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BeP_2: A Tetrahedral Structure of Type Order–Disorder Which Obeys a Coordination Rule for Short-Range Order

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Une étude structurale d'un monocristal de BeP_2 indique que ce composé possède une structure de type ordre–désordre. La sous-structure est caractérisée par une maille quadratique de paramètres: $a = 3{,}546$ Å, $c = 15{,}01$ Å, $Z = 4$, groupe spatial $I4_1$/amd. La valeur finale du facteur R est 0,033. Les sites d'atomes dans la sous-structure correspondent aux sites dans la structure de diamant, si la dernière est décrite avec une maille tétragonale où $a = (2^{1/2}/2)a_{\text{diamant}}$ et $c = 3a_{\text{diamant}}$. Un ordre à courte distance détermine l'occupation de ces sites par les atomes de Be ou P. Chaque Be a quatre voisins tétraédriques de P et chaque atome de P a 2 Be et 2 P comme proches voisins tétraédriques. En considérant les maxima sur les traînées de diffusion continue qui se situent entre les rangées de tâches de diffraction ponctuelles de la sous-structure, on trouve une maille intermédiaire avec $a = 7{,}09$ Å et $c = 30{,}02$ Å. La règle de coordinence permet de faire une proposition pour la structure intermédiaire qui est triclinique mais pseudoquadratique. La vraie maille est aussi pseudoquadratique avec $a = 7{,}09$ Å et $c = N \cdot 15{,}01$ Å où N est un grand entier.

Single-crystal studies on BeP_2 indicate that this compound possesses an OD structure. The substructure has a tetragonal unit cell with: $a = 3.546$ Å, $c = 15.01$ Å, $Z = 4$, space group: $I4_1/amd$. The final R factor has a value of 0.033. The atom sites in this substructure correspond to the sites of diamond if the latter is described with a tetragonal cell, where $a = (2^{1/2}/2)a_{\text{diamond}}$ and $c = 3a_{\text{diamond}}$. A short-range order governs the occupation of these sites with Be and P atoms. Each Be has four tetrahedral P neighbors and every P has two Be and two P neighbors. Consideration of the maxima on the diffuse streaks between the sharp reflections of the substructure leads to an intermediate unit cell with $a = 7.09$ Å and $c = 30.02$ Å. Coordination considerations allow a structure proposal to be formulated for this intermediate structure which is triclinic but pseudotetragonal. The true unit cell is also pseudotetragonal with $a = 7.09$ Å and $c = N \cdot 15.01$ Å, where N is a large integer.

Introduction

The first study of the system Be–P was undertaken by von Stackelberg and Paulus (*1*), who isolated a phase with formula Be_3P_2. Recently, El Maslout (*2*) and David and Lang (*3*) restudied the system and found two compounds: Be_3P_2 and BeP_2 While this manuscript was in preparation Brice et al. (*4*) published a paper on BeP_2. These authors prepared BeP_2 in powder form and indexed its Debye–Scherrer diagram with a tetragonal unit cell: $a = 7.08$ Å and $c = 15.06$ Å. They stated that this compound had an arrangement

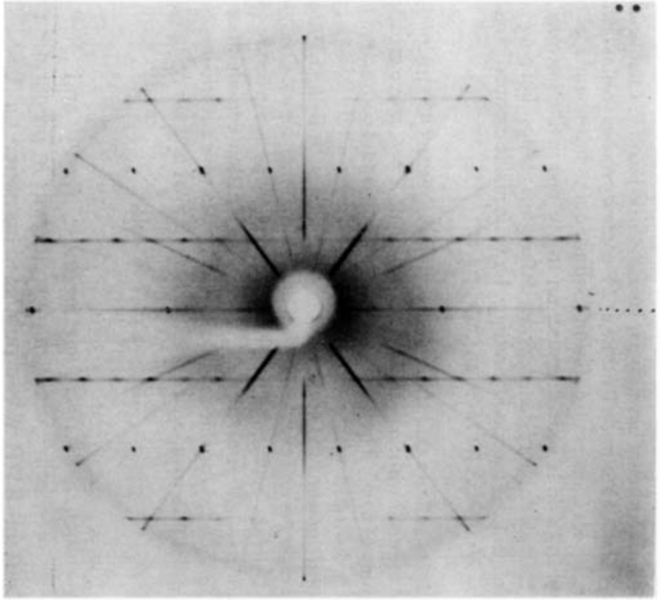


FIGURE 1.1

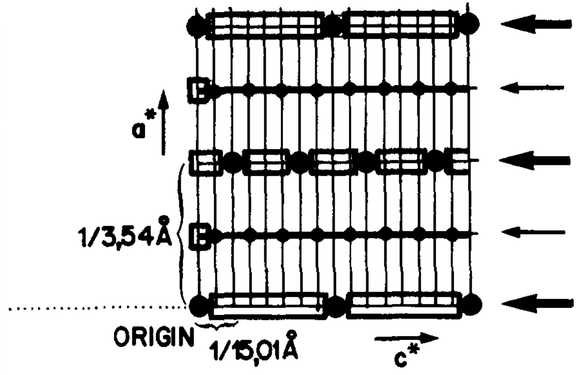


FIGURE 1.2

FIG. 1.1. Precession photograph of the *h*0*l* reciprocal plane of BeP_2. The vector **a*** is vertical and the vector **c*** is horizontal.

