

of the adjacent ring. Bond lengths and bond angles for the two molecules of *p,p'*-dimethoxybenzophenone are shown in Figs. 4 and 5.

### Discussion

The similarities in the distances and angles in the three molecules of the two compounds studied is quite striking. The six O-CH<sub>3</sub> bond lengths range from 1.419 to 1.435 Å, the six O-C<sub>ar</sub> bond lengths range from 1.350 to 1.374 Å, the five OC-C<sub>ar</sub> distances range from 1.480 to 1.501 Å, and the three C=O distances are 1.211, 1.213 and 1.220 Å. The C<sub>ar</sub>-C<sub>ar</sub> in deoxyanisoin average 1.392 Å and in *p,p'*-dimethoxybenzophenone 1.390 Å. The six C-O-C<sub>ar</sub> angles range from 116.3° to 118.9°. The O-C<sub>ar</sub>-C<sub>ar</sub> angles are unequal about the C<sub>ar</sub>-O bond and enlarged on the side of the methyl group, the enlargement probably due to steric hindrance between hydrogens on the ring and in the methyl group. These angles range from 123.7° to 125.1° in the three molecules. The deoxyanisoin molecule almost behaves as if it had a center of symmetry between C<sub>1</sub> and C<sub>9</sub>, judging from the similarity in the values of the angles at either end of the molecule. Even the C-C-C angle in the tetrahedral methylene group has been enlarged to nearly equal the C-C-C angle in the planar carbonyl group.

The environment of the molecules in the unit cell is quite similar in the two compounds. The planes of the rings in different molecules make angles of 60°-62° with each other. The carbonyl groups are surrounded by hydrogens from the methyl groups of adjacent molecules. The closest intermolecular approach in deoxyanisoin is 3.46 Å between methyl carbons atoms of adjacent molecules and the next closest is 3.54 Å for O<sub>3</sub>-C<sub>16</sub> and 3.56 Å for O<sub>2</sub>-C<sub>3</sub>.

Similarly in *p,p'*-dimethoxybenzophenone close approaches are found between the carbonyl oxygens and carbons of the methyl groups (3.47-3.53 Å) and between the methoxy oxygens and ring carbon atoms (3.41-3.54 Å). The closest approach of 3.38 Å is between O<sub>3</sub> and the atom related to it by a center of symmetry.

The isotropic temperature factors for both molecules are also quite similar. The average *B* values for all carbons except those in the methyl groups, for the methyl carbons, methoxy oxygens, and carbonyl oxygens are 3.64, 5.34, 4.35 and 5.08 for deoxyanisoin and 3.25, 5.93, 4.19 and 5.08 for *p,p'*-dimethoxybenzophenone. In each molecule, there is considerably more vibration at the terminal methoxy groups and in the central carbonyl than in the rings.

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## Structural Features of Some Phases Related to Cementite

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Investigations during the last few years have shown that a number of phases, especially borides, of the seventh and eighth group metals are isomorphous with cementite or crystallize in structures closely related to that of cementite. In this paper the recently obtained structural data are summarized and discussed. The influence of the radius ratio on trends in interatomic distances and lattice parameters is particularly considered. On basis of the presented data some general remarks on 'complicated' interstitial phases are also made.

### 1. Introduction

During the last few years the crystal structures of borides, silicides and phosphides of the seventh and

eighth group metals have been studied at this Institute with the principal aim of providing accurate data for a discussion of the crystal chemistry of these phases. In this paper the structures of a number of metal-rich

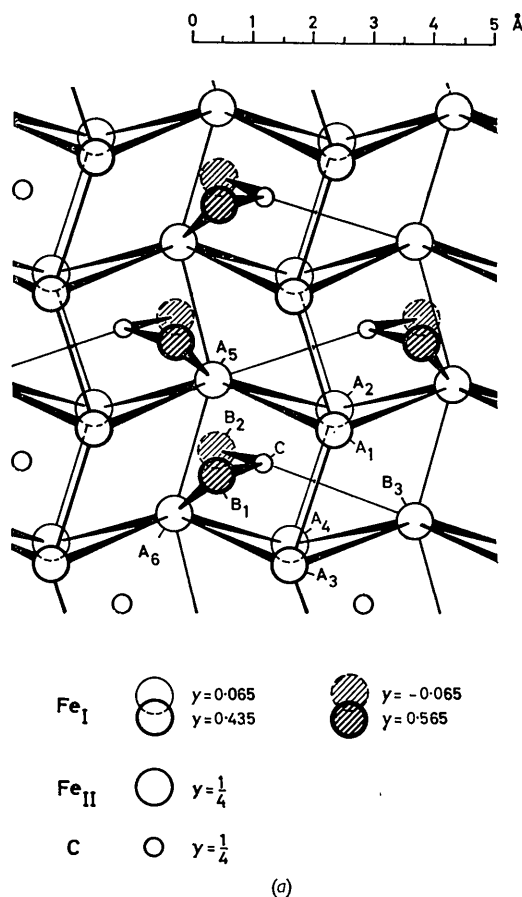
phases which have been found to be closely related to cementite will be presented and discussed. Some interesting trends in the shortest interatomic distances have been observed and are given particular consideration.

In all the phases presented in this paper the radius ratio\*  $r_X/r_{Me}$  exceeds 0.59. Thus they may be regarded as phases possessing 'complicated' interstitial structures. In view of the data presented some general remarks on phases with interstitial structures are given.

## 2. Structural data of phases isomorphous with $Fe_3C$ , $Re_3B$ , $Pd_5B_2$ and $Ru_7B_3$ ( $Th_7Fe_3$ -type)

The phases to be discussed in this paper crystallize in one of four closely related structures— $Fe_3C(DO_{11})$ ,  $Re_3B$ ,  $Pd_5B_2$ , and  $Th_7Fe_3(D10_2)$ . A projection of a representative of each type is shown in Figs. 1–4.

\* Unless otherwise stated, the radii used in the calculations of radius ratios and radius sums are the Goldschmidt radius (coordination number 12) for the metal atom—as given by Hume-Rothery & Raynor (1954)—and the tetrahedral radius for the non-metal atom (0.77, 0.88, 1.10 and 1.17 Å for carbon, boron, phosphorus, and silicon, respectively). Throughout the paper  $X$  denotes a non-metal and  $Me$  a metal.



Lattice parameters of phases crystallizing in the four types are listed in Tables 1 and 2.

The immediate environments of the atoms is very similar in the four types (see Tables 3 and 4). The metal atoms have 10–12 metal neighbours and in addition coordinate three or four non-metal atoms.

