Similarly the a-axis length is given by

$$a = 2\{[F(2)\text{–chain}]^2 - (c/8)^2\}^{1/2} + \sqrt{2}[Sb\text{–}F(2)] \tag{3}$$

and from a the value of δ can be calculated.

Since the Hg–Hg intrachain distance, chain–chain distance and F–chain distances are the same in both $Hg_{3-\delta}$ AsF_6 and $Hg_{3-\delta}SbF_6$ (Table 3), the values of a, c, u_0 and δ should depend only on the size of the anion. Table 4 shows that good predictions of these quantities can be made on this assumption. Prediction can also be made for all the positional coordinates as well as for the structural parameters expected for the hypothetical $Hg_{3-\delta}PF_6$ and $Hg_{3-\delta}BiF_6$ compounds. The small value of δ expected for the latter suggests that it might exist in a stoichiometric form.

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Single-Crystal Neutron Diffraction Study of Ammonium Nitrate Phase III

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Abstract

The crystal structure of ammonium nitrate phase III has been studied at room temperature by neutron diffraction using a single crystal containing 5% KNO_3 in solid-solution form. The space group is *Pnma*, with $a = 7.6772$ (4), $b = 5.8208$ (4), $c = 7.1396$ (5) Å, $Z = 4$. The final residual after full-matrix least-squares refinement was $R = 0.042$ for 348 observed reflections. The ammonium ions are thermally disordered into two orientations, displaced by an angle of approximately 42° about an axis parallel to the c axis.

Introduction

Ammonium nitrate (AN), NH_4NO_3, crystallizes in five different polymorphic forms, phase I, II, III, IV, V with transition temperatures of 398, 357, 305, and 255 K respectively. The crystal structures of phase IV (Choi,

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Mapes & Prince, 1972), phase II (Lucas, Ahtee & Hewat, 1979) and phase I (Ahtee, Kurki-Suonio, Lucas & Hewat, 1979) have been completely determined by neutron diffraction. The structure of phase III has also been determined for the non-hydrogen atoms by three independent studies: an X-ray single-crystal study by Holden & Dickinson (1975); a neutron powder diffraction study by Choi, Prask & Prince (1980); and a neutron powder diffraction study (ND_4NO_3) by Lucas, Ahtee & Hewat (1980). However, the orientation of the ammonium group was not clearly determined. The orientation of the ammonium group as reported by Lucas *et al.* (1980) has one of the 4 axes of the ammonium ion parallel to the unit-cell a axis, but that reported by Choi *et al.* (1980) shows the 4 axis parallel to the c axis. This study is aimed at clarifying the disputed orientation of the ammonium group by using the single-crystal neutron diffraction method. Since the crystal structures of AN, in all solid phases except phase I, contain hydrogen bonds, the orientation of the NH_4 group is particularly important for understanding AN phase transitions.

Experimental

The solid solution of KNO_3 (KN) in NH_4NO_3 (AN) crystallizes in the phase III structure at room temperature if the concentration of KN is about 3 wt% or more (Holden & Dickinson, 1975). Single crystals of AN containing 5 wt% KN in solid-solution form were grown from saturated aqueous solution by very slow evaporation at room temperature. An elongated six-sided single crystal with approximate dimensions of 1 × 1 × 6mm was mounted on a full-circle goniometer with the long axis of the crystal directed approximately parallel to the φ axis. The unit-cell parameters for the 5 wt% solid solution of KN in AN III, as obtained by the neutron powder diffraction study (Choi et al., 1980) (see Abstract), were in good agreement with this study. Using neutrons of wavelength 1·273 Å, two sets of equivalent reflections (hkl and $\bar{h}kl$) within the scattering angle of 120° were measured by the computer-controlled four-circle diffractometer at the NBS reactor. The μt values of the crystal for this diffraction geometry range from 0·20 for reflection 101 to 0·31 for 071, assuming that the incoherent cross section of H is 42 × 10^2 fm^2 [half of H_2O (Hughes & Schwartz, 1958)] for $\lambda = 1·273$ Å. No absorption corrections were made because the effect was small. The data were merged to a total of 460 independent reflections (R factor between two equivalent sets was 0·019), among which 348 reflections had observable intensity (i.e. peak intensity greater than twice the standard deviation). The integrated intensities of unobservable reflections were assumed to be half of each corresponding standard deviation. The integrated intensities were converted to structure factors for the refinement of the structure.

