

Refinement of Ammonium Perrhenate Structure Using a Pseudo-Spin Model for the Ammonium Ion Orientation

I. P. SWAINSON^a AND R. J. C. BROWN^{b*}

^aAECL, Chalk River Laboratories, Chalk River, Ontario, Canada K0J 1J0, and ^bChemistry Department, Queen's University, Kingston, Ontario, Canada K7L 3N6. E-mail: brownrjc@chem.queensu.ca

(Received 29 September, 1995; accepted 10 September, 1996)

Abstract

A new Rietveld refinement of previously reported powder neutron diffraction data on ND_4ReO_4 taken over a wide range of temperatures [Powell, Brown, Harnden & Reid (1993). *Acta Cryst.* B49, 463–468] is reported. Rigid-body constraints are applied to the cation geometry and occupation of a second cation orientation at higher temperatures is permitted. The resulting structure at higher temperatures is to be preferred to the previous structure with a single cation orientation and supports the pseudo-spin theory of cooperative disordering without a phase transition.

1. Introduction

Interest in the physical properties of NH_4ReO_4 began with the discovery of unusual features of the Re nuclear quadrupole resonance (NQR) spectrum. Both the temperature coefficient (Rogers & Rama Rao, 1973; Burkert & Eckel, 1973; Johnson & Rogers, 1974) and pressure coefficient (Brown, 1975; Brown & Segel, 1977) of the Re NQR frequency were found to be positive, contrary to all previous observations. The NQR anomalies were shown to be associated with highly anisotropic thermal expansion (Brown, Smeltzer & Heyding, 1976); the *a*- and *c*-axis linear thermal expansion coefficients are numerically very large and of opposite sign (Brown, Segel & Dolling, 1980; Powell, Brown, Harnden & Reid, 1993). The Raman spectrum shows large shifts in the low-frequency internal and external modes (Korppi-Tommola, Devarajan, Brown & Shurvell, 1978) and the temperature dependence of the heat capacity shows a broad peak which does not shift upon deuteration (Weir & Staveley, 1980; Brown, Callanan, Weir & Westrum, 1986, 1987*a*). Such anomalies are not found in any of the isostructural alkali metal perrhenates.

NH_4ReO_4 has the tetragonal scheelite structure (Beintema, 1937; Kruger & Reynhardt, 1978) and may be regarded as the prototype for a family of isostructural ammonium salts (ammonium scheelites) which share many unusual properties. There are two other ammonium salts of group VII oxyanions with the

scheelite structure, ammonium metaperiodate NH_4IO_4 and ammonium pertechnetate NH_4TcO_4 . For NH_4IO_4 the temperature and pressure coefficients of the NQR frequency are both positive (Segel, Brown & Heyding, 1978, 1979; Burkert, 1980); the thermal expansion coefficients (Brown, Segel & Dolling, 1980) and heat capacity (Brown, Callanan, Weir & Westrum, 1987*b*) are very similar to those of the perrhenate. NH_4TcO_4 has been studied in less detail than the other two salts, but the thermal expansion behaviour, although rather different from the perrhenate and metaperiodate, is highly anomalous (Faggiani, Lock & Poce, 1980). The temperature coefficient of the Tc NQR frequency is positive, as in the perrhenate and metaperiodate (Segel, 1989; Tarasov *et al.*, 1986). Ammonium tetrachlorothallate NH_4TlCl_4 and ammonium tetrachloroindate NH_4InCl_4 also crystallize in the scheelite structure (Thiele, Grunwald, Rink & Breiting, 1980), but the temperature dependences of their properties do not appear to have been studied.

