

TABLE II  
COMPUTATION OF  $E^\circ$  FOR " $a$ " = 11 Å.

No.	$x = ka$	I	III	V	$-\log f$	$\frac{-0.05915}{\log f}$	$E^\circ$
1	0.6541	+0.706	-0.088	+0.026	+0.768	0.0454	0.337
2	1.0258	.904	-.057	.018	.943	.0558	.338
3	1.1594	.958	-.048	.014	.992	.0587	.337
4	1.5466	1.084	-.028	.003	1.109	.0656	.336
5	2.1494	1.218	-.013	..	1.231	.0728	.338
6	2.5663	1.284	-.007	..	1.291	.0764	.338
7	4.9819	1.487	.....	..	1.487	.0880	.342
8	9.2466	1.611	.....	..	1.611	.0953	.346
9	12.0879	1.649	.....	..	1.469	.0975	.351

### Summary

The e. m. f. measurements of Hutchison and Chandlee on the activity coefficient of sulfuric acid in glacial acetic acid can be accounted for on the basis of the Gronwall, La Mer and Sandved extension of the Debye-Hückel theory on the assumption that sulfuric acid behaves as a binary electrolyte in this solvent with an " $a$ " value equal to 11 Å., for the concentration range  $m = 0.0025$  to  $0.038$ .

$E^\circ = 0.338$  volt for the cell  $H_2, H_2SO_4$  in glacial acetic acid,  $Hg_2SO_4, Hg$ .  
NEW YORK, N. Y.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS, DEPARTMENT OF AGRICULTURE, AND THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON]

## MOLECULAR ROTATION IN THE SOLID STATE. THE VARIATION OF THE CRYSTAL STRUCTURE OF AMMONIUM NITRATE WITH TEMPERATURE

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The phenomenon of molecular rotation in the solid state, first recognized by L. Pauling,<sup>1</sup> is proving of wide occurrence. In sodium nitrate<sup>2</sup> the picking up of rotational energy by the nitrate groups takes place over an extended temperature interval and is accompanied by *gradual* changes in such properties as coherent scattering of x-rays, heat capacity and specific volume. Pauling interpreted the *gradual* transitions shown by methane, hydrogen bromide, hydrogen iodide and the ammonium halides as accompanying molecular rotation. He also suggested that the *polymorphic* transitions shown by nitrogen (35.4°K.), oxygen (43.75°K.) and hydrogen chloride (93.36°K.) are accompanied by the excitation of molecular rotation.

The several gradual transitions shown by hydrogen bromide and hydro-

<sup>1</sup> L. Pauling, *Phys. Rev.*, **36**, 430 (1930).

<sup>2</sup> F. C. Kracek, E. Posnjak, S. B. Hendricks, *THIS JOURNAL*, **53**, 3339 (1931).

gen iodide<sup>3</sup> were supposed by Pauling to be connected with incipient rotation about various directions in the crystals. x-Ray powder diffraction photographs, recently obtained, from the various crystalline modifications of these compounds are not readily interpretable.<sup>4</sup> They are, however, in no sense incompatible with the concept of molecular rotation.

We have been fortunate in discovering in ammonium nitrate formal proof for the concept of molecular rotation in the solid state and evidence for the setting in of the rotation at a *polymorphic* transition point. The structures of the many modifications of ammonium nitrate have been studied in detail.

### I. The Polymorphism of Ammonium Nitrate

Ammonium nitrate has one high pressure and five low pressure crystalline modifications. The inversion temperatures, the volume changes, and the latent heats of inversion have been determined;<sup>5</sup> the most probable values of these constants are given in the following tabulation.

Phase reaction	Temp., °C.	Volume change, cc./g.	Heat of inversion, cal./g.	Authors
I $\longleftrightarrow$ II	125.2	0.013	11.9	Early and Lowry, Bellati and Finazzi, Bellati and Romanese, Behn
II $\longleftrightarrow$ III	84.2	-.008	5.3	Early and Lowry, Bellati and Romanese, Behn
III $\longleftrightarrow$ IV	32.3	.0221	4.99	Cohen and Kooy, Cohen and Heldeman
IV $\longleftrightarrow$ V	-18	-.016	1.6	Behn
		-.018		
II $\longleftrightarrow$ IV	45 to 51	...	..	Bowen, Behn

Three series of measurements of the relative dilatation of ammonium nitrate have been published, by Bellati and Romanese, Bellati and Finazzi, and U. Behn. These series are not in mutual agreement because of errors in the elimination of the expansion of the dilatometer liquid. We have recalculated the results employing the accurate values of specific volumes at 32.0 and 32.5° for modifications IV and III by Cohen and Kooy, and the density 1.725 *ca.* 18° (Behn, Retgers).<sup>6</sup> The recalculated results are represented in Fig. 1.

<sup>3</sup> W. F. Giaque and R. Wiebe, *THIS JOURNAL*, **50**, 2198 (1928); **51**, 1441 (1929).

<sup>4</sup> B. Ruhemann and F. Simon, *Z. physik. Chem.*, **15**, 389 (1932). See also G. Natta, *Nature*, **127**, 235 (1931).

<sup>5</sup> "International Critical Tables," Vol. IV, p. 7; P. Groth, *Chem. Krystallographie*, Leipzig, Vol. 2; Bellati and Finazzi, *Atti ist. Veneto*, **69**, 1151 (1909); U. Behn, *Proc. Roy. Soc. (London)*, **A80**, 444 (1908); Cohen and Kooy, *Z. physik. Chem.*, **109**, 81 (1924); Cohen and Helderman, *ibid.*, **113**, 145 (1924); N. L. Bowen, *J. Phys. Chem.*, **30**, 721 (1926).

<sup>6</sup> Other values quoted in the literature are largely accidental; thus Schröder is quoted as having determined  $\rho = 1.737$ , the actually measured values being 1.681 and 1.791. Many other determinations are vitiated by lack of physical homogeneity of the salt used.

The crystallographic observations on the various modifications indicate that ammonium nitrate is (I) cubic (optically isotropic) above  $125^\circ$ , (II) tetragonal (Wallerant) or trigonal (Lehmann, Gossner) between  $125$  and  $84^\circ$ , (III) orthorhombic (Lehman) or monoclinic pseudo-tetragonal (Wallerant) between  $84$  and  $32^\circ$ , (IV) orthorhombic pseudo-tetragonal (Wallerant) or orthorhombic pseudo-trigonal (Lehmann) between  $32$  and  $-18^\circ$ , and (V) tetragonal below  $-18^\circ$ . Only the room temperature orthorhombic modification (IV) has been measured crystallographically, with the result that two mutually incompatible sets of axial ratios have been published,

- (a) 0.5834:1:0.736 (Retgers, Wallerant, based on measurements by Marignac)  
 (b) 0.9092:1:1.0553 (Gossner)

The latter set of axial ratios (b) agrees with our structural determinations.

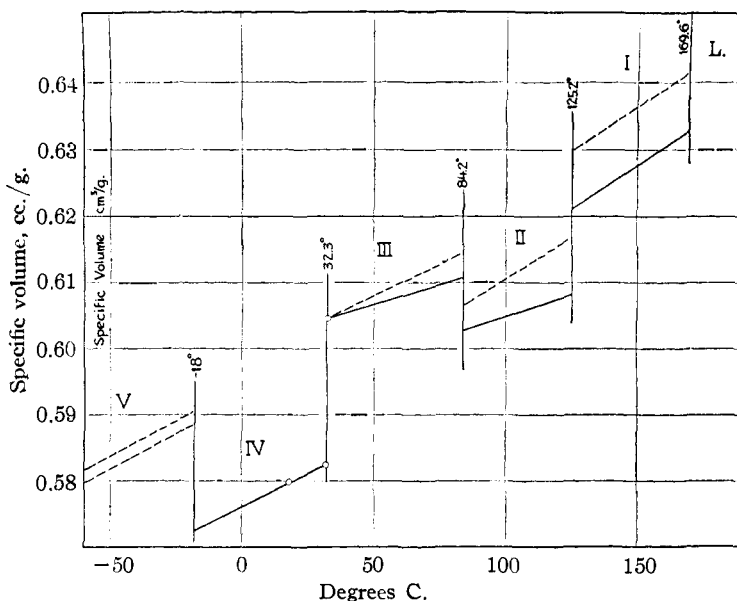


Fig. 1.—The specific volumes of the various modifications of ammonium nitrate. Circles represent the accurate values by Cohen and Kooy, and by Retgers. Full lines from relative expansion curves by Bellati and Romanese and Finazzi; broken lines, from relative expansion curves by Behn.

