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## THE PHYSICS OF THE DIAMOND

BY reason of its remarkable properties, diamond is a substance of extraordinary interest to the physicist interested in the study of solids. It exhibits in a characteristically striking fashion, many phenomena which are scarcely noticeable with other solids in ordinary circumstances. As an instance, we may recall the variation of specific heat with temperature. This was known as an experimental fact in the case of diamond for at least fifty years before it was recognised as a universal property of the solid state; the data for diamond published by Weber in 1875 formed the basis of Einstein's epoch-making paper of 1907 introducing the quantum theory of specific

heats. History has a way of repeating itself, and the study of diamond should therefore appeal strongly to the experimenter seeking new avenues of research and to the theorist seeking new and fruitful lines of physical thought concerning the solid state.

For the reasons stated, I have since the year 1930 been deeply interested in physical investigations on the diamond. The difficulty of obtaining the material in a form suitable for exact studies has, however, been a serious obstacle to progress. Indeed, in the early days, I was reduced to the expedient of borrowing diamond rings from wealthy friends who, though willing to oblige, were slightly apprehensive about

the fate of their property! More recently, these difficulties have diminished as the result of the discovery that flat plates of diamond of excellent quality are not very expensive and can be purchased in useful sizes from many jewellers in India. The collection of diamonds got together in this way has enabled studies with this crystal to figure prominently in the Bangalore researches on the solid state. Results of fundamental importance have been reached by spectroscopic investigations on light-scattering, on absorption in the visible and ultra-violet, on fluorescence and phosphorescence, and by X-ray studies on numerous diamonds. It is no exaggeration to say that the experimental facts revealed by these researches have opened up a completely new view of the physics of the crystalline state.

My knowledge of diamonds in their natural condition has improved and my personal collection of material for study has been notably enlarged, following a visit by me to the State of Panna in Central India where diamond-mining and diamond-working have been carried on since ancient times. I carried with me to Panna, a microscope, a strain-viewer, an ultra-violet lamp and a small quartz spectrograph. With the aid of this apparatus and with the kind cooperation of Mr. Balkrishna who is Director of Industries in the State, Mr. Nayar and myself were enabled to examine several hundred diamonds in their natural condition. We were also graciously permitted by His Highness the Maharaja of Panna to examine his famous garland of 52 large diamonds strung together in their natural state as crystals. The 25 uncut diamonds

I purchased and brought back to Bangalore form a representative collection chosen for their scientific interest. There is little doubt that their detailed examination will yield a rich harvest of results.

## 2. THE CRYSTAL FORMS OF DIAMOND

The reports on the diamond deposits in the Panna State published by E. W. Vredenburg (1906) and by K. P. Sinor (1930) include a good deal of information of interest to the physicist and crystallographer. Sinor has a whole chapter in his book, accompanied by drawing and illustrations, concerning the physical characters of the Panna diamonds. Personal observation, however, is necessary to enable one to appreciate the remarkable beauty of these diamonds in their natural condition. With their exquisitely perfect geometric form and their smooth lustrous surfaces, they look absolutely fresh from Nature's crucibles, though actually taken from sedimentary formations which according to the geologists, are a thousand million years old. The strongly-marked curvature of the crystal faces and smoothly rounded edges of the octahedral forms are a surprising feature of these crystals. It is clear, however, from the symmetry of shape, the smoothness of the faces and the fact that forms more complex than the octahedron are represented by sharp edges that the diamonds as we now see them are exactly in the same state as when they were first formed.

I wish to put forward tentatively a suggestion which seems to me to offer a reasonable interpretation of the facts stated above. If carbon liquefied under suitable

conditions of temperature and pressure when surrounded by molten silicious material, the form of the drops of the liquid diamond would be determined by the interfacial tension and would be spherical, provided the valence bonds between the atoms of carbon in the liquid were oriented completely at random. If, however, some measure of regularity in the orientation of the valence bonds could be assumed, the conditions within the liquid would roughly approximate to those in the solid crystal; in other words, *diamond in the molten state would be a liquid crystal*. The interfacial tension would then vary with direction and the surfaces of minimum energy would not be spherical, but would tend to show some resemblance to the forms exhibited by a cubic crystal. If the shapes assumed by diamond in the liquid crystalline state persisted on solidification or else suffered only minor changes, we would have an explanation of the forms now observed.

