

# The diffraction of X-rays by diamond—Part I

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## 1. Introduction

By reason of its remarkable physical properties, diamond stands out uniquely as the crystal which shows us the way to a correct understanding of the fundamental aspects of the physics of the solid state. The atomic vibrations in crystals, the theory of their specific heats and their spectroscopic behaviour may be mentioned in this connection. These topics formed the subject of recent memoirs published in these *Proceedings*, and the experimental results obtained with diamond figured very prominently in them. The present communication deals with the X-ray diffraction effects exhibited by diamond and considers them from both the theoretical and experimental standpoints. It emerges that diamond has a great deal to teach us regarding the fundamental aspects of the subject of X-ray crystallography and indeed compels us to approach the subject from new points of view.

The present investigation stems from a report from the author's laboratory published in the year 1940 under the title "A new X-ray effect" (*Curr. Sci.*, 1940, 9, 165-67). That report recorded the discovery of the very striking and indeed surprising features which reveal themselves in strongly exposed X-ray diffraction patterns of diamond. It was very clear that the phenomena stood outside the framework of the classical theory of X-ray diffraction. It was accordingly suggested that they had their origin in the quantum-mechanical excitation of the atomic vibrations in diamond by the monochromatic X-ray beam traversing it, the X-rays being themselves reflected as a result of such excitation with a change of frequency. It was explained in the report why it was possible for reflections of this nature to be observed even when the setting of the crystal was different from that ordinarily required for a reflection of the X-rays by the same lattice planes.

The instrumental equipment available for the research at that time was, unfortunately, not of sufficient power to enable the subject to be explored with any degree of completeness. The investigation had accordingly to be laid aside and the circumstances in which the author found himself did not, for many years, permit of its being resumed. Happily, however, it has now been possible to take up the work once again, not only with new and more powerful instrumental aid,

but also with fresh theoretical ideas derived from the work of the author in the related fields referred to earlier in this introduction. The results are now laid before the reader.

Part I of the paper considers the theory of X-ray diffraction by crystals in general from a fundamentally new standpoint. Part II considers the application of the theory to the particular case of diamond. Part III presents the results of a detailed experimental investigation of the case.

## 2. The structure of crystals

The conventional view of a crystal as an assembly of atoms arranged in a regular three-dimensional array in space is neither useful nor enlightening when we seek to obtain an insight into the behaviour of crystals when traversed by radiation in the different ranges of frequency. It is necessary indeed to lay aside that view and regard a crystal as a system composed of two kinds of charged particles, namely the nuclei and the electrons, their relative numbers being determined by the magnitudes of their charges. Diamond, for example, is an assembly of carbon nuclei and of electrons, the latter being six times as numerous as the former.

The atomic nuclei have enormously larger masses than the electrons and it is this circumstance that determines the manner in which the two sets of particles arrange themselves in space. According to the fundamental notions of the quantum theory, it is not meaningful to regard the electrons as located at any specifiable points in space, while on the other hand, it is permissible to do so in respect of the nuclei. The Coulomb forces exerted by the nuclei on the electrons tend to draw the latter together and hold them in dynamic equilibrium. Accordingly, what may be described as a cloud of negative charge gathers round each nucleus. But when we raise the question as to what determines the position of the nuclei in space, the answer, remarkably enough, is to be found in these very clouds of negative charge which each nucleus gathers around itself. Indeed, it is the electrons which determine the location and ordering in space of the nuclei. Accordingly, it would be appropriate to describe a crystal as consisting of two distinct assemblies, namely an assembly of nuclei whose positions it is possible to specify with some measure of precision, and an assembly of electrons. It is the interaction of these two assemblies with each other that determines the architecture of the crystal and its physical behaviour. This view of crystal structure will be found most illuminating when we proceed to consider the phenomena resulting from the passage of radiation through the crystal.

## 3. The response of crystals to radiation

The tremendous disparity in the masses of the nuclei and of the electrons justifies us in ignoring any movement of the atomic nuclei which results directly from the

action of the electric field of the radiation on the charges carried by the nuclei. What we need consider in every case is the effect of the radiation field on the electronic clouds. But since these are held in place by their interactions with the atomic nuclei, the latter would also tend to be disturbed when the electronic clouds are set in motion by the field. These considerations are valid irrespective of the individual features of the crystal structure and of the frequency or wavelength of the incident radiation. But since the response of the electrons to the field of the incident radiation would depend on these latter factors, the nature and extent of the movements of the atomic nuclei consequent thereon would also be influenced by those factors.

