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Crystals and photons*

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My first duty on this occasion is to express our gratitude to the authorities of the Andhra University for their generous sympathy and support to the work of the Academy and the opportunity they have afforded us of having our Annual Meeting in a truly academic atmosphere set amidst the beautiful scenery of Waltair. We appreciate very much the warmth of the welcome we have received. Our gathering here gives the Fellows of the Academy an opportunity of visiting the Andhra University at a time when many new developments are receiving attention, and of meeting men like Professor Bhagavantam, Professor Seshadri and Dr Nagendra Nath, whose research papers have filled the pages of the *Proceedings* of the Academy and whose work has shed lustre on the University. They have, like our many other Fellows in other parts of India, given ungrudgingly of their time and energy for the welfare of the Academy. Our special thanks are due to them and other local Fellows and to the Chairman and members of the Reception Committee for having worked to make this meeting a success.

In my Presidential Address last year at Bangalore, a long-term programme of research on the physics of crystals was outlined and put forward as likely to yield valuable results for our knowledge of the solid state. Looking over the *Proceedings* of the Academy for the last twelve months, I find that fourteen papers on crystal physics (listed at the end of this address) have appeared in it, of which three are from Waltair and the rest from Bangalore. We have no reason to be dissatisfied with the progress made so far, and indeed it may be claimed that some of these papers deal with the problems of the solid state from a quite novel standpoint and open up new pathways of investigation. I propose in this address to survey broadly the field of research dealt with in these papers which may be designated as the newer crystal optics based on the ideas of the quantum theory, to distinguish it from the older optics which considers the effects of passage of radiation through crystals on the wave-principles. The quantum optics links together the phenomena observed with infra-red radiation, visible light and X-rays in a remarkable way, and reveals the existence of a new type of X-ray reflection in crystals.

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As is well known, the behaviour of a crystal with respect to common light is intimately related with the geometric symmetry of the system to which it belongs. Rock-salt and diamond, for example, which are cubic crystals are isotropic or singly refracting; calcite and sodium nitrate which are rhombohedral crystals are doubly refracting but optically uniaxial; aragonite and barite which are orthorhombic are doubly refracting but optically biaxial. These characters of the respective crystals are determined by the optical polarisability of the substance in different directions. The polarisability may be geometrically represented by a surface which is a sphere for an isotropic crystal, a spheroid of revolution for a uniaxial crystal, and an ellipsoid with three unequal axes for a biaxial crystal. The polarisability is a bulk or molar property, which is intimately connected with the atomic architecture of the crystal, that is to say, by the properties of the atoms or ions or molecules composing the crystal, and by the manner in which they are spaced, orientated and linked together. The modern techniques for growing large crystals enable us to study and exhibit the very striking optical behaviour of many common substances. Sodium nitrate, for instance, can be grown into large crystals, and a block of it shows a birefringence which is even more obvious and striking than that of calcite. Still better is naphthalene which is a biaxial crystal and shows an extremely large birefringence. *The angles of internal and external conical refraction of naphthalene are about* 14°, *and are thus eight times larger than those of aragonite with which conical refraction is usually exhibited.* Needless to say, conical refraction as observed with a piece of naphthalene is far more striking than that exhibited by aragonite. As was shown by Bhagavantam in the very first paper he published as a research student, the strong birefringence of naphthalene is closely connected with the very great optical anisotropy of the molecules as well as the special orientation of the molecules in the crystal.

The classical optics of crystals prefers to ignore the atomic architecture of the solid and regards the substance as a continuum with specific molar properties. The crystal functions as a pathway for the passage of the radiation, taking part in its propagation but remaining essentially undisturbed in the process. Even when, as frequently happens, the radiation is partially absorbed by the crystal, this is fitted mathematically into the wave-picture by making the optical constants of the substance complex quantities instead of real numbers. Such a wave-picture is a satisfactory description of the phenomena which it is intended to cover. But it is not a complete descritpion of the facts. This was shown clearly by the studies on the scattering of light in crystals commenced by the writer in the year 1921 and culminating in the discovery of the effect of a change of frequency described in the lecture on "A New Radiation" in February 1928. The method of observation described in that lecture involves the use of monochromatic light and a spectroscope. To take a specific example, we allow the beam of light from a mercury arc lamp to pass through a crystal of diamond. Focussing an image of the illuminated diamond on the slit of a spectroscope, we observe in the light scattered in the substance of the diamond, new lines not present in the incident radiation. Corresponding to each monochromatic line in the incident radiation, there is a second and additional line, the wave-number of which is less by 1332 per centimetre than for the incident light. A third and much feebler line of which the wave-number *exceeds* that of the incident light by 1332 per centimetre is also weakly recorded in the spectrum. Numerous such studies of the scattering of light in crystals have been made since they were first described. It is abundantly clear from the observations that they cannot be explained on the basis of the ideas of the classical wave-theory alone. It is necessary to introduce the concept of the photon or a quantum of radiation, the energy of which is proportional to the frequency of the corresponding waves. The change of frequency as actually observed appears on the quantum theory as due to an exchange of energy between the photon and the crystal, a diminution of frequency if the photon is the donor and the crystal the acceptor, and an increase if the reverse is the case.

