

A new X-ray effect

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The discovery by Laue in 1912 of the diffraction of X-rays by crystals and the discovery by A H Compton in 1922 of the change of wavelength in X-ray scattering had both a profound influence on our concepts of the nature of X-radiation. Laue's discovery established beyond all question that X-rays are physically of the same nature as ordinary light but of much shorter wavelength, while the Compton effect showed in the clearest possible way that the interaction between X-rays and matter obeys quantum mechanical principles. The new X-ray phenomenon described and illustrated in the present communication has, in its physical nature, something in common with both the Laue and the Compton effects: it is a specular reflection of X-rays by crystals but with a change of frequency explicable only on quantum mechanical principles. Before proceeding to give particulars of the phenomenon, it would appear desirable to make a few prefatory remarks regarding the structure of crystals and the nature of their internal vibrations.

The ideal crystal is an ordered geometric arrangement of atoms or molecules held together in a space-lattice by interatomic forces. The electron density in such a crystal is a periodic function in space expressible as a three-dimensional Fourier series. Each term in this Fourier expansion contains as a multiplying factor the structure-amplitude which is the magnitude of the periodic variations of electron-density occurring as we proceed along the particular direction in the crystal. This same factor determines the amplitude and phase of X-rays reflected by the particular spacing in the crystal in the conditions indicated by the Bragg formula.

The internal vibrations possible in a crystal are of two types. The first type is the acoustic spectrum of elastic waves which traverse the crystal in all directions and range in frequency from zero up to a certain limiting value; these figure in the Debye expression for the specific heat of the solid. The second type consists of the characteristic vibrations of the crystal giving rise to well-defined spectral lines in infra-red absorption or in the scattering of monochromatic light; these appear as Einstein functions in the expression for the specific heat. We are here particularly concerned with the nature of the internal disturbances in the crystal corresponding to the Einstein functions. It would be wrong to identify them with incoherent

vibrations of the individual atoms or molecules in the lattice. Indeed, in a perfect crystal, the correct way to picture them would be to regard them as a vibration of the inter-penetrating lattices forming the crystal as rigid wholes relatively to each other, so that the phase of such vibration is the same everywhere throughout the crystal.

Since the structure-amplitude corresponding to any particular spacing in the crystal depends on the positions of the atoms in the unit cell of the lattice, it is clear that a periodic vibration of the inter-penetrating lattices would cause a corresponding variation with time of each structure-amplitude. If, therefore, the crystal is traversed by a beam of monochromatic X-rays, the Bragg reflections (where these are possible) would also be affected by the periodic variation of structure-amplitude. Viewed in a classical way, this would mean that the intensity of the Bragg reflection, instead of being constant with time, would be modulated by the infra-red frequency. In other words, if the X-ray reflections could be analysed by a spectroscope of sufficiently high resolving power, we would find three components, one having the original frequency of the incident monochromatic X-radiation, and the other two, a frequency greater and less respectively than this frequency by that of the internal vibration in the crystal.

The foregoing classical view-point, though it serves to indicate the possibility of X-ray reflections with altered frequency, is fundamentally inadequate. As in the case of the scattering of light with change of frequency, it fails to tell us exactly what we do observe. For instance, in the classical theory, reflections with relatively large changes of frequency could not occur, as the corresponding lattice vibrations would not be thermally excited to any appreciable extent. On the principles of the quantum theory, however, the position would be different; the lattice-vibration, even when of high frequency and therefore not initially present, would be excited by the incidence of the X-ray itself. The intensity of the reflection with change of frequency would in fact depend on the change of structure-amplitude as indicated by the classical considerations, but the law of temperature variation would be altogether different.

The quantum view-point also indicates that we may expect to be able to observe the modified reflections independently of the unmodified ones, instead of merely accompanying them as is indicated by the classical considerations. To appreciate why this is the case, we have only to recall that the reflection of the usual type cannot occur if the spacing in the crystal, the angle of incidence and the wavelength of the incident monochromatic X-rays do not satisfy the Bragg formula. The modified X-ray reflections are, however, not determined by the fixed positions of the atoms in the crystal, but by their displacements from the same. By a suitable adjustment of the phases of these displacements, the planes of constant phase may be inclined at an angle to the crystal spacings in such manner as to satisfy the Bragg relation for the modified reflections. In other words, we would get a modified reflection from a given set of crystal planes even when an unmodified one is not possible with the given X-ray wavelength.