FIG. 1.2. Schematic presentation of the *h*0*l* reciprocal plane of BeP_2. The heavy arrows indicate the rows of sharp diffraction spots and the light arrows indicate the directions of the diffuse streaks. The size of the circles is not an indication for the actual amount of diffracted intensity, but allows between sharp diffraction spots (large circles) and diffraction maxima on the diffuse streaks (small circles) to be differentiated. In the areas which have been framed, no diffracted intensity is observed. Any structure model based on a unit cell with $a = 7{,}09$ Å and $c = N \cdot 15{,}01$ Å has to account for these particular extinctions.

of Be and P atoms similar to a diamond, but they did not give the atomic coordinates. We have succeeded in obtaining single crystals which permitted us to study the crystal structure by single-crystal diffraction methods.

The Subcell, Intermediate Cell, and True Unit Cell

Weissenberg and precession photographs of BeP_2 indicate that this compound has an OD structure (structure of type order–disorder). The photographs show rows of sharp diffraction spots and between these rows, streaks of diffuse intensity which run parallel to **c***. Intensity maxima appear on these streaks at positions which are intercalated between the reciprocal lattice points of the substructure. In Fig. 1.1 we show a precession photograph representing the $h0l$ plane of the reciprocal lattice of BeP_2. Next to it, in Fig. 1.2, a schematic presentation of the same plane is presented.

The lattice formed by the sharp diffraction spots can be described with the tetragonal unit cell:

$$a_s = b_s = 3.546\ (1)\ \text{Å},$$
$$c_s = 15.01\ (1)\ \text{Å} \qquad Z = 4.$$

This unit cell corresponds to the substructure (notation after Buerger (5)). The condition for the systematic extinctions; $h+k+l \neq 2n$, indicates a body-centered Bravais lattice. The other extinctions, $h\ k\ 0$ with $h \neq 2n$ and hhl with $2h+l \neq 4n$, lead to the unique space group $I4_1/amd$.

The intensity maxima on the diffuse streaks and the sharp diffraction spots lead to a larger pseudotetragonal intermediate unit cell being assumed:

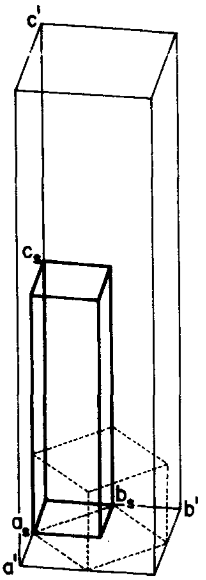


FIG. 2. The subcell and the intermediate unit cell of BeP_2 together with the unit cell of the diamond structure (shown with dashed lines).

$$a' = b' = 7.09\ \text{Å},$$
$$c' = 30.02\ \text{Å} \qquad Z = 32.$$

In Fig. 2 the relation between the subcell with a_s, b_s, c_s, and the intermediate unit cell with a', b', and c' is shown. The Laue photos indicate on first sight a $4/mmm$ symmetry. However, a detailed study of the intensities of the maxima on the diffuse streaks, shown in Fig. 1, indicates that $I(h0l) \neq I(h0\bar{l})$. This condition is incompatible with the tetragonal crystal system. Thus, the unit cell is only

TABLE I

THE UNIT CELLS OF BeP_2

	Symmetry	a (Å)	c (Å)	Z
Substructure	tetragonal	3.546 (1)	15.01 (1)	4
Intermediate structure	pseudotetragonal	7.09	30.02	32
True structure	pseudotetragonal	7.09	$N \cdot 15.01$ (1)	$N \cdot 16$
Density (g/cm³)		$D_{obs} = 2.49$	$D_{calc} = 2.496$	

pseudotetragonal. The condition for the systematic extinctions, $h+k+l \neq 2n$, corresponds to a lattice of type I. One notes that of all the maxima on the diffuse streaks those with $-h+k+l=4n$ are more intense than those with $h-k+l=4n$.

If one considers all the diffuse streaks, one finds the true unit cell of BeP_2 to be

$$a = b = 7.09\ \text{Å},$$
$$c = N \cdot 15{\cdot}01, \qquad Z = N \cdot 16,$$

where N can be a large integer.

In Table I we combine all the unit-cell data for BeP_2.

Determination, Refinement, and Description of the Substructure

The intensities of the diffraction peaks corresponding to the substructure have been measured on a Nonius CAD-4 automatic diffractometer up to $\theta = 50°$. A $\omega/2\theta$ scan was used with a scan width s which is a function of the Bragg angle according to: $s = m + n\tan\theta$ ($m = 1.20$; $n = 0.45$ in degrees). Two-hundred and fifteen independent reflections with $I > \sigma(\text{I})$ were available for the solution of the structure.

An interpretation of a three-dimensional Patterson map allowed two atom positions to be determined. For space group $I4_1/amd$ (International Tables for Crystallography, Vol. 1, No. 141; the origin at $0\ \frac{1}{4}\ \frac{7}{8}$ from the symmetry center), the first site corresponds to equipoint $4a$, 0 0 0, and the second site corresponds to equipoint $8e$, 0 0 z, with $z = 0.333$. At first it was assumed that both sites were fully occupied by P atoms and using an isotropic temperature factor, $B = 0.5$ Å^2, an R ($=\Sigma|\Delta F|/\Sigma F_0$) value of 0.13 was obtained. In the first refinement variations of the z parameter of the $8e$ equipoint as well as variations in the site occupation of this site by P atoms were considered. After some cycles the R value decreased to 0.043 with $z = 0.03348$ and a site occupation of 0.625. We have therefore concluded that this site is statistically occupied by 4Be + 4P with a site occupation of 0.5 for the two elements.

