

Reflexion and scattering of X-rays with change of frequency†

I. Theoretical

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The paper sets out in an elementary way the theory of two new phenomena of fundamental importance, namely the quantum reflexion and the quantum scattering of X-rays. (1) The quantum or modified scattering is due to the excitation of the elastic solid or low frequency vibrations of the crystal lattice by the X-ray photon. It has a very low specific intensity proportional to N (the number of lattice cells) and is distributed over a wide range of solid angles. The view expressed by some authors that the elastic solid vibrations of the lattice are responsible for the additional spots visible in Laue diagrams is consequently erroneous. (2) The quantum or modified reflexion is due to the excitation of the infra-red or characteristic high frequency vibrations of the crystal lattice by the X-ray photons. Its intensity, like that of the classical or unmodified reflexions is of the order N^2 , though usually smaller in absolute value than the intensity of the classical reflexions. The manner in which the direction and intensity of the quantum reflexions are connected with the specific modes of infra-red vibration is mathematically formulated and discussed. (3) The frequency changes which play a fundamental part in the theory of both phenomena appear as necessary consequences of both the classical and quantum theoretical points of view. The law of temperature dependence of intensity is, however, quite different in the classical and quantum formulations. The experimental study of intensity at low temperatures accordingly furnishes a conclusive criterion both for the reality of the frequency changes and for the quantum mechanical character of the effects. (4) The influence of the modified X-ray reflexions on the intensity of the classical reflexions and their variations with temperature is discussed and shown to be of even greater importance than the effect on the same of the X-ray scattering by the elastic solid vibrations.

I. INTRODUCTION

The scattering of light in crystals with a change of frequency, discovered by me in 1928, has been the subject of intensive investigations at this

† These papers were sent as a contribution to the discussion on 'Diffuse reflexions of X-rays by crystals', but arrived too late to be included in the special number of *Proceedings* (A 976) devoted to this discussion.

Institute during the past five years. These are described in numerous memoirs published during the period in the *Proceedings of the Indian Academy of Sciences* and have notably advanced our knowledge of crystal optics and crystal dynamics. That analogous effects should arise also in the X-ray optics of crystals naturally suggested itself, and inspired investigations directed towards placing the behaviour of crystals towards light and X-rays on a common footing. The natural outcome of these researches has been the discovery of two new X-ray phenomena of fundamental importance, namely, the quantum reflexion and the quantum scattering of X-rays in crystals. The observations and theoretical considerations establishing the existence of these effects were published in 1940 (Raman & Nilakantan 1940 *a, b*); they may be briefly summarized thus: *The phenomenon of quantum or modified reflexion arises when X-ray photons traverse a crystal and excite the infra-red or high-frequency vibrations of the crystal lattice; the lattice planes of the crystal then reflect the X-rays in geometrically defined directions, which are, in general, different from those of the well-known classical or Laue reflexions; the reflexions occur with a frequency ($\nu \pm \nu^*$), ν being the X-ray frequency, and ν^* one or another of the characteristic infra-red frequencies of the crystal. The quantum scattering by crystals, on the other hand, arises when the X-ray photons excite the elastic or low-frequency vibrations of the crystal lattice; the X-rays are then diffused over a wide range of solid angles and have a frequency ($\nu \pm \nu^*$), ν^* the frequency of the excited elastic solid waves being now dependent on the direction of scattering. The law of temperature dependence of the intensity of the effects is determined, in either case, by the relation between $h\nu^*$ and kT , k being the Boltzmann constant and T the absolute temperature. If $h\nu^* > kT$, the component of frequency ($\nu - \nu^*$) preponderates and the total intensity of quantum reflexion or scattering, as the case may be, is approximately independent of temperature, while if $h\nu^* < kT$ the two components ($\nu \pm \nu^*$) are of comparable intensities and their aggregate increases with rising temperature. The phenomenon of quantum reflexion comes under the first category at sufficiently low temperatures, while quantum scattering usually comes under the second category.*

The further investigations on the subject carried out at Bangalore have completely confirmed the foregoing conclusions. In particular, the general geometric law of quantum reflexion has been derived and has been quantitatively confirmed by measurements made with diamond and a variety of other crystals, both organic and inorganic. The quantum-mechanical nature of the effects and the changes of frequency indicated by the theory have also received experimental confirmation from comparative studies

of the intensity of the effects over a range of temperatures including that of liquid air, made with a series of crystals.