Refinement

The structure of an ordered model reported previously by Choi et al. (1980) was the starting point of the refinement. The occupancy factors for the ammonium site are 0·96 NH_4^+ ion and 0·04 K atom. The refinement with anisotropic thermal parameters for all atoms and with an isotropic secondary-extinction parameter (Zachariasen, 1968) reduced the residual indices to $R_w = 0·056$ and $R = 0·051$, where $R_w^2 = \sum w(\Delta F)^2/\sum wF_o^2$ and $R = \sum (\Delta F)/\sum F_o$ with $\Delta F = ||F_o| - |F_c||$. The thermal parameters of the H atoms obtained in this refinement were extremely large and anisotropic, which suggested a considerable amount of anharmonic motion probably due to orientational disorder of the ion. The rigid-body motions of the ammonium ion which were calculated from the anisotropic atomic thermal parameters by the method of Schomaker & Trueblood (1968) showed large librational motions with r.m.s. amplitudes about principal axes of 27, 22, and 20°, respectively. The

observed H—N—H angles of the NH_4^+ ion ranged from 104 to 113°, which indicated an unrealistically severe distortion from the expected tetrahedral angles. In the subsequent refinement, the NH_4^+ ion was constrained to an ideal tetrahedral structure with rigid-body motions using the method of Prince & Finger (1973). The computer program RFINE (Finger & Prince, 1975), which has a convenient and versatile option for applying constraints, including the TLS rigid-body motions, was used for this study. With these constraints, the number of refinement parameters was reduced from 50 to 41 and, hence, the residual indices increased slightly to $R_w = 0·059$ and $R = 0·056$. The libration motion of the constrained ammonium ion reduced to 25, 22, and 20° in r.m.s. amplitude.

An examination of the difference Fourier map obtained from the structure with all H atoms deleted revealed a pair of probable disorder sites for each H atom. In the ordered model, the NH_4^+ ions are oriented with one of the $\bar{4}$ axes lying on the crystal mirror plane and parallel to the c axis. A disordered model was constructed by reorienting the NH_4^+ ion in the ordered structure by a 20° rotation in either direction about the $\bar{4}$ axis in the mirror plane (Fig. 1). The pair of disordered orientations as obtained above are related by the mirror symmetry of the crystal. The disordered model was refined in two ways: conventional (unconstrained) refinement with anisotropic thermal parameters for all atoms, and a constrained rigid-body refinement with TLS motions for the ammonium group.

The anisotropic refinement of the disordered model reduced the residual indices to $R_w = 0·042$ and $R = 0·041$ for a total of 65 least-squares parameters. The structure of the NH_4^+ ion showed a severe distortion from the tetrahedral shape with the H—N—H bond angles ranging from 100 to 115°. The thermal parameters of H atoms were still very large even in the disordered structure. Because of the proximity of the two disordered sites (only 42° apart in reorientation
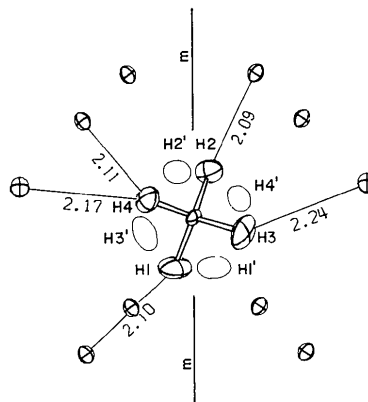

Fig. 1. ORTEP drawing (Johnson, 1965) of ammonium nitrate and its oxygen neighbors viewed along the c-axis direction. The open ellipsoids symbolize the alternate sites of the disordered model.

angle) and the large thermal motions, the density distributions around pairs of sites overlap significantly. It was concluded, therefore, that the structure of the NH_4^+ ion obtained by the unconstrained refinement is less meaningful despite the better residuals of the refinement.

