

On the Phase Transformation in Ta₃P

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In an earlier paper, [*Acta Chem. Scand. A* 32 (1978) 515], it was suggested that Ta₃P transforms from a high temperature modification β-Ta₃P, crystallizing with the β-V₃S-type structure (space group $P4_2/nbc$), into a low temperature modification α-Ta₃P, crystallizing with the Ti₃P-type structure ($P4_2/n$). A reinvestigation of the X-ray powder patterns of Ta₃P revealed that the reflections with an odd value of $h+k+l$ were broader and weaker in β-Ta₃P compared to α-Ta₃P. This observation indicates that β-Ta₃P could in fact be a transitional structure, with regions of a body-centered high temperature modification, crystallizing with either the Fe₃P- (space group $I4$) or the α-V₃S-type structure ($I42m$), and regions of the Ti₃P-type low temperature modification occurring simultaneously within a common coherent lattice. An estimation of the relative amounts of the high and low temperature modifications in the transitional structure was made using a Rietveld-type full profile analysis of Guinier-Hägg X-ray powder diffraction film intensity data. Analysis of the line broadening of the reflections with an odd value of $h+k+l$ yielded a second estimate of the proportions of the two modifications. The good agreement between the two independently determined results supports the proposed existence of a transitional structure in Ta₃P, corresponding to the phase formerly denoted by β-Ta₃P.

A phase transformation in Ta₃P was reported in Ref. 1. The transformation temperature was estimated to be less than 100 °C below the melting point of Ta₃P which is close to 2100 °C.

On the basis of single-crystal X-ray data obtained by the Weissenberg method, which indicated a primitive tetragonal symmetry and Laue symmetry $4/mmm$, it was suggested¹ that the high temperature modification (β-Ta₃P) crys-

tallizes with the β-V₃S-type structure [space group $P4_2/nbc$ (No. 133)]. A crystal structure refinement based on X-ray diffractometer data converged in a satisfactory manner with normal values of the isotropic temperature factors but with somewhat high R values (e.g. $R_w(F^2) = 0.224$). The low temperature modification (α-Ta₃P) crystallizes with the Ti₃P-type structure [space group $P4_2/n$ (No. 86)]. A single-crystal structure refinement of α-Ta₃P is reported in Ref. 2.

The unit cell dimensions, determined from X-ray powder diffraction data, are almost equal for the two forms; for β-Ta₃P: $a = 10.1542(4)$ Å, $c = 5.0137(3)$ Å and for α-Ta₃P: $a = 10.1550(3)$ Å, $c = 5.0128(2)$ Å.²

The proposed structures of the two modifications are very similar, and movements of the atoms of the order of some hundredths of an Ångström are sufficient to convert one structure into the other. In view of this, the transformation from the high to the low temperature form should occur so readily that it is surprising that the high temperature form can be retained by quenching. Furthermore, a heat treatment at 1100 °C for three days was not sufficient to complete the transformation from β-Ta₃P into α-Ta₃P.²

Recent studies of the phase transformations in Ta₃Ge^{3,4} and V₃S⁵ have revealed the occurrence of a novel type of transition between structures belonging to the Fe₃P–Ti₃P–V₃S family. The X-ray data did not show a separation into two distinct phases during the transformation but a continuous change in the unit cell parameters from the values of the body-centered high temperature modification to the values of the primitive low temperature modification. This observation suggested the existence of a tran-

sitional structure with regions of the high temperature modification alternating with regions of the low temperature modification within a common coherent lattice. At a stage of the transformation when the number and extent of the regions of the low temperature modification have become sufficiently large, reflections with an odd value of $h+k+l$ appeared in the diffraction patterns. The intensities and halfwidths of this category of reflections varied considerably. With a decreasing amount of the high temperature modification in the transitional structure the intensities and halfwidths of these reflections increased and decreased, respectively. With this new information at hand it seemed worthwhile to re-examine the phase transformation in Ta_3P in greater detail.

The X-ray powder diffraction films of Ta_3P showed that reflections with an odd value of $h+k+l$ were broader and weaker in β - Ta_3P compared to α - Ta_3P . The observed differences in intensity between corresponding reflections for β - Ta_3P and α - Ta_3P as reported earlier² cannot be explained by the difference in structure type. In fact, powder diffraction data calculated on the basis of positional parameters taken from the single-crystal structure refinements^{1,2} differ insignificantly between the β - V_3S - and the Ti_3P -type structures of Ta_3P . (Due to an input error in the computer program used, the calculated powder diffraction intensities for β - Ta_3P as published in Table 1 of Ref. 2 are incorrect. Values calculated in the correct manner are almost identical to the calculated intensities for α - Ta_3P listed in the same table.)

