

Ammonium Perrhenate at 295 and 135 K

BY G. J. KRUGER

National Physical Research Laboratory, CSIR, PO Box 395, Pretoria 0001, South Africa

AND E. C. REYNHARDT

Department of Physics, University of South Africa, PO Box 392, Pretoria 0001, South Africa

(Received 26 July 1977; accepted 14 August 1977)

Abstract. NH_4ReO_4 , tetragonal, $I4_1/a$, $Z = 4$, $M_r = 266.2$. At 135 K: $a = 5.995$ (3), $c = 12.440$ (5) Å; at 295 K: $a = 5.892$ (3), $c = 12.970$ (5) Å. Accurate single-crystal X-ray diffraction analyses were performed and least-squares refinement gave final R values of 0.017 and 0.016 at 135 and 295 K respectively. H atoms could be located at 135 K only. No change could be observed in anion distortion and structural changes are relatively small.

Introduction. The unusual temperature dependence of the ^{187}Re nuclear quadrupole resonance (NQR) frequency in NH_4ReO_4 was first reported by Burkert & Eckel (1973). Subsequent studies by Boguslavskii, Lotfullin, Magera & Pechenov (1975) and Johnson & Rogers (1974) confirmed that $(\delta\nu_Q/\delta T)_p$ is positive over the range 100 to 400 K as opposed to the negative values normally observed for most compounds.

NH_4ReO_4 is known to have the tetragonal scheelite structure in common with many other substances (Wyckoff, 1965). In a recent study of the temperature dependence of the cell dimensions, Brown, Smeltzer & Heyding (1976) found that the thermal-expansion coefficients are very large and opposite in sign, with $\alpha_a = -1.8 \times 10^{-4}$ and $\alpha_c = 3.9 \times 10^{-4} \text{ K}^{-1}$ over the temperature range 140 to 370 K. It has been suggested (Brown & Segel, 1977) that the anomalous behaviour of NH_4ReO_4 is due to a temperature-dependent distortion of the ReO_4^- ion, while Petch, Reynhardt & Watton (1977) explain their proton relaxation and second-moment results in terms of a model in which the motion of the NH_4^+ ion is changed from general reorientation at 100 K to isotropic tumbling at 400 K. In order to explain the anomalous behaviour of this compound, accurate structure determinations were performed at 135 and 295 K.

To minimize absorption errors, a very small but regular crystal was selected for data collection. The crystal was cooled in a stream of cold nitrogen gas. The temperature could be kept constant to within 0.5 K. Cell dimensions were obtained on the diffractometer by least-squares refinement of 25 reflections. The experimental conditions are given in Table 1. The scan rates

at 135 and 295 K were 0.075 and 0.05° s^{-1} respectively. All four equivalent reflections hkl , $\bar{h}\bar{k}l$, $k\bar{h}l$ and $\bar{k}hl$ were measured and averaged and the e.s.d. found to be 6%. No absorption corrections were applied.

The structures were refined by full-matrix least squares with anisotropic temperature factors and $1/\sigma^2(F)$ weights. Difference maps were calculated for both sets of data but the position of the H atom could only be found at the low temperature. This atom was included with an isotropic thermal parameter in subsequent refinement of the low-temperature data. Extinction was found to be negligible for the 135 K data but refinement of an isotropic extinction factor (Larson, 1967) reduced the R factor significantly for the 295 K data.

Refinement converged with R factors of 0.016 and 0.017 (R_w values of 0.017 and 0.019) for the 295 and 135 K data respectively. It is interesting that such a good fit could be obtained with data which suffered from systematic errors of 6%, probably mainly due to absorption. This reflects a surprising ability of the model to accommodate systematic errors. For the Re atom the anomalous-scattering factors of Cromer & Liberman (1970) were applied. All the calculations were performed with the XRAY system (1972). The

