The Crystal Structure of MoCoB and Related Compounds

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MoCoB crystallizes with an orthorhombic unit cell, space group *Pnma*, having the lattice constants $a = 5\cdot741 \pm 0\cdot003$, $b = 3\cdot232 \pm 0\cdot001$, $c = 6\cdot634 \pm 0\cdot001$ Å. The structure is of the ordered $PbCl_2$ type (TiNiSi type, *E*-phase). The positional parameters have been refined by the least-squares method with (limited) three-dimensional single-crystal data, giving a final *R* value of $0\cdot103$ (including the unobserved reflections). The compounds WCoB and WFeB are isotypic with MoCoB. A survey on the known $PbCl_2$ type compounds is given.

Introduction

The ternary system molybdenum–cobalt–boron has been the subject of several investigations recently. Haschke, Nowotny & Benesovsky (1966), later referred to as (1), and Kuz'ma, Nych & Skolozdra (1966) (2), have reported complete phase diagrams. Stadelmaier & Davis (1966) (3), have made an intensive study of the Co-rich section of this system. There is agreement between (1) and (3) about the occurrence of the phase MoCoB, which was first observed by Rieger, Nowotny & Benesovsky (1965). The diagram published by (2) contains no phase MoCoB; instead, a phase of the approximate composition $MoCo_4B$ has been reported, which in turn was not observed by (1) and (3). The present study was undertaken to clarify this question and to establish the crystal structure of the occurring phase (or phases) which might have had a structural relationship to MoAlB (Jeitschko, 1966).

Experimental

Samples of ternary alloys in the Co-rich section of the Mo–Co–B system were made by induction-melting compacted pellets of the mixed powder components. Parts of the reacted samples were annealed subsequently in sealed quartz tubes for three weeks at 950°C. The samples were examined metallographically and X-ray powder photographs were taken with a Guinier–de Wolff focusing camera and Cu $K\alpha$ radiation.

No evidence could be found for a phase near the composition $MoCo_4B$ and the phase diagrams reported by (1) and (3) were confirmed in this respect. MoCoB was found to be formed peritectically by reaction of Mo_2CoB_2 (Rieger, Nowotny & Benesovsky, 1966) with the liquid, as also observed by (3). This makes it difficult to isolate single crystals from a sample of this composition. However, metallographic examination of a sample Mo/Co/B = 9/70/21 at.% showed primary crystallization of MoCoB. The Co-rich matrix of the sample could be dissolved in concentrated boiling hydrochloric acid, which did not affect the single crystals of MoCoB. A flame emission analysis of the material gave the following result: Mo: $56\cdot8 \pm 1\cdot1$ and Co: $36\cdot8 \pm 0\cdot8$ wt%; the balance was assumed to be boron. This corresponds to $Mo_{32\cdot8}Co_{34\cdot5}B_{32\cdot7}$ and is compatible with the ideal composition MoCoB.

The single crystal used for the structure determination had the shape of a needle with a rectangular cross section and the dimensions $0\cdot080 \times 0\cdot009 \times 0\cdot010$ mm and was mounted with the needle axis – which later proved to be the [010] direction – perpendicular to the primary X-ray beam. Preliminary diffraction patterns were taken with a Buerger precession camera and Mo $K\alpha$ radiation. For the refinement of the structure, intensities were recorded with the multiple-film technique using an integrating Weissenberg camera and Cu $K\alpha$ radiation. The intensities of the zero and one upper level were estimated visually with the aid of an intensity strip. An absorption correction was made using the assumption that the crystal had a cylindrical shape with $\mu R = 1\cdot2$ (*International Tables for X-ray Crystallography*, 1959).

Determination of the structure of MoCoB

The precession photographs of MoCoB could be indexed with orthorhombic lattice constants which were refined by a least-squares fit of data taken with a focusing back-reflection camera (Cr $K\alpha$ radiation).

