The effect of this transition can best be considered in terms of the (010) layers illustrated in Fig. 3. In α -Na₂Cr₂O₇, these layers are identical and presumably similar to the corresponding (010) layer in Ag₂Cr₂O₇ [see Fig. 3(c)]. In β -Na₂Cr₂O₇, the two layers are different [see Fig. 3(a) and (b)]. Apart from small shifts in the cation, the most notable difference between the two layers lies in the configuration of the Cr_2O_7 ion. In layer I [Fig. 3(a)], the bridging oxygen atom lies directly between two opposite terminal oxygen atoms [O(11) and O(21)], the configuration found in most other 'dichromate' structures [see Fig. 1(a) and (c)]. In layer II, the bridging oxygen lies close to the plane of four terminal oxygen atoms [O(31), O(33), O(41), and O(42)]. The terminal oxygen atoms are also twisted slightly from the eclipsed configuration, so that layer II shows a strong similarity to the (010) layers in α -Mg₂P₂O₇ (Calvo, 1967) [Fig. 3(d)],* a derivative of the thortveitite structure. It would thus appear that at high temperatures, $Na_2Cr_2O_7$ has a type I 'dichromate' structure but that on reducing the temperature alternate (010) layers transform into a configuration similar to that found in the thortveitite-like α -Mg₂P₂O₇. We are presently studying the structure of α -Na₂Cr₂O₇ and the phase transition in more detail.

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The Structure of Ammonium Nitrate (IV)

BY C.S. CHOI* AND J.E. MAPES

Explosives Laboratory, Picatinny Arsenal, Dover, N.J. 07801, U.S.A.

AND E. PRINCE

Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234, U.S.A.

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The structure of ammonium nitrate (IV), the phase which is stable between -18 and 32.3 °C, has been refined by least-squares methods with three-dimensional neutron diffraction data. 188 independent reflections were observed on a four-circle diffractometer with a neutron wavelength of 1.232 Å and a limiting 2θ angle of 100°. The refinement, using anisotropic temperature factors and an isotropic secondary extinction parameter, gave a final weighted R index of 0.028. The structure is orthorhombic, space group *Pmmn*, with two NH₄NO₃ formula units per unit cell. A two-dimensional network of hydrogen bonds between the nitrogen atoms of the ammonium group and the oxygen atoms at one corner of the nitrate groups forms infinite sheets parallel to the (001) planes of the crystal. Adjacent sheets are bound together by van der Waals forces. This structure is simply related to the structures of the higher temperature phases.

Introduction

Ammonium nitrate, NH_4NO_3 , crystallizes in several polymorphic forms. The structure of the room-tempera-

ture phase, designated phase IV, was determined by West (1932), and by Hendricks, Posnjak & Kracek (1932) who also proposed possible structures for the higher temperature phases. The room-temperature phase is orthorhombic, space group *Pmmn*, with the cell constants (Swanson, Gilfrich, & Cook, 1957) a =

^{*} The unit cell of α -Mg₂P₂O₇ has been transformed from the space group $B2_1/c$ reported by Calvo (1967) to $P2_1/c$ to facilitate comparison.

^{*} Guest worker at Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234, U.S.A.

5.745, b=5.438, c=4.942Å, and Z=2. A neutron diffraction investigation was undertaken to determine the structure more accurately, and in particular to determine the structural role of the hydrogen atoms in the ammonium groups.