In the constrained rigid-body refinement, the ammonium group in each disordered orientation was constrained to maintain a tetrahedral shape and to undergo **TLS** motions. A special coordinate system was chosen for the rigid body with an origin on the N(H) atom, z axis parallel to the N(H)–H(1) bond, and y axis perpendicular to the H(1)–N(H)–H(2) plane as in Fig. 1. All H–N–H bond angles were constrained to be 109·47° (tetrahedral angle) and all N–H bonds were constrained to have identical lengths. The number of least-squares parameters was reduced to 49 compared to 65 for the anisotropic refinement. The final R indices were $R_w = 0.043$ and $R = 0.042$. The final least-squares parameters are given in Table 1, and the rigid-body parameters based on the special coordinate system are given in Table 2. The bond parameters are given in Table 3. The existence of mirror symmetry in the phase III structure was quite evident from the results of the refinement of the non-centrosymmetric structure with the space group $Pn2_1a$. The starting parameters were taken from the centrosymmetric structure given in Table 1 with nine atoms in an asymmetric unit. The refinement with anisotropic thermal parameters for all atoms reduced the R indices to $R_w = 0.040$ and $R = 0.044$ for a total of 82 parameters with no significant deviations from the mirror symmetry. Furthermore, all the parameters of the O(2) atom, particularly the y-axis-related parameters, highly correlated with the corresponding parameters of the O(3) [the pseudo mirror-symmetric pair of

Table 1. *The final least-squares parameters of the rigid-body refinement for the disordered model*

The ammonium group was constrained to an ideal tetrahedral structure. The hydrogen positions which were corrected for the librations are given in parentheses. B is the equivalent isotropic factor ($Å^2$), and n is the occupancy factor

	x	y	z	B	n
N(H)/K	−0·0097 (2)	$\frac{1}{4}$	0·3171 (2)	2·77	0·96/0·04
N(0)	0·1550 (2)	$\frac{1}{4}$	0·1263 (2)	2·38	1·0
O(1)	0·0599 (4)	$\frac{1}{4}$	0·2661 (4)	3·73	1·0
O(2)	0·2007 (3)	0·0660 (4)	0·0540 (3)	3·52	1·0
H(1)*	−0·1048 (9)	0·7022 (57)	0·3857 (13)	9·75	0·96
	(−0·1154)	(0·6936)	(0·3954)		
H(2)*	0·0793 (11)	0·7906 (57)	0·3974 (11)	7·18	0·96
	(0·0886)	(0·7964)	(0·4072)		
H(3)*	−0·0403 (16)	0·8751 (35)	0·2449 (20)	9·84	0·96
	(−0·0421)	(0·8919)	(0·2347)		
H(4)*	0·0270 (14)	0·6321 (35)	0·2403 (19)	7·32	0·96
	(0·0300)	(0·6180)	(0·2311)		

* The parameters of the ammonium hydrogens are derived from the rigid-body parameters as given in Table 2.

Table 2. *The rigid-body parameters of the constrained ammonium group (of the disordered model), based on a special orthonormal coordinate system (Å) with the origin at the ammonium N(H)*

ω, χ and φ are Eulerian angles for transformation to standard systems.

ω	20·9 (12)°	T_{11}	0·041 (2) $Å^2$
χ	−57·9 (6)°	T_{22}	0·030 (2)
φ	−1·5 (12)°	T_{33}	0·034 (2)
H(1)(x)	0·0	T_{12}	0·018 (2)
H(1)(y)	0·0	T_{13}	0·006 (1)
H(1)(z)	0·922 (11)	T_{23}	0·002 (2)
H(2)(x)	0·8697	L_{11}	0·117 (15) deg^2
H(2)(y)	0·0	L_{22}	0·117 (7)
H(2)(z)	−0·3075	L_{33}	0·108 (9)
H(3)(x)	−0·4348	L_{12}	−0·006 (10)
H(3)(y)	0·7532	L_{13}	−0·017 (9)
H(3)(z)	−0·3075	L_{23}	0·032 (10)
H(4)(x)	−0·4348	S_{11}	−0·019 (4) deg Å
H(4)(y)	−0·7532	S_{22}	0·015 (4)
H(4)(z)	−0·3075	S_{33}	0·004
		S_{12}	−0·013 (4)
		S_{13}	0·005 (4)
		S_{23}	0·011 (4)
		S_{21}	0·009 (4)
		S_{31}	−0·017 (5)
		S_{32}	−0·003 (4)

