ARGAY, GY. & KÁLMÁN, A. (1973). *Acta Cryst.* B**29**, 636–638.
ARGAY, GY. & SERES, J. (1973). *Acta Cryst.* B**29**, 1146–1149.
BAUDOUR, J. L. & MESSAGER, J. C. (1971). *Acta Cryst.* B**27**, 799–806.
CRUICKSHANK, D. W. J., PILLING, D. E., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis*. Oxford: Pergamon Press.
GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
LIQUORI, A. M. & VACIAGO, A. (1956). *Gazz. Chim. Ital.* **86**, 769–782.
MASON, R. (1961). *Acta Cryst.* **14**, 720–724.
SERES, J. (1970). *Investigations in the Field of Substituted Succinimides.* Dr Techn. Thesis, Techn. Univ. Budapest.

Acta Cryst. (1974). B**30**, 809

Anion Ordering in TaON: A Powder Neutron-Diffraction Investigation

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(*Received* 16 *October* 1973; *accepted* 7 *November* 1973)

The structure of tantalum oxynitride has been determined by the profile analysis of powder neutron-diffraction data collected at 4·2°K. The compound is monoclinic, space group $P2_1/c$, with $a=4{\cdot}9581$, $b=5{\cdot}0267$, $c=5{\cdot}1752$ Å, and $\beta=99{\cdot}640°$ (4·2°K). Complete ordering of the anions occurs in alternate layers normal to the [100] direction and this ordering is consistent with calculated site potentials. Short nitrogen–nitrogen distances of 2·51 to 2·64 Å are observed.

Introduction

Two polymorphs have been reported for TaON: a red low-temperature form with a complex hexagonal structure (Buslaev, Glushkova, Ershova & Shustorovich, 1966; Buslaev *et al.*, 1969) which transforms at approximately 800°C to a green modification, first reported by Brauer & Weidlein (1965) and Brauer, Weidlein & Strahle (1966). The latter has a monoclinic structure and is probably isostructural with baddeleyite (ZrO_2). Mixed anion compounds, including oxyfluorides, *e.g.* YOF (Mann & Bevan 1970), are often ordered in layers and oxynitrides may be similarly ordered. The difference in the neutron scattering lengths for oxygen and nitrogen allows this problem to be solved by the analysis of the diffraction profile obtained from neutron powder data.

Experimental

TaON was prepared by a method similar to that of Brauer *et al.* (1966). 'Specpure' grade Ta_2O_5, supplied by Johnson Matthey Chemicals Ltd, was heated to 830°C in a flow of dry ammonia until the weight change, colour and X-ray Debye-Scherrer photographs indicated complete conversion to TaON according to the equation

$$Ta_2O_5+2NH_3 \rightarrow 2TaON+3H_2O\ .$$

The product was analysed by reconversion to Ta_2O_5 in flowing oxygen on a thermogravimetric balance. Two separate determinations gave compositions of $TaO_{0{\cdot}98\,(2)}N_{1{\cdot}01\,(2)}$ and $TaO_{1{\cdot}01\,(2)}N_{0{\cdot}99\,(2)}$. Attempts to alter the O:N ratio on the oxygen-rich side of TaON gave a mixture of phases and Swisher & Read (1972) report that the non-stoichiometric range of TaON extends only to the nitrogen-rich side.

A room-temperature X-ray diffractometer trace was indexed on a monoclinic unit cell and a least-squares determination of the unit-cell parameters gave $a=4{\cdot}9692$ (3) (4·966), $b=5{\cdot}0330$ (3) (5·034), $c=5{\cdot}1821$ (3) (5·185) Å and $\beta=99{\cdot}682$ (5)° (99·65) where the Brauer *et al.* (1966) values are in parentheses. The systematic absences ($h0l$, $l=2n+1$; $0k0$, $k=2n+1$) indicate the space group $P2_1/c$.

Neutron-diffraction measurements were carried out on the PANDA powder diffractometer at AERE Harwell. The sample was contained in a thin-walled vanadium can which was suspended in a liquid-helium cryostat. A neutron wavelength of 1·537 Å [obtained by reflexion from the (331) planes of a germanium monochromator at a take-off angle of 72°] was employed and the diffraction pattern recorded from 12 to 85° (2θ) in steps of 0·02°.

