rhombic symmetry was performed; averaging gave 533 independent intensity values after a correction for absorption was made. A least-squares refinement (the heavy atoms having anisotropic temperature factors) gave the weighted $R = 0.068$. The average standard deviation of the M—O distances is 0.009 Å. The unit-cell dimensions are $a = 8.425$ (9), $b = 8.084$ (8) and $c = 5.909$ (7) Å.

(iii) *Adamite*. A crystal of adamite from Durango, Mexico, was measured on a Weissenberg-type diffractometer with Mo $K\alpha$ radiation. Altogether, 692 reflections were measured; they gave 330 independent reflections after averaging. An absorption correction was applied; the least-squares refinement with anisotropic temperature factors for the As and Zn atoms was used; final weighted $R = 0.045$. The average standard deviation of the M—O distances is 0.012 Å. The unit-cell dimensions are $a = 8.32$ (1), $b = 8.53$ (1) and $c = 6.05$ (1) Å; refinement was in *Pnnm*.

Publication of the full details of items (i) and (iii) is not contemplated because the atomic coordinates obtained agree within one or two standard deviations with previously published data (Toman, 1977; Hill, 1976). Details of item (ii) will be published in a paper on libethenite solid solutions.

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The Crystal Structure of ZrIr₃B~4

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ZrIr₃B~4 crystallizes in the hexagonal space group $P6_3/m$, with $a = 7.560$ (2), $c = 3.512$ (2) Å, $Z = 2$. HfIr₃B₄ is isotypic. The structure was determined and refined from single-crystal counter data: $R = 0.038$ for 237 reflections. The structure contains two different types of boron atoms: B(1), isolated, in distorted trigonal prisms, and B(2), at the centres of Ir octahedra, forming linear chains with B—B = 1.756 Å. The Zr atoms have tetrakaidecahedral metal coordination. The crystal structure of ZrIr₃B~4 is related to the Fe₂P-type structure.

Introduction

The ternary compound ZrIr₃B~4 was found in the course of an X-ray investigation of the Zr–Ir–B system at 1100°C (P. Rogl, unpublished results). The corresponding phase of the homologous system Hf–Ir–B reported by Brukl & Rudy (1967) has been recognized as being isotypic with the former. The purpose of the present work is the determination of the crystal structures of both these phases.

Experimental

Powders of the elements* were compacted in steel dies (without the use of binders or lubricants). The pellets (0.5–1 g) were presintered in vacuum on a boronitride substrate (5 × 10⁻⁶ Torr, 1000°C, 2 h) and finally

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* Zr: Koch Light Laboratories, Colnbrook, England; 99·9% Zr. Hf: Wah Chang, Albany, Oregon, USA; 3% Zr, 600 ppm O. Ir: Englehard Industries Inc., Newark, NJ; 99·9% Ir. B: crystalline, Koch Light Laboratories; 99% B.

Table 1. *Crystallographic data for* ZrIr$_3$B$_{\sim4}$ *and* HfIr$_3$B$_4$

Space group $P6_3/m$ (No. 176), $Z = 2$

ZrIr$_3$B$_{\sim4}$	HfIr$_3$B$_4$
$a = 7.560$ (2) Å	$a = 7.548$ (2) Å
$c = 3.512$ (2)	$c = 3.487$ (2)
$c/a = 0.466$	$c/a = 0.462$
$D_x = 13.5$ g cm^{-3}	$D_x = 15.4$ g cm^{-3}
$\mu(\text{Mo } K\alpha) = 1320$ cm^{-1}	

heated to 1200–1300 °C until melting occurred. After an additional heat treatment at subsolidus temperatures (~1200 °C) for 1 h, the samples were radiation cooled. Small crystals suitable for X-ray analysis were isolated by mechanical fragmentation of the reguli. Because of the small difference in the scattering power of Hf and Ir atoms, single crystals of the Zr compound were used for X-ray analysis. A single crystal of ZrIr$_3$B$_{\sim4}$ was obtained from a melted sample with the nominal composition Zr$_{0.10}$Ir$_{0.39}$B$_{0.51}$. Weissenberg photographs (axis: [001]) proved the crystal to be hexagonal with Laue symmetry $6/m$. The extinctions for $00l$ with $l = 2n + 1$ indicate $P6_3$ or $P6_3/m$ as possible space groups. Lattice parameters and intensities were measured with graphite-monochromated Mo $K\alpha$ radiation on a Philips PW 1100 four-circle goniometer. The crystallographic data are given in Table 1. The intensities of 237 non-equivalent reflections were recorded up to a limit of $\sin\theta/\lambda = 0.8$ Å^{-1}. Except for the ill-shaped peaks of the 002 and 004 reflections, all observed intensities were used in the structure determination. An absorption correction for the crystal ($\sim35 \times 35 \times 50$ μm) was applied, assuming a spherical shape ($\mu r = 2.3$, *International Tables for X-ray Crystallography*, 1968).

