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## X-Ray Studies of Molybdenum and Tungsten Phosphides.

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The Mo-P and W-P systems have been studied by X-ray powder methods. In addition to the previously reported phases  $\text{Mo}_3\text{P}$ , MoP,  $\text{MoP}_2$ , WP and  $\text{WP}_2$ , the occurrence of a phase with the approximate composition  $\text{MoP}_{0.75}$  has been established. The unit cell dimensions for  $\text{Mo}_3\text{P}$ , MoP and WP have been re-determined. Some data supporting the hypothesis of an ordered distribution of phosphorus atoms in MoP (WC-type structure) are given. The structures of the isostructural  $\text{MoP}_2$  and  $\text{WP}_2$  have been determined, and the  $\text{MoP}_2$  structure has been refined from X-ray powder data. The orthorhombic unit cell dimensions (in Å) are for  $\text{MoP}_2$  :  $\underline{a} = 3.145$ ;  $\underline{b} = 11.184$ ;  $\underline{c} = 4.984$ ; and for  $\text{WP}_2$  :  $\underline{a} = 3.166$ ;  $\underline{b} = 11.161$ ;  $\underline{c} = 4.973$ . The space-group is  $\underline{C} \underline{m} \underline{c} 2_1$  with four metal atoms and eight phosphorus atoms in three sets of fourfold positions. The structure is related to the  $\text{ZrSi}_2$  ( $\underline{C} 49$ ) type.

The systems Mo-P and W-P were studied by tensimetric and X-ray powder methods by Faller *et al.*<sup>1</sup> According to these authors, the following intermediate phases occur:  $\text{Mo}_3\text{P}$ , MoP,  $\text{MoP}_2$ , WP and  $\text{WP}_2$ . It was suggested that  $\text{Mo}_3\text{P}$  is isostructural with  $\text{Cr}_3\text{P}$  ( $\text{Fe}_3\text{P}$ -type structure) and WP with MnP (MnP-type structure), but unit cell dimensions were not given. Schönberg<sup>2</sup> confirmed the structures proposed for  $\text{Mo}_3\text{P}$  and WP, and determined the unit cell dimensions.

In addition, he reported that MoP crystallizes with the WC-type structure. Bachmayer et al.<sup>3</sup> reported unit cell dimensions for MoP and WP in agreement with Schönberg's values.

- The present investigation was undertaken principally to determine the crystal structures of MoP<sub>2</sub> and WP<sub>2</sub>. In addition, phase analyses in the Mo-P and WP systems were made in the range 0-70 at % phosphorus, using X-ray powder methods.

### Experimental

Phosphides of molybdenum and tungsten were prepared by heating metal powder (purity about 99.5 %) and red phosphorus (purity greater than 99 %) in evacuated and sealed silica tubes at temperatures between 600°C and 1100°C for several days. No attack on the silica tubes was detected, and from the analytical figures quoted by Faller et al.<sup>1</sup> it seems reasonable to assume that this method of synthesis does not lead to serious contamination of the products. The phosphides were obtained in the form of black powders. Single-crystals suitable for X-ray work were not found.

X-ray powder photographs were recorded in Guinier-type focussing cameras with CuK $\alpha$  or CrK  $\alpha_1$  radiation. Unit cell dimensions (estimated accuracy 0.04 %) were measured using silicon ( $a = 5.4305 \text{ \AA}$ ) as internal calibration standard. The intensities of the X-ray reflexions were obtained from photometer records of the films, using methods similar to those described by Hägg and Regnström<sup>4</sup>. Relative  $F_0$  - values were calculated from the equation derived by Hägg<sup>5</sup>. Absorption in the specimen was neglected.

For the structure determinations, preliminary Fourier summations were made using the automatic analogue computer described by Lundström and Klimecki<sup>6</sup>. Least squares refinements and calculations of structure factors and interatomic distances were made on the electronic digital computers BESK and FACIT EDB using programmes devised by Brändén and Åsbrink<sup>7</sup>, and by Liminga<sup>8</sup>. Atomic scattering factors were interpolated from tables given by Thomas and Umeda<sup>9</sup> for molybdenum, and by Tomie and Stam<sup>10</sup> for phosphorus. The real part of the dispersion correction for molybdenum, as calculated by Dauben and Templeton<sup>11</sup> was included in the scattering factor values.

#### Phase-analytical investigations

The Mo-P system. The present investigation confirms the occurrence in the Mo-P system of the phases  $\text{Mo}_3\text{P}$ , MoP and  $\text{MoP}_2$ . The nominal compositions of the single-phase preparations corresponded closely to the ideal formulae. A phase with the approximate composition  $\text{MoP}_{0.75}$  was also found to occur. Although Faller et al.<sup>1</sup> failed to detect this phase, their results do not contradict the present findings.