Results

The neutron-diffraction profile contained 91 reflexions consistent with $P2_1/c$. Refinements were carried out by means of a least-squares comparison of observed and calculated profiles (Rietveld, 1969). The program minimizes the function $\chi^2=\sum_i w_i[y_i(\text{obs})-1/c y_i(\text{calc})]^2$

where w_i is a weighting function, y_i the number of counts at a point i in 2θ and c is a scale factor. Neutron scattering lengths $b_{Ta}=0{\cdot}700\times10^{-14}$ m, $b_N=0{\cdot}940\times10^{-14}$ m and $b_O=0{\cdot}580\times10^{-14}$ m (Neutron Diffraction Commission, 1972) were used. The refinement involved 12 structural variables: nine positional parameters, effective scattering lengths for the two kinds of anion site and an overall temperature factor. In a structure of this type at 4·2°K the temperature factors are bound to be small (0·1–0·2 Å^2) so that the assumption of a single overall B is reasonable. The reliability index defined as

$$R_{\text{profile}}(\text{weighted})=100\,\frac{\sum_i w_i[y_i(\text{obs})-1/cy_i(\text{calc})]^2}{\sum_i w_i[y_i(\text{obs})]^2}$$

converged to a value of 12·9% after four cycles, compared with an idealized minimum of 8·9% expected from purely statistical errors.

The anion sites were assigned a mean scattering length of $0{\cdot}760\times10^{-14}$ m and the occupation numbers refined to give the total scattering for each site. The results of the refinement are given in Table 1 and it may be seen that anion sites A_1 and A_2 are exclusively occupied by N and O respectively. The observed and calculated profiles are illustrated in Fig. 1.

An investigation of TaON by differential thermal analysis did not reveal any features below the decomposition temperature (approximately 1000°C under nitrogen) which suggests that the monoclinic structure is maintained to this temperature, though we cannot be certain that the anions remained fully ordered.

Discussion

Fig. 2 is a projection on the (010) plane, showing the layer order of O and N. The coordination of tantalum

Table 1. *Structural parameters for* TaON *and* ZrO$_2$

Lattice parameters

TaON at 4°K	ZrO$_2$ at room temperature (Adam & Rogers, 1959)
$a=$ 4·9581 (5) Å	$a=$ 5·145 (5) Å
$b=$ 5·0267 (6)	$b=$ 5·2075 (5)
$c=$ 5·1752 (6)	$c=$ 5·3107 (5)
$\beta=$99·640 (7)°	$\beta=$99·23 (8)°

Positional parameters

TaON	x	y	z	ZrO$_2$ (Smith & Newkirk, 1965)	x	y	z
Ta	0·292 (1)	0·046 (1)	0·213 (1)	Zr	0·2758 (2)	0·0411 (2)	0·2082 (2)
A_1	0·4449 (8)	0·7566 (9)	0·4810 (8)	O$_{II}$	0·4423 (15)	0·7549 (14)	0·4789 (13)
A_2	0·064 (1)	0·324 (1)	0·345 (1)	O$_I$	0·0703 (15)	0·3359 (14)	0·3406 (13)

$B_{\text{overall}}=0{\cdot}12$ (8) Å^2

Total scattering from site relative to a Ta occupancy of 1·0.