The final refinement of the z parameter and the isotropic temperature factors lead to an R value of 0.033. In Table II we list the atomic parameters for the substructure of BeP_2.

The atomic scattering factors used in our study were those derived by Vand, Eiland, and Pepinsky (*6*) and modified by Forsyth and Wells (*7*), with constants given by Moore (*8*). The full matrix least-squares program used was devised by Prewitt (*9*). The weighting schemes described by Stout and Jensen (*10*), and by Grant, Killean, and Lawrence (*11*) were used.

In Fig. 3 we show the three-dimensional arrangement of the atoms in one unit cell of the substructure. All atoms have a tetrahedral coordination (see Fig. 4). The atom arrangement, disregarding the difference between P and Be atoms, is the same as in diamond. For the idealized structure the z parameter of equipoint $8e$ should be $\frac{1}{3}$. From a study of Fig. 2 one can conclude that the ideal c_s/a_s ratio should be $3/(2^{1/2}/2) = 4.24_2$.

TABLE II

THE ATOMIC POSITIONS IN THE SUBSTRUCTURE OF BeP_2 DESCRIBED WITH SPACE GROUP $I4_1/amd$[a]

	Equipoint	Site occupation	x	y	z	B (Å^2)
P	$4a$	1	0	0	0	0.415 (*7*)
P	$8e$	0.5	0	0	0.33453 (*2*)	0.441 (*6*)
Be	$8e$	0.5	0	0	0.33453 (*2*)	0.441 (*6*)

[a] The origin at $0\ \frac{1}{4}\ \frac{7}{8}$ from the symmetry center.

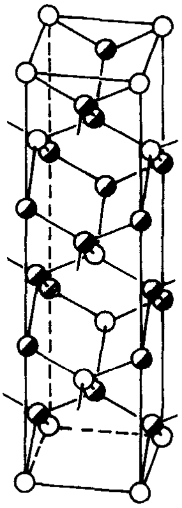


FIG. 3. The atom arrangement in the substructure of BeP_2. The open circles correspond to P atom sites, the half-open circles correspond to sites which are occupied in equal proportions by Be and P atoms.

A Coordination Rule which Determines the Order between Be and P Atoms

The presence of the diffuse streaks in between the rows of sharp diffraction spots is an indication for some kind of ordering between Be and P atoms. In Fig. 1.2 the areas in the *h*0*l* reciprocal plane where no diffracted intensity is found have been framed. Only those ordering models are acceptable for which the calculated intensities of the framed areas are zero.

When one considers the valence electron rules which have been developed for this kind of compound (*12*), it is possible to find a coordination rule which is applicable to our short-range-order problem. The total valence electron concentration, VEC, is 4. BeP_2 has therefore a normal tetrahedral structure where each atom has four tetrahedral neighbors. The partial valence electron concentration of the anion, $(VEC)_A$, is 6. BeP_2 is therefore a polyanionic valence compound for which one expects normally two anion–anion bonds per P atoms and no Be–Be bonds. The coordination rule thus requires that

(i) every Be atoms is tetrahedrally surrounded by four P atoms, and

(ii) each P atom has two P and two Be neighbors.

As will be shown below, only structural models which satisfy this coordination rule have the required diffraction extinctions.

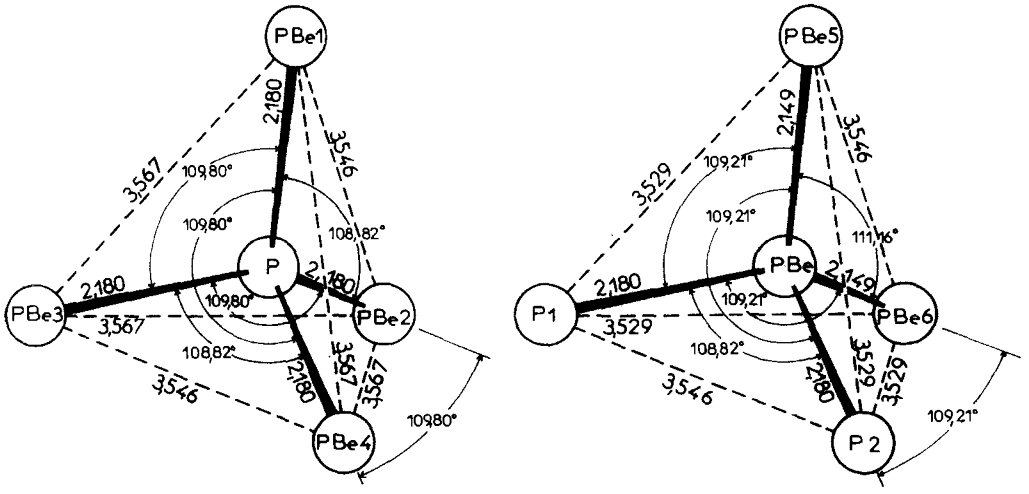


FIG. 4. The interatomic distances and angles in the two kinds of tetrahedra formed in the substructure of BeP_2. The errors in the distances are 0.002 Å and in the angles 0.01°.

