

The luminescence of diamond and its relation to crystal structure

SIR C V RAMAN and A JAYARAMAN
Raman Research Institute, Bangalore

Received August 14, 1950

1. Introduction

Studies on the luminescence exhibited by diamond under ultra-violet irradiation were commenced at Bangalore some ten years ago. Their scope enlarged as the collection of high-grade material available for the investigations grew and became more fully representative in character. The results of the researches of the first few years were reviewed in two papers^{1,2} published together in these *Proceedings* in the year 1944. The conclusions reached in those papers may be stated briefly as follows:

I. *Nearly all diamonds and especially those of the first quality exhibit luminescence: this effect is an inherent property of the material: the variations observed in its intensity and in its spectral character have a structural origin.*

II. *The symmetry of the electronic structure of diamond may be either tetrahedral or octahedral: in individual specimens there is a commingling of the different possible structures having these types of symmetry and the property of luminescence results therefrom.*

Experimental evidence was presented both at that time³ and also later^{4,5} that variations of behaviour having a structural origin present themselves not only in respect of luminescence, but also in respect of numerous other physical properties of diamond, viz., the intensity and angular divergence of the X-ray reflections by the crystal, its infra-red absorption spectrum of the first-order, the absorption spectra in the remote and near ultra-violet and in the visible region, structural birefringence and photo-conductivity. The variations observed in all these properties are manifestly correlated with each other, thereby demonstrating their common physical origin.

The structural origin of the luminescence of diamond can be very elegantly exhibited with the aid of polished cleavage plates of the crystal and by various methods of observation. One of these is an examination of the behaviour of such plates in respect of luminescence under ultra-violet irradiation and in respect of

birefringence in ordinary light. A remarkable parallelism between these two phenomena was discovered by one of us.⁶ Photographs were published in these *Proceedings*⁷ which were intended to exhibit them side by side for purposes of comparison. Unfortunately, however, the techniques employed were defective, and the pictures reproduced convey only a feeble idea of the very remarkable and precise character of the relationship between luminescence and birefringence in diamond. The present paper is intended to remedy this defect in the earlier work. The photographs now published in the plates accompanying the paper are a record of the luminescence and birefringence of some of our typical specimens. The photographs are on precisely the same scale and have the same orientation, thus enabling them to be readily compared with each other. There are over a hundred cleavage plates of diamond of the first quality in our collection, and the summary of the facts noticed in the case of the diamonds whose photographs are reproduced is equally a description of the behaviour of the rest of them.

2. Technique of study

The spectral character of the luminescence of diamond has been thoroughly investigated by P G N Nayar⁸ and by Anna Mani⁹ at Bangalore. On cooling the diamond down to low temperatures, it becomes evident that the luminescence has its origin in various electronic transitions in the crystal, either alone or in combination with its vibrational transitions. Comparison of the spectra of numerous specimens shows that the emission is of two distinct kinds, a *blue luminescence* and a *greenish-yellow luminescence* respectively. Their absolute and the relative intensities vary largely. The blue luminescence arises principally from an electronic transition giving a line at 4152 A.U. near the violet end of the spectrum, accompanied by a vibrational spectrum appearing in the blue and green regions. The greenish-yellow luminescence arises *principally* from an electronic transition giving a greenish-blue line at 5032 A.U. accompanied by a vibrational spectrum appearing in the green and yellow regions. The two types of luminescence may be viewed separately by observing the diamond through appropriately chosen colour filters. A piece of cobalt glass transmits only the blue luminescence and cuts off the other. For isolating the greenish-yellow luminescence, we have found that an orange-yellow filter which has a complete cut-off at 5400 A.U. is preferable to a yellow filter with a cut-off at about 5000 A.U., since the blue luminescence has a sensible intensity in the region between 5000 and 5400 A.U.

Sunlight concentrated by a large lens and passed through a nickel-oxide glass filter furnishes ultra-violet illumination of the requisite intensity to excite the luminescence. It is focussed on the diamond which is placed on a plate of black glass, both being carefully cleaned to minimise scattered light. It is arranged that the ultra-violet irradiation is almost tangential to the surface of the specimen and as nearly uniform over it as possible, while the visible luminescence is viewed

nearly normally to the surface. In this way, the trouble due to reflection and scattering of the red light simultaneously transmitted by the ultra-violet filter is minimised. In some cases, entry of light through the faceted edges of the diamond results in a streaky illumination of its interior. This trouble is avoided or minimised by a proper choice of the setting of the diamond in its own plane. The camera with which the specimen is photographed is a vertical one of rigid construction and of fixed focal length. It is fitted with a high-quality short-focus lens of the type used for making enlarged photographic prints from small negatives. The appropriate colour filter is interposed between the camera and the diamond. When the cobalt-blue glass is used as a filter, a cell containing sodium nitrite solution has to be interposed to prevent scattered and reflected ultra-violet radiation from entering the camera.

