# The Crystal Structure of $V_{12}P_7$

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The crystal structure of $V_{12}P_7$ has been investigated by single crystal X-ray methods. The symmetry is hexagonal, and the dimensions of the unit cell as determined from a sample containing copper are $a = 9.299$ Å; $c = 3.2790$ Å. The structure is the anti-type to $Th_7S_{12}$. $V_{12}P_7$ and $Th_7S_{12}$ are both partially disordered structures, which makes it difficult to assign a proper space group symmetry. The observed X-ray data for $V_{12}P_7$ are very well accounted for by a structure of $P6_3/m$ symmetry, where some of the positions are only half filled. An interpretation of the disorder phenomenon is proposed in terms of two ordered structure models with reasonable coordination geometries and interatomic distances. The actual crystal is composed of a random distribution of smaller regions, each with an ordered structure corresponding to one of the two models.

During the investigation of ternary transition metal phosphides undertaken by one of the present authors (E. G.),[1,2] attempts were made to prepare vanadium copper phosphides by arc-melting. A new intermediate phase was found as revealed by X-ray powder photographs and as it proved possible to obtain single crystals, it was decided to make an X-ray single crystal structure determination. This new phase turned out to be a vanadium phosphide with the ideal formula $V_{12}P_7$, but as the preparation was undertaken in the presence of copper there is probably small amounts of copper dissolved in it. The powder photograph showed, however, that the main part of the copper in the sample was distributed in phases based on elemental copper and $Cu_3P$.

An intermediate phase in the binary vanadium phosphorus system, denoted $VP_x$ $0.5 < x < 1$, has been reported by Lundström.[3,4] By comparison with Weissenberg photographs put at our disposal it has been possible to show that this phase actually is $V_{12}P_7$. Lundström also found that this phase existed both in a disordered and in an ordered form, the $a$ axis of the hexagonal unit cell being doubled when ordering taking place.

The crystal structure determination of the disordered form of $V_{12}P_7$ is that which is described in this paper.

## EXPERIMENTAL

*Preparation.* The first stage of the preparations involved heating of mixtures of the powdered components in evacuated and sealed silica tubes for several days. The sintered lump thus obtained was then rapidly arc-melted. Single crystals found in the solidified melt were used directly without further heat treatments.

*X-Ray work.* Cell dimensions were determined from powder photographs recorded in Guinier-type focussing cameras using strictly monochromatic $CuK\alpha_1$ radiation ($\lambda = 1.54051$ Å) and with silicon as internal calibration standard ($a = 5.4305$ Å). An aluminium foil was used to reduce the fluorescence radiation from the sample.

An approximately cylindrical crystal with radius about 0.02 mm was used for recording equi-inclination Weissenberg photographs with zirconium-filtered $MoK$ radiation. The multiple film technique was used with thin iron foils interleaving successive films. The intensities were estimated visually by comparison with a calibrated intensity scale. The data were corrected for the Lorentz and polarization effects as well as for absorption, taking the crystal as being cylindrical in form with the linear absorption coefficient equal to 123 cm$^{-1}$.

*Computing methods.* All the calculations were performed with a CD3600 computer using the following programs:

| | |
|---|---|
| Least squares refinement of unit cell dimensions. | CELSIUS: J. Tegenfeldt, Uppsala, Sweden. |
| Absorption correction. | DATACORR: R. Liminga, Uppsala, Sweden. |
| Lorentz-polarization corrections, Fourier summations and structure factor calculation. | DRF: A. Zalkin, Berkeley, U.S.A., modified by R. Liminga and J. O. Lundgren, Uppsala, Sweden. |
| Least squares refinements of positional parameters and temperature factors. | LALS: P. K. Gantzel, R. A. Sparks and K. N. Trueblood, Los Angeles, U.S.A.; Modified by A. Zalkin, Berkeley, U.S.A. and by C.-I. Brändén, R. Liminga and J. O. Lundgren, Uppsala, Sweden. |
| Interatomic distances. | DISTAN: A. Zalkin, Berkeley, U.S.A. |

Atomic scattering factors and factors correcting for the real part of the anomalous dispersion were taken from Ref. 5.

