THE LATTICE SPECTRUM AND THE RAMAN X-RAY REFLECTIONS BY ROCK-SALT

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1. Introduction

It has been shown in an earlier paper that the diffuse maxima observed by several authors in the Laue patterns of rock-salt are due mainly to the dynamic X-ray reflections by the monochromatic crystal vibrations as was originally explained by Raman and Nilakantan[1] (1940). In the present paper it is proposed to give an analysis of the lattice vibrations of the sodium chloride crystal and ascertain their part in determining the intensity and the geometric law of the Raman X-ray reflections from its principal planes.

2. Group Theory and the Lattice Spectrum of Rocksalt

The unit cube of the rock-salt lattice contains four sodium and four chlorine atoms, each group possessing tetrahedral symmetry. The co-ordinates of the atoms are

Na: $0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0; \frac{1}{2}, 0, \frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2}$.

Cl: $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, 0; 0, \frac{1}{2}, 0; 0, 0, \frac{1}{2}$.

There are twenty-four degrees of freedom for the atoms in the unit cell. The crystal vibrations may be classified among the different symmetry classes of the space group O_h to which the crystal belongs, according to the following character table. The notations employed are the same as those given by Placzek[2] and the procedure followed in drawing up the table is the same as that given by Bhagavantam and Venkatarayudu[3] (1939). It will be seen from Table I that there are altogether eight modes of vibrations for the crystal all of which are triply degenerate. One of these in class F_{2u} corresponds to the translations of the unit as a whole along the three axes and may, for the present, be assigned to the Debye elastic spectrum.

Of the remaining seven, two belonging to the class F_{1u} are active in infra-red and inactive in Raman, and five in class F_{2u} are inactive in both. One of the former class corresponds to the oscillation of the sodium lattice against the chlorine lattice, and is referred to in the following as inter-lattice vibration. The remaining one of this class and one of F_{2u} correspond to the

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TABLE I
Character Table for Rock-salt

O_h	E	$8\,C_3$	$3\,C_2$	$6\,\sigma$	$6\,S_4$	i	$8\,S_3$	$3\,\sigma$	$6\,C_2$	$6\,C_4$	n_i	Raman	Infra-red
A_{1g}	1	1	1	1	1	1	1	1	1	1	0		
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	0		
E_g	2	-1	2	0	0	2	-1	2	0	0	0		
F_{1g}	3	0	-1	-1	1	3	0	-1	-1	1	0		
F_{2g}	3	0	-1	1	-1	3	0	-1	1	-1	0		
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	0		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	0		
E_u	2	-1	2	0	0	-2	1	-2	0	0	0		
F_{1u}	3	0	-1	-1	1	-3	0	1	1	-1	2	f	Active
F_{2u}	3	0	-1	1	-1	-3	0	1	-1	1	6	f	Inactive
u_R	8	2	8	4	4	8	0	8	4	4			
ψ_j	24	0	-8	4	-4	-24	0	8	-4	4			
$h_j\psi_j$	24	0	-24	24	-24	-24	0	24	-24	24			

'breathing' oscillations of sodium and chlorine atoms in the unit, in one of which all the atoms move in the same phase (symmetric), and in the other the movements of the sodium and the chlorine atoms are opposite in phase (anti-symmetric). The author will go more fully into the vibrational spectrum of the crystal in a subsequent paper.

3. The Dynamic Reflections of X-rays by Rock-salt

The displacements of the atoms in the inter-lattice vibration are normal to the (100) planes and those of the 'breathing' oscillations are normal to the (111) planes. As a first approximation, we consider the effect of these three modes of vibrations on the intensities of Raman X-ray reflections. The other modes of vibrations would contribute only relatively feeble components normal to (100), (111) and (110) planes. If a and b are the amplitudes of the Na and Cl atoms in the direction of vibration, the co-ordinates of the eight atoms for the three vibrations are

1. *for the anti-symmetric*

$$\text{Na}: \frac{a}{\sqrt{3}}, \frac{a}{\sqrt{3}}, \frac{a}{\sqrt{3}}; \frac{1}{2} - \frac{a}{\sqrt{3}}, \frac{1}{2} - \frac{a}{\sqrt{3}}, \frac{a}{\sqrt{3}}; \text{ etc.}$$

$$\text{Cl}: \frac{1}{2} + \frac{b}{\sqrt{3}}, \frac{1}{2} + \frac{b}{\sqrt{3}}, \frac{1}{2} + \frac{b}{\sqrt{3}}; \frac{1}{2} + \frac{b}{\sqrt{3}}, - \frac{b}{\sqrt{3}}, - \frac{b}{\sqrt{3}} \text{ etc.}$$

2. *for the symmetric*

Na: Same as for 1.

$$Cl : \frac{1}{2} - \frac{b}{\sqrt{3}}, \frac{1}{2} - \frac{b}{\sqrt{3}}, \frac{1}{2} - \frac{b}{\sqrt{3}}; \frac{1}{2} - \frac{b}{\sqrt{3}}, \frac{b}{\sqrt{3}}, \frac{b}{\sqrt{3}} \text{ etc.,}$$

and 3. *for the interlattice, considering its triple degeneracy*

Na: a', a', a'; $\frac{1}{2} + a', \frac{1}{2} + a', a'$; etc.

