

Single-Crystal (Neutron) Diffraction Structure of III-Rubidium Nitrate

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Abstract. RbNO_3 , $M_r = 147.488$, cubic, $a = 4.40$ (1) Å, $V = 84.60$ (3) Å³, $Z = 1$, $D_m(300 \text{ K}) = 3.11$, $D_x = 2.90 \text{ Mg m}^{-3}$, 3D neutron single-crystal diffraction, $\lambda = 1.249$ (1) Å, $\mu = 0.0367 \text{ mm}^{-1}$, $F(000) = 68$, $T = 461 \text{ K}$. Full-matrix least-squares refinements for models with 4-, 8- and 12-fold NO_3 -group orientational disorder with each possible space group: $P432$, $P\bar{4}3m$, $Pm\bar{3}m$. $wR = 0.062$, 0.061, 0.036 for 20 reflections for the three space groups, respectively. High crystal symmetry and elevated temperature reduced data to 20 independent observed integrated intensities. Preference is indicated for 12-fold disorder of the NO_3 groups, each orientation being parallel to one of the cube faces defined by Rb atoms at its corners. The N atom is slightly displaced from the cube centre.

Introduction. RbNO_3 , at atmospheric pressure, has been reported to exhibit the polymorphic phase transitions (Plyushev, Markina & Shklover, 1956; Brown & McLaren, 1962)

IV–437 K–III–492 K–II–564 K–I.

X-ray powder diffraction photographic studies of III- RbNO_3 led Finbak & Hassel (1937) to suggest a cubic crystal structure, $a = 4.37$ Å, $Z = 1$, with the NO_3 group in 'free' rotation about its centre of mass, while Korhonen (1951) proposed an ordered cubic structure, $a = 8.74$ Å, $Z = 8$, space group $Pa\bar{3}$. Strømme (1971) pointed out that the large entropy change of $9.0 \text{ J mol}^{-1} \text{ K}^{-1}$ (Newns & Staveley, 1966) at the IV–III transition could indicate a disordered phase III crystal structure. Utilizing Korhonen's (1951) experimental data, he proposed a further cubic structure, $a = 4.37$ Å, $Z = 1$. The NO_3 group was considered orientationally disordered with mainly aragonite-type and partly calcite-type configurations within the Rb-atom cube.

Ahtee & Hewat (1980), using neutron powder diffraction data with Rietveld's (1969) profile structure refinement technique, have also considered the structure of III- RbNO_3 . The unit cell obtained was cubic, $a = 4.37$ Å (at 463 K), $Z = 1$. Their structural analysis showed a slight preference for a 12-fold orientationally disordered model for the NO_3 group (the plane of each group being parallel to a face of the surrounding Rb cube) over an eightfold disordered model (pure

aragonite-type configuration) for the NO_3 group (the plane being normal to the body diagonal of the Rb-atom cube).

Shinnaka & Yamamoto (1981, 1983) have studied the disk-like maxima in the observed single-crystal X-ray diffuse scattering intensity pattern (that occur perpendicular to the reciprocal-lattice axes) to obtain further information on the orientational disorder of the NO_3 group in III- RbNO_3 .

Owing to the conflicting findings of previous studies, an investigation was commenced to determine whether a three-dimensional single-crystal neutron diffraction experiment could add further information on the conformation and orientation of the NO_3 group within III- RbNO_3 .

