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Quantum theory of X-ray reflection and scattering— Part I. Geometric relations

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1. Introduction

The simplest example of the optical excitation of the vibrations of a crystal lattice is that afforded by the absorption of infra-red radiations by the crystal. In this case, the material vibrations of the lattice and the electromagnetic waves by which they are excited have the same frequency. When the incident radiations lie in the visible or ultra-violet region of the spectrum, they have a much higher frequency than the possible lattice vibrations, but may nevertheless excite the latter, as is shown by the fact that the light scattered by the crystal includes radiations of diminished frequency. The possibility of excitation in this case is due to the lattice vibrations altering the optical polarisability of the material of the crystal. In both cases, the excitation is essentially an optical process, as is clear from the fact that it occurs irrespective of the temperature of the crystal. That it is also a quantum-mechanical effect is particularly evident in the case of light scattering; the intensity of the lines appearing with diminished frequency in the spectrum of the scattered light is proportional to the Planck constant of action and varies but little with temperature, so long as this is moderate and the lattice vibrations are of sufficiently high frequency.

That the lattice vibrations of a crystal may be excited by X-rays in much the same way as in the case of ordinary light has been suggested and supported by experimental evidence in a recent series of papers in these *Proceedings.** It was there shown that the character of the resulting phenomena is different in the cases where the lattice vibrations lie respectively in the acoustic and the optical range of frequencies. This is to be expected, because in the vibrations of the acoustic class, the average electron density in the unit cell of the lattice varies periodically while its distribution within the cell remains nearly constant, while on the other hand, in the vibrations of the optical class, the mean electron density in the unit cell

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*Raman and Nilakantan, 1940, 11, 379–408.

remains approximately constant while its distribution within the cell varies periodically with time. The possibility of the vibrations of these two classes being induced by the incidence of X-rays therefore arises in different ways. In one case, it is the time-variation of the mean polarisability of the crystal and in the other case the time-variation of the structure amplitudes (Fourier components) of the electron density that is responsible for the excitation of the vibrations. It is not surprising therefore that the effects produced on the incident radiation differ even in respect of their geometric characters in the two cases.

It is proposed in these papers to develop in mathematical form the ideas outlined in the papers quoted above. In this first instalment, the purely geometric aspects of the phenomena will be discussed, the important question of intensities being only touched upon incidentally. The fuller treatment of the latter will be given in part II.

2. The acoustic case

From the remarks made above, it is evident that the cases in which the frequency of the lattice vibrations lie respectively in the acoustic and optical ranges must be considered separately. We shall proceed on the assumption that exchanges of energy and momenta take place between the incident X-radiation and the waves excited by it in the crystal, the substance of the latter otherwise taking no part in the phenomena. The conservation of energy and momentum requires

$$h\nu = h\nu' + h\nu^* \tag{1}$$

$$\frac{\vec{h}}{\lambda} = \frac{\vec{h}}{\lambda'} + \frac{\vec{h}}{\lambda^*} \tag{2}$$

ν, ν' and ν^* being respectively the frequency of the incident and scattered X-rays and of the excited acoustic waves; λ, λ' and λ^* are the corresponding wavelengths. Equation (1) shows that the frequency of the scattered X-rays is diminished relatively to the incident X-rays by the frequency of the sound-waves excited in the process. As, however, ν is far larger than ν^* we may in equation (2) take $\lambda = \lambda'$ without sensible error and proceed to solve it geometrically as shown in figure 1.

With O as centre, we draw a sphere having a radius equal to $1/\lambda$. The particular radius OI of the sphere which is parallel to the incident X-rays being marked out, we draw a second sphere with I as centre and $1/\lambda^*$ as radius which intersects the first sphere along the circle RR. It is evident that the generating lines of the cone ORR represent the possible directions of the scattered X-rays corresponding to the acoustic wavelength λ^*. The semi-vertical angle of this cone ψ is given by the relation