Ta	0·700 10^{-14} m
A_1	0·93 (1) 10^{-14} m
A_2	0·58 (1) 10^{-14} m

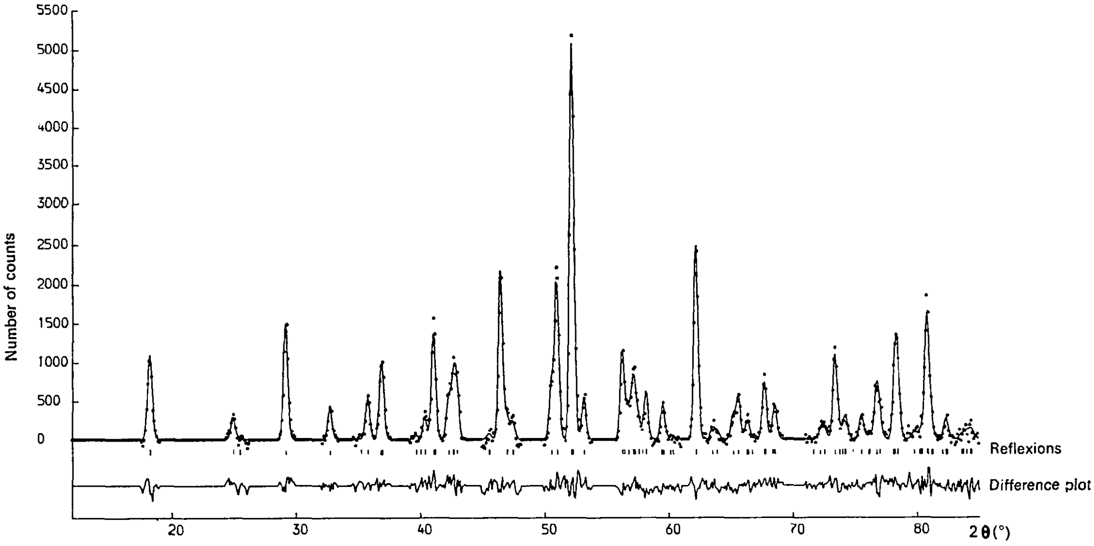

Fig. 1. Observed and calculated profiles for TaON. · observed; — calculated.

is also shown and coordinations of A_1 and A_2 are given in Fig. 3. Four nitrogen atoms are located on one side of the cation and three oxygens on the other and this ordered arrangement is that expected on simple electrostatic grounds. Madelung potentials for each unique site in the structure were calculated assuming integral charges for the ions. Three possible arrangements were considered: (*a*) random occupation of the two anion sites by O^{2-} and N^{3-}, (*b*) preferential occupation of A_1 by O^{2-} and A_2 by N^{3-} and (*c*) the alternative arrangement with A_1 occupied by N^{3-} and A_2 by O^{2-}. The results of these calculations are shown in Table 2. In every case it turns out that A_1 is more positive, *i.e.* more favourable for nitrogen occupation than A_2, entirely in line with the structural findings.

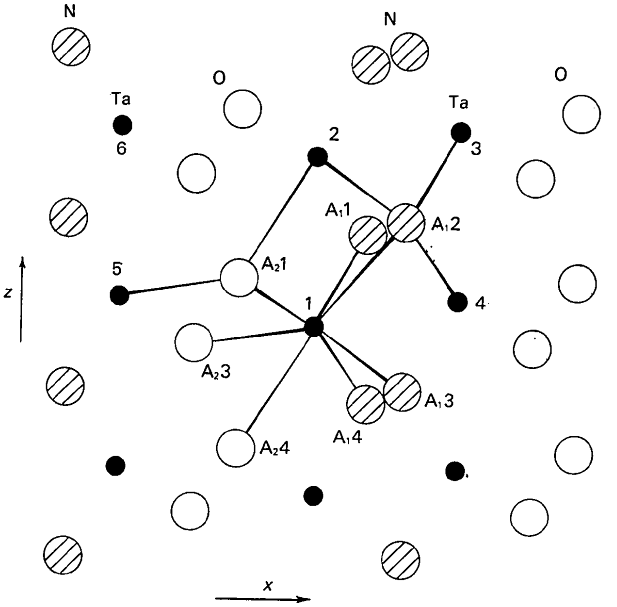

Fig. 2. A projection of the structure onto the (010) plane – angle β idealized as 90°. Black circles Ta; open circles O and hatched circles; N.

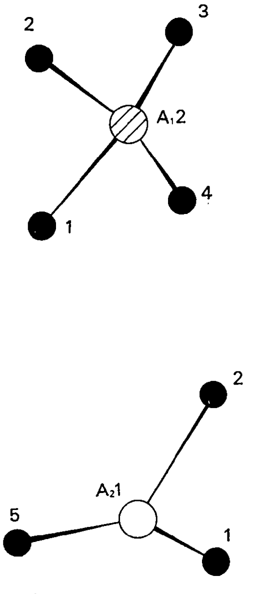

Fig. 3. (*a*) Coordination polyhedron for $A_1$2 (nitrogen). (*b*) Coordination polyhedron for $A_2$1 (oxygen).