## STRUCTURE DETERMINATION

Weissenberg photographs showed the Laue symmetry to be $6/m$. No systematic absences were found. It was not possible to check the $(00l)$ reflexions, however, since the crystal was rotated about the $c$ axis only. The short $c$ axis (3.279 Å) and the approximately constant value of the ratio $I(hkl)/I(hkl+2)$ strongly suggested that the atoms were confined to two planes perpendicular to the $c$ axis and spaced $c/2$ apart. With this restriction the following space groups are possible: $P6$, $P\bar{6}$, $P6/m$, $P6_3$, and $P6_3/m$. Using the $(hk0)$ and $(hk1)$ reflexions the Patterson sections $P(UV0)$ and $P(UV\,1/2)$ were calculated. These sections could be successfully interpreted in terms of the space group with the highest symmetry, $P6_3/m$, with 12 metal atoms distributed on two $6(h)$ positions and 6 phosphorus atoms in one $6(h)$ position. At this stage it was not quite clear if there were both vanadium and copper atoms present in the structure. An electron density calculation, based on observed structure factors with signs taken from calculated structure factors with vanadium as the only metal, suggested that one of the metal positions

might be occupied by vanadium and the other by copper. A least squares refinement of this structure proposal, where the scale factors and the positional parameters were varied, stopped at an $R$-value of 0.24 ($R = \sum ||F_o| - |F_c||/\sum |F_o|$). A difference synthesis then showed that the position which was assumed to be vanadium was split up into two maxima, one on each side of the position which had been obtained from the refinement. In the next step the split vanadium position was treated as two half-filled vanadium positions about 0.5 Å apart in a least squares refinement followed by a new electron density and difference synthesis. The $R$-value obtained was now 0.15. The difference syntheses indicated that too many electrons had been placed in the assumed copper position which accordingly was assumed to be occupied by vanadium. Moreover, there were indications that scattering power approximately equal to one phosphorus atom was associated with the line $(0, 0, z)$, however, it is not possible to determine the $z$ coordinate using only $(hk0)$ and $(hk1)$ reflexions. It can easily be shown that in space group $P6_3/m$ only reflexions with $l = 2n$ make any contribution to the electron density on the line $(0, 0, z)$. In the present case only $(hk0)$ reflexions contribute to the summation and consequently, a constant value independent of $z$ is obtained for the electron density along $(0, 0, z)$. As there is no onefold position in the actual space group it was assumed that one of the twofold positions 2 ($b$): $(0, 0, 0)$, $(0, 0, 1/2)$ and 2($a$): $(0, 0, 1/4)$, $(0, 0, 3/4)$ was occupied. However, the short $c$ axis of 3.28 Å excludes the possibility of one of these positions being completely filled as this would result in improbably short $P-P$ distances of 1.64 Å. The shortest $P-P$ distances known are about 2.2 Å and these distances occur only in very phosphorus rich compounds. It transpires that the line $(0, 0, z)$ is surrounded by the vanadium positions which were treated as half filled. It thus seemed as if some kind of disorder was associated with the line $(0, 0, z)$ and its nearest surroundings. As there are strong crystal chemical indications in favour of one of the twofold positions 2($a$) and 2($b$) it was not considered necessary to estimate intensities of layer lines with $l > 1$. With the 2($b$) position half filled with phosphorus the result will be that phosphorus is octahedrally surrounded by six vanadium atoms with at least three distances as short as 2.05 Å as compared with the radius sum of 2.46 Å. This can also be compared with the $P-Ti$ distances of 2.440 Å found for an octahedrally surrounded phosphorus atom in TiP.[11] On the other hand, with the 2($a$) position half filled it is possible to avoid such short distances using a model which is discussed in the next section. According to this model a phosphorus atom in 2($a$) would have a very reasonable ninefold coordination with $P-V$ distances ranging from 2.40 Å to 2.49 Å. Crystal chemical considerations are thus strongly in favour of the 2($a$) position which accordingly is used in the following. A new least squares refinement where this phosphorus atom was included together with the other changes mentioned above gave an $R$-value of 0.070 with quite normal temperature factors. It seems reasonable to assume that too close contacts between the phosphorus atoms are avoided through a partially ordered distribution on the 2($a$) sites in the following manner. Along any particular hexagonal axis in the structure, either $(0, 0, 1/4)$ positions only or $(0, 0, 3/4)$ positions only are occupied by phosphorus atoms. The distribution of "$(0, 0, 1/4)$ axes" and "$(0, 0, 3/4)$ axes" is entirely random.

