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## GRADUAL TRANSITION IN SODIUM NITRATE. II. THE STRUCTURE AT VARIOUS TEMPERATURES AND ITS BEARING ON MOLECULAR ROTATION

BY F. C. KRACEK, E. POSNJAK AND S. B. HENDRICKS

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Results of measurements which establish a gradual transition in crystalline sodium nitrate were presented in a previous paper.<sup>1</sup> It was shown that the transition is completed at 275°, but that the changes in heat capacity and volume are distributed over an extended temperature interval. These phenomena are markedly different from those accompanying a typical change of crystal phase in one component system. The experimental values at all temperatures are reproducible and wholly free from hysteresis. The results support the thesis that no abrupt change of phase takes place below the melting point. This conclusion is supported by observations on the optical properties of the crystals under a heating microscope.

A number of examples of the above type of behavior have been mentioned in the previous paper. We shall refer here specifically to the extensive observations on the behavior of ammonium chloride, ammonium bromide and certain other ammonium salts.<sup>2</sup> The transitions in these salts are complete at -50 to -30°, depending on the anion. It was first suggested that these abnormal characteristics were to be explained by transition of the ammonium ion from one energy state to another; the nature of the energy states was not specified.

A second explanation for gradual transition in the solid state has been suggested by L. Pauling.<sup>3</sup> He, and later T. E. Stern,<sup>4</sup> treated by the wave mechanics, the problem of a diatomic homopolar molecule free to rotate in an axially symmetrical field of force. From their analysis it follows that the temperature at which transition from oscillational to rotational motion takes place within the crystal can be calculated approximately as  $T = 2V_0/k$ , where  $V_0$  is a constant in the potential function  $V = V_0(1 - \cos 2\theta)$  and  $k$  is Boltzmann's constant. For the ammonium salts  $T$ , calculated, is 240° K., in approximate agreement with the observed values.

It has not yet been possible to differentiate between these two explanations, or to eliminate other hypotheses elucidating the behavior of the ammonium salts. The very direct method of studying the electronic

<sup>1</sup> F. C. Kracek, *THIS JOURNAL*, **53**, 2609 (1931).

<sup>2</sup> F. Simon, *Ann. Physik*, **68**, 241 (1922); Simon, Simson and Ruhemann, *Z. physik. Chem.*, **129**, 339 (1927).

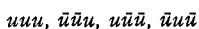
<sup>3</sup> L. Pauling, *Phys. Rev.*, **36**, 430 (1930).

<sup>4</sup> T. E. Stern, *Proc. Roy. Soc. (London)*, **130A**, 551 (1931).

distribution in the lattice as a function of the temperature, by the coherent scattering of x-radiation, is inapplicable as a criterion for the second explanation, in the case of these salts, since the scattering power of hydrogen is very small. X-ray diffraction photographs give no indication of structural change.<sup>5</sup> We may recall, however, the apparent conflict between the symmetry of ammonium chloride and ammonium bromide (note also the ammonium alums) at room temperature as deduced from the face development and etch figures in comparison with that deduced from the x-ray data if the hydrogen atoms are to occupy fixed positions. This conflict can be reconciled by assuming that the ammonium ion acts, crystallographically as well as chemically, as a single entity.<sup>6</sup> A rotating ammonium group would satisfy this requirement for the structure at room temperature.

The most important difference in the behavior of the ammonium salts is that the transition in ammonium chloride is accompanied by an increase in volume, while for ammonium bromide and ammonium dihydrogen phosphate there is a gradual contraction within the transition interval.<sup>7</sup> These observations have been verified by studying the effect of pressure on the transition for ammonium chloride and ammonium bromide.<sup>8</sup> It was suggested that this difference in behavior was indicative of two different processes. Neither of the two suggested explanations given above predicts the nature of the volume change accompanying the transition; in neither case is it justifiable, *a priori*, to expect the volume change always to be of the same sign.

