

Quantum theory of X-ray reflection: mathematical formulation

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Contents

1. Introduction
2. Secondary radiations from an oscillating atom
3. Dynamic stratifications of density
4. Geometric law of dynamic reflection
5. Dynamic structure factor
6. Quantum scattering by elastic vibrations
7. Quantum reflection by infra-red vibrations
8. Temperature factor for quantum reflections
9. Temperature factor for classical reflections
10. Summary

1. Introduction

As was pointed out by Laue (1926), the secondary radiations from the atoms in a crystal traversed by a monochromatic beam of X-rays suffer changes of frequency when the atoms oscillate about their positions of equilibrium. These changes of frequency play a fundamental rôle in determining the observed X-ray phenomena. For, the superposition of radiations which differ in frequency cannot give rise to observable interferences, while, on the other hand, secondary radiations of identical frequency are necessarily coherent and capable of interfering with each other even if the frequency differs from the primary X-ray frequency. Accordingly, if we fix our attention on a particular mode of vibration of the atoms in a crystal, the radiations of altered frequency arising therefrom can give rise to interference maxima in just the same way as the radiations from stationary atoms. It follows also, that if several vibrations co-exist in a crystal, each set of secondary radiations of different frequency thus arising would produce its own interference maxima independently of the others. If, further, the individual vibrations are of

infinitesimal amplitude, a considerable simplification becomes possible. For, then each vibration may be regarded as giving rise to its own secondary radiations and acting independently of all the others, provided its frequency is different from theirs. This statement, however, requires some qualification when the excursions of the atoms about their positions of equilibrium resulting from the totality of all the vibrations present have a finite amplitude. For, the total radiation amplitude of an atom is fixed and is equal to the superposed radiation amplitudes of various frequencies. Hence, the radiation amplitude due to any particular vibration frequency would naturally be less than it would be in the absence of all the others. It is evident also that as the atomic excursions increase, the strength of the secondary radiations of the original or primary X-ray frequency and of the interference maxima to which they give rise must progressively diminish, finally tending to zero.

The elastic or low-frequency modes of vibration have a continuous spectrum of frequencies and hence, as explained above, the optical effects of each vibration should be considered separately. Since the energy corresponding to a particular frequency is small and is further distributed over all the atoms in the crystal, the resulting atomic amplitudes are exceedingly small. Hence, the secondary radiations due to these separate vibrations are exceedingly weak, and since they are incoherent, their intensities and not their amplitudes should be added. In the final result, therefore, we have an effect which is inherently feeble and which can only become important when a large volume of the crystal is under consideration.

The position is different when we consider the effect of modes of vibration of the crystal which appear as monochromatic frequencies in its infra-red spectrum. Each such line in the spectrum represents N co-existent modes of vibration, where N is the number of the lattice cells in the crystal. In the ideal case when all the N modes are of identical frequency, it is evident that the secondary radiations of altered frequency due to these co-existing modes would all be coherent and must therefore be considered *together* and *not separately*. It is evident, therefore, that the vibrations of the infra-red type can give rise to effects of an altogether higher order of intensity than the elastic vibrations considered above. This result has already been deduced in an earlier paper from a consideration of the phase relations subsisting between the lattice cells in a crystal in an infra-red vibration. Its possibility, it may be remarked, is consequential on our rejection of the ideas of Debye and Born regarding the nature of the high frequency vibrations in a crystal lattice, and especially of the so-called postulate of the "cyclic lattice" due to Born which we have considered in detail and shown to be untenable.

It should be noted that the elastic and infra-red modes of vibration of a crystal also differ in other respects. In the former case, the basic grouping of the atoms in the lattice cells remains unaltered, while in the latter, it is to be regarded as essentially a variable. Then again, the wave-fronts of an elastic vibration may have any possible orientation within the crystal, while for the infra-red vibrations, there is *prima facie* no reason for assuming that this should be the case. It has also

to be remembered that the elastic vibrations are of lower frequency than the infra-red ones; this makes a considerable difference in considering the influence of thermal agitation in the two cases.

As already explained in the preceding paper, the recognition of the changes of frequency, the importance of which was first emphasised by Laue, leads us naturally to bring the X-ray problem within the scope of the quantum theory of radiation. It also makes the transition from the classical to the quantum mechanical considerations very simple. The changes of frequency indicated by the classical electrodynamics appear in the quantum theory as the result of exchanges of energy between the quantum and the crystal lattice. Similarly, the Laue conditions for a dynamic reflection are the same as those required for the conservation of momentum in the encounter between the quantum and the crystal. The principal difference between the classical and quantum points of view is in regard to the question of the absolute intensity of the secondary radiations and its dependence on temperature. Here, the quantum mechanical considerations replace such incorrect applications of the quantum theory to X-ray physics as are usually made by introducing the Planck factor and the zero point energy, neither of which is really relevant when considering the exchanges of energy between matter and radiation.

2. Secondary radiations from an oscillating atom

Under the influence of waves of unit amplitude, an atom emits secondary radiations which at a distance R from the origin of co-ordinates and in a direction making an angle 2ψ with the primary ray have the amplitude

$$f \sin \beta \cdot \frac{e^2}{mc^2} \cdot \frac{1}{R} \cos 2\pi \left(\nu t - \frac{R + 2D \sin \psi}{\lambda} \right), \quad (1)$$

where D is the perpendicular distance of the atom from a reference plane through the origin bisecting the angle between the primary and secondary rays, f is the atomic structure factor, and β the angle between the electric vector in the incident pencil and the diffracted ray. It is evident that this expression would remain invariable if the atom moves parallel to the reference plane but would alter periodically if it oscillates perpendicular to it.

Writing

$$D = d + \alpha \cos(2\pi\nu^*t + z) \quad (2)$$

the periodic part of (1) may be written as

$$\cos [2\pi\nu t - Z - \zeta \cos(2\pi\nu^*t + z)] \quad (3)$$

where

$$Z = \frac{2\pi(R + 2d \sin \psi)}{\lambda}, \quad \zeta = \frac{4\pi\alpha \sin \psi}{\lambda}. \quad (4)$$

The expression (3) may be expanded in a series of Bessel functions. Neglecting the functions of higher order than the first, it may be written as

$$J_0(\zeta) \cos(2\pi\nu t - Z) + J_1(\zeta) \sin [2\pi(\nu \pm \nu^*)t - Z \pm z]. \quad (5)$$

The three quantities Z , ζ and z appearing in (5) are all phase angles. Z is the phase of the secondary radiation from the atom when it is in the position of equilibrium, ζ the change of this phase produced by displacing the atom through a distance α in a direction normal to the reference plane, and z is the phase of the atomic vibration. Expression (5) indicates that the secondary radiation from the oscillating atom consists of three components whose amplitudes depend on the amplitude of the oscillation and which differ in frequency and phase. The first component has the frequency ν of the primary X-rays and its phase is determined solely by the equilibrium position of the atom. Its amplitude has however been diminished by the movement of the atom in the ratio $J_0(\zeta):1$. The second and third components have the same amplitude, namely $J_1(\zeta)$, but they differ in frequency and phase. The component $(\nu + \nu^*)$ has a phase angle $(Z - z)$, while the component $(\nu - \nu^*)$ has a phase angle $(Z + z)$. The secondary radiations of altered frequency thus increase in amplitude with increasing vigour of the atomic vibration, while their phases are determined jointly by the atomic positions and the phase of the atomic vibrations. The equality of the amplitudes of the components of increased and diminished frequency indicated by (5) is a typical consequence of the classical electrodynamics which will later be amended in the light of quantum mechanics.

