

Reflection of X-rays with change of frequency— Part I. Theoretical discussion

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1. Introduction

The present paper deals with the new type of X-ray reflection in crystals observed by the authors and described in an address to the Easter Conference of Scientific Societies at Bangalore on the 22nd March of this year. A brief account of the phenomenon with an illustrative photograph of the effect as observed in diamond appeared as a special article¹ in the issue of *Current Science* for April under the title "A new X-ray effect". The phenomenon was there described as having "in its physical nature, something in common with both the Laue and the Compton effects", and as being "a specular reflection of X-rays by crystals but with a change of frequency explicable only on quantum mechanical principles". More succinctly, we may describe it as the analogue in X-ray optics of the phenomenon of the scattering of light in crystals accompanied by a change of frequency. The appropriateness of these descriptions will be made evident as we proceed.

Twenty-two photographs grouped in eight plates accompany Parts II and III of the present paper (appearing in the same issue) and are intended to illustrate various aspects of the new phenomenon. Detailed studies have been made with two crystals, namely, diamond and sodium nitrate, which fully establish the nature of the effect and confirm the theoretical interpretations which have been put forward. These are also set out with full particulars.

2. Scattering of light in crystals

In the lecture² on "A New Radiation" (Raman 1928) describing the phenomenon of a change of frequency in the scattering of light by matter, the issue was raised whether such scattering should be considered as being coherent or non-coherent radiation, in other words, whether the different molecules in the substance emit

the scattered radiation with or without any definite phase-relationships as between themselves. It was suggested that though the assumption of incoherence might seem a natural one to make, nevertheless the question required investigation before a definite answer could be returned. Considering the purely theoretical issue, it is evident that if the molecules in a substance are independent oscillators, the scattered radiations arising from the transfer of energy to them need obviously have no specifiable phase-relationships. The position would however be different when the molecules are packed and held together as an ordered assemblage in a crystalline solid by interatomic forces. In such a case, the oscillations with which we are concerned would be those of the crystal lattice rather than those of the individual atoms or molecules. The transfer of energy from the radiation to the substance should then evidently be regarded as a process in which the crystal as a whole is the operative unit. This point of view was indeed suggested and adopted³ by Ig Tamm (1930) as the basis for a quantum-theoretical discussion of light-scattering in crystals.

The simplest mechanism by which a change of frequency can be produced in light by the co-operative action of the molecules in a substance is that considered many years ago by Leon Brillouin⁴ in a well known paper (1922). Addressing himself to the problem of the diffusion of light by the thermodynamic fluctuations of density in a substance, Brillouin considered the effect on a beam of light of a plane train of sound-waves traversing the medium. The sound-waves result in a periodic stratification of the optical density of the medium, and hence in accordance with a well known optical principle would selectively reflect the light-waves, provided these are incident on the stratifications at a glancing angle θ satisfying the relation

$$2\lambda^* \sin \theta = \lambda \quad (1)$$

λ and λ^* are the wavelengths of light and sound respectively as measured in the medium. The optical stratifications due to the sound-waves are, however, not static but travel through the medium with the usual acoustic velocity v . Accordingly, there would be a Doppler effect giving a change of frequency in the reflected light. This would be an increase or a decrease according as the sound-waves approach or recede from the light source. The change of frequency is given by the usual formula for reflection from a moving mirror, namely

$$v_{\text{reflected}} - v_{\text{incident}} = \pm 2 \cdot v \cdot \frac{v}{c} \sin \theta \quad (2)$$

c being the velocity of light in the medium. Writing $c = v\lambda$ and $v = v^*\lambda^*$ where v and v^* are the frequencies of the incident light and sound-waves respectively, and combining equations (1) and (2), we have the relation,

$$v_{\text{reflected}} - v_{\text{incident}} = \pm v^* \quad (3)$$

In other words, the change in the frequency of light in a Brillouin reflection is

merely the frequency of the periodic pulsation in the optical density of the medium.

