erhebliche Verstärkung der Wechselwirkung mit den Anionen gekoppelt.

Die Bindungsverhältnisse im Trihydrat der Hexachloroantimonsäure sind offenbar so, dass sich die Ausbildung einer monomeren Einheit $H^+(H_2O)_3$ verbietet. Dazu fehlt die erwähnte Stabilisierungsmöglichkeit im Kontakt mit Anionen. Vielmehr ist die Bildung des Dimeren eine interessante Alternative zur Kette. Warum letztere nicht realisiert ist, mag daran liegen, dass ein Kettensegment über drei Bindungen im Trihydrat des Chlorwasserstoffs die Länge von 6,3 Å hat. Das erscheint knapp im Vergleich zum mittleren Durchmesser des $SbCl_6^-$-Ions. Vielleicht ist aber auch die Kette ohne Anionenkontakte hinreichender Stärke nicht stabil.

Für kristallographische Berechnungen stand die Anlage Univac 1108 des Rechenzentrums der Universität Karlsruhe zur Verfügung. Verwendet wurden die Programme des XRAY-Systems (Stewart, Kundell & Baldwin, 1970), u. a. *FOURR* und *CRYLSQ*. Bei den Zeichnungen konnte auf *ORTEP*-II (Johnson, 1971) zurückgegriffen werden. Zu erwähnen bleibt der Übersichtsartikel von Lundgren & Olovsson (1976), aus dem die Diskussion wertvolle Anregung bezog.

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The Structure of Phase III Ammonium Nitrate

BY B. W. LUCAS

Department of Physics, University of Queensland, St Lucia, Brisbane, Queensland 4067, *Australia*

M. AHTEE

Department of Physics, University of Helsinki, Siltravuorenpenger 20*D*, 00170 *Helsinki, Finland*

AND A. W. HEWAT

Institut Laue–Langevin, Avenue des Martyrs, BP 156*X*, *Centre de Tri*, 38042 *Grenoble CEDEX, France*

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Abstract

Neutron powder diffractometer data from deuterated ammonium nitrate at 318 K have been used with the profile-refinement method to determine the crystal structure of phase III. The structure is disordered, with orthorhombic space group *Pnma*, $a = 7{\cdot}7184$ (3), $b = 5{\cdot}8447$ (1), $c = 7{\cdot}1624$ (2) Å, $Z = 4$. The orientations

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of the ions and disorder of the NH_4 ions have been determined, there being two alternative orientations for each NH_4 ion.

Introduction

Solid ammonium nitrate can exist in several different phases at atmospheric pressure, 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 (Lucas, Ahtee & Hewat, 1979) and to a cubic phase I structure above 328 K (Ahtee, Kurki-Suonio, Lucas & Hewat, 1979). The corresponding transitions have been found also for deuterated ammonium nitrate, the transition temperatures being only slightly affected by deuteration (Juopperi, 1972).

The crystal structures of all five phases (for the hydrogenous form) have been studied by X-ray diffraction, but only phase IV (Choi *et al.*, 1972), phase II (Lucas *et al.*, 1979) and phase I (Ahtee *et al.*, 1979) have been completely determined; these were by neutron diffraction methods.

The aim of the present study was to determine the phase III crystal structure. The profile-refinement method (Rietveld, 1969) for neutron powder diffraction measurements was employed.

Experimental

Approximately 20 g of a previously prepared deuterated ammonium nitrate powder sample (Lucas *et al.*, 1979) was sealed in an air-tight thin-walled vanadium can of diameter 16 mm. The sample was heated to 318 K in a furnace on the high-resolution powder diffractometer (D1A) at the high-flux reactor at the ILL (Grenoble) and neutron diffraction measurements were made, the wavelength used being 1·90818 Å. D1A has a bank of ten ^3He high-pressure counters with a 6° angular separation. The final measured intensity profiles were obtained by appropriately combining the intensities from these counters, covering an effective 2θ range of 10 to 160°.

Analysis

The profile-refinement method was used to analyse the powder diffraction data.* The least-squares refinement program was that of Rietveld (1969), with modifications by Hewat (1973). 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,

Table 1. *Atomic parameters of deuterated* III–NH_4NO_3 (318 K) *determined by neutron powder profile refinement*

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

	x	*y*	*z*
N(1)	0·5105 (3)	$\frac{1}{4}$	0·8177 (3)
H(1)	0·5806 (4)	$\frac{1}{4}$	0·7282 (6)
H(2)	0·5806 (4)	$\frac{1}{4}$	0·9118 (6)
H(3)	0·4374 (4)	0·3624 (7)	0·8177 (3)
N(2)	0·6557 (4)	$\frac{1}{4}$	0·3729 (4)
O(1)	0·5662 (6)	$\frac{1}{4}$	0·2367 (7)
O(2)	0·7004 (4)	0·4351 (5)	0·4442 (5)

$$R = \sum|sF_o^2 - F_c^2|/\sum F_o^2 = 0{\cdot}095$$

Table 2. *Interatomic distances* (Å) *and angles* (°) *for deuterated* III–NH_4NO_3

Calculated corrections for bond lengths are based on the riding (NH_4^+) and rigid-body motion (NO_3^-) models.

