THE QUANTUM REFLECTION AND THE QUANTUM SCATTERING OF X-RAYS IN ROCK-SALT

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1. *Introduction*

During the past year numerous papers have appeared concerning the origin of the diffuse spots and streaks observed by Wadlund[1] (1938) in well-exposed Laue photographs of rock-salt crystal. On the basis of their original observations on the sharply defined monochromatic X-ray reflections shown by the (111) planes of diamond over a wide range of the crystal settings, Raman and Nilakantan[2] (1940) put forward the view that the diffuse spots observed in rocksalt have also a similar origin, namely that they are due to a *reflection of the X-rays with a change of frequency* arising from the quantum mechanical excitation of the infra-red vibrations of the crystal lattice. About the same time Zachariasen[3] (1940) put forward the view that the Faxen[4]-Waller[5] (1923) theory of temperature-scattering of X-rays by crystals explains the phenomenon. This point of view has been supported by Preston,[6] Lonsdale[7] and Born[8].

In a paper in the course of publication in this *issue*, Sir C. V. Raman[9] has theoretically examined the effect of the atomic vibrations in a crystal on the X-rays traversing it, starting from certain classical considerations originally put forward by Laue[10], and has arrived at the following general conclusions: (1) The infra-red or high frequency vibrations of a crystal lattice are quantum-mechanically excited by the incident X-ray photons; as the result of the periodic variation of the structure amplitude of particular crystal planes resulting from such vibrations, the incident monochromatic X-rays are reflected by the crystal planes with a change of frequency. *These dynamic or quantum reflections are quite distinct from the static or unmodified reflections*, except that at the Bragg setting of the crystal they coincide with the latter in direction. The direction in which the dynamic reflection appears at other settings of the crystal is determined by the inclination of the phase waves to the crystal planes. (2) The elastic or low-frequency vibrations of the crystal give rise to diffuse maxima of scattering of the kind postulated in the Faxen-Waller-Zachariasen theory.

At the Bragg settings of the crystal, the maxima are sharpest, then coinciding with the regular reflections by the lattice planes. But they fall off rapidly in intensity and become much more diffuse when the glancing angle is altered in either direction. The formulæ indicate that the direction in which the hump of scattering intensity is to be expected alters with the crystal setting roughly—but by no means exactly—in the same way as the quantum reflection by the same lattice planes. (3) In addition to this, there is a general scattering of X-rays of the Brillouin type forming a diffuse cone round the primary beam, their change of frequency being dependent on the angle of scattering. The second and the third effects due to the *elastic waves in the crystal* come under what may be called the *quantum scattering of X-rays*. The relative intensity of the quantum scattering to the quantum reflection would depend upon various factors, including especially the structure of the crystal, and the temperature of observation.

The present investigation was undertaken with the object of examining the origin of the diffuse spots observed with rock-salt by some simple experimental tests capable of deciding between the alternative theories which have been proposed.

2. *Influence of the Volume of the Irradiated Crystal*

It is well known that as a result of the primary and secondary extinctions, the number of layers of a crystal effectively taking part in the Laue or Bragg reflections is limited to an extent depending upon the degree of its crystallographic perfection. The increase of the thickness of the crystal beyond such limit results only in the loss of the intensity of reflection due to the absorption by the medium traversed. From the preliminary considerations set forth above it will be evident that a similar situation should also exist in respect of *the quantum or Raman reflections of the X-rays*. In other words, the ratio of the intensity of a Raman spot in a Laue pattern to that of any of the Laue spots due to *approximately the same X-ray wave length* should remain the same irrespective of the thickness of the crystal plate used or the narrowness of the incident beam, other things remaining the same. The size of the spots due to the quantum reflections should also increase with the area and the thickness of the crystal traversed by X-rays and with the divergence of the incident beam in much the same manner as for the Laue spots.

The situation is, however, very different for the *quantum scattering* of X-rays of either of the kinds described above. The " extinctions " restricting the number of layers in the case of a reflection do not enter into consideration and therefore, the intensity of the quantum scattering should be proportional to the volume of the crystal irradiated except for the diminution due to absorption which arises also for the Laue or the Raman reflections. Thus, by taking a series of Laue photographs with different thickness of crystal and with varying widths of the X-ray beam traversing it, we should be in a position to decide whether we are dealing with a true reflection or a simple scattering by the crystal planes.