3. Dynamic stratifications of density

We may now proceed to deduce the optical effect of all the atoms vibrating with the same frequency but with a phase which may be assumed to vary slowly from

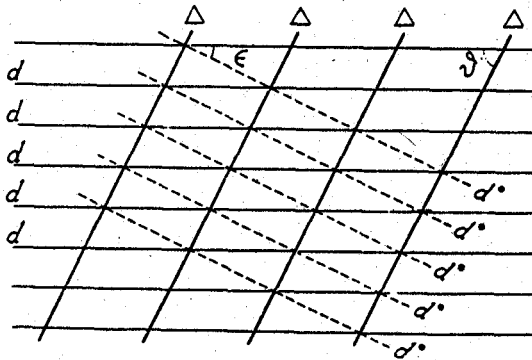


Figure 1. Graphical derivation of the dynamic spacings.

place to place within the crystal. For the purpose of a graphical derivation of the conditions for interference, it is not necessary at the present stage to distinguish between the elastic and infra-red modes of vibration. We consider a particular set of lattice planes in the crystal marked ddd in figure 1.

It is evident that for any given setting of the crystal the phase of the secondary radiations as received at a distance will vary from point to point within the crystal. In respect of the secondary radiations of unmodified frequency, this phase is given by Z . Hence, to obtain the maximum resultant intensity, Z must be invariable along a crystal plane and jump by 2π or an integral multiple thereof, as we pass from plane to plane. In other words, the planes ddd should make equal angles with the incident and diffracted rays, and their spacing d should satisfy the relation

$$2d \sin \theta_c = \lambda. \quad (6)$$

This is the familiar optical formula for a monochromatic reflection from a regularly stratified medium. θ_c indicates the glancing angle for a classical or unmodified reflection.

Considering now the secondary radiations of altered frequency, we see that their resultant is determined by the variation of $(Z - z)$ in one case and of $(Z + z)$ in the other. Let $\Delta \Delta \Delta$ in the figure represent the planes along which the phases of the atomic vibrations, in other words the values of z , are constant. In order to obtain the maximum intensity for the resultant of the secondary radiations, the crystal should be so set that $(Z - z)$ or $(Z + z)$ as the case may be, is constant along the lattice planes; it is evident from the figure that this would be the case if the setting of the crystal is such that the incident and diffracted rays are equally inclined to the planes which run diagonally cutting the ddd and $\Delta \Delta \Delta$ planes, e.g., $/^*d^*d^*d^*$ as shown in figure 1. For obtaining the maximum intensity, a further condition must be satisfied, namely

$$2d^* \sin \psi = \lambda, \quad (7)$$

where ψ is, as before, half the angle between the incident and diffracted rays. It is evident from the figure that there are two sets of diagonal planes possible. But the same set will satisfy equation (7) for both the frequency components $(\nu + \nu^*)$ and $(\nu - \nu^*)$, provided that we assume the phase angle Z advances in one case and recedes in the other case as we move across the figure. The diagonal planes $d^*d^*d^*$ thus represent the dynamic stratifications of electronic density resulting from the vibrations of the atoms contained in the lattice planes of the crystal. As the phase waves $\Delta \Delta \Delta$ move from left to right, the dynamic stratifications $d^*d^*d^*$ move upwards, keeping a constant spacing, while if the phase waves $\Delta \Delta \Delta$ move from right to left, the spacings $d^*d^*d^*$ move downwards in the same way. The changes of frequency from ν to $(\nu \pm \nu^*)$ may thus be regarded as analogous to the Doppler effect in the reflection from a moving mirror.

4. Geometric law of dynamic reflection

The spacing d^* of the dynamic stratifications is connected with the spacing d of the static ones and the phase-wavelength Δ of the atomic vibrations by the vectorial relation,

$$\frac{1}{d^*} = \frac{1}{d} + \frac{1}{\Delta}. \tag{8}$$

This is readily deduced by writing down the vectorial equation represented by the three sides of one of the triangles appearing in figure 1 and dividing the same by the area of the triangle. Denoting by ϑ the angle between the planes ddd and the phase waves $\Delta\Delta\Delta$, and by ϵ the angle between the planes ddd and $d^*d^*d^*$, we have from figure 1 and equation (8)

$$d^* \sin \vartheta = d \sin(\vartheta \pm \epsilon) = \Delta \sin \epsilon. \tag{9}$$

Substituting the first of these relations in (7), we obtain

$$2d \sin \psi \sin(\vartheta \pm \epsilon) = \lambda \sin \vartheta. \tag{10}$$

Equation (10) is the general geometric law of dynamic reflection deduced by Raman and Nath (1940). It will be noticed from (9) that when the phase wavelength Δ is infinite, $\epsilon = 0$ and $d^* = d$, from which it follows that $\psi = \theta$. In other words, the static and dynamic reflections then coincide in direction. This is also obvious directly from figure 1. In general, however, d^* and d are different, and the conditions for the possibility of static and dynamic reflections are not the same. While a static reflection can only occur at the particular setting of the crystal indicated by (6), a dynamic reflection is evidently possible over a wide range of settings of the crystal determined by the permissible values of the phase wavelength Δ . It is further to be remarked that while the glancing angles of incidence and reflection are equal for the static reflections given by (6), these angles when measured as usual with reference to the static crystal planes would generally differ from each other for the dynamic reflections. Further, the latter reflections would in general appear in a plane different from that of the incidence of the X-rays on the crystal spacings. To specify the actual plane of dynamic reflection, it is necessary to know the angle χ which determines the azimuth of the phase waves. We may put $\chi = 0$ in the case when the dynamic reflection appears in the plane of incidence, the phase waves then being evidently perpendicular to that plane. When $\chi \neq 0$, the dynamic reflection swings out of the plane of incidence to an extent determined by the values of Δ , ϑ and χ .

