

## Reflection of X-rays with change of frequency— Part III. The case of sodium nitrate

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### 1. Introduction

Sodium nitrate is very similar in crystalline form and structure to calcite, but owing to the lower atomic weight of sodium, is better suited than calcite for X-ray studies with a copper-target tube. Its physical properties present a striking contrast with those of diamond. The melting point of the crystal is  $309.5^{\circ}\text{C}$ , indicating that its characteristic frequencies are low. The unit cell contains two ions of Na and two of  $\text{NO}_3$  situated along the trigonal axis of symmetry. There are thus ten atoms in the cell occupying non-equivalent positions, and the possible modes of oscillation of the interpenetrating lattices are therefore numerous. Theory indicates that there should be eighteen fundamental frequencies of vibration, nine of them being doubly degenerate. Ten of these fundamentals should have low frequencies representing translatory movements of the Na and  $\text{NO}_3$  ions and rotational oscillations of the latter. The remaining eight fundamentals should have high frequencies corresponding to the internal vibrations of the  $\text{NO}_3$  ions. Actually, the crystal exhibits two low and three high frequencies in light-scattering, while in infra-red absorption, three low and three high frequencies have been observed, all these being different. Three low and two high frequencies are theoretically forbidden from appearing either in light-scattering or in infra-red absorption. The agreement with theory is thus nearly complete. Diagrams illustrating the different possible modes of oscillation will be found in a recent paper by Bhagavantam and Venkatarayudu (1939). Nedungadi (1939*a*) has studied in considerable detail, the influence of temperature on the spectrum of light-scattering in sodium nitrate, and has found that the two low frequency lines with wave-number shifts 98 and 185 are displaced to still lower frequencies and broaden greatly when the crystal is heated above  $180^{\circ}\text{C}$ , finally becoming diffuse bands as the melting point is approached. Nedungadi (1939*b*) has also identified the modes of vibration corresponding to these low frequencies by studies of the polarisation of light-scattering in orientated crystals.

The planes in the crystal structure parallel to the rhombohedral cleavages give

by far the most intense X-ray reflections. As in the case of diamond, therefore, we should expect these planes also to give intense modified reflections. The diagonal planes passing through the edges of the cleavage rhomb and bisecting the acute angle between its faces also give intense Bragg reflections, and by the same token should give strong modified reflections. The crystal planes normal to the trigonal axis of symmetry consist of alternate layers of Na and  $\text{NO}_3$  ions. The reflections due to these planes are not very strong. In view, however, of the fact that several of the fundamental modes of vibration consist of movements of the Na and  $\text{NO}_3$  ions along the axis of symmetry, marked variations of the structure-amplitude of these planes may be expected. We may therefore reasonably anticipate that these planes should give modified reflections with notable intensity.

Remarkable changes are observed in the intensity of the rings in the X-ray powder pattern of sodium nitrate when the temperature is raised above  $180^\circ\text{C}$  and up to a little below its melting point. These changes have been very fully studied by Kracek and co-workers (1931), whose results have been confirmed by Nedungadi at this Institute. The most interesting feature is that above  $180^\circ\text{C}$ , the rise of temperature affects the intensity of the X-ray reflections due to different spacings very unequally. Some are scarcely affected, some reflections diminish in intensity a little, while a few which are fairly strong below  $180^\circ\text{C}$  are practically wiped out when the temperature rises towards  $250^\circ\text{C}$ . It thus appears that the structure-amplitude of some of the spacings is very markedly a function of temperature in this range. Kracek and his co-workers have suggested that this is due to the rotational oscillations of the  $\text{NO}_3$  ions gradually increasing in amplitude and passing into continuous rotation in the temperature range from  $180^\circ\text{C}$  to  $290^\circ\text{C}$ . It may be mentioned that this is also the temperature range in which Nedungadi finds that the low frequency lines observed in light scattering broaden out and shift to lower frequencies.

To bring out the position clearly, we give below in table 1, a list of the principal planes and crystal spacings in sodium nitrate, and the intensities of the X-ray reflections due to them (on an arbitrary scale) as given by Kracek *et al.*, at  $25^\circ\text{C}$  and at  $280^\circ\text{C}$ .

The Millerian indices of the planes given in the first column of the table have reference to the axes of the elongated rhombohedron which is the unit cell of the crystal lattice. In this notation, (211) represents a cleavage face, (323) is a diagonal plane bisecting the acute angle between the cleavage faces and (222) is normal to the trigonal axis. It will be noticed from the table that the (211) and (323) planes give strong reflections which are scarcely influenced by temperature, while the (222) planes give a weaker reflection which falls off appreciably on heating. The (210) planes are specially remarkable as they give a strong reflection which disappears at high temperatures. The last column in the table indicates the manner in which the structure-amplitude of the respective planes is effectively determined by the contributions of the three species of atoms in the crystal, according to Kracek and his co-workers.

