Reflection of X-rays with change of frequency—
Part IV. Rock-salt

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1. Introduction

The second and third papers of this series (Raman and Nilakantan 1940) described an experimental study of the phenomena observed when X-rays incident on a crystal excite the characteristic vibrations of its lattice structure, resulting in a reflection of the X-rays with altered frequency. The experimental results disclosed remarkable differences between the behaviour of the two crystals studied, namely, diamond and sodium nitrate, in respect of the details of the phenomenon, viz., the geometric law of the modified reflection, the range of incidences over which it may be observed with any particular crystal spacing, the definition which it exhibits at various incidences, the influence of temperature on its intensity, and so forth. These observations indicated the importance of studying the phenomena with a variety of other substances with a view to correlating the results with the crystal structure and infra-red spectrum of the substance. Such a correlation should be possible in the light of the quantum-mechanical theory of X-ray reflection which has been developed and of which the first part has been published in these *Proceedings* (Raman and Nath 1940, I). The present investigation deals with the case of rock-salt, which is of special interest in view of the simplicity of its structure, and has resulted in an advance of our knowledge of the subject in several directions.

2. Lattice structure and lattice vibrations

The structure of rock-salt was one of the earliest to be established by the X-ray method. As is well known, the crystal is built up of sodium and chlorine ions grouped round each other and forming two similar interpenetrating face-centred cubic lattices. The crystal planes which contain equal numbers of sodium and

chlorine ions have the lattice spacing halved and give only the reflections of even orders, while the others in which layers of sodium and chlorine ions alternate exhibit the full lattice spacings and therefore give both odd and even order reflections. In the X-ray reflections of even orders given by both types of spacings, the sodium and chlorine ions co-operate and therefore enhance the intensity, while in the reflections of odd orders given by the undivided spacings, they subtract from each other's effects. The reflections of even and odd orders therefore form two different sequences in one of which the intensity is large and in the other it is small. In both sequences, the intensity falls off as the spacing diminishes (Bragg, James and Bosanquet 1921). Table 1 shows all the reflections observed with rock-salt of which the intensity is 5 per cent or more of the reflections given by the cleavage faces. The figures for the (100), (110) and (111) reflections are taken from the authors quoted, and those for the 210 (2), 211 (2) and 221 (2) reflections are obtained by interpolation from their curve.

Table 1. Spacings and reflection intensities

Halved spacings			Full spacings		
Miller indices	Spacings in A.U.	Reflection intensity	Miller indices	Spacings in A.U.	Reflection intensity
			111(1)	3·250	9
100(2)	2·814	100			
110(2)	1·990	50			
			111(2)	1·625	33
100(4)	1·407	20			
210(2)	1·259	15			
211(2)	1·149	12			
110(4)	0·995	6			
221(2)	0·938	5			
100(6)	0·938	5			

The reflecting power of rock-salt for infra-red radiation shows a large increase over the region of wavelengths from $40\,\mu$ to $80\,\mu$, the curve exhibiting a broad maximum at $52\,\mu$. The absorption of infra-red radiation by the crystal is very strong over the whole of this region, but by using a thin layer, it is possible to resolve the transmission curve and observe the principal maximum of absorption at $61\,\mu$ and feebler subsidiary maxima at $51\,\mu$ and $41\,\mu$ (Barnes 1932). It is obvious that an oscillation of the two interpenetrating lattices of sodium and chlorine atoms with respect to each other would give rise to a large electric moment along the direction of movement. Such an oscillation would be strongly active in the infra-red, and the absorption maximum observed at $61\,\mu$ ($164\,\mathrm{cm}^{-1}$) may therefore reasonably be identified with it. Symmetry considerations indicate that

the same oscillation would be inactive in light-scattering. Actually, as has been shown by Fermi and Rasetti (1931), rock-salt exhibits in a very strongly exposed spectrum of light-scattering, a band covering the region of frequency shift from $160\,\mathrm{cm}^{-1}$ to $365\,\mathrm{cm}^{-1}$ with a series of intensity maxima clearly visible within this range. This has been explained by Fermi and Rasetti as a second-order effect. The lower frequency limit of the band, it will be noticed, is about the same as the characteristic infra-red absorption frequency, and the upper limit approximately the octave of it. In view of these facts, it appears justifiable to conclude that the principal optical frequency of the rock-salt structure is $164\,\mathrm{cm}^{-1}$ and that this frequency corresponds to a movement of the two interpenetrating lattices with respect to each other.

Owing to the cubic symmetry of the crystal, the oscillation referred to above would be triply degenerate, that is, may take place in any arbitrary direction with the same frequency. It is also evident that the oscillation would influence the structure amplitude of all the crystal spacings except such as happen to be actually parallel to it. Considering the lattice planes containing equal numbers of sodium and chlorine ions, the average electron density exactly midway between such planes would be neither increased or decreased by an oscillation in which adjacent sodium and chlorine ions alternately approach and recede from each other. Nearer the planes, however, the electron density would be increased in one half of the oscillation and decreased in the other half, or *vice versa*. The wavelength of the oscillation of electron density would therefore be the same as the distance between such planes, and its time-period identical with that of the oscillation of the lattices. In the case of the planes which contain only sodium or chlorine ions alternately, the electron density midway between such planes is increased in one half of the oscillation and decreased in the other half, or *vice versa*. Here again, therefore, the wavelength of the oscillation of electron density is the same as the distance from one plane of atoms to the next of the same kind. In other words, the dynamic stratifications of electron density have their spacings halved or not halved, in the same way as the corresponding static periodicities.