In the paper by Faller et al., Fig. 2, the X-ray powder diagram for a product with the composition  $\text{MoP}_{0.7}$  is stated to contain reflexions from MoP and  $\text{Mo}_3\text{P}$ . A closer inspection indicates, however, that although this diagram undoubtedly contains MoP reflexions there are many reflexions which cannot be ascribed either to MoP or to  $\text{Mo}_3\text{P}$ . Further, Faller et al. quote results obtained by Köcher for the thermal decomposition of MoP at  $1200^\circ\text{C}$

in vacuum. Köcher found it impossible to obtain decomposition products containing less than about 45 at % phosphorus. Since the homogeneity range of MoP is very narrow (stated by Faller et al. and confirmed by Schönberg<sup>2</sup> and the present authors), the simplest explanation of Köcher's results seems to lie in the formation near the composition MoP<sub>0.75</sub> of an intermediate phase with a very low phosphorus vapour pressure at 1200°C.

For samples annealed at 1000°C, the following two-phase equilibria were observed: Mo + Mo<sub>3</sub>P, Mo<sub>3</sub>P + MoP<sub>0.75</sub>, MoP<sub>0.75</sub> + MoP and MoP + MoP<sub>2</sub>. Samples containing more than 66.7 at % phosphorus, heated at 1000°C and slowly cooled, gave no indications of a molybdenum phosphide with a phosphorus content higher than MoP<sub>2</sub>. Within the limits of experimental error, variations of the lattice parameters for the molybdenum phosphides were not observed. This indicates that all these phases have narrow homogeneity ranges below 1000°C

The W-P system. The only intermediate phases found in this system were WP and WP<sub>2</sub>; this confirms the results obtained by Faller et al.<sup>1</sup> and by Schönberg<sup>2</sup>. Attempts to prepare a "sub-phosphide", as reported by Hartmann and Orban<sup>12</sup>, were unsuccessful. Samples with the composition WP<sub>0.3</sub> were heated for several days at temperatures between 800°C and 1100°C, but the products contained only tungsten and WP.

The compositions of WP and WP<sub>2</sub> were found to correspond closely to the ideal formulae, and there were no indications of an extended homogeneity range in either instance.

X-ray crystallographic investigations.

Mo<sub>3</sub>P. The X-ray powder reflexions were indexed on the basis of a body-centred tetragonal cell, dimensions for which are given in Table 1. The values obtained differ considerably from those given by Schönberg<sup>2</sup>.

Faller et al.<sup>1</sup> and Schönberg<sup>2</sup> state that Mo<sub>3</sub>P has the Fe<sub>3</sub>P-type structure. However, there is also a possibility that Mo<sub>3</sub>P is isostructural with α-V<sub>3</sub>S, the structure of which was determined by Pedersen and Grønvoold<sup>13</sup>. α-V<sub>3</sub>S has a body-centred tetragonal unit cell with dimensions similar to those of Fe<sub>3</sub>P. The Laue symmetry is  $4/\underline{m} \underline{m} \underline{m}$  for α-V<sub>3</sub>S (space group  $I 4 2 \underline{m}$ ) and  $4/\underline{m}$  for Fe<sub>3</sub>P (space group  $I 4$ ). The general arrangements of the atoms, and consequently the intensities of the reflexions, are not very different for the two structures. Accordingly, it is difficult to decide from powder data alone whether Mo<sub>3</sub>P is isostructural with Fe<sub>3</sub>P or with α-V<sub>3</sub>S.

MoP<sub>0.75</sub>. The powder pattern of MoP<sub>0.75</sub> is highly complex, indicating a large unit cell and probably a low symmetry. Attempts to index the diffraction pattern were unsuccessful. Powder data for identification purposes are given in Table 2.

MoP. The hexagonal unit cell dimensions measured for MoP (Table 1) are in fair agreement with the values reported earlier<sup>2,3</sup>. Superstructure reflexions indicating a doubling of the c axis were not observed. This is in agreement with the results obtained by Schönberg<sup>2,14</sup>, who stated that MoP

crystallizes with the WC-type structure. In this structure the metal atoms are arranged in a simple hexagonal lattice, in which the non-metal atoms occupy half of the triangular prismatic voids. The distribution of the non-metal atoms may be ordered or random.

It was mentioned earlier that within the limits of experimental error the unit cell dimensions of the MoP phase are unchanged in alloys of different composition, and that any deviation from the ideal composition was not detected. If this phase has the stoichiometric composition MoP, the hypothesis of a totally random distribution of phosphorus atoms in the triangular prismatic voids would imply the occurrence of some P-P separations of only 1.86 Å in the (001) plane. The existence of such small P-P separations appears highly improbable, since the shortest P-P distances in black phosphorus as well as in all known metal phosphide structures exceed 2 Å. It is therefore reasonable to assume an ordered distribution of phosphorus atoms within each (001) layer. These layers may, however, be stacked in a more or less random way to give structures, which range from the ordered WC-type on the one hand to the ordered NiAs-type on the other<sup>14</sup>.

By using neutron diffraction methods, Leciejewicz<sup>15</sup> and Parthé and Sadagopan<sup>16</sup> have been able to show conclusively that the carbon atoms have the ordered arrangement in WC. The difference between an ordered and a disordered WC-type structure, as demonstrated by X-ray intensities, is very small when the scattering powers of the two constituents are very different. It was nevertheless decided to make an attempt to study the

distribution of the phosphorus atoms in MoP by the X-ray diffraction technique.

