

Fig. 2. Projection down [001] of the tetrahedral  $\text{NH}_4^+$  and  $\text{ReO}_4^-$  ions at  $z = 0$  and  $z = \frac{1}{4}$ . The dashed line  $PQ$  indicates the interatomic distance discussed in the text. (N is at  $x = \frac{1}{2}$ , Re is at  $x = 0$ .)

repulsive force between these O atoms forces the tetrahedra further apart causing an increase in the  $a$  and  $b$  cell dimensions. In spite of the expansion in the [100] and [010] directions, this closest contact between O tetrahedra nevertheless decreases from 3.243 to 3.107 Å. The  $\text{NH}_4^+$  ion is considerably distorted from the ideal tetrahedral configuration, being flattened along  $c$ .

The observed NMR results can be explained satisfactorily by using the atomic parameters determined in this study and are discussed elsewhere (Reynhardt & Kruger, 1977).

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## A Reinvestigation of the Structure of $\epsilon$ -Tantalum Nitride

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**Abstract.**  $\epsilon$ -TaN,  $a = 5.196(4)$ ,  $c = 2.911(2)$  Å,  $Z = 3$ , space group  $P6_2m$ . It was prepared by annealing tantalum nitride in nitrogen at 1450°C and 1.4 MPa for 70 h. The structure was determined by the powder profile refinement technique with neutron diffraction data. The coordination polyhedra are a planar regular  $\text{TaN}_3$  triangle and two regular three-sided  $\text{TaN}_6$  prisms.

**Introduction.**  $\epsilon$ -TaN has the composition  $\text{Ta}_{1.00}\text{N}_{1.00}$ .

within the limits of errors of X-ray and chemical analyses (Brauer & Mohr-Rosenbaum, 1971). In contrast to this, the two other tantalum nitrides (Gatterer, Dufek, Ettmayer & Kieffer, 1975),  $\beta$ - $\text{Ta}_2\text{N}$  and  $\delta$ -TaN, have broad composition ranges and are typical nonstoichiometric compounds.  $\delta$ -TaN has the NaCl structure (Gatterer *et al.*, 1975), and  $\beta$ - $\text{Ta}_2\text{N}$  a structure similar to that of  $\beta$ - $\text{Nb}_2\text{N}$  (Conroy & Christensen, 1977; Christensen, 1976). The structure of  $\epsilon$ -TaN has been determined from X-ray powder patterns (Brauer & Zapp, 1954). However, the Ta

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atoms contribute 99.1% of the intensity of the X-ray powder pattern, and the small scattering contribution from the N atoms is not sufficient for a determination of the N atom positions. In a neutron powder pattern the Ta atoms contribute only 35.1% of the intensity. Samples of  $\epsilon$ -Ta<sub>2</sub>N became available during a project concerning the preparation and characterization of transition-metal carbides and nitrides, and it was decided to reinvestigate the crystal structure of  $\epsilon$ -Ta<sub>2</sub>N by neutron diffraction.

Samples of tantalum nitride containing  $\epsilon$ -Ta<sub>2</sub>N and  $\beta$ -Ta<sub>2</sub>N were prepared from powders of Ta of nominal 99.9% purity and nitrogen gas of nominal 99.99% purity (Conroy & Christensen, 1977). The powders of tantalum nitride were placed in a container made of Ta foil and heated in a graphite crucible in pure nitrogen at 1450°C and 1.4 MPa for 15 h. The powder was ground in a boron carbide mortar and annealing in pure nitrogen was repeated for 70 h. A powder pattern obtained with a Guinier-de Wolff camera with Cu  $K\alpha_1$  radiation ( $\lambda = 1.54051$  Å) and Ge,  $a = 5.6576$  Å, as an internal standard showed that the product was  $\epsilon$ -Ta<sub>2</sub>N without traces of  $\beta$ -Ta<sub>2</sub>N.

Powder patterns were measured at room temperature at the DR3 reactor at Risø with a neutron wavelength of 1.007 Å. The sample was housed in a 10 mm diameter V container. One diffraction pattern (A) was measured in the  $2\theta$  interval 10.0 to 42.0°, and one (B) in the  $2\theta$  interval 10.0 to 112.0°, both in steps of 0.1°.