	Uncorrected	Corrected
N(1)–H(1)	0·839 (4)	1·02 (2)
N(1)–H(2)	0·864 (4)	1·04 (1)
N(1)–H(3)	0·866 (4)	1·17 (4)
N(2)–O(1)	1·195 (6)	1·231 (8)
N(2)–O(2)	1·245 (3)	1·275 (5)
H(1)–N(1)–H(2)	101·1 (4)	
H(1)–N(1)–H(3)	114·9 (3)	
H(2)–N(1)–H(3)	114·1 (3)	
O(1)–N(2)–O(2)	119·7 (2)	
O(2)–N(2)–O(2)	120·7 (3)	

Hydrogen bonds

	For alternative NH_4^+ orientations	
Bond type	N(1)–H(2)···O(1)	N(1)–H(3)···O(1)
O···H	2·330 (7)	2·299 (4)
O···N	3·032 (5)	3·007 (1)
N–H···O	138·5 (4)	139·1 (3)
	N(1)–H(1′)···O(2)	N(1)–H(3′)···O(2)
O···H	2·395 (4)	2·236 (5)
O···N	3·132 (4)	3·031 (4)
N–H···O	147·0 (2)	152·5 (3)

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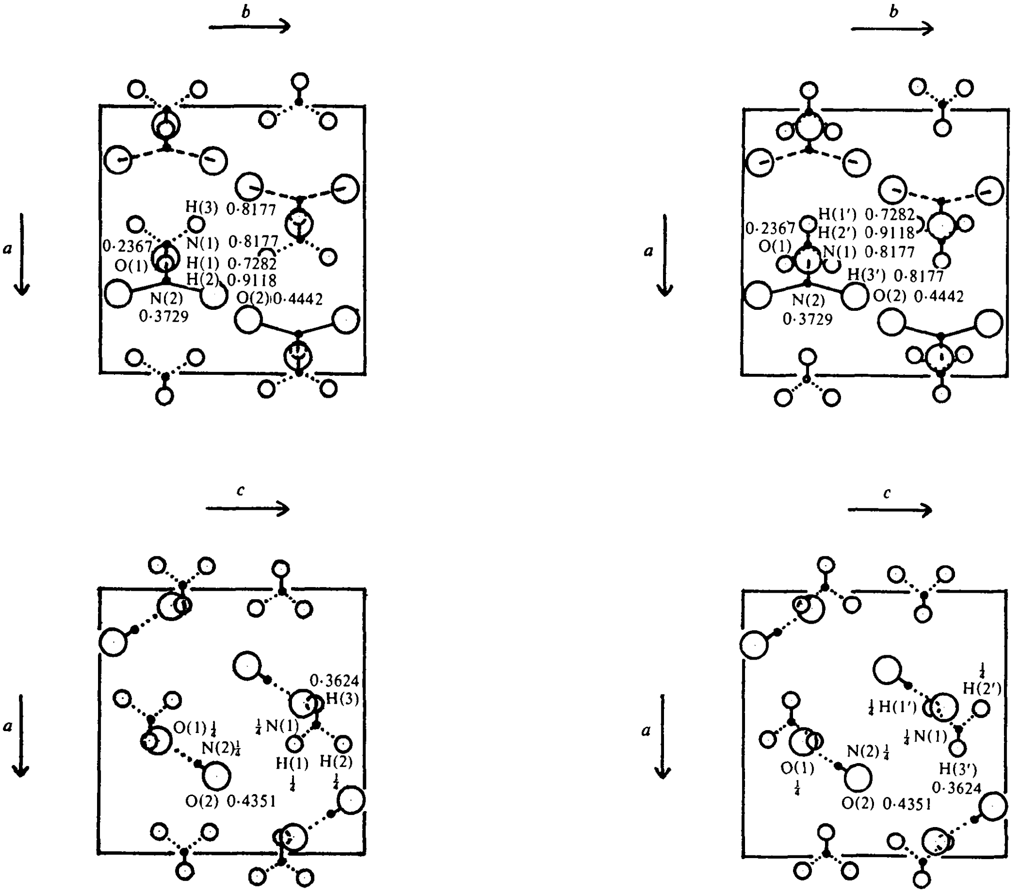
* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35303 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.



