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SYMPOSIUM OF PAPERS

ON

THE STRUCTURE AND PROPERTIES

OF

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CONTENTS

THE CRYSTAL SYMMETRY AND STRUCTURE OF DIAMOND

By Sir C. V. Raman

(From the Department of Physics, Indian Institute of Science, Bangalore)

Received April 17, 1944

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1. The Crystal Symmetry of Diamond

Diamond was assigned by the earlier crystallographers (*vide* Groth, 1895; Liebisch, 1896; Hintze, 1904) to the ditesseral polar or tetrahedrite class of the cubic system. The assignment was based on the fact that though diamond commonly exhibits octahedral symmetry of form, specimens showing only the lower tetrahedral symmetry were forthcoming, and it was therefore natural to suppose that the higher symmetry when observed was the result of a supplementary twinning of the positive and negative tetrahedral forms. In particular, the appearance of octahedral forms with grooved or re-entrant edges could be explained in this way. We may here quote from the first edition of Miers' *Mineralogy* (1902) where the forms of diamond are discussed at considerable length: "Much controversy has taken place upon the question whether the diamond is really octahedral as it appears or tetrahedral as is suggested by the grooves; the problem may now be regarded as decided in favour of the tetrahedrite class by the following two facts: (1) several crystals have been found which are undoubtedly simple crystals of tetrahedral habit..... (2) the supplementary twinning of such crystals sufficiently explains all the other peculiarities of form." Sutton (1928) who has written a treatise on the South African diamonds gives illustrations of crystals having the forms of hexakis-tetrahedra, truncated tetrahedra, duplex-tetrahedra and others which are entirely typical of ditesseral polar symmetry.

Van der Veen (1908) noticed that diamond does not exhibit any pyro-electric properties and expressed the view that this is irreconcilable with the assignment of tetrahedral symmetry. The results of the X-ray analysis of the crystal structure of diamond by W. H. Bragg and W. L. Bragg (1913) have also usually been regarded as demonstrating that diamond possesses holohedral symmetry (Tutton, 1922; W. L. Bragg, 1937). These contentions are, however, open to question. It may, in the first place, be pointed out that the evidence of the crystal forms on which the earlier assignment was based cannot be lightly brushed aside. Secondly, it is very significant that the X-ray data show the structure of diamond to be analogous to that of zinc blende which is a typical crystal of the tetrahedrite class, and this is a hint that the crystal symmetry of diamond might also be of the same class. It is thus evident that the matter deserves more careful consideration than it appears to have received so far. It is the purpose of the present paper critically to examine the question whether the crystal symmetry of diamond is octahedral or only tetrahedral. The investigation reveals that there are several alternative possibilities and thereby furnishes the key to an understanding of many remarkable and hitherto imperfectly understood facts regarding the diamond and its physical properties.

2. *The Four Possible Structures of Diamond*

We shall accept the X-ray finding that the structure of diamond consists of two interpenetrating face-centred cubic lattices of carbon atoms which are displaced with respect to one another along a trigonal axis by one-fourth the length of the cube-diagonal. Each carbon atom in the structure has its nucleus located at a point at which four trigonal axes intersect. Hence, we are obliged to assume that the electronic configuration of the atoms possesses tetrahedral symmetry. It must also be such that the alternate layers of carbon atoms parallel to the cubic faces have the same electron density. This is shown by the X-ray finding that the crystal spacings parallel to the cubic planes are halved. Hence, the possibility that the two sets of carbon atoms carry different total charges is excluded. In other words, diamond is not an electrically polar crystal in the ordinary sense of the term. It is readily shown, however, that the charge distributions may satisfy both of these restrictions and yet not exhibit a centre of symmetry at the points midway between neighbouring carbon atoms. To show this, we remark that when two similar structures having tetrahedral symmetry interpenetrate, centres of symmetry would not be present at the midpoints between the representative atoms unless the tetrahedral axes of the two structures point in opposite directions. We may, in fact, have *four* possible kinds of arrangement as indicated in Fig. 1. Of these the arrangements

shown in Td I and Td II have tetrahedral symmetry, while Oh I and Oh II would be distinct forms, both having octahedral symmetry.

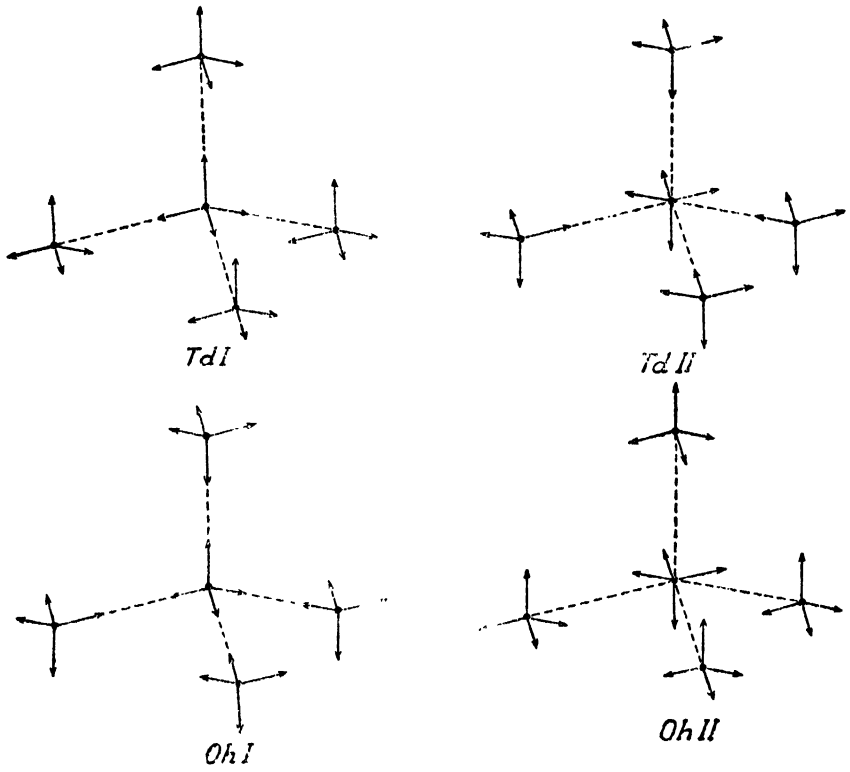

FIG. 1. The Four Possible Structures of Diamond

The tetrahedral symmetry of the atoms required by virtue of the special positions which they occupy in the crystal lattice must be satisfied both by the electrostatic distributions of charge and by the orientations of the orbital and spin moments of the electrons. When the structure as a whole is considered, the magnetic moments should be fully compensated, since the crystal is diamagnetic. But such compensation may be secured in several distinct ways which would endow the structure with different symmetry properties. On the one hand, four equal magnetic moments directed either all inwards or all outwards along the four tetrahedral axes of a cubic crystal would automatically cancel each other. On the other hand, if the pair of electrons which bind neighbouring atoms have opposite magnetic moments (directed inwards or outwards as the case may be), these would directly cancel each other. Considering these two pairs of possibilities, we have four different ways in which the extinction of the resultant magnetic moment

may be secured. It is seen that these correspond to the four possible structures of diamond indicated in Fig. 1.

It is readily shown that if the charge distributions which differ in their angular setting as shown in Fig. 1 are otherwise identical, the electron density in the alternate layers of atoms parallel to the cubic planes would be the same. This follows immediately from the fact that these planes are equally inclined to the tetrahedral axes. Hence, all the arrangements shown in Fig. 1 would be consistent with the observed halving of the spacing of these planes. Hence, the X-ray findings leave the question whether diamond possesses tetrahedral or octahedral symmetry entirely open.

The expectation that diamond would have pyro- or piezo-electric properties would only be justified if the neighbouring carbon atoms carry different electric charges. Since this is not the case, the absence of such properties cannot be regarded as a contradiction of the views of the earlier crystallographers regarding the symmetry class to which diamond belongs.

3. Confirmation of the Theory by Infra-Red Spectroscopy

Placzek (1934) has discussed the relation between the symmetry class of crystallographic groups and their activity in infra-red absorption, as also in the scattering of light with change of frequency. He has shown that for the groups which contain a symmetry centre, the selection rules for infra-red absorption and for light-scattering are complementary, *viz.*, the modes of vibration which can appear in light-scattering are forbidden in infra-red absorption, and *vice versa*. For those groups which do *not* have a centre of symmetry, there is a possibility that the same vibrations may appear both in the scattering of light and in infra-red absorption. The simplest illustration of these principles is furnished by the case of a diatomic molecule, its vibrations being active in light-scattering and inactive for infra-red absorption provided the atoms are similar, and active in both if they are dissimilar. Placzek's rules successfully explain the experimentally observed behaviour of many crystals in light-scattering and in infra-red absorption. Taking, for instance, the case of rock-salt which has holohedral symmetry, its fundamental frequency is that of the triply degenerate oscillation of the sodium and chlorine lattices with respect to each other. This is observed to be active in infra-red absorption and inactive in light-scattering, in accordance with the behaviour indicated by the selection rules.

The infra-red absorption of diamond was studied by Angstrom (1892), Julius (1893) and by Reinkober (1911), and has been investigated with especial thoroughness by Robertson, Fox and Martin (1934). From these studies, and especially from the work of the last mentioned investigators,

the remarkable fact emerges that diamonds are not all identical in respect of their behaviour in infra-red absorption. In the majority of diamonds the infra-red absorption coefficient rises very steeply from a comparatively moderate value to a maximum of about 90% in the wave-number range 1350–1300 cm.$^{-1}$ This steep rise in absorption as well as the entire band of which it is the head are, however, wholly absent in other diamonds which evidently form a second and rarer variety.

The significance of these facts becomes clearer when it is remarked that the fundamental frequency of the diamond structure is that of the triply-degenerate oscillation of the two lattices of carbon atoms with respect to each other, and that this falls precisely within the range of wave-numbers where the sudden rise of infra-red absorption occurs in the common variety of diamond. This is proved by the appearance of an intense line with a frequency-shift of 1332 cm.$^{-1}$ in the spectrum of the scattering of monochromatic light by diamond; the wave-number of the fundamental vibration of the diamond structure calculated from its specific heat data is also 1332 cm.$^{-1}$ (Ramaswamy, 1930). The investigations of Robertson and Fox (1930) have shown that both the commoner variety of diamond which exhibits the infra-red absorption in this region of frequency and the rarer variety in which it is missing, alike exhibit the strong line with a frequency shift of 1332 cm.$^{-1}$ in the spectra of the scattering of light.

Placzek's selection rules (*loc. cit.*) for the point-groups of the cubic system show that a triply-degenerate vibration in a crystal having octahedral symmetry can manifest itself *only* in infra-red absorption *or* in light-scattering *but not in both.* On the other hand, in a crystal with tetrahedral symmetry, such a vibration must appear *both* in absorption and light-scattering or else can appear in *neither.* Taking these selection rules in conjunction with the experimental facts, it follows at once that the commoner variety of diamond has only tetrahedral symmetry, while the rarer variety of diamond has octahedral symmetry. *The views of the earlier crystallographers assigning only the lower symmetry are thus completely vindicated by the infra-red absorption data and the selection rules so far as the commoner variety of diamond is concerned. The rarer variety of diamond must however be credited with the full or holohedral symmetry of the cubic system.*

Infra-red spectroscopy thus compels us to recognize the existence of two forms of diamond, a commoner form having only tetrahedral symmetry of structure, and a rarer form having octahedral symmetry. We have now to consider the further implications of the theory which indicates that each of these forms has two variants, namely those whose symmetry characters

are indicated in Fig. 1 as Td I and Td II respectively for the tetrahedral type of diamond, and as Oh I and Oh II respectively for the octahedral type. The question arises whether there is any physical evidence for the existence of these four types of diamond and in what manner, if any, it is possible to differentiate between them. In this connection, it is worthy of note that both the tetrahedral and octahedral types of diamond, as we may now designate them, exhibit the same frequency shift (1332 cm.$^{-1}$) in the scattering of light within the limits of observational error. This indicates that the forces which hold the carbon atoms together in the two kinds of diamond do not differ sensibly, despite the difference in the symmetry of their structures. Accepting this as an experimental fact, it follows that in respect of the energy of formation and the lattice spacings in the crystal, and therefore also all the commoner physical properties, such as density, elasticity, specific heat, refractivity, dielectric constant, diamagnetic susceptibility, etc., any differences which may exist between the four types of diamond must be small. It is very remarkable that though the symmetry of the electronic configuration is not the same in the two types of diamond, the strength of binding between the carbon atoms is not sensibly different. *Prima facie*, this result indicates that the electrostatic distributions of charge are the same. We are therefore led to assume that the differences which exist lie essentially in the orientations of the orbital and spin moments of the electrons, as already indicated.

4. *Interpenetration of Positive and Negative Tetrahedral Structures*

As the commoner type of diamond has only tetrahedral symmetry, crystallographic considerations compel us to admit the existence of two variants of the tetrahedral type, namely the positive and negative structures indicated by Td I and Td II respectively in Fig. 1. It is evident that these two sub-classes would be completely identical in respect of energy of formation and lattice spacing, and consequently also in respect of density, refractive index and such other physical properties. The question then arises how we can distinguish between them.

It is possible, of course, for diamond having the positive or negative tetrahedral structure to have an external form with octahedral symmetry. For, both positive and negative tetrahedral faces may appear in the same diamond—as they actually do in zinc-blende—and it is quite possible that they are equally well developed with nothing whatever to distinguish one from the other. The comparative infrequency of crystals having a simple tetrahedral habit would, however, be easier to understand on the basis of the supplementary twinning of the positive and negative tetrahedral forms.

That such twinning is possible and indeed common finds support in the various peculiarities of form (*e.g.*, the grooving of the octahedral edges) observed in actual specimens. Further, the identity of the physical properties of the positive and negative tetrahedral structures makes the assumed interpenetration highly probable on theoretical grounds. We are therefore justified in assuming that such interpenetration twinning is a phenomenon of very general occurrence.

It is well known that when interpenetrative twinning occurs, there is no " plane of composition ", in other words, the interpenetrating forms are separated from each other in an irregular way. In the present case, the interpenetration is often complete and it is a reasonable assumption that it may occur on a microscopic or even ultra-microscopic scale. Whether this is so or not, the identity of density and refractive index would make the direct observation of such internal twinning impossible, and we would have to depend on the study of structure-sensitive properties to demonstrate its existence. Diamond is rightly regarded as one of the most perfect crystals, if not the most perfect of them all, as shown by the extreme sharpness of the setting for the reflection of monochromatic X-rays exhibited by well-chosen specimens. It is evident however, that unless a specimen consists *exclusively* of sub-type Td I or of sub-type Td II, we cannot consider it as ideally perfect and homogeneous. Hence, the existence of the interpenetrative twinning should be capable of detection by X-ray methods. The *smaller* the volume-elements inside the crystal which are exclusively of one or the other sub-type, the more numerous would be the elementary blocks of which the crystal is built up, and the easier, therefore, would it be to observe the resulting non-homogeneity of the crystal by its X-ray behaviour or by other delicate methods of study.

5. *Lamellar Twinning of Octahedral Structures*

Fig. 1 indicates that the sub-types Oh I and Oh II cannot, unlike the sub-types Td I and Td II, be regarded as necessarily identical with each other in observable physical properties. They would nevertheless resemble each other sufficiently closely to make it highly probable that the Oh I and Oh II types would frequently appear together in the same specimens of diamond of the octahedral variety.

It is significant in this connection that a laminated structure in which layers parallel to one, two, three or even all the four faces of the octahedron appear simultaneously has been recognised as a characteristic phenomenon exhibited by some diamonds. Sutton (1928) describes and illustrates this kind of structure in diamond. He recognises that it is quite different from

the macling or twinning which has been often observed in diamond, since in the latter case, the components differ in orientation as shown by the difference in their planes of cleavage, and also, of course, by their X-ray patterns. Sutton therefore considers the lamellar structure to be an "illusory" type of twinning. Since, however, it is a real phenomenon it is no explanation of its existence to call it by such a name. Indeed, the appearance of a finely laminated structure is a well-known experience in crystallographic studies. It is observed for instance, in iridescent crystals of potassium chlorate and in various other substances. Hence, it is a reasonable assumption that when it is observed in diamond, it is also a specific form of twinning. We have already seen that an interpenetrative twinning of the Td I and Td II types would not exhibit any specific planes of composition. Hence, the presence of a lamellar structure in diamond parallel to the octahedral planes is a definite indication of the presence of the Oh types in the specimen and if, further, the specimen consists exclusively of these types, we may explain it on the basis that the Oh I and Oh II sub-types appear in alternate layers within the crystal. The simultaneous appearance of laminations parallel to more than one of the octahedral planes presents no difficulty of explanation on this view, since it would indicate merely that the two sub-types appear in the diamond as small blocks bounded by surfaces parallel to the laminations instead of as thin layers.

6. *Inter-Twinning of the Tetrahedral and Octahedral Structures*

Though diamonds having the lower and higher symmetry are physically different, yet they are so closely alike in their structure that the appearance of the two types simultaneously in the same individual crystal must be a not uncommon event. Indeed, since diamond has usually the lower symmetry, it may be expected that the higher symmetry would appear as an intrusion in diamond of the lower symmetry more frequently than as a type by itself. Since there are altogether four types of diamond, the number of possible modes of combination amongst them is fairly large, and we may have a wide range of possible space distributions of the different kinds of structure within the crystal.

Inter-twinning of the tetrahedral and octahedral forms of diamond may ordinarily be expected to exhibit a composition plane or planes parallel to each other within the crystal, thus dividing up the latter into layers which are physically different. The alternate layers may consist exclusively of the Td I or Td II types and of the Oh I or Oh II respectively. On the other hand, it is also possible that the Td I and Td II types may appear together in the layers having tetrahedral symmetry, while similarly, the Oh I and Oh II

types may appear as alternate finely-spaced laminæ within the layers having octahedral symmetry. Besides such cases, others may conceivably arise in which diamond of the lower symmetry is dispersed in microscopically small volume elements or even ultra-microscopically in diamond of the higher symmetry, or *vice versa*. The possibility of such cases is distinctly suggested by the situation which exists in relation to the individual types of diamond.

7. *Summary*

By virtue of the special positions which they occupy in the crystal lattice, the carbon atoms in diamond must have a tetrahedrally symmetric configuration of the electron orbital movements and spins. A tetrahedral axis has both direction and sense, and the carbon atoms in the two Bravais lattices may therefore be orientated in space and with respect to each other in four distinct ways, each of which corresponds to a possible structure for diamond. In two of these structures, diamond has only tetrahedral symmetry and in the two others the full or octahedral symmetry of the cubic system. The selection rules require that the fundamental vibration of the diamond lattice having a frequency 1332 cm.$^{-1}$ should appear both in light-scattering and infra-red absorption if the crystal has tetrahedral symmetry, while it would appear only in light-scattering and not in the infra-red absorption spectrum if the symmetry is octahedral. These predictions are in accord with the observed spectroscopic behaviours respectively of the commoner and rarer types of diamond recognised as such by Robertson, Fox and Martin. Hence, the assignment of tetrahedral symmetry to diamond by the earlier crystallographers is confirmed for the commoner type of diamond, while on the other hand, the rarer type is shown to have the full symmetry of the cubic system. The crystallographic facts also support the theoretical result that there should be two sub-types of diamond for each kind of symmetry. The positive and negative structures having tetrahedral symmetry have identical physical properties and can therefore interpenetrate freely. The two sub-types having octahedral symmetry cannot be considered as physically identical and their inter-twinning would therefore have composition planes. The lamellar structure parallel to the octahedral planes observed in some diamonds thereby becomes explicable. The possibility that diamond having the higher and lower types of symmetry may appear inter-twinned in the same crystal has also to be recognised.

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THE NATURE AND ORIGIN OF THE LUMINESCENCE OF DIAMOND

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Received April 17, 1944

Contents

1. Introduction

Not the least interesting of the many remarkable properties of diamond is that it emits visible light on excitation by appropriate methods. Many investigators have studied the luminescence of diamond since Robert Boyle in 1663 published his observations of the phenomenon. To the methods of exciting luminescence described by him, *viz.*, light, heat and friction, the advance of knowledge has added others, *viz.*, cathode-ray bombardment and X-rays. It has also provided instruments, *viz.*, the phosphoroscope and the spectroscope for the critical study of the phenomenon and extended the range of temperatures over which it may be observed downwards to the lowest values. A full summary of the earlier investigations is given in the fourth volume of Kayser's *Handbuch* (1908). In view of the fact that diamond is an elementary solid and is the typical valence crystal, it might have been supposed that its behaviour would figure prominently in any account of the subject of luminescence. Far from this being the case, the luminescence of diamond does not even find a mention in the two bulky treatises written by Lenard for the *Handbuch der Experimental Physik,* or in Pringsheim's article of 1928 in the *Handbuch der Physik.* The reason for this lack of interest is clear from the brief reference made in Pringsheim's book (1928) and in his earlier *Handbuch* article (1926), namely the belief

that the centres of luminescence in diamond are not the atoms of carbon of which it is composed, but some foreign atoms of undetermined identity present in it as impurity. The basis for this belief has been the variability of the intensity and colour of the emitted light, and the fact that not all diamonds show the phenomenon. The impurities suggested in the literature as the origin of the luminescence make a lengthy list, *viz.*, samarium, yttrium, sodium, aluminium, chromium, iron and titanium, and include even some hydrocarbons !

The considerations regarding the crystal symmetry and structure of diamond developed in the introductory paper of this Symposium (Raman, 1944) enable us to make a fresh approach to the problem of its luminescence. It is proposed to give a general outline of the experimental facts regarding the luminescence properties of diamond and to show that they fit naturally into the framework of the ideas developed in that paper, while, on the other hand, the facts remain wholly unintelligible on the impurity hypothesis. On the basis of the new ideas, it follows that the behaviour of diamond in respect of luminescence should stand in the closest relationship with its other properties, namely the absorption spectra in visible, ultra-violet and infra-red regions of the spectrum, the isotropy or birefringence observed in the polariscope, the X-ray reflection intensities, and so on. The evidence that such relationships actually exist, thereby placing the new ideas on a firm basis of experimental fact, is briefly set out in the present paper, and in fuller detail in others following it in the symposium.

2. *The Material for Study*

Opportunities for observing the luminescence of diamond in an impressive fashion first presented themselves to the writer in the year 1930 in connection with spectroscopic studies on the scattering of light in crystals. Several diamonds of exceptional size and quality (one of them as large as 143 carats) had been loaned by kind friends for use in those investigations. It was then found that the luminescence spectrum of diamond recorded itself on the spectrograms simultaneously with the scattering of light in the crystal, its leading feature being a band at 4155 A.U., and its intensity varying enormously from specimen to specimen (Bhagavantam, 1930). These observations on photo-luminescence suggested a comparison with the case of cathode-ray luminescence. A spectroscopic investigation of the latter phenomenon was then undertaken and showed very clearly the similarity between the results in the two cases (John, 1931). The very striking character of the photo-luminescence as observed visually with some of the diamonds indicated that its further study should prove a fascinating

line of research. The difficulty of obtaining suitable material, however, discouraged the pursuit of the subject.

About five years ago, the writer became aware that cleavage plates of diamond of good size and of excellent quality could be obtained at very modest prices. It was also recognized that diamond in this form is often more suitable for physical investigations than the high-priced brilliants of the jeweller's trade. The difficulty of obtaining material having thus disappeared, a sufficient number of specimens was acquired to make a start with the research, and a very fruitful series of investigations on the scattering and absorption of light in diamond and its photo-luminescence at various temperatures was carried out (Dr. P. G. N. Nayar, 1941, *a, b, c, d* ; 1942 *a, b*).

In June 1942, the writer was enabled through the kindness of the Maharaja of Panna to visit his State in Central India where diamond-mining has been carried on since very early times. The necessary instruments were transported to Panna and set up in a room in the State Treasury, and with the assistance of Dr. Nayar, a physical examination was made of some hundreds of diamonds in their natural state. In particular, the valuable opportunity was afforded to us of observing the crystal form and luminescence properties of a unique set of 52 large diamonds of the finest quality belonging to the Maharaja. The writer was also enabled during this visit and also a subsequent one in December 1942 to purchase a representative collection of the diamonds mined in the State and of enlarging his collection of polished cleavage plates. Preliminary reports of the observations made on the Panna diamonds have already appeared (Raman, 1942, 1943).

The observations made at Panna and the more detailed systematic studies made at Bangalore with the diamonds in the writer's collection have furnished ample material on which to base trustworthy conclusions. The material available for the laboratory investigations includes 310 specimens which may be classified as under:

(*a*) 29 Panna crystals in their natural condition, selected so as to be representative of the forms and qualities of diamond as found in the State.

(*b*) 65 Polished cleavage plates, for the greater part of Indian origin.

(*c*) 88 Brilliants, made from South African diamonds, and set together as a jewel.

(*d*) 10 Diamonds of various origins specially chosen for their interesting behaviour in regarding to luminescence or colour.

(*e*) 118 Other diamonds, mostly of Indian origin.

3. *Intensity and Colour of Luminescence*

The 88 *South African Diamonds.*—These diamonds are in the form of brilliants of varying size. Set in gold surrounded by a circle of pearls and interspersed by lines of rubies and emeralds, the pattern formed by them represents the double-headed eagle which is the heraldic emblem of the Mysore State (Fig. 1 in Plate III). The brilliants are not quite large enough to exhibit the inherent colour, if any, of the diamonds. So far as can be seen, however, they appear to be clear and colourless.

The ensemble of diamonds, pearls, rubies and emeralds formed by the ornament makes a striking exhibit when irradiated by ultra-violet light in the wave-length range 3500–3900 A.U. obtained by filtering the rays of the sun or of an electric arc through a plate of Wood's glass. The circle of pearls shines brightly with a uniform bluish-white lustre, while the lines of rubies appear a brilliant red and the emeralds a very faint yellow. The diamonds on the other hand, vary enormously in their appearance. A few of them irregularly scattered over the set emit a bright blue light of great intensity, while others not so luminous are also to be seen here and there. A cursory inspection suggests that only some ten or twelve of the diamonds emit any visible light. On a closer examination, however, it becomes evident that this is not really the case and that *all the* 88 *diamonds excepting three or four are luminescent,* though with enormously different intensities. This fact becomes particularly clear when the ultra-violet rays are focussed on each individual diamond so that the intensity of the light emitted by it is as great as possible. It is then noticed that the great majority of the diamonds exhibit luminescence of various shades of blue, the fainter ones appearing an indigo-blue and the brighter ones purer blue. Half a dozen of the diamonds, however, exhibit other colours, *viz.*, greenish blue, greenish yellow, or pure yellow.

The range of variation of intensity between the different diamonds may be roughly estimated from the photographic exposures necessary to record them on a plate. The appearance of the ornament as seen by daylight is shown in Fig. 1 and photographed by (Miss) Mani with different exposures under ultra-violet light in Figs. 2 to 6 in Plate III. A cell containing a concentrated solution of sodium nitrite was placed in front of the camera lens as a complementary filter when obtaining the luminescence photographs. Its effectiveness is shown by the fact that the gold setting and all the gems with the exception of the diamonds and one of the emeralds remain completely invisible. An exposure of two seconds was found to be sufficient to record the three mostly strongly luminescent diamonds. Exposures of

5 seconds, 15 seconds and 30 seconds respectively resulted in substantial increases in the number of diamonds visible in the photograph (Figs. 2, 3 and 4 respectively). An exposure of two minutes (Fig. 5) was necessary before the pattern bore any recognizable resemblence to its appearance as seen by daylight, while an exposure of 30 minutes was necessary in order to record the most feebly luminescent diamonds (Fig. 6). The brightest diamonds are, of course, then heavily overexposed. A ratio of the order of 1000: 1 or even more, between the strongest and the feeblest emission intensities, is thus indicated.

The 52 Large Panna Diamonds.—Crystals having smooth and lustrous faces and exquisitely beautiful geometric forms (rounded hexakis-octahedra or tetrakis-hexahedra) are to be found amongst those mined in the Panna State. Mr. Sinor's book (1930) on the diamond mines of Panna contains an illustration of a remarkable and probably unique set of 52 diamonds of this kind, all having the form of hexakis-octahedra, every one of them of the finest water, and their sizes forming a regular gradation from 24 carats for the largest to 1½ carats for the smallest. The diamonds are strung together as a garland in their natural state by thin girdles of gold which leave the crystal faces exposed. The luminescence properties of the entire set of diamonds could therefore be very conveniently examined one after another in succession. For this purpose, the light of a carbon-arc was filtered through a plate of Wood's glass and focussed by a lens on one of the faces of the crystal, and the track of the beam inside the diamond as made visible by the luminescence could be observed through another face. In this way, besides noting the colour of the luminescence, some idea of its relative intensity in the different diamonds could also be obtained.

Of the 52 diamonds in the set, the luminescence of 3 diamonds was visually classified as " intense", of 12 as " strong ", of 21 as " weak ", of 14 as " very weak " and of the remaining 2 diamonds as " unobservable ". The luminescence as observed in all the 50 fluorescent diamonds was of a blue colour, though, as stated, its intensity varied enormously.

The Writer's Collection of 29 Panna Diamonds.—The specimens in this collection fall into two groups. Group A comprises 10 diamonds of the best quality, colourless and transparent, having well-developed crystal forms and smooth lustrous faces. Group B comprises 19 so-called " industrial " diamonds, mostly of irregular shape and having a noticeable colour, grey, brown, or yellow. From a scientific point of view, however, some of these diamonds are of great interest, thereby justifying their inclusion in the collection.

The diamonds were in the first instance tested in the usual manner under ultra-violet irradiation and all of them were found to be luminescent. At a later stage in the investigations, it was found useful to immerse the diamonds, while irradiated, in a cell containing a highly refractive liquid and thereby diminish the disturbing effect of reflections and refractions at their external surfaces. The behaviour of the diamonds in the two groups showed many notable differences. Those in Group A were all blue-luminescent. So far as could be made out, the intensity was uniform within the substance of each crystal, though it differed enormously as between the different diamonds. The diamonds in Group B showed a very varied behaviour. Some exhibited a blue luminescence very similar to that given by the diamonds in Group A, but its intensity varied greatly, not only as between the different specimens but also within the volume of each individual crystal. Others, again, of the diamonds in Group B showed a greenish-yellow luminescence of which the intensity varied from specimen to specimen. Careful examination showed that luminescence of this colour was, in general, not uniformly distributed within the specimen, but appeared in parallel bands or stripes running through the volume of the crystal. The remaining crystals in Group B showed a mixed type of luminescence in which yellow bands or stripes of varying width appeared crossing a background of blue colour. In some of them, the yellow luminescence was most pronounced near projecting tips or bosses on the surface of the crystal, while the blue luminescence appeared in the interior.

The observations made with the Panna diamonds are of particular value, as the specimens were studied individually in their natural state and were in some cases also of considerable size. The observations with the brilliants of South African origin were not made under such favourable conditions, and hence they are not scientifically so significant. Broadly speaking, however, the results obtained with the two sets of diamonds are in excellent accord. The experimental situation may be summarised as follows:

(*a*) Luminescence under ultra-violet excitation is exhibited by the vast majority of diamonds, including especially those of the finest quality.

(*b*) A blue luminescence is characteristic of nearly all diamonds which are colourless and crystallographically perfect, its intensity, however, varying enormously from specimen to specimen.

(*c*) Imperfect diamonds show sometimes a blue luminescence, sometimes a greenish-yellow luminescence and sometimes a mixed

type of luminescence, the intensity of which varies not only from specimen to specimen but also within the volume of each specimen.

(*d*) A few diamonds are definitely non-luminescent.

4. Luminescence Patterns in Diamond

The difficulties which arise in working with the immersion method are altogether avoided by the use of polished cleavage-plates of diamond. 65 such plates are included in the writer's collection. Their thickness is generally small (from half a millimetre to one millimetre or more), but this is far from being a disadvantage in these investigations. The luminescence of the plates may be conveniently studied by placing them on a polished sheet of copper and irradiating them normally with ultra-violet light, a complementary filter of sodium nitrite solution being used when photographs are desired.

The enormous variations in the intensity of luminescence are best appreciated by viewing a group of diamonds at the same time (see Fig. 7, in Plate IV which includes 46 diamonds). Six plates in the collection exhibit no observable luminescence except very feebly at their edges, as shown by the bottom row in the figure. The luminescence of 34 plates is a blue, of 6 plates a yellowish-green, and of the remaining 19 plates a mixture of the two. The blue-luminescing plates may be divided into two groups of approximately equal number; in the first group, the luminosity is more or less uniform over the plate except at the unpolished edges which shine out brightly; in the second group, the luminosity is highly non-uniform over the area of the plate and exhibits a pattern of bright and dark regions, usually with geometric features related to the crystal structure, the lines of equal brightness running parallel to the inter-sections of one, two or three sets of octahedral planes with the surface of the plate. Most of the yellow-luminescent diamonds show a pattern of fine streaks running parallel to one another within the plate. In the plates showing the mixed type of luminescence, sets of yellow bands running parallel to one another in one or two or even three different directions within the crystal are a conspicuous feature. The appearance of these yellow bands is found to depend on the angle at which the plate is viewed; they appear as fine sharp lines at some angles of observation and as broad bands at others, thereby indicating that they represent thin luminescent layers within the substance of the crystal.

Many of the 46 cleavage plates appearing in Fig. 7 in Plate IV exhibit luminescence patterns, as may be seen in that figure. The scale of this photograph is however rather too small and the exposures in most cases either too great or too small to record the patterns satisfactorily. Six typical

patterns photographed on a larger scale are reproduced as Fig. 8 and Fig. 9 respectively in Plate V, appearing in the upper half of these pictures. The geometric character of the patterns shown by D38 in Fig. 8 and by D179 in Fig. 9 is particularly noteworthy. These, as well as D224 appearing in Fig. 8, are blue-luminescent diamonds. The non-uniform intensity and the appearance of dark streaks in the luminescence of D179 and D224 are also worthy of remark. D200 seen in Fig. 8 has a greenish-yellow luminescence in which the most prominent feature is a set of four parallel bands. D188 and D190 appearing in Fig. 9 are typical diamonds exhibiting the mixed variety of luminescence. The former shows an extremely interesting pattern consisting of an intense blue spot surrounded by a faint blue ground which is crossed by sets of parallel yellow bands running in different directions across the plate. D190 exhibits a pattern of parallel bands running in different directions, blue in one part of the diamond and yellow in other parts.

Many other examples of luminescence patterns and a detailed description of the same will be found in a paper by Mrs. K. Sunandabai (1944) appearing in this symposium.

5. *Luminescence and Ultra-Violet Transparency*

It has long been known that while the majority of diamonds are opaque to ultra-violet radiation of wave-lengths smaller than about 3000 A.U., there are some diamonds which transmit the ultra-violet rays freely up to about 2250 A.U. The investigations of Roberston, Fox and Martin (1934) have shown that this difference in ultra-violet transparency goes hand in hand with other notable differences in behaviour, especially in respect of infra-red absorption and in respect of photo-conductivity. It is therefore of obvious importance to ascertain whether the luminescence properties are in any way correlated with the empirical classification of diamond into two types which has been suggested by these investigators.

The ultra-violet transparency of diamond may be studied with a suitable source of radiation and a quartz spectrograph, and if quantitative results are desired, also an ultra-violet spectro-photometer of some kind. When a cleavage plate is employed, it is also possible by traversing its area in successive steps to investigate whether its ultra-violet transparency varies over the surface. A much simpler and more satisfactory procedure adopted by the author and Mr. Rendall for this purpose is to place the plate in contact with a sheet of uranium glass and illuminate the latter *through* the diamond with the 2537 A.U. radiations of a water-cooled quartz mercury arc, its other radiations being deflected aside with a quartz prism and a couple of quartz lenses. The plates which are opaque to the 2537 rays

are then seen as dark areas in the surface of the uranium glass lit up by these radiations, while those which transmit them are seen as bright areas. On placing a group of cleavage plates together on the sheet of uranium glass, it may be seen at a glance that a few of them transmit while others are opaque to the 2537 A.U. radiations. Further, it is noticed that the plates which are not opaque to the 2537 radiations may differ greatly in their degree of transparency. The method of observation also reveals that the extent of transparency may vary greatly over the surface of a given plate. Indeed, a plate may be perfectly opaque to the 2537 radiation in certain areas, perfectly transparent to it in other areas, and exhibit an intermediate behaviour elsewhere. *The procedure thus enables as visually to observe and photograph the ultra-violet transparency patterns of the cleavage plates of diamond.* Using this method of study, the following relations between luminescence and ultra-violet transparency have been established:

(*a*) A blue-luminescent diamond is invariably of the ultra-violet opaque type, but the opacity diminishes with increasing intensity of luminescence.

(*b*) Non-luminescent diamonds are invariably of the ultra-violet transparent type.

(*c*) The diamonds which exhibit an yellowish-green luminescence are of the intermediate type, in other words, are neither perfectly transparent nor perfectly opaque to the 2537 radiations.

(*d*) These statements are also valid in respect of the individual areas in a cleavage plate which exhibits a luminescence pattern.

It follows that the luminescence pattern should show a close resemblance to the ultra-violet transparency pattern in those cases where part of the diamond is blue-luminescent and another part is non-luminescent, or when the plate exhibits a greenish-yellow banded luminescence. On the other hand, if a cleavage plate consists exclusively of blue-luminescent diamond, it is ultra-violet opaque and can therefore show no transparency pattern, even though it may exhibit local variations in the intensity of the luminescence.

To illustrate these remarks, the luminescence and ultra-violet transparency patterns of the diamonds numbered D48, D198 and D235 in the collection are reproduced side by side in Fig. 10. D48 exhibits three different types of behaviour simultaneously in different areas, *viz.*, non-luminescence, blue-luminescence and the greenish-yellow banded luminescence, as can be seen from the pattern reproduced in the upper part of Fig. 10, while the corresponding variations in ultra-violet transparency are noticeable in the

lower part of the same figure. D198 is non-luminescent at the centre and around it shows a geometric pattern of bands of greenish-yellow luminescence, changing to blue at the outer margin. It will be noticed that the resemblance between the luminescence and ultra-violet transparency patterns is extremely striking. D235 shows patches which are non-luminescent and ultra-violet transparent, while in the main it is blue-luminescent and ultra-violet opaque. Where the opaque and transparent diamonds mix, we have an imperfect transparency, and streaks of greenish-yellow luminescence are observed. It may be remarked that none of these three diamonds shows the least trace of non-uniformity when critically examined in ordinary daylight.

Illustrations of many more ultra-violet transparency patterns and a detailed discussion of the same will be found in a paper by Mr. G. R. Rendall (1944) appearing in this symposium.

6. *Luminescence and Structural Birefringence*

Diamond is a cubic crystal. Hence, if the structure is the same throughout the volume of a specimen, it should be optically uniform and isotropic. If, however, structures which differ from each other ever so little in their lattice spacings are incorporated in the same specimen, it is inevitable that stresses would be set up, with the result that a strain pattern indicating the inhomogeneity of the specimen would be visible between crossed nicols in the polariscope. Cleavage plates with polished faces are particularly well-suited for such studies, as disturbing effects due to oblique reflection or refraction at the surfaces do not arise. Further, the cleavage which enables the plate to be detached from the crystal automatically releases the stresses arising from flaws, cracks or inclusions located outside the plate, and hence eliminates the purely accidental birefringence due to such causes, thereby enabling the true structural birefringence, if it exists, to be perceived.

The examination of the 65 cleavage plates in the writer's collection has furnished much valuable information regarding the nature and origin of the birefringence sometimes observed in diamond. These results will be fully dealt with in another paper appearing in the symposium. It will be sufficient here to state the following relations which the observations show to exist between luminescence and the presence or absence of birefringence in diamond.

(*a*) Diamond may be perfectly isotropic and strain-free; it is then invariably of the blue-luminescent type.

(*b*) Non-luminescent diamond exhibits a characteristic and readily recognisable type of birefringence, consisting of closely-spaced parallel streaks running in several directions through the crystal.

(*c*) Diamond exhibiting the greenish-yellow luminescence invariably shows a characteristic type of structural birefringence consisting of parallel dark and bright bands, usually rather wider apart than those shown by non-luminescent diamonds.

(*d*) Diamond in which the blue-luminescent and non-luminescent types, or the blue-luminescent and the greenish-yellow luminescent types are simultaneously present invariably shows structural birefringence.

To illustrate the structural birefringence which appears associated with luminescence in the particular circumstances explained above, the patterns seen between crossed polaroids of the diamonds D38, D224, D200, D188 D179 and D190 are reproduced in Figs. 8 and 9 (Plate V), side by side with the corresponding luminescence patterns. In all these cases, the general resemblance between the two kinds of pattern can be made out easily. It is most obvious in the case of the three diamonds which exhibit a greenish yellow luminescence, *viz.*, D200, in Fig. 8, and D188 and D190 in Fig. 9. Diamonds D38 and D224 in Fig. 9 and D179 in Fig. 10 are blue-luminescent, the two former strongly, and the latter weakly. The dark streaks appearing in their luminescence-patterns correspond to bright streaks in the birefringence patterns and arise from the intrusion of non-luminescent diamond into the blue-luminescent kind.

7. *Interpretation of the Experimental Facts*

We are now in a position to consider the question of the origin of the luminescence. As we have seen, Indian and South African diamonds exhibit essentially similar phenomena. The fact that the effects observed do not depend on the locality of origin makes it highly improbable that impurity atoms are responsible for the luminescence. Then again, it is the clearest and most colourless, in other words, the chemically purest diamonds which exhibit the blue luminescence in the most striking fashion. The necessity for rejecting the impurity hypothesis becomes even clearer when we consider the luminescence patterns exhibited by individual diamonds. In numerous cases, as we have seen, particular regions with sharply defined boundaries show a vivid luminescence, while adjoining regions are non-luminescent. The patterns observed in many cases have geometric configurations clearly related to the symmetry of the crystal, indicating that the luminescence is fundamentally connected with the crystal structure.

Positive proof that the luminescence is an inherent property of the diamond itself is furnished by the relationships between the phenomenon and the other physical properties of diamond which are also dependent on

crystal structure. Particularly significant is the fact that non-luminescent diamonds are completely transparent to the 2537 radiations of the mercury arc. According to the investigations of Robertson, Fox and Martin (*loc. cit.*), such ultra-violet transparency goes hand in hand with the absence of a prominent infra-red absorption band which is markedly present in diamonds opaque to the 2537 radiations. This infra-red absorption band has its head at the characteristic frequency of the diamond lattice (1332 $cm.^{-1}$), and its absence and presence respectively indicate, as shown in the preceding paper, that the diamond has full octahedral symmetry or only tetrahedral symmetry as the case may be.

In the light of the foregoing remarks, the experimental facts set out in the preceding sections may be re-stated in the following words:

(*a*) Diamonds with tetrahedral symmetry of structure are, in general, blue-luminescent.

(*b*) Diamonds with octahedral symmetry of structure are non-luminescent.

(*c*) Diamonds in which the tetrahedral and octahedral types of structure are intimately mixed exhibit the greenish-yellow type of luminescence.

It remains to explain the enormous variations found in the intensity of the luminescence. In the case of the blue-luminescent diamonds, the most natural interpretation of the facts is that the luminescent property arises from the interpenetration of the positive and negative tetrahedral structures and consequent heterogeneity of the crystal. The intensity of the luminescence would then be determined by the nature and extent of such interpenetration. Similarly, in the case of the greenish-yellow luminescence, its intensity would be determined by the extent and distribution of the tetrahedral structure which is present as an admixture with the octahedral type. The features exhibited by the luminescence patterns and the analogies and differences noticed between them and the patterns of ultra-violet transparency and of structural birefringence give strong support to these ideas.

8. *The Spectral Characters of Luminescence*

The blue and greenish-yellow types of luminescence should evidently show different spectra. Since as we have seen, the greenish-yellow luminescence is exhibited by diamonds in which the non-luminescent and blue-luminescent varieties are mixed, it follows that the spectrum of the greenish-yellow type should always be accompanied, feebly or strongly, with that of the blue type. Non-luminescent diamond, on the other hand, should show neither type of spectrum, even under the most prolonged exposures.

A striking experimental confirmation of these conclusions is furnished by the investigations of the luminescence and absorption spectra in the visible region carried out by (Miss) Anna Mani with 32 representative diamonds and reported in this symposium (Mani, 1944). She has shown that the spectra are of two types which may be designated as the 4152 and 5032 systems, these being respectively characteristic of the blue and greenish-yellow luminescence. These always appear together, though with varying intensities whenever a diamond is luminescent, while neither appears when it be non-luminescent. Each system consists of a principal electronic line appearing at the wave-length stated in emission as well as absorption, and this is accompanied by weaker electronic lines at other wave-lengths and by a subsidiary lattice spectrum in which the principal electronic frequency combines with the various possible frequencies of vibration of the crystal lattice. The lattice spectrum appears with mirror-image symmetry about the principal electronic frequency, towards longer wave-lengths in emission and towards shorter wave-lengths in absorption.

The significant facts which emerge from the spectroscopic studies of Nayar (*loc. cit.*) and of Miss Mani (*loc. cit.*) are the following:

(*a*) Given sufficient exposures, the type of diamond which is opaque to the 2537 A.U. radiations invariably records the 4152 system with an intensity which varies enormously as between different specimens.

(*b*) No trace of either the 4152 or the 5032 systems is recorded, either in emission or in absorption, with diamonds which are perfectly transparent to the 2537 A.U. radiations. But diamonds which are imperfectly transparent to these radiations show both the 4152 and 5032 systems, with varying relative strengths.

(*c*) Whenever the 5032 system is recorded with any specimen, the 4152 system is an invariable accompaniment, though its strength may be greater or smaller than that of the former system.

These facts fit naturally into the ideas regarding the structure of diamond and the origin of its luminescence developed in these pages. But it is not easy to reconcile them with the 'impurity' hypothesis.

9. *Luminescence and X-Ray Reflection Intensities*

A further striking confirmation of the idea that the luminescence of diamond is associated with the interpenetration of different crystal structures and the inhomogeneity resulting therefrom is furnished by X-ray studies. Actually, we have four possible structures, two with tetrahedral symmetry

designated as Td I and Td II, and two with octahedral symmetry designated as Oh I and Oh II. The two tetrahedral structures are physically identical but geometrically different. Hence, they can interpenetrate freely without any composition planes and without setting up stresses in the crystal. The mixed structure is nevertheless not ideally homogeneous, and its lattice planes should therefore give X-ray reflections stronger than those given by either structure individually. The smaller the blocks in which the structure is homogeneous, the more intense would be the X-ray reflections, as also the luminescence. Hence, a close correlation must exist between luminescence and X-ray reflection intensity. The lowest reflection-intensities should be given by the most feebly blue-luminescent diamonds which accordingly are the nearest approach to the ideal crystal. *Per contra*, the strongest X-ray reflection intensities and the largest departures from crystal perfection would be provided by the intensely blue-luminescing diamonds.

The theoretical inferences stated above have been confirmed experimentally by Dr. R. S. Krishnan. The effect is conspicuously seen in the two Laue diagrams obtained by him and reproduced in an article by the present writer (Raman, 1943). One of the diamonds (D31) is weakly blue-luminescent, while the other (D224) shows an extremely strong luminescence of the same colour and gives a much more intense Laue pattern than the other. A similar effect has also been observed by Dr. R. S. Krishnan on comparing the intensities of the Bragg reflections by the oscillating crystal method.

If the Oh I or Oh II type of diamond structure exists by itself, it should give the weak X-ray reflections characteristic of an ideal crystal. Actually, when the two structures appear in the same diamond, they exhibit planes of composition and a characteristic streaky birefringence, indicating that they are physically different and that their juxtaposition sets up stresses in the solid. Hence the Oh I–Oh II mixed type should show much more intense X-ray reflections than the most intensely blue-luminescing diamond having the Td I–Td II structure. For the same reason also, diamonds having the Td-Oh mixed structures and exhibiting the yellow luminescence should stand half-way between these in respect of X-ray reflection intensities, just as they do in respect of ultra-violet transparency. That this is actually the case has been shown by Mr. P. S. Hariharan by photometric comparison of the intensity of the Bragg reflections by a series of cleavage plates of diamond having different luminescent properties. A report of his work appears elsewhere in the symposium (Hariharan, 1944).

Luminescence patterns, ultra-violet transparency patterns and structural birefringence patterns are the various different ways in which the non-uniformity of structure of a plate of diamond may be made manifest to the

eye at a glance. Still another and quite different way of doing this is by the aid of X-rays, and the technique necessary for this purpose has been successfully worked out by Mr. G. N. Ramachandran. His results are reported in another paper in the symposium (Ramachandran, 1944). White X-radiation from a tungsten-target tube diverges from a pin-hole and falls upon the plate of diamond held at a sufficient distance from it. Each of the spots in the Laue pattern recorded on a photographic film is then seen as a topographic map of the diamond in which the variations of crystal structure are indicated by corresponding variations of X-ray reflection intensity. Very striking and interesting pictures are obtained in this way, the plate and the photographic film being so tilted that the Laue spot is recorded as an undistorted representation of the diamond.