Although the positions of the hydrogen atoms in crystalline ammonium chloride and ammonium bromide at some low temperature cannot now be determined, it is possible that they are at



or rotated  $45^\circ$  about the normal to (001) from such positions, in which case the unit of structure would have to contain more than  $1\text{NH}_4\text{X}$  or else the symmetry would have to be less than cubic. In the former case, an arrangement derivable from space group,  $P\bar{4}3m$ , it might be expected for structural reasons that displacement of the hydrogen atoms would, over some temperature range, result in a decrease in volume. In the second case the expected change would be for the volume to increase. No particular emphasis can be placed on this suggestion; it is brought forward merely as an illustration.

The hypothesis of molecular rotation within the lattice offers a plausible explanation of the anomalous behavior of several other substances. The

<sup>5</sup> Simon and Simson, *Naturwiss.*, **38**, 880 (1926).

<sup>6</sup> R. W. G. Wyckoff, "The Structure of Crystals," New York, 1924, p. 320.

<sup>7</sup> Simon and Bergmann, *Z. physik. Chem.*, **8B**, 255 (1930).

<sup>8</sup> P. W. Bridgman, paper presented at the spring meeting of the National Academy of Sciences in Washington, April, 1931.

consequences of this hypothesis are of great importance in the theory of the solid state; it is accordingly obvious that each new case must be tested for possible contradictions. In sodium nitrate the physical conditions are favorable for a detailed examination in view of the accessibility of the temperature region over which the gradual transition is extended. The structure, in addition to the other criteria of the transition as previously described, can be studied over the whole range of temperatures. The ambiguity encountered in the ammonium salts, due to the low scattering power of the hydrogen atoms, does not enter in this case to vitiate the results by uncertainties in the experimental data.

The treatment given in the following pages examines the applicability of the rotation hypothesis by a comparison of the observed diffraction data with what might be expected on the basis of the hypothesis. It may be pointed out at once that the observed changes in the structure are not those which would be expected from a polymorphic change. The most important criterion observed concerns the oxygen atoms, which, like the sodium and the nitrogen atoms, occupy equilibrium positions in the lattice at low temperatures. At temperatures above  $200^\circ$  the reflections from planes in which the oxygen atoms alone contribute are progressively weakened until at  $280^\circ$ , where the gradual transition is completed, only uncertain traces of these reflections could be found. Otherwise, there is no major change in the structure within the transition interval, in good agreement with the optical examination and the behavior as exhibited by other physical properties.

### The Structure of Sodium Nitrate below $185^\circ$

Sodium nitrate crystallizes in the ditrigonal scalenohedral division of the hexagonal system. At  $25^\circ$  the unit of structure containing  $2\text{NaNO}_3$  has  $a = 6.32 \text{ \AA}$ . and  $\alpha = 47^\circ 14'$ ,<sup>9</sup> corresponding to the crystallographically observed angle of  $102^\circ 42.5'$ . The atomic arrangement according to Wyckoff is

$$\begin{aligned} \text{Na atoms at } & \frac{1}{4} \frac{1}{4} \frac{1}{4}; \frac{3}{4} \frac{3}{4} \frac{3}{4} \\ \text{N atoms at } & 0 \ 0 \ 0; \frac{1}{2} \frac{1}{2} \frac{1}{2} \\ \text{O atoms at } & u \ \bar{u} \ 0; \frac{1}{2} - u, \frac{1}{2} + u, \frac{1}{2} \\ & \bar{u} \ 0 \ u; \frac{1}{2} + u, \frac{1}{2}, \frac{1}{2} - u \\ & 0 \ \bar{u} \ u; \frac{1}{2}, \frac{1}{2} - u, \frac{1}{2} + u \\ & \text{with } u = \frac{1}{4} \text{ within close limits.} \end{aligned}$$

<sup>9</sup> W. L. Bragg, *Proc. Roy. Soc. (London)*, **89A**, 468 (1913). R. W. G. Wyckoff, *Phys. Rev.*, **16**, 149 (1920).

The data obtained from powder photographs taken at temperatures below 185° are listed in Table I. Most of these were taken with a General Electric apparatus which was equipped with a special device for heating the sample; data from other photographs, taken by C. J. Ksanda at room temperature with a different apparatus, were also available to check the precision of the films. MoK $\alpha$  radiation was used throughout.