In the case considered by Brillouin, the sound-waves are those spontaneously existing as the result of the thermal agitation in the substance. The wavelength λ^* of the sound which is actually operative is automatically determined by the wavelength λ of the light and the glancing angle θ as per equation (1). As λ^* diminishes from ∞ to $\lambda/2$, θ varies from 0 to $\pi/2$, and hence the specular reflection by the sound-waves actually gives a scattering in all directions with a change of frequency depending on the direction as indicated by (2). As the velocity of sound is small compared with that of light, this change of frequency is also small. Nevertheless, it has been established experimentally for the case of light-scattering in liquids, and more recently⁵ also in crystals (Raman and Venkateswaran 1938).

It should be remarked, that the optical principles on which equations (1) and (2) rest are of very general validity, and we are not therefore restricted to the cases in which the dynamic stratification in the medium may be identified with ordinary sound-waves. We may, in fact, start from (3), and consider a case in which a pulsation of optical density occurs in the medium with a specified frequency ν^* which may be much higher than that of any sound-waves permissible in the medium. We may assume further that the pulsation, instead of occurring with identical phase throughout the otherwise homogeneous medium, appears as a periodic stratification having a wavelength λ^* and travelling through the medium with a phase-velocity which is not identical with the ordinary acoustic velocity and indeed may be vastly greater. The stratifications would then give rise to a reflection of the incident light-waves with a change of frequency ν^* as in the case already considered, provided that the wavelength of the stratifications and their inclinations to the incident light-waves satisfy the relation (1).

The foregoing discussion indicates that when light is scattered by a homogeneous crystalline solid with a change of frequency ν^* corresponding to one or other of the characteristic infra-red frequencies, the process which occurs may be pictured as follows: The effect of incidence of the light-waves on the crystal is to generate in the latter, periodic stratifications of optical density having the frequency ν^* and a wavelength λ^* , the latter depending on their inclination to the light-waves. These stratifications reflect the light with altered frequency in the manner indicated by equations (1) and (3). The appropriate wavelength of the stratifications and their inclination to the incident light-waves are determined by the act of reflection itself. Surprising as this picture may seem, it is difficult to avoid the acceptance of it, once we concede the idea that the process of light-scattering in a crystal is a coherent phenomenon. Indeed, it is obvious that a completely homogeneous medium can scatter no light even if it is pulsating periodically. The presence of appropriately spaced and inclined stratifications of the pulsation is therefore a necessity to explain the observed scattering.

We may, at this stage, well ask ourselves the question, is there any experimental

evidence to support the basic postulate of coherence? It should be remarked in this connection, that measurements of the intensities of the scattered radiations cannot furnish a direct reply to this question. At first sight, it might seem that 'coherent' scattering should give us a much larger scattering than the 'incoherent' variety, and indeed this would be the case if the strength of the optical dipoles in the scattering particle is prescribed beforehand. Actually, however, when numerous oscillators co-operate in taking up energy from the incident quantum of radiation, their individual dipole strengths are reduced in proportion, and hence, when they emit the quantum again in co-operation, the final result is practically unaffected. The evidence actually available which indicates that light-scattering in crystals is a coherent process is rather indirect. It is well known that the frequency shifts given by crystals often differ appreciably from those obtained in the gaseous or liquid condition of the same substance, and are generally represented by sharply defined lines in the spectrum. Further, the selection rules for the intensity and polarisation of the scattered radiations appear, at least in the cases so far examined, to be determined by the structure and symmetry of the crystal as a whole, rather than by the structure and symmetry of the ionic or molecular units contained in it. These facts are significant and clearly favour the coherence hypothesis. This evidence is however, not absolutely conclusive and we have to rely more on the a priori probabilities of the case. If we consider a crystal such as diamond or quartz consisting of chains of atoms linked together firmly and continuously by valence bonds, it would be difficult to concede that the scattering of light in it could be the result of incoherent local processes involving only individual atoms. Such a crystal as diamond or quartz has been aptly described as being itself a giant molecule, and it appears quite natural to regard the solid as a whole and not the individual atoms in it as the scattering units. Indeed it may be said that nothing so far observed definitely contradicts the postulate of coherence in light-scattering as applied to crystals.

