# Crystal Structure Refinement of $\alpha$-$Ta_3P$

YVONNE ANDERSSON, SUPANICH PRAMATUS * and STIG RUNDQVIST

Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden

The crystal structure of $\alpha$-$Ta_3P$ has been refined from X-ray single crystal diffractometer data. $\alpha$-$Ta_3P$ crystallizes with the $Ti_3P$ type structure: space group $P4_2/n$ (No. 86), $a = 10.1550(3)$ Å, $c = 5.0128(2)$ Å; all atoms in $8g$, Ta(1) $x = 0.15898(7)$, $y = 0.65557(7)$, $z = 0.7435(2)$; Ta(2) $x = 0.10483(7)$, $y = 0.25374(7)$, $z = 0.5044(2)$; Ta(3) $x = 0.05257(7)$, $y = 0.54548(7)$, $z = 0.2474(2)$; P $x = 0.0420(5)$, $y = 0.2583(5)$, $z = 0.0064(16)$; (origin at $\bar{1}$). The transformation from low-temperature $\alpha$-$Ta_3P$ to high-temperature $\beta$-$Ta_3P$ occurs at a temperature between 2000 and 2100 °C.

In a previous paper[1] on the crystal structure of $\beta$-$Ta_3P$ it was mentioned that $Ta_3P$ occurs in two modifications: $\beta$-$Ta_3P$ crystallizing with the $\beta$-$V_3S$ type structure, and $\alpha$-$Ta_3P$ with the $Ti_3P$ type structure. In the present paper we give some further information on the $\alpha/\beta$ transformation and present the results of a single crystal structure refinement of $\alpha$-$Ta_3P$.

## EXPERIMENTAL DETAILS AND RESULTS

*Synthetic and phase-analytical work.* As mentioned earlier,[2] TaP and $TaP_2$ are the only phases formed by reaction between tantalum and phosphorus under the conditions of the ordinary silica tube synthetic technique. At higher temperatures, however, tantalum and TaP react to form a number of intermediate phases.[2,3] $\beta$-$Ta_3P$, crystallizing with the $\beta$-$V_3S$ type structure, is obtained by arc melting appropriate mixtures of tantalum and TaP on a water-cooled copper hearth.[1] If this material is annealed at temperatures not too far below the melting-point, $\alpha$-$Ta_3P$, crystallizing with the $Ti_3P$ type structure, is rapidly formed.

Since a detailed investigation of the Ta-P equilibrium diagram presents formidable experimental difficulties, we restricted the present studies to a cursory X-ray diffraction examination of some alloys, which has been subjected to different heat-treatments.

X-Ray powder patterns were recorded in Hägg-Guinier-type focussing cameras (Philips XDC-700) using Cu$K\alpha_1$ or Cr$K\alpha_1$ radiation, and zone-refined silicon ($a = 5.431065$ Å)[4] as internal calibration standard. Powder diffraction data for the two forms of $Ta_3P$ are given in Table 1. The unit cell dimensions for both forms are almost equal, for $\alpha$-$Ta_3P$:

*Table 1.* Powder diffraction data for $\alpha$-$Ta_3P$ and $\beta$-$Ta_3P$. Philips XDC-700 camera, Cu$K\alpha_1$ radiation, intensities measured on SAAB automatic film scanner.