2. SOME CLASSICAL CONSIDERATIONS

The quantum theory of radiation phenomena is an application of quantum mechanics to the interactions between matter and the radiation field, the latter being itself considered as essentially Maxwellian. Hence, except in regard to the question of intensities, purely classical ideas suffice in many cases to give a general indication of the nature of the phenomena to be expected in such interactions. It may, in fact, be shown in an elementary fashion that any vibration of the atoms of a crystal through which X-rays pass necessarily involves a change of frequency in the secondary radiations resulting therefrom, and that such changes of frequency play a fundamental part in determining the observed radiation effects.

If the field due to the incident X-rays at the origin be denoted by $E \cos 2\pi\nu t$, the secondary radiations from an individual atom received at a distance R from the origin may be written as

$$\frac{E \sin \beta F(\alpha)}{R} \cos [2\pi\nu t - 2\pi(R + 2r \sin \alpha/2)/\lambda], \tag{1}$$

where α and β are respectively the angles which R makes with the primary rays and with the primary electric vector, $F(\alpha)$ is determined by the structure of the atom, and r is the perpendicular distance of the atom from a plane through the origin bisecting the angle between the incident and the scattered rays. Any oscillation of the atom perpendicular to r would leave the expression unaffected, while an oscillation parallel to r would introduce a periodic variation of the argument of the cosine function in (1). The expression for the scattered radiation may then be written in the form

$$\frac{E \sin \beta F(\alpha)}{R} \{ \cos (2\pi\nu t - Z) \cos [z \cos (2\pi\nu^* t + \zeta)] + \sin (2\pi\nu t - Z) \sin [z \cos (2\pi\nu^* t + \zeta)] \}, \tag{2}$$

Z being written for the constant part of $2\pi(R + 2r \sin \alpha/2)/\lambda$ and $z \cos (2\pi\nu^* t + \zeta)$ for its periodic part. The expression within the curly brackets in (2) may be expanded in a series of Bessel functions, and written as

$$\begin{aligned} J_0(z) \cos (2\pi\nu t - Z) \mp J_1(z) \cos [2\pi(\nu \pm \nu^*) t - Z \pm \zeta] \\ - J_2(z) \cos [2\pi(\nu \pm 2\nu^*) t - Z \pm 2\zeta] \\ \mp \text{etc., etc.} \end{aligned} \tag{3}$$

The principles of the wave theory indicate that all secondary radiations having the same frequency are necessarily coherent, while those which differ in frequency by howsoever little, are necessarily incoherent with each other. Hence, in considering the interferences of the secondary radiations from the oscillating atoms with each other, it is necessary first to separate them according to the distinct frequencies as indicated by (3) and consider the secondary radiations of frequency ν , $(\nu + \nu^*)$, $(\nu - \nu^*)$, $(\nu + 2\nu^*)$, $(\nu - 2\nu^*)$, etc., separately. The relative importance of these frequency components

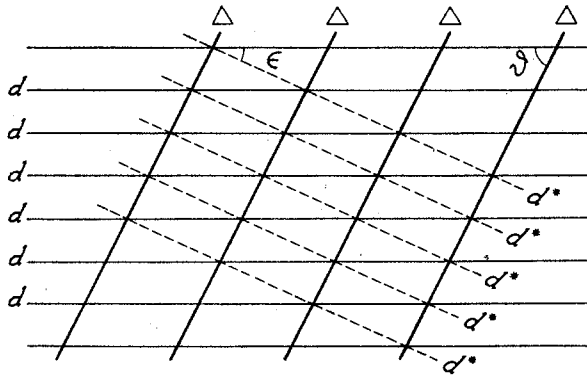


FIGURE 1. Geometric relation between static and dynamic stratifications.