3. *Experimental Results*

Figs. 1, 2 and 3 in the accompanying Plate illustrate the Laue patterns obtained with molybdeneum radiations incident normally to the 100 planes of rocksalt of thickness 0·5 mm. and 0·25 mm. respectively cleaved from the same block of a natural crystal. The diameter of the pin-hole used for the front lead slit was 1·32 mm. for Figs. 1 and 3 and 0·4 mm. for Fig. 2, which gave for the area of the crystal illumined 5·1 and 0·86 sq. mm. respectively. Since the intensity of the incident X-rays is diminished by the reduction of the size of the pin-hole, the time of exposure is suitably increased for the fine pin-hole in order to record the patterns with not too widely differing intensities. In comparing Figs. 1 and 2, it should be noted that the thickness of the crystal and the width of the incident beam are both different, the volume of the crystal irradiated being in the ratio 12 : 1 as between the two cases. The ratio of the intenstiy of the transmitted beam to that of the incident beam, I/I_0, for five wave-lengths is tabulated below from the known absorption data for rock-salt :

Thickness of Crystal	λ in A.U.	·417	·497	·631	·710	·88
·25 mm.	I_1/I_0	·915	·865	·75	·665	·49
·50 mm.	I_2/I_0	·84	·748	·559	·45	·32
	I_1/I_2	1·09	1·09	1·32	1·48	1·53

It will be seen from the table that the effect of absorption is small up to 0·5 Å. The effect of the absorption for the softer X-rays as between the crystals of different thickness can be made out from the patterns reproduced in Figs. 1 and 2. At the same time, it is clear that the relative intensity of the Laue spots and the diffuse maxima in the two photographs is practically unaltered in spite of the fact that the volume of the crystal irradiated for Fig. 2 is only one-twelfth of that for Fig. 1. Figs. 2 and 3 are reproductions of the Laue patterns obtained with identically the same crystal and the same setting, only the size of the pin-hole and the exposure time being varied. Although the Laue pattern in Fig. 3 is more intense than in Fig. 2, a microphotometric comparison of the intensity of the diffuse spot due to the Mo$\cdot$K$_\alpha$ rays with that of the weak Laue spots in the neighbourhood shows only an increase of intensity of the order of about 10% for Fig. 3 in spite of the irradiated volume on the crystal being increased nearly six-fold. It may also be noticed on comparing Fig. 2 with either Fig. 1 or 3 that the increased diameter of the pin-hole and the divergence of the incident beam produce very similar effects on the lateral extension of the Laue spots and the " diffuse maxima ". These experimental facts conclusively prove that the intensity of the extra spots or streaks observed with rock-salt are in the main not proportional to the irradiated volume but are determined by considerations of the same kind as the intensity of the Laue or Bragg reflections. If there is any true volume scattering, it is less than one-tenth of the observed effects in its intensity.

4. *The Intensity and Sharpness of the Dynamic Reflections*

In the theoretical paper by Raman already referred to, it has been shown that the intensity I of the scattering at an angle 2ψ due to the elastic vibrations of the crystal is given by

$$I \propto \frac{\sin^2\vartheta}{\sin^2\epsilon} = \left\{1 + \frac{\sin^2\theta_B}{\sin^2\psi} - 2\,\frac{\sin\theta_B}{\sin\psi}\cdot\cos\,\epsilon\right\}^{-1}$$

where θ_i is the angle of incidence, θ_B the Bragg angle, ϑ the inclination of the elastic wave-fronts to the crystal plane and $\epsilon = \psi - \theta_i$. Since

$$\cos\,\epsilon = 1 - 2\sin^2\,\epsilon/2 = 1 - 2\,(\epsilon/2)^2\ ;$$

$$I \propto \left\{\left(1 - \frac{\sin\theta_B}{\sin\psi}\right)^2 + \frac{\sin\theta_B}{\sin\psi}\cdot(\epsilon)^2\right\}^{-1} \qquad \text{(I)}$$

This corresponds to the factor

$$\cos^2\,(\theta_B - \psi)\,[1 + 2\cos^2\psi]/(\Delta\,\sin 2\,\theta_B)^2$$

in Zachariasen's modified formula[11] (1941) and tends to make the intensity infinity for small values of ϵ (or Δ *). As will be seen by the curves given later in Fig. 4, it also gives an asymmetrical distribution of the intensity and a shift of the maximum towards the Laue spot as in the case of the latter. But it has the added advantage that it remains valid for values of ϵ up to 20°.

In order to find whether the " diffuse maximum " in rock-salt falls off in intensity in the manner indicated by the above expression, the intensity distribution of the diffuse spots due to the 1st, 2nd and 3rd order reflections of the (200) plane of rock-salt have been determined microphotometrically from

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* $\Delta = \theta_i - \theta_B$.

the same Laue photograph. A very narrow beam of X-rays emerging from a pin-hole of diameter of 0·4 mm. and having a divergence of 30′ is let fall on the 100 planes of a rock-salt crystal, 0·42 mm. thick, at a glancing angle of 19°·49′. For this setting of the crystal, the maxima due to the first three orders are recorded with comparable intensities. The time of exposure is so chosen that the "maxima" are recorded with just sufficient intensity to give deflections in the microphotometer yielding a value between 0·3 and 0·6 for the log-intensities. The density-log. intensity curve for molybdenum radiations experimentally obtained was observed to be a straight line in this region and covers a range of intensity of about 1 : 20. Accuracy of measurement was thus ensured.