The considerations set out above indicate that table 1 which is a list of the spacings in rock-salt which give intense unmodified reflections would equally well represent a list of the spacings giving strong modified reflections as the result of the oscillations of the lattice structure. All the lattice planes except (111) should give the even order reflections only, and we may further expect the intensity of these reflections to fall off in a regular sequence with the diminution of the crystal spacings in much the same way as for the unmodified reflections. The case of the (111) planes, however, requires special consideration. The static structure amplitude of these planes is greater for the second order than for the first, the intensities of these reflections being in the ratio 33:9. The characteristic vibration of the crystal structure would however influence the structure amplitude more for the first order than for the second order, the movements of the two interpenetrating lattices being in opposite directions. Accordingly, the intensity of the modified

reflections of the first and second orders from the (111) planes should not exhibit such a large disparity as the unmodified reflections of these orders.

3. Geometry of modified reflection

The geometric relations entering in the modified reflection of X-rays have been discussed in detail on the basis of the quantum theory by Raman and Nath (1940) in a recent paper in these *Proceedings*. The results briefly stated are: the modified reflection appears in the plane of incidence of the X-ray beam on the crystal spacing under consideration; the glancing angles of incidence and reflection θ and ϕ respectively are, in general, not equal to each other, but satisfy the relation

$$2d \sin \tfrac{1}{2}(\theta + \phi) = n\lambda; \tag{1}$$

the intensity of the reflection is greatest when $\theta = \phi$ and falls off when θ and ϕ diverge from each other, at first very rapidly, and later more slowly. These three results enable us readily to determine the general features of the modified reflections appearing in a Laue pattern for any stated orientation of the crystal.

Equation (1) indicates that *the angular separation between the incident beam and the modified reflection from any particular spacing is independent of the setting of the crystal*. Round the centre of the pattern (viz., the point at which the incident beam meets the photographic plate), we draw a series of circles on the plate corresponding to this angular separation for each of the crystal spacings capable of giving modified reflections of sufficient intensity to be observed. It will be seen from equation (1) that the position of these circles on the plate would coincide with the rings in the powder-pattern of the crystal for the same plate distance. From the centre of the pattern, we then draw a set of radial lines on the plate such that each such line and the incident X-ray together define the plane of incidence of the latter on the particular crystal spacing under consideration. The points at which the circles and the radial lines intersect give the positions of the modified reflections. If the wave-length of the X-ray is changed, the powder-diagram circles would expand or contract, and the modified reflections would therefore move in or out along the radial lines. The modified reflection of the white radiation present in the incident pencil would therefore appear as a radial streak on the same line as the spots due to the monochromatic rays.

Since the angles θ and ϕ may have any values satisfying equation (1), it is not necessary for recording a modified reflection that the particular crystal plane should be in such an orientation as to give a Laue reflection observable on the plate. We may, for instance, have $\theta = 0$, in other words, the incident ray grazes the crystal plane, in which case the Laue reflection would be unobservable but the modified reflection would appear at an angle ϕ with the incident beam given by the relation

$$2d \sin \tfrac{1}{2}\phi = n\lambda. \tag{1a}$$
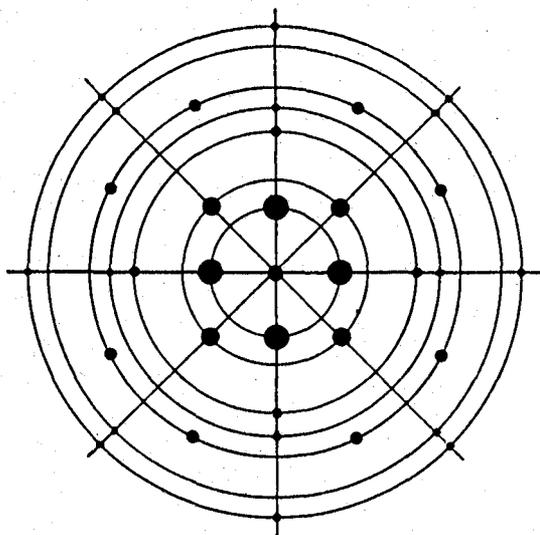
Figure 1. Pattern of modified reflections: direction of incidence [100].

It may be remarked also that θ and ϕ need not be positive. One of them may be positive and the other negative, and the integer n which gives the order of the reflection may be either positive or negative. The range of admissible values of θ and ϕ and the permissible values of n are, however, limited by considerations of intensity. If θ and ϕ differ too widely, or if n be too large, the modified reflection may be unobservable. Figures 1 and 2 represent the modified reflection patterns drawn in this way for the cases in which the incident X-ray beam traverses the [100] and [110] directions respectively within the crystal. The circles drawn in these figures are the Debye-Scherrer rings for the crystal spacings listed in table 1. Since the 441 and 600 spacings are identical, there are only nine rings to be considered. In figure 1, the 111 and 222 circles have been omitted, as the value of θ for these spacings would be too large for the corresponding modified reflection to be of observable intensity. They however appear in figure 2. In both of these cases, the incident X-ray grazes some of the planes giving the strongest modified reflections. For instance, a beam along [100] grazes the following planes: (001), (010), (011) and (01$\bar{1}$). A beam along [110] grazes the following planes: (001), ($\bar{1}$10), ($\bar{1}$11) and (1$\bar{1}$1). Accordingly, in these cases, the reflections by these planes appear in the directions given by the formula (1a) and form an important features of the observed patterns. Other reflections can also appear on the pattern if the orientation of the planes in question is not too remote from that necessary for a Bragg reflection. These have also been drawn in the figures.