Experimental procedure

Single crystals of NH₄NO₃ were grown by cooling, at the rate of 0.6°C per day, an aqueous solution of reagent grade material saturated at 31°C. The crystal used to collect the diffraction data was roughly spherical in shape, with a diameter of 4 + 0.3 mm. Because the crystal is hygroscopic, it was sealed in a tube of silica glass, along with a small quantity of anhydrous CaCl, dessicant. The crystal was mounted on a 4-circle diffractometer with a small angle between the *a* axis of the crystal and the φ axis of the diffractometer. Threedimensional data were taken under the control of an on-line computer (Alperin & Prince, 1970), using a program which determines, at each reciprocal lattice point, whether the peak intensity exceeds the background intensity by more than 2σ , where $\sigma = (I_p + I_b)^{1/2}$, where I_p and I_b are the peak and background intensities. For all observable reflections the program measures the integrated intensity by a θ -2 θ scan. With a neutron wavelength of 1.232Å and a limiting 2θ angle of 100°, 188 independent reflections are measureable. All reflections except h0l reflections were measured in two equivalent positions. The R index of equivalent reflections, $R = \sum |F_o(hkl) - F_o(h\bar{k}l)| / \sum F_o(hkl) + F_o(h\bar{k}l)|$ was 0.0253, when the sums were taken over 137 pairs of observed reflections. Twelve reflections did not have observable intensity, and 17 additional very weak reflections were considered to be too unreliable and were omitted from the refinement. The integrated intensities of all observed reflections were converted to F values, and each was assigned a standard deviation, $\sigma_F =$ $\frac{1}{2}[(T+B)/L(T-B)]^{1/2}$, based on counting statistics. Here, T is the total number of counts in a peak, B is the number of counts corresponding to the background, and L is the Lorentz factor. The crystal had a nearly spherical shape, with an effective absorption of $\mu R = 0.45$, so that the variation of the absorption factor as a function of scattering angle is less than 4%. Therefore no absorption corrections were applied.

Determination of the structure

The structure parameters for the heavy atoms, as determined by West (1932) were used to compute signs for an F_{o} Fourier synthesis. The resulting map contained clearly defined negative peaks, arranged tetrahedrally around the ammonium nitrogen atom, N(1). The coordinates of these peaks were used as the starting coordinates for hydrogen atoms. Three cycles of leastsquares refinement (program RFINE: Finger, 1968) with isotropic temperature factors gave a weighted Rindex, $\{wR = [\sum w(s|F_o| - |F_c|)^2 / \sum wF_c^2]^{1/2}$, where s is the scale factor and $w = 1/\sigma_F^2$, of 0.19. Further refinement, using anisotropic temperature factors, led to temperature factor matrices that were non-positive-definite. There was also evidence that certain reflections were strongly affected by secondary extinction. Accordingly, an extinction parameter, S, was included in the refinement, using the formula (Zachariasen, 1968) $|F|_{cor} =$ $|F|_c(1 + S\beta F_c^2)^{-1/4}$, where in the neutron case, $\beta = \lambda^2 \overline{T}/V^2 \sin 2\theta = k/\sin 2\theta$. \overline{T} is the average path length through the crystal and may be approximated by $\bar{T}=$ $-\log A/\mu$ (Coppens & Hamilton, 1970), where A is the transmission factor and μ is the linear absorption coefficient. With this parameter included, the refinement converged rapidly, giving a final weighted R index, wR = 0.028 when unobserved reflections were excluded. and 0.034 when they were included . The final secondary extinction parameter, kS, was 0.3463. There was no observable trend to the values of the weighted R index for subsets of the observed reflections, divided according to ranges of F and $\sin \theta / \lambda$. The three strongest reflections, 020, 001 and 110 were very severely affected by extinction, and were therefore omitted from the final stage of refinement. The 101 reflection appeared to be affected by some experimental error, and it was also omitted from the refinement. Shifts of position and thermal parameters were all less than 1% of their standard deviations in the last cycles. The final least-squares parameters are listed in Table 1, and the observed and calculated structure factors are given in Table 2. Table 3 is a summary of bond distances and angles.

Fig. 1 shows the structure as viewed along the a, b, and c axes. Tetrahedral ammonium groups and triangular nitrate groups occupy positions a and b, with

Table 1. Final least-squares parameters for the structure of NH₄NO₃ (IV)

Thermal parameters are the coefficients B_{ij} of the form:

 $\exp\left[-\frac{1}{4}(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)\right].$

