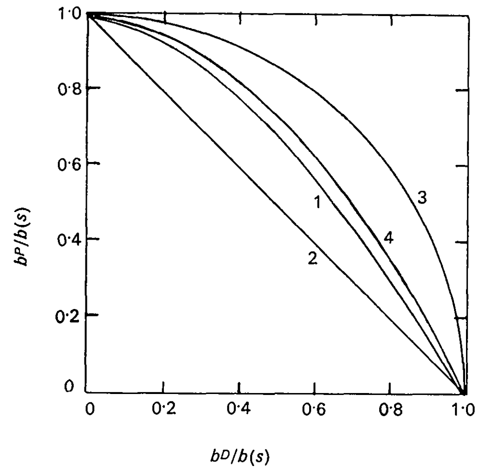

Fig. 1. Plots of $b^P/b(s)$ *versus* $b^D/b(s)$

Curve 1: $b(s)=b^D \exp[-(b^P/\sqrt{\pi} b^D)^2]/[1-\operatorname{erf}(b^P/\sqrt{\pi} b^D)]$
Curve 2: $b(s)=b^P+b^D$
Curve 3: $b(s)=[(b^P)^2+(b^D)^2]^{\frac{1}{2}}$
Curve 4: $b^P/b(s)=1-[b^D/b(s)]^2$

where ε_I and D_I are the integral breadth strain and particle size, respectively. Equation (1) is too complicated and cannot be handled conveniently to estimate the particle size and strain. We suggest that the equation

$$b^P/b(s)=1-[b^D/b(s)]^2 \qquad (5)$$

is a very good approximation to equation (1) and can be employed without difficulty. We plot $b^P/b(s)$ *versus* $b^D/b(s)$ from equations (1) and (5) and see that the difference between the two curves is at most 10%. This is illustrated in Fig. 1.

We analyzed the broadening of cold-worked pure tungsten and Ag–10 % In alloy by the Warren-Averbach analysis, by applying equation (5) and also by applying

$$b^2(s)=(b^D)^2+(b^P)^2 \,. \qquad (6)$$

Equation (6) is obtained when both the particle size and strain profiles are approximated by Gaussian functions.

Pure tungsten and Ag-10 %In filings were prepared at room temperature (23 °C) and powder pattern peaks were recorded on a Norelco diffractometer using the nickel-filtered copper radiation. The Fourier analyses of the powder pattern peaks were carried out by the Warren–Averbach technique and the instrumental correction for the integral breadths was made with the use of a parabolic relationship after Wagner & Aqua (1963). The particle size and strain calculated from the Warren-Averbach analysis, present method and pure Gaussian (considering both strain and particle size distribution as Gaussian) approximation are shown in Table 1.

Of the two materials investigated, Ag-10 %In is highly faulted and tungsten is free of faults. The particle sizes D_I^P for Ag-10 %In obtained by the present method are about twice as high as those obtained by Warren–Averbach analysis. As shown by Mitra & Halder (1964) and Wagner & Aqua (1965) in the case of h.c.p. metals and by Wagner & Aqua (1963) in the case of f.c.c. and b.c.c. metals, if fault broadening predominates, $D_I \simeq 2D_e$. The particle size D_I^G calculated from Gaussian approximation for both strain and particle size distribution is only slightly smaller than D_I^P.

For tungsten filings the integral breadth particle size D_I^P is also twice as large as the particle size $D_e=\bar{D}$. This is in agreement with the definitions of D_I and $\bar{D}$ since

$$D_I=\overline{D^2}/\bar{D}>\bar{D}.$$

As shown above, the approximation $A^P(L)\simeq\exp[-L/D_e]$ leads to the relation $D_I=2D_e$.

The lattice strains calculated with equation (5) are lower than those obtained with equation (6), and are in rather good agreement with the root-mean-square strains $\langle\varepsilon_L^2\rangle^{\frac{1}{2}}$ averaged over the dimensions of the coherently diffracting domains, *i.e.* $\varepsilon_I^P \simeq 1{\cdot}25\,\langle\varepsilon_L^2\rangle^{\frac{1}{2}}$.

References

Mitra, G. B. & Halder, N. C. (1964). *Acta Cryst.* **17**, 817.
Schoening, F. R. L. (1965). *Acta Cryst.* **18**, 975.
Wagner, C. N. J. & Aqua, E. N. (1963). *Advanc. X-ray Anal.* **7**, 46.
Wagner, C. N. J. & Aqua, E. N. (1965). *J. Less Common. Metals*, **8**, 51.
Warren, B. E. & Averbach, B. L. (1950). *J. Appl. Phys.* **21**, 595.
Warren, B. E. & Averbach, B. L. (1952). *J. Appl. Phys.* **23**, 1059.