Table 3. *Bond parameters for the disordered structure*

N(H)–H(1)	1·038 (11) Å	N(H)–H(4)	1·030 (3) Å
N(H)–H(2)	1·028 (11)	N(0)–O(1)	1·237 (3)
N(H)–H(3)	1·044 (3)	N(0)–O(2)	1·240 (2)

O(1)–N(0)–O(2)	120·2 (1)°	O(2)–N(0)–O(3)	119·5 (2)°
O(1)–N(0)–O(3)	120·2 (1)		

Hydrogen bonds

	H···O (Å)	N–H···O (°)
N(H)–H(1)···O(2)	2·10 (2)	148 (2)
N(H)–H(2)···O(2)	2·09 (2)	170 (2)
N(H)–H(3)···O(1)	2·24 (2)	127 (1)
N(H)–H(4)···O(1)	2·17 (2)	134 (1)
N(H)–H(4)···O(2)	2·11 (2)	157 (1)

O(2)]. The correlation coefficients were larger than 80% throughout, and the estimated standard deviations became very large, about a factor of four to eight times larger than the corresponding e.s.d.'s of the centrosymmetric structure.*

Discussion

The structure of the nitrate group determined in this study is essentially identical with previous studies

(Holden & Dickinson, 1975; Lucas *et al.*, 1980). However, the orientation of the ammonium group is different from that of Lucas *et al.*, having one of the $\bar{4}$ axes oriented approximately parallel to the c axis instead of the a axis. The NH_4^+ groups are disordered, with two different orientations related by mirror symmetry, as shown in Fig. 1. The orientational transition between them is achieved by a 42° rotation about the axis which passes through the ammonium nitrogen and is parallel to the c axis. This disorder is quite unusual and presents several interesting features:

(a) The ammonium group, which possesses mm symmetry in the ideal form, does not have mirror symmetry in the crystal despite the m symmetry of the site. Instead, the two disordered molecular orientations are related to each other through a mirror reflection.

(b) Although the two orientations are not related by any rotational symmetry besides the mirror-image relation, the reorientation of the ammonium ion is achieved by a rotational reorientation of 42° about an axis parallel to the c axis. This disorder makes a remarkable contrast to that of phase II where the rotational disorder of the ammonium ion is a fourfold rotation about the $4/m$ symmetry axis of the site (Choi *et al.*, 1980).

(c) The amplitude (42°) and direction of the reorientational rotation are not fixed by molecular or crystal symmetry, and hence may be temperature dependent.

(d) As shown in Fig. 1, H(3) and H(4) are not structurally equivalent; the H(3) site involves a weak hydrogen bond, whereas H(4) involves two strong hydrogen bonds. The rotational reorientations of 42° entail H(4) → H(3)′ and H(3) → H(4)′ so that each hydrogen alternates sites of relatively weak and strong bonding. The large librational components of the rigid ammonium ion (compared with phase II in Table 1) may possibly arise from the sudden change of external interaction at the two dissimilar sites.

The ammonium groups in the phase III structure are surrounded by 11 oxygen neighbors located within a distance of 3·21 Å, of which ten are shown in Fig. 1. Among them, eight atoms are involved in N—H···O type hydrogen bonding in the disordered structure, as given in Table 3. Similar oxygen surroundings for the ammonium group occur in other phases of ammonium nitrate: 12 oxygen neighbors within a distance of 3·27 Å for phase IV, and 16 oxygen neighbors (eight each for the two disordered orientations) for the phase II structure. In the case of ammonium perchlorate (Choi, Prask & Prince, 1974), they are surrounded by ten oxygen neighbors located within 3·25 Å. The librations of the ammonium groups in these structures are large because of the low potential barrier to rotation, and commonly exhibit a kind of orientational disorder.

The rigid-body motions and the disorder sites of the NH_4^+ ions in phases II, III, and IV are summarized in

Table 4. *Comparison of thermal disorder of the ammonium ions in phases* II, III *and* IV

Ion	Phase	Tempera-ture (K)	Disorder (angle)	Site symmetry	Principal axes T_{ii} (Å²)	L_{ii} (°)
ND_4	II[a]	357–398	90°	$4/m$	0·058	14·4
					0·058	14·4
					0·065	10·3
NH_4	III[b]	305–357	42°	m	0·055	22·4
					0·034	19·1
					0·015	16·0
NH_4	IV[c]	255–305	ordered	mm	0·051	18·9
					0·035	16·2
					0·035	11·1

References: (a) Lucas *et al.* (1979); (b) this work; (c) Choi *et al.* (1972).