The appearance of the broader and weaker reflections with an odd value of $h+k+l$ suggests, in analogy with the Ta_3Ge and V_3S transformations, that β - Ta_3P might be regarded as a transitional structure with regions of a body-centered high temperature form, in the following denoted by γ - Ta_3P , crystallizing with either the Fe_3P - or α - V_3S -type structure, alternating with regions of the low temperature modification α - Ta_3P . Whether γ - Ta_3P really is an equilibrium phase in the Ta - P system is not known. The transitional structure may be an intermediate step in the transformation from pure γ - Ta_3P into α - Ta_3P or due to stacking faults formed during the solidification of Ta_3P .

EXPERIMENTAL

The preparation of the samples of Ta_3P was described in Ref. 1. The intensity data for the Rietveld-type full profile analysis⁶ and the line broadening analysis were obtained by scanning X-ray powder diffraction films using a SAAB automatic film scanner^{7,8} connected to a Nord 100 computer. The films used were recorded using a Philips XDC 1000 or 700 Guinier-Hägg type focusing camera with $CuK\alpha_1$ (Rietveld analysis) and $CrK\alpha_1$ radiation (line broadening analysis), respectively.

The sample contained small amounts of tantalum metal. The tantalum reflections were removed from the intensity data without serious loss of intensity information for Ta_3P .

The halfwidths of certain reflections were obtained by plotting the intensity values obtained from the film scan against 2θ and measuring the full widths at half-maximum intensity in the graphs. The halfwidth for a reflection with an odd value of $h+k+l$ was corrected for instrumental broadening and particle size effects by simply subtracting the halfwidth of a neighbouring reflection with an even value of $h+k+l$.

STRUCTURE REFINEMENT

The details in the determination of the relative amounts of the high and low temperature forms in the transitional structure of Ta_3P using the Rietveld method are identical to the description given for the analogous determination in Ta_3Ge in Ref. 4. The refinement was performed assuming that the γ - Ta_3P -type regions have the Fe_3P -type structure.

The following parameters were refined: the profile parameters, which comprise the halfwidth (six parameters, three parameters for reflections with an even value of $h+k+l$ and three parameters for reflections with an odd value of $h+k+l$), the asymmetry (two parameters) and the 2θ zero point (one parameter), and the structure parameters which comprise the overall scale factor (one parameter), the lattice parameters (two parameters), the positional parameters (nine parameters, since only the tantalum positions were refined), the occupancy (one parameter) and the overall temperature factor (one parameter). Scattering factors corrected for the real part of the anomalous dispersion were interpolated from values given in the *International Tables for X-Ray Crystallography*.⁹ No

Table 1. Structure data for the transitional structure, corresponding to the phase formerly denoted by β -Ta₃P.^a

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>n_p</i>	<i>B</i> (Å ²)
Ta(1)	1598(6)	6542(6)	7458(17)		} 1.29(6)
Ta(2)	1053(3)	2539(13)	4873(12)	0.96(1)	
Ta(3)	0521(7)	5449(6)	2363(12)		
P ^b	0420	2583	0064	0.96(1)	

^a Space group $P4_2/n$ (No. 86); all atoms in position 8g; origin at $\bar{1}$. Positional parameters $\times 10^4$, standard deviations in parentheses. ^b Positional parameters from Ref. 2.

attempt was made to correct for absorption. The overall temperature factor obtained therefore includes the combined effects of thermal vibration and absorption.

Positional parameters from the α -Ta₃P structure² were used as starting values in the refinement. The final residual values obtained were; for the reflections with an even value of $h+k+l$ (for definitions see Ref. 10): $R_I=0.092$ and $R_F=0.071$, and for the reflections with an odd value of $h+k+l$: $R_I=0.149$ and $R_F=0.139$. The *R* values for the total profile (197 reflections) were $R_p=0.180$ and $R_{wp}=0.259$.

Structure data are presented in Table 1. The *z*-coordinates of the Ta(2) and Ta(3) atoms obtained using the Rietveld method differ by 14 and 9 standard deviations, respectively, from those of α -Ta₃P obtained using the single-crystal method.² The differences between the other positional parameters are within three standard deviations.

The occupancy parameter n_p is equivalent to the relative number of unit cells of α -Ta₃P in the transitional structure, while $1-n_p=N$ is thus equal to the relative number of unit cells of the high temperature modification γ -Ta₃P.