Bowen (1926) agrees with Wallerant that the  $84$  to  $125^\circ$  modification (II) is tetragonal, optically uniaxial and positive. He describes the  $32$  to  $84^\circ$  modification (III) as orthorhombic or monoclinic (optically biaxial), optic axial angle ( $2V$ ) nearly  $90^\circ$ , with a moderately high birefringence, in comparison with the orthorhombic room temperature (IV) modification which has a very high birefringence, optic axial angle  $2V$  about  $35^\circ$ .

We have studied the behavior of ammonium nitrate with the petro-

graphic microscope equipped with a heating stage. For reading the temperatures the stage is provided with a gold palladium-platinum rhodium thermocouple. The samples were prepared in the usual way, by melting a small quantity of the salt on an ordinary microscope slide, a cover-glass being then pressed down lightly to obtain a thin section. The lag in the inversions was clearly noticeable; the greatest lag is observed with the IV  $\rightleftharpoons$  III inversion, which started at 36 to 40° with rising temperature, and 28 to 25° with falling temperature. When both phases are initially present, the lag is very much less; the boundary can then be seen to move quite rapidly at 33° in one direction and at 31 to 32° in the other. On raising the temperature to the III  $\rightleftharpoons$  II inversion, the transformation starts quite promptly at about 85°. If the cooling is begun now before the temperature of the salt reaches 125°, modification II reverts to III directly, starting usually near 80°, but sometimes not until a temperature of 70 or even 65° is reached. If, on the other hand, the temperature is allowed to rise above the II  $\rightleftharpoons$  I inversion near 125°, then, on subsequent cooling, the form II does not invert directly back to III as above, but it persists down to 48 or 45°, when it changes apparently to form IV, as also described by Bowen (*op. cit.*, p. 723). If the slide is very thin, and the salt well dried, the transformation is very like a single crystal to single crystal transition, taking place very rapidly, with barely a noticeable change in orientation and birefringence. If the slide is a little thicker than before, or the salt not too thoroughly dried, the transformation proceeds by recrystallization. If the temperature is allowed to decrease further, no other transformation occurs, either with the thin or the thick preparations, down to 0°. On heating now, the thin slides always revert back to form II at about 50 to 52°, again very rapidly, with a hardly noticeable change in birefringence. This metastable inversion can be carried back and forth in the thin films almost indefinitely, the metastable condition persisting for many hours; it is, however, rapidly destroyed by moisture. In the thicker slides the metastable inversion can sometimes also be reversed a number of times, but usually after three or four reversals the stable modification III appears. Sometimes this happens following the metastable inversion on cooling, as observed by Bowen, but often also on heating, and then only after the metastable inversion on heating has taken place. The difference in behavior of the very thin and the thicker slides at the metastable inversion is striking, as is likewise the reluctance of the preparations, when in the metastable condition, to assume the stable form.

## II. The Crystal Structure of Ammonium Nitrate as a Function of Temperature

**The Modification Stable between 125 and 169.5° (Melting Point, Cubic I).**—x-Ray powder diffraction photographs were made with

MoK  $\alpha_1\alpha_2$  radiation of a revolving sample of ammonium nitrate at  $155^\circ$ . The sample was obtained by cooling a melt. Photographs were also made with CuK  $\alpha_1\alpha_2$  radiation of samples at  $130$ – $140^\circ$ . In these cases the ammonium nitrate was ground finely and placed in small glass tubes which were rotated throughout the time of exposure. On account of the high rate of crystal growth it was necessary to change the sample every hour. The data obtained from these photographs are summarized in Table I.

TABLE I  
POWDER PHOTOGRAPHIC DATA FROM CUBIC AMMONIUM NITRATE (I)

155° MoK  $\alpha_1\alpha_2$  radiation (NaCl reference)  
 $\sin^2\theta = 0.00648(h^2 + k^2 + l^2)$   $a_0 = 4.40 \text{ \AA.}$

Plane	$\sin^2\theta$ (obs.)	$\sin^2\theta$ (calcd.)	Int. obs.
(100)	0.00640	0.00648	v. s.
(110)	.01295	.01296	v. s.
(111)	.01955	.01944	w.
(200)	.0259	.0259	m.
(210)	.0321	.0324	v. w.
(211)	.0386	.0389	v. w.
(220)	.0522	.0518	v. w.
(300)(221)	.0588	.0583	w.
(310)	.0648	.0648	v. w.

The lattice required by these data is a simple cubic one. The unit of structure has  $a_0 = 4.40 \text{ \AA.}$  at  $155^\circ$ . The density calculated on the basis of such a unit containing  $1\text{NH}_4\text{NO}_3$  is 1.55 g./cc. in agreement with the experimentally observed value 1.57 g./cc.

The only possible atomic positions are:

$$\begin{array}{ll} \text{(a) } 000 & \text{(b) } \frac{1}{2}\frac{1}{2}\frac{1}{2} \\ \text{(3a) } \frac{1}{2}\frac{1}{2}0; \frac{1}{2}0\frac{1}{2}; 0\frac{1}{2}\frac{1}{2} & \text{(3b) } \frac{1}{2}00; 0\frac{1}{2}0; 00\frac{1}{2} \end{array}$$

Combinations of these positions lead to calculated intensities entirely out of agreement with the observed intensities. Moreover, but we must remark secondarily, such arrangements do not give nitrate groups. It is thus impossible, if the geometrical concepts of crystal symmetry are to be retained, for the oxygen atoms to be in fixed positions.

Several possible escapes from this conclusion might be considered.

(1) *Is the Symmetry Less than Cubic?*—The powder diffraction data would require the crystal axes to be approximately orthogonal and of equal lengths. The instance of  $\text{LiCl}\cdot\text{H}_2\text{O}$  might be recalled as an illustration. H. Ott<sup>7</sup> from powder photographic data concluded that the structure of  $\text{LiCl}\cdot\text{H}_2\text{O}$  was based upon a simple cubic lattice and that the unit of structure contains  $1\text{LiCl}\cdot\text{H}_2\text{O}$ . Since it is not possible to have three dissimilar atoms in such a unit he suggested that two of the atoms were associated, this pseudo atom being the one defined by the geometrical criteria. These observations, however, were inconsistent with the high birefringence and

<sup>7</sup> Ott, *Z. Krist.*, **63**, 231 (1926).

uniaxial character of  $\text{LiCl}\cdot\text{H}_2\text{O}$ . A closer examination<sup>8</sup> of the structure showed it to be tetragonal with an axial ratio of approximately unity. If the symmetry of ammonium nitrate were less than cubic and the unit of structure contained  $1\text{NH}_4\text{NO}_3$ , the birefringence would necessarily be high, as it is observed to be in the four modifications of ammonium nitrate stable below  $125^\circ$ , since the molecular birefringence of the nitrate group is high. It is thus improbable that the symmetry is less than cubic.

(2) *Is the Unit of Structure Larger?*—This would be possible if the atoms in question, oxygen atoms, had negligible  $F$  values in comparison with the other atoms in the compound. In ammonium nitrate the oxygen atoms are in no sense negligible, and there is no evidence for reflections other than the ones listed in Table I.

