

The nature and origin of the luminescence of diamond

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Contents

1. Introduction
2. The material for study
3. Intensity and colour of luminescence
4. Luminescence patterns in diamond
5. Luminescence and ultra-violet transparency
6. Luminescence and structural birefringence
7. Interpretation of the experimental facts
8. The spectral characters of luminescence
9. Luminescence and X-ray reflection intensities
10. Excitation of luminescence by X-rays
11. Phosphorescence
12. Summary

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 M 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 (figure 1 in plate I). 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 wavelength 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 figure 1 and photographed by (Miss) Mani with different exposures under ultra-violet light in figures 2 to 6 in plate I. 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 (figures 2, 3 and 4 respectively). An exposure of two minutes (figure 5) was necessary before the pattern bore any recognizable resemblance to its appearance as seen by daylight, while an exposure of 30 minutes was necessary in order to record the most feebly luminescent diamonds (figure 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 $1\frac{1}{2}$ 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 figure 7, in plate II 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 figure 7 in plate II 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 figure 8 and figure 9 respectively in plate III, appearing in the upper half of these pictures. The geometric character of the patterns shown by D38 in figure 8 and by D179 in figure 9 is particularly noteworthy. These, as well as D224 appearing in figure 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 figure 8 has a greenish-yellow luminescence in which the most prominent feature is a set of four parallel bands. D188 and D190 appearing in figure 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 Sunanda Bai (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 wavelengths smaller than about 3000 A.U., there are some diamonds which transmits the ultra-violet rays freely up to about 2250 A.U. The investigations of Robertson, 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 us 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 a 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 to 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 figure 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 figure 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 nonuniformity 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 figures 8 and 9 (plate III, 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 figure 8, and D188 and D190 in figure 9. Diamonds D38 and D224 in figure 9 and D179 in figure 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 wavelength stated in emission as well as absorption, and this is accompanied by weaker electronic lines at other wavelengths 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 wavelengths in emission and towards shorter wavelengths 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 wavelength range 4000 A.U. to 3500 A.U. Luminescence is also excited by longer wavelengths (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 wavelength of the exciting radiation, being greatest when it coincides with the wavelength 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 wavelengths. 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 figures 11 to 14 in plate IV with the sequence of figures 2 to 6 in plate I. 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

wavelength 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.