TABLE I

POWDER DIFFRACTION DATA ON SODIUM NITRATE TO 185°. MoK $\alpha$  RADIATION  
Room temperature,  $\sin^2\theta = 0.006956(h^2 + k^2 + l^2) - 0.005626(hk + hl + kl)$

hkl	Intensity		$\frac{\sin^2\theta}{\text{Calcd.}}$	$\sin^2\theta$ observed				
	Obs.	Calcd.		25° <sup>a</sup>	105°	150°	180°	185°
110	2	1.2	0.00829	0.00823	0.00828	0.00828	0.00833	0.00837
211	> 10	27	.01361	.01360	.01364	.01374	.01355	.01355
222	4	4.2	.01596	.01596	.01585	.01585	.01553	.01553
1 $\bar{1}$ 0	3	3.1	.01954	.01951	.01968	.01968	.01985	.01977
210 <sup>b</sup>	5,7	10.5	.02353	.02349	.02362	.02362	.02362	.02341
200	4	3	.02782	.02787	.02789	.02802	.02802	.02789
220	1	1.4	.03314	.03319	.03312	.03338	.03320	.....
323	7	9.3	.03489	.03495	.03474	.03437	.03400	.03400
321	3	5.6	.03550	.03544	.....	.03565	.03527	.03521
2 $\bar{1}$ 0 <sup>b</sup>	3	4.4	.04603	.04605	.04618	.04623	.04631	.04618
2 $\bar{1}$ 1	2	2.1	.04736	.04740	.04744	.04783	.04774	.04774
433	...	< 0.1	.05085	.....	.....	.....	.....	.....
310	1+	1.6	.05268	.0530	.0528	.0528	.0528	.0530
422	...	0.7	.05442	.....	.....	.....	.....	.....
432 <sup>b</sup>	1	2.8	.0554	.0554	.....	.....	.....	.0546
320 <sup>b</sup>	2	2.7	.0567	.0566	.0567	.0568	.0564	.0566
2 $\bar{1}$ 1	2	4.0	.0586	.0588	.0585	.0591	.0589	.0588
444	2	2.6	.0638	.0639	.0624	.0624	.0616	.0620
421 <sup>b</sup>	2	2.0	.0673	.0673	.0669	.0671	.0667	.0669
442	0.5	1.0	.0704	.0706	.....	.....	.....	.....
431	0.5	1.0	.0740	.....	.0734	.0734	.0733	.0730
411	}	1	0.7	.0746	.0743	.....	.....	.....
330								
2 $\bar{2}$ 0	0.5	0.5	.0782	.0782	.0782	.....	.0783	.....
543	1	0.8	.0834	.0835	.....	.....	.0808	.0789
3 $\bar{1}$ 0	...	< 0.1	.0854	.....	.....	.....	.....	.....
532	0.5	1.4	.0899	.0893	.0890	.....	.0887	.....
3 $\bar{2}$ 1	3	4.1	.0918	.0916	.0918	.0921	.0919	.0919
554	...	< 0.1	.0934	.....	.....	.....	.....	.....
420	...	< 0.1	.0941	.....	.....	.....	.....	.....
542 <sup>b</sup>	0.5	0.7	.0992	.0996	.....	.....	.....	.....
222	0.5	0.1	.1060	.1061	.....	.....	.....	.....
400	0.5	0.6	.1113	.1111	.....	.....	.....	.....
521	2	2.1	.1130	.1128	.1122	.1122	.1122	.1117

<sup>a</sup> Average of four determinations. <sup>b</sup> Planes in which O atoms alone contribute to reflections.

There are no significant changes in the intensities of the reflections in the region 25 to 185°. The agreement between the observed values of

$\sin^2\theta$  and values calculated on the basis of  $\alpha = 47^\circ 14'$  and  $a = 6.32$  is well within the error of measurement for the data at room temperature. With increase in the temperature the observed values of  $\sin^2\theta$  for some of the planes change progressively; due apparently to thermal expansion.