It is interesting to consider in what way the pattern represented in figure 1, would be altered if the orientation of the crystal is altered, step by step, by rotating
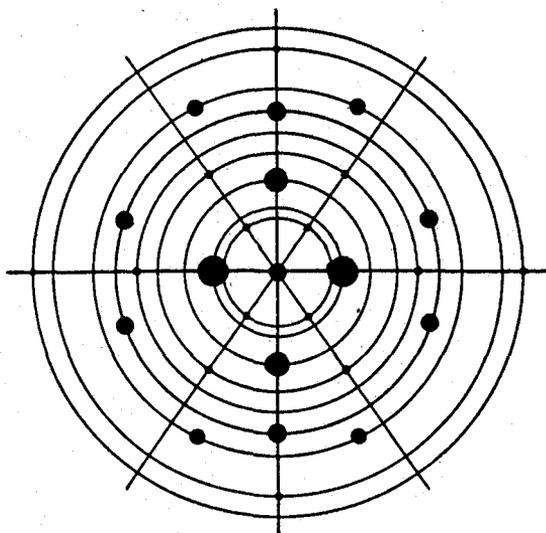
Figure 2. Pattern of modified reflections: direction of incidence [110].

it about a suitable axis. The X-ray beam has initially the direction [100] within the crystal, and the latter is then rotated about a perpendicular direction, say [010], a few degrees at a time. By virtue of formula (1), the modified reflections would in such a case continue to lie on their respective circles. It is obvious, however, that with the exception of the reflections appearing in the plane containing the axis of rotation, the modified reflections must move along the circles which are their loci in order that they may remain in the respective planes of incidence. To find their position rigorously, it would be necessary, at each setting of the crystal to find anew the planes of incidence and redraw the radial lines in the diagram the intersection of which with the circles of the powder-diagram gives the modified reflections. The trouble of doing this may, however, be avoided and the positions located with fair accuracy by a simple device, namely by finding the layer lines on which appear the Bragg reflections when the crystal is rotated or oscillated about the specified axis. It is evident that the points at which these layer lines intersect the powder-diagram circles represent the position of the modified reflections *rigorously* for the particular orientation of the crystal at which they coincide with the corresponding Bragg reflections, and therefore *approximately* also for a considerable range of orientations on either side of that position. In figure 3, the layer lines have been drawn for the case mentioned above, and the positions of the modified reflections marked therein. On comparing the same with figure 1, it will be seen that the displacements from their positions in the normal setting of the crystal are not large.
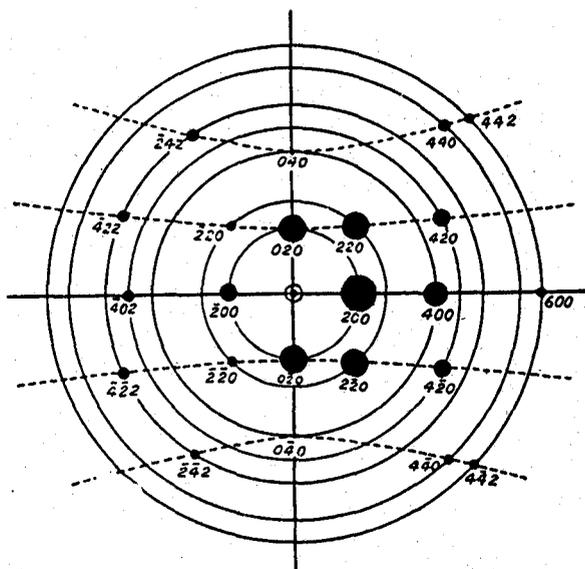
Figure 3. Pattern of modified reflections with crystal tilted about [010] axis.

4. Experimental results

Plates I, II and III reproduce a series of 12 Laue photographs (figures 4 to 15) obtained with a crystal of rock-salt and the unfiltered radiation from a molybdenum target, the distance from crystal to photographic film being 4·9 cms in the whole series. In obtaining figure 4, the crystal was set with the X-ray beam normal to a cube-face, in other words parallel to an axis of four-fold symmetry, and the pattern accordingly shows the same type of symmetry. In obtaining the remaining seven photographs of the series figures 5 to 11, the setting of the crystal was altered a few degrees at a time, being turned round a vertical axis of four-fold symmetry in the crystal. The patterns accordingly exhibit two-fold symmetry about a horizontal axis. The inclination of the X-ray beam to the four-fold axis of symmetry increased from 0° in figure 4 to 17° 46′ in figure 11. Figures 12 to 15 in plate III reproduce another series of Laue photographs obtained by the same procedure but at larger angular intervals for the setting of the crystal and covering a greater range of incidences. To permit of this being done, the photographic film was displaced sideways so that it exhibits only one half of the Laue pattern. The inclination of the X-ray beam to the four-fold axis of symmetry was 0° in figure 12 and 25° 21′ in figure 15. Plate IV reproduces two Laue photographs (figures 16 and 17) obtained with the unfiltered X-radiation from molybdenum and copper targets respectively, the rock-salt crystal being set so

that the X-ray pencil was parallel to a diagonal axis of symmetry, in other words inclined at 45° to the cube faces.

A careful study of the Laue photographs reproduced in the plates brings out clearly the laws of the modified reflection of X-rays. The series of figures 4 to 15 in the plates should be compared with figure 1 and figure 3 in the text above in which the theoretical positions of the modified reflections have been indicated. Figures 16 and 17 in the plate may also be compared with figure 2 in the text which refers to the same orientation of the crystal. It will be seen that there is a satisfactory agreement in each case between the theory and the experimental results. The most striking features brought out by the photographs are (1) the invariability of the angular separation between the incident beam and the modified reflections and (2) the remarkable resemblance between the pattern of modified reflections for an oblique setting of the crystal with the layer-line diagram of an oscillating or rotating crystal. This resemblance is clearly the consequence of the mechanism by which the modified reflections are brought into existence, namely the rotation of the dynamic stratifications of electron density with respect to the crystal spacings by the phase-waves of the lattice vibration. The rotation is of such magnitude that the angle $(\theta + \phi)$ between the incident pencil and the modified reflection by any particular plane remains invariant, though the crystal setting is altered. In other words, the modified reflection appears at the same angular separation from the primary beam as the Bragg reflection for a different setting of the crystal.