In the particular case when $\chi = 0$, it is evident that

$$\phi + \theta = 2\psi, \quad \text{and that} \quad \phi - \theta = 2\epsilon, \tag{11}$$

where θ and ϕ are respectively the glancing angles of incidence and dynamic reflection measured as usual from the crystal planes. Equation (10) may then be

written as

$$2d \sin \frac{\theta + \phi}{2} \sin \left(\vartheta \pm \frac{\theta - \phi}{2} \right) = \lambda \sin \phi. \quad (12)$$

The value of ϕ then depends on the angle ϑ . If we imagine ϑ to march from 0 to π , equation (12) shows that the relation between ϕ and θ will alter from

$$\phi = \theta, \quad \text{when } \vartheta = 0 \quad \text{or } \pi \quad (13)$$

to

$$d(\sin \theta + \sin \phi) = \lambda, \quad \text{when } \vartheta = \frac{\pi}{2}. \quad (14)$$

Thus, when the phase waves are *parallel* to the crystal planes, the dynamic reflection always satisfies the ordinary geometric law of reflection from the crystal planes, while if the phase waves are transverse to the crystal planes, it appears in the direction given by (14) which may be written *approximately* as

$$2d \sin \frac{\theta + \phi}{2} = \lambda, \quad (15)$$

thereby indicating that the angle between the incident and reflected rays is approximately constant and independent of the crystal setting.

5. Dynamic structure factor

To find the conjoint effect of the secondary radiations from all the atoms in the unit cell of the lattice, we have to sum them up considering each component of frequency separately. This summation for the radiations having the primary X-ray frequency gives (omitting constant factors),

$$\sum_p J_p J_0(\zeta_p) \cos(2\pi\nu t - Z_p). \quad (16)$$

The summation for the secondary radiations of frequency $(\nu \pm \nu^*)$ similarly gives

$$\sum_p J'_p J_1(\zeta'_p) \sin [2\pi(\nu \pm \nu^*)t - Z'_p \pm z'_p] \quad (17)$$

the index p referring to the p th atom in the cell, and the dashes in (17) indicating that the setting of the crystal and the angle of diffraction are not necessarily the same as those considered in (16). Remembering, however, the conditions for a dynamic reflection discussed in the foregoing section, namely that $Z \pm z$ should be constant along any particular lattice plane, we may simplify (17) and write it in the form

$$\sum_p J'_p J_1(\zeta'_p) \sin [2\pi(\nu \pm \nu^*)t - Z_p], \quad (18)$$

Z_p having now the same significance as in (16) for a static reflection by the same set of lattice planes. A further simplification arises when the angle between the primary and diffracted radiations does not differ greatly for (16) and (18). We may then write, approximately, $j'_p = f_p$. If, further, the setting of the crystal in the two cases is not so greatly different, we may also write, $\zeta'_p = \zeta_p$, as an approximation. Subject to the restrictions indicated, (17) now takes the form

$$\sum_p f_p J_1(\zeta_p) \cdot \sin [2\pi(v \pm v^*)t - Z_p]. \quad (19)$$

The static structure factor of the unit cell as influenced by the particular vibration may therefore be evaluated by diminishing the structure factor of each atom in the ratio $J_0(\zeta_p)$ to unity. At the same time, the lattice cell acquires a dynamic structure factor which is found in exactly the same way except that the structure factor of each atom is now multiplied by $J_1(\zeta_p)$.

Very significant differences now arise in considering respectively the elastic and the infra-red vibrations. For the elastic vibrations, ζ_p is the same for all the atoms in the unit cell. The suffix p may therefore be removed and the Bessel functions taken outside the summation sign. For an elastic vibration, therefore, the static and dynamic reflections may be evaluated from the expressions

$$J_0(\zeta) \cdot \sum_p f_p \cdot \cos(2\pi vt - Z_p), \quad (20)$$

$$J_1(\zeta) \cdot \sum_p f_p \cdot \sin [2\pi(v \pm v^*)t - Z_p]. \quad (21)$$

The static and dynamic structure factors in the case of an elastic vibration thus differ only by a multiplying factor which is the same for all the atoms in the unit cell. Thus, if a particular set of crystal planes gives zero intensity for a particular order of reflection, the dynamic reflections for the same planes and the same order of reflection must also vanish. The dynamic reflections by different sets of crystal planes would follow the same order of intensity as the static reflections by those planes, provided the amplitude of the elastic vibrations transverse to the planes may be assumed to be the same. A similar remark would also apply to the relative intensities of the successive orders of reflection by a particular set of planes, except that the factor $J_0(\zeta)$ diminishes while the factor $J_1(\zeta)$ increases as the angle of diffraction becomes larger, *vide* equation (4).

The position is greatly altered when we consider the infra-red vibrations of the lattice. Here, the displacements being different for the different atoms, the factors $J_0(\zeta_p)$ and $J_1(\zeta_p)$ must remain within the summation signs. Some of the atoms in the lattice cell must evidently move in directions opposite to the others if the centre of gravity of the cell is to remain undisplaced. Hence $J_1(\zeta_p)$ would be positive for some of the atoms and negative for the others in an infra-red vibration, while on the other hand $J_0(\zeta_p)$ would always be positive and nearly equal to unity. It follows that the static and dynamic structure factors for an infra-

red vibration are determined by quite different considerations and cannot, in general, exhibit the close parallelism indicated by the theory for the elastic vibrations. Indeed, it may well happen that in particular cases, the static structure factor vanishes while the dynamic structure factor remains finite, or vice versa.

6. Quantum scattering by elastic vibrations

The disturbance produced by an elastic vibration on X-ray propagation is of two kinds. Firstly, a compressional wave would evidently alter the average electronic density. It is thus itself a dynamic stratification of the medium capable of reflecting the X-rays with a frequency ($\nu \pm \nu^*$), increased or decreased as the case may be, depending on the direction of the wave. Such a reflection occurs when

$$2\Delta \sin \psi = \lambda, \quad (22)$$

large values of Δ corresponding to small values of ψ , and vice versa. Thus, since Δ may have any one of a practically continuous series of values determined by the dimensions of the crystal, and since the orientation of the wave is arbitrary, the reflection indicated by equation (22) would result in a cone of scattered X-rays (the Brillouin cone) having the direction of the primary beam as its axis. The angular extension of the cone depends on the smallest permissible values of Δ . The intensity of such scattering would depend on the energy of the vibration and the resulting variation of electron density. On the classical mechanics, the energy of an elastic vibration of thermal origin may be taken as KT , while if the wave is quantum-mechanically excited by the incident radiation, the energy would be $h\nu^*$. The latter assumption would be the appropriate one to make if $h\nu^* \gg KT$, while if $h\nu^* \ll KT$, the former assumption would be correct. This type of X-ray scattering should therefore be exhibited by crystals even at the lowest temperatures and in the absence of thermal agitation, and especially by crystals of high elasticity, e.g., diamond. We should expect the intensity of the X-ray scattering by such crystals to be greater than that indicated by the classical considerations even at ordinary temperatures.

The second kind of disturbance to X-ray propagation arises from the distortions which the elastic waves cause to the regular stratifications of the crystal structure. The formulae of the three preceding sections enable us to evaluate these effects quantitatively in a very simple manner. As explained in section 3 and illustrated in figure 1, the superposition of an elastic vibration on a specified set of crystal planes gives rise to dynamic stratifications of density. As further explained in section 4, these stratifications reflect the incident X-rays in the direction given by the general geometric law (10). The intensity of such reflection is determined by the dynamic structure factor as explained in section 5.

