CAHN, R. W. (1950). *Proc. Phys. Soc.* A, **63**, 323.

CLAREBROUGH, L. M., HARGREAVES, M. E., MICHELL, D. & WEST, G. W. (1952). *Proc. Roy. Soc.* A, **215**, 507.

COLLINS, J. A. & MATTHEWSON, C. H. (1940). *Trans. Amer. Inst. Min. (Metall.) Engrs.* **137**, 150.

CRUSSARD, C. & AUBERTIN, F. (1946). *Métaux et Corrosion,* **21**, 45.

DEHLINGER, U. & KOCHENDÖRFER, A. (1939). *Z. Kristallogr.* **105**, 393.

ESHELBY, J. D., FRANK, F. C. & NABARRO, F. R. N. (1951). *Phil. Mag.* (7), **42**, 351.

FRANK, F. C. (1948). *Rep. Conf. 'Strength of Solids'.* London: Physical Society.

FRANK, F. C. (1950). Carnegie Institute of Technology. Symposium on the Plastic Deformation of Crystalline Solids. Office of Naval Research.

GAY, P., HIRSCH, P. B. & KELLY, A. (1953). *Acta Metall.* **1**, 315.

GAY, P. & HONEYCOMBE, R. W. K. (1951). *Proc. Phys. Soc.* A, **64**, 844.

GAY, P. & KELLY, A. (1953a). *Acta Cryst.* **6**, 165.

GAY, P. & KELLY, A. (1953b). *Acta Cryst.* **6**, 172.

GUINIER, A. (1952). *Imperfections in Nearly Perfect Crystals.* New York: Wiley.

HALL, W. H. & WILLIAMSON, G. K. (1951a). *Proc. Phys. Soc.* B, **64**, 946.

HALL, W. H. & WILLIAMSON, G. K. (1951b). *Proc. Phys. Soc.* B, **64**, 937.

HEIDENREICH, R. D. (1951). *Bell System Tech. Journ.* **30**, 867.

HEIDENREICH, R. D. & SHOCKLEY, W. (1948). *Rep. Conf. 'Strength of Solids'.* London: Physical Society.

HIRSCH, P. B. (1952a). *Acta Cryst.* **5**, 168.

HIRSCH, P. B. (1952b). *Acta Cryst.* **5**, 172.

HIRSCH, P. B. & KELLAR, J. N. (1952). *Acta Cryst.* **5**, 162.

HONEYCOMBE, R. W. K. (1951). *J. Inst. Met.* **80**, 45.

JACQUET, P. A. (1945). *Rev. Métall.* **42**, 133.

KELLY, A. (1953). Ph. D. Thesis, University of Cambridge.

LOMER, W. M. (1951). *Phil. Mag.* (7), **42**, 1327.

MEGAW, H. D. & STOKES, A. R. (1945). *J. Inst. Met.* **71**, 279.

MERWE, J. H. VAN DER (1950). *Proc. Phys. Soc.* A, **63**, 616.

MOTT, N. F. (1951). *Proc. Phys. Soc.* B, **64**, 729.

MOTT, N. F. (1952). *Imperfections in Nearly Perfect Crystals.* New York: Wiley.

PATERSON, M. S. (1948). Ph.D. Thesis, University of Cambridge.

PAXTON, H. W., ADAMS, M. A. & MASSALSKI, T. B. (1952). *Phil. Mag.* (7), **43**, 257.

RÖHM, F. & KOCHENDÖRFER, A. (1950). *Z. Metallk.* **41**, 265.

SMITH, C. S. & STICKLEY, E. E. (1943). *Phys. Rev.* **64**, 191.

STOKES, A. R., PASCOE, K. J. & LIPSON, H. (1943). *Nature, Lond.* **151**, 137.

TAYLOR, G. I. & QUINNEY, H. (1934). *Proc. Roy. Soc.* A, **143**, 307.

WARREN, B. E. & AVERBACH, B. L. (1952). *Imperfections in Nearly Perfect Crystals.* New York: Wiley.