| | | $\alpha$-$Ta_3P$ | | $\beta$-$Ta_3P$ | | | | $\alpha$-$Ta_3P$ | | $\beta$-$Ta_3P$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| hkl | $d_o$ (Å) | $I_o$ | $I_c$ | $I_o$ | $I_c$ | hkl | $d_o$ (Å) | $I_o$ | $I_c$ | $I_o$ | $I_c$ |
| 110 | 7.173 | 4 | 3 | 3 | 2 | 331 | | 0 | 0 | - | - |
| 200 | | 0 | 0 | 0 | 3 | 421 | 2.069 | 8 | 8 | 4 | 4 |
| 101 | | 0 | 0 | 0 | 1 | 222 | 2.056 | 38 | 34 | 31 | 26 |
| 111 | | 0 | 0 | - | - | 302 | | 0 | 0 | 0 | 0 |
| 220 | 3.589 | 6 | 7 | 7 | 5 | 510 | 1.992 | 14 | 16 | 12 | 10 |
| 201 | 3.567 | 16 | 16 | 8 | 7 | 312 | 1.976 | 14 | 15 | 13 | 21 |
| 211 | | 0 | 0 | 1 | 6 | 431 | | 0 | 1 | 0 | 1 |
| 310 | 3.211 | 2 | 2 | 1 | 0 | 501 | | 0 | 0 | 0 | 0 |
| 221 | | 0 | 0 | - | - | 322 | | 0 | 0 | 0 | 0 |
| 301 | | 0 | 0 | 0 | 0 | 511 | 1.851 | 6 | 8 | 2 | 4 |
| 311 | 2.704 | 33 | 37 | 20 | 16 | 440 | | 0 | 1 | 0 | 0 |
| 400 | | 0 | 1 | 0 | 2 | 402 | 1.784 | 4 | 6 | 4 | 1 |
| 002 | 2.506 | 4 | 6 | 4 | 4 | 521 | | 0 | 2 | 0 | 1 |
| 321 | 2.456 | 100 | 100 | 89 | 100 | 412 | | 0 | 0 | 0 | 0 |
| 102 | | 0 | 0 | 0 | 0 | 530 | | 0 | 0 | 0 | 1 |
| 330 | 2.394 | 45 | 43 | 35 | 34 | 332 | 1.731 | 2 | 3 | 1 | 2 |
| 112 | 2.367 | 67 | 61 | 94[a] | 48 | 600 | | 0 | 1 | 0 | 0 |
| 420 | 2.271 | 35 | 35 | 39 | 30 | 441 | | 0 | 0 | 0 | 0 |
| 401 | 2.265 | 24 | 22 | | 9 | 422 | | 0 | 0 | 0 | 0 |
| 202 | 2.248 | 19 | 17 | 18 | 8 | 103 | | 0 | 0 | 0 | 0 |
| 411 | 2.211 | 82 | 87 | 64 | 62 | 531 | 1.645 | 2 | 3 | 0 | 1 |
| 212 | | 0 | 0 | 0 | 2 | | | | | | |

a) overlapped by Ta.

* On leave from the Faculty of Science, Chulalongkorn University, Bangkok 5, Thailand.

$a = 10.1550(3)$ Å; $c = 5.0128(2)$ Å and for $\beta$-$Ta_3P$: $a = 10.1542(4)$ Å; $c = 5.0137(3)$ Å, and remain unchanged within experimental error in alloys of different compositions. As seen from Table 1 there are only minor differences in intensity between corresponding lines, the most prominent difference being exhibited by the pair (220)/(201). The great similarities between the powder patterns made it very difficult to determine the relative proportions of the two $Ta_3P$ forms in samples containing both phases simultaneously. Examination of ground and polished specimens by optical microscopy provided no additional advantage from the phase-analytical point of view.

The heat-treatments of the alloys were made in an induction furnace under a protective atmosphere of argon. Since molten Ta-P alloys were found to attack conventional crucible materials severely, heating was performed using a water-cooled current concentrator specially designed for levitation melting. The temperatures of the samples were measured by optical pyrometry.

The melting-point of $Ta_3P$ was determined to be close to 2100 °C. After rapid quenching the solidified melt was found to consist of $\beta$-$Ta_3P$, as judged from the X-ray diffraction films. When $\beta$-$Ta_3P$ was heated at 1100 °C for three days in an evacuated and sealed silica tube, the films gave indications of an inchoate transformation, while heating at 1900 °C for 20 min in the induction furnace produced complete conversion into $\alpha$-$Ta_3P$. In an attempt to locate the transformation temperature more accurately, a sample was levitated for several minutes in such a way that the lower part was molten and the upper part solid. The alloy was then quenched rapidly. The part, which had been molten, was found to consist of $\beta$-$Ta_3P$, while the part, which had remained solid, was found to consist of $\alpha$-$Ta_3P$. The temperature of the solid $\alpha$-$Ta_3P$ part was about 2000 °C during the heating.