3. Effect of pulsation of structure-amplitude

In his paper of 1922, Brillouin applied his theory of reflection by sound-waves to the problem of the diffusion of X-rays when passing through a crystal which results from the thermal agitation in it. It is clear from equation (1) that such reflections would, as in the case of light, give rise to a diffusion or scattering of the radiation. But owing to the short wavelength of the X-rays, such diffusion would be limited to glancing angles ranging from zero up to a maximum determined by the shortest wavelength of sound present in the acoustic spectrum of the crystal. As this wavelength limit for sound can scarcely be smaller than the grating constant of the crystal, the diffusion of the Brillouin type would be limited to

glancing angles less than that at which any Bragg reflection of monochromatic X-rays by the crystal could appear.

As in the case of light, however, we are not restricted to considering stratifications which are identifiable with sound-waves, and may extend the application of equations (1), (2) and (3) in the X-ray region to any type of coherent pulsation capable of giving periodic stratifications of the electron density of the crystal. Excluding the case of small glancing angles, we see from (1) that the wavelength λ^* of the stratifications must be comparable with that of the incident X-rays, and would therefore also be of the same order of magnitude as the crystal spacings existing in solids which give the ordinary Bragg-reflections of unchanged frequency. It is therefore necessary to consider in what circumstances, the dynamic X-ray reflections with change of frequency here contemplated may be expected to occur with sensible intensity and be capable of being distinguished from the usual static reflections.

As is well known, the usual Laue spots given by X-rays with crystals are observed when the Bragg condition given by (1) is satisfied, λ^* now representing the spacings in the crystal structure, and λ the wavelength of the X-rays responsible for the reflection. The intensity of any such reflection is determined principally by a quantity known as the structure-amplitude of the spacing, which appears as a multiplying factor of the corresponding term in the three-dimensional Fourier analysis of the electron density in the crystal. This structure-amplitude is determined by the atomic arrangement in the unit cell of the crystal lattice. If, now, we postulate a periodic pulsation of the atomic positions in all the cells of the crystal lattice, its effect would be to vary the structure-amplitude of every spacing of the crystal periodically with the same frequency. In other words, the effect of such pulsation is to superimpose upon the each static structure-amplitude of the crystal, a dynamic structure-amplitude having the same spacing and capable of giving a reflection with changed frequency.

We may now, in the first instance, consider the consequences of assuming that the phase of the pulsation of electronic density is rigorously the same for all the unit cells in the crystal lattice. The static and dynamic stratifications of electron density would then everywhere run parallel to each other, and the geometric conditions (as given by the Bragg formula) for the appearance of static and dynamic X-ray reflections would therefore be identical. In other words, the unmodified and modified X-ray reflections would always appear or fail to appear, at the same time. Since the actual change of frequency in the X-ray reflections is beyond the resolving power of the most powerful X-ray spectrometer, we should be unable to detect the appearance of the modified reflections in the presence of the unmodified ones.

Actually, however, the assumption that the pulsations in the cells of the crystal lattice are coherent does not imply that their phases should be identical at all points of the crystal. Indeed, we have already seen that in order to explain the phenomena observed with ordinary light, it is necessary that the analogous