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Composition and crystallographic data for the highest boride of tungsten.

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Chretien & Helgorsky (1961) have described the highest boride of tungsten, which they called WB_4, as tetragonal with $a_0=6{\cdot}34$ and $c_0=4{\cdot}50$ Å. Goldschmidt, Catherall, Ham & Oliver (1963) also observed this compound but reported slightly different parameters ($a_0=6{\cdot}36$ and $c_0=4{\cdot}42$ kX). We have now made a detailed study of this compound and found the unit cell to be hexagonal with $a_0=5{\cdot}200$ and $c_0=6{\cdot}340$ Å. We have also found evidence that while the ideal formula is WB_4, the compound we studied may contain more than stoichiometric amounts of boron.

There are two problems in determining the composition of this compound. First, it is very difficult to produce a single-phase sample large enough for conventional methods of analysis. Second, owing to the large difference in atomic weight, very accurate analysis is necessary to distinguish between WB_4 and WB_5.

We solved the first problem by electron microprobe analysis of several individual grains in three-phase samples containing W_2B_5 and free boron as well as the highest boride. The tungsten concentration, calculated by the method of Philibert (1963) modified by Colby & Niedermeyer (1964) with an atomic number correction empirically determined from analyzed samples of WB and WB_2, was 78·0 ± 0·4 wt.% (compared with theoretical values of 77·3 for WB_5 and 80·9 for WB_4). The minimum tungsten value for the boron-saturated W_2B_5 phase was 88·2 wt.%, which corresponds to 69·4 at.% boron. This would seem to be a significantly higher boron content than the limit of 68·0 at.% reported for this phase by Keissling (1947) which he admitted was 'rather uncertain'.

Chretien & Helgorsky based their formula on analysis of a sample containing only free boron and the highest boride. They separated the boride from the free boron by dissolving it in aqua regia and then analyzed the solution by standard wet chemical methods. We analyzed several such samples by their method but with X-ray spectrography substituted for traditional wet methods for tungsten analysis in the solution. The results of these analyses generally fell between the theoretical values of WB_4 and WB_5 but were not consistent enough to indicate definitely one or the other. The analytical results are given in Table 1.

Table 1. *Analytical results* (*wt.* %)

	Theoretical		Wet analysis		Microprobe
Compound	W	B	W	B	W
WB	94·4	5·6	94·7	6·2	94·4
'WB_2'	89·5	10·5	89·0	11·2	89·0
W_2B_5 grains	87·2	12·8			88·2
WB_x grains					78·0
WB_x solution			77·0	20·3	
duplicate			75·5	20·9	
duplicate			79·3	22·1	
duplicate			79·7	20·3	
WB_4	80·9	19·1			
WB_5	77·3	22·7			

There is sufficient similarity between our X-ray powder data and both those of Chretien & Helgorsky and of Goldschmidt *et al.* to make it clear that the same compound is being studied in all three cases. Our choice of the hexagonal unit cell is based on Laue and precession photographs of a single crystal found in a bubble in an arc melted tungsten-boride sample containing a large excess of boron (41·4 wt.%). Chretien & Helgorsky based their tetragonal indexing on powder data only. The relationship between the hexagonal and tetragonal lattices is most obvious in the reciprocal lattice where the tetragonal a^* is equal to the hexagonal c^* and *vice versa*.

Our powder data were obtained with a Geiger counter diffractometer and copper radiation. Calculation of '*d*' spacings were based on a wavelength of 1·54050 Å for the $K\alpha_1$ radiation and 1·54178 Å for the unresolved peaks. A comparison of observed and calculated '*d*' spacings is presented in Table 2. The only extinctions observed are in *hhl* reflections with *l* odd and in *hkl* reflections when $h-k=3n$ and *l* is odd. These extinctions are consistent with space groups $P6_3mc$, $P\bar{6}2c$ and $P6_3/mmc$.

The samples studied were prepared by sintering, then arc melting a mixture of high purity tungsten and boron. Since the sample is in contact with a water cooled copper hearth, it is rapidly cooled after melting.