The intensities of reflexions from three different MoP samples were recorded and averaged. The powder camera used covers the range  $0^\circ < \theta < 45^\circ$ , which for  $\text{CuK}\alpha$  radiation includes only ten reflexions. Of these, the structure factors of the five reflexions (001), (110), (002), (111) and (112) are independent of the ordering of the phosphorus atoms and were therefore used to obtain a scale factor and an isotropic, over-all temperature factor. (A temperature factor with  $\underline{B} = 0.49_7 \text{ \AA}^2$  was found). These scale and temperature factors were then applied to the five remaining reflexions. The results are collected in Table 3. It is seen that the agreement between observed and calculated  $|\underline{F}|^2$ - values is much better for the ordered than for the disordered structure proposal. For the five independent reflexions,  $\sum (|\underline{F}_o|^2 - |\underline{F}_c|^2) / \sum |\underline{F}_o|^2$  is 0.07. For the remaining five reflexions, the value of this ratio is 0.04 in the instance of the ordered structure, and 0.11 for the disordered structure.

The experimental data quoted above may be influenced by systematic errors, such as preferred orientation in the powder samples; moreover, the number of recorded intensities is very small. Accordingly, only limited conclusions can be drawn. It seems safe to assume, however, that the distribution of the phosphorus atoms in the MoP structure is ordered within each (001) layer, and that the stacking of these layers corresponds mainly to the arrangement in the ordered WC-type structure.

Interatomic distances for MoP are listed in Table 4.

WP. Confirmation that WP has the MnP (B 31)- type structure has already been provided by one of the present authors<sup>17</sup>.

The unit cell dimensions are given in Table 1.

MoP<sub>2</sub> and WP<sub>2</sub>. The close similarity between the X-ray powder photographs of MoP<sub>2</sub> and WP<sub>2</sub> noted by Faller et al.<sup>1</sup> was confirmed in the present investigation. In each instance the diffraction pattern was indexed on the basis of an orthorhombic unit cell (see Table 1). Since MoP<sub>2</sub> offers the best conditions for an accurate determination of the phosphorus positions, it was decided to collect quantitative intensity material for this phase only. Visual comparison of intensities for corresponding reflexions in MoP<sub>2</sub> and WP<sub>2</sub> indicates that the atomic positions in the two structures are closely similar.

The unit cell volume for MoP<sub>2</sub> (175 Å<sup>3</sup>) suggests a cell of content four formula units. Reflexions (h k l) with h+k = 2n+1 were not observed. Among the (h 0 l) reflexions, those with l = 2n + 1 were not detected. If these extinctions are systematic, the alternative space groups are C m c 2<sub>1</sub>, C 2 c m and C m c m. The ratio F<sub>0</sub> (0 k l) / F<sub>0</sub> (2 k l) was found to be closely similar for all pairs of corresponding (0 k l) and (2 k l) reflexions. This observation, and the fact that a is only 3.145 Å, gives strong indication that all atoms are situated in two planes parallel to (100) and spaced a/2 apart.

The Patterson function was evaluated in the section P(0 y z). (The reliability of the Patterson map was limited

owing to overlaps among the reflexions combined with marked series termination errors). The number and distribution of peaks in  $\underline{P}$  ( $0 \underline{y} \underline{z}$ ) supported the hypothesis regarding the arrangement of the atoms in the  $\underline{a}$  direction. Further interpretation of the Patterson map was facilitated by the introduction of the following subsidiary assumptions; all Mo-P distances are larger than 2.2 Å and all P-P distances larger than 1.8 Å. With these restrictions, only one possible atomic arrangement could be derived. This has the symmetry  $\underline{C} \underline{m} \underline{c} 2_1$  with all the atoms situated in 4( $\underline{a}$ ) positions. Using  $\underline{F}_0$  values for 34 well resolved reflexions, atomic parameters and isotropic individual temperature factors were refined by the least squares method, until the shifts in the atomic parameters were smaller than  $10^{-5}$  and the shifts in the temperature factors smaller than  $10^{-3} \text{ Å}^2$ . The least squares programme used<sup>7</sup> minimizes the function  $\sum \underline{w}(\underline{F}_0 - |\underline{F}_c|)^2$ . The weighting factor  $\underline{w}$  was put equal to  $1/\underline{F}_0^2$  except for the three weak reflexions (220), (153) and (024), to which the weighting factors  $1/4 \underline{F}_0^2$  were assigned. The final  $\underline{R}$ -value was 0.04. The good agreement between observed and calculated structure factors (see Table 5) is taken as proof that the structure determination is correct. The following structure data for  $\text{MoP}_2$  were obtained:

Space group  $\underline{C} \underline{m} \underline{c} 2_1$  ( $\underline{C} \begin{smallmatrix} 12 \\ 2 \underline{v} \end{smallmatrix}$ );  $\underline{Z} = 4$ .

$\underline{a} = 3.145 \text{ Å}$ ;  $\underline{b} = 11.184 \text{ Å}$ ;  $\underline{c} = 4.984 \text{ Å}$ ;  $U = 175.3 \text{ Å}^3$ .