(*a*) (*b*)

Fig. 1. The disordered structure of phase III ammonium nitrate (318 K); (*a*) and (*b*), showing alternative NH_4 orientations, exist in equal proportions. N, H, and O atoms are represented sequentially by circles of increasing size. Bonds represented by full and dashed lines are towards and away from the observer respectively; dotted lines represent bonds in the plane of the page.

the fractional coordinates and thermal parameters of each atom. Corrections to the estimation of bond lengths were calculated (Busing & Levy, 1964) and the approximation to rigid-body motion for the ions was considered (Burns, Ferrier & McMullan, 1967).

Phase III ammonium nitrate structure

The model proposed by Goodwin & Whetstone (1947) was used as the starting model. This consists of an orthorhombic structure based on the space group *Pnma*. For the nitrate ions, the N atom and one O atom for each is considered to be positioned on a mirror plane, the other O atom positions being related across the mirror plane. The plane of the nitrate ions is inclined to the *ab* plane. The ammonium ions are also considered to have their N atoms on mirror planes. The Goodwin & Whetstone (1947) model does not provide the ammonium ion orientations, but these ions were found to be disordered (about their N atom positions) between two different orientations and their structural arrangements were determined in the present work. The H atoms of the ion are located essentially tetrahedrally about their N atom, a $\bar{4}$ axis of the ion being parallel to **a**. The second equivalent orientation is related to the first by an inversion, centred at the N atom position. The two possible orientations for the ammonium ion were considered equally probable and hence given equal weight in the full-matrix least-squares refinement. The refinement converged with the final atomic parameters given in Table 1. The structure is illustrated in Fig. 1 and the interatomic distances (with estimates of corrections for thermal motion) and angles are given in Table 2.

Conclusions

The phase III structure of ammonium nitrate has been determined and shows orientational disorder of the ammonium ions. The shortest distances of the H atoms to O atoms are 2·330 (7), 2·299 (4) Å for one orientation of the ammonium ion, compared to 2·395 (4), 2·236 (5) Å for the other. These distances tend to the upper limit of ~2·38 Å for H···O bonding (Hamilton & Ibers, 1968) and would not preclude the apparent large thermal vibrational motion of the ammonium ion obtained.

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Structure of Europium(II) Tetraborate

BY KEN-ICHI MACHIDA, GIN-YA ADACHI* AND JIRO SHIOKAWA

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita-Shi, Osaka-fu 565, Japan

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Abstract

EuB_4O_7 is orthorhombic, space group $Pnm2_1$, with $Z = 2$, $a = 4·435\ (1)$, $b = 10·731\ (1)$ and $c = 4·240\ (1)$ Å. The structure was refined to $R = 0·023$ for 510 observed reflections with isotropic thermal parameters. The structure framework consists of a three-dimensional $(B_4O_7)_\infty$ network of BO_4 tetrahedra. Each Eu atom is surrounded by nine O atoms with Eu—O distances from 2·531 to 2·841 Å to form an EuO_9 polyhedron. The mean interatomic distances between Eu nearest neighbors and between Eu next-nearest neighbors are 4·338 and 6·171 Å, respectively. The thermal, magnetic and luminescence properties of EuB_4O_7 were found to be closely related to its crystal structure.

Introduction

Compounds containing divalent europium (Eu^{2+}) have been synthesized because of their magnetic and spectroscopic properties. Since the Eu^{2+} ion exists in a divalent state under a limited condition (McCarthy & White, 1970), no Eu^{2+}-containing compound has been obtained as a natural product. Recently we have prepared a series of Eu^{II} borates, $Eu_3B_2O_6$, $Eu_2B_2O_5$, EuB_2O_4 and EuB_4O_7, by the solid-state reaction of appropriate amounts of Eu_2O_3, B (metal) and H_3BO_3, and their magnetic and luminescence properties have been studied (Hata, Adachi & Shiokawa, 1977; Machida, Hata, Okuno, Adachi & Shiokawa, 1979; Machida, Adachi & Shiokawa, 1979*a*). The borates EuB_4O_7 and $Eu_2B_2O_5$ are paramagnetic, while EuB_2O_4 and $Eu_3B_2O_6$ are an antiferromagnet with $T_N = 3$K and a ferromagnet with $T_c = 7·5$ K respectively. The tetraborate, EuB_4O_7, gives a band emission based on the $4f^7$–$4f^6\,5d$ transition of the Eu^{2+} ion.

In this paper we report the structure of EuB_4O_7 and discuss its thermal, magnetic and luminescence properties on the basis of the X-ray analysis.

Experimental

Single crystals were grown by the Bridgeman technique as follows: The polycrystalline EuB_4O_7 powder was

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* To whom correspondence should be addressed.

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