We may illustrate the foregoing remarks by considering first the cases in which the frequency of radiation lies in the infra-red range. Viewing the matter classically, the effect of the radiation on the electronic clouds in this case would be to produce periodic displacements to and fro of the electronic clouds with the same frequency. These displacements would, however, be limited by the binding of the electrons to the nuclei. Even when the frequency of the incident radiation coincides with a natural frequency of vibration of the atomic nuclei about their positions of equilibrium, it would not necessarily follow that such vibration is excited by the field. Indeed, it is well known that in many cases, the field does not excite the vibrations; in other words, the vibrations are not active in the absorption of the infra-red radiation. In order that any given mode of vibration should be excited by the incident radiation field and thereby rendered infra-red active, it is necessary that a certain lack of symmetry in the structure of the crystal or of the particular mode of vibration results in the movements of the nuclei being accompanied by a periodic displacement to and fro of the electronic clouds which hold the nuclei together. The selection rules which define the conditions under which any particular mode of vibration is active in the absorption of infra-red radiation are, indeed, based on considerations of this nature. That they are in agreement with experience demonstrates the validity of the present approach to the subject.

Coming now to the case of visible light, the response of the crystal to the field of the incident radiation would be determined by the relation between the frequencies of the incident radiation and the characteristic frequencies of vibration of the electronic clouds. Further, since the frequency of the radiation is much higher than the natural frequencies of vibration of the nuclei, the possibility of the incident radiation exciting the latter in the manner considered in the preceding paragraph would not arise at all. There are however possibilities of the nuclear vibration being excited by the electronic movements in a different way. Considering those electrons which hold together the different nuclei and thus form part of the architecture of the crystal, it is evident that any approach or recession of such nuclei from each other would influence the characteristic frequencies of the electronic clouds attached to them. This is equivalent to stating that the response of the electronic clouds to the field of the incident light would be

modified or modulated by the natural frequencies of the nuclear vibrations. That such an effect actually arises is demonstrated by the fact that when monochromatic light traverses a crystal, and the light diffused in its interior is spectroscopically examined, monochromatic radiations are observed in it whose frequencies differ from that of incident light by amounts equal to the characteristic infra-red vibration frequencies. Whether or not any particular mode of vibration of the nuclei thus reveals itself is determined by the circumstances of the case. The selection rules which express these circumstances are naturally different from those that determine the activity in infra-red absorption.

The frequency of X-radiation is very much higher than that of either visible light or of infra-red waves, and the phenomena arising from their passage through crystals would naturally be determined by the high frequencies and correspondingly short wavelengths of the rays. We have, in the first instance, to consider the effect of the radiation field on the electronic clouds. But it is not possible to ignore the fact that the electronic clouds are held in their places by the atomic nuclei and that, consequently, not only the electronic clouds but also the atomic nuclei would tend to be disturbed by the X-radiation. There is every reason therefore to expect that the effects arising from such disturbance of the nuclei would manifest themselves in the X-ray diffraction patterns of the crystal.

The foregoing represents the general point of view which will be developed and discussed in greater detail in the present series of papers. Its consequences will also be compared with the facts of observation. We shall find that it receives the clearest possible support in the phenomena exhibited by diamond in its X-ray diffraction patterns.

#### 4. X-rays and crystals

The observational basis of X-ray crystallography is the selective reflection of X-rays by the atomic layers in a crystal at angles of incidence determined by the wavelength of X-rays and the spacing of the layers. The phenomena is clearly analogous to the familiar effect of iridescence exhibited by regularly stratified media on which visible light is incident. Hence it is quite natural to explain the phenomena of X-ray diffraction by crystals on similar lines. We assume the crystal to be a material of which the optical polarisability for X-ray frequencies exhibits space-periodic variations in three dimensions. A determination of the settings of the crystal at which the X-ray reflections for a known wavelength are observed enables us to determine the spacings of the stratifications in various directions as also their relative orientations. A comparative study of the intensities of the various reflections enables us to go further and obtain a measure of the magnitude of the periodic variations of the polarisability for X-ray frequencies appearing in each set of stratifications. The entire procedure is phenomenological in character. In endeavouring to deduce from the experi-

mental results a picture of the ultimate structure of the crystal, various difficulties arise which we shall not discuss here. What we are actually concerned with is the meaning of the phrase "polarisability for X-ray frequencies" employed above in terms of the ultimate structure of the crystal.