Cl: $\frac{1}{2} - b', \frac{1}{2} - b', \frac{1}{2} - b'$; $\frac{1}{2} - b', -b', -b'$ etc.

Sir C. V. Raman has given the following expressions for the intensities of static (I_B) and dynamic (I_R) X-ray reflections at or very near the Bragg setting. For an imperfect crystal,

$$\sqrt{I_B} = \Sigma_P J_0(\zeta_p) f_p' \cos(2\pi vt - z_p) \qquad\qquad \text{I}$$

$$\sqrt{I_R} = \Sigma_p J_1(\zeta_p) f_p' \sin[2\pi(v \pm v^*)t - z_p] \qquad \text{II}$$

where $\zeta_p = \dfrac{2\pi \xi_p}{d}$, ξ_p being the component of the displacement of the pth atom normal to the crystal plane considered and d its lattice spacing. For an infra-red vibration of frequency v^*, the amplitude a_p is given by

$\Sigma_p \frac{1}{2} m_p a_p^2 = \dfrac{h}{4\pi^2 v^*}$ where m_p is the mass of the atom. The dynamic structure amplitude of any plane is then given by

$$|F|^2 = [\Sigma_p J_1(\zeta_p) f_p' \cos 2\pi N(hx_p + ky_p + lz_p)]^2 +$$
$$[\Sigma_p J_1(\zeta_p) f_p' \sin 2\pi N(hx_p + ky_p + lz_p)]^2 \qquad \text{III}$$

where h, k, l are the Miller indices of the plane, N is the order of reflection and x_p, y_p and z_p are the co-ordinates of the *displaced* atom. These expressions for the 1st and 2nd order reflections by the 111, 100 and 110 planes have been deduced for the three modes of vibrations. And assuming that the frequencies of these vibrations are all in the neighbourhood of 160 cm.$^{-1}$ and remembering that they are triply degenerate, the amplitude a_p is calculated for the three cases and hence the corresponding ξ_p, ζ_p, $J_0(\zeta_p)$ and $J_1(\zeta_p)$ for Na and Cl atoms separately in each case. Substituting these values in the expressions for intensities, we get the following table for the intensities of the static and dynamic reflections.

The data given in Table II lead to the following conclusions: (1) The intensities of the dynamic reflections from (222), (200) and (220) planes are proportional to the corresponding Bragg intensities. (2) The (100) and (110) dynamic reflections should appear weakly whereas their static reflections are forbidden. The dynamic structure amplitude of (100) reflections is sufficiently

TABLE II

Intensities of Raman and Bragg X-ray Reflections

Mode of Vibration	Intensities $|E|^2$	Miller Indics of Planes					
		111	222	100	200	110	220
Anti-Symmetric	Raman	·11	17·7	·003	43·8	9×10^{5}	27·6
	Bragg	310	2700	0	6624	0	4020
Symmetric	Raman	·11	17·7	·045	43·8	9×10^{5}	27·6
	Bragg	310	2700	0	6624	0	4020
Inter-Lattice	Raman	·21	5·5	0	14·2	0	8·6
	Bragg	310	2700	0	6600	0	4000
	Raman (Total)	·43	40·9	·0453	101·8	18×10^{5}	63·8
	$\frac{\text{Raman}}{\text{Bragg}}$	$\frac{1}{720}$	$\frac{1}{66}$		$\frac{1}{66}$		$\frac{1}{6}$

high (about $5 \times 10^{-?}$) to record the spot in well-exposed pictures. (3) The intensity of the (111) dynamic reflections is only 1/720 of the static reflections, while that of (222) is 1/66. As the Bragg intensities of (111) to (222) reflections are in the ratio 3:11, the corresponding ratio for the Raman intensities is 1:40.