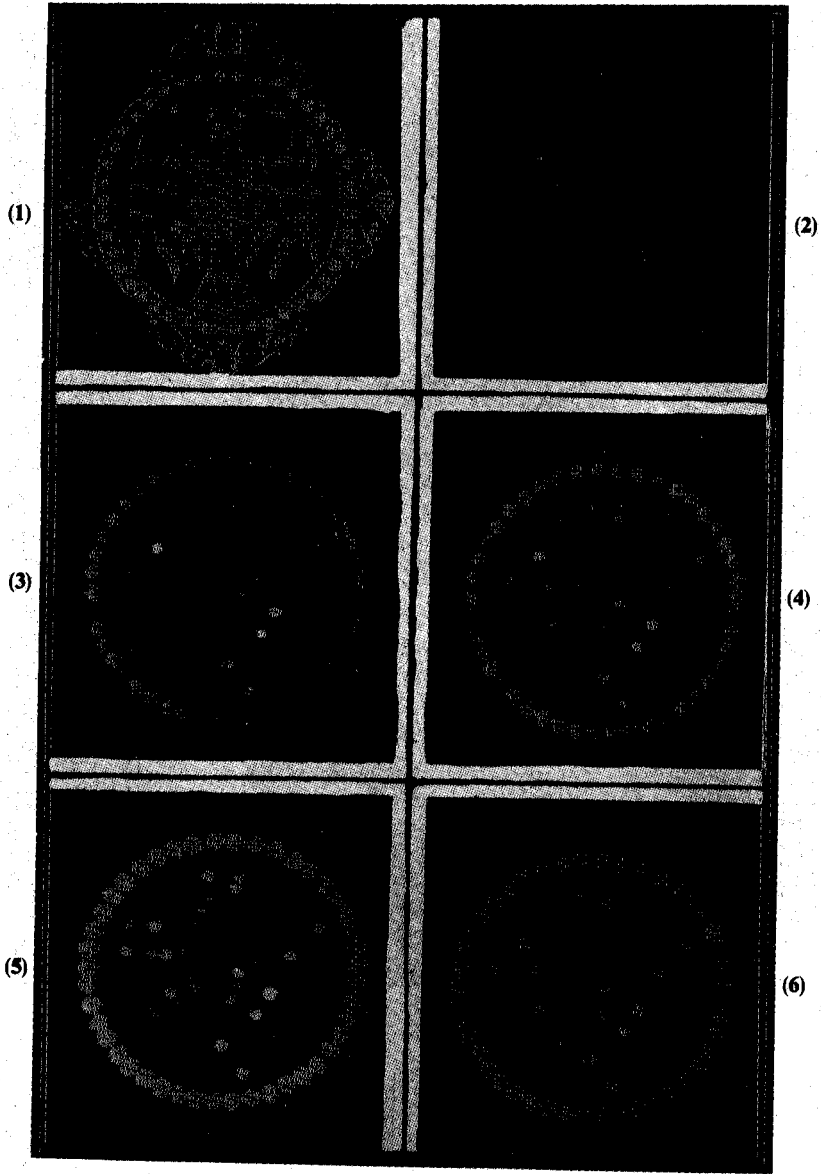
12. Summary

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.

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Luminescence of South African diamonds

Figure 1. Photograph in daylight.

Figures 2 to 6. Luminescence in ultra-violet with increasing exposures.

Plate I

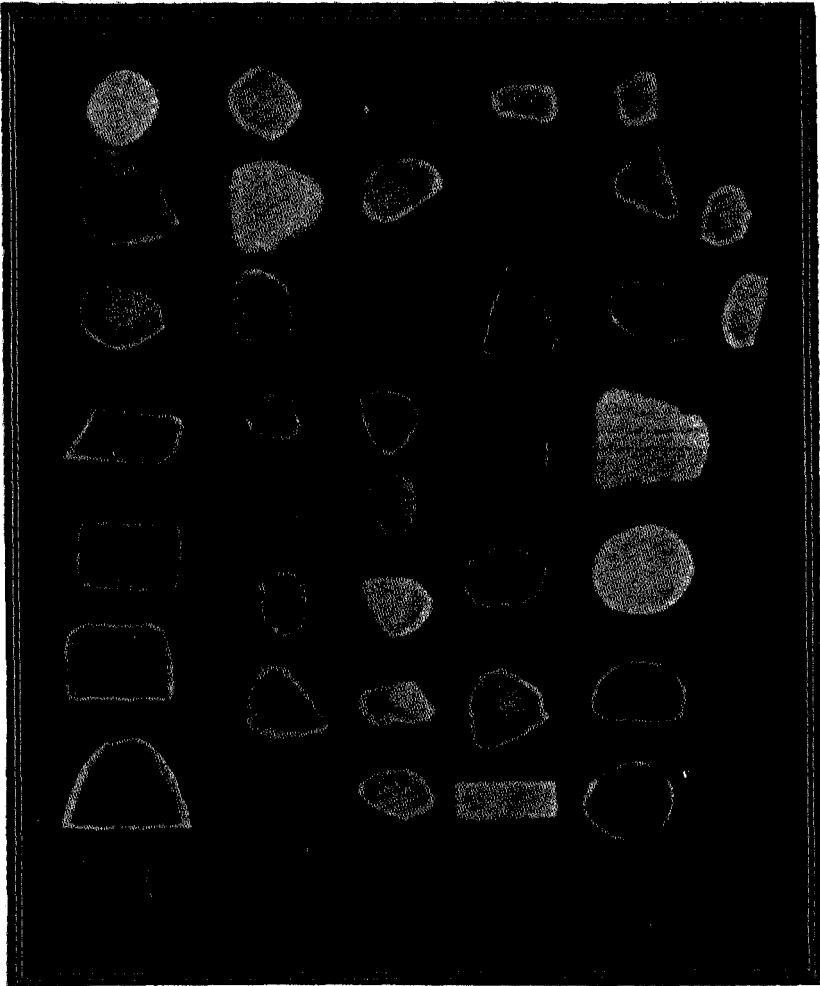


Figure 7. Luminescence of cleavage plates of diamond.