	<u>y</u>	<u>z</u>	<u>B</u> (Å <sup>2</sup> )
4 Mo in 4 ( <u>a</u> )	0.0934	0	2.7 <sub>3</sub>
4 P <sub>I</sub> in 4 ( <u>a</u> )	0.294 <sub>1</sub>	0.803 <sub>1</sub>	1.9 <sub>3</sub>
4 P <sub>II</sub> in 4 ( <u>a</u> )	0.426 <sub>9</sub>	0.121 <sub>7</sub>	3.6 <sub>9</sub>

(z<sub>Mo</sub> is arbitrarily put equal to 0).

It is difficult to assess the accuracy of this structure determination. The least squares refinement indicated the following standard deviations: for Mo  $\sigma(\underline{y}) = 0.0004$ ,  $\sigma(\underline{B}) = 0.1_2 \text{ \AA}^2$ , for P<sub>I</sub>  $\sigma(\underline{y}) = 0.002$ ;  $\sigma(\underline{z}) = 0.003$ ;  $\sigma(\underline{B}) = 0.3 \text{ \AA}^2$ , and for P<sub>II</sub>  $\sigma(\underline{y}) = 0.002$ ;  $\sigma(\underline{z}) = 0.004$ ;  $\sigma(\underline{B}) = 0.5 \text{ \AA}^2$ . Although these values have a reasonable magnitude, only limited confidence should be attached to them since only a small number of reflexions were used in the refinement. The differences between the individual "temperature factors" for the atoms in MoP<sub>2</sub> may well be spurious effects.

The X-ray powder data for MoP<sub>2</sub> are given in Table 5, and interatomic distances are listed in Table 6.

#### Description and discussion of the MoP<sub>2</sub> structure.

The structure of MoP<sub>2</sub> is shown in projection on (100) in Fig. 1. Each molybdenum atom is surrounded by seven near phosphorus neighbours and four more distant molybdenum neighbours. Of the phosphorus atoms, six are located at the corners

of a triangular prism, and the seventh lies outside one of the rectangular faces of the prism. A molybdenum atom lies outside each of the two remaining rectangular faces and each of the two triangular faces of the prism. The arrangement is shown in detail in Fig. 2. The average of the four Mo-Mo distances is 3.20 Å, exceeding the Goldschmidt metal diameter for 12-coordination (2.80 Å) by 14 %. The mean of the seven Mo-P distances is 2.49 Å, which corresponds to the sum of the Goldschmidt radius for molybdenum and the tetrahedral covalent radius for phosphorus (1.10 Å).

The phosphorus atom  $P_I$  is surrounded by one near phosphorus neighbour ( $P_{II}$ ) and three near molybdenum neighbours in a distorted tetrahedral configuration, while the phosphorus atom  $P_{II}$  has one near phosphorus neighbour ( $P_I$ ) and four near molybdenum neighbours in a distorted square pyramidal arrangement. The phosphorus atoms in  $MoP_2$  are thus linked in pairs (P-P distance 2.17 Å), the other P-P distances being 2.98 Å or longer. P-P pairs have also been found in other di-phosphides, *viz.*  $FeP_2$ ,  $RuP_2$  and  $OsP_2$  (marcasite-type structure), and  $PtP_2$  (pyrites-type).

It is interesting to compare the  $MoP_2$  structure with the  $ZrSi_2$  ( $C_{49}$ ) structure type. The  $ZrSi_2$  structure has the space group symmetry  $C_{4v}$  and has four zirconium atoms and eight silicon atoms in three sets of 4 ( $c$ ) positions. A (100) projection of the structure (according to Schachner *et al.*<sup>18</sup>) is shown in Fig. 3. A comparison of Fig. 3 with Fig. 1 shows the resemblance between the structures. The metal atom lattices

are almost identical, but the arrangement of the non-metal atoms is different in the two structures. In  $\text{MoP}_2$  the close contacts between non-metal atoms are restricted to isolated  $\text{P}_I$ - $\text{P}_{II}$  pairs, while in  $\text{ZrSi}_2$  short Si-Si contacts form infinite zig-zag  $\text{Si}_I$  chains extending in the  $c$  direction, and infinite  $\text{Si}_{II}$  layers parallel with the  $a$   $c$  plane.

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References:

1. Faller, F.E., Biltz, W., Meisel, K. and Zumbusch, M.  
Z. anorg. Chem. 248 (1941) 209.
2. Schönberg, N. Acta Chem. Scand. 8 (1954) 226.
3. Bachmayer, K., Nowotny, H. and Kohl, A. Monatsh. Chem. 86  
(1955) 39.
4. Hägg, G. and Regnström, G. Arkiv Kemi, Mineral. Geol. 18A  
(1944) Nr. 5.
5. Hägg, G. quoted in Berger, S. Acta Chem. Scand. 7 (1953) 612.
6. Lundström, T. and Klimecki, V. J. Sci. Instr. 38 (1961) 424.
7. Åsbrink, S. and Brändén, C.-I. Programme available at BESK.
8. Liminga, R. Programme available at BESK.
9. Thomas, L.H., and Umeda, K. J. Chem. Phys. 26 (1957) 293.
10. Tomiie, Y. and Stam, C.H. Acta Cryst. 11 (1958) 126.
11. Dauben, C.H. and Templeton, D.H. Ibid 8 (1955) 841.
12. Hartmann, H. and Orban, J. Z. anorg. Chem. 226 (1936) 257.
13. Pedersen, B. and Grønvold, F. Acta Cryst. 12 (1959) 1022.
14. Schönberg, N. Acta Met. 2 (1954) 427.
15. Leciejewicz, J. Acta Cryst. 14 (1961) 200.
16. Parthé, E. and Sadagopan, V. Monatsh. Chem. 93 (1962) 263.
17. Rundqvist, S. Acta Chem. Scand. 16 (1962) 287.
18. Schachner, H., Nowotny, H. and Kudielka, H. Monatsh. Chem.  
85 (1954) 1140.

Table 1. Crystallographic data for molybdenum and tungsten phosphides. (Unit cell dimensions in Å).

Phosphide	Structure type	Space group	<u>a</u>	<u>b</u>	<u>c</u>
Mo <sub>3</sub> P	(Fe <sub>3</sub> P or α-V <sub>3</sub> S)	(Body-centred tetragonal)	9.794		4.827
MoP	WC ( <u>B<sub>h</sub></u> )	<u>P</u> <u>6</u> <u>2</u> <u>m</u>	3.223		3.191
MoP <sub>2</sub>	MoP <sub>2</sub>	<u>C</u> <u>m</u> <u>c</u> <u>2</u> <sub>1</sub>	3.145	11.184	4.984
WP	MnP ( <u>B</u> 31)	<u>P</u> <u>n</u> <u>m</u> <u>a</u>	5.732	3.249	6.222
WP <sub>2</sub>	MoP <sub>2</sub>	<u>C</u> <u>m</u> <u>c</u> <u>2</u> <sub>1</sub>	3.166	11.161	4.973

Table 2. X-ray powder data for MoP<sub>0.75</sub>. (Guinier-type focussing camera, CrK $\alpha_1$  radiation,  $\lambda = 2.28962 \text{ \AA}$ )

$I_{\text{obs}}$	$\sin^2\theta_{\text{obs}} \cdot 10^4$	$d_{\text{obs}} (\text{\AA})$	$I_{\text{obs}}$	$\sin^2\theta_{\text{obs}} \cdot 10^4$	$d_{\text{obs}} (\text{\AA})$
v. w	117	10.600	v. w	2267	2.405
w	245	7.313	m	2361	2.356
w	341	6.208	st	2405	2.334
w	729	4.242	v. w	2439	2.318
w	796	4.058	m	2488	2.295
v. w	842	3.946	m	2529	2.276
w	968	3.679	v. st	2580	2.254
w	1046	3.541	w	2673	2.215
m	1118	3.424	m	2704	2.202
w	1123	3.416	m	2798	2.165
m	1214	3.285	st	2852	2.143
v. w	1345	3.122	m	2862	2.140
w	1430	3.028	st	2882	2.133
m	1469	2.988	w	2907	2.123
v. w	1483	2.973	m	2939	2.112
w	1596	2.866	v. w	3086	2.061
m	1641	2.826	st	3176	2.032
st	1685	2.789	w	3223	2.017
m	1779	2.715	w	3248	2.009
v. w	1860	2.654	m	3305	1.991
w	1877	2.642	st	3337	1.982
w	1902	2.625	m	3406	1.961
w	1937	2.601	w	3479	1.941
st	2099	2.497	m	3614	1.903
st	2109	2.493	m	3660	1.892
st	2156	2.466	v. w	3800	1.857
v. w	2187	2.448	v. w	3851	1.845
w	2204	2.438	st	3938	1.824
w	2225	2.427			
v. w	2248	2.414			

Table 3. Observed and calculated  $|F|^2$ - values for MoP.

<u>h</u> <u>k</u> <u>l</u>	$ \underline{F}_O ^2$	$ \underline{F}_C ^2$ ordered	$ \underline{F}_C ^2$ disordered
001	552		562
100	949	878	798
101	1292	1273	1212
110	1331		1190
002	1072		1181
111	293		287
200	480	458	415
102	486	452	410
201	758	733	693
112	735		747

Table 4. Interatomic distances (Å) in MoP.  
(Distances shorter than 4 Å listed)

Mo - Mo : 3.191 (2), 3.223 (6).

Mo - P : 2.451 (6)

P - Mo : 2.451 (6)

(The P-P distances are equivalent to the Mo - Mo distances  
for a completely ordered WC-type structure).