WILMAN, H. (1951). *Proc. Phys. Soc.* A, **64**, 329.

WOOD, W. A. (1939). *Proc. Roy. Soc.* A, **172**, 231.

WOOD, W. A. & RACHINGER, W. A. (1949a). *J. Inst. Met.* **75**, 571.

WOOD, W. A. & RACHINGER, W. A. (1949b). *J. Inst. Met.* **76**, 237.

The Crystal Structure of Rh₂B*

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The crystal structure of Rh_2B has been determined from X-ray rotation and Weissenberg photographs. The unit cell is orthorhombic, with dimensions $a = 5 \cdot 42 \pm 0 \cdot 01$, $b = 3 \cdot 98 \pm 0 \cdot 02$, $c = 7 \cdot 44 \pm 0 \cdot 03$ Å. The space group is D_{2h}^{16}–$Pnma$ with eight rhodium atoms in the unit cell. The atomic coordinates were found by means of Booth's method of 'steepest descents', using the intensity data from the $hk0$ and $0kl$ zones. The relation of this structure to other intermetallic borides is discussed and some comments are made on the type of intermetallic bonding which may exist.

Introduction

Boron is well known for its ability to form binary

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* The opinions contained herein are those of the authors and are not to be construed as official or as reflecting the views of the Navy Department or the Naval Establishment at large.

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compounds with many metals. The crystal structures of many of these borides have been studied by Kiessling, and a survey of some of his results has recently been published (Kiessling, 1950). In addition, a survey of the intermetallic compounds formed between boron and the noble metals was recently made (Buddery & Welch, 1951) in which it was shown that these compounds are easily prepared by direct synthesis and

that crystals of some of the noble-metal borides are readily obtainable. Rh_2B, being one of the compounds which showed promise of giving single crystals, was selected for this study.

Crystals of Rh_2B were prepared directly by mixing and sintering of the elements. Powdered rhodium metal of very high purity was kindly loaned by Johnson Matthey and Co. Ltd and relatively pure boron (98·8 % with slight amounts of iron and carbon) was obtained from A. D. Mackay, New York. Further purification or analysis of these elements was assumed to be unnecessary for the purposes of this investigation. A homogeneous mixture of the elements in the proper stoichiometric ratio was inserted in a silica tube, which was then evacuated and sealed off. The system was held at approximately 1200° C. in an electric furnace for 16 hr. and cooled slowly to room temperature. The resulting alloy was crushed and examined under a microscope. The crystals were rod shaped and varied in size from 0·5 mm. to 2·0 mm. in length and from 0·08 mm. to 0·20 mm. in average diameter. Two of the smaller crystals with no adhering sintered alloy were selected for investigation. The crystal used for the $h0l$ reflections, in which the long axis of the rod lay in a plane perpendicular to the collimated X-ray beam, was 1·0 mm. in length and had an average diameter of 0·12 mm.

Unit cell and space group

Zero-layer Weissenberg photographs taken about each of the three axes using Cu $K\alpha$ and Mo $K\alpha$ radiation showed that the unit cell was orthorhombic. The unit-cell dimensions were determined from high-order $hk0$ and $h0l$ reflections on the corresponding rotation photographs taken with Cu $K\alpha$ radiation. The data were extrapolated to $\theta = 90°$ giving the dimensions:

$$a = 5·42 \pm 0·01, \quad b = 3·98 \pm 0·02, \quad c = 7·44 \pm 0·03 \text{ Å}.$$

The volume of the unit cell is 160·5 Å³. The density was determined by displacement and found to be approximately 10·5 g.cm.⁻³, as compared to a calculated value of 8·96 g.cm.⁻³ for $4Rh_2B$ per unit cell and 11·20 g.cm.⁻³ for $5Rh_2B$ per unit cell. The space group and final structure analysis indicate that there are four units of Rh_2B per unit cell and therefore the experimentally determined value may be high. This could easily be accounted for if the sample used in the density determination contained a small amount of metallic rhodium.