Table 2. *X-ray powder data for* WB_4

Here, $I_c = kmF_c^2$, where *m* is the multiplicity factor and *k* an arbitrary scale factor ($1{\cdot}67 \times 10^{-3}$). No temperature factor was included in F_c.

hkl	d_{obs}	d_{calc}	I_o	I_c
100	4·51	4·50	4	12·5
101	3·67	3·67	100	73·5
002	3·17	3·17	30	37·5
110	2·600	2·600	65	88·4
102	2·596	2·592		11·7
200	2·25	2·25	< 0·3	3·5
201	2·125	2·122	27	17·6
112	2·010	2·010	82	100·0
103	1·911	1·914	20	15·8
202	1·836	1·835	0·3	4·7
210	1·70	1·702	0·5	3·1
211	1·644	1·644	26	15·9
004	1·584	1·586	10	8·1
203	1·540	1·541	12	8·1
300	1·501	1·501	20	22·6
212		1·500		4·5
104	—	1·496	< 0·3	1·9
302	1·356	1·357	19	20·0
114	1·353	1·354	20	19·8
213	1·325	1·326	12	9·4
220	1·300	1·300	7	10·9
204	—	1·296	< 0·3	1·6
310	—	1·249	< 0·3	1·1
311	1·225	1·226	12	6·4
105	1·220	1·221	4	3·8
222	1·202	1·203	19	19·5
312	1·162	1·162	0·3	2·2
214	1·160	1·160		2·3
400	1·125	1·126	< 0·3	0·4
401	1·109	1·109	3	2·4
205	1·105	1·105	3	2·9
304	1·090	1·090	19	15·8
313	1·075	1·075	6	5·6
402	1·061	1·061	< 0·3	0·8
006	1·057	1·057	2	1·8
320	1·034	1·033	< 0·3	0·7
106	—	1·029	< 0·3	0·8
321	1·020	1·020	6	4·2
215	1·017	1·017	6	5·1
224	1·003	1·005	6	10·1
403	0·9934	0·9938	2	2·5
410	0·9828	0·9828	8	11·8
322		0·9824		1·5
314	—	0·9812	—	1·7
116	0·9789	0·9791	11	13·4
206	0·9562	0·9568	0·5	0·7
412	0·9386	0·9387	17	26·6
323	0·9281	0·9283	5	4·1
404	0·9187	0·9180	< 0·3	0·9
500	—	0·9008	< 0·3	0·4
216	—	0·8980	< 0·3	1·5
501	0·8917	0·8918	3	2·2
315	0·8896	0·8900	5	5·3
107	0·8880	0·8883	3	2·2
330	0·8665	0·8668	6	9·0
502		0·8665		0·9
324		0·8656		2·0
306	0·8640	0·8643	10	11·1

Chretien & Helgorsky reported that WB_4 completely dissociated at 1600 °C. If this were the case, it would be impossible to produce this boride by arc melting. A considerable amount of the highest boride must exist near its melting point. As was observed at lower temperatures by Chretien & Helgorsky, it is necessary to have a large excess of boron (> 8:1, B:W) to produce a sample free of W_2B_5.

Chretien & Helgorsky reported a density of 8·3 for WB_4. Their measurements apparently were made on a polyphase powder, perhaps without adequate allowance for free boron.

We measured a density of 5·25 for a solid sample with a 12:1 atomic ratio of boron to tungsten. If the composition of the boride is WB_4, then allowing for the free boron, the density of the boride is 9·9. If the boride is WB_5, the experimental density is 8·7. Assuming 4 formula units per hexagonal unit cell, the theoretical density is 10·16 for WB_4 and 10·64 for WB_5, both reasonably close to 9·9.

In view of the large difference between atomic scattering factors of tungsten and boron it is very difficult to determine the locations of the boron atoms from X-ray measurements and it should be possible to calculate a first approximation of the structure factor by neglecting the contribution of the boron atoms. Partial structure factor calculations for the tungsten alone gave reasonable agreement with observed structure factors calculated from powder data when the following positions in space group $P6_3/mmc$ were used:

2W(1) in 2(*c*)	$\frac{1}{3}, \frac{2}{3}, \frac{1}{4}$; $\frac{2}{3}, \frac{1}{3}, \frac{3}{4}$
2W(2) in 2(*b*)	$0, 0, \frac{1}{4}$; $0, 0, \frac{3}{4}$

The above arrangement of tungsten atoms limits the boron atoms of the following positions:

12B(1) in 12(*i*)	x, 0, 0; *etc.*
4B(2) in 4(*f*)	$\frac{1}{3}, \frac{2}{3}, z$; *etc.*

A value of $\frac{1}{3}$ for X places the boron atoms of the first group equidistant from the surrounding tungsten atoms at a distance of 2·35 Å. Assuming a B–B distance of 1·72 Å (as in W_2B_5) for adjacent boron atoms of the second group, the W–B distance is 2·31 Å which is the same as the shortest W–B distance in W_2B_5. These values correspond to a z of 0·615. The distance of closest approach of two tungsten atoms is 3·00 Å compared with 2·98 Å for W_2B_5. Intensities calculated from the above tungsten and boron positions are included in Table 2.