Application of the Coordination Rule to the Substructure

Let us consider the sequence of atoms in the substructure in a direction parallel to c_s. Planes at $z = 0, \frac{1}{4}, \frac{1}{2}$, and $\frac{3}{4}$ are occupied by P atoms only (equipoint 4*a*). These planes, which will be called *welding* planes, divide the unit cell into four layers, each 3.75_2 Å high. Between these welding layers are inserted two planes containing Be and P atoms (equipoint 8*e*). This sequence of planes is presented in Fig. 5.

In each of these layers different distributions of Be and P atoms are possible but the unit cell is obtained by stacking of four layers (layer 1, 2, 3, and 4) for which the order is determined by the positions of the P atoms in the welding planes.

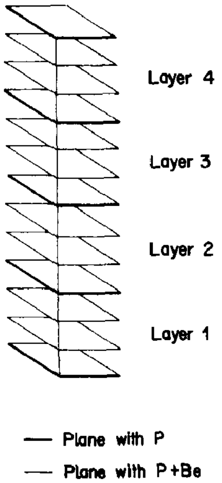
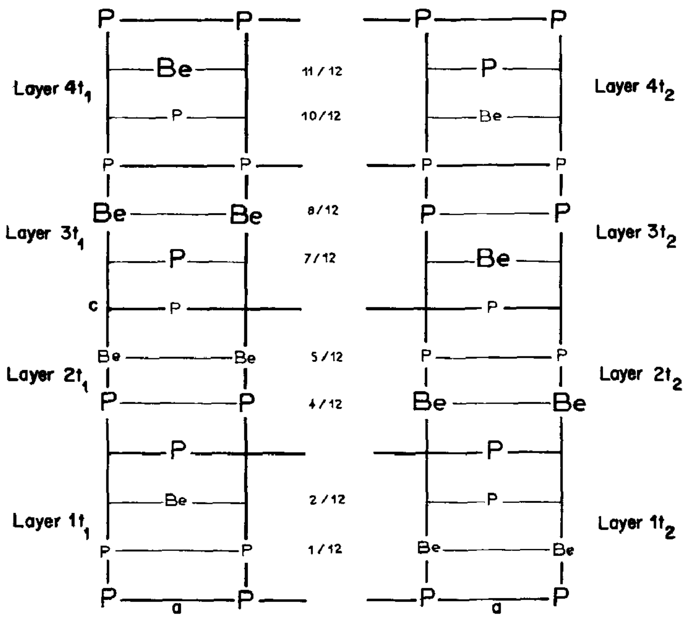


FIG. 5. Sequence of planes containing atoms in the substructure of BeP_2. The *welding* planes consisting of P atoms only are drawn with heavy lines.

Depending on whether a P or a Be atom is placed in the plane following a welding plane, the coordination rule imposes two atomic distributions to which correspond the atom sequences (with z increasing) of P–P–Be–P or P–Be–P–P, respectively. We will denote by t_1 and t_2 the two kinds of layers. By stacking



Stacking of t_1 layers, each having the atom sequence P–P–Be–P (with increasing values of z)

Stacking of t_2 layers, each having the atom sequence P–Be–P–P (with increasing values of z)

FIG. 6. Two hypothetical ordered structures of BeP_2 based on a unit cell with $a = b = 3.546$ Å and $c = 15.01$ Å. The large chemical symbols correspond to atoms at height $y = 0$ and the small chemical symbols to atoms at height $y = \frac{1}{2}$. The two structures are identical because by shifting the origin by $\frac{1}{2}\ \frac{1}{2}\ \frac{1}{6}$, the structure built up with t_2 layers becomes equal to the other structure constructed with t_1 layers only.

only layers t_1 or t_2 one obtains the two ordered structures shown in Fig. 6. They are identical except for a difference in origin. As the corresponding unit cells have the dimensions $a = 3.545$ Å and $c = 15.01$ Å, these ordered structures cannot correspond to the real structure of BeP_2.

Furthermore, a mixture of layers t_1 and t_2 is not permissible because in this case the coordination rule is not satisfied. The P atoms in the welding plane would then be surrounded either by four Be atoms or by four 4P atoms.

Application of the Coordination Rule to Stacking of Larger Layers

The experimental data indicate that the **a** value of the real structure is twice that of the substructure. Thus one has to consider the stacking of layers having the dimensions $a = b = 7.09$ Å and $c = 3.752$ Å. Respecting the coordination rule, one can formulate for each layer four different kinds of ordered atom distributions. They are conveniently presented in a projection along c, where the size of the chemical symbols increases with the z value of the atoms as shown in Fig. 7.