Experimental. Single crystals of IV- RbNO_3 were grown by slow evaporation of an aqueous solution at room temperature (RbNO_3 powder of stated 99.8% purity from Koch-Light Laboratories, England, was used). The IV- RbNO_3 specimen crystal of parallelepiped-type shape, approximately $0.65 \times 3.0 \times 5.8 \text{ mm}$, mounted with c axis almost parallel to the φ axis of a computer-controlled four-circle neutron diffractometer belonging to the Australian Institute of Nuclear Science and Engineering (AINSE), installed at the Australian Atomic Energy Commission (AAEC) research reactor HIFAR, at Lucas Heights: the IV- RbNO_3 crystal was heated to 461 K using a single-crystal neutron diffraction furnace (Lucas, 1976) and remained single crystal through the IV–III transition, attached crystal thermocouple indicated temperature ($\pm 1 \text{ K}$). D_m by flotation. Wavelength 1.249 (1) Å (graphite monochromator), obtained by previous calibration using a spherically shaped single-crystal standard: ω – 2θ scans, 2θ step size of 0.01° and width of 3.8° , background–peak–background measurements made for each of the 214 Bragg reflections, equivalent sets of Bragg intensities (for half of reciprocal-space sphere, $l \geq 0$) collected to a limit of $\sin \theta/\lambda \leq 0.493 \text{ \AA}^{-1}$. Cell dimensions obtained from the single-crystal neutron diffraction data collected; standard reflection (200) monitored after every 20 reflections. Measurements were repeated with specimen crystal removed and allowance was made for the furnace contributions to the measured Bragg intensities. Shinnaka & Yamamoto (1981, 1983)

have reported disk-like maxima in the observed single-crystal X-ray diffuse scattering intensity pattern for $h (=k=l) = 1.67, 2.67$, and allowance has also been made for the possible contributions to the measured integrated Bragg intensities.

The measured integrated intensities I (reflections greater than 1σ were considered as observed) and $\sigma(I)$ based on counting statistics alone were corrected for absorption by numerical integration. The crystal shape was divided into 125 volume elements, according to three-dimensional five-point Gaussian integration intervals. An examination of the absorption-corrected data revealed the Laue group to be $m\bar{3}m$. In order to define the reliability of the data, statistical analysis (F test at the 1% level) was performed on each set of equivalent hkl reflections and no reflections were thereby rejected. Lorentz-factor corrections were applied to the data and the equivalent reflections were combined to give 20 independent reflections. $\sigma(I)$'s used were from Poisson statistics if greater than $\sigma(I)$'s from equivalent reflections.

The point-group symmetries belonging to the Laue group $m\bar{3}m$ are: $432, \bar{4}3m, m\bar{3}m$. The observed lack of conditions on h, k, l (for both special and general hkl reflections) indicated the possible space groups $P432, P\bar{4}3m, Pm\bar{3}m$.

For each possible space group, the primitive cubic unit cell was defined by placing the only available Rb atom at its corners. Keeping the Rb...O distances somewhat greater than the sum of their effective atomic radii, 2.88 Å (*International Tables for X-ray Crystallography*, 1968), up to three possible ways were considered of positioning the planar triangular-shaped NO_3 group within the Rb-atom cube for each space group. These are shown as structural models (a), (b), (c), having 4-, 8- and 12-fold orientational disorder of the NO_3 group, respectively (Fig. 1).

For space groups $P432$ and $P\bar{4}3m$, corresponding $|F(hkl)|$'s are real and equal (for the same n -fold disorder model), if h (or k or l) = 0 or x (or y or z) = $\frac{1}{2}$ or (for $P432$) $h = \pm k$ (or $k = \pm l$ or $l = \pm h$). For $Pm\bar{3}m$, $F(hkl)$ is always real and equal to twice the corresponding $|F(hkl)|$ for $P432$ and $P\bar{4}3m$, unless $F(hkl)$ has an imaginary part for that particular reflection (*International Tables for X-ray Crystallography*, 1965). Hence, apart from the scale factor, the $|F(hkl)|$'s of each space group have identical form, except for reflections with $h \neq k \neq l$. In the present investigation, only the general reflection 123 was of sufficient intensity to be measured, although it did not subsequently assist in discriminating between the models (Table 2). Each model was incorporated into the three possible space groups, with the O atoms placed in their most general appropriate positions. It was found from initial trial least-squares refinements that these reduce to the three possibilities shown in Table 1, as the atoms could either be placed at the same

effective positions within differing space groups or the discrepancies between their positional coordinates (when trial refined) in the different space groups were within 1σ .

