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SIR C. V. RAMAN AND CRYSTAL PHYSICS*

OPTICAL theory and the physics of crystals are linked together almost inseparably in the history of their development. It is not surprising, therefore, that his love of optics has led Sir C. V. Raman to take an ever-increasing interest in crystal physics, as will be evident from the titles of the papers communicated by him to the Academy during the past decade or two. Many aspects of the subject have received his attention at some time or another. More recently, also, he has considered the fundamental problems of crystal physics from a standpoint which, while it is essentially novel, has proved highly successful in explaining the facts of observation. In these circumstances, it has appeared desirable to include in the present Symposium on Crystal Physics which commemorates his Sixtieth Birthday, a classified list of the papers on the subject which have emerged from his laboratories during the last thirty years. It is of particular interest to trace the development of his ideas and to indicate the fundamental character of the contributions made by him and his school. This will be done in the present survey.

Some of the most beautiful illustrations of optical principles are to be found in the phenomena of crystal optics. Haidinger's and Quetelet's rings in crystalline plates, the iridescence of twinned crystals of potassium chlorate, the optical effects observed with amethystine quartz, the diffraction of light by the lamellar boundaries in mica and the haloes observed in the Christiansen experiment with crystal powders are amongst the subjects of this kind investigated during the earliest years of Raman's professoriate by his pupils. The phenomena of conical refraction exhibited by biaxial crystals have also had a special fascination for him. Amongst the discoveries made in this field may be mentioned that of the formation of sharply focussed optical images by plane plates of biaxial crystals. That naphthalene crystals have an extremely large angle of conical refraction and exhibit the effects arising therefrom in a very striking way is another significant contribution. Many studies have also been published of the beautiful phenomena exhibited by the nacreous layer in molluscan shells and the manner in which they are influenced by the size, shape and relative orientation of the platelets of aragonite appearing in its stratifications.

2. THE SCATTERING OF LIGHT IN CRYSTALS

In the latter part of 1921, Raman commenced his studies on the diffusion of light in transparent media. These were systematically pursued over a period of years until finally they led to the discovery of the effect

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known by his name. The work of this epoch was of significance for crystal physics in several ways. The first major contribution which emerged at an early stage was the discovery of the phenomenon of the *thermal diffusion of light in crystals*. Raman was led to recognize its existence by the fact that the clearest crystals available to him, *viz.*, a polished sphere of quartz and a large transparent block of ice, both exhibited a blue opalescence when traversed by a concentrated beam of sunlight and that the intensities observed were of the right order of magnitude, both relatively and absolutely. Ice, which has a high compressibility, showed the phenomenon more conspicuously than quartz, in spite of the higher refractive index of the latter. The inference suggested by these facts, *viz.*, that the scattering had its origin in the fluctuations of optical density in the crystal due to the thermal agitation was confirmed by heating a quartz block. The intensity of the opalescence was then found to increase, as was to be expected.

Following these early observations, the work with crystals was laid aside and studies with gases and liquids were energetically pursued, as they offered a larger variety of promising material for quantitative work. In February 1928, Raman switched over from sunlight to the monochromatic radiations provided by the mercury arc for his studies on light scattering. When his pocket spectroscope revealed clearly the appearance of radiations of altered frequency in the light scattered by liquids, he instantly realised the importance of looking for a similar phenomenon in the light scattered by crystals as well as by amorphous solids. Observations with a large block of crystalline ice showed sharp displaced lines in approximately the same positions as those observed with distilled water. This fact and its theoretical significance are clearly brought out in the paper announcing the discovery of the effect. The magnitude of the frequency shifts observed with ice showed that the phenomenon was of a different nature from the thermal diffusion of light in crystals discovered in 1921, and was to be accounted for on the same basis as the corresponding effect observed with water, *viz.*, an exchange of energy between the incident light quanta and the vibrations of the structural units of the substance.

3. BIREFRINGENCE AND PLEOCHROISM IN CRYSTALS

Apart from the discovery of the Raman effect, the studies on the scattering of light in gases and liquids carried on during the years 1921 to 1927 opened up several other pathways of research. They threw a vivid light on the nature of the liquid state, showing clearly that it is far from being a random distribution in space of the molecules composing it. This led Raman to seek a confirmation of his ideas by undertaking with the aid of his collaborators a series of systematic studies on the X-ray diffraction haloes of liquids and glasses. The results obtained in these studies were found to be explicable on the same basis as the facts observed earlier in light-scattering. Of special significance to crystal physics were the deter-

minations of the optical anisotropy of the molecules or ions made possible by measurements of the intensity and depolarisation of light-scattering in fluids. A correlation became evident between the optical anisotropy of molecules in fluids and the birefringence exhibited by the same substances in the crystalline state. This indicated that the birefringence of crystals is determined principally by the optical anisotropy of the molecules or ions and by the manner in which they are orientated with respect to the crystal axes. Thus, from the known optical anisotropy and the observed features of the birefringence, it becomes possible to draw useful conclusions regarding the structure of the crystal. Indications of this kind were found to be particularly useful in cases where the optical anisotropy and the birefringence are both large, *e.g.*, organic crystals of the aromatic class.