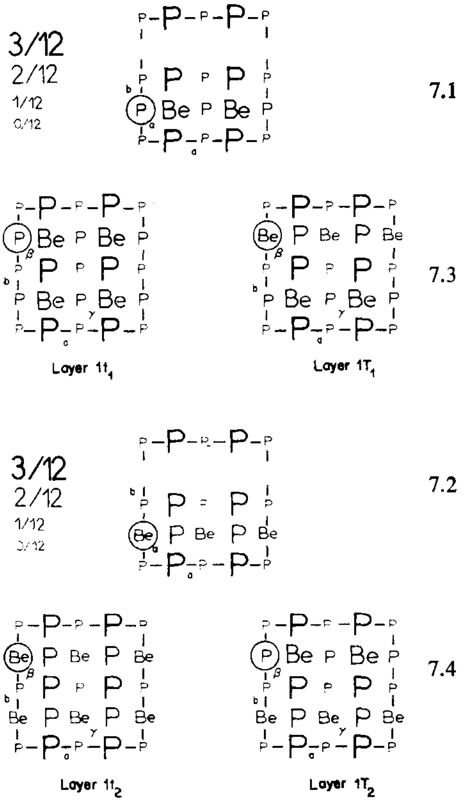


FIG. 7. The derivation of the four different kinds of layers in position 1: $1t_1$, $1t_2$, $1T_1$, and $1T_2$.

When one considers, for example, layer 1, which contains two welding planes at $z = 0$ and $z = \frac{1}{4}$ and the planes in between, starting from the origin at 0 0 0, one can place in the next site at $0\,\frac{1}{4}\,\frac{1}{12}$ either a P or a Be atom. Once a choice has been made, the positions of the other atoms in one-half of the layer are determined by the coordination rule and around point α one finds a helical sequence of atoms with z increasing which is either P–P–Be–P or P–Be–P–P (Figs. 7.1, 7.2). To fix the site occupation in the second-half of layer 1 we have to make a choice for the position $0\,\frac{3}{4}\,\frac{1}{12}$. Thus one obtains around point β one or the other of the two helical sequences mentioned above (Figs. 7.3, 7.4).

The designation of the different kinds of layers obtained is simple if one considers the points α, β, γ and denotes the helical sequences around these points. As can be seen in Table III, the arrangement of the atoms in the layers t_1 and t_2 is the same as for the layers t_1 and t_2 used above for the discussion of the substructure. Quite simply, the parameters a and b have now been doubled. However, the layers T_1 and T_2 present a new atom arrangement. In Fig. 8 we show 16 drawings which correspond to the four different kinds of layers in the four possible positions.

TABLE III

THE NOTATION OF THE FOUR KINDS OF LARGE LAYERS BASED ON THE HELICAL SEQUENCE OF ATOMS AROUND THE POINTS α, β, AND γ

Helical sequence of atoms around α	Identical helical sequences of atoms around β and γ	Different helical sequences of atoms around β and γ
P–P–Be–P	t_1	T_1
P–Be–P–P	t_2	T_2

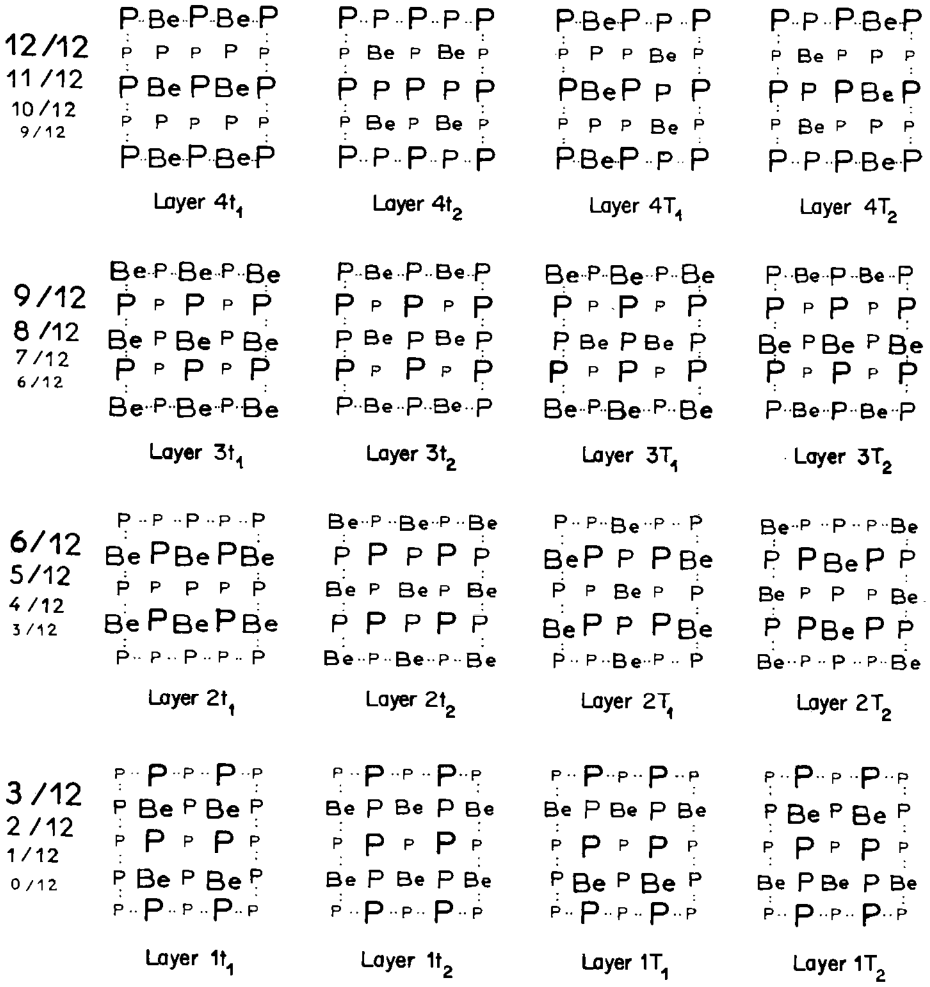


FIG. 8. The atom positions of the four different kinds of layers in the four possible successive positions which one can find in a unit cell with $a = 7.09$ Å and $c = 15.01$ Å.