### 3. ACCIDENTAL BIREFRINGENCE IN DIAMOND

Mr. Sinor examined many of the Panna diamonds under the polarisation microscope and writes as follows:—“*Very clear crystals in which all the faces were symmetrically developed showed very little or no double refraction. Crystals full of flaws and inclusions and distorted crystals showed the colour bands very well.*” This important finding agreed with the observations made by Mr. Nayar and myself at Panna with numerous diamonds placed between the nicols of a simple strain-viewer. It has since been fully confirmed by careful observations under the polarising microscope made at Bangalore with the 25 Panna dia-

monds, the disturbing effects produced by their external surfaces being eliminated by immersion of the specimens in a highly refractive liquid.

The absence of birefringence in clear and symmetrically developed diamonds and its presence in defective and distorted diamonds are precisely what we should expect if a liquid crystalline condition of molten carbon preceded the formation of solid diamond. If the fluid material attained complete uniformity as well as mechanical and thermal equilibrium with its surroundings before solidification, a homogeneous crystal would have formed, while if it did not, the resulting solid would exhibit a lack of homogeneity with consequent development of internal stresses and strains manifesting themselves in an observable birefringence. On this view, the birefringence when observed is essentially a macroscopic effect which does not differ in its physical nature from the birefringence artificially produced by the imposition of external stress on a homogeneous crystal. This interpretation is supported by the fact that the restoration of light is most strongly marked in the vicinity of visible flaws and defects and that by cleaving off the defective parts, the rest of the material may be freed from strain, with the result that the birefringence in it disappears. I have in my collection a plate of diamond which was cleaved into two pieces: as the result of the cleavage, one part was freed from birefringence and is now perfectly dark between crossed nicols, while the other part continues to show a marked restoration of light. It is clear from all these facts that the belief entertained by some writers that a condition of

strain is an inherent characteristic of diamond is completely without foundation.

Examination of the specimens in my collection also shows the lack of foundation for the idea which has gained currency in the literature that diamonds whose transparency extends into the ultra-violet beyond 3000 Å are strain-free, while those which transmit radiations only up to 3000 Å are subject to strains. Actually, I have several specimens of the less transparent variety which appear quite dark between crossed nicols, while the four plates of the more transparent kind in my possession all exhibit an intense restoration of light when viewed under the polarising microscope.

#### 4. THE SCATTERING OF LIGHT IN DIAMOND

Beliefs in arbitrary or artificial hypotheses, however plausible they may appear, is contrary to the spirit of science which should rely rather on well-ascertained facts of observation as the foundation of its activities. Galileo when he made his famous experiment of dropping weights from the leaning tower of Pisa, showed the way to deal with all such *ad hoc* beliefs, namely, to confront them with the results of a direct experimental test. Diamond which is the prince of crystalline solids gives us the means of making such tests of the assumptions on which Debye's theory of specific heat and the so-called lattice theory of Born are based.

The spectroscopic examination of the light scattered by a crystal when it is traversed by a beam of monochromatic radiation is perhaps the simplest of the experimental methods available for investigating

the possible modes of atomic vibration in a crystal. Diamond is readily examined in this way and yields very interesting results. Even with tiny diamonds, the spectroscopist records a remarkably intense and perfectly sharp line displaced from its parent radiation by 1332.1 wave-numbers at room temperature. Bhagavantam (1930) has shown that this line is many times more intense than the sharp bright line with a displacement of 992 wave-numbers observed with benzene which arises from the symmetric vibrations of the carbon ring. Using an exceptionally fine and clear diamond 20 carats in weight, he also recorded several other comparatively faint lines, their wave-number shifts being 1158, 1288, 1382, 1431, 1480, and 1585. More recently, Nayar (1941) has studied the scattering of light in diamond over a wide range of temperature and finds that the principal line remains sensibly sharp over the whole range from 83° T to 1130° T; its frequency-shift, however, falls from 1333.8 at the lowest to 1316.4 at the highest temperature of observation.

The appearance of no less than seven discrete frequencies as sharp lines in the spectrum of such a simple crystal as diamond is not easy to reconcile with the ideas underlying the Debye and Born theories of the solid state. If we lay aside the preconceived notions underlying these theories, the plain reading of the experimental facts is that the infra-red vibration spectrum of diamond is essentially similar to that of a polyatomic molecule and consists of discrete monochromatic lines. The experiments do not offer any *prima facie* support for the assumption inherent in the theories of

Debye and Born that the lattice spectrum is a continuous one.

