

## Refinement of the Crystal Structure of the Non-stoichiometric Boride $\text{IrB}_{\sim 1.35}$

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The structure of  $\text{IrB}_{\sim 1.35}$  has been refined using a single-crystal diffractometer technique. Variations in the cell dimensions have been observed, indicating a small homogeneity range.

The structure is described in terms of puckered boron layers and puckered metal double layers, which also contain boron atoms in trigonal prismatic interstices. The structure does not contain a three-dimensional boron network.

The microhardness of  $\text{IrB}_{\sim 1.35}$  was found to be  $(1380 \pm 80) \times 10^7$  N/m<sup>2</sup>.

Two of the phases in the iridium-boron system were characterized crystallographically in the early sixties by Aronsson and co-workers<sup>1-3</sup> using powder as well as single-crystal techniques. The phases were denoted  $\text{IrB}_{\sim 1.1}$  and  $\text{IrB}_{\sim 1.35}$ . Recently two further phases were discovered by Rogl, Nowotny and Benesovsky,<sup>4</sup> who claimed the composition to be close to  $\text{IrB}_{0.9}$  for both phases. One of these phases is stable at high temperatures, crystallizing in the WC-type structure. The other phase is a low-temperature modification, which crystallizes in a new, unique structure. Iridium-boron alloys were also studied by Reinacher,<sup>5</sup> using high-temperature microscopical techniques, and by Samsonov *et al.*,<sup>6</sup> who studied the sintering reaction between boron and iridium.

The purpose of the present investigation was to study the boron network of  $\text{IrB}_{\sim 1.35}$  using single-crystal diffractometry.

### EXPERIMENTAL DETAILS

The samples were prepared from iridium powder (Johnson, Matthey and Co., London, claimed purity min. 99.8 %) and crushed crystalline boron (H. C. Starck, Werk Goslar, claimed purity min. 99.8 %) by arc-melting under an inert atmosphere of purified argon. Many crystal fragments were examined in a Weissenberg camera until a crystal suitable for X-ray intensity measurement was found. The crystal fragment selected was taken from an alloy of nominal composition  $\text{IrB}_{\sim 1.4}$ , which in addition contained  $\beta$ -rhombohedral boron crystals. The *h0l* Weissenberg layer of the crystal selected displayed weak

streaks surrounding the reflexions and extending in directions perpendicular to the vector  $\vec{R}(hkl)$  in the reciprocal lattice. Weak streaks were also found in the  $b^*$  direction.

The X-ray intensities were measured with an automatic single-crystal diffractometer (PHILIPS-STOE) using  $\theta - 2\theta$  integration and monochromatized molybdenum radiation (graphite monochromator). A total of 1729 independent reflexions with  $2\theta < 120^\circ$  were recorded. All observed intensities less than  $2\sigma$  were excluded from the refinement procedure. Three standard reflexions (400,  $\bar{1}11$ , and 312) were measured 53 times each during the data collection period but no significant changes in their intensities were detected. Corrections were applied for Lorentz, polarization (correction factor  $p = (1 + \cos^2 2\theta_M \cos^2 2\theta) / (1 + \cos^2 2\theta_M)$  with  $\theta_M = 6.1^\circ$ ) and absorption effects using the program DATAPH, originally written by Coppens *et al.*<sup>7</sup> The calculated value of the linear absorption coefficient was  $1504 \text{ cm}^{-1}$ . The shape of the crystal was approximated by ten boundary planes. The size of the crystal was roughly  $41 \times 42 \times 27 \text{ }\mu\text{m}$  in the directions  $a$ ,  $b$ , and  $c$ , respectively. The agreement factor

$$\frac{\sum |F_o - F_{o,av}|}{\sum F_o}$$

decreased through the application of the absorption correction from 5.2 % to 4.0 % for 109 pairs of equivalent reflexions (those related by the two-fold axis).

#### CELL DIMENSIONS AND MICROHARDNESS

X-Ray powder photographs were taken with a Guinier-Hägg focusing camera using  $\text{CuK}\alpha_1$  radiation and zone-refined silicon ( $a = 5.43054 \text{ \AA}$ ) as internal calibration standard for the determination of the cell dimensions.

The cell dimensions were refined using a least-squares computer program (CELNE) written by J. Tegenfeldt and N.-O. Ersson of the Institute of Chemistry, Uppsala, Sweden.