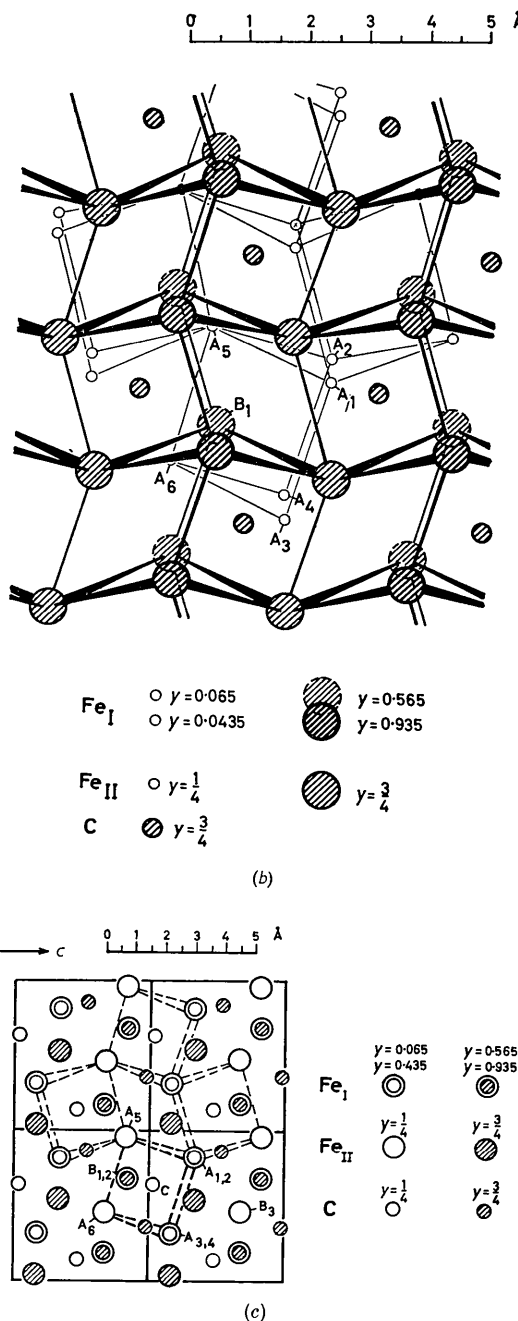


Fig. 1. The structure of cementite,  $Fe_3C$  (Lipson & Petch, 1940). (a) and (b) illustrate the interconnection of the triangular prisms of iron atoms which surround the carbon atoms. (c) shows a projection of the structure on the mirror plane. The atoms  $A_5$ ,  $A_6$ ,  $B_3$  and  $C$  lie in the mirror plane.

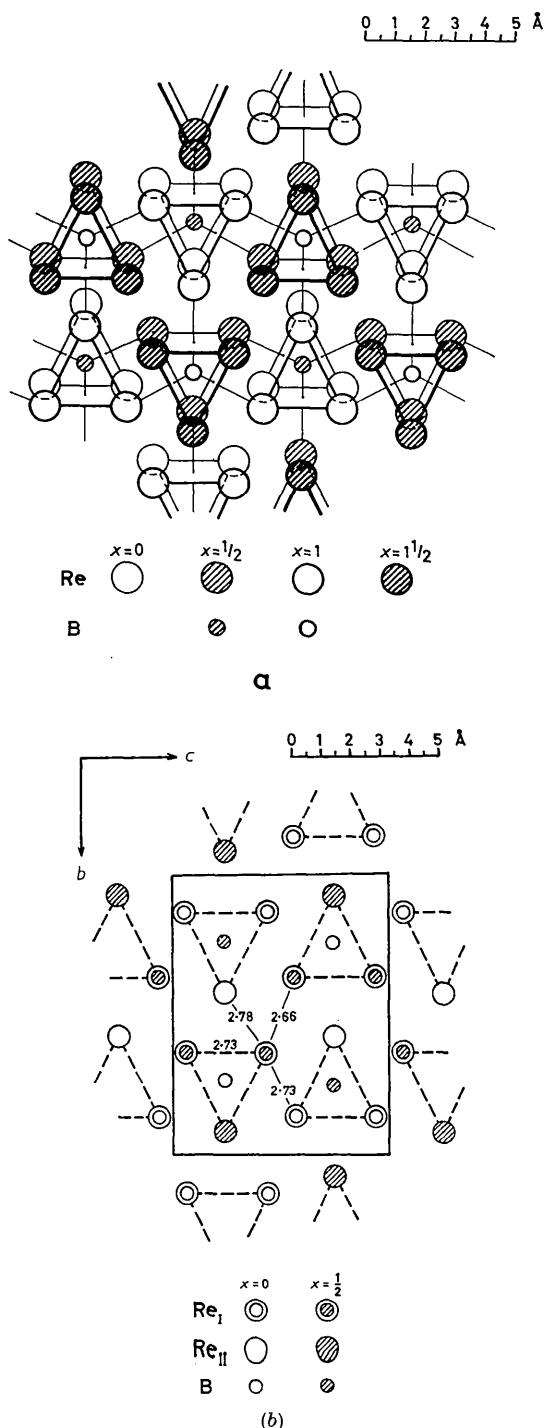


Fig. 2. The structure of  $\text{Re}_3\text{B}$  (Aronsson *et al.*, 1960b). (a) illustrates the interconnection of the triangular prisms of rhenium atoms which surrounds the boron atom. (b) shows a projection of the structure on the mirror plane ( $z = \pm \frac{1}{4}$ ).

The latter are surrounded by nine metal atoms; six of these occupy the corners of what is best described as a distorted trigonal prism, while the remaining (and sometimes rather remote) three metal neighbours

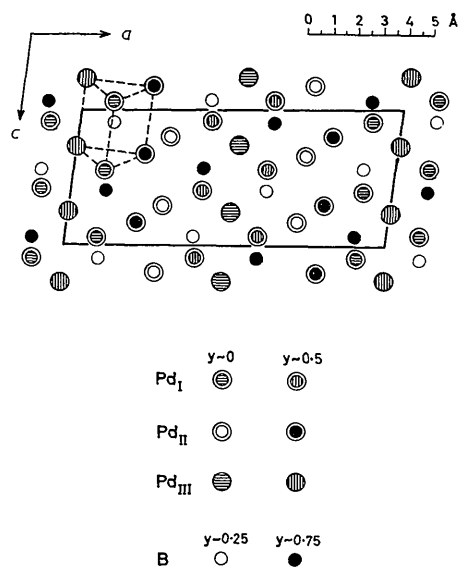


Fig. 3. The structure of  $\text{Pd}_5\text{B}_2$ , projected on the  $ac$ -plane. (Stenberg, 1961).

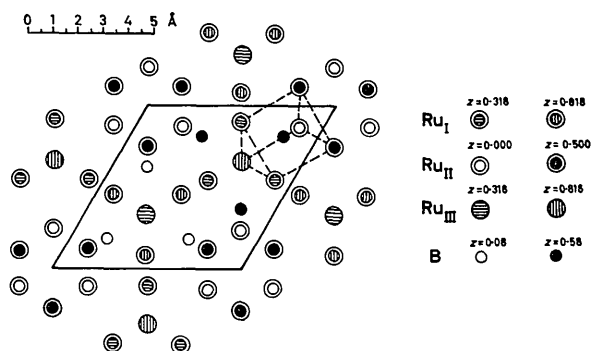


Fig. 4. The structure of  $\text{Ru}_7\text{B}_3$ , projected on the basal plane. (Aronsson, 1959).

are situated outside the foursided faces of the prism (Fig. 5). Ideally, the nine metal atoms are situated at the corners of a tetrakaidecaedron. However, since six metal atoms are always closer to the central atom than the other three, we prefer to describe the coordination around the non-metal atom as triangular prismatic.