Considering the *direction* in which the so-called dynamic reflection appears, it is evident from equations (9) and (10) that this depends on the wavelength Δ , the

angle ϑ which the wave-fronts make with the crystal spacings, and also upon the azimuth χ of the wave-fronts. A variation of χ would throw the dynamic reflection out of the plane of incidence, while if $\chi = 0$, the reflection would appear in that plane. A dynamic reflection is only possible when the X-ray wavelength, the dynamic spacing d^* and the glancing angle ψ of incidence of the X-rays thereon are suitably related. But since we have at our disposal two variables, namely Δ and ϑ , we may, as is evident from figure 1, by suitably altering both of them get a dynamic reflection in any desired direction. In other words, the resultant effect of all the elastic vibrations is a diffuse scattering of the X-rays over a wide range of solid angles and not a geometric reflection in any specified direction.

To find the X-ray scattering due to any particular set of crystal planes, we have only to evaluate the two expressions (20) and (21) given previously. Their magnitudes are in the ratio $J_0(\zeta):J_1(\zeta)$. If ζ be sufficiently small, $J_0(\zeta)$ is practically unity while $J_1(\zeta)$ would be equal to $\frac{1}{2}\zeta$. If m be the mass of a unit cell of the lattice, the energy of vibration of N such cells, each having an amplitude α with a frequency ν^* would be $2\pi^2 m N \alpha^2 \nu^{*2}$. This may be written in the form $2\pi^2 \cdot M \sigma^2 \cdot \alpha^2 / \Delta^2$, where M is the mass of the whole crystal, σ is the velocity of the elastic waves and Δ is their wavelength. Utilising equations (4), (7) and (9), we may write this in the simple form

$$\frac{1}{2}\zeta^2 \cdot M \sigma^2 \cdot \sin^2 \varepsilon / \sin^2 \vartheta. \tag{23}$$

This may now be put equal to KT (classical mechanics). Accordingly, we have

$$\frac{1}{2}\zeta^2 = KT / M \sigma^2 \cdot \sin^2 \vartheta / \sin^2 \varepsilon. \tag{24}$$

Equation (24) gives the ratio of the sum of the squares of the dynamic structure factors to the square of the static structure factor. It is evidently of the order $1/N$ and is thus an exceedingly small quantity. The X-ray scattering in any specified direction due to the distortion of the crystal planes by the elastic waves is therefore of vanishingly small intensity in comparison with the intensity of regular reflection by the same crystal planes and should be unobservable except when relatively large volumes of the crystal are under consideration.

The numerical factor $\sin^2 \vartheta / \sin^2 \varepsilon$ appearing in equation (24) determines the manner in which the intensity of the scattered radiation varies with direction. It may be written also as Δ^2 / d^{*2} , where Δ and d^* have the same significance as in equation (8). Thus the intensity of the scattering would be greatest in those directions for which the wavelength Δ of the elastic waves which effectively scatter the X-rays is greatest. This variation arises because the amplitude of the elastic waves is directly proportional to their wavelength, and the scattering is therefore greatest in the directions in which the waves of longest wavelength and lowest frequency are effective. The nature of the variation can be readily made out from figure 2, which represents the geometric relation between $1/d$, $1/d^*$ and $1/\Delta$ given by equation (8), as also the relation between $1/d^*$, $1/\lambda$ and $\sin \psi$ expressed by equation (7).

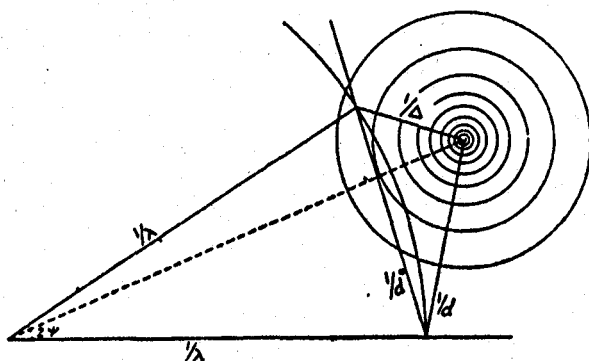


Figure 2. Distribution of intensity of diffuse X-ray scattering.

Spheres are drawn (sections of which by the plane of the figure appear as circles) round the terminus of the vector $1/d$ and with radii $1/\Delta$; points on the spheres represent various values and orientations of the vector $1/\Delta$ drawn from their common centre. The spheres are drawn closely together near their centre and further away at a distance from it to suggest the rapid diminution of the amplitude of the elastic waves with diminishing wavelength. A sphere of reflection is drawn with radius $1/\lambda$ around O as centre. It cuts across the "spheres of diffusion" having the radii $1/\Delta$ and the scattered radiations would therefore appear over the entire area of the sphere of reflection thus cut by the spheres of diffusion. When the sphere of reflection actually passes through the terminus of the vector $1/d$, the maximum of scattering intensity would fall on the sphere itself, but as it would then coincide with the regular reflection, the maximum would be unobservable. In other cases, the scattering would show a very broad and diffuse maximum of intensity corresponding to the minimum value of $1/\Delta$ on the sphere of reflection. This maximum however becomes rapidly weaker and more diffuse as the sphere of reflection passes further away from the centre of the spheres of diffusion with altered settings of the vector $1/d$. Hence, *nothing even remotely resembling a regular geometric reflection which persists over a wide range of settings of the crystal would be exhibited by the X-ray scattering due to the elastic waves.*

The same situation can be represented graphically by plotting the function $\sin^2 \vartheta / \sin^2 \varepsilon$ for various settings of the crystal. It is sufficient if this is done for the scattered radiations lying in the plane of incidence. With the aid of the formulae (6), (7), (9) and (11), it is readily shown that

$$\frac{\sin^2 \vartheta}{\sin^2 \varepsilon} = \frac{\sin^2 (\theta + \varepsilon)}{\sin^2 \theta_c - 2 \sin \theta_c \sin (\theta + \varepsilon) \cos \varepsilon + \sin^2 (\theta + \varepsilon)} \quad (25)$$

It is seen on differentiating the denominator of the expression on the right-hand side of (25) that it becomes a minimum and the whole expression is therefore a

maximum when

$$d \sin(\theta + \phi) = \lambda \cos \phi. \tag{26}$$

Equation (26) is equivalent to saying that $1/\Delta$ is then a minimum, as can be seen directly from figure 2. The values of $\sin^2 \vartheta / \sin^2 \epsilon$ have been plotted in figure 3, as