The birefringence is recorded with the same camera and under the same conditions as the luminescence, except that the illumination is by ordinary light transmitted normally through the diamond held between crossed polaroids, no filters being used. The photographs of luminescence and birefringence are thus on exactly the same scale and therefore strictly comparable. The record of the birefringence is to some extent influenced by the setting of the specimen in its own plane between the crossed polaroids. This is varied until the features which it is desired to exhibit are most clearly visible.

3. The facts of observation

Each of the figures 1 to 14 appearing in plates I to VII contains three photographs marked (a), (b), (c); these represent respectively the blue luminescence, the greenish-yellow luminescence and the birefringence of the diamond. They are placed together for ease of comparison. We shall not comment on the figures individually, but proceed to state the facts emerging on a careful study made with the specimens in our collection. The interested reader can readily verify these statements by an examination of the figures reproduced.

A. A few diamonds are non-birefringent. Such diamonds exhibit only blue luminescence, the greenish-yellow type being absent.*

*During a visit by one of us to Great Britain in May 1948, the opportunity arose of examining the luminescence of a great number of diamonds of the highest grade in their natural form as crystals. These had been sorted and arranged in cages in the order of their excellence, as judged by their water, freedom from colour and the absence of strong birefringence when examined between crossed polaroids. Each cage contained some fifty or sixty crystals. All the diamonds without exception from the first six cages showed luminescence of blue colour. Examples of green or yellow luminescence were very few even in the cages containing the lower grades. A blue or bluish-green luminescence was by far the commonest. The batch of diamonds studied was from the Congo, and the similarity between these results and those observed with Indian diamonds of high grade during a visit to Panna in June 1942 was very striking.

B. A few diamonds show neither the blue nor the greenish-yellow luminescence. Such diamonds exhibit a characteristic type of birefringence consisting of a set of fine streaks parallel to each other, or sets of such parallel streaks intersecting each other.

C. The majority of diamonds exhibit both types of luminescence. They also exhibit a birefringence pattern, the geometric character of which bears a recognisable relationship to the features observed in one or the other or both of the luminescence patterns.

D. The two kinds of luminescence often exhibit certain geometric features in common. In other cases, they appear to be complementary, dark regions in one being bright regions in the other, and vice versa. Frequently, also, the greenish-yellow luminescence exhibits features totally absent in the blue luminescence.

E. The blue luminescence is usually conspicuous in areas where the birefringence is weak or absent. It often exhibits a remarkably uniform intensity over such areas. On the other hand, in areas where there is strong birefringence, the blue luminescence is generally of non-uniform intensity and may exhibit a banding which is often straight, but may sometimes also be wavy.

F. The greenish-yellow luminescence frequently takes the form of sets of bands running parallel to each other. Sometimes, two or even three such sets of bands may be seen. Corresponding sets of bands are visible in birefringence.

G. The greenish-yellow luminescence is often conspicuous in the regions separating areas in which birefringence is weak or absent from those which exhibit a strong birefringence.

H. One can distinguish the character of the birefringence in the areas which display both blue and greenish-yellow luminescence or the latter alone, from the birefringence in the areas which display neither. The areas of the latter kind exhibit birefringence of the same character as the nonluminescent diamonds.

Figures 15 and 16 in plate VIII illustrate an effect observed with all diamonds which exhibit the greenish-yellow luminescence as a set of parallel bands. Inclining the plate about an axis parallel to the bands, it is found that the bands sharpen to fine lines when the plate is tilted to one side, while they become more diffuse when the tilt is on the opposite side. In the same circumstances, the bands in birefringence sharpen to fine lines or become more diffuse respectively, thus displaying a complete parallelism of behaviour with the bands in luminescence. Figures 15(b) and (c) exhibit these effects with a tilt to one side, and figures 16(b) and (c) with the tilt on the other.

In this connection, a reference should be made to the facts elicited concerning the birefringence of polished cleavage plates of diamond in the very thorough study by G N Ramachandran¹⁰. This author made use of a Zeiss petrographic microscope with a Federov universal stage on which the diamond could be placed and suitably orientated. He examined many plates apparently different in their behaviour, and the investigation showed that in all cases, the birefringence patterns were resolved by the microscope with a suitable tilt of the plate to a set of

laminations having a definite orientation parallel to either the octahedral or the dodecahedral planes in the crystal. This was found to be the case even when no laminations were visible when the plate was viewed *normally* between crossed nicols. Only in the diamonds which exhibited no visible birefringence were such laminations found to be absent. In other words, birefringence when observed in diamond is associated with a laminated structure in the crystal: the laminae run parallel to the octahedral or to the dodecahedral planes in the space-lattice.