The investigation of light scattering in crystals is a powerful method for the study of the solid state. But it is beset by peculiar experimental difficulties. Theory indicates that a perfectly homogeneous crystal would scatter no light at all; the diffusion of light theoretically possible is that due to the vibrations of the crystal lattice excited by the incident light and occurs in every case with a change of frequency. Unfortunately, however, actual crystals are far from being perfect. Internal flaws and surface imperfections result in a strong scattering of light with unaltered frequency. Theoretically this should not trouble us at all, but practically it does trouble us very much. The difficulty arises from the fact that the incident light is not truly monochromatic and usually contains additional components and some continuous spectrum. If the crystal is not clear, or if the spectrograph gives appreciable coma or scattered light of its own, there is not much hope of getting useful results. Truly monochromatic light sources, clear crystals of sufficient size with polished faces, and spectrographs of high optical perfection and illuminating power are needed for such work. When these requirements are satisfied, results of great interest and value are forthcoming.

To appreciate the significance of the results obtained in such studies, we must remember that a crystal is not a mere geometric array of atoms, molecules or ions in space, but is a coherent structure of such particles having identical properties which are held together by powerful forces, thereby forming a rigid solid. It is inappropriate to consider the observed results in terms of the vibrations of the individual ions, atoms or molecules in a crystal. For, it is obviously not possible for any one particle in a crystal to vibrate without setting all the other particles in resonant vibration. To understand the optical behaviour of a crystal rightly, we must consider it as a whole and set ourselves to discover the various modes of vibration of which its structure is capable. These vibrations divide themselves into two classes. In the first class of vibration, we can ignore the atomic architecture of the crystal and regard it as an elastic solid traversed by acoustic waves. The frequency of such vibration may be anything from zero upwards to a value so high that the corresponding wavelength becomes comparable with the spacing of the atomic planes in the crystal. In the second class of vibration, we are dealing with movements which can only be understood or described in terms of the atomic architecture of the crystal. Such vibrations are referred to as the optical vibrations of the lattice. Some of these optical vibrations may have no counterpart at all for the substance in a fluid state and arise as a consequence of the crystal fields which bind the chemical units together into a rigid and ordered assemblage. Some of the optical vibrations, however, may have frequencies roughly corresponding to those characteristic of the ions or molecules in the fluid state. Even so, they cannot be identified with the vibrations of the individual chemical units. The optical vibrations—quite as much as the acoustic ones—are characteristic of the crystal structure and not of the individual particles present in the lattice cells.

The simplest way in which we may picture an optical vibration of a crystal lattice is to imagine the interpenetrating lattices of the simplest type present in the crystal, each carrying a single atom at the lattice points, to oscillate as rigid units relatively to each other, the centre of the inertia of the whole assembly remaining at rest. In such an oscillation, the crystal would throughout remain a homogeneous structure, but the relative positions of the atoms in its lattice cells would vary periodically with time. Such physical properties as the electric dipole moment, optical polarisabilities, and structure-amplitudes which determine the behaviour of radiation in various ranges of frequency in its passage through the crystal – would, therefore, also vary periodically with the frequency of the oscillation. It can be readily seen, however, that optical vibrations of the general description indicated would also be possible in which the phase of the oscillation changes slowly from place to place within the crystal. If this phase varies regularly in such manner as to repeat itself over a series of regularly spaced planes, the spacing of such planes is the phase wavelength of the optical vibation. An infinite phase-wavelength indicates a vibration identically the same throughout the crystal, and the optical frequency has then its limiting value.