depends upon the absolute value of the quantity z which appears as the argument of the Bessel functions. If z be sufficiently small, $J_0(z)$ is nearly equal to unity, $J_1(z)$ may be written as $\frac{1}{2}z$, while $J_2(z)$, etc., may be neglected. From equation (3) it will be seen that the interferences of unmodified frequency are determined by the values of Z giving the phases of the secondary radiations, in other words, by the equilibrium positions of the atoms. The interferences of the radiations of modified frequency $(\nu + \nu^*)$ and $(\nu - \nu^*)$ are, on the other hand, determined by the values of $Z - \zeta$ and $Z + \zeta$ respectively, in other words, jointly by the equilibrium positions of the atoms and by the relative phases of their vibrations. The significance of these results is readily appreciated by reference to figure 1 in which the lines marked ddd represent a set of lattice planes in the crystal, the lines $\Delta\Delta\Delta$ represent a set of equidistant parallel planes along which the phases of the atomic vibrations are identical, while $d^*d^*d^*$ are the diagonal planes passing through the intersections of ddd and $\Delta\Delta\Delta$. It is evident from (3) that the lines $d^*d^*d^*$ represent the planes of atoms from which the secondary radiations of frequency $(\nu \pm \nu^*)$ have the same resultant phase. The differing signs of ζ in (3) indicate that the direction of advancing phase, in other words,

the direction of movement of the waves $\Delta\Delta\Delta$, must be opposite for the frequencies $(\nu + \nu^*)$ and $(\nu - \nu^*)$, if the same diagonal planes are to represent the resultant in both cases.

3. SCATTERING OF X-RAYS BY ELASTIC-SOLID WAVES

The planes marked ddd in figure 1 evidently represent a static periodicity of electron density in the crystal, while $d^*d^*d^*$ represent the dynamic stratifications due to the oscillation of the atoms in these layers, the resultant effect of which has the frequency $(\nu \pm \nu^*)$ as indicated by (3). If the waves marked $\Delta\Delta\Delta$ are of such a nature as directly to involve variations of electron density in the solid, viz. if they are longitudinal elastic waves producing compressions and dilatations, they should themselves be regarded as dynamic stratifications of electron density irrespective of the atomic layers in the crystal. Such longitudinal or compressional waves should therefore be capable of giving a scattering of X-rays by the sound waves entirely analogous to that actually observed with ordinary light in liquids and in crystals. The angle through which the rays are scattered is given by the familiar optical formula

$$2\Delta \sin \alpha/2 = \lambda, \tag{4}$$

and therefore ranges from the value $\alpha = 0$ for $\Delta = \infty$ upwards to the value of α found from (4) by putting Δ equal to the smallest permissible wavelength for sound waves in the crystal. The scattered rays thus form a diffuse cone surrounding the primary beam, their frequency change ν^* being dependent on the angle of scattering. Such a frequency shift in the acoustic scattering of radiation (originally predicted by L. Brillouin) has found experimental verification in the case of light. It is important to remark that though compressional and distortional elastic waves are both operative with light in the effect now under discussion, only the former need be considered in the case of X-rays.

