

Neutron Diffraction Studies of Ammonium Perrhenate and Ammonium Metaperiodate at Low Temperature

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(Received 18 February 1980; accepted 16 May 1980)

Abstract

The structures of ND_4ReO_4 at 100 and 205 K and of ND_4IO_4 at 100 K have been determined by neutron diffraction. The space group is $I4_1/a$ for all three structures. Cell constants are $a = 6.0148$ (18), $c = 12.4457$ (39); $a = 5.9340$ (14), $c = 12.6598$ (30); and $a = 6.0122$ (17), $c = 12.3813$ (43) Å, respectively. The ammonium ion is hydrogen bonded to the O atoms belonging to anions displaced relative to the N atom by $\pm c/4$ along c . Anisotropic temperature factor ellipsoids for the D atoms at 205 K are very elongated, and indicate large librational amplitudes.

Introduction

Ammonium perrhenate and ammonium metaperiodate are isostructural (scheelite) and have several unusual properties in common. The temperature dependencies of the ^{187}Re and ^{127}I nuclear quadrupole resonance frequencies were the original source of interest (Johnson, Rogers & Leroi, 1972; Segel, Brown & Heyding, 1978), and led to measurements of the pressure coefficients of the quadrupole couplings (Brown & Segel, 1977), thermal-expansion coefficients (Brown, Smeltzer & Heyding, 1976), proton-relaxation times (Armstrong, Lourens & Jeffrey, 1976), and several other properties. The atomic positions in NH_4ReO_4 were determined by X-ray diffraction at two temperatures by Kruger & Reynhardt (1978). The H atoms were located at 135 K but not at room temperature, because of ammonium ion rotational motion. NH_4IO_4 shares many of the unusual features of NH_4ReO_4 , but to a less marked extent. The present paper reports a study of ND_4ReO_4 and ND_4IO_4 by powder neutron diffraction at low temperatures.

Experimental

Ammonium metaperiodate and ammonium perrhenate were deuterated by repeated recrystallization from D_2O . All operations were carried out in a dry atmosphere. The extent of deuteration was checked by high-resolution NMR of samples dissolved in D_2O with added *p*-dioxane as internal standard; no protons were detected in either material, and in the treatment of the data it was assumed that deuteration was complete. For the neutron diffraction experiments the samples were contained in an air-tight thin-walled vanadium can which was rotated during the measurements. Temperatures were regulated by a thermostatically controlled cold finger cooled with liquid nitrogen.

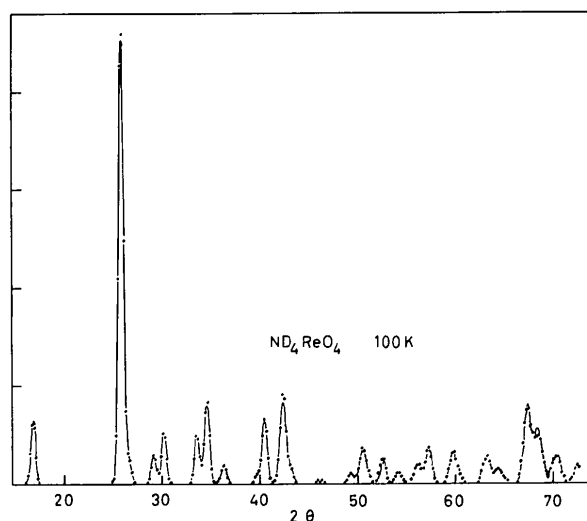


Fig. 1. The neutron diffraction pattern for ND_4ReO_4 at 100 K. The points represent observed intensities, and the line shows the calculated intensity profile. The corresponding diagrams for the other two sets of data are similar.