Table 2. *Results of site potential calculations*

	Potential for random distribution	Potential for $O^{2-}(A_1)$, $N^{3-}(A_2)$	Potential for $N^{3-}(A_1)$, $O^{2-}(A_2)$
Ta	−3·749	−3·705	−3·794
A_1	+2·333	+2·141	+2·524
A_2	+1·895	+2·088	+1·701

Interionic distances and angles are summarized and compared with ZrO_2 in Table 3. The detailed coordinates are close to those for monoclinic ZrO_2, and the nitrogen atoms occupy virtually the same positions as O_{II} in ZrO_2 [Smith & Newkirk (1965) notation]. The cell dimensions of ZrO_2 are larger than those of TaON (a consequence of the larger radius of Zr^{4+}) and therefore interatomic distances would be expected to be smaller in TaON. However, we see that the tantalum–oxygen distances are in fact similar to the Zr–O_{II} values and that there is a larger contraction of the Ta–N distances than would be predicted from the change in cell dimensions alone. This contraction implies a relative displacement of the tantalum ions towards the nitrogen layers (with a slight preference for nitrogen atom in sites $A_1$2 and $A_1$3). This effect is also seen in the separation of the metal ions. Cation–cation distances across the planes of anions O_I and O_{II} differ in ZrO_2 (3·93 and 3·46 Å respectively) with the shorter distance originating from the greater concentration of anions between metal ions sandwiching the O_{II} layer. In TaON the difference is more marked and Ta–Ta distances of 3·90 and 3·30 Å reflect the stronger Ta–nitrogen interaction.

Table 3. *Interatomic distances and bond angles in* TaON *and* ZrO_2

(*a*) Interatomic distances (Å) in TaON compared with values for ZrO_2 (Smith & Newkirk, 1965).

Metal–metal distances in the unit cell.

	TaON	ZrO_2
1–2	3·302 (7)	3·429 (7)
1–4	3·233 (7)	3·460 (7)
3–4	3·944 (7)	4·030 (7)
1–5	3·901 (7)	3·929 (7)
Metal–A_1 distances in the Ta(1) coordination polyhedron.		
1–$A_1$1	2·065 (7)	2·151 (7)
1–$A_1$2	2·122 (9)	2·285 (7)
1–$A_1$3	2·066 (8)	2·189 (7)
1–$A_1$4	2·153 (8)	2·220 (7)
Metal–A_2 distances in the Ta(1) coordination polyhedron.		
1–$A_2$1	1·989 (10)	2·051 (7)
1–$A_2$3	2·067 (7)	2·057 (7)
1–$A_2$4	2·147 (10)	2·163 (7)

Table 3 (*cont.*)

A_2–metal distances in the $A_2$1 coordination polyhedron.

$A_2$1–1	1·989 (10)	2·051 (7)
$A_2$1–2	2·147 (10)	2·163 (7)
$A_2$1–5	2·067 (7)	2·057 (7)

A_1–metal distances in the $A_1$2 coordination polyhedron.

$A_1$2–1	2·122 (9)	2·285 (7)
$A_1$2–2	2·066 (8)	2·189 (7)
$A_1$2–3	2·065 (7)	2·151 (7)
$A_1$2–4	2·153 (8)	2·220 (7)

A_1–A_i distances in the Ta(1) coordination polyhedron.

1–2	2·508 (6)	2·622 (14)
2–3	2·588 (6)	2·658 (14)
3–4	2·637 (6)	2·722 (14)
1–4	2·588 (6)	2·658 (14)

A_2–A_2 distances in the Ta(1) coordination polyhedron.

1–3	2·735 (7)	2·83 (1)
1–4	2·692 (7)	2·80 (1)
3–4	2·539 (7)	2·59 (1)

(*b*) Bond angles in TaON compared with ZrO_2.
Metal coordination polyhedron with metal as origin.