10. Excitation of Luminescence by X-Rays

The preceding discussion concerned itself with the effects observed under ultra-violet irradiation in the wave-length range 4000 A.U. to 3500 A.U. Luminescence is also excited by longer wave-lengths (5000 A.U. to 4000 A.U.) and by shorter waves (3500 to 2000 A.U.). This is readily demonstrated using the appropriate light-sources and a monochromator to isolate the desired exciting radiations. The intensity with which the 4152 and 5032 systems are excited would necessarily depend on the wave-length of the exciting radiation, being greatest when it coincides with the wave-length of the principal electronic radiation of the system concerned and becoming negligible when it is larger, while it would persist with appreciable but greatly diminished intensities for shorter wave-lengths. This has been shown to be the case for the 4152 system by Nayar (1941). In the ultra-violet beyond 3000 A.U., the imperfect transparency of the diamond also comes into play and causes the luminescence to be superficial and to be markedly enfeebled, these effects being the less conspicuous the more transparent the diamond under study is for the exciting radiations.

Diamonds also luminesce under the action of X-rays, unlike pearls and rubies which remain completely dark under such excitation. The intensity and also the colour of the luminescence varies as between different specimens, but the range of such variation is far less conspicuous than in the excitation by ultra-violet light. This is evident on a comparison of the series of Figs. 11 to 14 in Plate VI with the sequence of Figs. 2 to 6 in Plate III. Mr. G. N. Ramachandran who has made some observations on the subject has noticed a remarkable brightening up of the luminescence by increasing the voltage under which the X-ray tube is run, while the milliamperage seemed to have little or no obvious effect on the intensity. These effects obviously merit further investigation.

11. Phosphorescence

Diamonds which are strongly blue-luminescent emit a yellow phosphorescence when the exciting radiation is cut off. It follows that the spectrum of the emitted light should change rapidly with time when the incident radiation is cut off. Nayar (1941, *b, c*) has recorded some fluorescence and phosphorescence spectra showing this effect, as also the change in the spectrum of the emitted light when the wave-length of the incident light is altered by steps over the range 4000 A.U. to 6000 A.U. It is obviously desirable that the studies of the phosphorescence spectra should be extended to diamonds which show the 4152 and 5032 systems in fluorescence with comparable intensities. In this connection, it is noteworthy that strongly yellow-luminescent diamonds have a scarcely noticeable phosphorescence, thus markedly differing in their behaviour from blue-luminescing ones.

12. Summary

Luminescence is exhibited by nearly all diamonds, though with enormously varying intensities. Numerous specimens, both Indian and South African, in the form of natural crystals as also of cleavage plates, have been studied and the results are described and discussed. Observations with the cleavage plates are particularly significant, as many of them exhibit *luminescence patterns* having geometric characters obviously related to the structure of the crystal. The comparison of these luminescence patterns with *the patterns of transparency in the ultra-violet* beyond 3000 A.U. and with *the patterns of structural birefringence* observed between crossed polaroids is very instructive and shows that all these patterns have an essentially similar origin, *viz.*, the interpenetrative or lamellar twinning of the different possible crystal structures in diamond. The interpenetration of the positive and negative tetrahedral structures gives rise to blue luminescence without any structural birefringence, the diamond remaining ultra-violet opaque. The interpenetration of the tetrahedral and octahedral structures gives rise to the yellow luminescence accompanied by a banded structural birefringence and an imperfect ultra-violet transparency. The lamellar twinning of the two possible octahedral structures gives diamond which is both non-luminescent and ultra-violet transparent but with a characteristic finely streaky birefringence. Spectroscopic study of the emission and absorption spectra of diamonds in the visible region, and a study of the variation of the reflecting power of the lattice planes for X-rays confirm these conclusions and show that the luminescence is essentially physical in origin and not due to foreign atoms present as impurities.

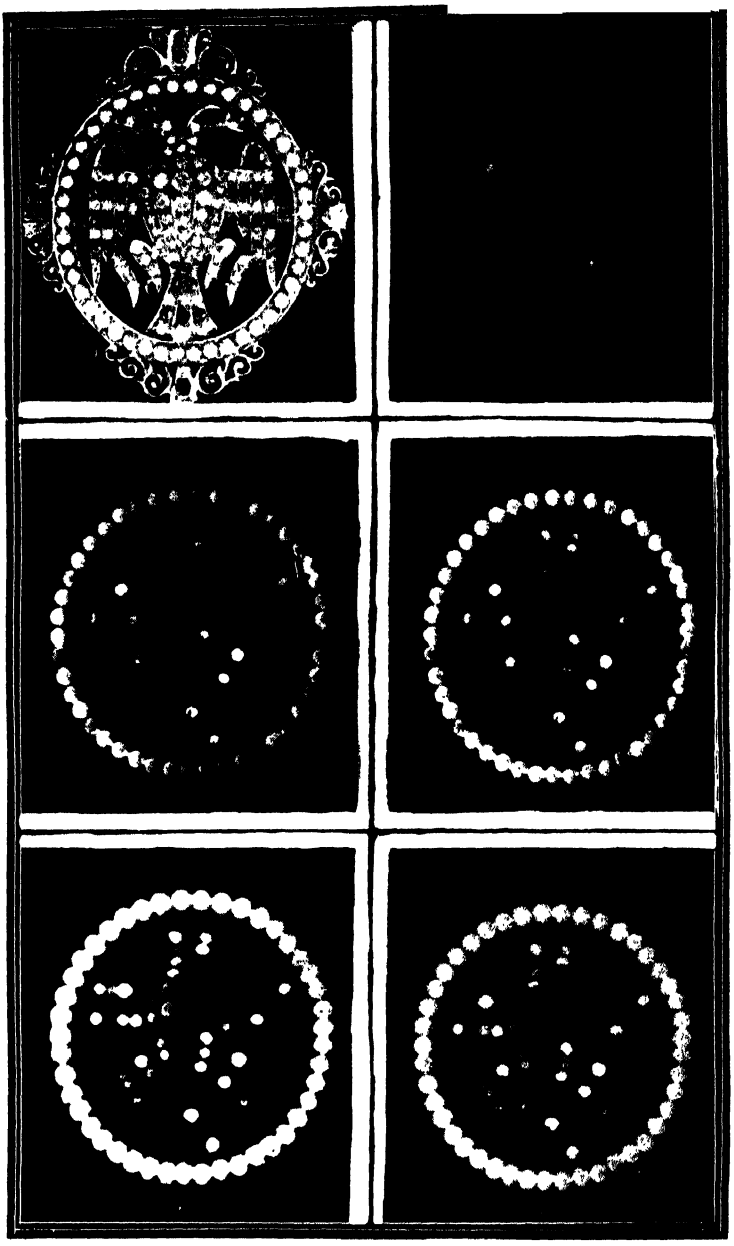


Fig. 3

Fig. 4

Fig. 5

Fig. 6

Luminescence of South African Diamonds

Fig. 1. Photograph in Daylight

Figs. 2 to 6. Luminescence in Ultra-Violet with Increasing Exposures

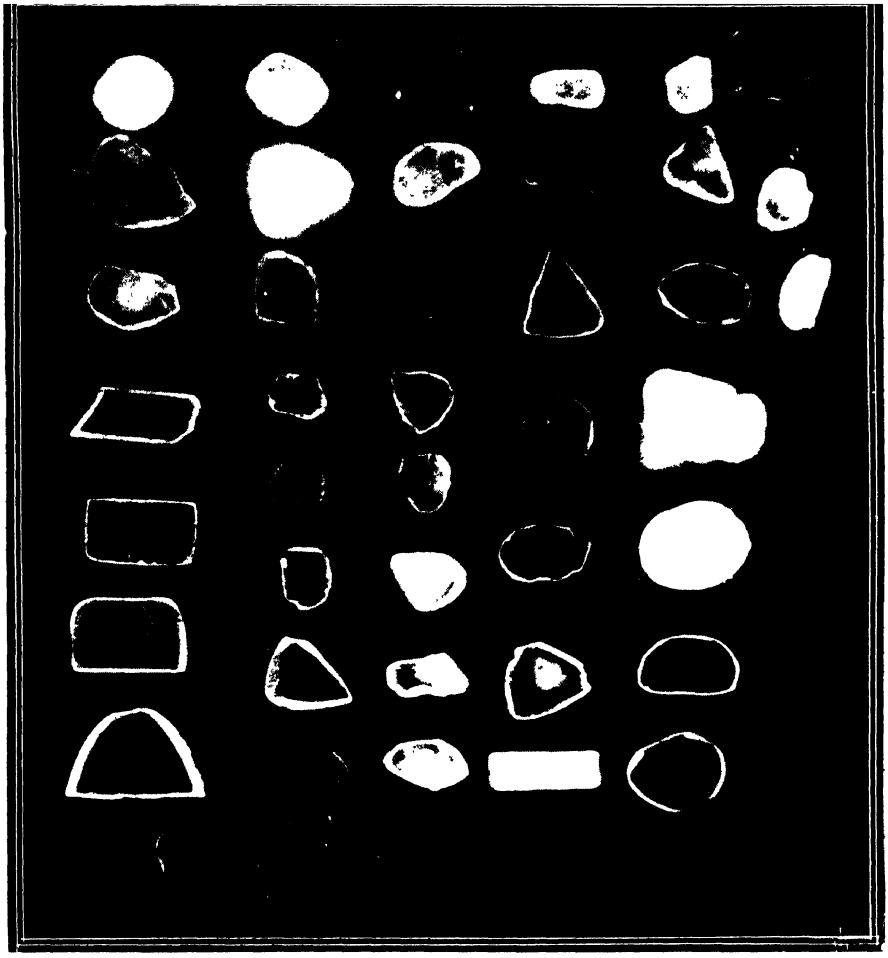
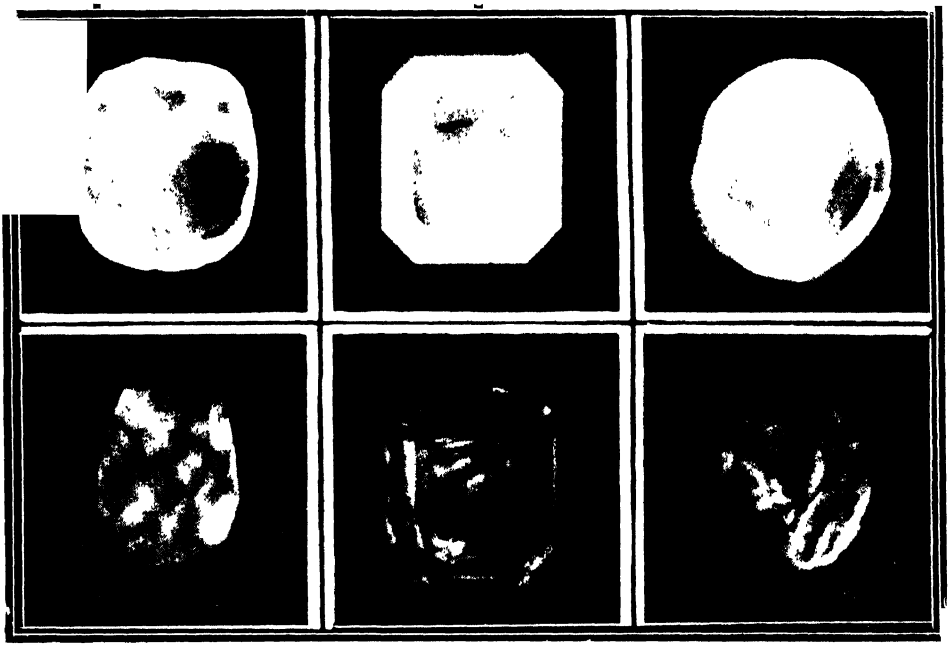


FIG. 7. Luminescence of Cleavage Plates of Diamond

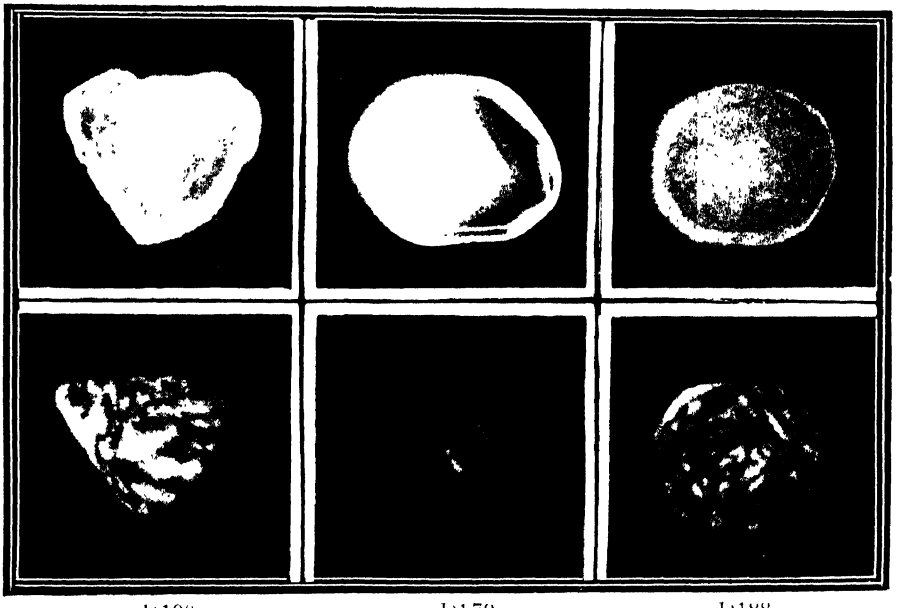
Catalogue Numbers					
D 188	200	199	196	193	191
175	190	192	198	48	194
185	210	211	195	177	202
31	231	182	178	34	
	176	183			
221	52	187	173	38	
36	174	189	180	181	
222	172	186	42	179	
57,208	209	206	39	207	



D200 D224 D38

FIG. 8. Comparison of Luminescence and Birefringence Pattern

D179 D188



D190 D179 D188

FIG. 9. Comparison of Luminescence and Birefringence Pattern

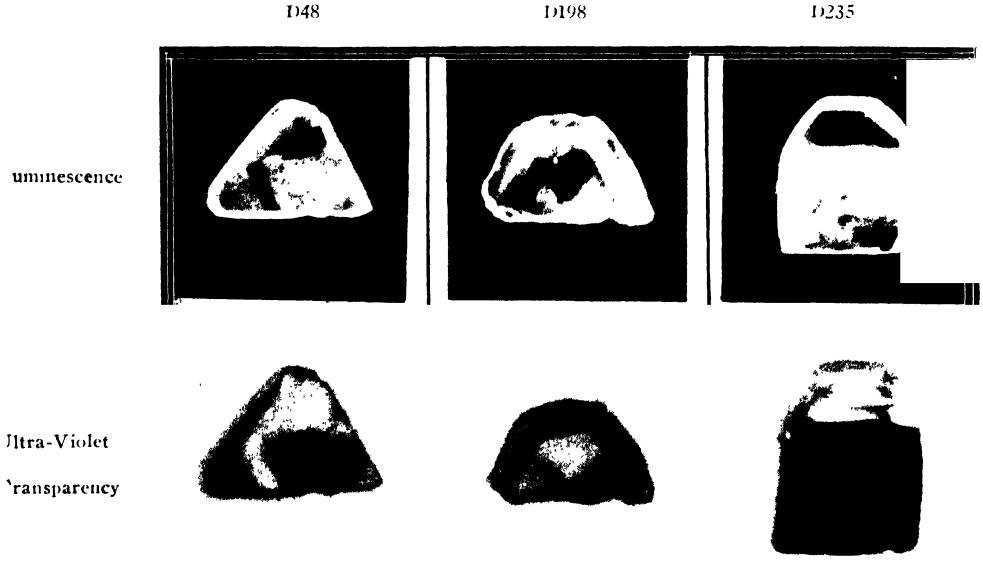


FIG. 10. Comparison of Luminescence and Ultra-Violet Transparency Patterns

FIG. 11
50 K.V. 10 minutes

FIG. 12
50 K.V. 30 minutes

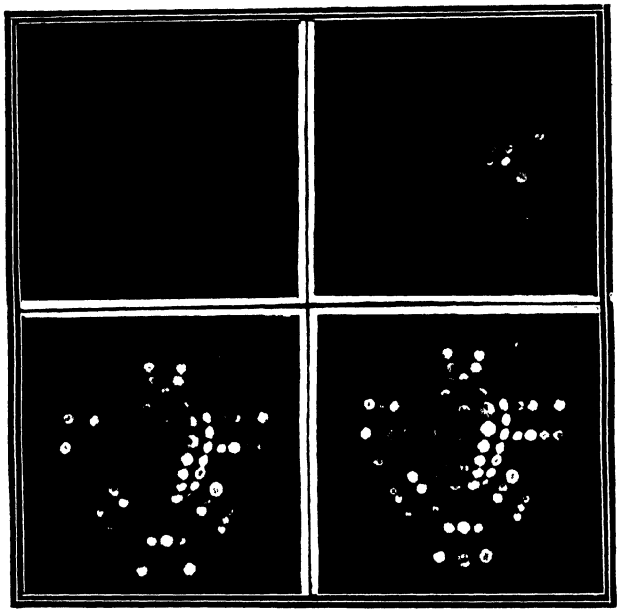


FIG. 13
70 K.V. 30 minutes

FIG. 14
70 K.V. 60 minutes

Luminescence of Diamonds under X-Rays with Increasing Exposures

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THE RAMAN SPECTRUM OF DIAMOND

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1. Introduction

Ramaswamy (1930), Robertson and Fox (1930) and Bhagavantam (1930) simultaneously and independently observed the Raman spectrum of diamond and found one sharp strong line with a frequency shift of 1332 cm.$^{-1}$ As was pointed out by Ramaswamy and later fully confirmed by the theoretical investigations of Nagendra Nath (1934) and of Venkatarayudu (1938), this frequency represents the fundamental vibration of the diamond structure, *viz.*, the mode in which the two interpenetrating Bravais lattices of carbon atoms oscillate against each other. This mode, according to the usual selection rules (Placzek, 1934) should be active in the Raman effect. The researches of Nayar (1941, 1942) on the luminescence and absorption spectra of diamonds have, however, demonstrated the existence of many more vibrations of the diamond structure with discrete frequencies, besides the one found in the Raman effect. Nayar's results have been confirmed and extended by the investigations of (Miss) Mani of which a report appears elsewhere in this symposium. The appearance of several discrete monochromatic frequencies in the vibration spectrum of the diamond lattice is unintelligible on the basis of the older theories of the specific heat of solids. It, however, finds a natural explanation in the new theory of the dynamics of crystal lattices due to Sir C. V. Raman (1943). On the basis of the Raman dynamics, the possible modes of atomic vibration in diamond have been fully worked out and described by Chelam (1943) and by Bhagavantam (1943). They have both given explicit expressions for the frequencies in terms of the force constants. There are, on the whole, eight fundamental frequencies, of which only the one having the highest frequency is active in the Raman effect. Though the seven other vibrations are forbidden as fundamentals, they are allowed as octaves in light-scattering, according to the usual selection rules. Besides overtones, some of the combinations may also be Raman-active. There is thus a clear possibility that octaves and combinations of the eight frequencies of the diamond lattice might appear recorded in strongly exposed Raman spectra. The present research was undertaken to investigate this possibility. Its successful confirmation places the Raman dynamics of crystal lattices on a firm foundation of experimental reality.

2. *Review of Previous Experimental Work*

Besides the investigations already referred to in the Introduction, mention may be made here of others relevant to the subject of this paper.

During the course of their systematic investigations on the properties of diamond, Robertson, Fox and Martin (1934) examined the Raman spectra of a few samples of the two types of which the existence was recognized by them. They found that the principal Raman line had exactly the same frequency shift in both cases. With the diamonds which are more transparent in the ultra-violet, the Raman effect studies could be extended further into that region.

Bhagavantam (1930 *a*) studied the Raman spectra of numerous large diamonds of the ultra-violet opaque type, using the 4046 and 4358 radiations of the mercury arc as exciters, with a view to discover whether there are any observable frequency shifts besides the principal one of 1332 cm.$^{-1}$ We shall consider his results on this point later in the present paper.

Contrary to a finding by Bhagavantam, Nayar (1941 *a*) reported that the intensity of the 1332 line did not vary with the specimen of diamond under study. He also made a careful study of the thermal behaviour of this line over a wide range of temperatures. He found the frequency shift to diminish from 1333·8 cm.$^{-1}$ at $-190°$ to 1316·4 cm.$^{-1}$ at 860 C., in a manner evidently connected with the thermal expansion of the crystal. Continuing his earlier work, Nayar (1942 *a*) found that the line showed no measurable variation either in its frequency shift or in its intensity when the setting of the crystal or the angle of scattering was altered. He also drew attention to an interesting case in which the 1332 line appears distorted in an imperfect crystal.

3. *Experimental Technique*

In the present investigation the well-known Rasetti technique of using the 2536 radiation of a water-cooled quartz mercury arc has been adopted, and diamonds of the ultra-violet transparent type have been chosen for study. The ordinary type of diamonds are usually fluorescent to varying extents, the fluorescent bands falling in a region extending from 4000 A.U. to about 6000 A.U. Even the diamonds which are the least fluorescent give a weak continuous radiation in the visible region, and the faint Raman lines, if present, would be lost in the general background and remain unobserved. These difficulties are completely eliminated by working in the ultra-violet region and using the 2536 monochromatic radiations of mercury vapour for exciting the Raman lines. The enormously increased scattering power of the 2536 line arising from its exceptional intensity as compared

with the other mercury lines and from the λ^{-4} law, also makes it possible to record fainter Raman lines which would remain unobserved otherwise. The study of the Raman spectra using the Rasetti technique is, however, necessarily restricted to diamonds which are transparent to the 2536 radiation.

From Sir C. V. Raman's personal collection two diamonds were selected which were suitable for the present investigation. Their serial numbers are 206 and 227. Diamond No. 206 was colourless and in the form of a thin plate ($10 \times 6 \times 0{\cdot}6$ mm.) and its weight was $0{\cdot}2$ of a carat. The other diamond was cut in the form of a faceted prismatic rod with oblique ends and had a slight tinge of colour. It was a centimetre long and about 3 mm. thick, its weight being roughly $1{\cdot}3$ carats.

A vertical quartz mercury arc of a special design was constructed in the laboratory with mercury cathode and tungsten anode. The arc was kept immersed in running water to a depth of about one centimetre above the cathode bulb and was kept continuously evacuated by an efficient pumping system. The central vertical portion of the arc was inserted between the poles of a powerful electromagnet which caused the deflection of the discharge against the front wall of the tube. The water-cooling and the continuous evacuation prevented the mercury from acquiring any considerable density, and the magnet by squeezing the discharge against the wall still further prevented the reversal of the 2536 line. Under these conditions, this line was so intense that the main Raman lines of calcite could be recorded in a couple of minutes.

Diamond No. 206 being a flat plate was illuminated through one of its faces and the scattered light was observed through one of the edges in the end-on position. The maximum depth of illumination equal to the length of the plate was thus secured. By aluminising the opposite face of the diamond, the incident radiations were reflected back, thereby increasing the intensity of the scattered light. Diamond No. 227 was fixed inside a copper rod at the junction of two perpendicular holes cut through it. This diamond was irradiated through one of its long prismatic facets and the scattered light was taken out normally through one of the pyramidal end facets. In this arrangement, the parasitic illumination entering the spectrograph was negligible and the displaced lines could be photographed on a very clear background.

The diamond under investigation was held facing the most intense portion of the arc near the front wall of the quartz tube towards which the discharge was deflected. To prevent any appreciable rise in temperature of the diamond, a continuous stream of cold air was directed towards it. The

light scattered from the diamond was condensed on the slit of a Hilger Intermediate spectrograph. The 2536 radiation in the scattered light was suppressed before its entry into the spectrograph by absorption in a column of mercury vapour contained in a cell placed in front of the slit. With these arrangements, the 1332 line could be recorded in about ten minutes. Longer exposures of the order of 15 hours or more are required to record the fainter Raman lines. These were obtained also with the smaller diamond. The efficiency of the optical set-up could be judged from the fact that the anti-stokes of 1332 was recorded in about 24 hours with the smaller diamond. For obtaining strongly-exposed spectrograms, the larger diamond was used. Numerous photographs were taken varying the time of exposure up to a maximum period of 60 hours. On every negative, a series of photographs of the direct mercury spectrum with graded exposures was also recorded by the side of the spectrogram of the scattered light. The slit width employed was 20 μ. The dispersion of the instrument was about 220 wave numbers per millimetre in the region of 2536. The plates were measured under a Hilger cross-slide micrometer. To measure the shift of very faint lines, an ordinary low-power microscope was used.

4. *Results*

An intense Raman spectrum of diamond with 2536 excitation is reproduced in Plate VII along with a photograph of the direct arc. The microphotometric record of a less intense spectrogram is also reproduced. The displaced lines are clearly seen on the microphotometric record. Most of them can also be identified on the reproduced photograph. Their positions have been marked for clarity. The Raman spectra obtained with the two diamonds are exactly similar in nature. The recorded spectra show,

TABLE I

Ser. No.	Frequency shift in cm.$^{-1}$	Intensity*	Nature	Assignment†
1	−1331·5	<1	Anti-stokes	F_2
2	1332·0	500	Fundamental	F_2
3	1925	<1	Combination	$H_1 + H_2$
4	2175·5	1	Octave	K_3^2
5	2245	1·5		
6	2267	2	Combination	$K_1 + M_1$
7	2300·5	4	Octave	H_1^2
8	2467	10		
9	2495	10	do.	H_4^2
10	2518	7		
11	2609·5	4·5	do.	M_1^2
12	2664·6	5	do.	F_2^2

* Intensity values are only approximate. † Notation taken from Bhagavantam's paper (1943).

besides the intense line with a frequency shift of 1332 cm.$^{-1}$, a host of lines of comparatively feeble intensity. The frequency shifts of the two extreme lines are 1925 and 2664·6 cm.$^{-1}$ Of these, some are rather broad, while others are sharp. The shifts of these lines have been carefully measured and are given in Table I. Rough estimates of the relative intensities of these lines have also been made and the values entered in the table. There is a weak continuum starting from a point separated by about 2300 wave numbers from the 2536 line. This continuum is sharply cut off at 2664 cm.$^{-1}$ which corresponds to the octave of 1332. Even in the most heavily exposed photographs, no trace of any Raman line having a frequency shift less than 1332 cm.$^{-1}$ could be detected. In the direct picture of the mercury arc, one notices a faint mercury line at λ 2625·2. The principal Raman line with the frequency shift of 1332 cm.$^{-1}$ falls on the top of this faint mercury line. The anti-stokes line corresponding to 1332 is also clearly recorded on the plate. The Raman line with a frequency shift of 2467 cm.$^{-1}$ unfortunately falls almost on the top of a faint mercury line in this region. This fact has been taken into account while estimating the intensity of this Raman line. The reproduced photograph shows the presence of a displaced line at 2749 A.U. which corresponds to the frequency shift of 1332 wave numbers excited by the strong mercury line λ 2652 A.U.

5. *Discussion of Results*

On the assumption that the diamond structure has octahedral (Oh) symmetry, it is possible to calculate the Raman-active frequencies of diamond. The appropriate character table for a super-lattice based on the Raman theory of crystal dynamics has been given by Bhagavantam (1943). Of the eight fundamental frequencies of oscillation which have been designated by Bhagavantam as F_2, H_1, H_2, H_4, K_1, K_3, M_1 and M_2 with degeneracies 3, 6, 6, 6, 4, 4, 8 and 8 respectively, only F_2 is active in the Raman effect, and it corresponds to the principal line of frequency shift 1332 wave numbers. The other seven modes which have frequency shifts less than 1332 cm.$^{-1}$ are inactive in light-scattering as fundamentals. This fact has been fully substantiated by the present experimental results. The use of the intense 2536 radiation and of exposures long enough to bring out the octaves, has failed to reveal the presence of any Raman line corresponding to a fundamental frequency of oscillation other than the principal one with the frequency shift of 1332 cm.$^{-1}$ Bhagavantam (1930 *a*) had reported the existence of some feeble lines on either side of the 1332 line excited by 4046 in some diamonds and by 4358 in some others. The luminescence studies of Nayar and of (Miss) Mani have shown that many fluorescent lines (some of which are sharp) fall in the regions separated by about 1100 wave numbers

from both the 4046 and 4358 mercury lines. These results together with the fact that no Raman line corresponding to a fundamental frequency of oscillation other than 1332 is excited by the 2536 radiation, suggest that the origin of the faint lines reported by Bhagavantam is in all probability fluorescence and not Raman effect.

The group characters for the various octaves and combinations have been determined and the selection rules applied for finding their activity in the Raman effect. The octaves of all the eight modes and four combinations, namely $H_1 + H_2$, $H_1 + H_4$, $K_1 + M_1$ and $K_3 + M_2$ should be Raman-active. The ten new Raman lines (see Table I) which are observed with intensities small compared with that of the principal 1332 line are therefore some of the allowed octaves and/or combinations. Of these, the line with the frequency shift of 2664·6 cm.$^{-1}$ can be easily identified as the octave of 1332, *i.e.*, F_2^2. In order to give proper assignments for the remaining nine observed Raman lines, it is necessary to know the fundamental frequencies (in wave numbers) of the various modes. The lattice frequencies which appear very prominently in the absorption and luminescence spectra of diamonds are (in wave numbers) 1332, 1283, 1251, 1149, 1088, 1013, 785 and 544. These values have been taken from the recent and more accurate measurements of (Miss) Mani. On the assumption that these represent the eight fundamental frequencies of the diamond lattice, it is possible to assign them. F_2 having the maximum and M_2 the minimum frequency, should be identified with 1332 and 544 cm.$^{-1}$ respectively. M_1 being the next highest, should correspond to 1283 cm.$^{-1}$ As the frequency of H_2 is $\sqrt{2}$ times that of M_2, 785 cm.$^{-1}$ should be assigned to H_2. Putting these values in the expressions for the frequencies given by Bhagavantam, one finds that 1251, 1149, 1088 and 1013 cm.$^{-1}$ represent the frequencies of H_4, H_1, K_3 and K_1 respectively. The Raman lines observed with frequency shifts of 2175·5, 2300·5, 2495, 2609 and 2664·6 cm.$^{-1}$ are thus the octaves of K_3 (1088), H_1 (1149), H_4 (1251), M_1 (1283) and F_2 (1332). The octave of K_1 (1013), even if present, would not be detected as it would fall roughly on the mercury line at 2675 A.U. No Raman lines have been observed corresponding to the octaves of H_2 and M_2 which have the lowest frequencies.

Next to the Raman line of frequency shift 2664·6 cm.$^{-1}$, the line at 2175·5 cm.$^{-1}$ is rather sharp and stands out clearly in the photograph. This is also true of the corresponding lattice frequency (1088 cm.$^{-1}$) in the luminescence spectrum. The octave of 1251 appears to have been split into three components in the Raman effect, these having approximately the

same intensity. The frequency shifts of these components are 2467, 2495 and 2518 cm.$^{-1}$

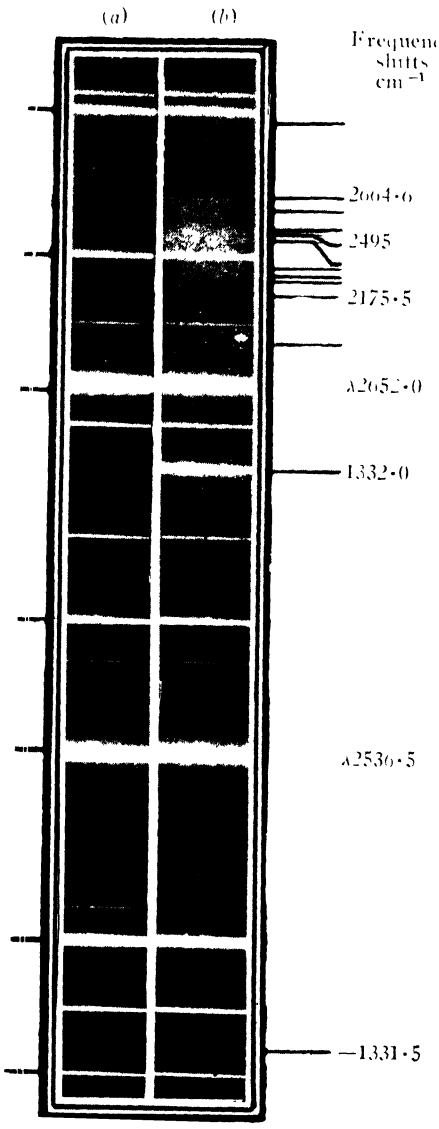
The observed Raman lines with frequency shifts of 1925 and 2267 cm.$^{-1}$ can be considered as combinations of H_1 and H_2 (1149 + 785) and of K_1 and M_1 (1013 + 1283) which are allowed in light-scattering. The combinations of H_1 and H_4 (1149 + 1283) and of K_3 and M_2 (1088 + 544), though Raman-active, could unfortunately not be detected, as the former would fall on the top of the mercury line at 2698·9 A.U., while the latter would be masked by the halation due to the intense mercury line at 2652 A.U. The microphotometric record shows other kinks which remain unassigned. It is reasonable to suggest that these represent lines due to some of the so-called forbidden combinations. They are forbidden in the Raman effect on the basis of the ordinary selection rules which are valid provided the vibrations are harmonic. But the fact that combinations and overtones appear in Raman effect shows that the amplitudes of such oscillations need not necessarily be small. When once anharmonicity sets in, the ordinary selection rules cease to be valid and more combinations become Raman-active.

The appearance of several new Raman lines in diamond as overtones and combinations of modes of oscillation of the diamond structure which are inactive as fundamentals is a direct experimental verification of the predictions of the Raman theory of crystal dynamics. These results cannot be explained satisfactorily on the basis of the Born dynamics.

In conclusion the author takes this opportunity to express his grateful thanks to Professor Sir C. V. Raman at whose suggestion the present investigation was carried out.

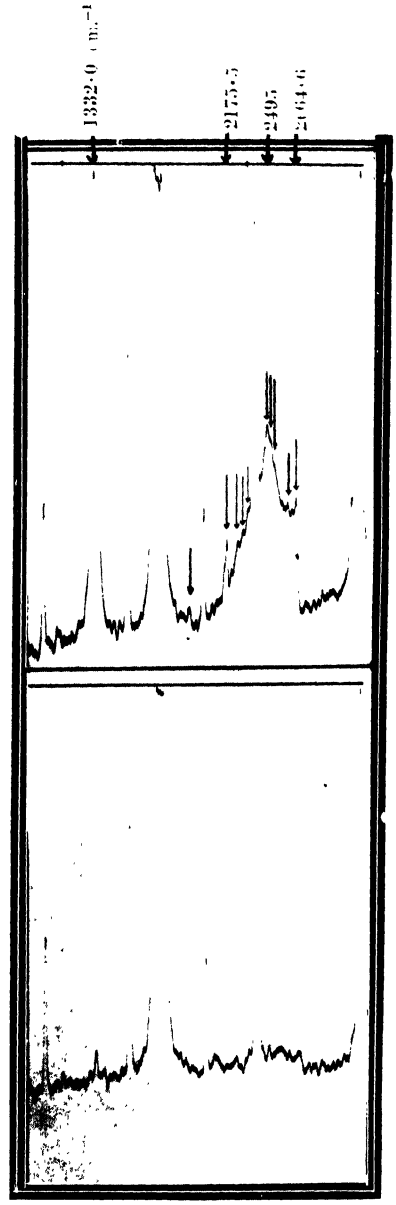
Summary

The Raman spectra of diamonds of the ultra-violet transparent type have been investigated using the 2536 resonance line of mercury as exciter. Besides the well-known 1332 Raman line, ten others with frequency shifts 1925, 2175·5, 2245, 2267, 2300·5, 2467, 2495, 2518, 2609·5 and 2664·6 cm.$^{-1}$ have been recorded. These new lines have been identified as the octaves and allowed combinations of some of the eight fundamental frequencies of oscillation of the diamond structure of which the existence is indicated by the Raman theory of crystal dynamics, but which are not themselves permitted to appear in light-scattering by reason of the selection rules.



(*a*) Mercury Spectrum
(*b*) Raman Spectrum

FIG. 1



Microphotometric Record
(*a*) Mercury Spectrum
(*b*) Raman Spectrum

FIG. 2

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THE LATTICE SPECTRUM AND SPECIFIC HEAT OF DIAMOND

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1. Introduction

The mathematical problem of finding the vibration spectrum of the atoms in a crystal about their positions of equilibrium has been solved by Sir C. V. Raman (1943) in a recent memoir, it being assumed that the external boundaries of the crystal have no sensible influence on the vibrations of high frequency under consideration. The treatment leads to the result that there are $(24p - 3)$ normal modes and frequencies of atomic vibration, p being the number of non-equivalent atoms in the crystal and $24p$ being, therefore, the total number of degrees of freedom of the atoms contained in the cell of a super-lattice which has twice the linear dimension of the cells of the crystal structure. The number of distinct frequencies is reduced by degeneracy in the case of crystals possessing symmetry elements. The particular case of the diamond lattice has been fully worked out on the basis of this theory by Bhagavantam (1943) and by Chelam (1943) by different methods which yield the same results. It is found that the diamond structure has eight distinct frequencies of atomic vibration which between them embrace 45 out of the 48 degrees of freedom of movement of the 16 atoms of carbon contained in the cell of the super-lattice.

A remarkable confirmation of the correctness of this new approach to crystal dynamics is furnished by some recent experimental work by Dr. R. S. Krishnan which is reported in another paper in this symposium. If, as is indicated by the theory, the diamond lattice has eight discrete frequencies of vibration, it should be possible to demonstrate their existence by means of the Raman effect under appropriate experimental conditions, whereas hitherto only the so-called fundamental vibration has been recorded as a frequency-shift in the Raman spectrum. Using the well-known Rasetti technique and a diamond having the requisite transparency in the ultra-violet, Raman spectra have been successfully recorded by Dr. R. S. Krishnan in which several of the additional frequencies appear as octaves as permitted

by the selection rules, though their fundamentals are not allowed. It is gratifying that the nature of the lattice spectrum as thus deduced from Raman effect data agrees with that deduced from other entirely independent methods of spectroscopic study, *viz.*, the investigation of the luminescence spectra and the absorption spectra of the diamond made by Dr. Nayar (1942) and recently in a more exhaustive way by (Miss) Anna Mani, a report of whose work appears as another paper in this symposium.

It is the purpose of the present writer to correlate the theoretical results of Bhagavantam and of Chelam with the experimental results of R. S. Krishnan, Nayar, and of (Miss) Mani, in other words, to identify the particular modes of vibration indicated by theory with the frequencies as spectroscopically observed. This enables us to ascertain the degeneracy attached to each particular observed frequency and hence to evaluate the specific heat of diamond in a manner fully justified by both theory and experiment.

2. *Identification of the Optical Frequencies*

The formulæ for the optical frequencies as given by Bhagavantam and Chelam have been reproduced in Table I where we have followed the group-theoretical designation of the former author and the force-constant notation of the latter. The force constants K and K″ arise from the mutual displacements of the neighbours and next nearest neighbours respectively, and K_α from the changes in the angle between the various valence bonds.

The most intense line at 1332 cm.$^{-1}$ in the Raman spectrum was interpreted by Ramaswamy (1930) as the fundamental lattice oscillation. The theoretical investigations of Nagendra Nath (1934), Venkatrayudu (1939) and Bhagavantam and Venkatrayudu (1939) have proved conclusively that the mode F_2 which is an oscillation of the two interpenetrating lattices of carbon atoms with respect to each other has this value. It follows from the formulæ of Table I that this is the highest lattice frequency. The two next highest frequencies taken in order evidently belong to the modes M_1 and H_4 and should satisfy the relation $\nu^2_{F_2} - \nu^2_{M_1} = \nu^2_{M_1} - \nu^2_{H_4}$. A line with a frequency shift of nearly twice 1284 has been observed by Krishnan in the Raman spectrum, while there is an indication of a line at twice 1248 also in his photographs. Both these lines have been observed by Nayar (*loc. cit.*) and (Miss) Mani (this symposium) in fluorescence and absorption. They approximately satisfy the above-mentioned difference relationship for these frequencies and there seems little doubt that they belong to the modes M_1 and H_4 respectively. The modes M_2 and H_2 should have low frequencies since they do not involve the largest force constant K, while the numerical

values of their frequencies are in the ratio $1 : \frac{1}{\sqrt{2}}$. No low frequency lines have been observed in light-scattering, but two lines at 565 and 784 satisfying the above relationship have been observed both by Nayar and (Miss) Mani, and have been assigned by us to the above two modes. The other three lines can also be assigned by inspection and have been given in Table I. In order to show that the assignment is correct, we have also given the calculated values of the frequencies in the same table. The force-constants have been calculated by approximately solving the equations for the frequencies belonging to the modes F_2, H_2 and M_2. It is seen that there is a good agreement between the theoretical and observed values. The values of the force-constants are

$$K = \cdot 314 \times 10^6 \text{ dynes cm.}$$
$$K'' = \cdot 039 \times 10^6 \quad ,,$$
$$K_\alpha = \cdot 0197 \times 10^6 \quad ,,$$

TABLE I

Lattice Frequencies of Diamond

Mode	Degeneracy	$4\pi^2\nu^2$	Calculated ν cm.$^{-1}$	Observed ν cm.$^{-1}$	Evidence
F_2	3	$\frac{8K + 64K_\alpha}{3m}$	1332	1332	Fundamental Raman and infra-red active, observed in luminescence and absorption.
H_1	6	$\frac{4K + 40K_\alpha}{3m} + \frac{8K''}{m}$	1185	1149	Octave at 2245 in Raman spectrum. Fundamental in fluorescence and absorption.
H_2	6	$\frac{12K_\alpha + 4K''}{m}$	745	784	Fluorescence and absorption.
H_1	6	$\frac{8K + 4K_\alpha}{3m} + \frac{4K''}{m}$	1200	1248	Fluorescence and absorption. Octave in Raman effect.
K_3	4	$\frac{2K + 8K''}{m}$	1153	1088	do.
K_1	4	$\frac{2(K + 32K_\alpha + 12K'')}{3m}$	1153	1013	Fluorescence and absorption.
M_1	8	$\frac{8K + 34K_\alpha}{3m} + \frac{2K''}{m}$	1269	1284	Fluorescence and absorption. Octave in Raman effect.
M_2	8	$\frac{6K_\alpha + 2K''}{m}$	527	565	Fluorescence and absorption.

3. Elastic Constants of Diamond

Nagendra Nath (1935) has investigated the relation between the elastic data and the force-constants of diamond. If we neglect the intravalence force-constant K‴, his expressions are

$$c_{11} = \frac{1}{3d}[K + 12K'' + 12K_a]$$

$$c_{12} = \frac{1}{3d}[K + 6K'' - 6K_a]$$

$$c_{44} = \frac{2}{d}[K'' + 3K_a]$$

where d is the lattice constant of diamond $= 3{\cdot}552 \times 10^{-8}$ cm. Substituting the values of the force-constants given earlier, we have

$$c_{11} = 9{\cdot}6 \times 10^{12} \text{ dyne/cm.}^2$$
$$c_{12} = 4{\cdot}0 \times 10^{12} \quad ,,$$
$$c_{44} = 5{\cdot}6 \times 10^{12} \quad ,,$$

The calculated value of the bulk modulus $\frac{1}{\kappa}$ is $\frac{1}{3}(c_{11} + 2c_{12}) = 5{\cdot}9 \times 10^{12}$ dyne/cm.^{2} This agrees well with the experimental values $6{\cdot}25 \times 10^{12}$ and $5{\cdot}56 \times 10^{12}$ determined by Adams (1921) and Williamson (1922) respectively, and is a fair check on the values of the force-constants and the assignment of frequencies.

4. Evaluation of the Specific Heat

We have now to ascertain the modes and the frequencies of the vibration which represent the three degrees of freedom of movement of the 16 atoms contained in the super-lattice cell which are left over after considering the optical modes of vibration. The exact knowledge of these modes and frequencies is of importance for the specific heat evaluation only in the lower ranges of temperature. Lacking such knowledge and in view of the fact that they represent only $\frac{1}{16}$ of the total number of degrees of atomic freedom, we may evaluate their contribution to the thermal energy by using the Debye approximation and assuming that they represent the elastic spectrum of the crystal lattice. The characteristic temperature θ_D, however, has to be altered by putting $\frac{3N}{16}$ in place of 3N in the usual Debye formula. The modified expression for it is

$$\theta_D = \frac{h}{k}\left(\frac{3N}{64\pi V}\right)^{\frac{1}{3}} v$$

where V is the atomic volume and $\bar{v}$ the average velocity obtained from

$$\frac{1}{\bar{v}^3} = \frac{1}{3}\sum_1^3 \frac{1}{4\pi}\int\int \frac{1}{v_i^3}\, d\omega$$

v_i is the velocity corresponding to the direction i and the summation is be made over the whole solid angle for all the three waves. The integ has been evaluated by Hopf and Lechner's interpolation method (19 from the above-mentioned theoretical elastic constants. The numeri value of θ_D thus obtained is 820 which has been used for the evaluation the specific heat. This is accordingly given by the formula

$$C_v = 3R\left[\sum_1^8 \sigma_s \, E\left(\frac{h\nu_s}{kT}\right) + \frac{1}{16} D\left(\frac{820}{T}\right)\right],$$

where E and D stand for Einstein and Debye functions respectively. σ_s is the statistical weight of frequency ν_s and can be obtained from the degeneracies given in Table I.

The calculated values of C_v are given in Table II. The experimental data below 273° K. have been taken from Pitzer (1938) and above that temperature from Magnus and Hodler (1926). Near the room temperature —the region common to both sets of observations—Pitzer's determinations of C_v are systematically lower than those of the other authors. The order of difference can be judged from the fact that the C_v measured by him at 276·6° K. coincides with that given by Magnus and Hodler for 273° K. If we accept the latter's result as standard, the experimental values of Pitzer given in Table II are about 5% lower near about 252° K.

Considering these facts, we find that the theoretical values follow the course of experimental data fairly closely above 200° K. It is, however, precisely this region of high temperatures where no arbitrary constants are involved in the calculation and where, therefore, the present theory is rigorously valid. The contribution of the elastic spectrum to the thermal energy reaches its limiting value at about 300° K., so that its value above this temperature is entirely determined by the optical frequencies and their degeneracies. Below 200° K, there is a small systematic deviation between the theoretical and calculated results, but owing to the increasing importance here of the contribution of the elastic branch, there are two uncertain factors involved in the calculations. In the first place, the elastic constants used in the calculation of the Debye characteristic temperature have been derived on certain simplifying assumptions about the nature of the forces between the atoms, and, secondly, the Debye function itself is only used as an approximation to represent the elastic spectrum. Further, the atomic

heats are particularly sensitive to changes of frequencies in the low-temperature region, so that small errors either in measurements of frequencies or estimation of the characteristic temperature can cause rather large deviations in the atomic heats.

TABLE II

Atomic Heats of Diamond

Temp. 0° K.	Optical frequencies	Elastic spectrum	Total C_v	Observed C_v
70·16	·0013	·0180	·0193	·022
81·59	·0046	·0280	·033	·036
105·1	·0284	·0547	·083	·079
125·3	·072	·082	·154	·138
162·8	·222	·135	·357	·318
200·9	·445	·183	·628	·595
252·4	·839	·231	1·070	1·032
273	1·014	·247	1·261	1·252
300	1·253	·263	1·516	1·520
400	2·122	·305	2·427	2·411
500	2·873	·326	3·199	3·149
600	3·442	·340	3·782	3·749
700	3·851	·348	4·199	4·222
800	4·200	·354	4·554	4·580
1000	4·630	·357	4·987	4·992
1100	4·780	·362	5·142	5·060

In the end the author wishes to express his indebtedness to Professor Sir C. V. Raman, Kt., F.R.S., N.L., for his kind suggestions and guidance in the course of the work.

Summary

The new view of crystal dynamics developed by Sir C. V. Raman indicates that the diamond lattice has eight distinct normal frequencies of vibration which comprise forty-five out of the forty-eight degrees of freedom of the atoms present in a group of eight lattice cells, while the remaining three degrees of freedom represent the elastic vibrations of lower frequency. These eight frequencies of atomic vibrations are actually observed in the Raman spectrum recorded by Dr. R. S. Krishnan and in the luminescence and the absorption spectra in the visible region investigated by Dr. P. G. N. Nayar and (Miss) Anna Mani. The modes corresponding to the observed frequencies and their respective degeneracies have been ascertained from the theoretical formulæ given by Bhagavantam and Chelam. The elastic constants have been calculated from the spectroscopic data with the aid of the same formulæ. The calculated and experimental values of the bulk modulus agree well. The thermal energy of diamond has been evaluated from the spectroscopically observed frequencies and the known degeneracies, the three degrees of

freedom not covered by these frequencies being considered as an elastic spectrum for which a formula of the Debye type with greatly reduced characteristic temperature is an approximate representation. The theoretical and experimental results agree throughout the whole range of temperature and particularly well in the temperature range between 200 and 1100° K. where the thermal energy content is principally determined by the optical frequencies of vibration.

