

Crystal Structure Refinements of the Ti_3P -Type Phosphides Nb_3P and Zr_3P

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The crystal structures of Nb_3P and Zr_3P have been determined and refined by single-crystal X-ray diffraction methods. Both compounds have the Ti_3P -type structure and the tetragonal unit cell dimensions are for Nb_3P : $a = 10.128 \text{ \AA}$; $c = 5.089 \text{ \AA}$ and for Zr_3P : $a = 10.799 \text{ \AA}$; $c = 5.354 \text{ \AA}$. The atomic arrangement in the two compounds is discussed and a comparison with related structures is made.

Recent investigations of the niobium phosphides¹ and zirconium phosphides² have led to the identification of the compounds Nb_3P and Zr_3P , both of which crystallize with the Ti_3P -type structure.^{3,4} Single-crystal structure determinations of Nb_3P and Zr_3P have now been made and the results are reported and briefly discussed below.

THE STRUCTURE OF Nb_3P

Nb_3P samples were prepared by arc-melting mixtures of niobium and NbP. Powder diffraction patterns were taken with $CuK\alpha_1$ and $CrK\alpha_1$ radiation in Guinier-Hägg type focussing cameras using silicon ($a = 5.43054 \text{ \AA}$) as the internal calibration standard. Cell dimensions were refined from the patterns using a least-squares computer program.⁵

A single-crystal fragment approximating to a parallelepiped with the dimensions $0.06 \times 0.08 \times 0.09 \text{ mm}$ was selected. By rotating the crystal about the b -axis, $h0l$ intensity data were recorded in a Weissenberg camera with zirconium-filtered $MoK\alpha$ radiation and the multiple-film technique, with thin iron foils interleaved between successive films. In a similar manner, $hk0$ intensity data were recorded after reorientating about the c -axis. The intensities were estimated visually by comparison with a calibrated intensity scale. The following calculations were performed on a CDC 3600 computer:

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correction for Lorentz and polarization factors, Fourier series summation and structure factor calculation,⁶ and least-squares refinements of positional parameters and temperature factors.⁷

The size of the crystal used for collection of the intensities should lead to considerable absorption effects, and an absorption correction of the data was therefore made.⁸ The linear absorption coefficient for Nb₃P was calculated from the tabulated values⁹ of the atomic absorption coefficients of Nb and P. Atomic scattering factors and anomalous dispersion factors were obtained from the values given in Ref. 9, using interpolated values where necessary.

The single-crystal data fully confirmed the proposed Ti₃P-type structure for Nb₃P. After some preliminary electron density calculations starting with atomic parameters taken from Ti₃P⁴ the structure was then refined by the least-squares method.⁷

Even after the absorption correction had been made, there were appreciable discrepancies between F_c and F_o for some of the strongest reflections, especially (400), (802), (170), (240), (330), (510), (550), (660) and (1,11,0). This was thought to be due to extinction effects, and these reflections, together with some very weak reflections, were therefore removed from the final refinements. The final discrepancy factor, $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, was 0.106 for the remaining 290 ($h0l$) and 407 ($hk0$) reflections. The weights assigned were set according to Cruickshank's formula,¹⁰ $w = 1/(A + |F_o| + C|F_o|^2)$, with the constants $A = 4.770$ and $C = 0.077$. Interatomic distances were calculated by using the positional parameters obtained from the last refinement.

The atomic parameters, individual temperature factors, and their standard deviations are listed in Table 1. Interatomic distances shorter than 4.0 Å are listed in Table 2. Standard deviations for Nb—Nb distances are calculated to be 0.002—0.003 Å, for Nb—P distances 0.006—0.007 Å and for P—P distances 0.010 Å.

