possède un voisinage constitué par six atomes d'oxygène appartenant à trois octaèdres TeO_6 et par la molécule d'eau O(*w*).

L'atome Na(2) est entouré seulement de six atomes d'oxygène, provenant par moitié des octaèdres TeO_6 et des tétraèdres PO_4.

Le Tableau 6 donne les principales distances interatomiques et angles de liaison.

La présence d'une molécule d'eau sur un axe ternaire pose un problème en ce qui concerne une localisation éventuelle des protons de cette molécule. La présence à proximité de cette dernière de groupements HPO_4 suggère la possibilité de l'existence d'un groupement hydronium H_3O^+. Dans cette hypothèse, les trois atomes d'oxygène O(1) distants de 2,64 Å de cette molécule d'eau seraient reliés à cette dernière par deux liaisons hydrogène provenant des protons de la molécule d'eau, la dernière liaison étant assurée par le proton du groupement HPO_4. Un essai de localisation des protons par minimisation d'énergie (Tordjman, 1979) conduit à leur attribuer une position générale 6(*c*) en x = 0,186, y = 0,682, z = 0,277. Dans cette configuration, on observe les distances suivantes: H—O(*w*) = 0,96, H—O(1) = 1,70 Å, avec des angles O(1)—H—O(*w*) = 167 et H—O(*w*)—H = 112°. Une étude par diffraction de neutrons est envisagée pour vérifier cette hypothèse.

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Structures of Ta_3As and $(Nb,Ta)_3As$*

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Abstract. Ta_3As (a new structure type), monoclinic, $B2/b$, a = 14·6773 (6), b = 14·5505 (4), c = 5·0954 (2) Å, γ = 90·572 (3)°, Z = 16; a full-matrix least-squares refinement gave R = 0·081 for 2440 observed *hkl*, using graphite-monochromated Mo radiation ($\lambda\alpha_1$ = 0·70932 Å). One $(Nb,Ta)_3As$ crystal, $P4_2/n$, a = 10·308 (1), c = 5·148 (1) Å, Z = 8, had the Ti_3P-type structure; a refinement on a twin-type model gave R = 0·072 for 3709 observed *hkl*. Both structures contain $[AsM_{10}]$ bicapped square antiprism units with average interatomic distances for Ta_3As and $(Nb,Ta)_3As$ of M—M = 3·12 and 3·13 Å, M—As = 2·74 and 2·74 Å and As—As = 3·87 and 3·92 Å respectively. Ta_3As is an ordered variant of Nb_3As.

Introduction. Ta_3As and Nb_3As were reported to have the Ti_3P structure by Ganglberger, Nowotny & Benesovsky (1966). This was confirmed for Nb_3As by Rundqvist, Carlsson & Pontchour (1969) but they suggested the Fe_3P or α-V_3S structure for Ta_3As and, in addition, found some of the lines in Ta_3As powder patterns split or broadened, but were unable to obtain single crystals. Ta_3As was characterized as monoclinic with a new structure type by Murray, Taylor, Calvert, Wang, Gabe & Despault (1976) on the basis of powder patterns and single-crystal precession photographs. Their powder patterns were not identical for all samples and their single crystals were twinned or of poor quality. Single-crystal studies were undertaken in an attempt to clarify these discrepancies. Many apparently good single crystals grown by iodide transport in tantalum crucibles (Murray *et al.*, 1976) were examined by Laue photographs and found to be twinned, *i.e.* Laue ellipses were doubled. The first good crystal found was mounted on a four-circle computer-controlled diffractometer. The symmetry was found to be tetragonal, not monoclinic as expected, with reflection conditions 00*l*, $l = 2n$ and *hk*0, $h + k = 2n$ and a c axis of 5·148 Å, intermediate between those of Ta_3As (5·0954 Å) and Nb_3As (5·189 Å; Waterstrat, Yvon, Flack & Parthé, 1975). Cell parameters were obtained by centring reflections with $\theta > 60°$ (Table 1). The Ta used in preparing these specimens was later found to have contained ~1% Nb. Intensities were measured (Table 1) using local programs (for details see Wang, Gabe, Calvert & Taylor, 1976*a*) and corrected for Lorentz, polarization and absorption effects. Because the composition was not certain the absorption coefficient was an experimental value. Intensities were measured at 10° intervals as the crystal was rotated around the diffraction vector ($0 < \psi < 180°$) for several reflections and the appropriate absorption corrections were calculated with different values of μ_l.