Intensities of reflections were calculated on the basis of the equation

$$\rho = c \cdot J \cdot \frac{1 + \cos^2 2\theta}{\sin 2\theta} \cdot F\bar{F}$$

employing the  $F$  values published by Bragg and West<sup>10</sup> for sodium and oxygen and assumed  $F$  values for nitrogen equal to three-fourths the corresponding values for oxygen. The agreement between observed and calculated intensities of reflections is satisfactory; note Table I, which lists all the possible planes having  $\sin^2\theta$  for  $\text{MoK}\alpha$  radiation less than 0.11. No reflections that are required to be absent by the structure are observed.

### The Structure of Sodium Nitrate in the Transition Region

Data from photographs taken at 215, 250 and 280° are listed in Tables II, III and IV and are graphically illustrated in Fig. 1. In this region the changes in the dimensions of the lattice accompanying thermal expansion are unusually large as compared with other substances and with sodium nitrate at lower temperatures. Considerable changes are necessary in the constants of the expressions used for calculating the values of  $\sin^2\theta$

$$\sin^2\theta = c_1(h^2 + k^2 + l^2) + c_2(hk + kl + hl)$$

$$\text{where } c_1 = (\lambda/4a^2) \frac{\sin^2 \alpha}{1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha}$$

$$c_2 = (\lambda/4a^2) \frac{2(\cos^2 \alpha - \cos \alpha)}{1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha}$$

The following values of the lattice dimensions at 280° were calculated using 0.710 Å. as the effective wave length

$$\left. \begin{array}{l} a = 6.56 \text{ \AA.} \\ \alpha = 45^\circ 35' \\ V = 131.2 \text{ \AA.}^3 \end{array} \right\} \text{at } 280^\circ$$

where  $V$ , the volume of the unit of structure containing  $2\text{NaNO}_3$ , is equal to  $a^3 \sin \alpha \sin \delta$ ,  $\sin(\delta/2) = \sin(\alpha/2)/\sin \alpha$ . The calculated density is 2.137. This agrees within the limits of experimental error, arising chiefly from variations in temperature during the exposure, with the measured values<sup>11</sup> 2.138 at 275° and 2.133 at 280°.

Extraordinary changes take place at temperatures above 215° in the intensities of reflections from some planes as compared with 25°. Oxygen atoms alone contribute to odd order reflections from planes with one odd and two even indices, whose sum is not divisible by four ( $\sigma e e$ ;  $(e_1 + e_2)/n$

<sup>10</sup> W. L. Bragg and J. West, *Z. Krist.*, **69**, 118 (1929).

<sup>11</sup> See the preceding paper, *THIS JOURNAL*, **53**, 2609 (1931).

TABLE II  
POWDER DIFFRACTION DATA ON SODIUM NITRATE AT 215°. MoK $\alpha$  RADIATION  
 $\sin^2\theta = 0.00694(h^2 + k^2 + l^2) - 0.00566(hk + hl + kl)$

<i>hkl</i>	Intensity		$\sin^2\theta$	
	Obs.	Calcd.	Obs.	Calcd.
110	2	1.2	0.00824	0.00822
211	> 10	27	.01336	.01334
222	3	4.2	.01525	.01536
$\bar{1}\bar{1}0$	3	3.1	.01985	.01954
210 <sup>a</sup>	5	10.5	.02341	.02338
200	4	3	.02789	.02776
220	...	1.4	.....	.03238
323	4	9.3	.03378	.03382
321	1	5.6	.03508	.03490
2 $\bar{1}0$ <sup>a</sup>	2	4.4	.04627	.04602
2 $\bar{1}1$	1	2.1	.04744	.04730
433	...	< 0.1	.....	.04918
310	0.5	1.6	.05244	.05242
422	...	0.7	.....	.05336
432 <sup>a</sup>	...	2.8	.....	.05410
320 <sup>a</sup>	0.5	2.7	.0560	.0563
$\bar{2}11$	1	4.0	.0590	.0586
444	0.5	2.6	.0610	.0614
421 <sup>a</sup>	0.5	2.0	.0667	.0665
442	...	1.0	.....	.0687
431	...	1.0	.....	.0729
330	...	0.7	.....	.0740
2 $\bar{2}0$	...	0.5	.....	.0782
543	...	0.8	.....	.0810
3 $\bar{1}0$	...	< 0.1	.....	.0854
532	...	1.4	.....	.0883
32 $\bar{1}$	1+	4.1	.0912	.0915

<sup>a</sup> Planes in which O atoms alone contribute to reflections.