With the exception of  $\text{Pd}_3\text{P}$  none of the binary phases reported in Tables 1 and 2 displays appreciable l.p. (lattice parameter) variations indicating that (except for  $\text{Pd}_3\text{P}$ ) each has a narrow homogeneity range. Since the real composition has not been determined accurately for any of the phases, it is not known whether or not the homogeneity range includes the ideal composition given in the tables. There is, however, no evidence for large deviations from stoichiometry.

The unit-cell volume of  $\text{Pd}_3\text{P}$  decreases with decreasing phosphorus content, suggesting that the homogeneity range is associated with a varying

Table 1. *Lattice parameters of phases with the cementite structure*  
(Space-group  $Pnma$ )

Phase	Lattice parameters (Å)			Ref.*
	<i>a</i>	<i>b</i>	<i>c</i>	
Mn <sub>3</sub> C	5.080	6.772	4.530	<i>a</i>
Fe <sub>3</sub> C:				
slowly cooled	5.0890	6.7428	4.5230	<i>b</i>
quenched from 900 °C.	5.0837	6.7475	4.5165	<i>b</i>
Co <sub>3</sub> B	5.225	6.629	4.408	<i>c</i>
Ni <sub>3</sub> B	5.211	6.619	4.389	<i>c</i>
Pd <sub>3</sub> B	5.463	7.567	4.852	<i>d</i>
Pd <sub>3</sub> P:				
phosphorus-rich limit (~ Pd <sub>3</sub> P) at 740 °C.	5.980	7.440	5.164	<i>e</i>
phosphorus-poor limit (~ Pd <sub>3</sub> P <sub>0.75</sub> ) at 740 °C.	5.645	7.558	5.071	<i>e</i>
Pd <sub>3</sub> Si	5.735	7.555	5.260	<i>f</i>
NiAl <sub>3</sub>	6.6115	7.3664	4.8118	<i>g</i>
Fe <sub>3</sub> B <sub>0.9</sub> C <sub>0.1</sub>	5.4052	6.6685	4.4500	<i>h</i>
Co <sub>3</sub> B <sub>0.8</sub> C <sub>0.2</sub>	5.195	6.635	4.415	<i>c</i>
Ni <sub>3</sub> B <sub>0.8</sub> P <sub>0.2</sub>	5.282	6.632	4.409	<i>i</i>
Fe <sub>3</sub> (B, Si):				
boron-rich	5.363	6.660	4.458	<i>j</i>
boron-poor	5.299	6.674	4.474	<i>j</i>

\* *a*: Kuo & Persson (1954); *b*: Petch (1944); *c*: Rundqvist (1958); *d*: Stenberg (1961); *e*: Rundqvist & Gullman (1960); *f*: Aronsson & Nylund (1960); *g*: Bradley & Taylor (1937); *h*: Nicholson (1957); *i*: unpublished results by Rundqvist (1961); *j*: Aronsson & Lundgren (1959).

Table 2. *Lattice parameters of phases with the Re<sub>3</sub>B-, Pd<sub>5</sub>B<sub>2</sub>-, and Th<sub>7</sub>Fe<sub>3</sub>-structures*

Phase	Structure type	Lattice parameters (Å)	Ref.*
Re <sub>3</sub> B	Re <sub>3</sub> B	<i>a</i> = 2.890, <i>b</i> = 9.313, <i>c</i> = 7.258	<i>a</i>
Pd <sub>5</sub> B <sub>2</sub>	Pd <sub>5</sub> B <sub>2</sub>	<i>a</i> = 12.786, <i>b</i> = 4.955, <i>c</i> = 5.472, $\beta$ = 97° 2'	<i>b</i>
Mn <sub>5</sub> C <sub>2</sub>	Pd <sub>5</sub> B <sub>2</sub>	<i>a</i> = 11.66, <i>b</i> = 4.573, <i>c</i> = 5.086, $\beta$ = 97° 45'	<i>c</i>
Re <sub>7</sub> B <sub>3</sub>	Th <sub>7</sub> Fe <sub>3</sub>	<i>a</i> = 7.504, <i>c</i> = 4.882	<i>d</i>
Ru <sub>7</sub> B <sub>3</sub>	Th <sub>7</sub> Fe <sub>3</sub>	<i>a</i> = 7.46 <sub>7</sub> , <i>c</i> = 4.71 <sub>3</sub>	<i>e</i>
Rh <sub>7</sub> B <sub>3</sub>	Th <sub>7</sub> Fe <sub>3</sub>	<i>a</i> = 7.47 <sub>1</sub> , <i>c</i> = 4.77 <sub>7</sub>	<i>d</i>

\* *a*: Aronsson *et al.* (1960b); *b*: Stenberg (1961); *c*: Kuo & Persson (1954); *d*: Aronsson *et al.* (1960a); *e*: Aronsson (1959).

number of vacancies on the phosphorus sites. It is noteworthy that the small l.p. variations of Fe<sub>3</sub>C are in the same directions as those of Pd<sub>3</sub>P. Thus, it seems very likely that also in Fe<sub>3</sub>C, as was suggested by Petch (1944), a varying number of the non-metal sites may be vacant.

For details regarding the accuracy of the interatomic distances (listed in Tables 3 and 4), original sources should be consulted. For the purposes of the subsequent discussion it is sufficient to know that (except in Fe<sub>3</sub>C and NiAl<sub>3</sub>) the standard deviation of individual *Me- $\bar{M}e$*  distances is about 0.01 Å or less, in Pd<sub>3</sub>P and Pd<sub>3</sub>Si that of individual *Me-X* distances is about 0.02 Å, while individual *Me-X* distances in borides and carbides are only approximate. In most of the borides as well as in Fe<sub>3</sub>C, the approximate

positions of the non-metal atoms have been unambiguously determined experimentally, but (except for Fe<sub>3</sub>C and Ni<sub>3</sub>B) the atomic parameters of the non-metal atoms have been chosen so as to make the shortest *Me-X* distances as equal as possible. The discussion of *Me-X* distances in borides and carbides must accordingly be confined to *average Me-X* distances which are accurate to about 0.01 Å. (Within the limits of experimental error, the position of the non-metal atoms in Pd<sub>3</sub>P and Pd<sub>3</sub>Si are the same as those obtained by making the six shortest *Me-X* distances as nearly equal as possible. Also, the prisms of metal atoms surrounding the boron or carbon atoms have a geometry which makes it possible to put the non-metal atom at very nearly the same distance from its six closest metal neighbours. Thus, it is reasonable to derive the atomic parameters of the boron and carbon atoms from space considerations.)