5. Intensity relations

We shall now proceed to consider in detail the remarkable changes which occur in the *intensity* of the modified reflections as the setting of the crystal is altered. These form an impressive feature in the photographs.

The most intense reflections are those given by the (100) planes, as is to be expected. These are observed over a wide range of incidences in the second, fourth and sixth orders, but in decreasing order of intensity. The second order may be positive or negative, the reflection in the latter case appearing on the side of the plane opposite to that on which the X-ray beam is incident, which is rather a noteworthy phenomenon. Modified reflections of several different orders may be simultaneously observed, and in such cases, the relative intensity of the different orders depends on the setting of the crystal. For instance, in figures 14 and 15, the second, fourth and sixth order reflections by the (100) planes may all be observed, but the fourth order is the most intense in figure 14 and the sixth order in figure 15. The intensity of a reflection of any particular order is greatest when θ and ϕ are nearly equal, that is when the modified reflection appears in the vicinity of an ordinary or Bragg reflection of the same order from the planes under consideration. The intensity falls off when θ and ϕ diverge from each other in either direction. This fall is very rapid when θ is nearly equal to ϕ, as is evident

from the photographs and strikingly illustrated by the fact (see for instance figure 9) that the K_β reflection may actually be stronger than the K_α reflection when it is nearer the Laue spot due to the same spacing. The fall of intensity however, becomes relatively slow when θ and ϕ differ greatly, and this fact enables the modified reflections to be observed over a wide range of incidences.

The (110) planes also give intense modified reflections, which may be observed in the second order, positive as well as negative and, though rather weakly, also in the fourth order (see figure 15). That these reflections are definitely weaker than the corresponding (100) reflections, may be seen for instance from figure 7, in which the second order (negative) reflections from the (110) planes have almost vanished, while those from the (100) are still quite strong. In some settings of the crystal, the (110) reflections may appear stronger than the corresponding (100) reflections, e.g., in figures 14 and 15 where the 220 spots are stronger than the 200 spots, but this is merely due to the great disparity in the relative values of θ and ϕ for the two reflections.

Next in order of intensity are the 420 modified reflections, i.e., those by the (210) planes in the second order. They may be seen above and below the 400 modified reflections and on the same layer line as the 020 and 220 modified reflections (figures 10, 11, 13, 14 and 15) and may be readily compared in intensity with them. It will be noticed that the (420) spots though less intense than the 020 and 220 spots are comparable in intensity with the 400 spots and in some photographs actually brighter than them (see for instance figure 15). These observations indicate that the modified reflections by the crystal planes appearing in the first column of table 1 follow the same order of intensity as the unmodified reflections by those planes. The figures given in table 1 further suggest that the 422 modified reflections should be weaker than the 420 and 400 modified reflections. That this is actually the case may be seen from figure 11 in which these reflections are seen in comparable circumstances (the 420 and 400 spots in the right half of the picture, and the 422 spots in the left half). See also figures 6, 8, 9 and 11. From table 1, we may also expect that the (221) planes should give modified reflections (in the second order) of comparable intensity with the fourth order reflections from the (110) planes and the sixth order reflections from the (100) planes. The 442 reflections may be seen clearly in figure 5 and their intensity is about the same as the 110 (4) and 100 (6) reflections seen in figure 15 in comparable circumstances.

6. Verification of the modified Bragg formula

In the theoretical paper by Raman and Nath quoted above, two alternative formulae have been deduced, namely

$$2d \sin \tfrac{1}{2}(\theta + \phi) = n\lambda, \tag{1}$$

$$d \sin (\theta + \phi) = n\lambda \cos \phi, \tag{2}$$

which connect the glancing angles of incidence and reflection θ and ϕ respectively with the crystal spacing d, the order of reflection n and the X-ray wavelength λ. It was indicated that the considerations on which formula (1) was derived were probably valid for the great majority of crystals. In the preceding discussion, formula (1) has been assumed to be correct, but it is evidently of importance that the experimental data should be compared with both of the formulae as a test of the theoretical considerations on which they were respectively based. The results given by the two formulae differ to a greater extent the more widely θ and ϕ diverge from each other. The formulae however become identical when $\theta = \phi$. Further, if the angles θ and ϕ are small,

$$2 \sin \tfrac{1}{2}(\theta + \phi) \approx \sin(\theta + \phi) \text{ and } \cos \phi \approx 1,$$

and hence in these circumstances the two formulae cease to be experimentally indistinguishable. Accordingly for a discrimination between them to be possible, it should be based on those cases when θ and ϕ differ considerably, and ϕ is as large as possible.

We give below in a series of tables, the data measured from the photographs for the various orders of reflections by the spacings listed in the first column of table 1.

The figures appearing in the last two columns of tables 2, 3, 4, 5, 6, 7, 8 and 9 all show in an unmistakable manner that the symmetric formula (1) and *not* the

Table 2. 200 Reflections: crystal spacing = 2·814 A.U.

Crystal planes and order of reflection	X-ray wavelength A.U.	Glancing angle of incidence θ	Glancing angle of reflection ϕ	$\theta + \phi$	Spacing calculated from	
					Formula (1) A.U.	Formula (2) A.U.
+ 100(2)	0·708	0°	14°19′	14°19′	2·84	2·77
		2°17′	11°55′	14°12′	2·86	2·82
		3°33′	10°46′	14°19′	2·84	2·81
		4°4′	10°21′	14°25′	2·82	2·80
		9°40′	4°45′	14°25′	2·82	2·83
		11°36′	2°43′	14°19′	2·84	2·86
		14°47′	−0°35′	14°12′	2·86	2·89
		17°46′	−3°34′	14°12′	2·86	2·88
		25°21′	−11°9′	14°12′	2·86	2·83
+ 100(2)	0·625	0°	12°39′	12°39′	2·83	2·79
		4°4′	8°35′	12°39′	2·83	2·82
		9°40′	2°46′	12°26′	2·89	2·90
		11°36′	1°3′	12°39′	2·83	2·85
− 100(2)	0·708	0°	−14°12′	−14°12′	2·86	2·80
		2°17′	−16°36′	−14°19′	2·84	2·74
		3·33′	−17°52′	−14°19′	2·84	2·72
		4°4′	−18°16′	−14°12′	2·86	2·74
		9°40′	−23°59′	−14°19′	2·84	2·62

Table 3. 220 Reflections: crystal spacing = 1·990 A.U.

