THE QUANTUM THEORY OF X-RAY REFLECTION: BASIC IDEAS

BY SIR C. V. RAMAN, KT., F.R.S., N.L.

(From the Department of Physics, Indian Institute of Science, Bangalore)

CONTENTS

1. Introduction

THE phenomena arising when a beam of X-rays traverses a crystal and ascribable to the possible or actual movements of the atoms in it from their positions of equilibrium are of very great interest, since their study may be expected to throw light on the nature of such atomic movements and also on the nature of the interaction between the X-rays and the material particles of the medium. In the analogous case of a beam of monochromatic light traversing a transparent crystal, the phenomenon of the scattering of light with change of frequency first observed by the present writer in 1928 renders a direct spectroscopic investigation of the atomic vibrations possible. Much light has been recently thrown on the subject of crystal physics by such spectroscopic studies. Indeed, the new knowledge derived in this way necessitates a radical revision of the ideas hitherto accepted concerning the dynamics of crystal lattices and the thermal energy of crystals. Further, the optical investigations show very clearly that the interchanges of energy and momentum between the radiation and the crystal lattice are determined by the principles of the quantum mechanics and not by the

317

classical ideas. Early last year (1940), it was observed by Dr. P. Nilakantan and the present writer that the (111) crystal planes of diamond exhibit mono-chromatic X-ray reflections of a new type which are as sharply defined as the ordinary or Laue reflections but which obey a wholly different geometric law. Further, the intensity of these reflections, though definitely smaller than the intensity of the classical X-ray reflections, is of the same order of magnitude and is not appreciably altered by either rise or fall of the tempe-rature of the crystal. These and other observations of a fundamental character revealed the existence of a whole group of X-ray phenomena which lie outside the scope of the existing theoretical developments of the subject. It thus becomes necessary to re-examine the assumptions on which the existing theories are based and to build a new theoretical structure in better accord with facts.

2. *The Failure of the Classical Mechanics*

In an essay on the molecular diffraction of light published in 1922, the present writer showed that, contrary to the opinion generally held at that time, transparent crystals such as quartz, rock-salt and ice traversed by a beam of light exhibit a true opalescence or diffusion of light associ-ated with the ultimate structure of the crystal. This diffusion was provi-sionally attributed to the disordering of the crystal lattice by thermal agitation. The subsequent observation by the present writer that the spectrum of the light so scattered by crystals exhibits changes of frequency placed a new complexion on the matter. The incident light being mono-chromatic, frequency differences between the incident and scattered radia-tions are observed which fall in the infra-red region of the spectrum and are therefore to be identified with certain specific modes of vibration of the crystal structure. If the appearance of such vibrations in the spectrum of the scattered light had been due to thermal agitation in the crystal, it would follow from the principles of optics and electrodynamics that the radiations of *increased* and *diminished* frequencies should appear with *equal intensity*. Actually, this is very far from being the case. Indeed, when the frequency differences are large, we observe *only* scattered radia-tions with diminished and *none* of increased frequencies. These facts indicate that the vibrations of the crystal lattice revealed by the spectro-scope are produced or induced by the light itself. Further, quantitative studies of intensity show that this is the correct view of the matter even if such vibrations are of sufficiently low frequency to be appreciably excited by thermal agitation. The light induces a step-down or a further step-up of the vibration as the case may be, appearing as scattered light with increased

and diminished frequencies respectively, though with greater intensity corresponding to the greater amplitude of vibration. The facts thus compel us to recognise that the observed scattering of light is in every case associated with the changes in the energy level of vibration induced by the light itself.

The spectroscopic evidence thus makes it clear that the scattering of light in crystals is a quantum-mechanical effect, the exchanges of energy between the photons and the crystal lattice occurring in discrete units or quanta of vibrational energy. When these units of energy are sufficiently small, in other words when the frequencies of mechanical vibration of the crystal lattice are sufficiently low, the quantum-mechanical picture of the facts tends asymptotically towards the purely classical picture in which the scattered light should appear with equal intensity with increased and diminished frequencies. In other words, the quantum description has a classical analogue; the latter, however, bears no resemblance to the facts except when the vibrations of the crystal are of very low frequency or the temperature of the crystal is very high. The lower the temperature of the crystal, and the higher the frequency of a particular vibration, the less would the actual facts resemble the picture suggested by the classical ideas.