Elastic waves of both types and especially waves of distortional type give rise to a diffuse scattering of X-rays in another way, namely, by disturbing the regularity of arrangement of the lattice cells in the crystal. The effect of such disturbance has been considered by Laue (*Ann. Phys., Lpz.*, December 1926) in a very complete manner, taking into account the changes of frequency indicated by classical considerations. Laue's results are readily intelligible from the geometric considerations indicated in figure 1. Here, the planes $\Delta\Delta\Delta$ represent the elastic solid waves traversing the crystal. Acting on the static atomic layers ddd , the waves create dynamic stratifica-

tions $d^*d^*d^*$ whose structure amplitude is proportional to $J_1(z)$ as indicated by equation (3). These stratifications have a sensible optical effect only when the relation

$$2d^* \sin \psi = n\lambda \quad (5)$$

is satisfied. Here, ψ is the angle of incidence of the primary X-rays on the dynamic stratifications, d^* being the spacing of the latter. From figure 1 we write

$$d^* \sin \vartheta = d \sin (\vartheta + \epsilon) = \Delta \sin \epsilon, \quad (6)$$

where ϑ and ϵ are the angles which the crystal spacings make respectively with the elastic waves and the dynamic stratifications. Combining (5) and (6), we obtain the formula

$$2d \sin \psi \sin (\vartheta + \epsilon) = n\lambda \sin \vartheta. \quad (7)$$

Now, the plane of the elastic waves is entirely arbitrary; in other words, the angle ϑ appearing in equation (7) may have all possible values, and hence the angle of scattering which is 2ψ and the plane in which the scattered rays appear are both completely indeterminate. In other words, *the elastic solid waves can give only a diffuse scattering of the X-rays spread over a wide range of solid angles.*

Since elastic waves displace the atoms in a lattice cell to the same extent, in other words involve no appreciable distortion of their basic grouping, the static and dynamic structure amplitudes are proportional to each other. The intensity of the scattering by waves of specified frequency ν^* acting on a particular set of crystal planes may therefore be readily expressed as a fraction of the intensity of the unmodified reflexion by the same planes in the absence of any disturbance. From equation (3), it is seen that, apart from the variations of the factor $\sin^2 \beta F^2(\alpha)$, the ratio under consideration would be $2J_1^2(z)$. When z is small, this may be taken as $\frac{1}{2}z^2$. Its magnitude is therefore directly proportional to the energy of vibration with frequency ν^* , the amplitude A of which is connected with z by the relation $z \approx 4\pi A \sin \psi / \lambda$. With the aid of equations (5) and (6), the energy of the oscillation may be written in the form $\frac{1}{2}z^2 Ms^2 \sin^2 \epsilon / \sin^2 \vartheta$, where M is the mass of the whole crystal, and s is the velocity of the elastic waves in it. Putting this expression equal to kT (classical mechanics) or $h\nu^*$ (quantum mechanics), it is easily seen that the intensity ratio $\frac{1}{2}z^2$ of the modified scattering in any specified direction to the intensity of the unmodified reflexion is an exceedingly small quantity, being, in fact, of the order of magnitude $1/N$, where N is the total number of lattice cells. For a crystal large enough to be the subject of experiment but not so large as to invalidate the simple theory, *this ratio becomes a vanishingly*

small quantity. In practice, it is easily possible to record the classical X-ray reflexions by using thin crystal plates and fine X-ray beams, and it is evident that when such a technique is employed the effect due to the scattering by the elastic solid waves would be inappreciable. The multiplying factor $\sin^2 \vartheta / \sin^2 \epsilon$ appearing as a numerical factor in the ratio cannot alter the position stated above. For it is a number which may range from say 100 \rightarrow 10,000, according

