

X-rays and crystals*

SIR C V RAMAN

It is familiar knowledge that every crystal is a three-dimensionally periodic grouping in space of atomic nuclei and electrons held together by their mutual interactions so as to form a rigid solid. We recognise in each crystal a unit of its structure containing, say, a group of p atoms, this group repeating itself at regular intervals along three directions which are designated as the axes of the structure. The atoms in the crystal may accordingly be regarded as consisting of p sets, all the atoms of a particular set being equivalent to each other and located at regular intervals in a space lattice whose axes are those of the crystal.

2. Diffraction of X-rays by crystals

That the geometric picture of crystal architecture briefly indicated above is not just a mathematical hypothesis but a physical reality was first demonstrated by the famous experiment of Laue and his collaborators. When a narrow pencil of X-rays traverses a crystal and is received on a photographic film held behind it, a pattern of spots surrounding the impress of the incident beam appears on the film when developed. It is well recognised that these Laue spots—as they are called—represents monochromatised reflections of the incident X-ray beam by the stratifications of the electron density parallel to the various crystallographic planes in the structure of the crystal. The intensity of each spot is indicative of the magnitude of the corresponding periodic variations of electron density normal to the planes under consideration. The theory of the Laue experiment can be dealt with in a purely classical manner by attributing a certain scattering power to each volume element in the electron cloud present in the crystal proportional to its local density. This scattering power derives from the fact that the electrons would be set in motion and oscillate with the same frequency as that of the electromagnetic field which the incident X-ray beam represents. On this basis, the scattered radiations from all the volume elements would have the same frequency as the incident X-rays, as also specific phase relationships determined by their

*Presidential Address to the Indian Academy of Sciences at the Hyderabad Meeting on 27th December, 1955.

relative positions. The scattered radiations therefore would be capable of reinforcing each other's effects in certain specific directions determined by the wavelength of the X-rays and the spacing of the stratifications, in accordance with recognised optical principles. Concentrations of intensity accordingly appear in the directions representing a highly restricted selection of wavelengths from the incident white X-radiation.

3. Atomic nuclei and X-ray diffraction

The foregoing picture is obviously however an over-simplification. It implicitly assumes that the electrons which scatter the X-rays remain firmly bound to the structure of the crystal and that the latter also remains otherwise unaffected by the passage of the X-ray beam. The strength of the binding of the electrons to the atomic nucleus or nuclei closest to them necessarily enters into the picture and would influence the intensity and phase of the scattered radiations to an extent determined by the approach of the frequency of the incident X-radiation to the characteristic X-ray absorption frequencies of the electrons. Indeed, recent X-ray researches have shown that these factors have to be taken into account in the theory of X-ray diffraction by crystals.

The foregoing remarks indicate that considerations somewhat analogous to those which enter into the theory of scattering of light in crystals need to be taken into account also in the theory of X-ray diffraction. When a beam of common light traverses a crystal, its wavelength is very great in comparison with the spacing of the electronic stratifications in the crystal and the latter do not therefore reflect the incident radiation but merely transmit it. On the other hand, it is known that the passage of the light excites vibrations of the atomic nuclei with the result that if the incident light be monochromatic, scattered radiations are observed exhibiting sharply defined shifts of frequency corresponding to the characteristic vibration frequencies of the atomic nuclei about their positions of equilibrium. The appearance of such scattered radiations indicates the existence of a coupling between the forced vibrations of the electrons under the influence of the incident electro-magnetic field and the natural or free vibrations of the atomic nuclei about their positions of equilibrium. In the language of the quantum theory of dispersion, the appearance of such frequency shifts is described by the statement that the system composed of the nuclei and electrons does not—following the virtual transitions to higher energy states induced by the incident radiation—return to the same level as previously but shifts to a third level in which the atomic nuclei are in a different energy state of vibration.

In the X-ray experiment, the frequency of the incident radiation is usually much higher than the characteristic frequencies of the electrons. Nevertheless, the ideas of the quantum theory of dispersion continue to be applicable and the question therefore arises whether the incident X-radiations can also excite

transitions in the energy state of the atomic nuclei by virtue of their mechanical coupling with the electrons and if so, what would be the observable result of such transitions. We shall now proceed to answer these questions.

4. The characteristic vibrations of crystal lattices

As remarked earlier, the fundamental feature of crystal architecture is that it is a repetitive pattern in three-dimensional space of a characteristic unit of the structure containing a finite number of atoms. Each unit of the structure is similar to and similarly situated with respect to the units surrounding it. Hence it follows that in respect of all their physical properties the units of the crystal structure would be similar to each other; in particular the dynamic behaviour of all the units of the crystal structure would be completely identical. We may put the same situation in slightly different language by saying that every crystal is an assembly of atomic oscillators all of which have identical modes and frequencies of vibration. What these modes and frequencies are is a matter for rigorous mathematical investigation. Such investigations have been carried out and published in recent papers which have appeared in the *Proceedings* of the Indian Academy of Sciences. It emerges that all the atoms in the crystal have $(24p - 3)$ modes and frequencies of vibration in common. $(3p - 3)$ of these frequencies represent modes in which equivalent atoms in neighbouring cells oscillate with the same amplitudes and in identical phases, while for the remaining $21p$ frequencies, equivalent atoms in adjacent cells oscillate with the same amplitudes but with phases which may be the same or else opposite along one, two or all three axes of the lattice. This picture of the dynamical behaviour of the atoms in a crystal has important consequences for the subject of X-ray diffraction which we shall now proceed to consider.