That the propagation of X-rays through a crystal is influenced by the atomic vibrations is shown by the diminishing intensity of the spots in a Laue pattern when the crystal is heated. Numerous physicists, amongst them Debye (1914), Brillouin (1922), Waller (1923, 1927), and Laue (1926), have considered this problem from a semi-classical point of view. Laue in his memoir of 1926 drew attention to a very important feature emerging from his treatment of the problem, namely that all secondary radiations from the crystal, except those appearing as the geometric reflections by the lattice planes, suffer a change of frequency. The origin of this change of frequency is readily understood. An atom occupying a fixed position in space would naturally emit secondary radiations having the same frequency as the primary X-ray falling upon it. An oscillation of the atom about its position of equilibrium would result in a periodic variation of phase of such secondary radiation. The analysis indicates that the secondary radiations would then include components with their frequency increased and diminished respectively by the oscillation frequency of the atom. These components appear with an intensity which rapidly increases with the amplitude of the atomic vibration, the intensity of the component of unmodified frequency diminishing *pari passu.* Laue emphasised that these changes of frequency play a fundamental rôle in determining the observed optical effects. For, only such radiations as have identically the same

frequency can be coherent with each other; any difference of frequency ho
ever small would render coherence impossible. A frequency analysis
the secondary radiations and therefore also of the atomic vibrations
thus a necessary preliminary to a proper investigation of the problem.

Laue showed that the secondary radiations from the atoms in t
crystal vibrating with a specified frequency yield a resultant in which t
*components with increased and diminished frequency appear superposed w
identical intensity*. The situation is thus exactly similar to that arising in t
theory of the scattering of light in a crystal when considered classical
and it automatically follows that the classical mechanics must also fail
the X-ray problem. The change over from classical to quantum mechan
is fortunately simple. The conservation of energy as between the X-r
quantum and the crystal is equivalent classically to a change of frequen
of the radiation, such change, however, occurring in one direction or t
other and not in both at once. The conservation of momentum in t
encounter between the X-ray quantum and the crystal is equivalent clas
cally to the usual formula for a monochromatic reflection of incident rad
tion by a stratified medium, the stratifications being now dynamic and n
static. The correct intensity for the radiation of modified frequency resu
ing from the encounter is found by associating one energy quantum of t
appropriate frequency with each degree of freedom of vibration of t
crystal lattice. The effect of thermal agitation in the crystal enters into t
quantum mechanical scheme for the X-ray problem in exactly the same w
as in the parallel problem of the scattering of light.

3. The Vibration Spectrum of a Crystal

Einstein who was the pioneer in the development of the quantu
theory of specific heats suggested that the vibrations of the atoms in a sol
have *monochromatic* frequencies and showed how these frequencies cou
be connected with the observed variation of specific heat with temperatu
He also explained how in simple cases the order of magnitude of the
frequencies could be inferred from the elastic properties of the solid. T
alternative hypothesis put forward by Debye, namely that the frequencies
atomic vibration in a solid form a continuous spectrum which may
identified with its elastic vibrations, subsequently however found its w
into general favour. The success of the Debye formula in representing t
course of the specific heat curve in several cases promoted the belief th
the hypothesis correctly represents the actual vibration spectrum of simp
solids. That this belief is illusory becomes evident on a closer examinatio
of the facts.