### 3. Discussion of the structures

Different authors put different emphasis on the relative importance of the 'size factor' and various 'electronic factors' in interpreting the structures. In this paper the discussion will be mainly confined to considerations of the 'size-factor', partly because it is felt that a study of this factor may be of great value in a preliminary systematization of the interatomic distances (given in Tables 3 and 4) and partly because no data are available for testing the influence of other factors. It is not implied that 'electronic factors' are of negligible importance.

It is obvious that a great deal of the structural data presented cannot be accounted for by simple consideration of atomic size. The occurrence of a particular structure type is certainly not determined by the radius ratio alone. For example, there are phases with the cementite structure in systems where the radius ratio  $r_X/r_{Me}$  lies between 0.61 (Fe<sub>3</sub>C) and 0.87 (NiAl<sub>3</sub>). A radius ratio between these values is found in a large number of *Me-X* systems, but only in a small fraction of these does a phase isomorphous with cementite appear. Similarly, no explanation can be given for the non-existence of platinum metal borides with the CuAl<sub>2</sub>-structure (or any other structure where the boron atom is surrounded by a square antiprism of metal atoms), although borides isomorphous with CuAl<sub>2</sub> are found in *Me-B* systems where the radius ratio is larger (e.g. Fe<sub>2</sub>B) as well as smaller (e.g. W<sub>2</sub>B) than in systems of boron with a platinum metal. It is also observed that in binary systems containing more than one intermediate phase, the environment of the non-metal atom may be rather different in different phases. Thus, the triangular prism of ruthenium atoms surrounding the B<sub>1</sub> atom in Ru<sub>11</sub>B<sub>8</sub> (Åselius, 1961) is considerably larger than the corresponding prism in Ru<sub>7</sub>B<sub>3</sub> (Aronsson, 1959), the average of the six shortest B-Ru distances being 2.22 and 2.16 Å, respectively. This is not under-

Table 3. *Environment of metal atoms in phases isomorphous with Fe<sub>3</sub>C, Re<sub>3</sub>B, Pd<sub>3</sub>B<sub>2</sub> and Ru<sub>3</sub>B<sub>3</sub>*

Phase	(Distances in Å)		Av.	2 <i>r</i> <sub>Me</sub>	Me-X distances	<i>r</i> <sub>Me+rX</sub>	Ref.*
	Me-Me distances						
Fe <sub>3</sub> C	FeI -11 Fe:	2.49, 2.52(1+2), 2.55(1+1), 2.65(2), 2.67, 2.68(1+1)	2.58	2.54	-3 C: 2.06, 2.15, 2.31	2.04	<i>a</i>
	FeII -12 Fe:	2.52(2), 2.55(2), 2.65(2), 2.67(2), 2.68(2+2)	2.62	2.54	-3 C: 1.86, 1.88, 3.02	2.04	
Ni <sub>3</sub> B	NiI -11 Ni:	2.43, 2.46(2), 2.50(1+1), 2.55, 2.57, 2.58, 2.71, 2.74(2)	2.57	2.49	-3 B: 1.99, 2.07, 2.30	2.13	<i>b</i>
	NiII -12 Ni:	2.50(2), 2.55(2), 2.57(2), 2.58(2), 2.71(2), 2.79(2)	2.62	2.49	-3 B: 2.02, 2.09, 2.60	2.13	
Pd <sub>3</sub> B	PdI -11 Pd:	2.72, 2.76(2), 2.79, 2.82(1+1), 2.83(2), 2.86, 2.87, 2.96	2.82	2.75	-3 B: 2.17(1+1), 2.71	2.26	<i>c</i>
	PdII -12 Pd:	2.82(2+2), 2.86(2), 2.87(2), 2.88(2), 2.96(2)	2.87	2.75	-3 B: 2.17, 2.18, 2.97	2.26	
Pd <sub>3</sub> P†	PdI -11 Pd:	2.78, 2.84, 2.85, 2.89(2), 2.93(1+1), 2.94, 3.11(2), 3.21	2.95	2.75	-3 P: 2.31, 2.39, 2.60	2.48	<i>d</i>
	PdII -12 Pd:	2.84(2), 2.93(2+2), 2.94(2), 3.21(2), 3.22(2)	3.01	2.75	-3 P: 2.31(1+1), 3.14	2.48	
Pd <sub>3</sub> Si	PdI -11 Pd:	2.78, 2.80, 2.85(1+2), 2.90, 2.93, 2.97(2), 3.01, 3.56	2.95	2.75	-3 Si: 2.35, 2.48, 2.56	2.55	<i>e</i>
	PdII -12 Pd:	2.78(2), 2.80(2), 2.85(2), 2.93(2), 3.29(2), 3.56(2)	3.03	2.75	-3 Si: 2.35, 2.37, 3.04	2.55	
Re <sub>3</sub> B	ReI -11 Re:	2.66, 2.73, 2.74(2+2), 2.78(2), 2.89(2), 3.04	2.79	2.75	-3 B: 2.23(2), 2.54	2.26	<i>f</i>
	ReII -12 Re:	2.74(4), 2.78(4), 2.89(2), 3.04(2)	2.83	2.75	-3 B: 2.23(2), 2.95	2.26	
Pd <sub>3</sub> B <sub>2</sub>	PdI -12 Pd:	2.77, 2.81, 2.83, 2.85, 2.89(2), 2.90(1+1+1), 2.96, 2.97, 3.08	2.90	2.75	-4 B: 2.18(1+1), 2.80, 3.06	2.26	<i>c</i>
	PdII -11 Pd:	2.70, 2.77(1+2), 2.81, 2.83(2), 2.90(1+1), 2.96, 3.08	2.85	2.75	-3 B: 2.18, 2.19, 2.60	2.26	
	PdIII -10 Pd:	2.70(2), 2.77(2), 2.83(2+2), 2.97(2)	2.82	2.75	-4 B: 2.18(2), 2.19(2)	2.26	
Ru <sub>3</sub> B <sub>3</sub>	RuI -11 Ru:	2.61(2), 2.72, 2.76(2), 2.81(2), 2.84(2), 2.86(2)	2.77	2.67	-4 B: 2.15(2), 2.66(2)	2.22	<i>g</i>
	RuII -11 Ru:	2.73(2), 2.81(2), 2.84(4), 2.86(2), 2.87	2.82	2.67	-4 B: 2.15, 2.16(2), 2.86	2.22	
	RuIII -12 Ru:	2.72(3), 2.84(6), 2.87(3)	2.78	2.67	-3 B: 2.20(3)	2.22	

\* *a*: Lipson & Petch (1940); *b*: Rundqvist (1958); *c*: Stenberg (1961); *d*: Rundqvist & Gullman (1960); *e*: Aronsson & Nylund (1960); *f*: Aronsson *et al.* (1960b); *g*: Aronsson (1959).

† There is a printing error in the original paper on Pd<sub>3</sub>P (Rundqvist & Gullman, 1960). The *x*-parameter of Pd<sub>1</sub> is erroneously given as 0.1783. The correct value is 0.1763. In calculating the interatomic distances in this paper as well as the original paper the correct *x* parameter of the Pd<sub>1</sub> atom has been used.

