and H—Cl = 2·55 Å with apex toward $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. It is then remarkable that the refinements show quite clearly that one of these two orientations is strongly preferred. We feel that a more comprehensive neutron diffraction investigation of the ammonium-based salts, particularly using deuterated specimens, may be able to provide information on this aspect of the structure.

Table 4 lists the bond lengths at room temperature.

We wish to thank Dr E. A. Harris for providing the powder sample and Dr J. B. Dunlop for making the susceptibility measurements. Financial assistance from the Science Research Council, and the help of the University Support Group at AERE, Harwell, are gratefully acknowledged. We would also like to thank Professor G. E. Bacon for his interest and encouragement throughout this investigation.

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Acta Cryst. (1979). B**35**, 1038–1041

The Crystal Structure of Phase II Ammonium Nitrate

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(*Received* 4 *December* 1978; *accepted* 18 *January* 1979)

Abstract

On heating dry (without occluded water) ammonium nitrate at atmospheric pressure, a solid-state phase transformation occurs from phase IV to phase II at 328 K. Neutron powder diffractometer data of the deuterated compound have been used with the profile-refinement method to first verify the reported phase IV structure and then determine the structure of phase II. For phase II, the structure is disordered, with tetragonal space group $P\bar{4}2_1m$, $a = 5{\cdot}7193$ (1), $c = 4{\cdot}9326$ (1) Å, $Z = 2$. The orientations and disorder of the NH_4 and NO_3 ions in this phase have been determined, there being two equivalent alternative positions for each ion.

0567-7408/79/051038-04$01.00

Introduction

At atmospheric pressure, solid ammonium nitrate can exist in several different phases depending on the temperature. Five distinct phases with reversible transitions between them in the sequence V–IV–III–II–I have been reported (Nagatani, Seiyama, Sakiyama, Suga & Seki, 1967). At room temperature, phase IV has an orthorhombic crystal structure (Choi, Mapes & Prince, 1972), which transforms to a tetragonal phase V structure (Amorós, Arrese & Canut, 1962) when cooled below 255 K. On heating above room temperature, transitions occur to an orthorhombic phase III structure at 305·3 K (Goodwin & Whetstone, 1947), a tetragonal phase II structure at 357 K (Shinnaka, 1956) and to a cubic phase I structure above 398 K (Shinnaka, 1959*a*). Dry crystals (without occluded water) have been found to transform directly from the phase IV structure to phase II on heating at 328 K (Brown & McLaren, 1962). The same transitions have been found also for deuterated ammonium nitrate, the transition temperatures being only slightly affected by the deuteration (Juopperi, 1972).

The crystal structures of all five phases (for the hydrogenous form) have been studied by X-ray diffraction, but only the room-temperature phase IV has been satisfactorily determined; this was by single-crystal neutron diffraction (Choi *et al.*, 1972). The direct transformation of phase IV to phase II has been the subject of several studies and a proposed structure for phase II from X-ray diffraction has been reported by Shinnaka (1956). Shinnaka (1959*b*) also made some X-ray diffuse-scattering photographic studies. The proposed structure was based on limited visually estimated intensities and only an approximate, incomplete structure could be suggested. It seemed evident from this work that disorder of the nitrate groups is present in the phase II structure, but the similar scattering powers of O and N atoms and the weak scattering power of H atoms, for X-rays, limited the structural information that could be obtained.

The aim of the present study was to confirm the reported phase IV neutron diffraction structure and then determine the structure of phase II. The method used was the profile-refinement method (Rietveld, 1969) for neutron powder diffraction measurements.

Experimental

Ammonium nitrate was deuterated by repeated recrystallization from saturated solutions with 99·6% D_2O. The powder was kept vacuum-sealed in a glass flask. Just before measurements were made, a sample of approximately 20 g was finely ground, after being unloaded in a He-filled glove bag containing P_2O_5, and sealed in an air-tight thin-walled vanadium can of diameter 16 mm. Neutron diffraction measurements were made on the high-resolution powder diffractometer (D1A) at the high-flux reactor in the ILL (Grenoble), the wavelength being 1·90818 Å. D1A has a bank of ten ^{3}He high-pressure counters with a 6° angular separation. In the measurements described here the intensity profiles were obtained by appropriately combining the intensities from these counters, covering an effective 2θ range of 10 to 160°.