The extensive data obtained regarding optical anisotropy also enabled some general conclusions to be drawn regarding the relation between this property and the chemical constitution of the molecule. It emerged that a large optical anisotropy is accompanied by the presence of absorption in the near ultra-violet or visible region of the spectrum. Further, in such cases, the crystals of the substance exhibit a marked pleochroism in which the axis of maximum absorption coincides with that of the largest optical polarisability, though there are some exceptions to this rule.

4. MAGNETIC ANISOTROPY OF CRYSTALS

Many papers on magnetism and magneto-optics figure in the published output of Raman's school. The early studies on light-scattering, remarkably enough, gave an impetus to work in this field. Magnetic birefringence in liquids owes its origin to the fact that while the magnetic field tends to orientate the molecules, their optical anisotropy results in double refraction. Thus, simultaneous studies on magnetic double refraction and on light-scattering in liquids enable the magnetic anisotropy of the molecules or ions to be evaluated and connected with the magnetic anisotropy of the solid crystal of the same substance. The known magnetic behaviour of the crystalline nitrates and carbonates was successfully explained by Raman and Krishnan in this way. The large magnetic anisotropy of the benzene ring deduced by them in the same fashion proved to be a fundamental discovery, since it led to the recognition of the still larger anisotropy of other aromatic molecules and opened the way to the interpretation of the magnetic behaviour of crystals of those substances. Indeed, magnetic studies were shown to be a powerful aid to crystal structure analysis by the early work of Bhagavantam with naphthalene and anthracene. So impressed was Raman by the importance of the method that he initiated studies on magnetic birefringence in many liquids in which it had not been previously observed. This work led to the discovery of the weak negative birefringence exhibited by water, the aliphatic hydrocarbons and other liquids. Crystals of substances exhibiting such negative magnetic birefringence show a relation

between their magnetic and optical behaviour quite different from that of crystals of substances, *e.g.*, the aromatic series, which show a positive magnetic birefringence in the liquid state.

5. RAMAN EFFECT STUDIES

Raman's discovery of 1928 opened up a vast new field of activity which was naturally taken up by his collaborators with enthusiasm, and many publications dealing with different aspects of the subject emerged from his laboratory. The effect exhibited by crystals was in the foreground of this activity from the beginning in view of its evident importance for an understanding of the theory of solids; indeed, during the last ten years, work with gases and liquids has been completely laid aside in favour of crystals which present both a challenge and an incentive to investigators in the field. They are a challenge since the difficulties of obtaining satisfactory material and of eliminating spurious effects due to parasitic illumination and instrumental defects are great. They are an incentive, since the sharpness of the Raman lines observed with crystals encourages employment of the most powerful instruments capable of revealing the maximum of detail and yielding data with the precision characteristic of spectroscopy. The major aim of the work in recent years has been that of elucidating the physical problems of the solid state, the substances chosen and the studies undertaken being both determined by this aim. Amongst the topics investigated are the following: the influence of temperature on the sharpness, position and intensity of the lines; the changes in the spectra accompanying thermal transitions in the crystal; the change from the solid to the liquid state; the identification of the modes of vibration active in light-scattering; the influence of crystal symmetry and structure on the spectra, and so forth. We cannot here describe either the techniques employed or the results obtained in these researches. It is necessary, however, to mention an important group of investigations designed to elucidate the fundamental problem of the nature of the vibration spectrum of a crystal. Taking for instance, the case of diamond, its Raman spectrum as ordinarily recorded is a single extremely sharp line with a frequency shift of 1332 cm.^{-1} . Obviously, this cannot represent the complete vibration spectrum and there should be other frequencies in it. The task of establishing their existence has been successfully accomplished by the present writer and the results are of very great interest. The results show in a perfectly unambiguous way that the vibration spectrum of diamond consists of a whole series of sharply defined discrete frequencies, of which only the highest is represented by the frequency shift of 1332 cm.^{-1} . The remaining frequencies do not appear in the first-order Raman spectrum ordinarily recorded. But with adequate exposures they appear as overtones and combinations in the so-called second-order Raman spectrum. The latter has also been successfully recorded with numerous crystals besides diamond.