In classical optics, where we are concerned with the behaviour of media which can be regarded as continuous, the term polarisability has a simple and definable meaning, namely, the strength of the electric dipole per unit of volume induced by an external electric field of unit strength. Difficulties arise when we endeavour to take over this description into the region of high frequencies and short wavelengths. These difficulties are of two kinds. Firstly, the medium can no longer be regarded as a continuous and structureless substance, since it actually consists of a set of discrete particles arranged in layers. The second difficulty is that these particles are not all similar and similarly circumstanced. In particular, the nuclei and the electrons have very different masses and are oppositely charged; the interactions between them enter fundamentally into the problem of determining the response of the medium to the field of the incident radiation.

A way of escape from the difficulties indicated above may be sought for by regarding the recognisable units in the structure as "diffracting particles" in the sense of classical optics. We find however that such a procedure is not sustainable. For example, the individual electrons in the crystal cannot be assigned the role of "diffracting units". For, as already remarked, an electron does not possess any precisely definable location in space and hence the phase of any radiation that it could diffract would be indeterminate. An even more fundamental difficulty is that if an individual electron does interact with X-rays, the result is a secondary radiation of altered wavelength, in other words the Compton type of scattering. The alternative approach of regarding the individual *atoms* in the crystal as the "diffracting units" is also not sustainable. For, in any actual crystal, the atoms are held in their places by the electrons which link them together and these electrons cannot therefore be regarded as the exclusive possession of any particular atom. Taking for instance the case of diamond, only two out of every six electrons can with any measure of justification be considered as attached to an individual carbon nucleus. The remaining four electrons enter into the architecture of the crystal and hence must be considered as held in common with other atoms.

In view of the situation stated above, it is clear that the only logically sustainable approach to the subject of X-ray diffraction is that which proceeds on the following basis: *the X-ray reflections by a crystal are a co-operative effort of the entire structure, meaning thereby all the nuclei and all the electrons included in it.*

## 5. The energy levels of crystals

The present approach to X-ray diffraction problems differs from that customarily adopted in two respects. In the first place we recognize that the atomic nuclei have

a part to play in the phenomena since on the one hand, they hold the electrons in place and on the other hand are themselves held in place by the electrons. Further, what we shall actually concern ourselves with is not the behaviour of the individual electrons or of the individual atoms in the crystal, but the behaviour of the two assemblies consisting of nuclei and of electrons respectively constituting the crystal when it is traversed by the X-radiation. This approach brings the phenomena of X-ray diffraction into the closest relationship with the behaviour of crystals when traversed by ultra-violet, visible or infra-red radiation. In all such cases we are concerned with the changes in the energy levels of a crystal which are or could be induced by the radiations traversing it. As we have two sets of particles which differ greatly in their masses, the possible changes in the energy levels are of two kinds which in the usual language of spectroscopy may be described as changes in the electronic levels and the vibrational levels respectively. The simplest cases are those in which there is no change in either the electronic or vibrational energy states of the crystal when traversed by radiation. This would correspond to a simple undisturbed transmission of the radiation through the crystal in the case of visible or ultra-violet light. In the case of X-radiation, however, the stratifications of optical polarisability in the structure of the crystal can in appropriate circumstances result in geometric reflections of X-rays in various directions. In the language of the quantum theory, such reflections would be described as the result of an exchange of momentum without an exchange of energy between the radiation and the crystal. Still another possibility has to be recognised, namely, that while the initial and final *electronic* energy states are the same, the radiation induces a change in the *vibrational* energy level which persists. When and in what circumstances such a process can occur as the result of the passage of X-radiation, and what would be the observable results of such a process are the questions which we shall proceed to consider.

The answers to the questions raised above emerge when we consider the effects observed respectively when a crystal is traversed by radiation in the infra-red and in the visible regions of the spectrum. In the former case we are concerned with an actual absorption of the radiation. In the latter case we have a simple transmission accompanied by a diffusion or scattering with shifts of frequency indicating that changes in the vibrational energy levels have been induced by the incident light. It should not be imagined that each and every characteristic mode of vibration can manifest itself in the infra-red absorption spectrum and in the scattering of light as a frequency shift. This is very far indeed from being the case. Whether a particular mode of vibration does or does not so manifest itself is determined by certain selection rules which are different for infra-red absorption and for light-scattering. Why this is so becomes clear when the mechanisms respectively of infra-red absorption and of the scattering of light with change of frequency are examined. The latter effect is explained as arising from the variations of the optical polarisability of the crystal for visible light which accompany changes in its infra-red energy levels. On the other hand, infra-red