The results of our experiments indicate that the transformation between high-temperature $\beta$-$Ta_3P$ and low-temperature $\alpha$-$Ta_3P$ occurs at some temperature less than 100 °C below the melting-point of $\beta$-$Ta_3P$. Whether $\beta$-$Ta_3P$ melts congruently or not remains to be determined by a complete thermal analysis of the Ta-P system.

*X-Ray single crystal work.* The intensities were recorded on a Stoe four-circle diffractometer with a graphite monochromator using Mo$K\alpha$ radiation. The measurements were made using the $\omega - 2\theta$ step scan technique, to a maximum in $2\theta$ of 70°. Totally 1418 reflexions were recorded, of these 1136 were nonequivalent. The intensities were corrected for absorption using the Gaussian grid method, and a calculated linear absorption coefficient of 1254 $cm^{-1}$. The transmissions varied between 0.04 and 0.11. Equivalent reflexions were averaged and the crystal structure was refined by the least-squares method in the same manner as described in Ref. 1.

For the 1133 reflexions refined the following agreement factors were obtained: $R(F^2) = 0.093$, $R(F) = 0.077$ and $R_w(F^2) = 0.124$. The final structure data obtained are presented in Table 2. Calculated interatomic distances are given in Table 3. A table of observed and calculated structure factors can be obtained from the authors on request.

## DISCUSSION OF THE RESULTS

The $Ti_3P$ type structure, and its relationships to the $Fe_3P$, $\alpha$-$V_3S$ and $\beta$-$V_3S$ types, have been described and discussed at length earlier.[5-9] Here, we restrict the discussion to a few observations on $Ti_3P$-type $\alpha$-$Ta_3P$ and $\beta$-$V_3S$-type $\beta$-$Ta_3P$.

These two structures are indeed very similar, and movements of the atoms of the order of tenths of an Ångström are sufficient to transform one structure into the other. One might even suspect that the $\beta$ crystals actually are polysynthetic twins of the $\alpha$ form, but the powder diffraction data (Table 1) and the reasonable values obtained for the temperature factors of the atoms in the $\beta$ structure[1] definitely exclude this possibility. Regarding the

*Table 2.* Structure data for $\alpha$-$Ta_3P$, including isotropic temperature factors, space group $P4_2/n$ (No. 86), origin at $\bar{1}$. $a = 10.1550(3)$ Å; $c = 5.0128(2)$ Å.

| Atom | Position | $x$ | $y$ | $z$ | $B$ |
|---|---|---|---|---|---|
| Ta(1) | 8$g$ | 0.15898(7) | 0.65557(7) | 0.7435(2) | 0.38(1) |
| Ta(2) | 8$g$ | 0.10483(7) | 0.25374(7) | 0.5044(2) | 0.40(1) |
| Ta(3) | 8$g$ | 0.05257(7) | 0.54548(7) | 0.2474(2) | 0.41(1) |
| P | 8$g$ | 0.0420(5) | 0.2583(5) | 0.0064(16) | 0.64(6) |

*Table 3.* Interatomic distances in α-$Ta_3P$. Distances shorter than 3.5 Å are listed.

