

The Structure of the Low-Temperature Phase V of Ammonium Nitrate, ND_4NO_3

BY M. AHTEE AND K. J. SMOLANDER

Department of Physics, University of Helsinki, Siltavuorenpenger 20 D, SF-00170 Helsinki 17, Finland

B. W. LUCAS

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

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. $M_r = 84.058$, $Pccn$, $a = 7.9804$ (1), $b = 8.0027$ (1), $c = 9.8099$ (1) Å, $V = 626.5$ (4) Å³, $Z = 8$, neutron powder diffraction (Rietveld method), $\lambda = 1.909$ Å, $F(000) = 336$, $T = 233\text{K}$, $R = 0.086$ for 470 integrated Bragg intensities. The crystal system has orthorhombic structure rather than the tetragonal structure reported earlier by Amorós, Arrese & Canut [*Z. Kristallogr.* (1962), **117**, 92–107].

Introduction. Ammonium nitrate undergoes several successive phase transitions below its melting point at 442 K, showing at least five separate phases at atmospheric pressure. All phases and the structures reported so far are listed in Table 1 together with the still disputed lowest-temperature phase VII. On cooling a dry sample, without occluded water, a direct

transition occurs from phase II to phase IV at 328 K. Deuteration slightly shifts the transition temperatures for NH_4NO_3 given in Table 1 by the following amounts: 0 K (V→IV), 3.2 K (IV→III), 3.6 K (III→II), –2.4 K (II→IV), 2.7 K (II→I) (Hovi, Järvinen & Pyykkö, 1966; Juopperi, 1972).

We have studied the different phases of deuterated ammonium nitrate using neutron diffraction. Applying Rietveld's profile refinement method to the powder data we have already determined the detailed crystal structures of phases I, II and III (Ahte, Kurki-Suonio, Lucas & Hewat, 1979; Lucas, Ahte & Hewat, 1979; Lucas, Ahte & Hewat, 1980). In the phase I cubic structure both ionic molecules, ND_4^+ and NO_3^- , are reorientating almost freely. The phase transitions with decreasing temperature are associated with a freezing

Table 1. *The phases of ammonium nitrate*

Phase	Transition temperature (K)	Symmetry, space group	Lattice constants (Å), Z	Ordering	References
I		Cubic $Pm\bar{3}m$	$a = 4.3655$ (2) $Z = 1$	Disordered	Brown & McLaren (1962)
II	398	Tetragonal $P4_2/m$ at 355 K	$a = 5.7193$ (1) $c = 4.9326$ (1) $Z = 2$	Disordered	Ahte, Kurki-Suonio, Lucas & Hewat (1979) Shinnaka (1956) Lucas, Ahte & Hewat (1979)
III	356	Orthorhombic $Pnma$ at 318 K	$a = 7.7184$ (3) $b = 5.8447$ (1) $c = 7.1624$ (2) $Z = 4$	Disordered	Goodwin & Whetstone (1947) Lucas, Ahte & Hewat (1980)
IV	305	Orthorhombic $Pmmn$ at 300 K	$a = 5.7574$ (1) $b = 5.4394$ (1) $c = 4.9298$ (1) $Z = 2$	Ordered	Choi, Mapes & Prince (1972) Lucas <i>et al.</i> (1979)
V	257	Tetragonal $P4_2$ at 120 K	$a = 7.98$ $c = 9.78$ $Z = 8$	Disordered	Amorós <i>et al.</i> (1962)
		Orthorhombic $Pccn$ at 233 K	$a = 7.9804$ (1) $b = 8.0027$ (1) $c = 9.8099$ (1) $Z = 8$	Ordered	This work
VII	103	Unknown	?	Ordered	Volfkovich, Rubinchik & Kozhin (1954)

out of the rotational degrees of freedom. Phase II shows orientational disorder of both the ammonium and nitrate ions, whereas in phase III the NO_3^- ions are ordered while the ND_4^+ ions still have two alternative orientations. The room-temperature phase IV has a completely ordered structure of orthorhombic symmetry.

