#### STACKING DISORDER IN NbP, TaP, NbAs AND TaAs

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#### Summary

Stacking disorder in the monophosphides and arsenides of niobium and tantalum was studied using X-ray diffraction techniques. Special attention was paid to the effects of the composition and the heat treatment of the samples. A metastable WC-type structure is formed during the early stages of the reaction while the sample is heating up. As the temperature increases, the metastable WC-type structure partially transforms into a stable NbAs-type structure, resulting in a disordered structure comprising variable amounts of the WC- and NbAs-type structures which coexist within a common coherent lattice. This transformation appears to be constrained by the presence of the metal phase so that the completeness of the transformation, and thus the amount of stacking disorder, varies with the sample composition.

#### 1. Introduction

NbP, TaP and TaAs crystallize in the NbAs-type structure [1] (space group,  $I4_1md$  (no. 109)). Boller and Parthé [1] reported a composition dependence of the X-ray powder diffraction patterns of NbP. The half-widths of all reflections with odd-*l* indices increased continuously while those of reflections with even-*l* indices were unaffected when the composition of the samples changed from NbP to Nb<sub>55</sub>P<sub>45</sub>. The line broadening was accompanied by a decrease in the integrated intensities of reflections with odd-*l* indices. Similar features have also been reported for TaP [1] and TaAs [2].

The variations in the linewidths and the integrated intensities of reflections with odd-*l* indices were accounted for by a model involving disordering along  $(001)_{NbAs}$  [1] in which regions of the NbAs- and WC-type structures [3] alternate. It was proposed that the apparent composition dependence of the amount of disorder was due to a homogeneity range for NbP which was estimated to extend from NbP to Nb<sub>55</sub>P<sub>45</sub>. The phosphorus deficiency was reported to be accompanied by a slight expansion of the *c* axis by 0.2%, while the *a* axis remained constant. However, a significant decrease in cell volume would be expected if as many as 20% of the phosphorus atoms were removed [4].

Similar variations in the linewidths and integrated intensities of a particular subset of X-ray powder diffraction reflections accompanied by variations in the unit cell dimensions have recently been observed during studies of the phase transformations in Ta<sub>3</sub>Ge [5, 6], Ta<sub>3</sub>P [7] and V<sub>3</sub>S [8]. Therefore it seemed worthwhile to re-examine the disorder phenomena in the monophosphides and arsenides of niobium and tantalum.

#### 2. Experimental details

The samples were prepared by heating mixtures of metal powder (particle size, less than  $45 \ \mu m$ ) with about 0.09 g of red phosphorus or arsenic in evacuated silica tubes. The metals (Highways International) had a nominal purity of 99.9% and the phosphorus (MCP Electronic Ltd.) and arsenic (Boliden Metal Ltd.) had nominal purities of 99.999%. To avoid the risk of explosion, the silica tubes were placed in a resistance furnace at room temperature and the temperature was gradually increased to its final value over a period of 12 h. The temperature was measured using a Pt-(Pt-10%Rh) thermocouple. The heating was terminated by cutting off the power supply to the furnace, and the samples were left in the furnace to cool slowly. In one series of experiments samples of NbP were taken out of the furnace at various temperatures during heating and were quenched with water. Subsequent annealing was performed by placing the samples directly in the hot furnace at the chosen annealing temperature.

The samples were examined by X-ray powder diffraction methods using a Philips XDC 1000 Guinier-Hägg focusing camera with Cu K $\alpha_1$  radiation. The unit cell dimensions were refined using the least-squares program CELNE [9], and silicon (a = 5.431065 Å [10]) was employed as an internal calibration standard.

The intensity data used in the line broadening analysis and the Rietveld profile analysis [11] were obtained by scanning X-ray powder diffraction films using a SAAB automatic film scanner [12, 13] coupled to a NORD 100 computer. The halfwidths of certain reflections were measured from the film scans. Reflections with odd l were corrected for instrument broadening and particle size effects by subtracting the halfwidths of neighbouring reflections with even l.