4. Experimental Results

Figs. 1-4 in the accompanying Plate are four photographs taken with a crystal of rock-salt set with one of the (111) planes normal to X-rays and then rotated about [110] axis. Fig. 1 shows the trigonal symmetry, when the X-rays are nearly normal to the plane and the glancing angle on (111) planes measured from their Laue spots is 19·36'. Figs. 2-4 are taken with X-rays making glancing angles of 11·32', 4·46' and nearly 2·30' with the 111 plane. On account of the great thickness of the crystal traversed by X-rays due to oblique incidence, the absorption is great and it was observed that the effective X-ray wave-length maximum is 0·46 Å. The corresponding Bragg angle for the first order of (111) reflection is 3·40' and for the second order is 7·37'. The strong Raman spot of the (222) reflections may be seen in all pictures. On the other hand, the (111) Raman spot appears very weakly only in Fig. 4 in which it is very near the Bragg setting. In Fig. 3, the (111) reflection is nearer to the Laue spot than the (222) reflection and yet it is not recorded while the latter comes out with great intensity. The investigation thus clearly shows that the first order of the dynamic reflection by the (111) plane is

extremely weak which is in qualitative agreement with the theoretical calculations. These results again demonstrate that the new spots in rock-salt do not owe their origin to the scattering of X-rays by the elastic waves, for which the relative intensities of the first and second order maxima should be nearly* of the same order as of the Bragg Reflections, *viz.*, 3 : 11. The (222) Raman spots show also a drift towards the Laue spot as the crystal is rotated.

5. *Phase-waves and the Geometric Law of the Raman X-ray Reflections*

It may be reasonably assumed that the phase waves associated with the lattice vibrations of rock-salt will be parallel to the planes containing only either sodium atoms or chlorine atoms. Secondly the phase-waves responsible for the Raman spot lying approximately on the line joining the central and the Laue spots, should be one having the minimum azimuthal angle. From these two considerations it is assumed that the phase-waves will be parallel to the {311} planes. There are altogether twenty-four planes belonging to this "form". The geometric law of the dynamic reflections is given by Raman and Nath[5] (1940) as $2\,d \sin \dfrac{\theta + \phi}{2} \sin \left(\vartheta - \dfrac{\phi - \theta}{2}\right) = \lambda \sin \vartheta$, where d is the lattice spacing, θ is the glancing angle of incidence, $\theta + \phi$, the angle between the incident and reflected rays, ϑ is the angle made by the reflecting plane with one of the {311} planes.

Jauncey and Baltzer[6] (1941) have shown by an elegant experimental method that the diffuse maxima of the (400) and (620) planes drift towards the Laue spot as the crystal is rotated. In order to verify their data, the author has reinvestigated the case of rock-salt with Mo radiations, using a fine aperture lead-slit and a thin crystal and taking care in setting the crystal so that the plate distance remains constant for all crystal orientations. It was observed that the dynamic reflections for the 200, 400, 220 and 440 planes for Mo K_α do not show any measureable drift from the Bragg position, as is only to be expected from the above formula. Since no shift has been noticed the measurements are not given here. The extrapolated data furnished by Zachariasen[7] (1941) from a re-measurement of the reproduced photographs of Raman and Nilakantan (1940) are thus unjustifiable and are indeed contradicted by his own rigorous formula given later (Zachariasen[7], 1941).

In Tables III–V, the results of Jauncey and Baltzer[6] are given along with those of the present author. The readings in the neighbourhood of the Bragg

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* According to Zachariasen's rigorous formula[4] (1941) the intensity varies as $1/\cos^2 \theta_B$ for small values of $\theta_i - \theta_B$. This gives an increase of only 1·4% for the second order reflection over the first order.

angle are omitted. The phase-wave angle, *i.e.*, the angle made by the reflecting plane with one of the {311} planes, in each case is shown in the beginning of each table.

TABLE III

$$\vartheta = 72 \cdot 27' \quad 100 \quad 113$$

(400) reflection : $d = 2 \cdot 81 \text{Å}$ Jauncey : CuK$_a$				(680) reflection : $d = 2 \cdot 81 \text{Å}$ Author : MoK$_a$			
2θ	$\theta \pm \phi$	$\phi \quad \cdot$	d	2θ	$\theta \quad \cdot$	$\phi \quad \cdot$	d
80 · 14'	68 · 38'	11 · 36	2·831	89 · 12	44 · 14	·	· 81 ·
78 · 14'	68 · 38	9 · 36	2·810	46 · 12	44 · 41	1 · 41	· 81 ·
76 · 14'	68 · 20	7 · 84	2·808	50 · 8	45 ·	· ·	2·82
74 · 14'	67 · 80	6 · 24	2·809	54 · 20	45 · 24	6 · 36	· 81 ·
72 · 14'	67 · 32	4 · 42	2·804				
60 · 14'	65 · 2	4 · 48	2·825				
58 · 14'	64 · 26'	6 · 12	2·840				
56 · 14'	64 · 26'	8 · 12	2·830				