The crystal structure of the low-temperature phase V has been attempted by Amorós, Arrese & Canut (1962) with single-crystal X-ray methods. Table 1 shows that their proposed structure for phase V is inconsistent with the structures of the other phases. In the transition IV→V the symmetry would increase from orthorhombic to tetragonal and there would again be disorder as in the high-temperature phases, whereas there is no disorder in phase IV. Furthermore, when examined more closely, the interatomic bonding in their phase V gives an asymmetrical arrangement for the NO_3^- and NH_4^+ molecules.

It is not surprising, therefore, that the proposed structure for phase V has recently been the subject of inquiry, since it has been found to be inconsistent also with infrared (Oxton, Knop & Falk, 1976) and Raman (Kearley, Kettle & Oxton, 1980) data. Furthermore, when we tried to refine the structure given by Amorós *et al.*, it soon became evident from our neutron powder diffraction data that there was something wrong with the proposed structure. In the present paper we report a new ordered structure for the low-temperature phase V.

Experimental. Ammonium nitrate was deuterated by repeated recrystallization from saturated solutions with 99.6% D_2O . A previously prepared powder sample (Lucas *et al.*, 1979) of approximately 20 g was sealed in an air-tight thin-walled vanadium can of diameter 16 mm. The measurements were performed with the high-resolution neutron powder diffractometer (D1A) at the high-flux reactor of the ILL (Grenoble). D1A has a bank of ten counters with high-efficiency Mylar collimators (Hewat & Bailey, 1976) and a focusing monochromator. The sample was kept in a He gas flow cryostat at 233 K. The diffractometer was programmed to make steps of 0.05° in 2θ , effective 2θ range of 10 to 160° . The diffraction pattern was collected in about 22 h, with contributions to the different counters being added.

The background under the peaks was determined by linear interpolation from the regions in which no reflections contribute. No corrections for absorption or extinction were necessary. The scattering lengths used are: $g_{\text{N}} = 9.4$, $g_{\text{O}} = 5.8$ and $g_{\text{D}} = 6.67$ fm (Bacon, 1972).

It proved impossible to refine the data on the model with space group $P4_2$ suggested by Amorós *et al.* (1962). Therefore further data were collected at lower temperatures down to 5 K with wavelengths varying from 2.98 to 1.21 Å. The data collected at 5 K with the longest wavelength showed splitting in the 400 reflec-

tion, indicating an orthorhombic structure. When powder indexing techniques (see Shirley, 1980) were used to index these data, the space group $Pccn$ proved the most appropriate. Pawley (1981) has written a program for refining cell constants without knowing the structure. When this program was applied to the data collected with a neutron wavelength 2.98 Å at 5 K the cell constants were found to be 7.88, 7.91 and 9.80 Å.

The diffraction patterns were analysed by the Rietveld method (Rietveld, 1969) with modifications for anisotropic thermal motion (Hewat, 1973). In the refinement, two sets of parameters were refined, those describing the crystal structure and those describing the characteristics of the diffractometer. The latter group consisted of five parameters: the counter zero point, the three half-width parameters which describe the variation with 2θ of the angular width of the Gaussian curve, and a parameter for correction of asymmetry of the reflection curves caused by the fact that the sample has a finite height and cannot be regarded simply as a point on the axis of the diffractometer. The structural parameters refined were the scale factor, the lattice constants, the fractional coordinates and the thermal parameters for each atom. The program calculates four R factors: the R factor for the profile intensities R_p , a related weighted profile R factor R_{wp} , the R factor for integrated Bragg intensities R_I and the expected R factor R_E , which would be expected if the differences between the observed and calculated profiles were purely statistical in origin. $R_p = 10.90$, $R_{wp} = 11.17$, $R_I = 8.56$, $R_E = 6.99\%$.