$\neq 4$ ). At 250° only (120) persists, and at 280° only uncertain traces of any reflections due to oxygen atoms alone are observable on the films. This indicates that the oxygen atoms at temperatures above 275°, the temperature at which the gradual transition is completed, scatter x-radiation as if they were on the trigonal axes. This observation is in harmony with the postulate that the nitrate ions are rotating about the trigonal axes.

If it is assumed that the nitrate groups, at temperatures above 275°, scatter x-radiation as pseudo-atoms on the trigonal axes, the  $F$  values reduce to the following two cases

$$\begin{aligned} (a) \quad (h + k + l)/4 = n, \quad F = 2\text{NO}_3 + 2\text{Na} \\ (b) \quad (h + k + l)/4 \neq n, \quad F = 2\text{NO}_3 - 2\text{Na} \end{aligned}$$

For large values of  $\sin^2\theta$  only reflections from planes of type (a) would be expected to persist. This is true; note Table IV, at 280° for values of  $\sin^2\theta > 0.05204$  ((422)).

TABLE III  
POWDER DIFFRACTION DATA ON SODIUM NITRATE AT 250°. MoK $\alpha$  RADIATION  
 $\sin^2\theta = 0.00692(h^2 + k^2 + l^2) - 0.00568(hk + hl + kl)$

$hkl$	Intensity		$\sin^2\theta$	
	Obs.	Calcd.	Obs.	Calcd.
110	2	1.2	0.00828	0.00816
211	> 10	27	.01320	.01312
222	2	4.2	.01488	.01488
1 $\bar{1}$ 0	4	3.1	.01977	.01952
210 <sup>a</sup>	1	10.5	.02341	.02324
200	5	3	.02776	.02768
220	...	1.4	.....	.03264
323	7	9.3	.03280	.03296
321	2	5.6	.03452	.03440
2 $\bar{1}$ 0 <sup>a</sup>	...	4.4	.....	.04596
2 $\bar{1}$ 1	1+	2.1	.04774	.04720
433	...	< 0.1	.....	.....
310	...	1.6	.....	.0522
422	1	0.7	.0528	.0525
432 <sup>a</sup>	...	2.8	.....	.0530
320 <sup>a</sup>	...	2.7	.....	.0559
2 $\bar{1}$ 1	2	4.0	.0590	.0586
444	...	2.6	.....	.0595
421 <sup>a</sup>	...	2.0	.....	.0658
442	...	1.0	.....	.0674
431	1-	1.0	.0718	.0720
330	...	0.7	.....	.0734
2 $\bar{2}$ 0	1	0.5	.0783	.0781
543	...	0.8	.....	.0790
3 $\bar{1}$ 0	...	< 0.1	.....	.0862
532	0.5	1.4	.0870	.0869
32 $\bar{1}$	1	4.1	.0913	.0912
554	...	< 0.1	.....	.....
420	...	< 0.1	.....	.....
542 <sup>a</sup>	...	0.7	.....	.....
2 $\bar{2}$ 2	...	0.1	.....	.....
400	...	0.6	.....	.1107
521	1	2.1	.1109	.1110

<sup>a</sup> Planes in which O atoms alone contribute to reflections.