(3) *Molecular Rotation.*—Randomness in positions of the oxygen atoms may be interpreted as evidence for rotation of the nitrate groups. In order to calculate intensities of reflection it is necessary, on the basis of such data, to assume certain types of distributions. Several distributions were tried. The centers of the ammonium groups can be taken at 000, of the  $\text{NO}_3$  groups at  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ . Structure factors are listed in Table II calculated on the basis of the following assumptions: (1) the centers of the oxygen atoms are assumed to be randomly arranged on a sphere of 1.25 Å. radius about  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ , all positions of the oxygen atoms being considered equally probable; (2) the nitrate groups are assumed to be rotating with constant angular velocity in three orthogonal planes. In each case, the values of the structure factors, which are only approximate, lead to calculated intensities on the basis of assumed  $F$  curves, which are still not in good agreement with

TABLE II  
STRUCTURE FACTORS FOR VARIOUS PLANES OF CUBIC AMMONIUM NITRATE (I)

Plane	$\sqrt{S} = A (B = 0)$				No. of planes in form	Intensity observed
	$1F_{\text{NH}_4}$	$-1F_{\text{N of NO}_3}$	(1)	(2)		
(100)			$-1.7F_0$	$-1.5F_0$	6	s.
(110)	1	+1	+0.7	+0.7	12	v. s.
(111)	1	-1		0	8	w.
(200)	1	+1	+0.2	-0.2	6	m.
(210)	1	-1	+0.3	+0.5	24	v. w.
(211)	1	+1		-0.6	24	v. w.
(220)	1	+1	-1.0	-0.4	12	v. w.
(300)	1	-1	-0.9	0.4	6	} w.
(221)	1	-1		0.4	24	
(310)	1	+1	+0.2	-0.3	24	v. w.

(1) Calculated for the nitrate groups rotating with constant angular velocities in three orthogonal planes normal to the cubic axes.

(2) These calculations are based upon the assumption that the nitrate groups are rotating with approximately spherical symmetry.

<sup>8</sup> S. B. Hendricks, *Z. Krist.*, **66**, 298 (1927).

the observed intensities. This lack of agreement is merely indicative of over-simplification in the assumed models. It is quite probable that the nitrate groups do not rotate with constant angular velocities and that they do not generate any simple geometrical figure. In any case, however, it should be pointed out that all reflections beyond (110) are characteristically weak. Either of the above cases qualitatively requires this. It can be seen that if the oxygen atoms approach such arrangements they will contribute partially out of phase for all reflections.

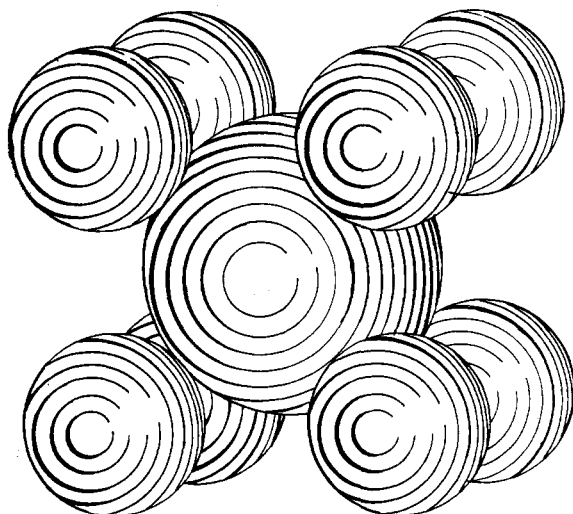


Fig. 2a.—Cubic ammonium nitrate (I). The small spheres represent ammonium groups, the large sphere a nitrate group rotating with spherical symmetry.  $a_0 = 4.40 \text{ \AA}$ . ( $155^\circ$ ).

One factor of importance to geometrical crystallography is brought into clear relief by this structure of ammonium nitrate. It would seem that the unit of structure is the smallest element that *statistically* has the symmetry of the crystal. If this is true the figure generated by a rotating nitrate group must have at least the symmetry of the point group T-23. The minimum symmetry might be that of any cubic point group, the actual that of a sphere.

The unit of structure with the rotating nitrate group represented as a spherical shell is shown in Fig. 2a. In Fig. 2b the nitrate group is represented as rotating in three orthogonal planes. If the angular velocity were constant, the symmetry of the generated figure would be that of the point group  $O_h-4/m\bar{3}2/m$ . The minimum separation of points  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$  is  $4.40 \text{ \AA}$ ,  $a_0$ . If the nitrogen to oxygen distances within the nitrate group are  $1.25 \text{ \AA}$ , the oxygen ions would, in either case, approach within  $1.90 \text{ \AA}$ . of one

another at some time if the nitrate groups were rotating independently in phase. This value is improbably small.<sup>9</sup>

Finally, it is interesting to note that ammonium chloride is soluble to the extent of *ca.* 8% by weight in cubic ammonium nitrate<sup>10</sup> and is not soluble, in detectable amounts, in the other crystalline modifications. If it is assumed that the ionic radius of  $\text{NH}_4^+$  is 1.46 Å., the apparent radius of  $\text{NO}_3^-$  is 2.35 Å., in comparison with *ca.* 1.90 Å., the radius of  $\text{Cl}^-$  with a coordination number of eight. On this basis solid solution would be expected with the nitrate group acting as a structural unit (rotating).

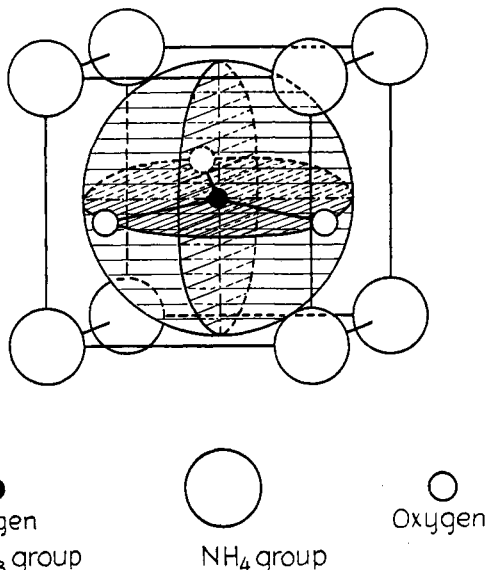


Fig. 2b.—Cubic ammonium nitrate (I). The structure is shown with the nitrate groups rotating in three orthogonal planes normal to the cubic axes.  $a_0 = 4.40$  Å. ( $155^\circ$ ).

#### The Modification Stable between 125 and $84.2^\circ$ (Tetragonal, II).—

A number of powder photographs were made, with  $\text{CuK}\alpha$  and  $\text{MoK}\alpha$  radiation, from revolving samples of ammonium nitrate at  $100 \pm 10^\circ$ . The samples were prepared and photographed as for the cubic modification. Some of the results obtained are summarized in Table III.

The data require a tetragonal unit of structure with  $a = b = 5.74$  Å.,  $c = 5.00$  Å.

$$\text{CuK } \alpha_1 \sin^2 \theta = 0.0181 (h^2 + k^2) + 0.0236 l^2$$

$$\text{MoK } \alpha_1 \sin^2 \theta = 0.00380 (h^2 + k^2) + 0.00501 l^2$$

The density calculated on the basis of such a unit containing  $2\text{NH}_4\text{NO}_3$  is 1.60 g./cc. in agreement with the observed value 1.64.

<sup>9</sup> Note for instance, W. H. Zachariasen, *Z. Krist.*, **80**, 137 (1931).

<sup>10</sup> N. L. Bowen, *J. Phys. Chem.*, **30**, 726 (1926).