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The value which gave the best fit was chosen. This corresponded to Nb_2TaAs, a composition consistent with the results of the structure refinement. The structure was solved by direct methods. Refinement by full-matrix least squares with allowance for anomalous dispersion converged to $R_1 = \sum |\Delta F|/\sum |F_o| = 0{\cdot}16$ with Nb scattering factors used for all metal-atom sites but occupancies refined with the scale held constant. Two sites, $M(1)$ and $M(3)$, were later changed to Ta scattering factors. Careful inspection showed that the agreement for the 344 observed hhl and $h0l$ reflections was better ($R_1 = 0{\cdot}09$) than for the hkl ones. A disordered model, derived by a 180° rotation around $\langle 1\bar{1}0\rangle$, did not refine successfully. A 'twin' model was successfully refined on structure factors defined as $F^2 = F_1^2 + tF_2^2$ where F_1 is calculated from x,y,z for the normal structure and F_2 from $y,x,-z$ for the twin fragment, and t is the ratio of twin present and is refined as a parameter. This model refined to $R_1 = 0{\cdot}072$ with $t = 0{\cdot}225$ for the 3709 observed hkl. Occupancies for two sites [$M(1)$ and $M(3)$] were 0·70 and 0·67 of Ta respectively and these are therefore believed to be mixed Ta and Nb sites. At this stage a difference map, computed for 'twin-free' F_o, showed residual features on the two sites [$M(2)$ and As] which interchange metal for As after the twin operation. These residual features were removed by adding 0·12 Nb in the $M(2)$ 'twin' site and 0·11 As in the As 'twin' site. The final parameters (corresponding to F_1) are given in Table 2. This approximates Nb_2TaAs but in view of the uncertain absorption correction and the refinement problems, the composition must be considered as tentative. Although this model refined successfully there may be other equally valid models. An attempt at obtaining a microprobe analysis for this crystal failed because the crystal was lost during polishing. However, a previous X-ray fluorescence analysis on this crystal had confirmed the presence of Nb. It seems clear from the structure derived, the values of the cell parameters and the intermediate powder patterns observed (Murray *et al.*, 1976) that Nb_3As can dissolve some Ta_3As without change of structure.

A continued search produced a monoclinic crystal of Ta_3As. Lattice parameters were in good agreement with those of Murray *et al.* (1976) for Ta_3As and two sets of data were measured for this crystal and averaged (Table 1). A trial based on a 45° rotation of the $(Nb,Ta)_3As$ structure with two Ta_3As in the asymmetric unit did not refine. A refinement of x,y coordinates only, based on the 168 $hk0$ reflections, converged ($R_1 = 0{\cdot}11$); z coordinates were then added and a difference map showed that atoms corresponding to $M(2)$ and As of the Nb_3As structure were shifted by $c/2$ relative to the trial structure (Fig. 1). Full-matrix refinement with anisotropic thermal parameters and allowance for anomalous dispersion and isotropic extinction converged to $R_1 = 0{\cdot}081$ for 2440 hkl ($I > 2\sigma$). A difference Fourier map showed no significant residual features other than small irregular residuals near the Ta sites, probably attributable to inadequacies in the absorption corrections. Considerable pains were taken to define the shape of the crystal and check the calculated transmission factors by azimuthal scans around the diffraction vector; these checks were satisfactory. Refinement of the data without absorption corrections converged to $R_1 = 0{\cdot}18$

Table 1. *Structure refinement details*

	Ta_3As	$(Ta,Nb)_3As$
Crystal size (mm)	0·05 × 0·10 × 0·13	0·03 × 0·05 × 0·12
μ_l (mm^{-1})	138·5	62·3
Transmission factors	0·0025–0·0518	0·06–0·19
Scan range (°)	0·5 + 0·7 tan θ + 0·5	0·5 + 0·7 tan θ + 0·7
$2\theta_{max}$	75°	120°
Measurements	2888 × 2	4429
Observed, $I > 2\sigma$	2440	3709
Reflections used for cell parameters	50	32

Table 2. *Atomic parameters for* $(Nb,Ta)_3As$

The temperature factor was of the form $\exp[-8\pi^2 U(\sin\theta/\lambda)^2]$.

	Occupancy	Scattering factor used	x	y	z	U (Å^2)
$M(1)$	0·703 (4)	Ta	0·15544 (5)	0·66315 (5)	0·23449 (11)	0·0043 (1)
$M(2)$	1·007 (7)	Nb	−0·10159 (7)	0·75909 (7)	0·48680 (16)	0·0017 (1)
$M(3)$	0·673 (4)	Ta	−0·03971 (6)	0·44440 (6)	0·25573 (11)	0·0043 (1)
As	0·783 (8)	As	−0·23299 (12)	0·54330 (12)	0·51476 (26)	0·0039 (2)
*$M(2')$	0·119 (8)	Nb	−0·2594 (8)	−0·1032 (8)	0·484 (2)	0·006 (11)
*As'	0·114 (10)	As	0·538 (2)	−0·263 (2)	0·505 (4)	0·020 (3)

[$t = 0{\cdot}225$ (4)]

* No twin component in the refinement.