The microhardness measurements were performed with the DURIMET Micro hardness tester (LEITZ, Wetzlar). The indentations were made with a pyramidal Vickers diamond, using a load of  $49.03 \times 10^{-2} \text{ N}$  (50 p).<sup>\*</sup> The load was applied for ten seconds for all measurements. An oil immersion objective in combination with a green-filter was used in measuring the indentations. The hardness determination was based on the measurements of both diagonals for 17 ( $=n$ ) crack-free indentations, at different parts of the specimen. A hardness value was calculated for each indentation, based on the arithmetic mean of the two diagonals. The calculated standard deviation was obtained using the following expression:

$$\sigma = \left[ \frac{\sum_{i=1}^n (H_{v_i} - \bar{H}_v)^2}{(n-1)} \right]^{1/2}$$

The surface was prepared for the hardness measurements by sawing, wet grinding on carborundum disks and polishing with diamond paste. No etching procedure was performed on the polished surface.

Cell dimensions and microhardness were measured at room temperature and are collected in Table 1.

<sup>\*</sup> 1 N (Newton) = 101.972 p.

Table 1. Cell dimensions and microhardness [ $49.03 \times 10^{-2}$  N (50 p) load] for the monoclinic IrB<sub>~1.35</sub>. Standard deviations are given in parentheses.

Compound	Cell dimensions (Å)	Monoclinic angle (°)	Cell volume (Å <sup>3</sup> )	Microhardness (N/m <sup>2</sup> × 10 <sup>-7</sup> )
IrB <sub>~1.35</sub> B-rich	$a = 10.5300(9)$	$\beta = 91.119(9)$	186.52(6)	$1380 \pm 80^a$
	$b = 2.9038(3)$			
	$c = 6.1013(5)$			
IrB <sub>~1.35</sub> B-poor	$a = 10.5421(10)$	$\beta = 91.143(6)$	185.85(6)	
	$b = 2.8905(3)$			
	$c = 6.1003(4)$			

<sup>a</sup> 1 N/m<sup>2</sup> =  $1.01972 \times 10^{-7}$  kp/mm<sup>2</sup>.

### STRUCTURE REFINEMENT AND RESULTS

The crystal structure of IrB<sub>~1.35</sub> was refined using alternatively a least-squares procedure and Fourier difference technique. The programs used were the full-matrix program UPALS<sup>8</sup> and the Fourier summation program DRF.<sup>9</sup> The atomic scattering factors were taken from Refs. 10 and 11 and were corrected for dispersion effects.<sup>12</sup> The least-squares refinements were based on statistical weights modified according to  $w = 1/\{(C_1\sigma)^2 + (C_2F_o)^2\}$ . The best weighting analysis was obtained using  $C_1 = 1.0$  and  $C_2 = 0.08$ . The discrepancy indices,  $R$  and  $R_w$ , are based on  $F_o$  using unity weights and the weights described above, respectively.

An analysis of the corrected intensity data corroborated the choice of space groups proposed by Aronsson,<sup>3</sup> namely  $C2/m$ ,  $Cm$ , or  $C2$ . The atomic coordinates given in Ref. 3 were used in the first refinement cycles, using space group  $C2/m$ . A very high temperature factor was obtained for the B(5) atom (notation according to Ref. 3), which indicated non-occupancy of the proposed atomic position. A Fourier difference synthesis, based solely on the iridium contributions to  $F_c$ , supported this conclusion. The refinement further yielded approximately 50% occupation of the atomic position of B(6) as obtained with a fixed value for the temperature factor for this atom. The composition of the crystal investigated is thus IrB<sub>~1.25</sub>, which is of a slightly but not necessarily significantly lower boron content than that proposed by Aronsson.<sup>3</sup> The Fourier difference map also displayed electron density peaks approximately 0.1 Å outside the mirror plane, which indicated that the metal atoms might partially occupy a general atomic position close to the mirror plane. Refinement of this model yielded  $y$  coordinates for the iridium atoms that were significantly different from those of the mirror plane ( $\sim 60\sigma$ ). The metal atoms thus occupy positions on one side or the other of the mirror plane in a more or less disordered way.

It is possible, however, that the observed disorder of the metal atoms in the  $b$  direction may be described as anisotropic thermal vibrations of the atoms. The structure was accordingly refined using anisotropic temperature factors for the atoms. This refinement yielded 10% lower estimated standard

deviations for the atomic coordinates and  $R_w = 9.3\%$ . The thermal vibrations of the metal atoms were significantly anisotropic, the r.m.s. vibrations in the  $b$  direction being  $18\sigma$  larger than those in the  $ac$  plane. However, the difference synthesis based on the anisotropic refinement displayed peaks extending in the  $b$  direction from the mirror plane, which supports the model described above with the iridium atoms in general positions. Furthermore, there are no evident physical grounds for markedly anisotropic thermal vibrations of the metal atoms in the structure. These circumstances infer that the most likely structure model involves the iridium atoms in general positions outside the mirror plane.

The structure was also refined in the lower space groups  $C2$  and  $Cm$ , in order to investigate possible disorder in the  $ac$  plane, for which some indications were found in the Fourier difference synthesis. These refinements did not improve the agreement between observed and calculated structure factors. Consequently the space group  $C2/m$  was chosen for the description of the structure.