### 5. THE BLUE FLUORESCENCE OF DIAMOND

The experimental situation becomes even clearer in the light of the facts revealed by the recent studies of Nayar (1942) of the blue fluorescence spectrum of diamond and of the corresponding absorption spectrum observed with the crystal held at liquid air temperature. Both in fluorescence and in absorption, diamond when so cooled down exhibits a close doublet centred at  $4152 \text{ \AA}$  in the spectrum, the same appearing bright in fluorescence and dark in absorption. Spreading out towards lower frequencies in fluorescence and towards higher frequencies in absorption, appears depicted the lattice spectrum of diamond; this is located with perfect mirror-image symmetry of frequency respectively on the two sides of the  $4152$  doublet. Even at liquid air temperature, the width of the  $4152$  band is sufficiently small to enable the details of the lattice spectrum to be seen clearly resolved. No fewer than 19 discrete frequencies can be made out, the values derived from the fluorescence and absorption spectra being in complete agreement. These frequencies range from 1387 wave-numbers down to 178 wave-numbers, and include (within the limits of experimental error) those found by Bhagavantam from his studies on light-scattering in the same region.

Three distinct methods of spectroscopic study, namely, scattering, fluorescence, and absorption, thus agree in indicating that the lattice spectrum of diamond is essentially similar to that of a polyatomic molecule, consisting of a series of discrete mono-

chromatic frequencies. The experimental facts are evidently irreconcilable with the

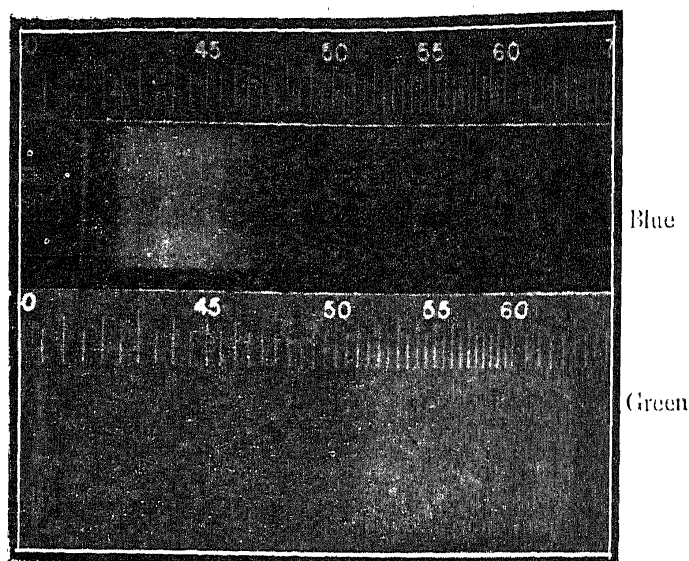


FIG. 1

Blue and green fluorescence spectra

basic ideas of the Debye and the Born theories of the solid state according to which the diamond lattice should have a continuous spectrum of frequencies.

### 6. X-RAY REFLECTIONS OF THE SECOND KIND

The spectroscopic evidence showing that the vibration spectrum of diamond consists of discrete monochromatic frequencies has very important consequences for the X-ray physics. Since diamond has a rigid structure which is a three-dimensional repeating pattern in space, each of the possible vibrations of this structure must be assumed to occur in the same way in all the volume elements chosen as the units of the space-pattern, since otherwise we would have an infinite number of possible frequencies, instead of a finite number of discrete vibrations as actually observed. In other words, a diamond in which the atoms oscillate with any one of its infra-red frequencies continues to be a three-

dimensionally periodic structure in space. Thus, for the same reason which enables the crystal planes of the static crystal to give the well-known Laue and Bragg reflections of unaltered frequency, the crystal planes of the vibrating crystal should also give dynamic reflections with altered frequency.

It has been shown by Dr. Nilakantan and myself that the (111) crystal planes in diamond do exhibit dynamic X-ray reflections of the kind indicated above and that their characters as actually observed in experiment, namely, their perfectly specular sharpness, the geometric law which they follow and their practical independence of temperature, can only be understood if they are associated with the high-frequency infra-red vibrations of the crystal structure in the manner suggested. Indeed, exact experimental studies have confirmed this view of their origin in a most remarkable and complete fashion. In particular, it may be remarked that the theory indicates that corresponding to the principal or 1332 vibration of the diamond lattice, the (111) planes should give *three* quantum reflections and not one, the geometric position of these varying with the setting of the crystal, being strictly calculable when it is known. The beautiful confirmation of this prediction furnished by the experiments is illustrated in the accompanying Laue diagram obtained by R. V. Subramanian, where the three quantum-reflections appear as sharply defined lines in displaced positions on one side of the usual Laue reflection.