The proposed structure is closely related to the AlB_2 structure which consists of close packed layers of metal atoms located directly above one another with boron atoms in the interstices. The WB_4 structure can be derived from the AlB_2 structure by replacing one third of the metal atoms with pairs of boron atoms systematically so that the remaining metal atoms form layers of open hexagons with alternate layers displaced by one atom. It is possible that additional tungsten atoms might be randomly replaced by boron pairs which could account for the experimental composition we observed.

References

CHRETIEN, A. & HELGORSKY, J. (1961). *C. R. Acad. Sci., Paris*, **252**, 742.

COLBY, J. W. & NIEDERMEYER, J. F. (1964). USAEC Report NLCO-9H.

GOLDSCHMIDT, H. J., CATHERALL, E. A., HAM, W. M. & OLIVER, D. A. (1963). Wright Patterson AFB Report No. ASD-TDR-62-25, Part II.

KEISSLING, R. (1947). *Acta Chem. Scand.* **1**, 893.

PHILIBERT, J. (1963). *X-Ray Optics and X-Ray Microanalysis*. pp. 379–392. New York: Academic Press.

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The neutron coherent scattering amplitude of caesium.

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The neutron coherent scattering amplitude of the caesium atom, equal to $0{\cdot}49 \times 10^{-12}$ cm according to *International Tables for X-Ray Crystallography* (1962), was used in neutron diffraction investigations of the crystal structure of caesium uranyl nitrate*. The positions of heavy atoms in this structure, including caesium, are known from the X-ray study of Malčić & Manojlović (1961). However, the difference Fourier syntheses applied in our refinement showed the presence of high positive peaks in the caesium atom position. Assuming the work of Malčić & Manojlović to be correct, this suggests that the value taken for the neutron scattering amplitude of caesium is probably too low. To solve the problem, we have reinvestigated this constant.

The neutron diffraction measurements were made on a powder sample of CsCl, Merck's product of a quality normally used in preparing crystals for structure analysis. The sample was contained in a 5 cm long vanadium tube of 0·1 mm wall thickness and 10 mm diameter. The powder diagrams were recorded on a neutron diffractometer on the nuclear reactor RA of this Institute. The neutron wavelength was 1·031 Å. The intensities were brought to an absolute scale by scaling from a nickel powder diagram, obtained under the same experimental conditions.

The powder diagram of CsCl is shown in Fig. 1. The accuracy of the diffraction peak areas was estimated to 3 % or better. The absorption correction was made, and the experimentally determined value of μR for CsCl was found to be 0·17 cm^{-1} and $\varrho'/\varrho_0 = 0{\cdot}645$.

The scattering amplitude of caesium was calculated following the method described by Shull & Wollan (1951) and Sidhu, Heaton & Mueller (1959). The integrated intensities of the reflexions with $h+k+l=2n$ were used. The numerical value of the experimental constant K was obtained from the nickel sample, the scattering amplitude being $1{\cdot}03 \times 10^{-12}$ cm. The plot of F_{hkl} observed *versus* $(\sin\theta)^2/\lambda^2$, for nickel and $h+k+l=2n$ reflexions of CsCl, is shown in Fig. 2. The value of $F(0)_{hkl}$ for CsCl as determined by least squares is found to be $1{\cdot}742 \times 10^{-12}$ cm. From the expression $F(0)=b_{Cs}+b_{Cl}$ for the $h+k+l=2n$ reflexions and the known value of the scattering amplitude of chlorine, equal to $0{\cdot}99 \times 10^{-12}$ cm, as given in *International Tables for X-Ray Crystallography* (1962), we found the coherent scattering amplitude of caesium to be $(0{\cdot}75 \pm 0{\cdot}02) \times 10^{-12}$ cm.

The values of the coherent scattering amplitude of caesium and rubidium quoted in *International Tables for X-Ray Crystallography* (1962) were determined by Shull & Wollan (1951). Our value of b_{Cs} is considerably higher than the previously reported one of $0{\cdot}49 \times 10^{-12}$ cm. The recently

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