Table 2. Final structure data for  $\text{IrB}_{\sim 1.35}$ . Standard deviations are given in parentheses. Space group  $C2/m$  (No. 12). Cell dimensions:  $a = 10.5300(9)$  Å,  $b = 2.9038(3)$  Å,  $c = 6.1013(5)$  Å and  $\beta = 91.119(9)^\circ$ .

Atom	Position	$x$	$y$	$z$	$B$	Occupancy
Ir(1)	8( $j$ )	0.09933(9)	0.0310(5)	0.13856(13)	0.56(2)	1/2
Ir(2)	8( $j$ )	0.35745(9)	0.0292(5)	0.28858(13)	0.59(2)	1/2
B(3)	4( $i$ )	0.5545(37)	0	0.3808(56)	1.3(3)	1
B(4)	4( $i$ )	0.1804(22)	0	0.4689(35)	0.6(2)	1
B(6)	4( $i$ )	0.745(10)	0	0.056(16)	1.9(9)	0.51(15) <sup>a</sup>

<sup>a</sup> Refined with fixed temperature factor.

The final structure data are collected in Table 2. The final  $R_w$  was 0.100, based on all observed reflexions (1006), while  $R$  was 0.082 based on 632 reflexions with  $0.5 < \sin\theta/\lambda < 1.04$ . The interatomic distances are presented in Table 3.

## DISCUSSION

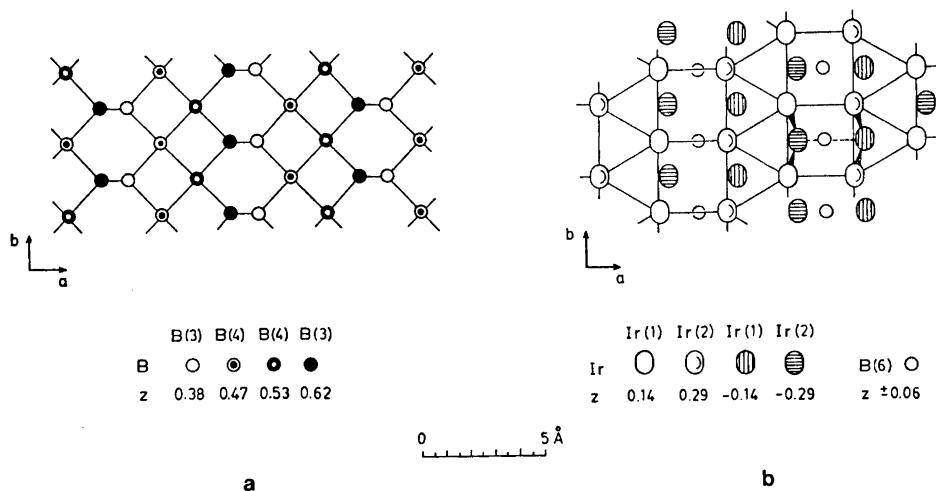
Since diffractometer data were used, the agreement between observed and calculated structure factors as obtained in the refinement was not so good as might have been anticipated. There are at least two factors that might be responsible for the less satisfactory agreement. One factor is the imprecise nature of the absorption correction originating in the large absorption coefficient and the irregular shape of the crystal. Secondly, there is a possibility that for different reflexions different proportions of the X-ray intensity within the streaks have escaped measurement. It is estimated that for this reason some of the reflexions may have up to 15% too low observed intensity.

Table 3. Interatomic distances for  $\text{IrB}_{\sim 1.35}$  (in Å units). Distances listed are  $0.2 \text{ Å} < \text{Ir}-\text{Ir} < 3.8 \text{ Å}$ ,  $\text{Ir}-\text{B} < 3.5 \text{ Å}$ , and  $\text{B}-\text{B} < 2.6 \text{ Å}$ . The estimated standard deviations are given in parentheses.