6. THE THERMAL SCATTERING OF LIGHT

We return to the phenomenon discovered by Raman in 1921, namely the thermal diffusion of light in crystals. The thermal agitation which gives rise to it may be identified with stationary elastic vibrations of various modes and frequencies determined by the elastic constants and by the size and shape of the crystal. The diffusion itself would arise from the modulation of the optical wave-motion by the elastic vibrations and should therefore exhibit frequency shifts, while its strength would be determined by the photoelastic properties of the crystal. It would evidently not be easy to determine the distribution of intensity in the resulting spectrum unless, following L. Brillouin, we regard the crystal as of infinite extension. Whether this is always permissible is a question.

The frequency shifts to be expected theoretically are small and therefore not easily determined; lack of perfect monochromatism in the incident radiation and any Tyndall scattering present give rise to serious experimental difficulties. The subject is, nevertheless, of great interest and many studies have been published. Particular success has been achieved in the case of diamond which gives large frequency shifts not requiring interferometric aid for their observation. A perfect elimination of the Tyndall scattering is also possible by the use of the resonance radiation of mercury and a mercury vapour filter. An experimental result of great importance which has been established with this technique is that the elastic vibrations in a crystal are wholly incapable of giving rise to an observable diffusion of light, unless their "wave-lengths" are such as to give a regular Brillouin reflection. The behaviour of the elastic vibrations in the crystal is thus in complete contrast with that of the modes of vibration with discrete frequencies which readily record themselves in the second-order Raman spectrum even when they do not appear in the first order.

7. THE VIBRATION SPECTRA OF CRYSTALS

A fundamental question in the theory of the solid state is the nature of the vibration spectrum of a crystal. The new approach to the solution of this problem made by Raman is based on the idea that since we are concerned with the vibrations of a mechanical system, we have necessarily to consider its "normal modes". Further, the approach to the problem of finding these modes is necessarily different for the "elastic" vibrations in a continuum, and the "atomic" vibrations in a discrete structure. In the former case the vibrational modes and frequencies are determined by the external boundary conditions, while in the latter case, the time-periodic movements in the units of the structure are analogous to the vibrations of a polyatomic molecule and hence the external boundary conditions are wholly irrelevant. Following up this idea in a straightforward way, Raman derived his fundamental proposition that the structure of a crystal having

p atoms in each of the cells of its structure has $(24p-3)$ normal modes of vibration, and the same number of discrete frequencies of vibration unless this is reduced by reason of symmetry of the crystal and consequent degeneracy of the modes. This is a result of far-reaching importance which explains in a completely quantitative fashion the experimental results mentioned in the preceding two sections. In particular, the experimental fact that the 'elastic vibrations' of a crystal are wholly inactive in light-scattering (except in the case of a Brillouin reflection), while the structural vibrations are active in the second-order if they are not active in the first-order is a clear indication that they are different in their physical nature. The recognition of such a difference is, in fact, the starting point of the new theoretical approach.

8. THE STRUCTURE AND PROPERTIES OF DIAMOND

Diamond is a substance of extraordinary interest to the physicist engaged in the study of crystals, since it exhibits the characteristic properties of the solid state in an exceptional degree. For this reason the investigation of the physical behaviour of diamond has of recent years formed one of the principal activities of Raman's laboratory and many papers have been published describing the results.

The properties of diamond may be broadly divided into two groups. The first group comprises those that do not exhibit significant variations as between different specimens of diamond. This group includes density, hardness, elasticity, thermal expansion, specific heat, thermal conductivity, refractivity, dispersion, photoelasticity, dielectric constant, magnetic susceptibility, Faraday effect, Raman effect, and infra-red absorption of the second and higher orders. The second group of properties are those which exhibit variations, often of a most striking character, as between different diamonds. Amongst them may be listed infra-red absorption of the first order, absorption spectra in the visible and ultra-violet regions, fluorescence excited by visible and ultra-violet light and by X-rays, phosphorescence, photoconductivity, optical birefringence, intensity and sharpness of the Laue and Bragg X-ray reflections, and dynamic X-ray reflections. If the variations in the properties listed above had been unrelated to each other, the study of the diamond would indeed have been a very perplexing subject. Happily, this is not so, as has been shown by Raman and his collaborators by studies covering all the properties listed above with an extensive collection of material. The results present such striking correlations between the variations of the different properties as to leave no room for doubt that differences are systematic and arise from fundamental differences in crystal structure. This inference receives direct observational support from studies on the crystal morphology of diamond. The situation may be summed up broadly by the statement that the electronic structure of diamond may possess either tetrahedral or octahedral symmetry. Assuming each atom

of carbon to possess only tetrahedral symmetry, geometric consideration indicate that there must be two sub-species (positive and negative, respectively) of the tetrahedral type and two sub-species of the octahedral type. The recognition of the existence of these four species of the diamond structure, appearing separately or together in any actual specimen of diamond enables the varied behaviours actually met with to be satisfactorily described and interpreted.