In the first place, it may be pointed out that while a knowledge of the vibration spectrum enables us uniquely to determine the specific heat curve, it can scarcely be suggested that a knowledge of the specific heat curve enables us uniquely to determine the vibration spectrum. Indeed, whenever it has been possible to make a direct spectroscopic study of the vibration spectrum of a solid, the claim of the Debye hypothesis to represent the same is shown to be false. Taking for instance the case of diamond, the studies of Bhagavantam (1930) on the scattering of light in this crystal, and the recent investigations of Nayar (1941) on its luminescence at low temperatures show the lattice spectrum of diamond to consist of numerous discrete or monochromatic frequencies, some of them being much smaller than the so-called limiting frequency calculated from the Debye formula. The spectrum of the scattering of light in sulphur and phosphorus similarly exhibits numerous discrete lines, including some with very low frequency shifts, indicating that most of the degrees of freedom of atomic vibration are represented by monochromatic vibrations as originally pictured by Einstein. The position is equally striking when we consider crystals of apparently simple chemical composition, *e.g.*, quartz. Mr. Saksena (1940) has shown by a detailed investigation that no less than 24 out of every 27 degrees of freedom are represented in the vibration spectrum of this crystal by monochromatic frequencies.

It is known that the Debye formula fails to represent the specific heat curves correctly in several cases. It may be pointed out that these failures are actually more significant than the successes of the formula in other cases. Elaborate hypothesis have been put forward to explain away these failures, overlooking the simple explanation indicated by the spectroscope, namely, that the vibration spectrum of every crystal, however simple in its chemical composition, includes several monochromatic frequencies. When these frequencies are known, the specific heat formula necessarily contains corresponding Einstein terms, and this involves a reduction (usually very drastic) in the number of degrees of freedom allotted to the Debye term, as also of its " limiting frequency ". In the case of diamond, for example, it is shown in a forthcoming paper by Mr. V. B. Anand that the specific heat data are perfectly expresssed in this way by the spectroscopically observed frequencies, only one-eighth of the total number of degrees of freedom being included in a term of the Debye type. On the other hand, a Debye function alone even with an arbitrarily assumed " limiting frequency " shows large deviations from the observed specific heats. It may reasonably be inferred that in other cases, *e.g.*, metallic silicon or grey tin, where the Debye formula altogether fails to represent the specific heat data, the cause of failure is the same,

namely that the vibration spectrum includes several monochromatic frequencies.

Thus, both the spectroscopic and specific heat data show unmistakably that the Debye picture of the vibration spectrum of a solid bears no resemblance to the facts, except in the region where it is *prima facie* appropriate, namely in respect of the elastic solid vibrations of the lowest frequencies whose wave-length is large compared with the lattice spacings of the crystal. The maximum possible contribution which such vibrations can make to the specific heat of the solid can be found by treating the lattice cell in the crystal as a single unit and assigning it three degrees of freedom of translatory movement. All other degrees of freedom of movement are necessarily associated with monochromatic or Einstein frequencies of vibration of the crystal structure. Thus, in all crystals, including even those which are elementary or of the simplest chemical composition, the vibration spectrum is essentially of the type pictured by Einstein, and consists of discrete or monochromatic frequencies lying in the infra-red or high-frequency region. This is accompanied in the region of low frequencies by a continuous spectrum of elastic vibrations. The contribution of the latter to the thermal energy would be relatively of minor importance for the vast majority of crystals except at the lowest temperatures.

4. Character of the Einstein Vibrations

We may now proceed to consider the nature of the monochromatic vibrations. It is evident that they arise from a periodic variation with time of the basic grouping of the atoms in the unit cells of the lattice. Such a vibration obviously cannot be confined to an individual cell, for its energy would then be rapidly passed on to the neighbouring cells and would be immediately damped out. We must, in fact, picture the vibrations as taking place simultaneously and in identically the same way in all the cells of the lattice. The frequency of such vibrations as well as their modes would be determined by the internal architecture of the crystal, in other words by the geometric grouping of the atoms and the forces which they exert on each other. If the number of the lattice cells be sufficiently large, as would be the case even for a sub-microscopic crystal, these frequencies and modes would be wholly independent of the size or shape of the crystal. The vibrations must, in the limiting case, be pictured as having an identical frequency, amplitude, and phase in all the cells of the lattice, as only then could the motion be truly monochromatic. Any variation in the phase of the vibration at different points in the crystal would involve a departure from perfect monochromatism, but this would be negligible provided the

phase wave-length is sufficiently great to include a large number of lattice cells. Phase wave-lengths comparable with the dimensions of the lattice cells would be altogether excluded, and in general the smaller wave-lengths would be much less probable than the larger ones for which the frequency is independent of wave-length. The possible orientations of the phase waves would be determined by the geometry of the atomic grouping and especially by its symmetry characters.