			E.s.	d.'s are in pare	ntheses.						
	Fractional j	position paran	neter	Thermal parameter (Å ²)							
	x	У	Ζ	<i>B</i> ₁₁	B ₂₂	B ₃₃	B ₁₂	<i>B</i> ₁₃	B ₂₃		
N(1)	$\frac{3}{4}$	1	-0.0836(4)	2.12 (9)	3.48 (10)	2.25 (9)	0	0	0		
N(2)	14	4	0.5067 (3)	2.57 (8)	2.46 (7)	1.51 (8)	0	0	0		
O(1)	1 4	4	0.7629 (6)	2.80 (11)	3.71 (14)	1.57 (10)	0	0	0		
O(2)	0.4342 (5)	4	0.3832 (5)	4.11 (12)	5.86 (15)	2.96 (10)	0	1.66 (8)	0		
H(1)	0.6045 (12)	<u>1</u> 4	−0 ·1898 (17)	6.87 (32)	5.92 (30)	8.73 (38)	0	-4.77 (32)	0		
H(2)	34	0.1011 (16)	0.0324 (16)	6.19 (28)	8.33 (37)	7.28 (34)	0	0	3.64 (31)		

Table 2. Observed and calculated structure amplitudes for NH_4NO_3

The values of F_{cal} are calculated on an absolute scale and then multiplied by the secondary extinction correction factor. The unobserved reflections and the three strongest reflections, which were excluded from the final refinement, are marked with asterisk (*) and double asterisk (**) respectively.

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2	4	0	1.97	1.95	2	1	1	1.89	1.85	0	0	2	1.25	1.10					• • • •
- 4	- 4	0	2.33	2.00	5	1	1	1.30	1.2/	1	0	s	•64	.68	0	- 2			
1	- 3	. 0	1.12	1.16	4	1	1	1.76	1.74	2	0	ş	• 33			- 2		1.47	1.45
- 3	5	0	1.10	1.16	5	1	1	1+84	1.82	3	0	5	2.20	5.55	1 2	3		.10	
5	- 3	0	.79	• 79	6	1	1	•53	.53	- 4	0	2	• 52	.50	3	3		1.94	1.89
•• 0	5	6	2.30	2.45	** 0	0	1	1.73	1.75	* 5	0	2	•13	+12	4	3	4	• 34	• 35
2	5	0	5.00	2.07	+ 1	0	1	• 31	•16	6	0	2	• 54	.59	0	2	4	• 48	
	5	0	2.30	2.35	+ 5	0	1	•16	•06	* 0	5	3	.20	.05	1	2	4	1.41	1.41
6	2	0	1.91	1+97	3	0	1	.48	• 39	1	5	3	•68	.85	5	2	4	1.58	1.63
** 1	ī	U	1.70	1.81	4	0	1	.54	.60	2	5	3	•61	.60	3	2	4	1.00	1.01
- 3	ī	ū.	. 91	.87	5	0	1	.64	.64	3	5	3	•89	.88	4	5	4	1.23	1.24
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1.5	6	1	•16	•13	1 3	2	2	• 33	•25				1.40	12	1	ň	ū	1.28	1.23
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- 2	5	1	1.09	1.05	1 1	4	2	• 52	17	1 - 6	2	- 2			1 2		5	1.24	1.24
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۷	4	+ 1	•53	• 5 3	0	3	2	1.51	1.45	5	2	3	1.43	1.42	1	2	2	. • ! •	
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. 4	- 4	+ 1	+19	+05	5	3	2	•45	• 39	1	1	3	1.11	1.13	• 3	s	2	. 21	
* 5	4	1	+11	• 20	. 5	3	2	.23	•17	2	1	3	1.59	1.61	0	1	5	1.71	1.70
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ī		i i	2.17	2.17	+ 5	- 3	2	.12	.09	4	1	3	. 39	.34	2	1	5	1.10	1.08
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- 5		ĩ	1.71	1.70	1 i	2	2	.54	.44	• 6	1	3	.15	,20	0	0	5	1.04	1.09
		í i	1. 15	1.37	1.5	2	2	1.13	1.19	6	0	3	.76	.79	1 1	0	5	•56	. 59
			1.43	1.78	1 5	2	5	2.01	1.98	l ĭ	ŏ	3	2.15	2.14	1 2	ō	5	1.80	1.48
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				1.37	1.5	5	5	.12	.03	1 5	ŏ	3	1.06	1.05	4	ŏ	5	1.01	1.03
			1.30		1 2	5	5	70	77	1	ň	ž	1.71	1.76	l á	š	6	.59	.63
1	, č	1	+25	. 29	1 8	ŝ	5		1 07	1.2	ň	1	1.66	1.63	l ő.	å	6	.60	.64
		1	1.05	1.13	1	÷.	ŝ	1.01		12					1 .	ŏ	6	. 42	. 33