9. LUMINESCENCE AND ABSORPTION SPECTRA

The luminescence of diamond, a long-known but neglected phenomenon, has been studied with great thoroughness by Raman and his collaborators with results of exceptional interest. Two distinct types of luminescence based on different electronic transitions are observed, and the same electronic transitions can also appear in absorption. They may be coupled with vibrational transitions in the crystal lattice and as the result, the principal emission or absorption in each case appears accompanied by subsidiary radiations of less and greater frequency respectively. The emission and absorption spectra exhibit mirror-image symmetry with respect to each other about the electronic frequency. The lattice frequencies deduced from the spectra agree with those given by the new crystal dynamics, which was in fact first developed to explain the effects observed in the luminescence spectrum of diamond.

The coupling of electronic with vibrational transitions so clearly manifested in the case of diamond is a general feature in the luminescence spectra of crystals. As a consequence, Raman effect studies are of great assistance in interpreting such spectra. As an illustration, one may cite the case of the fluorescence and absorption of the uranyl salts, as also the cases of alumina and of topaz investigated by the present writer. The lattice frequencies of magnesium oxide calculated on the basis of theory fit very well with those deduced from its luminescence spectra resulting from the presence of a trace of chromic oxide as impurity.

10. INFRA-RED ABSORPTION SPECTRA

All diamonds without exception exhibit an infra-red absorption spectrum of the second order, while the diamonds of the tetrahedral class exhibit also a first order absorption. These spectra have been thoroughly investigated and are explicable in all their details on the basis of the new lattice dynamics. Particularly interesting is the fact that the two weakest second-order Raman lines (2176 cm.^{-1} and 2015 cm.^{-1}) are represented in the second-order infra-red absorption by its two most conspicuous peaks, as is to be theoretically expected. A feature which manifests itself conspicuously in the first order infra-red absorption by diamond is that all the nine fundamental modes of vibration of the lattice are active, though in different degrees, and not merely the so-called principal oscillation having the highest frequency.

The absorption curves exhibit distinct peaks corresponding to the different modes, but their resolution is far from perfect. These features are explicable as due to the coupling of the different modes with each other due to anharmonicity. Such coupling would necessarily manifest itself even more strongly in the case of strongly infra-red active crystals and offers a basis for an explanation of the features exhibited by their absorption spectra.

11. THERMO-OPTIC PROPERTIES OF CRYSTALS

Studies of the effect of temperature on the optical properties of diamond have pointed the way to the development of a successful quantitative theory of the thermo-optic behaviour of crystals. The refractive index of diamond increases instead of diminishing with rise of temperature, this increase becoming more rapid as we approach the violet end of the spectrum. In consequence, the dispersion of diamond is enhanced by rise of temperature even more rapidly than its refractive index. The sharply defined electronic absorption lines in the visible and ultra-violet region exhibited by diamond at low temperatures are observed to drift towards lower frequencies when the temperature is raised. It may therefore be reasonably assumed that the characteristic frequency in the extreme ultra-violet principally responsible for the dispersion also shifts downwards with rise of temperature. Such a shift would result in an increase of dispersion and refraction which would only be partially set off by the diminution caused by the thermal expansion. Not only does this idea work successfully in the case of diamond, but it is found to be remarkably successful also in explaining the facts observed with numerous other crystals, both those which are isotropic, *e.g.*, the alkali halides and those which are birefringent, *viz.*, quartz, calcite and aragonite. The basis of the theory, namely the diminution of the characteristic frequencies in the remote ultra-violet with temperature, also finds direct observational support.

12. PHOTOELASTIC PROPERTIES OF CRYSTALS

One of the earliest attempts to develop a quantitative theory of the photoelastic behaviour of crystals was that made at Raman's suggestion in 1927 by Kedareshwar Banerji. The subject has acquired considerable importance in recent years by reason of its relationship to other phenomena, *viz.*, the optical effects arising from mechanical oscillations in a crystal and the thermal diffusion of light. The theory of the diffraction of light in ultrasonic fields originally put forward by Raman and Nath to explain the effects observed in liquids, applies *mutatis mutandis* to the case of a crystal when the relevant piezo-optic constants are introduced in the formulæ. The recent determination of the piezo-optic constants of diamond was, in fact, made with a view to work out the consequences of Brillouin's theory of the thermal scattering of light in it. Measurements with other crystals will no doubt prove of great value in this field of research.