In the refinement the scattering lengths for Ta and N were 0.691 and 0.940 ( $\times 10^{-12}$  cm) respectively (Bacon, 1972), and the profile-analysis method was used (Rietveld, 1969).

Diagram A: The diagram had nine peaks. The first eight were resolved and the last had contributions from three reflexions. From the nine peaks, intensities for 10 reflexions were calculated (multiplicity and Lp corrections were made). A Patterson function had peaks at the positions: (I) (0.37,0,0) (0,0.37,0) (0.37,0.37,0), and (II) (0.33,0,0.5) (0,0.33,0.5) (0.33,0.33,0.5). Peaks (I) were interpreted as Ta–N vectors and peaks (II) as Ta–Ta vectors. This gives the two following possibilities for the structure: (1) three Ta in (0,0,0) ( $\frac{1}{3}, \frac{2}{3}, \frac{1}{2}$ ) ( $\frac{2}{3}, \frac{1}{3}, \frac{1}{2}$ ), and three N in (0.37,0,0) (0,0.37,0)

(0.63,0.63,0); (2) the same positions for the Ta atoms and three half N in (0.37,0,0) (0,0.37,0) (0.37,0.37,0), and three half N in (0.63,0,0) (0,0.63,0) (0.63,0.63,0). Refinement of these two structures showed that model (2) could be ruled out.

Diagram B: The diagram had 12 sharp and 10 broad peaks corresponding to contributions from 88 reflexions. The structure was refined in space group  $P\bar{6}2m$  with one Ta in 1(a), two Ta in 2(d), and three N in 3(f). The parameters refined were: one positional parameter for the N atom, three isotropic temperature-factor parameters, one scale factor, three half-width parameters, a zero-point parameter, and two unit-cell parameters, a total of eleven parameters. The results of the refinements are listed in Table 1.\*

**Discussion.** The structure of  $\epsilon$ -Ta<sub>2</sub>N determined from X-ray powder patterns (Brauer & Zapp, 1954) has atoms in the point positions 1(a) and 2(d) for three Ta, and in 3(f) for three N atoms, all in space group  $P6/mmm$ . This structure is unusual because the Ta atoms form alternating layers of centred and uncentred hexagons, and the N atoms are placed in centres of deformed octahedra. The model, however, agrees with the X-ray powder pattern, and the positions of the Ta atoms could thus be assumed to be correct. This investigation confirms the positions of the Ta atoms. The Ta atoms are closely packed with Ta(1)–Ta(1<sup>i</sup>) = 2.911 (2), Ta(2)–Ta(2<sup>i</sup>) = 3.000 (5), and Ta(1)–Ta(2) = 3.334 (5) Å. The packing is displayed in Fig. 1. Ta(1) is coordinated by three N atoms in a planar triangle with Ta(1)–N = 2.041 (5) Å. Ta(2) and Ta(2<sup>i</sup>) are coordinated by six N atoms in a three-sided prism, with Ta(2)–N = 2.163 (5) Å. The N atoms are coordinated by five Ta atoms in a four-sided pyramid, with N–Ta =

\* A list of structure factors is available from the authors and has also been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33008 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atomic coordinates and isotropic temperature-factor parameters for  $\epsilon$ -Ta<sub>2</sub>N

Standard deviations are in parentheses.					
	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
Ta(1)	1(a)	0	0	0	0.36 (4)
Ta(2)	2(d)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{2}$	0.14 (3)
N	3(f)	0.3928 (2)	0	0	0.23 (1)

Scale factor 0.0150 (1),  $R(F^2)$  3.58%,  $R(F)$  3.70%.

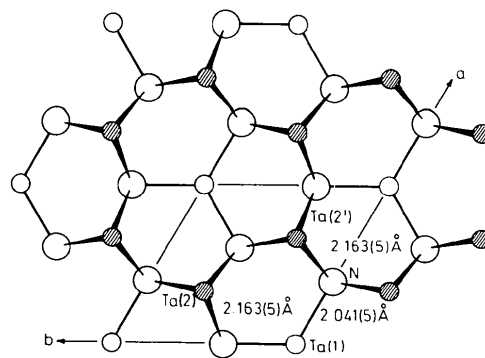


Fig. 1. Projection of the structure of  $\epsilon$ -Ta<sub>2</sub>N along [001]. Ta atoms with  $z = \frac{1}{2}$  are hatched.