absorption arises from the displacements of electric charge produced by the incident radiation. The question arises whether effects of the same nature can be induced by X-radiation. It is obvious that any change in the optical polarisability for X-rays produced by the changes in the infra-red energy levels of the crystal would, in view of the very high frequencies of X-radiation, be entirely negligible. On the other hand, the periodic displacements of electric charge associated with vibrational transitions which are active as absorbers of infra-red radiation necessarily involve periodic displacements of the stratifications of optical polarisability which give us the X-ray reflections by the crystal. *It follows that when X-radiations traverse a crystal, they can induce changes in its vibrational energy levels, provided that such changes involve displacements of electric charge—in other words, provided that the modes of vibration under reference are active as absorbers of infra-red radiation.*

## 6. X-ray reflection with change of frequency

We have now to consider what would be the consequence of a change in the vibrational energy levels of crystals induced by X-rays in the circumstances stated above. The question arises whether the observable result of such a process would be a diffusion of the X-rays in various directions or else a reflection similar to that ordinarily observed involving no exchange of energy. Before this can be answered, we have to ask ourselves: What is the nature of the vibration spectrum of a crystal? This question has already dealt with by the author in various recent publications and the same ground need not therefore be traversed here once again. As has been shown in the publications referred to, theory and experiment alike indicate that the vibration spectrum of a crystal containing  $p$  atomic nuclei in each unit cell consists of a set of  $(24p - 3)$  monochromatic frequencies, accompanied by a residue representing the three omitted degrees of freedom which constitutes a continuous spectrum of low frequencies. Amongst the  $(24p - 3)$  modes, in  $(3p - 3)$  modes which are the only ones with which we are concerned in the present paper, the vibration repeats itself with identical frequency and amplitudes and phases in the successive cells of the crystal structure. It follows from this that the changes in the corresponding vibrational levels induced by the incident X-radiation would extend over the entire volume of the crystal traversed by the incident X-ray beam. As a consequence of this again, the X-rays would be regularly reflected by the stratifications of the crystal; such reflection involves a transfer of energy between the radiation and the crystal equal to the vibrational frequency multiplied by Planck's constant. *Hence, the frequency of the reflected X-rays would differ from that of the incident X-ray beam by the frequency of the vibrational mode excited.* As has been explained in the preceding section, such a process is only possible in respect of the modes of vibrational which are active in the absorption of infra-red radiation.

The result stated above has a classical analogue in the reflection of light by a stratified medium which is assumed to execute oscillations of small amplitude normal to its layers. (An oscillation parallel to the layers would obviously be without effect.) It can readily be shown that the reflected wave of the original frequency  $A \sin 2\pi\nu t$  would be accompanied by *two* additional components which are respectively of diminished and increased frequency,

viz.,

$$\pi \cdot A \cdot d^*/d \cdot \sin 2\pi(\nu + \nu^*)t,$$

and

$$\pi \cdot A \cdot d^*/d \cdot \sin 2\pi(\nu - \nu^*)t,$$

where  $d$  and  $d^*$  are respectively the spacing of the stratifications and the amplitude of their oscillation, while  $\nu$  and  $\nu^*$  are respectively the frequencies of the incident radiation and of the oscillation of the stratifications. The equality of amplitude of the reflected waves of enhanced and diminished frequency is a natural consequence of our assuming the oscillations of the layers to subsist of themselves. In the quantum theory, on the other hand, the oscillations are *induced* by the incident radiation; and hence the two components would, in general, be of very different intensities; their ratio is determined by thermodynamic considerations and is expressible in terms of the Boltzmann factor  $\exp(-h\nu^*/kT)$ .

The classical analogy referred to above leads to some general inferences regarding the intensity of the X-ray reflections with altered frequency in relation to the intensity of the X-ray reflections of unmodified frequency given by the same set of lattice planes. We notice in the first place that the two are proportional to each other. Hence, if one is absent, the other would also be absent. In other words, the so-called missing reflections familiar to the X-ray crystallographer would also fail to manifest themselves as dynamic reflections. Further, we could normally expect to observe the latter only as accompaniments of the stronger reflections of the ordinary kind. Their relative intensity is determined by the square of the ratio  $d^*/d$ , where  $d^*$  is the amplitude of oscillation of the stratifications and  $d$  is their spacing. Since  $d^*$  is a measure of the displacement of electric charge which is responsible for the activity of the mode in the absorption of infra-red radiation, it follows, firstly, that inactive modes would not give rise to dynamic X-ray reflections, and secondly, that the greater the infra-red activity of a mode, the more intense would be the dynamic X-ray reflections associated with it.