The importance of the considerations set out above becomes clear when we consider the effect of radiations falling on a crystal. We may first refer to the case of a beam of infra-red radiation incident normally on the surface of a crystal. It is a well-known experimental fact that if the frequency of such radiation is within certain ranges characteristic of the particular substance, the radiations are powerfully reflected backwards by the crystal. This is the result of the optical vibrations of the crystal lattice being strongly excited by the incident waves. That such an excitation results in a directed reflection and not a diffuse scattering clearly indicates that the vibration of the crystal lattice is in the same phase at every point on the surface of the crystal. In the more general case of oblique incidence, in order that a regular geometric reflection may result, the excited lattice vibrations have necessarily to be coherent in phase, having everywhere the same relation to the phase of the resultant electric force due to the superposition of the incident and reflected waves. Since the waves necessarily penetrate to a certain depth, it follows that such coherence in phase must extend also into the interior of the crystal.

Passing on to the case of the scattering of light within a crystal, it is evident that an optical vibration of the crystal lattice cannot be excited by the incident light if the phase of such vibration is the same throughout the volume of the crystal. This is evident from the principle of interference, as the effects of all the secondary radiations, irrespective of their frequency, would completely cancel out. In fact, it is easy to show that a scattering of light with altered frequency within a crystal would only be possible if the lattice-vibrations have phase waves which are equally inclined to the incident and scattered waves and so spaced that the scattering is in effect a monochromatic reflection by an optically stratified medium. A very similar situation also arises when we consider the scattering of light as the result of the acoustic vibrations of the crystal lattice. The usual formula for a monochromatic reflection connects the wavelength of the incident radiation, the spacing of the optical stratifications and the glancing angle which is half the angle of scattering. This formula which follows from the classical wave-principles has its counterpart in the quantum theory, appearing as a consequence of the conservation of energy and momentum in the collision between the photon and the acoustic or optical disturbance in the crystal.

Having considered the cases of infra-red radiation, and of ordinary light, we naturally pass over to the X-ray optics of crystals. It is fairly obvious that, as in the case of ordinary light, an acoustic vibration of the lattice can only give rise to a diffuse scattering of the X-rays. The position is entirely different in regard to the optical vibrations of the crystal lattice. It follows from the very nature of an optical vibration that it does not involve any variation in the mean electronic density of a unit cell in the lattice, but can cause only periodic variations of the structure-amplitudes of the crystal. In other words, the effect of an optical vibration is to cause a variation having its own frequency in the reflecting power of the regular crystal spacings. We may put this a little differently by stating that the optical vibration creates dynamic stratifications of electron density, and that these can give regular X-ray reflections but with a change of frequency, in much the same way as the static planes give the classical reflections without change of frequency. The spacing and orientation of the dynamic stratifications are identical with those of the static spacings when the phase-wavelength is infinite. More generally, these quantities and, therefore, also the geometric law of the modified reflection, would depend on the wavelength of the phase-waves and the angles which they make with the crystal spacings and with the plane of incidence. The geometric law of quantum X-ray reflection for the most general case has been deduced by Raman and Nath in a paper published in the *Proceedings* of the Academy for November 1940, and takes a quite simple form. It will suffice here to remark that the theory shows that the reflection should appear in precisely specifiable directions. In other words, *the spacings of a crystal should give, in addition to the classical or unmodified reflections, quantum or modified reflections* *obeying a different geometric law.* It is no exaggeration to remark that this new result is of the greatest importance both to X-ray optics and to crystal physics. For the experimental proof of this thesis, it is necessary that sharply defined X-ray reflections of which the positions agree with those theoretically deduced should be found in association with every crystal plane of which the structure amplitude is sufficiently large and is strongly modulated by the possible vibrations of the lattice. That this is actually the case has been demonstrated in a series of communications published during the year by Raman and Nilakantan. A specially detailed investigation for the case of diamond is appearing shortly in the *Proceedings*, which brings out in a convincing way the physical reality of the phase-waves associated with the optical vibrations of the crystal lattice. The prediction made earlier in the year that the intensity of the modified reflections given by diamond should remain unaffected at liquid air temperatures has also been completely confirmed. *The quantum theoretical character of the new reflections has thus been completely established.*

Returning to the case of the scattering of ordinary light, it may be remarked that both the acoustic and optical vibrations of the crystal lattice reveal themselves in it. The vibrations of the latter class are usually subdivided into external and internal vibrations. Though this distinction is somewhat arbitrary, it is in many cases useful; and indeed, in relation to the crystal structure, the external vibrations, the frequency of which is determined by the crystal fields and are usually much lower, are even more important than the internal vibrations. The thermal behaviour of the external oscillations is particularly interesting. The very careful studies of the temperature effect which have been made by Nedungadi in the cases of sodium nitrate and of quartz have been very illuminating. Nedungadi's studies indicate that any transformation in crystalline form is usually *preceded* by notable changes in the magnitude and character of the low-frequency shifts. The changes observed in the case of α-quartz greatly assist in understanding the remarkable variations of physical properties which precede the α–β transformation of quartz.

