

considered to be the case at the time of the controversy between Pauling and Huggins^{4,7} on the one hand and Buerger^{6,8} on the other (*vide supra*). These differences between the two modifications, which are related to the structural dissimilarities, will be subject to discussion in a forthcoming paper.

As a consequence of the cubic symmetry of the pyrite type structure and the fact that there is only one positional parameter, knowledge of the lattice constant a and estimates of the length of the bonding $X-X$ ($a\sqrt{3}(1-2x)$) or $T-X$ ($a(3x^2-2x+\frac{1}{2})^{\frac{1}{2}}$) distance enables prediction of the value of x (*cf.*, *e.g.*, Pauling and Huggins⁴). More conveniently, however, the value of x may be estimated from the ratio between these distances ($\sqrt{3}(1-2x)/(3x^2-2x+\frac{1}{2})^{\frac{1}{2}}$), since it may be easier to judge this quantity with reliability. (In the relevant range of x , *i.e.* $0.35 < x < 0.42$, the ratio can to a good approximation be simplified to the linear function $4.4454 - 9.0722x$.)

Substitution of the observed distance ratio for the marcasite modification of FeS_2 in the above expression, gives $x=0.381$ for pyrite, which accords reasonably well with the experimental value 0.3840. Similarly, the recent values for the distance ratios in the marcasite modifications of FeTe_2 ,¹⁴ CoTe_2 ,¹⁴ and $\beta\text{-NiAs}_2$,¹⁵ may be utilized for the prediction of the x -values 0.364, 0.367, and 0.377, respectively, for the corresponding modifications with the pyrite type structure which have recently been prepared^{12,16} by high pressure syntheses. The hitherto unobserved pyrite variant of NiSb_2 may be predicted to have $a=6.204$ Å and $x=0.367$ on the basis of the structural data¹⁶ for the marcasite modification. It must be emphasized, however, that these predictions are subject to some uncertainty (in particular in the latter case) since, *e.g.*, the size of transition metal atoms appears to correlate with their localized configurations of unpaired electrons (*cf.* Pearson¹⁷).

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New Metal-rich Arsenides of Niobium and Tantalum

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In several earlier investigations of the Nb-As and Ta-As systems,¹⁻⁷ the method of synthesis has been the direct reaction between the component elements at temperatures up to 1000°C. Under these conditions the only intermediate phases formed in each system are a monoarsenide and a diarsenide. Ganglberger,^{8,9} who employed higher temperatures for his syntheses, was able to prepare the metal-rich compounds Nb_3As and Ta_3As , both of which were reported to crystallize with the Ti_3P -type structure.

In the present paper, some results are reported from an examination of the

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Nb—As and Ta—As systems at higher temperatures.

The alloys were prepared in the following manner. Samples of the monoarsenides were synthesized by heating mixtures of niobium (rod, 3N, Koch-Light) or tantalum (powder, ~99.5 %, Herman Starck) with arsenic (5N, Koch-Light) in evacuated and sealed silica tubes for a few days at 900–1000°C. Mixtures of monoarsenides and niobium or tantalum in various proportions were then arc-melted under purified argon. In some cases, the arc-melted products were further heat-treated under purified argon in an induction furnace at temperatures up to 1700°C.

The products were studied by X-ray powder diffraction methods using Guinier-Hägg type focusing cameras with $\text{CuK}\alpha_1$ or $\text{CrK}\alpha_1$ radiation. Single crystals picked from the alloys were examined using Weissenberg cameras with CuK or MoK radiation.

Unit cell dimensions were determined by a combination of single crystal and powder methods and refined from powder data by the least squares method. Silicon ($a=5.43054$ Å) was used as an internal calibration standard, and the least squares calculations were made on a CDC 3600 computer.

In the Nb—As system, the occurrence of four intermediate phases, Nb_3As , Nb_7As_4 , Nb_5As_3 , and $\text{NbAs}_{\sim 0.75}$, was established in the composition range 0–45 at. % arsenic. Crystallographic data for these compounds are given in Table 1.

Nb_3As appears to be the most metal-rich compound in the system. The crystallographic results obtained in the present study are in good agreement with those reported by Ganglberger.^{8,9} By a direct comparison of the Weissenberg photographs of Nb_7As_4 with the corresponding films for Nb_7P_4 (the structure of which has been determined earlier¹⁰) it was established that the two compounds are isotypic. In the same way it was determined that Nb_5As_3 is isotypic with Nb_5P_3 and Hf_5As_3 .¹¹ (The crystal structure of Nb_5P_3 has been determined by Hassler¹² and will shortly be reported in this journal.) The compound $\text{NbAs}_{\sim 0.75}$ crystallizes with a new structure type. The single crystal data indicate space group symmetry $C222_1$. The composition of the compound could not be determined very accurately, but from the available phase-analytical and crystallographic data it seems likely that the ideal composition is Nb_4As_3 , and the unit cell content is eight

formula units. A complete single crystal determination is in progress.