In order to obtain further information about the degree of disorder and to what extent copper was dissolved in the crystal, another least squares refinement was started in which the following parameters were varied: two scale factors, one overall temperature factor, all the positional coordinates which, according to space group restrictions, are allowed to be varied and four multiplier parameters defining the degree of occupancy for four atomic positions. The degrees of occupancy assumed as starting values were as follows: one completely filled vanadium position in $6(h)$, two half filled vanadium positions in $6(h)$, one completely filled phosphorus position in $6(h)$ and one half filled phosphorus position in $2(a)$. The multiplier parameter for the phosphorus atoms in $6(h)$ was kept constant in order to avoid a singular matrix. After four cycles of refinement no further changes were indicated. The deviations from the assumed occupancies were then in one case 2.6 standard deviations ($V_{II}$) and in the other cases about 1 standard deviation. Although this method is not very sensitive it can be concluded with a fairly high degree of accuracy that the composition of the crystal is close to the formula $V_{12}P_7$. As already has been mentioned this phase does exist in the binary vanadium phosphorus system. However, it seems reasonable to assume that small amounts of copper have been taken up into solid solution in the crystal used in the present study.

Attempts were also made to treat the crystal as an ordered one in space groups of lower symmetry. In $P\bar{6}$, for example, it is possible to select only half of the disordered atoms in $P6_3/m$, and to leave out atoms not in agreement with restrictions imposed by space considerations. However, all trial models proved difficult to refine and the $R$ values stopped at about 0.15.

In the least squares refinements the reflexions were assigned weights according to a formula given by Cruickshank et al.[6] $w = 1/(a + |F_o| + c|F_o|^2)$ The values $a = 16.0$ and $c = 0.015$ proved suitable as shown by a weight analysis.

The final crystallographic data obtained are as follows:

$a = 9.299$ Å          $\sigma = 0.001$  Å
$c = 3.2790$ Å          $\sigma = 0.0007$ Å
$V = 245.5$ Å$^3$

Space group: $P6_3/m$          $C_{6h}^2$          $Z = 1$
Calculated density: 5.600 g/cm$^3$

The atoms are in $6(h)$ and $2(a)$ positions with the parameter values:

|  |  | $x$ | $\sigma(x)$ | $y$ | $\sigma(y)$ | $B$ (Å$^2$) | $\sigma(B)$ (Å$^2$) |
|---|---|---|---|---|---|---|---|
| $V_I$ | $6(h)$* | 0.0143 | 0.0005 | 0.2646 | 0.0006 | 0.65 | 0.07 |
| $V_{II}$ | $6(h)$* | 0.0055 | 0.0005 | 0.2046 | 0.0006 | 0.71 | 0.07 |
| $V_{III}$ | $6(h)$ | 0.3771 | 0.0003 | 0.5095 | 0.0003 | 0.74 | 0.04 |
| $P_I$ | $6(h)$ | 0.7133 | 0.0005 | 0.1640 | 0.0004 | 0.82 | 0.07 |
| $P_{II}$ | $2(a)$* | — | — | — | — | 0.68 | 0.19 |

* Half filled position, see the text.

$R = 0.070$ for 151 observed independent $F$ values.

Interatomic distances are given in Table 1. Tables of observed and calculated structure factors may be obtained on request from the authors.

*Table 1.* Interatomic distances and their standard deviations (Å units) in disordered $V_{12}P_7$. In the case of $V_{III}$ and $P_I$ some of the distances are dependent on which position is chosen for $P_{II}$. The first distance given is with $P_{II}$ in (0, 0, 1/4), the second with $P_{II}$ in (0, 0, 3/4). For details, see the text. Distances shorter than 3.5 Å listed.