Discussion. Critical assessment of the previously proposed structure for phase V

Amorós *et al.* (1962) determined the crystal structure for phase V NH_4NO_3 at 120 K on the basis of single-crystal X-ray diffraction data. They observed the following systematic absences: $h+k$ odd for $hk0$, l odd for $0kl$ and h odd for hhl . The systematic absences gave the space group $P4_2/ncm$ (No. 138), which, however, did not give any sensible arrangement for the NO_3^- and NH_4^+ groups. Amorós *et al.* (1962) concluded, therefore, that the symmetry was $P4_2$ (No. 77) with eight formula units in the unit cell. That the observed extinctions $h+k$ odd for $hk0$ and l odd for $0kl$ are not forbidden in this space group was supposed to be due to the particular positions of the atoms.

Amorós *et al.* (1962) based their structure determination on the Fourier projection onto the (001) and ($\bar{1}10$) planes. The agreement was rather poor; from the observed and calculated structure factors the discrepancy factor was $R(hhl) = 25\%$. When a 25% disorder of the NO_3^- ions was introduced, the R factor dropped to 18% for the observed intensities. The (001) projection of this structure is illustrated in Fig. 1. This structure, with the positional parameters given by Amorós *et al.* (1962) (corrected for misprints), was used as a starting model for the profile refinement.

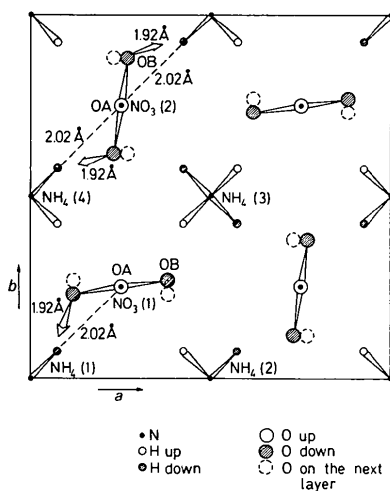


Fig. 1. The structure of phase V NH_4NO_3 proposed by Amorós *et al.* (1962) as viewed along the c axis. The bondings of the two non-equivalent NO_3 molecules with NH_4 molecules are marked with arrows and dashed lines; the bond lengths are also given. The asymmetry of the bonding of the $\text{NO}_3(1)$ group is clearly seen.

However, it proved impossible to obtain agreement between the observed and calculated intensities. The structure was then critically re-examined and the following points were noted.

In ammonium nitrate the ND_4^+ and NO_3^- molecules are usually distorted only to a minor extent in successive phases. This means that both ionic molecules can be represented by rigid units in which the shape and bond lengths remain almost the same through phase transitions. In the ND_4^+ molecule, N is at the centre of four D atoms arranged at the corners of a regular tetrahedron. The NO_3^- molecule is represented by a planar equilateral triangle with N at the centre and O atoms at the corners. The bonding in ND_4NO_3 is principally determined by the hydrogen bonds between the O atom and the D atoms.

It is characteristic of the phase transitions in molecular crystals that with decreasing temperature the rotational degrees of freedom of the molecules gradually freeze out so that in the phase stable at the lowest temperatures the molecules do not rotate, and are not disordered. While the rotations of the molecules diminish with decreasing temperature, the bonds between the molecules strengthen. At each temperature T the most stable structure is that for which the Gibbs free energy $G = U - TS$ assumes its lowest value. The rotations of the molecules affect principally the entropy term TS , whereas the bonds contribute mainly to the internal energy U . This means that the structure which allows the molecules to rotate as freely as possible is stable at higher temperatures, whereas a structure which has stronger bonds between the molecules is preferred at lower temperatures. It is to be expected, therefore, that the low-temperature phases possess a

lower symmetry than the high-temperature phases. Accordingly, one does not expect the symmetry of phase V to be tetragonal but rather orthorhombic or lower (see Table 1). It is also unlikely that the low-temperature phase V should contain 25% disorder of the NO_3^- molecules, while there is no disorder in phase IV (Choi, Mapes & Prince, 1972; Lucas *et al.*, 1979). Diffuse-scattering studies reveal no evidence of disorder in phase V.