The ammonium scheelites thus constitute a recognizable group of crystalline salts and their unusual properties should be explainable within a single theoretical framework. Three theoretical approaches are found in the literature. Smith (1983*a,b*) gave a qualitative discussion of the heat capacity and thermal expansion in terms of the rotational energy levels of the ammonium ion. The pseudo-spin model of ammonium perrhenate proposed by Taylor (1987, 1989) assumes the existence of two inequivalent orientations of the ammonium ion in the scheelite lattice; the anomalous temperature dependence of various properties of the crystal are ascribed to a cooperative coupling between lattice strain and the energy difference between the two orientations. A molecular dynamics study of the crystal by Brown & Lynden-Bell (1994) gave a reasonable account of some of the anomalies, but predicted only a single ammonium ion orientation.

In a previous powder neutron diffraction study of ND_4ReO_4 using Rietveld refinement (Powell, Brown, Harnden & Reid, 1993), the attempt to define the two possible ammonium ion orientations on the basis of deuterium atomic positions was not successful, because the resulting ammonium ion geometries were far from

tetrahedral. The analysis of the higher temperature data using a single orientation resulted in a very elongated thermal ellipsoid for the D atom. This result, which appeared to be confirmed by the molecular dynamics calculations, is hard to reconcile with the ammonium ion librational frequencies in the Raman spectrum (Park, Shurvell & Brown, 1986), with their temperature dependence (Korppi-Tommola, Devarajan, Brown & Shurvell, 1978) and with nuclear spin relaxation time measurements (Szabo & Brown, 1994).

With this background of conflicting theories and experiments, further consideration of the neutron diffraction experiment was thought desirable. The present paper presents the results of a re-refinement of the previously published data using rigid-body constraints for the cation and allowing a second orientation with a variable population. The results confirm the pseudo-spin theory and give a more satisfactory and consistent picture of the ammonium ion disorder.

2. Rietveld analysis

The experimental details have been published previously (Powell, Brown, Harnden & Reid, 1993). The measurements were carried out in two separate series, labelled I (covering 20 to 140 K) and II (covering 140 K to room temperature); there is some inconsistency between the lattice parameters for the two series, which was discussed in the previous paper. The refinements reported in the present paper were carried out using the GSAS Rietveld refinement code (Larson & Von Dreele, 1987). The profile data were corrected for absorption; this eliminated the negative thermal parameters for the Re atom which were noted previously (Powell, Brown, Harnden & Reid, 1993). The background was fitted to a three-term cosine Fourier series and correction for line asymmetry was made. T_d symmetry for the ammonium ion was maintained using rigid-body constraints. The N—D bond length was determined to be 1.025 Å from the 20 K data and this value was used at all temperatures. At temperatures up to 140 K, a single cation orientation was used and at temperatures of 160 K and above, a second cation orientation with variable occupancy was introduced. The rigid-body thermal parameters for the cation were taken to be the same for the two orientations in order to limit the number of variables in the refinement.

3. Discussion

In the NH_4ReO_4 structure, each cation is surrounded by eight O atoms, which can be divided into two groups of four (Brown, Segel & Dolling, 1980). O atoms from one group belong to anions which lie at the same level along the c axis as the cation; these O atoms are

Table 1. Cell dimensions

These data were obtained from the neutron diffraction profiles assuming neutron wavelengths of 1.49978 (9) Å for series I and 1.49935 (6) Å for series II. Results at 160 K and above are taken from the analyses of the two-orientation model. E.s.d.'s are given in parentheses. The space group is $I4_1/a$. R_{wp} has been multiplied by 10^2 . In the last column N is the number of cation orientations used in the refinements.