The calculation of intensities of reflections for planes having spacings greater than that of (422) presents a most interesting difficulty. A rotating NO<sub>3</sub> group would be expected to have a time average electronic distribution more closely resembling a torus or a hollow sphere than a sphere. In the case of a torus its scattering power would certainly not be a function of  $\theta$  alone but would depend markedly upon the orientation of the NO<sub>3</sub> group relative to the reflecting plane. For planes having approximately the same values of  $\theta$ , the maximum value of  $F$  would be expected for that plane most closely perpendicular to the trigonal axes; the minimum for a plane parallel to the trigonal axes. That such an effect

TABLE IV

POWDER DIFFRACTION DATA ON SODIUM NITRATE AT 280–290°. MoK $\alpha$  RADIATION

$$\sin^2\theta = 0.00691(h^2 + k^2 + l^2) - 0.00569(hk + hl + kl)$$

$hkl$	$\sin^2\theta$			Intensities		
	Calcd.	Obs.	Obs.	Obs.	Calcd.	B
110	0.00813	0.00815	0.00824	3, 2	1.2	10
211	.01301	.01295	.01320	> 10	27	27
222	.01464	.01457	.01459	2, 5	4.2	1.5
1 $\bar{1}$ 0	.01951	.01938	.01968	3, 4	3.1	15.3
210 <sup>b</sup>	.02317	(.02332)	.....	< 0.5	10.5	0.0
200	.02764	.02742	.02789	2, 4	3	0.5
220	.03252	.03247	.03254	7, 7	9.3	7.5
332	.03253					
321	.03415					
2 $\bar{1}$ 0 <sup>b</sup>	.04593	.....	(.04516)	< 0.5	4.4	0.0
2 $\bar{1}$ 1	.04715	.04679	.04778	1, 2	2.1	0.6
433	.....	.....	.....	.....	< 0.1	< 0.1
310	.05203	.05226	.05244	1, 1	0.7	3.8
422	.05204					
432 <sup>b</sup>	.05245					
320 <sup>b</sup>	.0557	(.0560)	.....	< 0.5	2.7	0.0
2 $\bar{1}$ 1	.05853	.0579	.0586	1, 2	2.6	1
444	.05856					
421 <sup>b</sup>	.0655					
442	.0667	.....	.....	.....	1.0	< 0.1
431	.0716	.0718	.0721	0.5, 0.5	1.0	4
330	.0732	.....	.....	.....	0.7	< 0.1
2 $\bar{2}$ 0	.07804	.0781	.0785	0.5, 1	0.8	3.5
543	.07807					
3 $\bar{1}$ 0	.....					
532	.0862	.....	.....	.....	1.4	< 0.1
32 $\bar{1}$	.0911	.0905	.0917	1, 1	4.1	2.5
554	.....	.....	.....	.....	< 0.1	< 0.1
420	.....	.....	.....	.....	< 0.1	< 0.1
542 <sup>b</sup>	.....	.....	.....	.....	0.7	0.0
2 $\bar{2}$ 2	.....	.....	.....	.....	0.1	< 0.1
400	.1106	.1101	.1107	0.5, 1	2.1	2.2
521	.1106					

<sup>a</sup> A, oxygen atoms in fixed positions. B, NO<sub>3</sub> group at a point on trigonal axes.

<sup>b</sup> Planes in which oxygen alone contributes to reflections.

plays a prominent role can be ascertained from attempts to calculate intensities of reflections for (110) (222), (1 $\bar{1}$ 0) and (200) on the basis of any assumed monotonic type of F curve for the nitrate group. A similar factor was encountered in a minor degree in the analysis of the crystal structure of potassium chlorate.<sup>12</sup>

We have calculated the intensities of reflections for planes of the type mentioned above, assuming that  $F(\text{NO}_3) = F(\text{N}) + F(3\text{O}) = F(3\frac{3}{4}\text{O})$ .

<sup>12</sup> W. H. Zachariasen, *Z. Krist.*, 71, 501 (1929).



