

## The two types of X-ray reflection in crystals\*

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### 1. Introduction

One of the most remarkable and fruitful discoveries in modern science was made when Max von Laue applied the principles of the wave-theory to find the effect of passage of a pencil of X-rays through a crystalline plate and arrived at conclusions which were strikingly confirmed by experiment. When the pencil after traversing the crystal is received on a photographic plate, we find recorded on the plate, as predicted by Laue, numerous spots in geometric array, their positions being closely related to the internal atomic architecture of the crystal and the direction of passage of the incident X-rays. The location of the spots in the Laue pattern is determined by the consideration that the secondary radiations from the atoms in the crystal co-operate in the directions indicated by the spots by reason of an agreement in phase, such agreement being itself a consequence of the arrangement of the atoms in a regular space-lattice. The Laue conditions which express this situation are mathematically equivalent to the Bragg formula; the latter follows very simply from the consideration that the crystal is a regularly stratified medium and should, therefore, selectively reflect the radiations falling on its strata at an angle of incidence appropriate to their spacing and to the wavelength of the X-rays in accordance with a general principle familiar to students of optics.

Laue's discovery was a vindication of the wave-theory and was naturally regarded as finally settling the issue, then being keenly debated, whether X-rays were corpuscles or waves, in favour of the latter hypothesis. Actually, however, the position is not quite as simple as this. As we know at the present time, there is an essential duality in the behaviour of the fundamental physical entities. They

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\*The new type of X-ray reflection forming the subject of this paper was first described and an explanation of it on the basis of the quantum theory given in a series of papers published earlier this year by Raman and Nilakantan in these Proceedings and elsewhere. The present report is intended to be a self-contained theoretical exposition of the subject and incorporates the ideas already expounded in the papers by Raman and Nilakantan, as also the fuller mathematical treatment by Raman and Nath published in these Proceedings for July 1940. Recent experiments by Nilakantan with diamond completely establish the quantum theoretical explanation of the phenomenon.

have a wave-aspect as well as a particle aspect, and these two characters are complementary and not contradictory. To get a complete picture of the observable phenomena, therefore, we can ignore neither one aspect nor the other. It is thus necessary to bear in mind the particle aspect as well as the wave-aspect of the Laue phenomena, and indeed, when we approach the subject from this point of view, the possibility of there being two distinct kinds of X-ray reflection becomes apparent. From the particle point of view, the X-ray reflections of the Laue type are *elastic* collisions of the photon with the crystal lattice, while from the wave-point of view, they arise from the fact that the crystal has a static periodicity of structure. This suggests that a second type of X-ray reflection in crystals should be possible, that from the particle stand-point is an *inelastic* collision in which the photon gives up a part of its energy during the encounter and excites the vibrations of the crystal lattice, while from the wave-standpoint, the reflection is due to the *dynamic stratifications of density* arising from such vibrations of the lattice. From either point of view, a change of frequency is seen to be a necessary feature of the second type of X-ray reflection; we may, therefore, refer to it as the quantum or modified reflection to distinguish it from the classical or unmodified reflections.

## 2. Theory of modified reflection

We may now proceed to consider a little more closely the mechanism of the modified X-ray reflection and its relation to the structure of the crystal. The classical or unmodified X-ray reflections arise from the fact that the electron density in the crystal is a periodic function of the co-ordinates in three dimensions. The intensity of the reflection by any particular set of crystal planes is determined by a quantity known as its structure amplitude which specifies the variation of the mean electron density over a plane when such plane is moved normally to itself through the crystal. The positions occupied by the atoms in the unit cell of the lattice are the most important factor in determining the structure amplitudes, though other factors such as the number of electrons and the distribution of electron density in each atom also enter into it.