5. A classical analogue

It is useful in the first instance to consider the position from a purely classical standpoint so that the consequences arising therefrom may be taken over into the quantum-mechanical treatment of the problem. We shall restrict ourselves here to a consideration of the $(3p - 3)$ modes of vibration of the atomic nuclei in which the vibrations in the different cells of the crystal lattice are identical in all respects. In such a vibration it would follow that the stratifications of electron density in the crystal would not remain in fixed positions but would oscillate to and fro with the frequency equal to that of the mode of vibration concerned. An X-ray beam traversing such stratifications would continue to be reflected in the same direction as in the static case. But in consequence of the periodic motion of the stratifications (assumed to be of small amplitude), the reflected X-ray beam would

now consist of three spectral components having frequencies respectively ν , $(\nu + \nu^*)$ and $(\nu - \nu^*)$, ν being the incident X-ray frequency and ν^* that of the oscillation of the lattice. The additional components arising by virtue of the oscillations may be regarded as Doppler shifts of frequency resulting from the movement of the stratifications normal to themselves. The amplitudes of the additional components would be determined by the ratio of the amplitude of the oscillations to the wavelength of the X-rays.

The above classical result translated into the language of quantum mechanics would mean that the incident X-radiation traversing the crystal may excite the characteristic vibrations of the lattice, and if such excitation actually occurs, the beam would be reflected in the same direction as in the absence of such excitation but with diminished frequency. If, on the other hand, the characteristic vibration is already present by reason of thermal agitation, the crystal may be de-excited and the incident X-radiation would then be reflected with increased frequency.

6. Infra-red activity and X-ray diffraction

It will be seen from the foregoing that the mechanism which can give rise to X-ray reflections of altered frequency is altogether different from the mechanism which results in the scattering of light with frequency shifts in crystals. In the latter case it is known that a change in the internuclear distances gives rise to a change in the optical polarisability of the elements of the structure and hence also to secondary radiations with altered frequency; the selection rules which determine whether a particular mode of vibration is or is not active in light-scattering are different from those which determine whether or not the same mode is active in infra-red absorption. In the X-ray problem, the shifts of frequency in the X-ray reflections arise from the periodic movements of the stratifications of the electron density associated with the nuclear oscillation. Hence, it may be expected that the excitation and the de-excitation of the lattice vibrations resulting from the passage of X-rays would appear in circumstances analogous to those in which infra-red absorption manifests itself. In other words, X-rays may be expected to excite or de-excite those oscillations of the lattice which are also infra-red active.

7. The geometry of the X-ray reflections

In the foregoing we have assumed that the vibrations in the crystal structure appear in all the cells of the crystal lattice not only with the same frequency but also with identical phases. This is evidently a highly idealised situation, which when it actually exists indicates that the X-ray reflection with altered frequency would appear in precisely the same direction as that of unmodified frequency. The modes and frequencies of the lattice vibrations are determined by the interatomic

forces which may be assumed to fall off rapidly in magnitude with increasing interatomic distances. Hence, a change of phase of the oscillations occurring progressively as we pass from cell to cell—provided it be small enough—would involve a relatively small change in the actual frequency of vibration. This would give rise to the possibility of observing X-ray reflections with a change of frequency even in settings of the crystal different from those in which the ordinary or unmodified reflections are observed. Such reflections may be regarded as arising from a forced oscillation of the lattice with slightly altered frequency and with the appropriate phases induced by the incidence of the X-radiation. In such circumstances the intensity of the X-ray reflection of altered frequency may be expected to fall off more or less rapidly as the setting of the crystal is altered from the setting needed for an ordinary reflection.

8. The influence of thermal agitation

As already indicated, it necessarily follows that if X-rays can excite an infra-red active oscillation of the lattice, they can de-excite such an oscillation if it already exists and thereby give rise to an X-ray reflection of increased frequency. The relative intensities of the X-ray reflections with increased and diminished frequencies respectively would be determined by the Boltzmann factor for the particular frequency of the oscillation of the lattice. The reflections of increased and of diminished frequencies would, of course, appear in the same direction, and it is the summation of their intensities that would determine the observed effects. Accordingly, measurements of the variations in intensity of this observable effect with temperature would enable us to estimate the frequency of the vibrations responsible for them.

9. Summary

The quantum theory of dispersion indicates that the infra-red active vibrations of the atoms in a crystal would be excited by the passage of a beam of X-rays through it. Such excitation would result in the incident beam being reflected by the lattice planes of the crystal with appropriately diminished frequency. Such reflections would also be observable but with diminished intensity when the setting of the crystal is moved away from the position in which X-rays of the given wavelength are selectively reflected by the lattice planes in question with unaltered frequency. The effect of thermal agitation is also considered.