$$2\lambda^* \sin \psi/2 = \lambda. \tag{3}$$

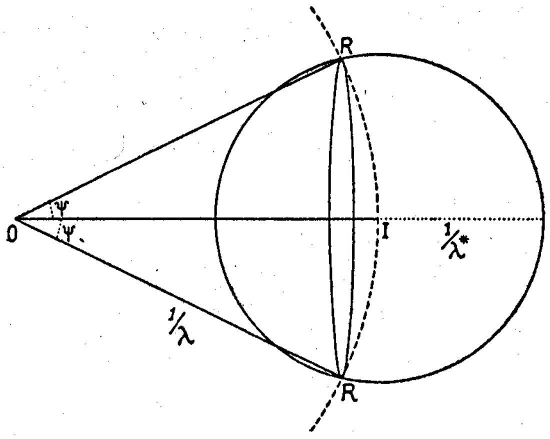

Figure 1

When λ^* is infinite, ψ vanishes and the cone of scattered X-rays collapses to a line along the incident ray. As λ^* diminishes however, the cone opens out, reaching its maximum semi-vertical angle when the wavelength of the acoustic waves is the minimum physically possible in the crystal. In the case of a cubic crystal, this minimum wavelength would certainly be greater than the grating constant of the crystal, and it is clear from (3) that in any setting of the crystal, the directions in which the Bragg reflections by the crystal could be observed would lie outside the cone of monochromatic radiations scattered by it. The distribution of energy in the cone of scattered X-rays is a special problem into which we shall not here enter. It is obvious, however, that if the acoustic spectrum of the crystal has a concentration of energy at or near a particular wavelength which may be greater than the minimum possible, the scattered X-rays may be expected to show a concentration of intensity in the vicinity of a corresponding cone of rays.

3. The optical case

Equations (1) and (2) are equally applicable in the optical case, ν^* being now one of the characteristic optical frequencies of the crystal lattice and λ^* is the wavelength of the periodic stratifications of electron density resulting from the lattice vibrations of that frequency excited in the crystal by the incident X-rays. ν^* is, of course, much larger than in the acoustic case, but even so, it is small compared with the X-ray frequency. Hence, though the change of frequency in the act of reflection indicated by equation (1) is an essential part of the phenomenon, we may without sensible error take $\lambda = \lambda'$ in equation (2). We shall, however, retain the ascent in λ' to indicate that the vector $1/\lambda'$ refers to the direction of the reflected X-ray. In the acoustic case, the vector $1/\lambda^*$ has an arbitrary direction and an arbitrary magnitude subject to only a maximum limit, with the result that the vector $1/\lambda'$ representing the direction of the scattered X-rays has an arbitrary direction lying within a certain cone. In the optical case, however, conditions are different, as we shall presently see, with the result that the vector $1/\lambda'$ is restricted to specifiable directions and the observed effect is in the nature of a well-defined reflection and not an irregular scattering.

We shall first consider the particular case in which the optical vibrations excited in the cells of the crystal lattice are everywhere of identical phase; in other words, the phase-waves of the lattice vibrations have an infinite wavelength ($\Delta = \infty$). As already remarked, the possibility of optical excitation of the lattice vibrations depends on the fact that these vibrations produce time-periodic variations in the Fourier components of the space distribution of electron density, in other words, produce periodic pulsations of the structure amplitudes of the crystal. When $\Delta = \infty$ the wavelength of these pulsations is the same as that of the crystal spacings, or a harmonic thereof; and the wave-fronts also run parallel to the crystal spacings. Accordingly, we may write

$$\frac{\vec{1}}{\lambda^*} = \frac{\vec{n}}{d}, \tag{4}$$

where n is an integer (1, 2, 3,...) and $1/d$ is a vector normal to any chosen set of crystal spacings, its magnitude being the reciprocal of that spacing. Combining (2) and (4), we have

$$\frac{\vec{1}}{\lambda} - \frac{\vec{1}}{\lambda'} = \frac{\vec{n}}{d}. \tag{5}$$

Representing this graphically, (figure 2), we derive the formula $2d \sin\theta = n\lambda$, θ being the glancing angle of incidence and of reflection. Equation (5) thus shows that *when the phase-wave length Δ of the lattice vibrations is assumed to be infinite, the quantum reflection of X-rays with diminished frequency occurs under the same geometric conditions as the classical X-ray reflections.*

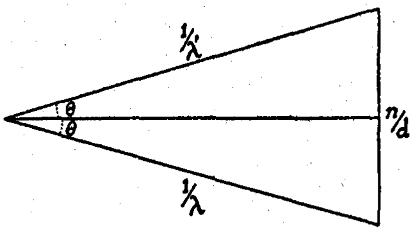

Figure 2

The case when Δ is finite corresponds to a lattice vibration in which the phase of the atomic vibrations alters progressively from cell to cell. The phase of the pulsation of structure-amplitude will therefore also alter from cell to cell, and *in general*, both the direction of the wave-fronts along which this phase is constant, and the spacing between successive such wave-fronts will differ from the crystal spacings. These quantities are indicated by the vector $1/\lambda^*$ and the reciprocal of its magnitude. We may readily find the relation between λ^*, the lattice wavelength Δ and the crystal spacing d/n (see figure 3).