Table 5. Powder diffraction data for MoP<sub>2</sub>  
 (CuK<sub>α</sub> radiation, λ = 1.5418 Å)

<u>hkl</u>	$\sin^2\theta_o$ .10 <sup>4</sup>	$\sin^2\theta_c$ .10 <sup>4</sup>	$I_o$	$I_c$	$F_o$	$ F_c $
020	190	190	200.2	159.2	51.8	46.2
021	431	429	680	712	91.2	93.4
110	649	648	142.4	173.9	54.0	59.7
040	761	760	119.3	123.9	77.3	78.7
111	888	888	669	582	100.4	93.6
002	958	957	133.4	132.6	91.9	91.6
041	1000	999	221.7	235.0	86.1	88.5
130 <sup>1,2</sup>	-	1028	< 1	0.0	< 6	0.9
022	1147	1147	174.5	166.8	80.7	78.9
131	1269	1268	947	811	139.5	128.9
112	1606	1605	303.7	326.9	87.2	90.4
060 <sup>1</sup>	1711	1710	} 231.0	123.0	-	114.4
042 <sup>1</sup>	1717	1717		123.3	-	81.0
150	1789	1789	208.4	200.3	107.6	105.5
061	1950	1950	46.9	49.2	53.5	54.8
132	1986	1985	48.8	49.9	38.5	39.0
151	2028	2028	44.6	41.9	37.3	36.2
023	2342	2343	173.7	162.5	108.4	104.8
200	2404	2403	131.3	134.1	133.3	134.6
220 <sup>2</sup>	-	2593	5.0	7.0	18.7	22.2
062	2667	2667	88.6	88.3	80.2	80.0
152	2745	2746	102.6	107.6	61.4	62.9
113	2801	2801	17.1	17.3	25.3	25.4
221	2832	2833	74.8	76.1	52.8	53.3
043	2914	2913	28.4	29.7	46.4	47.4
170 <sup>1,2</sup>	-	2929	< 1	0.0	< 9	1.6
080 <sup>2</sup>	-	3041	6.6	8.0	31.9	35.1

Table 5. (cont.)

<u>hkl</u>	$\sin^2\theta_o$ .10 <sup>4</sup>	$\sin^2\theta_c$ .10 <sup>4</sup>	$I_o$	$I_c$	$F_o$	$ F_c $
240 <sup>1</sup>	} 3167	3163	}	25.2	-	44.0
171 <sup>1</sup>		3168		291.2	-	57.2
133 <sup>1</sup>		3182		135.5	-	72.2
081	3281	3280	44.8	43.2	58.8	57.4
202	3360	3360	37.1	34.6	53.2	51.6
241	3403	3403	78.8	76.1	54.6	53.7
222	3551	3550	61.3	62.5	47.7	48.3
004	3828	3828	21.7	22.4	54.9	55.8
063 <sup>1,2</sup>	-	3864	3	4.1	15	16.7
172	3887	3886	80.4	76.2	52.5	51.1
153 <sup>2</sup>	-	3942	3.6	4.5	10.9	12.3
082 <sup>1,2</sup>	-	3998	2.7	1.4	13.2	9.7
024 <sup>2</sup>	-	4018	6.0	5.7	19.8	19.4
260 <sup>1</sup>	4115	4114	172.4	74.1	-	68.9
242 <sup>1</sup>	4118	4120		78.9	-	50.3
261	4353	4353	35.5	43.1	32.3	35.6
190 <sup>1</sup>	-	<del>4449</del>	} 183.3	11.4	-	25.7
114 <sup>1</sup>	4476	4476		123.2	-	59.5
044 <sup>2</sup>	-	4588		20.2	220.2	33.5
191	4688	4688	165.2	137.1	66.4	60.4
223 <sup>1</sup>	} 4745	4746	} 278.2	170.8	-	66.7
0 10 0 <sup>1</sup>		4751		40.3	-	64.8

<sup>1</sup> Reflexion not used in least squares refinement.

<sup>2</sup> Reflexion too weak for accurate measurement of diffraction angle.

Table 6. Interatomic distances (Å) in MoP<sub>2</sub>.  
(Distances shorter than 4 Å listed)

Mo - Mo : 3.145 (2), 3.25<sub>1</sub> (2).

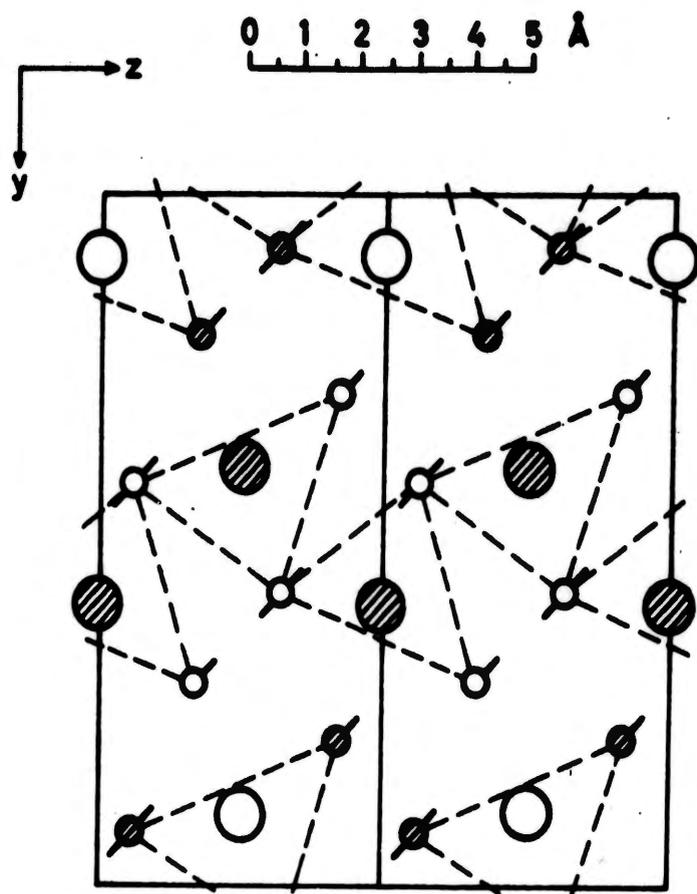
Mo - P<sub>1</sub> : 2.45, 2.52 (2), 3.83 (2), 3.99 (2).