Table 4. Interatomic distances in Å between unlike atoms in phases isomorphous with  $\text{Fe}_3\text{C}$ ,  $\text{Re}_3\text{B}$ ,  $\text{Pd}_3\text{B}_2$  and  $\text{Ru}_7\text{B}_3$ 

$r_X/r_{Me}$	Phase	Distances between the X atom and Me atoms at the corners of the prism (A atoms)		Av.	$r_{Me} + r_X$	Distances between the X atom and Me atoms outside the prism (B atoms)		Ref.*
		(Me atoms in 4(c))	(Me atoms in 8(d))			(Me atoms in 8(d))	(Me atoms in 4(c))	
	$\text{NiAl}_3$	2.44, 2.46	2.42(2), 2.44(2)	2.44		2.52(2)	2.72	a
0.61	$\text{Fe}_3\text{C}$	1.86, 1.88	2.06(2), 2.15(2)	2.03	2.04	2.31(2)	3.02	b
0.71	$\text{Ni}_3\text{B}$	2.02, 2.09	1.99(2), 2.07(2)	2.04	2.13	2.30(2)	2.60	c
0.64	$\text{Pd}_3\text{B}$	2.17, 2.18	2.17(2+2)	2.17	2.26	2.71(2)	2.97	d
0.80	$\text{Pd}_3\text{P}$	2.31(1+1)	2.31(2), 2.39(2)	2.34	2.48	2.60(2)	3.14	e
0.85	$\text{Pd}_3\text{Si}$	2.35, 2.37	2.35(2), 2.48(2)	2.39	2.55	2.56(2)	3.04	f
0.64	$\text{Re}_3\text{B}$		2.23(4+2)	2.23	2.26	2.54(2), 2.95		g
0.64	$\text{Pd}_3\text{B}_2$	2.18(1+1+1+1), 2.19(1+1)		2.18	2.26	2.60, 2.80, 3.06		d
0.66	$\text{Ru}_7\text{B}_3$	2.15(1+2), 2.16, 2.20		2.16	2.22	2.66(2), 2.86		h

\* a: Bradley & Taylor (1937); b: Lipson & Petch (1940); c: Rundqvist (1958); d: Stenberg (1961); e: Rundqvist & Gullman (1960); f: Aronsson & Nylund (1960); g: Aronsson *et al.* (1960b); h: Aronsson (1959).

stood if the atoms are believed to be characterized by a constant radius.

Although factors other than size have to be taken into account in explaining many experimental facts, some features of the close-packed structures under consideration may be regarded as largely determined by the relative size of the atoms. The non-metal atoms are surrounded by a (more-or-less distorted) triangular prism of metal atoms (Fig. 5). This is what one would expect from packing considerations when the radius ratio  $r_X/r_{Me}$  exceeds the value favourable for an octahedral environment of the non-metal atom. The ideal radius ratio  $r_X/r_{Me}$  for a non-metal atom to fit in a trigonal prismatic 'hole' is 0.528 as compared with 0.414 for an octahedral 'hole'. (The next regular arrangement of neighbours would be a square anti-prism—ideal radius ratio 0.645—but, as pointed out earlier, the non-metal atoms do not have this environment in the phases under discussion although in some of them the radius ratio is larger than 0.645.)

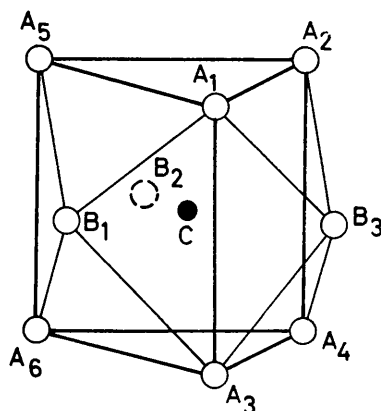


Fig. 5. Triangular prism of metal atoms  $A$  (unfilled circles) surrounding a non-metal atom  $C$  (filled circle).

In order to study more quantitatively the influence of the radius ratio on the short interatomic distances, let us consider the arrangement of spherical atoms

shown in Fig. 5. (For clarity, only the centre of each atom is indicated.) The  $A$  atoms, situated at the corners of a triangular prism, are assumed to have the same radius as the  $B$  atoms, which are placed outside each four-sided face of the prism in contact with four  $A$  atoms. The radius of the  $C$  atom at the centre of the prism is smaller than that of the  $A$  and  $B$  atoms. If the prism is an ideal trigonal prism and the radius ratio  $r_C/r_{A,B}$  equals 0.528, each  $A$  atom contacts the central  $C$  atom (distance  $1.528 r_{A,B}$ ) as well as three other  $A$  atoms (distance  $2r_{A,B}$ ). The  $B$ - $A$  distances equal  $2r_{A,B}$ , while the  $B$ - $C$  distances are  $1.992r_{A,B}$ , which is considerably larger than the radius sum  $r_{A,B} + r_C$ . When the radius ratio  $r_C/r_{A,B}$  increases beyond 0.528, the  $A$  and  $C$  atoms are still in contact, but one or more of the distances between each  $A$  atom and its three close  $A$  neighbours must necessarily be larger than  $2r_{A,B}$ . The  $B$  atoms, still in contact with four  $A$  atoms, move closer to the  $C$  atom.

In structures containing building elements similar to that in Fig. 5, space considerations of the above type might to a large extent explain the spread of the shortest interatomic distances, and should be particularly valuable for comparisons of isomorphous phases with varying radius ratio.

A discussion along these lines is possible in structures such as that of  $\text{Re}_3\text{B}$  where adjacent prisms only share edges of the same kind ( $A$ - $A$  or  $A$ - $B$ ) (that is, the prisms are not linked together so that an  $A$ - $A$  contact in one prism is identical with an  $A$ - $B$  contact in an adjacent prism). The interatomic distances in  $\text{Re}_3\text{B}$  (Figs. 2 and 7(b)) are well accounted for by considering the atoms to be spherical with the radii 1.375 Å and 0.85 Å respectively. The  $A$ - $C$  distances are closely equal to the radius sum. The  $A$ - $A$  distances are larger than the metal diameter, consistent with the radius ratio being 0.62. As expected, the  $A$ - $B$  distances are close to the metal diameter, while the  $B$ - $C$  distances are larger than the radius sum. The way in which the prism of rhenium atoms is distorted,

two rectangular faces being larger than the third one, is obviously associated with the packing of the prisms. A more uniform expansion of the prism would result in a very short distance (corresponding to the distance marked 2.66 in Fig. 2) between rhenium atoms in adjacent prisms. It should be noted that the deviation of two  $A-B$  distances (2.78 and 2.73 in Fig. 2) from the ideal value of 2.75 Å as well as the shortening of one  $A-A$  distance to 2.73 Å are such as to prevent the short rhenium-rhenium distance of 2.66 Å becoming still shorter. Thus, the structure of  $\text{Re}_3\text{B}$  may be regarded as a simple close-packed arrangement of nearly spherical atoms with the radii 1.37<sub>5</sub> and 0.85 Å respectively.