pulsations of optical density in the crystal should *not* be of identical phase throughout, but should appear as stratifications having the appropriate wavelength and inclination to the incident light-waves and thus satisfying the condition for a coherent reflection. In our present case, the spacing or wavelength of the dynamic stratifications is fixed, being in fact the atomic spacings in the crystal, but their phases are capable of adjustment and should, in fact, automatically adjust themselves, as in the case of light, so as to secure the condition necessary for reflection. *It is readily seen, that a progressive change of phase in the atomic pulsations as we move in a direction parallel to a particular plane of atoms is equivalent to a tilt of the wave-front of that pulsation away from the crystal planes in a direction perpendicular to them.* When a pencil of X-rays is incident obliquely on a particular spacing of the crystal, the phase of the electrical vibration reaching successive atoms in any particular layer alters progressively in the plane of incidence. A compensating change in the phase of the structure-amplitude variation along the same direction would, in effect, tilt the wave-fronts of the atomic pulsation to such an obliquity that the Bragg condition for the particular spacing may be satisfied. In other words, we can get a dynamic or modified X-ray reflection from a particular atomic spacing at an angle of incidence at which we cannot obtain the usual Bragg reflection for the same X-ray wavelength. The modified reflection would in these circumstances appear in a direction which is displaced from the usual geometric position.

The foregoing discussion indicates that the unmodified and modified X-ray reflections are separable by the simple device of tilting the crystal away from the correct glancing angle for the X-ray wavelength employed. The unmodified reflection obeys the usual geometrical laws of reflection from the atomic spacings besides satisfying the Bragg condition. The modified reflection also appears in the plane of incidence of the X-ray on the atomic spacings, but in general, in a direction different from that of geometric reflection from such planes. This failure of geometrical optics is, however, more apparent than real; as we have already seen, the modified reflections satisfy both the geometrical laws of reflection and the Bragg condition, provided that we recognise the surfaces of constant phase of the structure-amplitude pulsations and not the atomic spacings themselves as the reflecting planes responsible for them.

4. Modified reflection as a quantum effect

It is well recognised that the scattering of light with a change of frequency as actually observed is a quantum effect and cannot be explained on the classical dynamics, though there is a classical analogue which agrees with it in certain particulars. The inadequacy of the classical theory is evident even in the case of scattering by individual molecules and becomes clearest when we consider the question of intensities. Taking, for instance, the scattering of light by a hydrogen

molecule, the characteristic vibration frequency is 4156 cm^{-1} in spectroscopic units. Classically, the spectrum of monochromatic light scattered by hydrogen gas should exhibit two spectral lines of equal intensity shifted from the primary radiation in either direction by this frequency. But the intensity of either of the displaced lines on the classical theory would be very small, while in actual fact, this is true only of the line displaced to a higher frequency, whereas the line shifted to a lower frequency is remarkably intense. When we consider light-scattering in crystals, the failure of the classical theory is even more acute. Classically, a crystal if it is an ideally homogeneous solid, should scatter no light at all; in order to explain the observed diffusion of light, we have to postulate that stratifications having the desired frequencies and of specially suitable wavelengths and orientations are present which reflect the incident radiations with a change of frequency. Except for the lowest frequencies of pulsation or at sufficiently high temperatures, thermal agitation would scarcely be adequate to account for the presence of such stratifications. This difficulty disappears when light scattering is regarded as a quantum-mechanical phenomenon, as the production of the stratifications which reflect the radiations would then itself be a part of the process.

In our present X-ray problem, the stratifications with which we are concerned have, in part, a physical basis, namely, the atomic spacings in the crystal, and this fact is responsible for the resulting effects being directed reflections analogous to the Laue spots instead of being a diffuse scattering. The atomic pulsations which give the periodic variations of structure-amplitude have the same origin as the characteristic internal vibrations revealed in light-scattering or in infra-red absorption, and their frequencies may be so high that the thermal excitation of the same is entirely negligible. Nevertheless, as in the optical case, we should expect them to be excited and give rise to the modified reflection of X-rays even at ordinary temperatures. Further, on the quantum view, such modified reflections should persist without serious diminution of intensity when the crystal is cooled down to low temperatures. *Per contra*, when the crystal is heated, the intensity of the modified reflections should increase but not very greatly until temperatures are reached at which the characteristic vibrations concerned contribute notably to the thermal energy content of the crystal.