Table 1. *Unit-cell dimensions and X-ray densities of complex borides with ordered* $PbCl_2$ (*E*-TiNiSi)
type structure (Cr $K\alpha_1$: $\lambda = 2\cdot28962$)

Compound	a (Å)	b (Å)	c (Å)	V (Å³)	ϱ (g.cm⁻³)
MoCoB	$5\cdot741 \pm 0\cdot003$	$3\cdot232 \pm 0\cdot001$	$6\cdot634 \pm 0\cdot001$	$123\cdot1$	$8\cdot94$
WCoB	$5\cdot724 \pm 0\cdot001$	$3\cdot240 \pm 0\cdot001$	$6\cdot632 \pm 0\cdot001$	$123\cdot0$	$13\cdot69$
WFeB	$5\cdot823 \pm 0\cdot002$	$3\cdot161 \pm 0\cdot001$	$6\cdot810 \pm 0\cdot002$	$125\cdot3$	$13\cdot27$

Some range of homogeneity has been reported for MoCoB by Stadelmaier & Davis (1966); therefore, the lattice constants, given in Table 1, apply to the Co-rich side of the phase.

The conditions for possible reflections are $0kl$ only with $k+l=2n$ and $hk0$ only with $h=2n$, indicating the space group is $Pnma$ or $Pn2_1a$. On the precession diagrams it was noticed that the intensities of the spots hkl were equal to those of $h, k+2, l$, apart from the Lp factor and normal decline. It was concluded that the atoms in the cell lie on two planes perpendicular to [010] at a distance of $y/2$; thus, space group $Pnma$ was assumed. Using the experimental density value of 8.78 g.cm^{-3}, the number of formula units per cell was calculated to be $3.93 \simeq 4$. Space considerations led to only one possible structure model: that of the ordered (*anti-*) $PbCl_2$ (*E*-TiNiSi)-type (Shoemaker & Shoemaker, 1965). An intensity calculation with trial parameters, derived from this model, was in good agreement with the observed powder diffraction intensities.

The structure was refined on the University of Illinois IBM 7094 computer using a full-matrix least-squares program originally written by Gantzel, Sparks & Trueblood (1961) and later revised by Okaya. The function minimized was $\Sigma w^2(\Delta F)^2$ with $w = 1/F_{obs}$. A total of nine parameters (six positional, the isotropic temperature parameters of molybdenum and cobalt and one scale factor) were refined in the three main cycles. The program was then used to refine scale factors for the two layer lines separately, following which the next three main cycles were run. This procedure was then repeated. The values of the atomic scattering factors f_0 were taken from *International Tables for X-ray Crystallography* (1962), and were corrected for the real part of the anomalous dispersion (Dauben & Templeton, 1955). However, a structure factor calculation including the imaginary part of the anomalous dispersion correction (Templeton, 1955) showed that seven very weak reflections were affected by more than 10% by this correction and, therefore, were ascribed zero weight in the last cycles. Thus the total of the reflections used for the last refinements was 84. For the calculation of the structure factors listed in Table 2, both the real and the imaginary part of the anomalous dispersion correction were applied giving a final R value $(R = \Sigma |F_o - F_c| / \Sigma F_o)$ of 0.103 including the unobserved reflections. The final parameters are listed in Table 3.

Since Stadelmaier & Davis (1966) have reported a homogeneity range for MoCoB, three least-squares cycles were run with the assumption that 10% of the Mo sites were occupied by Co atoms. This, however, resulted in an increase of the R value. Also a difference

Fourier synthesis using the program by Sly, Shoemaker & Van den Hende (1962) did not suggest any weaker occupation of the molybdenum places. Finally, the result of the spectrographical analysis mentioned above did not show any substantial deviation from the ideal formula MoCoB. It was, therefore, concluded that the deviation of the ideal composition on the Co-rich side must be small and that any such deviation did not affect the structure refinement.