4. The origin of the luminescence

The view formerly held regarding the luminescence of diamond was that it did not represent a characteristic property of that substance and that the emission was due to some undetermined impurity present in it; the impurities suggested from time to time made a long list, viz., samarium, yttrium, sodium, aluminium, chromium, iron, and titanium, and included even some hydrocarbons! However, it became clear from even the earliest Bangalore investigations that this view was irreconcilable with the observed spectral characters of the luminescence and of the associated absorption. Nayar in his papers of 1941 recognized that the spectroscopic evidence showed the luminescence to be a characteristic property of diamond itself. He ventured further to suggest that the variations of its intensity were in some way connected with the question of the structural perfection of the crystal. A more extensive collection of material became available soon afterwards, and other methods of investigation were also applied to the problem. These enabled more definite conclusions to be reached and published, as already mentioned in the introduction.

It is clearly not possible to reconcile the view which regards the luminescence of diamond as an emission by some undetermined impurity with the experimental facts which we know today about the subject. It is not possible, either, to entertain the alternative but scarcely less naive hypothesis put forward by some authors, namely that the luminescence is that of diamond *activated* by a trace of some unknown impurity. Indeed, it is obvious that no activator, however distributed within the crystal, could account for the curious and remarkable relationships between luminescence and birefringence observed to exist, as set out in the foregoing pages. Nor would it be capable of accounting for the quantitative relationships which exist between luminescence intensity and X-ray reflection phenomena in diamond as demonstrated by G N Ramachandran^{11, 12, 13} by three different methods. These relationships form a direct and convincing demonstration that luminescence in diamond has a structural origin. In these circumstances, it seems almost superfluous to refer to many other facts which have been fully established for which it would scarcely be possible to offer any reasonable explanation on the "activator" hypothesis. We shall content ourself

here with mentioning the very striking results obtained by K G Ramanathan,¹⁴ who has shown that the luminescence intensity and the infra-red absorption by diamond stand in the closest relation with each other.

5. Luminescence and crystal structure

The clue to an understanding of the luminescence properties of diamond is to be found in a consideration of the symmetry properties of the structure of that crystal.* The leading crystallographers of the nineteenth century, including especially Groth, came to the conclusion that the crystal symmetry of diamond was of the tetrahedral class, and that the octahedral symmetry frequently exhibited by it was a pseudo-symmetry arising from an interpenetration of the positive and negative tetrahedral forms. Fersmann and Goldschmidt made a thorough study of the subject¹⁵ and arrived at the same conclusions. The crystal forms of diamond have been re-examined from completely new point of view,¹⁶ and the results support the earlier findings with one modification, namely that the possibility of the structure of diamond being octahedral in some cases is not excluded. The position thus reached is that there are alternative possibilities, in other words that the symmetry of the structure may be either tetrahedral or octahedral.

The existence of structures belonging to the two different symmetry classes would at once explain why the strength of the infra-red absorption of the first order in diamond is highly variable. Spectroscopic theory permits us to identify the structures which are infra-red active with those possessing tetrahedral symmetry and those which are inactive as possessing octahedral symmetry. We can also understand without difficulty why some diamonds which are infra-red active are optically isotropic. The positive and negative tetrahedral forms are physically identical and only geometrically different. Hence their interpenetration would not lead to birefringence. On the other hand, the lamellar structure of the infra-red inactive diamonds indicates that there are also two sub-types of octahedral structure: but these are physically different and therefore do not interpenetrate but appear in distinct layers, the octahedral or dodecahedral planes of the lattice being the planes of junction, analogous to be the composition

*In the article on diamond in volume 3 (pp. 69-89) of the *Encyclopedia of Chemical Technology* (Edited by Professors Kirk and Othmar of the Brooklyn Polytechnic Institute, and issued by the Interscience Publishers, 1949), it is shown how this also enables the remarkable variations in physical properties exhibited by diamond to be correlated and interpreted in a coherent and intelligible manner.

planes in polysynthetic twinning. Such a juxtaposition naturally results in birefringence.

Viewed against the theoretical background sketched above, the facts stated in the preceding sections naturally fall into place. Tetrahedral and octahedral symmetries do not give us different kinds of diamond but only different kinds of structure. If the positive and negative tetrahedral structures co-exist, interpenetrating each other, we have non-birefringent blue luminescent diamond. If the two sub-types of octahedral symmetry co-exist, we have birefringent non-luminescent diamond. In the great majority of cases, however, the tetrahedral and octahedral structures co-exist with the result that the diamond is birefringent and exhibits both blue and greenish-yellow luminescence. The latter arises at the junction planes between the tetrahedral and octahedral structures, and it is readily understood, therefore, why it exhibits a banded structure.

