

The Structure of ND_4NO_3 Phase V by Neutron Powder Diffraction

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Abstract

The crystal structure of ND_4NO_3 phase V was determined by the Rietveld refinement method for a series of neutron powder diffraction data measured at temperatures ranging from 10 to 250 K using a 90% deuterated sample. The unit cell was found to be orthorhombic, *Pccn*, with (at 78 K) $a = 7.8850(2)$, $b = 7.9202(2)$, $c = 9.7953(2)$ Å, and $Z = 8$. The final R indices were $R(\text{integ.}) = 0.036$, $R(\text{prof.}) = 0.024$ for the 78 K structure. The cations and anions are packed with a distorted CsCl-type arrangement and are linked together by two sets of three-dimensional hydrogen-bond chains. At ambient pressure, there are no other polymorphic phases (*i.e.* phase VII) down to 10 K. The thermal expansions of phases V, IV, III, and II were also measured accurately in this study (residual standard deviation less than 0.05 \AA^3).

Introduction

Ammonium nitrate, NH_4NO_3 , has been studied extensively by X-ray diffraction (Holden & Dickinson, 1975, and references cited therein), differential thermal analysis (Konkoly-Thege, 1977, and references cited therein), calorimetry (Nagatani, Seiyama, Sakiyama, Suga & Seki, 1967, and references cited therein), dielectric measurements (Yamashita & Asai, 1963), optical microscopy (Seiyama & Yamazoe, 1968), NMR (Riggin, Knispel & Pintar, 1972, and references cited therein), Raman (Tang & Torrie, 1978, and references cited therein), infrared (Theoret & Sandorfy, 1964, and references cited therein), and neutron scattering (Jayasooriya, Kearley, Kettle & Lauter, 1981, and references cited therein) and diffraction (Choi & Prask, 1982, and references cited therein). Ammonium nitrate in the solid state is an ionic crystal consisting of tetrahedral NH_4^+ cations and planar NO_3^- anions. These ions are coupled not only by electrostatic forces but also by hydrogen bonds in the crystal and, at ambient pressure, form five stable polymorphic

phases, I, II, III, IV, and V in order of decreasing temperature, with transition points 398, 357, 305, and 255 K, respectively (Hendricks, Posnjak & Kracek, 1932). Phase VI is a high-temperature, high-pressure phase (Bridgman, 1915). The crystal structures of phases I through IV have been determined completely by neutron diffraction studies (based on the numerous previous X-ray studies): cubic *Pm3m* for I (Ahtee, Kurki-Suonio, Lucas & Hewat, 1979); tetragonal *P4/mbm* for II (Choi, Prask & Prince, 1980; and *P42₁m* symmetry by Lucas, Ahtee & Hewat, 1979); orthorhombic *Pnma* for III (Choi & Prask, 1982); and orthorhombic *Pnma* for IV (Choi, Mapes & Prince, 1972). Among them the three high-temperature phases are thermally disordered, each with a different degree of molecular rotation. The ions in phase IV have an ordered structure, but the thermal motions of the NH_4 group are still very large. The structure of phase V, which was proposed to be tetragonal *P4₂* (Amorós, Arrese & Canut, 1962), has been subject to question in recent years, being inconsistent with infrared (Oxton, Knop & Falk, 1976), Raman (Kearley, Kettle & Oxton, 1980), and neutron powder diffraction studies (Lucas, referenced by Jayasooriya *et al.*, 1981). There are several conflicting reports regarding the existence of a seventh phase below 156 K from studies of Raman spectra, specific heat, and NMR, as discussed by Abolin'sh, Karpov & Shultin (1977) and by Tang & Torrie (1978). This study was aimed at solving the complete structure of phase V and other phases, if existent.

The dilation of ammonium nitrate exhibits a sharp change at each transition temperature (Hendricks *et al.*, 1932; Griffith, 1963). The volume change at the IV–III transition point is particularly severe. It is known that the IV–III transition is the primary cause for dimensional instability, *i.e.* caking, breakage of prills, and swelling during long-term storage (Sjolin, 1972, and references cited therein). In the present work the linear and volumetric thermal-expansion coefficients were measured accurately over the temperature range 10 to 393 K by analysis of lattice parameters derived from the Rietveld (1969) refinement technique.