The systematic absence of $hk0$ reflections when h is odd and of $0kl$ reflections when $k+l$ is odd show that the space group is either C_{2v}^9-Pn2a or $D_{2h}^{16}-Pnma$. It is impossible to accommodate the eight rhodium atoms in the general eightfold positions of $Pnma$ owing to the shortness of the b axis, and therefore the rhodium atoms must be situated in the fourfold general positions of $Pn2a$ or the special fourfold positions of

$Pnma$. The very strong $0k0$ reflections and the general diminishing of intensity for a given h or l in the $hk0$ (k even), $hk0$ (k odd) and $0kl$ reflections as k was increased, can be explained only if the rhodium atoms are located on or very close to the $y = \frac{1}{4}$ and $y = \frac{3}{4}$ plane. Since all of the data are compatible with the assumption that the space group is $D_{2h}^{16}-Pnma$ with the metal atoms in special positions (c), the equivalent positions of the rhodium and boron atoms are given by the coordinates

$$x, \tfrac{1}{4}, z; \quad \bar{x}, \tfrac{3}{4}, \bar{z}; \quad \tfrac{1}{2}-x, \tfrac{3}{4}, \tfrac{1}{2}+z; \quad \tfrac{1}{2}+x, \tfrac{1}{4}, \tfrac{1}{2}-z.$$

Determination of the structure

Weissenberg photographs were taken in the $h0l$ zone using Ni-filtered Cu $K\alpha$ radiation and in the $hk0$ and $0kl$ zones using Zr-filtered Mo $K\alpha$ radiation. The relative intensities were estimated using a standard Hilger photometer by taking the logarithm of the ratio of the background transmitted light to the transmitted light at the most dense point of the reflected spot. This procedure was checked against the more accurate but time-consuming process of taking the integrated intensity over the entire spot and the results indicated that the measured intensities were sufficiently accurate for this structure determination. The intensities so determined were corrected in the usual manner for Lorentz and polarization factors. Owing to the very high absorption coefficient of Rh_2B for Cu $K\alpha$ radiation ($\mu r = 10$), the $h0l$ intensities were corrected (Bradley, 1935) assuming that the specimen had a circular cross-section. In the $hk0$ and $0kl$ zones the absorption effects were assumed at first to be negligible, owing to the use of the shorter wavelength radiation. However, in the later stages of the analysis it was noted that the observed structure amplitudes of the low-angle reflections were low when compared to the calculated factors. Accordingly, an empirical correction was determined as a function of the reciprocal spacing by plotting $\log F_c/F_o$ against $\sin\theta$. This exponential correction was applied to the intensities of the seven reflections in the $hk0$ and $0kl$ zones with $\sin\theta$ less than 0·25. The magnitude of the corrections varied from a factor of 1·06 for the 220 reflection to 2·00 for the 011 reflection. The direction in which this correction was applied would make it seem likely that it was due to absorption in these zones, even with the use of the more penetrating Mo radiation. It is unlikely that this effect is due to extinction since the strong reflections at high angles were unaffected. No temperature correction was applied to the data. The resulting values of F_o were placed on an absolute scale by comparison with the calculated amplitudes and by comparison of the $h00$, $0k0$, and $00l$ spots common to the separate zones. For the calculation of structure amplitudes the scattering curve for rhodium was taken from *Internationale Tabellen*. The scattering due to boron was assumed to be negligible in comparison with the heavy rhodium scattering.