One can now construct structure models by stacking different kinds of layers. Ten different mixing combinations using the layers t_1, t_2, T_1, and T_2 are possible. The results are presented in Table IV. For five combinations the coordination rule is not satisfied for the P atoms in the welding planes and, therefore, these five have to be rejected. For a number of models, diffraction intensity calculations have been made. One finds that whenever the coordination rule is not satisfied then the extinction laws are not respected either. Under the five combinations which are acceptable, four lead to unit cells which are too small. There remains thus the combination $T_1 + T_2$ to which corresponds a unit cell with parameters $a = 7.09$ Å and $c = N \cdot 15.01$ Å, where N is a large integer. Only a structure model based on such a large unit cell allows the appearance of the diffuse streaks in the diffraction photograph to be explained.

Structure Proposal for the Intermediate and the True Structure

In the intermediate structure which has a unit cell with $a = 7.09$ Å and $c = 30.02$ Å one has a stacking of eight layers of kind T_1 and

TABLE IV THE TEN POSSIBLE COMBINATIONS WHEN MIXING LAYERS t_1, t_2, T_1, AND T_2

Mixture of layers	Coordination rule satisfied	Extinction laws satisfied	Required unit cell		
			$a = 3.546$ $c = 15.01$	$a = 7.09$ $c = 15.01$	$a = 7.09$ $c = N \cdot 15.01$
$t_1 + t_1$	Yes	Yes	√		
$t_1 + t_2$	No	No			
$t_1 + T_1$	No	No			
$t_1 + T_2$	No	No			
$t_2 + t_2$	Yes	Yes	√		
$t_2 + T_1$	No	No			
$t_2 + T_2$	No	No			
$T_1 + T_1$	Yes	Yes		√	
$T_1 + T_2$	Yes	Yes			√
$T_2 + T_2$	Yes	Yes		√	

TABLE V

STRUCTURE DATA FOR THE INTERMEDIATE STRUCTURE OF BeP_2

P in	0	0	0,	$\frac{1}{2}$	0	0,	0	$\frac{1}{2}$	0,	$\frac{1}{2}$	$\frac{1}{2}$	0,	1st Welding plane
Be in	$\frac{23}{24}$	$\frac{7}{24}$	$\frac{1}{6}$,	$\frac{11}{24}$	$\frac{7}{24}$	$\frac{1}{6}$,	$\frac{1}{6}$	$\frac{5}{6}$	$\frac{1}{3}$,	$\frac{2}{3}$	$\frac{5}{6}$	$\frac{1}{3}$,	Lower layer
P in	$\frac{23}{24}$	$\frac{19}{24}$	$\frac{1}{6}$,	$\frac{11}{24}$	$\frac{19}{24}$	$\frac{1}{6}$,	$\frac{1}{6}$	$\frac{1}{3}$	$\frac{1}{3}$,	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{1}{3}$,	
P in	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{2}$,	$\frac{5}{8}$	$\frac{1}{8}$	$\frac{1}{2}$,	$\frac{1}{8}$	$\frac{5}{8}$	$\frac{1}{2}$,	$\frac{5}{8}$	$\frac{5}{8}$	$\frac{1}{2}$,	2nd Welding plane
Be in	$\frac{5}{6}$	$\frac{1}{6}$	$\frac{2}{3}$,	$\frac{5}{6}$	$\frac{2}{3}$	$\frac{2}{3}$,	$\frac{7}{24}$	$\frac{11}{24}$	$\frac{5}{6}$,	$\frac{7}{24}$	$\frac{23}{24}$	$\frac{5}{6}$,	Upper layer
P in	$\frac{1}{3}$	$\frac{1}{6}$	$\frac{2}{3}$,	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{2}{3}$,	$\frac{19}{24}$	$\frac{11}{24}$	$\frac{5}{6}$,	$\frac{19}{24}$	$\frac{23}{24}$	$\frac{5}{6}$,	

Note: $a = 7.09$ Å, $b = 7.09$ Å, $c = 7.91_3$ Å, $\alpha = 102.94_5°$, $\beta = 77.05_6°$, $\gamma = 90°$ space group: $P1$, $Z = 8$.

T_2. It has been stated above that the positions of the intensity maxima on the diffuse streaks indicate a body-centered Bravais lattice. Thus, the sequence of layers cannot be arbitrary. Each fourth layer above every T_1 layer must be a T_2 layer and vice versa. By considering this restriction there are only two possibilities for the stacking of these eight layers. It can be shown that all other body-centered stacking combinations can be transformed to these two cases by translations or rotations. If we denote the first stacking by

$$1T_2 + 2T_2 + 3T_2 + 4T_2 + 1T_1 + 2T_1 + 3T_1 + 4T_1,$$

then the second stacking consists of layers which have been turned upside down (which may be achieved by changing the signs of the z parameters of the atoms). The structure and its inverse are only pseudotetragonal, the space group being $P1$. One can describe the structure with a triclinic unit cell, only one-quarter in volume, by using the vector equations:

$$\mathbf{a} = \mathbf{a}', \qquad \mathbf{b} = \mathbf{b}', \qquad \mathbf{c} = \tfrac{1}{4}\mathbf{a}' - \tfrac{1}{4}\mathbf{b}' + \tfrac{1}{4}\mathbf{c}'.$$

The structure data of the intermediate structure described with a triclinic unit cell are given in Table V.