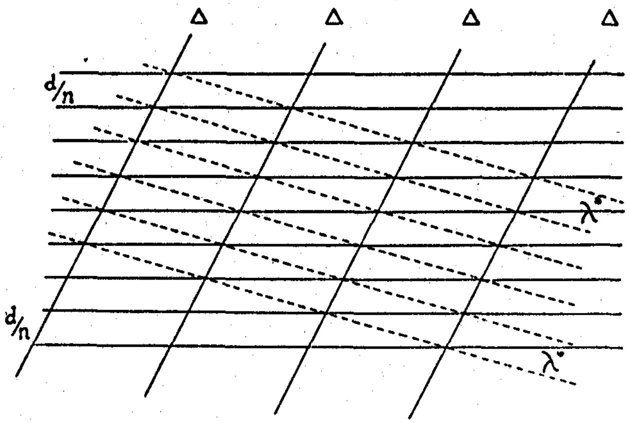

Figure 3

The crystal spacings are a set of equidistant planes marked d/n in the figure and the phase waves of the lattice vibrations are another set of planes marked Δ crossing them at an angle as in figure 3. It is evident that the planes along which the phase of the pulsations of electron density would be constant would be the set of planes crossing both diagonally and marked λ^* in the figure. The spacings of the three sets of planes are evidently connected by the vector relationship between their reciprocals (see note at the end of the paper).

$$\frac{\vec{1}}{\lambda^*}=\frac{\vec{n}}{d}+\frac{\vec{1}}{\Delta}. \tag{6}$$

Combining (6) with (2), we have, in the most general case

$$\frac{\vec{1}}{\lambda}-\frac{\vec{1}}{\lambda'}=\frac{\vec{n}}{d}+\frac{\vec{1}}{\Delta}. \tag{7}$$

Equation (7) reduces, as it should, to equation (5) when Δ is infinite. It states the most general law of the quantum reflection of X-rays which may be put into words thus: *We combine vectorially the reciprocals of the crystal spacing and of the wavelength of the optical vibrations of the crystal lattice. The reciprocal of the resultant gives the spacing of the dynamic stratifications of electron density and its direction that of their normal: these dynamic stratifications give a geometric reflection of the X-rays with diminished frequency.*

The optical vibrations of a crystal lattice have well-defined frequencies, as is shown by the sharpness of the lines observed in the spectrum of the light scattered by the crystal. The fact that the frequency shifts observed in light scattering have not so far been found to depend appreciably on the angle of scattering is also significant and shows that the lattice frequencies are approximately independent of the lattice wavelengths. Regarding the observed frequencies as due to the characteristic vibrations of the unit cells in the lattice, it is evident that the frequency as observed with an actual crystal would be N-fold degenerate, N being the number of lattice cells in the fragment of crystal used. Actually, the N frequencies should be regarded as forming an aggregate which is densest at the frequency corresponding to an infinite lattice wavelength ($\Delta = \infty$) and rapidly thins out as Δ diminishes. These considerations enable us to understand the effects to be expected on the basis of equation (7). Δ can always be considered as large compared with d/n. Hence, the effect of its appearance in the right-hand side of equation (7) on its scalar magnitude is a small quantity of the first order. It serves, however, to alter the orientation of the wave-fronts of the dynamic stratifications with respect to the crystal spacings. Indeed this would be its only effect if the vectors $1/\Delta$ and n/d are mutually perpendicular, as the resultant of their addition would then be practically n/d. In the limiting case when Δ is infinite, equation (7) shows that the quantum reflection appears under the same conditions as the classical reflection and coincides with it in position. It is also then of maximum intensity, as the N-fold aggregate of optical frequencies of the lattice is densest for infinite values of Δ. As the crystal is tilted away from the setting for the ordinary Bragg reflection, equation (7) shows that Δ must diminish in magnitude, and the intensity of the quantum reflection must therefore fall off in proportion to the diminished density of the aggregate of frequencies for smaller values of Δ. As we shall see presently, the quantum reflection also then separates out from the Bragg reflection and can be observed by itself.