Table 1. Crystal spacings in sodium nitrate

Indices	Spacing Å at 25° C	Spacing Å at 280° C	Intensity at 25° C	Intensity at 275° C	Structure- amplitude
110	3.902	3.921	2	3	N + O - Na
211	3.035	3.121	> 10	> 10	N + O + Na
222	2.802	2.932	4	2.5	N + O - Na
1 $\bar{1}$ 0	2.534	2.543	3	3.4	N + O + Na
210	2.310	2.313	6	< 0.5	O
		at 250° C			
200	2.122	2.138	4	2.4	N + O - Na
220	1.943	1.964	1	7.7	N + O + Na
323	1.893		7		N + O + Na
321	1.880	1.914	3	2.2	N + O - Na
2 $\bar{1}$ 0	1.649	—	3	< 0.5	O
2 $\bar{1}$ 1	1.626	1.637	2	1.2	N + O - Na

## 2. Experimental results

Figures 1 and 2 in plate I, figures 3 and 4 in plate II, figures 5 and 6 in plate III, figures 7 and 8 in plate IV, figures 9 and 10 in plate V are Laue patterns of sodium nitrate obtained with the unfiltered radiation from a copper target. They illustrate the phenomena exhibited by this crystal in various circumstances. Figures 1, 2, 3, 4, 5 and 6 show the modified reflections by some of the principal planes at various angles of incidence, while figures 7, 8, 9 and 10 exhibit the effect of raising the temperature from 25° C successively to 200°, 225° and 275° C, the position of the crystal remaining unaltered.

In obtaining all these photographs, the crystal was placed with one of its cleavage faces in a vertical plane, the longer diagonal of this face being vertical. The incident X-ray beam passed through the cleavage face in a horizontal direction, and its angle of incidence on the various crystal planes could be altered by rotating the crystal about the vertical diagonal. In all the settings of the crystal, the trigonal axis of the crystal remained horizontal, its inclination to the X-ray beam being varied. The Laue patterns accordingly exhibit two-fold symmetry about a horizontal axis. The two other cleavage faces of the crystal being inclined to the vertical, the reflections from them appear in two directions symmetrically inclined to the horizontal. The (222) and (323) planes being always vertical, the reflections from them appear on the horizontal axis of the pattern in suitable settings of the crystal.

The most conspicuous features in figures 1, 2, 3 and 4 besides the usual Laue spots, are the modified reflections from the two cleavage planes. In figures 2 and 3, the  $K_\alpha$  and  $K_\beta$  modified reflections appear as distinct spots adjacent to the Laue

reflections from the same planes, while the modified reflections of the white radiation appear as radial streaks stretching towards the centre of the pattern and distinctly separated from the  $K_\alpha$  and  $K_\beta$  reflections. In figures 1 and 4, the Laue reflections are far removed from the modified reflections of the  $K_\alpha$  and  $K_\beta$  rays in one direction or the other; but the latter continue to be visible in approximately the same positions as in figures 2 and 3, though only as diffuse spots or clouds. The radial streaks are also seen in approximately the same positions. That the latter are due to the modified reflection of the white radiation will be very evident on comparing figures 1 and 4. When the Laue spots are nearer the centre of the pattern than the modified reflections of the  $K_\alpha$  and  $K_\beta$  radiations, they are traversed by the radial streaks, whereas when the Laue spots are further away, they are not overlaid by the streaks.

The inclination of the X-ray beam to the trigonal axis of the crystal in figures 1, 2, 3 and 4 was successively  $56^\circ$ ,  $50^\circ$ ,  $44^\circ$  and  $39^\circ$ . It is a notable fact that the modified reflections from the cleavage planes continue to be visible in spite of the large change in the angle of incidence which is indicated by the displacement of the Laue reflection from near the centre of the photograph to near its outer margin. On comparing figures 2 and 3, the great increase in the intensity of the modified reflection of the  $K_\alpha$  radiation when it approaches the Laue spot will be evident. This phenomenon has already been noted in the case of diamond. It is evident, however, that the modified reflections are more conspicuous in intensity and observable over a wider range of incidences in sodium nitrate than in diamond. They are also somewhat more diffuse than is the case with diamond.