TABLE III  
POWDER PHOTOGRAPHIC DATA FROM TETRAGONAL AMMONIUM NITRATE (II)  
100 ± 10°

Plane	Int.	MoK $\alpha_1\alpha_2$ radiation		Plane	Int.	MoK $\alpha_1\alpha_2$ radiation	
		Sin <sup>2</sup> $\theta$ calcd.	Sin <sup>2</sup> $\theta$ obs.			Sin <sup>2</sup> $\theta$ calcd.	Sin <sup>2</sup> $\theta$ obs.
(100)	a	0.00380	...	(201)	1	0.02021	0.0202
(001)	3	.00501	0.0047	(102)	a	.02384	...
(110)	7	.00760	.0074	(121)	3	.02401	.0238
(101)	a	.00881	...	(112)	1	.02764	.0280
(111)	10	.01261	.0125	(220)	2	.03040	.0303
(200)	6	.01520	.0150	(221)	0.5	.0354	.0361
(120)	3+	.01900	.0187	(113)	0.5+	.0527	.0539
(002)	a	.02004	...	(132)	0.5+	.0580	.0583

The presence of reflections from (001), (120), (111) and (112) and the assumptions that the nitrate group has approximately the same configuration as found in other nitrates and that two such groups, irrespective of orientation, must be separated by at least 2.6 Å. eliminate all space groups save

$$P4mm, P4bm, P4, P\bar{4}2_1m, P\bar{4}, C\bar{4}2m$$

If it is assumed that the separation of the ammonium groups and of the ammonium and nitrate groups must be greater than 2.5 Å., that is,  $\frac{1}{2}c$ , the most general projection of the atomic arrangement on (001) is



If it is assumed that the closest oxygen to oxygen distances in the nitrate groups are about 2.2 Å., then the intensities, as listed in Table IV, of ( $hk0$ ) require  $x = 0.14$ ,  $y = 0.36$ , the values probably being accurate to  $\pm 0.03$ . This might correspond to positions  $u, \frac{1}{2} - u, v$ , etc., with  $u = 0.14$ , arrangements derivable from space groups  $P\bar{4}2_1m$ , and  $P4bm$ . The paucity of the data does not permit the evaluation of the three or four parameters determining the atomic arrangement in the  $c$  direction. It might be stated, however, that an arrangement derivable from space group  $P4 - (C_4^1)$  seems to be required by the data.

TABLE IV  
CALCULATED INTENSITIES FOR SOME ( $hk0$ ) OF TETRAGONAL AMMONIUM NITRATE (II)

Plane	Obs. int.	Intensity calculated			
		$x = 0.31$ $y = 0$	$x = 0.33$ $y = 0.08$	$x = 0.35$ $y = 0.12$	$x = 0.36$ $y = 0.14$
(100)	a	1.7	0.7	0.1	0.0
(110)	7	1.6	1.8	2.0	1.8
(200)	6	6.7	5.5	4.5	4.0
(120)	3+	1.6	2.4	2.7	2.8
(210)					
(220)	2	0.2	1.1	1.9	2.1
(300)	a	1.2	0.3	0.0	0.0
(310)	a	0	0.1	0.3	0.4
(130)					

The projection of the atomic arrangement on (001), which is only approximate since  $x$  and  $y$  might be appreciably different from 0.14 and 0.36, respectively, is shown as Fig. 3. The nitrate groups probably are not rotating in this modification of ammonium nitrate.

It was very difficult to obtain reliable intensity measurements since the particle size increased rapidly at  $100^\circ$ . In particular on some films reflections from (110) and (220) were weak or absent. The absence of these reflections would be compatible with an entirely different type of structure that we have previously described in a letter to the Editor of *Nature*.<sup>11</sup> We are not certain at this time that these data are to be explained by crystal orientation.

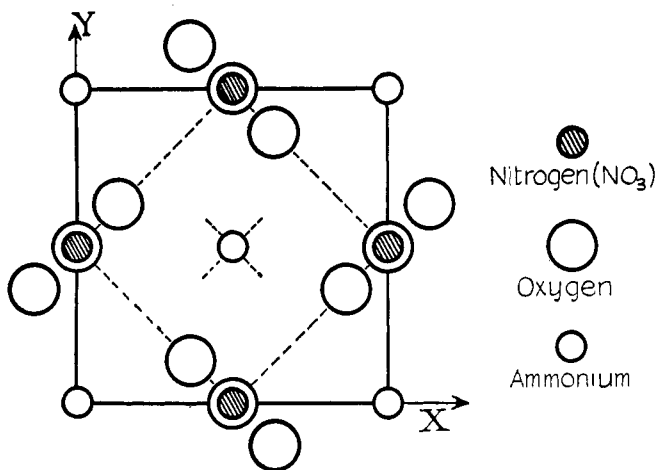


Fig. 3.—Tetragonal ammonium nitrate (II). Projection on (001).

In the microscopic work it was observed that the tetragonal modification II inverts directly to III, when it had originally been formed from III. On the other hand, if it had been formed from I by cooling from above  $125^\circ$ , it inverts metastably at  $50^\circ$  apparently to (IV) (orthorhombic room-temperature modification). It was also observed that the character of the metastable inversion depends on the specific experimental conditions of the sample, sometimes proceeding by distinct recrystallization with a high change in birefringence, at other times apparently as a single crystal transformation with practically no change in birefringence. This behavior might be due, partly or wholly, to the orientation of the crystals on the slide. The supposition suggests itself, however, that the character of the phases II and IV depends upon the previous thermal history of the salt such that II' and IV' closely similar to, but not identical with, II and IV, are formed under suitable conditions. Structures can be suggested

<sup>11</sup> F. C. Kracek, S. B. Hendricks and E. Posnjak, *Nature*, **128**, 410 (1931).

for hypothetical II' and IV' that would have optical properties identical with or closely similar to II and IV; these are not described since we have been unable to prove the existence of the hypothetical II' and IV'.

**The Modification Stable between 84.2 and 32.3° (Orthorhombic III).**—Single crystals of this modification were prepared by slowly cooling saturated solutions of ammonium nitrate in absolute alcohol from 50 to 35°. The crystals were usually long needles often showing well-developed side faces. In all cases the angles between the only four developed side faces were 90°0'. Photographs were made with a crystal rotating about its needle axis and about axes normal to the needle axis. Weissenberg photographs were made of the equatorial zone in the former case. The room in which the photographs were made was maintained at a temperature greater than 35°. CuK radiation was used in all instances.

The Weissenberg photographs show two planes of symmetry at 90° to one another. Since the crystals are biaxial it follows that the symmetry is probably orthorhombic. This modification has previously been said to be monoclinic, by Wallerant.

The dimension of the unit of structure along the needle axis as determined from the layer line separations on the rotation photographs is

$$c = 5.80 \pm 0.05 \text{ \AA.}$$

The other two dimensions of the unit of structure were determined from equatorial zone Weissenberg photographs about the *c* axis. They are

$$a = 7.06 \text{ \AA.} \qquad b = 7.66 \text{ \AA.}$$

These values are not particularly accurate since all reflections from (100) and (010) were quite weak and high orders were missing. The density calculated on the basis of such a unit of structure containing  $4\text{NH}_4\text{NO}_3$  is 1.68 g./cc. in comparison with the observed value, 1.66.

The data obtained from Weissenberg and rotating crystal photographs are in part summarized in Tables V and VI. Planes of the type (*Ok*l) with *k* odd and (*h*0l) with (*h* + *l*) odd are observed to be characteristically absent in odd orders. All space groups requiring planes of other types to be absent are eliminated by the presence of observed reflections. These absences are consistent with the requirements of space group  $Pbnm (V_h^{16})$ . It should be borne in mind that there is no indication that the crystals are orthorhombic bipyramidal, and even if they were, space groups  $Pmmm$ ,  $Pmbm$  and  $Pnmm$  could not be eliminated. The final justification for selecting space group  $Pbnm$  is that it leads to calculated intensities in agreement with the observed ones.

Possible atomic positions from  $Pbnm (V_h^{16})$  are, in general

$$(a) \quad xyz; \bar{x}, \bar{y}, z + \frac{1}{2}; \bar{x} + \frac{1}{2}, y + \frac{1}{2}, \bar{z} + \frac{1}{2}; x + \frac{1}{2}, \bar{y} + \frac{1}{2}, \bar{z} \\ \bar{x}\bar{y}\bar{z}; x, y, \bar{z} + \frac{1}{2}; x + \frac{1}{2}, \bar{y} + \frac{1}{2}, z + \frac{1}{2}; \bar{x} + \frac{1}{2}, y + \frac{1}{2}, z$$

on the reflection planes

$$(b) \quad uv\frac{1}{2}; \bar{u}\bar{v}\frac{1}{2}; \bar{u} + \frac{1}{2}, v + \frac{1}{2}, \frac{1}{2}; u + \frac{1}{2}, \bar{v}, + \frac{1}{2}, \frac{1}{2}$$

without degrees of freedom, at symmetry centers

$$(c) \quad 000; 00\frac{1}{2}; \frac{1}{2}\frac{1}{2}0; \frac{1}{2}\frac{1}{2}\frac{1}{2}$$

$$(d) \quad \frac{1}{2}00; \frac{1}{2}0\frac{1}{2}; 0\frac{1}{2}0; 0\frac{1}{2}\frac{1}{2}$$

If it is assumed that  $\text{NO}_3$  groups are present in the structure, then the observations that the maximum axis of the optical ellipsoid is parallel to  $c$  and that the intensities of reflection from (001) are second order  $m$ , and fourth order  $m. s.$ , require the ammonium ions to be on the reflection planes (b) and the oxygen ions to be at (a) and (b). The intensities of reflections from the two orders of (001) are compatible with  $z = 0.06$ , a value to be expected if the nitrate groups are stationary with a configuration similar to that found in other nitrates.