The packing of the NH_4^+ and NO_3^- molecules in the structure proposed by Amorós *et al.* (1962) is close to body centred (see Fig. 1). Both the molecules are regular and fixed at their special positions, although the space group would allow rotation and different N—H bond lengths for the NH_4^+ molecules and a small distortion and displacement from their special positions for the NO_3^- molecules. An unusual feature in the proposed tetragonal structure is also that every fourth NH_4^+ molecule on the (001) planes is rotated 90° around the z axis with respect to the others. As a result of this arrangement, the NO_3^- molecules are bonded with the NH_4^+ molecules in such a way that alternate NO_3^- molecules have an asymmetric bonding, *i.e.* bonded only on one side, whereas every other NO_3^- molecule has a symmetric bonding, *i.e.* bonded on both sides.

In the room-temperature structure IV (Choi *et al.*, 1972), the nitrate groups within a given column parallel to the z axis have the same orientation, whereas the orientations in adjacent columns are opposite. In the structure proposed by Amorós *et al.* (1962) for phase V all the NO_3^- molecules have the same orientation with regard to the z axis. In the projection along $[\bar{1}10]$ Amorós *et al.* obtained ghost peaks which were explained by disorder. These ghost peaks, which indicate some systematic difference in $F_k(\text{obs}) - F_k(\text{calc})$, indicate that in reality the NO_3^- molecules are not all similarly oriented.

Further evidence for rejection of the tetragonal structure for phase V proposed by Amorós *et al.* (1962) has been put forward by Oxtan *et al.* (1976) who studied the infrared spectra from the isotopically dilute NH_3D^+ ion. They concluded that the observed spectrum can be explained so that in the crystal there are either two non-equivalent sets of NH_4^+ ions of molecular symmetry C_{2v} (point symmetry mm) or a single set of NH_4^+ ions of molecular symmetry C_1 (point symmetry 1). These observations were re-iterated by Kearley, Kettle & Oxtan (1980), who studied the Raman spectrum of phase V. However, Jayasooriya, Kearley, Kettle & Lauter (1981) did not find any inconsistency between the Amorós structure and their inelastic neutron scattering results and Raman and infrared vibrational spectra data.

Possible structure alternatives for phase V

In spite of the foregoing criticism, the structure put forward by Amorós *et al.* (1962) can be taken as the

starting point for a more correct structure determination. It is evident that the dimensions of the unit cell and the packing of the molecules are more or less appropriate. In particular, the Fourier projection along [001] seems to be correct, whereas one is inclined to reject the projection along $[\bar{1}10]$. To restrict the number of possible structures which fulfil the above mentioned conditions, the following additional constraints were assumed: (i) the structure does not contain disorder, and (ii) the bonds between the molecules should be as symmetrical as possible.

It turns out that there is no tetragonal structure which satisfies all of the above mentioned conditions. Starting from splitting of the 400 reflection found at 5 K, we extended the possible structures to include also orthorhombic symmetry, and were left with three candidate space groups *Pccn* (No. 56), *Pnmm* (No. 48) and *I222* (No. 23). The experimental diffraction pattern shows clearly more reflections than are allowed by the body-centred symmetry so that the last space group is out of the question. Altogether, the systematic absences of reflections in the observed pattern give preference to space group *Pccn*. All three space groups give the constraint $h+k=2n$ for $hk0$, as was found by Amorós *et al.* (1962) from their single-crystal data. Both space groups *I222* and *Pnmm* require in addition that $k+l=2n$ for $0kl$ and $l+h=2n$ for $h0l$, whereas space group *Pccn* has the condition $l=2n$ for $0kl$, in accordance with Amorós *et al.*, plus an extra condition $l=2n$ also for $h0l$.