Temperatures were measured with a copper-constantan thermocouple, and contain possible errors of ± 5 K. Neutrons (C4 beam hole of the NRU reactor) were made monochromatic ($\lambda = 1.5471$ Å) by reflection from the (113) plane of a germanium single crystal. Intensity profiles were obtained over the 2θ range 15 to 73° for ND_4ReO_4 and 21 to 73° for ND_4IO_4 in steps of 0.2°. The profile for ND_4ReO_4 at 100 K is given in Fig. 1.*

* Neutron profiles for ND_4ReO_4 at 205 K and ND_4IO_4 at 100 K have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35352 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Refinement

The profile-refinement method (Rietveld, 1969; Hewat, 1973) was used to determine the cell dimensions, the O and D positions and the anisotropic temperature factors. The counter zero point and the overall scale factor were refined, but the three line-width parameters were held fixed. The starting position parameters for the refinement were taken from the known structures of NH_4ReO_4 , KReO_4 (Lock & Turner, 1975), or NaIO_4 (Kálmán & Cruickshank, 1970). The results of the refinements for NH_4ReO_4 at 100 and 205 K and for ND_4IO_4 at 100 K are summarized in Tables 1, 2, and 3, and structural data calculated from these parameters are given in Table 4.

Table 1. Cell dimensions

These data were obtained from refinement of the neutron diffraction profiles, assuming a neutron wavelength $\lambda = 1.5471$ Å. E.s.d.'s are given in parentheses. The space group is $I4_1/a$.

	<i>T</i> (K)	<i>a</i> (Å)	<i>c</i> (Å)
ND_4ReO_4	100	6.0148 (18)	12.4457 (39)
ND_4ReO_4	205	5.9340 (14)	12.6598 (30)
ND_4IO_4	100	6.0122 (17)	12.3813 (43)

Discussion

In NH_4XO_4 ammonium salts having the scheelite structure, the ammonium ion is surrounded by eight O atoms, which can be divided into two groups of four. One group belongs to the XO_4^- anions in which the X atoms lie at the same level along *c* (i.e. with the same *z* value) as the N atom in the NH_4^+ ion. This group will be referred to as equatorial O atoms. The four equatorial

Table 2. Fractional position parameters

Parameters are given relative to the origin at $\bar{1}$, and have been multiplied by 10^4 . E.s.d.'s are given in parentheses. N is at (0, 7500, 3750) and Re or I is at (0, 2500, 1250).

	<i>T</i> (K)	<i>R</i>	<i>x</i> _D	<i>y</i> _D	<i>z</i> _D	<i>x</i> _O	<i>y</i> _O	<i>z</i> _O
ND_4ReO_4	100	2.88%	4420 (34)	6089 (41)	1746 (20)	2051 (18)	3852 (22)	467 (8)
ND_4ReO_4	205	3.69%	4570 (30)	6198 (34)	1723 (18)	2159 (13)	3770 (19)	518 (6)
ND_4ReO_4	100	2.74%	4705 (30)	6069 (28)	1726 (20)	2086 (21)	3897 (16)	439 (8)
$\text{NH}_4\text{ReO}_4^*$	135	—	4557 (129)	6218 (161)	1582 (59)	2045 (7)	3714 (7)	452 (3)
NH_4ReO_4	295	—	—	—	—	2119 (8)	3617 (8)	492 (4)

* Results of X-ray refinement by Kruger & Reynhardt (1978), transformed to the origin at $\bar{1}$.

Table 3. Anisotropic thermal parameters

The anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The parameters β_{ij} in the table have been multiplied by 10^4 ; e.s.d.'s are given in parentheses.

	<i>T</i> (K)		β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
ND_4ReO_4	100	N	101 (176)	101	53 (62)	0	0	0
		D	469 (74)	354 (135)	22 (32)	-60 (115)	56 (36)	-69 (38)
		Re	150 (41)	150	-1 (16)	0	0	0
		O	54 (50)	227 (60)	24 (16)	55 (47)	92 (29)	-11 (23)
ND_4ReO_4	205	N	483 (96)	483	85 (49)	0	0	0
		D	1591 (153)	325 (88)	138 (26)	134 (87)	211 (34)	-216 (43)
		Re	236 (36)	236	14 (16)	0	0	0
		O	301 (94)	136 (56)	25 (10)	114 (39)	68 (19)	58 (12)
ND_4IO_4	100	N	46 (141)	46	21 (63)	0	0	0
		D	304 (53)	215 (128)	20 (23)	98 (101)	-59 (37)	-29 (34)
		I	242 (68)	242	25 (28)	0	0	0
		O	10 (41)	66 (38)	6 (10)	95 (71)	47 (22)	57 (25)

