The hydrogen bond system may be divided into four types:

(i) two strong water–thiosulphate oxygen hydrogen bonds, O(4)–H(1)$\cdots$O(3) (2·73 Å) and O(5)–H(3)$\cdots$O(3) (2·77 Å),

(ii) two weak water–thiosulphate oxygen hydrogen bonds, O(4)–H(2)$\cdots$O(2) (2·94 Å) and O(5)–H(4)$\cdots$O(3*) (2·81 Å),

(iii) two water–water oxygen hydrogen bonds O(6)–H(5)$\cdots$O(4*) (2·73 Å) and O(7)–H(8)$\cdots$O(8*) (2·79 Å),

(iv) three water–sulphur hydrogen bonds, O(6)–H(6)$\cdots$S(1*) (3·30 Å) O(7)–H(7)$\cdots$S(1*) (3·13 Å) and O(8)–H(10)$\cdots$S(1) (3·40 Å).

In the case of the water molecule H(9)–O(8)–H(10), Taylor & Beevers have suggested that both the hydrogen atoms are bonded to the sulphur atom. As revealed by the neutron study, the existence of a hydrogen bond between the atom H(9) and the sulphur atom is doubtful, since the distance H(9)$\cdots$S(1*) is 2·68 Å and the angle O(8)–H(9)$\cdots$S(1*) is 119°, a considerable deviation from linearity. Apart from the sulphur atom, the nearest atom is O(2) which makes an angle O(8)–H(9)$\cdots$O(2) of 163°, but in this case H(9)$\cdots$O(2) is 2·48 Å and O(8)$\cdots$O(2) is 3·39 Å. Hence it is reasonable to assume that the atom H(9) does not participate in any meaningful hydrogen bonding. The hydrogen atoms H(6), H(7) and H(10)

may be regarded as being involved in hydrogen bonding to the sulphur atom. In these cases the H$\cdots$S distances range from 2·38 to 2·59 Å and the O$\cdots$S distances from 3·13 to 3·40 Å. The O–H$\cdots$S angles are in the region 142·8 to 145·2°. Recently Muir (1969) has reported an O–H$\cdots$S bond in BaS$_2$O$_3$. H$_2$O with O$\cdots$S, 3·298, H$\cdots$S, 2·367 Å and an O–H$\cdots$S angle of 163°. These are the first reports of hydrogen bonding to a sulphur atom revealed by neutron diffraction.

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The Crystal Structure of NbCoB

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The crystal structure of NbCoB has been determined by single-crystal X-ray analysis. The lattice constants are $a = 3·266$ (1), $b = 17·177$ (3), $c = 5·947$ (3) Å, the unit cell contains 30 atoms, and the space group is *Pmmn* (D_{2h}^{13}). The atomic parameters have been refined by least-squares analysis to a final R value of 0·086, based on the 265 observed reflections. The NbCoB structure is a combination of the TiNiSi- and ZrAlNi-type structures (isostructural with Cl$_2$Pb and Fe$_2$P respectively): the slightly deformed trigonal prisms [BM$_6$] form columns of three types – isolated, connected by two, and by three edges. The nets (two per cell) perpendicular to the x axis are built of pentagons, quadrangles and triangles. The coordination numbers are 17 (Nb), 12 (Co) and 9 (B); the coordination polyhedra are derived from pentagonal, tetragonal and trigonal prisms respectively.

Introduction

The ternary compound NbCoB was revealed in the course of an X-ray investigation of the Nb–Co–B

system; at 800°C it exists in equilibrium with Co, NbCo$_2$, NbB and Nb$_2$Co$_{21}$B$_6$. The following dimensions of the orthorhombic NbCoB cell were found: 3·26, 5·93 and 17·08 Å (Kuz'ma, Ciolkovsky & Baburova, 1968). Stadelmaier & Schöbel (1966) ascribe the composition NbCo$_2$B, rather than NbCoB, to the second ternary compound in this system.

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The purpose of the present work is the determination of the crystal structure of NbCoB.