Full-matrix least-squares refinements were made for each structural model. The refinements were based on comparison of $|F(hkl)|^2$ values: the function minimized was $\sum(wF_o^2 - F_c^2)^2$ and the weighting factor was $w(hkl) = \{\sigma^2[|F(hkl)|^2]\}^{-1}$. The coherent scattering lengths used throughout were: Rb = 7.18 (Shamsuz-zoha & Lucas, 1982), N = 9.4 (*International Tables for X-ray Crystallography*, 1974) and O = 5.83 fm (Schneider, 1976). The parameters refined for each model were a scale factor, positional coordinates, isotropic temperature and isotropic extinction factors. The results are shown in Tables 1 and 2.

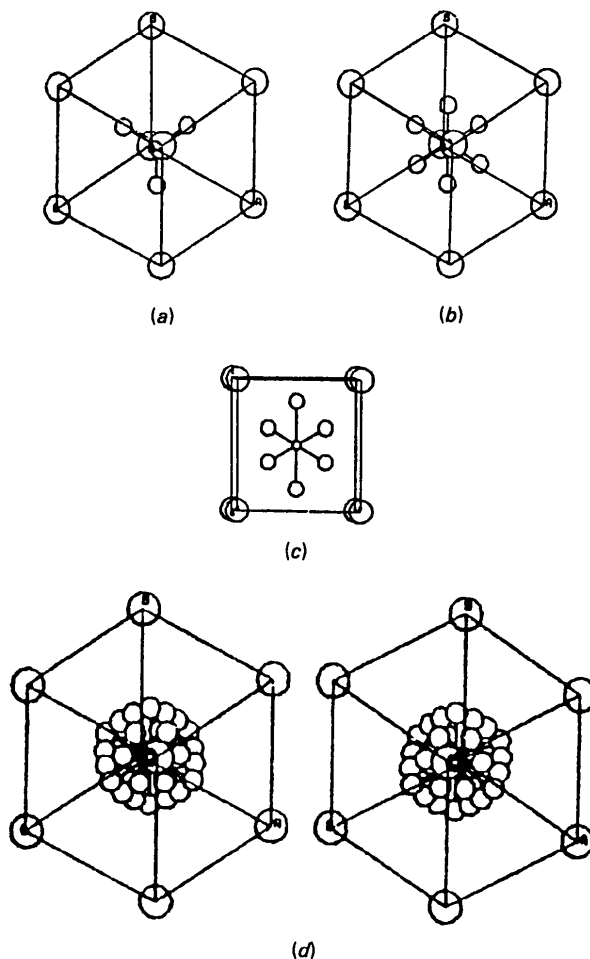


Fig. 1. The unit-cell contents of III-RbNO₃ for (a) 4-fold, (b) 8-fold, and (c) 12-fold NO₃-group disorder models. In (a) and (b) the disordering is about the body diagonals, in (c) about the cell-axis directions, of the cube. For clarity, only representative positions are shown. (d) A stereoview of the preferred 12-fold disorder structure, with all equivalent O-atom positions shown. $\{[111]$ out of paper for (a), (b), (d), $[100]$ for (c).}

Interatomic bond distances and interbond angles are shown in Table 3, where distances of the N atom from its O-atom plane are also given.

All calculations were made with the University's PDP-10 computer (using a suite of programs from various sources), except for the initial stages of the data reduction which were carried out on the IBM 370 computer at the AAEC.

Discussion. The elevated specimen temperature required to achieve phase III restricted to 214 the number of significantly measurable Bragg intensities and the high crystal symmetry reduced these to only 20 non-equivalent reflections. The structural investigation was further complicated by disorder of the NO₃ group.

Table 1. Atomic positional and thermal parameters of III-RbNO₃ (at 461 K) for 4-, 8- and 12-fold disorder models, as determined by least-squares refinement

B(N) and *x(N)* were refined alternatively owing to high correlation.