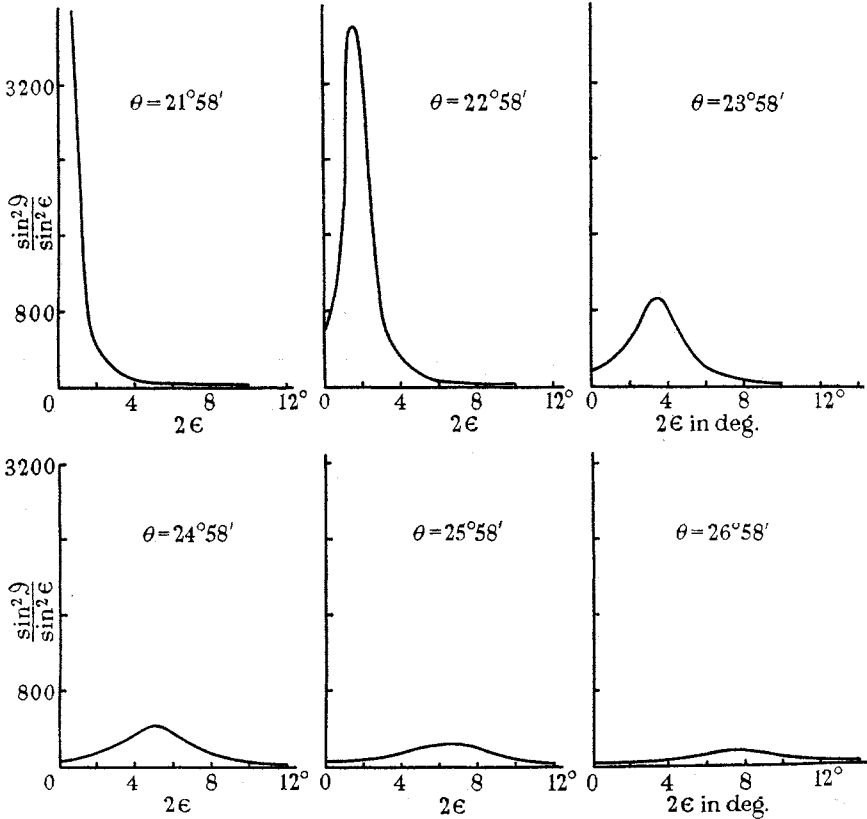


FIGURE 2. Graph of $\sin^2 \vartheta / \sin^2 \epsilon$ against 2ϵ (in degrees of angle); crystal spacing is that of (111) planes in diamond, using Cu K_α radiation.

to the setting of the crystal and the direction of the scattered ray, while, on the other hand, the value of N is of an altogether larger order of magnitude, say 10^{12} , for a crystal traversed by X-rays in the circumstances in which these considerations are valid.

Omitting the variation of the structure factor $F^2(\alpha)$, the function $\sin^2 \vartheta / \sin^2 \epsilon$ represents the manner in which the intensity of the scattered

radiation varies with the direction of the scattered ray. Its value can readily be calculated using the formulae (5), (6) and (7), and its variation with 2ϵ (the angle between the Laue spot and a scattered ray assumed to lie in the plane of incidence) is shown graphically in figure 2 for a series of settings of the crystal. It will be seen from the graphs that the scattering intensity shows a maximum or 'peak' when the setting of the crystal planes is nearly that required for reflecting the incident monochromatic X-rays. The position of this peak for each setting corresponds to the direction in which the elastic waves having the longest wave-length or the lowest frequency (and therefore possessing the largest amplitude) are effective in scattering the X-rays. It will be seen, however, that the peak falls away very rapidly both in height and in sharpness and becomes an extremely diffuse 'hump' when the crystal is moved away from the setting at which the peak coincides with the Laue spot. It is evident from figure 2 and from the considerations regarding the absolute intensity of the scattering already set out, that *such scattering cannot give rise to any phenomenon even remotely resembling a geometric reflexion which persists over a wide range of settings of the crystal and is of sufficient intensity to be observed under the same experimental conditions as the ordinary Laue spots.*

It may be remarked here that Zachariassen, Lonsdale, Jahn and others who have considered the possible effects arising from the scattering of X-rays by the elastic solid waves have perhaps overlooked the fundamental considerations dealt with above. The conclusions which they have arrived at are, in consequence, in my opinion wholly illusory. As will be shown in Part II of this paper, all the observed characters of the 'modified' reflexions, namely, their intensity, their sharpness, geometric positions, and their behaviour at low temperatures, seem to contradict completely the idea that the scattering by elastic solid waves is responsible for their origin.