| | | | |
|---|---|---|---|
| Ta(1) – P | 2.550(6) | Ta(3) – P | 2.552(6) |
| – P | 2.572(6) | – P | 2.584(6) |
| – Ta(1) | 2.664(1) | – Ta(2) | 2.845(1) |
| – Ta(3) | 2.933(1) | – Ta(3) | 2.854(2) |
| – Ta(3) | 2.964(1) | – Ta(2) | 2.874(1) |
| – Ta(3) | 2.967(1) | – Ta(3) | 2.900(2) |
| – Ta(2) | 3.085(1) | – Ta(1) | 2.933(1) |
| – Ta(2) | 3.093(1) | – Ta(1) | 2.964(1) |
| – 4Ta(1) | 3.136(1) | – Ta(1) | 2.967(1) |
| – Ta(3) | 3.178(1) | – P | 3.159(5) |
| – Ta(3) | 3.180(1) | – Ta(1) | 3.178(1) |
| | | – Ta(1) | 3.180(1) |
| Ta(2) – P | 2.561(5) | – Ta(2) | 3.274(1) |
| – P | 2.577(8) | – Ta(2) | 3.395(1) |
| – P | 2.595(5) | – P | 3.414(5) |
| – P | 2.597(8) | | |
| – Ta(3) | 2.845(1) | P – Ta(1) | 2.550(6) |
| – Ta(3) | 2.874(1) | – Ta(3) | 2.552(6) |
| – Ta(2) | 2.950(1) | – Ta(2) | 2.561(5) |
| – Ta(1) | 3.085(1) | – Ta(1) | 2.572(6) |
| – Ta(1) | 3.093(1) | – Ta(2) | 2.577(8) |
| – 2Ta(2) | 3.227(2) | – Ta(3) | 2.584(6) |
| – Ta(3) | 3.274(1) | – Ta(2) | 2.595(5) |
| – 2Ta(2) | 3.295(2) | – Ta(2) | 2.597(8) |
| – Ta(3) | 3.395(1) | – Ta(3) | 3.159(5) |
| | | – Ta(3) | 3.414(5) |

nature of the α/β transition, the structural similarities indicate a diffusion-less mechanism. The available data provide no definite information on this point.

The major structural difference between a β-$V_3S$ type compound and a typical representative of the $Ti_3P$ type structure lies in the nonmetal atom coordination. The phosphorus atoms in β-$Ta_3P$ have eight near metal atom neighbours. Two additional metal atoms are situated at considerably larger distances. In $Ti_3P$, the phosphorus atoms have nine near metal neighbours at almost the same distances. A tendency to eight-coordination for the non-metal atoms in $Ti_3P$-type compounds has been observed for $Nb_3P$ [10] and $V_3P$,[11] and this tendency is most pronounced for α-$Ta_3P$. The members in the series $V_3P$, $Nb_3P$, α-$Ta_3P$ thus exhibit a gradual structural change towards the ultimate β-$V_3S$-type atomic arrangement. This and other structural features will be discussed in a more extensive survey of coordination and bonding in $Fe_3P$, $Ti_3P$, α-$V_3S$ and β-$V_3S$ type compounds to be published later.

*Acknowledgements.* Financial support from the Swedish Natural Science Research Council is gratefully acknowledged. S.P. thanks the International Seminars at the University of Uppsala and the Swedish International Development Authority (SIDA) for a travel grant.

## REFERENCES

1. Phavanantha, P., Pontchour, C.-O., Pramatus, S., Andersson, Y. and Rundqvist, S. *Acta Chem. Scand. A 32* (1978) 515.
2. Rundqvist, S. *Nature (London) 211* (1966) 847.
3. Björkegren, J. and Andersson, Y. *New Phases in the Ta–P System,* Institute of Chemistry, University of Uppsala, Uppsala 1976, UUIC-B18-53.
4. Deslattes, R. D. and Henins, A. *Phys. Rev. Lett. 31* (1973) 972.
5. Rundqvist, S. *Acta Chem. Scand. 16* (1962) 1.
6. Rossteutscher, W. and Schubert, K. *Z. Metallkd. 56* (1965) 813.
7. Lundström, T. and Snell, P. O. *Acta Chem. Scand. 21* (1967) 1343.
8. Rundqvist, S. *Ark. Kemi 20* (1962) 67.
9. Lundström, T. *Ark. Kemi 31* (1969) 250.
10. Nawapong, P. C. *Acta Chem. Scand. 20* (1966) 2737.
11. Jawad, H., Lundström, T. and Rundqvist, S. *Phys. Scr. 3* (1971) 43.

Received May 29, 1978.