4. Geometric law of quantum reflection

The geometric interpretation of equation (7) is facilitated by first considering a case in which the vector $1/\Delta$ besides being small compared with n/d is perpendicular to it and lies in the same plane with it as the incident X-rays. In this case, it is evident that the result of combining $1/\Delta$ and n/d vectorially is to tilt the reflecting planes in the plane of incidence with respect to the crystal spacings but without any alteration of these spacings. If therefore we consider a case in which the crystal-spacings are so inclined to the incident monochromatic X-rays that they *cannot* give a Bragg reflection, in other words, when

$$\frac{\vec{1}}{\lambda}-\frac{\vec{1}}{\lambda'}\neq\frac{\vec{n}}{d} \tag{8}$$

they would nevertheless give a quantum reflection according to the formula

$$\frac{\vec{1}}{\lambda}-\frac{\vec{1}}{\lambda'}=\frac{\vec{n}}{d'} \tag{9}$$

where d' has the same magnitude as the crystal spacing d, but its direction has been altered so as to satisfy the vectorial relation (9). This relation indicates that *the incident X-rays give a reflection with diminished frequency in the plane of incidence even when the Bragg reflection is not possible, and that the direction in which it appears with reference to the incident X-rays is unaffected by the setting of the crystal,* though as remarked above, *its intensity would fall off rapidly as the crystal is turned away from the Bragg setting.*

Equation (9) is represented graphically in figure 4 for two cases in which the crystal has been turned away from the Bragg setting in one direction or the other.

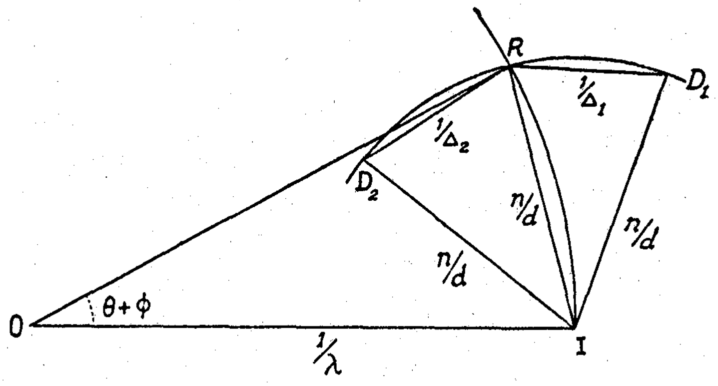

Figure 4

In both cases, the direction of the reflected ray OR is the same and is given by the trigonometric formula

$$2d\sin\tfrac{1}{2}(\theta+\phi)=n\lambda, \tag{10}$$

where θ and ϕ are the glancing angles of incidence and reflection with respect to the crystal spacings.

The postulate made above which results in the formulae (9) and (10), namely, that the vectors $1/\Delta$ and $1/d$ are perpendicular to each other, physically interpreted, means that the lattice-waves excited by the X-rays have wave-fronts perpendicular to the crystal spacings giving the quantum reflection. There is good reason to believe that this must be actually the case with most crystals. For, the atomic vibrations which are effective in altering the structure-amplitude of any particular spacing are those in which the displacements are normal to the crystal spacing. If the lattice wave-fronts are parallel to the crystal spacings, the phase of the atomic vibrations would alter as we pass from one spacing to the next, whereas if they are perpendicular to the crystal spacings, the phase of the vibration would change along the crystal spacings but not perpendicular to them. The forces brought into play between the neighbouring cells of the lattice by such phase-changes would obviously be much greater in the former case than in the latter. Accordingly, the N-fold aggregate of frequencies would be spread out over a much wider range of frequencies when Δ and d are parallel than when they are perpendicular. So far as the reflection of X-rays is concerned, therefore, we would be justified in considering only the case where Δ and d are perpendicular and ignoring the case where they are parallel. Equation (10) could then be regarded as the generally valid geometric law for the quantum reflection of X-rays with diminished frequency.