## 3. Results

## 3.1. NbP and TaP

Overexposed X-ray powder diffraction films indicated the presence of minute amounts of oxide contaminants in the samples, which are probably the result of a reaction between the metals and the silica tube.



Fig. 1. The variation in the c axis of NbP with the temperature at which the heating was interrupted during the preparation of the monophosphide: peak temperature, 1000 °C; nominal sample composition, NbP. X-ray reflections characteristic of unreacted niobium metal were observed for all samples except the one which was heat treated for 20 h.

Unreacted phosphorus condensed on the inner wall of the silica tube when samples with nominal composition NbP were removed from the furnace at various stages during the gradual temperature increase to the final reaction temperature of 1000 °C. According to the X-ray data, the solid reaction products consisted of niobium metal and NbP; no NbP<sub>2</sub> was present. The *c* axis of NbP in these samples depended strongly on the temperature at which the heating had been interrupted (Fig. 1). The *a* axes of NbP (a = 3.3340(3) Å) and TaP (a = 3.3184(3) Å) were constant within experimental error in all samples.

The c axis of NbP depended on both the reaction temperature and the sample composition (Fig. 2) as reported in ref. 1. Similar behaviour was observed in the Ta-P system (Fig. 2). The c axis became less dependent on the composition at lower reaction temperatures.

The sample size did not affect the diffraction patterns of NbP in samples with nominal compositions  $Nb_{52}P_{48}$  and NbP in which the amount of phosphorus present in the starting material varied from 0.01 to 0.06 g. Furthermore, a change in the nominal composition of a  $Ta_{55}P_{45}$  sample prepared at 1000 °C to  $Ta_{49}P_{51}$  by the addition of phosphorus pieces and subsequent annealing at 1000 °C for 4 days did not produce any alteration in the diffraction pattern for TaP.

Overexposed X-ray powder diffraction films of samples of both NbP and TaP with nominal compositions  $M_{51}P_{49}$  (M = Nb, Ta) prepared at 1000 °C revealed the presence of unreacted metal. The composition-dependent variation in the *c* axis of these monophosphides is thus not due to an extended homogeneity range.

The thermal history of the metal-rich samples affected the value of the c axis of both NbP and TaP. The value of the c axis in metal-rich samples prepared at 1000 °C (NbP samples) and 1100 °C (TaP samples) was



(b)

Fig. 2. The influence of the sample composition on the *c* axis of (a) NbP and (b) TaP prepared at various temperatures:  $\bigcirc$ , 1100 °C for 110 h;  $\Box$ , 1000 °C for 96 h;  $\triangle$ , 900 °C for 118 h;  $\bigtriangledown$ , 800 °C for 134 h;  $\bullet$ , 690 °C for 168 h;  $\blacksquare$ , 650 °C for 145 h;  $\blacktriangledown$ , 1000 °C for 96 h, 1350 °C for 24 h;  $\blacklozenge$ , from ref. 1.

significantly different from the values obtained in samples prepared at lower temperatures (NbP, 650 °C; TaP, 1000 °C) and subsequently annealed at 1000 °C and 1100 °C respectively (Fig. 3). Analogous heat treatments of  $M_{49}P_{51}$  samples did not result in any differences in the values of the *c* axes of the corresponding samples. The lowest values for the *c* axis in metalrich samples of both NbP and TaP were obtained when two samples with nominal compositions Nb<sub>55</sub>P<sub>45</sub> and Ta<sub>53</sub>P<sub>47</sub> prepared at 1000 °C were annealed at 1350 °C for 24 h (Fig. 2). The only other *c* values in this range