THE STRUCTURE OF Zr₃P

A sample of Zr₃P prepared by the technique described in Ref. 3 was kindly provided by Dr. Lundström. A single-crystal with a triangular prismatic shape was selected. The dimensions of the triangular edges were 0.012, 0.016 and 0.024 mm and the length was 0.053 mm. By rotating the crystal about the c -axis, $hk0$ intensity data were recorded. After reorientation the crystal was rotated about the b -axis and the intensities of the $h0l$ reflections were

Table 1. Atomic parameters, isotropic temperature factors in (Å²) and standard deviations. Nb₃P: Ti₃P-type structure, space group $P4_2/n$ with origin at 1. $a = 10.1282 \pm 0.0004$ Å, $c = 5.0891 \pm 0.0003$ Å.

| Atom in 8(g) | x | $\sigma(x)$ | y | $\sigma(y)$ | z | $\sigma(z)$ | B | $\sigma(B)$ |
|-----------------|--------|-------------|--------|-------------|--------|-------------|-------|-------------|
| Nb I | 0.1634 | 0.0001 | 0.6529 | 0.0001 | 0.7256 | 0.0004 | 0.259 | 0.014 |
| Nb II | 0.1051 | 0.0001 | 0.2632 | 0.0001 | 0.5154 | 0.0004 | 0.287 | 0.015 |
| Nb III | 0.0590 | 0.0001 | 0.5368 | 0.0001 | 0.2406 | 0.0004 | 0.249 | 0.014 |
| P | 0.0425 | 0.0004 | 0.2748 | 0.0004 | 0.0185 | 0.0013 | 0.366 | 0.037 |

Table 2. Interatomic distances and their standard deviations (Å units) in Nb₃P. Distances shorter than 4 Å are listed.

| | | Dist. | S.d. | | | Dist. | S.d. |
|-------|------------|-------|------------|-----------|------------|-------|-------|
| Nb I | — 1 P | 2.569 | 0.005 | Nb III | — 1 P | 2.534 | 0.005 |
| | — 1 P | 2.592 | 0.005 | | — 1 P | 2.635 | 0.005 |
| | — 1 Nb I | 2.635 | 0.002 | | — 1 Nb III | 2.819 | 0.003 |
| | — 1 Nb III | 2.931 | 0.002 | | — 1 Nb II | 2.833 | 0.002 |
| | — 1 Nb III | 2.966 | 0.002 | | — 1 P | 2.888 | 0.004 |
| | — 1 Nb III | 3.061 | 0.003 | | — 1 Nb II | 2.903 | 0.002 |
| | — 2 Nb II | 3.100 | 0.002 | | — 1 Nb I | 2.931 | 0.002 |
| | — 4 Nb I | 3.154 | 0.001 | | — 1 Nb I | 2.966 | 0.002 |
| | — 1 Nb III | 3.182 | 0.002 | | — 1 Nb III | 2.999 | 0.003 |
| | — 1 Nb III | 3.189 | 0.002 | | — 1 Nb I | 3.061 | 0.003 |
| Nb II | — 1 P | 2.549 | 0.004 | — 1 Nb II | 3.140 | 0.002 | |
| | — 1 P | 2.607 | 0.007 | — 1 Nb I | 3.182 | 0.002 | |
| | — 1 P | 2.618 | 0.004 | — 1 Nb I | 3.189 | 0.002 | |
| | — 1 P | 2.643 | 0.007 | — 1 Nb II | 3.527 | 0.002 | |
| | — 1 Nb III | 2.833 | 0.002 | — 1 P | 3.666 | 0.004 | |
| | — 1 Nb III | 2.903 | 0.002 | P | — 1 Nb III | 2.534 | 0.005 |
| | — 1 Nb II | 2.946 | 0.002 | | — 1 Nb II | 2.549 | 0.004 |
| | — 2 Nb I | 3.100 | 0.002 | | — 1 Nb I | 2.569 | 0.005 |
| | — 1 Nb III | 3.140 | 0.002 | | — 1 Nb I | 2.592 | 0.005 |
| | — 2 Nb II | 3.175 | 0.003 | | — 1 Nb II | 2.607 | 0.007 |
| | — 2 Nb II | 3.405 | 0.003 | | — 1 Nb II | 2.618 | 0.004 |
| | — 1 Nb III | 3.527 | 0.002 | | — 1 Nb III | 2.635 | 0.005 |
| | | | | | — 1 Nb II | 2.643 | 0.007 |
| | | | | | — 1 Nb III | 2.888 | 0.004 |
| | | | — 1 Nb III | | 3.666 | 0.004 | |
| | | | — 2 P | 3.810 | 0.010 | | |

collected. A normal-incidence Weissenberg camera and the multiple film technique were used as in the case of Nb₃P. The exposure time with zirconium-filtered MoK α was longer than that in the previous case. This was due to the smaller crystal size.