Table 1. *Comparison of observed and calculated structure amplitudes*

hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c
020	217	−258	033	108	−155	502	60	−105
040	170	180	053	111	−119	103	139	−116
060	140	−136	073	78	−92	203	150	130
080	89	104	004	< 40	− 6	303	59	−66
200	64	64	015	74	−71	403	77	−50
210	193	−160	035	74	−60	503	87	−55
220	53	52	006	96	−67	603	55	41
230	154	−118	026	62	−62	104	97	−80
240	—	39	017	90	76	204	65	54
250	121	−90	037	52	66	304	44	47
270	70	−69	008	151	−134	404	—	40
400	46	32	028	123	−126	504	143	130
410	33	27	048	86	−107	105	108	150
420	33	29	068	70	−87	205	94	59
430	< 30	23	019	—	− 1	305	60	13
440	< 30	24	0,0,10	113	83	405	63	−52
600	140	132	0,2,10	· 84	79	505	60	64
610	84	−70	0,1,11	160	120	106	99	−36
620	100	124	0,3,11	131	110	206	89	75
630	61	−62	0,5,11	99	96	306	—	−41
640	90	106	101	—	−21	406	73	62
650	—	−52	201	—	14	506	37	−39
800	—	−17	301	161	141	107	—	−29
810	137	−124	401	153	−104	207	—	−35
830	103	−113	501	—	−22	307	129	−143
850	96	−98	601	83	−67	407	< 35	−12
011	90	75	102	88	−122	108	—	57
031	55	51	202	151	−141	208	55	−32
002	< 40	−38	302	94	−32	308	42	22
013	143	−209	402	128	−95	109	58	38

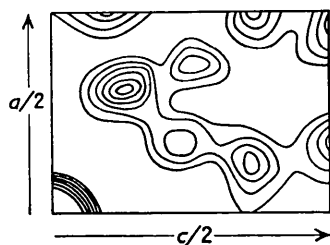An unsharpened Patterson projection of the $h0l$ data is shown in Fig. 1. Approximate x and z para-

Fig. 1. Unsharpened Patterson projection of the $h0l$ data. Contours at arbitrary equal intervals.

meters were calculated from the information provided by this projection, assuming that only the intermetallic vectors would show up. All of the peaks shown in the projection could be accounted for by the approximate structure derived in this manner. The x and z parameters were then refined by the method of 'steepest descents' (Booth, 1947), using the $hk0$ and $0kl$ data. As mentioned previously, the very strong $0k0$ reflections, together with the gradual decrease in intensity of the $hk0$ (k even), $hk0$ (k odd), and $0kl$ reflections with increasing values of k, make it extremely likely that the metal atoms are located on the $y = \frac{1}{4}$ and $y = \frac{3}{4}$ planes. Using these values of the y parameters, the calculations of the x and z parameters by the method of 'steepest descents' are greatly simplified since the calculated structure amplitudes in

the $hk0$ and $0kl$ zones are functions only of the x and z parameters respectively. The final results of these calculations gave values of the factor $R = \Sigma ||F_o| - |F_c|| \div \Sigma F_o$ of 0·14 and 0·18 for the $hk0$ and $0kl$ reflections respectively. The values of the x and z parameters so determined were used to calculate the structure amplitudes in the $h0l$ zone and gave a value of R of 0·26 or an overall value of 0·20. The values of the observed and calculated structure amplitudes are compared in Table 1, and the final atomic coordinates in fractions of the unit cell edges are given in Table 2.

The resulting structure makes the metal atoms approximately equidistant and leaves holes for four boron atoms. However, these holes have an average diameter of 2·16 Å and therefore are considerably larger than the minimum required to accommodate a boron atom with a diameter of approximately 1·74 Å. For this reason it is impossible to assign definite atomic parameters to the boron atoms, and instead approximate parameters were calculated by trial and error so as to place the boron atom in the approximate center of the hole. The parameters calculated in this manner are given in Table 2.

Table 2. *Final atomic parameters*

	x/a	y/b	z/c
Rh$_1$	0·026	0·250	0·200
Rh$_2$	0·167	0·250	0·577
B	0·73	0·25	0·60

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Table 3. *Interatomic distances*

				Average
Rh_1:	8 Rh	at	2·75(2), 2·80(2), 2·81(2), 2·84, 2·90	2·81
	6 B	at	2·49, 2·54(2), 2·63(2), 3·07	2·57 (first five)
Rh_2:	8 Rh	at	2·75(2), 2·80(2), 2·84, 2·90, 2·93(2)	2·84
	4 B	at	2·38, 2·42, 2·45(2)	2·42
B:	11 Rh	at	2·38, 2·42, 2·45(2), 2·49, 2·54(2), 2·63(2), 3·07, 3·39	2·50 (first nine)
	2 B	at	3·51(2)	