A data set was first collected with the powder sample at room temperature. The sample was then placed in a furnace and heated to 355 K and a further scan was made at this temperature for phase II.

Analysis

The profile-refinement method was used to analyse the powder diffraction data* obtained for both phase IV

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34215 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic parameters of* IV–ND_4NO_3 (298 K) *and* II–ND_4NO_3 (355 K) *determined by neutron powder profile refinement with values for* IV–NH_4NO_3 *from neutron single-crystal measurements* (*Choi et al.*, 1972) *included for comparison*

E.s.d.'s are in parentheses; parameters without e.s.d.'s were fixed in refinement by space-group requirements. *R* factors are for integrated intensity reflexions.

Crystal data		*x*	*y*	*z*
IV–ND_4NO_3 (298 K)				
	N(1)	$\frac{3}{4}$	$\frac{1}{4}$	−0·0834 (4)
Orthorhombic	D(1)	0·6110 (4)	$\frac{1}{4}$	−0·1932 (6)
a = 5·7574 (1) Å	D(2)	$\frac{3}{4}$	0·0990 (5)	0·0244 (6)
b = 5·4394 (1)	N(2)	$\frac{1}{4}$	$\frac{1}{4}$	0·5059 (4)
c = 4·9298 (1)	O(1)	$\frac{1}{4}$	$\frac{1}{4}$	0·7613 (6)
Z = 2	O(2)	0·4338 (4)	$\frac{1}{4}$	0·3857 (5)
Space group: *Pmmn*				
$R = \sum[sF_o^2 - F_c^2]/\sum F_o^2 = 0{\cdot}037$				
IV–NH_4NO_3 (Choi *et al.*, 1972)				
	N(1)	$\frac{3}{4}$	$\frac{1}{4}$	−0·0836 (4)
Orthorhombic	H(1)	0·6045 (12)	$\frac{1}{4}$	−0·1898 (17)
a = 5·745 Å	H(2)	$\frac{3}{4}$	0·1011 (16)	0·0324 (16)
b = 5·438	N(2)	$\frac{1}{4}$	$\frac{1}{4}$	0·5067 (3)
c = 4·942	O(1)	$\frac{1}{4}$	$\frac{1}{4}$	0·7629 (6)
Z = 2	O(2)	0·4342 (5)	$\frac{1}{4}$	0·3832 (5)
Space group: *Pmmn*				
$R_w = [w(s\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum wF_c^2]^{1/2} = 0{\cdot}028$				
II–ND_4NO_3 (355K)				
	N(1)	0	0	$\frac{1}{2}$
Tetragonal	D(1)	0·1404 (4)	−0·0171 (16)	0·3850 (4)
a = 5·7193 (1) Å	N(2)	0	$\frac{1}{2}$	0·0230 (26)
c = 4·9326 (1)	O(1)	0	$\frac{1}{2}$	0·2742 (9)
Z = 2	O(2)	0·6287 (4)	$\frac{1}{2} + x$	0·1029 (10)
Space group: $P42_1m$ (disordered)				
R = 0·022				

and phase II. The least-squares refinement program was that of Rietveld (1969), with modifications by Hewat (1973). In the refinements, two sets of parameters were refined: those describing the characteristics of the diffractometer and those describing the crystal structure. The former group consisted of five parameters: the counter zero point, the three half-width parameters and an asymmetry parameter. The structural parameters refined were the scale factor, the lattice constants, the fractional coordinates and the thermal parameters for each atom.

Phase IV ammonium nitrate structure

The starting model was that reported by Choi *et al.* (1972) for the hydrogenous compound, the details of which are reproduced in Table 1. The correctness of the structure was immediately confirmed and the details of the deuterated phase IV structure are given in Table 1. In the final cycles of refinement, the occupation numbers of the D atoms were also refined to check the degree of deuteration of the sample, before proceeding to the study of the unknown phase II structure. The value obtained was 2·039 (9) compared to 2 that would have been expected for 100% sample deuteration, showing that virtually complete deuteration had been achieved.