$4 \times 2.163$  (5) and  $2.041$  (5) Å. The structure of  $\epsilon$ -TaN described above is thus different from that arrived at previously (Brauer & Zapp, 1954).

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## Cadmium Diiodate

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**Abstract.**  $\text{Cd}(\text{IO}_3)_2$ , orthorhombic,  $P2_12_12_1$ ,  $a = 5.856$  (1),  $b = 17.470$  (3),  $c = 5.582$  (1) Å,  $Z = 4$ ,  $D_m = 5.31$ ,  $D_x = 5.373$  g cm<sup>-3</sup>. The structure was solved by Patterson methods and refined to an  $R$  of 0.038 for 1876 independent reflexions. The coordination number of Cd is seven, the surrounding O atoms form a distorted pentagonal bipyramid, and the Cd–O distances range between 2.262 and 2.510 Å. The I atoms are closely bonded to three O atoms at distances between 1.81 and 1.83 Å and weakly bonded to three further O atoms at distances between 2.58 and 2.77 Å. Thus, a distorted octahedral coordination is achieved. The O atoms link neighbouring Cd and I atoms in a nearly planar trigonal configuration.

**Introduction.** Recently attention was drawn to different salts of iodic acid in view of their piezoelectric and

electrooptical applications. Single crystals of  $\text{Cd}(\text{IO}_3)_2$  with a size of several mm in all directions were grown by Bach (1976) at a temperature of 70°C by evaporation of an aqueous solution containing 60%  $\text{HNO}_3$ . A small sample was ground in a Bond chamber to an approximately spherical shape of 0.140 mm diameter. Intensities were collected with an automated Stoe two-circle diffractometer STADI 2. With Mo  $K\alpha$  radiation 1876 independent reflexions ( $hkl$ ,  $l = 0$  to 7) were recorded in the range  $2.3^\circ < \theta < 35.0^\circ$ . With respect to anomalous dispersion,  $hkl$  and  $\bar{h}\bar{k}l$  were averaged separately from the group of  $hkl$  and  $\bar{h}\bar{k}l$  reflexions. The 46 weakest reflexions with  $F_o < 10$  were not considered. An absorption correction was applied ( $\mu_{\text{MoK}} = 146.1$  cm<sup>-1</sup>), assuming spherical shape.

Computations were carried out with the XRAY system (Stewart, Kundell & Baldwin, 1970). Approxi-

Table 1. Fractional atomic coordinates and thermal parameters  $U_{ij}$  (Å<sup>2</sup> × 10<sup>2</sup>)

Standard deviations given in parentheses refer to the last significant digits in the parameter values. The temperature factor is of the form  $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ .

	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Cd	0.17191 (7)	0.09346 (2)	0.70714 (13)	1.14 (2)	1.18 (2)	1.28 (19)	-0.05 (1)	-0.03 (2)	0.11 (2)
I(1)	0.21417 (6)	0.20870 (2)	0.25443 (11)	1.02 (2)	0.90 (2)	1.07 (18)	-0.05 (1)	0.02 (2)	-0.06 (2)
I(2)	0.63699 (6)	0.07754 (2)	0.02919 (11)	0.93 (2)	0.88 (2)	1.32 (18)	0.02 (1)	-0.01 (2)	0.07 (2)
	$x$	$y$	$z$	$U$	$x$	$y$	$z$	$U$	
O(1)	0.0203 (11)	0.1650 (4)	0.0417 (19)	1.81 (12)	O(4)	0.8169 (8)	0.0482 (3)	-0.2196 (15)	0.80 (9)
O(2)	0.3694 (10)	0.1249 (4)	0.3645 (16)	1.27 (10)	O(5)	0.5057 (8)	0.1613 (3)	-0.1070 (14)	0.72 (9)
O(3)	0.0327 (10)	0.2081 (4)	0.5185 (18)	1.52 (11)	O(6)	0.3977 (8)	0.0148 (3)	-0.0456 (14)	0.80 (9)