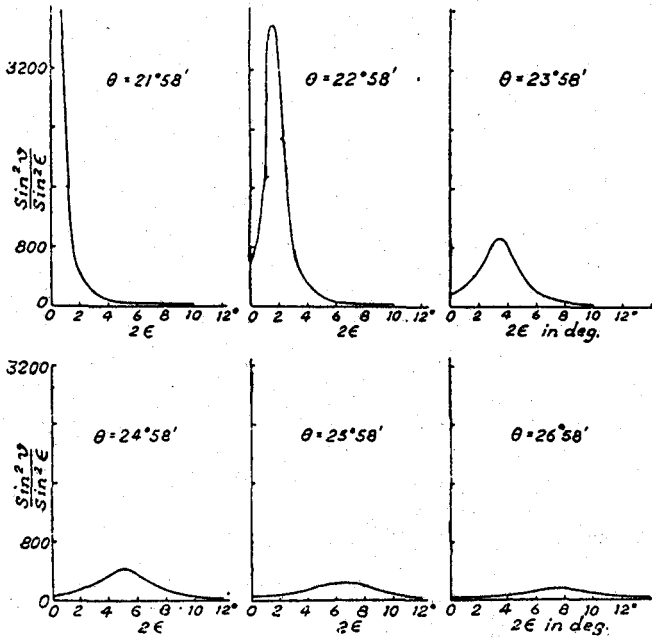


Figure 3. Graph of the function $\sin^2 \vartheta / \sin^2 \epsilon$.

functions of the angle 2ϵ for six settings of the crystal indicated by the different glancing angles of incidence θ entered in the figures. The particular case chosen is one in which $\theta_c = 21^\circ 58'$; in the first of the six settings, θ has the value θ_c , and in the others increases by successive steps of one degree. It will be seen that the peak of intensity which appears in the first setting coinciding with the classical reflection rapidly falls off and is replaced by a relatively weak hump in the curve which spreads over many degrees of arc. The actual value of the numerical factor $\sin^2 \vartheta / \sin^2 \epsilon$ also falls off rapidly and becomes insignificant as the crystal is turned away from the correct setting for a classical reflection.

We have in the foregoing analysis tacitly made certain simplifying assumptions, viz., that there is only one kind of elastic waves to be considered, that the velocity of the waves is a constant and that the atomic displacements due to the waves are in every case normal to the crystal planes. In reality, there are three sets of elastic waves possible, their velocity is a function of the direction of travel of the

waves, and the directions of the displacement are different for the three sets of waves. It should be remembered, however, that the three sets of waves would not all be equally effective in varying the structure amplitudes of the lattice planes. A movement of the atoms parallel to the lattice planes would have no X-ray effect and we may therefore exclude from consideration the types of waves which give rise to such displacements. Further, only such waves as have their wave-fronts roughly transverse to the lattice planes would produce a scattering of X-rays in directions which are appreciably displaced from the static reflections, and are therefore within the range of observation. It follows that we are principally concerned with distortional waves travelling in directions nearly parallel to the lattice planes under consideration and giving atomic displacements nearly normal to them. Hence, the simplified treatment we have adopted should be a fair approximation to the truth. The variation of the velocity of the elastic waves with the direction of travel may be readily taken account of in our formulae. In any event, such corrections as may be necessary would not affect the broad result which emerges from the theory, namely that the elastic waves produce only a diffuse scattering of the X-rays with very low intensity and not a geometric reflection of the X-rays in any particular direction.

It may be emphasized that the humps of intensity in the X-ray scattering curves appearing in figure 3 correspond to the elastic waves of greatest wavelength or lowest frequency operative in such scattering. Indeed, the smaller the angle at which the hump or maximum appears, and the more pronounced it therefore is, the lower would be the frequency of the elastic waves responsible for it. Accordingly, it is sufficient, as we have done, to take the energy of the individual vibrations as KT and to treat the problem classically. *At low temperatures, therefore, these maxima of scattering intensity should weaken still further and become altogether negligible. This should be so even for crystals of high elasticity, such as diamond, so long as we are considering the X-ray effects due to the elastic vibrations of lowest frequency for which $h\nu^* < KT$.*

7. Quantum reflection by infra-red vibrations

The geometric law of dynamic reflection (10) indicates that when the X-rays are incident on the lattice planes at an appropriate angle, the static and dynamic reflections appear simultaneously and in the same direction. The length of the phase waves Δ of the lattice vibration is then infinite, in other words, the atomic vibrations have everywhere the same phase. To enable us to evaluate the dynamic structure factor, we require to know the geometry of the particular mode of vibration as well as its actual amplitude. The former may be derived from a knowledge of the crystal structure and atomic forces, while the latter is determined by the energy of the vibration. The entire crystal being regarded as a single dynamic unit, the energy associated with a single non-degenerate mode of

its vibration would be KT on the basis of classical mechanics or $h\nu^*$ according to quantum mechanics. In considering the infra-red or monochromatic vibrations, however, the crystal must be considered as a system having a great number of identical or nearly identical frequencies. To obtain an idea of the results to be expected in consequence of this fact, we may make the simplifying assumption that all the N frequencies of the system are identical, N being the number of lattice cells in the crystal. It follows that the amplitude of the N modes of vibration should be superposed. Each cell in the lattice would then have energy KT (classical mechanics) or $h\nu^*$ (quantum mechanics). The resulting amplitudes of vibrations would be considerable and the dynamic structure factor would no longer be negligibly small in comparison with the static structure factor. Considering also the identity of the phase of the vibration in the N cells, it follows that it would result in a dynamic X-ray reflection having an intensity proportional to N^2 and comparable with the intensity of the usual static reflections. In the language of quantum mechanics, we may express this by saying that the crystal takes up an energy of vibration $h\nu^*$ from the X-ray photon $h\nu$ which is reflected by the lattice planes with diminished energy $h(\nu - \nu^*)$, but that the probability of such a process occurring is increased N -fold by the fact that all the N cells co-operate, their frequencies, amplitudes and phases of vibration being identical.

On the basis of these ideas, we may evaluate the structure factor for a dynamic reflection when it appears in the same direction as a possible static reflection. Denoting by m_p the mass of the p th atom in the unit cell and by ξ_p its displacement from the position of equilibrium, the energy of a vibration of frequency ν^* may be written as

$$\sum_p 2m_p \xi_p^2 \pi^2 \nu^{*2} = h\nu^*. \quad (27)$$

From this we have

$$\sum \frac{1}{2} m_p \xi_p^2 = \frac{h}{4\pi^2 \nu^*}. \quad (28)$$

If the geometry of the vibration is known, we may evaluate the ξ_p 's from (28). Resolving each ξ_p in a direction normal to the chosen crystal planes, we obtain its component α_p and thence also ζ_p , which appears in the dynamic structure factor. The latter may thus be determined for any particular mode of vibration and for the particular set of crystal planes. A similar procedure would have to be followed if we wish to consider any other possible mode of infra-red vibration or any other set of lattice planes. Taking $h = 6.55 \times 10^{-27}$ erg sec and with $m_p = 40 \times 10^{-24}$ gm and $\nu^* = 6 \times 10^{12}$ sec⁻¹ as representative values, the quantity $\sqrt{h/4\pi^2 m_p \nu^*}$ comes out as a length of the order 0.1 Å, U. The ratio of $J_1(\zeta_p)$ and $J_0(\zeta_p)$ appearing respectively in the expressions for the dynamic and static factor is then of the order 1:20 for an average crystal. In other words, under the most

favourable conditions, the quantum or modified reflections have intensities which are of the same order of magnitude as the classical or unmodified reflections though, as a rule, definitely weaker.