The structure with space group *Pccn*, which has proved to be the correct one for phase V at 233 K, is illustrated in Fig. 2. The structure with space group *Pnmm* differs from this in that successive NO_3^- molecules along the z axis are oppositely directed with respect to the z axis. On the other hand, space group *I222* implies that all ND_4^+ molecules are oriented in the same sense, while adjacent NO_3^- molecules along the z direction are opposed. In fact, in all the three structures which were considered in this work, the ND_4^+ molecules in the same (001) plane are oriented in the same way except for small distortions allowed by the space groups. Contrary to the tetragonal structure proposed by Amorós *et al.* (1962), there is no ferroelectric polarization in any of the three structures under consideration, since as many NO_3^- triangles point in the direction of the positive z axis as point along the negative z axis. Each O atom in the top corner of the NO_3^- triangle is bonded linearly with the two D atoms, while the O atoms at the ends of the base of the NO_3^- triangle are each bonded only with one D atom. In this way, all the D atoms of the ND_4^+ tetrahedra are each bonded with one O atom, which is more reasonable than the Amorós *et al.* structure.

Pccn structure for phase V ND_4NO_3

The structure with space group *Pccn* was refined with the aid of the Rietveld method. In the starting model the

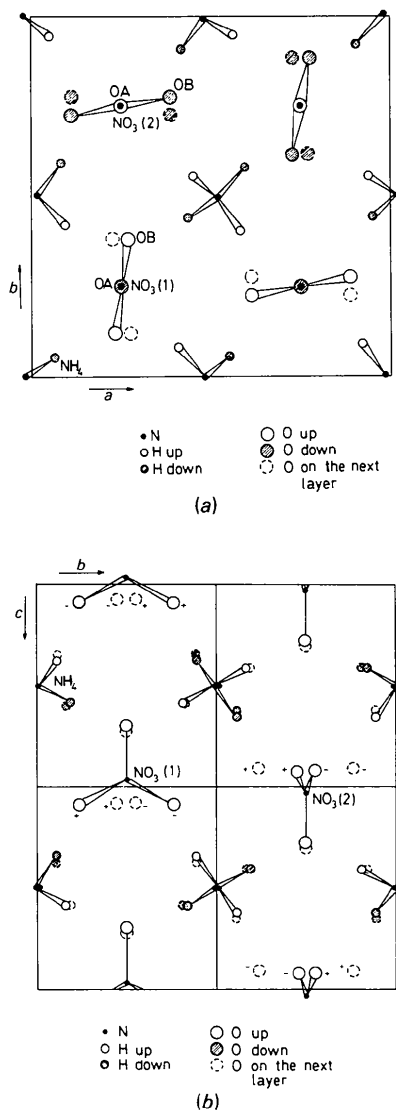


Fig. 2. The correct structure of phase V NH_4NO_3 , with space group *Pccn* (a) as viewed along the c axis, (b) as viewed along the a axis. The planes of the NO_3^- triangles are inclined with respect to the plane of projection. The levels of the O atoms are qualitatively depicted by + and - signs to indicate their relative displacements along the a direction, with respect to the N atom.

NO_3^- triangles and the ND_4^+ tetrahedra were assumed to be regular and the bond lengths were those found by Amorós *et al.* (1962), *i.e.* $\text{N}-\text{D} = 1.04$ and $\text{N}-\text{O} = 1.21$ Å. The bases of the NO_3^- triangles deviated arbitrarily from the symmetry directions of the x and y axes; the initial angle of deviation being chosen to be 10° . The results of the refinement are listed in Table 2, where the atomic positional parameters and the isotropic temperature factors are given. When the anisotropic temperature factors were included in the refinement the R factor for integrated intensities dropped from 0.086 to 0.050 which is not significant

Table 2. Atomic positional parameters of ND_4NO_3 phase V at 233 K as determined by neutron powder profile refinement with wavelength 1.909 Å

Standard deviations are in parentheses and the parameter without a deviation was fixed to define the origin.