An intensity calculation for a powder pattern of BeP_2 assuming the intermediate structure is given in Table VI. In the first column we give the Miller indices of the substructure. The next two columns contain the Miller indices of the intermediate structure of BeP_2, first described with the pseudotetragonal unit cell and then with the triclinic unit cell. One notes that all the pseudotetragonal indices with $h - k + l = 4n$ have equivalent

TABLE VI

INTENSITY CALCULATION FOR A POWDER DIAGRAM OF BeP_2 ASSUMING THE INTERMEDIATE STRUCTURE ($CuK\alpha$ RADIATION).

Substructure tetragonal *h k l*	Intermediate structure					
	Pseudotetragonal *h k l*	Triclinic *h k l*	$\sin^2\theta_{calc}\cdot 1000$	$\sin^2\theta_{obs}\cdot 1000$	I_{calc}	I_{obs}
	004	001	10.55	—	0	—
	$011/10\bar{1}$ $101/01\bar{1}$	$010/100$ —	12.48	—	5.0 —	—
	$103/01\bar{3}$ $013/10\bar{3}$	$101/01\bar{1}$ —	17.76	17.7	28.5 —	vvvw
	110 $1\bar{1}0$	110 —	23.64	—	0 —	—
	$1\bar{1}2/1\bar{1}\bar{2}$ $112/11\bar{2}$	$1\bar{1}1/1\bar{1}0$ —	26.28	—	0 —	—
	$015/10\bar{5}$ $105/01\bar{5}$	$011/10\bar{1}$ —	28.31	28.4	41.4 —	vvvw
	$114/11\bar{4}$ $1\bar{1}4/1\bar{1}\bar{4}$	$111/11\bar{1}$ —	34.20	—	0 —	—
004	008	002	42.21	42.2	33.5	vw
	$107/01\bar{7}$ $017/10\bar{7}$	$102/01\bar{2}$ —	44.13	44.3	39.8 —	vvvw
	$1\bar{1}6/1\bar{1}\bar{6}$ $116/11\bar{6}$	$11\bar{2}/1\bar{1}\bar{1}$ —	47.38	—	0 —	—
101	$022/202/02\bar{2}/20\bar{2}$	$020/201/02\bar{1}/200$	49.93	49.9	53.5	w
	$121/21\bar{1}/2\bar{1}1/1\bar{2}1$ $211/12\bar{1}/1\bar{2}\bar{1}/2\bar{1}\bar{1}$	$120/210/2\bar{1}1/1\bar{2}1$ —	59.77	59.8	84.9 —	w
	$213/12\bar{3}/1\bar{2}\bar{3}/2\bar{1}\bar{3}$ $123/21\bar{3}/2\bar{1}3/1\bar{2}3$	$211/12\bar{1}/1\bar{2}0/2\bar{1}0$ —	65.05	65.2	63.0 —	vw
	$019/10\bar{9}$ $109/01\bar{9}$	$012/10\bar{2}$ —	65.24		31.4 —	
	$118/11\bar{8}$ $1\bar{1}8/1\bar{1}\bar{8}$	$112/11\bar{2}$ —	65.85	—	0 —	—
103	$206/026/20\bar{6}/02\bar{6}$	$202/021/20\bar{1}/02\bar{2}$	71.03	71.0	1000.0	vvvst
	$125/2\bar{1}5/21\bar{5}/1\bar{2}5$ $215/1\bar{2}\bar{5}/12\bar{5}/2\bar{1}\bar{5}$	$121/2\bar{1}2/21\bar{1}/1\bar{2}2$ —	75.60	75.5	34.8 —	vvw
	$1\ \bar{1}\ 10/1\ \bar{1}\ \overline{10}$ $1\ 1\ 10/1\ 1\ \overline{10}$	$1\bar{1}3/1\bar{1}\bar{2}$ —	89.59	—	0 —	—
	$217/1\bar{2}\bar{7}/12\bar{7}/2\bar{1}\bar{7}$ $127/2\bar{1}7/21\bar{7}/1\bar{2}7$	$212/1\bar{2}\bar{1}/12\bar{2}/2\bar{1}\bar{1}$ —	91.42	91.4	16.5 —	vvw
	$1\ 0\ 11/0\ 1\ \overline{11}$ $0\ 1\ 11/1\ 0\ \overline{11}$	$103/01\bar{3}$ —	91.61		21.9 —	
	$220/2\bar{2}\bar{0}$	$220/2\bar{2}1$	94.58	—	0	—
	$0\ 0\ 12$	003	94.96	—	0	—
112	$224/22\bar{4}/2\bar{2}\bar{4}/2\bar{2}4$	$221/22\bar{1}/2\bar{2}0/2\bar{2}2$	105.13	105.05	36.9	vw
	$301/03\bar{1}$ $031/30\bar{1}$	$301/03\bar{1}$ —	107.06	—	0.3 —	—
	$033/30\bar{3}$ $303/03\bar{3}$	$030/300$ —	112.34	—	2.4 —	—
	$129/2\bar{1}9/1\bar{2}9/21\bar{9}$ $219/1\bar{2}\bar{9}/2\bar{1}\bar{9}/12\bar{9}$	$122/2\bar{1}3/1\bar{2}3/21\bar{2}$ —	112.53	—	4.7 —	—
105	$2010/0210/02\bar{1}\bar{0}/02\bar{1}\bar{0}$	$203/022/20\bar{2}/02\bar{3}$	113.23	113.6	16.0	vw