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	
52,208	209	206	39	207	

Non-luminescent

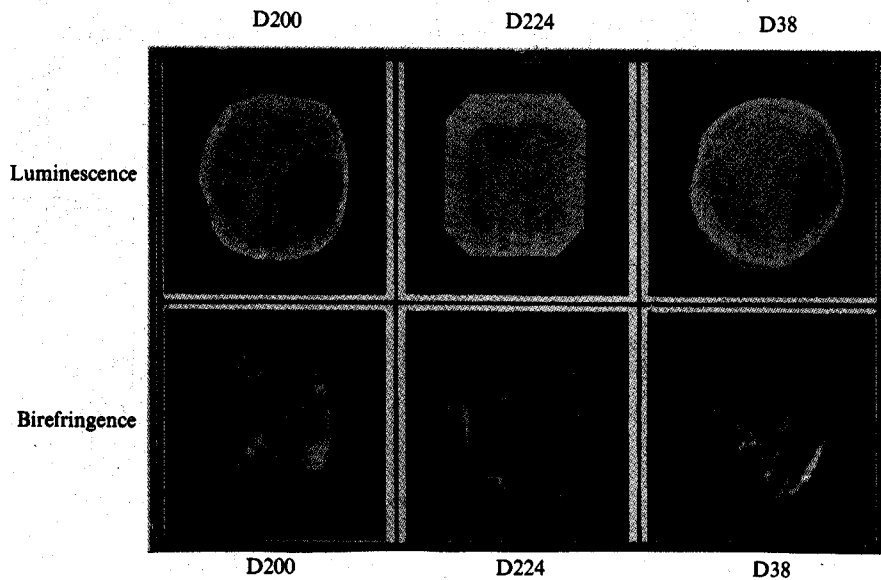


Figure 8. Comparison of luminescence and birefringence patterns.

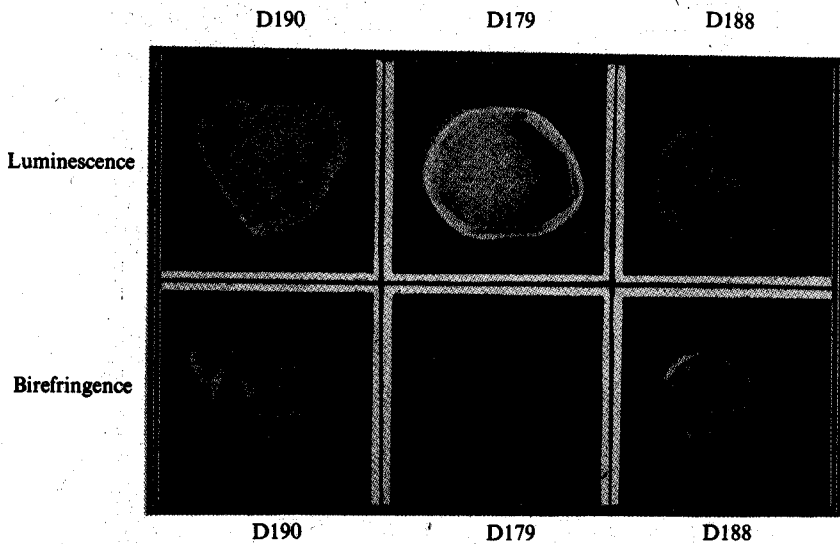


Figure 9. Comparison of luminescence and birefringence patterns.