4. CLASSICAL THEORY OF MODIFIED X-RAY REFLEXION

We now proceed to consider the effect on the X-rays of vibrations in the crystal having one or another of the characteristic infra-red frequencies. The character of such vibrations differs fundamentally from those of the elastic-solid type, and the resulting optical effects are therefore also completely different. While the elastic-solid vibrations displace the lattice cells without disturbing the atomic grouping within them, the situation is reversed in the infra-red vibrations; the lattice cells now remain undisturbed in their equilibrium positions, while the atoms within the cells oscillate

relatively to each other. As the result of such vibration the structure amplitudes of the lattice planes become periodic in time and give rise to geometric reflexions having a dynamic character and an altered frequency. Viewed from a purely classical standpoint, the preliminary discussion in § 2 continues valid; a change of frequency of the secondary radiations appears as a necessary consequence of the classical wave principles. The considerations contained in § 3, however, require radical modification in view of the altered nature of the vibrations with which we are now concerned.

It is obvious that in the present case the manner in which the secondary radiations from the different atoms in the unit cell sum up is different for the modified and the unmodified radiations. The resultant of the latter is expressed by

$$\sum_p F_p(\alpha) J_0(z_p) \cos Z_p, \quad (8)$$

and of the former by

$$\sum_p F_p(\alpha) J_1(z_p) \cos Z_p, \quad (9)$$

it being remarked that the displacements z_p for the p atoms are different though their phases ζ_p may be taken as identical. Formula (9) indicates that the vibration amplitudes of the atoms in any particular infra-red mode as well as their positions enter into the calculation of the final resultant. It may well happen that in a particular case, expression (9) vanishes while (8) is finite, or vice versa.

A general idea of the results to be expected in the present case may be obtained by regarding the N cells of the lattice as N oscillators having an identical vibration frequency, namely, ν^* . Each lattice cell may then be assigned a vibration energy kT (classical mechanics) or $h\nu^*$ (quantum mechanics). If we further assume that the phases of the secondary radiations from the N cells are in complete agreement as received in the direction of observation, their final effect would be the maximum possible and would be proportional to N^2 multiplied by the square of the expression (9). The amplitude of the oscillation of the atoms in the individual cells would be of the order $\sqrt{(kT/2\pi^2\mu\nu^{*2})}$ (classical mechanics) or $\sqrt{(h/4\pi^2\mu\nu^*)}$ (quantum mechanics), μ being the reduced mass of the lattice cell. Choosing appropriate values for μ and ν^* , the expressions may be evaluated, *and it is readily verified that the intensity of the modified X-ray reflexions would be from a hundredth to a thousandth part of that of the unmodified ones.* The general procedure indicated above would be approximately valid even when the coupling between the N cells is taken into account. For, the effect of such coupling is to endow the crystal with N separate frequencies of which a large proportion cluster round some particular value. Accordingly, though

the resultant intensity would be smaller than that indicated above, it would still remain proportional to N^2 .

The phase relations subsisting between the vibrations of the different lattice cells determine the directions in which the resultant of the modified secondary radiations is observable. The geometric representation in figure 1, and the formulae (5), (6) and (7), continue to be applicable. The same diagram and formulae were employed in § 3 to represent the diffuse scattering by the elastic-solid waves. In the present case they describe a geometric reflexion because the nature of the vibrations is quite different. The orientation and azimuth of the phase waves are properties of the particular mode of vibration under discussion and would be determined by the symmetry of the mode in relation to the symmetry properties of the crystal. They may be expected, therefore, to have specific values in relation to the lattice planes of which the structure amplitude is varied by the vibration. The situation may be pictured geometrically by setting out the possible values of $\vec{1/\Delta}$ as vectors from the origin in a three-dimensional diagram. The vectors thus drawn would then all be in the same straight line (or along one or another of a few straight lines determined by symmetry considerations) having a specific inclination to the reciprocal vector $\vec{1/d}$ of the crystal spacing. It follows immediately that the direction of the resulting dynamic reflexion would be represented by a single point (or a few specific points) on the sphere of reflexion.