Space group and unit cell

The lattice constants refined on the basis of the rotation (a) and Weissenberg patterns (b, c) are the following:

$$a = 3 \cdot 266(1), \quad b = 17 \cdot 177(3), \quad c = 5 \cdot 947(3) \text{ Å} .$$

The unit cell contains 10 formula units $(d_{exp} = 7 \cdot 99$ g.cm^{-3}, $d_{calc} = 8 \cdot 03$ g.cm^{-3}). The extinctions in the diffraction pattern indicate only the presence of an n plane perpendicular to c; thus the structure has the
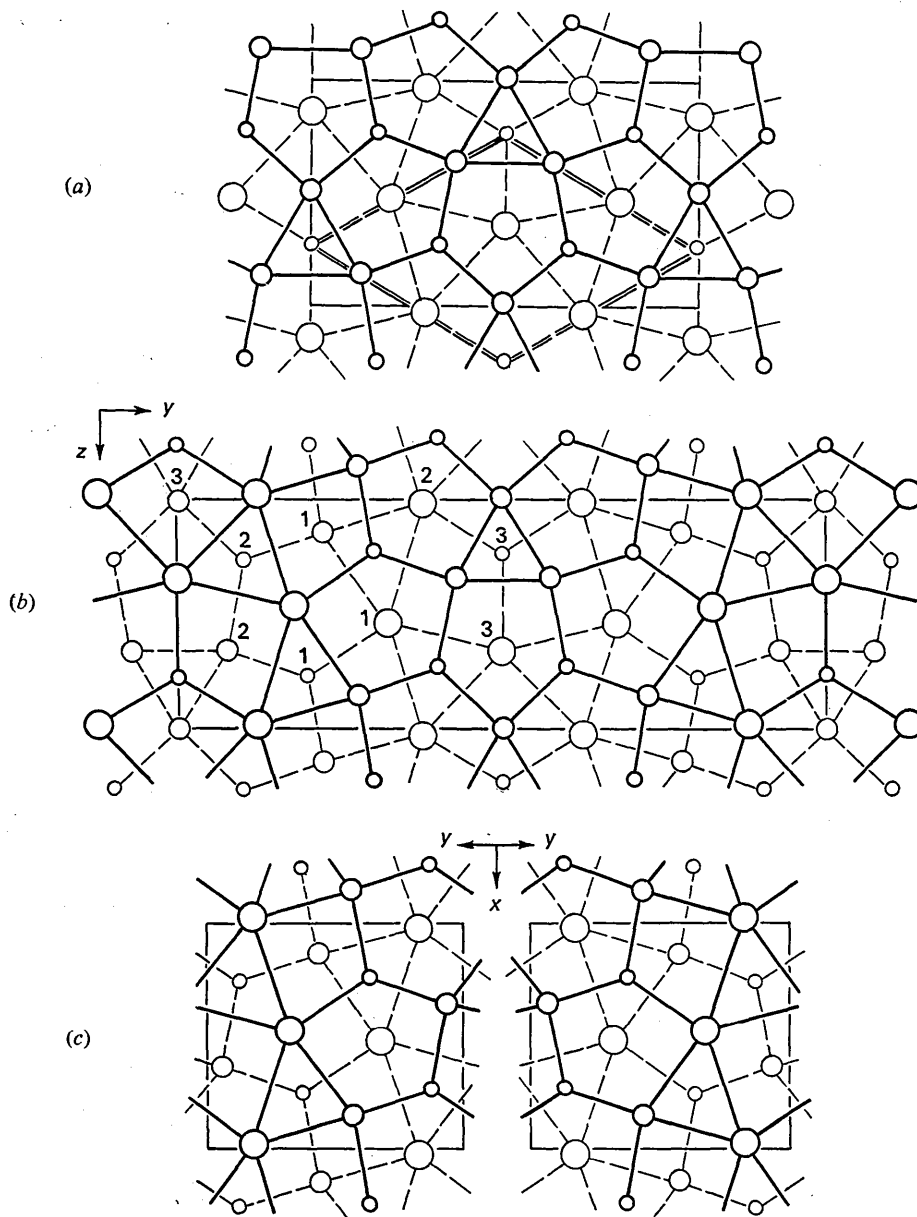

Fig. 1. The genesis of the NbCoB structure $[(b)$; origin at mmn, that is at $(\frac{1}{4}\frac{1}{4}0)$ from origin used in Table 1] from the ZrAlNi $[(a)$; hexagonal and orthorhombic cells] and TiNiSi (c) type structures.

Projection on	Nets		Circles		
	Solid line	Broken line	Large	Intermediate	Small
(a)	(001)	$z = 0$	$\frac{1}{2}$	Zr	Al	Ni
(b)	(100)	$x = \frac{1}{2}$	0	Nb	Co	B
(c)	(001)	$z = \frac{3}{4}$	$\frac{1}{4}$	Ti	Ni	Si

diffraction group $mmmPn--$, i.e. the space groups $Pmmn$ or $Pm2_1n$. [The choice of axes does not comply with the setting rules adopted in *Crystal Data* (1963)].