The intensities of both the $hk0$ and $h0l$ sets of reflections were estimated visually using a calibrated scale in the normal way and the data were corrected for Lorentz and polarization factors. The F_o values for the corresponding reflections of Nb₃P and Zr₃P were then compared. It was found that they were relatively similar. A preliminary electron density calculation was thus thought unnecessary. On the basis of the atomic parameters obtained from Nb₃P, the refinement by the method of least-squares⁷ was started directly. The constants in Cruickshank's weighting formula were given the final values $A = 4.264$ and $C = 0.065$. The refinement converged rapidly and the final R -value for 149 F_o ($hk0$) and 116 F_o ($h0l$) was 0.097. The atomic parameters, individual temperature factors, and their standard deviations are listed in Table 3. Interatomic distances shorter than 4.0 Å are listed in Table 4. Standard deviations for Zr—Zr distances are calculated to be 0.002–0.006 Å, for Zr—P distances 0.007–0.011 Å and for P—P distances 0.014 Å. Tables of observed and calculated structure factors for Nb₃P and Zr₃P can be obtained from the Institute of Chemistry, Uppsala, on request.

Table 3. Atomic parameters, isotropic temperature factors in (\AA^2) and standard deviations. Zr_3P : Ti_3P -type structure, space group $P4_2/n$ with origin at $\bar{1}$. $a = 10.7994 \pm 0.0003 \text{ \AA}$, $c = 5.3545 \pm 0.0003 \text{ \AA}$.

| Atom in $8(g)$ | x | $\sigma(x)$ | y | $\sigma(y)$ | z | $\sigma(z)$ | B | $\sigma(B)$ |
|----------------|--------|-------------|--------|-------------|--------|-------------|-------|-------------|
| Zr I | 0.1649 | 0.0002 | 0.6423 | 0.0002 | 0.7131 | 0.0007 | 0.261 | 0.031 |
| Zr II | 0.1128 | 0.0002 | 0.2777 | 0.0002 | 0.5274 | 0.0007 | 0.267 | 0.031 |
| Zr III | 0.0707 | 0.0002 | 0.5346 | 0.0002 | 0.2367 | 0.0006 | 0.269 | 0.031 |
| P | 0.0443 | 0.0006 | 0.2910 | 0.0006 | 0.0328 | 0.0019 | 0.351 | 0.082 |

Table 4. Interatomic distances and their standard deviation (\AA units) in Zr_3P . Distances shorter than 4 \AA are listed.