In obtaining the Laue patterns reproduced as figures 5 and 6, the crystal was turned over by  $180^\circ$  about the vertical diagonal. This made it possible to get the reflections from the (222) planes to the left of the pattern simultaneously with those from the (211) and the (323) planes on its right. A slightly smaller plate distance was also used. The modified reflection of the  $K_\alpha$  radiation from the (222) planes is clearly seen in figures 5 and 6 to the right and left of the Laue spots respectively, the actual glancing angle of the beam on this plane in the two photographs being  $18^\circ$  and  $11^\circ$ , being thus respectively greater and less than the Bragg angle of  $15^\circ 55'$ . The spacing of the (323) planes being  $1.893 \text{ \AA}$ , the Bragg angle for these planes and the  $K_\alpha$  radiation is  $23^\circ 57'$ . This being much greater than the actual glancing angle in either of the two patterns, we do not observe the modified reflection of the  $K_\alpha$  and  $K_\beta$  radiations from the (323) planes but only those of the white radiations of shorter wavelength. These appear as intense horizontal streaks passing through the Laue reflections. It is obvious that the modified reflection of monochromatic rays by a particular set of crystal planes cannot be observed if the wavelength of the rays used is too great to give a Bragg reflection, or if the glancing angle differs too largely from that required for such reflection. In such cases, however, if the white radiation present in the X-ray beam is sufficiently intense, its modified reflection may be observed as a radial streak passing through the Laue spot. Numerous examples of this may be seen in the photographs reproduced.

## 3. Geometry of modified reflection

In Part II of the paper, it was mentioned that an empirical formula of an unsymmetrical type fitted the observations with diamond, namely,

$$d \sin(\theta + \phi) = \lambda \cos \phi \quad (1)$$

$\theta$  and  $\phi$  being the glancing angles of incidence and of modified reflection and  $d$  the crystal spacing. An alternative formula was also given which is symmetrical in  $\theta$  and  $\phi$ , namely,

$$2d \sin \frac{1}{2}(\theta + \phi) = \lambda. \quad (2)$$

This formula would have a theoretical basis if it be assumed that as the wave-fronts of the stratification giving the modified reflections tilt round, they maintain the same spacing as the crystal planes of which they are the structure-amplitude fluctuations. In table 2 are collected the values of  $\theta$  and  $\phi$  as given by the observed positions of the Laue spot and of the modified reflection, the spacing  $d$  as calculated from formulae (1) and (2), and as known from the crystal structure. The data refer to the crystal at room temperature.

**Table 2.** Modified reflections by sodium nitrate (211) planes: crystal spacing = 3.035 A.U. (The symbol  $\alpha$  indicates  $K_\alpha$  reflection;  $\beta$  indicates  $K_\beta$  reflection)

Character of reflection	Glancing angle		Spacing calculated from formula (1) in A.U.	Spacing calculated from formula (2) in A.U.
	Incidence $\theta$	Reflection $\phi$		
Very diffuse	5° 24'	23° 44' $\alpha$	2.896	3.060
"	6° 20'	22° 48' $\alpha$	2.942	3.090
"	6° 44'	22° 26' $\alpha$	2.920	3.056
"	7° 48'	21° 22' $\alpha$	2.944	3.056
Diffuse	10° 27'	18° 58' $\alpha$	2.966	3.029
"		15° 33' $\beta$	3.055	3.031
"	11° 34'	17° 46' $\alpha$	2.994	3.040
		14° 57' $\beta$	3.007	3.092
Fairly sharp	11° 6'	18° 19' $\alpha$	2.975	3.029
"		15° 22' $\beta$	3.007	3.035
"	11° 50'	17° 20' $\alpha$	3.016	3.056
"		14° 38' $\beta$	3.017	3.035
Sharp	15° 52'	13° 28' $\alpha$	3.057	3.040
"		10° 36' $\beta$	3.064	3.035
"	15° 58'	13° 17' $\alpha$	3.065	3.046
"		10° 20' $\beta$	3.084	3.054
Very diffuse	19° 58'	9° 12' $\alpha$	3.085	3.022
"	20° 47'	8° 23' $\alpha$	3.092	3.022

Tables 2 and 3 include the data for the modified reflections observed in all the six Laue patterns and the corresponding spacings. It is clear from the figures that the experimental results for sodium nitrate fit the symmetrical formula (2) very well, and that the unsymmetrical formula (1) is not applicable in the case of this crystal. The figures for the (111) spacing in diamond given in Part II are compiled in table 4 in the same way as for sodium nitrate. It is clear that the experimental data for diamond agree better with the unsymmetrical formula (1) though even here there is a systematic deviation. The symmetrical formula (2) is evidently inapplicable in the case of diamond.

**Table 3.** Modified reflections by sodium nitrate

Glancing angle		Spacing calculated from formula (1) in A.U.	Spacing calculated from formula (2) in A.U.
Incidence $\theta$	Reflection $\phi$		
(222) Planes: crystal spacing = 2.802 A.U.			
11° 50'	20° 48' $\alpha$	2.669	2.739
	17° 29' $\beta$	2.707	2.740
18° 29'	14° 1' $\alpha$	2.779	2.750
	10° 50' $\beta$	2.787	2.740
(210) Planes: crystal spacing = 2.310 A.U.			
18° 12'	20° 29' $\alpha$	2.307	2.325
	16° 41' $\beta$	2.327	2.317
19° 17'	19° 57' $\alpha$	2.289	2.292
	15° 36' $\beta$	2.340	2.317
(200) Planes: crystal spacing = 2.122 A.U.			
21° 51'	20° 27' $\alpha$	2.144	2.132
22° 31'	20° 8' $\alpha$	2.133	2.115