Structure determination

Comparison of the atomic volumes with the volume of the unit cell – assuming a space filling of $\sim70\%$ – indicates two formula units of ZrIr$_3$B$_{\sim4}$. Inspection of a three-dimensional Patterson map showed prominent peaks corresponding to six Ir atoms in $6(h)$ of space group $P6_3/m$. From an electron density map the position of the Zr atoms in $2(d)$ was obvious. A difference Fourier map clearly resolved the peaks due to B atoms in $6(h)$ as well as in $2(b)$. It is of interest to note that the B peaks for the $2(b)$ position are definitely smaller by $\frac{1}{4}$ than those for the $6(h)$ position.

The structure was refined with the program *CRYLSQ* (XRAY 70, Stewart, Kundell & Baldwin, 1970). Hartree–Fock scattering factors were used for Zr, Ir and B atoms (Cromer & Mann, 1968). The anomalous-dispersion correction (Ir) was taken from Cromer & Liberman (1970). Unit weights were

attributed to all observed reflections. A relatively high temperature factor for B(2) in $2(b)$ also indicated partial occupation of this site. Because of the high correlation coefficients between occupancy and temperature factor the occupancy 0.76 (5) was determined using a constant temperature factor equal to that of B(1) in $6(h)$. Thus the precise formula is ZrIr$_3$B$_{3.75}$. The final R ($= \Sigma |\Delta F|/\Sigma |F_o|$), calculated for 213 observed reflections ($|F_o| > 2\sigma$) and isotropic temperature factors, was 0.038. At this point a difference Fourier map was featureless. The final positional parameters, and occupancy and temperature factors are given in Table 2; atomic distances are shown in Table 4. As this structure is of a new type a listing of reflections with corresponding intensities for X-ray powder diagram identification is given in Table 3.*

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33081 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Atomic parameters for* ZrIr$_3$B$_{\sim4}$

Standard deviations are in parentheses. Isotropic temperature factors are expressed as $T = \exp[-2\pi^2 10^{-2} U(2 \sin\theta/\lambda)^2]$.

	Site	x	y	z	Occupancy factor	U(Å^2)
Ir	$6(h)$	0.0734 (2)	0.3285 (2)	$\frac{1}{4}$	1.0	0.7 (1)
Zr	$2(d)$	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	1.0	0.9 (1)
B(1)	$6(h)$	0.395 (10)	0.439 (10)	$\frac{1}{4}$	1.0	1.3 (2)
B(2)	$2(b)$	0	0	0	0.76 (5)	1.3

Table 3. *Calculated powder data for* ZrIr$_3$B$_{\sim4}$ *for* Cr $K\alpha$ *radiation* ($\lambda = 2.29092$ Å)

Intensity data were calculated with the point positions obtained from single-crystal data. $I = mF^2(1 + \cos^2 2\theta)/\sin^2 \theta \cos \theta$ is normalized to the strongest reflection having an intensity of 100.