Table 4. The TLS motions of the phase II structure were calculated from the atomic thermal ellipsoids of the ND_4^+ ion (Lucas *et al.*, 1979) using the method of Schomaker & Trueblood (1968). The NH_4^+ ion in the phase IV structure undergoes an intense librational motion, but maintains an ordered structure, unlike those in the higher-temperature phases. The NH_4^+ ion in phase III exhibits a strong anharmonic motion, mostly in the form of orientational disorder. The NH_4^+ group at each disordered site of phase III still exhibits large librational motion, as given in Table 4. This may be attributable to the lack of rotational symmetry about the reorientation axis and also to the significantly different hydrogen bondings for the two alternate sites of the H(3) or H(4) atom as described above. The ammonium group of the phase II structure occupies a position at the $4/m$ symmetry site with one of the $\bar{4}$ axes of the ion coinciding with the fourfold axis (Choi *et al.*, 1980), and undergoes an orientational disorder involving a 90° rotation about the $\bar{4}$ axis of the ion. In this case, the reorientation of the ion is in complete harmony with the crystal site symmetry, and hence the libration amplitudes of the ion at each disordered site are quite normal, as shown in Table 4.

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Structure Determination of Calcium Neodymium Potassium Double Phosphate CaKNd(PO₄)₂

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Abstract

The structure of $(Ca_{1.5}Nd_{1.5})K_{1.5}(PO_4)_3$ [CaKNd(PO₄)₂] has been determined using single-crystal X-ray diffraction data. The material crystallizes in the hexagonal system with space group $P6_222$ ($P6_422$) and the parameters (refined from powder data) $a = 7.033$ (5) and $c = 6.397$ (5) Å, $Z = 1$. The least-squares anisotropic refinement led to $R = 0.042$ for 407 reflexions. The structure is similar to that of hexagonal LnPO₄ except that the K atom occupies a large tunnel in the lattice and the Ln position is statistically occupied by both Nd and Ca atoms. It is made up of (Nd,Ca)–PO₄–(Nd,Ca)– chains running along the c axis, linked to similar chains by corner sharing with four PO₄ tetrahedra coplanar with the (001) plane.

Introduction

The importance of new luminophores has recently motivated research on new materials containing rare-earth ions. Phosphors containing neodymium ions can be used as high-power microlaser sources.

The study of the optical properties of various phosphates such as NdP₅O₁₄ (Albrand, Attig, Fenner, Jeser & Mootz, 1974), KNdP₄O₁₂ (Hong, 1975), K₃Nd(PO₄)₂ (Hong & Chinn, 1976) has shown that such phases possess a covalent two- or three-di-

mensional framework in which the rare-earth ion is found relatively isolated ($d_{Ln-Ln} \simeq 5$ Å).

The phosphates LnPO₄ (Ln = La, Ce, Nd) seem to crystallize in two allotropic varieties. One has the monazite-type structure with monoclinic symmetry, the second has hexagonal symmetry, its structure being characterized by large tunnels running along the c axis. Ordinarily, the LnPO₄ hexagonal phases are hydrated (LnPO₄.½H₂O), but no evidence exists proving that the presence of water is necessary for stabilizing their structure (Mooney, 1950; Mooney-Slater, 1962).

The existence of the large tunnels in the lattice has l Et-Tabirou & Daoudi (1980) to prepare phases such as ACaNd(PO₄)₂ (A = K, Rb, Cs) with the large alkali ions inserted in the tunnels.

The necessity of studying and giving an interpretation of the optical properties of such phases has led us to carry out a detailed structural determination of CaKNd(PO₄)₂.

Preparation and characterization

The starting materials (NH₄)₂HPO₄, K₂CO₃, CaCO₃ and Nd₂O₃ are mixed together in stoichiometric amounts and pressed into discs. These are first heated for several hours at 673 K followed by two heat treatments for 48 h at 1323 K with interposed grinding.

Single crystals were grown by recrystallization of the powder at 1873 K in a sealed platinum tube, followed by slow cooling.

The X-ray powder patterns of the ground crystals suggest an isotypy with hexagonal LnPO₄. A qualitative X-ray fluorescence analysis shows only the

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