Similar considerations enable us to understand the variations in the behaviour of diamond in respect of infra-red activity, as also in respect of their ultra-violet absorption. In sufficiently thin layers,¹⁷ all diamonds exhibit ultra-violet transmission up to 2250 A.U., there being an intense absorption at still shorter wavelengths. A weaker absorption at longer wavelengths is characteristic of the electronic structures having tetrahedral symmetry. Hence, the strength of such absorption varies from diamond to diamond in a manner closely correlated with their behaviour in respect of luminescence. If the diamond is completely non-luminescent, the cut-off appears at 2250 A.U. even with thick plates. On the other hand, if the diamond is of the luminescent kind, the thicker plates exhibit absorption at wavelengths greater than 2250 A.U., and in the case of the feebly blue-luminescent non-birefringent diamonds this extends up to about 3000 A.U.

6. Some remarks on nomenclature

References continue to appear in the literature which assume that any actual diamond must belong to either the one or the other of two species designated as type I and type II respectively. This assumption does not correspond with reality. The original proposers of that nomenclature noted that the great majority of diamonds showed optical birefringence and also infra-red activity in the 8μ region of the spectrum. They assumed that such optical anisotropy and infra-red activity were characteristic of a particular type of diamond including the great majority of specimens which they designated as type I. On the other hand, they found that a small minority of diamonds were inactive in infra-red absorption in the 8μ region and exhibited a lamellar structure. These diamonds, they designated as belonging to type II. Actually as we have seen, diamonds are forthcoming which show the infra-red activity strongly but do not show any visible birefringence. Moreover, examination on the Federov stage with a polarising microscope shows that all diamonds which show birefringence also

exhibit a lamellar structure. Further, the infra-red activity of diamond in the $8\ \mu$ region is variable and may be anything from zero upwards. Hence it is not possible to divide diamond into two classes on the basis of the presence or absence of such activity. Neither is it possible to base such a classification on the degree of transparency of diamond in the ultra-violet region of the spectrum between 2250 A.U. and 3000 A. U., since this varies in a continuous manner from diamond to diamond.

It is thus clear that the classification of diamond as belonging to type I or type II was based on erroneous beliefs concerning the actual facts of the case. A proper scientific classification must be based on a definite physical idea of what the structural differences actually observed represent and should be capable of correctly describing and interpreting the observed facts. Since this is not the case for the division of diamond into two types and since such division does not correspond with reality, it is meaningless and quite misleading and should therefore be discarded. The truth of the matter is that the great majority of diamonds have a structure which does not permit of their being labelled as belonging to any single type.

Acknowledgement

We take this opportunity of acknowledging the generous assistance which was forthcoming when one of us visited London in May 1948, facilities for study and specimens for further investigations having been freely placed at his disposal by several persons and authorities. We wish to mention and specially offer our thanks to Dr Paul Grodzinski and to Mr B W Anderson. The diamond of which the photographs are reproduced as figure 1 was one of the specimens received as a gift during the visit. To the Instruments and Chemicals Ltd. of Ambala, we are also much indebted for the prompt construction of the stand-camera used in obtaining the photographs and for their generosity in making a gift of it to this Institute.

Summary

The relationships which exist between the luminescence of diamond and its behaviour in respect of birefringence are described and illustrated in the paper by a new series of photographs obtained with improved technique and with diamonds of the first quality. It is shown that the results fully support the conclusions reached earlier, viz., that the luminescence of diamond has a structural origin. It is also pointed out that the classification of diamond into two species as type I and type II does not correspond with reality and must therefore be discarded.

References

1. C V Raman, *Proc. Indian Acad. Sci.*, A19 189 (1944).
2. C V Raman, *Ibid.*, 19, 199 (1944).
3. First symposium on diamond, *Ibid.*, June issue 19 (1944).
4. Second symposium on diamond, *Ibid.*, July issue 24 (1946).
5. Symposium on the vibration spectra of crystals, *Ibid.*, December issue 26 (1947).
6. C V Raman, *Curr. Sci.*, 12 33 (1943).
7. G R Rendall, *Proc. Indian Acad. Sci.*, 24 168 (1946).
8. P G N Nayar, *Ibid.*, 13 483 (1941).
P G N Nayar, *Ibid.*, 13 534 (1941).
P G N Nayar, *Ibid.*, 14 1 (1941).
P G N Nayar, *Ibid.*, 15 293 (1942).
9. (Miss) Anna Mani, *Ibid.*, 19 231 (1944).
10. G N Ramachandran, *Ibid.*, 24 65 (1946).
11. G N Ramachandran, *Ibid.*, 19 280 (1944).
12. G N Ramachandran, *Ibid.*, 19 304 (1944).
13. G N Ramachandran, *Ibid.*, 24 95 (1946).
14. G N Ramachandran, *Ibid.*, 26 469 (1947).
15. Fersmann and Goldschmidt, *Der Diamant, C Winter, Heidelberg* (1911).
16. C V Raman and S Ramaseshan, "Second symposium of diamond," *Proc. Indian Acad. Sci.*, A24 1 (1946).
17. K G Ramanathan, *Ibid.*, 24, 137 (1946).