TABLE IV

$$\vartheta = 55 \cdot 6' \quad 311 \quad 110$$

(620) reflection : $d = \cdot 89 \text{Å}$

Jauncey : CuK$_a$				Author : MoK$_a$			
2θ	$\theta \quad \phi$	$\phi \quad \cdot$	d	2θ	$\theta \quad \phi$	$\phi \quad \cdot$	d
126 · 8'	123 · 54'	4 · 14	·889	44 · 81'	46 · 28	2 · 42	·884
125 · 8'	122 · 36'	2 · 42	·890	50 · 45	47 · 21	3 · 24	·881
113 · 8'	115 · 36	2 · 28	·894	52 · 46	47 · 41	5 · 5	·882
111 · 8'	114 · 54'	3 · 46	·891				
109 · 8'	114	4 · 52'	·890				

TABLE V

$\vartheta = 82° \cdot 15' = 13\bar{1} \wedge 201$, *X-ray wave-length* $\cdot 708$ Å

(402) reflections: Lattice Spacing $= 1 \cdot 26$ Å

| 2θ	$\theta + \phi$	$\phi - \theta$	d
$25° \cdot 58'$	$32° \cdot 17'$	$6° \cdot 19'$	$1 \cdot 267$
$35° \cdot 24'$	$32° \cdot 33'$	$-2° \cdot 59'$	$1 \cdot 272$
$41° \cdot 24'$	$32° \cdot 49'$	$-8° \cdot 35'$	$1 \cdot 275$
$45° \cdot 46'$	$33° \cdot 5'$	$-12° \cdot 41'$	$1 \cdot 271$
$47° \cdot 30'$	$33° \cdot 5'$	$-14° \cdot 25'$	$1 \cdot 276$
$49° \cdot 50'$	$33° \cdot 20'$	$-16° \cdot 20'$	$1 \cdot 273$

Considering the limitations for accurate experimental measurements, Tables III, IV and V show that the lattice spacing obtained in every case is fairly constant and nearly equal to. the theoretical value. It may be remarked here that as has been indicated by some authors, the geometric law for the new reflections is more or less similar whether they are considered as arising from the infra-red vibrations (Raman), elastic waves (Faxén-Waller-Zachariasen), or mosaic blocks (Preston-Bragg[8]). As such, any agreement between the theoretical and experimental values (see also Zachariasen[9], 1941) cannot be regarded as being in favour of one or other of these theories. Indeed, the present study shows that the geometric behaviour of the Raman reflection gives us a valuable method of determining the direction of the phase-waves in the crystal.

6. Origin of the Streamers in the Rock-salt Patterns

The Laue photographs of rock-salt reproduced by Raman and Nilakantan (1940) show that many of the quantum reflections have faint streamers running in different directions associated with them. These are also clearly seen in the pattern obtained by Gregg and Gingrich (1940) using monochromatic radiations, an original print of which kindly sent by them to Sir C. V. Raman was placed at the disposal of the author. These streamers have obviously a similar origin to those recorded by Raman and Nilakantan (1940) for diamond and explained in a complete fashion by Pisharoty (1941) on the assumption that associated.with each of the (111) planes there are three phase waves parallel to the (100) planes. In the case of rock-salt the (311) planes take the place of the (100) planes of diamond. Calculations made on the lines indicated by Pisharoty for diamond and taking three (311) phase-waves symmetricaly situated with respect to the reflecting plane shows that the angle between streamers connected with (220) and (402) planes lies betwen 80° and 85°. Observations made on the photograph furnished by Dr. Gingrich are in