	x	y	z	B(Å ²)
N(1)	$\frac{1}{4}$	$\frac{1}{4}$	-0.0186 (5)	0.5 (1)
OA(1)	$\frac{1}{4}$	$\frac{1}{4}$	-0.1440 (9)	1.1 (2)
OB(1)	0.2701 (7)	0.3825 (6)	0.0432 (6)	1.9 (1)
N(2)	$\frac{1}{4}$	$\frac{3}{4}$	0.0173 (6)	1.1 (1)
OA(2)	$\frac{1}{4}$	$\frac{3}{4}$	0.1399 (10)	2.0 (2)
OB(2)	0.3846 (6)	0.7774 (8)	-0.0405 (7)	2.5 (1)
N(3)	-0.0177 (3)	0.0023 (9)	0.2500	1.6 (1)
D(1)	0.0634 (10)	0.0535 (11)	0.1844 (9)	3.4 (2)
D(2)	0.0443 (9)	-0.0603 (11)	0.3246 (10)	4.9 (2)
D(3)	-0.0917 (9)	-0.0772 (9)	0.2020 (7)	2.2 (1)
D(4)	-0.0841 (11)	0.1004 (12)	0.2890 (7)	5.1 (2)

Table 3. Interatomic distances (Å) and angles for phase V ND_4NO_3 at 233 K

$\text{NO}_3(1)$		$\text{NO}_3(2)$	
N(1)-OA(1)	1.230 (10)	N(2)-OA(2)	1.203 (11)
N(1)-OB(1)	1.232 (6)	N(2)-OB(2)	1.234 (6)
OB(1)-N(1)-OB(1)	121.1 (0.5)	OB(2)-N(2)-OB(2)	125.3 (0.6)
OB(1)-N(1)-OA(1)	119.5 (0.3)	OB(2)-N(2)-OA(2)	117.3 (0.4)
ND_4			
N(3)-D(1)	1.000 (9)	D(1)-N(3)-D(2)	110.5 (0.7)
N(3)-D(2)	1.016 (10)	D(1)-N(3)-D(3)	110.1 (0.7)
N(3)-D(3)	0.986 (9)	D(1)-N(3)-D(4)	105.2 (0.9)
N(3)-D(4)	1.022 (11)	D(2)-N(3)-D(3)	108.5 (0.9)
		D(2)-N(3)-D(4)	111.2 (0.8)
		D(3)-N(3)-D(4)	111.3 (0.7)
Hydrogen bonds			
Bond type	O...D	O...N	N-D...O
N(3)-D(1)...OB(1)	1.987 (10)	2.978 (6)	170.7 (3.1)
N(3)-D(2)...OB(2)	1.939 (11)	2.931 (8)	164.7 (2.0)
N(3)-D(3)...OA(1)	1.958 (8)	2.932 (6)	147.4 (2.7)
N(3)-D(4)...OA(2)	1.916 (10)	2.921 (6)	167.1 (1.4)

when the increase in the number of parameters is taken into account.*

In phase V, all the ND_4^+ molecules are symmetrically equivalent whereas the four D atoms of each molecule are all non-equivalent. This means that the ND_4^+ molecules are slightly distorted from the ideal tetrahedral shape, as can be seen from Table 3. The NO_3^- molecules which lie in the same ($hh0$) plane are equivalent, whereas the NO_3^- molecules which lie on adjacent planes are non-equivalent. There are thus two types of NO_3^- molecules, which are distorted in slightly different ways. The structure can be called

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38379 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

'pseudotetragonal' as the lattice constants a and b are almost equal, and in the projection along the z direction the packing of the molecules looks tetragonal except that in adjacent ($0k0$) planes the NO_3^- molecules point in opposite directions along the z axis.

The interatomic distances and angles given in Table 3 correspond closely with the bond lengths and angles for similar compounds given in the literature (*International Tables for X-ray Crystallography*, 1968). The average N-D bond lengths and angles are 1.006 (10) Å and $109.5 (0.8)^\circ$, respectively. The average N-O bond lengths for the two non-equivalent NO_3^- triangles are 1.231 (8) and 1.224 (8) Å.

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