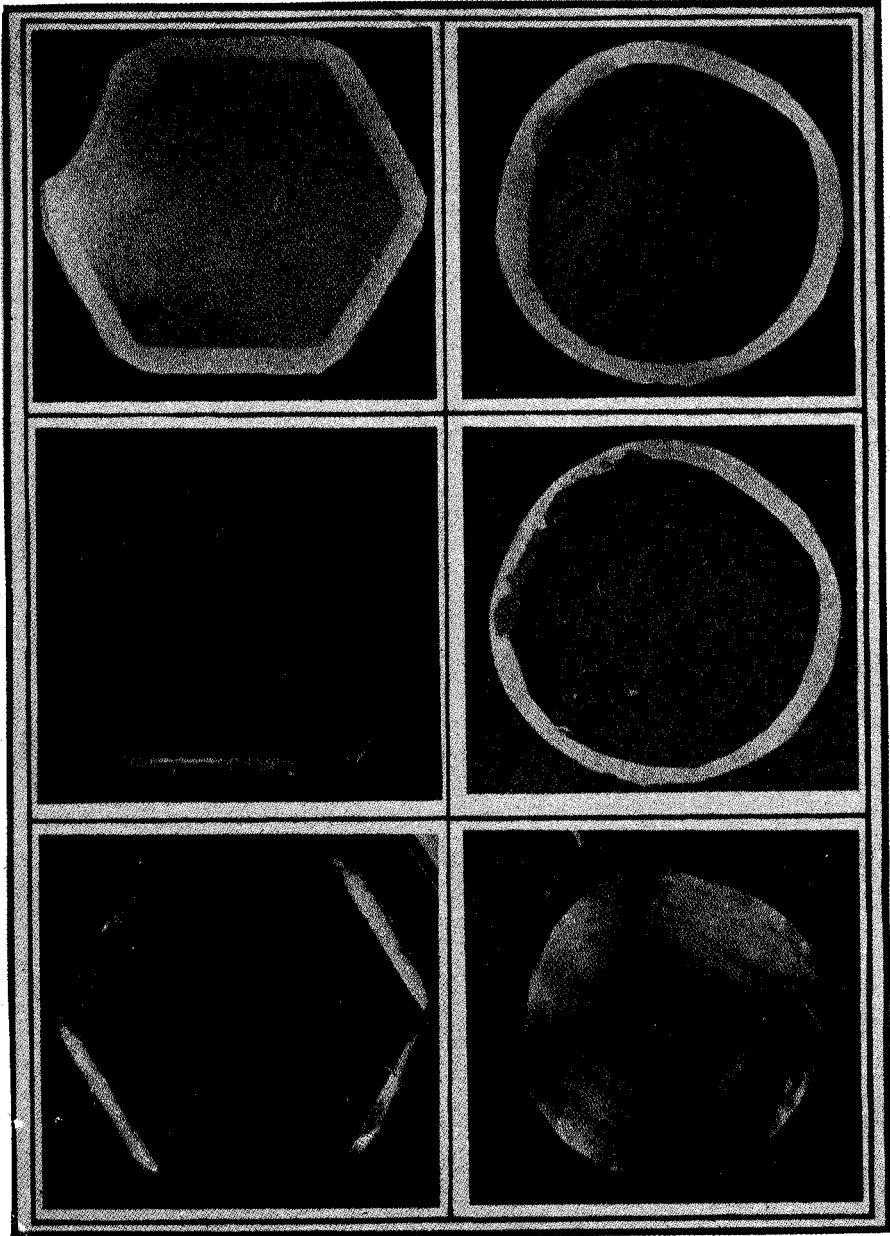


Figure 1

Figure 2

Plate I