Experimental

The sample used in this study was deuterated by six cycles of repeated recrystallization from solutions with 99.6% D₂O at about 376 K. The concentration of D atoms at the H sites was determined by the least-squares refinement of the occupancy factor, using room-temperature powder data for the phase IV structure (the structural parameters are well known), and was found to be 0.903 ± 0.003 . The sample was ground to a fine powder and placed in a cylindrical vanadium container, 10 mm in diameter. A closed-cycle helium-gas cryostat equipped with a temperature controller was used for the low-temperature measurements. The neutron diffraction measurements were made on the high-resolution five-detector powder diffractometer at the NBS Reactor, using 1.542 Å wavelength neutrons from a Cu (220) monochromator and collimation of 10, 20, and 10', before and after the monochromator and before the detectors, respectively. The powder patterns were obtained within a 120° scattering angle with 0.05°-step increments at the temperatures 293 (room temperature), 10, 78, and from 130 to 270 K in 20 K steps. Among them the measurements at 270 and 293 K were for the phase IV structure. Subsequently, the sample was transferred from the cryostat to a furnace for the high-temperature measurements, and a series of powder patterns was measured at 308, 333, and 353 K for phase III and at 363 and 393 K for the phase II structures.

Analysis of structure

The Rietveld refinement method was used to determine the crystal structure of phase V and also to measure the unit-cell dimensions as a function of temperature. A total of 458 unique reflections (2101 data points) were refined at each temperature. The least-squares program was that of Rietveld (1969) with modifications by Hewat (1973) and Prince (1980). An initial attempt was made to refine the structure of phase V proposed by Amorós *et al.* (1962), and it was unsuccessful. A close examination of the observed and calculated profile showed small but clear disagreements in many peak positions, which indicated an error in the crystal system. In fact, the proposed structure and the systematic absences reported in their single-crystal study are consistent with a different space group, orthorhombic *Pccn*. They found that the unit cell of phase V is a supercell of phase IV with the transformation matrix: $110/\bar{1}10/002$. Since the [110] direction is exactly identical to the $[\bar{1}10]$ direction in the phase IV structure (*Pmnm* space group), the crystal obtained from phase IV by the above transformation is expected to be twinned (if it is not a tetragonal cell) with the *a*- and *b*-axis directions interchanged ran-

domly. If the transformed unit cell is orthorhombic and the axial ratio *a/b* is close to unity (or approaches a rational number) to satisfy the twinning condition, its diffraction pattern would show tetragonal symmetry. A new model structure was constructed by modifying the Amorós structure to fit the new space-group symmetry. The correctness of the new model was immediately confirmed by the rapidly converging *R* values. The parameters in the refinement were a scale factor, 10 background parameters, three unit-cell dimensions, and the structural parameters. The three half-width parameters and the occupancy factor of D atoms were determined by the profile refinement of the phase IV structure at the beginning of the study, and the same values were used for all other profiles. Absorption corrections were made by applying an equivalent Debye-Waller factor [(Hewat, 1979, $B = -0.3 \text{ \AA}^2$ which is equivalent to $\mu r = 0.53$ obtained by a transmission measurement)] to the calculated structure factors. The coherent scattering lengths used were $b(\text{N}) = 9.40$, $b(\text{O}) = 5.80$, $b(\text{D}) = 6.67$, $b(\text{H}) = -3.74$ fm. The refinements were carried out with isotropic temperature factors assigned to all atoms for the structures from 130 to 250 K. The structures at 78 and 10 K were analyzed more rigorously by assigning rigid-body thermal motions to all atoms in the ammonium group. To reduce the number of least-squares parameters, the rigid-body motions were

Table 1. *The final least-squares parameters for ND₄NO₃ (phase V) at 78 K*

The ammonium group was constrained to centrosymmetric rigid-body motions. The hydrogen positions which were corrected for the librations are given underneath each raw value.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
N(1)	$\frac{1}{4}$	$\frac{1}{4}$	0.0154 (4)	0.76 (9)
N(2)	$\frac{1}{4}$	$\frac{1}{4}$	0.0155 (4)	0.99 (9)
N(3)	-0.0167 (3)	-0.0021 (9)	0.2511 (8)	1.33
O(1)	$\frac{1}{4}$	$\frac{1}{4}$	0.1444 (8)	1.6 (1)
O(2)	0.1135 (4)	0.2723 (6)	-0.0410 (5)	1.6 (1)
O(3)	$\frac{1}{4}$	$\frac{1}{4}$	0.1446 (7)	1.0 (1)
O(4)	0.7679 (5)	0.1126 (4)	-0.0480 (4)	0.8 (1)
D(1)	0.0622 (9)	-0.0527 (9)	0.1756 (7)	2.2*
	0.0638	-0.0529	0.1745	
D(2)	-0.1005 (9)	0.0836 (9)	0.2023 (7)	2.6*
	-0.1028	0.0845	0.2009	
D(3)	-0.0821 (9)	-0.0961 (9)	0.2904 (7)	2.4*
	-0.0840	-0.0977	0.2911	
D(4)	0.0527 (9)	0.0575 (9)	0.3207 (7)	2.7*
	0.0553	0.0584	0.3222	