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THE FLUORESCENCE AND ABSORPTION SPECTRA OF DIAMOND IN THE VISIBLE REGION

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1. Introduction

The luminescence of diamond has long been familiar knowledge, but spectroscopic studies of it have not been very numerous. E. Becquerel (1859) and W. Crookes (1879) were amongst the earlier observers. The latter noticed some bright lines in the spectrum of the cathode luminescence of diamond and ascribed them to the presence of foreign atoms. Walter (1891) who studied the absorption of light by diamond and noticed a dark band at 4155 A.U., also ascribed it to the presence of impurities. The luminescence of diamond appears in the spectrum along with the scattering of light when the Raman effect is studied, thus directing attention to itself [Ramaswamy (1930), Bhagavantam (1930), Robertson and Fox (1930), and Robertson, Fox and Martin (1934)]. The important observation was made by these authors that a bright line appears in luminescence which coincides with the dark line at the same wave-length noticed in absorption by Walter. John (1931) observed the cathode luminescence spectrum of diamond and found it to be very similar to that excited by ultra-violet irradiation.

Dr. P. G. N. Nayar (1941 *a*, *b*, *c*, *d*; 1942 *a*, *b*) made a notable advance by his comparative studies of the luminescence and absorption spectra of diamond over a wide range of temperatures. His investigations at liquid air temperatures, in particular, yielded highly interesting and valuable results. His most important findings were, however, made with one single strongly blue-luminescent diamond. It is well-known that diamond may also emit luminescence of other colours and that the intensity of such luminescence may vary over a wide range of values. It is therefore of importance that the investigation of the luminescence and absorption spectra should be extended to specimens showing the widest range of behaviour. Such studies may be expected to throw light on the question of the reason for such difference of behaviour and ultimately also on the general question of the nature and origin of the luminescence of diamond.

The present paper describes a detailed investigation of the fluorescence and absorption spectra of 32 diamonds from Sir C. V. Raman's collection, so selected to be as widely representative as possible of the behaviour of this substance. To enable this wide range of specimens to be successfully studied, a spectrograph of high light-gathering power combined with good resolution was found to be necessary. A two-prism Hilger glass spectrograph (E 328) was used which gave a dispersion of 28 A.U./mm. in the 4358 A.U. region and 63 A.U./mm. in the 5500 A.U. region. To study the absorption spectra under high dispersion in a few cases, a spectrograph of three-metre focal length (Hilger E 185) having a dispersion of 2 A.U./mm. in the 4200 A.U. region and 6 A.U./mm. in the 5200 A.U. region was employed.

Except with regard to the spectrographs employed, the technique of the investigation was generally similar to that followed by Nayar. A specially designed demountable Dewar flask was used to hold liquid air, and the diamonds were mounted in copper blocks screwed on to the bottom of its inner metal tube. This ensured the specimen reaching and remaining at the liquid air temperature. The source of ultra-violet light was a small carbon arc run at 5 amperes, the light from it being filtered through a plate of Wood's glass. The fluorescent light was focussed on the slit of the spectrograph by a short-focus cylindrical lens. The light-source for the absorption studies was a gas-filled incandescent lamp with a straight filament run at 30% more than the usual voltage. In every case, the diamonds were set so that the maximum thickness was employed. The spectra were photographed on Ilford selochrome plates in the blue region of the spectrum, on Ilford HP_2 plates in the green, and on Kodak extra-rapid infra-red plates in the red.

The fluorescence spectrum of each diamond was recorded both at room and at liquid air temperature, while the absorption spectrum was similarly recorded in each case with a graded series of exposures. In all, some 67 fluorescence spectra and 590 absorption spectra were obtained. Except where specifically mentioned, however, the data given in the paper always refer to the measurements of the plates taken at liquid air temperature.

2. *Description of the Diamonds*

As mentioned above, the 32 specimens chosen for examination covered a wide range of behaviour. Four of them were totally non-fluorescent; sixteen showed a blue luminescence with intensities ranging from extreme brilliance to almost complete invisibility; seven showed a greenish-blue and five a greenish-yellow fluorescence, in each case with widely different

intensities. By placing all the diamonds together under the ultra-violet lamp they could be sorted out, and those in each class of luminescence arranged in order of their apparent brightness. Table I shows the catalogue numbers of the 32 diamonds arranged in the order of decreasing intensity of luminescence as visually observed. The twelve diamonds with catalogue numbers between D1 and D30 were crystals from Panna in their natural state. Ten of the other diamonds were cleavage plates with their faces polished flat, while the rest had been fashioned into different shapes for use as jewellery.

TABLE I

List of Diamonds Studied

Diamonds which were non-fluorescent : (4)

D39	D206	D207	D227	
6·6	7·2	6·8	11·2	millimetres

Diamonds showing a blue fluorescence : (16)

D223	D224	D40	D226	D34	D27	D32	D3	
4·4	8·7	4·6	3·8	9·2	7·0	11·5	7·0	millimetres
D8	D38	D33	D43	D42	D36	D221	D31	
6·0	7·6	7·6	7·8	7·7	8·4	8·2	10·0	millimetres

Diamonds showing a greenish-blue fluorescence : (7)

D225	D4	D15	D10	D11	D7	D47	
10·3	7·9	6·7	8·9	6·2	6·7	4·4	millimetres

Diamonds showing a greenish-yellow fluorescence : (5)

D13	D12	D19	D1	D197	
6·5	5·0	5·0	9·8	9·4	millimetres

The great majority of the non-fluorescent and blue-fluorescent stones were colourless as seen in daylight. The exceptions were the following: in the non-fluorescent class, D227, a rod-shaped diamond with a slight brownish tinge; in the blue-fluorescent class, D226, a small brilliant with a lively pink colour; D27, a grey hexakis-octahedron from Panna; D32, a heart-shaped diamond with a distinct yellow tinge.

On the other hand, the majority of the diamonds with a greenish-blue or greenish-yellow fluorescence showed various shades of brown or yellow or yellowish brown difficult to describe exactly. The exceptions were D47, a small colourless octahedron with an extremely feeble bluish-green fluorescence, and the two diamonds D225 and D13 which exhibited a greenish tint by daylight, possibly due to their fluorescing with that colour.

The maximum linear dimension (in millimetres) of each diamond has been entered under it. This is of importance, as it influences the observed results, especially in the case of the absorption spectra.

3. General Results of the Investigation

Nayar's published studies (*loc. cit.*) relate to the class of diamonds which exhibit a blue fluorescence of greater or less intensity. Such diamonds show a bright band in luminescence at 4156 A.U. and a dark band in absorption at the same wave-length. A summary of the results obtained by him with regard to the fluorescence and absorption spectra of such diamonds appears in the preface to his doctorate thesis. It is useful to quote the same here *in extenso*, in view of its bearing on the present investigations and to enable it to be better appreciated how the latter have advanced our knowledge of the subject.

" The fluorescent band at 4156 Å varies enormously in intensity between different diamonds, but is nevertheless found to be present with every one of the specimens examined, and is thus evidently characteristic of diamond. The 4156 band occurs also in absorption, the peak of intensity coinciding exactly with that observed in fluorescence, and the intensity varying with the specimen studied in precisely the same fashion. Both in absorption and fluorescence, the 4156 band sharpens at liquid air temperature, shifting to 4152 Å and appears resolved into a close doublet. On the other hand, at higher temperatures, there is a shift to greater wave-lengths, the band becomes progressively more diffuse, and fades off to invisibility above 600°K.

" The 4156 Å band in the spectrum is accompanied by subsidiary bands between 4156 Å and 4900 Å in fluorescence, and between 4156 Å and 3600 Å in absorption. These are present strongly in crystals in which the 4156 band is intense. The bands in absorption exhibit a perfect mirror image symmetry about the 4156 frequency with respect to the bands observed in fluorescence. When the diamond is cooled to liquid air temperature, and the bands are examined under high dispersion, they appear resolved into a spectrum of discrete frequencies. The frequency shifts from the principal band at 4152 Å in fluorescence and in absorption are found to be exactly equal but of opposite sign. They lie in the infra-red range, indicating that the subsidiary bands arise from a combination of certain infra-red or atomic vibrations with the electronic frequency manifesting itself both in emission and absorption at 4152 Å.

" The 18 discrete infra-red frequencies ranging from 137 cm.$^{-1}$ to 1332 cm.$^{-1}$ deduced as explained above from the fluorescence and absorption spectra of diamond at low temperature, are interpreted as the characteristic

vibration frequencies of the diamond lattice. This interpretation is confirmed by the agreement of the frequency shifts with the Raman effect data reported by Bhagavantam, and with the infra-red absorption frequencies reported by Julius, Reinkober and by Robertson *et al.* The fact that the lattice spectrum of diamond consists of 18 discrete frequencies covering such a wide range, is evidently irreconcilable with the assumptions on which the Debye theory of specific heats is based."

* * * * * * *

The present investigation shows the appearance of a *second system of subsidiary bands which may be designated as the* 5032 *system* to distinguish it from the 4152 system described in Nayar's thesis. As will be set out later in the paper, this 5032 system is related to a line observed at 5032 Å, appearing at longer wave-lengths in emission and at shorter wave-lengths in absorption in a manner generally analogous to, but differing in important details from the relation between the 4152 system and the 4152 Å line. The important point is that both the 4152 and 5032 systems appear in the fluorescence and absorption spectra, but that their relative as well as their absolute intensities vary enormously from diamond to diamond. The great differences in the intensity and colour of the light emitted by different stones as perceived by the unaided eye arise from these variations. These points are illustrated by the five fluorescence spectra reproduced as Fig. 8 in Plate X appearing at the end of the paper. The spectra were those obtained with two diamonds of the blue-fluorescing type, two of the greenish-blue and one of the yellowish-green fluorescing type.

Another important result of the present investigation has been to show that besides the 4152 and 5032 lines and the bands which accompany them in luminescence and in absorption, there are numerous other lines which are quite sharply defined at liquid air temperature and of which the positions as observed in emission and in absorption coincide. These are interpreted as electronic frequencies. No fewer than 36 such lines have been recorded in the present investigation, their wave-lengths ranging between 3934 and 6358 Å. They may roughly be divided into two groups, the behaviour of which in respect of intensity is similar to that of the 4152 and 5032 systems respectively in the spectra.

The present investigation also shows that the relations between emission and absorption observed by Nayar in respect of the 4152 line and its associated bands are much more general, and extend also to the lines and bands of the 5032 system and to the numerous other electronic frequencies mentioned above. A particular case of this correlation which is of great importance is that of the non-fluorescent diamonds. It has been found that

these show no trace of any absorption lines in the visible spectrum even under the most favourable conditions, namely with the longest possible absorption paths and the exposures most suitable for their detection. No trace of any emission lines, either, appears with such diamonds even after prolonged exposures.

Still another interesting result of the present investigation is that the doublet structure of the 4152 line detected in *absorption* by Nayar in a particular diamond is observable also in the *emission spectra* of numerous diamonds. Further, it has been found that the width and separation of the components of the doublet varies from diamond to diamond in a manner generally related to the intensity of the luminescence of the specimen.

4. The Colour of Fluorescence and its Spectrum

The 22 diamonds whose fluorescence spectra have been studied may be arranged in the order of the *relative* intensities of the band systems accompanying the 4152 and 5032 lines, beginning with those in which the former is the principal feature while the latter is barely recorded, and ending with those in which the 5032 system is much more prominent than the 4152 system. It should be mentioned that in no case does the 5032 system appear in the spectrum without the 4152 system being also recorded.

TABLE II

Order of Relative Intensities of the 4152 *and* 5032 *Systems in Emission*

D33,	D8,	D27,	D36,	D38,	D34,	D40,	D42,	D223,	D224,	D32,
D12,	D226,	D3,	D225,	D7,	D4,	D47,	D15,	D1,	D13,	D19

Examining this list and comparing it with Table I, it will be noticed that all the diamonds which appear earliest in Table II are those classified as blue-luminescent in Table I, while those which appear last are mostly those shown in it as having a greenish-yellow luminescence. The diamonds shown in Table I as giving a greenish-blue fluorescence appear somewhere midway between the beginning and the end of the list in Table II. There are a few anomalies, *e.g.*, D12 appears high up in the list instead of towards the end. The order in which the blue-fluorescent diamonds appear in Table II is also not the same as that in which they are shown in Table I. It is quite clear, however, on a comparison of the two tables that the difference in the relative intensities of the 4152 and 5032 band systems in the spectrum is the origin of the differences in the colour of the fluorescence as visually observed.

5. Relation between Fluorescence and Absorption

The intensity of the luminescence of diamond varies enormously. An idea of the range of this variation may be obtained by phtographing a

group of stones with a series of graded exposures and counting the number rendered visible by their luminescence. Such photographs also enable a large group of diamonds to be sorted to small groups of approximately equal brightness and their relative intensities to be estimated microphotometrically. The figures obtained in this way for a group of 88 South African diamonds are:—

5(0), 2(1), 4(3), 9(10), 16(20), 4(30), 14(50), 7(100), 6(200), 4(400), 3(700), 2(1,000), 6(1.800), 3(3,000), 1(5,000), 1(10,000), 1(12,000).

It will be seen that the majority of the diamonds have small intensities of fluorescence, while a few exhibit intense luminescence or else are entirely non-fluorescent.

The diamonds whose emission and absorption spectra have been studied in the present investigation exhibit similar variations in their intensities of luminescence. While the spectra of the most intensely fluorescent diamonds were recorded in a few minutes, to photograph the emission spectrum of the weakly fluorescent diamonds, long exposures of the order 15 to 20 hours were found to be necessary even when thinner plates of Wood's glass and broader slits were used, and the source of light was brought much nearer the diamond.

Accompanying these large differences in the intensities of luminescence, we have corresponding differences in the intensity of absorption of the electronic lines, especially those at the wave-lengths 4152 and 5032. There is also a corresponding increase in the intensity of the subsidiary absorption bands associated with these two electronic lines and appearing towards shorter wave-lengths. It should be mentioned that if the diamonds are arranged in the order of the relative intensities of the two systems of bands as they appear in absorption, the list would be the same as Table II. The absolute intensities of absorption would, however, depend on the length of the absorbing column and cannot therefore be directly compared unless the latter is equal.

Figs. 9 and 10 in Plate XI illustrate the 4152 and 5032 systems respectively, as seen in absorption in a sequence of seven diamonds in one case, and a sequence of five in the other. We have only to compare the spectra of D36 and D224 in Fig. 9 or those of D1 and D197 in Fig. 10 to realise that great differences in the strength of absorption go hand in hand with the differences in the intensity of luminescence. It is not unlikely that the absorption coefficients for the electronic lines are proportional to the intensity of their emission and that the subsidiary band-systems also vary proportionately in intensity. No quantitative measurements have, however, been made to test these points.

It is important to remark that the intensity with which *the 4152 and 5032 electronic lines* are actually recorded in emission would be affected by the absorption of these same radiations before they emerge from the diamond. Hence, the apparent intensities of these lines as recorded in the spectra would not be proportional to the intensity of the luminescence as visually observed, especially when considerable thicknesses are involved. The subsidiary bands accompanying the electronic lines are a better criterion for the visually observed intensity of luminescence. The effect of self-reversal in reducing the intensity of the 4152 and 5032 lines compared with that of the band systems accompanying them is clear on an inspection of several of the spectrograms reproduced in Figs. 1, 7 and 8 in Plates VIII and X. This is also startlingly evident in the emission spectrum of D32 reproduced in Fig. 7, where the 4152 line has completely disappeared due to self-reversal in passing through a thickness of over one centimeter of diamond.

6. The Electronic Frequencies

In the fluorescence spectra taken at liquid air temperature, the presence is noticed of several sharply defined lines, besides those at 4152 and 5032 Å and the emission band-systems associated with these which appear at longer wave-lengths. The absorption spectra of luminescent diamonds similarly show several sharply defined dark lines other than 4152 and 5032 and the absorption band-systems associated with these toward shorter wave-lengths. When the absorption and emission spectra are compared, the positions of the bright and dark lines respectively noticed in them are found to coincide, and their identification as distinct electronic frequencies is thereby confirmed.

It must not be supposed, however, that an electronic absorption line would necessarily be observable in the same position in the spectrum as every electronic emission line. The effective absorption dependson the luminescent intensity of the diamond, the intrinsic strength of the electronic absorption and the length of the path available, and when these factors (or all of them working together) make the effective absorption very small, the absorption line in the spectrum would be overpowered by the transmission on either side of it and become unobservable. In general, therefore, a weak electronic line would be more easily observed in emission than in absorption, and only the strongest electronic lines could be expected to be recorded with very weakly luminescent diamonds, unless very long absorption paths are available. Another inherent difficulty in observing weak electronic lines arises when the region in which they appear coincides with the regions in which the subsidiary bands associated with the 4152 and 5032 lines appear.

The latter regions are fortunately different in emission and in absorption, and the relative intensity with which the two systems appear differs greatly with different diamonds. These facts and the sharpness and intensity of the electronic lines are an aid to their discrimination from the background of the band-system on which they may appear superposed.

The foregoing remarks will enable the results shown in Appendices I and II at the end of the paper to be better understood. These appendices give a list of the electronic lines observed in the emission and absorption spectra of the 28 diamonds investigated. Where a column has been left blank under either emission or absorption, it is to be understood that the same has not been studied. The figures recorded in these tables reveal the following features:—

(*a*) The most strongly luminescent diamonds show the largest number of electronic lines, and the number of such recorded in emission is generally greater than in absorption, for the reasons already explained.

(*b*) The blue-fluorescing diamonds show characteristic electronic lines at the wave-lengths 4090, 4109, **4152, 4189. 4197, 4206, 4959** and **5032** Å.

(*c*) The yellow-fluorescing diamonds show characteristic electronic lines at the wave-lengths 4060, 4123, **4152, 4194,** 4222, 4232, **4277, 4907,** 5014, **5032, 5359,** 5658, 5695, **5758,** 6177, 6265 and 6358 A.U.

The more intense lines are printed in heavy type. They may be recognised in the spectrograms reproduced in the Plates. Fig. 11(*a*), (*b*) and (*c*) indicate diagrammatically the changes of the electronic spectrum occurring in the transition from yellow to blue fluorescence. While the diagram represents the facts generally both as regards the positions of the lines and (qualitatively) also their relative intensities, individual diamonds show peculiarities of behaviour, as will be seen from the data given in Appendices I and II. For instance, D42 shows 4907, 6177, 6265 and 6358 but not 4959, 5359 or 5758. Then again, D13 shows strong lines at 4388 and 4833, D32 a strong line at 5895, and D47 strong lines at 4175 and 6043 which are not usually observed in other diamonds. A remarkable observation worthy of special mention is the appearance of an extremely sharp and intense absorption line at 3934 Å with D225 and D36.

7. *Structure of the* 4152 *and* 5032 *Lines*

In one particular diamond, the 4152 line in absorption was observed by Nayar to exhibit a doublet structure. In the present investigation it is

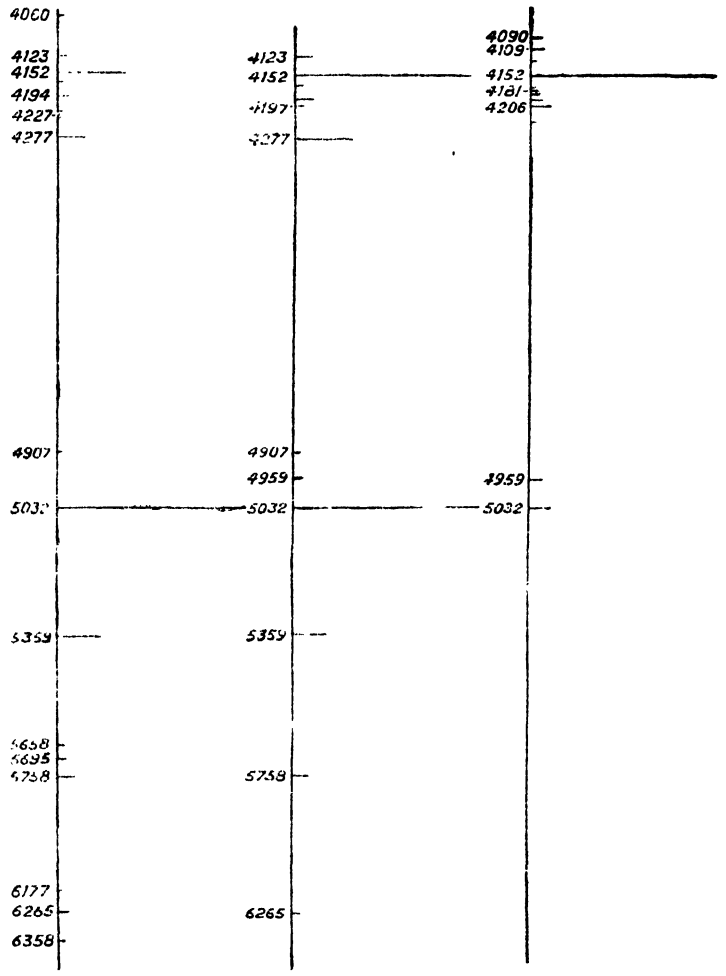

FIG. 11. Electronic Spectrum of Diamond for (*a*) yellow, (*b*) green and (*c*) blue fluorescence.

found that in most diamonds the 4152 line appears as a doublet with widely separated components in both emission and absorption. The width and separation of the components generally increases with the intensity of luminescence. In very weakly fluorescent diamonds, the doublet is so close as to be scarcely resolved. With increasing intensities of luminescence, the separation as well as the width of each component increases, so that in the most intensely fluorescent diamonds the 4152 line is the most diffuse and the separation of the components the largest. This is strikingly illustrated in Fig. 13, Plate XII, where the microphotometer tracings of the 4152

line for 6 diamonds of increasing intensities of blue luminescence are reproduced. Table III gives the wave-lengths, width and separation of the two components of the 4152 line for 13 diamonds. It will be noticed that the two components always appear centred about the mean wave-length at 4152 A.U. and that the line is thus symmetrically split with regard to the positions of the two components. The intensity and the width of the component of longer wave-length are, however, larger than those of the component of shorter wave-length.

TABLE III

Structure of the 4152 *Line*

Number of Diamond	Component I		Component II		Separation in A.U.
	Wave-length in A.U.	Width in A.U.	Wave-length in A.U.	Width in A.U.	
D223	4155	3	4149	3	6
D224	4156	3	4150	2	6
D27	4155	3	4149	2	6
D40	4155	2	4149	2	6
D226	4155	5	4150	4	5
D42	4154	3	4149	2	5
D225	4154	3	4150	2	4
D34	4154	3	4151	3	3
D3	4153	2	4151	2	2
D38	4153	2	4151	2	2
D15	4153	2	4151	2	2
D13	4153	2	4151	1	2
D4	4153	2	4151	1	2

The four diamonds D3, D33, D34 and D226 appear to be exceptions to the general rule stated above as existing between the intensity of luminescence and the structure of the 4152 line. In D3, D33 and D34, the separation of the components is not as high as we might expect from their luminescence intensity. In D226 the two components of the 4152 doublet are extremely broad and more diffuse than in D223 or D224. It is likely that D226 owes its pink colour to some extraneous impurities and that these are responsible for the observed diffuseness of the line. It should be remarked however,

that in the case of diamonds showing a tinge of yellow or brown colour, impurities if present, appear to have no effect on the sharpness of the electronic lines.

In the case of two diamonds D223 and D225, it was observed that different portions of the same diamond give the 4152 line respectively as a well-separated doublet and as a single line. In D223, where the 4152 appears as a line, it is accompanied by two wings of high intensity extending to 4 A.U. on either side. D225 showed in the same spectrogram the upper portions of the doublet clearly split, while in the lower portion the two components were very close to each other. These observations become intelligible when it is remembered that in many cases diamonds show definite regions of both high and low luminosity and patterns of blue and green fluorescence. The weakly blue-fluorescent portions of the same diamond will show 4152 as a close doublet or a single line, while with the strongly fluorescent parts it will appear as a well-separated doublet.

Under the high dispersion of the three-metre spectrograph and at liquid air temperature the 4152 line in D42 appears as a triplet, the central line at 4152·2 A.U. being very much sharper and fainter than the two outer components. Absorption photographs of the 4152 line taken at room temperature and at liquid air temperature respectively on the three metre spectrograph are reproduced in Fig. 3(*a*) and (*b*) Plate VIII.

The principal electronic line appearing in fluorescence and absorption at 5032 A.U., on the other hand, does not alter in its width and structure with variations in the intensity of luminescence. As will be noticed in the photographs of the 5032 system for different diamonds reproduced in Fig. 8 (emission) and Fig. 10 (absorption), there is no marked broadening of the line as the intensity of yellow luminescence increases, the width of the line in the strongest and weakest fluorescing diamonds being approximately the same, *viz.*, 7 to 8 A.U. In all yellow-fluorescing diamonds, with the exception of D1, D13 and D15 where it appears as a very close doublet, 5032 is present as a single line. Absorption spectra taken on the three-metre spectrograph also failed to reveal any clear splitting of the 5032 line. No definite relationship thus seems to exist between the intensity of yellow luminescence and the structure of the 5032 line. In D226, the 5032 line as well as the other electronic frequencies at 4206, 4388 and 4959 are broader than in other diamonds. This, as mentioned before, is to be ascribed to probable impurities in this diamond.

8. *The Lattice Spectrum of Diamond*

(*a*) *The 4152 System.*—The wave-lengths, intensities and frequencies of the principal electronic line at 4152 and the associated subsidiary bands

in both fluorescence and absorption are given in Table IV. Column 6 gives the descriptions of the lines and bands, and columns 5 and 9 the frequency differences of the subsidiary bands from 4152 in fluorescence and absorption respectively. The microphotometer tracing of the 4152 system in emission for D4 is reproduced in Fig. 14 Plate XIII, and the prominent lattice frequencies indicated by their frequency shifts. The bands are numbered from II to XI, extending to 4825 A.U. in fluorescence and to 3730 A.U. in absorption. The continuous spectrum in fluorescence lies between 4110 and 6500 A.U. A number of new lines have been observed in the present investigation, *viz.*, 4158, 4164, 4169, 4189, 4215, 4248, 4279, 4373, 4386 and 4401 in fluorescence and 4140, 4135, 4123, 4116, 4109, 4092, 4060, 3952 and 3930 in absorption. The bands X and XI in fluorescence could not be obtained in absorption, owing to the lack of sensitiveness of the selochrome plates in the 3500–3700 Å region.

An examination of the 4152 system in both emission and absorption reveals that though the intensity of the subsidiary bands relative to that of 4152 varies from diamond to diamond, the relative intensities of the lattice bands among themselves are constant. The only exception to this rule is the first subsidiary band II which generally consists of two faint lines at 4164 and 4169 in fluorescence and at 4140 and 4135 in absorption. In D47 this appears as a fairly intense band with limits at 4158 and 4169 and is observed in D3, D4, D19, D40 and D225 but weakly. This band is however present in fluorescence and absorption with identical frequency shifts in both the 4152 and 5032 systems and hence 34, 70 and 98 cm.$^{-1}$ are classed as genuine lattice frequencies.

The lattice lines at 4060, 4109, 4175, 4189, 4197 and 4304 coincide with electronic lines present at the same wave-lengths and this is evidently responsible for the observed small variations in the relative intensities of these lines.

A number of lines which could not be classified with any certainty as either lattice or electronic lines are listed separately in Table V.

D32 exhibits the lattice spectrum in absorption also at wave-lengths greater than 4152. The bands in absorption at longer wave-lengths disappear at low temperatures and are therefore probably thermally excited. D32 also exhibits three broad bands in absorption with approximate limits at 4494 and 4538, 4602 and 4701 and 4758 and 4794 A.U., which are apparently unrelated to either the 4152 or 5032 systems. The last one at 4776 A.U. is the most intense of the three and appears in the fluorescence spectrum as a dark band.

TABLE IV

Lattice Spectrum in the 4152 System

No.	Fluorescence: Wavelength in A.U.	Intensity	Frequency in cm.$^{-1}$	Frequency differences from 4152	Description of the Bands	Absorption: Wavelength in A.U.	Frequency in cm.$^{-1}$	Frequency differences from 4152 in cm.$^{-1}$
	4152	20	24077	..	Intense line	4152	24077	
	4158	½	24043	34	Sharp edge			
	4164	½	24009	68	Discrete line	(4140)	24148	(71)
	4169	½	23980	97	Discrete line	(4135)	24177	100
III	4175	½	23945	132	Sharp limit	4130	24206	131
	4183	1	23900	177	Discrete line	(4123)	24247	(170)
	4189	½	23865	212	Discrete line	(4116)	24288	(211)
	4197	1	23820	257	Discrete line	(4191)	24330	(253)
	4215	1	23718	359	Discrete line	(4092)	24431	(354)
	4230	1	23634	443	Sharp limit	4077	24521	444
IV	4246	3	23545	532	Very sharp edge	4062	24611	533
	4248	4	23534	543	Discrete line	4060	24624	544
	..	..	..	..	Discrete line	4057	24642	565
	4273	5	23396	681	High int. edge	4038	24758	681
	4279	5	23363	714	Discrete line	4032	24795	717
	4292	6	23293	784	Sharp edge	4021	24862	785
V	4304	½	23228	849	Discrete line	4011	24924	847
	4322	1	23131	946	Discrete line	3995	25024	947
	4334	3	23067	1010	Discrete line	3984	25093	1016
	4349	4	22987	1090	Discrete line	3973	25163	1086
VI	4357	3	22945	1132	Sharp edge	3966	25207	1130
	4360	4	22929	1148	Discrete line	3963	25226	1149
	4373	4	22861	1216	Discrete line	(3952)	25296	1219
	4380	5	22825	1252	Discrete line	3947	25328	1251
	4386	5	22793	1284	Discrete line	3942	25360	1283
	4395	6	22747	1330	Discrete line	3935	25406	1329
	4397	5	22736	1341	Sharp edge	3933	25419	1342
VII	4401	2	22716	1361	Sharp line	3930	25438	1361
	4406	2	22690	1387	Sharp limit	3927	25457	1380
	(4461)	1	22410	(1667)	Limit approx.	(3890)	25700	(1623)
VIII	(4490)	2	22265	(1812)	Limit approx.	(3865)	25865	(1788)
	(4511)	3	22162	(1915)	Peak approx.	(3850)	25967	(1890)
	(4547)	3	21986	(2091)	Limit approx.	(3827)	26123	(2046)
IX	(4611)	2	21681	(2396)	Limit approx.	(3782)	26434	(2357)
	(4635)	2	21569	(2508)	Peak approx.	(3758)	26602	(2525)
	(4667)	2	21421	(2656)	Limit approx.	(3742)	26716	(2639)
X	(4678)	1	21370	(2707)	Limit approx.	..	..	..
	(4700)	1	21271	(2806)	Peak approx.	..	..	..
	(4710)	1	21225	(2852)	Limit approx.	..	..	..
XI	(4760)	1	21002	(3075)	Limit approx.	..	..	..
	(4795)	1	20849	(3228)	Peak approx	..	..	..
	(4825)	1	20719	(3358)	Limit approx	..	..	..

N.B.—The figures within brackets refer to lines which are doubtful or to those whose frequencies could not be measured accurately.

The sharpness of the lattice lines in the 4152 system is closely associated with the structure of the 4152 line. In strongly fluorescing diamonds where the 4152 is broad and diffuse, the lattice lines are broad and the edges of the bands slightly diffuse, while in weakly fluorescent diamonds, where the 4152 is sharp, the lattice lines and edges are correspondingly sharp. This is clearly seen in the spectra of D3, D1, D42 and D225 in the Plates and may more readily be noticed in the case of the lines at 4334 and 4349 which are a prominent feature of every spectrum. In D226, these two lines are scarcely observable owing to their diffuseness. In D3 and D1 they are seen to be very sharp. The variations in the breadth of the lattice lines with the broadening and splitting of the 4152 line suggest that both components of the doublet are capable of exciting the lattice frequencies. Therefore the procedure adopted in Table IV of considering neither of the components but the central wave-length at 4152 as responsible for exciting the lattice spectrum appears justified.

TABLE V

Unassigned Frequencies

No.	Wave-length of lines in		Diamonds in which present	Frequency in cm.$^{-1}$
	Emission	Absorption		
1	5128	..	D225	19495
2	4200	..	D3	23803
3	4310	..	D223	23195

(*b*) *The* 5032 *System.*—Preliminary investigations by Nayar on the yellow luminescence and absorption of diamond had shown that the fluorescence spectrum is similar to that in the blue and consists of a principal band accompanied by subsidiary bands at longer wave-lengths in fluorescence and at diminished wave-lengths in absorption. A photograph of the 5032 system in emission and absorption taken by Nayar is reproduced in an article by Sir C. V. Raman in *Current Science* for January 1943.

At room temperature the principal electronic line lies at 5038 A.U. and is about 15 A.U. broad. The subsidiary bands, as will be seen in Fig. 5(*a*), are correspondingly broad and diffuse. As the temperature is lowered, both the main and subsidiary bands become more intense and sharper and shift towards shorter wave-lengths. The peak of the band at liquid air temperature as determined by a microphotometer curve was found to be at 5032·0 A.U. Descriptions of the bands, their wave-lengths, intensities

and frequencies are given in Table VI for both emission and absorption. Columns 5 and 9 give the frequency shifts of the subsidiary bands from 5032 in fluorescence and absorption respectively. A microphotometer tracing of the 5032 system in emission is reproduced in Fig. 15, Plate XIII.

TABLE VI

Lattice Spectrum in the 5032 System

No.	Fluorescence				Description of the Bands	Absorption		
	Wavelength in A.U.	Intensity	Frequency in cm.$^{-1}$	Frequency Shifts from 5032 in cm.$^{-1}$		Wavelength in A.U.	Frequency in cm.$^{-1}$	Frequency Shifts from 5032 in cm.$^{-1}$
I	5032	20	19867	..	Intense line	5032	19867	..
II	5040	4	19836	31	Sharp limit	..	..	..
	(5049)	4	19800	(67)	Fall in intensity	(5015)	19934	(67)
	(5056)	2	19773	94	Diffuse limit	(5009)	19958	(91)
III	(5062)	2	19750	(117)	Diffuse limit	(5002)	19986	(119)
	(5080)	4	19680	(187)	Rise in intensity	(4985)	20054	(187)
	(5100)	7	19602	(265)	Further rise in intensity	(4966)	20131	(264)
	(5130)	7	19488	(379)	Fall in intensity	(4930)	20278	(411)
	(5144)	3	19435	(432)	Diffuse limit	(4920)	20320	(453)
IV	(5170)	3	19337	(530)	Diffuse limit	(4900)	20402	(535)
	(5180)	5	19300	(567)	Rise in intensity	(4890)	20444	(577)
	..	..	..	..	..	..	..	..
	(5216)	5	19166	(701)	Fall in intensity	..	..	..
	(5230)	3	19115	(752)	Diffuse limit	(4840)	20655	(788)
V	(5260)	2	19006	(861)	Diffuse limit	(4825)	20720	(853)
	(5284)	3	18920	(947)	Rise in intensity	..	..	..
	(5304)	3	18848	(1019)	Fall in intensity	(4788)	20880	(1013)
	(5320)	2	18792	(1075)	Diffuse limit	(4768)	20967	(1100)
VI	(5335)	1	18739	(1128)	Fairly sharp limit	(4762)	20994	(1127)
	5341	2	18718	1149	Sharp line	4757	21016	1149
	5372	3	18610	1257	Sharp limit	4733	21122	1255
	5381	2	18579	1288	Sharp limit	4727	21149	1282
	5393	2	18537	1330	Sharp limit	4716	21198	1331
	(5397)	1	18524	(1343)	Fairly sharp limit	(4713)	21212	(1345)
VII	(5420)	2	18445	(1422)	Limit approx.	(4692)	21307	(1440)
	(5455)	2	18327	(1540)	Peak approx.	(4673)	21394	(1527)
	(5492)	2	18203	(1664)	Limit approx.	(4645)	21522	(1655)
VIII	(5520)	1	18110	(1757)	Limit approx.	(4611)	21681	(1814)
	(5560)	1	17980	(1887)	Peak approx.	(4588)	21790	(1923)
	(5602)	1	17846	(2021)	Limit approx.	(4566)	21895	(2028)
IX	(5639)	1	17729	(2138)	Limit approx.	..	..	..
	..	..	..	..	Peak approx.	(4468)	22375	(2508)
	..	..	..	..	..	..	..	..

The sharpness of the lattice lines in the 4152 system is closely associated with the structure of the 4152 line. In strongly fluorescing diamonds where the 4152 is broad and diffuse, the lattice lines are broad and the edges of the bands slightly diffuse, while in weakly fluorescent diamonds, where the 4152 is sharp, the lattice lines and edges are correspondingly sharp. This is clearly seen in the spectra of D3, D1, D42 and D225 in the Plates and may more readily be noticed in the case of the lines at 4334 and 4349 which are a prominent feature of every spectrum. In D226, these two lines are scarcely observable owing to their diffuseness. In D3 and D1 they are seen to be very sharp. The variations in the breadth of the lattice lines with the broadening and splitting of the 4152 line suggest that both components of the doublet are capable of exciting the lattice frequencies. Therefore the procedure adopted in Table IV of considering neither of the components but the central wave-length at 4152 as responsible for exciting the lattice spectrum appears justified.

TABLE V

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No.	Wave-length of lines in		Diamonds in which present	Frequency in cm.$^{-1}$
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3	4310	..	D223	23195

(*b*) *The* 5032 *System.*—Preliminary investigations by Nayar on the yellow luminescence and absorption of diamond had shown that the fluorescence spectrum is similar to that in the blue and consists of a principal band accompanied by subsidiary bands at longer wave-lengths in fluorescence and at diminished wave-lengths in absorption. A photograph of the 5032 system in emission and absorption taken by Nayar is reproduced in an article by Sir C. V. Raman in *Current Science* for January 1943.

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and frequencies are given in Table VI for both emission and absorption. Columns 5 and 9 give the frequency shifts of the subsidiary bands from 5032 in fluorescence and absorption respectively. A microphotometer tracing of the 5032 system in emission is reproduced in Fig. 15, Plate XIII.

TABLE VI

Lattice Spectrum in the 5032 System

No.	FLUORESCENCE				Description of the Bands	ABSORPTION		
	Wave-length in A.U.	Intensity	Frequency in cm.$^{-1}$	Frequency Shifts from 5032 in cm.$^{-1}$		Wave-length in A.U.	Frequency in cm.$^{-1}$	Frequency Shifts from 5032 in cm.$^{-1}$
I	5032	20	19867	..	Intense line	5032	19867	..
II	5040	4	19836	31	Sharp limit	..	..	..
	(5049)	4	19800	(67)	Fall in intensity	(5015)	19934	(67)
	(5056)	2	19773	94	Diffuse limit	(5009)	19958	(91)
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	(5080)	4	19680	(187)	Rise in intensity	(4985)	20054	(187)
	(5100)	7	19602	(265)	Further rise in intensity	(4966)	20131	(264)
	(5130)	7	19488	(379)	Fall in intensity	(4930)	20278	(411)
	(5144)	3	19435	(432)	Diffuse limit	(4920)	20320	(453)
IV	(5170)	3	19337	(530)	Diffuse limit	(4900)	20402	(535)
	(5180)	5	19300	(567)	Rise in intensity	(4890)	20444	(577)
	..	..	..	..	..	..	..	..
	(5216)	5	19166	(701)	Fall in intensity	..	..	..
	(5230)	3	19115	(752)	Diffuse limit	(4840)	20655	(788)
V	(5260)	2	19006	(861)	Diffuse limit	(4825)	20720	(853)
	(5284)	3	18920	(947)	Rise in intensity	..	..	..
	(5304)	3	18848	(1019)	Fall in intensity	(4788)	20880	(1013)
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VI	(5335)	1	18739	(1128)	Fairly sharp limit	(4762)	20994	(1127)
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	(5560)	1	17980	(1887)	Peak approx.	(4588)	21790	(1923)
	(5602)	1	17846	(2021)	Limit approx.	(4566)	21895	(2028)
IX	(5639)	1	17729	(2138)	Limit approx.	..	..	..
	..	..	..	..	Peak approx.	(4468)	22375	(2508)
	..	..	..	..	..	..	..	..

The bands are numbered from II to IX and extend to 5700 A.U. in fluorescence and to 4400 in absorption. The continuous spectrum in this system extends to 6500 A.U., and beyond 5600 A.U. is as intense as the subsidiary bands whose limits could not therefore be located with any certainty. The relative intensities of the subsidiary bands as in the 4152 system are always constant with the exception of the band II which is generally weak, but appears with fairly high intensity in D225 (see Fig. 7*c* and Fig. 8*c*).

(*c*) *Lattice Frequencies.*—An examination of Tables IV and VI shows that the frequency shifts of the subsidiary bands in both the 4152 and 5032 systems are identical within the limits of accuracy of measurement and that these bands arise from a combination of the lattice frequencies of the diamond lattice with the electronic frequencies at 4152 and 5032 respectively. The intensity and structure of the bands in the two systems are, however, very different. In the 4152 system, the bands II to VI consist of sharp lines or bands with extremely sharp edges, while in the 5032 system all the bands with the exception of VI are broad and diffuse. The lattice bands in the 4152 system alternate in intensity, II, V, VII, IX and XI being weaker than IV, VI and VIII. In the 4152 system VI is the most intense band and III one of the weakest. On the other hand in the 5032 system, the bands progressively decreasing in intensity as we proceed away from 5032, III is the most intense band of the group and VI one of the weakest.

The lattice frequencies derived from fluorescence and absorption measurements may be classified into ten groups: 34–98, 132–443, 532–784, 848–1088, 1131–1341, 1361–1667, 1800–2090, 2400–2660, 2700–2850 and 3100–3350 cm.$^{-1}$ The principal discrete frequencies are listed below:—

34, 70, 98, 132, 178, 212, 258, 359, 443, 533, 543, 565, 681, 716, 784, 848, 946, 1013, 1088,1131, 1149, 1218, 1252, 1284, 1330.

9. *Effect of Temperature Variation on the* 5032 *System*

The general effect of cooling the crystal from room temperature to liquid air temperature is to increase the intensity of fluorescence and absorption in the whole region of the 5032 system. The bands become considerably sharper and shift towards the blue, the general behaviour being analogous to that of the 4152 system. The changes in absorption in every case are parallel to those in fluorescence. In Table VII are given the wave-lengths and frequencies of the principal electronic line and the lattice bands of the 5032 system at room temperature and at liquid air temperature respectively. In column (3) are shown the shifts of the bands in cm.$^{-1}$ as the temperature is lowered from 25° C. to − 189° C. In column (6) the changes in

TABLE VII

Effect of Temperature Variation on Electronic and Lattice Lines

No.	25° C.		−189° C.		Wave-numbers shift	Shift per 1000 cm.$^{-1}$
	Wave-length in A.U.	Frequency in cm.$^{-1}$	Wave-length in A.U.	Frequency in cm.$^{-1}$		
I	5038	19844	5032	19868	24	1·2
III	5123	19514	5115	19545	31	1·6
IV	5204	19210	5198	19233	23	1·2
V	5292	18891	5286	18912	21	1·1
VI	5367	18627	5359	18655	28	1·5
VII	5455	18327	5451	18340	13	0·71
XI	5701 5768	17536 17332	5695 5758	17554 17362	18 30	1·0 1·7
1	4156	24057	4152	24077	20	0·83
2	3450	28975	3447	28999	24	0·83
3	3304	30257	3299	30303	46	1·5
4	3159	31648	3154	31699	51	1·6
5	Raman line	1332·1	Raman line	1333·8	1·7	1·3

frequencies in each case are shown as a shift per 1000 cm.$^{-1}$ In the lower half of the table are given similar data for the prominent electronic lines in the 4152 system and in ultra-violet absorption along with those of the 1332 line in Raman effect (taken from Nayar's tables). An examination of the last column shows that the shifts per 1000 cm.$^{-1}$ are more or less of the same order and about the same as that of the 1332 line in Raman effect.

In conclusion, the author wishes to express her respectful thanks to Professor Sir. C. V. Raman for his constant guidance and encouragement during the course of this work.

10. Summary

A detailed study of the fluorescence and absorption spectra of 32 diamonds of widely different intensities and colours of luminescence has been made at room temperature and at liquid air temperature, using a two-prism spectrograph of good resolution and large light-gathering power. A clear relation is observed to exist between the fluorescence and absorption spectra in the visible region and this is shown to extend both to the

The bands are numbered from II to IX and extend to 5700 A.U. in fluorescence and to 4400 in absorption. The continuous spectrum in this system extends to 6500 A.U., and beyond 5600 A.U. is as intense as the subsidiary bands whose limits could not therefore be located with any certainty. The relative intensities of the subsidiary bands as in the 4152 system are always constant with the exception of the band II which is generally weak, but appears with fairly high intensity in D225 (see Fig. 7*c* and Fig. 8*c*).

(*c*) *Lattice Frequencies.*—An examination of Tables IV and VI shows that the frequency shifts of the subsidiary bands in both the 4152 and 5032 systems are identical within the limits of accuracy of measurement and that these bands arise from a combination of the lattice frequencies of the diamond lattice with the electronic frequencies at 4152 and 5032 respectively. The intensity and structure of the bands in the two systems are, however, very different. In the 4152 system, the bands II to VI consist of sharp lines or bands with extremely sharp edges, while in the 5032 system all the bands with the exception of VI are broad and diffuse. The lattice bands in the 4152 system alternate in intensity, II, V, VII, IX and XI being weaker than IV, VI and VIII. In the 4152 system VI is the most intense band and III one of the weakest. On the other hand in the 5032 system, the bands progressively decreasing in intensity as we proceed away from 5032, III is the most intense band of the group and VI one of the weakest.

The lattice frequencies derived from fluorescence and absorption measurements may be classified into ten groups: 34–98, 132–443, 532–784, 848–1088, 1131–1341, 1361–1667, 1800–2090, 2400–2660, 2700–2850 and 3100–3350 cm.$^{-1}$ The principal discrete frequencies are listed below:—

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VI	5367	18627	5359	18655	28	1·5
VII	5455	18327	5451	18340	13	0·71
XI	5701 5768	17536 17332	5695 5758	17554 17362	18 30	1·0 1·7
1	4156	24057	4152	24077	20	0·83
2	3450	28975	3447	28999	24	0·83
3	3304	30257	3299	30303	46	1·5
4	3159	31648	3154	31699	51	1·6
5	Raman line	1332·1	Raman line	1333·8	1·7	1·3

frequencies in each case are shown as a shift per 1000 cm.$^{-1}$ In the lower half of the table are given similar data for the prominent electronic lines in the 4152 system and in ultra-violet absorption along with those of the 1332 line in Raman effect (taken from Nayar's tables). An examination of the last column shows that the shifts per 1000 cm.$^{-1}$ are more or less of the same order and about the same as that of the 1332 line in Raman effect.

In conclusion, the author wishes to express her respectful thanks to Professor Sir. C. V. Raman for his constant guidance and encouragement during the course of this work.

10. Summary

A detailed study of the fluorescence and absorption spectra of 32 diamonds of widely different intensities and colours of luminescence has been made at room temperature and at liquid air temperature, using a two-prism spectrograph of good resolution and large light-gathering power. A clear relation is observed to exist between the fluorescence and absorption spectra in the visible region and this is shown to extend both to the

general character of the spectra and to their intensities. In spite of the enormous variations in the intensity and colour of luminescence, the spectra in all diamonds consist mainly of the 4152 and 5032 systems which consist of (*a*) a set of lines appearing as bright and dark at the same wave-lengths respectively in fluorescence and absorption, (*b*) subsidiary or lattice lines appearing at greater wave-lengths in fluorescence and at diminished wave-lengths in absorption, associated with the principal electronic lines at 4152 and 5032 Å respectively. In blue-fluorescing diamonds the 4152 system is more prominent than the 5032 system. In yellow-fluorescent diamonds the reverse is the case. More generally, the two systems appear with comparable intensities. The intensity and colour of luminescence is thus determined by the absolute and relative intensities of the two systems.

Thirty-six electronic lines other than 4152 and 5032 are found to be present in the visible region. Of these the lines at 4060, 4123, 4194, 4222, 4232, 4277, 4907, 5359, 5695, 5758, 6177, 6265 and 6358 are characteristic of yellow fluorescence while those at 4090, 4109, 4189, 4197, 4206 and 4959 are characteristic of blue fluorescence.

The 4152 line appears in most diamonds as a doublet in both emission and absorption, the width and separation of the components increasing with the intensity of blue luminescence. The 5032 line shows no such variation with changes in the intensity of yellow fluorescence.

The frequency differences between the principal electronic lines at 4152 and 5032 and the lattice lines associated with them are the same in fluorescence and absorption, and lie in the infra-red range; they thus represent the vibration frequencies of the diamond lattice. Their values as derived from the 4152 and 5032 systems are identical, but the degree of sharpness and the intensity distributions are different in the two systems. From the observed frequency differences 25 monochromatic frequencies, *viz.*, 34, 70, 98, 132, 178, 212, 258, 359, 443, 533, 543, 565, 681, 716, 784, 848, 946, 1013, 1088, 1131, 1149, 1218, 1252, 1284 and 1330 have been obtained as constituting the lattice spectrum of diamond.