Mo - P<sub>II</sub>: 2.47 (2), 2.51 (2), 3.48 (2), 3.78.

P<sub>I</sub> - P<sub>I</sub> : 3.11 (4), 3.145 (2).

P<sub>I</sub> - P<sub>II</sub>: 2.17, 3.07 (2), 3.25, 3.71, 3.82 (2).

P<sub>II</sub> - P<sub>II</sub>: 2.98 (2), 3.145 (2).



	$x=0$	$x=\frac{1}{2}$
Mo	○	●
P <sub>I</sub>	⊙	⊙
P <sub>II</sub>	⊙	⊙

Fig. 1. The structure of MoP<sub>2</sub> projected on (100)

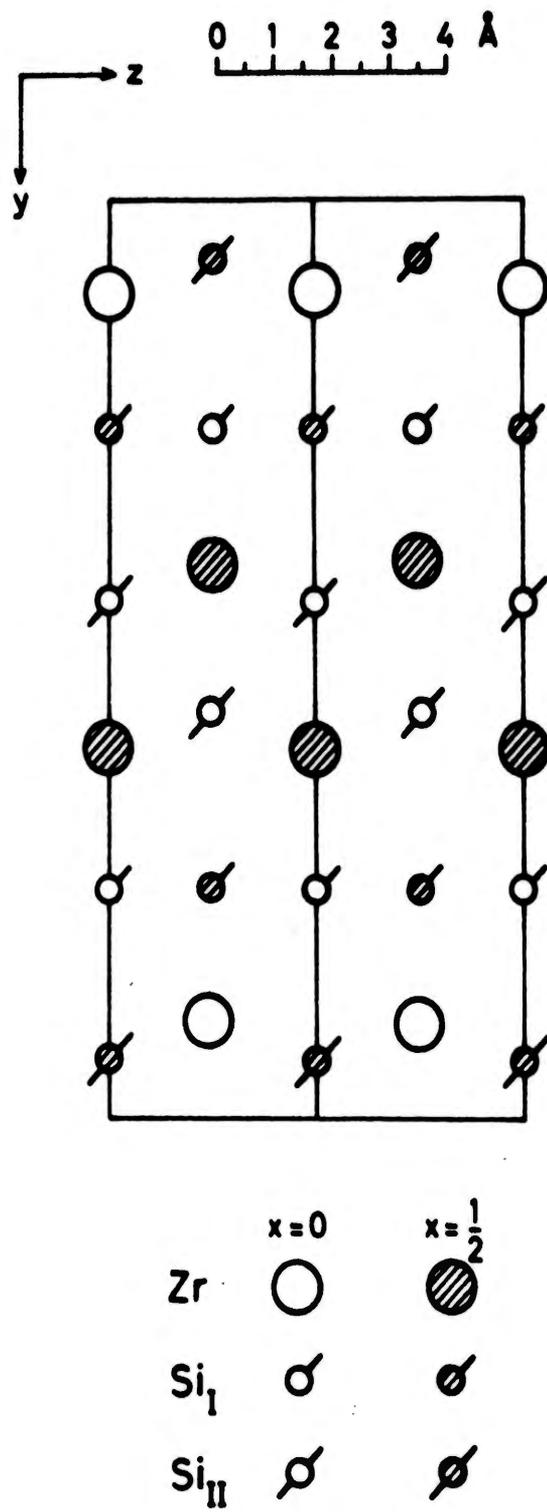


Fig. 3. The structure of  $ZrSi_2$  projected on (100)