T (K)	a (Å)	c (Å)	V (Å ³)	R_{wp}	N
Series I					
20	5.99986 (16)	12.3976 (4)	446.29 (3)	6.36	1
40	6.00092 (16)	12.3989 (4)	446.50 (3)	6.52	1
60	6.00193 (17)	12.4027 (4)	446.78 (4)	6.47	1
80	6.00313 (17)	12.4118 (4)	447.29 (4)	6.59	1
100	6.00301 (18)	12.4258 (4)	447.78 (4)	6.51	1
120	6.00091 (19)	12.4466 (5)	448.22 (4)	6.63	1
140	5.99564 (21)	12.4783 (5)	448.57 (4)	6.84	1
Series II					
140	5.98872 (14)	12.4660 (3)	447.09 (3)	5.09	1
160	5.97765 (14)	12.5160 (3)	447.23 (3)	5.06	2
180	5.95898 (15)	12.5916 (4)	447.12 (3)	5.22	2
200	5.93240 (16)	12.6897 (4)	446.59 (3)	5.45	2
220	5.91124 (18)	12.7765 (5)	446.45 (4)	5.74	2
240	5.89725 (19)	12.8464 (5)	446.77 (4)	5.73	2
298	5.88050 (21)	12.9874 (6)	449.11 (4)	5.97	2

described as *equatorial* relative to this particular cation. O atoms from the other group belong to anions which are displaced along c by distances of $\pm c/4$ from the cation; these O atoms are described as *axial* relative to the cation. Each group forms a slightly distorted tetrahedron around the cation site, consistent with S_4 cation site symmetry.

Energy considerations suggest that the cations should be oriented so the N—D bonds point to either the axial or equatorial O atoms. This defines two special cation orientations, described as axial and equatorial according to whether the N—D bonds point towards the axial or equatorial O atoms. Given the site symmetry, the cation orientation relative to the unit-cell axes can be described by one angle which can be taken as $\alpha = \tan^{-1}[(x_N - x_D)/(y_N - y_D)]$; for the two special orientations α is $\sim 19^\circ$ in the axial orientation and $\sim -53^\circ$ in the equatorial orientation. In ND_4ReO_4 the N—O_{ax} distance is smaller than the N—O_{eq} distance and the cation orientation is found to be axial at low temperatures. The anion orientation is described by the angle $\beta = \tan^{-1}[(y_O - y_{Re})/x_O - x_{Re}]$. The angles α and β are illustrated in Fig. 3 of Powell, Brown, Harnden & Reid (1993).

The results of refinements are given in Tables 1–6. Refinements using a single orientation led to results similar to those obtained in the previous analysis, except that the cell dimensions given in Table 1 are slightly larger than the previous results by a factor close to 1.0005, which may result from a different treatment of linewidth and asymmetry parameters by the GSAS software. The introduction of a second orientation with a variable occupancy gave satisfactory refinements with

Table 2. *Fractional atomic positions and rotation angles for the ammonium ion*

Parameters are given relative to the origin at $\bar{1}$. N is at (0.5, 0.75, 0.125). α is defined in the text and refers to the cation orientation relative to the unit-cell basis vectors. Above 20K the N—D bond length was fixed at 1.025 Å and so no standard deviation is shown for z_D .

T (K)	x_D	y_D	z_D	α	Population
Series I					
20	0.4546 (3)	0.61813 (20)	0.17273 (7)	19.0 (1)	1.000
40	0.4550 (3)	0.61800 (9)	0.17273	18.8 (1)	1.000
60	0.4548 (3)	0.61808 (10)	0.17271	18.9 (1)	1.000
80	0.4550 (3)	0.61805 (10)	0.17268	18.8 (1)	1.000
100	0.4551 (3)	0.61802 (10)	0.17263	18.8 (1)	1.000
120	0.4561 (3)	0.61762 (11)	0.17255	18.3 (1)	1.000
140	0.4576 (4)	0.61702 (12)	0.17243	17.7 (2)	1.000
Series II					
140	0.4568 (3)	0.61709 (9)	0.17247	18.0 (1)	1.00
160	0.4535 (6)	0.61794 (22)	0.17228	19.4 (3)	0.898 (8)
	0.562 (5)	0.624 (3)	0.17228	-26.2 (24)	0.102 (8)
180	0.4536 (6)	0.61743 (19)	0.17200	19.3 (2)	0.852 (6)
	0.578 (3)	0.633 (2)	0.17200	-33.8 (14)	0.148 (6)
200	0.4546 (7)	0.61644 (21)	0.17164	18.8 (3)	0.776 (6)
	0.5910 (18)	0.6422 (15)	0.17164	-40.2 (10)	0.224 (6)
220	0.4562 (8)	0.6154 (3)	0.17132	18.0 (3)	0.706 (6)
	0.5962 (15)	0.6461 (14)	0.17132	-42.8 (8)	0.294 (6)
240	0.4553 (10)	0.6153 (3)	0.17107	18.4 (4)	0.648 (8)
	0.5964 (15)	0.6458 (14)	0.17107	-42.8 (8)	0.352 (8)
298	0.4524 (14)	0.6159 (5)	0.17057	19.6 (6)	0.590 (10)
	0.6011 (18)	0.6499 (18)	0.17057	-45.3 (10)	0.410 (10)