Table 1. General information

Instrument: Philips PW 1100 diffractometer with an Enraf–Nonius Universal low-temperature device		
Source: Mo $K\alpha$, $\lambda = 0.7107$ Å, graphite monochromator		
Crystal size: $0.04 \times 0.04 \times 0.04$ mm		
ω - 2θ scan, scan width = 1.5° (θ)		
Scan limits: 3° to 30° (θ)		
$\mu = 284 \text{ cm}^{-1}$		
Systematic absences: hkl , $h + k + l \neq 2n$; $hk0$, h , $(k) \neq 2n$; $00l$, $l \neq 4n$		
Space group $I4_1/a$		
	135 K	295 K
Unique reflections	327	325
Observed reflections	259	256
$\Sigma F^2 - \langle F^2 \rangle / \Sigma F^2$	0.058	0.059
D_c (g cm^{-3})	3.955	3.927

Table 2. *Positional and thermal parameters* ($\times 10^4$)

The temperature factor is defined as $\exp[-2\pi^2(h^2a^{*2}U_{11} + 2hka^*b^*U_{12} + \dots)]$. Extinction parameter $g = 100(6) \times 10^{-6}$.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{11} or U	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
135K									
Re	0*	0*	0*	85 (1)	85*	62 (2)	0*	0*	0*
N	0*	0*	5000*	153 (25)	153*	90 (37)	0*	0*	0*
O	2045 (7)	3786 (7)	1702 (3)	136 (19)	154 (19)	119 (18)	33 (16)	14 (16)	5 (16)
H	3718 (129)	4557 (161)	332 (59)	244 (239)					
295K									
Re	0*	0*	0*	189 (2)	189*	217 (2)	0*	0*	0*
N	0*	0*	5000*	320 (29)	320*	247 (43)	0*	0*	0*
O	2119 (8)	3883 (8)	1742 (4)	361 (24)	349 (24)	353 (23)	85 (20)	132 (21)	-10 (21)

* Special position.

Table 3. *Interatomic distances* (Å) *and angles* ($^\circ$)

	135 K	295 K
Re—O	1.737 (5)	1.720 (5)
N—H	0.91 (8)	
N—O ⁱ	2.855 (5)	2.902 (5)
N—O ⁱⁱ	3.046 (5)	3.014 (6)
O—H	2.03 (8)	
O—O ⁱⁱⁱ	3.107 (7)	3.243 (7)
O—Re—O	110.3 (2)	110.3 (2)
O—Re—O	109.1 (2)	109.1 (2)
H—N—H	126 (7)	
H—N—H	102 (8)	
N—H—O	149 (7)	
Re—O—H	137 (3)	

Equivalent positions: (i) $x - \frac{1}{2}, y - \frac{1}{2}, z + \frac{1}{2}$; (ii) $x - \frac{1}{2}, y, \frac{3}{4} - z$;
(iii) $-x, \frac{1}{2} - y, \frac{1}{4} - z$.

atomic parameters are listed in Table 2.* Interatomic distances and angles are given in Table 3.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32930 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion. Fig. 1 illustrates the crystal packing and hydrogen bonding at 135 K. The NH_4ReO_4 structure consists of tetrahedral NH_4^+ and ReO_4^- ions linked by hydrogen bonds. The cations are surrounded by eight O atoms, four of which are closer than the others.

The low- and room-temperature structures differ very little. The small changes that do occur can be seen as a result of the H atom occupying a preferential equilibrium position at lower temperatures. The closest N—O contact decreases from 2.902 (5) Å at 295 K to 2.855 (5) Å at 135 K indicating a strengthened hydrogen bond. Simultaneously, the other N—O distance increases from 3.014 (6) to 3.046 (5) Å. The main component of the hydrogen bond is along the *c* axis and the decreased N—O separation results in a contraction of the cell in this direction.