Note: $I_{calc} = mF^2((1 + \cos^2 2\theta)/\sin^2\theta\cdot\cos\theta)$ is normalized to the strongest reflection having intensity 1000.

triclinic indices, but there are no corresponding triclinic indices for pseudotetragonal $h\,k\,l$ values with $-h+k+l=4n$ and thus the calculated intensities are zero. For the structure having a stacking of inverse layers one finds the same values for the intensities but now reflections with $-h+k+l=4n$ have triclinic equivalents and those with $h-k+l=4n$ do not exist in the triclinic description. One can see from Fig. 1.1 that the intensity maxima on the diffuse streaks with $-h+k+l=4n$ are more intense than those with $h-k+l=4n$. Thus, the predominant intermediate structure in the crystal studied has a stacking of inverse layers. In a powder diagram, the difference between these two structures is unimportant. However, in the crystal studied there is also diffracted intensity between the intensity maxima. As a consequence, the observed intensities for the superstructure reflections will be smaller than calculated for the intermediate structure as can be verified in Table VI.

Concerning the true structure of BeP_2, one can conclude that the unit cell must have the dimensions $a=7.09$ Å and $c=N\cdot 15.01$ Å. It is possible to state the $x\,y\,z$ values of all the atomic sites, however, only for sites in the welding planes can one specify with certainty that these sites are occupied by P atoms. The coordination rule implies that the structure consists of a stacking of layers of kind T_1 and T_2. The stacking is not completely arbitrary. One finds domains with a layer sequence corresponding to that described for the intermediate structure. Since the crystal studied shows differences in the intensities between reflections with $-h+k+l=4n$ and those with $h-k+l=4n$, one can conclude that the domains with a stacking of inverse layers are more frequent than the others with a stacking of noninverse layers. One can see in Fig. 1.1 that the intensity maxima on the diffuse streaks are not sharp but are extended along the diffuse streaks. By measuring their integral widths and by using the Scherrer formula, one finds that the domains have on the average a height of 150 Å which corresponds to five unit cells of the intermediate structure. Thus, the value of N in the true structure must at least be 10. It is however, impossible, using the available experimental data, to obtain more precise results on the true structure of BeP_2.

In conclusion, BeP_2 belongs to the family of phosphides $M^{II}P_2$ with tetrahedral structure. It differs from the compounds with zinc (*13*, *14*) and cadmium (*15*, *16*) by having an OD structure. This might possibly be related with the close similarity of the covalent tetrahedral radii of the two elements ($r_P=1.10$ Å, $r_{Be}=1.06$ Å).

For $BeAs_2$, a tetragonal unit cell with $a=7.53$ Å and $c=31.65$ Å has been reported recently (*17*). This unit cell corresponds to the unit cell of the intermediate structure of BeP_2. It would be interesting to know if $BeAs_2$ also has an OD structure similar to BeP_2. A study of this subject is in progress.

References

1. M. Von Stackelberg and R. Paulus, *Z. Phys. Chem.* **B22**, 305 (1933).
2. A. El Maslout, Thèse d'Etat, Nancy (1974).
3. J. David and J. Lang, *C.R. Acad. Sci., Paris, Ser. C* **282**, 43 (1976).
4. J. F. Brice, R. Gerardin, M. Zanne, Ch. Gleitzer, and J. Aubry, *Mater. Res. Bull.* **10**, 1237 (1975).
5. M. Buerger, "Vector Space," p. 312, Wiley, New York (1959).
6. V. Vand, P. F. Eiland, and R. Pepinsky, *Acta Crystallogr.* **10**, 303 (1957).
7. J. B. Forsyth and M. Wells, *Acta Crystallogr.* **12**, 412 (1959).
8. F. H. Moore, *Acta Crystallogr.* **16**, 1169 (1963).
9. C. T. Prewitt, SFLS 5, A Fortran Crystallographic Least-Squares Program, Report ORNL-TM-305, Oak Ridge National Laboratory, Tennessee (1962).
10. G. H. Stout and L. H. Jensen, "X-Ray Structure Determinations," Macmillan, New York (1968).
11. D. F. Grant, R. C. G. Killean, and J. L. Lawrence, *Acta Crystallogr.* **25**, 374 (1969).
12. E. Parthé, "Cristallochimie des structures tétraédriques," Gordon and Breach, Paris (1972); *Acta Crystallogr.* **B29**, 2808 (1973).
13. J. G. White, *Acta Crystallogr.* **18**, 217 (1965).
14. I. J. Hegyi, E. E. Loebner, E. W. Poor, and J. G. White, *J. Phys. Chem. Solids* **24**, 333 (1963).
15. J. Horn, *Bull. Acad. Polon. Sci.* **17**, 69 (1969).
16. J. Goodyear and G. A. Steigmann, *Acta Crystallogr.* **B25**, 2371 (1969).
17. R. Gerardin and J. Aubry, *J. Solid State Chem.* **17**, 239 (1976).