The structure of WCoB and WFeB

In the paper by Haschke, Nowotny & Benesovsky (1966), the existence of the phases WCoB and WFeB was reported. It was suspected that the structures of these phases might be related to or isotypic with MoCoB. The procedure which proved to be successful in the preparation of MoCoB crystals was also used to obtain single phase WCoB and WFeB. Guinier powder diagrams of both phases could be indexed with orthorhombic unit cells similar to that of MoCoB. The lattice constants given in Table 1 were obtained by a least-squares refinement of the last lines observed on a powder diffraction diagram taken with the asymmetric film setting in a 114.6 mm diameter Debye–Scherrer camera and Cr $K\alpha$ radiation. The isotypy with MoCoB was proven by an intensity calculation (Jeitschko & Parthé, 1966) using the positional parameters of MoCoB. Since the unit-cell dimensions and the atomic radii for MoCoB and WCoB are very similar, the atomic parameters of both phases should be almost the same. The axial ratios of WFeB, however, are somewhat different and therefore the parameters of MoCoB should be regarded only as an approximation

Table 2. *Calculated and observed structure factors of* MoCoB (Cu *Kα radiation*)

hkl	F_c	F_o	hkl	F_c	F_o	hkl	F_c	F_o	hkl	F_c	F_o
200	94.3	99.5	004	35.3	48.1	208	43.1	42.9	613	22.3	21.2
400	40.5	36.1	104	32.5	30.4	210	106.2	100.9	114	62.3	60.0
600	62.1	53.4	204	29.6	28.7	410	37.5	36.2	214	1.8	<5.2
101	18.1	22.6	304	28.8	24.9	610	38.1	35.7	314	113.3	125.9
201	16.4	17.8	404	33.9	37.8	011	84.5	84.8	414	24.2	29.4
301	105.6	89.5	504	85.3	86.1	111	40.5	32.4	514	48.4	57.1
401	63.2	55.4	604	5.1	4.9	211	113.7	86.9	614	19.1	18.6
501	27.1	29.2	105	68.4	60.0	311	2.4	<4.5	015	108.9	102.2
601	67.9	63.2	205	67.9	67.6	411	75.3	69.2	115	14.5	16.4
701	13.9	15.2	305	42.1	43.8	511	69.9	60.6	215	55.2	60.9
002	20.8	28.1	405	15.6	20.5	611	28.7	29.1	315	30.9	42.5
102	48.2	46.6	505	31.7	32.6	711	20.5	22.8	415	13.0	17.0
202	79.9	80.5	006	65.7	53.1	112	127.6	103.7	515	27.7	28.5
302	64.8	71.3	106	37.3	38.3	212	26.3	25.3	116	39.0	46.3
402	76.3	77.9	206	76.8	78.3	312	38.2	38.4	216	8.5	9.4
502	22.0	22.8	306	15.4	19.3	412	52.9	52.9	316	11.3	10.0
602	5.6	<7.5	406	68.4	69.3	512	45.7	45.9	416	50.9	53.7
702	56.2	46.6	506	10.7	6.8	612	49.7	54.9	017	52.0	55.0
103	137.6	113.5	107	31.8	33.0	013	74.6	87.8	117	27.9	28.8
203	56.3	63.5	207	6.6	7.6	113	50.8	50.9	217	68.7	67.8
303	65.4	72.8	307	8.3	10.7	213	5.5	6.0	317	10.6	6.6
403	13.3	10.2	407	49.1	42.0	313	50.3	60.6	118	47.6	46.6
503	48.2	47.9	008	73.6	81.8	413	20.8	26.7			
603	12.6	14.5	108	12.0	12.6	513	44.6	51.1			

Table 3. *Atomic parameters of* MoCoB *and their standard deviations*

Atoms	x	$\sigma(x) \cdot 10^4$	y	z	$\sigma(z) \cdot 10^4$	$B \cdot 10^{-16}$ cm^2	$\sigma(B)$
4 Mo in 4(c)	0.0271	6	$\frac{1}{4}$	0.1733	4	0.27	0.14
4 Co in 4(c)	0.1478	11	$\frac{1}{4}$	0.5556	9	0.52	0.17
4 B in 4(c)	0.2705	54	$\frac{1}{4}$	0.8614	49	0.1	—

to those of WFeB. To facilitate identification of the three complex borides, the intensities as recorded with a Debye–Scherrer camera are listed in Table 4.