Fig. 3. The effects of heat treatment and sample composition on the *c* axis of (a) NbP ( $\Box$ , 650 °C, 6 days (initial synthesis);  $\circ$ , 650 °C for 6 days, 1000 °C for 4 days;  $\bigtriangledown$ , 650 °C for 6 days, 1000 °C for 4 and 33 days;  $\blacktriangle$ , 1000 °C, 4 days (initial synthesis)) and (b) TaP ( $\Box$ , 690 °C, 7 days (initial synthesis);  $\triangle$ , 690 °C for 7 days, 1000 °C for 3 days;  $\bullet$ , 690 °C for 7 days, 1000 °C for 3 and 33 days;  $\bigtriangledown$ , 1000 °C, 4 days (initial synthesis);  $\circ$ , 1000 °C for 4 days, 1100 °C for 5 days;  $\blacksquare$ , 1100 °C, 4 days (initial synthesis);

were obtained in samples with near-equiatomic compositions. No change in the c axis was observed when samples of NbP and TaP prepared at 1000  $^{\circ}$ C were annealed at temperatures of 800  $^{\circ}$ C or below.

The increase in the c axis of NbP and TaP in samples with increasing metal content was accompanied by the appearance of a reflection which could be indexed as (100). The intensity of this reflection increased with increasing c axis.

Simultaneously with the variation in the c axis, the linewidths and integrated intensities of odd-l reflections were also affected by the nominal composition and the reaction temperature. The line broadening increased and the integrated intensities decreased when the value of the c axis increased (Table 1). In samples with a metal content exceeding Nb<sub>55</sub>P<sub>45</sub> and Ta<sub>53</sub>P<sub>47</sub> or which had been prepared at temperatures below 800 °C, reflections with odd-l indices were only visible in overexposed X-ray diffraction films. In addition to the (100) reflection, another extra reflection which could be indexed as (214) was also present.

Reflections with even l also became somewhat broader when the metal content of the samples increased. This effect reduced the accuracy of the measurement of the diffraction line positions and resulted in an increased standard deviation for the values of the c axis in these samples.

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The halfwidth  $\beta^{a}$  of some odd-*l* reflections and the corresponding  $\gamma$  values calculated using eqn. (1) for various NbP and TaP samples (reaction temperature, 1000 °C)

Nominal	C C		$\beta$ and $\gamma$ valu	ues for the fo	llowing reflec	tions			
composition	(A)		(101)	(103)	(105)	(102)	(213)	(109)	(217)
$Nb_{49}P_{51}$	11.375(1)	$\beta(rad)$	0.0001	0.0007	0.0003	0.0006	0.0005	0.0009	0.0001
$Nb_{51}P_{49}$	11.379(2)	$\gamma \\ \beta(rad)$	0.0006	0.0012	0.002 0.0016	0.004 0.0025	0.0009	0.0030	0.0012
		٢	0.014	0.013	0.013	0.017	0.015	0.018	0.009
$Nb_{53}P_{47}$	11.385(3)	$\beta(rad)$	0.0025	0.0039	0.0054	q─	0.0034	q	q
		٢	0.060	0.040	0.042		0.053		
$\mathrm{Nb}_{55}\mathrm{P}_{45}$	11.392(3)	$\beta(rad)$	0.0058	٩	۹ 	q	٩	q	٩
		٢	0.13						
$Ta_{48}P_{52}$	11.347(3)	$\beta(rad)$	0.0006	0.0011	0.0022	0.0011	0.0007	q	<b>q</b>
		٢	0.014	0.012	0.018	0.008	0.011		
TaP	11.347(2)	$\beta(rad)$	0.0008	0.0012	0.0024	0.0033	0.0013	q	<b>م</b> 
		٢	0.020	0.013	0.019	0.022	0.021		
$Ta_{52}P_{48}$	11.377(5)	$\beta(rad)$	0.0085	0.0160	q	q	0.0091	q	q 
		γ	0.18	0.14			0.13		
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<sup>a</sup>The  $\beta$  values are corrected empirically for instrument broadening and particle size effects. <sup>b</sup>Reflection too weak and diffuse to permit measurement of the halfwidth.



Fig. 4. The appearance of alternating regions of NbAs- and WC-type structures in the disordered structure.