Crystal planes and order of reflection	X-ray wavelength A.U.	Glancing angle of incidence θ	Glancing angle of reflection ϕ	$\theta + \phi$	Spacing calculated from Formula (1) A.U.	Formula (2) A.U.
+(110)(2)	0·708	0°	20°10′	20°10′	2·02	1·93
		4°21′	15°55′	20°16′	2·01	1·97
		6°53′	13°31′	20°24′	2·00	1·98
		7°58′	12°26′	20°24′	2·00	1·98
		12°20′	7°50′	20°10′	2·02	2·03
+(110)(2)	0·625	6°53′	10°53′	17°46′	2·02	2·01
		10°20′	7°32′	17°52′	2·01	2·02
		12°20′	5°20′	17°40′	2·04	2·05
−(110)(2)	0·708	0°	−20°10′	−20°10′	2·02	1·93
		1°39′	−21°49′	−20°10′	2·02	1·91
		1°51′	−22°1′	−20°10′	2·02	1·90
		2°14′	−21°53′	−19°39′	2·07	1·95

Table 4. 400 Reflections: crystal spacing = 2·814 A.U.

Crystal planes and order of reflection	X-ray wavelength A.U.	Glancing angle of incidence θ	Glancing angle of reflection ϕ	$\theta + \phi$	Spacing calculated from Formula (1) A.U.	Formula (2) A.U.
(100)(4)	0·708	9°40′	19°18′	28°58′	2·83	2·76
		11°36′	17°26′	29°2′	2·82	2·78
		17°46′	11°22′	29°8′	2·82	2·85
		19°21′	9°57′	29°18′	2·80	2·85
		25°21′	3°57′	29°18′	2·80	2·89
(100)(4)	0·625	9°40′	15°58′	25°38′	2·82	2·78
		11°36′	14°8′	25°44′	2·81	2·79
		14°47′	10°57′	25°44′	2·81	2·83
		17°46′	7°58′	25°44′	2·81	2·85

asymmetric formula (2) gives results in agreement with experiment in the case of rock-salt. The differences between the actual crystal spacings and those calculated from the asymmetric formula are systematic and in the expected direction: they increase when θ and ϕ diverge from each other, being positive when θ is greater than ϕ and negative when θ is less than ϕ. The differences become great when ϕ is numerically large, just as we should expect. The errors in measurements of the angles of θ and ϕ are relatively the greatest in the case of the 200 reflections, both because the absolute values of θ and ϕ are then smallest, and also because the spots being intense, are heavily overexposed and therefore

Table 5. 240 and 420 Reflections: crystal spacing = 1·259 A.U.

Crystal planes and order of reflection	X-ray wavelength A.U.	Glancing angle of incidence θ	Glancing angle of reflection ϕ	$\theta + \phi$	Spacing calculated form	
					Formula (1) A.U.	Formula (2) A.U.
(120)(2)	0·708	13°3'	19°27'	32°30'	1·27	1·24
and		13°17'	19°13'	32°30'	1·27	1·24
(210)(2)		14°53'	17°37'	32°30'	1·27	1·26
		15°24'	17°14'	32°38'	1·26	1·25
		15°32'	17°2'	32°34'	1·26	1·26
		16°59'	15°35'	32°34'	1·26	1·27
	0·625	13°3'	15°27'	28°30'	1·27	1·26
		13°17'	15°19'	28°36'	1·27	1·26
		14°53'	13°59'	28°52'	1·25	1·26
		15°24'	13°20'	28°44'	1·26	1·26
		15°32'	12°58'	28°30'	1·27	1·28
		16°59'	11°53'	28°52'	1·25	1·27

Table 6. 242 and 422 Reflections: crystal spacing = 1·149 A.U.

Crystal planes and order of reflection	X-ray wavelength A.U.	Glancing angle of incidence θ	Glancing angle of reflection ϕ	$\theta + \phi$	Spacings calculated from	
					Formula (1) A.U.	Formula (2) A.U.
(121)(2)	0·708	15°6'	20°36'	35°42'	1·15	1·13
and		15°32'	20°20'	35°52'	1·15	1·13
(211)(2)		16°29'	19°27'	35°56'	1·15	1·14
		16°59'	18°57'	35°56'	1·15	1·14
		18°32'	17°24'	35°56'	1·15	1·15
		20°29'	15°27'	35°56'	1·15	1·16
		20°35'	15°21'	35°56'	1·15	1·16
	0·625	15°6'	16°24'	31°30'	1·15	1·15
		15°32'	16°4'	31°36'	1·15	1·15
		16°29'	16°11'	31°40'	1·15	1·14
		16°59'	14°53'	31°52'	1·14	1·15
		18°32'	13°8'	31°40'	1·15	1·16

subject to photographic broadening. It is therefore not surprising that the agreement between the actual crystal spacings and those calculated from the symmetric formula and shown in the penultimate column of table 2 is not as excellent as it is in the case of the reflections listed in tables 3 to 9. Even so, the

Table 7. 440 Reflections: crystal spacing = 1·990 A.U.