Discussion

Borides are usually classified according to the linking of the boron atoms (Kiessling, 1950; Aronsson, 1961). In boron-rich compounds the boron atoms form three-dimensional frameworks. With increasing metal content the boron–boron interaction gradually decreases, the boron atoms thus forming nets, double chains, single chains, pairs and finally in boron-poor compounds the boron atoms are isolated from each other. The environment of isolated boron atoms is either an octahedron as in the borides of the large metal atoms with the NaCl type (for references see Pearson, 1967), a tetragonal antiprism with the borides of the $CuAl_2$ type and $Cr_{23}C_6$ type (Stadelmaier, Draughn & Hofer, 1963) as the most numerous representatives, or a trigonal prism as in the borides with Fe_3C type and Th_7Fe_3 type structures. Sometimes the three metal atoms outside the rectangular faces of the trigonal prism approach the central boron atom so closely that the coordination number of the boron atom must be considered to be nine. This is also the environment of the boron atoms in the TiNiSi type borides MoCoB, WCoB and WFeB.

It is interesting to note that the corresponding binary borides Mo_2B, W_2B, Co_2B and Fe_2B are all of the $CuAl_2$ type. The main difference between the two types can be seen in the environment of the metal atoms (Table 5). The TiNiSi type allows the larger metal atoms the higher coordination number whereas the smaller metal atom has the lower number of neighbors. Thus, as already mentioned by Rundqvist & Nawapong (1966), the TiNiSi type is particularly suited for ternary compounds containing two kinds of metal atoms with different radii.

An examination of the list of interatomic distances of MoCoB (Table 6) reveals a strong interaction Mo–Co, while the interactions Mo–Mo and Co–Co are somewhat weaker in general, although there are two short Co–Co distances. Due to the weak scattering power of boron the boron–metal distances have wider standard deviations; the mean distances, however, are more reliable. They are slightly larger than the corresponding distances in the binary borides of the $CuAl_2$ type. This is consistent with the higher coordination number of the boron atom in MoCoB. A drawing of the TiNiSi type has been given earlier in this journal (Shoemaker & Shoemaker, 1965).

It has been mentioned by Shoemaker & Shoemaker (1965) and Rundqvist & Nawapong (1966) that the compounds with the $PbCl_2$ type structure can be divided into two groups, depending on the a/c ratio (setting *Pnma*), giving rise to considerable differences in the number of nearest neighbors. The length of the short b axis is an additional parameter determining the coordination number. A convenient expression for this is the ratio $(a+c)/b$. The slightly higher $(a+c)/b$ ratio

Table 4. *Calculated and observed intensities of complex borides with E-TiNiSi type structure. Debye–Scherrer camera, Cr Kα radiation*

MoCoB

hkl	$d_c(\text{Å})$	I_c	I_o
101	4.3412	2.9	vvvw
002	3.3170	0.9	vvvw
011	2.9055	41.7	m
102	2.8721	16.0 }	m
200	2.8705	25.6 }	
201	2.6345	0.9	vvvw
111	2.5924	19.2	w
202	2.1706	20.1	w
112	2.1469	100.0 }	vvs
210	2.1462	37.4 }	
103	2.0635	52.3	s
211	2.0420	68.4	s
301	1.8387	25.8	w
013	1.8250	13.2	vw
212	1.8019	3.8	vvvw
203	1.7518	7.2	vvw
113	1.7393	10.7	vw
004	1.6585	1.0 }	vw
302	1.6576	7.6 }	
020	1.6160	28.1	w
311	1.5982	0.0	—
104	1.5933	2.3	vvvw
213	1.5401	0.2	—
121	1.5145	0.4	—
312	1.4749	3.7	vvvw
022	1.4528	0.2	—
303	1.4471	6.3	vvw
204	1.4360	1.5 }	vvvw
400	1.4352	0.9 }	
114	1.4291	11.3	vw
122	1.4084	5.0 }	vw
220	1.4082	8.6 }	
401	1.4028	7.2	vvw
221	1.3775	0.5	—
313	1.3207	10.6	vw
402	1.3172	13.1	vw
214	1.3123	0.0 }	vvvw
410	1.3117	2.2 }	
222	1.2962	16.8	vw
105	1.2927	10.4	vw
411	1.2868	26.4	w
123	1.2723	55.0	s
304	1.2533	1.7	—
015	1.2274	39.3	m
412	1.2198	19.3	w
321	1.2138	47.5	m
205	1.2044	19.3 }	w
403	1.2039	0.9 }	
115	1.2003	1.7	—
223	1.1878	17.9	w
314	1.1685	163.9	vvs
024	1.1574	6.3 }	s
322	1.1571	44.9 }	