Table 3. *Fractional atomic positions and rotation angles for the perrhenate ion*

Parameters are given relative to the origin at $\bar{1}$. Re is at (0, 0.25, 0.125). β defines the anion orientation relative to the unit-cell basis vectors. Bond lengths in Å and bond angles in $^\circ$.

T (K)	x_O	y_O	z_O	β	Re—O	O—Re—O
Series I						
20	0.2028 (3)	0.3751 (2)	0.04560 (12)	31.68 (6)	1.736 (2)	110.9 (1)
40	0.2026 (3)	0.3748 (2)	0.04554 (12)	31.62 (6)	1.735 (2)	110.8 (1)
60	0.2028 (3)	0.3747 (3)	0.04559 (12)	31.59 (6)	1.735 (2)	110.8 (1)
80	0.2028 (3)	0.3742 (3)	0.04567 (13)	31.48 (7)	1.734 (2)	110.8 (1)
100	0.2030 (3)	0.3738 (3)	0.04582 (13)	31.37 (7)	1.734 (2)	110.8 (1)
120	0.2035 (3)	0.3728 (3)	0.04569 (14)	31.11 (7)	1.735 (2)	110.6 (1)
140	0.2039 (3)	0.3722 (3)	0.04590 (16)	30.93 (8)	1.733 (2)	110.6 (1)
Series II						
140	0.2024 (3)	0.3715 (2)	0.04594 (12)	30.97 (6)	1.724 (1)	110.2 (1)
160	0.2037 (3)	0.3706 (2)	0.04617 (12)	30.63 (6)	1.725 (1)	110.2 (1)
180	0.2056 (3)	0.3695 (3)	0.04645 (13)	30.16 (6)	1.728 (2)	110.2 (1)
200	0.2076 (3)	0.3677 (3)	0.04684 (15)	29.55 (7)	1.728 (2)	110.0 (1)
220	0.2102 (3)	0.3672 (3)	0.04758 (17)	29.14 (8)	1.733 (2)	110.4 (2)
240	0.2115 (4)	0.3662 (4)	0.04809 (18)	28.78 (8)	1.733 (2)	110.5 (2)
298	0.2143 (4)	0.3639 (5)	0.04920 (21)	28.00 (11)	1.734 (2)	110.8 (2)

occupancies greater than 0.1 for temperatures of 160 K and above; at lower temperatures the occupancy was too low for the refinements to yield reliable information about the second orientation and so the results of refinements for a single orientation are given in the tables.

At low temperatures, where a single orientation of the cation is assumed, α is close 19° , corresponding to the axial orientation. With the introduction of a second cation orientation at 160 K and above, α for one orientation remains close to the axial value, while for the second orientation α is -45° at 298 K and, with

increasing temperature, is tending towards the value of -53° expected for the equatorial orientation. The occupancy of the equatorial orientation, shown in Fig. 2, increases smoothly with temperature and agrees well with the population calculated from the pseudo-spin model using previously published parameters (Taylor, 1987).