It must be recognised, however, that there may be cases where the considerations set forth above cannot reasonably be expected to be valid. It may, for instance, be possible that the binding forces which hold the crystal lattice together are of such a nature that though the atomic vibrations are normal to the crystal planes under consideration, a change in the phase of such vibrations along the crystal planes may evoke forces and disturb their frequencies quite as much as a change of phase normal to them. In such a case, the postulate that the vectors $1/\Delta$ and $1/d$ are perpendicular may cease even to be approximately true. In such cases, that is, when the effective lattice-waves have an arbitrary inclination to the crystal spacings, an alternative principle suggests itself giving the selection rule for the vector $1/\Delta$, namely, that the direction of the vector is such that its scalar magnitude necessary to satisfy equation (9) is a minimum. Such a principle would not be unreasonable in view of the remark already made that the frequency-aggregate of the optical vibrations becomes rapidly less dense for increasing values of Δ. It can readily be shown that this principle gives the same result as equation (10) when θ and ϕ are nearly equal to each other, that is to say when the setting of the crystal is not far from the Bragg position. More generally, however, it deviates from that result.

Figure 5 represents equation (7) graphically for two cases in which the crystal has been turned away from the Bragg setting in one direction or the other, and Δ is chosen to have the minimum necessary length required to satisfy the equation. The direction of the reflected ray is OR_1 in one case and OR_2 in the other. It will be noticed that the effective resulting spacing is in one case greater than d/n, and in the other case less than d/n. At the correct Bragg setting, therefore, OR_1 and OR_2 become coincident. The geometric law of the quantum reflection is seen

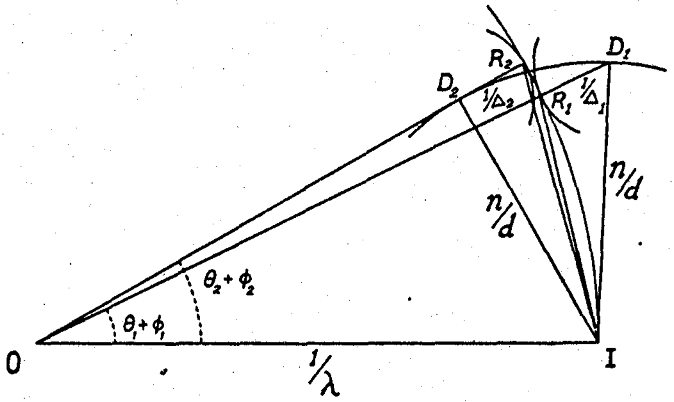

Figure 5

from figure 5 to be

$$d \sin(\theta + \phi) = n\lambda \cos \phi. \tag{11}$$

Equations (10) and (11) give results which differ the more widely, the greater the difference between θ and ϕ, but become identical when $\theta = \phi$. It will be noticed that they correspond respectively to the results which have been found experimentally valid for the cases of sodium nitrate and diamond. The divergence between the results given by the two formulae when $\theta \neq \phi$, and the fact that they have been derived on quite different considerations suggests that when the crystal is tilted away from the correct Bragg setting, the definition of the quantum reflection should progressively deteriorate. Such an effect is actually observed, but whether it is due solely to the cause stated or is due partly also to other disturbing effects, e.g., thermal agitation or the mosaic structure of the crystal, is a matter for further investigation.

Summary

When X-rays fall upon a crystal, the characteristic vibrations of the crystal lattice may be excited thereby, in much the same way as in the phenomenon of the scattering of light in crystals with diminished frequency, the excitation being a quantum mechanical effect. From the equations for the conservation of energy and momentum, the geometrical relations entering in this effect are deduced theoretically for the two cases in which the lattice vibrations fall within (1) the acoustic range of frequency and (2) the optical range. In the first case, the incident X-rays are scattered in directions falling within a cone having the incident ray as axis and with a semi-vertical angle $2 \sin^{-1} \lambda/2\lambda^*$ where λ^* is the minimum

acoustical wavelength. In the second case, we have a quantum-mechanical reflection of the X-rays with diminished frequency in a direction which generally follows the geometric formula $2d \sin \frac{1}{2}(\theta + \phi) = n\lambda$ where θ and ϕ are the glancing angles of incidence and reflection on the crystal spacings. For crystals with specially rigid bindings, the alternative formula $d \sin (\theta + \phi) = n\lambda \cos \phi$ is indicated as being more appropriate. In either case, the intensity of the reflection should fall off rapidly as θ and ϕ diverge.

Note: Equation (6) may be very simply derived from the construction shown in figure 3. The vector sum of the two sides of a triangle is equal to the third side. Dividing this equation by the area of the triangle, we get a vector relation between the reciprocals of the three perpendiculars from the vertices on the sides.