

The effect of this transition can best be considered in terms of the (010) layers illustrated in Fig. 3. In α - $\text{Na}_2\text{Cr}_2\text{O}_7$, these layers are identical and presumably similar to the corresponding (010) layer in $\text{Ag}_2\text{Cr}_2\text{O}_7$ [see Fig. 3(c)]. In β - $\text{Na}_2\text{Cr}_2\text{O}_7$, 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 - $\text{Mg}_2\text{P}_2\text{O}_7$ (Calvo, 1967) [Fig. 3(d)],* a derivative of the thortveitite structure. It would thus appear that at high temperatures, $\text{Na}_2\text{Cr}_2\text{O}_7$ 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 - $\text{Mg}_2\text{P}_2\text{O}_7$. We are presently studying the structure of α - $\text{Na}_2\text{Cr}_2\text{O}_7$ and the phase transition in more detail.

* The unit cell of α - $\text{Mg}_2\text{P}_2\text{O}_7$ has been transformed from the space group $B2_1/c$ reported by Calvo (1967) to $P2_1/c$ to facilitate comparison.

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The Structure of Ammonium Nitrate (IV)

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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 \AA 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 $Pm\bar{m}n$, with two NH_4NO_3 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-

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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 $Pm\bar{m}n$, with the cell constants (Swanson, Gilfrich, & Cook, 1957) $a =$

5.745, $b=5.438$, $c=4.942\text{\AA}$, 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 NH_4NO_3 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_2 desiccant. 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. Three-dimensional 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 $\theta-2\theta$ scan. With a neutron wavelength of 1.232\AA and a limiting 2θ angle of 100° , 188 independent reflections are measurable. 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 least-squares refinement (program *RFINE*: Finger, 1968) with isotropic temperature factors gave a weighted R index, $\{wR = [\sum w(s|F_o| - |F_c|)^2 / \sum wF_c^2]^{1/2}$, 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) $|F|_{\text{cor}} = |F|_c(1 + S\beta F_c^2)^{-1/4}$, where in the neutron case, $\beta = \lambda^2 \bar{T}/V^2 \sin 2\theta = k/\sin 2\theta$. \bar{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 NH_4NO_3 (IV)

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

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

E.s.d.'s are in parentheses.

Fractional position parameter			Thermal parameter (\AA^2)						
	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N(1)	$\frac{3}{4}$	$\frac{1}{4}$	-0.0836 (4)	2.12 (9)	3.48 (10)	2.25 (9)	0	0	0
N(2)	$\frac{1}{4}$	$\frac{3}{4}$	0.5067 (3)	2.57 (8)	2.46 (7)	1.51 (8)	0	0	0
O(1)	$\frac{1}{4}$	$\frac{1}{4}$	0.7629 (6)	2.80 (11)	3.71 (14)	1.57 (10)	0	0	0
O(2)	0.4342 (5)	$\frac{1}{4}$	0.3832 (5)	4.11 (12)	5.86 (15)	2.96 (10)	0	1.66 (8)	0
H(1)	0.6045 (12)	$\frac{1}{4}$	-0.1898 (17)	6.87 (32)	5.92 (30)	8.73 (38)	0	-4.77 (32)	0
H(2)	$\frac{3}{4}$	0.1011 (16)	0.0324 (16)	6.19 (28)	8.33 (37)	7.28 (34)	0	0	3.64 (31)

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 $\rho(r) = \exp[-(r^2/2q^2)]$ 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 1.03\AA found in $L(1)$ is in good agreement with values found for the ammonium ion in other crystals (*International Tables for X-ray Crystallography*,