With scarcely an exception, the actual crystals with which we are concerned contain more than one atom per unit cell, indeed usually several atoms of the same or of different kind. These atoms are held together in their places as the result of forces acting between each atom and its neighbours. Each individual atom is capable of vibrating about its position of equilibrium, but in view of the existence of the interatomic forces, it is more appropriate to consider the crystal lattice as a whole and to fix our attention on some one or another of its possible modes of vibration. These modes fall into two divisions, namely, the vibrations of the acoustic type and those of the optical type. The vibrations of the acoustic class lie for the greater part in the lower ranges of frequency, while the optical

vibrations have frequencies falling in the infra-red region of the spectrum. The character of the movements involved in these two classes differs essentially. The acoustic vibrations consist chiefly of translatory movements of the unit cells of the lattice relative to each other, while in the vibrations of the optical class the atoms within each unit cell oscillate relatively to each other about their common centre of gravity. The interatomic displacements within the unit cells for the acoustic vibrations and the translations of the unit cells for the optical vibrations are in each case of relatively minor importance.

We may now fix our attention on the optical vibrations of the crystal lattice and consider their effect on the structure amplitudes responsible for the X-ray reflections. In the first instance, we may make the simplifying assumption that the oscillation in all the unit cells is of the same frequency, amplitude and phase. It is evident that with this restriction, the atomic vibrations do not affect the uniformity of the crystal structure; the spacing and orientations of the crystal planes remain completely unaltered. The structure amplitudes of the crystal, however, alter periodically with time to an extent depending on the magnitudes and directions of the atomic displacements of which only the components normal to the spacing under consideration are effective. It is evident that the electronic density in the crystal would in these circumstances exhibit two different kinds of space variation, a static structure amplitude which is not a function of time, and a dynamic structure amplitude which varies with time and has the same frequency as the optical vibration of the crystal lattice. If the vibration of the lattice is sufficiently intense, the existence of a dynamic structure amplitude should evidently result in an alteration of the static structure amplitude, in most cases making it smaller than what it would be in the absence of such vibration.

From optical theory, it is evident that a dynamic structure amplitude would result in sharply defined monochromatic reflections in the same way as a static structure amplitude, except that the reflections would now occur with a change of frequency. Since under the assumptions made, the dynamic structure amplitudes do not differ from the static ones in respect of their spacings and orientations, the geometric conditions necessary for the observation of the static and dynamic reflections would also be identical, in other words, these reflections would either appear or not appear together in the same circumstances. If, for instance, the incident X-radiation be monochromatic, neither the modified nor the unmodified reflection would be observable unless the Bragg condition is satisfied.

### 3. Geometric law of modified reflection

We may now remove the restrictive assumption made that the atomic oscillations occur in identically the same phase in all the unit cells comprising the crystal. The oscillation will be assumed to have the same frequency and amplitude everywhere, but its phase will be regarded as variable from cell to cell. While this

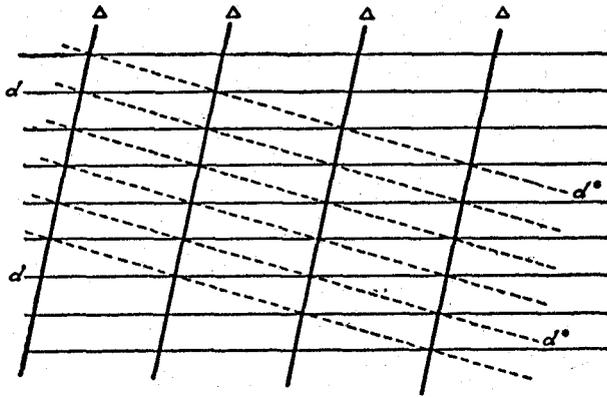


Figure 1

variation of phase would not affect the *static structure amplitudes* giving the unmodified reflections, it would profoundly influence the *dynamic structure amplitudes* and the effects produced by them. This is very readily seen from the accompanying diagram (figure 1), in which the thin lines represent a set of crystal planes and therefore also the planes among which the time-variations of electron density would be the same if the phase of the atomic vibrations were everywhere identical. The heavy lines crossing these at an angle represent the planes along which the phase of the atomic vibrations is constant. It is then evident that the dynamic stratifications of electron density would be along the diagonal planes cutting through the crystal spacings and the phase wave-fronts of the atomic vibration. These diagonal planes are indicated by the dotted lines in the figure, and their spacing and orientation are given by the vectorial formula:

$$\frac{\vec{1}}{d^*} = \frac{\vec{1}}{d} + \frac{\vec{1}}{\Delta}. \quad (1)$$

Here  $d^*$  is the spacing of the dynamic stratifications of electron density,  $d$  is the static crystal spacing, and  $\Delta$  the spacing of the phase-waves of the atomic vibration in the crystal lattice. Equation (1) shows that in the limiting case when  $\Delta$  is infinite,  $d^*$  becomes identical with  $d$  both in magnitude and direction. The classical and quantum reflections then coincide as already remarked.