The parameters to be determined are

$x, y$  for oxygen in the general positions

$u_1, v_1$ , for oxygen on the reflection planes

$u_2, v_2$ , for ammonium groups on the reflection planes

$u_3, v_3$ , for nitrogen atoms, of  $\text{NO}_3$  group, on the reflection planes.

In this place only an outline of the method used in the parameter determination can be given. In the first approximation the effect of the nitrogen atoms of the nitrate groups on the intensities of reflection can be neglected. The remaining six parameters, which in both instances can be evaluated owing to unusual combinations of data, are separable into two groups of three each. Since structure factors for even order reflections from ( $hkl$ ) are of the type

$$A = 8F_0 \cos 2\pi n(hx) \cos 2\pi n(ky) \cos 2\pi n(lz) + 4 \sum_{r=1}^3 F_r \cos 2\pi n(hu_r) \cos 2\pi n(kv_r) \cos 2\pi n(l/4)$$

the observed absence or low intensities of reflections from (400) and (402) require  $x$  to be  $\neq 0.07$ ;  $\neq (\frac{1}{4} \neq 0.07)$ ;  $(\frac{1}{2} \neq 0.07)$  since  $\cos 2\pi(4x)$  must be approximately zero.

The high value of the optic axial angle ( $2V \text{ ca. } 90^\circ$ ) clearly indicates that the planes of the nitrate groups are not approximately parallel to (010) or (100). This and the assumption that the  $\text{NH}_4\text{-O}$  distances must be greater than 2.5 Å. greatly facilitate the determination of the other two parameters in the  $a$  direction. In particular the observations

(400)a	(200)v. s.	(101)m. s.	(600)a
(402)a	(202)s	(303)m. s.	

limit  $u_1, u_2$  and  $x$  to the following combinations

$u_1 = -0.32$	$u_1 = -0.18$	$u_1 = -0.32$	$u_1 = -0.18$
$u_2 = 0.18$	$u_2 = 0.18$	$u_2 = 0.32$	$u_2 = 0.32$
$x = -0.43$	$x = -0.07$	$x = -0.43$	$x = -0.07$

If it is now assumed that the nitrate groups have approximately the same configurations as found in other nitrates, then the above parameter limitations require  $v_1 = y \neq 0.22$ . The values of the two remaining parameters

$y$  and  $v_2$  can be determined from the intensities of reflections ( $0kl$ ) and ( $hkl$ ) in combination with the above values. The final values are

$$\begin{array}{lll} u_1 = -0.19 & x = -0.07 & v_3 = -0.19 \\ u_2 = 0.30 & v_1 = -0.05 & y = -0.27 \\ u_3 = -0.09 & v_2 = 0.52 & z = 0.06 \end{array}$$

These values are probably accurate to  $\pm 0.03$ .

TABLE V

WEISSENBERG PHOTOGRAPHIC DATA FROM ORTHORHOMBIC AMMONIUM NITRATE (III)  
ABOVE  $32^\circ$

(001) Axis of rotation; equatorial zone; CuK radiation; temperature, $35^\circ$							
	$h00$	$h10$	$h20$	$h30$	$h40$	$h50$	$h60$ $h80$
$0k0$			v. w.		m.		w. w.
$1k0$		m.	m. s.	s.	a.	m. w.	a.
$2k0$	v. w.	v. v. s.	s.	m. w.	a.	v. w.	
$3k0$		m. m. s.	m.	v. w.	m. m. s.	w.	
$4k0$	v. w.	m. m. s.	w. <sup>-</sup>	w. - v. w.			
$5k0$		m.	w. <sup>+</sup>				
$6k0$	v. w.						

The agreement between observed and calculated intensities of reflection is shown in Table VI. The intensities were calculated on the basis of the

TABLE VI

ROTATING CRYSTAL PHOTOGRAPHIC DATA FROM ORTHORHOMBIC AMMONIUM NITRATE  
(III) STABLE ABOVE  $32^\circ$

(001) Axis of rotation; CuK  $\alpha$  radiation; temperature,  $35^\circ$

Equatorial zone		1st layer line		2d layer line		3d layer line	
Plane	Int. obs. Int. calcd.	Plane	Int. obs. Int. calcd.	Plane	Int. obs. Int. calcd.	Plane	Int. obs. Int. calcd.
(010)	a. 0	(011)	a. 0	(012)	a. 0		
(100)	a. 0	(101)	v. s. 4000	(102)	a. 0		
(110)	m. 550	(111)	s. 1300	(112)	s. 400		
(020)	a. 1	(021)	s. 70	(022)	v. s. 1250		
(200)	v. w. 8	(201)	a. 0	(202)	s. 750		
(120)	s. 370	(121)	m. s. 240	(122)	s. 280	(123)	a. 20
(210)	v. s. 3000	(211)	m. s. 15	(212)	w. 80	(213)	w. 25
(220)	s. 500	(221)	m. w. 30	(222)	w. 65	(223)	m. w. 22
(030)	a. 0	(031)	a. 0	(032)	a. 0	(033)	a. 0
(130)	s. 270	(131)		(132)	a. 10	(133)	m. s. 160
(300)	a. 0	(301)	m. 200	(302)	a. 0	(303)	m. s. 160
(310)	m. 10	(311)	a. 0	(312)	m. s. 280	(313)	m. s. 35
(230)	m. s. 140	(231)	w. 5	(232)	m. 100	(233)	v. w. 30
(320)	m. 90	(321)	m. s. -s. 130	(322)	m. 15	(323)	v. w. 30
(040)	m. 660	(041)	a. 20	(042)	a. 2	(043)	m. w. 10
(140)	a. 200	(141)	m. 4	(142)	m. w. 30	(143)	m. 40
(400)	a. 8	(401)	a. 0	(402)	a. 3	(403)	a. 0
(330)	v. w. 80	(331)	a. 37	(332)	a. 0	(333)	a. 25
(410)	s. 400	(411)	a. 7	(412)	s. 140	(413)	m. 90
(240)	a. 15	(241)	m. w. 70	(242)	m. 180	(243)	v. w. 33
(420)	a. 50	(421)	a. 2	(422)	a. 3	(423)	a. 2
(050)	a. 0	(051)	a. 0	(052)	a. 0	(053)	a. 0

*F* curves described in the next section. The agreement is only moderate but since the calculated intensities are sensitive to slight changes in parameter values no particular significance can be attached to the discrepancies observed.

The atomic arrangement is illustrated in Fig. 4, which is a projection on (001). The structure is hardly as simple as that of aragonite<sup>12</sup> or potassium nitrate<sup>13</sup> in which the planes of the NO<sub>3</sub> groups are parallel to one of the pinacoids.