The case of α-quartz has been very exhaustively investigated by Saksena with a view to identifying the various modes of optical vibrations appearing in the spectrum of the scattered light and correlating these with the known infra-red spectrum of α-quartz and with the specific heat of the crystal. The investigation must be considered to have been highly successful, as the theoretically predicted and experimentally observed behaviours show an almost complete agreement. The theoretical part of the investigation was based on an application of the methods of the group theory to the known structure of the crystal and the determination of its symmetry modes of vibration. The verification of the theoretical conclusions required an investigation of the spectra with the incident light polarised in different ways and with the crystal in different orientations, as also an analysis of the scattered light in each case. Such an investigation is naturally laborious and time-consuming, but the results in the case of quartz appear fully to have justified the trouble taken. It is very satisfactory to find from the work of Bhagavantam with calcite, and of Saksena with quartz, that the theoretical selection rules for the appearance and non-appearance of certain vibrations in the spectra are found to be obeyed. These selection rules may be deduced geometrically from the known form of the optical polarisability ellipsoid of the crystal and the character of the deformations it should undergo for vibrations of the different possible types of symmetry. The fact that the results deduced are in accord with the experimental results shows clearly that we are dealing with the vibrations of the crystal lattice and not of the individual chemical units in it, as remarked earlier in this address.

Summary

The excitation of the optical modes of vibration of a crystal lattice by radiations incident on the crystal is discussed. The optical vibrations can be described as oscillations of the interpenetrating lattices in the crystal with respect to one another. They give rise to a periodic variation of the physical constants, e.g., electric dipole-moment, optical polarisabilities, structure amplitudes, which influence the behaviour of radiation in various ranges of frequency in its passage through the crystal. The phenomena observed in the different ranges of frequency have a common feature, namely that the incident radiation excites the crystal vibrations of which the phases are everywhere in coherent relationship with the phase of the radiation field. The scattering of light or the reflection of X-rays with change of frequency appears as the result of the phase of the lattice vibrations varying from point to point in such manner that the crystal is, in effect, an optically stratified medium giving a monochromatic reflection of the incident rays at the appropriate angle of incidence determined by the spacing of the stratifications and the wavelength of the incident radiation. The description of the observed effects in the language of the wave-theory and in terms of the quantum hypothesis are complementary and do not in any way contradict each other.

The paper includes a review of 14 communications dealing with this field of research published during the year 1940 in the *Proceedings of the Indian Academy of Sciences.*

References

Proceedings of the Indian Academy of Sciences, Vols. XI and XII, 1940

Quantum reflection of X-rays

1. C V Raman and P Nilakantan, "Reflection of X-rays with change of frequency—Part I. Theoretical discussion."

2. C V Raman and P Nilakantan, "Reflection of X-rays with change of frequency—Part II. The case of diamond."
3. C V Raman and P Nilakantan, "Reflection of X-rays with change of frequency—Part III. The case of sodium nitrate."
4. C V Raman and N S Nagendra Nath, "Quantum theory of X-ray reflection and scattering."
5. C V Raman and P Nilakantan, "Reflection of X-rays with change of frequency—Part IV. Rock-salt."
6. S Bhagavantam and J Bhimasenachar, "Modified reflection of X-rays in crystals: calcite."
7. C V Raman and N S Nagendra Nath, "The two types of X-ray reflection in crystals."

See also Raman and Nilakantan, *Current Science*, April 1940 and *Nature*, April 27th, June 1st and October 19th, 1940.

Scattering of light: Infra-red specta

8. S Bhagavantam, "Effect of crystal orientation on the Raman spectrum of calcite."
9. T M K Nedungadi, "Effect of temperature on the Raman spectrum of quartz."
10. B D Saksena, "Raman effect and crystal symmetry."
11. T M K Nedungadi, "Raman effect in Rochelle salt crystals."
12. B D Saksena, "Analysis of the Raman and infra-red spectra of α-quartz."
13. K Venkateswarlu, "Raman spectrum of sulphur."
14. P Rama Pisharoty, "The Young's modulus of diamond."