An identical refinement of a sample of pure α -Ta₃P [no broadening of the reflections with odd values of $h+k+l$ was visible in the X-ray powder pattern] resulted in an n_p value of 1.01(2), the estimated standard deviation in parenthesis.

RESULTS AND DISCUSSION

The transitional structure proposed for Ta₃P is very similar to the transitional structures in Ta₃Ge and V₃S. A detailed description of the transitional structure in Ta₃Ge was given in Ref. 4. The regions of γ -Ta₃P type in the transitional

structure of Ta₃P can adopt either the Fe₃P- or α -V₃S-type structure without affecting the main features of the discussion below.

The halfwidths of the reflections with an odd value of $h+k+l$ depend on the number and extensions of the regions of γ -Ta₃P in the transitional structure. Only γ -Ta₃P-type regions with an extension of ma in a direction parallel to an *a* axis, where m is an integer and *a* is equal to the length of the *a* axis, contribute to the broadening of the reflections with an odd value of $h+k+l$. This is because the atoms in one of the regions of α -Ta₃P surrounding such a region of γ -Ta₃P are shifted by approximately $(a+a+c)/2$ from the positions corresponding to the other region.⁴

If the extension of the region of γ -Ta₃P is equal to $(m+1/2)a$ in a direction parallel to an *a* axis, there are no shifts in the atomic positions of the surrounding regions of α -Ta₃P with respect to each other. This type of region will thus not contribute to the line broadening of the reflections with odd values of $h+k+l$.

The relation between the integral breadth of the reflections with an odd value of $h+k+l$ and the relative number γ of regions of the high temperature modification with an extension of ma was given in Ref. 4,

$$\beta(2\theta) = - \frac{\lambda(|h|+|k|) \ln(1-2\gamma)}{2a \cos\theta (h^2+k^2+(ac)^2)^{1/2}} \quad (1)$$

where $\beta(2\theta)$ is the integral breadth in radians, λ is the wavelength of the radiation used, *a* and *c* are the lengths of the *a* and *c* axes, respectively, θ is the diffraction angle (in degrees) for the hkl reflection. The values of γ calculated using eqn. (1) for some reflections are presented in Table 2.

The line broadening in powder patterns from different parts of the same sample varies. This

Table 2. The breadth of some reflections with an odd value of $h+k+l$ and the corresponding γ values calculated using eqn. (1) for a sample of the transitional structure (β -Ta₃P) and α -Ta₃P.

Sample and heat treatment		$h k l$	201 ^d	311	412 ^d	511	
β -Ta ₃ P ^{a,b} arc-melted		$\beta(\text{rad})^c$	0.0016	0.0021	0.0022	0.0032	
		γ	0.009	0.008	0.008	0.010	
		$\bar{\gamma}^e$					0.009(1)
β -Ta ₃ P ^a arc-melted		$\beta(\text{rad})^c$	0.0021	0.0046	0.0074	0.0057	
		γ	0.012	0.017	0.022	0.018	
		$\bar{\gamma}^e$					0.017(4)
α -Ta ₃ P 1700 °C 20 min		$\beta(\text{rad})^c$	— ^f	0.0	— ^f	0.0001	
		γ	—	—	—	0.0005	

^a Samples from different parts of the same master alloy. ^b Sample used in the Rietveld analysis. ^c The halfwidths corrected for instrumental broadening and particle size effects. ^d Reflection overlapped by a reflection with an even value of $h+k+l$. The halfwidth of the reflection with an odd value of $h+k+l$ was obtained by resolving the reflections by means of a least-squares method assuming an asymmetric Lorentzian peak shape. ^e Arithmetic mean value with standard deviation in parenthesis. ^f Reflection not measured.

variation indicates that the amount of γ -Ta₃P varies between different parts of the same sample which, for instance, might be due to local differences in the cooling rate.

Because of the low amount of the γ -Ta₃P-type regions in the transitional structure, around 4 % according to the Rietveld analysis (Table 1), it is reasonable to assume that the regions of γ -Ta₃P type are very narrow and m is of the order of unity. Furthermore, by assuming that γ -Ta₃P occurs with equal probability in regions with an extension of either a or $3a/2$ in directions parallel to an a axis, it is possible to estimate the fraction γ of regions of extension a using the value of $N(=1-n_p)$ as obtained from the Rietveld analysis:

$\gamma + 3\gamma/2 = N$; $\gamma = 0.4N = 0.4 \cdot 0.04 = 0.016(5)$, the estimated standard deviation in parenthesis. This value should thus be compared to 0.009(1) as obtained from the line broadening analysis (Table 2).