APPENDIX I

List of Electronic Lines

Observed in Diamond	Wave-lengths in A.U. and intensities (on a scale of 20) of the lines present in	
	Fluorescence	Absorption
D3	4152 (20), 4189 (0), 4197 (1), 4206 (2), 4959 (5), 5032 (6)	4152 (20), 5032 (4), 4959 (2)
D7	4152 (20), 5032 (3)	
D8	4152 (20)	
D12	4152 (20), 4206 (2), 5032 (1)	
D27	4152 (20), 4206 (4), 4222 (2)	
D31		4152 (20)
D32	4152 (–), 4197 (6), 4206 (6), 4227 (15), 5895 (20)	4152 (20), 4189 (1), 4197 (1), 4206 (2), 4304 (1), 4380 (1), 4252 (1), 4959 (1), 5032 (1)
D33	4152 (20), 4197 (3), 4206 (2)	4152 (20)
D34	4152 (20), 4189 (1), 4197 (1), 4206 (2), 4959 (2), 5032 (1)	
D36	4152 (20), 4197 (1), 4206 (3), 4227 (1), 5032 (0)	4152 (20), 3934 (5),
D38	4152 (20), 4206 (2), 4227 (2), 5032 (4)	
D40	4152 (20), 4189 (0), 4197 (0), 4206 (1), 4227 (1), 4959 (2), 5032 (6), 5233 (1)	
D42	4152 (20), 4189 (1), 4197 (2), 4206 (4), 4907 (2), 5032 (8), 6177 (1), 6265 (2), 6358 (1)	4152 (20), 5032 (4)
D42+D43		4152 (20), 4206 (1), 5014 (1), 5032 (3)
D221		4152 (20)
D223	4090 (1), 4109 (1), 4152 (20), 4175 (2), 4189 (1), 4197 (2), 4206 (3), 5233 (2)	
D224	4090 (2), 4109 (1), 4152 (20), 4189 (2), 4197 (3), 4206 (4)	4152 (20)
D226	4152 (20), 4206 (2), 4388 (5), 4959 (2), 5032 (7)	4152 (20), 5032 (5)

APPENDIX II

List of Electronic Lines

Observed in Diamond	Wave-lengths in A.U. and intensities (on a scale of 20) of the lines present in	
	Fluorescence	Absorption
D1	4060 (1), 4123 (1), 4152 (20), 4194 (2), 4222 (1), 4227 (0), 4232 (1), 4277 (3), 4907 (2), 5014 (0), 5032 (20), 5359 (4), 5658 (1), 5695 (1), 5758 (2), 6177 (0), 6265 (0), 6358 (0)	4152 (20), 4907 (2), 5014 (1) 5032 (20), 5359 (4)
D4	4152 (20), 4175 (1), 4206 (2), 4907 (3), 4959 (1), 5032 (7), 5359 (1)	4152 (20), 5032 (6)
D10		4152 (15), 4907 (2), 5032 (20), 5359 (3)
D11		4152 (5), 4907 (1), 5032 (20), 5359 (4)
D13	4123 (1), 4152 (20), 4175 (1), 4194 (3), 4222 (1), 4227 (0), 4232 (1), 4277 (5), 4388 (6), 4590 (1), 4606 (2), 4833 (4), 5014 (0), 5032 (20), 5359 (3), 5658 (0), 5695 (0), 5758 (2), 6177 (0), 6265 (0), 6358 (0)	
D15	4123 (1), 4152 (20), 4194 (3), 4222 (1), 4227 (0), 4232 (1), 4277 (6), 4907 (2), 4959 (1), 5032 (15), 5359 (6), 5658 (0), 5695 (0), 5758 (1), 6177 (0), 6265 (0), 6358 (0)	4152 (15), 4907 (2), 5032 (20), 5359 (5)
D19	4152 (10), 5032 (20), 5359 (3)	
D47	4152 (20), 4175 (4), 4959 (1), 5032 (12), 5233 (2), 5359 (2), 5758 (2), 5895 (1), 6043 (4)	
D197		4060 (1), 4152 (6), 5014 (1), 5032 (20)
D225	4152 (20), 4189 (2), 4197 (3), 4206 (4), 4959 (18), 5032 (12)	3934 (10), 4152 (20), 4245 (1), 4295 (2), 4304 (1) 4959 (6), 5032 (10)

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Raman, C. V. .. *Curr. Sci.*, 1943, **12**, 33.
Ramaswamy, C. .. *Ind. Journ. Phys.*, 1930, **5**, 97.
Robertson and Fox .. *Nature*, 1930, **125**, 704.
Robertson, Fox and Martin .. *Phil. Trans.*, 1934, **232**, 494.
Walter .. *Wied. Ann.*, 1891, **42**, 505.

DESCRIPTION OF PLATES VIII TO XIII

FIG. 1. Fluorescence spectra, (*a*) at room temperature, and (*b*), (*c*), (*d*) at liquid air tempe-ture. In these, 4152 appears at the extreme left and 5032 at the extreme right. The latter is much brighter than the former for D1 which is a yellow-luminescing diamond, while the reverse is the case for D3 and D42 which are blue-luminescing diamonds. 4152 is clearly seen as a doublet in Fig. 1 (*d*). The electronic frequency at 4959 is seen with D3 but not with D1. Note other electronic frequencies at 4194, 4222, 4232. 4277 in (*c*) and 4189, 4197 and 4206 in (*b*).

FIG. 2. Fluorescence and absorption spectra juxtaposed after inverting the latter to exhibit the mirror-image symmetry of the lattice lines about the electronic frequency at 4152.

FIG. 3. The 4152 line of D42 in absorption at room temperature and at liquid temperature with the three-meter spectrograph.

FIG. 4. The 5032 system of D1 in emission and absorption at liquid air temperature, showing mirror-image symmetry. Note the two prominent electronic lines at 5359 and 5758 A.U.

FIG. 5. (*a*) The 5032 system in emission at room temperature ; (*b*) and (*c*), the same in emission and absorption at liquid air temperature, with the latter inverted.

FIG. 6. (*a*) and (*b*). The 4152 and 5032 systems in emission for diamonds D1 and D3 respectively.

FIG. 7. (*a*), (*b*), (*c*) and (*d*). Emission spectra of four diamonds, showing variations in the appearance of the 4152 line, and its effect on the associated lattice spectrum. In Fig. 7 (*a*) the 4152 has disappeared by self-reversal, while in Fig. 7 (*c*), it has been much weakened.

FIG. 8. (*a*), (*b*), (*c*), (*d*) and (*e*). Sequence showing progressive change in the relative intensities of the 4152 and 5032 systems. Notice also the changes in the appearance of the 4152 line.

FIG. 9. Sequence showing the appearance of the 4152 system in absorption and its increased intensity with increasing intensity of luminescence. Note also the increased width of the 4152 line in the sequence. D227 is non-fluorescent and shows no lines.

FIG. 10. Sequence showing the 5032 system in absorption and its increasing intensity with intensity of luminescence.

FIG. 12. The complete fluorescence and absorption spectra of diamond in the visible with wave-length scale, to illustrate the general relationship between fluorescence and absorption.

FIG. 13. Microphotometer tracings of the 4152 line for six diamonds of increasing intensities of luminescence, illustrating the corresponding variations in the structure of the line.

FIG. 14. Microphotometer tracing of the 4152 system of D4 in fluorescence at liquid air temperature. The prominent electronic frequencies are indicated by their wave-lengths in A.U. and the lattice lines by their frequency shifts in cm.$^{-1}$ from the 4152 line.

FIG. 15. Microphotometer tracing of the 5032 system of D15 in fluorescence at liquid air temperature. The electronic and lattice lines are indicated as in Fig. 14.

APPENDIX II

List of Electronic Lines

Observed in Diamond	Wave-lengths in A.U. and intensities (on a scale of 20) of the lines present in	
	Fluorescence	Absorption
D1	4060 (1), 4123 (1), 4152 (20), 4194 (2), 4222 (1), 4227 (0), 4232 (1), 4277 (3), 4907 (2), 5014 (0), 5032 (20), 5359 (4), 5658 (1), 5695 (1), 5758 (2), 6177 (0), 6265 (0), 6358 (0)	4152 (20), 4907 (2), 5014 (1) 5032 (20), 5359 (4)
D4	4152 (20), 4175 (1), 4206 (2), 4907 (3), 4959 (1), 5032 (7), 5359 (1)	4152 (20), 5032 (6)
D10		4152 (15), 4907 (2), 5032 (20), 5359 (3)
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D15	4123 (1), 4152 (20), 4194 (3), 4222 (1), 4227 (0), 4232 (1), 4277 (6), 4907 (2), 4959 (1), 5032 (15), 5359 (6), 5658 (0), 5695 (0), 5758 (1), 6177 (0), 6265 (0), 6358 (0)	4152 (15), 4907 (2), 5032 (20), 5359 (5)
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Raman, C. V. .. *Curr. Sci.*, 1943, **12**, 33.

Ramaswamy, C. .. *Ind. Journ. Phys.*, 1930, **5**, 97.

Robertson and Fox .. *Nature*, 1930, **125**, 704.

Robertson, Fox and Martin .. *Phil. Trans.*, 1934, **232**, 494.

Walter .. *Wied. Ann.*, 1891, **42**, 505.

DESCRIPTION OF PLATES VIII TO XIII

FIG. 1. Fluorescence spectra, (*a*) at room temperature, and (*b*), (*c*), (*d*) at liquid air tempeture. In these, 4152 appears at the extreme left and 5032 at the extreme right. The latter is much brighter than the former for D1 which is a yellow-luminescing diamond, while the reverse is the case for D3 and D42 which are blue-luminescing diamonds. 4152 is clearly seen as a doublet in Fig. 1 (*d*). The electronic frequency at 4959 is seen with D3 but not with D1. Note other electronic frequencies at 4194, 4222, 4232. 4277 in (*c*) and 4189, 4197 and 4206 in (*b*).

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FIG. 3. The 4152 line of D42 in absorption at room temperature and at liquid temperature with the three-meter spectrograph.

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FIG. 15. Microphotometer tracing of the 5032 system of D15 in fluorescence at liquid air temperature. The electronic and lattice lines are indicated as in Fig. 14.

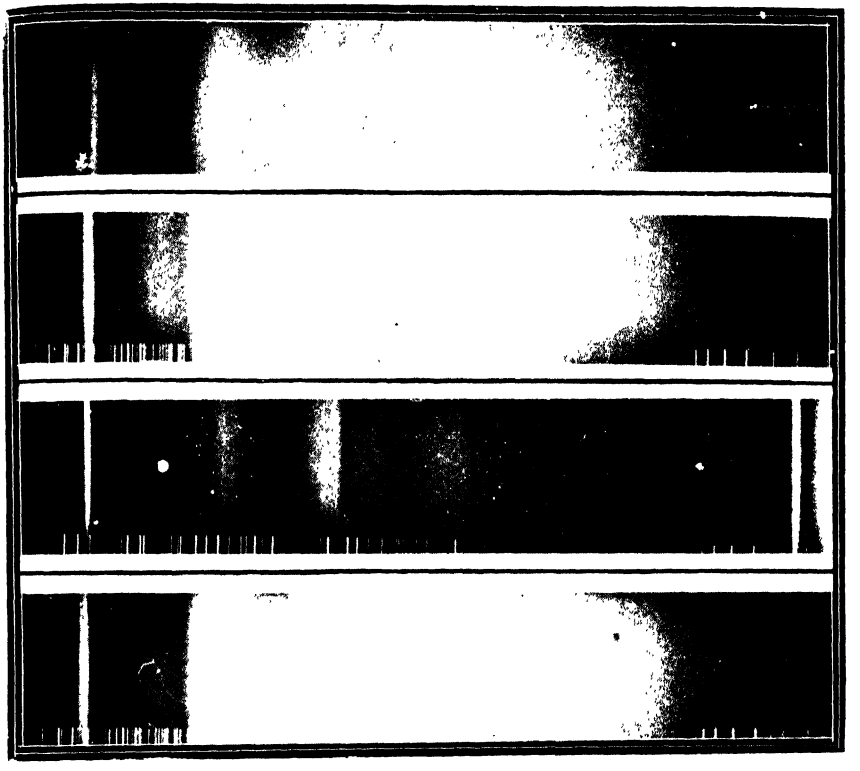
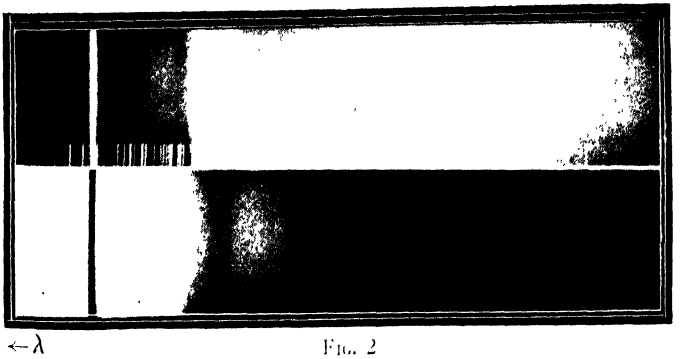


FIG. 1

$\lambda \rightarrow$



$\leftarrow \lambda$

FIG. 2

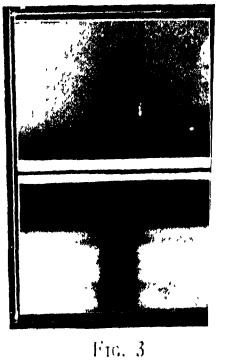


FIG. 3

FIG. 4

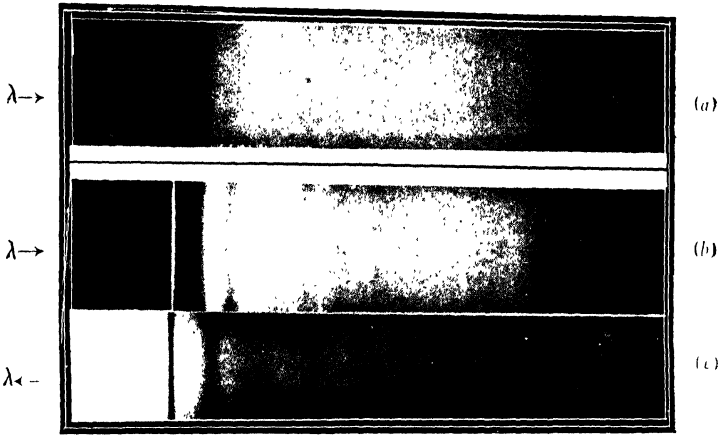
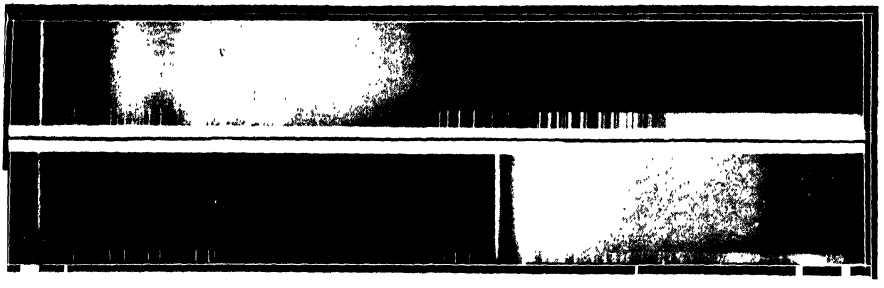


FIG. 5



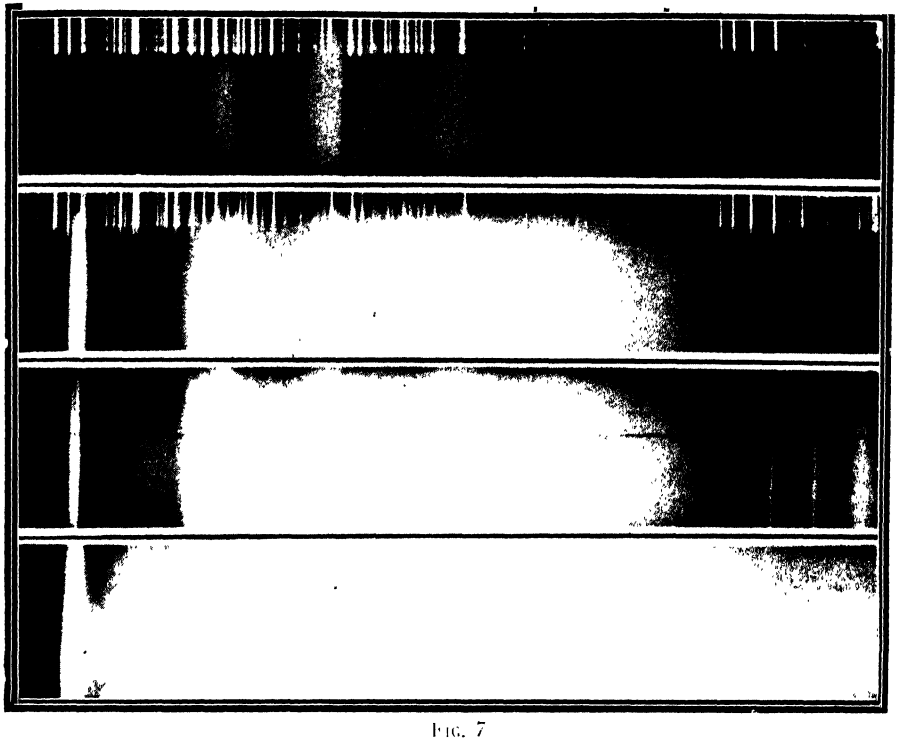


FIG. 7

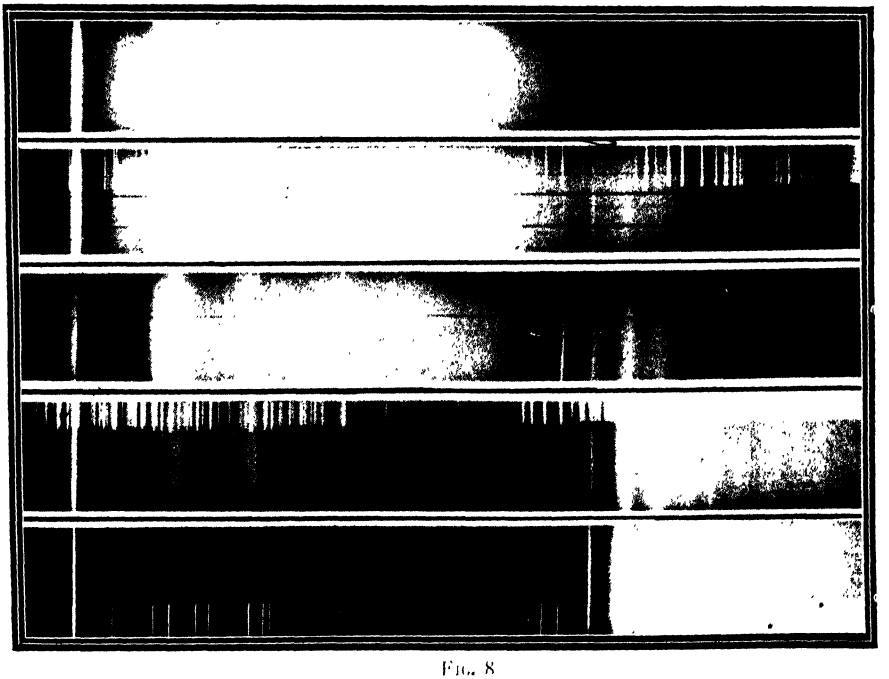


FIG. 8

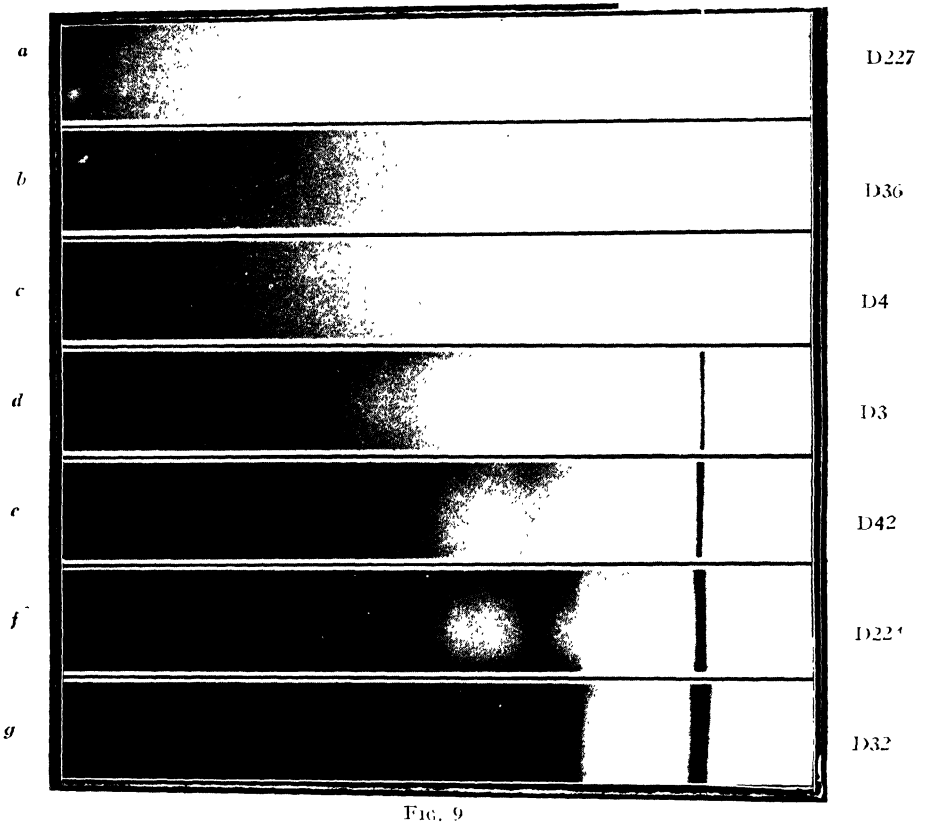


FIG. 9

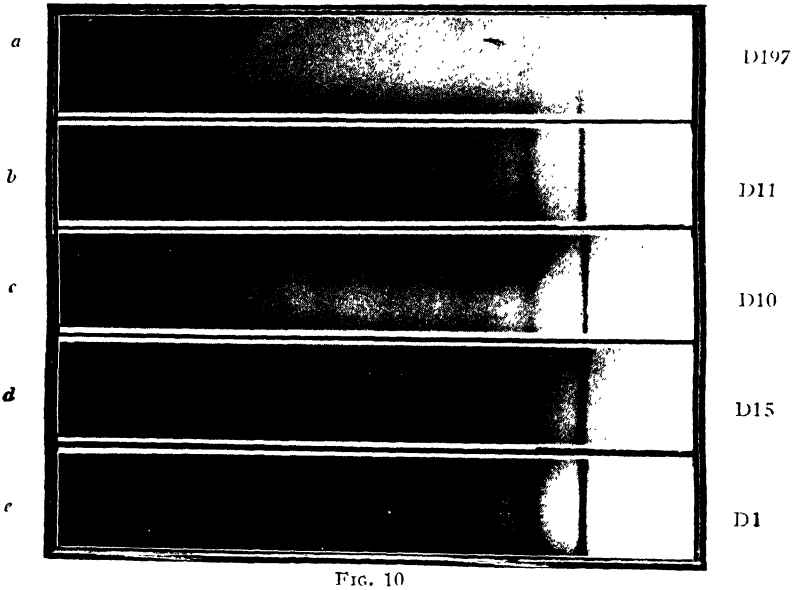


FIG. 10

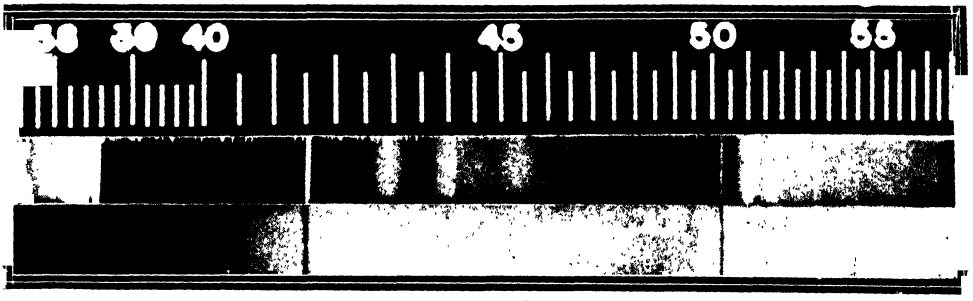


FIG. 12

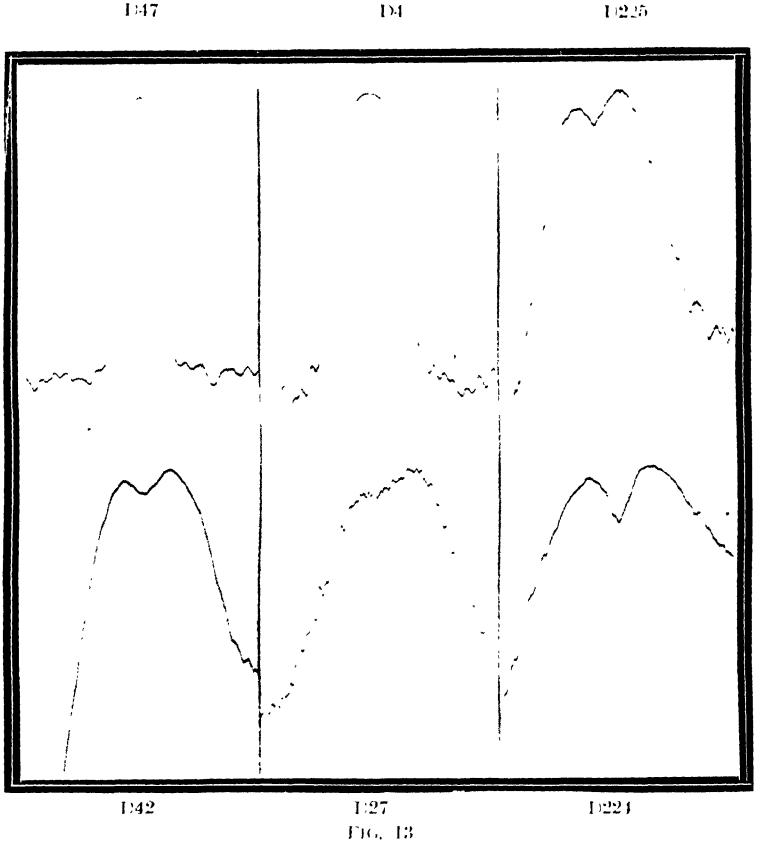


FIG. 13

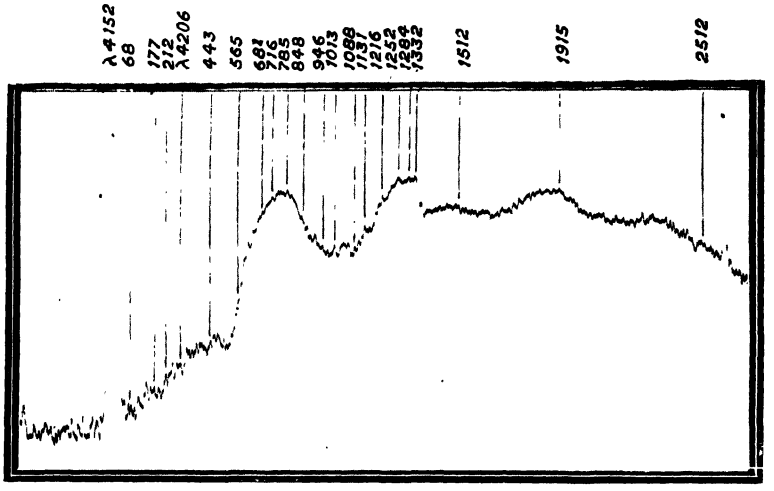

λ4152
68
177
212
λ4206
443
565
681
716
785
848
946
1013
1088
1131
1216
1252
1284
1332
1512
1915
2512

FIG. 14

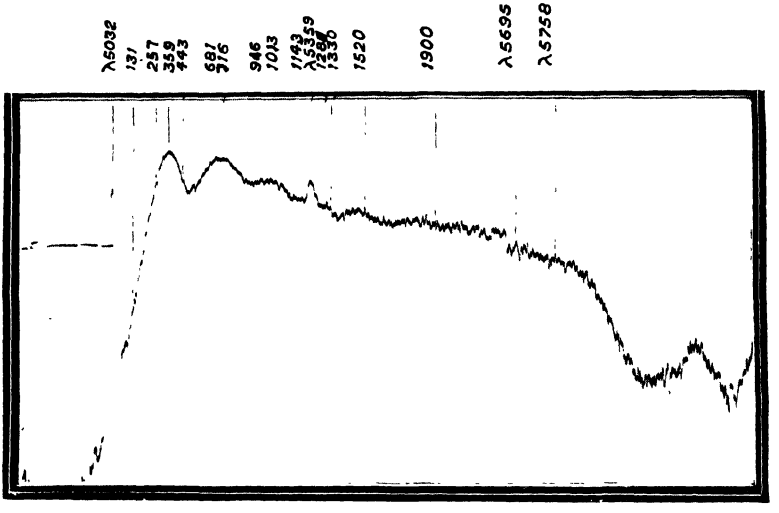

λ5032
131
257
358
443
681
716
946
1013
1143
1336
1520
1900
λ5695
λ5758

FIG. 15

THE ULTRA-VIOLET ABSORPTION SPECTRUM OF DIAMOND

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1. Introduction

It has long been known that the transparency of diamond in the ultra-violet region of the spectrum is variable, some specimens allowing transmission only a little farther into the ultra-violet than ordinary window glass, while others transmit the major part of the spectrum to which quartz is transparent. It was also recognized (Gudden and Pohl, 1920, Pringsheim, 1928) that these differences in ultra-violet transparency go hand in hand with striking variations of the behaviour of diamond in other respects, *viz.*, in the excitation of luminescence and of photo-conductivity by the incident radiation. More recently, Robertson, Fox and Martin (1934) noticed that these variations in ultra-violet transparency are accompanied by significant differences in the infra-red absorption spectrum of diamond of the kind to which attention had been drawn earlier by Reinkober (1911). They accordingly suggested that there are two distinct types of diamond, one giving a complete cut-off of the ultra-violet spectrum beyond about 3000 Å while the other shows a similar cut-off at 2250 Å.

The studies made at this Institute during recent years have however shown that neither the description given of the behaviour of diamond nor the interpretation of the same suggested by Robertson, Fox and Martin is adequate. Dr. P. G. N. Nayar (1941, 1942) found that there is no complete cut-off at 3000 Å in the spectrum transmitted by the commoner varieties of diamond and that the limit could be extended progressively into the ultra-violet up to about 2700 Å by reducing the thickness of the specimen and by suitably increasing the photographic exposures. It was observed that a system of five absorption bands at 2715, 2770, 2845, 2950 and 2975 Å appeared in this extended region of transmission. Nayar also found that all such diamonds are blue-luminescent in greater or less degree and that their behaviour in the region of wave-lengths greater than 3000 Å depended greatly on the intensity of such luminescence. Working at liquid air temperatures with diamonds which fluoresced only feebly, he observed a

set of 25 sharply defined absorption lines in the region of wave-lengths between 3000 Å and 3500 Å, eight of the strongest of which had been recorded earlier by Robertson, Fox and Martin. The width and intensity of these lines, however, showed a striking dependence on the luminescence properties of the diamond; the strongest of them lying in the region between 3000 Å and 3300 Å were practically unobservable in his most intensely luminescent specimen. Later, Nayar also found that while some diamonds transmitted freely up to 2250 Å, there are others in which the absorption progressively increases as this limit is approached, and in which also a clearly marked absorption band appears in the vicinity of 2370 Å. Pictures of the different types of absorption spectra in the ultra-violet region exhibited by diamond are reproduced in an article by Sir C. V. Raman in *Current Science* for July 1942. They clearly show a much wider range of behaviour than can be described in terms of two alternatives only.

It is thus evident that the absorption spectrum of diamond and its luminescence properties are intimately connected with each other. This relationship also manifests itself, though in a different way, in the visible region of the spectrum. This has been clearly shown by Nayar (*loc. cit.*) in the case of blue-luminescent diamonds and by (Miss) Mani (1944) in a paper appearing in this symposium in respect of other varieties of luminescence. It is obviously important, therefore, that study of the absorption spectrum of diamond in the ultra-violet region should be extended to specimens showing the widest range of behaviour in respect of the intensity and spectral character of their luminescence and that the results should be correlated with the variations of the latter properties. The present investigation was undertaken with the object stated, and the results obtained will now be described.

2. *Materials and Methods*

The diamonds used in the present investigation were chosen from the personal collection of Sir C. V. Raman. 45 of them were polished cleavage plates, while two were crystals in their natural condition. Most of the cleavage plates were the same as those of which photographs are reproduced in another paper by the author on the luminescence patterns in diamond appearing in this symposium. As will be noticed from those photographs, several of the plates show a uniform or practically uniform luminescence, while others exhibit striking variations of its intensity over their area. The very great differences in the intensity of luminescence with which we are concerned will be appreciated on a reference to the group picture of 46 cleavage plates reproduced with Sir C. V. Raman's paper on the nature and origin of the luminescence of diamond. For our present purpose, the

diamonds may be grouped into four classes: (*a*) non-fluorescent diamonds; (*b*) diamonds exhibiting a yellowish-green fluorescence; (*c*) diamonds showing a blue fluorescence and (*d*) diamonds showing a mixture of the two types of fluorescence. Enormous variations in the intensity of luminescence in each of the three groups (*b*), (*c*) and (*d*) appear, both in respect of different specimens and also over the area of an individual specimen in the case of those diamonds which show a luminescence pattern.

The source of ultra-violet light used for recording the absorption spectra was a water-cooled hydrogen lamp with an exit-window of quartz made by the firm of Hilger. It was run with 200 to 300 milliamperes current at 3000 volts, and produced an intense continuous spectrum extending up to 1800 Å. The diamonds to be studied were set in small apertures made in a sheet of lead so as to completely cover the same except for the exposed area of the plate. The procedure for recording the spectra was slightly different according as it was desired to study the transmission by the whole area of the specimen, or the local variations of the transmission spectrum over the different parts of the area. In the former case, an image of the quartz window of the lamp was thrown on the slit of the spectrograph by a short-focus quartz lens. In the latter case, an image of the cleavage plate was carefully focussed on the slit of the spectrograph by a quartz lens, and by moving the specimen, different parts of the image were made to pass over the slit. In this way, a series of spectra with equal exposures could be obtained exhibiting the local variations of the absorption in the case of diamonds showing luminescence patterns.

When it was desired to record the absorption spectrum of the specimen at liquid air temperature, the diamond was embedded in a cylindrical copper rod with two circular apertures for the entrance and exit of light. This rod was fixed at the bottom of a long-thin-walled brass cylinder in which liquid air is kept. In order to ensure good thermal contact, Wood's metal was used to fix the diamond in the copper rod. Another jacket of pyrex glass with putty seal between the metal and the glass formed a vacuum jacket round the metal cylinder. The system was kept continuously evacuated by a Cenco pump. With this arrangement, the crystal attained the temperature of liquid air within a few minutes.

As already remarked, the thickness of the specimen and the photographic exposures employed are factors of very considerable importance in determining the nature of the recorded spectra. In the case of all the cleavage plates used, the light passed normally through the specimens. The slit width of the spectrograph and the exposures employed were varied according to the nature of the investigation. A few minutes usually sufficed for

recording the region of free transmission by the specimen, while exposures up to one hour had to be employed fully to record the regions of partial transparency.

A Spekker ultra-violet photometer by Hilger was also used to investigate the transmission spectra of two diamonds D221 and D39 by comparison with that of the tungsten-iron spark used as the source in this instrument, their intensity-ratio being altered step by step over a wide range of values.

3. *Non-Fluorescent Diamonds*

The absorption spectra of seven non-fluorescent diamonds, *viz.*, D39, D57, D206, D207, D208, D209 and D227 have been recorded and the effect of cooling them to liquid air temperature has also been studied with D39. These diamonds were found to be all of the ultra-violet transparent type. At room temperature, the intensity of the transmitted radiation falls off rapidly beyond 2350 Å, a cut-off being observed at about 2255 Å. At liquid air temperature, the absorption beyond 2350 Å disappears, and the cut-off shifts to 2251 Å. These results completely confirm similar observations reported by Robertson, Fox and Martin. A new result obtained in the present investigation is the appearance of a region of feeble transparency extending beyond the edge at 2255 Å up to about 2242 Å at room temperature. This effect becomes more pronounced at liquid air temperature. Fig. 5 reproduces two spectra taken at room temperature and at liquid air temperature respectively, using a Hartmann diaphragm and the same time of exposure. The region of feeble transmission and the shift of the edge at liquid air temperature towards the ultra-violet are both clearly seen. A careful examination of the spectra of D39 and D57 revealed no local variations in transparency over the area of these plates. The Spekker-photometer records of D39 show that at room temperatures, there is a fairly strong absorption commencing at 2350 Å which increases up to the absorption edge at 2255 Å, there becoming very large.

In all the four diamonds studied which fluoresce with a greenish-yellow colour, *viz.*, D199, D200, D201, D202, the recorded spectra for shorter exposure times showed a progressive increase in absorption beyond 2750 Å. When the exposure time was increased, the recorded spectra extended clearly up to 2250 Å and rather weakly beyond to about 2242 Å, as in the case of the non-fluorescent diamonds. No local variations in their transparency were noticed in these diamonds as well.

4. *Blue-Fluorescent Diamonds*

Nayar's observation that the absorption bands at 3030, 3060, 3075 and 3157 Å which are exhibited by weakly blue-fluorescing diamonds tend to

disappear in strongly fluorescent specimens has been completely confirmed in the present investigation. It is noticed that whether these bands are recorded or not depends both on the thickness employed as well as on the fluorescence intensity of the specimen. Thus, in the case of diamonds D31 (thickness 0·97 mm.) and D36 (thickness 0·80 mm.) which are only feebly blue-fluorescent, no trace of these bands could be observed. On the other hand, the crystal D234 of which the fluorescence was much weaker and indeed scarcely observable showed the absorption bands very clearly, though its thickness was only 1·4 millimeters. Then again, with D34 (thickness 1·22 mm.) and D224 (thickness 1·5 mm.) in which the fluorescence was strong and very intense respectively, the bands were wholly unobservable. They were, however, feebly recorded with the crystal D3 which had a moderate intensity of fluorescence, evidently because an absorption thickness of 4 millimeters was employed in this case.

A new and remarkable result noticed in the present investigation is that the ultra-violet transparency of diamonds increases with their intensity of fluorescence. This effect appears to be closely related to the one mentioned above. The extension of the spectrum transmitted in the ultra-violet depends on the thickness of the specimen, its luminescence intensity, and to some extent, also the photographic exposures employed. We may illustrate this by the behaviour of the same specimens as those mentioned above.

The crystal D234 which shows the absorption bands at 3060, 3075 and 3157 Å very clearly exhibits a practically complete cut-off at 3050 Å, even the most prolonged exposures failing to record an extension beyond that wave-length. On the other hand D31, D36 and D34 which do not show these bands show a transmission into the ultra-violet far beyond 3000 Å, increasing in the order stated which is also the order of their luminescence intensities. Even with moderate exposures, D31 goes up to 2850 Å and D36 to 2750 Å, while the transmission of D34 goes up to 2550 Å with sufficient exposures, an absorption band being clearly visible at 2845 Å. On the other hand, the crystal D3 with an absorption thickness of 4 millimeters which shows the bands at 3060, 3075 and 3157 Å (though very feebly) shows a practically complete cut-off at about 3000 Å.

The highly blue-luminescent diamond D224 of which the ultra-violet transmission spectra are reproduced as Fig. 3 in Plate XV affords a very striking illustration of the new effect now under consideration. It will be noticed that its transmission extends up to 2450 Å, a series of step-like falls in intensity occurring at 2845, 2715 and 2570 Å. The first two edges coincide with the positions of absorption bands reported previously by

Nayar. It should not be supposed, however, that only highly luminescent diamonds have a transmission extending so far into the ultra-violet. Actually, the feebly luminescent diamond D221 which is a plate 0·68 millimeters thick of which two Spekker-photometer records are reproduced as Fig. 4 in Plate XV, shows a transmission extending up to 2570 Å. The smaller thickness and the much greater exposures employed (about 6 hours) have contributed to enable the very feeble transmissions of this diamond extending so far into the ultra-violet to be successfully recorded.

5. *Diamonds showing the Mixed Fluorescence*

For short exposure times, the recorded absorption spectra of the diamonds which exhibit both the blue and yellowish-green types of fluorescence showed a gradual fall of intensity beyond 2700 Å. As the photographic exposures are increased, the spectra recorded approach the transmission limit at 2250, however still exhibiting a region of absorption beyond 2500 Å. 19 diamonds belonging to this class, *viz.*, D48, D53, D56, D175, D180, D185, D186, D188, D189, D190, D191, D192, D193, D194, D195, D196, D197, D210, D235, exhibit an absorption band with a clearly resolved doublet structure at about 2360 Å accompanied by a group of absorption bands on either side of it. The strength of these absorption bands varies enormously with the specimen under examination and is found to depend on its luminescence properties. D190 which is the most intensely luminescent diamond in the whole group shows them with the greatest strength, D189 less strongly, while in D210 and D191 which are only weakly fluorescent, they are very feeble (Fig. 1 in Plate XIV). These differences are most clearly seen in the doublet 2360–2357 Å and also in the bands at longer wave-lengths, but not so clearly in those nearer the absorption edge. Table I shows their positions both at room and at liquid air temperature.

The effect of cooling the diamond is to increase the transmission in the whole region between 3000 and 2250 Å. The diamonds D190 and D195 have been investigated at liquid air temperature as well as room temperature, their spectra being recorded side by side with identical exposures, using a Hartmann diaphragm. These are reproduced in Fig. 2 (Plate XIV). It is noticed that at liquid air temperature, the bands became sharper and shift towards the ultra-violet. The extent of this shift could be accurately determined only in the case of the principal doublet, and the extent of the shift is shown in Table I. The change of frequency between 29° C. and − 180° C. is found to be 1·6 per 1,000 wave numbers.

TABLE I

Ultra-Violet Absorption Bands

Robertsan *et al.*	Author		
λ in A.U.	29° C. λ in A.U.	− 180° C. λ in A.U.	−180° C. ν in cm.$^{-1}$
		2405 (weak)	41567
		2399 (strong)	41671
		2396 (weak)	41723
		2395 (weak)	41740
		2388 (weak)	41863
2363 to 2359	2364·5	2359·9 (very strong)	42361
	2359·5	2356·5 (very strong)	42423
		2314 (weak)	43202
2312 to 2300		2309 to 2306 (strong band)	43295 to 43352
		2300 to 2296 (strong band)	43464 to 43540

As will be noticed from Fig. 2, the components of the principal doublet in the highly fluorescent diamond D190 have considerable breadth, while they are much sharper in the weakly fluorescent D195. This is also observed in the case of some of the subsidiary bands, especially those at shorter wave lengths.

In conclusion, the author wishes to record her grateful thanks to Prof. Sir C. V. Raman, KT., F.R.S., N.L., for the suggestion of the problem and for helpful advice during the course of the investigation.

6. *Summary*

The ultra-violet absorption spectra of 47 diamonds in the region between 3300 and 2200 Å have been investigated. A striking correlation between the nature of these spectra and the intensity and spectral character of their fluorescence has been noticed. In non-fluorescing diamonds and those showing yellowish-green fluorescence, the recorded absorption spectra extend up to 2250 Å and even a little beyond, though long exposures were necessary for this purpose in the case of the latter. In the case of weakly blue-fluorescent diamonds, the spectrum shows a cut-off at 3050 Å preceded by a group of three sharp and intense bands at 3060, 3075 and 3157 Å. In strongly blue-fluorescent diamonds these bands disappear, but the region of transmission is enlarged, extending up to 2450 Å with three steep step-like falls in intensity at 2845, 2715 and 2570 Å.

In diamonds showing both the blue and greenish-yellow types of fluorescence, the spectrum recorded with long exposures shows a transmission extending up to 2250 Å. Absorption lines appear in these

diamonds at 2359·0 and 2356·5 Å with five bands on one side and three on the other, *viz.*, 2405, 2399, 2396, 2395, 2388 and 2314, 2309 to 2306, 2300 to 2296. The intensity and breadth of these absorption lines and bands are directly correlated with the intensity of luminescence, being great in highly fluorescent diamonds and small in weakly fluorescent ones. The bands sharpen and shift towards shorter wave-lengths at liquid air temperature.

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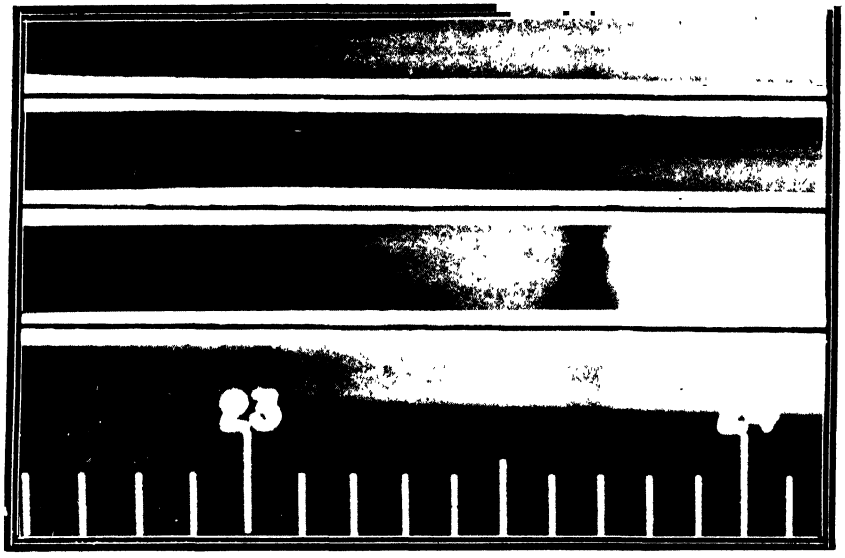
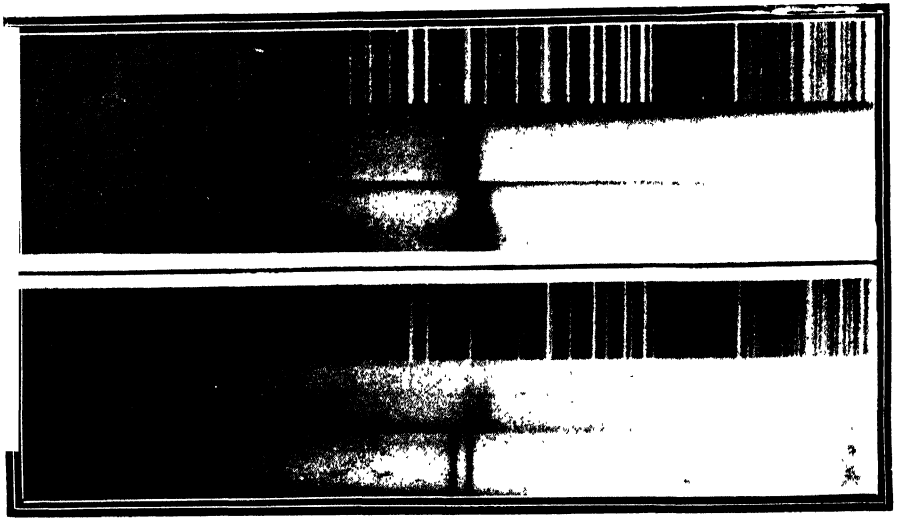
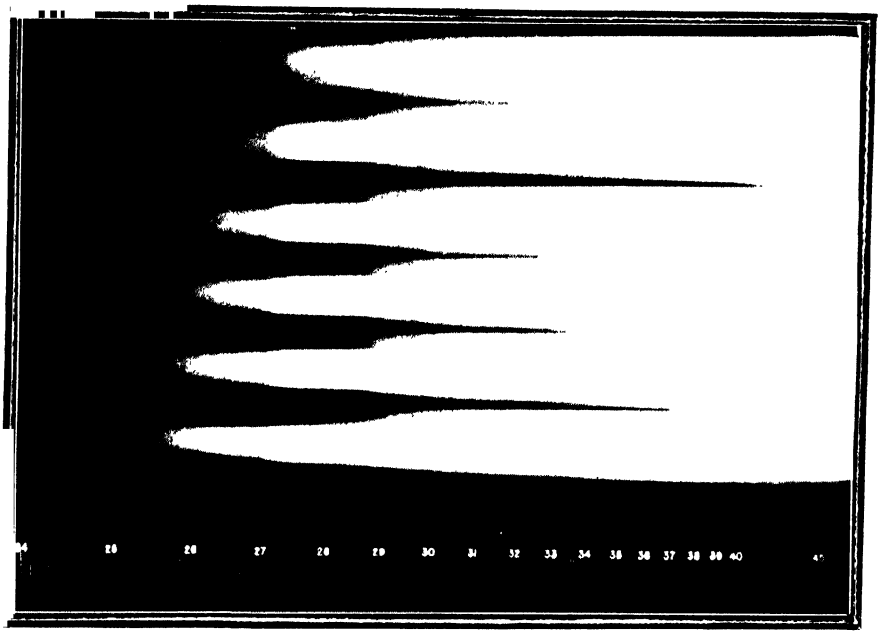


FIG. 1 Absorption in relation to Intensity of Fluorescence



d Shift of Absorption Bands at Low Temperatures



D224

Ultra-Violet Transmission by Strongly Blue Luminescent Diamond

D221

D39

Liquid

Room

Transmission Spectra in Ultra-Violet

INTENSITY OF X-RAY REFLECTION BY DIAMOND

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

It is a well-known fact that X-ray reflections from crystals are affected by the imperfections of the crystal lattice. The subject has been investigated by many authors, and it has been shown that the defects in the lattice structure have a tendency to increase the intensity of X-ray reflections. Ehrenberg, Ewald and Mark (1928) have studied the case of diamond, and found that some specimens give extraordinarily sharp geometric reflections, indicating a high degree of crystal perfection, while other specimens gave decidedly less satisfactory results. More recently, Lonsdale (1941) showed that diamonds which belong to the ultra-violet-transparent type give a very intense (111) reflection compared with diamonds of the other type. These observations indicated the desirability of a more complete study of the subject.