Discussion of the structure

A projection of the structure on to the 010 plane is shown in Fig. 2. The structure may be described as
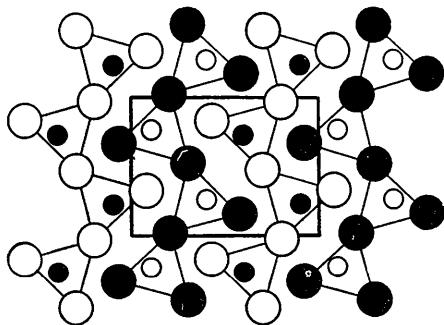
Fig. 2. Projection of the Rh_2B structure down the *b* axis. Large circles represent Rh atoms; small circles, B atoms. The solid circles are located on the $y = \frac{1}{4}$ plane; the others, on the $y = \frac{3}{4}$ plane. The unit cell is shown by the heavy lines. The light lines between metal atoms illustrate the triangular nature of this structure.

consisting of trigonal prisms of metal atoms with boron atoms situated at the approximate center of each prism. The borides of the FeB type (Bjurström, 1933) and the compound δ-Ni_2Si (Toman, 1952) have the same type of packing of metal atoms about non-metal atoms and the same space group as Rh_2B. The ratios of the lengths of the three orthorhombic axes are:

Rh_2B	1·36:1:1·87
FeB	1·38:1:1·87
δ-Ni_2Si	1·34:1:1·90

The phases are not isomorphous, however, owing to the different number of atoms when compared to FeB and to different atomic parameters for both FeB and δ-Ni_2Si. The structure of Rh_2B is not the same as the Me_2B- borides of the $CuAl_2$-type (Kiessling, 1950), which have tetragonal symmetry. The only similarity between Rh_2B and these metal borides is that in both cases the boron atoms are loosely accommodated in isolated holes between the metal atoms.

Each rhodium atom is coordinated to eight other rhodium atoms lying between distances of 2·75 Å and 2·93 Å. If the boron atoms are in the positions of Table 2, each boron atom is coordinated to eleven rhodium atoms: nine lying between distances of 2·38 and 2·63 Å and two others at substantially greater distances of 3·07 and 3·39 Å. Six of these rhodium atoms are at the corners of a trigonal prism with boron

situated at the center; the other five, including the two at 3·07 Å and 3·39 Å, are located in the same *y* plane as the boron atom. No B–B bonds exist in the structure. The rhodium atoms seem to be of two types with regard to their coordination to boron. The Rh_1 atoms have six B atoms surrounding them in a distorted octahedron; however, five of these Rh-B bonds are considerably shorter than the sixth. The Rh_2 atoms have four B atoms surrounding them in a distorted tetrahedron. The interatomic distances are summarized in Table 3.

With the B atoms in the assigned positions, it is interesting that the average Rh–B distance for the Rh_1 atoms which are coordinated to five or six boron atoms is 0·15 Å larger than the Rh–B distance for the Rh_2 atoms which are coordinated to four boron atoms. The differences in the average Rh–Rh spacings for the two types of rhodium atoms are not significant.

On the assumption (Pauling, 1949) of a linear relationship between the single-bond radius and the amount of *d* character of the *dsp* hybrid bond orbitals the following equation may be derived:

$$R_1(\text{Rh}) = 0.840 + 1.073\delta \,,$$

where δ represents the fractional amount of *d* character of the bond orbital. Using the experimentally observed intermetallic distances, the *d* character of the bond orbitals involved in metallic bonding may be calculated to be approximately 54 %. This is slightly greater than the 50 % *d* character predicted by Pauling, as would be expected since the experimentally observed metallic radius is slightly greater than the value of 1·342 for the metallic radius of rhodium with a coordination number of 12 (Pauling, 1947). The high percentage of *d* character may be the result of an effort to form stronger Rh–Rh bonds in the structure by the use of all five *4d* orbitals for intermetallic bonding. It is consistent with the electronic structure of rhodium since there are nine electrons available for bonding in the *4d*, *5s* and *5p* orbitals and therefore the maximum number of bonds may be formed with this element.