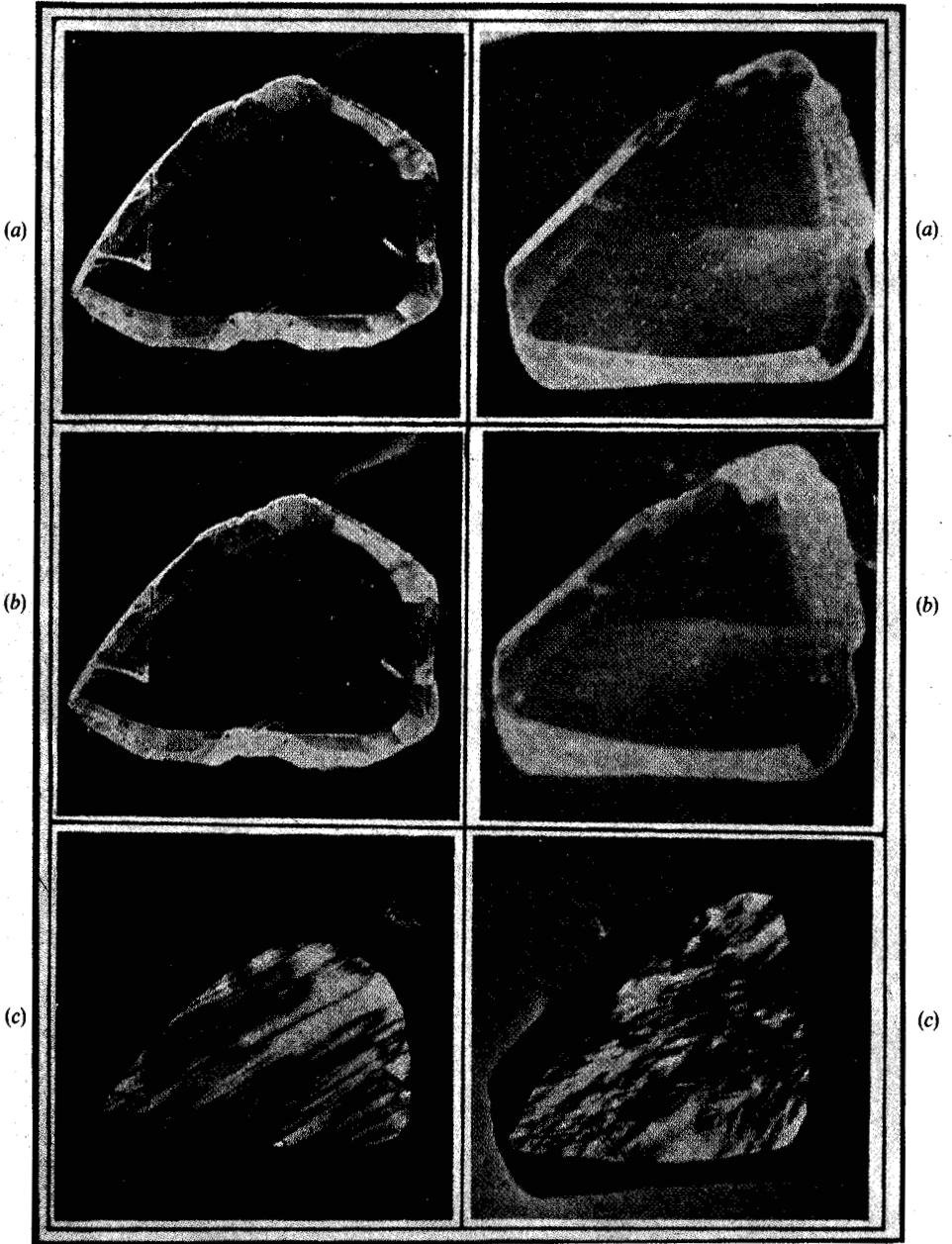


Figure 3

Figure 4

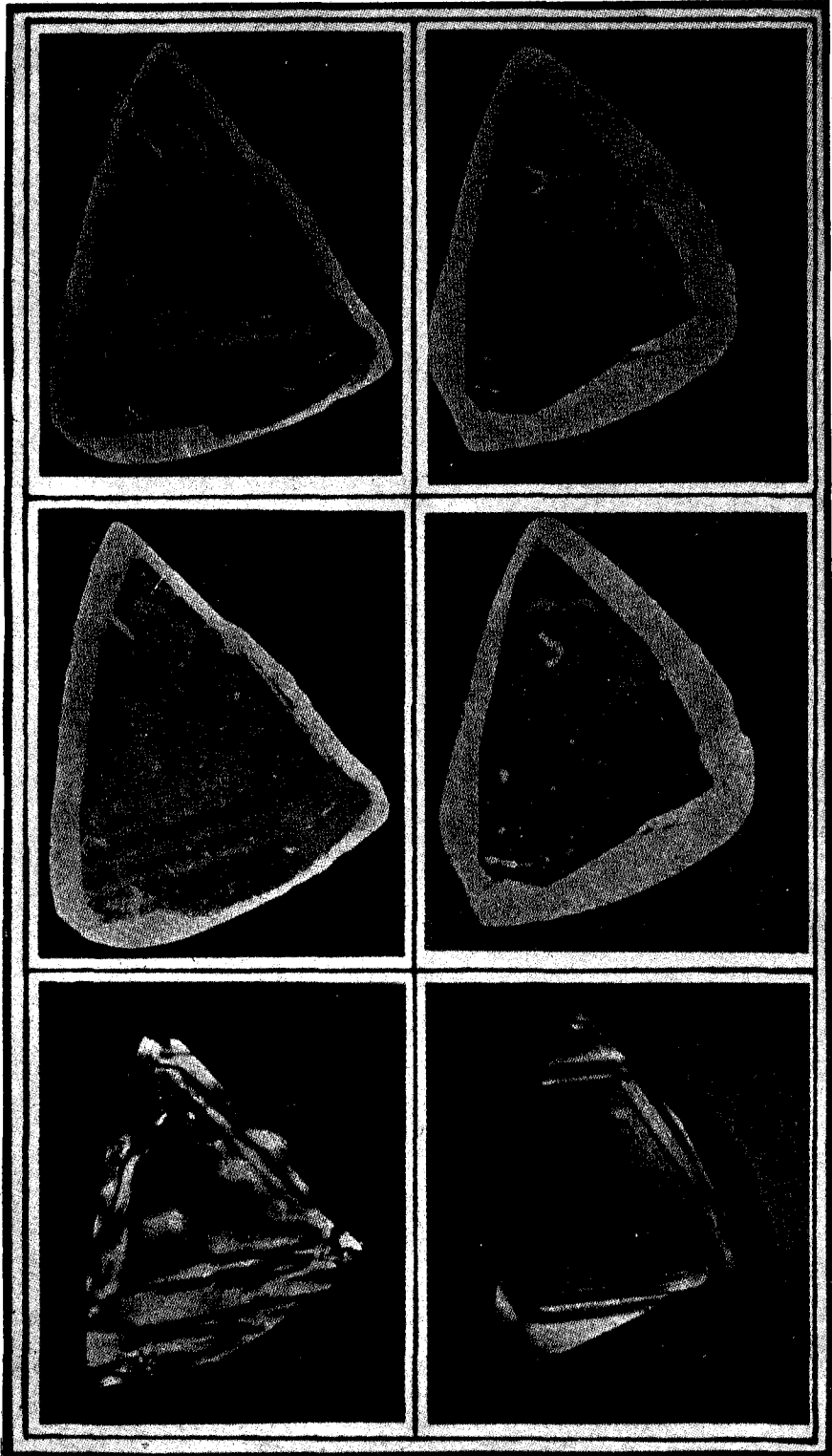