As would be expected, there is no agreement between the observed and calculated intensities of reflections. As a matter of fact, the better agreement for planes of this type is obtained by assuming that the oxygen atoms occupy fixed positions. Such an assumption is more nearly in

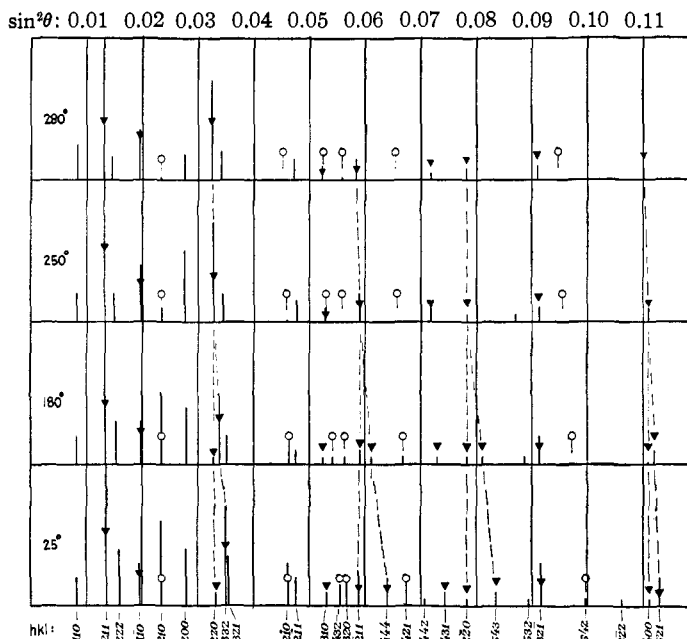


Fig. 1.—Representation of powder diffraction data on sodium nitrate at various temperatures, showing the positions (abscissa) and relative estimated intensities (ordinate) of the lines. Three types of planes required by the structure are differentiated by circles, triangles and absence of marking. The ordinates of the circles and triangles bear no relation to intensities (calculated values may be found in the tables). Circles differentiate planes in which only oxygen contributes to reflections; note the great changes in the observed intensities of these lines with temperature. Triangles mark lines due to mixed planes in which the effect due to Na adds to that due to N and O ( $h + k + l = e = 4n$ ); the remaining lines result from planes in which the effect due to Na subtracts from that of the other atoms ( $h + k + l = e \neq 4n$ ).

harmony with the physically allowable electronic distribution for a torus (three points on the rim) rather than the electronic distribution concentrated at points on the trigonal axes.

We may conclude, then, that there is no serious objection to the hypothesis of molecular rotation as an explanation for the gradual transition in sodium nitrate. At absolute zero the sodium, nitrogen and oxygen atoms occupy equilibrium positions in the lattice. As the temperature

is increased, particularly from above 150 to 275°, the average amplitudes of vibration of the oxygen atoms about their equilibrium positions progressively increase. This change is accompanied by changes in the intensities of x-ray reflections from the crystal planes. At 280° the rotational degree of freedom is apparently fully excited, the nitrate groups rotating about the trigonal axes of the solid. The lattice probably expands normally from this temperature to the melting point at 309.5°. There has been no abrupt change in phase at any one temperature, hence instead of polymorphism we have morphotropism associated with the rotation of the nitrate ions.

It is significant that during the transition interval the axial angle  $\alpha$  decreases as the temperature increases. The net increase in volume during this interval is produced by an abnormal increase in the value of  $a$ .

The rotational degree of freedom of the nitrate group about an axis normal to the plane of the group is apparently the one excited in the region 150 to 280°. The other two rotational degrees of freedom about axes in the plane of the nitrate group are probably degenerate below the melting point. The moment of inertia is greatest in the first case. It is probable that this characteristic is to be accounted for by a considerably smaller value of  $V_0$ , which indeed is suggested by the atomic arrangement at room temperature.

### Summary

It has been shown on the basis of powder diffraction data at a number of temperatures from 25 to 280° that the gradual transition observed in sodium nitrate can be satisfactorily accounted for by the initiation of rotation of the nitrate ion about the trigonal axes of the crystal. The symmetry of the crystal remains trigonal; the constants of the lattice at 280° are  $\alpha = 45^\circ 35'$ ,  $a = 6.56 \text{ \AA}$ ., as compared with  $\alpha = 47^\circ 14'$  and  $a = 6.32 \text{ \AA}$ . at 25°.

WASHINGTON, D. C.