Rigid-body motions (T and L) of the constrained ND₄⁺ ion, based on an orthonormal system with the origin at the N(3) atom and the coordinate axes parallel to those of the crystal

<i>i, j</i>	<i>T</i> _{<i>i, j</i>} (Å ²)	<i>L</i> _{<i>i, j</i>} (deg ²)	<i>i, j</i>	<i>T</i> _{<i>i, j</i>} (Å ²)	<i>L</i> _{<i>i, j</i>} (deg ²)
11	0.0144 (12)	0.006 (3)	12	-0.0041 (22)	-0.007 (3)
22	0.0227 (12)	0.034 (3)	13	0.0002 (17)	-0.009 (3)
33	0.0134 (9)	0.020 (2)	23	0.0037 (7)	0.003 (1)

* Equivalent isotropic temperature factors.

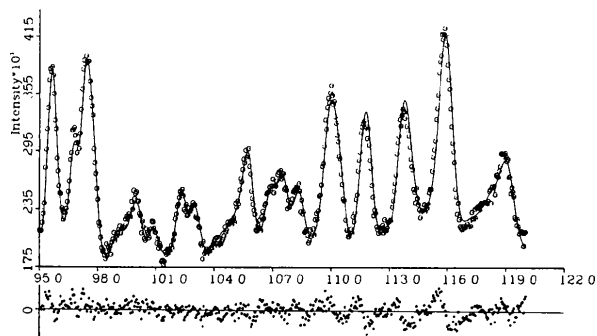
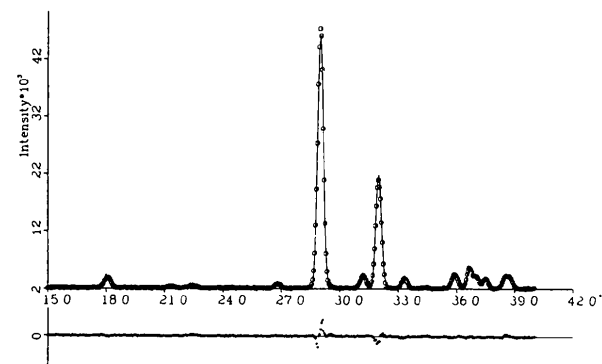


Fig. 1 (cont.)

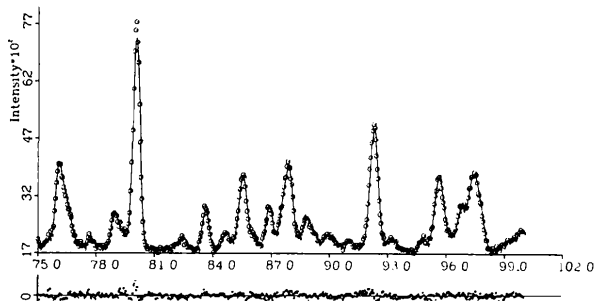
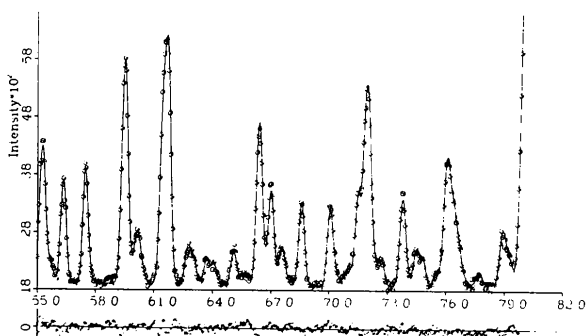
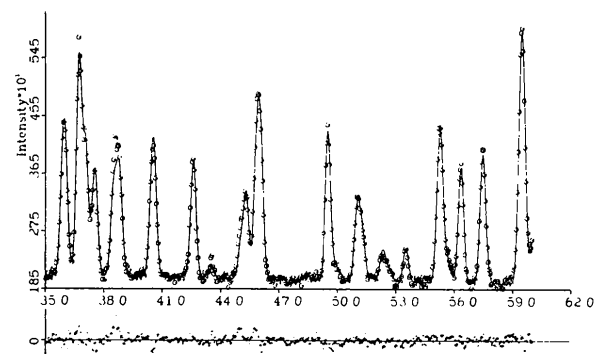


Fig. 1. The observed and calculated profiles of ammonium nitrate phase V at 78 K, with circles for the observed and lines for the calculated profile. Residual profiles ($Y_o - Y_c$) are given directly underneath each profile with the same scale.

constrained to a centrosymmetric type with translational and librational motion only. The final least-squares parameters* obtained for the 78 K structure are given in Table 1, and the observed and calculated profiles are shown in Fig. 1.