WCoB

hkl	$d_c(\text{Å})$	I_c	I_o
101	4.3332	25.5	w
002	3.3160	9.7	vw
011	2.9112	74.1	s
102	2.8693	9.8 }	m
200	2.8620	42.2 }	
201	2.6278	3.8	vvvw
111	2.5948	4.5	vvvw
202	2.1666	21.0	w
112	2.1481	100.0 }	vs
210	2.1450	23.3 }	
103	2.0622	57.1	m
211	2.0409	77.3	s
301	1.8336	17.4	vw
013	1.8261	6.4	vvw
212	1.8010	0.2	—
203	1.7495	2.9	vvvw
113	1.7397	6.7	vvw
004	1.6580	1.5 }	vvw
302	1.6538	7.1 }	
020	1.6200	24.3	w
311	1.5958	0.5	—
104	1.5925	0.3	—
213	1.5394	0.0	—
121	1.5174	3.7	vvvw
312	1.4730	12.4	vw
022	1.4556	2.7	vvvw
303	1.4444	12.5	vw
204	1.4346	2.3	vvvw
400	1.4310	3.5 }	w
114	1.4292	25.7 }	
122	1.4107	3.3 }	vw
220	1.4098	15.8 }	
401	1.3988	8.5	vvw
221	1.3790	1.9	vvvw
313	1.3193	13.3	vw
402	1.3139	10.7 }	vw
214	1.3118	0.2 }	
410	1.3090	6.1	vw
222	1.2974	19.2	vw
105	1.2922	13.0	vw
411	1.2842	31.4	w
123	1.2739	64.8	s
304	1.2515	4.2	vvvw
015	1.2275	34.9	m
412	1.2176	17.4	vw
321	1.2140	34.3	m
205	1.2034	11.7	vw
403	1.2013	0.1	—
115	1.2002	1.7	—
223	1.1887	7.4	vvw
314	1.1674	152.6	vvvs
024	1.1587	9.2	vvw
322	1.1573	43.8	m

WFeB

hkl	$d_c(\text{Å})$	I_c	I_o
101	4.4257	29.0	w
002	3.4050	11.3	vw
102	2.9394	9.9	vw
200	2.9115	45.1	m
011	2.8672	72.7	s
201	2.6771	4.3	vvvw
111	2.5723	3.7	vvvw
202	2.2128	22.3	w
112	2.1525	100.0	vvs
210	2.1415	22.2	w
103	2.1150	61.6	s
211	2.0429	77.8	vs
301	1.8667	17.7	w
013	1.8438	6.2	vvw
212	1.8128	0.1	—
203	1.7902	2.9	vvw
113	1.7578	6.7	vvw
004	1.7025	1.6	vvvw
302	1.6863	7.3	vw
104	1.6341	0.2	—
311	1.6073	0.6	—
020	1.5805	22.8	vw
213	1.5577	0.0	—
121	1.4884	3.9 }	vw
312	1.4878	13.1 }	
303	1.4752	12.9	vw
204	1.4697	2.3	vvvw
400	1.4557	3.7	vvvw
114	1.4516	26.6	m
022	1.4336	2.9	vvvw
401	1.4236	8.5	vw
122	1.3920	3.1 }	w
220	1.3890	16.3 }	
221	1.3610	2.1	vvvw
402	1.3385	10.1 }	w
313	1.3368	12.9 }	
214	1.3327	0.2	—
105	1.3262	12.2 }	w
410	1.3223	6.2 }	
411	1.2980	30.1	m
222	1.2861	19.6	w
304	1.2799	3.9	vvvw
123	1.2660	66.4	s
015	1.2508	30.5	m
205	1.2337	9.2 }	m
412	1.2326	15.6 }	
403	1.2254	0.1	—
115	1.2229	1.4	—
321	1.2062	34.9	m
314	1.1864	111.0 }	vvs
223	1.1848	7.1 }	
024	1.1583	9.6	vvw
322	1.1532	53.1	m