Crystal planes and order of reflection	X-ray wavelength A.U.	Glancing angle of incidence θ	Glancing angle of reflection ϕ	$\theta + \phi$	Spacing calculated from	
					Formula (1) A.U.	Formula (2) A.U.
(110)(4)	0·708	17°29'	24°19'	41°48'	1·99	1·94
	0·625	17°29'	18°49'	36°18'	2·01	2·00

Table 8. 442 Reflections: crystal spacing = 0·938 A.U.

Crystal planes and order of reflection	X-ray wavelength A.U.	Glancing angle of incidence θ	Glancing angle of reflection ϕ	$\theta + \phi$	Spacing calculated from	
					Formula (1) A.U.	Formula (2) A.U.
(221)(2)	0·708	20°48'	23°36'	44°24'	0·937	0·927
		21°27'	22°47'	44°14'	0·940	0·935

Table 9. 600 Reflections: crystal spacing = 2·814 A.U.

Crystal planes and order of reflection	X-ray wavelength A.U.	Glancing angle of incidence θ	Glancing angle of reflection ϕ	$\theta + \phi$	Spacing calculated from	
					Formula (1) A.U.	Formula (2) A.U.
(100)(6)	0·708	19°21'	24°45'	44°6'	2·83	2·74
		25°21'	19°3'	44°24'	2·81	2·87

failure of the asymmetric formula for the 200 reflections is as evident as in the other cases.

7. Significance of the results

The asymmetric formula (2) referred to above may be written in the form

$$d(\sin \theta + \cos \theta \tan \phi) = n\lambda. \tag{2'}$$

A formula of identically the same form as (2') appears as equation (12) of a theoretical paper by Faxen (1923) *in which ϕ now denotes the direction of maximum intensity in the diffuse thermal scattering of monochromatic X-rays by a cubic crystal.* Faxen's theory has been recently revived and developed by Zachariasen

(1940) in an attempt to explain the radial streaks in Laue patterns observed by many workers as well as the more recent experimental results obtained in this connection by Wadlund (1938), Preston (1939) and of Siegel and Zachariasen (1940). As we have seen above, the formula (2') fails to represent the actual position of the modified reflections observed with rock-salt when the incidences are varied over a sufficient range of angles to make a real test of its validity. The experimental results thus clearly indicate that the Faxen–Zachariasen theory is inadequate to explain the phenomena under consideration in the present series of papers. Further, the success of the modified Bragg formula (1) in giving correctly the position of the spots as observed in the present investigation over a wide range of incidences indicates clearly that we are dealing here with a distinctive phenomenon which is in the nature of a specular reflection of the X-rays, and not a diffuse scattering.

It will be noticed that the modified reflections given by rock-salt are much better defined than those obtained with sodium nitrate, especially when the angles of incidence and reflections differ greatly. This is not surprising when it is remembered that the melting point of rock-salt is 804° C as against 308° C for sodium nitrate, and that the characteristic frequencies of the latter substance (at any rate some of them) are much lower than that of rock-salt. The disturbing effect of thermal agitation on the modified reflections should therefore be much more serious with sodium nitrate than with rock-salt. The theoretical derivation of the symmetric formula makes it clear that the reflections given by that formula should appear in sharply defined directions, and any lack of definition must therefore be due to disturbing causes such as thermal agitation or the mosaic structure of the crystal. The question here raised can be resolved by experiments with the substance at low temperatures. Such experiments have been taken in hand.

8. Summary

The paper presents an experimental study and theoretical discussion of the modified reflection of X-rays in rock-salt. It is shown that the oscillation of the interpenetrating lattices of sodium and chlorine ions would vary the structure amplitudes of the crystal in such a way that the halved spacings which give strong unmodified reflections would also give strong modified reflections in the same order of relative intensity. This is supported by the experimental results. A geometrical construction is given for deriving the modified reflection patterns in various cases and it is shown that for an oblique setting of the crystal, there is a remarkable similarity between the patterns and the layer-line diagram of the Bragg reflections by an oscillating crystal. The modified Bragg law $2d \sin \frac{1}{2}(\theta + \phi) = n\lambda$ is in very satisfactory agreement with the experimental result.

References

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Fermi and Rasetti *Ibid.* **71** 689 (1931).
Faxen *Ibid.* **17** 266 (1923).
Zachariasen *Phys. Rev.* **57** 597 (1940).
Wadlund *Ibid.* **53** 843 (1938).
Preston *Proc. R. Soc.* A **172** 116 (1939).
Siegel and Zachariasen *Phys. Rev.* **57** 795 (1940).

(4) (5)