It is remarkable that the geometric law of the modified reflections should differ so markedly with the two different crystals. It is, of course, not possible to generalise on the evidence of these two cases only. But it is permissible to suggest that these and other differences already noticed between the cases of diamond and sodium nitrate are connected with the great difference in their crystal structure and properties, and especially with the fact that diamond has a very high characteristic frequency, while sodium nitrate has numerous low frequencies and is therefore influenced to a far greater extent by thermal agitation. There is also the possibility that there may be a difference in the behaviour of "ideal" crystals and of those with a "mosaic structure". Diamond almost certainly belongs to the first class, and sodium nitrate probably to the second. The

**Table 4.** Modified reflections by diamond (111) planes: crystal spacing = 2.056 A.U. (The symbol  $\alpha$  indicates  $K_{\alpha}$  reflection;  $\beta$  indicates  $K_{\beta}$  reflection)

Glancing angle		Spacing calculated from formula (1) in A.U.	Spacing calculated from formula (2) in A.U.
Incidence $\theta$	Reflection $\phi$		
17° 11'	24° 33' $\alpha$	2.104	2.161
	21° 0' $\beta$	2.098	2.123
17° 48'	24° 24' $\alpha$	2.086	2.142
	21° 0' $\beta$	2.070	2.091
18° 41'	23° 50' $\alpha$	2.084	2.122
	20° 18' $\beta$	2.071	2.081
19° 53'	23° 12' $\alpha$	2.070	2.094
20° 10'	23° 2' $\alpha$	2.069	2.090
20° 40'	22° 43' $\alpha$	2.067	2.080
20° 49'	22° 43' $\alpha$	2.062	2.073
	19° 11' $\beta$	2.041	2.031
21° 4'	22° 41' $\alpha$	2.052	2.065
	19° 6' $\beta$	2.034	2.023

pulsations of structure-amplitude could scarcely be expected to be coherent as between consecutive units in a "mosaic" structure, while in an ideal crystal, a strict coherence of phase might well be possible. Until the intensity problem for the modified reflection of X-rays is fully worked out, however, it would be premature to discuss the probable influence of mosaic structure on the results.

#### 4. Influence of temperature

The series of four photographs (figures 7, 8, 9 and 10) reproduced in plates 4 and 5 exhibit the effect of heating the crystal from 25° C to 200° C, 225° C and 275° C respectively. It will be noticed that as the crystal is heated, the separation between the Laue and  $K_{\alpha}$  modified reflections diminishes, until at 275° C they are superposed on each other. This naturally involves a large increase in the intensity of the modified reflections of both the  $K_{\alpha}$  and  $K_{\beta}$  radiations. Apart from this incidental circumstance which is due to thermal expansion, we notice the following interesting effects:

- (1) There is a marked increase in the intensity of the modified reflection of the white radiation from all the planes in the crystal, including the (211) planes.
- (2) While there is a distinct diminution in the intensity of all the Laue spots, the changes in their *relative intensity* are extremely conspicuous. Indeed, on a

careful comparison, it will be seen that some spots which are larger and brighter than others at 25° C have become much feebler or almost disappeared at 275° C.

- (3) Figure 10 shows four *faint* Laue spots which are accompanied by *strong* modified reflections, while in figure 7, the same Laue spots are intense but the modified reflections are invisible. Figures 8 and 9 show a progressive *diminution* in the intensity of these Laue spots and a progressive *increase* in the intensity of the modified reflections accompanying them. These spots have been identified from their positions as due to the (210) planes.

On a reference to table 1, it will be noticed that the (210) planes give strong Bragg reflections at 25° C, but the intensity of these reflections falls to a very small value at 280° C. We have thus *the very interesting result that the planes of which the structure-amplitude falls to zero with rising temperatures show simultaneously a large increase in the intensity of the modified reflection.*

So far from being surprising, these results are entirely in accord with the general ideas developed in Part I. The variations of structure-amplitude produced by the lattice vibrations determine the intensity of the modified reflections. In the limiting case when the thermal agitation is negligible, the lattice oscillations are themselves to be regarded as excited by the incident radiation, the modified reflection being then a pure quantum effect. With rise of temperature, however, the thermal excitation of the lattice vibrations begins to assume importance, especially when, as in the case of sodium nitrate, these are of sufficiently low frequency. The dynamic part of the structure-amplitudes would increase progressively and even rapidly, and the intensity of the modified reflection would show a corresponding increase. It must be remembered in this connection that the static and dynamic structure-amplitudes cannot be regarded as completely independent of each other. For an infinitesimal disturbance of the lattice it might be correct to regard the dynamic variation of the structure-amplitude as superposed on the static structure-amplitude without sensibly influencing it. This would however cease to be true when the amplitudes of vibration are finite. The actual influence of the vibration on the static structure-amplitude would naturally depend on the circumstances of each case. Broadly speaking, however, it may be said that with increasing amplitude of vibration, the static structure-amplitudes would diminish and the dynamic amplitudes would increase, the two effects being closely correlated. In other words, with rise of temperature, the unmodified or Laue reflection would diminish in intensity, and the modified reflections would correspondingly become more intense. It is thus clear that the modified reflection of X-rays plays a very important role in the theory of the temperature effect in X-ray diffraction. This is particularly well brought out by the case of the (210) planes in sodium nitrate which, as we have seen, show a static structure-amplitude tending to zero with rise of temperature and a dynamic structure-amplitude rising to a correspondingly high value.