The tetrahedral angles of the ReO_4^- ion stay constant but the Re—O bond distances increase with decreasing temperature as a result of the strengthened hydrogen bonds. To accommodate these enlarged anions in the shorter cell, the O tetrahedra rotate about [001] increasing the angle β with the [100] plane (shown in Fig. 2) by 3° . This rotation, however, reduces the contact distance between the O corners of neighbouring tetrahedra (distance *PQ* in Fig. 2). The

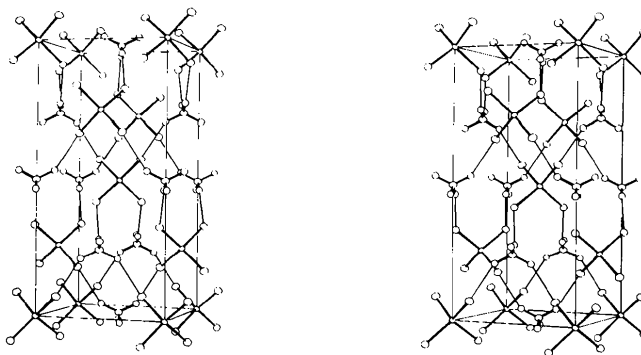


Fig. 1. Stereoview of the unit-cell contents of NH_4ReO_4 at 135 K. Thermal ellipsoids are drawn at the 0.5 probability level. H atoms are on an arbitrary scale. Hydrogen bonds are represented by thin lines.

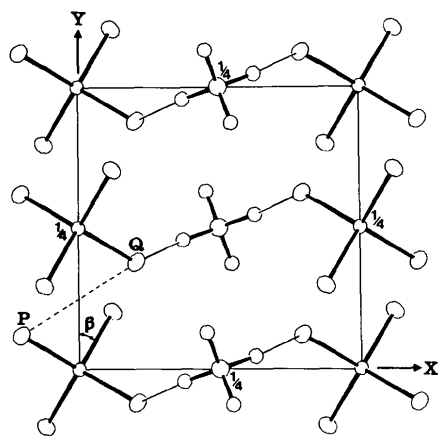


Fig. 2. Projection down [001] of the tetrahedral NH_4^+ and ReO_4^- ions at $z = 0$ and $z = \frac{1}{4}$. The dashed line PQ indicates the interatomic distance discussed in the text. (N is at $x = \frac{1}{2}$, Re is at $x = 0$.)

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 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).

References

- BOGUSLAVSKII, A. A., LOTFULLIN, R. SH., MAGERA, R. V. & PECHENOV, V. V. (1975). *Sov. Phys. Solid State*, **16**, 1602–1603.
- BROWN, R. J. C. & SEGEL, S. L. (1977). Private communication.
- BROWN, R. J. C., SMELTZER, J. G. & HEYDING, R. D. (1976). *J. Magn. Reson.* **24**, 269–274.
- BURKERT, P. K. & ECKEL, M. F. (1973). *Z. Naturforsch. Teil B*, **28**, 379–382.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
- JOHNSON, R. A. & ROGERS, M. T. (1974). *J. Magn. Reson.* **15**, 584–589.
- LARSON, A. C. (1967). *Acta Cryst.* **23**, 664–665.
- PETCH, H. E., REYNHARDT, E. C. & WATTON, A. (1977). *J. Magn. Reson.* To be published.
- REYNHARDT, E. C. & KRUGER, G. J. (1977). *J. Magn. Reson.* Submitted for publication.
- WYCKOFF, R. W. G. (1965). *Crystal Structures*, Vol. 3. New York: Interscience.
- XRAY SYSTEM (1972). Tech. Rep. TR-192, edited by J. M. STEWART, G. J. KRUGER, H. L. AMMON, C. DICKINSON & S. R. HALL. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Acta Cryst. (1978). B34, 261–263

A Reinvestigation of the Structure of ϵ -Tantalum Nitride

BY A. NØRLUND CHRISTENSEN*

Department of Inorganic Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark

AND B. LEBECH

Physics Department, Risø National Laboratory, DK-4000 Roskilde, Denmark

(Received 17 June 1977; accepted 14 September 1977)

Abstract. ϵ -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 TaN_3 triangle and two regular three-sided Ta_2N_6 prisms.

Introduction. ϵ -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), β - Ta_2N and δ -TaN, have broad composition ranges and are typical nonstoichiometric compounds. δ -TaN has the NaCl structure (Gatterer *et al.*, 1975), and β - Ta_2N a structure similar to that of β - Nb_2N (Conroy & Christensen, 1977; Christensen, 1976). The structure of ϵ -TaN has been determined from X-ray powder patterns (Brauer & Zapp, 1954). However, the Ta

* To whom correspondence should be addressed.