(6) (7)
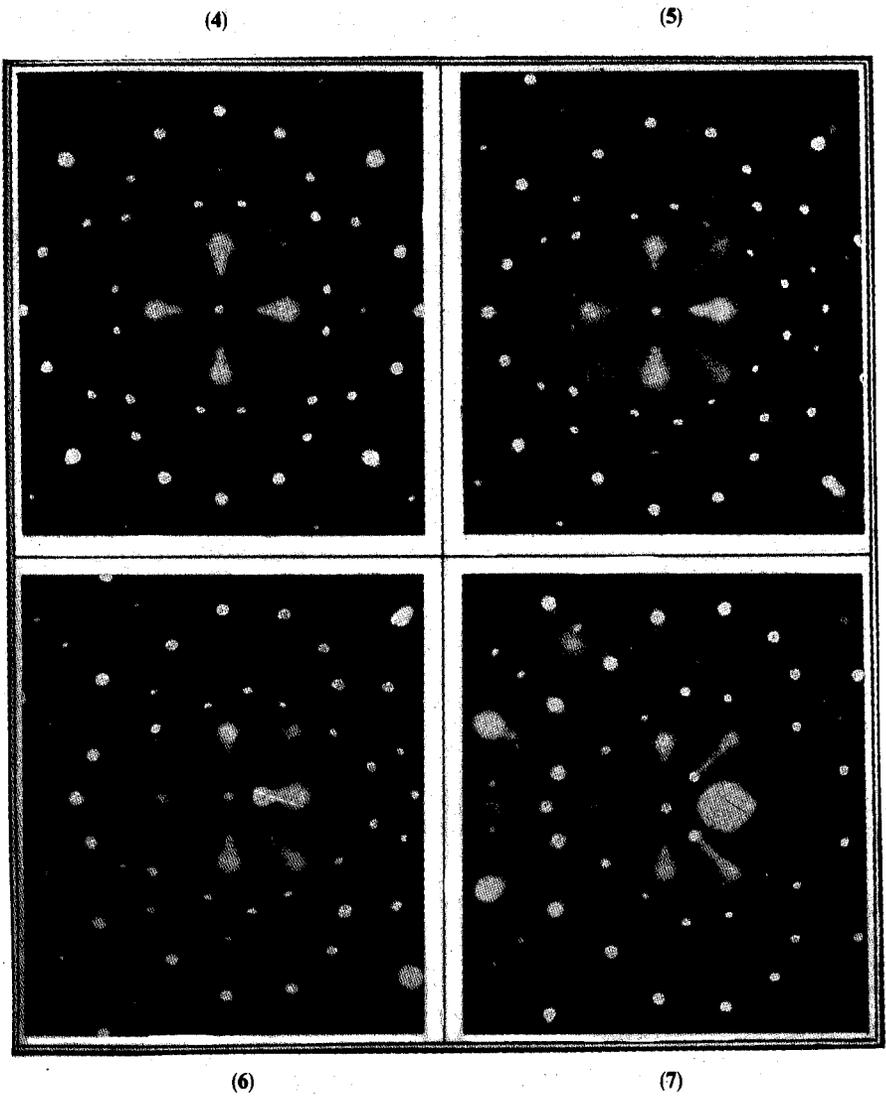
Figures 4–7. Laue photographs with rock-salt showing modified reflections.

Plate I

(8)   (9)

(10)   (11)
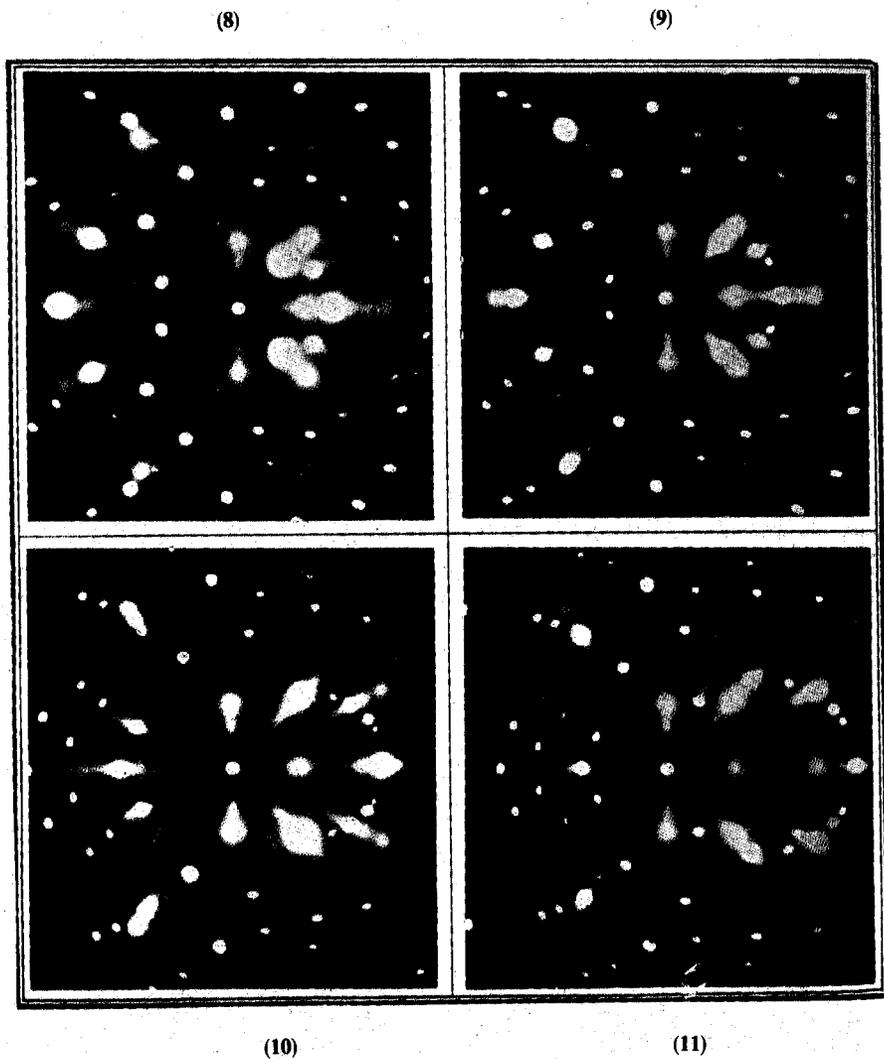
Figures 8–11. Laue photographs with rock-salt showing modified reflections.