13. MAGNETO-OPTIC BEHAVIOUR OF CRYSTALS

One of the many remarkable properties of diamond is the feebleness of the Faraday effect observed with it when considered in relation to its high dispersive power. The rotation of the plane of polarisation of light produced by a magnetic field is only one-fourth of that to be expected on the basis of the well-known Becquerel formula. The measurements which revealed this fact were made possible by the plates of diamond free from birefringence included in Raman's collection. The explanation for the low value is evidently to be found in the covalent character of the bonding of the atoms of carbon in the crystal with each other. The case of diamond thus clearly indicates that measurement of the "magneto-optic anomaly" exhibited by a crystal offers a method of ascertaining the nature of the electronic states in its atoms or ions. Studies with other crystals have since been pursued with this aim in view.

14. ELASTIC PROPERTIES OF CRYSTALS

Methods based on the use of piezo-electrically excited oscillations have opened out new possibilities for the accurate determination of the elastic constants of crystals. The recent work of Bhagavantam and his collaborators at Waltair may be specially mentioned in this connection. The problem naturally arises of seeking to connect these experimentally observed constants with the known crystal structure and if possible to derive them theoretically on the basis of that structure. The first step in any such attempt is evidently the evaluation of the interatomic forces arising from the displacements of the atoms from their positions of equilibrium. One way of finding these forces is to connect them with the frequencies of atomic vibration made accessible to observation by the Raman effect and from these frequencies as actually observed to evaluate the forces. A rigorous method of accomplishing this has been worked out in the case of various crystals. Difficulties arise in the next step, namely that of evaluating the elastic constants from the interatomic forces, but we shall not discuss them here.

15. THE THERMAL PROPERTIES OF CRYSTALS

The evaluation of the specific heat of a crystal requires a knowledge of its vibration spectrum. The proposition that this spectrum consists of $(24p-3)$ discrete frequencies places the theory of specific heats on a very simple and intelligible basis. Further, when these frequencies are accessible to direct spectroscopic observation, a comparison between the actual and calculated specific heats becomes possible. It may be remarked that the three excluded degrees of freedom represent the spectrum of elastic vibrations in the crystal. These appear at the very lowest end of the frequency range. Hence in most cases it is a sufficient approximation to regard them as fully excited at the temperature of observation and make the necessary addition to the specific

heat; a more exact calculation may, however, be necessary if p be small and if the temperature is very low. Calculations of the specific heat made in this manner for crystals for which the necessary spectroscopic data are available, e.g., diamond, show a satisfactory agreement with the facts.

Another property of a crystal which is intimately related to its vibration spectrum is its thermal expansion. Data regarding the thermal expansion coefficient of crystals are rather meagre. For example, no data were available for diamond above the room temperature. The present writer has developed a new precision method of measuring the coefficient of thermal expansion of crystals and applied it to the case of diamond which, as is well known, has a very small dilatation. Attempts to evaluate the thermal expansion of diamond and of other crystals theoretically on the basis of the spectroscopic data as in the case of their specific heats have given very encouraging results.

16. X-RAY STUDIES

The striking developments in X-ray physics which followed in the wake of Laue's great discovery of 1912 were already accomplished facts when Raman commenced his professoriate. Hence, neither X-ray spectroscopy nor crystal structure analysis was ever adopted by him as a part of his regular research programme. Nevertheless, these subjects have interested him greatly, as will be evident from the numerous X-ray studies published from time to time from his laboratory.

In April 1940, Raman and Nilakantan published in an article in *Current Science* under the title "A new X-ray effect", some strongly exposed Laue photographs obtained with an octahedral cleavage plate of diamond and the X-radiation from a copper target. These photographs showed some remarkable features which they explained as arising from dynamic reflections of the incident X-radiation by the (111) planes of the crystal. They gave reasons for believing that the crystal planes giving these reflections were set in vibration with the same frequency as that observed in the Raman spectrum of diamond and that the excitation was quantum-mechanical as in the case of the Raman effect. The reality of the effect is indisputable and on the basis of the explanation indicated, it is clearly of fundamental importance. Raman and Nilakantan subsequently published further experimental results which confirmed the correctness of the explanation given by them. We shall not here enter further into the subject except to remark that the explanation of this X-ray effect stands in the closest relation to the problem of the nature of the vibration spectrum of a crystal. The same question also enters fundamentally into the theory of the diffraction of X-rays by crystals and of the influence of temperature on the same.

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