To account for the broadening of odd-l reflections Boller and Parthé [1] suggested that blocks of NbAs are displaced by [1/2, 1/2, 0] with respect to one another. This displacement leads to a change from the NbAstype structure to the WC-type structure around the interface between two blocks (Fig. 4). The relation between the atomic positions in two regions of NbAs type adjoining a WC block depends on the extension of the WC block along  $\langle 001 \rangle_{\rm NbAs}$ . The atomic positions in two regions of NbAs type are identical if the extension of the WC block is equal to  $(m + 1/2)c_{\text{NbAs}}$ . where m is an integer and  $c_{NbAs}$  is the length of the c axis of the NbAstype structure. If, however, the extension of the WC block is equal to  $mc_{\rm NbAs}$ , the atoms in one region of the NbAs type adjoining the WC block are shifted by [1/2, 1/2, 0] with respect to the atomic positions in the next NbAs-type region. The arrangement is thus analogous to an antiphase domain structure and is the reason for the broadening of the odd-l reflections. By using the [1/2, 1/2, 0] shift vector and following a treatment given by Warren [14] an expression for the dependence of the integral width of odd-l reflections on the relative number of regions of the second type of WC block can be derived:

$$\beta(2\theta) = \frac{-\lambda l \ln(1-2\gamma)}{2c_{\rm NbAs} \cos \theta \left\{ (c/a)^2 (h^2 + k^2) + l^2 \right\}^{1/2}}$$
(1)

#### TABLE 2

Transformation data for NbP in two different samples (reaction temperature, 1000 °C)

Nominal sample composition	N <sup>a</sup>	0.4N <sup>b</sup>	γ <sup>c</sup>
Nb <sub>51</sub> P <sub>49</sub>	0.04(2)	0.016(10)	0.014(3)
Nb <sub>53</sub> P <sub>47</sub>	0.15(2)	0.06(1)	0.049(9)

<sup>a</sup>The relative amount of WC-type structure in the transitional structure obtained by the Rietveld method.

<sup>b</sup>The relative amount of WC-type structure producing the line broadening of odd-*l* reflections estimated by the Rietveld method.

<sup>c</sup>The relative amount of WC-type structure producing the line broadening of odd-*l* reflections deduced from the halfwidths of these reflections (arithmetic mean value of the results of Table 1).

where  $\beta(2\theta)$  is the integral width in radians (approximated by the halfwidth in the following),  $\lambda$  is the wavelength of the radiation used, *a* and *c* are the lengths of the *a* and *c* axes respectively,  $\theta$  is the diffraction angle for a specific reflection and  $\gamma$  is the relative number of regions of the WC type with an extension of  $mc_{NbAs}$  along  $\langle 001 \rangle_{NbAs}$ . The values of  $\gamma$  calculated using eqn. (1) for some odd-*l* reflections in various samples are presented in Table 1.

The WC-type regions do not contribute to the integrated intensities of odd-*l* reflections. Accordingly, the intensities of these reflections decrease when the relative amount of WC-type structure increases, while even-*l* reflections remain unaffected. By analogy with the determination of the relative amounts of high and low temperature modifications present in samples of Ta<sub>3</sub>Ge [6] and Ta<sub>3</sub>P [7], the relative amounts of WC- and NbAstype structures present in the disordered structure of two different NbP samples were refined using the Rietveld method (Table 2) in terms of two occupancy parameters N and 1 - N respectively in space group  $I4_1md$ .