FIG. 1   FIG. 2
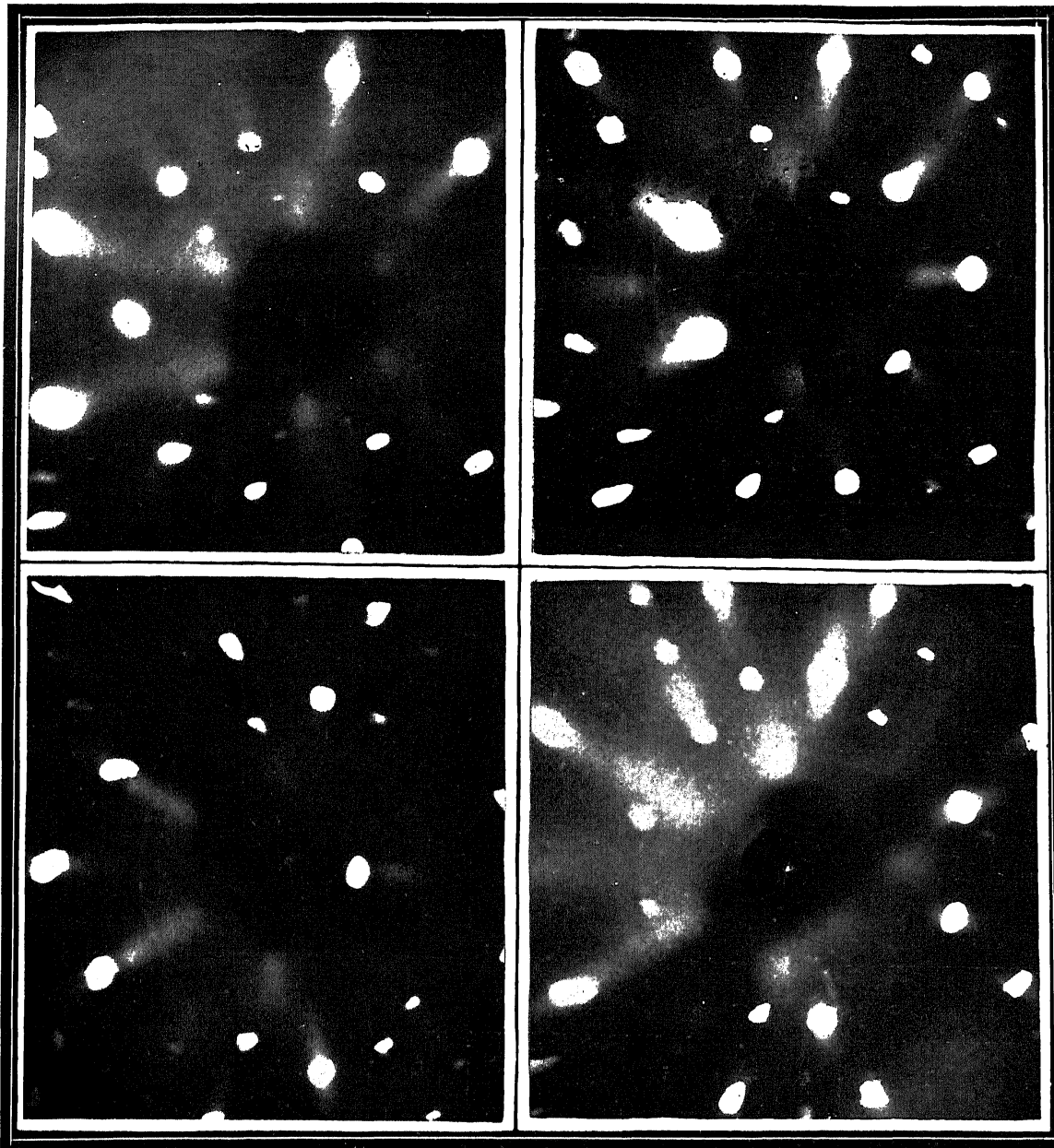
←— 222
Reflection

← 111 and
222
Reflections

FIG. 3   FIG. 4

Raman X-Ray Reflections in Rock-salt

agreement with this calculation. It is also possible that the cross-streamers connecting the ' maxima ' are due to the combined effect of different phase-waves and require further careful consideration. A faint spot corresponding to 100 reflection is also discernible in the latter photograph and if substantiated by observations on the original negative would confirm the theoretical expectation made earlier in the paper.

In conclusion I take this opportunity to thank Sir C. V. Raman, F.R.S., for his continued interest in my work. The author's thanks are also due to Mr. Rama Pisharoty for some discussions he had with him in the calculation of intensities.

7. Summary

The lattice vibrations of rock-salt are analysed and the intensities of the first and the second orders of the Raman X-ray reflections from the (111), (100) and (110) planes are calculated for the three principal modes of vibration. These calculations show that the intensities of the (222), (200) and (220) Raman reflections are proportional to those of their corresponding Bragg reflections. The intensity of the (111) Raman reflection is only 1/40 of that due to (222) whereas the ratio of the corresponding Bragg reflections is 9/33. This is in agreement with experimental observations with rock-salt. The (100) and (110) Raman reflections should be very weak. The drift of the Raman spot observed by Jauncey and Baltzer for 400 and 620 and also by the present author for 600, 620 and 420 planes for different crystal orientations is satisfactorily explained on the assumption that the phase-waves are parallel to {311} planes of the crystal. The ' streamers ' that are observed in association with the ' maxima ' in rock-salt are also explained on the basis of the co-existence of at least three such waves effectively connected with any particular plane.

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