h k ℓ	$10^4 \sin^2\theta$	Intensity	h k ℓ	$10^4 \sin^2\theta$	Intensity
1 0 0	306	3.2	4 0 1	5951	0.3
1 1 0	918	23.2	2 1 2	6397	11.6
2 0 0	1224	30.6	1 2 2	6397	5.2
1 0 1	1370	1.1	4 1 0	6428	0.1
1 1 1	1982	100.0	1 4 0	6428	0.0
2 1 0	2143	18.6	3 2 1	6879	22.2
1 2 0	2143	10.5	2 3 1	6879	18.9
2 0 1	2288	88.3	3 0 2	7009	21.3
3 0 0	2755	27.8	4 1 1	7492	2.7
2 1 1	3206	5.8	1 4 1	7492	0.9
1 2 1	3206	12.9	5 0 0	7652	10.0
2 2 0	3673	2.7	2 2 2	7928	3.1
3 0 1	3818	0.1	3 1 2	8234	21.7
3 1 0	3979	11.1	1 3 2	8234	53.3
1 3 0	3979	30.8	3 3 0	8264	0.2
0 0 2	4255	18.8	4 2 0	8570	17.1
1 0 2	4561	0.1	2 4 0	8570	10.2
2 2 1	4737	8.5	5 0 1	8716	88.4
4 0 0	4897	0.0	4 0 2	9152	0.0
3 1 1	5042	27.1	3 3 1	9328	40.5
1 3 1	5043	1.4	5 1 0	9489	2.6
1 1 2	5173	5.4	1 5 0	9489	1.8
2 0 2	5479	9.4	4 2 1	9634	2.3
3 2 0	5816	5.2	2 4 1	9634	57.8
2 3 0	5816	1.1	1 0 3	9879	1.1

Table 4. *Interatomic distances* (Å) *in* $ZrIr_3B_{\sim4}$

Zr–6 Ir	2·908	B(1)–2 Zr	2·661
3 Ir	3·093	1 Zr	2·550
3 B(1)	2·661	1 Ir	2·140
3 B(1)	2·550	1 Ir	2·137
		2 Ir	2·209
Ir–4 Ir	2·861	[2 B(1)	2·233]
2 Zr	2·908		
1 Zr	3·093	B(2)–6 Ir	2·423
1 B(1)	2·140	2 B(2)	1·756
1 B(1)	2·209		
2 B(1)	2·137		
2 B(2)	2·423		

Fig. 1. Projections along [001] of the crystal structures of (a) $ZrIr_3B_{\sim4}$ and (b) TaFeB.

Isotypic $HfIr_3B_4$

Powder patterns of newly prepared Hf–Ir–B samples with the approximate composition $HfIr_3B_4$ confirmed the existence of the ternary boride phase T_2 ($Hf_{0.07}$-$Ir_{0.42}B_{0.51}$), reported earlier by Brukl & Rudy (1967).

Single-phase powder patterns with sharp reflections have been obtained for samples of composition $Hf_{0.13}Ir_{0.37}B_{0.50}$. The powder patterns were indexed completely on the basis of a primitive hexagonal cell (Table 1). Within the limits of error no changes of the lattice parameters were obtained from multiphase samples, indicating a very narrow homogeneous range for $HfIr_3B_4$. Using the atomic parameters, derived for $ZrIr_3B_{\sim4}$ [Table 2, but according to the composition full occupancy of B(2) in 2(b)], the observed and calculated intensities are in good agreement for $HfIr_3B_4$. An evaluation of the powder diffraction data reported by Brukl & Rudy (1967) gave, within the limits of error, practically the same lattice parameters [$a = 7.545$ (2), $c = 3.485$ (1) Å]. Some extra lines due to the difference in composition were attributed to $IrB_{1.1}$ (α-ThSi$_2$ type).

Description of the structure and discussion

A projection in [001] of the $ZrIr_3B_{\sim4}$-type structure is shown in Fig. 1(a): The Ir atoms form a distorted Kagomé net, 3.6.3.6, which among borides also occurs in the crystal structure of TaFeB (Krypyakevich, Markiv & Melnyk, 1967; Fe$_2$P type, Fig. 1b). However, only one layer (Ta atoms in TaFeB) appears to be fully developed in Fe$_2$P-type phases, as the Fe atoms (second layer in TaFeB) do not bond along the dashed lines indicated in Fig. 1(b). Hexahedral arrays of trigonal prisms have also been observed for the crystal structure of NbCoB (Krypyakevich, Kuz'ma, Voroshilov, Shoemaker & Shoemaker, 1971).