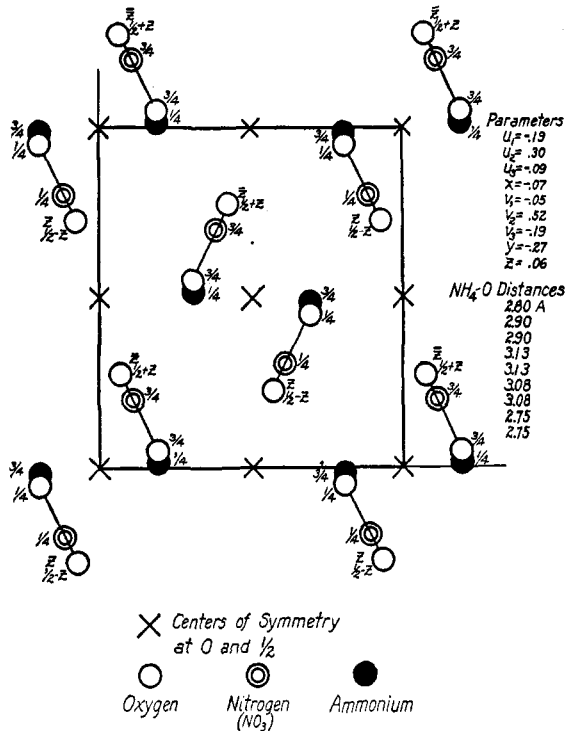


Fig. 4.—Orthorhombic ammonium nitrate (III) stable between 32.3 and 84.2°. Projection on (001) with distances above projection plane indicated.

An ammonium ion is approximately equidistant from nine oxygen ions. With the above parameter values these distances are: 2.75, 2.75, 2.80, 2.90, 2.90, 3.08, 3.08, 3.13, 3.13 Å. Each oxygen ion is approximately equidistant from three NH<sub>4</sub> groups.

An element of the structure in the *c* direction is shown as Fig. 5. This element is also to be found in the orthorhombic modification stable at room temperature. The dimension determined by it is 5.7–5.8 Å. This dimen-

<sup>12</sup> W. L. Bragg, *Proc. Roy. Soc. (London)*, **A105**, 16 (1924).

<sup>13</sup> D. A. Edwards, *Z. Krist.*, **80**, 154 (1931).

sion is further found as  $d_{(100)}$  for the tetragonal modification although it apparently is not determined by the same structural element.

**The Modification Stable between 32.3 and  $-18^\circ$  (Orthorhombic IV).—**The modification of ammonium nitrate stable at room temperatures has been described as orthorhombic bipyramidal. Single crystals were obtained by slowly cooling to  $5^\circ$  a 95% alcohol solution saturated at  $25^\circ$ . The crystals showed characteristic elongation and were plastic, as also were crystals of the other orthorhombic modification.<sup>14</sup> Weissenberg and rotating crystal photographs were made with CuK radiation and some rotating crystal photographs were made with MoK  $\alpha$  radiations. These data are in part listed in Tables VII and VIII.

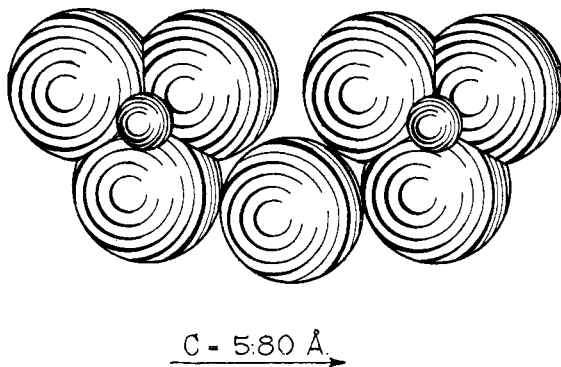


Fig. 5.—A structural element along the  $c$  axis in orthorhombic ammonium nitrate (III), stable between  $32.3$  and  $84.2^\circ$ , along the  $a$  axis in the room temperature modification (IV) ( $-18$  to  $32^\circ$ , orthorhombic), and possibly along the  $a$  (?) axis of the form (V) stable below  $-18^\circ$ . In this, and in Fig. 6, the ammonium group is represented as a sphere, the nitrate group as three oxygen spheres around a central nitrogen atom.

The value of  $b$  determined from the spacings of high orders of (010) on Weissenberg photographs is

$$b = 5.45 \text{ \AA.}$$

The values of  $a$  and  $c$  were determined approximately from the layer line separation on a rotating crystal photograph around the long direction of the crystal and from Weissenberg data, respectively. These approximate values are  $a = 5.74$ ,  $c = 4.96 \text{ \AA.}$  The measured and crystallographically determined axial ratios are:

Measured:	$c:b:a = 0.909:1:1.053$
Crystallographic:	$a:b:c = 0.909:1:1.0553$

<sup>14</sup> Compare W. L. Bond, *Phil. Mag.*, [6] **41**, 1 (1921).

Assuming that  $b$  is most accurately measured and that the crystallographic axial ratios are correct, the dimensions of the unit of structure are:

$$a = 5.75 \text{ \AA.} \qquad b = 5.45 \text{ \AA.} \qquad c = 4.96 \text{ \AA.}$$

The density calculated on the basis of such a unit of structure containing  $2\text{NH}_4\text{NO}_3$  is 1.70 g./cc. in agreement with the observed value, 1.72.

If it is assumed that the crystallographically assigned symmetry is correct and that nitrate groups similar to those found in other compounds must be preserved, then all space groups save  $Pmma$  and  $Pmmn$  are eliminated. The observed presence of reflections from (001), (110), (103) and (012) cannot be accounted for by  $Pmma$ . A satisfactory structure can be derived from  $Pmmn(V_h^{14})$ . The possible atomic positions are

N of $\text{NO}_3$	(a)	$00u; \frac{1}{2}\frac{1}{2}\bar{u}$
O of $\text{NO}_3$	(a)	$00w; \frac{1}{2}\frac{1}{2}\bar{w}$
N of $\text{NH}_4$	(b)	$0\frac{1}{2}v; \frac{1}{2}0\bar{v}$
O of $\text{NO}_3$	(e)	$0\bar{x}y; 0xy; \frac{1}{2}, \frac{1}{2} - x, \bar{y}; \frac{1}{2}, \frac{1}{2} + x, \bar{y}$
or	(f)	$x0y; \bar{x}0y; \frac{1}{2} - x, \frac{1}{2}, \bar{y}; \frac{1}{2} + x, \frac{1}{2}, \bar{y}$

An atomic arrangement with oxygen atoms at (e) is eliminated by the normal decline in the intensities of reflection from  $(0k0)$  ( $0k_{\text{even}}l$ ) and  $(0k_{\text{odd}}l)$ . There are five parameters to be determined, four in the  $c$  direction and one in the  $a$  direction.

The observation that  $(420) ca. = (220)$  and  $(600) ca. = (400)$  requires  $x = 0.18$  to  $0.20$ . Its value is taken as  $0.19 \pm 0.01$ . If it is assumed that the oxygen atoms of the nitrate groups are at the corners of equilateral triangles with the nitrogen to oxygen distance  $1.25 \text{ \AA.}$ , then

$$w = u + 0.25 \qquad y = u - 0.125$$

Two parameters defining the relative positions of the  $\text{NO}_3$  and  $\text{NH}_4$  groups remain to be determined.

It is assumed that  $F_{\text{NH}_4}$  for CuK radiation is approximately the same as determined for MoK radiation diffracted from  $\text{NH}_4\text{Cl}$ ,<sup>15</sup> that for oxygen the same as  $F_0$  for oxygen in nickel oxide (CuK radiation),<sup>16</sup> and that for  $F_{\text{N of NO}_3} = 0.35 F_0$  independent of  $\sin \theta/\lambda$ . Allowing wide variations from these assumptions the observations

$$(220) \text{ m. w. } > (311)\text{a} \\ > (101)\text{a}$$

and the observed intensities of reflections from  $(00l)$  and  $(0kl)$  require

$$u = 0.03 \pm 0.01 \qquad v = 0.57 \pm 0.03$$

It is not considered justifiable to attempt a closer restriction of the parameter values. The agreement between observed and calculated intensities of reflections is shown in Tables VII and VIII.

<sup>15</sup> R. W. G. Wyckoff and A. H. Armstrong, *Z. Krist.*, **72**, 319 (1929).

<sup>16</sup> R. W. G. Wyckoff, *Phys. Rev.*, **35**, 583 (1930).