Turning now to the continuous spectrum of elastic or low frequency vibrations, the situation here is totally different. The atomic structure of the solid does not enter into the picture. The possible frequencies of vibration are explicitly determined by the macroscopic dimensions of the crystal and their relation to the velocity of the wave propagation, the spectrum extending continually towards lower frequencies as the dimensions of the crystal are enlarged. The frequencies vary with the wave-lengths, being inversely proportional to them. The possible wave-lengths being determined by the dimensions of the crystal, it follows from simple geometry that the cases in which the wave-lengths are small are much more numerous than those in which they are large. Further, the orientation of the wave-fronts is entirely arbitrary and bears no relation whatsoever to the symmetry characters of the crystal or its atomic architecture.

5. The Fallacy of the Born Postulate

As shown in the preceding pages, facts and principles alike compel us to reject the hypothesis of Debye as a description of the vibration spectrum of a crystalline solid except in the restricted region of low frequencies. We have also seen that these low-frequency vibrations are altogether different in their character from the vibrations of higher frequency lying in the infra-red region of the spectrum. It follows that any treatment of the problems of crystal dynamics based on the concepts of Debye is necessarily fallacious. It may be remarked that the basic idea underlying Max Born's crystal dynamics is essentially the same as that of Debye, namely that all the possible vibrations of a crystal lattice are analogous to the elastic vibrations, having the same distribution of the phase-waves in respect of the wave-lengths and their relation to the size of the crystal, as well as an identically similar distribution of the phase waves in respect of orientation in space. No proof or justification of this postulate seems ever to have been put forward. The so-called postulate of the " cyclic lattice " is in fact nothing more than an *ad hoc* hypothesis adopted for mathematical convenience. It is evident that this postulate is in total conflict with the conclusions at which we have arrived regarding the characters of the mono-

chromatic vibrations of the crystal lattice. We shall therefore proceed to examine the Born postulate critically with reference to its claims to represent the actual state of affairs in a crystal.

One of the most remarkable facts brought into evidence by the study of the scattering of light in crystals is the extreme sharpness of the lines observed in the spectra of such scattering. Even in those few cases where the spectrum exhibits bands having an observable breadth, these sharpen to the finest lines when the crystal is cooled down to low temperatures. A perfect monochromatism of the vibrations of the lattice in the infra-red region is thus to be regarded as a characteristic property of the crystalline state, at least under ideal conditions. Not only is this true in respect of such vibrations as are also observable with the substance in the molten or dissolved condition, but it is equally so in respect of such vibrations as are specially characteristic of the crystalline state. It is obviously impossible to reconcile this situation with the idea that these vibrations are of the same nature as the elastic vibrations giving a continuous spectrum of frequencies.

To exhibit the fundamental error in Born's postulate, we may consider the behaviour of a model consisting of N Planck oscillators of identically the same kind regularly arranged in geometric order inside a box. The postulate of Born assumes that the dynamic behaviour of these oscillators could be represented by a three-dimensional Fourier series whose wavelengths are sub-multiples of the dimensions of the box and in which all the terms have equal weight. The assumption is, *prima facie*, unjustifiable because we are not here concerned with possible translatory movements of the oscillators which would involve collisions with the walls of the box, but only with the internal oscillations of the individual units in fixed positions. Accepting the postulate however for a moment, we may consider its implications in regard to the behaviour of the oscillators in our model. The essence of a Fourier representation is that the summation of the terms can reproduce the most arbitrary kind of disturbance. In the present case, since the series contains the full number of terms, namely N, all of which have equal weight, it would mean that their superposition would result in the phases of the individual oscillators being entirely arbitrary and un-correlated with each other. This is evidently a *reductio ad absurdum*, since such a state of affairs could only exist when the Planck oscillators are entirely independent of each other, as would be the case if we were consider-ing the molecules of a gas. It is a fundamental aspect of the crystalline state that the oscillators of which it is composed are coupled to each other more or less firmly. In diamond, for example, the bonds connecting the different lattice cells with each other are exactly of the same kind as those