| | | | | | | | |
|-------|------------|-------|-------|--------|------------|-------|-------|
| Zr I | — 1 P | 2.734 | 0.008 | Zr III | — 1 P | 2.678 | 0.008 |
| | — 1 P | 2.765 | 0.008 | | — 1 P | 2.813 | 0.008 |
| | — 1 Zr I | 2.965 | 0.005 | | — 1 P | 2.863 | 0.008 |
| | — 1 Zr III | 2.982 | 0.005 | | — 1 Zr I | 2.982 | 0.005 |
| | — 1 Zr III | 3.193 | 0.003 | | — 1 Zr III | 3.052 | 0.006 |
| | — 1 Zr III | 3.201 | 0.005 | | — 1 Zr II | 3.088 | 0.004 |
| | — 1 Zr II | 3.317 | 0.004 | | — 1 Zr II | 3.103 | 0.004 |
| | — 1 Zr III | 3.338 | 0.003 | | — 1 Zr I | 3.193 | 0.003 |
| | — 1 Zr II | 3.377 | 0.004 | | — 1 Zr I | 3.201 | 0.005 |
| | — 4 Zr I | 3.401 | 0.002 | | — 1 Zr II | 3.214 | 0.004 |
| | — 1 Zr III | 3.407 | 0.003 | | — 1 Zr III | 3.292 | 0.006 |
| | | | | | — 1 Zr I | 3.338 | 0.003 |
| Zr II | — 1 P | 2.739 | 0.007 | | — 1 Zr I | 3.407 | 0.003 |
| | — 1 P | 2.745 | 0.007 | | | | |
| | — 1 P | 2.754 | 0.011 | P | — 1 Zr III | 2.678 | 0.008 |
| | — 1 P | 2.809 | 0.011 | | — 1 Zr I | 2.734 | 0.008 |
| | — 1 Zr II | 3.022 | 0.005 | | — 1 Zr II | 2.739 | 0.007 |
| | — 1 Zr III | 3.088 | 0.004 | | — 1 Zr II | 2.745 | 0.007 |
| | — 1 Zr III | 3.103 | 0.004 | | — 1 Zr II | 2.754 | 0.011 |
| | — 2 Zr II | 3.201 | 0.006 | | — 1 Zr I | 2.765 | 0.008 |
| | — 1 Zr III | 2.214 | 0.004 | | — 1 Zr II | 2.809 | 0.011 |
| | — 1 Zr I | 3.317 | 0.004 | | — 1 Zr III | 2.813 | 0.008 |
| | — 1 Zr I | 3.377 | 0.004 | | — 1 Zr III | 2.863 | 0.008 |
| | — 2 Zr II | 3.660 | 0.006 | | — 2 P | 3.958 | 0.014 |

DISCUSSION

The Ti_3P -($\varepsilon_1(\text{Fe}-\text{P}-\text{B})$)-type structure has been thoroughly described elsewhere^{12,13} and only some brief comments are given here.

In the Ti_3P -type structure, the non metal atoms are surrounded by nine metal neighbours. According to unpublished results by Lundström and Snell,³ the phosphorus atoms in Ti_3P have nine titanium neighbours at distances ranging between 2.49 and 2.63 \AA . In Nb_3P however, each phosphorus atom has eight near niobium neighbours at distances between 2.53 and 2.64 \AA , while a ninth niobium atom is situated as far as 2.89 \AA from the central phosphorus atom. The difference in metal atom coordination about the phosphorus atom for Ti_3P and Nb_3P can hardly be explained by the size-factor effects, since the radius ratios for the two compounds are nearly equal (0.76 and 0.75, respectively). The tendency toward 8-coordination about phosphorus is even more pronounced in Mo_3P . In this compound, which crystallizes with the $\alpha\text{-V}_3\text{S}$ -type structure,¹⁴ the phosphorus atoms have eight molybdenum neighbours at distances ranging between 2.43 and 2.50 \AA .

Two additional molybdenum atoms are situated at distances of nearly 3.2 Å from the phosphorus atoms.

The packing of the metal atoms in Nb₃P is dense, each niobium atom having 11–12 niobium neighbours at an average distance of 3.09 Å, which exceeds the Goldschmidt metallic diameter for 12-coordination (2.94 Å) by 5 %. One Nb–Nb distance is particularly short, 2.63 Å. As mentioned in Ref. 14, the occurrence of this very short distance can be explained in terms of the geometrical packing effects discussed by Frank and Kasper.¹⁵

In Zr₃P, the average of the Zr–Zr distances shorter than 4.0 Å is 3.27 Å, which exceeds the Goldschmidt metal diameter (3.20 Å) by only 2 %. The nine shortest Zr–P distances range between 2.68 and 2.86 Å, and there is thus no tendency toward 8-coordination as observed for Nb₃P. It appears that the tendency toward a lower coordination number for phosphorus in Me₃P phosphides is connected with the group number of the transition metal rather than with the radius ratio. Thus, in both Ti₃P and Zr₃P there is a fairly even 9-coordination, in Nb₃P there are eight normal and one much longer Nb–P distances and in Mo₃P there are eight normal and two very long Mo–P distances.

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* Program available at the CDC 3600 computer in Uppsala.

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