Plate II

(12)   (13)

(14)   (15)
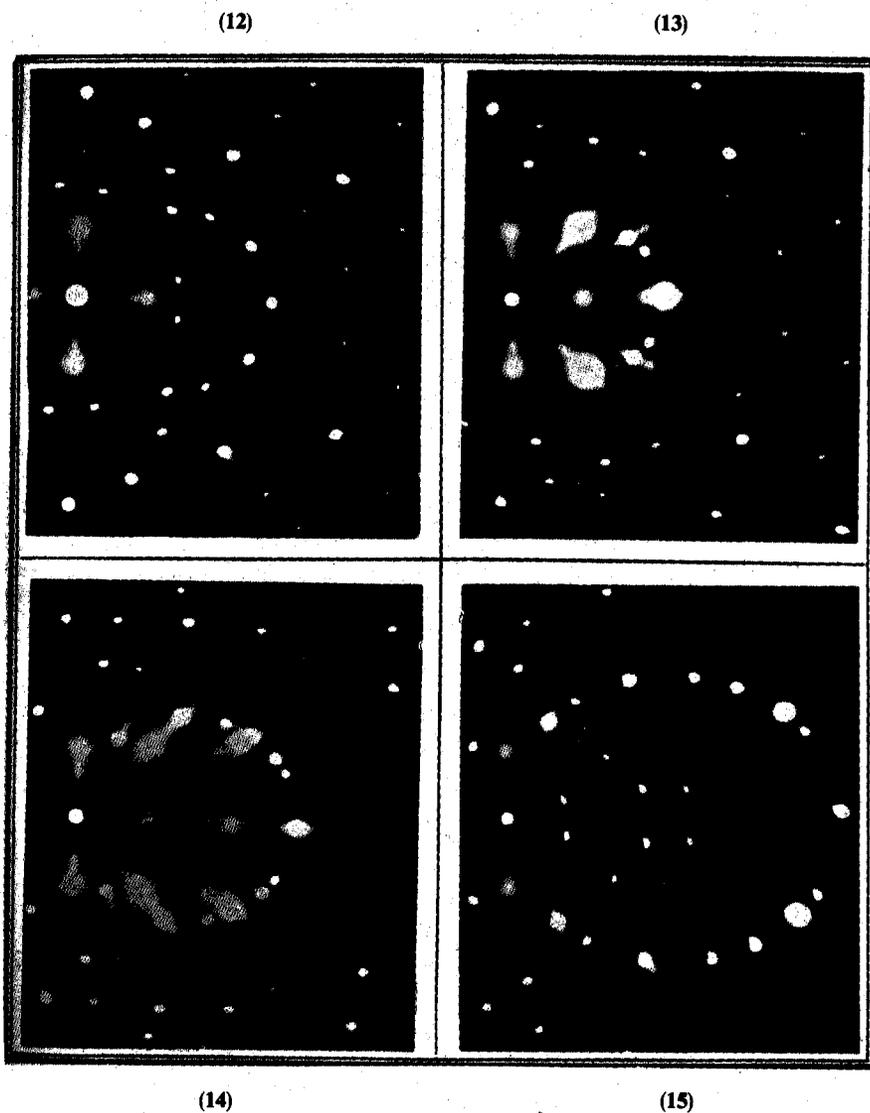
Figures 12–15. Laue photographs with rock-salt showing modified reflections.

Plate III
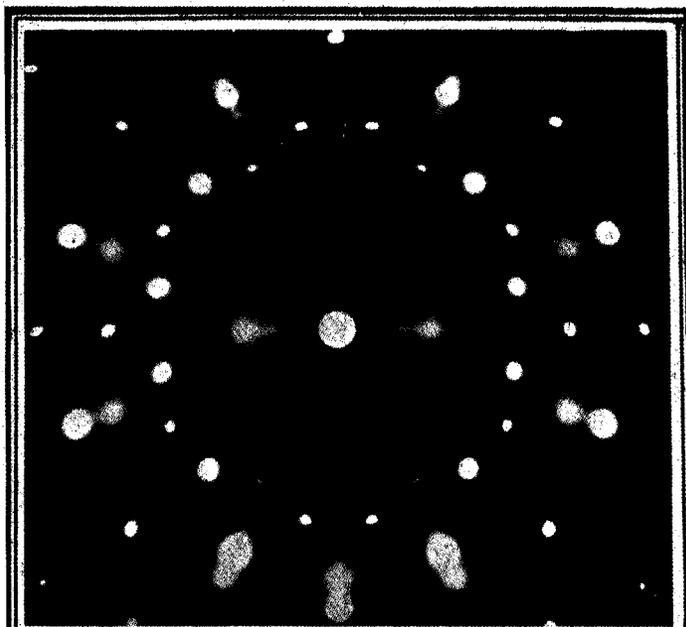
(16)
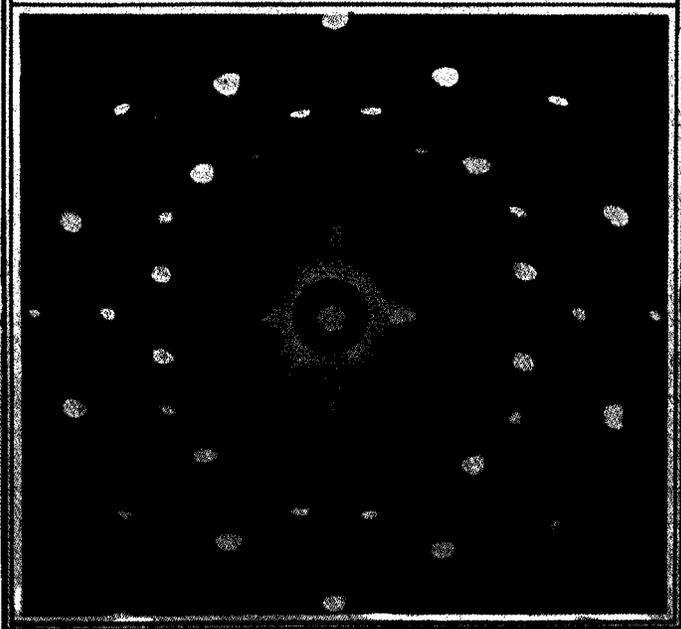
(17)

Figures 16 and 17. Laue photographs with rock-salt showing modified reflections.

Plate IV