Description of structure of phase V

The structural parameters presented in the discussion are based on the 78 K structure unless explicitly specified otherwise. The molecular packing of the phase V structure is similar to that of phase IV (and II), except for the marked differences in the orientations of the nitrate ions. The arrangement of ions is essentially the same as that proposed by Amorós *et al.* (1962) except for the existence of the inversion-symmetric relationship between the same type of ions. Both ammonium and nitrate ions are arranged to form slightly distorted pseudo-tetragonal lattices, with CsCl-type coordination. That is, each nitrate anion is surrounded by eight ammonium cations and *vice versa*. The nitrate anions are in narrow layers centered at $z = 0$ and 0.5 , and occupy the two twofold symmetry sites of the *Pccn* space group, with the N(1)-nitrate at site *c* and N(2)-nitrate at site *d*. The ammonium ions are located approximately at the body-center of the nitrate lattice and are linked tetrahedrally to four of the eight nearest nitrate ions by four strong hydrogen bonds, one for each hydrogen. There are two sets of three-dimensional hydrogen-bond chains which are related mutually by *c*-glide mirror symmetry. The two hydrogen-bond chains are interpenetrating to each other and make a tight van der Waals contact with very short $\text{N}\cdots\text{O}$ and $\text{O}\cdots\text{O}$ intermolecular distances. Fig.

* Lists of profile intensity data and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38407 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

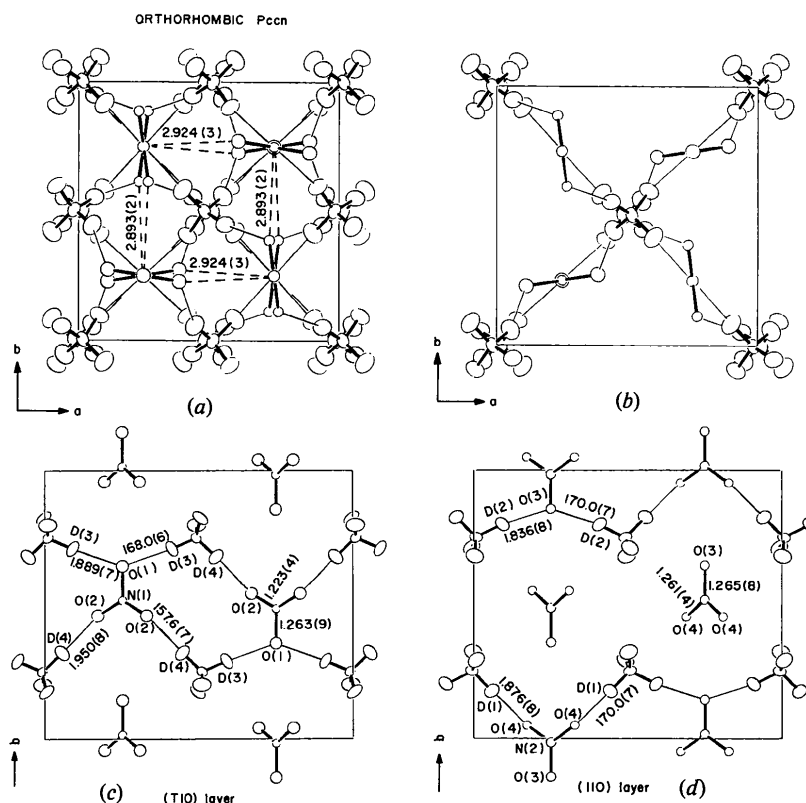


Fig. 2. ORTEP drawings of the phase V structure at 78 K. The thin lines indicate hydrogen bonds. There are two independent sets of three-dimensional hydrogen-bond chains which are related mutually by c -glide mirror symmetry. One of the two chains runs along $(\bar{1}10)$ and (110) of the unit cell, as shown in (b). The details of the hydrogen bonds are shown in (c) and (d).

Table 2. Bond lengths (\AA) and angles ($^\circ$) of phase V at 78 K

The parameters of the hydrogen bonds are also included.