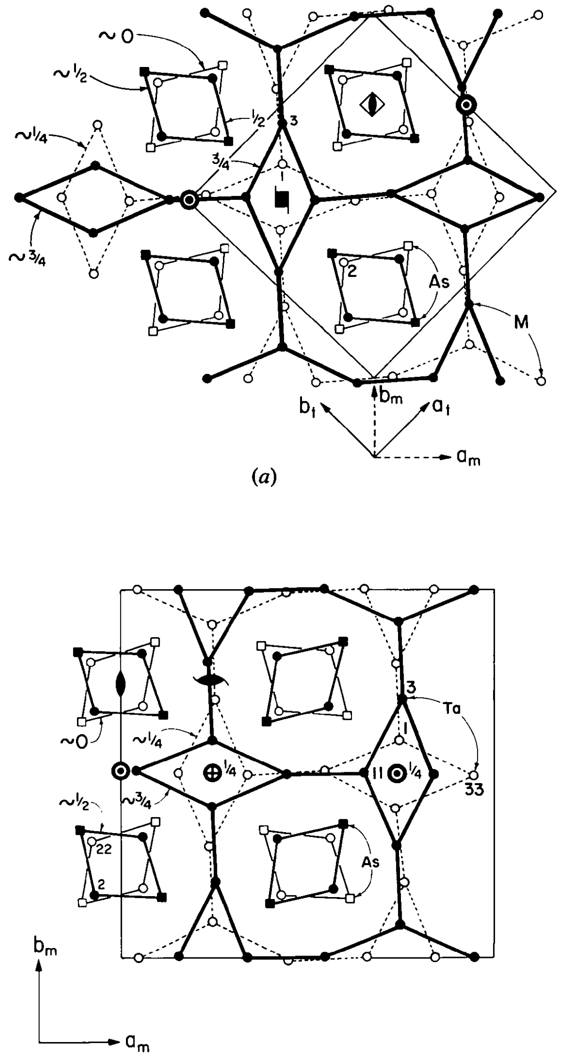

Fig. 1. The (001) projections of (*a*) the tetragonal M_3As structure (Ti_3P type) and (*b*) the monoclinic Ta_3As structure. Corresponding sets of symmetry elements are marked in both cells; symmetry centres are marked by ⊙. Corresponding sets of metal sites are numbered as in Tables 2 and 3.

Table 3. *Positional parameters* ($\times 10^4$) *of* Ta_3As

	x	*y*	*z*
Ta(1)*	−2531 (1)	4087 (1)	2283 (2)
Ta(11)	−1584 (1)	−41 (1)	2541 (2)
Ta(2)	−667 (1)	1715 (1)	5002 (2)
Ta(22)	−745 (1)	3215 (1)	−115 (2)
Ta(3)	−2423 (1)	2025 (1)	2533 (2)
Ta(33)	−484 (1)	−60 (1)	7509 (2)
As(1)	−3862 (2)	1553 (2)	−146 (6)
As(11)	−999 (2)	1402 (2)	−12 (6)

* Atoms are numbered for comparison with the Ti_3P-type structure of Nb_3As: Ta(1) and Ta(11) correspond to Nb(1).

with negative isotropic temperature factors. The final positional parameters are given in Table 3.*

Discussion. The intermediate $(Nb,Ta)_3As$ structure (Fig. 1*a*) is of the Ti_3P type which has been discussed by Nawapong (1966), Chen & Franzen (1972) and Waterstrat (1975) and thus needs no detailed description here. Lundström & Snell (1967) described the As coordination as tricapped trigonal prismatic (CN = 9) but this was modified by Waterstrat (1975) to a bicapped square antiprism description (CN = 10). The Ta_3As structure (Fig. 1*b*) contains open columns of octagonal antiprisms of Ta atoms at $z = \frac{1}{4}$ and $\frac{3}{4}$ forming $38^2 + 3^28^2$ (1:1) networks. These are centred by $[Ta_2As_2]$ diamonds at $z = 0$ and $\frac{1}{2}$ which form $4^4 + 4^4$ (1:1) nets. In both structures As has 10 Ta neighbours (both averages = 2·77 Å); Ta(1) and Ta(11) are coordinated to 12 Ta (both averages = 3·10 Å) plus 2 As (both averages = 2·63 Å) while Ta(2), (22), (3) and (33) have 11 Ta [overall averages 3·15 and 3·14 Å for $(Nb,Ta)_3As$ and Ta_3As respectively] plus 4 As neighbours at both 2·64 and 2·98 Å in both cases. The coordinations in Nb_3As, $(Nb,Ta)_3As$ and Ta_3As are compared in Table 4 in detail.*