In cementite, one of the short metal-metal distances is an  $A-A$  as well as an  $A-B$  contact. (In Figs. 1 and 6(a) the distances  $A_1-A_5$  and  $A_3-B_3$  are equivalent.) However, since there is no ambiguity as to whether the other short metal-metal distances are of the  $A-A$  or  $A-B$  type, an analysis of interatomic distances in

cementite should still be in general conformity with the principles described above. In the three isomorphous phases  $\text{Pd}_3\text{B}$ ,  $\text{Pd}_3\text{P}$  and  $\text{Pd}_3\text{Si}$  the influence of the radius ratio on the short interatomic distances is very well illustrated. The increasing metal-metal separations (Table 3, Fig. 6) in this series are mainly confined to  $A-A$  distances while the  $B-A$  distances remain nearly the same. The average value of the nine  $A-A$  distances in a prism is 2.84, 3.03 and 3.12 Å, respectively, while that of the twelve  $B-A$  distances is 2.82, 2.88 and 2.86 Å in  $\text{Pd}_3\text{B}$ ,  $\text{Pd}_3\text{P}$  and  $\text{Pd}_3\text{Si}$ . As seen in Fig. 6 two four-sided faces are particularly expanded in this series and, as a result of this expansion, the  $B_1$  and  $B_2$  atoms outside these faces are brought nearer to the centre of the prism. This results in a decrease of the corresponding  $B_{1,2}-C$  distance which is 2.70, 2.60 and 2.56 Å, respectively. We can thus see why certain interatomic distances ( $A-A$  and  $A-C$  distances) increase, while some ( $B-C$  distances) decrease, and others ( $B-A$  distances) remain approx-

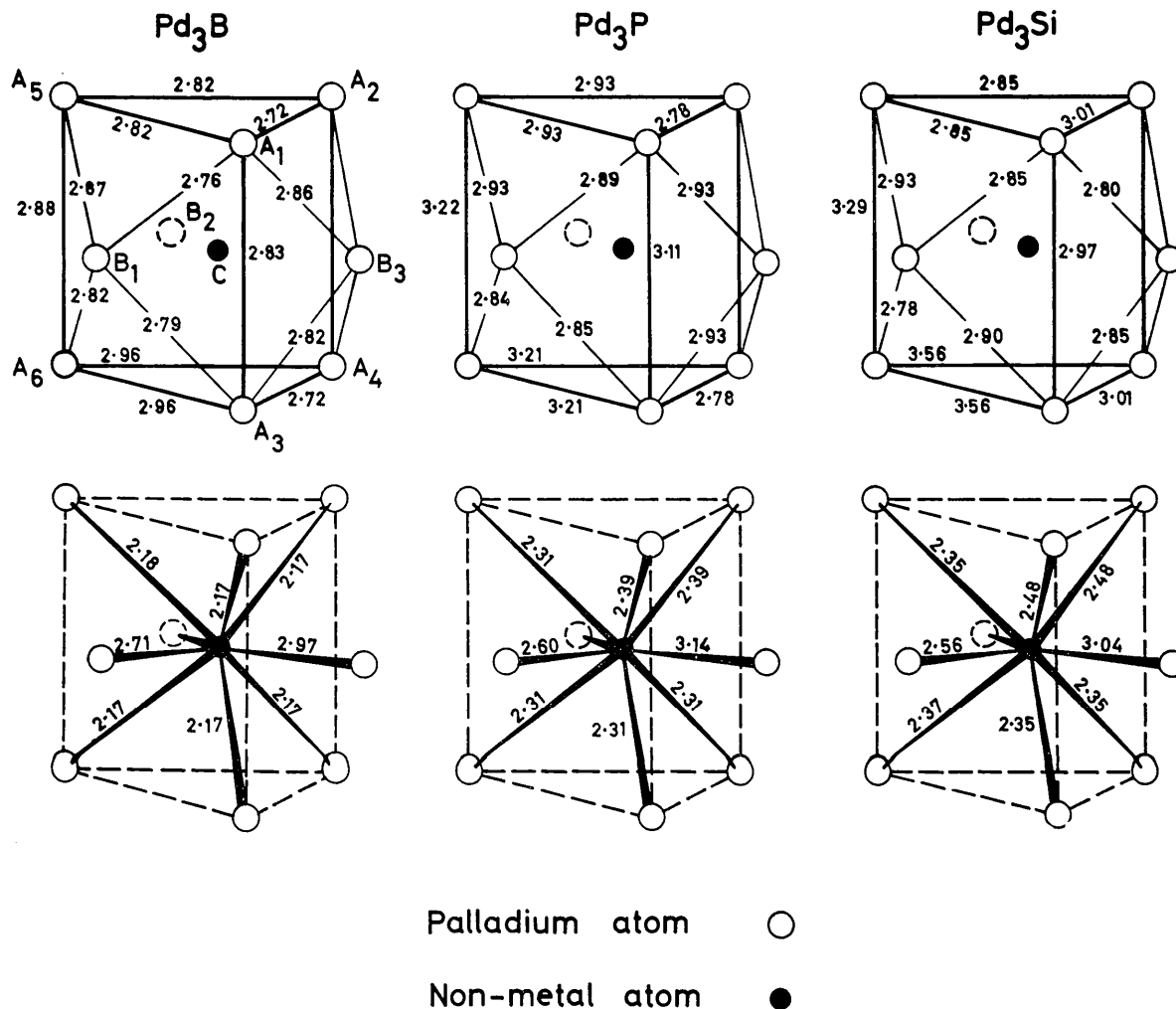


Fig. 6. The environment of the non-metal atoms in  $\text{Pd}_3\text{B}$ ,  $\text{Pd}_3\text{P}$ , and  $\text{Pd}_3\text{Si}$ . (The atoms  $A_5$ ,  $A_6$ ,  $B_3$ , and  $C$  lie in the mirror plane).

imately constant in the mentioned series of isomorphous phases. As mentioned earlier, the  $A_1-A_5$  distance (Figs. 1 and 6) is an  $A-B$  distance of an adjacent prism. This is consistent with the fact that this distance increases much less than the other  $A-A$  distances and thereby causes the metal atom very surrounding the non-metal atom to expand very unsymmetrically in the series  $\text{Pd}_3\text{B}$ ,  $\text{Pd}_3\text{P}$  and  $\text{Pd}_3\text{Si}$ .

Since the  $B-C$  distances lie in a plane nearly parallel to the  $bc$ -plane in cementite (Fig. 1) one would not expect the unit cell dimensions to change by similar amounts on isomorphous substitution in phases with the cementite structure. As explained above, some  $B-C$  distances will decrease when a small non-metal atom is replaced by a larger one, and consequently one or both of the  $b$ - and  $c$ -axes should increase less than the  $a$ -axis when such a substitution takes place. In  $\text{Pd}_3\text{B}$ ,  $\text{Pd}_3\text{P}$  and  $\text{Pd}_3\text{Si}$  the decreasing  $B_1-C$  and  $B_2-C$  distances (Fig. 1) are nearly parallel to the  $b$ -axis and consequently the  $b$ -axis decreases slightly in spite of the increasing unit-cell volume in this series.