## 7. The phase-waves of dynamic reflection

The possibility of X-radiation exciting one of the  $(3p - 3)$  characteristic modes of nuclear vibration and being itself reflected in the process was deduced above on the assumption that the wavelength of the X-rays, the spacing of the stratifications, and the angle of incidence on them are related to each other in the same



manner as that necessary for a reflection of the ordinary kind. In these circumstances, the excited vibration necessarily repeats itself with the same frequency and also with the same amplitudes and phases in every cell of the structure traversed by the X-rays.

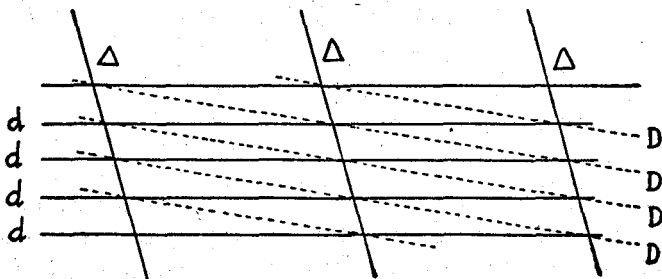


Figure 1

For X-ray reflections with a change of frequency to be observable at other settings of the crystal, it is necessary that the vibrations excited are everywhere similar, but that the phase of the excited vibration in the individual cells of the structure alters progressively through the crystal in such a manner that the vibrations excited in all the irradiated cells conspire to give a coherent reflection. The condition for this to be possible is most readily stated in the form of a diagram (figure 1 in the text). The lines marked *ddd* represent the traces on the plane of the paper of the stratifications in the crystal. The planes marked  $\Delta\Delta\Delta$  similarly represent the traces on the plane of the paper of the *phase-waves*, in other words of the planes along which the internal vibrations of the crystal have identical phases. It is evident from the figure that the planes marked *DDD* cutting across both of them would represent the stratifications which play the same role for the dynamic reflections that *ddd* play for the static ones. The relationship between the spacings *D*, *d* and  $\Delta$  is given by the vectorial formula

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

It needs to be explained why the situation indicated in figure 1 can arise consistently with the principles of dynamics and of the quantum theory. A vibration in which the frequency as well as the amplitudes and the phases are the same in every cell of the crystal structure is the only possible vibration having the characters of a normal mode. Since, however, the interatomic forces in crystals are essentially short-range forces, it is permissible to regard a crystal as made up of a great number of quasi-independent oscillators which have common modes and frequencies of vibration. Indeed, this is the approach which has necessarily to be adopted in developing the theory of the specific heats of crystals. It leaves

out of account the small uncertainties in the frequency of vibration incidental to a limitation in size of the individual oscillators. In our present problem, therefore, it is permissible to consider modes of internal vibration which are the same everywhere in the crystal but in which the phase of vibration in the individual cells alters progressively as we move through the crystal. If  $\Delta$  is large enough compared with  $d$ , the vibration would be practically indistinguishable from the limiting case in which  $\Delta$  is infinite. But as  $\Delta$  is diminished, what we have in the crystal is not a normal mode but a *forced* oscillation of which the frequency is different, the more so, the smaller  $\Delta$  is. In other words, a dynamic reflection in these circumstances results from a forced oscillation excited by the X-rays with a frequency differing slightly from that of the free oscillations of the structure. Hence, using the language of the quantum theory, we may infer that the probability of such an event happening would diminish rapidly as  $\Delta$  becomes smaller. In consequence, we would find that the dynamic reflection has the maximum intensity when the setting of the crystal is that at which the ordinary reflections also appear; the intensity would fall off rapidly as the crystal is moved away from that setting in either direction.