### Summary of parts I, II and III

These papers deal with a new type of X-ray reflection in crystals which is dynamic in character and thus differs from the static reflections of the Laue type.

Part I considers the broad theoretical aspects. The optical analogy of the scattering of light in crystals indicates that when X-rays traverse a crystal they excite pulsations in the crystal lattice having the characteristic infra-red frequencies, and these pulsations in turn cause periodic variations in the structure-amplitude of the crystal spacings and therefore result in reflections of the X-rays with change of frequency. At the Bragg angle of incidence, the modified and unmodified reflections are superposed, but when the incidence is increased or decreased, the unmodified reflections disappear, thus enabling the modified reflections to be observed by themselves. They are seen in the plane of incidence on the crystal spacing, but at an angle greater or less than that of geometric reflection by the crystal planes. The modified reflection is a quantum effect and is not primarily a thermal phenomenon, though for low lattice frequencies or at high temperatures it may be thermally influenced.

Part II describes the experimental results obtained by the study of the modified reflection from the (111) planes in diamond. The lattice vibration which is effective is that characteristic of the crystal which also appears in light-scattering with a frequency of  $1332 \text{ cm}^{-1}$ . This is confirmed by the character of the effects as described in detail.

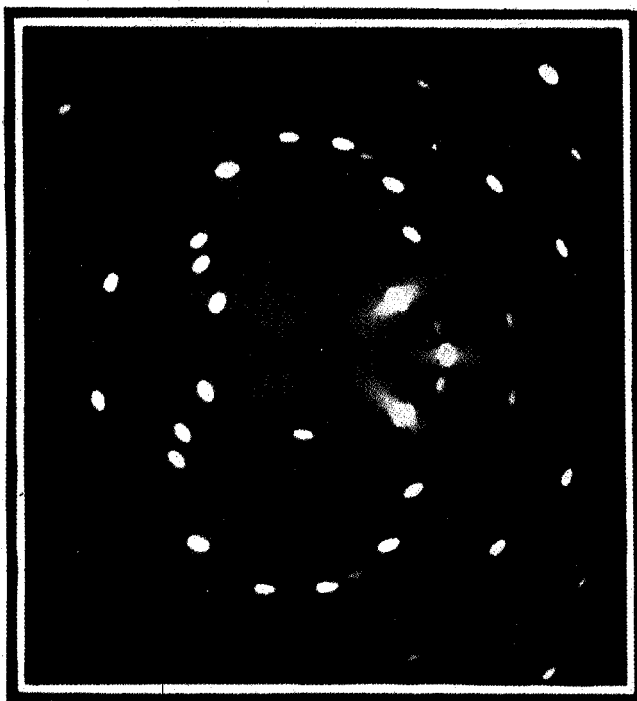
Diamond exhibits a diffuse halo with a distinct darkening at the centre of the pattern and a maximum of intensity at a distance from it. This is explained as due to acoustic waves of high frequency excited by the incident monochromatic X-rays and reflecting them in the usual way.

Part III describes the results obtained with sodium nitrate which exhibits intense modified reflection by several of the crystal spacings. The geometric law of modified reflection is discussed in relation to the experimental data for both crystals. A study of the temperature effects observed with sodium nitrate indicates that a diminution in the intensity of the unmodified reflection is accompanied by an increase in the intensity of the modified reflection. The modified reflections therefore play an important point in the theory of the temperature effect in X-ray diffraction.