In phases of metals of the first transition period the expansion of the metal prism on increasing radius ratio seems to be mainly confined to the face  $A_1-A_2-A_3-A_4$  resulting in a considerable decrease of the  $B_3-C$  distance which is nearly parallel with the  $c$ -axis. This would explain the pronounced decrease of the  $c$ -axis when boron substitutes for carbon in  $\text{Fe}_3\text{C}$ . A comparison of  $\text{Fe}_3\text{C}$  and  $\text{Ni}_3\text{B}$  (Tables 3 and 4) also shows that the  $B_3-C$  distance is very different in these phases (being 3.02 and 2.60 Å, respectively). As expected, the smallest values of the  $b/a$  and  $c/a$  axial ratios are found in  $\text{NiAl}_3$  which has the greatest radius ratio of the cementite-type phases.

As illustrated by the above examples, some features of the structures under discussion may be explained as arising when nearly spherical atoms are arranged in a close-packed manner consistent with the radius ratio. One may assign special radii to the atoms and a preliminary discussion of trends in the shortest interatomic distances is very much simplified if it is given in terms of these radii.

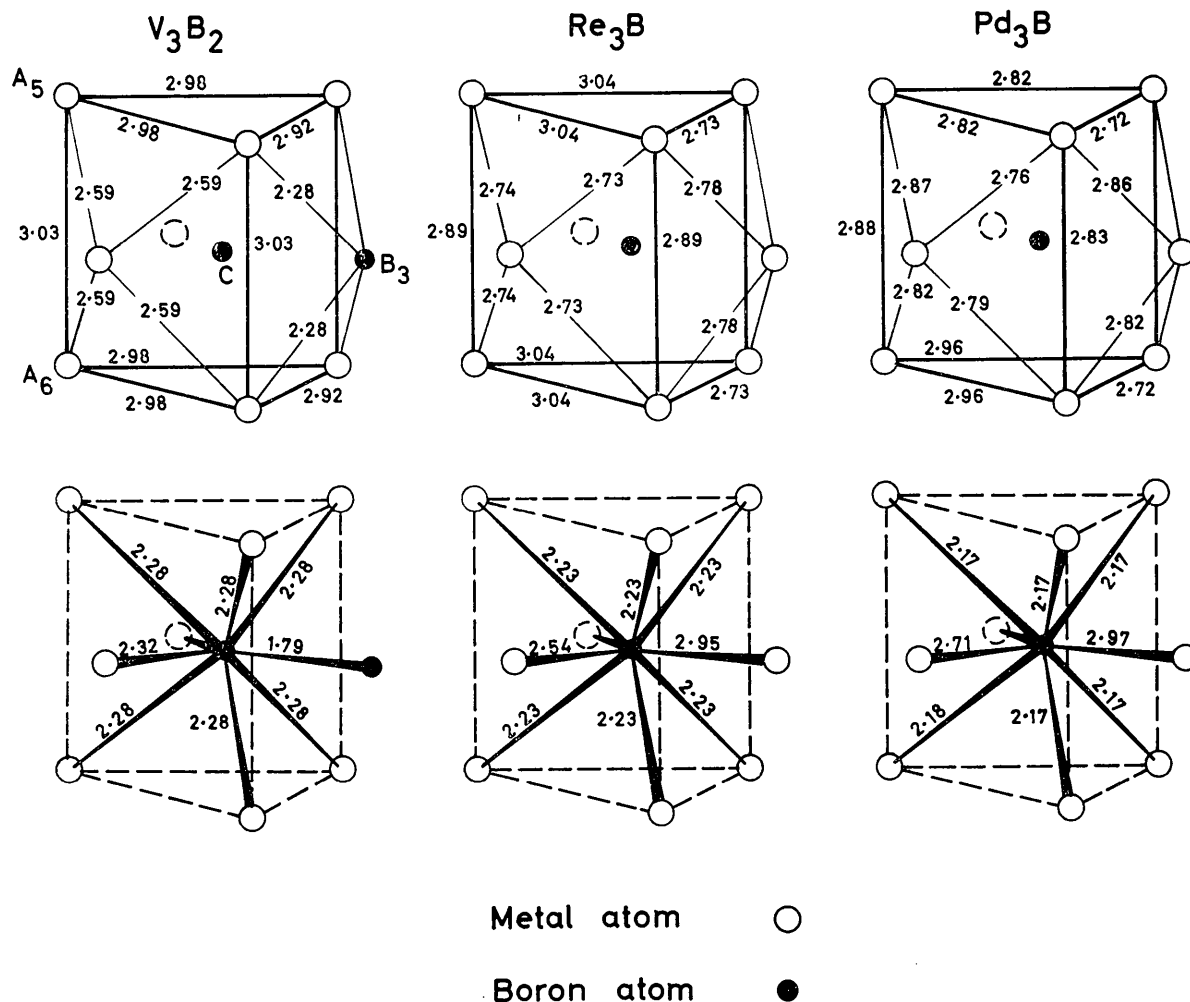


Fig. 7 The environment of the boron atom in  $\text{V}_3\text{B}_2$ ,  $\text{Re}_3\text{B}$ , and  $\text{Pd}_3\text{B}$ . (In all prisms, there is a mirror plane through the  $A_5$ ,  $A_6$ ,  $B_3$ , and  $C$  atoms).



These special radii may deviate considerably from the conventional radii quoted in the introduction. This is illustrated by a comparison of the boron environment in the three phases  $V_3B_2$  (Nowotny & Wittman, 1958),  $Re_3B$  and  $Pd_3B$  (Fig. 7). The metal atoms in these three phases have nearly the same Goldschmidt radius (1.36, 1.375 and 1.375 Å, respectively, for coordination number 12), but the size of the triangular prism of metal atoms surrounding the boron atom decreases markedly in the above-mentioned series. The average of the six shortest  $Me-B$  distances is 2.28, 2.23 and 2.17 Å in  $V_3B_2$ ,  $Re_3B$  and  $Pd_3B$ , respectively. In the same series the intermetallic distances of the  $B-A$  type (Fig. 5) display a considerable increase from 2.59 to about 2.80 Å. The tendency towards forming closer metal-boron contacts as the group number of the metal increases seems to be of general character. In a recent survey of borides (Aronsson, 1960) it was pointed out that the average of the shortest metal-boron distances in borides of the fourth to sixth group transition metals always exceeds the Goldschmidt radius for the metal by 0.90 Å or more, while in borides of the metals from the seventh and eighth groups this figure is usually considerably lower. As seen in Table 3 the closest  $Me-B$  distances are found in  $Ni_3B$ ,  $Pd_3B$  and  $Pd_5B_2$  where the average of the six shortest metal-boron distances exceeds the metal radius (C.N. 12) by only 0.80 Å. A similar trend seems to prevail among the silicides. In  $Pd_3Si$  for instance, the closest Pd-Si contacts are shorter than the radius sum by an amount much greater than in silicides of the earlier transition-group metals. The phosphides of the seventh and eighth group metals are also characterized by short  $Me-P$  distances. However, there is no definite trend to forming closer  $Me-P$  contacts as the position of  $Me$  moves from the manganese group to the nickel group in the periodic table. The data available for phosphides of the fourth to sixth group transition metals are too inaccurate to be discussed, and the sodium-chloride-type phosphides of the rare-earth metals will not be considered here since there is probably a large amount of ionic bonding in these compounds.