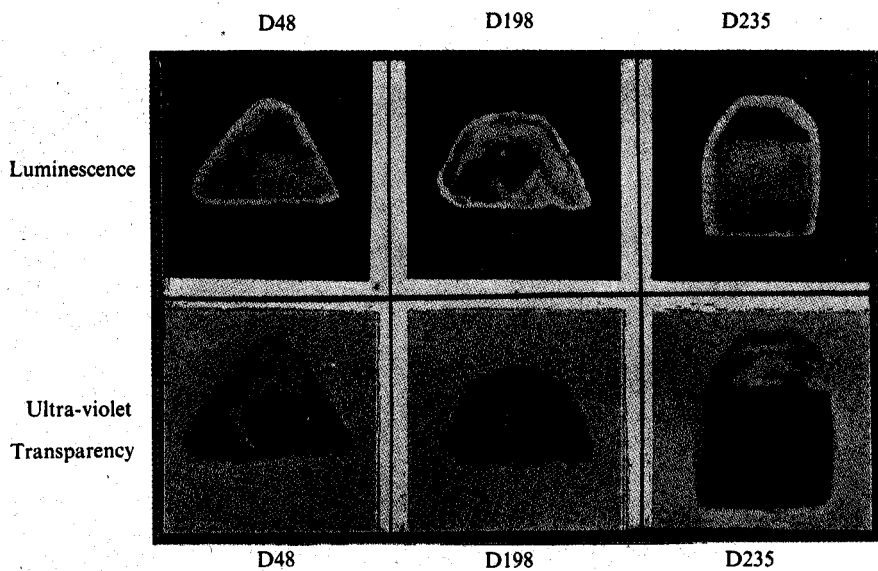
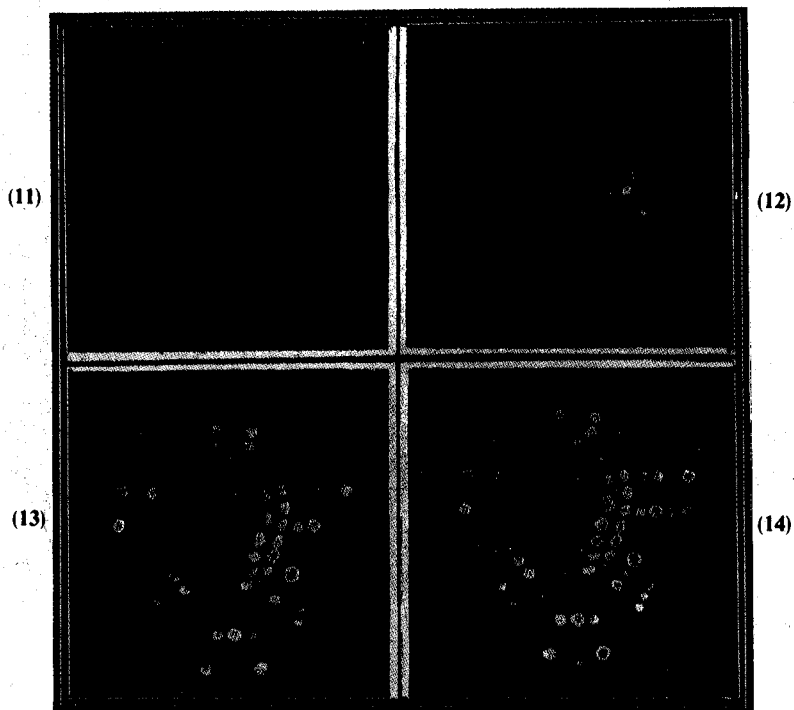


Figure 10. Comparison of luminescence and ultra-violet transparency patterns.



Figures 11 to 14. 11. 50 K.V. 10 minutes 12. 56 K.V. 30 minutes; 13. 70 K.V. 30 minutes; 14. 70 K.V. 60 minutes.