N(1)—O(1)	1.263 (9)	O(1)—N(1)—O(2)	116.9 (3)
N(1)—O(2)	1.223 (4)	O(2)—N(1)—O(2)'	126.3 (5)
N(2)—O(3)	1.265 (8)	O(3)—N(2)—O(4)	119.5 (2)
N(2)—O(4)	1.261 (4)	O(4)—N(2)—O(4)'	120.9 (5)
N(3)—D(1)	1.062 (9)	D(1)—N(3)—D(2)	107.1 (9)
N(3)—D(2)	1.083 (9)	D(1)—N(3)—D(3)	107.8 (8)
N(3)—D(3)	1.004 (8)	D(1)—N(3)—D(4)	109.2 (4)
N(3)—D(4)	1.019 (8)	D(2)—N(3)—D(3)	108.9 (5)
		D(2)—N(3)—D(4)	111.2 (9)
		D(3)—N(3)—D(4)	112.4 (10)

Hydrogen bonds and intermolecular distances between NH_4^+ and NO_3^-

Bonding type	N...O (\AA)	D...O (\AA)	N—D...O ($^\circ$)
N(3)—D(3)...O(1)	2.879 (6)	1.889 (7)	168.0 (6)
N(3)—D(4)...O(2)	2.918 (8)	1.950 (8)	157.6 (7)
N(3)—D(2)...O(3)	2.908 (7)	1.836 (8)	170.0 (7)
N(3)—D(1)...O(4)	2.928 (7)	1.876 (8)	170.0 (7)
N(3)...O(1)	3.082 (6)		
N(3)...O(2)	3.066 (8)		
N(3)...O(3)	3.053 (6)		
N(3)...O(4)	2.936 (7)		

Intermolecular distances (\AA) between NO_3^- groups

N(1)...O(4)	2.893 (3)	O(2)...O(4)	3.083 (6)
N(2)...O(2)	2.924 (3)	O(2)...O(4)	3.005 (6)
O(1)...O(4)	3.026 (4)	O(3)...O(4)	3.143 (6)
O(1)...O(2)	3.269 (8)	O(2)...O(4)	3.205 (7)

2 is a set of ORTEP (Johnson, 1965) drawings that illustrate the hydrogen-bonded structure. The bond lengths and angles and the short intermolecular distances are given in Table 2.

The N(1)-nitrate ion is hydrogen-bonded to four adjacent ammonium ions by two $\text{O}(1)\cdots\text{D}(3) = 1.889 \text{ \AA}$ and two $\text{O}(2)\cdots\text{D}(4) = 1.950 \text{ \AA}$ bonds, as shown in Fig. 2(c). The $\text{O}(1)\cdots\text{D}(3)-\text{N}(3)$ and $\text{O}(2)\cdots\text{D}(4)-\text{N}(3)$ bond angles are 168.0 and 157.6° , respectively. The structure of the N(1) group is distorted considerably from the ideal threefold-symmetric structure with an elongated bond, $\text{N}(1)-\text{O}(1) = 1.263 \text{ \AA}$, and an enlarged bond angle, $\text{O}(2)-\text{N}(1)-\text{O}(2') = 126^\circ$. This distortion is attributed mainly to the large elongation of the $\text{N}(1)-\text{O}(1)$ bond which is caused by the distinctly stronger hydrogen bonding of one O(1) atom in the nitrate. The N(2) nitrate ion is also hydrogen-bonded to four ammonium ions (Fig. 2d) in a similar way with two $\text{O}(3)\cdots\text{D}(2) = 1.836 \text{ \AA}$ and two $\text{O}(4)\cdots\text{D}(1) = 1.876 \text{ \AA}$. Both of the $\text{O}\cdots\text{D}-\text{N}$ bond angles are 170° . All three N—O bonds of the N(2)-nitrate are elongated almost equally ($1.263 \pm 0.002 \text{ \AA}$), and, hence, the nitrates maintain the pseudo-trigonal symmetry of the free state. The N(1)-nitrates are oriented with their plane normals approximately

parallel to the b axis (deviation of 9.3° in angle), and the N(2)-nitrate normals are almost parallel to the a axis (7.4° deviation). All nitrate ions are located in a layer perpendicular to the c -axis direction and make tight intermolecular contact along the a -axis and the b -axis directions. The short $\text{N}\cdots\text{O}$ contacts are shown in Fig. 2(a). In Table 2, the $\text{O}\cdots\text{O}$ contacts with distances less than 3.2 \AA only occur between the nitrates in the same layer. This two-dimensional contact between nitrate ions is correlated to the anisotropic thermal expansion (smaller c -axis expansion) as discussed in a later section.