The manner in which the N degrees of freedom corresponding to a particular infra-red mode of vibration are distributed amongst the various possible values of $\vec{1/\Delta}$ is evidently a matter of great importance, since it determines the intensity of the observed reflexions. It is evident that when Δ is large, the vibrations in neighbouring cells do not appreciably differ in phase. *Prima facie*, therefore, the frequency of a vibration of the atomic grouping within a cell would be influenced to a negligible extent by the value of Δ , so long as this is many times greater than the lattice spacing; the frequencies would diverge from the limiting value only when Δ becomes a small multiple of the lattice spacing. In other words, the discrete frequencies of the system cluster together very densely round the limiting frequency and are more sparsely distributed when they diverge from it. Accordingly, in the enumeration of the modes of vibration and their geometric representation on the vector diagram of $\vec{1/\Delta}$, the great majority of the representative points would be located at or near the origin of the diagram, while the remainder are distributed along the line or lines mentioned in the preceding paragraph, the density falling off quickly with increasing distance from the origin. Accordingly, also, the intensity of the modified

reflexion would be a maximum when it falls upon the classical reflexion, and would diminish rapidly when it separates and moves away from the same in altered settings of the crystal.

5. QUANTUM THEORETICAL CONSIDERATIONS

The theory so far developed indicates that the components of the modified radiations with frequencies $(\nu \pm \nu^*)$ have equal intensities. This is a characteristic consequence of a classical treatment of the interaction between matter and radiation; in the analogous case of the light scattering in crystals, the result is definitely contradicted by experiment, the spectral component of diminished frequency having an enormously greater intensity than the component of increased frequency when $h\nu^* > kT$. This feature finds a ready explanation on the quantum mechanical view of the interactions. The incidence of the photon on the crystal induces a transition from a lower to a higher level of energy of vibration or vice versa, the photon supplying or taking up the requisite quantum of energy and appearing after the encounter with diminished or increased energy, as the case may be. When $h\nu^* \gg kT$, the crystal finds itself at the lowest energy level, and transitions are therefore only possible in one direction. As the temperature is raised, some of the higher energy states are thermally excited, and hence the photon can induce transitions either to the next higher states or in the reverse direction to the next lower states of energy. The quantitative formulation of these ideas shows that the intensity of the component of frequency $(\nu - \nu^*)$ should be proportional to $1/(1 - e^{-h\nu^*/kT})$ and that of the component of frequency $(\nu + \nu^*)$ to $1/(e^{h\nu^*/kT} - 1)$. At low temperatures, therefore, the former component reaches the limiting value unity, while the latter vanishes. At high temperatures, on the other hand, the intensities of both components approach equality and ultimately become proportional to the absolute temperature.

The foregoing considerations are of such general validity and so closely related to our present problem that they must necessarily be regarded as applicable to it. Indeed, the change of frequency indicated classically by equation (3), and the classical condition for reflexion indicated in equation (5), appear independently from the quantum theory as consequences of the conservation of energy and momentum respectively in the encounter between the photon and the crystal. The modified reflexion and modified scattering must therefore necessarily be regarded as quantum effects and their intensities as determined by the principles of the quantum mechanics. From an experimental point of view, we are concerned now with the summation of the intensities of the two components of frequency $(\nu \pm \nu^*)$, since

they both overlap. In the parallel case of light scattering, this sum is proportional to

$$(e^{h\nu^*/kT} + 1)/(e^{h\nu^*/kT} - 1), \quad (10)$$

and this expression should therefore also represent the intensity of modified X-ray reflexion as a function of temperature, unless the latter be so high that the basic assumptions of theory cease to be valid.