Table 5. *Coordination numbers of transition metal borides T_2B with the $CuAl_2$ type structure as compared with the coordination numbers of the ordered $PbCl_2$ type structures MoCoB and TiNiSi*

First number: neighbors within 1·15 (r_A+r_B), second number: within 1·30 (r_A+r_B); r_A and r_B are the atomic radii for C.N. 12.

T_2B

	T	B	Σ
T	11	4	15
B	8	—	8

MoCoB

	Mo	Co	B	Σ
Mo	4+2	6	5	15+2
Co	6	2+2	4	12+2
B	5	4	—	9

TiNiSi

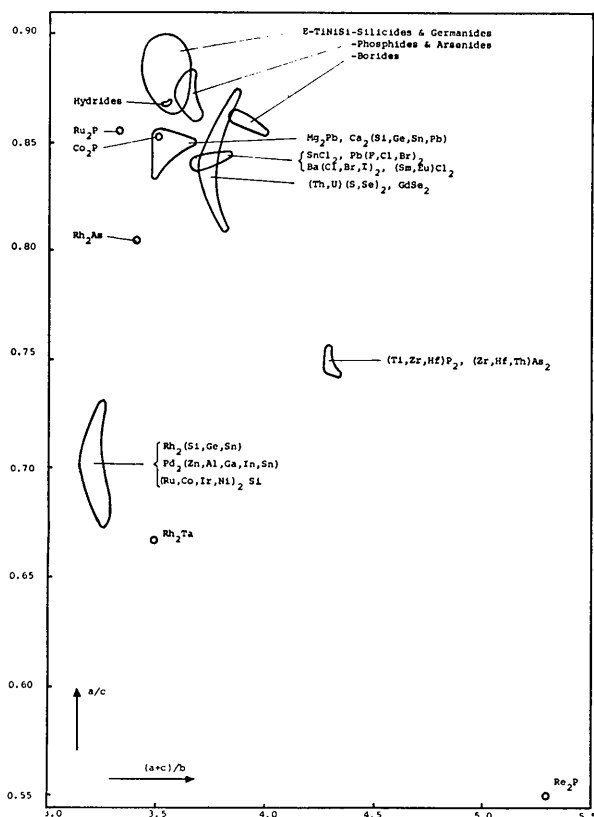|	Ti	Ni	Si	Σ
Ti	4+2	6	5+1	15+3
Ni	6	2	4	12
Si	5+1	4	—	9+1

Fig. 1. Grouping of PbCl₂ type compounds according to their axial ratios a/c and $(a+c)/b$.

of MoCoB as compared with that of TiNiSi gives rise to some differences in the coordination numbers of the two compounds (Table 5).

The two parameters a/c and $(a+c)/b$ can be used for grouping the various PbCl₂ type structures (Fig. 1). Since the atomic parameters are not too different within one group, the coordination polyhedra differ only slightly within the group, but are entirely different going from one group to another.

The group, with by far the largest number of representatives (a/c from 0·80 to 0·90; $(a+c)/b$ from 3·3 to 4·0) contains all the salt-like compounds (for references see Schubert, 1964; Pearson, 1967): $SnCl_2$, $Pb(F,Cl,Br)_2$ (for a refinement of the $PbCl_2$ structure see Sass, Brackett & Brackett, 1963a), Pb(OH)Cl (Brasseur, 1940), $Ba(Cl,Br,I)_2$, $(Sm,Eu)Cl_2$, $(Ca,Sr,Ba)H_2$, $(Yb,Eu)D_2$ and YbH_2. Also contained in this group are pseudoionic, intermetallic compounds: Mg_2Pb,* $Ca_2(Si,Ge,Sn,Pb)$; chalcogenides of the actinides and the rare earth metals: $(Th,U)(S,Se)_2$, $GdSe_2$; the phosphides Co_2P and Ru_2P and Rh_2As. Almost forty ternary silicides and germanides of the ordered $PbCl_2$ type (E-phase, TiNiSi type) in the systems {Ti,Zr,Hf,V,Nb,Ta} {Fe,Co,Ni,Pd,Pt,Cu} {Si,Ge} (Spiegel, Bardos & Beck, 1963; Gangelberger, Nowotny & Benesovsky, 1967; Nickl & Sprenger, 1967) belong to this group. The number of E phases has been further increased by almost twenty ternary phosphides and arsenides in