The structure of phase V projected on the (001) plane possesses a pseudo fourfold symmetry and also a pseudo-tetragonal lattice, as shown in Fig. 2(a). This explains why phase V was misassigned as tetragonal (Amorós *et al.*, 1962). The b axis is very slightly longer than the a axis, 0.035 \AA at 78 K. This difference arises from the following two components: first, the $\text{O}(4)\cdots\text{O}(4)$ distance of the N(2)-nitrate is $0.014 (6) \text{ \AA}$ longer than the corresponding distance in the N(1)-nitrate; and, second, the orientational staggering of nitrate ions about each twofold axis is about 4° larger for the N(1)-nitrate.

The ammonium ion is slightly distorted from the ideal tetrahedral structure with the D–N–D angles ranging from 107 to 112° . Each ammonium ion is surrounded by eight O atoms with $\text{O}\cdots\text{N}$ distances within 3.1 \AA . Among them, four are involved in hydrogen bonds. There is no evidence of orientational disorder in phase V.

Investigation of the existence of phase VII

There are many studies on the possible existence of a phase VII in ammonium nitrate. However, the evidence for phase VII was not always in agreement and often contradictory. Nagatani *et al.* (1967) proposed the existence of phase VII near 156 K based on the slight kink observed in their heat-capacity curve, although the same study conducted earlier by Stephenson, Bentz & Stevenson (1955) showed no such singularity in the curve. In a Raman-scattering study on NH_4NO_3 (and ND_4NO_3), Iqbal (1976) observed a sudden change in the slope of a linewidth *vs* temperature curve in the vicinity of 100 K and interpreted it as a singular jump in the ionic librational amplitudes occurring at the V–VII phase transition. However, the evidence from the Raman linewidth was directly challenged by a similar Raman study conducted later by Tang & Torrie (1978). To investigate the possible existence of the new phase, we have studied the low-temperature structure at $10, 78$ and 130 to 250 K in 20 K steps, as described in the previous sections. The structures at all temperatures were determined successfully with the same space group, $Pccn$, as demonstrated by the R indices in Table 3, with essentially identical crystal structures. There were no unusual sudden changes in the temperature dependence of the parameters, *i.e.* lattice parameters, atomic thermal motions, and positional coordinates. It is concluded that there is no other phase besides phase V in the temperature range 255 to 10 K .

Table 3. ND_4NO_3 unit-cell dimensions obtained by the profile refinements of neutron powder patterns

R_i , R_p , and R_w refer to the residual indices of the integrated intensity, profile intensity, and weighted profile intensity, respectively, and R_e to expected residual (Hewat, 1973).

Temperature (K)	a (Å)	b (Å)	c (Å)	V (Å ³)	R_i (%)	R_p (%)	R_w (%)	R_e (%)
Phase V, $Z = 8$								
10	7.8767 (2)	7.9106 (2)	9.7894 (2)	609.97 (2)	4.07	3.48	4.58	2.21
78	7.8850 (2)	7.9202 (2)	9.7953 (2)	611.72 (1)	3.63	2.40	3.06	1.88
130	7.9039 (2)	7.9372 (2)	9.7990 (3)	614.74 (2)	5.63	3.57	4.63	3.14
150	7.9144 (2)	7.9465 (2)	9.8004 (2)	616.37 (2)	4.69	2.97	3.83	2.69
170	7.9249 (2)	7.9558 (2)	9.8002 (2)	617.89 (2)	5.79	3.07	3.92	2.40
190	7.9370 (3)	7.9664 (2)	9.7986 (3)	619.56 (2)	5.44	2.81	3.61	2.70
210	7.9459 (2)	7.9743 (2)	9.7960 (3)	620.71 (2)	6.26	3.08	4.03	2.22
230	7.9640 (3)	7.9879 (3)	9.7928 (2)	622.98 (2)	6.00	2.86	3.67	2.50
250	7.9745 (3)	7.9960 (3)	9.7899 (3)	624.25 (2)	6.54	3.19	4.04	3.08
Phase IV, $Z = 2$								
270	5.7542 (1)	5.3858 (1)	4.9174 (1)	152.40 (1)	5.51	2.94	3.73	2.79
293	5.7503 (1)	5.4287 (1)	4.9239 (1)	153.71 (1)	4.08	2.62	3.35	2.45
Phase III, $Z = 4$								
308	7.6971 (3)	5.8327 (3)	7.1479 (3)	320.90 (2)	7.37	3.00	3.75	2.99
333	7.7203 (3)	5.8398 (3)	7.1524 (4)	322.47 (2)	8.95	3.25	4.23	3.34
353	7.7406 (3)	5.8461 (3)	8.1556 (3)	323.80 (2)	8.03	2.75	3.47	2.72
Phase II, $Z = 2$								
363	5.7012 (1)	–	4.9219 (2)	159.98 (1)	5.38	2.74	3.43	2.72
393	5.7181 (1)	–	4.9285 (3)	161.15 (1)	5.59	2.93	3.70	3.28