The structure is partially illustrated in Fig. 6. The structural element shown in Fig. 5 is here repeated in the  $a$  rather than in the  $c$  direction, the corresponding dimension being 5.75 Å. An ammonium ion is approximately equidistant from six oxygen ions of nitrate groups in the

TABLE VII  
WEISSENBERG PHOTOGRAPHIC DATA FROM ORTHORHOMBIC AMMONIUM NITRATE (IV)  
BELOW 32°

(100) Axis of rotation, equatorial zone.		CuK $\alpha$ radiation.					Room temperature.
	0k0	0k1	0k2	0k3	0k4	0k5	0k6
00l		v. v. s.	w.	a.	a.	a.	w.
01l		m.	v. s.	m.-m. s.	a.	m. w.	v. w.
02l	v. v. s.	s.	w.	a.	a.	a.	w.
03l		m. w.	m. s.	m. w.	a.	w.	
04l	s.	m.	a.	a.	a.		
05l		v. w.	m. w.	a.			
06l	m.	a.	a.				
08l	m. <sup>a</sup>						

<sup>a</sup> Intensity estimated from CuK  $\beta$  line.

$$\text{Calculated intensities } I = C \frac{1 + \cos^2 2\theta}{\sin^2 \theta} F\bar{F}$$

Plane	Calcd. int.	Plane	Calcd. int.
(001)	1200 C	(011)	130 C
(002)	60 C	(012)	2100 C
(003)	5 C	(013)	1300 C
(004)	10 C	(014)	20 C
(005)	40 C	(015)	30 C
(006)	60 C	(016)	10 C

TABLE VIII  
ROTATING CRYSTAL PHOTOGRAPHIC DATA FROM ORTHORHOMBIC NITRATE (IV) BELOW  
32°

(100) Axis of rotation; MoK $\alpha$  radiation; room temperature, about 29°.

Equatorial zone			1st layer line		
Plane	Obs. int.	Calcd. int.	Plane	Obs. int.	Calcd. int.
(010)	a.	0	(110)	s.	2100
(001)	v. s.	1200	(101)	a.	140
(011)	v. w.-a.	130	(111)	v. s.	4500
(020)	v. v. s.	10000	(120)	a.	0
(002)	v. w.	60	(102)	a.	1
(021)	w.	400	(121)	a.	12
(012)	v. s.	2100	(112)	w.	400
(022)	a.	40	(122)	} w.	9
(030)	a.	0	(130)		500
(031)	a.	10	(131)	m. w.	550
(003)	a.	5	(103)	m. w.	860
(013)	m.	1300	(113)	a.	40
(032)	m.	1300	(132)	a.	30
(023)	a.	5	(123)	m. w.	1000
(040)	m.	1000	(140)	a.	0

TABLE VIII (Concluded)

2d layer line			3d layer line			4th layer line		
Plane	Obs. int.	Calcd. int.	Plane	Obs. int.	Calcd. int.	Plane	Obs. int.	Calcd. int.
(210)	a.	0	(310)	m.	240	(410)	a.	0
(201)	m. s.	1100	(301)	a.	500	(401)	a.	10
(211)	v. s.	4000	(311)	a.	60	(411)	m. w.	260
(220)	m. w.	770	(320)	a.	0	(420)	m. w.	700
(202)	a.	50	(302)	m. s.	500	(402)	a.	2
(221)	m.	1100	(321)	a.	600	(421)	a.	10
(212)	a.	100	(312)	a.	360	(412)	a.	90
(222)	a.	60	(322)	} m. w.	540			
(230)	a.	0	(330)		6			
(231)	m.	800	(331)	a.	40			
(203)	w.	160	(303)	a.	1			
(213)	a.	270	(313)	m. w.	150			

plane of the nitrate groups and from six other oxygen ions at a slightly greater distance, three each in planes  $\frac{1}{2}b$  above and below it. The distances for the parameter values listed above are: 2.96, 2.96, 2.93, 2.93, 3.14, 3.14, 3.07, 3.07, 3.33, 3.33, 3.33, 3.33 Å. The structure indicates weaker binding normal to the planes of the nitrate groups than in the planes. The slippage accounting for the plasticity of the crystals is, as would be expected, parallel to the plane of the nitrate groups.

**The Modification Stable below  $-18^\circ$  (Hexagonal? V).—**

Wallerant observed this modification to be uniaxial positive and suggested that the symmetry was tetragonal. Crenshaw and Ritter have recently<sup>17</sup> measured the heat capacities from  $-90$  to  $0^\circ$ . They observed a pronounced maximum in the neighborhood of  $-60^\circ$ , the transition being similar in character to that exhibited by certain other ammonium salts. Transitions of this type were

interpreted by Pauling as accompanying initiation of molecular rotation. In the case of ammonium chloride x-ray powder diffraction photographs of

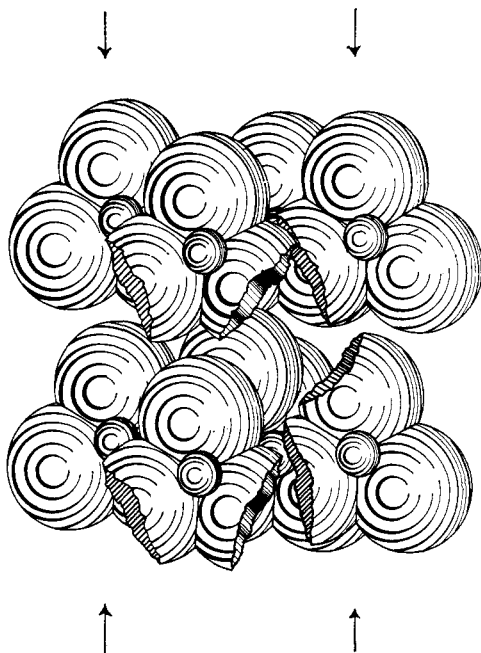


Fig. 6.—Orthorhombic ammonium nitrate (IV) stable between  $-18$  and  $32.3^\circ$ , showing the nitrate groups surrounding an ammonium group.

<sup>17</sup> Crenshaw and Ritter, *Z. physik. Chem.*, **B16**, 143 (1932).

samples below and above the transition region showed no essential changes other than those due to expansion of the lattice.<sup>18</sup> As we have previously pointed out, these results are not inconsistent with the concept of molecular rotation.<sup>2</sup>

The transition  $V \rightleftharpoons IV$  ( $-18^\circ$ ) was not recorded by Crenshaw and Ritter. There is, however, no possible ambiguity about the existence of this phase transformation. We have observed it under the microscope, by thermal analysis, and with a dilatometer. The x-ray powder diffraction patterns give final evidence of a change in phase. Although this transition is sluggish, and often is delayed so that it occurs on heating in the neighborhood of  $-5^\circ$ , it nevertheless seems as if it should have been observed in the heat capacity measurements.

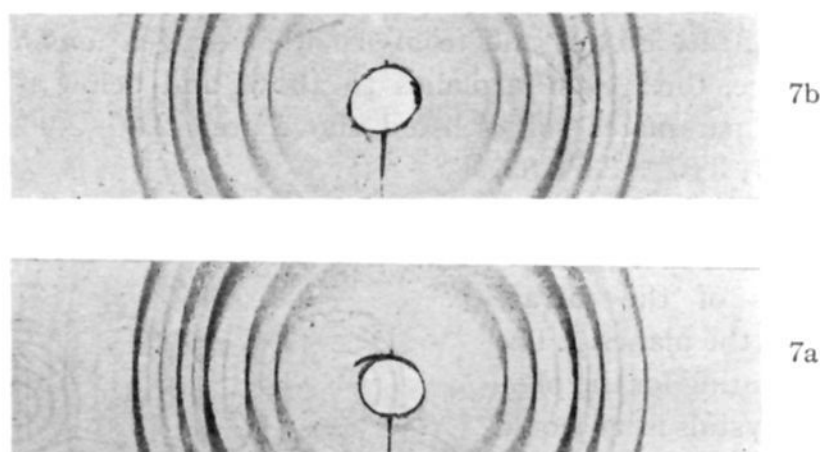


Fig. 7.—(a) A powder diffraction pattern of hexagonal ammonium nitrate (V) at  $-33^\circ$ .  $\text{CuK } \alpha$  radiation. (b) Same as (a), at  $-78^\circ$ .