Table 3. Interatomic distances and angles for NH₄NO₃

(a) Bond lengths (Å)

	Uncorrected	Riding model	L(1)	<i>L</i> (2)
N(2) - O(1)	1.266 (4)	1.274		_
N(2) - O(2)	1.222(3)	1.254	_	_
N(1) - H(1)	0.987(7)	1.069	1.029	1.066
N(1)-H(2)	0.992 (7)	1.072	1.032	1.063
(b) Bond angles	; (°)			
0	(1) - N(2) - O(2)	120.0	(3)	
ŏ	(2) - N(2) - O(2)	120.0	(3)	
Ĥ	(1) - N(1) - H(1)	115.7	(1.2)	
Н	(1) - N(1) - H(2)	107.9	(0.4)	
Н	(2) - N(1) - H(2)	109.4	(1.2)	
(c) Hydrogen b	onds			
Bond type	О…Н(Å) O…N	(Å) N-	H · · · O (°)
$N(1)-H(1)\cdots O$	(1) $2.050(7)$	2.971	(3) 1	54.4 (8)
$N(1)-H(2)\cdots O$	(1) 2.161 (7	3.147	(3) 1	72.6 (9)
$N(1)-H(1)\cdots O$	(2) 2.326 (7	ý 3·200	(4) 1	47.0 (9)
(d) Short intera	atomic distances	s (Å)		
	$N(1) \cdots O(2)$	2.935	(4)	
	$N(2) \cdots H(1)$	2.529	(6)	
	$O(2) \cdots O(2)$	3.049	(4)	
	$O(2) \cdots H(2)$	2.637	(7)	
	$N(1) \cdots O(2)$	3.272	(3)	

mm symmetry in space group Pmmn. There are infinite hydrogen-bonded chains parallel to the *a* axis, formed by N(1)-H(1)...O(1)...H(1)-N(1), etc. [H(1)...O(1) =2.05Å]. These chains are linked by somewhat weaker hydrogen bonds [H(2)...O(1)=2.16Å] to form infinite sheets parallel to (001). The H(1)-O(2) distance is 2.326Å, which is barely within the limit of 2.4Å (Hamilton & Ibers, 1968) for hydrogen bonding to oxygen. There is probably a weak interaction just sufficient to prevent rotation of the nitrate group around the O(1)-N(2) bond. The N(2)-O(1) distance is 1.266(4)Å, which is longer than the N(2)-O(2) distance of 1.222(3)Å. This is consistent with the fact that O(1) is involved in four strong hydrogen bonds and O(2) is not. Adjacent sheets are bound together only by van der Waals forces, accounting for the cleavage parallel to (001).

A particularly notable feature of the structure is the fact that the nitrate group is attached to the sheets by one corner only, and this is clearly reflected in the thermal motion. It is apparent from Fig. 1(b) that the nitrate group is librating as a unit about a point close to the oxygen atom, O(1), which is bonded to the sheet, rather than about N(2), its center of mass.

The amplitudes of thermal motion of the hydrogen atoms are large (the equivalent isotropic B is approximately 7.2Å^2), and are highly anisotropic, with the shortest axis of the thermal ellipsoids nearly parallel to the N–H bond [see Fig. 1(a) and (b)]. The thermal motion of the nitrogen atom in the ammonium group is much less extreme (the equivalent isotropic B is only 2.6Å²) and also much less anisotropic. This picture is consistent with a model which attributes most of the motion of the hydrogen atoms to the libration of the ammonium group. Because of this, the motions of the ammonium group were fitted to the rigid-body model by the method of Schomaker & Trueblood (1968) with the results shown in Table 4. The libration amplitudes are very large, as expected. The principal axes of the L tensor, parallel to the a and b axes, do not pass through the center of mass of the ammonium group, which is located close to the center of the nitrogen atom, but are each displaced toward the H-H vector which is parallel to the same axis. It is as if the tetrahedron is partially constrained to librate around the $N-H\cdots O\cdots H-N$ chain, which pins it at the corners. The mean-square deviation between the observed vibration amplitudes and those calculated from the rigidbody parameters is 0.0037Å². The fact that the fit is not better than this can be ascribed to the very large amplitudes of libration, and to the fact that an ammonium group is not a particularly rigid body.