Table 4. *Structural parameters for NH₄XO₄*

Interatomic distances (Å)							
	<i>T</i> (K)	X—O	N—H	N—O _{ax}	N—O _{eq}	H—O _{ax}	O—O(interionic)
ND ₄ ReO ₄	100	1.770 (11)	1.106 (24)	2.894 (10)	2.985 (18)	1.839 (27)	3.057 (22)
ND ₄ ReO ₄	205	1.752 (8)	1.010 (21)	2.902 (8)	2.932 (15)	1.941 (23)	3.227 (17)
ND ₄ IO ₄	100	1.813 (11)	1.058 (20)	2.854 (11)	2.961 (15)	1.868 (26)	3.038 (23)
NH ₄ ReO ₄ *	135	1.737 (5)	0.91 (9)	2.855 (5)	3.046 (5)	2.03 (8)	3.107 (7)
NH ₄ ReO ₄ *	295	1.720 (5)	—	2.902 (5)	3.014 (6)	—	3.243 (7)

Angles (°)						
The <i>c</i> axis bisects the interatomic angles. The angle β is defined in the text.						
	<i>T</i> (K)	O—X—O	H—N—H	O _{ax} —N—O _{ax}	O _{eq} —N—O _{eq}	β
ND ₄ ReO ₄	100	113.2 (0.7)	112.1 (2.5)	84.8 (0.4)	141.9 (0.5)	33.4 (0.5)
ND ₄ ReO ₄	205	116.1 (0.5)	107.3 (2.5)	79.0 (0.3)	143.2 (0.4)	30.5 (0.4)
ND ₄ IO ₄	100	112.7 (0.7)	112.3 (2.5)	85.8 (0.4)	140.3 (0.6)	33.8 (0.4)
NH ₄ ReO ₄ *	135	110.3 (0.2)	126 (7)	78.6 (0.2)	141.9 (0.2)	30.7 (0.2)
NH ₄ ReO ₄ *	295	110.3 (0.2)	—	77.7 (0.3)	141.9 (0.3)	27.8 (0.2)

* Results of X-ray refinement of Kruger & Reynhardt (1978).

O atoms are equidistant from the N atom, and form a distorted tetrahedron with its S_4 axis along the c axis of the unit cell. The other group belongs to the XO_4^- anions in which the X atoms are displaced along c by distances of $\pm c/4$ from the N atom in the NH_4^+ ion, *i.e.* $z_X = z_N \pm 0.25$. This group will be referred to as axial O atoms. The four axial O atoms are equidistant from the N atom, and form a distorted tetrahedron with its S_4 axis along the c axis of the unit cell. The distortions of the axial and equatorial tetrahedra of O atoms, though related, are not the same and the N—O_{ax} and N—O_{eq} distances are not equal. There are, therefore, two possible natural orientations for the ND_4^+ ion, in which the D atoms are close to either the axial or equatorial O atoms and energy minima might be expected due to hydrogen bonding. The axial and equatorial orientations of the ammonium ion are in general not equal in energy. Kruger & Reynhardt (1978), in their X-ray study, were able to locate the positions of the H atoms in NH_4ReO_4 at 135 K and showed that the NH_4^+ orientation is axial rather than equatorial. That result is confirmed by the present experiments for both ND_4ReO_4 and ND_4IO_4 at low temperatures. Table 2 contains the position parameters given by Kruger & Reynhardt transformed to the origin at $\bar{1}$ for comparison. Table 4 summarizes the interatomic distances and angles, calculated from the lattice parameters, and position parameters.

The D—N—D angle in the ND_4^+ ion is not significantly different from the angle in a regular tetrahedral ion in any of the three cases studied. However, the XO_4^- anion is slightly compressed along c . The present results indicate that the O—Re—O angle is (a) larger than the value based on X-ray measurements, and (b) temperature dependent. The angle $\beta = \tan^{-1} [(y_O - 0.25)/x_O]$ defined by Kruger & Reynhardt

specifies the orientation of the anion relative to the edge of the unit cell; β is found to be somewhat larger in the neutron results than in the X-ray results for NH_4ReO_4 , but its temperature dependence is similar. The X—O distances in both ND_4ReO_4 and ND_4IO_4 at 100 K are found to be about 0.04 Å longer than the corresponding distances in NH_4ReO_4 , $KReO_4$ (Lock & Turner, 1975) and $NaIO_4$ (Kálmán & Cruickshank, 1970) measured by X-ray diffraction at room temperature.