An important feature of the new X-ray reflections observed with diamond is that

the crystal-spacing associated with such reflections, if calculated on the basis of the

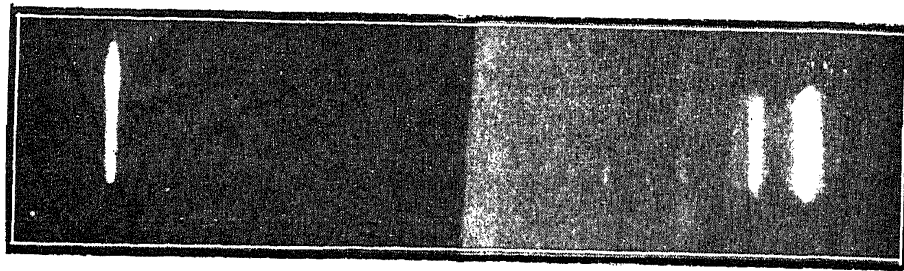


FIG. 2

The triple quantum X-ray reflections

ordinary Bragg formula, is not constant but varies rapidly with the setting of the crystal. It is also a function of the wave-length of the X-rays employed. Further, the orientation and azimuth of the plane in which the reflections are observed are also dependent on the setting of the crystal and the wave-length of the X-rays. These facts and especially the existence of three simultaneous reflections in geometric relation to each other are in complete accord with the dynamic view of their origin. It is evident, on the other hand, that attempts to explain away these phenomena by *ad hoc* assumptions, e.g., an arbitrarily postulated inherent static "strain" in diamond are wholly inadmissible and indeed quite meaningless. It should be emphasised also that the perfect sharpness at all settings of the crystal exhibited by these reflections excludes any attempt to explain them as due to the disturbance of the crystal lattice by vibrations of the kind assumed in the Debye and Born theories of the solid state.

#### 7. THE LATTICE SPECTRUM OF DIAMOND

The spectroscopic and X-ray results obtained with diamond and briefly summarised above thus compel us to reject the Debye and Born theories as incompatible with the facts. We may summarise the experimental

situation by stating that the possible vibrations of the crystal lattice of the diamond are spectroscopically similar to those of a polyatomic molecule, while geometrically they must be considered as repeating themselves in space with three-dimensional periodicity. A simple way of reconciling these results is to regard the entire crystal as an aggregate of interpenetrating space-lattices of a very simple kind, and to assume that these lattices oscillate as rigid wholes relatively to each other, while their common centre of gravity remains at rest. Such an oscillation would cause the structure of the crystal to vary with time periodically, while retaining its perfect three-dimensional periodicity in space. This picture is, however, only an idealisation, since the X-ray results show that a slow variation of phase of the lattice oscillation at different parts of the crystal is permissible.

The crystal structure of diamond is well-known, and the various possible normal modes of vibration of the lattice which can arise in this way can therefore be theoretically ascertained. Their frequencies can also be calculated in terms of the force resisting the movements of the carbon atoms, namely, those involved in an alteration of the length of the valence bonds and those resisting a change of the angles between them. The lattice spectrum of diamond can thus be theoretically worked out and compared with the experimental data. In particular, it becomes clear that the vibration having a frequency of 1332 wave-numbers is that in which the adjacent planes of carbon atoms parallel to the (111) faces of diamond alternately approach and recede from each other. It is readily understood