Phase II ammonium nitrate structure

The model proposed by Shinnaka (1956), with a change of origin to $(0,0,\frac{1}{2})$, was used as the starting model. This consists of a disordered tetragonal structure based on the space group $P\bar{4}2_1m$. The nitrate ions are considered to be positioned about the points $(\frac{1}{2},0,0)$ and $(0,\frac{1}{2},0)$. The planes of the nitrate ions make angles of 45°, about [001], to the lattice planes (010) and (100) respectively, the rotations being in opposite senses for the two lattice planes. One nitrate ion orientation has a N—O bond along [001], the other has N—O along [00$\bar{1}$]. The N atoms for the two nitrate ion orientations are slightly displaced from the respective $(\frac{1}{2},0,0)$ and $(0,\frac{1}{2},0)$ positions in equal magnitude but opposite sense along *c*. Further, the ion at each position is considered to be disordered between two orientations and positions, each related by a 60° rotation in its own plane and a small translation of its centre to the symmetrical position along *c*. The ammonium ions are considered to have their N atoms positioned at the points $(0,0,\frac{1}{2})$ and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. Shinnaka's (1956) model does not provide the ammonium ion orientations, but these ions were also found to be disordered about their N atom positions between two different orientations and their structural arrangements were determined in the present work. The D atoms of the ion are located tetrahedrally about their N atom, one $\bar{4}$ axis of the ion being coincident with [001], the other two nearly parallel to [100] and [010]. The second equivalent orientation is related to the first by a 90° rotation about [001]. The two possible orientations for each ion were considered equally probable and hence given equal weight in the

Table 2. *Interatomic distances* (Å) *and angles* (°) *for* IV–ND_4NO_3 (298 K) *and* II–ND_4NO_3 (355 K), *with values for* IV–NH_4NO_3 (*Choi et al.*, 1972) *included for comparison*

	IV–ND_4NO_3	IV–NH_4NO_3	II–ND_4NO_3	
N(1)–H(1)	0·966 (3)	0·987 (7)	0·988 (2)	
N(1)–H(2)	0·978 (3)	0·992 (7)		
N(2)–O(1)	1·259 (4)	1·266 (4)	1·239 (14)	
N(2)–O(2)	1·213 (3)	1·222 (3)	1·212 (7)	
H(1)–N(1)–H(1)	111·9 (0·3)	115·7 (1·2)	109·47	
H(1)–N(1)–H(2)	107·7 (0·1)	107·9 (0·4)		
H(2)–N(1)–H(2)	114·2 (0·3)	109·4 (1·2)		
O(1)–N(2)–O(2)	119·3 (0·2)	120·0 (0·3)	120·8 (0·6)	
O(2)–N(2)–O(2)	121·5 (0·2)	120·0 (0·3)	118·4 (0·6)	
Hydrogen bonds			For alternative relative orientations of the ions	
Bond type				
N(1)–H(1)···O(1)				
O···H	2·090 (2)	2·050 (7)	2·658 (4)	2·130 (3)
O···N	2·979 (1)	2·971 (3)	3·069 (2)	3·069 (2)
N–H···O	152·1 (3)	154·4 (8)	105·2 (2)	158·0 (4)
N(1)–H(2)···O(1)				
O···H	2·173 (3)	2·161 (7)		
O···N	3·149 (2)	3·147 (3)		
N–H···O	176·2 (3)	172·6 (9)		
N(1)–H(1)···O(2)				
O···H	2·313 (4)	2·326 (7)	2·008 (6)	2·622 (8)
O···N	3·188 (3)	3·200 (4)	2·981 (4)	2·981 (4)
N–H···O	150·3 (3)	147·0 (9)	163·3 (4)	101·5 (3)