Structure determination

In deriving the trial structure we noted the proximity of the value of the smallest lattice constant of NbCoB to those constants of MoCoB [TiNiSi type, Shoemaker & Shoemaker (1965) isostructural with Cl_2Pb; $b=3\cdot251$ Å, Kuz'ma, Krypyakevich & Chepiha (1968); $b=3\cdot232$ Å, Jeitschko (1968*)] and NbFeB [ZrAlNi type, Krypyakevich, Markiv & Melnyk (1967) isostructural with Fe_2P; $c=3\cdot20$ Å, Kuz'ma (1967)]; these constants are equal to the altitudes of the trigonal prisms [BM_6] which one can regard as an essential feature of the structures.

The diffraction pattern shows that the intensities for layer lines $h+2$ are equal to the corresponding ones for layer lines h(except for normal decline). The atoms are therefore arranged in layers perpendicular to the shortest axis, with a spacing of half the lattice translation in that direction, as is also the case in the previously mentioned structures. Taking into account the cell dimensions of these structures, a trial structure (see Fig. 1) was derived in space group $Pmmn$ consisting essentially of two mirror-reflected MoCoB cells (total content: 24 atoms) connected by six additional atoms situated simultaneously in 'horizontal' and 'vertical' m planes, as is the case in NbFeB and also in Re_3B (Aronsson, Bäckman & Rundqvist, 1960). The possibility of small deviations from space group $Pmmn$, leading to $Pm2_1n$, is not excluded, but the trial structure refined satisfactorily in the higher space group.

The refinement of the atomic parameters was carried out with the intensity data for 265 reflections estimated visually from Weissenberg photographs (Mo $K\alpha$ radiation); 106 additional reflections were too weak to be observed. Only layer lines with $h=0$, 1 and 2 were recorded. The intensities were reduced to a common scale by means of precession photographs (y and z axes). The structure factors were calculated taking into account the real part of the corrections for anomalous

dispersion (Cromer, 1965) and the reflections with $F_o>150$ were corrected for secondary extinction by means of the formula $F_o^{corr}=F_o(1+gI_o)$ with $g=4\cdot37\times10^{-6}$ (Zachariasen, 1963; largest correction about 15%). For the absorption correction (the dimensions of the irregularly shaped crystal fragment were $0\cdot015\times0\cdot008\times0\cdot005$ cm; $\mu=206$ cm^{-1}, $\mu/d=25\cdot19$ cm^2.g^{-1}) we used the program written by Wuensch & Prewitt (1965). The correction factor applied to the intensities varied between $1\cdot97$ and $1\cdot60$. The atomic parameters were refined by the full-matrix least-squares program of Busing, Martin & Levy (1962) as modified by Stewart & Kundell to conform with the X-ray 67 (1967) Program System.* The function minimized was $\sum w(|F_o|-|F_c|)^2$. The standard errors in the structure amplitudes, on which the weights were based, were set equal to 10 for all reflections with $|F_o|\leq100$ and to $0\cdot10\ |F_o|$ for $|F_o|>100$. The 22 parameters varied were: one scale factor, all positional parameters and isotropic temperature factors on the Nb and Co atoms.

The structure refined to an R index ($\sum|\Delta F|/\sum|F_o|$)= $0\cdot123$ for observed reflections only; the weighted R was $0\cdot145$ and the standard deviation of an observation of unit weight was $1\cdot29$. At this point one of the referees pointed out that most differences $|F_o|-|F_c|$ were positive for $|F_o|<93$. This seemed to indicate that a systematic intensity-dependent error had been made in the estimation of the intensities. To correct for this the explicit extinction correction was taken out and all $|F_o|$ were multiplied by the function: $-0\cdot0000152\ F_o^2 +0\cdot00614\ |F_o|+0\cdot528$, derived empirically from a plot of $|F_c|/|F_o|$ versus $|F_o|$. The structure was now refined with individual layer scale factors to an R index of $0\cdot086$ (observed reflections only); $R_w=0\cdot109$ and the standard deviation of an observation of unit weight $=0\cdot95$. In the last cycles 27 parameters were varied: all positional parameters, and isotropic temperature factors and occupancy factors of Nb and Co (the three layer scale factors being kept constant). The temperature and occupancy factors of the boron atoms were not refined, because of the very large standard deviations on them. The correlation coefficients between

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* The b and c axes are interchanged between TiNiSi and MoCoB.