As we have already seen, the appearance of the modified reflections in directions other than that of the unmodified ones involves a suitable progression of the phase of the atomic pulsation in the plane of incidence. This "tilting of the wave-fronts" so as to secure the possibility of a Bragg reflection at any arbitrary angle of incidence might seem a very surprising postulate to make when we view the subject classically. But it fits in perfectly with the quantum mechanical point of view according to which the incident radiation itself creates the atomic pulsations which result in its reflection, and the conditions necessary for such reflection are therefore automatically secured. Even on a purely classical view, it is not inevitable that the pulsations in the crystal lattice should be of identical

phase everywhere, though the more rigidly constructed the crystal lattice is, the more closely this ideal might be expected to be approached, and the more sharply would the modified reflections be limited to directions approaching that of the unmodified ones.

5. Analogy with the Compton effect

As is well known, the change of wavelength in X-ray scattering discovered by A H Compton in 1922 was explained by him⁶ as the result of the transfers of energy and momentum which occur when a photon impinges on a free electron. In the wave-mechanical picture of the same process given by Schrodinger⁷ in 1927, the scattering of the photon appears as a reflection of the incident waves by the periodically stratified distribution of charge density obtained on superposing the De Broglie waves of the electron before and after the collision. The Doppler effect due to the movement of these stratifications explains the change of frequency in reflection. That the effect as actually observed is a diffuse scattering follows from the fact that the recoil of a free electron and therefore also the reflection of the incident radiation is in an arbitrary direction. The wave-mechanical picture of the Compton effect is thus rather similar to Brillouin's classical treatment of the reflection of light by travelling sound-waves. The analogy would be closer still if the stratifications of optical density in the medium were considered as resulting from the incidence of the radiation, as in Schrodinger's treatment, instead of being postulated to exist in advance.

That the change of wavelength in the Compton scattering is a function of the angle of observation follows from the manner of its origin. Several attempts have been made in the past to observe the change of wavelength independent of the angle of scattering which might be expected if the electron which scatters the radiation shifts to a higher energy level while remaining bound to the atom. The theoretical problem has been considered⁸ by Sommerfeld in whose note will be found references to various papers in this connection. It is clear that if such an effect exists, the change of wavelength would be much smaller than the Compton shift. Then again, the more firmly the electron is bound to the atom, the less likely it is as the result of the scattering process, to pass to an unoccupied level of higher energy. These circumstances and the necessarily feeble intensity of any effect which appears as a diffuse scattering would militate against its successful detection in experiment. It may be recalled in this connection that the attempts so far made to discover the analogous phenomenon of a change of frequency in light scattering due to the transfer of a bound electron from one energy level to another within an atom have also been unsuccessful.

The preceding discussion prepares us for recognising that the modified reflection of X-rays by crystals and the Compton effect are essentially analogous phenomena, as they both arise from the reflection of radiation by a stratified

distribution of electric charge density. There are however also significant differences. In our present case, the electrons remain bound to the crystal lattice of which they form a part, and the stratifications arise from the crystal lattice being set in vibration and causing a periodic variation of the electronic charge density in the crystal structure. Accordingly, in our present case, the resulting effect appears as a directed reflection instead of as a diffuse scattering. The frequency changes in the modified reflection of X-rays are necessarily much smaller than in the Compton effect, indeed so small as to be beyond spectroscopic detection. The differences between the laws of modified and of unmodified reflection of X-rays by crystals should however enable us to recognise their existence.

The analogy between the modified reflection of X-rays and the Compton effect will also be obvious when it is recalled that in the present case as well, the change of frequency and the change in direction of the reflected X-rays may be regarded as a consequence of the exchange of energy and momentum between the incident quantum of radiation and the crystal lattice. The discussion of this point may however be more suitably undertaken in a later paper in which the intensity problem for modified X-ray reflection will be more fully dealt with.

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