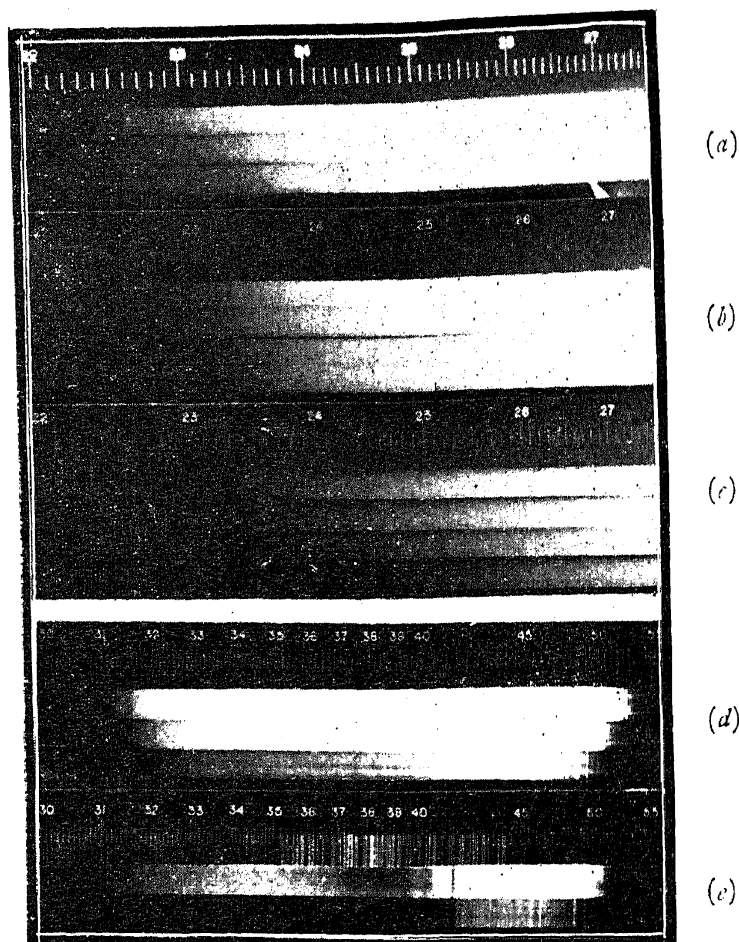


FIG. 3

The absorption spectra of different diamonds

why such an oscillation results in an intense reflection of the X-rays with altered frequency by those planes. Other lattice frequencies observed in the fluorescence spectrum may be similarly identified as various types of oscillations relative to each other of the atomic planes parallel or perpendicular to important faces of the diamond, *e.g.*, the cube, the octahedron and the dodecahedron. A complete account of the X-ray phenomena exhibited by diamond would include a detailed consideration of the effects of each of these possible modes of oscillation on the lattice planes capable of giving sufficiently strong X-ray reflections.

## 8. THE ABSORPTION SPECTRUM OF DIAMOND

It has already been mentioned that the blue fluorescence of diamond is associated

with a corresponding absorption in the violet and near ultra-violet regions of the spectrum. The intensity of this fluorescence and of the corresponding absorption varies enormously from diamond to diamond, though their spectral characters remain otherwise sensibly the same. For instance, in a small octahedral diamond in my possession, the 4152 band is only recorded after extremely prolonged exposures. The fluorescence, when present, is accompanied by phosphorescence in the green, yellow and red regions of the spectrum. Several of the Panna diamonds in my collection, on the other hand, show an intense fluorescence in the green, yellow and red regions, the blue fluorescence though present being weak in comparison. There are other diamonds again which show both the blue and green fluorescence in roughly comparable intensities.

These remarkable variations in the luminescence properties of diamond appear to bear a relation, not yet fully elucidated, to the equally obvious variations in the transparency of diamonds in the visible and ultra-violet regions of the spectrum. So far as transparency in the ultra-violet is concerned, Mr. Nayar's studies show that at least *three* distinct kinds of variation should be recognised, as they are accompanied by clearly recognisable features in the absorption spectra. *The first and most transparent kind of diamond* has a sharp cut-off at about 2250 A.U. in the ultra-violet. *The second type* has a clearly marked absorption band at about 2370 A.U. followed by a very feeble transmission at shorter wave-lengths. *The third type* has a cut-off at

about 3000 A.U., accompanied by subsidiary absorption bands at longer wave-lengths. The majority of diamonds appear to belong to the third type, a characteristic of which is the emission of the blue fluorescence with greater or less intensity. It is noteworthy also that some diamonds exhibit simultaneously more than one or even all the three types of spectroscopic behaviour. A continuous transition between the three types of behaviour is thus shown to be possible. The ultra-violet absorption of the third or ordinary type has been pretty fully investigated by Nayar. No fewer than some 25 sharply defined electronic absorption frequencies have been recorded by him between 3000 A.U. and 3600 A.U. at liquid air temperatures.

## 9. CONCLUDING REMARKS

It will be obvious from what has been stated above that the investigation of the physics of the diamond is full of promise for the future. I have made no reference in this article to further results of great interest which have been obtained but which could not appropriately find a place in a general account of the subject. I may, however, briefly mention the progress which has been made in the study of the relations between the spectroscopic behaviour of different specimens of diamond and the X-ray phenomena exhibited by the same specimens. It is sufficient here to remark that the results obtained in this connection do not in any way contradict the broad results stated above, but on the other hand afford them the fullest support.

C. V. RAMAN.