<i>n</i> -fold NO ₃ disorder (space group)	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)	NV	<i>wR</i>
4 (<i>P43m</i>)	Rb	0.000	0.000	0.000	5.44 (46)		
	N	0.445 (2)	<i>x</i>	<i>x</i>	8.21	7	0.062
	O	0.555 (4)	<i>x</i>	0.234 (3)	12.24 (70)		
8 (<i>P432</i>)	Rb	0.000	0.000	0.000	5.69 (57)		
	N	0.444 (3)	<i>x</i>	<i>x</i>	8.23	8	0.061
	O	0.533 (14)	0.575 (18)	0.231 (4)	12.15 (69)		
12 (<i>Pm3m</i>)	Rb	0.000	0.000	0.000	9.65 (42)		
	N	0.525 (14)	0.500	0.500	14.80	9	0.036
	O(1)	0.832 (5)	0.500	0.500	9.52 (88)		
	O(2)	0.500	0.732 (4)	0.373 (6)	10.61 (93)		

Table 2. III-RbNO₃ (at 461 K): observed and calculated integrated intensities for models (a) 4-fold, (b) 8-fold, (c) 12-fold NO₃-group disorder

<i>h</i>	<i>k</i>	<i>l</i>	<i>I</i> (obs)	σ [<i>I</i> (obs)]	<i>I</i> (calc)	Model (b)	<i>I</i> (calc)
0	0	1	147.29	1.95	141.09	141.11	147.86
0	0	2	223.78	1.73	225.00	225.17	222.83
0	0	3	10.62	1.22	0.04	0.01	8.70
0	0	4	27.19	2.49	24.28	23.54	30.49
0	1	1	276.35	9.12	309.87	307.08	283.04
1	2	0	9.54	1.52	7.21	8.22	9.14
1	3	0	76.16	1.54	76.15	76.77	77.55
1	4	0	1.34	2.72	5.19	5.12	0.56
2	2	0	56.03	1.29	54.15	53.63	57.69
2	3	0	5.38	1.93	7.97	8.06	2.00
3	3	0	21.57	2.86	15.33	14.38	13.21
1	1	1	7.88	0.67	8.03	7.82	7.79
1	2	1	72.57	1.36	74.92	74.91	71.17
1	3	1	10.36	1.78	9.02	8.57	5.85
1	4	1	11.53	2.66	15.07	14.29	5.90
1	2	2	35.10	1.22	35.35	35.30	35.76
1	2	3	25.33	2.66	25.47	25.44	20.46
1	3	3	4.00	2.12	5.59	5.28	0.23
2	2	2	22.27	2.16	18.39	19.47	22.75
2	2	3	7.44	3.30	8.87	8.21	0.45

Isotropic extinction
mosaic spread (μrad)
domain size (μm)

(a)	(b)	(c)
3.3	3.9	3.4
0.1	0.2	0.1

Table 3. Interatomic distances (Å) and angles (°) for III-RbNO₃ (at 461 K) from 4-, 8- and 12-fold disorder models

	4-fold	8-fold	12-fold
N—O(1)	1.15 (2)	1.17 (5)	1.35 (7)
N—O(2)			1.22 (4)
Rb...O(1)	2.95 (2)	2.96 (7)	3.20 (1)
Rb...O(2)			2.99 (2)
O(1)—N—O(2)	120.0 (1.5)	120.0 (4.9)	123.3 (2.7)
O(2)—N—O(2')			113.4 (5.1)
Perpendicular distance of N to O plane	0.03 (1)	0.01 (1)	0.00

The results in Tables 1, 2 and 3 show that all three models produce converged refinements with relatively low *wR*-factor magnitudes. The structure has Rb atoms at the corners of the cubic unit cell with an N atom close to its centre. The O atoms of the NO₃ group lie essentially on a spherical shell (radius approximately equal to the N—O bond length) about the cell centre, the atom location on the surface depending on the preferred model.