The existence of very short  $Me-X$  distances in the borides, phosphides and silicides of the seventh and eighth group metals is an important feature in the crystal chemistry of these phases. If the origin of these short distances were clarified, one would also better understand why phases of the platinum metals have structures different from those of corresponding phases of the earlier transition-group metals, although the radius ratios (as derived from the conventional set of radii) are nearly the same. At present, it does not seem possible to give any explanation for the trends in  $Me-X$  distances which have been described. In view of the electronegativities of the elements involved it is very unlikely that the trend is associated with a gradual change in ionic character of the  $Me-X$  bonds; more probably it has to be ascribed to 'elec-

tronic factors'. Such factors have been considered by Pauling (1949) in his discussion of  $Fe_3C$  which is also characterized by close contacts between metal and non-metal atoms. According to this author the short distances in  $Fe_3C$  either arise because the structure is under some strain or depend on the fact that those iron orbitals involved in Fe-C bonding have a large amount of  $d$ -character. These suggestions are interesting but it is not clear why the  $Fe_3C$  structure should be under some strain or why certain orbitals should have a larger amount of  $d$ -character than others.

As pointed out above, short  $Me-X$  distances are not only found in  $Fe_3C$  but in a number of related phases, and this has to be taken into account in any speculations on the 'bonding' in these phases. More elaborate discussions on this topic lie outside the scope of this paper.

#### 4. Concluding remarks on phases with 'complicated' interstitial structures

Recent studies at this Institute and elsewhere have demonstrated the close structural similarities between carbides and borides of the seventh and eighth group metals. Thus, several of these phases ( $Mn_3C$ ,  $Fe_3C$ ,  $Co_3B$ ,  $Ni_3B$  and  $Pd_3B$ ) crystallize in the cementite structure and, as shown by Stenberg (1961),  $Mn_5C_2$  is isomorphous with  $Pd_5B_2$ . In addition, the  $Me_7B_3$  borides are structurally very closely related to  $Cr_7C_3$  and  $Mn_7C_3$ . As shown in Table I boron and carbon can largely substitute for each other in phases of the seventh and eighth group metals. Such a substitution also takes place in the ternary phase  $Fe_{23}(C,B)_6$  (Carrol *et al.*, 1954) which crystallizes in the  $Cr_{23}C_6$ -structure.

The intimate structural relationships between borides and carbides makes it very natural to include (as is commonly done) the borides among the interstitial phases for which the metallic carbides, nitrides, hydrides (and also some oxides) of the transition metals are the typical representatives. It should be strongly emphasized, however, that interstitial phases in this broad sense are not clearly distinguished from other metallic phases, at least not from a crystal chemical point of view. A great number of borides and also some 'complex' carbides are isomorphous with silicides and phosphides and also with typically intermetallic phases, e.g.  $NiAl_3$  (cementite-structure) and  $Th_7Fe_3$ . It is difficult to make a judicious division of structures found among metallic phases into interstitial and intermetallic types. It seems most appropriate to use the concept of interstitial structure in the restrictive sense it was originally given by Hägg (1931) who only considered the simple structures of phases in which  $r_X/r_{Me} < 0.59$  to be of the interstitial type.

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## The Crystal Structure of Di-*p*-Chlorodiphenyltellurium Diiodide

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Crystals of  $(p\text{-ClC}_6\text{H}_4)_2\text{TeI}_2$  are triclinic with the following cell dimensions:

$$\begin{array}{ll} a = 9.751 \pm 0.006 \text{ \AA} & \alpha = 115.7 \pm 0.1^\circ \\ b = 10.681 \pm 0.006 & \beta = 87.2 \pm 0.1 \\ c = 9.531 \pm 0.006 & \gamma = 116.4 \pm 0.1 \end{array}$$

The space group is  $P\bar{1}$  and  $Z=2$ .

The Te, I and Cl atoms were located by use of two-dimensional Patterson and Fourier syntheses but location of the carbon atoms required a three-dimensional ( $F_o - F_c$ ) synthesis based on approximately 2500 independent  $|F_o|$  values. The structure was refined by use of full-matrix least-squares procedures and was checked by a final ( $F_o - F_c$ ) synthesis.

The molecular structure approximates the symmetry 2 and is similar to structures already reported for the dichlorides and dibromides of several  $\text{R}_2\text{Se}$  and  $\text{R}_2\text{Te}$  compounds. The observed bond distances and bond angles are:

Te-I <sub>1</sub>	2.947 ± 0.002 Å	Te-I <sub>2</sub>	2.922 ± 0.002 Å
Te-C <sub>1</sub>	2.13 ± 0.02	Te-C <sub>7</sub>	2.10 ± 0.02
Cl <sub>1</sub> -C <sub>4</sub>	1.75 ± 0.03	Cl <sub>2</sub> -C <sub>10</sub>	1.74 ± 0.03
I <sub>1</sub> -Te-I <sub>2</sub>	173.5 ± 0.1°	C <sub>1</sub> -Te-C <sub>7</sub>	101.1 ± 1.0°
C <sub>1</sub> -Te-I <sub>1</sub>	87.3 ± 0.7	C <sub>7</sub> -Te-I <sub>1</sub>	88.1 ± 0.7
C <sub>1</sub> -Te-I <sub>2</sub>	89.1 ± 0.7	C <sub>7</sub> -Te-I <sub>2</sub>	87.3 ± 0.7

Although  $(p\text{-ClC}_6\text{H}_4)_2\text{TeI}_2$  is definitely not a molecular complex of the type found for  $\text{C}_4\text{H}_8\text{Se}_2 \cdot 2\text{I}_2$  (which involves  $\text{Se} \cdots \text{I}-\text{I}$  bonding) the long Te-I distances and the short (3.85 Å) I<sub>1</sub>-I<sub>2</sub> separation observed in the present study suggest some tendency toward molecular complex bonding.

### Introduction

Previous studies on compounds of the type  $\text{R}_2\text{SeCl}_2$ ,  $\text{R}_2\text{SeBr}_2$ ,  $\text{R}_2\text{TeCl}_2$  and  $\text{R}_2\text{TeBr}_2$  have shown that

molecules of these substances contain nearly linear X-Se-X and X-Te-X bonding (Christofferson & McCullough, 1958). By contrast, the iodine complexes of 1,4 diselenane and 1,4 dithiane have been found to contain nearly linear  $\text{Se} \cdots \text{I}-\text{I}$  and  $\text{S} \cdots \text{I}-\text{I}$  bonding (Chao & McCullough, 1960, 1961). No com-

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