* All calculations were carried out at the Computation Center of the Massachusetts Institute of Technology.

Table 1. *Atomic parameters for* NbCoB

Space group $Pmmn$; origin at $\bar{1}$, standard deviations in parentheses; occ. represents apparent occupancy factor.

	Position	y	z	occ	B	CN
Nb(1)	$4(e)\frac{1}{4}yz$	0·5710 (2)	0·5288 (6)	0·99 (2)	−0·06 (10)	17
Nb(2)	$4(e)$	0·6259 (2)	0·0245 (6)	1·02 (2)	0·03 (11)	17
Nb(3)	$2(b)\frac{1}{4}\frac{3}{4}z$		0·6456 (9)	0·98 (3)	−0·14 (14)	17
Co(1)	$4(e)$	0·4761 (3)	0·1457 (9)	0·94 (3)	0·10 (16)	12
Co(2)	$4(e)$	0·3224 (3)	0·6441 (10)	1·01 (3)	0·48 (16)	12
Co(3)	$2(a)\frac{1}{4}\frac{1}{4}z$		0·0085 (13)	1·01 (5)	0·32 (23)	12
B(1)	$4(e)$	0·451 (2)	0·770 (7)		0·05	9
B(2)	$4(e)$	0·348 (2)	0·271 (7)		0·05	9
B(3)	$2(b)$		0·230 (10)		0·05	9

temperature factor and occupancy factor are about 0·84 for Nb and Co.

The final parameters, occupancy and B factors are given in Table 1 and the comparisons of F_o and F_c in Table 2. The temperature factors of two of the Nb atoms are negative by no more than one standard deviation (they were set back to zero in the structure factor calculation). The occupancy factors indicate that within the accuracy of this determination there is no disorder in the occupancy of the Nb and Co sites. No chemical analysis of the compound was made.

Table 2. Observed (left column) and calculated (right column) structure factors for NbCoB

Asterisk indicates non-observed reflection; value listed under F_o is $\frac{1}{2}$ F(min). Each block headed by HKL gives values for reflections starting with given HKL. Subsequent entries are for increase of 1 in k for $l \neq 0$, and increase of 2 in k for $l = 0$.

The introduction of the correction function resulted in reduction of the R index and the standard deviations of the parameters. The changes in the distances were for the most part smaller than the new σ; in three instances changes as large as twice the new σ were obtained.

Description of the structure and discussion

With respect to the atomic coordination the NbCoB structure bears resemblance to the generating structure types TiNiSi and ZrAlNi: for each structure three different coordination numbers (17, 12 and 9) are characteristic, corresponding to the atoms of three different sizes [the atomic radii of Nb, Co and B are respectively 1·45, 1·25 and 0·91 Å for CN12 (Boky, 1954)]. In each case the coordination polyhedra are deformed pentagonal, tetragonal and trigonal prisms with 7, 4 and 3 extra vertices. The interatomic distances are given in Table 3; the Nb–Nb distances are greater than the sum of the atomic radii, of the other distances some are greater and some are smaller. The common feature of the NbCoB-, TiNiSi- and ZrAlNi-type structures is the puckered sheet of edge-connected columns of trigonal prisms. This puckered sheet looks in the projection on (001) in the TiNiSi-type structure like

Table 3. Observed interatomic distances in Å for NbCoB

Values listed under atom types are sum of C.N. 12 radii. Numbers preceding distances indicate number of neighbors of that distance for atom heading column (when reading down). Standard deviations are given in parentheses.