| | Dist. | S.d. | | | | Dist. | S.d. |
|---|---|---|---|---|---|---|---|
| $V_I$ — 2 $V_I$ | 3.279 | 0.001 | | $V_{II}$ — 2 $V_I$ | | 2.696 | 0.005 |
| 2 $V_{II}$ | 2.696 | 0.005 | | 2 $V_I$ | | 2.766 | 0.005 |
| 2 $V_{II}$ | 2.766 | 0.005 | | 2 $V_{II}$ | | 3.279 | 0.001 |
| 1 $V_{III}$ | 2.980 | 0.005 | | 2 $V_{II}$ | | 3.252 | 0.008 |
| 1 $V_{III}$ | 2.940 | 0.005 | | 2 $V_{III}$ | | 2.994 | 0.005 |
| 2 $V_{III}$ | 2.659 | 0.004 | | 1 $V_{III}$ | | 3.454 | 0.005 |
| 1 $P_I$ | 2.468 | 0.006 | | 1 $V_{III}$ | | 3.191 | 0.005 |
| 2 $P_I$ | 2.282 | 0.004 | | 2 $P_I$ | | 2.592 | 0.004 |
| 1 $P_{II}$ | 2.397 | 0.005 | | 1 $P_I$ | | 2.549 | 0.006 |
| | | | | 2 $P_{II}$ | | 2.493 | 0.003 |
| | | | | | | | |
| $V_{III}$ — 1 $V_I$ | 2.980 | 0.005 | or | $V_{III}$ — 1 $V_{II}$ | | 3.191 | 0.005 |
| 1 $V_I$ | 2.940 | 0.005 | or | 1 $V_{II}$ | | 3.454 | 0.006 |
| 2 $V_{II}$ | 2.994 | 0.004 | or | 2 $V_I$ | | 2.659 | 0.004 |
| 2 $V_{III}$ | 3.279 | 0.001 | | | | | |
| 2 $V_{III}$ | 2.948 | 0.004 | | | | | |
| 2 $V_{III}$ | 2.889 | 0.003 | | | | | |
| 1 $P_I$ | 2.485 | 0.004 | | | | | |
| 2 $P_I$ | 2.415 | 0.003 | | | | | |
| 2 $P_I$ | 2.410 | 0.003 | | | | | |
| | | | | | | | |
| $P_I$ — 1 $V_I$ | 2.468 | 0.006 | or | $P_I$ — 1 $V_{II}$ | | 2.549 | 0.006 |
| 2 $V_{II}$ | 2.592 | 0.005 | or | 2 $V_I$ | | 2.282 | 0.004 |
| 1 $V_{III}$ | 2.485 | 0.004 | | | | | |
| 2 $V_{III}$ | 2.410 | 0.003 | | | | | |
| 2 $V_{III}$ | 2.415 | 0.003 | | | | | |
| 2 $P_I$ | 3.279 | 0.001 | | | | | |
| 2 $P_I$ | 3.171 | 0.006 | | | | | |
| | | | | | | | |
| $P_{II}$ — 3 $V_I$ | 2.397 | 0.005 | | | | | |
| 6 $V_{II}$ | 2.493 | 0.004 | | | | | |
| 2 $P_{II}$ | 3.279 | 0.001 | | | | | |

## DESCRIPTION AND DISCUSSION OF THE DISORDERED $V_{12}P_7$ STRUCTURE

In the previous section the experimental evidence for a disorder phenomenon along the hexagonal axis and its nearest surroundings was described. The interpretation proposed for this disorder phenomenon involved a half filled phosphorus position on the six fold axis and two half filled vanadium positions about 0.5 Å apart surrounding this axis. There is obviously a connection between the disorder on the axis and the splitting observed for the vanadium positions. In the following description of the structure an attempt is made to interpret the disorder in terms of two co-existing idealized models.

Fig. 1 shows the two models of the disordered $V_{12}P_7$ structure. One phosphorus atom ($P_{II}$) has been placed on the hexagonal axis, either at the height 1/4 or at the height 3/4, and then the closest vanadium neighbours have been chosen either as $V_I$ or $V_{II}$ (the two half-filled positions). If the $P_{II}$ atom is in 1/4, the $V_I$ atoms has been placed on the same height, while the $V_{II}$ atom replaces $V_I$ in 3/4, and conversely, if the $P_{II}$ atom is in 3/4 the $V_{II}$ atom has
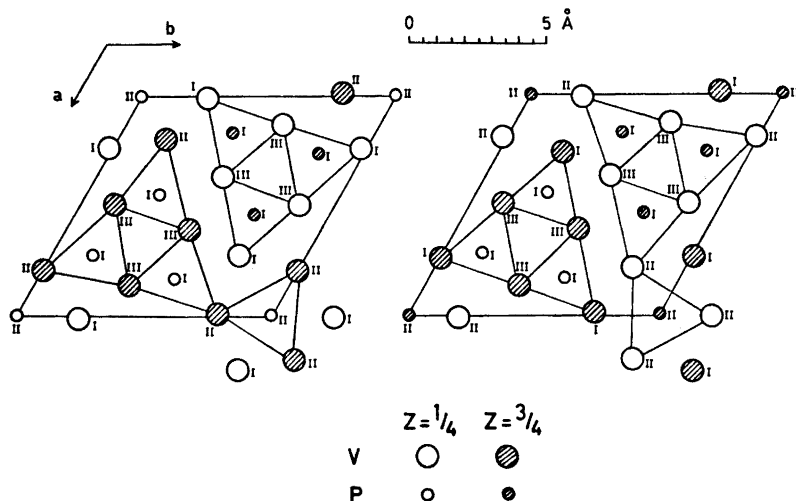
*Fig. 1.* Two idealized models of the $V_{12}P_7$ structure projected on (010). The vanadium atoms forming the trigonal prisms are connected with thin lines.

been put in 1/4 with the $V_I$ atom replacing it in 3/4. $V_{III}$ and $P_I$ are in the two cases in the same positions. By selecting $V_I$ or $V_{II}$ according to this model, reasonable atomic distances and coordination polyhedra are obtained. If the two types of atomic arrangement co-exist to about the same extent in the investigated crystal, either in some kind of domain structure or by a completely random distribution of the two types of arrangement the electron density will show the features described in the previous section.