The graphs *a*, *b* and *c* in Fig. 4 are drawn with 2 ψ for the abscissæ and the intensities as ordinates for the three orders. Curve 1 gives the intensity

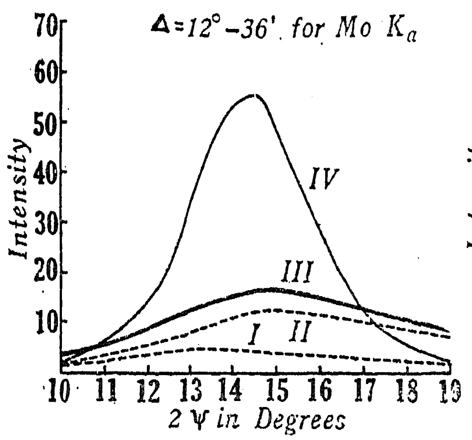

FIG. 4 (*a*) 200 Reflections from Rock-salt

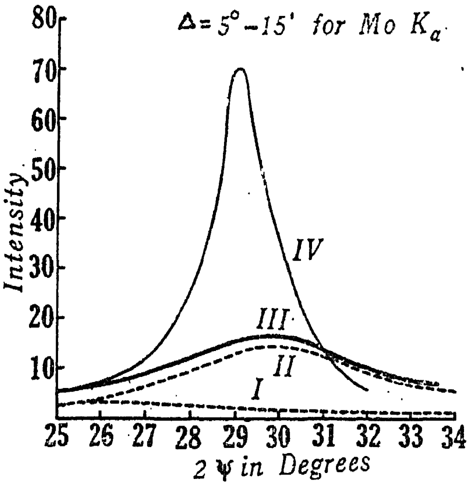

FIG. 4 (*b*) 400 Reflections from Rock-salt

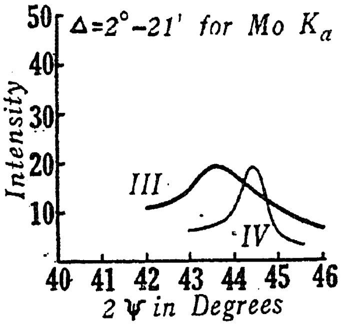

FIG. 4 (*c*) 600 Reflections from Rock-salt

distribution due to molybdenum K_β obtained by making use of formula 1 and reduced to 40% corresponding to its relative intensity to K_α; curve 2 is that due to K_α, and curve 3 gives the sum of the two intensities. The formula takes into account the increased scattering in the higher orders of reflection. In plotting the intensities of 1st, 2nd and 3rd orders to the same scale, the calculated values were reduced in the ratio 100 : 19 : 4·87 respectively. Thus, the curves 3 in Fig. 4 *a*, *b* and *c* indicate the relative magnitudes of the intensities of the three orders and the nature of their distribution to be expected if formula I holds. Curves 4 give the observed form of distribution, the peak intensity of the 3rd order being made equal to its theoretical maximum. From a study of the curves the following conclusions may be drawn:

The half-widths obtained from the theoretical curves 3 for the 1st, 2nd and 3rd orders and measured in a direction opposite to the central spot are

$3^\circ\cdot 24'$, $2^\circ\cdot 42'$ and $1^\circ\cdot 40'$. The corresponding values obtained for K_α only from the simplified formula of Zachariasen[3] (*viz.*, $\Delta \sin 2\,\theta_B$) are 2°54′, $2^\circ\cdot 33'$ and $1^\circ\cdot 40'$ respectively. On the other hand, the experimental data obtained from curves 4 in Fig. 4 are $1^\circ\cdot 50'$ for the 1st, 1° for the 2nd and 35′ for the 3rd order. It must be remarked that the finite divergence of the incident beam only tends to make the experimental values somewhat higher. For regions in the close neighbourhood of the Bragg setting ($\Delta = \pm 60'$), the theoretical half-widths calculated from the simplified formula are more than 70% higher than the experimental values furnished by the careful experiments of Zachariasen and Siegel[12] (1940). The modified formula recently given by Zachariasen[11] (1941) also gives a higher value for the half-width.* Thus we may conclude that the Raman reflections in rock-salt are much sharper than is indicated by the formula $\frac{\sin^2/\vartheta}{\sin^2/\epsilon}$. Secondly, it may be seen from the curves 3 in Fig. 4 that if the peak intensity of the 3rd order is taken as unity, that of the 1st and 2nd orders should be $0\cdot 9$ and $0\cdot 85$ respectively. On the contrary, the observed peak intensity of the 1st order is $2\cdot 9$ times and that of the second order $3\cdot 7$ times these theoretical values, showing thereby that the fall of intensity of the spot with increasing values of ϵ is much less rapid than is represented by the above formula. These experimental facts clearly demonstrate that neither as regards the variation of half-width of the spot nor of its intensity with crystal orientation, do the so-called " diffuse maxima " in the Laue pattern of rock-salt obey the laws appropriate to the scattering of X-rays by the elastic vibrations of the thermal origin in the crystal.

