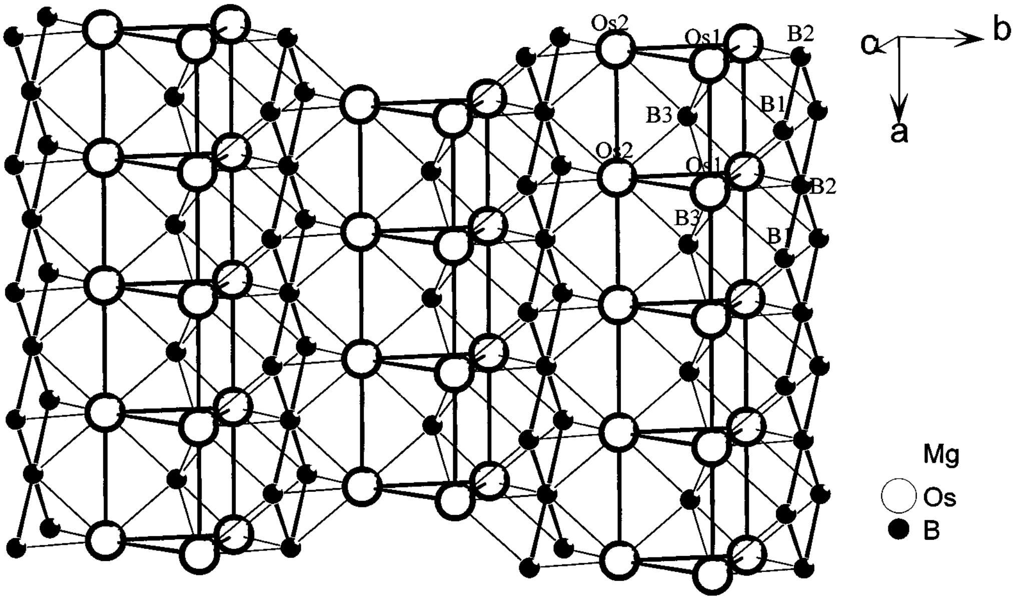

FIG. 3. Selected area of the Os/B framework in the $MgOs_3B_4$ structure. The two characteristic building elements, columns of triangular Os_6B prisms and boron ribbons consisting of corner-sharing, slightly distorted squares, are stressed by heavy lines.

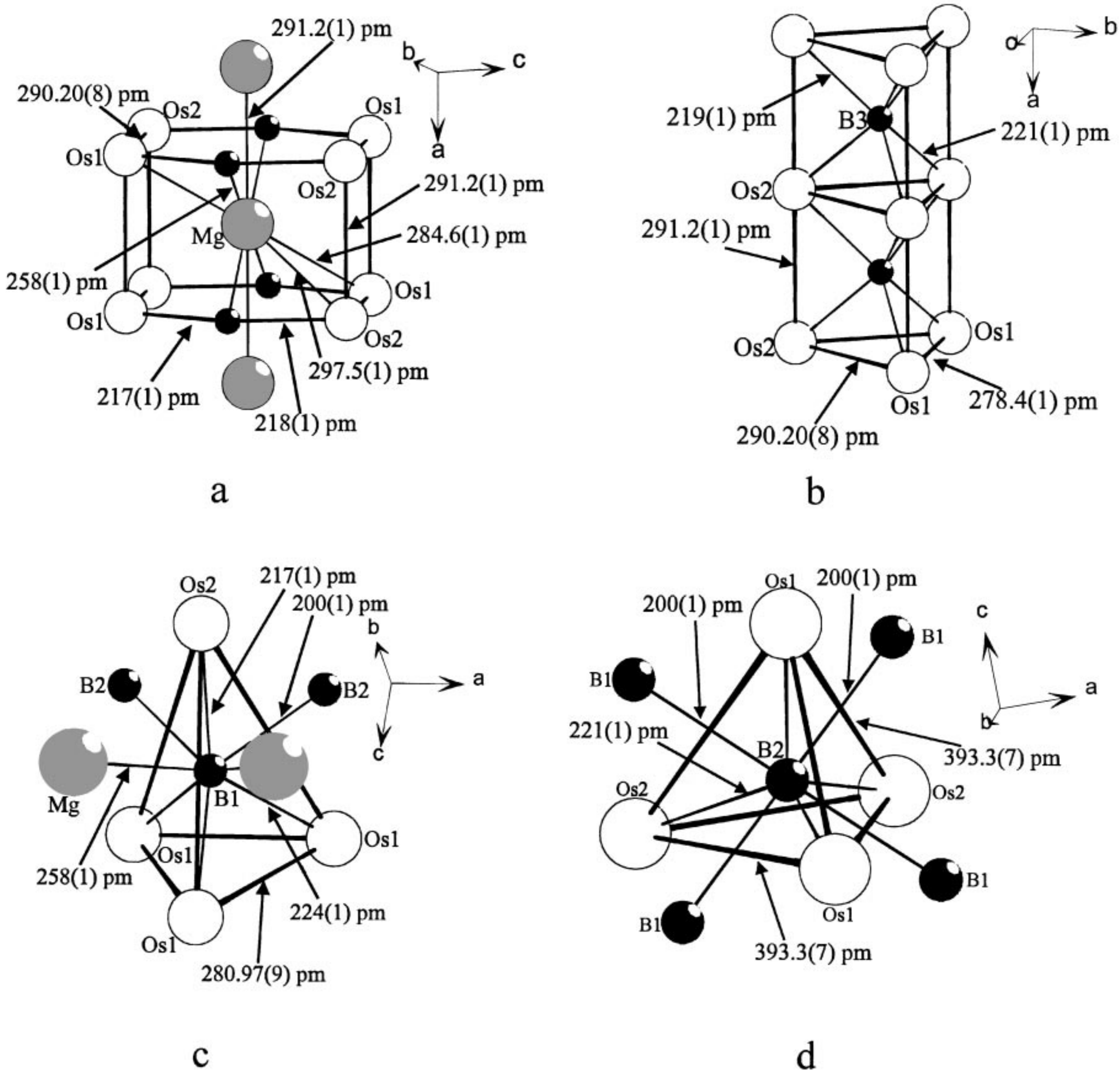

FIG. 4. Environments of (a) Mg, (b) B3, (c) B1, and (d) B2 in the $MgOs_3B_4$ structure.