		TaON	ZrO_2
Metal to $A_1$1	and $A_1$2	73°33′	72°30′
$A_1$2	$A_1$3	76°20′	72°54′
$A_1$3	$A_1$4	77°22′	76°6′
$A_1$4	$A_1$1	75°41′	74°48′
$A_2$1	$A_2$3	84°45′	87°6′
$A_2$3	$A_2$4	74°4′	75°36′
$A_2$1	$A_2$4	81°8′	83°24′
$A_1$1	$A_2$2	85°45′	88°18′
$A_1$2	$A_2$1	74°16′	72°42′
$A_1$3	$A_2$1	104°22′	101°
$A_1$3	$A_2$4	72°13′	72°42′
$A_1$4	$A_2$3	84°48′	88°12′
$A_1$4	$A_2$4	84°25′	83°30′
$A_2$1 coordination polyhedron.			
$A_2$1 to Ta(5)	and Ta(1)	148°12′	142°54′
(5)	(2)	106°23′	104°
(1)	(2)	105°51′	109°6′
$A_1$2 coordination polyhedron.			
$A_1$2 to Ta(3)	and Ta(1)	106°25′	107°36′
(2)	(4)	98°17′	100°24′
(2)	(3)	103°1′	105°42′
(3)	(4)	138°18′	134°18′
(4)	(1)	98°17′	100°24′
(1)	(2)	102°39′	103°54′

Errors in measurements of angles are ±14′ for TaON and approximately ±16′ for ZrO_2.

The most striking feature of the TaON structure is the close approach of the nitrogen ions to each other. The values observed here range from 2·51 to 2·64 Å, compared with 3·655 Å in Li_3N (Zintl & Brauer, 1935) and 2·8 Å in Th_3N_4 (Bowman & Arnold, 1971). The only comparable nitrogen–nitrogen separation is one of 2·66 Å in UN_2 reported (as a high-pressure phase) by Rundle, Baenziger, Wilson & McDonald (1948). The distances are similar to some of the shortest observed oxygen–oxygen approaches in oxides (*e.g.* O–O is 2·52 Å in Al_2O_3 and 2·60 Å in SiO_2) and must arise from considerable covalency in the Ta–N interaction.

We are grateful to Dr A. K. Cheetham for useful discussions and to Professor W. Van Gool for supplying the computer program on which the site potential calculations were based. We acknowledge the Science Research Council and AERE, Harwell, for the provision of neutron facilities and thank Mr D.H.C. Harris and members of the University Support Staff for some experimental assistance. One of us (D.A.) thanks the S.R.C. for the provision of a studentship.

References

ADAM, J. & ROGERS, M. D. (1959). *Acta Cryst.* **12**, 951–957.
BOWMAN, A. L. & ARNOLD, G. P. (1971). *Acta Cryst.* B**27**, 243–244.
BRAUER, G. & WEIDLEIN, J. R. (1965). *Angew. Chem.* **77**, 218, 913.
BRAUER, G., WEIDLEIN, J. & STRAHLE, J. (1966). *Z. anorg. allgem. Chem.* **348**, 298–308.
BUSLAEV, YU. A., GLUSHKOVA, M. A., ERSHOVA, M. M. & SHUSTOROVICH, E. M. (1966). *Neorg. Mat.* **2**, 2120–2124.
BUSLAEV, YU. A., SAFRONOV, G. M., PAKHOMOV, V. I., GLUSHKOVA, M. A., REPKO, V. P., ERSHOVA, M. M., ZHUKOV, A. N. & ZHDANOVA, T. A. (1969). *Neorg. Mat.* **5**, 45–48.
MANN, A. W. & BEVAN, D. J. M. (1970). *Acta Cryst.* B**26**, 2129–2131.
NEUTRON DIFFRACTION COMMISSION (1972). *Acta Cryst.* A**28**, 357–358.
RIETVELD, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.
RUNDLE, R. E., BENZIGER, N. C., WILSON, A. S. & MCDONALD, R. A. (1948). *J. Amer. Chem. Soc.* **70**, 99–105.
SMITH, D. K. & NEWKIRK, W. (1965). *Acta Cryst.* **18**, 983–991.
SWISHER, J. H. & READ, M. H. (1972). *Met. Trans.* **3**, 489–494.
ZINTL, E. & BRAUER, G. (1935). *Z. Elektrochem.* **41**, 102.