The N atom to O-atom plane distances (within the group) compare reasonably with those for similar nitrates, e.g. KNO₃ 0.02 (298 K) and 0.03 Å (373 K) (Nimmo & Lucas, 1973). The *wR*-factor magnitudes, NO₃ dimensions and the close similarity between the single-crystal X-ray diffuse intensity pattern according to Shinnaka & Yamamoto (1981, 1983) and that for cubic I-NH₄NO₃ (Yamamoto & Shinnaka, 1974), which has been shown to exhibit 12-fold orientational disorder of the NO₃ group by multipole analysis (Ahtee, Kurki-Suonio, Lucas & Hewat, 1979), suggests that III-RbNO₃ also exhibits 12-fold disorder of the NO₃ group. Hamilton's (1965) *R*-factor test was applied to consider the hypotheses that either the 4-fold [$\mathcal{R} = wR(4)/wR(12) = 1.722$; $\mathcal{R}_{2,11,0.005} = 1.619$] or 8-fold [$\mathcal{R} = wR(8)/wR(12) = 1.694$; $\mathcal{R}_{1,11,0.005} = 1.453$] disorder models were preferable to the 12-fold model and in both cases these hypotheses could be rejected at a significance level of < 0.5%. The preferred 12-fold disorder is in general agreement with that proposed by Ahtee & Hewat (1980).

A stereoview of the structure is shown in Fig. 1(d).

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Structure of Partially Deuterated TIH_2AsO_4

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Abstract. $M_r = 345.304$ for TIH_2AsO_4 , monoclinic, $P2_1/c$, $a = 6.635$ (2), $b = 4.652$ (1), $c = 14.574$ (4) Å, $\beta = 92.31$ (2)°, $V = 449.48$ Å³, $Z = 4$, $D_x = 5.102$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 434.82$ cm⁻¹, $F(000) = 592$, $T = 293$ K, final $R = 0.0524$, $wR = 0.0461$, for 364 independent reflections. The heavy-atom structure of thallium(I) dideuterium-arsenate is isomorphous with TIH_2PO_4 . The bond lengths and angles of the AsO_4 tetrahedron were found to be fairly regular. AsO_4 groups are linked by suggested deuterium atoms, D(1) and D(2) at the centre of inversion and D(3) along the b axis in infinite chains. The suggested D positions connect the AsO_4 groups in a continuous chain along the b as well as a axes.

Introduction. Thallium(I) dihydrogenarsenate, TIH_2AsO_4 (TDA), and its deuterated analogue TID_2AsO_4 (DTDA) may be regarded as KDP-type compounds. Since the discovery of ferroelectricity in TIH_2PO_4 (TDP) (Montagner & Donche, 1966), some experimental work on its heat capacity and dielectric constant (Matsuo & Suga, 1977), Raman scattering and specific heat (Vignalou, Tranquard, Couzi & Huong, 1976) and structure (Nelmes & Choudhary, 1981) have been reported. From these studies a phase transition at 230 K has been established in TDP. The large isotope effect on T_c has suggested that TDP is also of KDP type. A proton spin-lattice relaxation study (Blinic,

Rožmarin, Milia & Melisavopoulou, 1978) in TDA has suggested a structural phase transition at 251 K. No further study has been reported so far. It is well known that replacement of P by As and/or H by D in KDP-type compounds leads to a variety of crystal structures and physical properties. In view of this, a structural study of partially deuterated TIH_2AsO_4 has been carried out as part of our systematic study of thallium(I) compounds. The present study reports the heavy-atom structure of TID_2AsO_4 .

Experimental. Colourless, needle-shaped single crystals of TIH_2AsO_4 were grown by slow evaporation at room temperature (301 K) from aqueous solution containing stoichiometric amounts of thallose carbonate (Johnson Matthey Chemicals Ltd) and orthoarsenic acid (BDH). Deuterated crystals of TDA were obtained by slow evaporation of a heavy water (99.4% supplied BARC) solution after recrystallization. D_m not determined. Estimated D level (80 ± 5%) by NMR.

Crystal of size 0.3 × 0.3 × 0.2 mm, Syntex R3 single-crystal diffractometer, graphite monochromator, lattice parameters and orientation matrix by least-squares refinement with 25 carefully centred high-angle reflections, $\text{Mo } K\alpha$, Wyckoff (ω) scans, two check reflections measured for every 50 reflections, no significant variation, data collected in range 4° < 2 θ < 50°, max. $(\sin\theta)/\lambda = 0.51$ Å⁻¹. A total of 1766