At 20 K, the N—O_{ax} and N—O_{eq} distances are 2.867(2) and 3.035(2) Å, respectively, and at higher temperatures the difference between them is reduced, which is consistent with the supposition in pseudo-spin theory that the difference in energy between the two

Table 4. *Rigid-body thermal motion parameters for the ammonium ion*

Translational parameters T_{ii} have been multiplied by 10^2 and have units \AA^2 . Librational parameters L_{ii} have units of deg^2 . For temperatures of 160 K and above, the thermal parameters refer to both ammonium ion orientations.

T (K)	T_{11}	T_{33}	L_{11}	L_{33}
Series I				
20	1.91 (3)	1.17 (10)	61 (4)	81 (6)
40	1.95 (4)	1.29 (11)	61 (4)	79 (6)
60	1.97 (4)	1.52 (11)	65 (4)	88 (7)
80	2.09 (4)	1.48 (12)	68 (4)	81 (7)
100	2.26 (4)	1.77 (13)	68 (4)	89 (8)
120	2.42 (4)	1.90 (15)	82 (5)	98 (9)
140	2.73 (5)	2.35 (16)	88 (6)	145 (10)
Series II				
140	2.23 (3)	2.42 (12)	90 (4)	162 (8)
160	2.48 (3)	2.31 (11)	106 (4)	83 (10)
180	2.92 (4)	1.97 (11)	137 (5)	86 (11)
200	3.52 (5)	2.09 (14)	169 (6)	106 (13)
220	3.83 (5)	2.50 (16)	162 (8)	144 (16)
240	3.98 (5)	2.96 (17)	206 (8)	184 (18)
298	5.16 (7)	3.21 (21)	249 (10)	255 (25)

cation orientations decreases with increasing temperature as a result of changes in the structure. The D—O distances and N—D—O angles fall within normal ranges for these interactions.

The thermal motion of the cation, expressed as rigid-body TLS parameters (Larson & Von Dreele, 1987), is shown in Table 4; the thermal parameters were constrained to be equal for the two orientations at the higher temperatures. The addition of the screw motion, although permitted by the site symmetry, did not lead to significant improvement and the correspond-

ing parameters were set equal to zero in the final refinements. The thermal parameters increase smoothly with temperature, apart from the discontinuity resulting from introduction of the second orientation at 160 K. The two librational parameters permitted in S_4 site symmetry are approximately equal at all temperatures, indicating almost isotropic librational motion. In the low-temperature Raman spectrum the A_g and E_g librational modes have almost equal frequencies (Park, Shurvell & Brown, 1986) and there is no evidence that the rather weak A_g mode shifts to lower frequency with increasing temperature, as would be required by the highly elongated thermal ellipsoid for deuterium obtained in the previous refinement assuming a single cation orientation (Powell, Brown, Harnden & Reid, 1993).

The results of the new refinements using two cation orientations at temperatures of 160 K and above are to be preferred over the previous results based upon a single cation orientation (Powell, Brown, Harnden & Reid, 1993) since (a) the two orientations are close to the ideal axial and equatorial orientations defined by the neighbouring O atoms, and (b) the thermal parameters for deuterium show more reasonable values and temperature dependences than in the single orientation model. The results are consistent with pseudo-spin theory since (a) the observed occupancies agree satisfactorily with calculations and (b) the difference between the N—O_{ax} and N—O_{eq} distances decreases as the temperature increases. This establishes ammonium perrenate as an example of cooperative disordering without a phase transition, which is well represented by an Ising model with a longitudinal field.