Such a study is particularly interesting in view of the new theory of the structure of diamond put forward by Sir C. V. Raman (1944). According to him, diamonds which are opaque to the ultra-violet consist exclusively of the tetrahedral varieties (Td I and Td II), and the interpenetration of these gives rise to the blue fluorescence. So also, the ultra-violet transparent and non-fluorescent type of diamonds consists solely of the octahedral structures, while the yellow fluorescent diamonds contain both the tetrahedral and octahedral structures intermixed. Obviously, such an interpenetration of different structures would give rise to discontinuities in the crystal, so that one should expect the intensity of X-ray reflection to vary with the nature and intensity of its fluorescence.

This paper sets out the results of the investigations carried out by the author on the intensity of the (111) Bragg reflection given by a large number of diamonds in the collection of Prof. Sir C. V. Raman. The problem has specially been taken up with a view to correlate the intensity of X-ray reflection with the intensity of fluorescence. The fluorescence of diamonds has been studied by Nayar (1941), and his results made it very improbable that fluorescence is due to the presence of chemical impurities, and that, on the other hand, it has a physical origin. Fresh light has been thrown on the question by the work of Dr. R. S. Krishnan (Raman, 1943) who obtained

the Laue patterns of a couple of diamonds, and also the Bragg reflections from the (111) planes by the oscillation method. He found that in the case of two diamonds exhibiting blue fluorescence with widely different intensities, the whole Laue patterns as well as the (111) Bragg reflections were much more intense in the case of the intensely fluorescing crystal. The present investigation was taken up with a view to study this effect in greater detail, and in particular to extend the investigation to a variety of diamonds.

2. *Experimental Arrangement*

A metal Shearer tube with a copper anti-cathode was the source of X-rays. The tube was excited by a transformer, the voltage applied being in the neighbourhood of 50 K.V., and the current, 9 milliamperes. The X-ray beam was collimated through a slit 0·2 mm. wide, 6 mm. high and 130 mm. deep.

The diamond was mounted on a goniometer kept at a distance of about 2 cm. from the exit end of the slit. The goniometer was provided with an oscillating device, and the patterns were photographed on a plane X-ray film kept normal to the incident X-rays at a distance of about 4 cm. from the crystal.

The diamonds used were all cleavage plates with their plane faces parallel to the octahedral plane. One could therefore get the (111) Bragg reflection either by reflection from the (111) planes parallel to the surface, or by internal reflections from any one of the other three sets of (111) planes. As the diamonds examined were of varying thickness, surface reflections only were studied in the present investigation.

The crystal was set on the goniometer with the surface (111) planes vertical and the glancing angle approximately equal to the Bragg angle for the CuK_α radiation. The crystal was then oscillated over an angle of 4° through the Bragg position with uniform angular velocity. The exposures varied from 1 to 10 minutes.

The absolute intensity of the incident X-ray beam was not measured directly in every case. The voltage applied and the current passing through the X-ray tube were maintained at specific values during each exposure and also for different exposures. The distance of the photographic film was also kept constant. Identical exposures were given, and the films which were taken from the same packet were developed in the same stock developer under identical conditions of time and temperature.

The integrated intensity of the Bragg spot was determined using a Moll microphotometer. The density-log intensity curve for the grade of X-ray film used was drawn employing the step-wedge method. The microphoto-

metric curve for the Bragg spot was converted into a curve of intensity *versus* distance, and the area of this was taken to be proportional to the intensity of the Bragg reflection.

3. *Results and Interpretation*

The table below gives the relative values of the integrated intensities of reflection of the Cu K_α radiation from the (111) planes for the samples studied. The type, and a qualitative estimate of the intensity of fluorescence are also included in the table.

TABLE 1

Blue-fluorescing diamonds			Non-fluorescing and yellow-fluorescing diamonds		
Diamond	Integrated intensity	Colour of fluorescence	Diamond	Integrated intensity	Colour of fluorescence
36	1·0	Very faint blue	48	5·6	Blue and green
45	1·1	do.	56	6·2	Green
31	1·3	Faint blue	53	7·1	do.
52	2·1	Moderate blue	51	10·1	do.
44	2·2	do.	39	11·8	Non-fluorescent
33	2·6	Bright blue	57	14·0	do.
54	3·4	Very bright blue			
41	3·5	do.			
34	4·5	Intense blue			

The following facts emerge out of a study of the table:—

(1) In the case of the blue-fluorescing diamonds, the intensity of X-ray reflection increases steadily with intensity of fluorescence. This confirms Dr. Krishnan's observation.

(2) The green-fluorescing diamonds, in general, give greater intensities of X-ray reflection than the blue-fluorescing ones.

(3) The non-fluorescing diamonds give the greatest intensity of X-ray reflection. These, together with the green-fluorescent diamonds, belong to the ultra-violet transparent type of diamonds. Thus, it appears, that in this type, there is an inverse correlation between the intensity of yellow fluorescence and that of X-ray reflection.

These results form a good confirmation of Sir C. V. Raman's theory of the structure of diamonds. In the blue-fluorescing diamonds, the tetrahedral structures Td I and Td II intermix, and the extent of the interpenetration decides the intensity of fluorescence. Obviously, a greater interpenetration produces a greater " mosaic structure " in the crystal, so that it should give more intense X-ray reflections.

The high intensity of X-ray reflection given by the non-fluorescent diamonds is also to be expected on this theory, for these diamonds consist of the Oh I and the Oh II structures. The two are physically different, so that their intermixing sets up strains, and a consequent high mosaicity. The evidence of the polarising microscope also points to such a possibility, for the non-fluorescent diamonds exhibit a fine criss-cross pattern when viewed through it.

The yellow-fluorescent diamonds fall midway between the other two types, since they contain both Td and Oh types of structures. Consequently, they should exhibit properties intermediate between the blue and non-fluorescent varieties. In fact, their ultra-violet absorption shows such an intermediate behaviour, and their X-ray behaviour also thus fits in with Sir C. V. Raman's theory.

It is with great pleasure that I take this opportunity of expressing my grateful thanks to Prof. Sir C. V. Raman for suggesting the problem, for the loan of the diamonds used for the investigation and for the kind interest he has taken in the investigation. My thanks are also due to Dr. R. S. Krishnan for helpful suggestions in the course of the experiment.

Summary

The paper deals with the study of the intensity of the Bragg reflections from the (111) planes of diamond, and its variation from specimen to specimen. The diamonds were chosen so as to include a variety exhibiting different types and intensity of fluorescence. The study brings out the following facts :

(1) In blue-fluorescing diamonds, the intensity of X-ray reflection increases with intensity of fluorescence.

(2) Yellow-fluorescent diamonds give greater intensity than the blue ones.

(3) Among these, the intensity decreases with increasing intensity of yellow-fluorescence, and is largest for non-fluorescent diamonds. A discussion is given regarding these phenomena, and it is shown that they fit in with Sir C. V. Raman's new theory of the structure of diamond.

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BIREFRINGENCE PATTERNS IN DIAMOND

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1. Introduction

Mineralogists have long been familiar with the fact that diamonds exhibit a very varied behaviour when examined under the polarising microscope. Sinor (1930) made extensive observations on the diamonds mined in the Panna State and found that very clear crystals in which all the faces were symmetrically developed showed very little or no double refraction. On the other hand, crystals containing flaws and inclusions, distorted crystals, and brownish tinted crystals showed bands and stripes of colour between crossed nicols. Since perfection of external form and of optical quality are both indicative of a homogeneity of structure, the specimens exhibiting them should naturally also show the optical isotropy characteristic of a cubic crystal. *Per contra*, it is not surprising that diamonds having an irregular form or visible internal flaws or inclusions should exhibit birefringence. Even a small difference in crystal orientation in the different parts of a diamond which has solidified under unsatisfactory conditions would result in enormous stresses and strains being set up which would reveal themselves in the polariscope. Such birefringence would necessarily be irregular. The variations of crystal orientation within the diamond giving rise to it should be evident on an X-ray examination, *e.g.*, in a Laue photograph, the spots in the pattern being distorted or drawn out into streaks or even appearing multiplied in number.

Birefrigence of a wholly different kind which may be described as *structural* and not as accidental, is also exhibited by many specimens of diamond. Such birefringence is distinguished by the geometric character of the figures observed in the polariscope, as also by the relationship of the figures to the crystal architecture and symmetry. Birefringence of this kind in diamond and its interpretation forms the subject of the present paper. Somewhat analogous patterns are exhibited by crystal plates of isomorphous mixtures of substances crystallising in the cubic system, *e.g.*, the nitrates of barium, strontium and solids, and especially by crystal plates of the mixed alums when examined between crossed nicols (Liebisch, 1896). As is shown in the introductory paper of this symposium, crystallographic considerations as well as spectrocospic evidence compel us to admit

the possibility of four different structures for diamond, two with tetrahedral and two others with octahedral symmetry, which may coexist in one and the same specimen. This fact opens the way to an understanding of the geometric birefringence patterns observed in diamond, as also of other properties which vary with its structure, *e.g.*, its luminescence, its transparency in the visible, ultra-violet and infra-red regions of the spectrum, its reflecting power for X-rays and its photoconductivity, all of which stand in close relation to each other.

2. *Crystals in their Natural Form*

Observations with diamonds in their natural state placed between crossed nicols are of interest in view of the fact that the absence of birefringence is a very delicate test of crystal perfection. Consider for instance, an octahedral diamond of 20 carats which would be about a centimeter thick and the optical path through which would be some 50,000 wave-lengths of visible light. A difference of one part in a million in the refractive indices for vibrations in different directions would produce an easily observable restoration of light between crossed nicols, while a difference of one part in a hundred thousand would give polarisation colours. It will be evident that the test is an extraordinarily sensitive one for crystal perfection, especially where large diamonds are concerned.

Owing to the high refractivity of diamond, such observations are necessarily be confined in any one setting of the crystal to small portions of it bounded by parallel faces. These regions would be further restricted if, as is often the case, the surfaces of the crystal are curved. The difficulties mentioned are least serious in the case of large regular crystals with nearly plane faces and most serious for small crystals having highly curved surfaces and with irregular diamonds. They may, however, be minimised by immersing the crystal in a cell containing a transparent liquid of sufficiently high refractive index.

The optical behaviour of numerous diamonds, including some of large size and in particular, the Maharajah's necklace of 52 octahedral crystals was studied by Sir C. V. Raman and Dr. P. G. N. Nayar during their visit to Panna State in July 1942. More recently at Bangalore, 42 Panna crystals of various sizes and qualities have been critically examined for birefringence when immersed in liquid monobromnaphthalene. The conclusions indicated by these studies are as follows:—

(*a*) Diamonds which are of the blue luminescent and ultra-violet opaque type are optically isotropic, their birefringence, if any, being less than 1 part in 100,000. This is subject to the proviso that the

crystal is of perfect form, free from flaws and inclusions, and colourless.

(*b*) Small diamonds of the kind stated above may be optically isotropic even if the crystal form is not absolutely regular.

(*c*) Other diamonds usually exhibit marked birefringence of which there are two kinds, appearing each by itself or together, *viz.*, birefringence which is wholly irregular, and birefringence which is related to the crystal architecture and exhibits a geometric character.

(*d*) While birefringence of the latter kind may appear in blue-luminescent diamonds, it is an invariable feature in the yellow-luminescing ones.

3. *Observations with Polished Cleavage Plates*

There are notable advantages in the study of the birefringence patterns in diamond gained by the use of polished cleavage plates, such as are readily obtainable. As these plates are parallel to the octahedral planes (more rarely to the dodecahedral planes) in the crystal, the relationship of the pattern seen in the polariscope to the crystal architecture is immediately apparent. Moreover, the pattern over the whole area of the plate is visible and can be photographed at the same time, while the disturbing effects due to oblique reflection and refraction which are so troublesome in working with crystals in their natural form do not arise at all. There is also another notable gain in the use of cleavage plates. The act of cleavage releases the material in the plate from stresses having their origin in faults or irregularities elsewhere in the original crystal from which it is split off. The accidental or irregular birefringence due to those stresses is thereby eliminated and the real optical character of the material in the plate made accessible to observation.

A beautiful illustration of the foregoing remarks is furnished by the case of the cleavage plates D36 and D45, the birefringence patterns of which are reproduced in juxtaposition in Fig. 4 of Plate XIX. These two diamonds originally formed a single plate, the whole area of which exhibited a strong restoration of light between crossed nicols. This had its origin in certain irregularities located in the lower part included in D36 and which are clearly seen in the pattern of the latter. When D45 broke off, the stresses in it were released with the result that the birefringence in it has disappeared, while that in D36 remains undiminished (possibly even a little enhanced)

The birefringence patterns as seen between crossed polaroids of several cleavage plates are reproduced as Figs. 1, 2, 3 and 4 in Plates XVI to XIX accompanying this paper. These were chosen from amongst a large number so as to be generally representative of the whole and at the same time to illustrate points of special interest. The significance of these patterns becomes evident when they are carefully compared with the luminescence patterns, the ultra-violet transparency patterns and X-ray topographs of the same diamonds appearing with the papers immediately following the present one in the symposium.

4. *Description of the Patterns*

The diamonds D221 (Fig. 1) and D45 (Fig. 4) are opaque to the 2536 Å radiations of the quartz mercury arc lamp and are both feebly blue-luminescent. It will be noticed from the figures that they give no sensible restoration of light between the crossed polaroids, thereby confirming the essentially isotropic character of diamonds of this class already made evident from the study of the best Panna crystals. The statement made by Robertson, Fox and Martin (1934) that Type I or ultra-violet opaque diamonds are optically anisotropic is thus clearly not justified.

D174, D178 and D179 (Fig. 1) are three diamonds which exhibit rather striking patterns of geometric type. These diamonds are, over the greater part of their area, of the blue-fluorescent and ultra-violet opaque type. That they are optically isotropic in the same regions is evident from the fact that nearly the whole area of D178, the central region of D174 and the major part of the area of D179 remain quite dark as seen at all settings between crossed polaroids. The symmetric patterns shown rather feebly in D178 and more strongly in D174 and D179 consist of bands running parallel to the octahedral planes in the crystal. The region of the diamond which appears as a particularly bright line in the birefringence pattern of D179 appears as a dark line in its luminsecence pattern and as a line of diminished opacity in its ultra-violet transparency pattern, thereby clearly showing that it is an intrusive layer of diamond having different properties from the rest of the material in the plate. The same result is indicated by the X-ray topographs of D174 and D179 obtained by Mr. G. N. Ramachandran (1944), where the intruding layers reveal themselves by the increased intensity of X-ray reflection at precisely the same regions in the plates. D181 and D38 illustrated in Fig. 1 are also blue-luminescent diamonds. The strong birefringence which they exhibit has essentially the same explanation, *viz.*, the intrusion into the blue-luminescent diamond of thick layers of non-luminescent diamond. This is clearly

shown by the X-ray topographs which exhibit a perfect correspondence with the birefringence patterns.

The appearance between crossed polaroids of D206, D207, D208, D209 and of D39 and D57 is illustrated in Figs. 2, 3 and 4. All these six diamonds are of the ultra-violet transparent and non-fluorescent class, and it will be seen that the birefringence which they exhibit is of a highly characteristic type, *viz.*, sets of parallel dark and bright streaks running through the crystal in various directions. The spacing of these streaks is extremely variable, and indeed, both coarsely and finely-spaced streaks may often be seen at the same time in any particular specimen. A special remark is necessary regarding D39, which at first sight seems different in its behaviour from the others. In this diamond, an irregular birefringence is present, due to some obvious imperfections in the crystal which are also revealed by X-ray examination. This obscures the characteristic streaky birefringence of diamonds of this class over a greater part of its area. Careful examination under higher magnification, however, reveals the presence of the latter, and especially clearly when the irregular birefringence is eliminated in a particular area by an appropriate setting of the plate between the crossed polaroids. The patterns of D57 appearing in Fig. 4 have been reproduced under rather high magnification in order to exhibit the characteristic criss-cross streakiness of the field more clearly.

The case of D39 (and also of some other diamonds in the collection) shows clearly that diamonds of the ultra-violet transparent class *may* exhibit irregular birefringence. The statement made by Robertson, Fox and Martin in their paper that diamonds of this class are optically isotropic is therefore not justified. While all diamonds may exhibit irregular birefringence if they have imperfections, perfect crystals of the blue-fluorescent ultra-violet opaque type are, as we have seen, essentially isotropic and free from birefringence, while diamonds of the non-fluorescent ultra-violet transparent type have a characteristic structural birefringence of the kind illustrated in Figs. 2, 3 and 4 in the Plates. The situation is thus actually the reverse of that stated to exist by Robertson, Fox and Martin.

The remaining patterns illustrated in the Plates accompanying the paper fall into two groups. Some of them are essentially of the same nature as the patterns of the six ultra-violet transparent diamonds considered above. The diamonds D199 and D202 are of this kind. They exhibit a yellow fluorescence. They are not fully ultra-violet transparent, but as has been shown in the paper by Sunanda Bai (1944), if adequate exposures are given, the recorded absorption spectra of these diamonds extend to the same

limit as that of the fully ultra-violet transparent diamonds. It is therefore scarcely surprising that the birefringence patterns are also of the same nature for the two sets of diamonds. The other two plates whose patterns have been reproduced, *viz.*, D48 and D235, are typical *mixed* diamonds, showing in different parts of their area all the three kinds of behaviour in respect of luminescence, *viz.*, blue-luminescence, non-luminescence and yellow-luminescence, and the corresponding three different behaviours in their ultra-violet absorption, *viz.*, opacity, perfect transparency and partial transparency. The respective regions in the areas of the plate can be distinguished in the luminescence and ultra-violet transparency patterns, while the X-ray topographs show clearly the intrusion into each other of the different types of diamond. The corresponding variations in the nature of the birefringence in different areas of the plate can also be readily made out in Figs. 2 and 4.

5. *The Origin of Structural Birefringence*

The origin of *irregular* birefringence has already been considered and pointed out earlier in the paper, *viz.*, accidental imperfections of the crystal structure. The appearance of such imperfections is scarcely surprising when the structure of diamond and the nature of the atomic forces in it are considered. The binding forces acting directly between neighbouring atoms of carbon are the strongest of these and are sufficient to secure the coherence of all the atoms in a specimen even when the circumstances of formation of the crystal are such that complete uniformity of the inter-atomic distances and especially of the valence angles throughout its volume is not possible. Atomic equilibrium can then only be secured by the existence of a system of macroscopic stresses and strains in the solid.

The origin of the kind of birefringence with which we are principally concerned in this paper is, however, of an altogether different nature. As we have seen, it arises from the co-existence in the same specimen and inter-penetration into each other of kinds of diamond having different physical properties. Considering, first, the diamonds of the blue-luminescent ultra-violet opaque class, these have tetrahedral symmetry, the two variants Td I and Td II having this symmetry being co-existent and interpenetrating to varying extents. The absence of birefringence in such diamonds indicates that the crystal spacings of these two structures are perfectly identical and that they can therefore fit into each other without any stresses or strains arising. Indeed, the relationship between neighbouring carbon atoms in Td I and Td II is physically the same, but geometrically different. Hence, the identity of crystal spacing and the absence of any birefringence in

diamonds of this class is fully to be expected. *Per contra*, the appearance of a characteristic streaky or lamellar birefringence in the non-luminescent ultra-violet transparent diamonds indicates that the Oh I and Oh II structures of which these diamonds consist, and the co-existence and interpenetration of which gives rise to their lamellar structure, are not physically identical. It is evident that even a small difference in the crystal spacing of the two interpenetrating forms would give rise to a streaky or lamellar birefringence, and that it would also give rise to marked inhomogeneities giving a greatly increased intensity of X-ray reflection.

The explanation of structural birefringence in diamond indicated above is confirmed in a striking manner by the existence of observable variations of crystal spacing in diamonds of the ultra-violet transparent class. This is shown in another paper by Dr. R. S. Krishnan (1944) appearing in this symposium. His experiments were made with the diamond D209 whose birefringence pattern is reproduced in Fig. 2 of the Plates accompanying this paper. The variations in crystal spacing in alternate layers of the diamond were revealed by X-ray methods and found to be accompanied by periodic variations in the intensity of the X-ray reflections from these layers, indicating the existence of a close physical relationship between the two effects. The periodic variations in crystal spacing found were of the order of 5 parts per 10,000. Small though these are, they are clearly sufficient to explain the observed birefringence which is itself small and is so readily noticed only because of the delicacy of the method of observation.

X-ray observations with specimens, such as D48 and D235, in which the tetrahedral and octahedral varieties of diamond appear juxtaposed in adjacent areas should similarly be capable of ascertaining the differences in crystal spacing of the Td structures from those of the Oh I and Oh II types. A knowledge of these differences would assist in a fuller elucidation of the birefringence patterns observed in such cases. In some of these patterns, *e.g.*, those of D174 and D178 appearing in Fig. 1, only the intruding layers of octahedral diamond show an appreciable restoration of light, while in others *e.g.*, the patterns of D181 and D38, the entire diamond shows a restoration though of varying intensity, though the intrusions extend over only part of its area. It would seem that in cases of the latter kind, the stresses set up by the presence of the intruding layers extend over the entire diamond and are of sufficient magnitude to cause an appreciable birefringence to be exhibited by it.

6. *Nature and Magnitude of the Stresses*

Since the birefringence patterns are photoelastic effects due to the variations of the crystal spacing in diamond, it follows that the axes of

birefringence should be related to the orientation of the layers in the crystal in a determinate way. In particular, when there is only one set of laminations in the crystal, the axes of birefringence should be parallel and perpendicular respectively to the laminations. This is readily tested by placing the diamond between crossed polaroids and observing the changes in the pattern as the diamond is rotated in its own plane. As is to be expected, it is found that the bands in the pattern appear most intense when they run at an angle of 45° with the axes of the polaroids and vanish when they are set parallel or perpendicular to them.

In more complicated cases when there are two or more sets of parallel laminations running in different directions and intersecting each other, both the nature of the pattern and the axes of birefringence would be determined by their joint effect, and not by any one of them separately. A striking illustration of this is furnished by D209, the birefringence patterns of which taken at two different settings of the diamonds are reproduced in Fig. 2. It will be noticed that in one setting, the pattern is very bright and shows a rectangular patchwork of dark and bright lines, while in the other setting, it is of much smaller intensity and of irregular character. It is found that the pattern is most intense when the bands in the birefringence pattern are inclined at 45° to the axes of the crossed polaroids, and least intense when they are parallel and perpendicular respectively to these axes. It may be remarked that the X-ray topograph of D209 shows the presence of *two* sets of strongly reflecting layers of diamond which are inclined to each other at an angle of 60°, while the birefringence pattern, on the other hand, shows a rectangular pattern of bright and dark bands. This difference is, however, entirely to be expected in view of the remarks made above. Indeed, the resemblances as well as the differences noticed between the birefriengence pattern of this diamond and its X-ray topograph form a striking confirmation of the explanations put forward of the origin of the former pattern.

Quantitative measures of the birefringence are obviously desirable to enable a more complete account of the subject to be given. A knowledge of the elastic-optic constants of diamond, the orientation and thickness of the intruding layers, and of their crystal spacings, should enable the expected birefringence to be computed and compared with the observed values. Such an investigation should be well worth undertaking. It should be remarked also that the birefringence patterns reveal only the *differences* in the refractive index for vibrations along the principal axes of stress. Observations of interference patterns may conceivably reveal the *absolute* variations of the refractive index, though these would naturally be very small. A knowledge of them would be necessary for a complete evaluation of the stress system of pressures and shears present in the diamond.

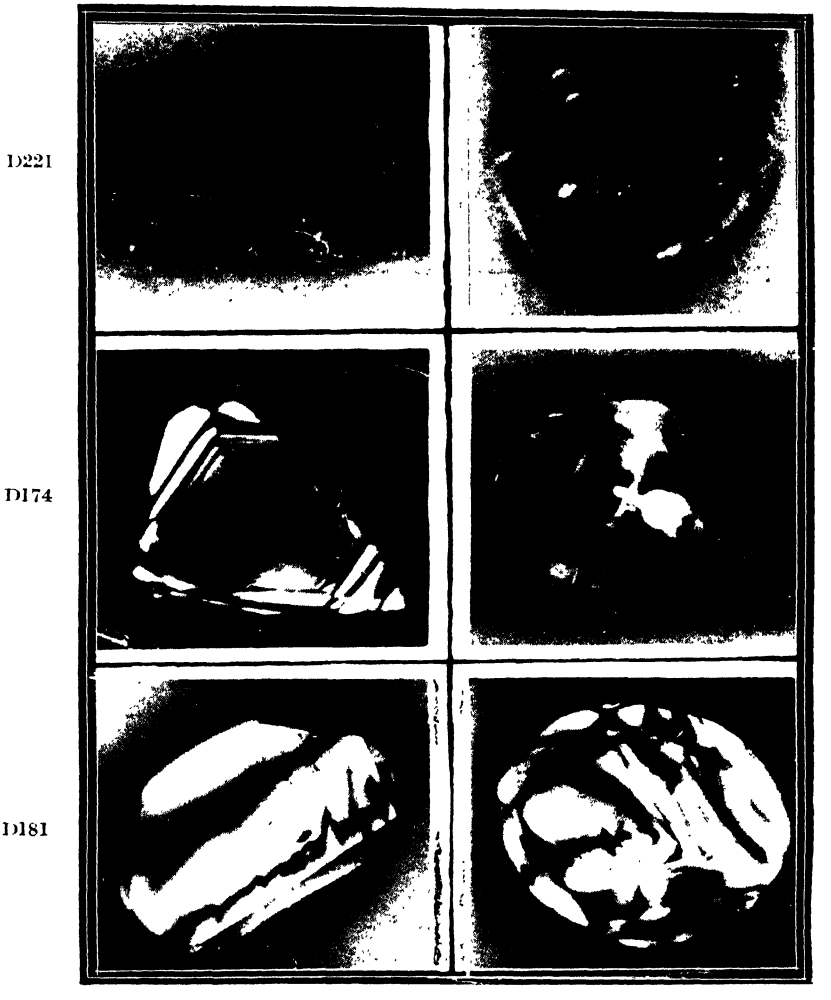

FIG. 1. Birefringence Patterns in Blue-Luminescent Diamonds

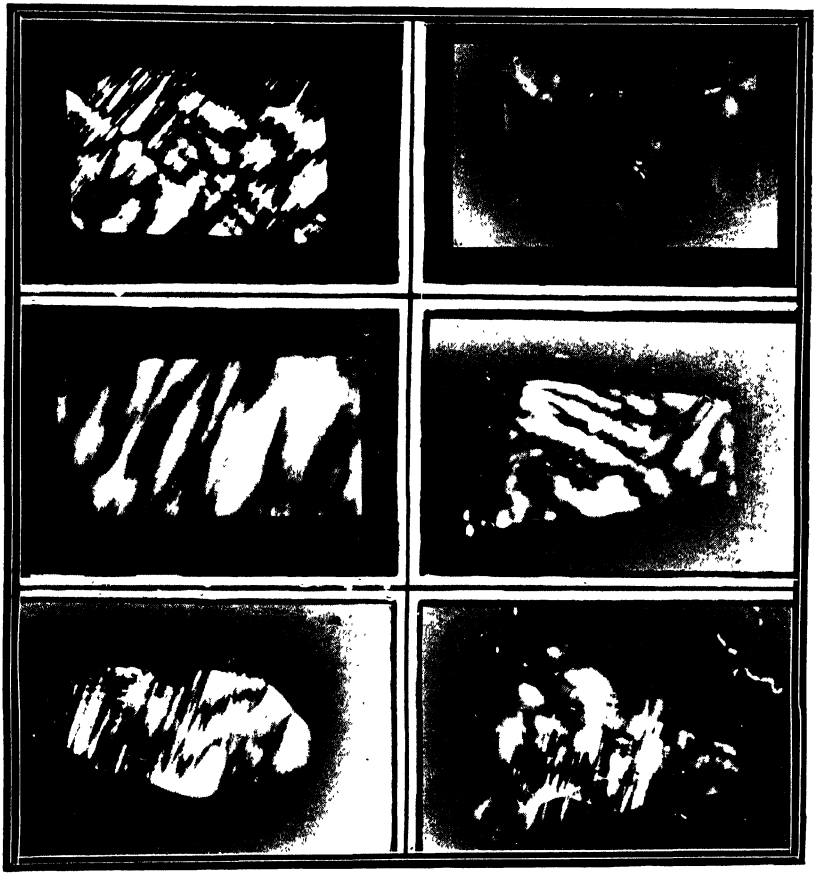

FIG. 2. Streaky Birefringence in Diamonds

FIG. 3. Birefringence in Non-Luminescent Diamonds

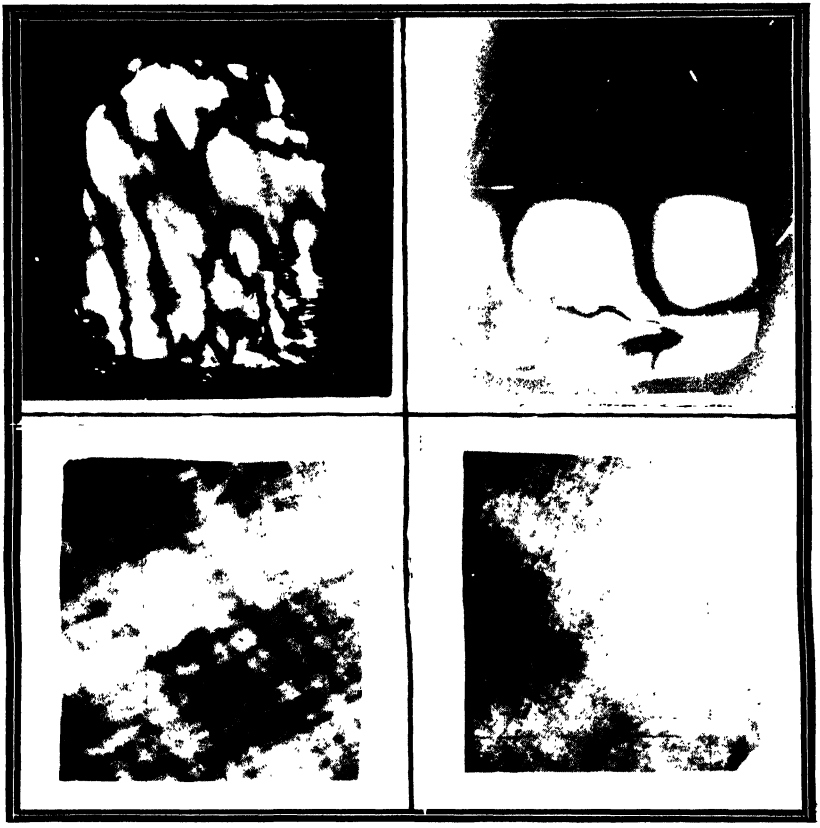

FIG. 4. Birefringence in Diamonds

7. *Summary*

Birefringence in diamond may be either *irregular* or of *geometric* character. In the former case, it is due to structural imperfections, but its magnitude is negligible in well-formed perfect crystals. *Geometric* or *structural* birefringence manifests itself in regular patterns related to the symmetry of the crystal. It arises from the co-existence in the crystal of structures with different properties and crystal spacings. Extensive studies prove that diamond of the blue-luminescent ultra-violet opaque type is isotropic, while diamond of the non-luminescent ultra-violet transparent type invariably shows a structural birefringence. These facts find a natural explanation when the relationships existing between the four possible structure-types in diamond namely Td I, Td II, Oh I and Oh II are considered. A difference in the crystal spacings of the Oh I and Oh II structures present in the ultra-violet transparent diamonds is proved by X-ray studies and is the origin of the streaky or laminar birefringence exhibited by such diamonds. Birefringence patterns may also arise from the intrusion of the Oh structure into Td diamonds. This is fully confirmed by the variations of luminescence, ultra-violet transparency, and of X-ray reflection intensities over the area of the specimen exhibited by such diamonds.

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LUMINESCENCE PATTERNS IN DIAMOND

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

The luminescence of diamond can be readily observed with sunlight and a simple fluoroscope, *viz.*, a piece of Wood's glass and a condensing lens at one end of a tube, a holder for the diamond inside it and a transversely-mounted eyepiece. Examining the specimens in his personal collection with this simple instrument, Sir C. V. Raman made the interesting observation that polished cleavage plates of diamond not infrequently exhibit *patterns of luminescence, viz.*, striking variations of its intensity and colour over the area of the plates. He noticed also that the luminescence pattern often bears a surprising resemblance to the birefringence pattern shown by the same specimen when viewed between a pair of crossed polaroids. Photographs exhibiting such resemblance have been secured by the author for some selected specimens and are reproduced with the paper appearing in the symposium in which Sir C. V. Raman (1944) has discussed the nature and origin of the luminescence of diamond.

To elucidate the nature of the structures which give rise to luminescence, the author undertook a systematic study of the ultra-violet absorption spectra of the diamonds in the collection. The results of the investigation are described in another paper appearing in the symposium. They show clearly that there is an intimate relationship between the ultra-violet absorption spectrum of diamond on the one hand and the colour and intensity of its luminescence on the other. Hence, it follows that a diamond which exhibits a luminescence pattern should also exhibit notable variations in its ultra-violet absorption spectrum over its area. This has also been shown to be actually the case, using the technique which has been described in the paper referred to. Typical absorption spectra illustrating such variations obtained with the diamonds D38 and D235 are reproduced as Fig. 8 in the Plates accompanying this paper.

In view of the great experimental and theoretical interest of the luminescence patterns shown by diamond, it appeared desirable to classify and describe the patterns of all the cleavage plates in the collection and also

to record them, thereby facilitating comparison with other effects exhibited by the same diamonds. Photographs in black and white convey but a faint reflection of the beauty and interest of these patterns with their varied colours. Nevertheless, they are not without value, since they can be studied at leisure, and in the case of the faintly luminescent specimens exhibit features which are not easy to observe visually.

2. *Photographing the Luminescence Patterns*

It has been shown by Miss Anna Mani (1944) in another paper appearing in the symposium, that the variations in the intensity and of the colour of the luminescence of diamond arise from variations in the absolute and relative intensities of two distinct sets of radiations which appear respectively in the regions of shorter and longer wave-lengths of the visible spectrum. For brevity, these will be referred to respectively as the " blue " and " yellow " luminescence spectra. The luminescence patterns may therefore also be ascribed to the local variations of the absolute and relative intensities of these spectra in the emitted light. The rendering of the patterns given by a photographic plate naturally depends on its sensitivity to the two spectral regions under consideration. The most satisfactory arrangement would evidently be to use appropriate filters and obtain two photographs in which the " blue " and the " yellow " luminescence are separately recorded. On setting these side by side, we should obtain an accurate idea of the distribution in the diamond of the structures responsible for their emission. In the present investigation, for the sake of simplicity, no such special arrangements were made, and only one photograph was obtained in each case. It should be mentioned that the patterns of " yellow " luminescence exhibit some fine detail which is not recorded except when high magnifications and plates specially sensitive to the yellow were employed, and long exposures given.

The source of light employed in securing the photographs reproduced was a carbon arc run at 220 volts with 6 to 8 amperes current. A box lined inside with black velvet served as an enclosure for the diamond during the exposure. The light of the arc, after passage through a water-cell and an aperture covered by a plate of Wood's glass, was focussed by a quartz lens on the plate of diamond. The latter was stuck on a polished sheet of copper, and its inclination to the incident beam was so adjusted as to secure a uniform irradiation. Occasionally, some trouble was encountered from the reflections at the bevelled edges of the plate which resulted in bright streaks appearing which ran across the area of the plate. By suitably varying the setting of the diamond, however, these streaks could usually be eliminated.

A rectangular glass cell containing a concentrated solution of sodium nitrite placed in front of the camera lens served as a complementary filter. A camera with a 5-inches focus lens was employed and set so that the image of the diamond appeared suitably enlarged on the plate. The Ilford selochrome plates used for the photographs gave a satisfactory rendering of the " blue " luminescence, but only weakly recorded the " yellow " luminescence even in the areas where actually it was strong. This fact has to be remembered in examining the figures reproduced in the paper. The advantage of using plates sensitive to the yellow region in some cases is illustrated by the striking photograph obtained with D198 (Fig. 5) for which a HP2 plate was employed. It should be mentioned that both the degree of enlargement employed and the photographic exposures were such as to secure the most satisfactory picture in each case. Neither the relative sizes of the diamonds nor their relative intensities of luminescence can therefore be judged from the reproductions.

3. Description of the Patterns

Photographs of 42 diamonds (mostly flat cleavage plates) are reproduced as Fig. 1 to 7 in Plates XX to XXIII. They have been grouped in these figures according to the nature of the effects exhibited by them. Fig. 1 shows the diamonds having a more or less perfectly uniform blue luminescence. (The streaks in D178 are spurious.) Fig. 2 and Fig. 3 also represent diamonds of this kind, the latter of those which exhibit striking patterns. Figs. 4, 5, 6 and 7 represent (with a few exceptions) diamonds showing a mixed blue and yellow luminescence. The exceptions are D200 and D202 in Fig. 7 which exhibit a yellow luminescence, and D182 and D236 in Fig. 7 which are blue-luminescent.

Striking examples of geometric patterns of luminescence are D38, D179 and D180 in Fig. 3, D191 and D194 in Fig. 4, D195, D198 and D235 in Fig. 5, D48 and D56 in Fig. 6, and D186 in Fig. 7. A common feature in many of the patterns is that the lines tend to run parallel to the edges of the plate; these, it may be recalled, represent its intersections with the faces of the crystal from which it was cleaved off. This feature is particularly well shown by D180 in Fig. 3, D191 in Fig. 4, D195 and D198 in Fig. 5, and indeed also by several others. It is a general feature in diamonds showing a yellow luminescence that numerous bright streaks appear running parallel to each other, sometimes in several directions simultaneously. Indications of this feature appear in some of the photographs, *viz.*, D194 in Fig. 4, D196 and D198 in Fig. 5, D48 in Fig. 6, D200 and D202 in Fig. 7. Only traces of the numerous parallel bands seen visually in D193 can be made out in its reproduced photograph (Fig. 4). D188

shows visually numerous yellow bands traversing a blue field in several directions simultaneously, but only with difficulty can this feature be noticed in the photograph (Fig. 6).

The lack of sensitiveness of the selochrome plates has resulted in the areas showing a greenish-yellow luminescence appearing as darker in the photographs than the blue-luminescent ones. The dark areas in the photographs of D191, D192, D193 and D194 in Fig. 4 and of D210 in Fig. 5 are actually areas of greenish-yellow luminescence, while the bright areas in these figures represent a blue luminescence. In D195 (Fig. 5), a band of bright yellow luminescence running parallel to one of the sides of the triangle of blue luminescence is recorded as a dark strip. Many other examples of this kind can be quoted.

4. Origin of the Patterns

The first and most important point to be borne in mind in considering the origin of the luminescence in diamond is that the behaviour of different specimens is very varied. Some are non-luminescent, some are blue-luminescent, some are yellow-luminescent, while others again show both types of luminescence. Further, the intensity of each kind of luminescence may also show enormous variations. The natural interpretation of these facts and of the existence of the patterns is that any given specimen may be a mixture of different species of diamond intertwinned with or inter-penetrating each other. As the different species are isomorphous, the geometric character of the patterns immediately becomes intelligible.

Accompanying the differences in the luminescence of diamond, we have also differences in other properties of which the ultra-violet absorption spectrum of diamond is one which is readily accessible to observation. The variation in ultra-violet absorption and its correlations with luminescence have been described in detail in another paper, and it is not necessary to set them out again here. It is sufficient to remark that using the knowledge gained by that investigation, it is possible from a study of the ultra-violet absorption over the different areas of a given specimen to infer the nature of the variations in the diamond which give rise to the luminescence pattern. *Vice versa*, the existence of such correlations between the local variations of luminescence and ultra-violet absorption spectra is evidence for the existence of a relationship between the crystal structure of diamond and its luminescence properties.

A striking example of the presence of material having very different properties in the same specimen of diamond is the dodecahedral cleavage plate D235 whose luminescence pattern appears in Fig. 5. As visually

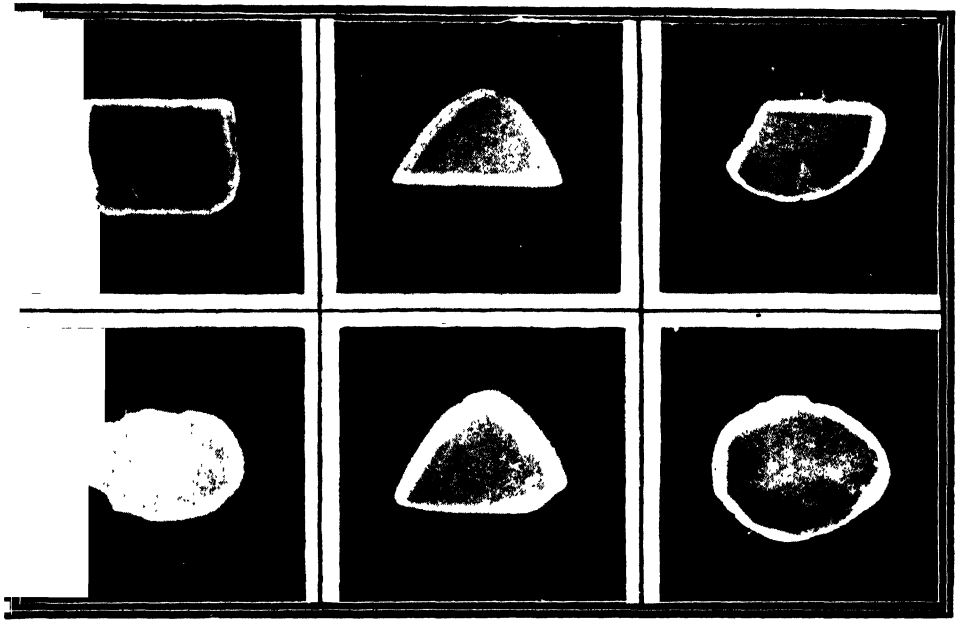
observed, the central area of this plate shows a fairly bright blue luminescence, while dark patches appear towards both of the extremities as seen in the figure. Visually, some faint bands of yellow luminescence can be seen traversing the plate obliquely from end to end. The ultra-violet absorption spectrum shows corresponding variations over the area of the plate. The non-luminescent areas exhibit a free transmission up to 2250 Å, while the blue-luminescent area shows a transmission extending up to about 2700 Å with moderate exposures, but with prolonged exposures right up to 2250 Å crossed by an absorption doublet at 2360 Å. The latter feature is characteristic of the diamonds which show both the blue and yellow types of luminescence.

Another example illustrating the correlation between luminescence and ultra-violet absorption is D210 (Fig. 5). The central dark region showing a yellow fluorescence gives an ultra-violet transmission spectrum which extends with sufficiently long exposures to 2250 Å traversed, however, by a set of absorption bands in the region between 2500 Å and 2250 Å. On the other hand, the blue-fluorescent marginal region of the diamond shows a transmission only up to 2500 Å even with long exposures. Another interesting case is D180. The brightly blue-luminescent part in the centre of its area shows an ultra-violet transmission up to 2600 Å only, while the marginal non-luminescent areas show a transmission extending to 2250° (with absorption bands between) when sufficiently long exposures are given. The blue-luminescent diamond D38 which shows a very striking pattern (Fig. 3) has a free transmission up to 2900 Å followed by a weak transmission up to 2600 Å in the luminescent areas. On the other hand, the non-luminescent strips give bands of free transmission up to about 2400 Å, showing clearly that they represent the intrusion of a more transparent variety of diamond into a less transparent one.

Considering the whole complex of facts, *viz.*, the existence of two distinct varieties of luminescence, the enormous variations possible in their intensities, and the appearance of patterns of blue and yellow luminescence with distinctive features in each case, it appears scarcely possible to reconcile it with the idea that there are only two alternatives possible for the crystal structure of diamond. The wider range of possibilities indicated in the papers by Sir C. V. Raman in the symposium appears easier to reconcile with the observed facts.

In conclusion, the author desires to record her grateful thanks to Prof. Sir C. V. Raman, Kt., F.R.S., N.L., for his valuable help and inspiring guidance throughout the course of this investigation.