Every remaining possibility of combining the half filled positions $V_I$, $V_{II}$, and $P_{II}$ results in atomic distances too short to be reasonable. For instance, there would be $V-P_{II}$ distances of 1.88 Å as compared with the normal radius sum of 2.46 Å. (Goldschmidt metal radius for 12-coordination for vanadium 1.36 Å, tetrahedral radius for phosphorus 1.10 Å.) According to the proposed model no $V-P_{II}$ distance is shorter than 2.40 Å and the mean of the nine $V-P_{II}$ distances is 2.46 Å. Moreover, the shortest $P-P$ distance is 3.17 Å, and the absence of short $P-P$ distances is a characteristic feature in metal rich transition metal phosphides as has been pointed out by Rundqvist.[7]

The proposed model results, however, in two sets of distances to $V_{III}$ and $P_I$, which is obviously a consequence of these two atoms having unchanged positions in the two types of atom arrangement. It is to be expected that the positions for $V_{III}$ and $P_I$ will to some extent depend on the actual position for the vanadium atoms surrounding the sixfold axis. It has not been possible, however, to obtain any information on this question from electron density calculations. This may be taken to indicate that the disorder effect is small for $V_{III}$ and $P_I$. It is possible that two different sets of distances never occur in the structure. In all probability the mean values are a better representation of the actual situation. The complete set of distances is to be found in Table 1.

According to the model proposed both the non-equivalent phosphorus atoms have a trigonal prismatic environment with two ($P_I$) or three ($P_{II}$) additional vanadium atoms outside the rectangular faces. This type of coordination is typical for phosphorus in metal rich phosphides of transition elements.[4,7,8] $P_{II}$ has thus a complete tetrakaidecahedral environment, the geometry of which has been discussed at length by Rundqvist.[7] He has shown that if the radius ratio $R_P/R_{Me} > 0.79$ ($R_P/R_V = 0.81$), simple geometrical considerations indicate that the $Me-P$ distances should equal the radius sum, while the $Me-Me$ distances can be divided into two different sets, both larger than the radius sum. The distances between Me atoms forming the trigonal prims should be considerably longer than the radius sum, while distances between those and Me atoms outside the rectangular faces should be only slightly longer than the radius sum. This is in fact the case for the tetrakaidecahedral surrounding of $P_{II}$. The $V-P$ distances are close to the expected value of 2.46 Å, and for the two types of $V-V$ distances the mean values are 3.26 Å and 2.73 Å, respectively ($2R_V = 2.72$ Å). The crystal chemical indications are thus strongly in favour of the interpretation proposed for the disorder effect. The model requires that the positions for the vanadium atoms surrounding the sixfold axis depend on the height at which the $P_{II}$ atom is situated.

The coordination numbers for the metal atoms are 14, 15, and 17, respectively. Coordination numbers as high as 17 seem to exist only among phosphides with metal atoms from groups IV and V.

The same type of disorder has already been observed in $Th_7S_{12}$ by Zachariasen.[9] On account of the large difference in scattering power between thorium and sulphur he was not able to detect any splitting of the sulphur atom positions surrounding the sixfold axis. However, in order to obtain acceptable distances he calculated tentative coordinates for such a splitting. $V_{12}P_7$ is accordingly the anti-type to $Th_7S_{12}$. The structural relationships between $Th_7S_{12}$ and $Fe_2P$ have earlier been pointed out by Engström.[10]

As already has been mentioned, Lundström[3] observed a tendency for $V_{12}P_7$ to become ordered as revealed by a doubling of the $a$ axis. There are several possibilities for explaining this doubling as a result of ordering with or without a change in composition. A small homogeneity range was observed [9] for $Th_7S_{12}$, and it appears probable that there is a corresponding effect in $V_{12}P_7$. Attempts to solve the ordered structure in space group $P\bar{6}$ using intensities from Weissenberg films put at our disposal by Lundström were unsuccessful. Either the intensities were not accurate enough to distinguish the different possibilities or the crystal was only partially ordered. Further work on the ordered phase should be preceded by careful heat treatments and detailed investigations concerning the possible occurrence of a homogeneity range.

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