Table 4. Rigid-body analysis of thermal motionof ammonium group

 $T(Å^{2}) \text{ and } L(^{\circ 2}) \text{ relative to the } a, b, c \text{ axis.}$ $T = \begin{pmatrix} 0.0353 & 0 \\ 0 & 0.0511 & 0 \\ 0 & 0 & 0.0353 \end{pmatrix} \quad L = \begin{pmatrix} 263.4 & 0 & 0 \\ 0 & 357.9 & 0 \\ 0 & 0 & 124.0 \end{pmatrix}$ Principal axes of L.
Angle (°) Direction mass center (Å) $L_{1} \qquad 18.9 \qquad b \text{ axis} \qquad 0.138$

a axis

c axis

0.282

0

16.2

11.1

 \mathbf{L}_2

 L_3

The corrections to the N-H bond distances in the ammonium group, as calculated by several models, are shown in Table 3. The correction designated L(1) is the formula given by Cruikshank (1965), in which the breadth parameter, q, for the scattering length distribution of the hydrogen atom was determined by fitting

the function $\varrho(r) = \exp[-(r^2/2q^2)]$ to the N(1) atom peak in a Fourier map. The correction designated L(2) is derived from the formula given by Johnson (1970, eq. 16). The value 1.03Å found in L(1) is in good agreement with values found for the ammonium ion in other crystals (*International Tables for X-ray Crystallography*,





1968). Both the riding model (Busing & Levy, 1964) and the L(2) formula appear to cause over-correction.

Relationship to higher temperature phases

NH₄NO₃ has several other phases which have been extensively studied (Hendricks et al., 1932; Goodwin & Whetstone, 1947; Tanaka & Fukuyama, 1953; Shinnaka, 1956; Amoros, Canut, Alonso, Riano, Banerjee, Moreno, Arrese, & Abasolo, 1960). Phase III (Hendricks et al., 1932; Goodwin & Whetstone, 1947), which is stable from 32.3 to 84.2°C, and phase II (Shinnaka, 1956), which is stable from 84.2 to 125.2° , have structures that are very closely related to that of the room-temperature phase. Under some conditions, phase II and phase IV are both metastable with respect to phase III, and reversible transitions between phases II and IV can take place without passing through phase III, suggesting that phase II and phase IV are in fact more closely related to each other than either one is to phase III. The structure of orthorhombic phase III may be derived from that of phase IV by breaking one half of the longer hydrogen bonds in the (001) sheets, thereby converting the sheets to double chains [see Fig. 1(a)].

There is some uncertainty as to the details of the structure of phase II, which has tetragonal symmetry (Shinnaka, 1956; Amoros *et al.*, 1960). Fig. 1(c) shows the room-temperature structure (phase IV) as viewed

Table 5. Calculated X-ray powder diffraction intensities for the possible structure of NH_4NO_3 (II), as compared with the data in the ASTM index

N, O(1), and O(2) have been assumed to have isotropic temperature factors equal to 3.0, 4.0, and 6.0 Å² respectively.

hkl	I/I ₀ (obs)	$I/I_o(cal)$
001	30	34.2
110	70	57.8
1 1 1	100	100
200	60	31.8
120	35	19.1
201	10	2.1
121	30	29.2
112	10	9.7
220	20	14.4
221	5	2.7
1 1 3	8	2.9
132	8	1.6

along the c axis. It is immediately apparent that if one ignores the O(2) oxygen atoms of the nitrate group, the remainder of the structure has essentially tetragonal symmetry. An ordered tetragonal structure belonging to space group $P\overline{42}_1m$ can be constructed by rotating the nitrate group 45° around the N(2)-O(1) bond, and shifting the z coordinates of the ammonium nitrogen atoms to zero. Table 5 shows the calculated intensities of X-ray powder diffraction lines, according to this structure, as compared with the data given in the ASTM index (Hendricks *et al.*, 1932). The structure suggested by Shinnaka (1956), in which the nitrate groups are disordered by 60° rotation in the plane of the groups, is unlikely, in view of the role played by N(1)-H...O(1) hydrogen bonds in the structure.

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