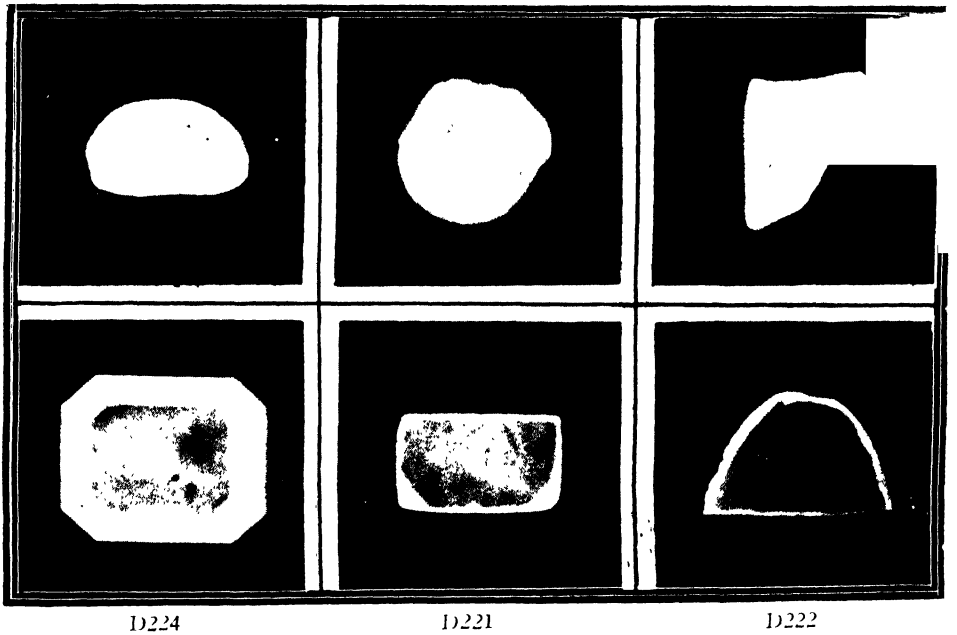
D36 D45



D173 D174 D178

FIG. 1

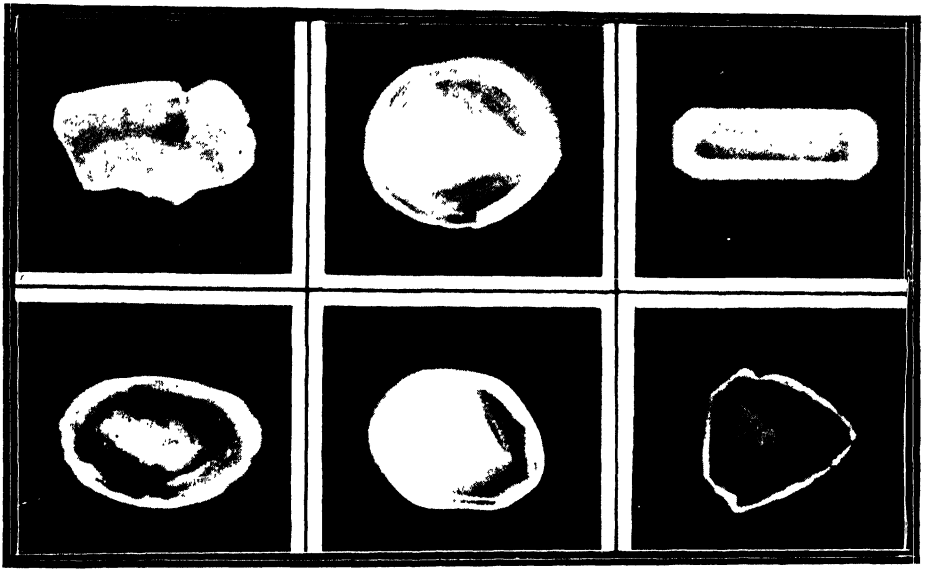
D184



D224 D221 D222

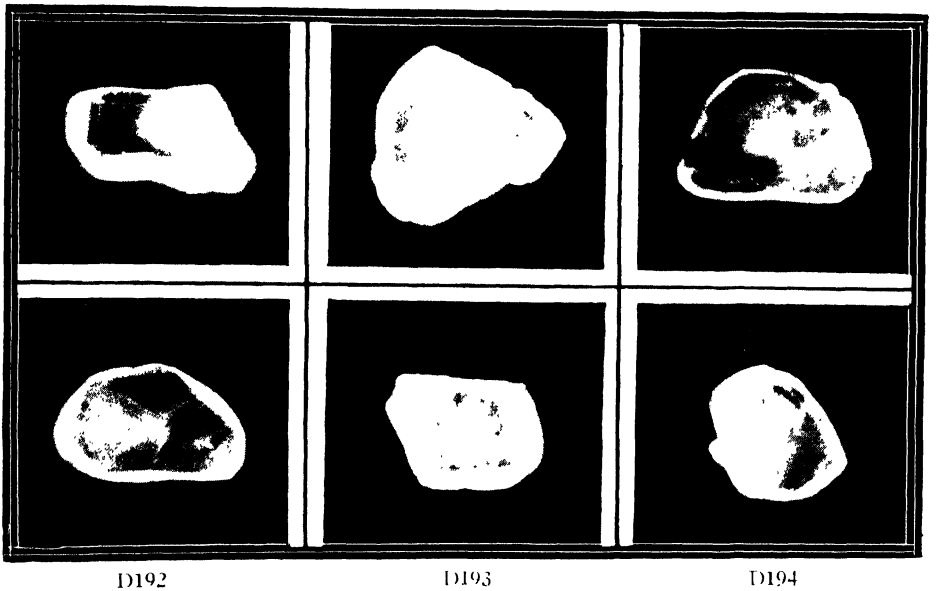
FIG. 2

D34 D38 D43



D177 D179 D180

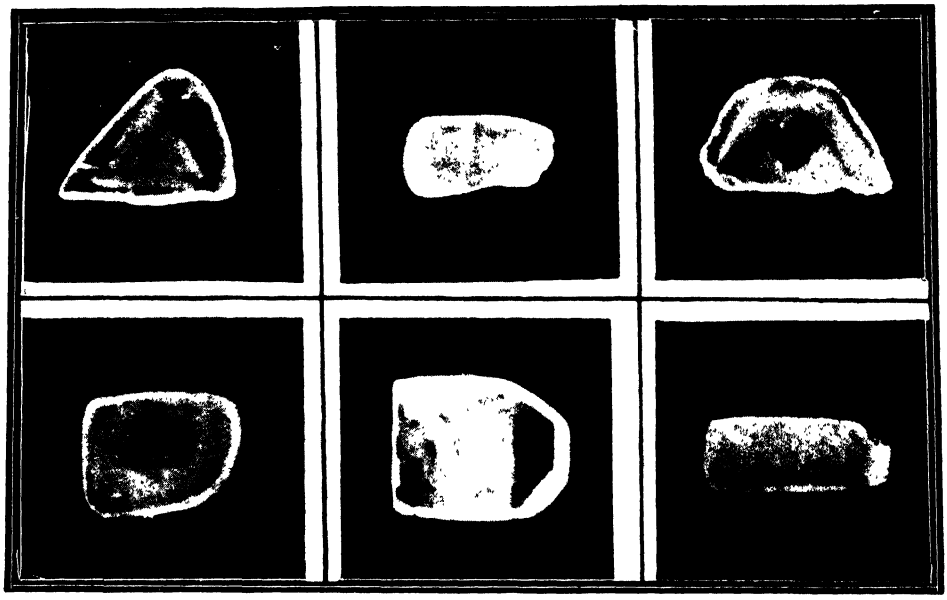
Fig. 3



D192 D193 D194

Fig. 4

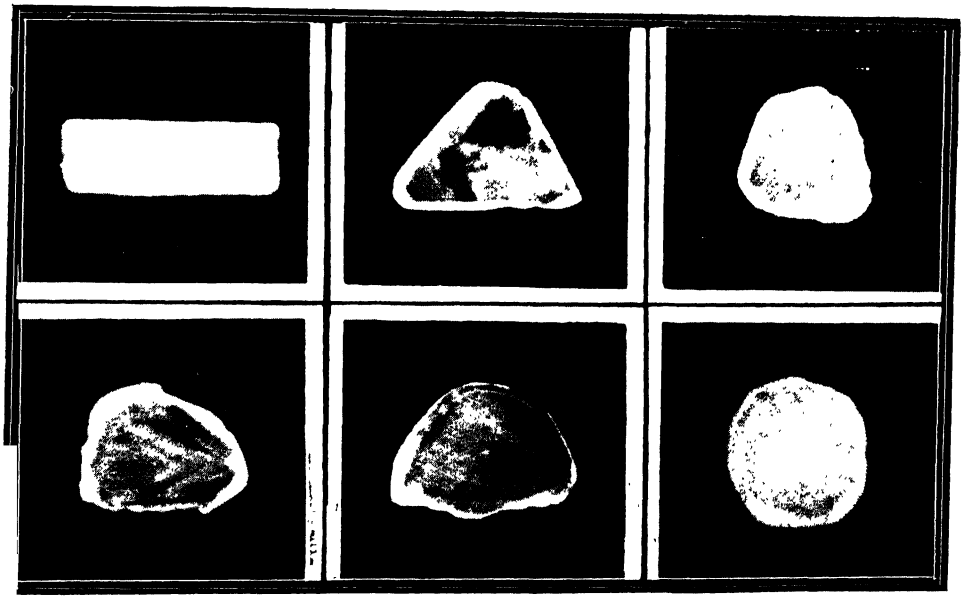
D195 D196 D198



D210 D235 D197

Fig. 5

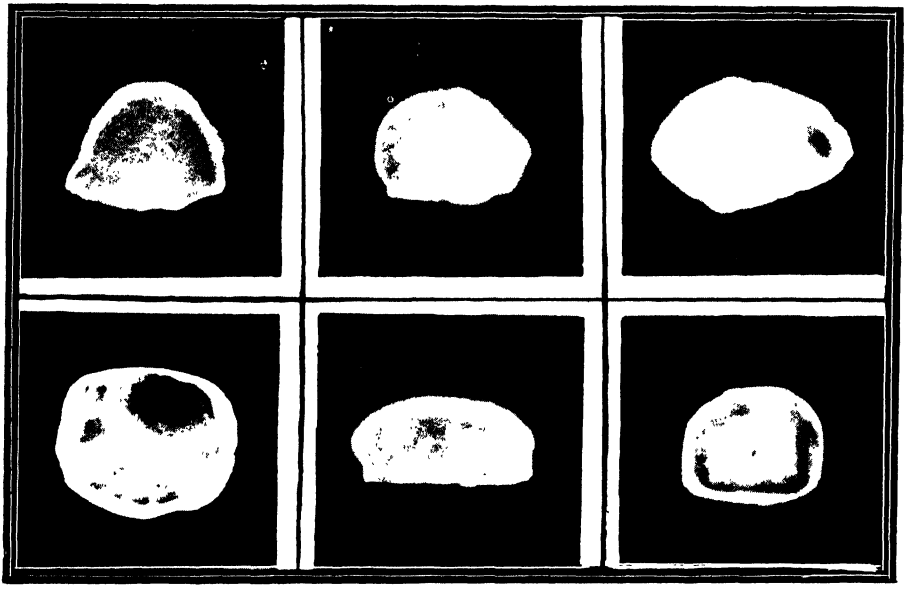
D42 D48 D53



D56 D175 D188

Fig. 6

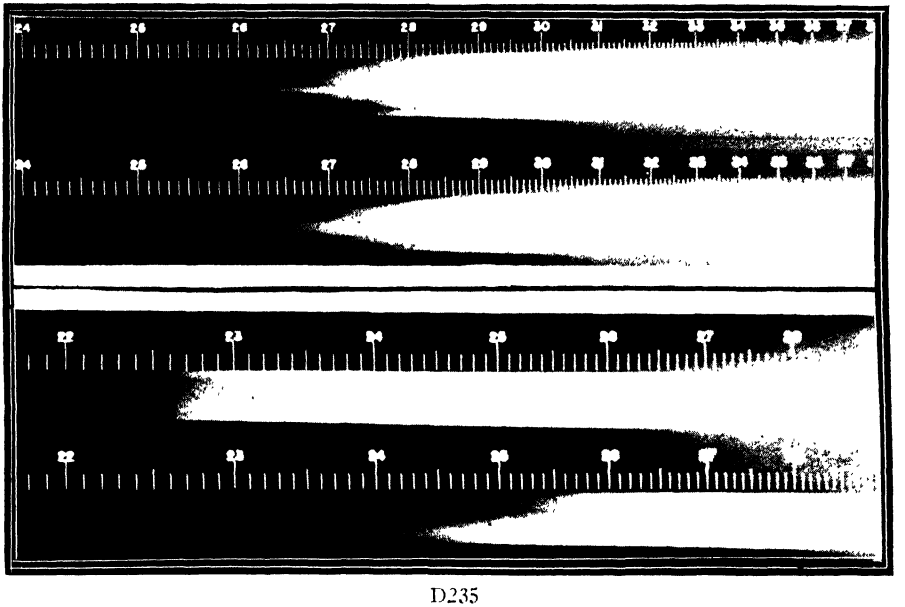
D182 D185 D186



D200 D202 D236

FIG. 7

D38



D235

FIG. 8

5. *Summary*

Geometric patterns showing variations of intensity or colour or of both are often observed in the luminescence of cleavage plates of diamond excited by long-wave ultra-violet irradiation. The lines in the pattern not infrequently also run parallel to the natural faces of the crystal from which the plate was cleaved. Such patterns may be altogether lacking in some cases where the diamond shows a uniform blue luminescence. On the other hand, such patterns are always present when the diamond shows both blue and yellow luminescence. The appearance of numerous bright streaks running parallel to each other, sometimes in several directions simultaneously, is characteristic of yellow luminescence. A study of the local variations of the ultra-violet absorption spectrum of the diamond is usually successful in revealing that the luminescence patterns, when observed, arise from intrusion into the crystal of diamond having properties different from the rest of the material.

42 luminescence photographs are reproduced with the paper.

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Sunanda Bai, K. .. *Ibid.*, 1944, **19**, 253.

X-RAY TOPOGRAPHS OF DIAMOND

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Received May 3, 1944

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

As is well known, the spots in the Laue pattern of a crystal arise from the reflection of X-rays by particular sets of lattice planes. The size of each spot in the pattern increases with the extension of the area of the crystal traversed by the X-ray beam, and reaches its maximum when the crystal is completely bathed in the latter. In the particular case when the crystal is in the form of a thin plate, its form and size would determine those of the Laue spot, and each spot in the X-ray pattern becomes, in effect, a geometric representation of the crystal plate. The representation would be perfect if there is no blurring and no distortion. The former condition may be secured by arranging that the beam emerging from the target of the X-ray tube is limited by a fine pinhole, and that the crystal plate is placed at a sufficient distance from the latter to ensure that it is completely bathed by the beam diverging from the pinhole. The fact that the spots in Laue patterns as usually recorded with an X-ray beam of circular cross-section are elliptical shows that, in general, distortion will occur in the present arrangement. It is possible, however, to secure that it is practically eliminated in respect of a chosen Laue spot by suitably inclining the photographic film, or the crystal plate, or both, to the beam of X-rays incident on the latter. The particular spot whose definition and freedom from distortion are thus secured, thereby making it an exact representation of the crystal plate, would evidently be formed by the reflection of white X-radiation by the chosen set of lattice planes over a small range of angles of incidence. Each point in the area of the particular Laue reflection would correspond to a particular point in the crystal plate, and if the strength of the incident beam and the reflecting power of the lattice planes are uniform over its area, the reflection would also appear of uniform intensity. The proviso must however be made that the range of angles of incidence employed does *not* include the Bragg angle for any of the monochromatic components present in the incident X-ray beam.

The considerations set out above become of practical interest, if, for any reason, the reflecting power for X-rays is *not constant* over the area of the

crystal plate under study. The geometric representation of the plate obtained by the method explained would then exhibit corresponding variations in intensity over its area, thereby revealing the local variations in the structure of the crystal which are responsible for the variations of reflecting power. The Laue spot becomes, in effect, a topographic map (or for brevity, a *topograph*) of the crystal plate exhibiting these variations of structure.

Topographs of 18 polished cleavage plates of diamond selected from Sir C. V. Raman's personal collection with their catalogue numbers entered against them, obtained in the manner briefly explained above, are reproduced in Figs. 4 to 6 in Plates XXIV and XXV, accompanying the present paper. Their significance will be discussed later in the course of the paper. To appreciate the X-ray topographs fully, they must be compared with the luminescence patterns (Sunanda Bai, 1944), the ultra-violet transparency patterns (Rendall, 1944), and the birefringence patterns (Raman and Rendall, 1944) of the same diamonds reproduced in the plates accompanying other papers published in this symposium.

2. *Practical Details and Theory for Obtaining the Topographs*

The experimental arrangement used is as follows, and is represented diagrammatically in Fig. 1. A fine pinhole P of diameter 0·3 mm. made in a sheet of lead, and placed in front of the window of a tungsten target X-ray tube forms a point-source of diverging white X-radiation. The diverging cone of X-rays is limited by an aperture A_1, placed at a suitable distance (20 cm.) from the pinhole. The crystal plate CD is mounted on a two-circle X-ray goniometer, kept at a distance of 30 cm. from the pinhole, which is adjusted so that one of its axes of rotation is vertical, and the other coincides with the axis of the cone of X-rays. Just in front of the crystal, a second aperture A_2 is placed. This aperture is of such a size that the direct X-ray beam just passes through it, without striking its boundary. In this way, it effectively prevents the X-rays scattered by A_1 from striking the photographic film F. The apertures are of such a size that the crystal is completely bathed in the X-rays. The film holder of the X-ray camera is capable of rotation about a vertical axis. It is also capable of longitudinal motion along the line joining the pinhole and the crystal. The film holder was always set such that the film was tangential to the circular head of the goniometer and the normal distance of the film from the crystal was a constant (2·5 cm. in the present case).

The diamond plates that were employed were usually octahedral cleavage plates with their surface parallel to one set of (111) planes, or slightly

inclined to it at angles of 1° or 2° owing to errors in polishing. A few specimens were however found which were dodecahedral cleavage plates. The setting required for getting the topograph was different in the two cases. Although any one of the Laue spots can be used for the purpose, it is an

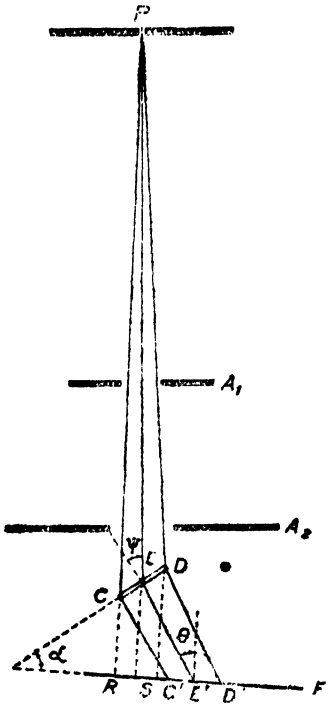

Fig. 1. Arrangement for obtaining topograph

advantage to use a strongly reflecting plane in order to minimise the exposure. For the octahedral cleavage plates, any one of the three sets of internal octahedral planes, *viz.*, (111), ($1\bar{1}1$) or ($11\bar{1}$) can be used. For dodecahedral cleavage plates with their surface parallel to the (110) planes, any one of the reflections ($\bar{3}13$), ($3\bar{1}3$) ($\bar{1}33$), ($1\bar{3}3$) can be employed.

The crystal plate (whether of octahedral or dodecahedral cleavage) is first mounted so that its surface is normal to the incident X-ray beam. A photograph is taken with this arrangement, and with its help, the requisite reflection, the (111) or the (331) as the case may be, is brought so as to be in the same horizontal line as the central spot, by rotating the crystal about the axis of the cone of X-rays. Next, the crystal is rotated about the vertical axis through an angle of $33\frac{1}{2}°$ for the octahedral plate and 38° for the dodecahedral plate, so that the same reflection occurs on the opposite side at an

angle of 14° and 19° respectively. The film holder is then rotated in a direction opposite to that of the crystal through an angle of 14° and 3° respectively. An exposure is then taken with this arrangement when an undistorted X-ray topograph is obtained. It may be pointed out that in these settings, the angles of incidence were beyond the Bragg angle for any of the characteristic lines of tungsten, and that the topograph was produced by white radiation alone.

We shall now develop the theory of the method for eliminating distortion, and show how the elimination is secured in the settings described above. Let CD be the crystal, and C′D′ the image of it produced on the film F, E and E′ being the middle points of these (Fig. 1). Let α be the angle between the plane of the crystal and of the film, θ the angle made by the X-ray reflected by E with the normal to the film, ψ the angle between the axis of the X-ray beam and the normal to the crystal, and ϕ the divergence of the incident X-ray beam, *i.e.*, the angle subtended by CD at the source P. The rest of the symbols are clear from the figure.

$$\text{Now, } C'D' = RD' - RC' = SD' - RC' + RS$$
$$= SD \tan(\theta - \phi) - RC \tan(\theta + \phi) + CD \cos\alpha.$$

This must be equal to CD if there is to be no distortion.

$$\text{Now, } SD = r + \frac{CD}{2}\sin\alpha, \quad RC = r - \frac{CD}{2}\sin\alpha.$$

Also, since ϕ is a small quantity, putting $\tan\phi = \phi$, and writing t for $\tan\theta$, $\tan(\theta + \phi) = t + \phi + \phi t^2$, $\tan(\theta - \phi) = t - \phi - \phi t^2$.

Substituting these, the condition for no distortion comes out as

$$2r\phi(1 + t^2) - (CD \sin\alpha)\, t \quad CD(1 - \cos\alpha) = 0.$$

Divide this equation by R, the distance PE of the crystal from the pinhole. Then, since $CD \cos\psi / R = \phi$, one obtains

$$\frac{2r}{R}\frac{1}{\cos\psi}(1 \quad t^2) \quad \frac{\phi}{\cos\psi}\, t \sin\alpha + \quad \frac{\quad}{\cos\psi} = 0.$$

Putting $R - r = K'$, this can be written in the form

$$t^2 - \frac{K'}{2\cos\psi}\, t \sin\alpha + \left[1 \quad \frac{K'}{2\cos\psi}(1 - \cos\alpha)\right] = 0.$$

or, if $K'\cos\psi = K$, $t^2 - \frac{K}{2}\, t \sin\alpha + \left[1 + \frac{K}{2}(1 - \cos\alpha)\right] = 0.$

If this equation is satisfied, then there will be no distortion laterally.

Before proceeding further, it is interesting to notice that when θ and α satisfy the above equation, the image is a normal representation of the crystal. In other words, if F is any point on the crystal, and F′ is the corresponding one in the reflected image, then CF = C′F′, and this is true for all points F in the cross-section CD. This is easily seen to be so, for the final equation is independent of ϕ, which alone depends on the dimensions of the crystal. Of course, the above theory rests on the assumption that ϕ is a small quantity, but this is true in the present experiment where the dimensions of the crystal never exceeded 10 mm., for which ϕ is less than 1°30. For these, the image will be a true reproduction of the object.

In order to make the theory capable of practical application, curves have been drawn for different values of K, connecting the values of θ and α which satisfy the equation for no distortion These are reproduced in Fig. 2. It will be noticed that all the curves are closed. Only for conditions corresponding to points on the curves will there be no lateral distortion;

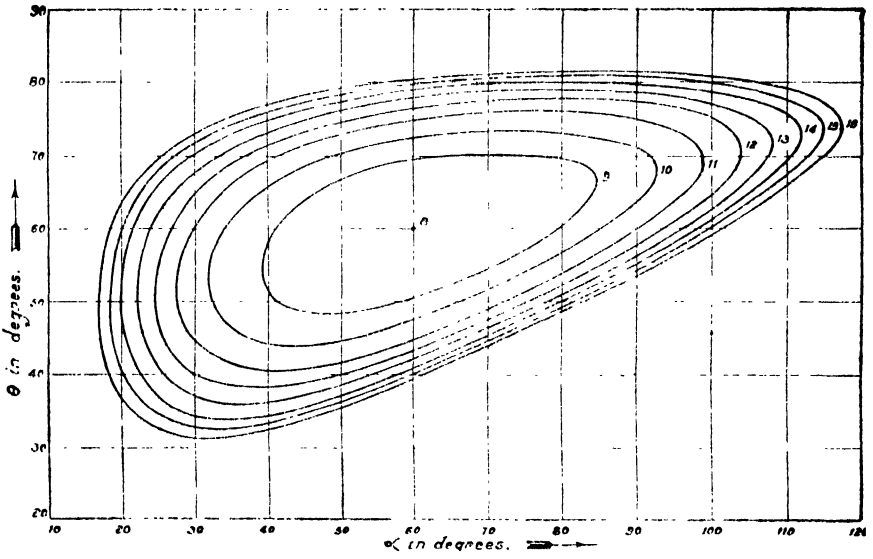

FIG. 2. Curves showing relation between θ and α

if the point is outside, the lateral dimensions of the image will be smaller than that of the object. while if it is inside, the reverse will be the case. It is also found that there is a limiting value of K, (K = 8), below which there can be no undistorted position for any values of θ or α. For this particular value of K, the curve reduces to a point (θ = 60° α = 60°), which is the only position of no distortion.

Taking now the particular case of an octahedral cleavage plate of diamond, it is clear that when it is mounted with the surface normal to the X-rays, the internal (111) planes reflect at an angle of $19\frac{1}{2}°$. As already said, the crystal is rotated through $33\frac{1}{2}°$, so that the same planes reflect at an angle of 14° in the opposite direction (which may be denoted by $-14°$). In this case, $\psi = 33\frac{1}{2}°$, and with the present arrangement for which $R/r = 12$, the value of $K = 14{\cdot}4$. If the film is rotated through 5° in a direction opposite to that of the crystal, then it is easily seen that α and θ have the values $38\frac{1}{2}°$ and 33°, which thus satisfy the condition for no lateral distortion.

It must be mentioned that even with this arrangement, the image will not be a perfect reproduction of the crystal, for there is a small divergence in the vertical direction. The arrangement only secures that the horizontal dimensions are unaltered, but does not compensate for the vertical divergence. However, even this small distortion can be eliminated by further increasing the tilt of the film, so that the working point moves inside the curve of no lateral distortion, and the horizontal dimensions of the image become actually greater than that of the object. The additional tilt can be adjusted so that the lateral dimensions are also increased in the same ratio as the vertical ones. This quantity was not calculated, but was determined by trial to be nearly 9°. Thus the total tilt necessary is 14°, which is the one used. With this arrangement, the distortion, if any, would be less than 2%. It might be pointed out that even if the vertical divergence were not corrected for, the consequent increase in the vertical dimensions would only be about 8%.

In the case of the dodecahedral plates, the method employed is to rotate the crystal through 38°, so that $\psi = 38°$ and $K = 15{\cdot}2$ for this setting. From the curves in Fig. 2 it is seen that there is no distortion if $\theta = 32°$ and $\alpha = 32°$. Here also, the additional tilt necessary to compensate for the vertical divergence is 9°, and the final setting is $\theta = 41°$, $\alpha = 41°$, which can be realised by rotating the film in a direction opposite to that of the crystal through 3°. This justifies the arrangement used.

It will not be out of place here if it is pointed out that this method of obtaining X-ray topographs is quite general, and can be used for any crystal, provided it is available in the form of a plate. Even the indices of the spot need not be known; what is needed is only the angle which the corresponding plane makes with the surface of the plate, which can easily be determined by taking a picture with the plate normal to the X-ray beam. If we call this angle by β, the author found that it is most convenient to make the planes reflect at $-\beta$, rotating the crystal through an angle $\psi = 2\beta$.

Then, the reflected beam is normal to the surface of the plate. In fact, this was the procedure adopted for obtaining the topographs of dodecahedral cleavage plates. For octahedral plates, the method is not feasible on account of the fact that the angle β ($19\frac{1}{2}°$) is in the neighbourhood of the Bragg angle for the characteristic lines of tungsten, so that the angle $-14°$ had to be employed.

If, however, it is required to obtain the X-ray topograph by surface reflection, an exactly similar method can be used. It may be remarked that, in this case, the condition for no distortion is extremely simple, namely that the film must be parallel to the crystal. This is because the reflected beam is divergent both in the horizontal and the vertical directions, so that if the photographic film is parallel to the crystal plate, the impression on it is merely an enlarged picture of the crystal, and will in fact be a true reproduction of the object.

3. *Intensity of X-Ray Reflection in Diamond*

As a preliminary to an examination of the individual topographs and of their significance, we may briefly consider here the problem of the structure of diamond in relation to the intensity of X-ray reflections given by it. Many of the physical properties of diamonds are highly variable, *viz.*, the colour and intensity of the visible luminescence exhibited by it under ultra-violet irradiation, as also its transparency to the visible, ultra-violet and infra-red radiations and the corresponding absorption spectra. The question arises as to what the origin of these variations is. An answer to this has been given by Prof. Sir C. V. Raman in two papers appearingearlier in this symposium. According to his theory, diamond can exist in four allotropic modifications. Two of these modifications have tetrahedral symmetry and the other two octahedral. In any actual crystal, these structures may appear either alone, or intermingled with one another and the properties of the specimen are determined by the nature and the extent of interpenetration of the structures that are present in it. Such an interpenetration may be on a macroscopic, microscopic or sub-microscopic scale. Now, any variations from perfect regularity in a crystal will give rise to an enhanced intensity of X-ray reflection as is well-known. But the scale in which these variations occur is an important fact to be considered. If the interpenetration of the different structures is on a macroscopic scale, then what one expects is not an increased reflection, but only what is to be expected for a perfect crystal, except that different parts of the crystal may conceivably behave differently, giving slightly varying intensities of X-ray reflection. On the other hand, if the interpenetration and the consequent

inhomogeneity of the structure is on a microscopic or sub-microscopic scale, the crystal can be considered to possess a mosaic structure, which at once leads to an increased intensity of X-ray reflection.

Striking support is given to these considerations by the fact that the crystallographically most perfect diamonds, which exhibit a blue luminescence, show variations in the X-ray reflection intensity, which is clearly correlated to their luminescence intensity. Diamonds of this class show a strong absorption in the ultra-violet at wave-lengths below 3000 Å.U., and the best specimens appear perfectly isotropic and free from birefringence. According to Sir C. V. Raman, diamonds of this class have an inherently tetrahedral symmetry of structure, but this is, in general, disguised by an intimate interpenetration of the positive and negative tetrahedral forms with the result that the higher octahedral symmetry of form is simulated. The resulting heterogeneity, however, reveals itself in the capacity of the diamond to luminesce. In agreement with this view, it is found that specimens of this class of diamond which exhibit the feeblest blue luminescence show the lowest X-ray reflection intensities, while those showing an intense blue luminescence give enhanced reflection intensities. This is beautifully shown by the Laue patterns of two diamonds, one feebly and the other strongly blue luminescent, obtained by Dr. R. S. Krishnan, and reproduced in Sir C. V. Raman's article in *Current Science* for January 1943. A similar pair of photographs obtained by the author under strictly comparable conditions for diamonds D31 and D41 are reproduced in Fig. 3, Plate XXIV of the present paper. These two diamonds are of equal thickness, but differ enormously in the intensity of blue luminescence, D31 being very weak and D41 very strong. It will be seen that the Laue pattern of the former is much the weaker. A quantitative study of the patterns, and a theoretical discussion of the same appears as another paper of the symposium.

It has long been known that some diamonds are completely non-luminescent and that these exhibit a higher degree of transparency to the ultra-violet, transmitting freely upto 2300 Å.U., or even shorter wave-lengths. According to Sir C. V. Raman, these belong to the class of diamonds having octahedral symmetry, there being two variants of this class (Oh I and Oh II), which are physically different. In general, both the variants are present in specimens of diamond belonging to this class, exhibiting a lamellar twinning parallel to one, two, three or even all the four sets of octahedral planes in the crystal. The existence of such lamellar twinning is proved by the external striations visible on the surface of the crystals, and by the finely spaced streaky birefringence patterns, running parallel to the planes of lamination, which are seen when plates of such diamonds are

examined between crossed nicols. The multiple lamellar twinning, in effect, divides the crystal into a great number of very small, and slightly disoriented crystal blocks, with the result that the X-ray reflection intensities of this type of diamond is much greater than even for the most intensely blue-luminescent diamond (Lonsdale, 1942; Hariharan, 1944).

Finally, we have to consider the kind of diamond in which the tetrahedral and the octahedral structures are more or less closely intermingled, and which exhibits a partial transparency in the spectral region between 2300 and 3000 Å.U. These diamonds show a mixed type of luminescence. They also exhibit an X-ray reflecting power intermediate between the two extremes, represented by the feebly luminescent tetrahedral and the non-luminescent octahedral types (Hariharan, *loc. cit.*).

A natural consequence of the possibility of interpenetration or intertwinning of the four possible structures of diamond is that the structure of any particular specimen may vary from part to part within its volume. Hence, it follows that a cleavage plate of diamond may exhibit variations of its various properties over its area, such as the colour and intensity of its luminescence, its transparency to the ultra-violet and its absorption spectra in the visible, the ultra-violet and the infra-red. It also follows that diamonds in which the tetrahedral and octahedral forms of diamond intrude into each other should exhibit a birefringence pattern related to the nature and extent of such intrusions. These conclusions are strikingly supported by a comparison between the luminescence, ultra-violet transparency and the birefringence patterns of the same diamond placed side by side. The existence of such variations of structure should also reveal itself as corresponding variations of X-ray reflection intensity, the nature of which would depend upon the precise details of the case.

4. *Description of the Topographs*

The 18 topographs reproduced as Figs. 4, 5 and 6 in Plates XXIV and XXV show great differences amongst themselves. The cleavage plates of diamond with which they were recorded were, in fact, selected so as to be representative of a wide range of variation of the behaviour of diamond as exhibited in other physical properties, *viz.*, colour and intensity of luminescence, ultra-violet transparency and the absence or presence of birefringence as seen between crossed nicols. The interpretation of the topographs is greatly facilitated by a knowledge of the behaviour of the specimens under study in these respects. While each diamond shows individual peculiarities, the topographs may be broadly classified into three groups:

(A) Those in which the reflecting power of the crystal plate is more or less uniform over its surface, so that but little detail is visible in the topographs, *e.g.*, D36, D45, D221. It should be mentioned that in these cases the intensity of the X-ray reflection is so weak that exposures of from two to three hours were found necessary to get a satisfactory picture.

(B) Those in which the topograph exhibits a great general intensity of X-ray reflection, so that from ten to twenty minutes of exposure was found to be sufficient. D206, D207, D208, D209 are examples of this class. It will be noticed that in all of them, sets of parallel streaks running in different directions through the plate are a characteristic feature. This is seen in a particularly striking manner in D208 and D209.

(C) Those diamonds in which the features described in classes (A) and (B) appear to coexist, so that while the crystal as a whole exhibits comparatively weak X-ray reflection, overlying this some intense regions also appear. These intense regions may be of several kinds. They may consist of:

(i) small areas of comparatively intense, but fairly uniform reflection, or

(ii) a few fine streaks running through the crystal in different directions, or

(iii) a combination of both these features. D180 shows both these features in a very striking way, *viz.*, a central bright patch with fine streaks running out in different directions. D181 is a fine example of a diamond showing a fairly uniform weak X-ray reflection, which is overlaid by a set of intensely reflecting parallel streaks. All the diamonds not mentioned under class (A) or (B) may be included in this class.

5. *Interpretation of the Topographs*

The interpretation is somewhat simplified on account of the fact that the classification in the preceding section also follows the classification that one would make considering the other properties of diamond. Thus, the diamonds in class (A) are weakly blue-luminescent, are opaque to the ultra-violet, and show no noticeable birefringence. They must therefore belong to the tetrahedral variety, and the extent of interpenetration of the two types Td I and Td II must be uniform throughout these specimens, as is shown by the uniform intensity of their luminescence. The mosaic structure in these diamonds must be on an extremely fine scale, showing no gross variations in the structure.

Diamonds belonging to the class (B) are transparent to the ultra-violet upto 2250 Å.U., are non-luminescent and show an intense birefringence, the

restoration under crossed nicols consisting of a large number of parallel streaks, related to, but not necessarily identical with, those in the topograph. It is clear, therefore, that they are purely of the octahedral type, in which the intense reflection arises from the fact that the two modifications Oh I and Oh II interpenetrate. The fact that the intensity is not uniform, but that the topograph exhibits parallel bands of intense reflection shows that the extent of interpenetration of the two structures is variable.

Diamonds belong to class (C) exhibit the properties of both the above classes. In fact, they are mixtures of the two structures, part of them being of the octahedral type, and the remainder of the tetrahedral. The mixing of the two types may occur in different ways. The whole diamond may consist of the tetrahedral type, and a few streaks of the other type may intrude into it. In this case, the intrusions alone will give a strong X-ray reflection, while the rest of it will be very weak. On the other hand, there may be an intimate mixture of the two types on a rather fine scale. It is not then possible to detect it by X-ray methods alone. Here, it may be pointed out that an intense X-ray reflection given by a portion of a diamond may mean one of two things—either it may be due to an increased interpenetration of the Td I and Td II structures, or it may be due to the presence of the octahedral structure.

The results obtained from the X-ray topographs confirm, and are confirmed by, those from the other patterns. First, we shall take up the evidence of the luminescence patterns. As already said, D36, D45 and D221 exhibit practically uniform fluorescence over their body, as is to be expected from their X-ray behaviour. D180 shows an intense central triangular region in the X-ray topograph, and this beautifully corresponds with a similar bright region in the luminescence photograph. A few bright streaks running in various directions are also seen in the topograph in addition. These are presumably due to the intrusion of the octahedral diamond, and are not shown by the luminescence pattern, although they are revealed by a spectroscopic study of the light transmitted by the various parts of the diamond. The topograph of D38 shows a few streaks brighter than the surrounding, but these correspond to dark regions in luminescence, showing that they are streaks of the octahedral diamond. A similar relation exists between the two patterns of D188. This diamond exhibits an intensely blue-fluorescing region at its centre, which is surrounded by a feebly blue-fluorescing background traversed by yellow bands running in various directions, and forming a figure similar to that of a spider web. In the X-ray topograph, the central portion shows itself as an intensely reflecting region.

The portions corresponding to the yellow bands also come out as bright streaks, showing that they arise from the intrusion of the octahedral strcture.

In the ultra-violet transparency patterns, the transparent and consequently bright portions in the pattern are of the octahedral type, while the opaque portions must contain the tetrahedral structure. D235 is a fine example of a mixed type, in which the top semi-circular portion, and one of the bottom corners show transparent patches, while the rest is mostly opaque to the ultra-violet. The X-ray picture confirms this, since the same two portions give more intense reflections than the rest of the diamond. The other parts of the picture are however crossed by a few bright bands, showing that these portions are not purely of the tetrahedral structure Another interesting example of the correlation between the ultra-violet and the X-ray patterns is that of D188, already described, whose ultra-violet pattern also shows transparent bands surrounding the centre of the diamond.

Intrusions of the octahedral variety in the other type will clearly set up strains, and give rise to birefringence. Hence, the X-ray topographs of the mixed type of diamonds must show some similarities to the birefringence pattern. One of the finest examples is that of D181, which shows practically uniform blue fluorescence, but in which a few faint yellow bands could be seen only with difficulty. The presence of these streaks of octahedral diamond is, however, clearly demonstrated by the X-ray topograph in which they reveal themselves as a set of bright parallel streaks. The birefringence pattern of this diamond shows features remarkably corresponding to those in the X-ray patterns, and thus confirms the finding of the latter. So also, the two patterns of D179 show a very close similarity. In the topograph of D174, there is a bright central region, surrounded by a bright boundary in the form of an irregular pentagon. In the birefringence pattern of the diamond, the same figure is visible, and outside it, there are a number of bands parallel to the sides of the figure.

The X-ray patterns of other mixed diamonds are too complicated to be resolved and interpreted. But the case of D195 is interesting. Here, there is a central triangular portion which luminesces strong blue, and corresponding to this, there is also a bright triangular patch in the X-ray pattern. Round this triangle, and parallel to its sides, there are a few bands in the topograph, showing that the octahedral structure is present in these portions. These regions either luminesce green or are non-luminescent.

I wish to record my heartfelt gratitude to Prof. Sir C. V. Raman for the suggestion of the problem, and for the many helpful hints which he gave me during the course of the experiment.

6. Summary

The paper reports a method by which it is possible to obtain topographic maps representing the variations in the reflecting power for X-rays over the area of a plate of any crystal. The method consists in using white X-radiation diverging from a pinhole, and photographing the Laue reflection from any set of crystallographic planes within the crystal. The distortion, which is inevitable in such an arrangement, can be eliminated by suitably tilting the crystal and the photographic plate. Eighteen such "topographs" of cleavage plates of diamond in the collection of Sir C. V. Raman are reproduced in the plates accompanying the paper. A discussion is given of the relation of these to other patterns, such as the luminescence, ultra-violet transparency and birefringence patterns of the same diamonds. It is shown that the evidence of these corroborates and supports that of the X-ray topographs, and that the increased intensity of X-ray reflection arises out of the mosaic structure produced by the interpenetration of the various possible structures of diamond.

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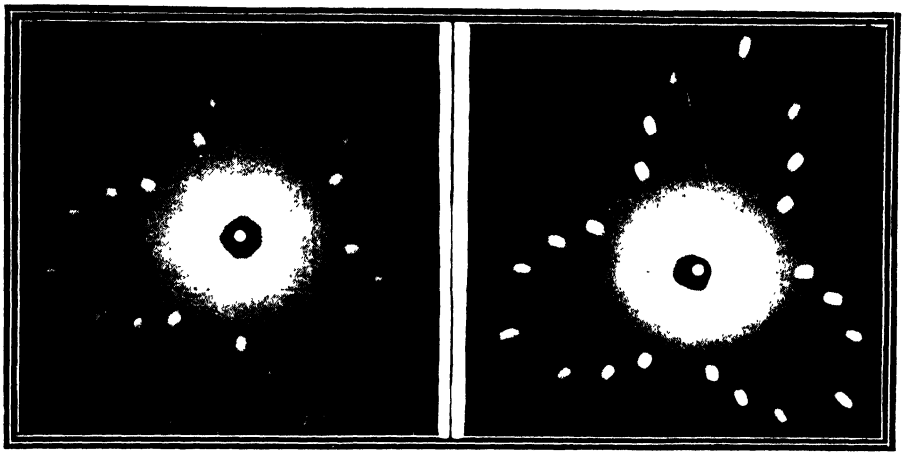
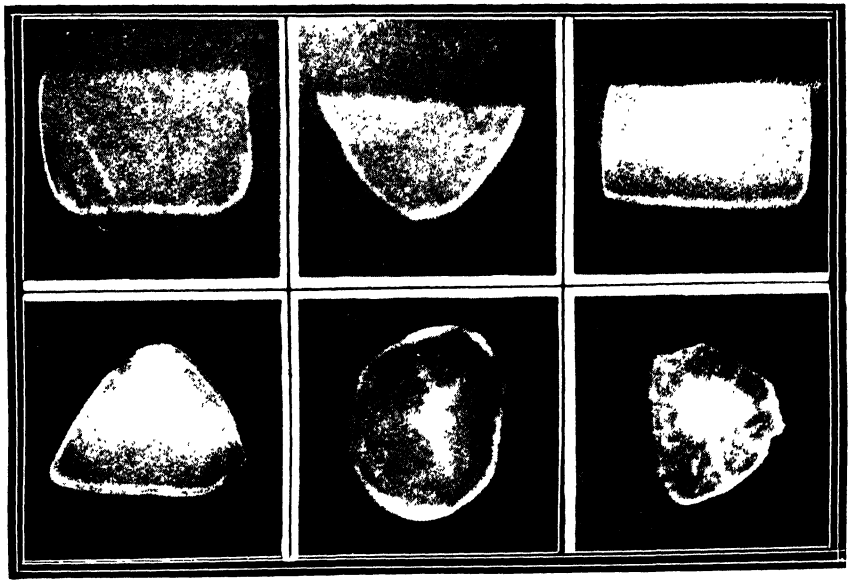


D31 D41

FIG. 3. Laue Photographs of two Blue-Fluorescent Diamonds

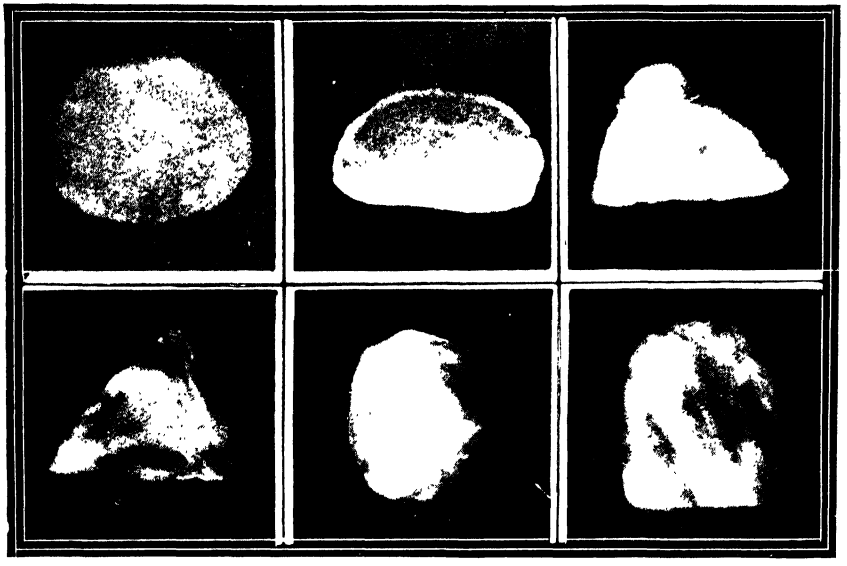
D36 D45 D221



D174 D179 D180

FIG. 4. X-Ray Topographs of Blue-Luminescent Diamonds

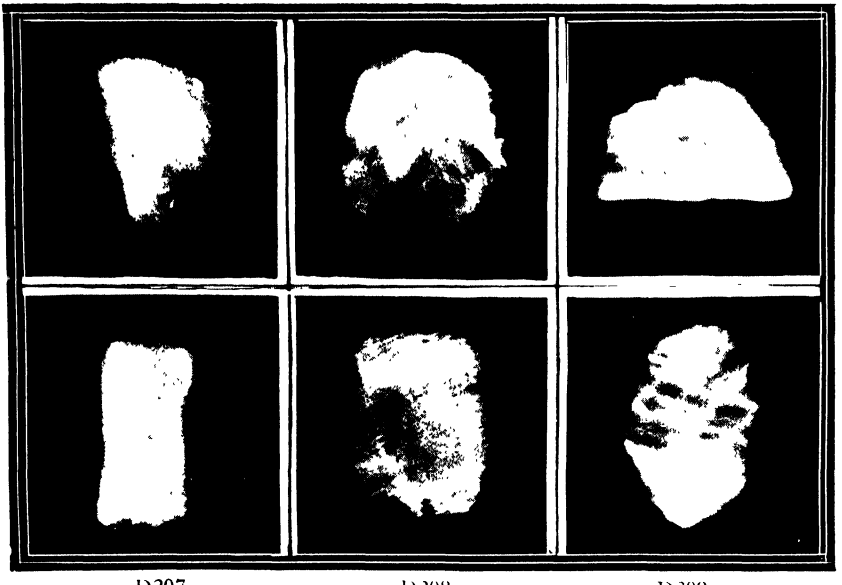
D38 D181



D195 D188 D235

FIG. 5. X-Ray Topographs of Blue-Luminescent and Yellow-Luminescent Diamonds

D199 D200 D206



D207 D208 D209

FIG. 6. X-Ray Topographs of Yellow-Luminescent and Non-Luminescent Diamonds

ULTRA-VIOLET TRANSPARENCY PATTERNS IN DIAMOND

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1. Introduction

The observation by Sir C. V. Raman (1943) that luminescence patterns are shown by some of the cleavage plates of diamond in his collection pointed the way to further researches in various other directions. Working with one such diamond which showed a pattern prominently, Mrs. K. Sunanda Bai (1944) noticed that the extent of the ultra-violet spectrum which it transmits is highly variable over its area. This observation indicated the desirability of developing a method by which such variations of ultra-violet transparency could be more conveniently observed and exhibited. The present paper describes the successful realisation of this idea. The method developed renders evident to the eye at a glance both the degree of transparency of the diamond as a whole and also its local variations for the chosen wave-length in the ultra-violet region. The current belief that a diamond is either opaque or transparent—oftener opaque—to the ultra-violet spectrum beyond 3000 A.U. is shown to be incorrect. Actually, every behaviour ranging between the extremes of transparency and opacity is observed—even inside a single individual piece of diamond.

2. Experimental Technique

The familiar way of examining whether an object is transparent is to hold it up against an extended source of light, *e.g.*, a window lit by the sky. An imperfect transparency of the object or of any portion of it then immediately reveals itself. In endeavouring to apply this simple technique to the study of the transparency of diamond in the ultra-violet, the principal difficulty is that of isolating the desired region of the spectrum and eliminating the rest. If the unwanted radiations are not completely excluded, wholly erroneous conclusions would be arrived at from the observations. The use of filters and of monochromators or of a combination of them were amongst the devices thought of and rejected after trial as unsuitable for the present purpose.

A procedure which has been found to be both simple and successful in practice is the use of an ultra-violet light-source in which the radiations of a chosen suitable wave-length are of such preponderating intensity that the other radiations can be easily and effectively eliminated without prejudice to the main purpose of the arrangement. Such a source is furnished by a water-cooled magnet-deflected mercury arc in quartz which emits an extremely intense radiation of wave-length 2536 A.U. The highly monochromatic image of the arc formed by this radiation and a suitable optical system is thrown on a plate of uranium glass and made visible by the resulting intense fluorescence of the latter. If a piece of diamond is stuck on to the front surface of the uranium glass, its behaviour in respect of the transmission through it of the 2536 radiations is immediately rendered evident by its screening effect on the fluorescence of the uranium glass.

Some experimental details may be worth recording. A small horizontal Heraus quartz mercury arc 5 cms. long and 1·5 cms. diameter was employed. It was held dipped in a trough containing flowing water so that the electrodes were completely immersed and remained cool when the arc was running. The discharge was deflected to the upper wall of the quartz tube by a small electromagnet, and the light emerging from it upwards was reflected horizontally forwards by a small stainless steel mirror. A quartz lens of 50 cms. focus, a constant-deviation quartz prism 5 cms. high (which could be adjusted) and a second quartz lens of 60 cms. focus were the successive items in the optical train which formed monochromatic images of the light source on a plate of uranium glass. The image formed by the 2536 radiations and made visible by the fluorescence of the plate could be readily picked out by its great intensity. By enclosing the lenses and prism in a wooden box with darkened sides and suitable apertures, extraneous light was avoided. Even so, there was some parasitic illumination due to the scattering of light at the surfaces of the lenses and prism, but this gave no trouble whatever, *provided the uranium glass plate was viewed by the fluorescent light alone in a slightly oblique direction and not by the parasitic light which came directly through it.* The appearance of the diamond as seen on the fluorescent screen could be readily photographed with the same precautions as those noted above. A camera with 5 cms. focus lens and Ilford selochrome plates gave good pictures, the exposures being regulated according to the nature of the case.

3. Some General Observation

The method of observation described above is so quick and convenient that a great many specimens can be rapidly examined by its use. It is not even necessary that they should be flat cleavage plates. For, if a specimen

of diamond were opaque to the 2536 radiations, it would appear opaque and throw a black shadow on the fluorescent screen having the shape of its external boundary irrespective of its shape, while if it were wholly or partially transparent, some evidence of this would appear on the screen when the specimen is suitably orientated.

On examining the transparency to the 2536 radiations of a batch of diamonds whose behaviour in respect of luminescence under long-wave ultra-violet irradiation (4000–3000 A.U.) is known, it becomes immediately evident that there is a very intimate relationship between these two characters of diamond. At one extreme, we have the diamonds which exhibit a blue luminescence of feeble or moderate intensity. These appear *perfectly opaque* to the 2536 radiations. Remarkably enough however, the diamonds that show an *intense blue luminescence* are *not* opaque to the 2536 radiations nor are they fully transparent to them. The partial transparency to the ultra-violet of highly luminescent diamonds was earlier and independently noticed by Sunanda Bai in spectroscopic tests. It is very readily exhibited by the present method of observation with all the diamonds in the collection which luminesce at all strongly with a blue colour.

At the other extreme, we have the diamonds which do not luminesce at all. With regards to these, we have the opposite situation, *viz.*, the more perfectly non-luminescent they are, the more perfect is their transparency. The merest trace of yellow luminescence results in a detectable deviation from complete ultra-violet transparency, while the more strongly yellow-luminescing diamonds approach nearer and nearer to complete opacity.

The situation as described above is, however, complicated by the fact, that in numerous cases, the ultra-violet transmission by the diamond is not uniform but patchy, often showing patterns of various kinds, and a comparison of these with the luminescence patterns shown by the same specimens indicates an intimate relationship between the two. The present paper is, in fact, principally concerned with these patterns, 24 of which have been photographed and are reproduced in Plates XXVI and XXVII. The catalogue numbers of the diamonds have been entered against them. With one or two exceptions, the luminescence patterns of all these diamonds have been reproduced with the paper by Sunanda Bai (1944) preceding the present one in the symposium. It is thus readily possible to compare them critically and determine the nature of the relationship between them.