### 8. The geometric law of dynamic reflection

The construction shown in figure 1 enables us to deduce some general results regarding the geometric behaviour of the dynamic reflections. If the phase wavelength  $\Delta$  is infinite, the dynamic stratifications  $DDD$  would coincide with the static layers  $ddd$ . Hence, if the X-rays are incident on the latter at the correct angle for a regular reflection of the ordinary kind, the dynamic reflection would also appear in the same direction superposed on it. In the general case, the direction in which the reflection would appear would be determined by the orientation and the magnitude of the phase-vector. If both of these quantities can vary arbitrarily, then nothing in the nature of a regular reflection would be possible. If, however, the orientation of the phase-vector is precisely defined, a monochromatic X-ray beam incident at a precisely defined angle on the lattice planes of a crystal can result in a dynamic reflection also appearing in a precisely defined direction; but unlike the static reflection in similar circumstances, it would be observable over a wide range of settings of the crystal. The plane of reflection would naturally be the plane of incidence of the X-rays on the dynamic stratifications and the angles of incidence and of reflection with respect to them would also be equal.

Figure 2 exhibits the geometric laws of dynamic reflection of X-rays in a readily comprehensible fashion. The directions of the vectors  $\vec{1/d}$ ,  $\vec{1/D}$ ,  $\vec{1/\Delta}$  are represented by points on the surface of a sphere, the X-ray beam being assumed to traverse the crystal along the polar axis of the sphere. Three meridional circles have been drawn on the sphere passing respectively through those three points.

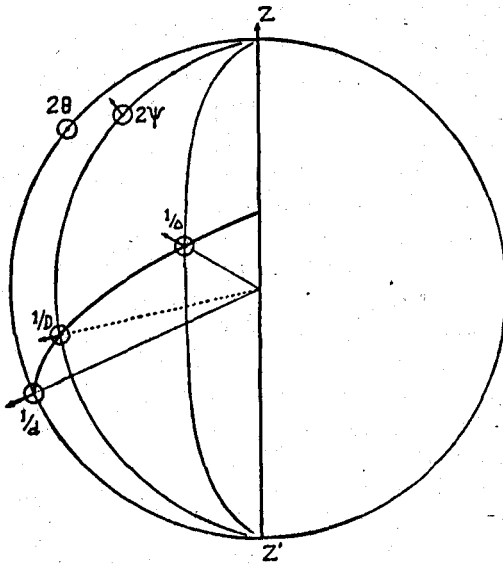


Figure 2

The first circle is evidently the plane of incidence of the X-rays on the lattice layers whose spacing is  $d$ . The second is the plane of incidence of the X-rays on the dynamic stratifications. The third circle is the plane containing the incident X-rays and the normal to the phase-waves. From equation (1) connecting the three vectors  $1/d$ ,  $1/D$  and  $1/\Delta$ , it follows that the point representing  $1/D$  on our sphere would lie on a great circle drawn through  $1/d$  and  $1/\Delta$ , its actual position on that circle being determined by the relative values of  $d$  and  $\Delta$ . If  $\theta$  be the glancing angle of incidence of the X-rays on the lattice layers of the crystal, a reflection would appear in a direction making an angle  $2\theta$  with the polar axis of the sphere on the first meridional circle, provided the condition  $2d \sin \theta = \lambda$  is satisfied. This would correspond to the case in which the phase wavelength  $\Delta$  is infinite. In the actual case to which the figure refers, the dynamic reflection would appear in a direction making an angle  $2\psi$  with the polar axis of the sphere,  $\psi$  being the glancing angle of the incident X-rays on the dynamic stratifications. It is here assumed that the condition  $2D \sin \psi = \lambda$  is satisfied. The figure indicates that the dynamic reflection deviates from the direction in which it would appear for an infinite phase wavelength, both along the meridional circle and transverse to it, to extents determined by the angle between the first and the third meridional circles as also by the angle of incidence of the X-rays on the lattice planes under consideration.

## 9. Summary

The theory of X-ray diffraction in crystals is discussed and it is shown that the X-ray reflections must be regarded as a co-operative effort of the entire structure in which the nuclei as well as the electrons play their respective roles. It is further shown that the passage of X-rays through a crystal and their reflection by the stratifications of electron density can simultaneously result in vibrational energy transitions, provided that the modes of vibration thus excited involve displacements of electric charge and are therefore active as absorbers of infra-red radiation. Vibrational modes of this kind when excited result in periodic displacements of the stratifications of electron density. Consequently, reflections appear whose frequencies are less (or greater, as the case may be) than the frequency of the incident X-radiation. It is explained why it is possible for such reflections to appear even when the setting of the crystal is different from that required for the usual or unmodified reflections. The geometry of the X-ray reflections which then appear in displaced positions is also discussed.