Ir(1) — B(6)	2.04(11)	Ir(2) — B(4)	2.059(16)
— B(3)	2.07(3)	— B(3)	2.14(4)
— B(6)	2.12(8)	— B(4)	2.175(15)
— B(4)	2.18(2)	— B(4)	2.19(2)
— B(3)	2.19(3)	— B(3)	2.21(4)
— B(6)	2.24(8)	— B(6)	2.28(8)
— Ir(1)	2.664(2)	— B(6)	2.35(10)
— Ir(1)	2.670(2)	— B(6)	2.39(8)
— Ir(1)	2.723(3)	— Ir(2)	2.734(3)
— Ir(2)	2.851(1)	— Ir(1)	2.851(1)
— Ir(2)	2.856(1)	— Ir(1)	2.856(1)
— 2Ir(1)	2.904(0)	— 2Ir(2)	2.904(0)
— Ir(2)	2.946(1)	— Ir(1)	2.946(1)
— Ir(2)	3.008(2)	— Ir(1)	3.008(2)
— Ir(2)	3.023(1)	— Ir(1)	3.023(1)
— Ir(2)	3.028(1)	— Ir(1)	3.028(1)
— Ir(2)	3.084(2)	— Ir(1)	3.084(2)
— Ir(2)	3.089(2)	— Ir(1)	3.089(2)
— Ir(2)	3.113(1)	— Ir(1)	3.113(1)
— Ir(2)	3.172(2)	— Ir(1)	3.172(2)
B(3) — B(3)	1.87(7)	B(4) — 2B(3)	2.03(3)
— 2B(4)	2.03(3)	— 2Ir(2)	2.059(16)
— 2Ir(1)	2.07(3)	— 2B(4)	2.09(3)
— 2Ir(2)	2.14(4)	— 2Ir(2)	2.175(15)
— 2Ir(1)	2.19(3)	— 2Ir(1)	2.18(2)
— 2Ir(2)	2.21(4)	— 2Ir(2)	2.19(2)
B(6) — 2B(6)	1.61(9)	B(6) — 2Ir(2)	2.28(8)
— 2Ir(1)	2.04(11)	— 2Ir(2)	2.35(10)
— 2Ir(1)	2.12(8)	— 2Ir(2)	2.39(8)
— 2Ir(1)	2.24(8)		

However, the results as regards the boron network were unambiguous, although the standard deviation of the occupational parameter of the B(6) atom is large.

The structure can be described most concisely as a stacking in the  $c$  direction of puckered boron layers (B) and puckered double layers of metal atoms (A). The stacking is simple without displacements, *i.e.* the stacking sequence is ABAB... . Projections of these layers in the  $c$  direction are shown in Fig. 1. The B(3) and B(4) atoms form the boron layer, having three and four close boron neighbours, respectively, within the layer. The iridium atoms have five close iridium neighbours within a layer and another two or three adjacent iridium atoms in the other half of the double layer. Boron atoms are also found in the trigonal prismatic interstices of the metal double layer. A full occupation of these interstices would imply the formation of boron chains with a B—B distance of 1.61 Å. However, the B(6) atoms occupy the position only to approximately 50%. If these atoms occupy the interstices in an ordered way, there are no B—B contacts between B(6) atoms. If on the other hand the occupation is disordered, boron pairs or short boron chains might occasionally



*Fig. 1.* The crystal structure of  $\text{IrB}_{\sim 1.35}$  may be described as a simple stacking of puckered boron layers (B) and double layers of metal atoms (A). (a) A puckered boron layer. (b) A puckered double layer of metal atoms containing isolated boron atoms. These boron atoms have a trigonal prismatic environment of metal atoms as indicated in (b). The metal atoms of the upper half of the double layer are connected with unbroken lines.

occur. The accuracy of the present investigation does not permit a choice between these two possibilities.

The structure differs in some respect from that earlier proposed by Aronsson,<sup>3</sup> based on photographic data. The iridium atoms occupy partially a general position close to the mirror plane while they were earlier believed to be situated exactly on the mirror plane. One proposed boron position, B(5), does not occur at all in the present refinement, which precludes the possibility of a three-dimensional boron network. Similar non-occurrence of boron atoms was recently demonstrated in the crystal structures of  $\text{Ru}_2\text{B}_3$ ,<sup>13</sup>  $\text{WB}_{2.0}$ ,<sup>13</sup> and  $\text{Mo}_{1-x}\text{B}_3$ .<sup>14</sup>

In general the interatomic distances obtained in this investigation do not differ appreciably from those obtained by Aronsson,<sup>3</sup> disregarding distances associated with the non-existent B(5) position.

From Table 1 it is apparent that  $\text{IrB}_{\sim 1.35}$  displays a range of homogeneity. The unit cell volume of boron-rich  $\text{IrB}_{\sim 1.35}$  is larger than that of boron-poor composition. Furthermore, an increase of the boron content of the phase involves a decrease of the *a* axis and an increase of the *b* axis while the *c* axis is not influenced. It appears as if the B(6) atoms may explain this behaviour to some extent. If it is assumed that the boron-poor composition corresponds to a half occupation of the B(6) position, the introduction of further boron atoms into the structure would involve the formation of more and more boron chains in the *b* direction. Since the B–B contacts formed are shorter than the remaining B–B distances in the structure (see Table 3), an expansion in the *b* direction is expected. The rigidity of the boron layer causes a minor contrac-

tion in the *a* direction. The *c* axis is not very much affected, since the bonding in the *c* direction mainly consists of metal-metal bonds between the two halves of the double layer and metal-boron bonds between the two types of layers.

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