which bind the atoms within the cell. The proposition that the internal oscillations occurring in the neighbouring cells of the lattice are uncorrelated in phase is thus entirely indefensible. Indeed, it would be more reasonable to make exactly the contrary assumption, namely that the phases of the oscillations in neighbouring cells are so highly correlated with each other that to all intents and purposes, the entire piece of diamond functions as a single oscillator with N times the statistical weight of a Planck oscillator of the same frequency. Only on some such view could we hope to understand the extraordinarily perfect monochromatism of the lattice vibrations in diamond.

We may summarise the situation by stating that the Born postulate does not represent the true state of affairs in a crystal except in regard to the low-frequency elastic vibrations, in which case, of course, it is of no particular significance. The real state of affairs in a crystal demands that if the distribution of phase of the Planck oscillators in a specified volume could be represented as a three-dimensional Fourier series, only the terms which have wave-lengths large compared with the lattice spacings and orientations specifically related to the geometry of the crystal structure would be allowed, while terms with phase wave-lengths of the same order as the lattice spacings would be altogether excluded. The stronger the atomic forces and the tighter the resultant mechanical coupling between the lattice cells, the more nearly would we approach a state of affairs in which the entire crystal behaves as a single oscillator with N times the statistical weight of a Planck oscillator of the same frequency.

6. *Fundamental Defects of the Existing Theories*

Born's postulate of the cyclic lattice which has been discussed in the foregoing pages and shown to be untenable was the basis on which Debye, Waller and Laue developed their treatments of the problem of the temperature effect in X-ray diffraction. It follows that, quite apart from the incompetence of the classical mechanics to deal correctly with the problem, these earlier investigations were also otherwise fundamentally defective, being in fact based on an erroneous conception of the nature of the vibrations in a crystal lattice. The picture of the X-ray phenomena which they present differs radically from the truth, failing as it does to indicate the fundamental difference between the low-frequency or continuous spectrum of elastic vibrations and the high-frequency or monochromatic vibrations in the infra-red, in respect of the X-ray effects to which they give rise. This is not surprising as the theories start from the assumption that these modes of vibration are essentially similar.

To make the foregoing points clear, we proceed to show from first principles how essentially the X-ray effects due to these two types of vibration of the lattice must differ. We shall consider first the elastic vibrations of the crystal lattice. These involve translatory movements of the lattice cells of the crystal from their positions of equilibrium. It is evident that if there are N lattice cells in the crystal, such translations would involve 3 N degrees of freedom. They may therefore be regarded as due to the superposition of 3 N sets of elastic waves of all the possible wave-lengths and frequencies, these having equal weight. It follows that the movements of any individual cell resulting from such superposition would be uncorrelated with that of any other lattice cell in the crystal. Hence, the secondary radiations of modified frequency sent out from the individual cells would be incoherent. In other words, the elastic vibrations would result in a secondary radiation of which the aggregate intensity is proportional to the number of lattice cells and which is in the nature of a diffuse or scattered radiation. This argument is not invalidated by the fact that the oscillation of a *particular* frequency expressed by one of the terms in the Fourier representation has a specifiable phase-relation in respect of the different lattice cells. The contradiction disappears when we remember that the number of degrees of freedom allotted to a *particular* frequency in a continuous spectrum is only one out of the very large number N. Hence, in spite of the fact that an elastic vibration of a specified frequency may be considered to be a coherent type of oscillation, the effect of all such vibrations taken together is essentially an incoherent radiation or diffuse scattering of which the intensity is proportional to N the number of lattice cells and not to N^2.