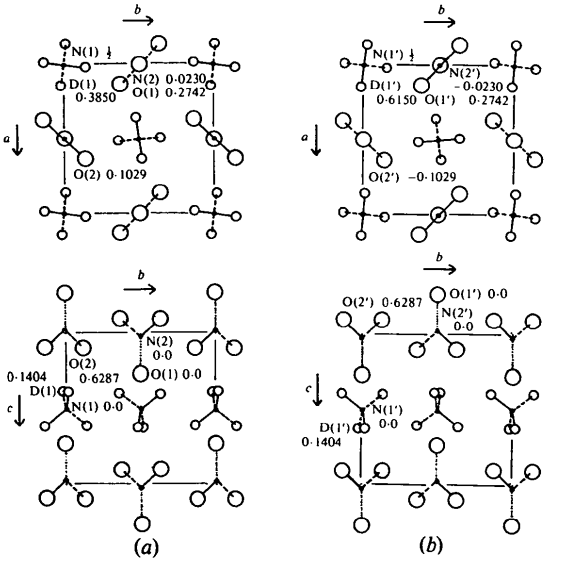

Fig. 1. (*a*) The structure of phase II ammonium nitrate (355 K) and (*b*) its equivalent (with equivalent NH_4 and NO_3 orientations and positions). Bonds represented in full and dashed lines are towards and away from the observer respectively; dotted lines represent bonds in the plane of the page.

full-matrix least-squares refinement. The refinement converged with the final atomic parameter values given in Table 1. The structure is illustrated in Fig. 1 and the interatomic distances and angles are given in Table 2.

Conclusion

The phase IV structure of ammonium nitrate has been confirmed. The phase II structure has been determined and shows orientational disorder of both the ammonium and nitrate ions. The shortest distances of the H atoms to O atoms in phase II are 2·008 (6), 2·658 (4) Å for one relative orientation of the ammonium and nitrate ions, compared with 2·622 (8), 2·130 (3) Å, respectively, for the other relative orientation. As the limit for H···O bonding is ~2·38 Å (Hamilton & Ibers, 1968), this would suggest that the NH_4, and probably the NO_3, ions are in dynamic (as opposed to static) disorder between their two equivalent positions.

The help of Dr K. Österlund in preparing the deuterated ammonium nitrate is gratefully acknowledged. We thank the French Government (BWL) and the Finnish Academy (MA) for their support, and the ILL for making all facilities available to us.

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Acta Cryst. (1979). B**35**, 1041–1046

Pseudo-Symmetry and Hydrogen Bonding in the Crystal Structure of $NaH_2PO_2.\frac{4}{3}H_2O$

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(*Received* 7 *September* 1978; *accepted* 25 *January* 1979)

Abstract

$NaH_2PO_2.\frac{4}{3}H_2O$ crystallizes in space group $P2_1/n$ with $a = 11{\cdot}127$ (4), $b = 13{\cdot}572$ (4), $c = 12{\cdot}930$ (4) Å, $\beta = 102{\cdot}98$ (8)°, $Z = 20$. The structure was refined to $R = 0{\cdot}043$ for 2684 counter reflexions. H atoms were refined isotropically. All atomic positions are consistent with a strong *C* pseudo-symmetry. The distorted tetrahedral configurations of the $[H_2PO_2]^-$ ions are discussed in terms of atomic repulsion forces. Two very low O···*W*···O′ angles (76·2 and 78·4°) are shown by hydrogen bonds, O···O′ being edges of the Na coordination polyhedra. The Na octahedra form [101] chains by sharing faces and edges; a weak link between chains is provided by sharing vertices (water molecules only) between polyhedra and by hydrogen bonding. On the basis of the structural topology, a dehydration mechanism is proposed.

Introduction

A series of hydrated sodium hydrogenorthophosphates have recently been the subject of structural studies to clarify the relative role of the Na–O coordination bonds and of hydrogen bonding in determining their structural topology and stability *vs* dehydration (*cf.* Catti, Ferraris & Ivaldi, 1978). Since the stoichiometric ratio O/Na and the number of acidic hydrogen atoms are the crucial parameters controlling the condensation of the Na coordination polyhedra (Catti & Ivaldi, 1977), it seemed interesting to change them by substituting the $[PO_2(OH)_2]^-$ or $[PO_3(OH)]^{2-}$ oxyanions by the hypophosphite ion $[H_2PO_2]^-$, where the two hydrogen atoms are not acidic and not involved in hydrogen bonds. The structure of the only known hydrated sodium hypophosphite $NaH_2PO_2.\frac{4}{3}H_2O$ has therefore been examined. This study can also provide

0567-7408/79/051041-06$01.00