Both the axial and equatorial tetrahedra of O atoms about the ammonium ion are considerably distorted. The equatorial tetrahedron is flattened and the axial tetrahedron elongated along c . The N—O_{ax} distance is significantly shorter than the N—O_{eq} distance in both salts at 100 K, which is no doubt correlated with the axial orientation of the ammonium ion. However, the N—O_{ax} and N—O_{eq} distances in ND_4ReO_4 are almost equal at 205 K. The D—O_{ax} distance of about 1.85 Å is consistent with hydrogen bonding between the ammonium ion and its surrounding O atoms.

The temperature factors given in Table 3 show that the N and Re (or I) atoms are more restricted in their thermal motion along c than in the ab plane. This effect was also observed in the X-ray analysis, although the anisotropy was not so marked. These observations suggest further consideration of the assignment of the translational-mode frequencies of the ReO_4^- ion. The B_g mode, consisting primarily of motion along c , has been assigned a lower frequency (49 cm^{-1}) than the E_g mode (68 cm^{-1}) which consists primarily of motion in the ab plane (Johnson, Rogers & Leroi, 1972; Korppi-Tommola, Devarajan, Brown & Shurvell, 1978). These vibrational assignments imply that there ought to be a larger amplitude of motion along c than in the ab plane, which is not observed. The thermal factors for the D

atoms at 100 K also show that motion in the *ab* plane is of larger amplitude than motion along *c*. At 205 K, the deuterium thermal ellipsoid in ND_4ReO_4 becomes very elongated along *a*, suggesting high-amplitude librational motion about *c*. Preferred reorientation of the NH_4^+ ions about *c* at 4.2 K was demonstrated by Lalowicz, McDowell, Raghunathan & Srinivasan (1978) by proton magnetic resonance. The presence of large-amplitude *c*-axis librations of the ammonium ion at 205 K is also consistent with the broadening and disappearance of the ammonium ion lattice modes in the Raman spectra in the vicinity of 200 K (Korppi-Tommola, Devarajan, Brown & Shurvell, 1978), and suggests that higher librational-rotational energy levels become significantly populated at about this temperature. Petch, Reynhardt & Watton (1978) proposed a similar model in which general reorientation of the ammonium ion takes place at temperatures above 100 K. The present results indicate that ammonium ion rotational motion remains restricted until temperatures above 200 K are reached.

This work was supported by the National Research Council of Canada. The sample of ND_4IO_4 was supplied by Dr H. F. Shurvell. The assistance of Mr David Groves with the NMR measurements is gratefully acknowledged. We thank Dr John Copley for supplying a deck for the profile preparation and

refinement programs. One of us (SLS) thanks AECL for hospitality during the course of these experiments.

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Acta Cryst. (1980). **B36**, 2198–2202

Straight Si—O—Si Bridging Bonds Do Exist in Silicates and Silicon Dioxide Polymorphs

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(Received 4 February 1980; accepted 8 April 1980)

Abstract

In 109 precisely determined crystal structures 247 different SiO_4 tetrahedra have been found which have a total of 293 unique O atoms involved in bridging Si—O—Si bonds. Eight of the O atoms are located on symmetry elements and have straight bridging angles of 180° . In four more cases of essentially straight Si—O—Si angles (177.7 to 179.9°) the O atoms are located in less symmetrical positions. The number of straight angles is surprisingly large if one considers the frequency of their occurrence per unit solid angle. The frequency distribution corrected per unit solid angle of

the bridging angle in silicates has peaks at 139 , 157 and 180° (with a mean of 154°), while the silica polymorphs have peaks at 147 , 157 and 180° (with a mean of 162°). The latter distribution is different from the distribution found experimentally for vitreous silica.

Introduction

About twenty years ago Liebau (1961) studied the question as to whether or not the angle Si—O—Si in silicates can assume a value of 180° . The answer given then was that normally the average value of the