So far as the optics of the cases is concerned, the classical and quantum reflection are on a similar footing. For the former to occur, the Bragg condition, namely,

$$2d \sin \theta = n\lambda, \quad (2)$$

must be satisfied, while for the quantum reflections it is similarly necessary that

$$2d^* \sin \psi = n\lambda, \quad (3)$$

$\theta$  and  $\psi$  being the glancing angles of the incident beam on the static and dynamic stratifications measured in the respective planes of incidence. Denoting by  $\vartheta$  and  $\varepsilon$ , the angles which the crystal planes make respectively with the phase-waves and with the dynamic stratifications, we have from equation (1) and figure 1,

$$d^* \sin \vartheta = d \sin (\vartheta + \varepsilon) = \Delta \sin \varepsilon. \quad (4)$$

Substituting the first of these relations in (3), we obtain,

$$2d \sin \psi \sin (\vartheta + \varepsilon) = n\lambda \sin \vartheta. \quad (5)$$

From equation (4), we see that if the wavelength  $\Delta$  is large compared with the crystal spacing  $d$  or the dynamic stratification  $d^*$ , the angle  $\varepsilon$  would be small compared with  $\vartheta$  or  $(\vartheta + \varepsilon)$ . Hence, provided  $\vartheta$  is not nearly equal to 0 or  $\pi$ , we may write (5) in the *approximate* form

$$2d \sin \psi = n\lambda, \quad (6)$$

which, it will be seen, is merely (3) with  $d$  written for  $d^*$ , that is to say, with the spacing of the dynamic stratifications put equal to that of the crystal planes from which they are derived. *Equation (6) is the same as equation (2) with  $\psi$  written for  $\theta$  and is thus the geometric law for quantum reflections analogous to the Bragg law for the classical reflections.* Since the angular separation between the incident beam and the quantum reflection is  $2\psi$ , equation (6) indicates that within the limits of its validity, *the angular separation of the quantum reflection and the incident beam is independent of the setting of the crystal and is equal to the angular separation of the classical reflection from the incident beam at the Bragg setting of the crystal.*

If  $\Delta$  is infinite, it follows from (4) that  $\varepsilon = 0$  and the approximate equation (6) becomes identical with the rigorous equation (5). How nearly this continues to be true when  $\varepsilon$  is finite depends on the angle  $\vartheta$ . If  $\vartheta = \pi/2$ ,  $\sin \vartheta = 1$  and differs little from  $\sin (\vartheta + \varepsilon)$  even when  $\varepsilon$  is as much as  $\pm 10^\circ$ . *Hence, for the particular case in which the phase wave-fronts are transverse to the crystal planes, the simple formula (6) may be regarded as practically the rigorous geometric law of quantum reflection.* If, however, the inclination  $\vartheta$  of the phase wave-fronts to the crystal planes is much less than  $\pi/2$ , it is not permissible to write  $\sin \vartheta = \sin (\vartheta + \varepsilon)$  except for very small values of  $\varepsilon$ , and hence in such a case, the rigorous formula (5) should be employed. It is evident that the angular separation  $2\psi$  of the quantum reflection from the incident beam would not then be independent of the crystal setting, but would be greater or less than the fixed value given by equation (6) according as  $\varepsilon$  is negative or positive, that is to say, according as the tilt of the dynamic stratifications with respect to the crystal planes is one way or the other.