The close agreement between the two independently determined results supports the view that the β -Ta₃P modification is, in fact, a transitional structure with regions of α -Ta₃P alternating with regions of the body centered γ -Ta₃P within a common coherent lattice.

No significant broadening of reflections with odd values of $h+k+l$ was observed in α -Ta₃P (Table 2), which is in accordance with the value of $N = -0.01(2)$ as obtained using the Rietveld method.

Weissenberg films showed that single-crystals of β -Ta₃P apparently possessed the Laue symmetry $4/mmm$.¹ Single-crystals with this symmetry seem to occur frequently in these samples since they have been isolated both at our institute in Uppsala and by the X-Ray Crystallography Group at Chulalongkorn University in Bangkok, Thailand. The appearance of the Laue symmetry $4/mmm$ of the transitional structure, consisting primarily (96 %) of regions with the Ti₃P-type structure, which possesses the lower Laue symmetry $4/m$, may seem rather surprising. However, this observation may be explained considering the regions of γ -Ta₃P type with an extension of a . As was mentioned above, the atomic positions in one of the regions of α -Ta₃P surrounding such a region of γ -Ta₃P are shifted by approximately $(a+a+c)/2$ from the positions corresponding to the other region. The relation between the two regions of α -Ta₃P can also be described as a rotation of one of the regions by 90° around the tetragonal axis with respect to the other region. In reciprocal space, this rotation means that the $(hkl)_1$ reflections will be overlapped by the $(khl)_2$ reflections (the subscripts 1 and 2 are used to distinguish between the reflections scattered from the two different regions of α -Ta₃P). Assuming that the regions of γ -Ta₃P, with an extension of a , are distributed randomly over the transitional structure, the amount of the two types of α -Ta₃P regions will be almost equal.

Accordingly, on a Weissenberg film, $I_{hkl} = I_{(hkl)_1} + I_{(hkl)_2}$ will thus be equal to $I_{(hkl)} = I_{(hkl)_1} + I_{(hkl)_2}$ and the transitional structure will appear to possess the Laue symmetry $4/mmm$, although both its constituents possess the lower Laue symmetry $4/m$.

The Laue symmetry $4/mmm$ of the transitional structure can possibly be explained in another way. The actual structure of the regions of γ -Ta₃P in the transitional structure is not known and, as was mentioned above, they could adopt the α -V₃S structure type. The free energy of the transitional structure may then be lowered if the low temperature modification adopts the β -V₃S-type structure instead of the Ti₃P structure type. The Laue symmetry $4/mmm$ of the transitional structure is then easily understood, since both α -V₃S and β -V₃S possess the Laue symmetry $4/mmm$.¹¹ A β -V₃S-type structure of the low temperature modification may thus be stabilized by the α -V₃S-type structure of the regions of γ -Ta₃P. However, in the instance when all regions of γ -Ta₃P have transformed into the low temperature modification, all atoms can shift over into the Ti₃P-type structure and the Laue symmetry $4/m$ is then observed.

The alternative model of the transitional structure consisting of regions adopting the α -V₃S and β -V₃S structure types has also been refined using the Rietveld method but no significant improvement was obtained.

There is no increase in the c/a ratio on passing from the transitional structure into α -Ta₃P although the c/a ratio increases with an increasing degree of transformation in both the Ta₃Ge and V₃S transformations.^{3,5} This difference between the transformation in Ta₃P and the Ta₃Ge and V₃S transformations may simply be due to the specific effect of the relative amounts of the high and low temperature modifications on the cell parameters of the transitional structure in Ta₃P. In the Ta₃Ge transformation the relative change in the cell dimensions of the transitional structure decreased with an increasing degree of transformation.⁴ This indicates that when the last regions of the high temperature modification disappear in the transitional structure of Ta₃P, the effect on the cell dimensions may be too small to be observed.

The transformation in Ta₃P, whether it is from pure γ -Ta₃P into pure α -Ta₃P or from the transitional structure into α -Ta₃P, is very similar

to the transformations in Ta₃Ge and V₃S, and the Ta₃P transformation may thus occur through a similar shear type mechanism.^{3,5} The more extensive atomic movements needed in this type of transformation compared to those involved in a transition from the β -V₃S- into the Ti₃P-type structure explain the low rate of transformation observed in annealing experiments of β -Ta₃P.

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