### References

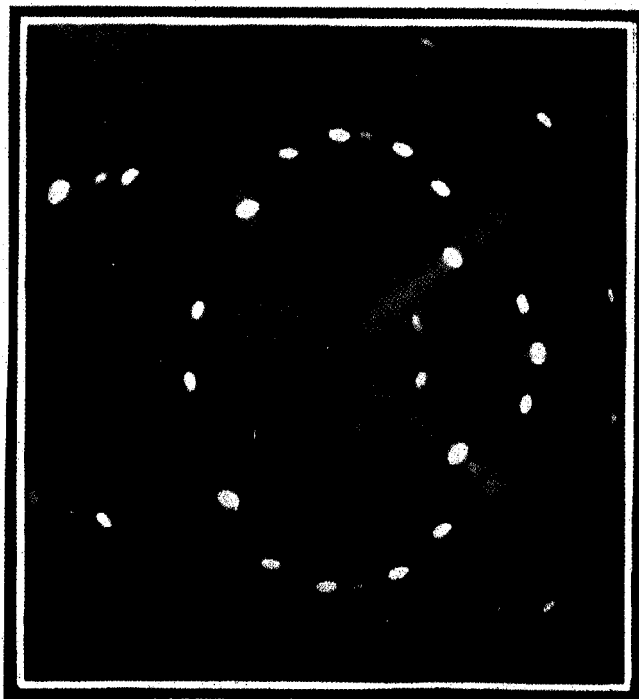
- Bhagavantam and Venkatarayudu *Proc. Indian Acad. Sci.* **9** 224 (1939).  
Nedungadi T M K *ibid.* **8** 397 (1938); **10** 195 (1940).  
Kracek, Posnjak and Hendricks *J. Am. Chem. Soc.* **53** 3339 (1931).

(1)



X-ray beam  
inclined  $56^\circ$   
to the  
trigonal  
axis

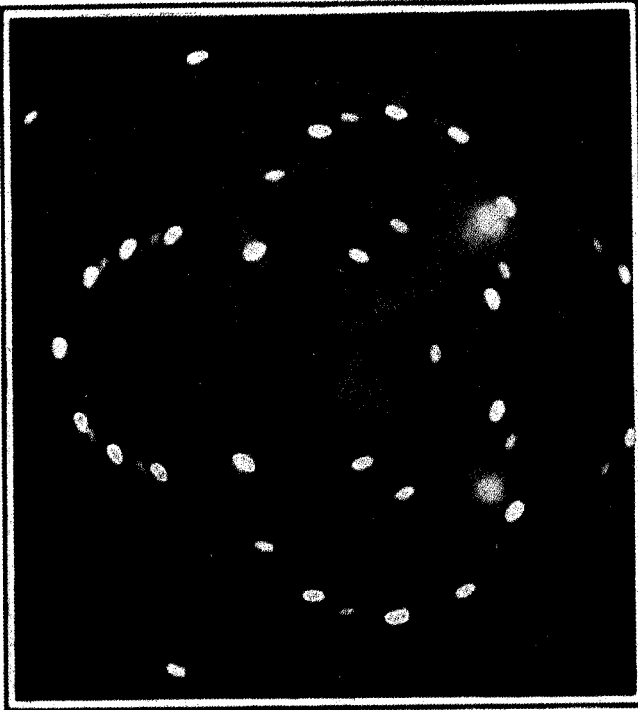
(2)



X-ray beam  
inclined  $50^\circ$   
to the  
trigonal  
axis

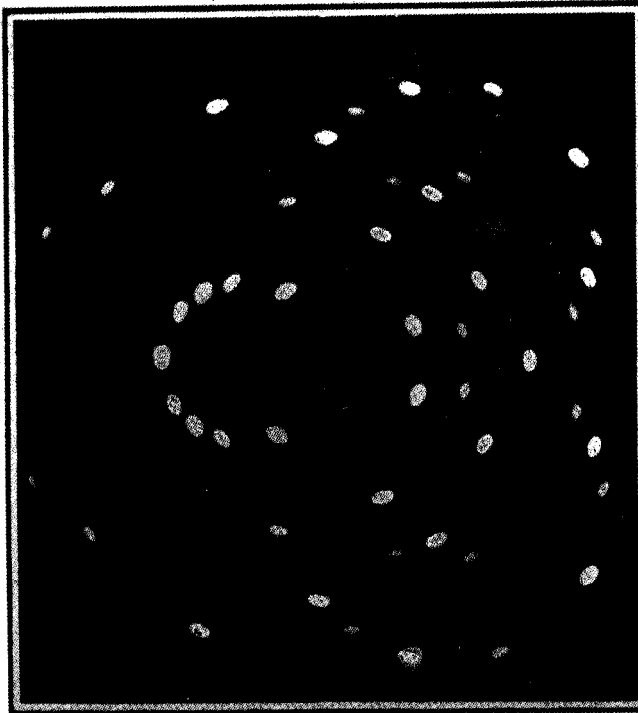
Figures 1 and 2. Laue pattern of sodium nitrate (trigonal axis horizontal).  
Plate I

(3)