The static and dynamic reflecting planes are coincident when  $\Delta$  is infinite and  $\varepsilon$  is therefore zero. The planes of incidence for both reflections are, therefore, identical in this particular case. If this result be true generally, *it would follow that the quantum reflection by any particular crystal spacing appears in the same plane of incidence as the usual Laue reflection.* We may then write  $2\psi = (\theta + \phi)$  and

$2\varepsilon = (\phi - \theta)$ ,  $\phi$  being the glancing angle of the quantum reflection measured with reference to the crystal planes. Equation (5) then becomes

$$2d \sin \frac{\phi + \theta}{2} \sin \left( \vartheta + \frac{\phi - \theta}{2} \right) = n\lambda \sin \vartheta, \quad (7)$$

while equation (6) takes the form

$$2d \sin \frac{1}{2}(\phi + \theta) = n\lambda. \quad (8)$$

It is easily seen that the rigorous formula (7) would in every case give values of  $\phi$  closer to  $\theta$  than the approximate formula (8), the difference being least when  $\vartheta = \pi/2$ . In general, therefore, when  $\vartheta$  is less than  $\pi/2$ , the quantum reflection is nearer the Laue reflection than the fixed position indicated by the approximate formula; it moves in the same direction as the Laue spot, though much more slowly, as the crystal is rotated; it coincides with and is overtaken by the Laue spot at the Bragg setting and continues to follow its further movement as the crystal is turned away from that setting. In the limiting case when  $\vartheta = 0$ , equation 7 indicates that  $\phi = \theta$ , in other words, the quantum reflection appears superposed on the Laue spot.

#### 4. Intensity of modified reflection

The modified reflection is the result of the crystal taking up a quantum of energy  $h\nu^*$  and the photon going off with the remainder of the energy  $h(\nu - \nu^*)$ ,  $\nu$  and  $\nu^*$  being the frequency of the incident radiation and of the lattice vibrations respectively. The energy  $h\nu^*$  being shared by all the lattice cells in the crystal, the amplitude of vibration and the resulting dynamic structure amplitude would be exceedingly small. It might, therefore, seem at first sight that the probability of the process occurring would be negligible. Actually, however, the small probability of the individual process is set off by the fact that the number of lattice cells  $N$  in the crystal is enormously large, and the system therefore possesses  $N$  discrete frequencies of vibration ranging around the value  $\nu^*$ . The fraction  $dN/N$  of this large number which becomes effective in any particular circumstances determines the observed intensity of the quantum reflection. This fraction should clearly be a function of the magnitude and direction of the phase vector  $1/\Delta$  which we shall denote for convenience by the symbol  $\delta$ . We may, therefore, write

$$dN/N = \frac{1}{4\pi} G(\delta, \chi, \vartheta) \sin \vartheta d\vartheta d\chi d\delta. \quad (9)$$

In this equation,  $\vartheta$  is the angle already introduced, namely the inclination of the phase wave-fronts to the crystal strata.  $\chi$  is the azimuth of a plane normal both to the crystal strata and to the phase wave-fronts, the reference plane for which  $\chi = 0$

being the plane of incidence on the crystal strata.  $\sin \vartheta d\vartheta d\chi$  is, therefore, the elementary solid angle within which the vector  $\delta$  lies.

The dependence of the  $G$ -function upon the value of  $\delta$  should evidently be very pronounced. Since the characteristic frequency  $\nu^*$  corresponds to a zero value of  $\delta$ , we may expect the possible degrees of freedom to cluster densely around small values of  $\delta$  and to thin out for large values of  $\delta$ . In other words, the  $G$ -function would have a strongly marked maximum when  $\delta = 0$  and diminish rapidly as  $\delta$  increases. If, therefore we regard the other variables in the function as having fixed values, e.g.,  $\chi = 0$  and  $\vartheta = \pi/2$ , the variation of intensity of the quantum reflection would depend solely on the value of  $\delta$  determined by the angles of incidence and reflection. It would then follow from equation (1) that *the intensity of the quantum reflection would be a maximum at the Bragg setting of the crystal for which  $\phi = \theta$  and would fall off rapidly as the crystal is moved away from this setting in either direction.*

It will be noticed that we have written the  $G$ -function with the angles  $\chi$  and  $\vartheta$  appearing explicitly in it, thereby indicating that the number of degrees of freedom lying between given limits of  $\delta$  depends on the inclination of the wave-fronts to the crystal planes and also on the azimuth of the plane which is normal to both the static and dynamic stratifications of density. Such a dependence is to be expected on dynamical grounds. It is well known that in a crystal, the relation between wavelength and frequency for vibrations of the *acoustic class* is a function both of the direction of vibration and the direction of propagation, the wave-front splitting up into a surface of three sheets even in a cubic crystal. There would, therefore, be no justification for assuming that for vibrations of the optical class, the distribution of the degrees of freedom would be independent of either the orientation of the wave-fronts in the crystal, or of the directions of the atomic vibration in them. In our present problem, we are concerned with the modes of vibration in which the displacements of the atoms are predominantly normal to the particular crystal planes under study, since displacements parallel to the planes have no effect on their structure amplitudes. We may, therefore, reasonably anticipate that the  $G$ -function should show a strongly marked dependence on the angles  $\vartheta$  and  $\chi$  which enter in our problem.