C.N.	Nb(1)	Nb(2)	Nb(3)	Co	Co(1)	Co(2)	Co(3)	B	B(1)	B(2)	B(3)
Nb 17				12				9			
Nb 2·90				2·70				2·36			
Nb(1)	2 3·266 (1)	1 3·144 (5)	2 3·151 (4)	2·70	1 2·802 (7)	2 2·660 (5)	4 2·692 (3)	2·36	1 2·51 (4)	2 2·45 (3)	2 2·46 (3)
	2 2·957 (5)	1 3·095 (5)	2 3·101 (5)		2 2·659 (5)	2 2·709 (6)	2 2·626 (7)		2 2·45 (3)	2 2·44 (3)	1 2·47 (6)
	1 3·144 (5)	2 3·266 (1)	2 3·266 (1)		1 2·672 (6)	2 2·679 (6)			2 2·43 (3)	2 2·39 (3)	
	1 3·095 (5)				2 2·601 (5)						
	1 3·151 (4)										
Nb(2)	1 2·802 (7)	1 2·672 (6)	4 2·679 (6)	2·50	2 2·519 (6)	1 2·485 (7)	2 2·498 (9)		1 2·27 (4)	1 2·33 (4)	4 2·18 (2)
	2 2·659 (5)	2 2·601 (5)	2 2·626 (7)			1 2·498 (9)			2 2·11 (3)	1 2·26 (4)	2 2·16 (4)
	2 2·660 (5)	2 2·709 (6)							1 2·34 (4)	1 2·29 (4)	
		2 2·692 (3)									
Nb(3)	1 2·51 (4)	2 2·43 (3)	4 2·39 (3)	2·16	1 2·27 (4)	1 2·34 (4)	2 2·29 (4)				
Co	2 2·45 (3)	2 2·44 (3)	1 2·47 (6)		2 2·11 (3)	1 2·26 (4)	2 2·16 (4)				
Co(1)	2 2·45 (3)	1 2·46 (3)			1 2·33 (4)	2 2·18 (2)					
Co(2)											
Co(3)											
B											
B(1)											
B(2)											
B(3)											

a zigzag ribbon of triangles, running along the x direction. In the ZrAlNi structure there are columns connected by three prism edges and forming hexahedral tubes with an isolated shifted column inside each tube. In the TiNiSi structure the columns are connected by two edges and the sheets are shifted (the prism vertex of a given sheet takes place opposite to the face center of the prism belonging to the other sheet). The NbCoB structure possesses the intermediate location: it contains, like ZrAlNi, tubes with isolated columns inside, and, as in TiNiSi, the sheets are shifted (Fig. 2); the columns are connected by three edges ($[B^{(2)}M_6]$ prisms), by two edges ($[B^{(1)}M_6]$ prisms) or isolated ($[B^{(3)}M_6]$ prisms). There are no B–B bondings in the NbCoB structure as well as in its constituents. The binary compound with the NbCoB structure is not known as yet, contrary to the ZrAlNi and TiNiSi cases (Fe_2P and Cl_2Pb types respectively).

In the Nb–Co–B system the close structural analogues of NbCoB are the binary compounds Co_3B (Fe_3C type), Nb_3B_2 (U_3Si_2 type), NbB (CrB type), CoB (FeB type), Nb_3B_4 (Ta_3B_4 type) and NbB_2 (AlB_2 type) with the structures containing trigonal prisms $[BM_6]$. The binary M_2B compounds containing such prisms in their structures (i.e. the compounds of the

Cl_2Pb and Fe_2P types) do not exist in this system. The only binary M_2B compound (Co_2B) has the structure of the Al_2Cu type with C.N. 10 (tetragonal-antiprismatic coordination of the B atom by $Co+2B$ at 2·11 Å) and C.N. 15; the replacement of half of the Co atoms in Co_2B by Nb results in forming of the NbCoB structure with a trigonal-prismatic coordination of the B atom and with the ordered distribution of metal atoms in the positions with unequal coordination numbers (17 and 12).

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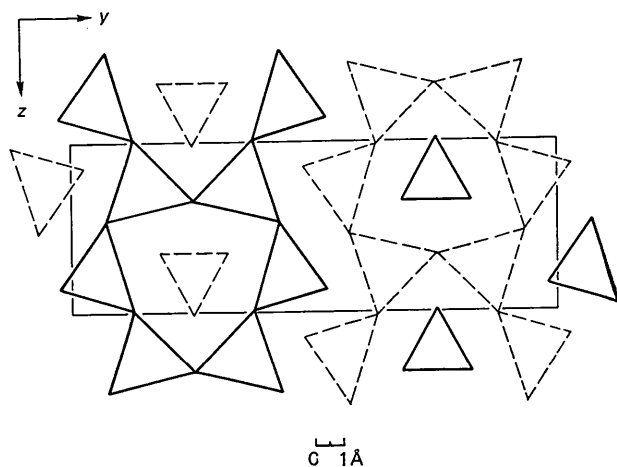

Fig. 2. The NbCoB structure as the packing of trigonal prisms. Origin at $\bar{1}$ (as in Table 1), projection on (100); solid-line triangles (prism bases) at $x=\frac{3}{4}$, broken line triangles at $x=\frac{1}{4}$.