The position is entirely different when we consider the monochromatic vibrations of the lattice cells. The monochromatism implies that all the N degrees of freedom refer to a single mode of oscillation, which in the limiting case is pictured as having identically the same frequency, amplitude and phase in all the lattice cells of the crystal. The movements of the atoms within a cell results in secondary radiations from the atoms, and therefore also from the cells, possessing components of modified frequency. The identity of the oscillation in all the lattice cells ensures that these secondary radiations received at any external point have coherent phase-relationships. Hence, these are capable, exactly as in the case of the secondary radiations of unmodified frequency, of giving rise to interference effects. Indeed, it is clear that they would result in a *geometric reflection of the X-rays by the lattice planes of the crystal but with modified frequency*. In the limiting case when all the cells vibrate in identical phase, the direction in

which this modified geometric reflection would appear is the same as that of unmodified reflection.

We thus see that the elastic vibrations of the solid and the infra-red vibrations of the lattice cells give rise to X-ray effects which are fundamentally different and which, in fact, portray in a geometric form the radically different spectroscopic characters of the two modes of vibration. The elastic vibrations give a diffuse scattering of the incident X-rays with an intensity proportional to N, the number of lattice cells, while the infra-red vibrations give geometric reflections of altered frequency of which the intensity (subject to the same limitations as in the case of the unmodified reflections) is proportional to N^2. It will be noticed that these results are consequential on our rejection of the Born postulate. Had the latter been valid, both types of vibration would have given a diffuse scattering proportional to N, the number of lattice cells; this, in fact, is the result emerging from the investigations of Debye, Waller and Laue, except that the actual result due to the elastic vibrations appears exaggerated in their papers by the assignment to them of $3\,p\,$N degrees of freedom instead of $3\,$N the correct number, p being the number of atoms in the unit cell of the lattice. That the internal vibrations within the lattice cells are not considered at all is clear from Laue's memoir where the positions of the atoms within the unit cell are explicitly regarded as constants.

7. *Quantum Reflection of X-Rays*

The preceding discussion enables us to proceed further and give a quantitative picture of the geometric reflection of X-rays by the lattice planes of a crystal with altered frequency. We consider the individual cells of the crystal lattice as Planck oscillators of frequency v^*, so that, when excited, the energy of each oscillator is hv^*. An oscillation with this energy would result in the atoms in the cell being set in vibration such that the sum total of their kinetic energies in passing through the position of equilibrium is equal to hv^*. We then write down the expressions for the secondary radiations of various frequencies from each of the atoms in the cell. These are then summed up in the usual way, taking the positions of the atoms into account, to find the structure factor of the lattice cell. *This is done separately for each of the different frequencies of secondary radiation.* If the frequency v^* is sufficiently high in relation to the temperature of the crystal, in other words, if $hv^* \gg kT$, it is sufficient to consider only the component having the primary or unmodified frequency v and the component with diminished frequency $(v - v^*)$. Assuming that the setting of the crystal is such that the Laue conditions are satisfied for a particular set of lattice

planes, it would follow that the primary X-rays of frequency ν would then be reflected by these planes. Simultaneously, the modified radiations of frequency $(\nu - \nu^*)$ would also be reflected by the same planes and in the same direction, provided we assume that the phase of the vibration of frequency ν^* is the same for all the cells in the crystal. The intensity of the modified reflection of frequency $(\nu - \nu^*)$ would be determined by the dynamic structure factor of the lattice cell, in exactly the same way that the intensity of the unmodified reflection of frequency ν is determined by the static structure factor.