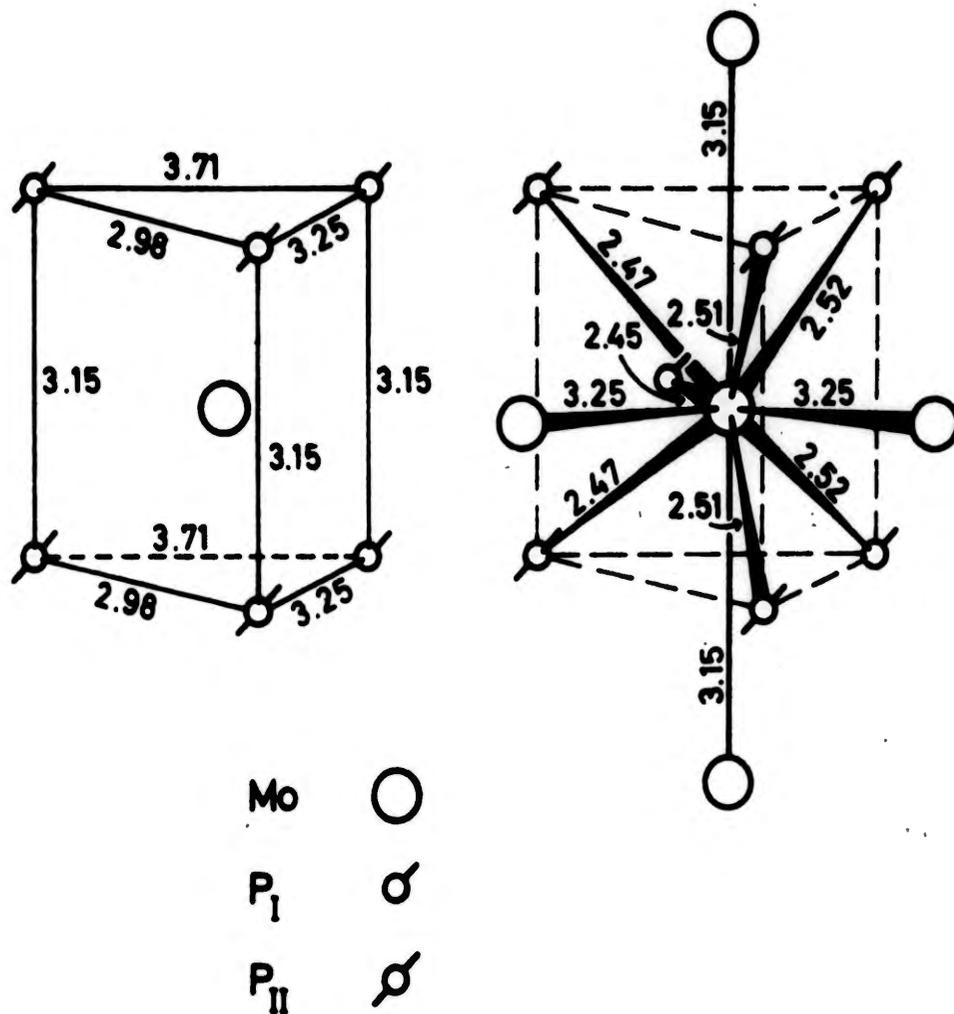


Fig. 2. The environment of the molybdenum atom in MoP<sub>2</sub>.

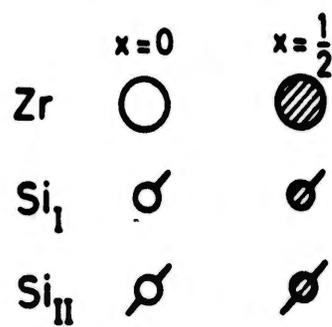
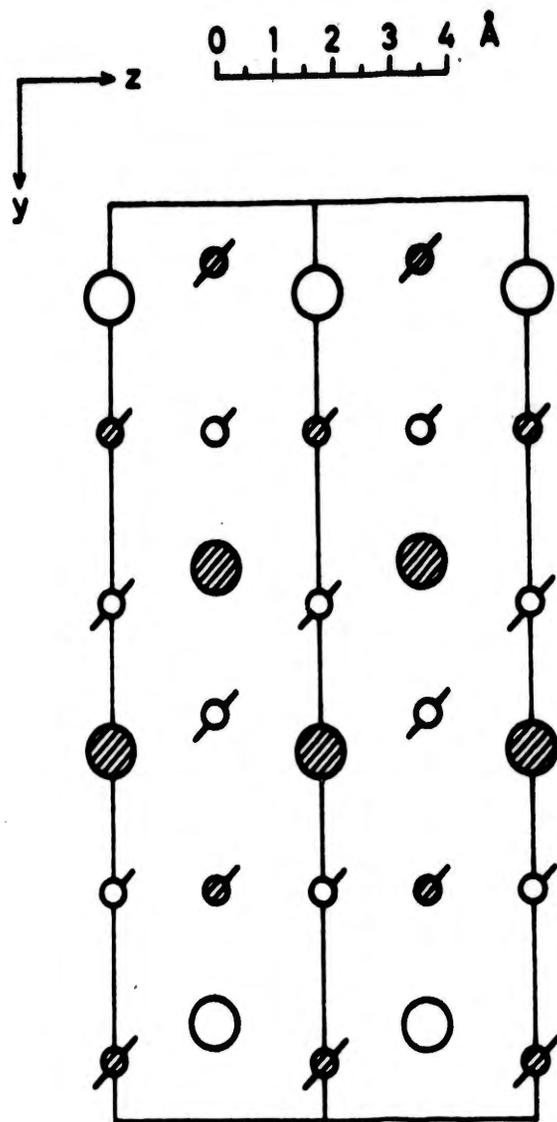


Fig. 3. The structure of  $ZrSi_2$  projected on (100)

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