It is evident that if the angles  $\vartheta, \chi$  defining the orientation of the phase-waves are regarded as entirely arbitrary, the optical conditions necessary for a reflection of the X-rays would be insufficient to indicate a unique direction for such reflection for any given setting of the crystal. It is, however, easily shown analytically or geometrically that they suffice to indicate a direction which would correspond to a minimum value of  $\delta$  and therefore also to a maximum observable intensity of reflection, the values of  $\chi$  and  $\vartheta$  corresponding to such direction being  $0$  and  $(\pi/2 - \phi)$  respectively. The zero value of  $\chi$  indicates that the reflection would be in the plane of incidence, while the value  $(\pi/2 - \phi)$  on substitution for  $\vartheta$  in (7) yields the formula

$$d \sin(\phi + \theta) = n\lambda \cos \phi, \quad (10)$$

which may also be written as

$$d(\sin \theta + \cos \theta \tan \phi) = n\lambda, \quad (11)$$

both reducing to the Bragg formula when  $\theta = \phi$ .

*The considerations on which equation (11) is based would, however, be invalid and the results given by this formula would be contradicted by experiment, if the angles  $\vartheta$  and  $\chi$  appear explicitly in the distribution function  $G(\delta, \chi, \vartheta)$  as assumed in our equation (9). For, when this is the case, the maximum of this function would be determined, not solely by the variations of  $\delta$ , but also by the independent variations of  $\chi$  and  $\vartheta$ , and the preferred values of these angles which make the G-function a maximum must, therefore, influence both the intensity of the modified reflection as well as the plane and direction in which it is observed. The value of  $\chi$  determines the plane of reflection, while that of  $\vartheta$  notably influences the direction of reflection in that plane. Hence the more precisely these angles can be specified, the more sharply defined would the direction of reflection be. The dependence of the distribution function on the angle variables thus plays an important part in determining all the observable features of the quantum reflection, namely, the plane and the direction in which it is to be found, its sharpness and its intensity. The preferred value of  $\vartheta$  is in particular of special importance and may be expected to depend on the substance chosen for investigation and possibly even on the particular set of crystal planes from which the reflections are observed. It may be evaluated by observing the quantum reflections over a sufficiently wide range of settings of the crystal and comparing the experimental results with the general formula (5) or its near equivalent (7).*

## 5. Effect of acoustic vibrations

We may now briefly discuss the phenomena resulting from the excitation of those crystal vibrations which lie in the acoustic range of frequency. When the number of atoms in the unit cell of the lattice is fairly large, the proportion of the aggregate number of degrees of freedom appearing as acoustic vibrations is small and the effects due to them are of small importance compared with those arising from the optical vibrations. Nevertheless, they deserve some consideration. The distinguishing feature of the acoustic vibrations is that they involve translatory movements of the unit cells, in other words a disordering of the crystal lattice, while the optical vibrations involve such movements to a negligible extent and may, therefore, be excited without distorting the crystal lattice. We have already noticed the latter as the special feature which enables the crystal to give modified or quantum reflections. We shall presently see that no such reflections would result from crystal vibrations of the acoustic class, and that on the contrary these vibrations would give rise only to a diffuse scattering of the X-rays.