It is worthy of remark that if a crystal has several possible infra-red modes of vibration, those of the lowest frequencies would in general, as indicated by (28), produce the most important X-ray effects. The special importance of the modes of lower frequency would however be less marked on the quantum theory than on the classical mechanics; this becomes evident on writing KT instead of $h\nu^*$ on the right-hand side of (27). We would then have ν^{*2} instead of ν^* in the denominator of (28). The question as to which of the possible infra-red modes is most effective is, however, not so summarily to be disposed of. Actually, each set of crystal planes would have to be considered separately in relation to the various possible modes of vibration in the lattice. It may well happen that the dynamic structure amplitude of a particular set of crystal planes is largely derived from one of the possible modes of vibration, while another set of planes is chiefly influenced by some other mode. It may also well happen that the dynamic structure factors determined by the aggregate effect of all the possible modes of vibration are widely different for different sets of crystal planes and bear no simple relation to the static structure factors of the same planes. Such special features would be characteristic of the individual crystal structure and of the particular modes of its infra-red vibration.

The simplifying assumption made above that all the N modes of vibration of the lattice have an identical frequency is equivalent to stating that the only possible phase wavelength is the largest possible, viz., $\Delta = \infty$. This is evidently an extreme assumption, and it would be more reasonable to expect that while the great majority of the possible modes of vibration correspond to a very great phase wavelength, the remainder correspond to lesser values of Δ , thus enabling the dynamic reflections to appear at other settings of the crystal as indicated by equation (10). It would then follow that the intensity of the dynamic reflections should diminish rapidly as the crystal is moved away from the setting at which the static and dynamic reflections appear superposed. The fall in intensity would, in fact, represent the distribution of the possible modes of vibration in respect of phase wavelength.

The situation indicated above is indicated graphically in figure 4. The reciprocal of the phase wavelength, namely $1/\Delta$, which we may denote by δ is represented as a vector drawn from the terminus of the vector $1/d$ which gives the spacing and setting of the crystal planes. The great majority of the possible values of δ congregate at the origin $\delta = 0$. There are, however, some which spread out along the lines representing the permitted directions of the phase-wave normal. The quantum reflections would then appear at the point or points on the sphere of reflection at which the vectors δ thus drawn meet the latter. As already explained, the dynamic reflections need not necessarily lie in the plane of incidence. The restriction of the vector δ to fall in specific directions differentiates our present

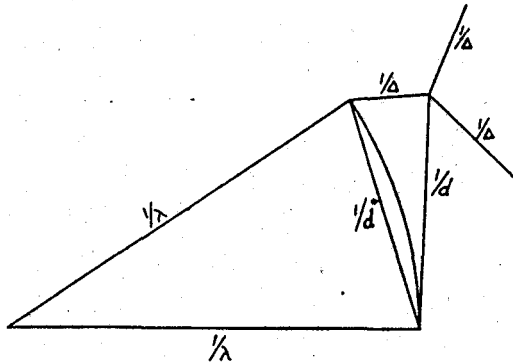


Figure 4. Geometry of quantum reflection.

case (figure 4) from that of quantum scattering also represented geometrically in figure 2. Such a restriction arises naturally from the fact that we are now concerned, *not* with a displacement of the lattice cell as a whole in some *arbitrary direction*, but with a *specific* mode of vibration of the atomic grouping within the cell. The symmetry of such atomic grouping, the nature and magnitude of the interatomic forces and especially the geometrical characters of the particular mode of vibration are superposed, or when the binding forces in the crystal are relatively the ideal case, therefore, we may expect this to lie in one or another of certain *precisely* defined directions related to the symmetry of the crystal and the symmetry of the mode of vibration. The quantum reflection would then appear, as indicated in figure 4, in a *sharply defined* direction (or in sharply defined directions, if, for instance, considerations of symmetry require that there should be several possible directions of the vector δ). It is evident that such a restriction of the phase-vector δ to specific directions would result in a very great increase in the intensity of the observable effects; in fact, the sharper the reflection, the more intense it would be and therefore the more easily observed. Thus, even if only a small fraction of the total number N of possible modes of vibration appear as stragglers from the point $\delta = 0$, their restriction to specific directions of δ should enormously increase the visibility of their effects.

We cannot however always expect the dynamic reflections to exhibit the same sharpness and precisely defined geometric character as the static reflections by the crystal planes. When, for instance, the effects of different possible modes of vibration are superposed, or when the binding forces in the crystal are relatively weak and are further disturbed by thermal agitation, a certain lack of precision in the direction of the phase-vectors would be inevitable. In such a case, the quantum reflections would necessarily be a little diffuse. Since, however, the majority of values of the vector δ congregate at the point $\delta = 0$, all the possible directions of the vector must necessarily crowd together as we approach the common origin. Hence, the reflections should appear not only more intense but

also more sharply defined as the crystal setting approaches the position in which the static and dynamic reflections coincide. The same considerations indicate that at the lowest possible temperatures when the disturbing influence of thermal agitation is removed, the diffuseness, if any, of the quantum reflections arising from its presence should diminish and disappear.

As indicated in earlier discussions, the distribution of the N possible modes of vibration amongst various values of the phase-wave vector δ is closely connected with the perfection of the monochromatism of the vibration frequency. The distribution should, in fact, run parallel to the distribution of the N modes amongst the various possible frequencies of vibration. The fine structure of the spectral lines in the infra-red region should thus stand in the closest relation to the variation in intensity of the quantum X-ray reflections with the crystal setting. It is known from studies on light scattering that the spectral lines representing the lattice vibrations, especially those of the lowest frequencies, become sharper at low temperatures. This effect is presumably due to the removal of the thermal agitation which disturbs the precisely defined geometric character of the infra-red vibrations and therefore also their monochromatism. Observations at low temperature should thus indicate a closer approach of the X-ray effects towards the ideal behaviour, viz., the appearance of sharply defined and correspondingly more intense dynamic reflections. Whether temperature directly affects the distribution of the N possible modes in the δ diagram, in other words tends to transfer a larger proportion of the modes to the origin $\delta = 0$, thereby diminishing the number of stragglers must, for the present remain, an open question. It can only be answered when we are in a position quantitatively to formulate the distribution law. The strength of the inter-atomic bindings within the lattice cell, and the strength of the forces which link the lattice cells to each other and make the whole crystal a coherent solid must necessarily enter into such a distribution law. Only in the ideal case when the lattice cells are firmly linked with each other and the influence of thermal agitation is negligible would be the assumption that the atoms within the lattice cells all vibrate together with identical frequency, amplitude, and phase approach towards the complete truth. It follows that our calculation of the intensity of the quantum reflection from equations (27) and (28) should be regarded as setting an upper limit to the intensity of such reflections which would be approached only in the most favourable cases.