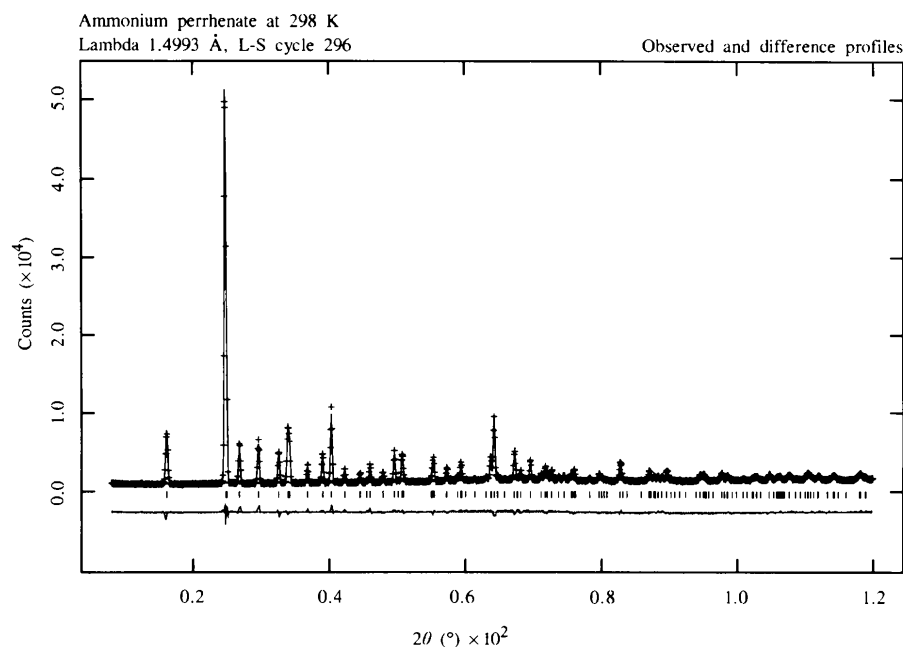


Fig. 1. Observed (+), calculated and difference intensity profiles for ND_4ReO_4 at 298 K, assuming two cation orientations.

Table 5. *Thermal motion parameters for the perrhenate ion*

The parameters have been multiplied by 10^2 and have units \AA^2 .

T (K)	Rhenium		Oxygen					
	U^{11}	U^{33}	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Series I								
20	0.67 (6)	0.77 (9)	1.46 (7)	1.55 (8)	1.15 (7)	0.21 (8)	0.00 (6)	0.44 (7)
40	0.78 (6)	0.84 (10)	1.57 (8)	1.58 (9)	1.19 (8)	0.10 (9)	0.01 (6)	0.40 (8)
60	0.92 (6)	0.93 (10)	1.73 (8)	0.76 (9)	1.37 (8)	0.21 (9)	0.07 (6)	0.31 (8)
80	0.92 (7)	1.11 (11)	1.84 (9)	1.90 (10)	1.37 (8)	0.07 (10)	0.13 (6)	0.33 (8)
100	1.10 (7)	1.20 (11)	2.00 (9)	2.21 (10)	1.42 (9)	0.15 (10)	0.22 (6)	0.36 (9)
120	1.11 (8)	1.58 (12)	2.31 (10)	2.42 (11)	1.49 (9)	-0.11 (11)	0.20 (7)	0.22 (9)
140	1.26 (8)	1.91 (13)	2.54 (11)	2.73 (12)	1.96 (11)	-0.10 (12)	0.46 (8)	-0.08 (10)
Series II								
140	1.74 (6)	0.92 (8)	2.77 (9)	2.90 (9)	1.97 (8)	-0.54 (10)	0.88 (6)	0.11 (8)
160	1.94 (6)	1.14 (8)	2.87 (9)	3.15 (10)	2.09 (8)	-0.71 (10)	1.06 (7)	0.31 (8)
180	1.91 (6)	1.60 (9)	2.87 (10)	3.44 (11)	2.36 (8)	-0.58 (11)	1.22 (7)	0.19 (8)
200	2.31 (7)	1.76 (12)	3.15 (12)	3.71 (13)	2.87 (9)	-0.54 (12)	1.58 (9)	-0.07 (9)
220	2.17 (8)	2.22 (14)	3.90 (15)	4.10 (15)	3.12 (12)	-1.14 (14)	1.90 (11)	-0.01 (10)
240	2.43 (8)	2.30 (14)	4.05 (16)	4.27 (14)	3.50 (12)	-1.20 (14)	1.93 (11)	0.05 (10)
298	2.86 (10)	3.14 (17)	4.96 (20)	5.53 (18)	4.86 (16)	-1.69 (19)	2.77 (14)	-0.08 (14)