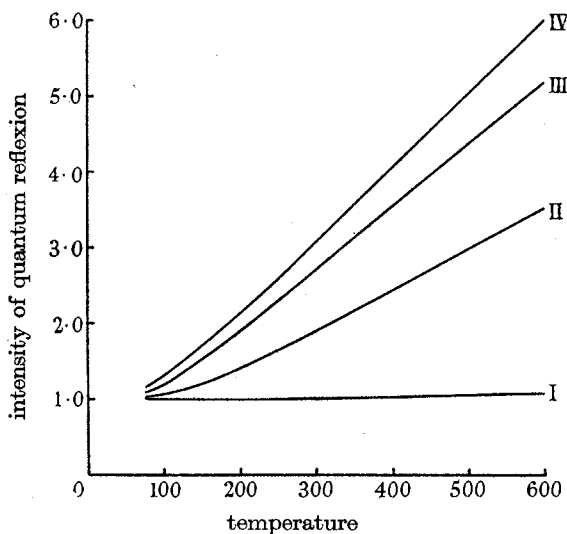


FIGURE 3. Intensity of quantum reflexion as a function of temperature.
I, Diamond; II, NaF; III, NaCl; IV, KCl.

In figure 3 the function appearing in (10) has been represented graphically for four different values of ν^* , being respectively the characteristic frequencies for diamond, sodium fluoride, sodium chloride and potassium chloride. It will be seen that the increase of intensity with temperature is quite negligible in the case of diamond and becomes the more conspicuous the lower the characteristic frequency of the crystal. The graph, however, indicates that in all cases, the function remains finite and reaches the limiting value unity at low temperatures. In other words, the *modified reflexions should persist at the lowest temperatures and their intensity should then be independent of temperature variations.*

6. RELATION TO THE INTENSITY OF CLASSICAL REFLEXION

We have already seen that the theory of the quantum or modified reflexion essentially rests on the fact that each of the characteristic infra-red modes represents the superposition of N co-existent vibrations of the crystal

having practically identical frequency. It is easily seen that the result of such superposition would be to endow the atoms of the crystal with relatively large amplitudes of vibration. Indeed, if all the N modes were assumed to possess identical frequencies and phases, their amplitudes would be superposed and the secondary radiations from a lattice cell would be expressed by

$$\sum_p F_p(\alpha) J_0(Nz_p) \cos Z_p \quad (11)$$

and

$$\sum_p F_p(\alpha) J_1(Nz_p) \cos Z_p \quad (12)$$

respectively. Though the values of z_p would be very small compared with unity, the arguments Nz_p of the Bessel functions $J_0(Nz_p)$ and $J_1(Nz_p)$ may easily assume large values; the greatly increased values of the expression (12) for the modified reflexion would then involve a corresponding diminution in the expression for the classical or unmodified reflexions given by (11).

The effect of the co-existence of N modes of vibrations having slightly different frequencies may, of course, be worked out completely ab initio from the expression (1) of § 2. It is obvious, however, that the general nature of the result, so far as it concerns the intensity of the unmodified reflexion, cannot differ much from the situation indicated in (11) and (12) above, namely, that the existence of strong modified reflexions by any particular set of crystal planes would usually involve a large diminution of the intensity of the unmodified reflexion by the same planes. Combining this with the indications of the graphs in figure 3, it also follows that the *increased intensity of the modified reflexions at high temperatures involves a diminished intensity of the unmodified ones. Further, the expressions (11) and (12) indicate that these reciprocal relationships would usually be selective, in other words, just those planes which show increased intensity of modified reflexions would also show a large diminution of intensity of the unmodified reflexion.*

From the foregoing discussion, it is evident that the characteristic infra-red vibrations of the crystal lattice play a fundamental part in the theory of the temperature effect in X-ray reflexion, even more than the elastic vibrations considered by Laue and his predecessors in the field. As in the majority of actual crystals the number of degrees of freedom associated with the infra-red modes is much larger than the number associated with the elastic vibrations of the lattice, the importance of this remark should be evident.

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