Os–Os distances in the range 278 to 291 pm ($ScOs_3B_4$: 278 to 295 pm) compare to 268 and 274 pm in osmium metal and indicate weak bonding interactions.

The structure contains three crystallographically distinct boron atoms. The B3 atoms are isolated and show the usual trigonal prismatic coordination (Fig. 4b) with short Os–B distances (average value 220 pm), indicative of strong covalent bonds. Of special interest are, however, B1 and B2 forming the boron ribbons described above. In Fig. 5 such a ribbon is shown as a projection along [010]. The boron squares are slightly distorted with angles of 87° and 93°. The B1–B2 distance is 200 pm ($ScOs_3B_4$, 203 pm). This is rather large compared with B–B distances in borides with boron chains which are typically in the range 174 to 186 pm (15). So only weak bonding interactions are to be expected. The bond strength calculated with the Pauling formula $d = d_1 - 60 \cdot \log n$ (d, observed distance (pm); d_1, metallic single bond distance (82 pm for boron); n, bond strength) (16) is 0.25 ($ScOs_3B_4$, 0.23). The complete environments of B1 and B2 comprising four additional osmium atoms at the vertices of distorted tetrahedra and, in the case of B1, two magnesium atoms are shown in Figs. 4c and 4d. With all these neighboring atoms the bonding strengths of B1 and B2 sum up to $\Sigma n = 3.39$ and 3.48, respectively, ($ScOs_3B_4$: 3.36 and 3.33). These are reasonable values for the metallic valence of boron. They are, however, relatively low if compared with B3 (3.87 for $MgOs_3B_4$ and 3.89 for $ScOs_3B_4$) and boron atoms in other ternary transition metal borides containing an electropositive nontransition metal as a third component. In such compounds, where electron transfer

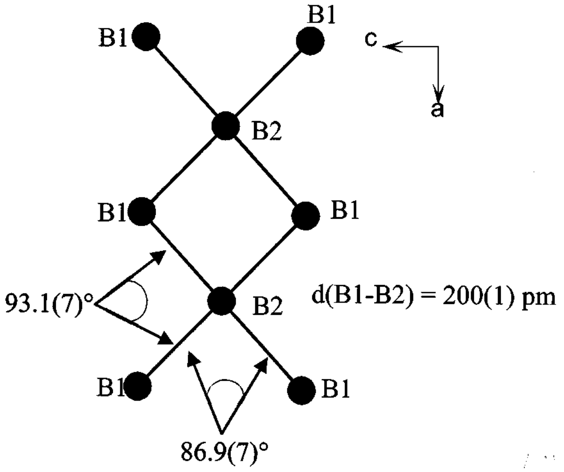

FIG. 5. Boron ribbon consisting of corner-sharing, slightly distorted squares. Projection along [010].

to the boron atoms increasing their metallic valence is likely to occur, Σn values slightly below 4 are usually observed.

ACKNOWLEDGEMENT

Financial support from the Fonds der Chemischen Industrie is gratefully acknowledged.

REFERENCES

1. R. N. Shelton, B. A. Karcher, D. R. Powell, R. A. Jacobson, and H. C. Ku, *Mater. Res. Bull.* **15,** 1445 (1980).
2. Yu. B. Kuźma and S. I. Svarichevskaya, *Sov. Phys. Crystallogr.* **17**(3), 569 (1972).
3. S. R. Hall and J. M. Stewart, XTAL 3.2, Universities of Western Australia and Maryland, 1992.
4. G. M. Sheldrick, SHELXL-97, Programm zur Kristallstrukturlösung, Univ. Göttingen, 1997.
5. K. Brandenburg, M. Berndt, and G. Bergerhoff, DIAMOND 1.1, Visuelles Informationssystem für Kristallstrukturen, Bonn 1995.
6. Yu. B. Kuźma, P. I. Kripyakevich, and N. S. Bilonizhko, *Dopov. Akad. Nauk Ukr. RSR A*, **10,** 939 (1969).
7. K. Niihara and S. Yajima, *Bull. Chem. Soc. Jpn.* **46,** 770 (1973).
8. H. C. Ku and G. P. Meisner, *J. Less-Common Metals* **78,** 99 (1981).
9. W. Jung and D. Quentmeier, *Z. Kristallogr.* **151,** 172 (1980).
10. P. Rogl, *Mh. Chemie* **104,** 1623 (1973).
11. J. Schiffer and W. Jung, unublished.
12. W. Jung, *Z. Naturforsch.* **32b,** 1371 (1977).
13. K. Schweitzer and W. Jung, *Z. Anorg. Allg. Chem.* **530,** 127 (1985).
14. P. Rogl, *J. Solid State Chem.* **55,** 262 (1984).
15. R. Kiessling, *Acta Chem. Scand.* **4,** 209 (1950).
16. L. Pauling, “Die Natur der Chemischen Bindung.” Weinheim, 1973.
17. A. C. Larson, “Cystallographic Computing” (F. R. Ahmed, Ed.), p. 291. Munksgaard, Copenhagen, 1970.