If it is assumed that the WC-type structure occurs with equal probability in regions with an extension of  $c_{NbAs}$  or  $3c_{NbAs}/2$  along  $\langle 001 \rangle_{NbAs}$ , the relative amount N of WC obtained in the Rietveld analysis can be compared with the  $\gamma$  values obtained in the line broadening analysis (Table 2):

$$\gamma + \frac{3\gamma}{2} = N \tag{2}$$
$$\gamma = 0.4N$$

# 3.2. NbAs and TaAs

Murray *et al.* [2] reported the appearance of several extra reflections in the X-ray powder patterns of TaAs prepared at temperatures below 1200 °C. These extra reflections could be indexed by relaxing the

body-centring condition. The following reflections were observed: (100), (201), (212) and (214). Furthermore, all reflections were broadened and the odd-*l* reflections were weaker. No variations in the unit cell dimensions (a = 3.4367(2) Å; c = 11.6437(6) Å) were observed, and the presence of the extra reflections was reported to be independent of the composition of the samples. These results were confirmed in this investigation, except that the presence of the extra reflections was found to be composition dependent in samples prepared at 1000 °C. The extra reflections and the broadening were absent in a sample with nominal composition Ta<sub>48</sub>As<sub>52</sub>, whereas these features appeared in a sample with nominal composition Ta<sub>52</sub>As<sub>48</sub>. The extra reflections and the broadening of all reflections were clearly visible in both metal-rich and metal-deficient samples prepared at 880 °C.

Samples of NbAs with nominal compositions Nb<sub>52</sub>As<sub>48</sub> and Nb<sub>48</sub>As<sub>52</sub> prepared at 880 and 1000 °C did not show any line broadening or reduction in intensity for odd-*l* reflections. However, the characteristic line broadening and decrease in the intensities of odd-*l* reflections, observed for NbP and TaP, were clearly visible in samples with the same compositions as above which had been prepared at 700 °C (heating period, 9 days). Reflections with odd values of h + k + l or variations in the unit cell dimensions (a = 3.4520(1) Å; c = 11.6754(7) Å) were not detected. Furthermore, no differences between the metal-rich and metal-deficient samples were observed; however, by analogy with the features in NbP, TaP and TaAs it is likely that such a difference should develop on increasing the preparation temperature slightly.

## 4. Discussion

The good agreement between the values of  $\gamma$  and 0.4N (Table 2) supports the disorder model proposed by Boller and Parthé [1] for NbP and TaP with regions of the NbAs type alternating with regions of the WC type within a common coherent lattice (Fig. 4). The appearance of the (100) reflection, which is solely attributable to regions of the WC type in samples consisting primarily of the NbAs type, also supports the suggested orientational relation between the different regions within this disorder model. Although the extension of the WC-type regions along  $(001)_{NbAs}$  is assumed to be of the order of 11 - 16 Å, the extension of these regions perpendicular to  $(001)_{NbAs}$  is much larger; in fact, it is of the order of the powder grain size of the samples. The diffraction coherency length required for the (100) reflection to appear is thus sufficiently large within this model.

The additional extra reflections observed in samples of TaAs cannot be accounted for by this model, however, and Murray *et al.* [2] have suggested that the appearance of these reflections is due to shifts in the atomic positions of the NbAs-type structure which are compatible only with the less symmetric space group  $P4_1$  (no. 76). The presence of the metal phase in samples of both NbP and TaP with nominal composition  $M_{51}P_{49}$  excludes the possibility of an extended homogeneity range as the origin of the composition dependence of the *c* axis in these monophosphides. By analogy with the Ta<sub>3</sub>Ge [5, 6] and V<sub>3</sub>S [8] transformations, the variation in the *c* axis of NbP and TaP is more likely to be due to changes in the relative amounts of the NbAs- and WC-type structures in the disordered structure. The misfit in the coherent interfaces between the NbAs- and WC-type regions may cause an elastic stress field which will affect the average cell dimensions of the mixed structure. A large value of the *c* axis thus indicates a large relative amount of WC-type structure, and accordingly a small *c* value indicates a large relative amount of the NbAstype structure. The simultaneous variations in the *c* axis, integrated intensities and linewidths of odd-*l* reflections are all consistent with this model.