The 'twin' mechanism for $(Nb,Ta)_3As$ leaves the atomic distribution on the planes $z = \frac{1}{4}, \frac{3}{4}$ unchanged but interchanges metal and As atoms at $z = 0, \frac{1}{2}$ (Wang, Gabe, Calvert & Taylor, 1976*b*). The basic unit

* Lists of structure factors for Ta_3As and $(Nb,Ta)_3As$, anisotropic thermal parameters for Ta_3As, and Table 4 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34288 (57 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

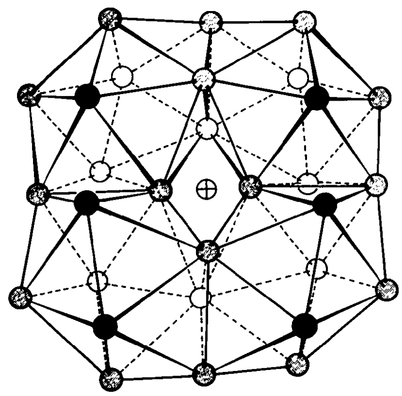

Fig. 2. A perspective view of the fourfold $[AsTa_{10}]$ grouping, which is centred on a centre of inversion (marked by ⊕ both here and in Fig. 1*b*). The As atoms are omitted from the $[AsTa_{10}]$ groups.

in both Nb_3As and Ta_3As is the $[AsM_{10}]$ bicapped square antiprism. In Ta_3As four such units surround a centre of inversion (Fig. 2), sharing two edges and two triangular faces. In Nb_3As these centres become 4_2 axes. Consequently the columns of $[Ta_2As_2]$ diamonds are displaced by $c/2$ in alternate octagonal columns in Ta_3As (Fig. 1*b*), whereas in Nb_3As (Fig. 1*a*) the $[Nb_2As_2]$ diamonds are all at the same height and the $[AsM_{10}]$ units share two edges and two corners.

A similar displacement of alternate columns is found between the structures of α-V_3S and β-V_3S (Pedersen & Grønvold, 1959) which contain columns of octagonal antiprisms, centred by $[M_2S_2]$ diamonds, arranged in a more symmetric manner. Ni_3P (Aronsson, 1955) is analogous to α-V_3S and Ta_3As.

The twinning mechanism found in the refinement of $(Nb,Ta)_3As$ provides a possible explanation for the variability of powder patterns and the difficulties of obtaining good single crystals reported by Rundqvist, Carlsson & Pontchour (1969) and Murray *et al.* (1976) as Nb is a frequent contaminant in Ta.

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Structure du Pyrochlore, $Tl_{0,51}Sb^{III}_{0,71}Sb^{V}_{2}O_{6,32}$

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Abstract. $Tl_{0.51}Sb^{III}_{0.71}Sb^{V}_{2}O_{6.32}$, cubic, $Fd3m$, $a = b = c = 10.3127$ (4) Å, $D_m = 6.479$ (5) Mg m^{-3}, $Z = 8$. X-ray data were collected on a three-circle diffractometer. The final unweighted R was 0·037 for 186 independent reflexions. As in $K_{0.51}Sb^{III}_{0.67}Sb^{V}_{2}O_{6.26}$, the Sb^{III} ions are located in a 96(*g*) position.

Introduction. Nous avons récemment décrit la structure du pyrochlore $K_{0,51}Sb^{III}_{0,67}Sb^{V}_{2}O_{6,26}$ dans laquelle l'antimoine(III) occupe au sein des tunnels communicants, délimités par la charpente Sb_2O_6, une position 96(*g*) (Piffard, Dion & Tournoux, 1978). C'est la première fois qu'il était démontré qu'un cation, dans ce type structural, pouvait occuper une position extérieure à l'axe [111]. Une phase de ce type, dans laquelle l'alcalin est remplacé par le thallium(I), a été obtenue à l'état de poudre microcristalline par Bouchama (1973).

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Nous avons obtenu des monocristaux de ce pyrochlore par chauffage à l'air pendant 3 h à 1273 K d'un mélange d'oxyde thallique et de Sb_2O_3 dans un rapport molaire initial Tl_2O_3/Sb_2O_3 de 0,25. La valeur élevée de la température de préparation entraîne des pertes en thallium par volatilité et rend peu probable la présence de thallium(III) dans les cristaux obtenus. Les cristaux se présentent sous forme d'octaèdres réguliers de couleur orange. Leur composition a été déterminée par différentes techniques: analyse à la microsonde de CASTAING du monocristal ayant servi à l'étude structurale, dosage par spectrophotométrie d'absorption du thallium et de l'antimoine, étude Mössbauer et détermination très précise de la densité à partir de cristaux. L'étude Mössbauer montre la présence d'antimoine(III) mais ne permet pas une détermination précise du rapport Sb^{III}/Sb^{V} car l'antimoine(III) est beaucoup moins fortement lié que l'antimoine(V) et présente un environnement très irrégulier. La présence

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