Thermal expansion

The specific volume of NH_4NO_3 as a function of temperature has been studied by Hendricks *et al.* (1932). The expansion curve of the specific volume is markedly discontinuous with a distinct step-change at each transition point. In particular, the step-changes at the IV–III and the IV–V phase transitions are very large, more than 3% in volumetric ratio. The thermal-expansion profiles published in the literature (Hendricks *et al.*, 1932; Griffith, 1963) are qualitative representations with unknown accuracy. To determine an accurate thermal-expansion profile of ND_4NO_3 , a series of neutron powder diffraction patterns were measured as a function of temperature from 10 to 393 K, using the procedure described in *Experimental*. The unit-cell dimensions were determined by the Rietveld-refinement method starting with the structural par-

ameters reported in the literature, *i.e.* phase IV by Choi *et al.* (1972), phase III by Choi & Prask (1982), and phase II by Choi *et al.* (1980). The structural parameters and the unit-cell dimensions were all varied in the final stage of the refinement. The cell dimensions found are given in Table 3.

In general, the observed linear and volumetric thermal expansion are described by polynomials of the form $A = A_0 (1 + A_1 t + A_2 t^2 + A_3 t^3)$ where $t = T - T_0$, A and A_0 are the linear (or volumetric) dimensions at temperatures T and T_0 , respectively. However, because the data were limited for certain phases, the following procedure was used.

In the case of $\text{ND}_4\text{NO}_3(\text{V})$, the lattice parameters and volumes of Table 3 were least-squares fit with the cubic-form equations, as given above, to obtain the linear (Table 4a) and volumetric (Table 5) thermal-expansion coefficients.

The thermal expansion for $\text{NH}_4\text{NO}_3(\text{IV})$ had been determined in a previous study, using ammonium nitrate doped with 2.0% NiO in solid-solution form (Choi *et al.*, 1980). Although the unit-cell dimensions of the doped sample are slightly different from those of $\text{ND}_4\text{NO}_3(\text{IV})$, *i.e.* the a axis is 0.006 Å shorter and the c axis longer by 0.005 Å, the unit-cell volumes at both 270 and 293 K agree within one e.s.d. Therefore, the l_0 and v_0 coefficients for this phase were adjusted to give the observed $\text{ND}_4\text{NO}_3(\text{IV})$ values of Table 3, with the remaining coefficients fixed as indicated in Tables 4(b) and 5.

In the case of phase II, it was noted that the specific cell volume measured at 363 and 393 K deviates only about 1 Å³ from the extrapolated expansion of phase V. This similarity in specific cell volume between phase V and II is not surprising when we consider the close similarity of the two structures. A volumetric thermal-expansion formula which includes phases V and II was determined from the combined data of the two phases by the procedure described above and given in Table 5.

In the phase V structure, the expansion rate of the c axis is either very small or negative, but those of the a and b axes are very large and essentially identical to each other (Table 3). This two-dimensional expansion profile of phase V can be explained by the two-

Table 4. *The linear-expansion coefficients for ND_4NO_3 for the form: $l = l_0 (1 + l_1 t + l_2 t^2 + l_3 t^3)$, where $t = T - T_0$*

The residual standard deviations are expressed in the form $R = [\sum (l_{\text{obs}} - l_{\text{calc}})^2 / N]^{1/2}$, where N is the number of degrees of freedom.

(a) Phase V (l_0 and T_0 were held constant)

	a	b	c
l_0 (Å)	7.8767	7.9106	9.7894
l_1 ($\times 10^6$)	-5.3 (6.0)	-1.5 (4.5)	8.3 (2.0)
l_2 ($\times 10^8$)	33.5 (6.9)	30.7 (5.2)	3.6 (2.3)
l_3 ($\times 10^{11}$)	40. (19)	-47. (14)	-30. (6)
T_0 (K)	10	10	10
R (Å)	0.0016	0.0010	0.0006
N	6	6	6

(b) Phase IV [the values for l_1 , l_2 , and l_3 are those of NH_4NO_3 (2% NiO)]

	a	b	c
l_0 (Å)	5.7505 (9)	5.437 (1)	4.9246 (5)
l_1 ($\times 10^6$)	-21.7	365.	50.3
l_2 ($\times 10^8$)	-13.0	140.	5.5
l_3 ($\times 10^{11}$)	-27.0	278.	-18.0
T_0 (K)	298	298	298
R (Å)	0.0011	0.0019	0.0007
N	1	1	1

Table 5. *The least-squares parameters of volumetric expansion of ND_4NO_3*

The underlined numbers are fixed values as explained in the footnotes; v_0 is the specific cell volume (per molecule) at temperature T_0 ; R is the residual standard deviation, and N is the number of degrees of freedom.