8. Temperature factor for quantum reflections

The quantum theory of radiation is an application of quantum mechanics to a consideration of the interrelations between matter and radiation. In our present problem we are concerned with the effect of passage of a train of waves through a regularly stratified medium in the particular case when the stratifications, may, in part, be time-periodic. If the existence of such time-periodic stratifications be

assumed, classical optics indicates – quite independently of all atomistic or quantum theoretical considerations – that both static and dynamic reflections would be observable under appropriate conditions, the latter appearing with a change of frequency. We translate this result into the language of the quantum theory by saying that the change of frequency arises from the exchange of energy between the photon and the medium, while the optical condition for a dynamic reflection is equivalent to the conservation of momentum in their encounter (Tamm 1930). Quantum theory indicates that there is a finite probability of a vibration quantum being created or destroyed in the encounter if there be a finite interaction energy between the radiation field and the vibrations of the solid. The fundamentally new feature arising in the quantum mechanics not indicated by the classical or semi-classical theories is that the vibrations, even if non-existent in the absence of the radiation, would be created by it. This is the basis of our equation (27) in which the energy of the oscillation is put equal to $h\nu^*$ and which correctly represents the situation at the lowest temperatures. In the presence of thermal agitation, we have to merely add a contribution due to its effect. In other words, instead of $h\nu^*$ we write the energy of the vibration in equation (27) as

$$h\nu^* \left(1 + \frac{1}{\exp(h\nu^*/KT) - 1} \right). \quad (29)$$

The second term within the brackets is the Planck factor. The justification for its inclusion is that the probability of the creation of a vibration quantum would be proportional to the number of such quanta present, and (29) is therefore only valid when we are considering encounters in which the number of vibration quanta is *increased* by the incidence of radiation. In considering the cases in which the number is *diminished*, we must evidently take the energy as

$$h\nu^* \cdot \frac{1}{\exp(h\nu^*/KT) - 1} \quad (30)$$

In our present problem, the effects of both types of encounters appear superposed, and we may therefore take the energy as the sum of (29) and (30), viz.,

$$h\nu^* \cdot \frac{\exp(h\nu^*/KT) + 1}{\exp(h\nu^*/KT) - 1}. \quad (31)$$

The effect of thermal agitation would be thus to increase the intensity of the quantum reflection or the quantum scattering as the case may be, by the factor

$$\frac{\exp(h\nu^*/KT) + 1}{\exp(h\nu^*/KT) - 1}, \quad (32)$$

which we shall refer to as the temperature factor in what follows.

In the particular cases when $h\nu^* \gg KT$, viz., when the frequency of vibration is very high or the temperature is very low, the temperature factor reduces to unity

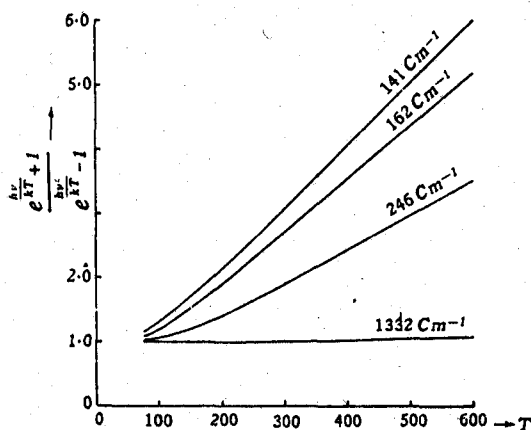


Figure 5. Temperature factor of quantum reflection.

and (31) becomes simply $h\nu^*$. On the other hand, when $h\nu^* \gg KT$, viz., when the frequency of vibration is very low or the temperature is very high; the expression (31) reduces to $2KT$. The numerical factor 2 indicates that we are now dealing with the sum of the two effects having the frequencies $(\nu \pm \nu^*)$, whereas previously we are only concerned with $(\nu - \nu^*)$. Thus, at sufficiently high temperatures, the intensities of dynamic reflection and scattering become proportional to the absolute temperature. At what stage this occurs depends on the value of ν^* . To illustrate this feature, the value of the temperature factor has been drawn as a function of the absolute temperature in figure 5 for a number of different values of ν^* . These are indicated in each case in spectroscopic units against the curves. It will be seen that all the curves tend asymptotically to the value unity at low temperatures. For low values of ν^* , the curve begins to rise steeply at a fairly low temperature, while for high values of ν^* , it remains nearly horizontal over a large range of temperature.

The foregoing is, of course, a simplified treatment, but it is sufficient to indicate the main features of the case. The treatment assumes that the intensity of dynamic reflection is proportional to the energy of the vibration giving rise to it. Such proportionality does not necessarily hold good when the thermal agitation is too violent. It should also be remarked that we are considering the different possible modes of infra-red vibrations as independent of each other, in other words, we are neglecting their mutual influence. Even when such neglect of the interactions is justified, we must necessarily consider their effects as superposed on each other. When there are several infra-red modes of widely different frequencies, it is possible that the temperature factor may be effectively different for the different sets of lattice planes in the crystal. In other words, those lattice planes whose structure amplitude is noticeably affected by the infra-red vibrations of lowest

frequency would show a large temperature factor, while those which are sensibly influenced only by the modes of higher frequency would show a relatively small temperature variation. That such a situation would arise in crystals which are highly anisotropic in structure is extremely probable. That it may occur even in isotropic crystals becomes evident when we recall that the atomic density and the structure amplitude vary enormously for the different planes of a crystal. Some of the planes in a crystal have special properties, e.g., cleavage, determined by the grouping of the atoms and the nature of the atomic bindings. These factors also determine the modes of atomic vibration possible. Hence, it should not be a matter for surprise to find that the temperature factor for dynamic reflection varies greatly for different planes also in isotropic crystals.