In conclusion the author expresses his sincere gratitude to Sir C. V. Raman, KT., F.R.S., N.L., for his stimulating interest in the work.

5. *Summary*

The ' diffuse maxima ' in the Laue patterns of rock-salt are obtained for two different crystal thickness and two different sizes of the pin-holes in the lead slit; the ratio of the volumes of the crystal irradiated by X-rays in the two cases being nearly 1 : 6 and 1 : 12. A comparison of their intensity with the weak Laue spots in the same pattern does not show any appreciable change due to the increase of the volume of the crystal. It is also noticed that the increase of the diameter of the pin-hole and the divergence of the X-ray beam has the same effect on the shape and dimensions of the Laue

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* The half-widths given by curves I and II in Fig. 4 in the paper by Zachariasen (1941) are for a pin-hole and give therefore only the lower limit for the linear slit used by Zachariasen nd Siegel.

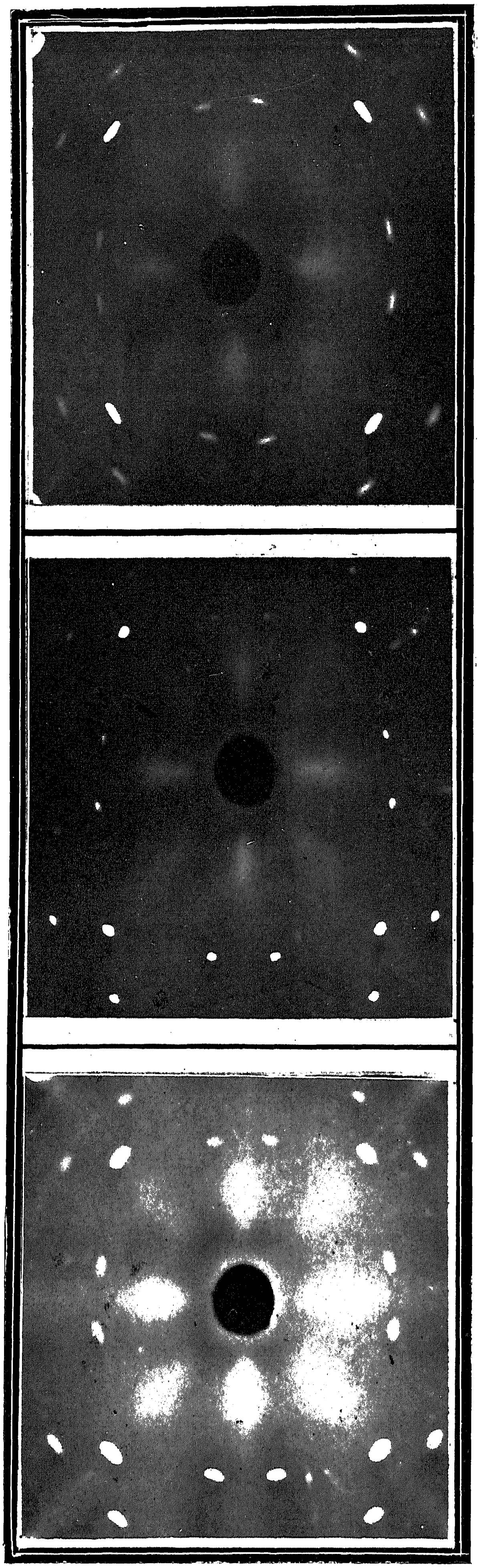

FIG. 1

Crystal thickness 0·5 mm.

Area illumined 5·1 sq. mm.

FIG. 2

Crystal thickness 0·25 mm.

Area illumined 0·86 sq. mm.

FIG. 3

Crystal thickness 0·25 mm.

Area illumined 5·1 sq. mm.

Laue Patterns of Rock-salt Crystals

spots and of the diffuse maxima. A microphotometric study of the intensity distribution of the 1st, 2nd and 3rd order spots due to the (200) planes of rock-salt reveals that they are much sharper and that the fall of intensity for increased angles of reflection is much less rapid than is to be expected if they were due to the scattering of X-rays by the thermally excited elastic waves in the crystal. It is therefore concluded that these diffuse maxima in rock-salt are due mainly to the *quantum or Raman reflections* of the X-rays due to the excitation by the X-ray quanta of the monochromatic or infra-red vibrations of the crystal lattice.

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