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References

BJURSTRÖM, T. (1933). *Ark. Kemi Min. Geol.* A, **11**, No. 5.

BOOTH, A. D. (1947). *Nature, Lond.* **160**, 196.
BRADLEY, A. F. (1935). *Proc. Phys. Soc.* **47**, 879.
BUDDERY, J. H. & WELCH, A. J. E. (1951). *Nature, Lond.* **167**, 362.
KIESSLING, R. (1950). *Acta chem. Scand.* **4**, 209.
PAULING, L. (1947). *J. Amer. Chem. Soc.* **69**, 542.
PAULING, L. (1949). *Proc. Roy. Soc.* A, **196**, 343.
TOMAN, K. (1952). *Acta Cryst.* **5**, 329.

On the Structure of Epidote

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The structure of epidote, $HCa_2(Al, Fe)Al_2Si_3O_{13}$, has been refined by two- and three-dimensional syntheses. The revised structure, in favour of which an earlier proposal was withdrawn, has now been confirmed. The structure is of the mixed silicate type containing both SiO_4 and Si_2O_7 groups bound together by Al, Al(Fe), Ca and O atoms and OH groups. Epidote is an alumino-silicate, like cyanite etc., as the Al and O atoms and OH groups form octahedral chains which occupy the bulk of its structure.

Introduction

One of the present writers several years ago proposed for epidote a structure (Ito, 1947) which was later abandoned in favour of another structure (Ito, 1950, p. 50). The latter structure should be preferred, we argued, because it was better able to derive the structure of the closely related mineral, zoisite. As far as the agreement between calculation and the experimental data then available was concerned, however, a different conclusion might have been drawn (Evans, 1952), and indeed our aim was rather to illustrate the usefulness of the concept of polysymmetric synthesis in dealing with a certain class of polymorphic crystals. We give below an account of our later work undertaken to determine the structure more precisely.

Experimental

In addition to those used in the previous studies, a great many further experimental data were accumulated. The $h0l$ reflexions observed on the ionization spectrometer (Ito, 1950, p. 54) were checked and supplemented by the data obtained photographically, correcting in particular those weak reflexions which were hard to measure accurately with the spectrometer. Relative intensities estimated visually in the $b(0)$ Weissenberg photographs (Mo and Co $K\alpha$) were correlated with the absolute values and incorporated into the $h0l$ spectra. Together with these, the evaluated

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reflexions deduced from the $a(0, 1, 3)$, $b(1, 2)$ (Co $K\alpha$) and $b(3, 4, 5)$ (Mo $K\alpha$) Weissenberg–Buerger photographs and rendered absolute (Harker, 1948; $B = 1.0 \times 10^{-16}$ cm.^{2}) cover practically the whole reciprocal space ordinarily observable and form the bulk of the experimental information on which the present study is based.

The photographs were processed by the multiple-film technique (Lange, Robertson & Woodward, 1938). For the intensities of reflexions only the Lorentz and polarization factors were taken into account, no correction for absorption or extinction having been made.

The specimens examined were the same as those used previously (Prince of Wales Island, Alaska), having an almost ideal composition of $HCa_2FeAl_2Si_3O_{13}$ (Ito, 1950, p. 51). The unit cell has the dimensions

$$a = 8.96, \quad b = 5.63, \quad c = 10.30 \text{ Å}, \quad \beta = 115° 24',$$

and contains four units of the above formula. The space group is $P2_1/m$, the reflexions $0k0$ being absent when k is odd.

Refinement by the Patterson–Harker functions

Our previous analysis was based on the finding that the y coordinates of all the atoms in epidote are $0, \frac{1}{4}, \frac{1}{2}$ or $\frac{3}{4}$. This was derived by considering the peculiarity of the $0k0$ reflexions and the geometry of the lattice with reference to the size of the constituent ions. Quite generally, the $b(n)$ and $b(n+4)$ Weissenberg–Buerger photographs display a virtually identical intensity distribution. This is possible in space group