Table 6. *Cation-oxygen distances (\AA) and angles ($^\circ$)*

T (K)	$\text{N}-\text{O}_{\text{ax}}$	$\text{D}_{\text{ax}}-\text{O}_{\text{ax}}$	$\text{N}-\text{D}_{\text{ax}}-\text{O}_{\text{ax}}$	$\text{N}-\text{O}_{\text{eq}}$	$\text{D}_{\text{eq}}-\text{O}_{\text{eq}}$	$\text{N}-\text{D}_{\text{eq}}-\text{O}_{\text{eq}}$
Series I						
20	2.867 (2)	1.880 (2)	160.6 (1)	3.035 (2)	—	—
40	2.866 (2)	1.880 (2)	160.6 (1)	3.037 (2)	—	—
60	2.867 (2)	1.880 (2)	160.5 (1)	3.037 (2)	—	—
80	2.868 (2)	1.881 (2)	160.5 (1)	3.040 (2)	—	—
100	2.870 (2)	1.884 (2)	160.3 (1)	3.041 (2)	—	—
120	2.867 (2)	1.882 (2)	160.1 (1)	3.043 (2)	—	—
140	2.870 (2)	1.887 (2)	159.7 (1)	3.043 (2)	—	—
Series II						
140	2.872 (2)	1.887 (2)	159.9 (1)	3.047 (2)	—	—
160	2.872 (2)	1.888 (2)	159.8 (1)	3.042 (2)	2.189 (23)	139.3 (23)
180	2.871 (2)	1.891 (2)	159.0 (1)	3.033 (2)	2.127 (9)	146.1 (13)
200	2.873 (2)	1.896 (2)	158.0 (1)	3.023 (2)	2.085 (5)	151.0 (7)
220	2.876 (2)	1.906 (2)	156.9 (1)	3.005 (2)	2.058 (3)	152.6 (5)
240	2.882 (2)	1.914 (2)	156.4 (1)	3.000 (2)	2.052 (3)	152.5 (5)
298	2.897 (2)	1.933 (2)	155.3 (1)	2.991 (2)	2.038 (4)	153.6 (5)

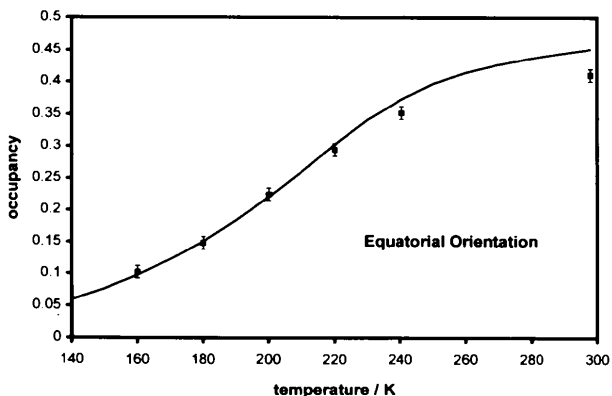


Fig. 2. The occupancy of the equatorial orientation of the ammonium ion as a function of temperature (Table 2). The line shows the occupancy calculated from the pseudo-spin theory with the parameters given by Taylor (1987).

This work was supported by the Natural Sciences and Engineering Research Council of Canada. We are grateful to Dr D. R. Taylor for helpful comments.