Figure 5

Figure 6

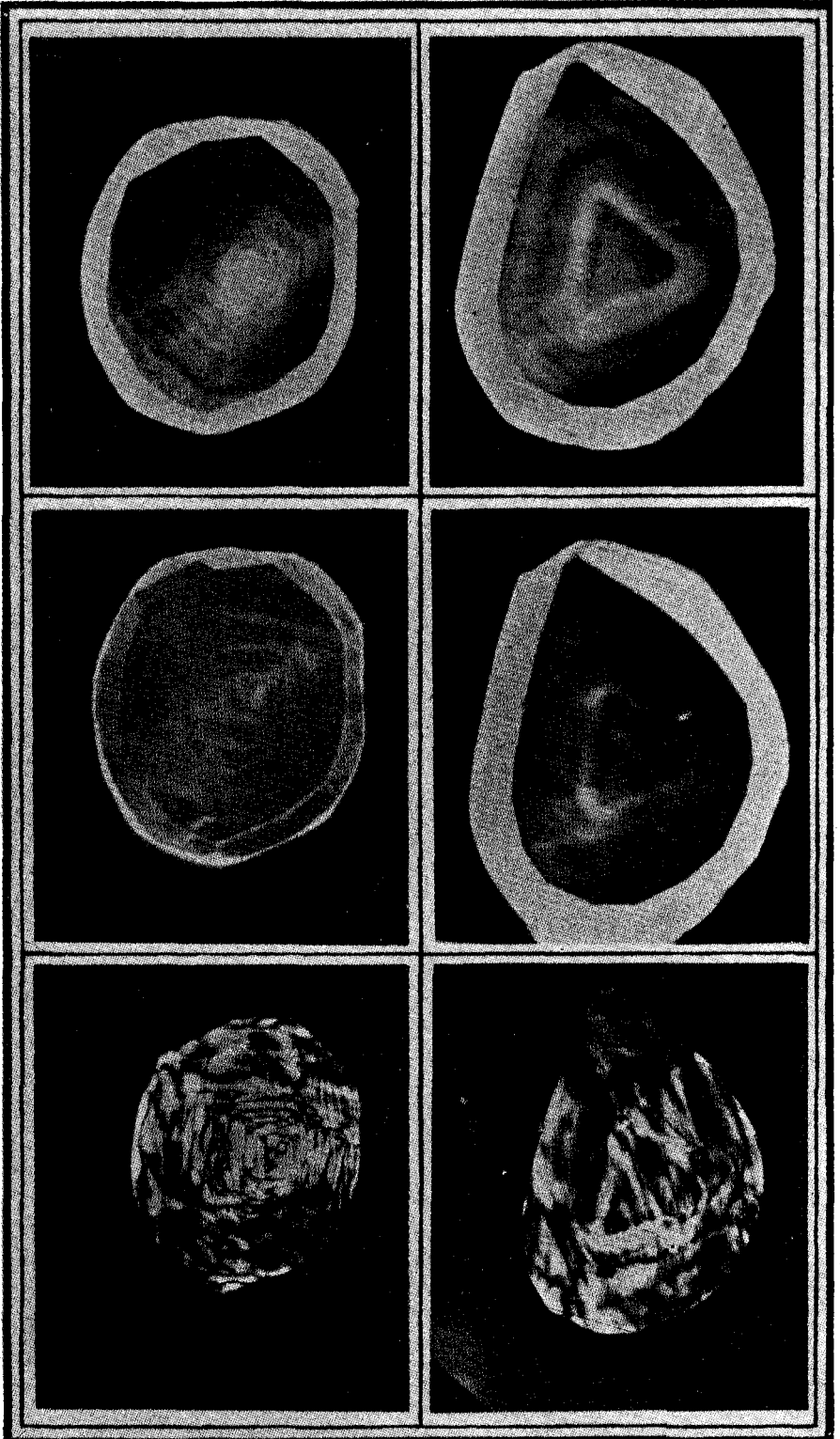


Figure 7

Figure 8