It will be noticed that this argument assumes that each of the N cells of the lattice is excited with an energy $h\nu^*$. It might seem at first sight that this would involve the entire crystal abstracting an energy $Nh\nu^*$ from the energy $h\nu$ of the incident X-ray photon, which of course, is impossible, besides being inconsistent with the assumed frequency $(\nu - \nu^*)$ of the reflection. Actually, all that the argument assumes is that the crystal functions as a single oscillator of frequency ν^* but with a statistical weight N times greater than that of a single lattice cell. This of course is only possible when all the cells vibrate in identically the same way, as is actually assumed in the argument. The intensity of the reflection calculated in this way would be the maximum possible. It may be regarded as an estimate of intensity to be expected in the most favourable setting of the crystal, viz., when the Laue conditions are satisfied also for the unmodified reflection. It may be emphasized that the quantum reflection is the result of a transition of the crystal from the ground state to a higher energy level of vibration, the energy required for the transition being derived from the incident radiations themselves and not from the energy of the thermal agitation of the crystal. Indeed in the circumstances considered, namely when $h\nu^* \gg kT$, thermal agitation is non-existent and can therefore play no part in the phenomenon. It may be remarked also that the so-called zero point energy which finds a place in the earlier semi-classical investigations of the X-ray problem becomes irrelevant from our present point of view.

8. Quantum Scattering of X-Rays

We now proceed to consider the X-ray effects arising from the elastic or low-frequency vibrations of the crystal lattice. As already remarked, these vibrations displace the lattice cells as a whole from their positions of equilibrium. Considering an elastic vibration of a particular wave-length, we notice that the stratifications in the medium arising from it are of two distinct kinds. Firstly, the elastic wave may itself, if it be of the longitudinal type, be regarded as a periodic stratification of electron density in a medium

which may otherwise be considered as uniform. This view of the matter is appropriate when we are concerned with stratifications with a spacing greater than the largest grating intervals in the crystal. Secondly, the elastic waves, more particularly those of the transverse type, disturb the regular arrangement of the lattice cells, so that the structure amplitudes of the crystal plane are diminished and, *per contra*, new dynamic stratifications are created due to the superposition of the elastic waves and the static crystal planes. This is the point of view developed in detail in Laue's memoir. The scattering of the X-rays by either of the processes indicated would necessarily involve a change of frequency. The scattering by the elastic waves themselves would appear in directions making smaller angles with the primary X-ray beam (assumed to be monochromatic) than the scattering due to their combinations with the crystal spacings. The two effects together give the background or diffuse scattering of X-rays by the crystal.

Since the elastic vibrations are of relatively low frequency, the situation may be represented in the majority of such cases by the inequality $h\nu^* \ll kT$, ν^* being the frequency of elastic vibration. When this is the case, the results to be expected from the classical and quantum theories would be identical. In other words, the effects observed may be described as the result of each of the elastic modes of vibration possessing an energy kT, the scattered radiations appearing with equal intensity in the two frequencies $(\nu \pm \nu^*)$. It must not be assumed, however, that a treatment on these lines would represent the facts of X-ray scattering in every case. Whenever the elastic frequency ν^* under consideration is high or the temperature T of the crystal is low so that $h\nu^* \gg kT$, the situation would be reversed. The intensity of X-ray scattering would then be the result of assigning an energy $h\nu^*$ to each vibration, and it follows that it would then be much greater than that given by the classical considerations. Since the energy is abstracted from the incident quantum, the scattered radiation would then appear only with diminished frequency $(\nu - \nu^*)$. It is evident also that the semi-classical considerations based on the Planck specific heat formula and the existence of zero point energy of the kind which figure in the earlier X-ray investigations cannot describe the situation correctly and are therefore irrelevant.

9. *Characters of the Two Effects*

It is evident from the foregoing discussion that the effects arising respectively from the vibrations in the infra-red and the elastic ranges of frequency are entirely different. Numerous criteria present themselves which make it possible to distinguish the one from the other.

Firstly.—The geometric distribution of the secondary X-radiations is widely different in the two cases, being a regular reflection of the incident X-rays by the lattice planes in one case and a diffuse scattering in the other. The influence of the setting of the crystal on the two phenomena is determined by considerations of a wholly distinct kind and should therefore also be quite different.

Secondly.—The intensity in one case is proportional to N^2, *viz.*, the square of the number of effective lattice cells and in the other case to N. Variations of the thickness of the crystal plate and of the cross-section of the X-ray beam traversing it would therefore influence the two phenomena in entirely different ways.