X-ray beam  
inclined  
 $44^\circ$  to the  
trigonal  
axis

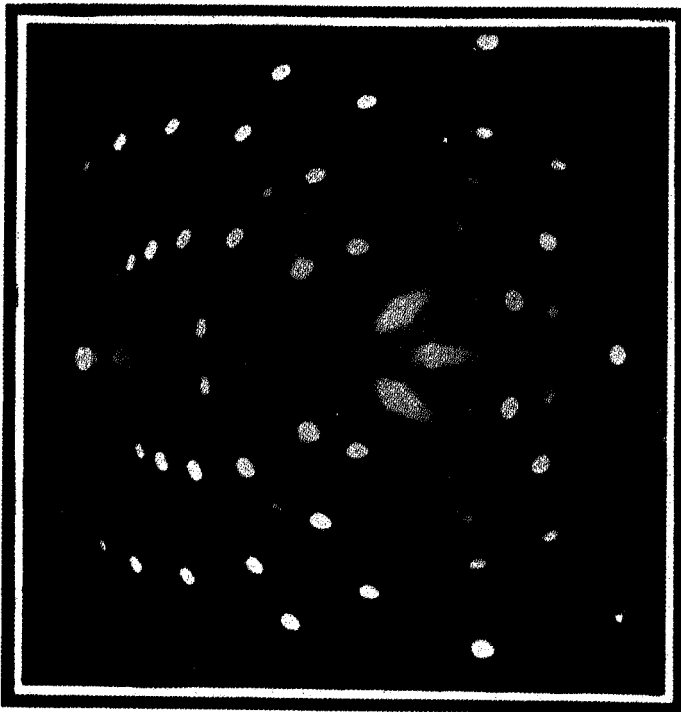
(4)



X-ray beam  
inclined  
 $39^\circ$  to the  
trigonal  
axis

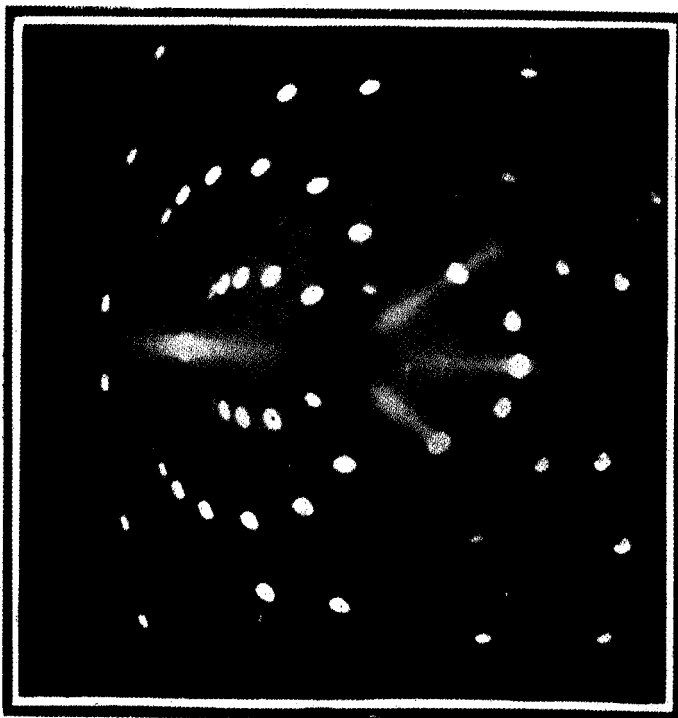
Figures 3 and 4. Laue pattern of sodium nitrate (trigonal axis horizontal).

(5)



X-ray beam  
inclined  $18^\circ$   
to  $[222]$   
planes

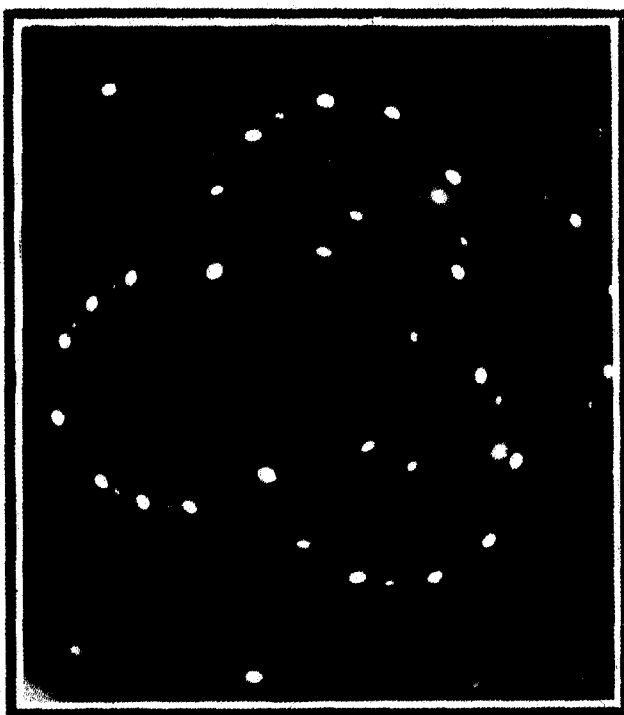
(6)