The Zr atoms are located at the centres of each second trigonal prism in a tetrakaidecahedral metal coordination (6 + 3Ir) (Fig. 1a). On the other hand, the metal environment of the Ir atoms is a rather distorted
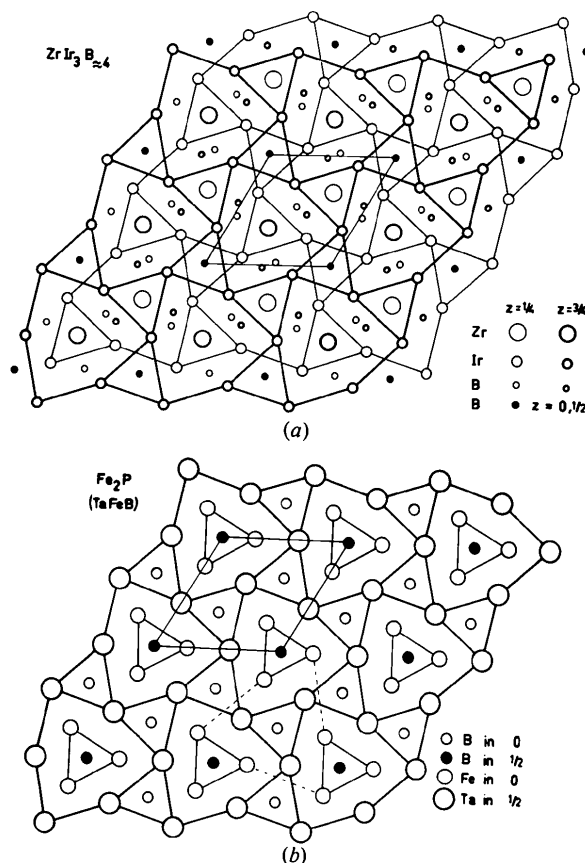
trigonal prism with one additional Zr atom at a distance of 3·093 Å (2 + 1Zr, 4Ir). Additional polyhedra originate from the combination of the two symmetry-related analogous layers of the host lattice: Ir octahedra, face-connected and stacked in rows along [001], as well as chains of distorted Zr_3I_3 trigonal prisms running in the same direction. Thus the metal host lattice in $ZrIr_3B_{\sim4}$ offers two types of interstitial sites for occupation by B atoms. In the octahedral voids (shortened along the c axis) the B(2) atoms form linear chains along [001]: B—B = 1·756 Å. The chain formation is incomplete due to the occupancy of ~75%. The B(1) atoms are located in strongly distorted trigonal prisms. The B(1)—B(1) distances of 2·23 Å can no longer be regarded as bonding. One of the faces of the Zr_3Ir_3 trigonal prisms has an additional neighbour (an Ir atom at a distance of 2·137 Å).

Filling of octahedral voids by B atoms is seldom observed; nevertheless, there are examples, such as RhB, PtB (anti-NiAs type; Lundström, 1969) or perovskite borides in the system (Sc,Y,Ln,Th,U)–(Ru,Rh)–B (Holleck, 1973). In all these phases the B atoms are at the centres of octahedral cages formed by

Group VIII*a* metals only. In RhB and PtB the B atoms form linear chains.

Ternary complex borides have been classified by B aggregation (Nowotny & Rogl, 1977). From the viewpoint of structural chemistry the formation of B chains with B atoms in trigonal-prismatic coordination is the typical element in borides with a B content of ~50 at.% B, whereas isolated B atoms tend to occur with much lower B contents in typical metal host-lattice structures. The crystal structure of $ZrIr_3B_{\sim4}$ can be described as a combination of B chains and isolated B atoms with CN 7. A similar combination occurs with IrB_{1-x} (low-temperature form; Rogl, Nowotny & Benesovsky, 1969). In this case isolated B atoms are surrounded by seven Ir atoms.

The geometry (space group) of the $ZrIr_3B_{\sim4}$ structure type is also found among chalcogenides in the Nb_3Te_4 structure type (Selte & Kjekshus, 1964). A comparison of the exploded formulae illustrates the formal relationship; however, positional parameters and the architecture of the two crystal structures differ considerably: $Ir_6Zr_2B_6B_{2-x} = Nb_6Te_2Te_6\square_2$ [where $\square$ means unoccupied octahedral void in 2(*b*)].

Considering the B aggregation and the strong metal–metal interaction, the crystal structure of $ZrIr_3B_{\sim4}$, despite its high B content, has to be grouped among the metal host-lattice structure types with B atoms accommodated in the interstitial sites of the metal lattice, rather than among typical chain boride structures such as CrB and FeB.

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