We have made x-ray powder diffraction photographs with  $\text{CuK}$  radiation of samples of ammonium nitrate at  $-33^\circ$  (liquid ammonia) and  $-78^\circ$  (solid carbon dioxide). Two such photographs are reproduced as Fig. 7. The photographs, with the exception of a displacement of the pattern due to thermal expansion, are the same within the limits of observation (fine lines will probably not show in the reproduced photographs). The ammonium group is probably rotating at  $-33^\circ$ , and in the four modifications stable at higher temperatures and atmospheric pressure. This comment is speculative in that x-ray diffraction characteristics are not sufficient to afford an answer to the question.

Data obtained from photographs of ammonium nitrate at  $-78^\circ$  are listed in Table IX. There apparently is one diffraction maximum very close to the central image; however, it was not definitely proved that this actually is a part of the diffraction pattern. The positions of the maxima, including the innermost, are given by

<sup>18</sup> Simon and Simson, *Naturwissenschaften*, **38**, 880 (1926).

$$\sin^2 \theta = 0.0242 (h^2 + hk + k^2) + 0.00234 l^2$$

for CuK  $\alpha_1$  radiation. This corresponds to a hexagonal lattice having  $a = 5.72$ ,  $c = 15.9$  Å. The density calculated on the basis of a unit of structure containing  $6\text{NH}_4\text{NO}_3$  is 1.76 g./cc. in agreement with 1.74, the determined value. It is to be emphasized that this integral number, 6, of  $\text{NH}_4\text{NO}_3$ , in the unit of structure would be most unusual if the lattice dimensions were obtained from a spurious agreement between observed and calculated  $\sin^2 \theta$  values.

TABLE IX

POWDER PHOTOGRAPHIC DATA FROM HEXAGONAL (?) AMMONIUM NITRATE (V) BELOW  $-16^\circ$

CuK  $\alpha$  radiation; temperature,  $-78^\circ$ ;  $\sin^2 \theta = 0.0242 (h^2 + hk + k^2) + 0.00234 l^2$ .

Plane	$\sin^2 \theta$ (calcd.)	$\sin^2 \theta$ (obs.)	Est. intensity	Plane	$\sin^2 \theta$ (calcd.)	$\sin^2 \theta$ (obs.)	Est. intensity
(001)	0.00234	0.0018	w.	(113)	0.0937	0.0912	0.5
(002)	.00936			(200)	.0968	.0984	2.0
(003)	.0211			(201)	.0991		
(100)	.0242	.0245	5.0	(202)	.1062		
(101)	.0265			(106)	.1085	.1086	2.0
(102)	.0335			(114)	.1100		
(004)	.0375	.0375	6.0	(007)	.1136		
(103)	.0453			(203)	.1178	.1174	8.0
(005)	.0585			(115)	.1311		
(104)	.0616	.0621	10.0	(204)	.1342	} .1356	0.5
(110)	.0726	.0725	1.0	(107)	.1378		
(111)	.0749	.0744	0.5	(008)	.1497	.1463	0.5
(112)	.0819	.0804	0.5	(205)	.1553	.1550	0.5
(105)	.0827	} .0832	8.0				
(006)	.0842						

The value of  $a_0$  (5.72 Å.) is approximately the same as  $a_0$  (5.75 Å.) of the room temperature modification,  $c_0$  (5.80 Å.) of the second orthorhombic modification, and  $a_0$  (5.74 Å.) of the tetragonal form. It is possible that it coincides with the direction of characteristic elongation, as is the case for the two orthorhombic modifications. This, the positive optical character, and the value of maximum index of refraction, clearly show that the planes of the nitrate groups are approximately parallel to the  $c$  axis. The intensities of reflections from the various orders of (001) are most unusual; (001) w. or a., (002)a., (003)a., (004)m. s., (005)a., (007)a., (008)w. w. We were unable to see the manner in which such an intensity distribution could be obtained in a hexagonal lattice with the atomic arrangement restricted as mentioned above. The, at least, pseudo-uniaxial character and hexagonal lattice require the nitrate groups to be approximately repeated in one or two groups of three planes containing the optic axis at angles of  $20^\circ$ . If in such a case the nitrate groups were not distributed according to hexagonal symmetry along the  $c$  axis, the crystals would

nevertheless be approximately uniaxial. For these reasons we would consider it quite possible that the symmetry may be orthorhombic, monoclinic or triclinic.

### Summary

The structures of three of the six crystalline modifications of ammonium nitrate have been determined and data, leading to partial structure determinations, have been obtained from two other forms. The nitrate groups are rotating in at least three orthogonal directions in the cubic (I) form which is stable between 125.2 and 169.5°;  $a_0 = 4.40 \text{ \AA}$ .,  $1\text{NH}_4\text{NO}_3$  in the unit of structure. The structural characteristics of the other modifications examined are:

Tetragonal (II) (125.2 – 84.2°)  $a = b = 5.75 \text{ \AA}$ .,  $c = 5.00 \text{ \AA}$ .,  $2\text{NH}_4\text{NO}_3$  in the unit of structure.  $2\text{NH}_4$  at  $00$ ;  $\frac{1}{2}\frac{1}{2}$ ;  $2\text{N}$  of  $\text{NO}_3$  at  $0\frac{1}{2}$ ,  $\frac{1}{2}0$ ; 2 oxygen at  $0\frac{1}{2}$ ,  $\frac{1}{2}0$ ; 4 oxygen at  $xy$ ,  $\bar{x}\bar{y}$ ,  $\bar{y}x$ ,  $y\bar{x}$ , with  $x = 0.14$ ,  $y = 0.36$ . The arrangement in the  $c$  direction was not determined.

Orthorhombic (III) (84.2 – 32.3°)  $a = 7.06 \text{ \AA}$ .,  $b = 7.66 \text{ \AA}$ .,  $c = 5.80 \text{ \AA}$ .,  $4\text{NH}_4\text{NO}_3$  in the unit of structure. Space group  $Pbnm(V_h^{16})$ , 8 oxygens in general positions with  $x = -0.07$ ,  $y = -0.27$ ,  $z = 0.06$ , 4 oxygen on reflection planes with  $u_1 = -0.19$ ,  $v_1 = -0.05$ ,  $4\text{NH}_4$  on reflection planes with  $u_2 = 0.30$ ,  $v_2 = 0.52$ , 4 nitrogen on reflection planes with  $u_3 = -0.09$ ,  $v_3 = -0.19$ . The parameter values are probably accurate to  $\pm 0.03$ .

Orthorhombic (IV) (32.3° to  $-18^\circ$ )  $a = 5.75 \text{ \AA}$ .,  $b = 5.45 \text{ \AA}$ .,  $c = 4.96 \text{ \AA}$ ., with  $2\text{NH}_4\text{NO}_3$  in the unit of structure. Space group  $Pmnm(V_h^{18})$  with 4 oxygen at  $x0y$ ;  $\bar{x}0y$ ;  $\frac{1}{2} - x, \frac{1}{2}\bar{y}$ ;  $\frac{1}{2} + x, \frac{1}{2}\bar{y}$ , with  $x = 0.19$ ,  $y = -0.095$ , oxygen and 2 nitrogen at  $00u$ ,  $\frac{1}{2}\frac{1}{2}\bar{u}$ , with parameter 0.28 and 0.03, respectively, and  $2\text{NH}_4$  at  $0\frac{1}{2}v$ ;  $\frac{1}{2}0\bar{v}$  with  $v = 0.57$ .

The form (V) stable below  $-18^\circ$  gives a powder diffraction pattern in agreement with a hexagonal unit of structure having  $a = 5.75 \text{ \AA}$ .,  $c = 15.9 \text{ \AA}$ . containing  $6\text{NH}_4\text{NO}_3$ . The data indicate that the true lattice might be only pseudo-hexagonal. Diffraction patterns of samples at  $-33$  and  $-78^\circ$  are identical save for displacement due to expansion, despite the existence of a gradual transition at  $ca. -60^\circ$ .

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