9. Temperature factor for classical reflections

We have already noticed in section 5 that the presence of a vibration which endows the lattice units with a dynamic structure factor simultaneously results in a reduction of the static factor. The reduction arises from the term $J_0(\zeta_p)$ which multiplies the atomic structure factor, this being the same for all the p atoms in the unit cell in the case of an elastic vibration, but different for the p different atoms in the case of an infra-red vibration. The energy of an *individual* vibration being only $h\nu^*$ multiplied by the relevant factors, see (29) and (30), the diminution of the static structure factor produced by it is negligible. The infra-red vibrations, however, have an N -fold degeneracy. The vibration of the atoms resulting from the superposition of the N modes would therefore be sensible and therefore also the diminution of the static structure factor produced by it. When the static reflection appears, the dynamic reflection is also superposed on it and is therefore effectively an addition to its intensity. Nevertheless, if the intensities of the two types of reflection are assumed to be proportional to the squares of their respective structure factors, the diminution of intensity is not compensated by such superposition. In other words, *the possibility of a quantum X-ray reflection by the crystal planes necessarily diminishes the intensity of the classical X-ray reflections by the same planes.*

In practice, there may be several modes of infra-red vibration possible. Their effect and also the *aggregate* effect of the low-frequency elastic vibrations of the lattice on the static structure factor of the atoms requires consideration. We therefore proceed to examine the case in which several different modes of vibrations are superposed. We write for the displacement of the p th atom.

$$D_p = d_p + \sum_n \alpha_{pn} \cos(2\pi\nu_n^* t + z_{pn}). \quad (33)$$

The secondary radiations from the atom have then as their periodic part

$$\cos \left[2\pi\nu t - Z_p - \sum_n \zeta_{pn} \cos(2\pi\nu_n^* t + z_{pn}) \right]. \quad (34)$$

The expansion of this in a series of Bessel functions is most easily carried out by writing (34) in an exponential form. It then appears as a product of a series of terms containing ν , ν_1^* , ν_2^* , etc., in the exponentials. On writing out the products after expansion in a series of Bessel functions, we get terms which are periodic in ν , $(\nu \pm \nu_1^*)$, $(\nu \pm \nu_2^*)$, etc., and also periodic terms involving overtones and combinations of ν_1^* , ν_2^* , etc. Neglecting these latter, the multiplier of the atomic structure factor for the frequency ν comes out as

$$\prod_n J_0(\zeta_{pn}). \quad (35)$$

While the multiplier for the atomic structure factor for the frequency $(\nu \pm \nu_m^*)$ is

$$J_1(\zeta_{pm}) \cdot \prod_{n \neq m} J_0(\zeta_{pn}). \quad (36)$$

For values of ζ which are not too large, we may use the approximation

$$J_0(\zeta) = \exp(-\frac{1}{4}\zeta^2) \quad \text{and} \quad J_1(\zeta) = 12\zeta. \quad (37)$$

Thus, the multiplier for the static structure factor of the atom is

$$\exp\left(-\sum_n \frac{1}{4}\zeta_{pn}^2\right), \quad (38)$$

the summation in the exponent being over all the n different frequencies of vibration. The multiplier for the dynamic structure factor of the atom for the frequency $(\nu \pm \nu_m^*)$ is

$$\frac{1}{2}\zeta_{pm} \cdot \exp\left(-\sum_{n \neq m} \frac{1}{4}\zeta_{pn}^2\right), \quad (39)$$

the summation in the exponent being now made over all the frequencies of vibration except ν_m^* . It appears from (38) that all the modes of vibration assist in diminishing the static structure factor, while (39) indicates that the dynamic structure factor for a particular frequency of vibration is diminished in the same way by all the other modes of vibration. The ratio of (39) to (38) is

$$\frac{1}{2}\zeta_{pm} \cdot \exp(-\frac{1}{4}\zeta_{pm}^2), \quad (40)$$

and depends only on the displacements of the atom due to the vibration of frequency ν_m^* . In this particular sense, each different vibration may be regarded as acting independently of all others, in other words as giving a quantum reflection of which the intensity in relation to the classical reflection is determined exclusively by its own amplitude.

In the summation indicated by the exponent in (38), we have to include all the frequencies of vibration of the lattice. We recall that

$$\zeta_{pn} = \frac{4\pi\alpha_{pn} \sin \theta}{\lambda}, \quad (41)$$

where α_{pn} is the displacement of the p th atom resolved normal to the crystal plane due to the vibration of frequency ν_n^* , the actual displacement ξ_{pn} being given by the geometry of the vibration and its energy. Considering the elastic vibrations first, we have already noticed that those of the lowest frequencies give the largest atomic displacements. On the other hand, the modes of the higher frequencies are far more numerous. Thus, the entire range of possible frequencies of elastic vibration would contribute towards determining the product (38) which alters the atomic structure factor. The treatment of the problem by Debye, Waller and Laue however greatly exaggerates the part which the elastic vibrations of the lattice play in this respect. Firstly, there is no justification for assigning all the $3Np$ degrees of freedom to the elastic vibrations. The maximum number which can properly be so assigned is $3N$, the remaining $(3p - 3)N$ degrees of freedom representing the infra-red or monochromatic vibrations of the lattice. Then again, the actual frequency limit for the elastic spectrum is automatically reduced by the diminution in the number of degrees of freedom allotted to it. Thirdly, the semi-classical way in which the quantum theory of specific heats and the zero point energy are usually brought into the X-ray problem is, of course, invalid. Finally, in the vast majority of actual crystals, the Einstein or monochromatic vibrations, besides being more numerous, have often quite low frequencies and therefore make a notable contribution to the thermal energy. Their influence on the intensity of the classical reflections indicated by (38) should therefore be of great importance, in fact much more so than that of the elastic vibrations of the lattice.

It follows from what has been stated above that there should be a considerable degree of correlation between the intensity of the quantum reflection by a particular set of crystal planes and the temperature variation of the intensity of the classical reflection by the same set of planes. An intense quantum reflection can only arise if the structure amplitudes are strongly influenced by the possible modes of infra-red vibration with a corresponding diminution of the static structure factor. We should then ordinarily expect a notable temperature effect of the intensity of classical reflection, *pari passu* with an increase of the intensity of quantum reflection with rising temperature. Since however, the static and dynamic structure factors for the unit cell are determined by different considerations, the factors for the unit cell are determined by different considerations, the correlation indicated above is not necessarily to be observed in all cases.

10. Summary

The ideas indicated in the preceding paper are here worked out quantitatively. The secondary radiation from an oscillating atom in a crystal traversed by X-rays is analysed into its frequency components. It is shown that the interferences to which each component of altered frequency gives rise are determined jointly by

the positions of the atoms and the phases of their vibration. It follows that besides the static reflections of unmodified frequency by the crystal planes, we would also have dynamic reflections of altered frequency. The geometric law of such dynamic reflection is derived. The static and dynamic structure factors are deduced and it is pointed out that the elastic and infra-red vibrations of the lattice stand on a different footing in respect of these factors. Considering first the elastic vibrations, formulae are obtained and graphs are drawn which show that such vibrations give rise to a diffuse scattering of the X-rays with low intensity proportional to the number of lattice cells. The N-fold degeneracy of the monochromatic infra-red vibrations, on the other hand, results in their giving true geometric reflections with altered frequency and with intensity proportional to the square of the number of lattice cells. The intensity of such reflection is evaluated on the basis of the quantum theory of radiation. The variation of the intensity, direction and sharpness of the quantum reflections with crystal setting is discussed. A formula is then obtained for the temperature variation of the intensity of the quantum reflections. The temperature factor for the intensity of the classical reflection is also written down and the extents to which the elastic and infra-red vibrations respectively contribute to it are discussed.

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