A longitudinal sound-wave causes the mean electronic density in a crystal to

vary periodically, and if its wavelength is sufficiently large in relation to the spacing of the lattice planes, we may ignore the latter and regard the wave itself as a time-periodic stratification of electronic density. Accordingly, the X-ray photon impinging on the crystal should excite such sound waves by inelastic collision and itself be reflected in the process, provided that the length  $\Delta$  of the sound-wave, the glancing angle  $\theta$  on its wave-fronts and the X-ray wavelength  $\lambda$  satisfy the relation

$$2\Delta \sin \theta = \lambda. \quad (12)$$

Accordingly, since both  $\Delta$  and  $\theta$  are arbitrary, the effect here contemplated would give rise to a diffuse scattering in directions surrounding the incident beam and lying within a cone of semi-vertical angle  $2\theta$  determined by the limiting value of  $\theta$  at which the argument fails, namely, when  $\Delta$  is of the same order of magnitude as the lattice spacings in the crystal.

To find the phenomena in directions lying outside this cone, the procedure to be followed would be formally analogous to that indicated earlier for the optical vibrations, namely, to analyse the structure amplitudes of the crystal into a static part and a dynamic part having the frequency of the acoustic vibration, and to consider the effect of the latter separately. The detailed results would, however, be quite different from those obtained for the optical vibrations. While an infinite wavelength  $\Delta$  for the optical vibrations corresponds to one or other of the characteristic frequencies at which there is a maximum concentration of the degrees of freedom of the system, we have exactly the opposite situation in the acoustic case, the infinite wavelength then corresponding to zero frequency and a minimum concentration of the degrees of freedom. Hence the arguments which indicate that in the optical case the reflected beam is limited to particular directions in the plane of incidence are wholly inapplicable for the acoustic vibrations.

We conclude that *the acoustic vibrations of the crystal lattice, though they may be excited by an inelastic collision of the photon, give rise to a diffuse scattering without any pronounced directional effects.*

## 6. Analogy with light scattering

As is well known, when monochromatic light traverses a crystal and the light diffused by it is spectroscopically examined, the scattered radiations exhibit diminished and in some cases also enhanced frequencies. The frequency shifts fall into two classes. Some of them are very small and require for their observation the use of a Lummer-Gehrcke plate or a Fabry-Perot etalon; the shifts are found to depend on the direction of observation and evidently arise from the acoustic vibrations of the crystal lattice. The second group of frequency shifts may be observed with an ordinary spectroscope and correspond to those optical

vibrations of the crystal lattice which are active in light scattering. In the latter case, no variations with the direction of observation have been reported, though no very careful investigations appear to have been made on this question.

It is recognised that the scattering of light with change of frequency is a quantum effect, though it has a classical analogue which fails to represent the observed facts in essential particulars. There is thus a clear analogy between the modified scattering of light and the quantum reflection of X-rays, both phenomena arising from the inelastic collisions of photons with crystals. The wavelength of the incident radiation is widely different in the two cases, and this is largely responsible for the difference in the character of the resulting effects. Despite the obvious differences, the fundamental similarity in the processes involved and the phenomena observed should be useful as a guide to research in both fields of investigation. In particular, it is desirable to emphasise that, as in the case of X-rays, the change of frequency observed in light-scattering should be regarded as the co-operative effort of extended domains in the crystal and not the effect of the individual ions or molecules in it.

In the literature of light-scattering, we are familiar with the idea that certain optical modes are active while others are inactive, the distinction being largely determined by the symmetry characters of the vibration. In the X-ray problem, the question whether an optical vibration is 'active' in giving a modified reflection depends on whether it modifies the structure amplitude of the particular crystal spacing under study. It is evident, however, that in the X-ray problem we are dealing with the superposed effect of all the characteristic optical modes, and cannot isolate the effect of any one of them in particular. On the other hand, we can observe the modified reflection from numerous individual crystal planes and the geometric relation of such planes to the various optical modes of vibration of the lattice cells would naturally be different. The X-ray method is also capable of application to crystals with which optical study is difficult or impossible. Hence a study of the phenomena of the modified X-ray reflection may be expected to lead us to a deeper understanding of the problem of crystal physics, and to supplement in important respects the results of spectroscopic studies.