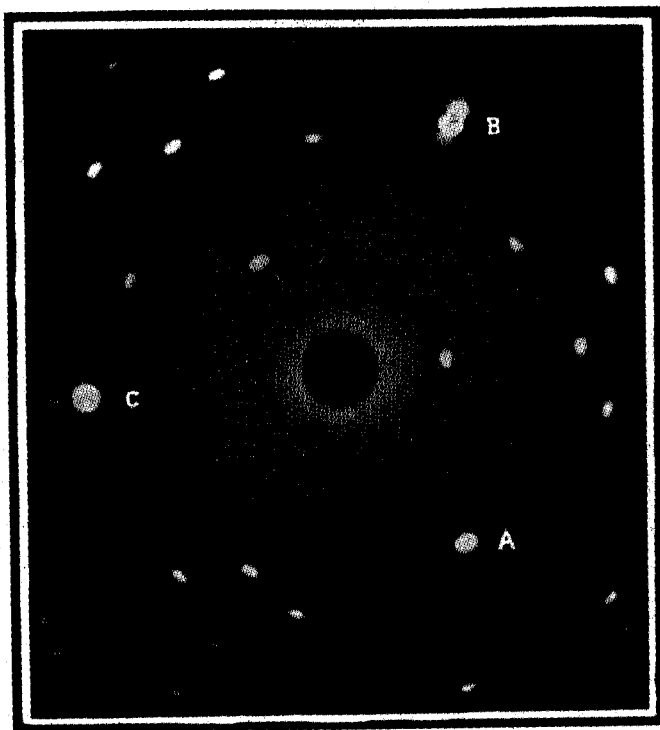


Figure 1. Laue pattern of diamond showing the new effect.

Modified X-ray reflections of the kind discussed above are to be seen in figure 1 which is a Laue photograph obtained with a crystal of diamond, the X-rays being from a tube with copper target excited at 41,000 volts. The crystal plate which had its faces parallel to one of the octahedral cleavages of diamond was so set that the incident X-ray beam was nearly normal to the crystal faces. The white radiation present gives the usual Laue spots, the pattern exhibiting approximate trigonal symmetry. The three most intense spots in the pattern (marked A, B, C in the figure) are the reflections from the $[111]$ planes parallel to the three other octahedral cleavages of the diamond. It will be noticed that these spots are accompanied by companions which lie on the radial lines joining them with the centre of the pattern, the positions and intensities of the companions being however different. Spot A has two faint companions lying outside. Spot B has also two companions lying one on either side of it, while spot C coincides with the inner one of its own companions. These companions are the modified reflections of the Cu K_α and Cu K_β radiations, and the spacing of the planes responsible for them is the same as that of the $[111]$ planes in the crystal, though of course, their inclination to the incident beam is different, as explained above. The striking

variation in the intensity of the spots is evident in the picture and is clearly related to their position relatively to the [111] Laue reflections. In fact, the intensity of the modified reflection is seen to fall off rapidly with the increasing inclination of the phase-waves to the [111] spacings.

The case of the diamond is of exceptional interest, both because of the fact that it approaches closely to an ideal crystal, and also because of the simplicity of its crystal structure which consists of two similar interpenetrating lattices. The frequency of the vibration of these two lattices relatively to each other is known from studies on light-scattering in diamond to have the high value of 1332 cm^{-1} in spectroscopic units or in absolute measure, 40×10^{12} per second. It will be seen on examining a crystal model of diamond that an oscillation of the two lattices relatively to each other would cause a large variation of the structure-amplitude of the crystal for the [111] spacings. The frequency of the vibration is so high that at the ordinary temperature its thermal excitation is negligible. The fact that the modified reflections are as intense as they are is thus explicable only on the quantum point of view.

In addition to the modified reflections, figure 1 shows other features of great interest, e.g., a diffuse halo falling off in intensity as the [111] reflections are approached and faint streamers stretching out obliquely from the modified reflections. Into the explanation of these features, we shall not here enter.