Phase	v_0 (Å ³)	v_1 ($\times 10^6$)	v_2 ($\times 10^8$)	v_3 ($\times 10^{11}$)	T_0 (K)	R (Å ³)	N
V	78.47 (9)	101. (28)	-32. (19)	-113. (38)	<u>298.</u>	0.028	5
IV ^(a)	76.99 (2)	<u>394.</u>	<u>134.</u>	<u>235.</u>	<u>298.</u>	0.023	1
III ^(b)	<u>80.075</u>	<u>184.5</u>	<u>25.7</u>	<u>—</u>	<u>298.</u>	—	—
(V + II) ^(c)	78.81 (3)	202. (3)	35.5 (4.8)	16.6 (15.6)	<u>298.</u>	0.047	7

Notes: (a) Fixed coefficients from $\text{NH}_4\text{NO}_3/0.02\text{NiO}$ (Choi *et al.*, 1980). (b) Obtained from three experimental data. (c) From combined (V + II) data discussed in text.

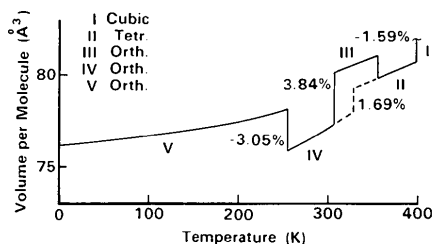


Fig. 3. The volumetric thermal expansion of ND_4NO_3 , given as specific cell volume *vs* temperature, over the temperature range from 10 to 393 K. The dashed line indicates the IV–II transition. The magnitude of the volumetric change at each transition point is also included.

dimensional intermolecular contacts between the nitrate ions described earlier. For ammonium nitrate, which consists of tetrahedral ammonium ions and planar nitrate ions, the thermal-expansion properties are determined primarily by the amplitudes of the nitrate librations, particularly by the out-of-plane mode. Therefore, it is expected that the largest expansion rate occurs in the direction perpendicular to the nitrate plane, which is the *a*- and *b*-axis direction for phases V and II and is the *b*-axis direction for phase IV.

Fig. 3 shows the volumetric thermal expansion of ND_4NO_3 (unit-cell volume per molecule) over the temperature range from 10 to 393 K, obtained from the cubic formulas in Table 5. The volumetric changes are -3.05 , 3.84 , and -1.59% at the V–IV, IV–III, III–II transition points, respectively. The specific cell volume of phase IV is distinctly smaller than those of V and II, although the three phases are essentially identical in molecular packing. This is attributed to the fact that the nitrate ions in phase IV are stacked with their planes parallel to each other to occupy the least space. The unusually large specific cell volume of phase III is related to the oddly irregular packing mode of molecules in the unit cell (Holden & Dickinson, 1975).

Note added in proof: After the acceptance for publication of our paper, we were notified of the existence of another independent study, entitled *The Structure of the Low Temperature Phase V of Ammonium Nitrate*, ND_4NO_3 , by Ahtee, Smolander, Lucas & Hewat (1983). Their paper consists of three parts, namely a critical assessment of the previously proposed structure, possible structure alternatives for phase V, and *Pccn* structure assignment for phase V based on neutron powder diffraction measurements at 233 K. The *b* axis of their unit cell is equivalent to the $-b$ axis of our cell. The essential features of the phase V structures are in agreement in the two studies. However, some quantitative differences arise because of the difference in sample temperatures, *i.e.* 233 K in their study, 78 K in ours. Even at 78 K we find that deuterium positional parameters change by more than

one standard deviation when correction for librational motion is applied. In general, the Ahtee *et al.* N–O bond lengths are shorter than our values, which may also be related to thermal-motion effects. Conversely, their O···D distances are longer than our values. One of the N–O bond lengths [N(1)–O(1) in our notation] was reported by Ahtee *et al.* to be $1.203(11)$ Å, which seems unusually short, and disagrees with our value of $1.263(9)$ Å.

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