There is no true polymorphism between the WC- and NbAs-type structures in these monophosphides and arsenides since it has not been possible to produce a transformation from the NbAs-type structure to the WC-type structure [2, 15, 16]. The large relative amount of the WC-type structure obtained in the early stages of the preparation of the monophosphides, as indicated by the high value of the c axis (Fig. 1), is most probably due to favourable reaction kinetics. On increasing the temperature, the regions of the metastable WC-type structure transform into the stable NbAs-type structure owing to higher thermal activation. The completeness of the transformation is dependent on the final reaction temperature and the sample composition. This is shown by the variation in the c axis of these monophosphides (Fig. 2). Above certain temperatures and with a sufficiently low metal content the WC-type regions transform almost completely into the NbAs type during the initial synthesis of the sample. If, however, the preparation of the monophosphide is completed at temperatures favouring the presence of a large proportion of the WC-type structure in the disordered structure, the transformation taking place during annealing at a higher temperature appears to be hindered by the presence of the metal phase.

The large difference in the ease with which the transformation takes place between metal-rich and phosphorus-rich samples and the effect of the thermal history of the samples (Fig. 3) suggest a diffusionless transformation. The shape and volume changes associated with a diffusionless transformation may be constrained by the presence of metal phase-monophosphide interfaces, which could thus give rise to the observed composition dependence of the transformation. If the metal content of the sample is not too high, the hindrance caused by the probable interface interaction appears to be reduced during the initial synthesis.

## 5. Conclusions

The monophosphides of niobium and tantalum are, to a variable extent, disordered along  $(001)_{NbAs}$  with alternating regions of the NbAs- and

WC-type structures. The large proportion of WC-type structure obtained in the disordered structure during the initial reaction of the elements while the sample is warming up is most probably due to favourable reaction kinetics. As the temperature increases, the regions of the metastable WC type transform into the stable NbAs type. The transformation appears to be constrained by the presence of the metal phase, so that the final relative amounts of the WC- and NbAs-type structures vary with sample composition. The variable amounts of WC- and NbAs-type structures in the disordered structure cause variations in the unit cell dimensions, the linewidths and the integrated intensities of the odd-*l* reflections. There are no indications that the unit cell variations can be related to a range of homogeneity in the monophosphides.

An analogous disordering also occurs in NbAs and TaAs, but the effect on the unit cell and the line broadening is less pronounced. This indicates a smaller variation in the relative amount of the WC-type structure in these phases.

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#### References

- 1 H. Boller and E. Parthé, Acta Crystallogr., 16 (1963) 1095.
- 2 J. J. Murray, J. B. Taylor, L. D. Calvert, Y. Wang, E. J. Gabe and J. G. Despault, J. Less-Common Met., 46 (1976) 311.
- 3 E. Parthé and V. Sadagopan, Monatsh. Chem., 93 (1962) 263.
- 4 T. Lundström, Ark. Kemi, 31 (1969) 227.
- 5 J.-O. Willerström, J. Less-Common Met., 86 (1982) 85.
- 6 J.-O. Willerström, J. Less-Common Met., 86 (1982) 105.
- 7 J.-O. Willerström, Y. Andersson and S. Rundqvist, Acta Chem. Scand., Ser. A, 37 (1983) 409.
- 8 J.-O. Willerström, J. Less-Common Met., 92 (1983) 41.
- 9 N. O. Ersson, Institute of Chemistry, Uppsala, unpublished work, 1982.
- 10 R. D. Deslattes and A. Henins, Phys. Rev. Lett., 31 (1973) 972.
- 11 G. Malmros and J. O. Thomas, J. Appl. Crystallogr., 10 (1977) 7.
- 12 S. Abrahamsson, J. Sci. Instrum., 43 (1966) 931.
- 13 SAAB Film Scanner Manual, SAAB AB, Datasaab, Linköping, 1967.
- 14 B. E. Warren, X-ray Diffraction, Addison-Wesley, Reading, MA, 1969.
- 15 A. Reinecke, F. Wiechmann, M. Zumbusch and W. Biltz, Z. Anorg. Chem., 249 (1942) 14.
- 16 M. Zumbusch and W. Biltz, Z. Anorg. Chem., 246 (1941) 35.