Both the arc-melting and the annealing treatments at high temperatures of the Nb—As samples were accompanied by considerable losses of arsenic. Since there are great experimental difficulties involved in maintaining an atmosphere with a controlled partial pressure of arsenic at these high temperatures it is far from easy to obtain reliable information about the high-temperature state of the Nb—As system.

Annealing experiments of the arc-melted alloys at 1000–1100°C for several weeks in sealed silica tubes indicated that the diffusion is too slow for attainment, within a reasonable time, of conditions approaching thermodynamic equilibrium. It is obvious that the present results for the solid part of the Nb—As system cannot be claimed to represent a complete survey under well-defined thermodynamic conditions. Further studies might well reveal the occurrence of additional phases.

The problems discussed above were even greater in the case of the Ta—As system. The most arsenic-rich phase which could be prepared in a pure state, was Ta_2As . The isotypism between Ta_2As and Ta_2P was established by comparison of the powder diffraction films for the two compounds.^{13,14} Powder diffraction patterns of arc-melted mixtures of Ta_2As and TaAs indicated the presence of a phase more arsenic-rich than Ta_2As , but owing to the rapid evaporation of arsenic, this phase could not be prepared in a pure state. Heat-treatment of mixtures of Ta_2As and TaAs in sealed silica tubes produced no reaction as judged from the powder diffraction examination of the products.

The powder diffraction lines belonging to the new phase could be indexed on the basis of a tetragonal unit cell. The cell dimensions indicated that the tetragonal phase might belong to the Ti_5Te_4 type structure,¹⁵ and an intensity calculation based on the atomic positional parameters given by Jensen and Kjekshus¹⁶ for Mo_5As_4 strongly supported this assumption. The new phase is therefore denoted as Ta_5As_4 in Table 1.

Ganglberger^{8,9} reported the occurrence of a Ti_3P -type tantalum arsenide. In the present investigation, the powder diffraction patterns of arc-melted alloys of composition near Ta_3As revealed the presence of a tetragonal phase with dimensions fairly close to those reported by Ganglberger.

Table 1. Crystallographic data for some metal-rich niobium and tantalum arsenides.

Phase	Structure type	Space group	Cell dimensions and their standard deviations (Å)	Cell volume (Å ³)
Nb ₃ As	Ti ₃ P	<i>P4₂/n</i>	$a = 10.2937 \pm 0.0008$ $c = 5.1971 \pm 0.0006$	550.7
Nb ₇ As ₄	Nb ₇ P ₄	<i>C2/m</i>	$a = 15.3716 \pm 0.0007$ $b = 3.5242 \pm 0.0002$ $c = 14.1920 \pm 0.0007$ $\beta = 104.742^\circ \pm 0.006^\circ$	743.5
Nb ₅ As ₃	Nb ₅ P ₃	<i>Pnma</i>	$a = 26.0701 \pm 0.0010$ $b = 3.5198 \pm 0.0002$ $c = 11.7869 \pm 0.0005$	1081.6
NbAs _{~0.75}		<i>C222₁</i>	$a = 14.6605 \pm 0.0010$ $b = 3.5161 \pm 0.0003$ $c = 18.8303 \pm 0.0011$	970.7
Ta ₂ As	Ta ₃ P	<i>Pnmm</i>	$a = 14.7680 \pm 0.0011$ $b = 11.8373 \pm 0.0009$ $c = 3.4696 \pm 0.0004$	606.5
Ta ₅ As ₄	Ti ₅ Te ₄	<i>I4/m</i>	$a = 9.8038 \pm 0.0008$ $c = 3.4344 \pm 0.0009$	330.1

However, reflexions with $h+k+l=2n+1$ were missing, which indicates that the structure is rather of the Fe₃P or α -V₃S type. The powder patterns of arc-melted samples annealed at 1700°C had a similar appearance, but some of the reflexions were broadened or split, indicating changes in symmetry and cell dimensions. These patterns bore a certain resemblance to those of the Hf₃As phase mentioned in a previous investigation.¹¹ For a complete crystallographic characterization of the Ta₃As phases it is necessary to employ single-crystal methods, but unfortunately no single crystals suitable for X-ray examination were found in any of the Ta-As alloys.

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