Thirdly.—The dynamic structure amplitudes for the quantum reflections are determined by the modes of atomic vibration and are not necessarily proportional to the static structure amplitudes. It is quite possible, for instance, that the dynamic structure amplitude for a particular set of crystal planes is zero while the static structure amplitude for the same planes is finite, or *vice versa.* In other words, the intensities of the classical and quantum reflections by any given set of crystal planes are not necessarily proportional to each other. Such a situation cannot rise in the quantum scattering of the X-rays, as this is due to the simple translatory movements of the lattice cells.

Fourthly.—Since the two phenomena arise from vibrations of the crystal lattice lying in widely different ranges of frequency, their intensity variations with temperature would be markedly different. In either case, a finite limiting intensity would be reached at low temperatures, but this would be far greater relatively to the intensity at ordinary temperatures for the infra-red vibrations than for the elastic ones.

Fifthly.—The characters of the quantum reflections and their variation with physical conditions such as temperature should exhibit a close correlation with the spectroscopic behaviour of the substance in the infra-red region; the quantum scattering, on the other hand, should show a correlation with the elastic behaviour of the substance.

Sixthly.—The changes of frequency, if directly observable, would naturally be much greater for the quantum reflections than for the quantum scattering.

10. Summary

The paper examines the views generally current at the present time regarding the nature of the vibrations possible in a crystal lattice which

are based largely on the specific heat theory of Debye and the crystal dynamics of Max Born and his school. The latter has for its starting point the so-called postulate of the "cyclic lattice". It is here shown that this postulate is an *ad hoc* supposition adopted for mathematical convenience and that, far from being justifiable, its consequences are definitely contradicted by the known spectroscopic behaviour of crystals and that it is also contrary to the dynamic behaviour which should be expected from a set of coupled Planck oscillators such as the lattice cells of a crystal constitute. It is also shown that the modes of vibration of the elastic type forming a continuous spectrum and the modes of vibration having discrete or monochromatic frequencies in the infra-red region have fundamentally different dynamic characters. Starting from the proposition established by Laue that the secondary X-radiation from an oscillating atom exhibits components of modified frequency, it is shown how the resultant effects of the secondary radiations of modified frequency due respectively to these two types of vibration can be evaluated. It is shown further that the infra-red vibrations result in geometric reflections by the lattice planes of the crystal but with altered frequency, their intensity (subject to the same limitations as for the classical reflections) being proportional to N^2, that is, to the square of the number of lattice cells in the crystal. On the other hand, the elastic vibrations of low frequency give a diffuse scattering of the X-rays of which the intensity is proportional to N. As both these effects involve changes of frequency, the classical mechanics is incompetent to describe them correctly, and has therefore to be replaced by quantum-mechanical considerations. It is shown how this can be done quantitatively. The temperature dependence of both these effects is discussed. Finally, numerous experimental criteria are presented distinguishing the two effects which should prevent them from being mistaken for each other.

REFERENCES

1. Raman and Nilakantan .. *Curr. Sci.*, 1940, **9**, 165.
2. ———————————— .. *Proc. Ind. Acad. Sci.*, 1940, **11**, 379.
3. ———————————— .. *Ibid.*, 1940, **11**, 389 and 398.
4. Debye .. *Ann. d. Phys.*, 1914, **43**, 49.
5. Brillouin .. *Annales De Phys.*, 1922, **17**, 88.
6. Waller .. *Zs. f. Phys.*, 1923, **17**, 398.
7. ———————————— .. *Ann. d. Phys.*, 1927, **83**, 153.
8. Laue .. *Ibid.*, 1926, **81**, 877.
9. Bhagavantam .. *Ind. Jour. Phys.*, 1930, **5**, 573.
10. Nayar .. *Proc. Ind. Acad. Sci.*, 1941, **14**, 1.
11. Saksena .. *Ibid.*, 1940, **12**, 93.