## 7. Influence of temperature

The analogy with light scattering is particularly useful in considering how the intensity of modified X-ray reflection would be influenced by varying the temperature of the crystal. As is well known, the character of the phenomena observed in light scattering differs essentially in the two cases in which  $h\nu^* \gg KT$  and  $h\nu^* \ll KT$  respectively. In the first case, the thermal agitation of the system plays an insignificant role, and the scattering is due to its transitions from the lowest to higher energy-levels induced by the incident radiation. Hence, the

scattering is with diminished frequency only, and its intensity is independent of temperature, being much greater than that indicated by classical considerations for a vibration with energy  $KT$ . In the second case in which  $h\nu^* \ll KT$ , the observed effects are practically describable in terms of the classical theory: the intensity of the scattering increases in proportion to the absolute temperature and appears to an equal extent with diminished and with increased frequencies. In the intermediate cases when  $h\nu^*$  and  $KT$  are of comparable magnitudes, the scattering with diminished frequency is of greater intensity than that with increased frequency. The ratio of the two tends to approach unity as the temperature is raised, and the absolute intensities of both types of scattering also become larger. This is because the transition probabilities from a thermally excited state are greater than from the ground state of the system.

We may naturally expect very similar results in the case of modified X-ray reflection, except that as it is not possible to separate the reflections with diminished and increased frequencies, we are only concerned with the result of their summation. As indicated by the theory, the nature of the results would depend on the characteristic optical frequencies of the crystal. At sufficiently low temperatures, the indications of the classical theory should in every case fail completely, and the quantum reflections, instead of vanishing, should continue to be observable. Further, for crystals with high characteristic frequencies, the intensity of reflection should be much greater than that indicated by the classical considerations, and its increase with rise of temperature should also be slower. On the other hand, for crystals with relatively low characteristic frequencies, the increase of intensity with temperature should be very marked. Further, since this increase indicates a larger population of thermally excited states and therefore also a diminution of the static structure amplitudes, *the increase of intensity of the modified X-ray reflections with rise of temperature would be accompanied by a falling off in the intensity of the unmodified reflections.*

It follows from the foregoing remarks that theories of the temperature effect in X-ray diffraction based on classical considerations cannot be expected to be in full accord with the facts either at low or high temperatures. This is indeed evident from the published literature of the subject. In the treatments usually given, however, the classical considerations are modified by taking into account the zero-point energy of the vibrations of the crystal and assuming that these have an optical effect analogous to that of thermal agitation. The static structure amplitudes of the crystal at low temperatures are thereby brought into better accord with the observed facts. It is evident, however, that except in regard to the classical or unmodified reflections, the effects produced by the crystal on the incident radiation depend on the change in the energy-state of the crystal and not upon its initial energy. The zero-point energy is therefore not really relevant to the discussion of such effects.

## 8. Summary

The X-ray reflections of the Laue type are elastic collisions of the photons with the crystal considered as a structure with static space periodicities. The modified or quantum reflections are inelastic collisions in which the photon excites the vibration of the crystal lattice and is itself reflected by the dynamic stratifications of electron density arising from such vibrations. The quantum reflections obey the Bragg principle with respect to the dynamic spacings, these however, in general, differing from the static spacings, besides being differently oriented, except when the incidence on the static spacings is at the Bragg angle for the given monochromatic radiation, in which case they are identical. The general geometric formula for the quantum reflection is

$$2d \sin \frac{\phi + \theta}{2} \sin \left( \vartheta + \frac{\phi - \theta}{2} \right) = n\lambda \sin \vartheta,$$

where  $\theta$  and  $\phi$  are the glancing angles of incidence and reflection, and  $\vartheta$  is the inclination of the phase-waves to the crystal spacings. If  $\vartheta$  does not differ greatly from  $\pi/2$ , this reduces approximately to the symmetric formula  $2d \sin \frac{1}{2}(\theta + \phi) = n\lambda$ . All the observable features of the quantum reflection are determined by the properties of the  $G$ -function which gives the distribution of the degrees of freedom of optical vibration as determined by the reciprocal of the length of the phase-waves of the optical vibration of the lattice and the angle variables  $\vartheta$ ,  $\chi$  defining their orientation. The dependence on temperature of the intensity of quantum reflection is very different in the two cases where  $h\nu^* \gg KT$  and  $h\nu^* \ll KT$  where  $\nu^*$  is the optical frequency of the lattice vibration. The increase of intensity of the modified X-ray reflections with rise of temperature is accompanied by a falling off in the intensity of the unmodified reflections from the same spacings.