4. The Patterns and Their Origin

Some of the most striking patterns have been grouped together as Fig. 1 in Plate XXVI. Though those reproduced in Figs. 2, 3 and 4 do not all

exhibit such vivid detail, nevertheless there is much in them worthy of careful examination, especially in relation to the corresponding luminescence patterns.

A very striking feature of the ultra-violet transparency patterns is that several of them bear nearly the same relation to the corresponding luminescence patterns as a lantern-slide does to the photographic negative from which it is prepared. Comparing for instance, the patterns of D48, D198, D235, D56, D189, D210, D194, D192, and D177, one finds an almost perfect correspondence of the kind indicated. This feature becomes intelligible in the light of the general observations made earlier regarding the relationships between luminescence and ultra-violet transparency, when we remember that the patterns have the same origin, *viz.*, the intrusion of one type of diamond into another. If one kind of diamond is luminescent and ultra-violet opaque, and the other kind is non-luminescent and ultra-violet transparent, we would have an explanation of the kind of relationship between the patterns which we have noted.

The matter is, however, not quite so simple as might appear from what has been said. There are cases where the relationships are quite different. Taking the instance, D180 which shows a bright blue patch surrounded by a dark area in its luminescence, its ultra-violet transparency shows no indication of this. The outline of the patch however appears as a faint line on a dark field. Take again the case of D179 which shows a striking luminescence pattern. But little of this can be made out in the ultra-violet transparency pattern except for a bright streak which appears where a dark streak appears in the .luminescence pattern. These and other examples could be quoted to show that variations in the intensity of blue luminescence do not necessarily show up prominently in the ultra-violet transparency pattern.

A striking characteristic of yellow luminescence is the appearance of numerous bright streaks running parallel to one another, sometimes in several directions simultaneously. Such an effect, for example, is exhibited very prominently in the luminescence of D188, D193, D199, D200 and D202. Their ultra-violet transparency patterns do also give indications of the presence of parallel streaks, but nothing at all comparable in fulness of detail with what is seen in luminescence. This is a point worthy of closer investigation.

It must of course, be admitted that many blue-luminescing diamonds which show a vivid pattern, *e.g.*, D38, and others which show by their birefringence, *e.g.*, D181 that they include non-luminescent diamond, are completely opaque to the 2536 radiations and therefore yield no result

D48

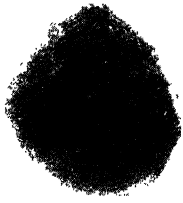
D56

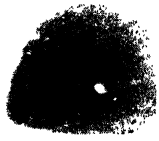
D195

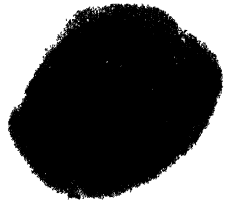
Fig. 1 Ultra-Violet Transparency Pat

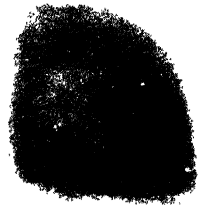
D180

D188









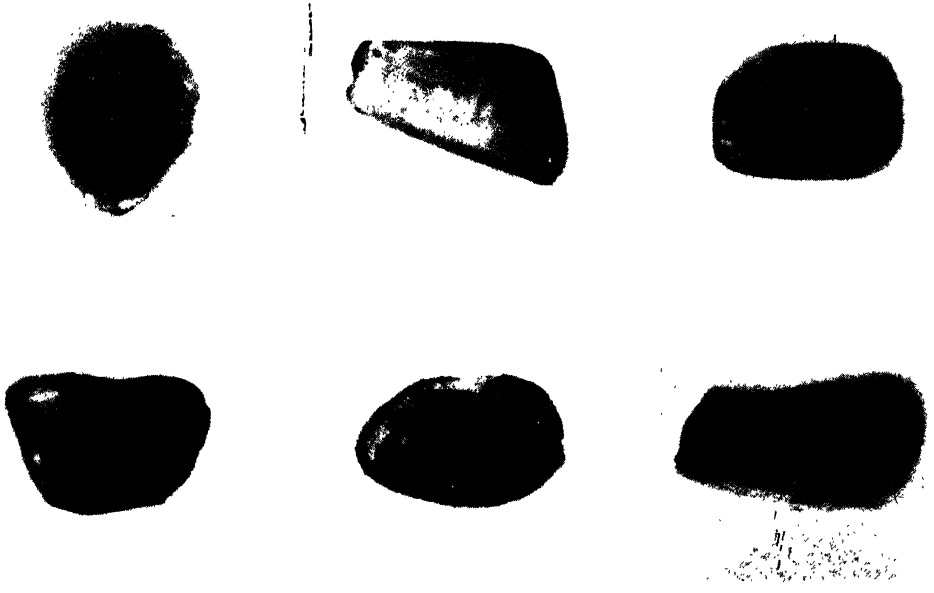
D210

D193 D194 D192

D185 D177 D202

FIG. 3. Ultra Violet Transparency Patterns

D178 D199 D236



under the present technique. It is possible that if a suitable light source of a somewhat longer wave-length could be developed, it would extend the range of investigation.

In conclusion, the author wishes to place on record his deep gratitude to Prof. Sir C. V. Raman, KT., F.R.S., N.L., for suggesting the problem and for his inspiring guidance.

5. *Summary*

Using the 2536 A.U. radiations of a water-cooled magnet-deflected mercury arc in quartz, and an optical system which forms an intense monochromatic image of it on a plate of uranium glass, it is possible to examine the ultra-violet transparency of diamond very conveniently and thoroughly. The investigation reveals that the current idea that diamonds are either opaque or transparent in this region is incorrect. A wide range of behaviour ranging between complete opacity and complete transparency is possible, and it stands in the closest relationship to the luminescence properties of the diamond. The same method enables the ultra-violet transparency patterns of cleavage plates of diamond to be photographed. In not a few cases, these patterns are very similar to the luminescence patterns but reversed. In other cases, again, such a similarity is not observed. The origin of these resemblances and differences is discussed.

24 photographs are reproduced with the paper.

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EXPERIMENTAL EVIDENCE FOR THE EXISTENCE OF THE FOUR POSSIBLE STRUCTURES OF DIAMOND

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1. Introduction

In the introductory paper of this symposium, Sir C. V. Raman has set out the theoretical considerations which indicate that the crystal structure of diamond has four possible forms. Two of these (Td I and Td II) have only tetrahedral symmetry, while the other two (Oh I and Oh II) have the full symmetry of the cubic system. These considerations receive support from the known spectroscopic behaviour of diamond, as also from the observed crystallographic facts. The fundamental oscillation of the two interpenetrating lattices of carbon atoms with respect to each other should be active in the infra-red absorption in the tetrahedral varieties of diamond, since these do not possess a centre of symmetry. On the other hand, this vibration should be infra-red inactive in the octahedral types of diamond, since these possess a centre of symmetry. The well-known fact that an intense infra-red absorption in the neighbourhood of 7·5 μ (corresponding to the lattice frequency of 1332 wavenumbers) is exhibited by some diamonds, while such absorption is absent in others, thus receives a natural explanation.

Accepting the conclusion indicated by the infra-red absorption data and the observed crystal forms that diamond may have either tetrahedral or octahedral symmetry, it is difficult to resist the further implication of the theory that there are two variants under each class. It is obviously of great importance to obtain convincing experimental evidence for the physical existence of all the four forms postulated. Since *prima facie*, all the four types should have closely similar properties, such evidence must be sought in measurements where the highest degree of precision is possible, *viz.*, in X-ray and in spectroscopic data. It is the object of this paper to present such evidence.

2. The Two Tetrahedral Structures

It is obvious that the two tetrahedral types of diamond, namely, the positive and the negative forms, are physically identical and only geometrically

different. Hence, they should possess precisely the same crystal spacing and lattice vibration frequency, and therefore apparently be indistinguishable from each other. If, however, both forms co-exist in one and the same specimen of diamond, this would give rise to a heterogeneity, and variations in the physical properties should arise depending upon the extent of their interpenetration. The spectroscopic studies of Nayar (1941), (Miss) Mani (1944) and Mrs. Sunanda Bai (1944) on the absorption and the luminescence spectra of diamonds show clearly the existence of such large variations. These may be regarded as fairly convincing evidence for the existence of the interpenetration and consequent variations in structure.

A clearer and more direct proof is, however, forthcoming from X-ray studies. The interpenetration of the positive and negative tetrahedral structures and consequent heterogeneity should evidently manifest itself in increased intensity of X-ray reflections from the lattice planes of the crystal. This conclusion was experimentally tested out by the author as early as May 1942. The diffraction of X-rays in a few typical diamonds of the tetrahedral variety exhibiting luminescence in varying degrees, was studied both by the Laue and by the Bragg methods, in the latter case with oscillating crystals. It was found that there was a direct correlation between the intensities of X-ray reflections and of luminescence of the diamond. The diamond exhibiting the blue luminescence with the least observable intensity were also the diamonds which gave the least intensities of X-ray reflections, showing thereby that these diamonds approached more closely to the ideal homogeneous structure. The strongly blue fluorescent diamonds gave rise to intense Laue and Bragg reflections, suggesting thereby that these specimens had a heterogeneous or mosaic structure arising from the interpenetration of the two tetrahedral types. These observations of the author have later been confirmed and extended by Hariharan (1944) and Ramachandran (1944).

3. The Two Octahedral Structures

Unlike the two forms of the tetrahedral type, the possible forms of the octahedral type, namely, Oh I and Oh II should be physically different from one another. Consequently, whenever interpenetration of the two octahedral forms occurs, the specimen exhibits a lamellar structure parallel to one or more of the cleavage planes of the crystal. Such specimens of diamond often show a streaky birefringence. Because of their physical difference, it is reasonable to expect the two octahedral forms of diamond structure to show a small but measurable difference in crystal spacing. The direct way of testing out the above conclusion would consist in an accurate determination of the lattice spacing in two perfectly homogeneous specimens

belonging to the Oh I and Oh II types respectively and comparing the values thus obtained. There is, however, ample evidence to show that the two structures do not ordinarily occur apart from each other, but that they co-exist in the same specimen, endowing it with a finely laminated structure. Such a structure may be expected to show periodic variations in crystal spacing detectable by appropriate methods. Indeed, the fact that diamonds of this type show characteristic birefringence patterns exhibiting their laminated structure may itself be regarded as a proof that the alternate layers in it do not have an identical crystal spacing. For, if the lattice spacings were the same throughout, there is no *prima facie* reason why any birefringence should arise.

From the large collection of diamonds of this kind in the possession of Sir C. V. Raman, diamond D209 which showed a well-defined streaky birefringence between crossed polaroids was selected for the present investigation. The geometric character of the birefringence pattern and its periodic disappearance as the crystal is rotated between the crossed polaroids, indicated that this sample would be an ideal one for the purpose of the present test. The diamond (an octahedral cleavage plate) was mounted on a goniometer with its faces vertical. The X-rays from a copper target after passing through an extremely fine vertical slit (5 mm. $\times$ 0·4 mm.) were allowed to fall on the crystal nearly at the Bragg angle for the surface reflection. The crystal was oscillated through a small angle about this position and the resulting Bragg reflection from the front surface of the crystal was recorded on a photographic film. The film was kept normal to the diffracted beam at a distance of about 40 cm. from the crystal. A typical oscillation photograph obtained is reproduced in Fig. 1 (*b*) in the accompanying plate. The reflections due to the Cu $K\alpha_1$, and Cu $K\alpha_2$ radiations are seen well resolved in the photograph; the intense one corresponds to Cu $K\alpha_1$. It will be noticed that these Bragg reflections instead of being linear in shape and of uniform intensity are wavy in nature and also show a periodic variation of intensity. The most intense portions are bent towards the direct beam and hence correspond to smaller values of θ, while the less intense portions are bent away from the direct beam. If the crystal were perfectly homogeneous through the section where the X-rays were incident, the Bragg reflections would give rise to a linear and true image of the slit. As the crystal used was heterogeneous with periodic variation in crystal spacing, the Bragg reflections would show a corresponding waviness. From a measurement of the amplitudes of the waviness and the average separation of the $K\alpha_1$ and $K\alpha_2$ reflections, the difference in crystal spacing has been estimated. It is found that the difference is of the order of 5 parts in 10,000. The inter-

penetration of one octahedral form into the other has not only caused a periodic variation in the crystal spacing, but also given rise to a mosaicity, as is evident from the increase in intensity of Bragg reflections from these layers.

Oscillation photographs were also taken for various settings of the same crystal and the Bragg reflection in every case showed the wavy character. The distribution of the intense and weak spots was different in each case. A typical oscillation photograph for a different setting of the crystal is reproduced in Fig. 1 (*c*) in Plate XXVIII. The experiment was repeated with a second diamond (D45 in Sir C. V. Raman's collection) which was only very feebly fluorescent and belonged to the tetrahedral type. The oscillation photograph is reproduced in Fig. 1 (*d*). As is to be expected, the Bragg reflection from D45 does not exhibit any wavy character. The reflected image is quite linear and of uniform intensity.

Very recently, Mrs. Lonsdale (1944) has carried out measurements of the crystal spacing in a large number of diamonds. She found no variation in the spacing greater than 2 parts in 10,000 in the various specimens examined by her. Very few diamonds which were transparent to the ultra-violet were included in her list. As already mentioned, however, the transparent variety of diamond usually occurs as a mixture of the two octahedral structures. Hence what Mrs. Lonsdale measured was the mean of the spacings of the two octahedral structures and her observations leave the question of the difference between the Oh I and Oh II spacings with which we are here concerned entirely untouched. It should be remarked that the success attained in the present investigation is largely due to the choice of the specimen in which the spacings of the laminations were sufficiently great to exhibit the waviness of the Bragg reflections. Specimens in which the laminations are very fine would obviously fail to show the effect.

4. The Spectroscopic Evidence

As has already been pointed out earlier in the paper, the two octahedral structures are physically different. It is therefore reasonable to suppose that the frequency of the fundamental lattice oscillation would be different for the two structures. The expected variation in lattice frequency would probably be of the same order of magnitude as the variation in the crystal spacing, namely, about 5 parts in 10,000. Even such a small difference in lattice frequency should, however, be sufficient to give rise to an observable broadening of the fundamental Raman line in the case of a diamond containing a mixture of the two forms. The experiment was carried out as follows :—

The Raman spectrum of diamond D227 (which belonged to the octahedral variety) was photographed through a Hilger E_1 quartz spectrograph using as fine a slit as possible. The 2536 resonance radiations of a water-cooled quartz mercury arc were used for exciting the Raman line. Visual observation of the recorded spectrum showed that the 1332 line had a finite breadth greater than that of any of the mercury lines of comparable intensity. This was confirmed by taking a microphotometric record of the spectrum. The microphotometric records of the mercury triplet at 2655·1, 2653·7 and 2652·0 A.U. and that of the Raman line are reproduced in Figs. 2 *a*, *b c*, and *d* respectively in the accompanying Plate. The mercury line at 2655·1 A.U. has nearly the same intensity as the 1332 Raman line, whereas the width of the Raman line is a little more than one and a half times that of the mercury line. The difference in width between the two is approximately one wavenumber. This is of the same order of magnitude in relation to 1332 as the observed difference in lattice spacings. Thus, the spectroscopic data also lend support to the view that there are two different structures in the octahedral type of diamond, though, no doubt, the observed width of the Raman line is, in part, due to the finite width of the 2536 line itself.

As the two tetrahedral forms of diamond are physically identical, their lattice vibrations should have identical frequencies but different from that of either of the octahedral forms. It is conceivable, however, that the *mean* lattice frequency of the octahedral types might be the same as that of the tetrahedral variety. In order to test these points, the Raman spectra of two diamonds D36 and D227 (the former of the tetrahedral type, while the latter of the octahedral type) were photographed side by side through a Fuess spectrograph using a Hartmann diaphragm. The spectrogram is reproduced in Fig. 1*a* in Plate XXVIII. The top picture represents the Raman spectrum of D227, while the bottom picture represents the Raman spectrum of D36. As far as can be made out, there is no difference in the frequency shifts and the Raman line appears in exactly the same position for the two diamonds. An enlarged picture of the 1332 Raman line excited by the 4046 radiation with suitable adjustment of the background intensity is reproduced in Fig. 1*e*. The upper portion of the figure represents the spectrum in D36, while the lower portion represents the spectrum in D227. The Raman line in D227 appears to be definitely broader than the corresponding line in D36, in agreement with the general considerations indicated above.

In conclusion, the author wishes to express his grateful thanks to Prof. Sir C. V. Raman for suggesting the problem and for valuable discussions during the progress of the investigation.

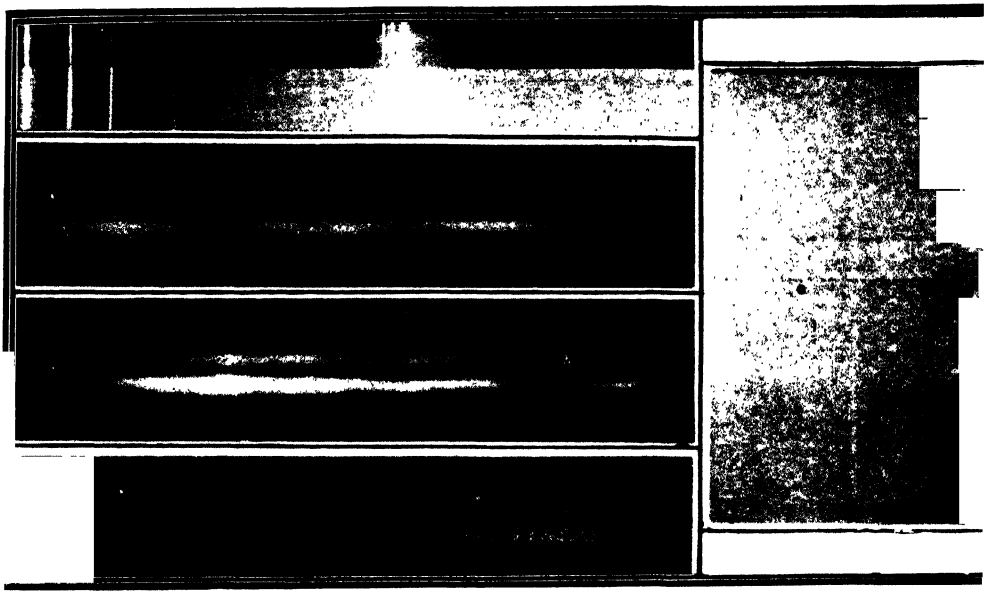
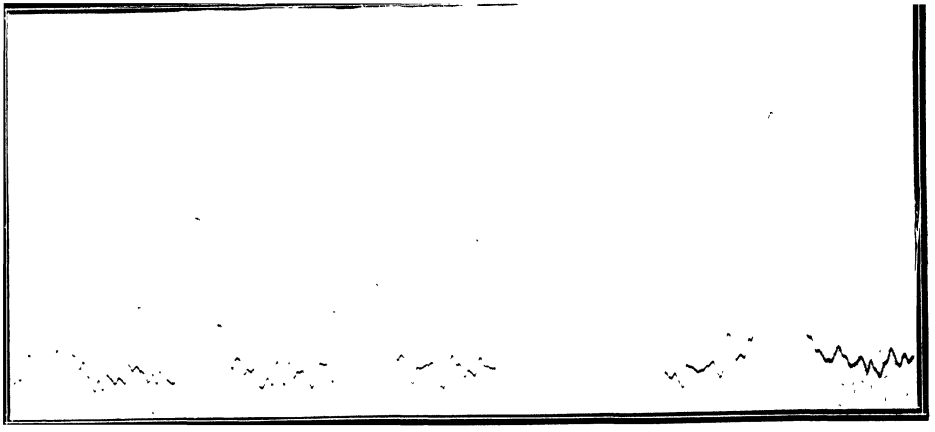


FIG. 1



5. Summary

Experimental evidence has been obtained for the existence of the four possible structures of diamond from X-ray and spectroscopic studies. The co-existence of the two variants of the tetrahedral structure in one and the same specimen and the heterogeneity arising therefrom have been confirmed from the observed increased intensities of X-ray reflections in such diamonds. Using the oscillating crystal method and a diamond in which the two structures of the octahedral type co-exist in adjacent layers of the crystal, it is observed that the Bragg reflections exhibit a waviness such as should be observed if there be a difference in the crystal spacings of the alternate layers. The observed difference in crystal spacings thus deduced is of the order of 5 parts in 10,000. The Raman line corresponding to the fundamental lattice vibration shows a definite width in the case of the octahedral type of diamond which agrees at least, in the order of magnitude, with the expected difference in the vibration frequencies of the two octahedral structures.

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X-RAY REFLECTION AND THE STRUCTURE OF DIAMOND

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

According to the well-known Ewald-Darwin theory of the reflection of X-rays by perfect crystals, the integrated reflection, or the total intensity reflected as the crystal is swung through the Bragg angle, is proportional to the structure factor of the particular set of planes concerned. On the other hand, if the crystal were ideally imperfect, so that one can neglect the effect of both primary and secondary extinction, then the integrated reflection becomes proportional to the square of the structure factor (Darwin, 1914 *a*, 1922). In general, therefore, the intensity of reflection is much greater for an imperfect crystal than for a perfect one. Crystals have generally been classified as either perfect or ideally imperfect, according as the integrated reflection approximates to the theoretical value calculated for the one or the other. To the latter class are assigned most of the crystals like rocksalt, fluorspar and barytes (Bragg, Darwin and James, 1926). Calcite is the only example for which values of the integrated intensity approaching that for a perfect crystal have been obtained (for references see Compton and Allison, 1935, pp. 399 to 405). Although the integrated reflection has not been measured for diamonds, measurements of the width of reflection have been made by Ehrenberg, Ewald and Mark (1928), who found values remarkably close to that for a perfect crystal with some specimens.

As already said, ordinary crystals either belong to the perfect or to the imperfect variety. It is not easy to get samples of the same crystal possessing varying degree of mosaic structure. However, in the case of diamond, such a procedure is possible. For, diamond can exist in four allotropic modifications, and, in an actual crystal, these can appear either alone, or two or more structures can appear intermingled (Raman, 1944 *a* and *b*). The extent of interpenetration of the different structures may also vary from sample to sample. Thus, one can obtain various types and degrees of mosaic structure by having crystals of diamond which exhibit different

colour and intensity of fluorescence. *Vice versa,* by studying the reflection of X-rays by different crystals of diamond, one can obtain some knowledge of the nature of the mosaic structure in diamond.

That such a mosaic structure exists in blue-fluorescent diamonds was first shown by R. S. Krishnan (Sir C. V. Raman, 1942), who obtained the Laue photographs of two such diamonds, one of which D31 was feebly blue-fluorescent and the other D224 was strongly fluorescent, also blue. He found that all the spots in the Laue pattern of the latter were more intense than the corresponding ones of the former. Following this discovery, P. S. Hariharan (1944) studied the intensity of the (111) Bragg reflection given by a number of diamonds, and found that there is a direct correlation between the intensity of X-ray reflection and of blue-fluorescence. It was therefore thought worthwhile to extend the investigation to some of the other important reflections given by diamond. This was done by taking the Laue patterns of two typical blue-fluorescent diamonds, which differ widely in their intensity of fluorescence.

2. *Experimental Details and Results*

The specimens used were carefully selected out of the collection of Sir C. V. Raman so as to have as nearly as possible the same thickness, and to be as perfectly isotropic as could be obtained. The diamonds used were D31 and D41, both octahedral cleavage plates of very nearly the same thickness, about 1 mm. The actual thicknesses were 0·96 mm. and 1·0 mm. D31 was feebly blue-fluorescent, while the other one was intensely fluorescent, also blue.

The source of X-rays consisted of a self-rectifying Shearer tube, excited by a transformer, and worked at 50 K.V. and 9·5 milliamperes. This was kept steady by continuous adjustment of the air-leak and the resistance in the primary circuit of the transformer. The X-ray beam was collimated through a pinhole 1 mm. in diameter and 10 cm. long.

The diamond plate could not be mounted on a goniometer since this prevented the photographic film from being brought close to the crystal so as to record the complete pattern. Consequently, the goniometer was dispensed with, and the diamond was placed straight against the exit end of the slit and stuck to it by means of wax. As already said, the surface of the diamond was parallel to the (111) plane, so that it was most convenient to mount the plate with the surface (111) planes normal to the X-ray beam. This was done by hand, the normality being judged by taking a picture of the $(11\bar{1})$, $(1\bar{1}1)$, and $(\bar{1}11)$ Laue spots and verifying

that they are at equal distances from the central spot. After this adjustment was made, the complete pattern was photographed by placing the film quite close to the crystal (at a distance of 9·5 mm.) and normal to the X-ray beam. An exposure of 3 hours was required to obtain a clear picture. Throughout the exposure, both the voltage applied and the current through the tube were maintained rigorously constant by continuous manipulation.

With diamond 31, standard pictures with exposures of 5, 90 and 180 minutes were taken. Then, using diamond 41, a series of pictures were taken with exposures varying from 2 to 180 minutes (for reasons to be explained shortly) under the same conditions as for D31. All the films were developed under standard conditions in the same stock developer.

The photographs obtained with an exposure of three hours in the two cases are reproduced in Fig. 3, Plate XXIV in a previous paper by the author appearing in this symposium. The Laue pattern consists of spots lying in the three zones, the $(1\bar{1}0)$, $(10\bar{1})$ and $(01\bar{1})$, and the indices of the spots in any zone belong to the forms {111}, {211}, {311}, {511}, {711} and {100}. It will be seen from the figure the intensities of the spots are greater in the pattern of D41 than of D31.

A detailed microphotometry of the peak intensities of the various spots was then undertaken. In this connection, it must be noted that the wave-lengths of the X-rays giving rise to the different Laue spots are different. Consequently, the calibration curve for the determination of the intensity had to be plotted for each wave-length required. It was for this purpose that a number of photogarphs were taken with a wide range of exposures, with the diamond giving stronger reflections. Using these photographs, and assuming the well-known result that the Schwarzchild's constant for X-rays does not differ appreciably from unity, the density-log intensity curve was drawn for each of the wave-lengths. From this curve, the intensity of the corresponding spots in the pattern of D31 were evaluated. It may be remarked in this connection that the Laue photographs obtained are not absolutely symmetrical, but that there is a small asymmetry. In order to avoid the errors arising from this, the intensity of all the six or three (as the case may be) spots having the same indices were measured, and the average was taken as the correct value.

The ratios of the intensities obtained in this way are shown in the second row in Table I.

TABLE I

Indices of the reflection ..	111	422	311	511	711	400
I_{41}/I_{31}	3·36	2·24	2·31	1·93	1·49	2·72
I_{224}/I_{31}	..	3·20	3·61	2·55	1·81	4·61
I_{224}/I_{41}	..	1·54	1·56	1·32	1·21	1·69

It will be seen from the table that the ratio of the intensities given by the two diamonds is not a constant for all the planes, but that it varies from one to another. In order to confirm this fact, the photographs taken by Dr. R. S. Krishnan with diamonds 31 and 224, which were reproduced in *Current Science* (Sir C. V. Raman, 1943) were subjected to microphotometry. The original negatives of these were kindly lent to the author by Dr. Krishnan. Although the thicknesses of these two diamonds were not the same, still the photographs could be used for the purpose of a check. The values obtained for the ratio I_{224}/I_{31} are shown in the third row in Table I. The ratios deduced for I_{224}/I_{41} from the above are tabulated in the fourth row. Although no claim is made as to the accuracy of the values of I_{224}/I_{31} and of I_{224}/I_{41}, it is clear that the ratio of the intensities of reflection given by two blue-fluorescent diamonds is not the same for all the planes, but that it varies. Further, the plane whose intensity is affected most is the same for all diamonds, and the order in which the intensities are enhanced is also the same.

3. *Interpretation of the Results*

From the experimental results described in the preceding section, it is clear that the enhancement in intensity produced by the mosaic structure which is present in blue-fluorescent diamonds is not the same for the various planes. A clue to the understanding of the cause for this comes out of a study of the intensity of X-ray reflection by perfect and by ideally imperfect crystals. According to Darwin (*loc. cit.*), the expressions for the integrated intensity reflected out of a crystal plate are, for a perfect one,

$$I_p = \frac{8}{3\pi} N\lambda^2 F \frac{e^2}{mc^2} \cdot \frac{1 + |\cos 2\theta_0|}{2 \sin 2\theta_0},$$

and for an ideally imperfect one,

$$I_i = \frac{N^2\lambda^3}{2\mu} \cdot \left(F\frac{e^2}{mc^2}\right)^2 \cdot \frac{1 + \cos^2 2\theta_0}{2 \sin 2\theta_0},$$

where N is the number of unit cells per c.c., F is the crystal structure factor for the unit cell, λ is the wave-length reflected, and θ_0 is the angle of

incidence for the particular reflection, μ is the linear absorption coefficient, and e, m and c have their usual significance. The perfect crystal formula is true only for a non-absorbing crystal, and for one which is not so I_p would obviously be less. Consequently, while comparing the two quantities I_p and I_i, we need not consider the factor $1/\mu$ in the expression for I_i, and the ratio of the two may be written as

$$\frac{I_i}{I_p} \propto N\lambda F \frac{e^2}{mc^2} \cdot \frac{1 + \cos^2 2\theta_0}{1 + |\cos 2\theta_0|}$$

Here, e^2/mc^2 is a universal constant, and N is a constant for a particular crystal, so that one may write

$$I_i/I_p \propto k\lambda F,$$

where k stands for the ratio $(1 + \cos^2 2\theta_0)/(1 + |\cos 2\theta_0|)$.

The above expression relates to the increase in intensity when a perfect crystal is completely broken up. However, in the case of diamond, with which we are concerned, the crystal approaches perfectness, but possesses a slight mosaic structure, which increases with increase in the intensity of blue-fluorescence. Therefore, we may expect the ratio of the intensities for two blue-fluorescent diamonds to be some function of $(k\lambda F)$. In Fig. 1, the quantities I_{41}/I_{31}, I_{224}/I_{31} and I_{224}/I_{41} (which may be denoted by r_1, r_2 and r_3 respectively) are plotted as ordinates against $(k\lambda F)$ as abscissæ.

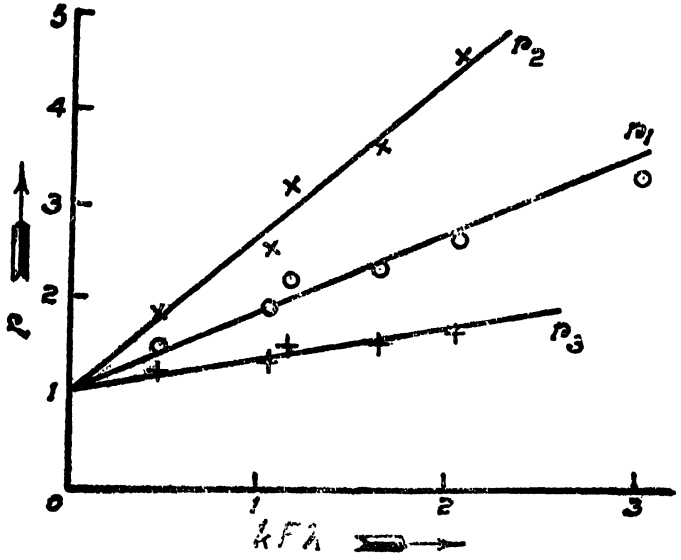

FIG. 1. X-Ray Reflection and the Structure of Diamond

The plotted points are found to lie approximately on straight lines, the equations to which are:

where the c's are constants. Thus the ratio r depends linearly on the product $(k\lambda F)$, having a value unity when the structure factor F is zero.

The author is not in a position at present to give a theoretical explanation for this empirical relation connecting r and $(k\lambda F)$. It may be remarked that even if r is plotted against (λF), then also the points lie on straight lines intersecting the r axis at $r = 1$.

In conclusion, I wish to express my deep sense of gratitude to Prof. Sir C. V. Raman for the suggestion of the problem and for the encouraging guidance which he gave me during the investigation. My thanks are also due to Dr. R. S. Krishnan for the loan of the two negatives taken by him.

Summary

Laue photographs with the X-ray beam normal to the surface (111) planes have been taken for two typical blue-fluorescent diamonds exhibiting widely different intensities of fluorescence, but similar in other respects. Microphotometry of the peak intensity of the various spots shows that although the intensity of all the spots is greater with the more fluorescent diamond, the ratio (r) of the intensities of the corresponding spots varies. Empirically, it is found that $(r - 1)$ is proportional to the product of the structure factor, the wave-length reflected and a function of the angle of incidence.

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MAGNETIC SUSCEPTIBILITY OF DIAMOND

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1. Introduction

Diamond is a solid of which several of the physical characters show remarkable variations. While the finest specimens are perfectly colourless and transparent, this is far from being generally the case. The majority of the so-called "industrial" diamonds have noticeable tints such as gray, brown or yellow, while some highly prized specimens exhibit quite definite colours such as pink or blue. Under long-wave ultra-violet irradiation many diamonds luminesce, the intensity and colour of the emitted light varying enormously from specimen to specimen, while some diamonds remain completely dark. It is a statement often made in the literature that the colours of diamond and its luminescent properties owe their origin to the presence of impurities. One method of testing these suppositions which does not involve the destruction of the diamond by chemical analysis is the accurate measurement of its magnetic susceptibility. As is well known, diamond is diamagnetic and it is therefore a possibility that such measurements may indicate the presence of para-magnetic or ferromagnetic impurities even in small amounts. The present investigation was undertaken to find whether there are any observable variations in the susceptibility of diamond, and if so, whether they show a correlation with the colour of the specimen, its luminescence and also with such other properties as have been known to vary, *viz.*, the transparency in the ultra-violet region of the spectrum and the photo-conductivity.

The 40 specimens examined were chosen from the personal collection of Sir C. V. Raman. Many of them were crystals in their natural form from the Panna diamond mines in Central India. Some of the others were cleavage plates, mostly of Indian origin, while the rest were diamonds of South African origin which had been faceted and polished for use as jewellery.

2. *Experimental Arrangements*

The susceptibility measurements were made by a Curie balance constructed by the author. An electromagnet with arrangement to clamp the coils at any suitable angle was used. A light aluminium beam was suspended by a torsion wire from a drum-head capable of rotation. The specimen was placed in a container made of thin silver foil and suspended in the field by a thin fibre from one end of the beam. The deflections of the beam were measured by the lamp and scale method. The non-homogeneous field was produced by pole pieces 5 cm. in diameter which were fixed at a suitable inclination so as to give a flat maximum for the factor $H.dH/dx$. Its variation in this region was investigated by finding the force on water enclosed in small glass bulbs of different sizes. The force was found to be proportional to the mass of water taken within the experimental error, showing that the " nonhomogeneity " was uniform. Further, for plates of diamond, closely fitting containers were made to hold the diamond as well as the standard substance, and they were suspended so as to have the broader side parallel to the field. The specimen was always brought to this region of the field by rotating the drum-head. This was accurately done by using a plane mirror placed below the specimen with its plane at an angle of 45° to the vertical, a tele-microscope being arranged to view the reflected image.

The diamonds were cleaned thoroughly in alcohol before taking measurements with them. Double distilled water was used as the standard substance and its susceptibility taken as $-0{\cdot}72$. The deflections were measured with the container alone, then with the diamond inside the container, and finally with the standard substance. The mass susceptibility was calculated by the relation

$$\frac{D_d}{D_\omega} = \frac{\chi_d M_d - K_a V_d}{\chi_\omega M_\omega - K_a V_\omega},$$

where D_d and D_ω are the deflections due to the diamond and water; χ_d, M_d and V_d are the mass susceptibility, mass and volume respectively of the diamond, χ_ω, M_ω and V_ω are those for water and K_a the volume susceptibility of air at room temperature. The volume of diamond was calculated from its mass, assuming its density to be 3·5. The volume susceptibility of air was taken as 0·0296. The working of the apparatus was tested by determining the susceptibility of pure samples of KCl, NaCl, etc., and the standard values were obtained within an error of 1%. For each specimen, independent repetitions were made and values differing by about $\frac{1}{2}$% were obtained.

3. *Results*

The values obtained for the susceptibility of diamond and the description of the shape and colour of the specimen are tabulated below.

Catalogue No.	Mass in mgm.	Shape	Colour	$-\chi \times 10^6$
14	177·0	Irregular crystal	Light brown	·456
8	278·0	Regular crystal	Colourless	·455
224	195·5	Faceted tablet	do.	·452
27	343·8	Regular crystal	do.	·451
12	183·5	Irregular crystal	Pale yellow	·450
9	222·5	Regular crystal	Colourless	·450
47	46·6	do.	do.	·449
19	56·3	Irregular crystal	Yellow	·448
199	24·2	Cleavage plate	Colourless	·447
226	39·0	Faceted tablet	Pink	·447
48.	42·0	Cleavage plate	Colourless	·446
16	173·6	Irregular crystal	Light yellow	·446
22	41·1	Regular crystal	Colourless	·445
24	31·8	do.	do.	·445
209	49·5	Cleavage plate	do.	·444
206	38·6	do.	do.	·444
207	65·8	do.	Light brown	·443
179	56·8	do.	Colourless	·443
6	341·1	Irregular crystal	Light yellow	·442
197	88·0	Cleavage plate	Light brown	·441
23	37·7	Irregular crystal	Colourless	·440
20	54·3	Regular crystal	do.	·438
18	61·3	do.	do.	·438
21	50·2	do.	do.	·437
200	49·1	Cleavage plate	do.	·437
201	23·4	do.	do.	·437
223	54·7	Faceted brilliant	do.	·435
181	43·2	Cleavage plate	do.	·434
178	32·6	do.	do.	·433
210	47·1	do.	do.	·428
198	35·7	do.	do.	·428
13	182·4	Irregular crystal	do.	·426
5	342·6	do.	Brown	·421
39	75·7	Cleavage plate	Colourless	·418
29	29·9	Twin crystal	do.	·416
28	214·3	do.	do.	·411
*227	270·6	Faceted rod	Pale brown	·398
*30	93·6	Irregular crystal	Light brown	·372
*15	174·8	do.	do.	·326
*2	790·6	do.	Dark brown	·29

* See Text.

4. *Discussion*

The above results show that the susceptibility of most of the specimens lie between $-0{\cdot}456$ and $-0{\cdot}411$. The few specimens which give still lower values were examined for ferromagnetic impurities. No. 227 (pale yellow in colour) showed a definite fall of the numerical value of the susceptibility as the magnetising field was diminished (the values being $-0{\cdot}398$, $-0{\cdot}386$ and $-0{\cdot}366$ for magnet currents 4·5 amp., 3·5 amp. and 2·6 amp. respectively), thereby indicating the presence of ferromagnetic impurities in it.

These values of susceptibility were plotted against the corresponding values of 1/H and the value at infinite field was obtained by extrapolation to be $-0{\cdot}448$. Nos. 30 and 15 (susceptibility $-0{\cdot}372$ and $-0{\cdot}326$ respectively) both light brown in colour and both having very small quantities of inclusions showed no variation of susceptibility with field strength. No. 2 a dark brown crystal having visible inclusions gave a very low value $-0{\cdot}29$. In these cases the low value of susceptibility has to be attributed to the inclusions. It is a surprising and remarkable fact that some of the coloured diamonds gave the normal values. No. 226 is pink; No. 19 is yellow, Nos. 14, 12, 6 and 16 are light yellow or brown and these specimens gave values ranging from $-0{\cdot}456$ to $-0{\cdot}442$. In these cases, if impurities are present, their effect on the susceptibility is unobservable. A comparative study of the values with the other properties shows that there is no systematic variation of susceptibility with the difference in shape or colour. There is also no correlation between the susceptibility and fluorescence. For example, 224 is a colourless diamond with an intense blue fluorescence, 47 is faintly luminous, 48 has a strong green fluorescence and 206 is non-fluorescent and they gave very nearly the same values ($-0{\cdot}452$, $-0{\cdot}449$, $-0{\cdot}446$ and $-0{\cdot}444$ respectively). Similarly, there is no correlation between the susceptibility and the differences in ultra-violet absorption or photo-conductivity.

The susceptibilities found by the author are slightly lower than the values obtained by the previous authors. Honda (1910) obtained the value $-0{\cdot}49$, Paramasivan (1929) obtained the value $-0{\cdot}47$ while P. Pascal* (1923) and S. Meyer* (1899) gave values $-0{\cdot}52$ and $-0{\cdot}33$ respectively.

The effect of illuminating the diamond on its susceptibility was investigated with two crystals, No. 224 and No. 48, the former being intensely blue fluorescent and the latter strongly green fluorescent. The sensitiveness of the apparatus was increased considerably by using a fine quartz fibre for the suspension of the beam, which gave large angles of torsion for the force acting on the diamonds and by detecting the deflection of the beam by the lamp and scale. The deflection due to the diamond was compensated by suspending in the magnetic field a container slightly above the diamond and adding bits of aluminium wire to it. When an intense beam of light from a carbon arc was focussed on the diamond by a condensing lens, after cutting off the infra-red, no change in the reading of the scale was detected.

* Quoted by J. W. Mellor,

In conclusion the author wishes to record his deep sense of gratitude to Professor Sir C. V. Raman, for his helpful interest and encouragement in this work.

5. *Summary*

The magnetic susceptibilities of 40 specimens of diamond were measured with a Curie balance. The specimens employed were very varied in their physical properties, *viz.*, colour, absorption, luminescence and photoconductivity. No systematic changes in the susceptibility with the differences in these properties were found. The values obtained ranged between $-0{\cdot}456$ to $-0{\cdot}411 \times 10^{-6}$. They are slightly lower than those found by earlier workers.

Observations on two specimens of highly fluorescent diamond showed that there was no change of the magnetic susceptibility. when they were exposed to an intense beam of light.

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THE PHOTO-CONDUCTIVITY OF DIAMOND

Part I. Experimental Results

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1. Introduction

AMONGST the many remarkable properties of diamond is that when illuminated by visible or ultra-violet radiation, it has a detectable electrical conductivity, while ordinarily it is an excellent insulator. This property of diamond which it shares with certain other highly refractive solids was discovered by Gudden and Pohl (1920) and was the subject of extended researches by them designed to elucidate the nature of the phenomenon. Under controlled conditions of illumination and applied voltages, Gudden and Pohl observed what they describe as the primary photo-electric current, which under appropriate conditions satisfied the quantum equivalence law, namely the release of one electron per absorbed quantum of radiation. With stronger or more prolonged illumination and larger applied voltages, what is known as a secondary current is produced. The action of red light in producing an extra current in previously illuminated diamond is another remarkable phenomenon studied by Gudden and Pohl.

Even in these earliest researches, it was clear that not all diamonds behaved alike. Gudden and Pohl found that the photo-conductivity was much more conspicuous with one specimen which was transparent to ultra-violet radiation upto λ 2300 A.U. than with two others which were opaque to wavelengths smaller than λ 3000 A.U. The spectral distribution of photo-conductivity was also different. In the former case the curve had a pronounced tail, the photo-current continuously rising with shorter wavelengths, while in the latter there was a maximum at approximately λ 3400 A.U. and a minimum at λ 3000 A.U. followed again by a rise in the photo-current for still smaller wavelengths. In their later work, Gudden and Pohl (1922) found a marked selective effect for incident light at λ 2260 A.U. Generally similar results have been observed by other workers, notably Robertson, Fox and Martin (1934). These authors found that the differences in ultra-violet transparency and photo-conductivity were accompanied

by differences in the infra-red absorption spectrum, and they therefore suggested a formal recognition of the existence of two distinct types of diamond. But that such a classification is inadequate to explain the facts is evident even from their own observations. The spectral distribution curves of photo-conductivity reproduced in Fig. 13 on page 505 of their memoir for four ultra-violet transparent diamonds differ widely amongst themselves, indeed nearly as much as any one of them differs from the spectral distribution curves for the two ultra-violet opaque diamonds given in Fig. 12 on page 503 of the same paper. Both in respect of the actual magnitude of the photo-current and the shape of the spectral distribution curve, their six diamonds, D_{21}, D_{16}, D_{22}, D_2, D_1 and D_{10} evidently form a continuous sequence. The suggested classification of diamonds into two distinct types is therefore incapable of describing the facts in respect of photoconductivity in a satisfactory manner.

It is evident from what has been said that we cannot hope to understand the true nature and origin of photoconductivity in diamond unless we start with correct ideas regarding the crystal structure of the substance and its possible variations in different specimens. The introductory paper by Sir C. V. Raman of the present symposium (1944) deals with just these questions, and the results of that paper afford a fresh starting point for a consideration of the phenomena of photoconductivity and enable us to present an intelligible picture of the facts. In Part I of this paper, some observations by the author will be described which exhibit the wide range of variation of the phenomena amongst different specimens of diamond. The theoretical interpretation of the results will be considered in Part II.

2. *Experimental Arrangements*

The apparatus employed was a D.C. valve-bridge amplifier, the detailed working of which, with a circuit diagram, was described by Anantha-krishnan (1934). However, in the present case, the photo-electric cell of the set-up was replaced by a diamond holder. The latter was made of two brass rods which passed through two small ebonite pillars fixed on an ebonite base. The tips of the brass rods were made of lead which for its softness and stability was found to be more suitable than any other metal or graphite. The diamond could be tightly screwed between the two electrodes and good contact could be secured. The source of light was a quartz mercury arc of moderate intensity; the light from it was focussed on the diamond with a quartz lens. When required, the diamond could be illuminated simultaneously with red light from the opposite side, *viz.*, the white light from a 500-watt tungsten lamp filtered through a red glass. The high tension

source was a set of dry batteries giving up to 250 volts. The same high tension set was used for the plate voltage of the amplifier as well as for applying a voltage to the diamond. The linearity of amplification was tested by measuring the photoconductivity of a specimen of diamond at different voltages (small compared to the saturation potential of the photo-current in diamond). The strict proportionality found between the applied voltage and the corresponding observed current showed the correct working of the amplifier.

It was found necessary, at least in some cases, that the diamond should be heated to a temperature of nearly 100° C. to remove any dark current due to moisture or previous excitation of the crystal. Since the applied voltage was small and the intensity of the mercury arc not very great, troubles due to secondary currents were mostly absent. An ordinary needle-galvanometer, therefore, served the purpose of measuring the photo-currents. However, a few diamonds which showed secondary effects on being illuminated for too long a time were examined by applying a smaller voltage to them. In each case, therefore, only the primary photo-electric current was measured.

The photo-conductivity of numerous diamonds from the personal collection of Sir C. V. Raman was measured, as far as possible under identical conditions. The crystals were either sandwiched between the electrodes so that the light entered through the edges of the plate (position A), or they were screwed tightly between them such that one of the broad faces alone could be illuminated (position B). Most of the diamonds studied were cleavage plates having a thickness of between half a millimetre and one millimetre, their linear dimensions varying between a few millimetres and one centimetre. Owing to the varying thickness and area of the plates, any comparison of the photo-currents obtained with them is necessarily only qualitative. Nevertheless, the variation in the magnitudes of the primary photo-currents observed in position A with different diamonds was so marked, that it could easily be recognised as due to an inherent property of the diamond and not to its varying dimensions. This becomes clearer on correlating the variations in photo-conductivity with the variations in other properties of the diamond.

3. Photo-Currents under Ultra-Violet Irradiation

Tables I, II and III give the values of the photo-currents of 36 diamonds arranged in the decreasing order of magnitude of the photo-currents observed in the position A. For all these measurements, the illumination was the total light of the quartz mercury arc and the applied voltage was

150 volts. The 36 diamonds have been grouped in three tables according to the magnitude of the photo-currents given by them in the position A. Table I refers to five diamonds giving high photo-currents of the order of 10^{-8} ampere; Table II to eleven diamonds which give moderate photo-currents of the order of 10^{-9} ampere and Table III to twenty diamonds giving small photo-currents of the order of 10^{-10} ampere. It will be noticed that the diamonds listed in the first two tables show higher photo-conductivity in the position A than in the position B, while under similar conditions, the diamonds appearing in the third table usually show slightly higher photo-conductivity in the position B than in position A.

TABLE I

Five diamonds exhibiting large photo-currents

Unit = 10^{-8} ampere

Diamond No.	Distance between electrodes in millimetres		Photo-current in the unit stated	
	Position A	Position B	Position A	Position B
208	0·62	3·4	7·0	1·0
227	2·10	3·1	3·0	1·5
39	1·12	4·9	2·5	0·5
57	0·75	..	0	..
206	0·63	3·9	·0	0·5

TABLE II

Eleven diamonds exhibiting moderate photo-currents

Unit = 10^{-9} ampere

Diamond No.	Distance between electrodes in millimetres		Photo-current in the unit stated	
	Position A	Position B	Position A	Position B
201	0·53	3·5	5·2	0·9
207	0·94	3·8	5·0	2·0
48	0·82	5·4	5·0	0·8
209	0·71	4·3	4·0	1·8
200	0·74	4·7	4·8	0·6
47	2·50	2·5	1·8	1·8
199	0·68	3·6	1·6	1·3
202	0·72	2·7	1·5	1·8
198	0·59	4·2	1·4	1·0
195	0·60	5·9	1·4	0·7
49	2·40	2·4	1·1	1·1

TABLE III

Twenty diamonds exhibiting small photo-currents

Unit = 10^{-10} ampere

Diamond No.	Distance between electrodes in millimetres		Photo-current in the unit stated	
	Position A	Position B	Position A	Position B
31	0·96	4·2	9·6	8·8
36	0·76	5·8	8·7	12·0
210	0·64	4·7	8·0	0·8
180	0·48	5·5	7·6	3·2
45	0·68	4·7	7·6	9·6
197	0·88	3·1	5·6	8·8
53	0·78	4·0	5·2	2·5
196	0·62	2·6	4·8	2·4
188	0·71	4·7	4·8	2·4
221	0·68	5·1	4·0	11·0
211	0·55	4·3	4·0	4·0
187	0·52	5·4	4·0	4·4
171	0·67	3·5	4·0	1·2
224	1·52	7·4	4·0	2·8
41	1·10	4·7	3·6	1·8
34	1·20	7·2	3·2	1·8
40	2·70	..	3·2	..
181	0·60	4·6	2·0	4·0
184	0·81	3·1	2·8	0·8
38	0·85	7·0	1·6	4·0

4. *Photo-Conductivity in the Visible Spectrum*

Table IV gives the spectral sensitivity data of a few selected diamonds showing high or moderate photoconductivity for wavelengths lying in the visible region. The source of light was a 500-watt pointolite lamp and the various regions of the visible spectrum were isolated by means of suitable light filters. The observations were made only in the position A.