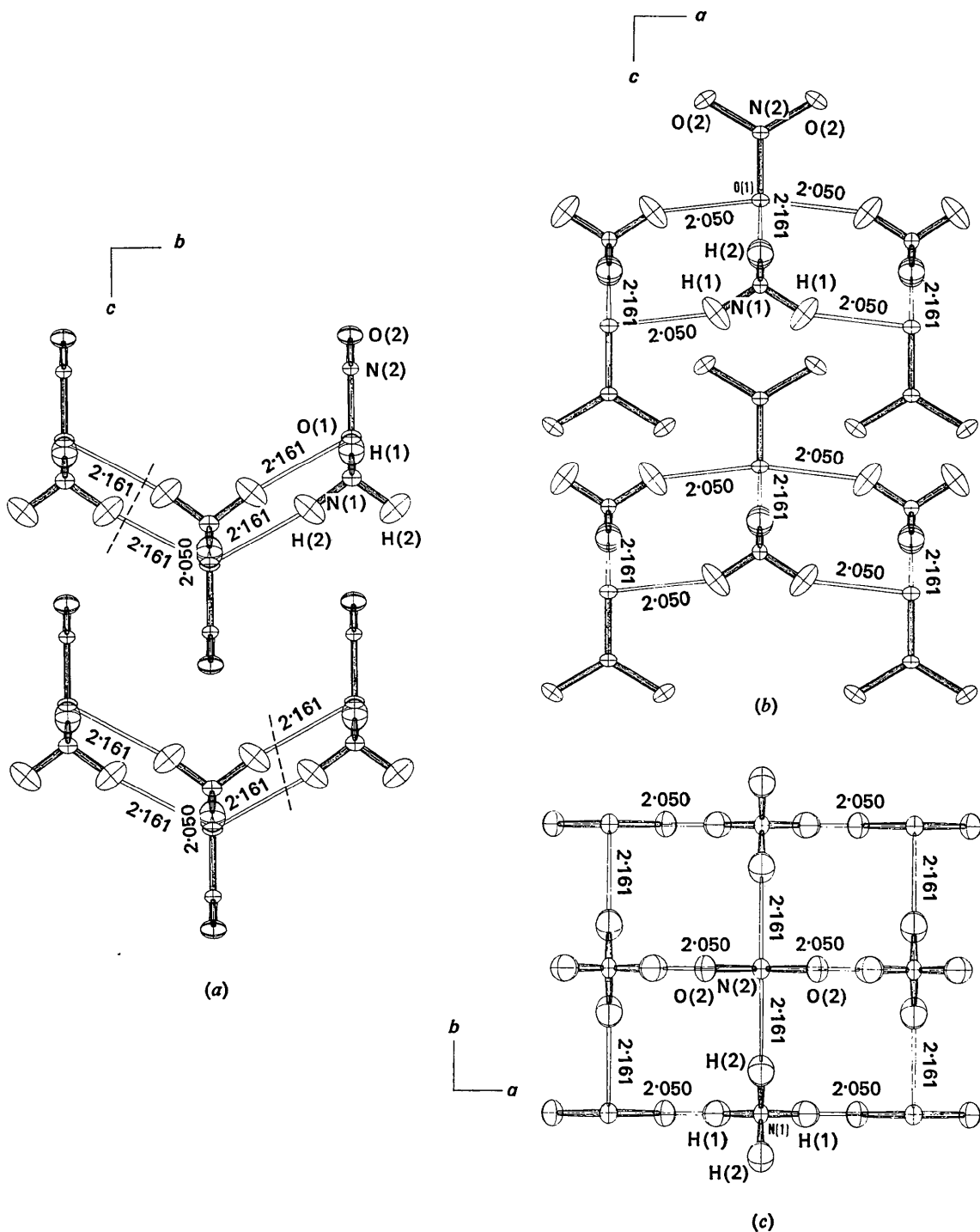


Fig. 1. The structure of NH_4NO_3 (IV) as viewed (a) along the a axis, (b) along the b axis, and (c) along the c axis. The dashed lines in (a) mark the bonds which must be broken to transform from the sheets of phase IV to the double chains of phase III.

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

Relationship to higher temperature phases

NH_4NO_3 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°C, 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.

$h k l$	$I/I_0(\text{obs})$	$I/I_0(\text{cal})$
0 0 1	30	34.2
1 1 0	70	57.8
1 1 1	100	100
2 0 0	60	31.8
1 2 0	35	19.1
2 0 1	10	2.1
1 2 1	30	29.2
1 1 2	10	9.7
2 2 0	20	14.4
2 2 1	5	2.7
1 1 3	8	2.9
1 3 2	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 $P4_2m$ 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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