X-ray beam  
inclined  $11^\circ$   
to  $[222]$   
planes

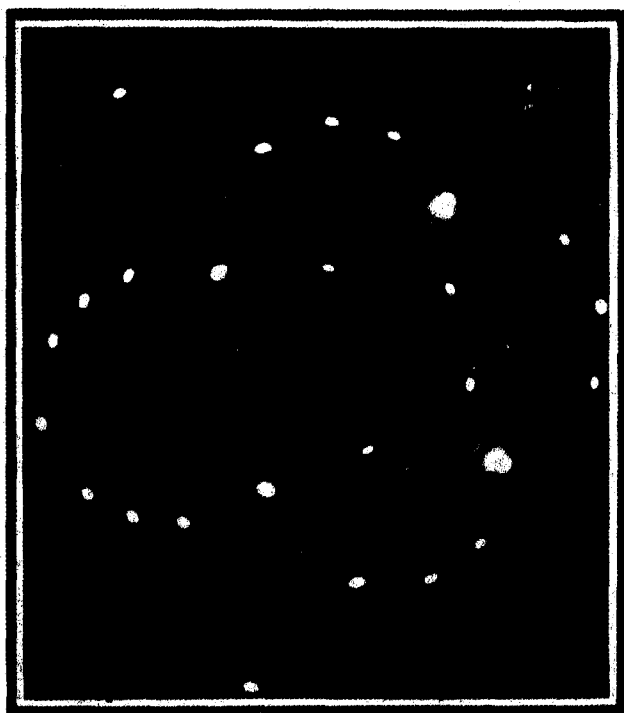
Figures 5 and 6. Laue pattern of sodium nitrate.  
Plate III

(7)



25° C

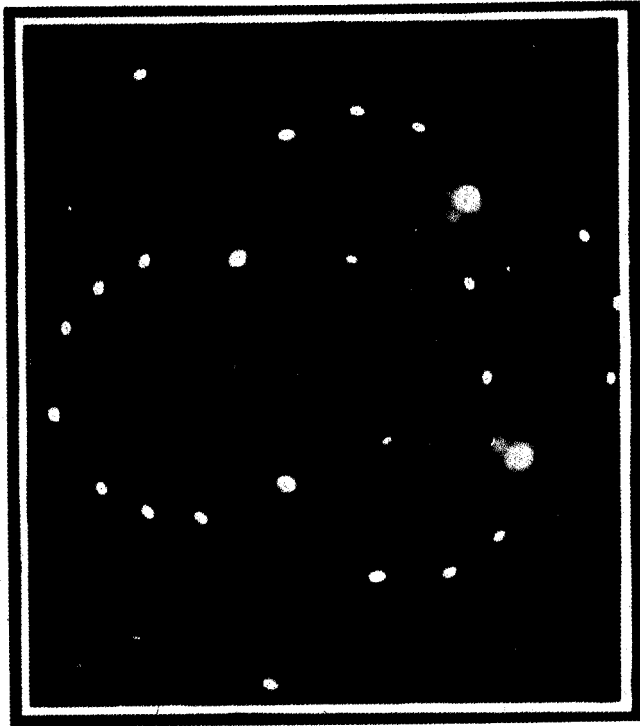
(8)



200 °C

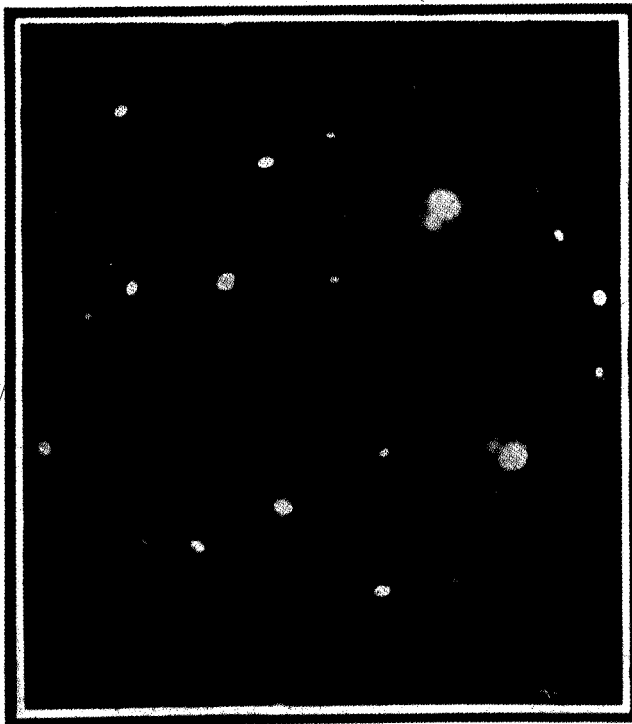
Figures 7 and 8. Temperature studies with sodium nitrate (X-rays perpendicular to one of the cleavage faces).  
Plate IV

(9)



225° C

(10)



275° C

Figures 9 and 10. Temperature studies with sodium nitrate (X-rays perpendicular to one of the cleavage faces).