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* *Note added in proof.:* – Eu₂Pb (a/c = 0·783; $(a+c)/b$ = 3·31) also crystallizes with the PbCl₂ structure (McMasters & Gschneidner, 1967).

Table 6. *Interatomic distances in the structure of* MoCoB

All distances shorter than 1·3 $(r_A + r_B)$ are listed. The sum of the atomic radii (C.N. 12) and the transition metal (T)–boron distances in Mo₂B (Kiessling, 1947) and Co₂B (Bjurström, 1933), respectively, are given in the last column.

Atom	Neighbors	Distance (Å)	Mean	$2r_T$, or T–B in Mo₂B, Co₂B
Mo	2Mo	2·828 ± 5		
	2Mo	3·046 ± 3		2·80
	2Mo	3·232 ± 1		
	2Co	2·589 ± 7		
	2Co	2·618 ± 6		
	1Co	2·629 ± 8	2·62	2·66
	1Co	2·655 ± 8		
	2B	2·349 ± 24		
	2B	2·363 ± 24	2·38	2·37
	1B	2·497 ± 33		
Co	2Mo	2·589 ± 7		
	2Mo	2·618 ± 6		
	1Mo	2·629 ± 8	2·62	2·66
	1Mo	2·655 ± 8		
	2Co	2·457 ± 10		
	2Co	3·232 ± 1		2·52
	2B	2·119 ± 22		
	1B	2·147 ± 34	2·16	2·15
	1B	2·235 ± 33		
B	2Mo	2·349 ± 24		
	2Mo	2·363 ± 24	2·38	2·37
	1Mo	2·497 ± 33		
	2Co	2·119 ± 22		
	1Co	2·147 ± 34	2·16	2·15
	1Co	2·235 ± 33		

the systems {Ti, Zr, Hf, Nb, Ta} {Fe, Co, Ni} {P, As} (Rundqvist & Nawapong, 1966; Rundqvist & Tansuriwongs, 1967) and by the borides of this work.

The second group of $PbCl_2$ type compounds (a/c from 0·66 to 0·74; $(a+c)/b$ from 3·1 to 3·3), referred to as Co_2Si subclass by Rundqvist & Nawapong (1966), consists of a number of binary zincides, aluminides, gallides, silicides, germanides and stannides of group VIII transition metals: $Rh_2(Si, Ge, Sn)$, $Pd_2(Zn, Al, Ga, In, Sn)$, $(Ru, Co, Ir, Ni)_2Si$ and of Rh_2Ta.

There is a third group of $PbCl_2$ type compounds with a rather limited range of axial ratios ($a/c \sim 0·75$; $a+c/b \sim 4·3$) consisting of phosphides and arsenides of group IV transition metals: $(Ti, Zr, Hf)P_2$ and $(Zr, Hf, Th)As_2$ (Trzebiatowski, Weglowski & Lukaszewicz, 1958; Jeitschko & Nowotny, 1962; Hulliger, 1964, 1966; Lundström, 1966).

Finally the structure of Re_2P (Rundqvist, 1961) stands alone in this classification of $PbCl_2$ type structures ($a/c = 0·55$; $(a+c)/b = 5·3$).

Rh_2B and $SrCl_2$ had been assigned the $PbCl_2$ type previously but later investigations (Aronsson, Åselius & Stenberg, 1959; Sass, Brackett & Brackett, 1963b) did not confirm this.

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