References

- Beintema, J. (1937). *Z. Krist.* **97**, 300–322.
 Brown, R. J. C. (1975). *J. Magn. Reson.* **18**, 558–559.
 Brown, R. J. C. & Lynden-Bell, R. M. (1994). *J. Phys. Condens. Matter*, **6**, 9903–9928.
 Brown, R. J. C. & Segal, S. L. (1977). *J. Chem. Phys.* **67**, 3163–3169.
 Brown, R. J. C., Callanan, J. E., Weir, R. D. & Westrum, E. F. (1986). *J. Chem. Phys.* **85**, 5963–5970.
 Brown, R. J. C., Callanan, J. E., Weir, R. D. & Westrum, E. F. (1987a). *J. Chem. Phys.* **86**, 3759.
 Brown, R. J. C., Callanan, J. E., Weir, R. D. & Westrum, E. F. (1987b). *J. Chem. Thermodyn.* **19**, 1173–1182.

- Brown, R. J. C., Segel, S. L. & Dolling, G. (1980). *Acta Cryst.* **B36**, 2195–2198.
- Brown, R. J. C., Smeltzer, J. G. & Heyding, R. D. (1976). *J. Magn. Reson.* **24**, 269–274.
- Burkert, P. K. (1980). *Z. Naturforsch. Teil B*, **35**, 1349–1354.
- Burkert, P. K. & Eckel, M. F. (1973). *Z. Naturforsch. Teil B*, **28**, 379–382.
- Faggiani, R., Lock, C. J. L. & Poce, J. (1980). *Acta Cryst.* **B36**, 231–233.
- Johnson, R. A. & Rogers, M. T. (1974). *J. Magn. Reson.* **15**, 584–589.
- Korppi-Tommola, J., Devarajan, V., Brown, R. J. C. & Shurvell, H. F. (1978). *J. Raman Spectrosc.* **7**, 96–100.
- Kruger, G. J. & Reynhardt, E. C. (1978). *Acta Cryst.* **B34**, 259–261.
- Larson, A. C. & Von Dreele, R. B. (1987). Report no. LA-UR-86-748. Los Alamos National Laboratory, New Mexico, USA.
- Park, Y. S., Shurvell, H. F. & Brown, R. J. C. (1986). *J. Raman Spectrosc.* **17**, 351–354.
- Powell, B. M., Brown, R. J. C., Harnden, A. M. C. & Reid, J. K. (1993). *Acta Cryst.* **B49**, 463–468.
- Rogers, M. T. & Rama Rao, K. V. S. (1973). *J. Chem. Phys.* **58**, 3233–3235.
- Segel, S. L. (1989). Private communication.
- Segel, S. L., Brown, R. J. C. & Heyding, R. D. (1978). *J. Chem. Phys.* **69**, 3435–3436.
- Segel, S. L., Brown, R. J. C. & Heyding, R. D. (1979). *J. Chem. Phys.* **71**, 2738.
- Smith, D. (1983a). *J. Chem. Phys.* **78**, 6238–6242.
- Smith, D. (1983b). *J. Chem. Phys.* **79**, 2995–3001.
- Szabo, A. J. & Brown, R. J. C. (1994). *Z. Naturforsch. Teil A*, **49**, 302–310.
- Tarasov, V. P., Petrushin, S. A., Privalov, V. I., German, K. E., Kryuchkov, S. V. & Buslaev, Yu. A. (1986). *Koord. Khim.* **12**, 1227–1236.
- Taylor, D. R. (1987). *J. Chem. Phys.* **87**, 773–774.
- Taylor, D. R. (1989). *Phys. Rev. B*, **40**, 493–499.
- Thiele, G., Grunwald, B., Rink, W. & Breiting, D. (1980). *Z. Naturforsch. Teil B*, **34**, 1512–1518.
- Weir, R. D. & Staveley, L. A. K. (1980). *J. Chem. Phys.* **73**, 1386–1392.