TABLE IV

Five diamonds with large or moderate photo-conductivity

Diamond No.	Applied voltage	Photo-current in amperes					
		White light	Red	Yellow	Yellow-green	Blue	Blue-violet
	Volts						
57	120	$4·0\times10^{-8}$	$2·7\times19^{-9}$	$1·5\times10^{-9}$	$9·0\times10^{-9}$	$1·2\times10^{-9}$	$1·0\times10^{-9}$
39	120	$7·6\times10^{-9}$	$2·0\times10^{-10}$	$1·4\times10^{-10}$	$1·5\times10^{-9}$	$1·0\times10^{-9}$	$6·0\times10^{-10}$
206	220	$4·2\times10^{-9}$	$8·0\times10^{-11}$	$4·0\times10^{-11}$	$3·2\times10^{-10}$	$7·6\times10^{-10}$	$4·4\times10^{-10}$
48	220	$1·6\times10^{-9}$	..	..	$1·2\times10^{-10}$	$2·8\times10^{-10}$	$1·6\times10^{-10}$
56	220	$8·4\times10^{-10}$	..	..	$1·6\times10^{-10}$	$8·0\times10^{-11}$	$6·0\times10^{-11}$

Table V gives the data for four weakly photo-conducting diamonds. The readings were taken both for the positions A and B, the source of light being the 500-watt pointolite lamp without any filters.

TABLE V

Four diamonds with small photoconductivity

Diamond No.	Applied voltage	Photo-current in amperes	
		Position A	Position B
	Volts		
36	150	$4{\cdot}4\times10^{-10}$	$1{\cdot}2\times10^{-10}$
31	150	$4{\cdot}0\times10^{-10}$	$1{\cdot}2\times10^{-10}$
224	150	$3{\cdot}2\times10^{-10}$	$4{\cdot}0\times10^{-10}$
221	150	$1{\cdot}6\times10^{-10}$	..

It will be noticed that with these diamonds, white light gives a higher photo-current in the position A.

5. *The Effect of Red Light*

Ordinarily, no photo-conductivity is produced even with strong illumination by red or infra-red light. A very interesting phenomenon, however, arises when the diamond is illuminated simultaneously by strong red or infra-red light and by light of a shorter wave-length which excites photo-conductivity. It is then noticed that the photo-current given by the shorter wave-length light is greatly enhanced by the presence of the red light, increasing under suitable conditions to double its original value. The extra current produced by red light in the manner stated above is known as the positive primary, ersatz or substitution current. This effect was demonstrated by Gudden and Pohl as early as 1924 and it is of interest to study its variation in different diamonds. Table VI gives the data for the red light effect with some eighteen diamonds. It will be seen that it is conspicuously shown by the strongly and moderately photo-conducting diamonds, but is scarcely noticeable or altogether absent in the weakly photoconducting ones.

6. *Secondary Current Phenomena*

The primary photo-electric current which is observed when the crystal is illuminated for a short time starts or falls down to zero instantaneously with the imposition or cutting off of the irradiating light. But if the crystal is illuminated for too long a time, the current begins to increase and finally reaches a steady maximum value which is often several times the initial

TABLE VI

Effect of red light

Diamond No.	Photo-current in amperes			
	Hg. Arc	Hg. Arc + Red light	Red light alone	Extra current due to red light
208	$7{\cdot}0\times10^{-8}$	$10{\cdot}0\times10^{-8}$	$2{\cdot}4\times10^{-10}$	$3{\cdot}0\times10^{-8}$
39	$2{\cdot}5\times10^{-8}$	$4{\cdot}2\times10^{-8}$	$2{\cdot}0\times10^{-10}$	$1{\cdot}7\times10^{-8}$
206	$2{\cdot}0\times10^{-8}$	$2{\cdot}8\times10^{-8}$	$8{\cdot}0\times10^{-11}$	$8{\cdot}0\times10^{-9}$
207	$5{\cdot}0\times10^{-9}$	$7{\cdot}4\times10^{-9}$	nil	$2{\cdot}4\times10^{-9}$
201	$5{\cdot}2\times10^{-9}$	$7{\cdot}8\times10^{-9}$	nil	$2{\cdot}6\times10^{-9}$
200	$4{\cdot}8\times10^{-9}$	$6{\cdot}8\times10^{-9}$	nil	$2{\cdot}0\times10^{-9}$
209	$4{\cdot}0\times10^{-9}$	$4{\cdot}4\times10^{-9}$	nil	$4{\cdot}0\times10^{-10}$
199	$1{\cdot}6\times10^{-9}$	$2{\cdot}0\times10^{-9}$	nil	$4{\cdot}0\times10^{-10}$
195	$1{\cdot}4\times10^{-9}$	$2{\cdot}2\times10^{-9}$	nil	$8{\cdot}0\times10^{-10}$
198	$1{\cdot}4\times10^{-9}$	$1{\cdot}9\times10^{-9}$	nil	$5{\cdot}0\times10^{-10}$
210	$8{\cdot}0\times10^{-10}$	$9{\cdot}6\times10^{-10}$	nil	$1{\cdot}6\times10^{-10}$
180	$7{\cdot}6\times10^{-10}$	$8{\cdot}0\times10^{-10}$	nil	$4{\cdot}0\times10^{-11}$
36	$8{\cdot}7\times10^{-10}$	$8{\cdot}7\times10^{-10}$	nil	nil
221	$4{\cdot}0\times10^{-10}$	$4{\cdot}0\times10^{-10}$	nil	nil
31	$9{\cdot}6\times10^{-10}$	$9{\cdot}6\times10^{-10}$	nil	nil
45	$7{\cdot}6\times10^{-10}$	$7{\cdot}6\times10^{-10}$	nil	nil
224	$4{\cdot}0\times10^{-10}$	$4{\cdot}0\times10^{-10}$	nil	nil
184	$2{\cdot}8\times10^{-10}$	$2{\cdot}8\times10^{-10}$	nil	nil

of the primary photo-electric current. If the light is now cut off, this increased current, unlike the primary photo-electric current, does not fall down instantaneously but decays with a considerable time-lag. This current which starts as well as decays with a time-lag is known as the secondary current. High applied voltages and strong intensity of light help the production of the secondary current.

In the present case although high voltages were not applied, yet on continued illumination for a long time some diamonds did show secondary currents, the magnitudes of which were in some cases 3 to 5 times the initial or primary photo-electric current. On sufficiently lowering the applied voltage, no diamond showed the secondary current. The diamonds which gave the secondary currents are those listed in Table I and a few others, namely D202, D199, and D195, appearing in Table II. None of the diamonds appearing in Table III gives any secondary current. It should also be remarked that secondary currents developed much more promptly in the position A than in B. In fact D202, D199, D195 did not show any secondary currents in the position B.

As mentioned above, the secondary current persisted even after the illumination was cut off and as a result of this a " dark current " in other

words, a current without illumination was observed. A diamond in this state when exposed to light of a longer wave-length gave a current which was much larger than that obtained when this radiation was imposed on the normal diamond. With red light, this increased current showed a close relationship with the dark current and decayed in a manner similar to the latter, finally coming to a constant value which was still higher than that produced by red light in the normal diamond (Fig. 1, curves I and II). A somewhat similar effect has been described by Robertson, Fox and Martin (*loc. cit.*)

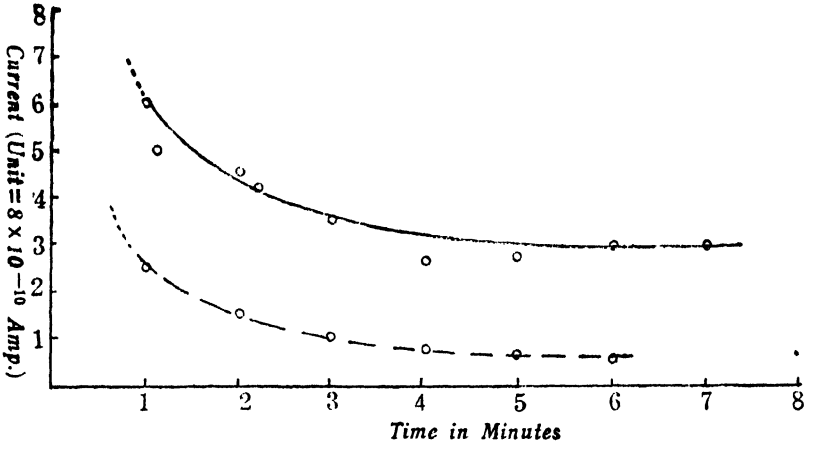

FIG. 1. Relation between I_r and I_d

----- Curve showing the decay of I_d with time

——— Curve showing the decay of I_r with time

7. *Relation to Other Optical Properties*

The remarkable variations in photo-conductivity described above admit of being correlated with other properties of the specimens, namely (*a*) their transparency to the radiations exciting photoconductivity, (*b*) their absorption spectra, and (*c*) their luminescence. These latter properties have been studied extensively and are being reported on in other papers appearing in the symposium (Sunanda Bai, 1944; Rendall, 1944; Mani, 1944). It has accordingly been easy to establish the relationships between them and photoconductivity.

The division of the 36 diamonds into three groups (Tables I, II and III) according to the magnitude of the photo-currents developed under ultra-violet irradiation, also practically represents their classification according to their degree of transparency to the 2537 radiation of the quartz mercury

arc. The diamonds appearing in Table I are transparent to those radiations, those in Table II are partially transparent in greater or less degree, while those in Table III are practically opaque to those radiations. The absorption spectra of the diamonds appearing in the three Tables also differ widely. The diamonds in Table I have a transmission extending up to λ 2250 A.U. in the ultra-violet and even beyond. Nearly all the diamonds in Table II show a similar transmission, but this is much weaker and there are several absorption bands in the region of wave-lengths greater than λ 2250. The diamonds in Table III show strong absorption bands in the region between λ 3000 and λ 2800 A.U. and a practically complete extinction at shorter wavelengths. The diamonds in Table III may also be subdivided into two classes, those nearer the top of the table which are more or less completely transparent in the visible spectrum, and those nearer the bottom which show strong absorption bands in that region. A classification is also possible on the basis of the luminescence properties. The five diamonds listed in Table I are non-luminescent. Of the eleven diamonds in Table II D207 is non-luminescent, while the luminescence of all the others is very weak with the exception of the three yellow diamonds D200, D201 and D202. The twenty diamonds appearing in Table III are moderately or strongly luminescent. Those nearer the top of the table have relatively small intensities, while those near the bottom, especially D187, D224, D41, D34, D40 and D38 exhibit very intense luminescence. There is, thus, a clear inverse correlation between photoconductivity and luminescence in the diamonds studied.

In conclusion, the author wishes to express his indebtedness to Prof. Sir C. V. Raman for suggesting the problem and for guidance during the course of the work.

8. *Summary*

The photo-conductivity of 36 diamonds, mostly in the form of polished cleavage plates, has been studied. They may be roughly classified into three groups showing respectively high, moderate or weak photo-conductivity. But there is no sharply defined demarkation between these groups and it is therefore not possible to make a clear-cut division of diamonds into two distinct types on the basis of their photoconductivity as proposed by Robertson, Fox and Martin.

The diamonds which are highly photo-conducting under ultra-violet irradiation are also those which give high photo-conductivity with visible light. They also exhibit the well-known red light effect and give rise on continued illumination to a secondary current which persists when such

illumination is cut off. A diamond in this state gives a larger current when illuminated by red light, and the magnitude of this is quantitatively related to that part of the secondary current which persists even without illumination. The weakly photo-conducting diamonds do not give these effects. The correlations which exist between photo-conductivity, ultra-violet transparency, spectral transmission curves and the intensity of luminescence of the diamond are pointed out.

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THE PHOTO-CONDUCTIVITY OF DIAMOND

Part II. Theoretical Considerations

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. The Structure of Diamond

ACCORDING to the theory put forward by Sir C. V. Raman (1944), the crystal structure of diamond has four possible variants; two of these, namely, Td I and Td II, have tetrahedral symmetry and the remaining two, namely, Oh I and Oh II, have the full or octahedral symmetry of the cubic system. The structure of any actual specimen of diamond is, in general, composite and includes more than one of the possible variants. Thus, in the non-fluorescent and ultra-violet transparent variety of diamonds, the Oh I and Oh II sub-types interpenetrate giving rise to lamellar twinning; the two sub-types are separated in the crystal by extended surfaces of discontinuity or laminations and the diamond is highly non-homogeneous. In the blue-fluorescent and ultra-violet opaque variety of diamond, the Td I and Td II sub-types are present, interpenetrating each other. As these two sub-types are not physically but only geometrically different, such interpenetration is irregular and occurs without any composition planes. Hence, diamonds of this class have a much higher degree of crystal perfection than those in which the Oh I and Oh II are mingled. Nevertheless, the interpenetration of the Td I and Td II does give rise to a non-homogeneity of the crystal which shows itself in the development of luminescence in diamonds of this class. The irregularities of crystal structure are of an entirely different type from those observed in the non-fluorescent diamonds, being in the present case closely connected with the intensity of the luminescence exhibited. The theory indicates further the possibility of the mixing up of the tetrahedral and octahedral types of structure in various ways. When there is an intimate mixing of tetrahedral and octahedral structures, the diamond gives a yellow luminescence and is of an intermediate type; the diamond in parts may exclusively be of the transparent type and in others it may be of the other variety; finally, in some cases a small quantity of a particular variety may be embedded in the bulk of the other variety. On account of these different

possibilities, the properties of diamond vary greatly from specimen to specimen.

These conclusions find unmistakable support in the experimental results contained in the various papers appearing in the present symposium. However, from our point of view we wish to draw attention to the results regarding the imperfection or mosaicity of structure of diamond obtained from the X-ray studies made at this Institute by R. S. Krishnan (1944), P. S. Hariharan (1944) and G. N. Ramachandran (1944). These studies show clearly that the mosaicity of the ultra-violet transparent variety of diamond is of a very high degree and varies not only from diamond to diamond but also from place to place in the same specimen. On the other hand, the mosaicity of structure of the blue fluorescent diamonds is comparatively low and increases with the intensity of blue fluorescence. The yellow fluorescent diamonds in this respect also are intermediate between these types.

2. The Photo-Electrically Active Centres

In view of the extremely small magnitude of the primary photo-electric current and the absence of any definite threshold frequency for its generation, it is hard to believe that the normal atoms of the crystal form the photo-electrons. Gudden and Pohl expressed the opinion that only a few "privileged atoms" are responsible for photo-conductivity. These atoms, which are probably those situated at slight irregularities, form the photo-electrically active centres, while the normal atoms of the lattice remain photo-electrically inactive. If these conceptions are correct, the greater the mosaicity of structure, the greater should be the photo-conductivity of the diamond. The high photo-conductivity of the highly imperfect ultra-violet transparent variety of diamond and the low photo-conductivity of the more perfect ultra-violet opaque variety thus becomes intelligible. A slight anomaly is presented by the weakly photo-conducting, strongly blue-fluorescent diamonds, namely, that in such diamonds higher mosaicity gives lower photo-conductivity. But this is not surprising in view of the fact that the mosaic structure revealed by the intensity of X-ray reflections being closely connected with the intensity of luminescence, it produces the luminescent centres and not the photo-electrically active centres. That the two are quite distinct in the present case is obvious from the fact that while a photo-electrically active centre is ionised by the absorption of a suitable quantum and the liberated electron is raised to the condition level, the luminescence centre absorbs a quantum of radiation only to raise its electron to an intermediate level below the conduction band (production of an exciton). The dependence of the intensity of the 4152 absorption band on the intensity of

blue-fluorescence is a proof of this statement. Incidentally, since the absorbed energy is radiated again as luminescence energy, it is obvious that high intensity of fluorescence will only diminish the photo-conductivity. A close relationship between photo-conductivity and luminescence should be expected only in those solids where the mechanism of luminescence is analogous to that operating in the Lenard phosphors, *viz.*, when by the absorption of light energy, the electron is completely separated from the parent centre and is trapped at a distance from it, the luminescence occurring when the trapped electron comes back to the ionised centre.

3. The Spectral Distribution Curves of Photo-Conductivity

An atom situated at a lattice defect will have one or more of its bonds ruptured due to the presence of the discontinuity, the electron or electrons of which the valence bonds are broken being attached to the atom only loosely. This atom, which for all practical purposes, may be taken as a combined electron-positive charge system, will be ionised by absorption of a lower energy quantum than is necessary for a normal atom of the lattice and will constitute a photo-electrically active centre. The energy of the quantum necessary to ionise the centre will depend on the strength of the binding of the electron to the positive charge. This in turn will depend on the degree of the rupture of the bond and the environment of the centre. The discontinuity will not equally affect all the atoms situated at it ; some will have their electrons more loosely bound than the others and so on. The centres would, therefore, not have a definite threshold frequency, and a long-wave-length tail in the spectral sensitivity curve would be an invariable accompaniment, the magnitude and the length of the tail depending on the mosaicity of the diamond. At the characteristic edge however, where the normal atoms of the lattice get ionised, the coefficient of absorption is so high that the whole phenomenon is confined to an extremely thin layer of the crystal. A high rate of absorption, therefore, naturally leads to a high rate of recombination and the two are probably so adjusted that before a liberated electron can move appreciably under an applied field, it recombines with the positive charge. The photo-conductivity, therefore, vanishes in the characteristic absorption region (Gurney and Mott, 1940). The spectral distribution curve of the transparent variety of diamond which has a pronounced long-wave-length tail, the photo-current dropping down at λ 2250 A.U., is thus clearly understood. The selective excitation of photo-conductivity for λ 2300 A.U. merely shows that the absorption of light is photo-electrically active in the volume of the crystal.

Sometimes, the normal atoms of the lattice absorb energy even in the region far removed from the characteristic absorption region and here also the

absorption is photo-electrically inactive. An interesting fact is then observed, namely, that though the quantity of absorbed energy is large, the observed photo-conductivity becomes less. The spectral distribution curve for photo-conductivity of the opaque variety of diamond shows a continuous rise in photo-conductivity upto λ 3400 A.U. but for wave-lengths between 3400–3000 A.U., the photo-current falls down in magnitude, showing a minimum at λ 3000. In the absorption spectra (Nayar, 1942), several absorption bands are observed in this region, clearly indicating that most of the energy absorbed is photo-electrically inactive and is spent only in raising the atoms to some higher levels. Even more interesting than this is the photo-conductivity of this variety of diamond in the region between $\lambda\lambda$ 3000–2250 A.U. Although the diamond is practically opaque to these wave-lengths, the photo-conductivity does not fall down to zero but rises, showing a broad maximum and falling down to zero only at λ 2250 A.U. But the curious fact is that although the energy absorbed by this variety of diamond is far greater than absorbed by the transparent variety, the observed photo-conductivity is far smaller in the former case. The absorption is not photo-electrically inactive, since a considerable rise in the photo-conductivity is observed for these wave-lengths. The answer to this anomaly lies in the peculiar absorption characteristic of these diamonds. It is most probable that the characteristic absorption edge for these diamonds is also at λ 2250 A.U. and that absorption of the type where simultaneous ionisation and recombination occur as described previously, takes place only at this edge. For other wave-lengths in the region between λ 2250 A.U. and λ 3000 A.U., the absorption coefficient may not be very high and the absorbed energy is then confined to a thin though not to an extremely thin layer of the diamond. The recombination between the positively charged ion and the electron produced by absorption of light does take place but only after the electron has moved a short distance (short compared to the mean free path). The photo-current will be smaller than expected on the quantum equivalence law, yet it will always be observed, the magnitude depending on the distance the electrons travel before recombination.

In the intermediate type of diamonds where the octahedral and the tetrahedral types of structures get mixed up, the spectral distribution curve of photo-conductivity also takes an intermediate shape depending upon the extent to which the diamond approaches more closely the opaque or the transparent variety. The diamonds D2 and D22, whose special sensitive curves are figured by Robertson, Fox and Martin (1934), appear to be of this intermediate type, D2 approaching rather closely to the opaque variety in its behaviour both in the magnitude of the photo-current given by it and in

the presence of a subsidiary maximum at λ 3400 A.U. in the spectral sensitivity curve, which is quite analogous to that shown by their ultra-violet opaque diamonds D1 and D10.

4. The Secondary Current

The quantity of electricity that flows in the secondary current is so large that it is impossible to interpret it as a simple photo-electric effect. It is generally believed that this current is generated in the crystal on account of the reduction in the resistance of the crystal brought about by the flow of the primary photo-electric current. In ionic crystals, Tubandt (1920–21), Joffe (1928) and Gudden and Pohl (1926) maintain that the secondary currents are due to the conductivity being ionic, but as Hughes and Du Bridge (1932) remark, an alternative explanation is necessary in the case of crystals like diamond.

We may expect that the same irregularities in the crystal structure which give rise to the production of the photo-electrically active centres also serve as good trapping centres for the liberated electrons. In crystals with repeated twinnings, tablets of compressed powders and some glasses, which may be regarded as the collection of tiny crystals welded together, the primary photo-electric current is largely suppressed and only a high secondary current is observed, except when the intensity of light is low and the applied voltage is small. The facts that even when the primary photo-electric current is large, time is required for the development of the secondary current, and that flaws and irregularities of structure help its production show that the trapping of electrons along the surfaces of discontinuity is responsible for the secondary current. If the discontinuity is such that it extends from one end of the crystal to the other even along irregular paths, in due course of time, due to the trapping of the electrons, a sort of " conducting channel " will be formed from one electrode to the other. The trapped electrons can deliver the charge from one place to the next close by, even if they are not free in the same sense as in the metallic conductors. All the trapped electrons are not equally free to move in the channel; those trapped in the vacant lattice points or at other obstacles are held more firmly than those which are in the middle of the channel. The electrons are attracted to the anode and at the same time they enter the crystal from the cathode, delivering charge from one place to the other in the manner stated above. The net result is a flow of electrons belonging to the metallic electrodes. Also, it is easy to see that due to the surplus of the electrons, all the positive ions left in the crystal would be neutralised in due course of time. Further, it is clear that time would always be required for establishing and destroying

the " conducting channels " in the crystal and that the secondary current would always develop or decay with a time lag. It would develop more promptly if the primary photo-electric current be large and also if the thickness of the crystal between the electrodes be small. In the latter case, many more channels bridging over the electrodes can be formed, and it is due to these reasons that the secondary current is produced more easily in the diamond in the position A. It will also be seen that when all the conducting channels are established, the secondary current would reach a steady maximum value.

The absence of the secondary current in the opaque variety of diamond is due to the absence of the extended surfaces of discontinuity and the small magnitude of the primary photo-electric current.

5. *Relation between I_r and I_d*

It is well known that when electrical charges are left behind in the crystal (the activated crystal), the absorption curve broadens towards the longer wave-lengths (Gudden and Pohl, 1925) and consequently the photo-electric effect for longer wave-lengths increases. From the picture given already for the production of the secondary current, it can be visualised that the trapped electrons will produce a similar effect on the atoms situated in the neighbourhood. This happens because the active centre which is more of a combined electron-positive charge system than an actual atom, is further influenced by the presence of the charge in its vicinity. If the trapped charge is an electron, it will attract the positive charge and repel the electron of the centre, producing a further instability in the centre. Again, if the trapped electron comes quite close to an active centre, the instability produced in the latter may be so great that it can now lose its electron even by the absorption of a quantum of red light. Any other active centre which is not close to the electron or which itself is not much affected by the discontinuity would not so much be influenced; only by absorption of a higher energy quantum than that of red light could such a centre be deprived of its electron. In short, the photo-conductivity of the crystal for longer wave-lengths would increase and on illumination by a long-wave-length light say, red light, it would give an increased current I_r. Since this increase is due to the presence of the trapped electrons, I_r must have a close dependence on their number. Again, as the dark current I_d (*i.e.*, decaying secondary current) depends on the number of the conducting channels and the latter on the number of the trapped electrons, a linear relation I_r–KI_d obviously follows. But not all the trapped electrons are capable of contributing to the dark current, for unless they are so arranged that a chain of them along the

channels from one end of the crystal to the other is created, their irregular distribution would not be of any help. But such electrons influence their neighbours as well as the electrons taking part in the production of the secondary current. Clearly, therefore, I_r is due to the sum of two currents, one produced by the presence of the electrons for the dark current and the other by the rest of the trapped electrons.

If, at any instant, N be the number of trapped electrons of which n_1 are responsible for the dark current and n_2 are irregularly distributed, we must have

$$I_d = xn, \text{ where } x \text{ is a constant.}$$

But $I_r = K'y(n_1 + n_2)$ where K′ depends on the intensity of red light and y depends on the number of centres per trapped electron which will be ionised by absorption of red light. Therefore,

$$I_r = K'y\left(\frac{I_d}{x} + n_2\right) = K'\frac{y}{x}(I_d + n_2x)$$
$$= K(I_d + n_2x) = K(I_d + \alpha),$$

where α depends on the degree of activation. It will be seen that this relation is the same as that obtained by Robertson, Fox and Martin (*loc. cit.*).

Now, when the trapped electrons are ejected out of the channels by an absorption of energy (or by thermal agitation) sufficiently large to overcome the potential barrier presented by the boundaries of the channel, the diamond would come back to its normal state. Not all but a great majority of these electrons would have the same potential barrier to overcome and, hence, although there would be no definite frequency necessary for bringing back the diamond to its original state, there would be an optimum frequency required for this purpose. Probably this corresponds to λ 2800 A.U. Red light being unable to eject the electrons from their trapped position would continue to excite a constant current.

6. *The Effect of Red Light*

This phenomenon has been explained by Gudden and Pohl by suggesting that the positive charges left behind in the crystal as a result of the removal of the electrons by the primary photo-electric current are released by the absorption of red light. A more specific theory of the effect of red light again has been put forward by Gudden and Pohl (1926) which suggests that due to the presence of the positive charges, a temporary photo-electric effect by longer wave-lengths becomes possible. Electrons are separated from the active centres until the accumulated charge builds up to a maximum value. At this stage, a sort of rearrangement (or local recrystallisation) takes place, whereby the location of the positive charges slips

towards the space element adjacent on the side next to the cathode. The commonly accepted view to-day is that not the positive charges but their locations slip towards the cathode (Hughes, 1936).

The principal effect of red light in producing the positive primary current should be the same as for the production of I_r already discussed, the difference arising only due to the fact that the charges left behind in the crystals are positive charges, and not electrons. A particular space-element of the surface of discontinuity, after the separation of the primary photo-electric current, will have accumulated a large positive charge and will have formed what is called an excitation centre. Now, the total effect of the excitation centre will be so great on the neighbouring active centres that they can be ionised by the absorption of red light even if they are not quite close to it. The liberated electrons will travel to the anode under the external applied field and will be caught by the excitation centre, turning the latter into neutral centres. The location of the excitation centre will thus slip continuously towards the cathode by a repetition of this process (Fig. 1).

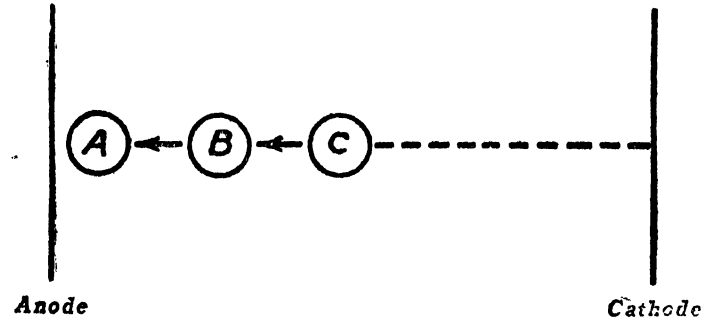

FIG. 1

It is easy to see that no electrons on the side towards the anode of the excitation centre can be released by red light after the excitation centre has begun to travel. For, as soon as the photo-electric effect in the centres (B) adjacent to the excitation centre (A) take place, A shifts to B. The liberated electrons have not time enough to reach the previous excitation centre A which still remains positively charged. The excitation centre at B, therefore, cannot release any positive charges from A and by continuation of the above process travels to C and so on.

It is easy to see now that as long as the active centres lie in the neighbourhood of the excitation centre so that by the presence of the latter a temporary photo-electric effect by red light is possible in them, the effect of red light will be observed. But as soon as this condition breaks down, the excitation centre can no longer slip towards the cathode, for the influence of

the positive charges on the normal atoms will be negligible. In the opaque variety of diamonds where there are only a very few centres and these are distributed in an irregular way, no positive primary current will be observed.

In conclusion, the author wishes to express his grateful thanks to Sir C. V. Raman, Kt., F.R.S., N.L., with whom he has had many useful discussions on the topics dealt with in this paper.

7. *Summary*

The variations in the photo-conductivity of diamond have been explained in this paper on the basis of the variations in the structure of the crystal, evidence for the existence of which is forthcoming from other directions, especially the study of the X-ray reflection intensities. Assuming that the non-homogeneities and irregularities in the crystal produce the photo-electrically active centres, the differences in the magnitudes of the photo-currents given by the different types of diamonds are explained. Various other observed facts regarding photo-conductivity also become intelligible, *viz.*, the spectral distribution curves of photo-conductivity, the absence of a definite threshold frequency, the effect of red light, and the production of a secondary current. The differences between the spectral distribution curves for the ultra-violet opaque and transparent types of diamond, and in particular the rising of the curve for wavelengths below 3000 A.U. are explained. A theoretical relation is also derived connecting the magnitude of the dark current and that of the current produced on excitation by red light.

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THE CRYSTAL FORMS OF THE PANNA DIAMONDS

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(Communicated by Sir C. V. Raman, KT., F.R.S., N.L.)

1. Introduction

THE opportunity for the present study arose from the visits made by Sir C. V. Raman two years ago to the State of Panna in Central India where diamonds have been mined since very ancient times. One result of these visits was the acquisition by him of 29 diamonds in their natural state as crystals. This material has been placed at the disposal of the author for a report on the crystal form of these specimens. Not one of them exhibits the plane faces and straight edges demanded by the ordinary rules of crystallography. Nevertheless, several of them show a high degree of geometric symmetry, as also smooth lustrous faces and rounded contours which endow them with a distinctive beauty. They also show various other characteristic features which appear to merit careful study and description. It has been found convenient to adopt the usual crystallographic nomenclature in classifying the specimens, though this procedure has no strict scientific justification, even in the case of the more regularly shaped diamonds.

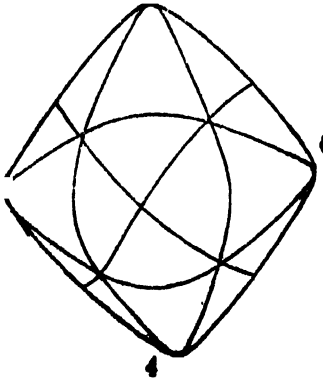


FIG. 4. Form of D9

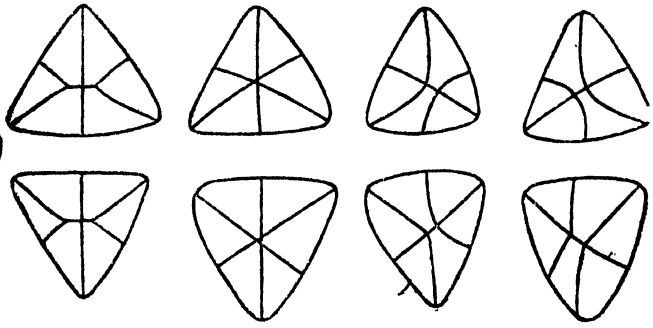


FIG. 5. The Eight Faces of D9

2. The Hexakis-Octahedral Forms

Three of the diamonds in the collection, namely D8, D9 and D27, approach sufficiently to the general form of the cubic system with 48 faces

to justify their being compared with it. Fig. 4 represents D9 which is the most perfect of this group. The resemblance, it will be noticed, is far from being exact. The six vertices or protuberances are, no doubt, present and convey to the eye the suggestion that the crystal has an octahedral form. The edges separating the octahedral faces are however missing, these regions being smoothly rounded off. The transverse curvature along them is sufficiently great, however, especially in D8 and D9, to suggest a resemblance to the octahedral form. Sharp edges cutting across the octahedral faces and dividing them into segments are observed. Four such edges meet at each vertex of the octahedron and run across to the opposite vertex, intersecting at or near the centre of the faces. Since, however, the octahedral edges are absent, the curved surface of the crystal appears actually divided up into 24 clearly defined and approximately equilateral triangles and not into the 48 faces required for the hexakis-octahedron. It should be remarked also that the angle between the curved surfaces meeting along these edges is highly variable. It is greatest near the vertices of the octahedron and diminishes to a relatively small value midway between them. This circumstance makes the observed form tend somewhat towards the triakis-octahedron.

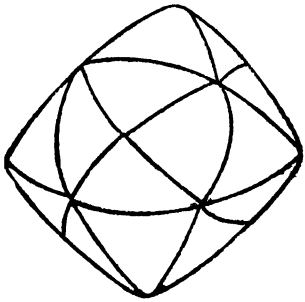
There are, however, certain minor irregularities. Instead of the edges meeting exactly at the centre of the octahedral faces, they may deviate slightly, or even meander, with the result that their meeting point is on one side or another of the centre. The edges in such cases do not run a continuous course from each vertex to the opposite one. It is an interesting point that in D9 even these irregularities appear symmetrically. Fig. 5 shows its eight octahedral faces, their features being qualitatively indicated and parallel faces being drawn one above the other.

D27 is the largest of the three diamonds and weighs 341 milligrams. It has a grey tinge which is probably superficial. D8, which is the next in size and weighs 279 milligrams, has a delicate greenish tinge which is particularly evident at the octahedral tips. This is a superficial tint characteristic of many of the best Panna diamonds which disappears when they are cut and polished (Sinor, 1930). D9 which weighs 226 milligrams is perfectly colourless. Both D8 and D9 have lustrous surfaces, while D27 has rather a dull appearance.

3. The Tetrakis-Hexahedral Forms

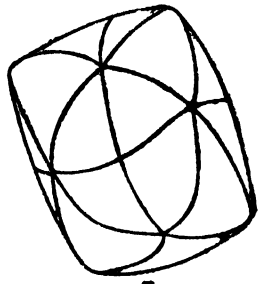
The six diamonds D18, D20, D21, D22, D24 and D25 may reasonably be compared with this ideal form. They are relatively small diamonds weighing 61, 56, 51, 41, 32 and 22 milligrams respectively. All of them

have the common feature that the surface of the crystal appears divided up into 24 distinct areas bounded by sharply defined edges. These are, however, not plane figures but are curved surfaces, with the result that all these diamonds, at a first glance, appear like small transparent globules. These features will be evident from the photographs of D18 and D20 in Plate XXIX which are the two largest diamonds in the group. It is evident that the three diamonds described in the preceding section, and the six now under consideration, have in reality the same basic form, a solid having 24 curved faces bounded by sharply defined edges. These edges meet on the surface quite exactly at six vertices in groups of four each and more or less exactly at eight points in groups of six each. In the ideal case, therefore, the surface appears divided up into 24 triangles. The general shape of the crystal is determined by the size and shape of these triangles, as well as by the angles which they make with each other along the lines where they meet.



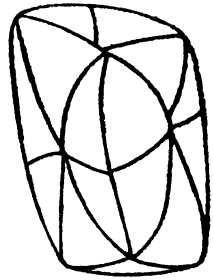
6

FIG. 6. Form of D18



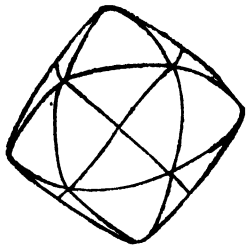
7

FIG. 7. Form of D20



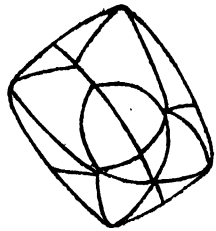
8

FIG. 8. Form of D21



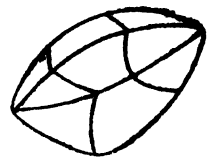
9

FIG. 9. Form of D22



10

FIG. 10. Form of D24



11

FIG. 11. Form of D 25

Each of the six diamonds has 6 protuberances like those of the octahedron or the tetrakis-hexahedron, but they are not equally prominent in all the crystals. They are particularly conspicuous in D18 and D22 which most nearly resemble the ideal form and less conspicuous in the other four

diamonds. The angle between the faces meeting along the shorter diagonal of the rhombus (Fig. 6) is much less than that between the faces which meet along one of its sides, thereby suggesting an approach to the dodecahedral form. This is a common feature in the Panna diamonds. D20 (Fig. 7) is a beautiful crystal which shows some resemblance to the octahedral form. Here again, the edges are sharp and clear. D21, D24 and D25 (Figs. 8, 10 and 11) are ellipsoidal crystals which are comparatively irregular. The faces are unequal and the edges meander so much that it would not be correct to call some of the faces triangular in shape. These irregularities are evident from the figures. D25 in some positions, presents a very flat surface which is divided into 6 faces. Such a view is portrayed in Fig. 11.

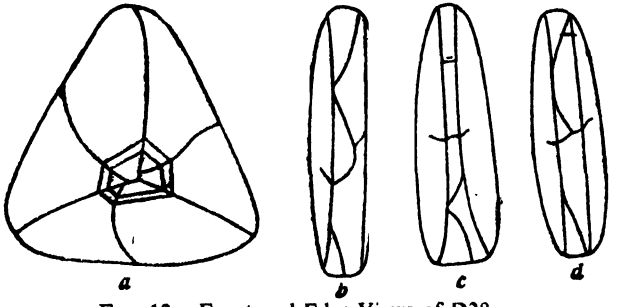


FIG. 12. Front and Edge Views of D28

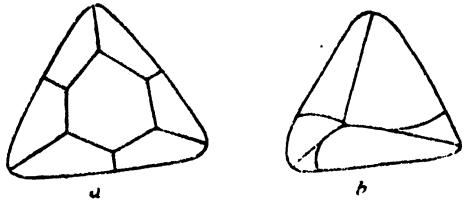


FIG. 13. Front and Rear of D29

The remaining crystals can only be classed as irregular and most of them are heavy distortions of the tetrakis-hexahedron. These diamonds can be divided into two groups, those which are colourless and transparent and those which are coloured yellow or grey. Some irregular crystals are illustrated in Fig. 2, Plate XXIX. As examples, a few of them are described below.

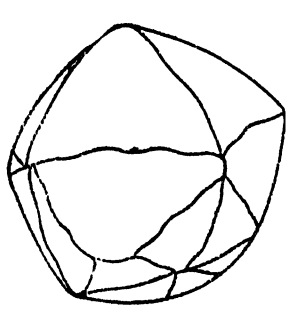
D3 is a colourless transparent crystal which appears highly distorted, but a close examination shows that it resembles a hexakis-octahedron whose growth has been restricted in one particular direction. The crystal can be described as a hexakis-octahedron cut by a plane which is approximately parallel to one of the octahedral faces. This intersecting plane is

a natural face and it has six well-marked lines on it which divide it into six segments. The crystal exhibits practically all the characteristics of the hexakis-octahedron which have already been described. It weighs 405 mgm.

D1 and D12 (Figs. 14 and 15) are both yellow crystals which are heavy distortions of the tetrakis-hexahedral form, but nevertheless display its characteristics. The most striking feature about these diamonds is the enormous variation in the area of the faces. The crystals are flattened and the flat portions are those where six faces meet. These faces are much larger in area than the others. The edges are sharp but wavy and are distinctly seen on the surface. The faces are curved but the variation in curvature is not always continuous as in the other diamonds. Sometimes on a convex surface, a small concave depression is present.

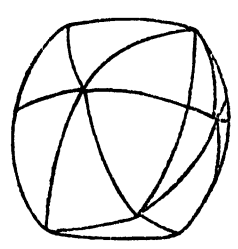
4. Twinned Crystals

There are two flat triangular crystals in the collection which closely resemble the macled diamonds of the Kimberley mines and have been found by X-ray examination to be actually twins. D28 (Fig. 12) weighs 214 milligrams and D29 (Fig. 13) weighs 29·9 milligrams. The crystals appear to have 24 faces, 6 faces being found on either of the flat sides and the remaining 12 being distributed on the thin girdle which connects the two components. The line of demarcation or seam between the two components (which is a common feature of the Kimberley twins) is absent. The edge view presents distinct faces (Fig. 12 *b, c, d*). The edges on the flat side are fairly sharp ; but those on the thin sides are faint and wavy.



14

FIG. 14. Form of D1



15

FIG. 15. Form of D12

The two sides of D29 do not appear alike (Figs. 13 *a* and *b*). On one side there is a flat area which is full of rugged triangular pits. The faces are, as usual, curved and the curvature increases as one moves from the centre to the edge of the triangle.

5. Surface Characters

The surface markings of the Panna diamonds show great variety and beauty. All the diamonds examined have striations on the surface, but their nature varies from crystal to crystal. The striæ on the clear colourless diamonds are very close together and they have a kind of satiny sheen to the surface. They are so disposed on the octahedral face as to give the appearance of a spider's web. A microphotograph of such striations on D3 is given in Fig. 3 *a* in Plate XXX. The lines found on the yellowish diamonds are quite different. The surfaces reveal somewhat rough and bold striæ, each face having two or three sets of such parallel lines. The criss-crossing of these lines gives a drusy appearance to the surface. Sometimes, but not often, tiny tetrahedral pits are found at the intersections of these lines. Under fairly high magnification the lines, although absolutely straight, are found to be discontinuous (Fig. 3 *c*) in Plate XXX. Most of the striations are parallel to the intersection of the octahedral planes with the surface.

The faint milky white appearance of D20 and D3 is due to the scattering of light by the large number of pits which abound on their surface. These pits are rather peculiar in nature, being circles with the circumference sunk into the diamond, the central area being shiny. Some of the pits are incomplete circles and occasionally only semi-circular. A few such pits are also seen in Fig. 3 *a*. D29 has triangular pits on its surface, all the triangles pointing in the same direction. Microscopic examination of these pits shows that they are really tetrahedral cavities with flat sides. Some of these sides are striated. The angle between two faces of a " trigon " was measured and was found to be near about the angle between the octahedral planes. A microphotograph of the pits on D29 is given in Fig. 3 *b* in Plate XXX.

6. Photographic Study of the Diamonds

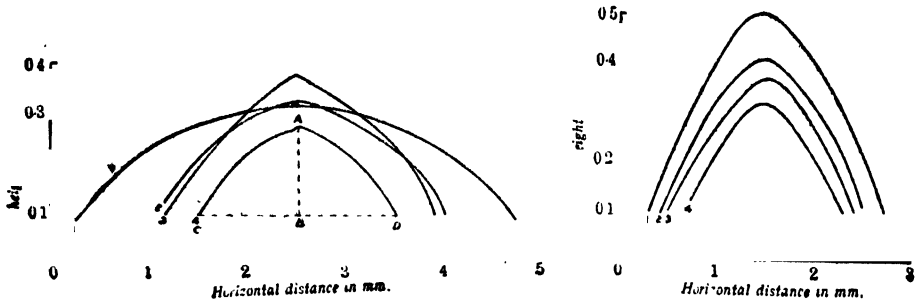
It is difficult to obtain a satisfactory photograph of a crystal of diamond showing the detail on its faces. The strong internal and surface reflections conspire to defeat any attempt to bring out the outlines and natural beauty of crystal form. However, in the case of small crystals, these difficulties are not insuperable. Seven out of the twelve photographs reproduced in Plate XXIX, *viz.*, the representations of D20, D18, D9, D3, D12, D4 and D10, were obtained by illuminating the diamond obliquely and avoiding any direct reflection from its surfaces entering the camera. The remaining five pictures, *viz.*, those of D27, D28, D9, D8 and D1 were obtained by photographing the diamond by its luminescence under ultra-violet irradiation. This was done by passing sunlight through a plate of Wood's

glass, a cell of sodium nitrite solution being used as a complementary filter. The bright patch at the centre of the green fluorescent D1 represents an intensely blue fluorescent region.

7. *Measurements of Curvature*

It appeared to be of interest to study the curvature of the surface in some of the more regular diamonds, and to find in what respects they differed from each other. As already stated, the surface of every such diamond consists of 24 similar triangles, and it is sufficient therefore to determine the configuration of the area included within a rhombus formed by a pair of adjacent triangles of this kind. The two vertices at the ends of the longer diagonal of the rhombus are points where four edges meet, and the two other vertices are points where six edges meet on the surface of the crystal. The measurements could be made by setting the crystal on the movable stage of a microscope and focussing the latter on a series of points on the area of the rhombus and reading off the vertical and horizontal displacements.

Figs. 16 and 17 represent the results of such a study for the four diamonds D9, D20, D18 and D22, the graphs for which are numbered serially in that order.

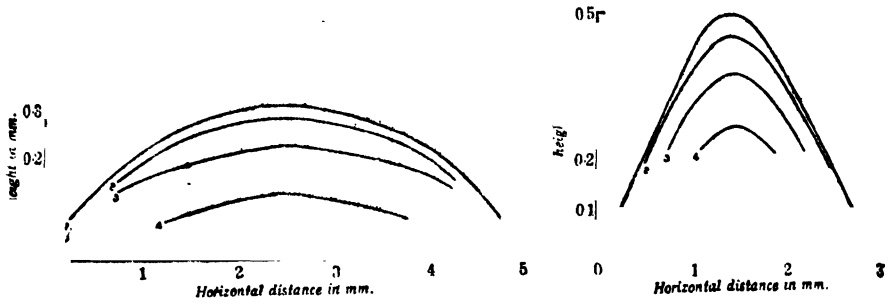


16 17

FIG. 16. Sections through the longer diagonal for D9, D20, D18 and D20
FIG. 17 Sections through the shorter diagonal for D9, D20, D18 and D22

It will be seen from the figures that the general shape of the section along the shorter diagonal is very similar for these four diamonds. On the other hand, the sections along the longer diagonal show conspicuous differences, the curve being very open in the case of the approximately octahedral diamond D9. A further idea of the configuration of the surface of this particular diamond is conveyed by Figs. 18 and 19 respectively, in which its sections by a series of planes 0·25 millimetre apart are shown. The

graphs are numbered in serial order moving away from the diagonal referred to in the caption of the figures.



18 19

FIG. 18. Sections of D9 by a series of planes parallel to the longer diagonal

FIG. 19. Sections of D9 by a series of planes parallel to the shorter diagonal

As we pass along the longer diagonal of the rhombus, we meet an edge or discontinuity of direction when crossing the shorter diagonal of the rhombus. This discontinuity is small, but it becomes more pronounced when we move to one side or another of the longer diagonal. This is shown by the series of graphs in Fig. 18. No such discontinuity is encountered as we move along the shorter diagonal or parallel to it, but the curvature becomes distinctly more marked as we approach the vertices of the rhombus (Fig. 19).

The angles between the tangents to the surface of the four diamonds at the ends of the longer and shorter diagonals were carefully measured. They are given in Table I together with the theoretical angles for the ideal geometric forms with which the crystals have been compared. It is clear from these figures that the crystals cannot in strictness be assigned to any particular form of the kind usually considered in geometric crystallography.

TABLE I

Crystal	Angle between ends of longer diagonals	Angle between ends of shorter diagonals
D9	152°	124° 30′
D20	144°	130°
D18	140° 30′	137° 30′
D22	140°	138° 30′
Tetrakis-hexahedron	143° 8′	180°
Octahedron	180°	109° 30′
Triakis-octahedron	180°	141°
Hexakis-octahedron	157° 30′	158° 30′
Dodecahedron	180°	180°

In conclusion, the author wishes to thank Prof. Sir C. V. Raman for his guidance throughout the course of this investigation.

8. *Summary*

The external forms and surface characters of 29 diamonds from the Panna mines in the personal collection of Sir C. V. Raman have been studied. Drawings and photographs of a selection from amongst them have been reproduced with the paper. In all the specimens examined, the surface of the crystal exhibits a set of sharply defined edges dividing up the area into 24 segments. In the best specimens, these segments have the shape of triangles, and the edges bounding them meet at points or vertices on the surface of the crystal respectively in groups of four and six. Measurements have been made of the curvatures of the surface in four of the best specimens. They show that these curvatures are highly variable both in an individual diamond and also as between different specimens.

REFERENCE

Sinor, K. P. .. *Diamond Mines of the Panna State*, 1930.

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