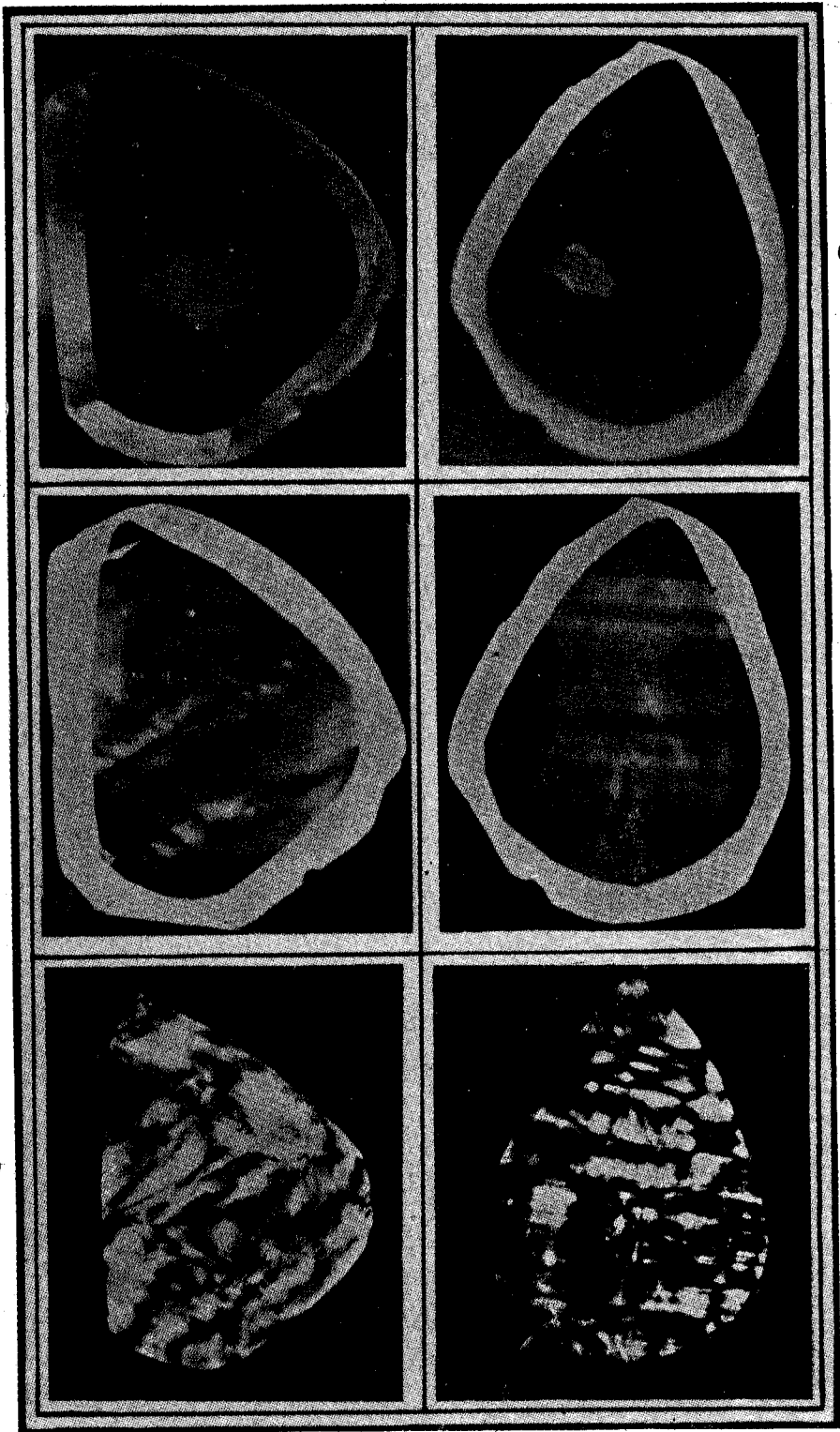


Figure 9

Figure 10



Figure 11

Figure 12

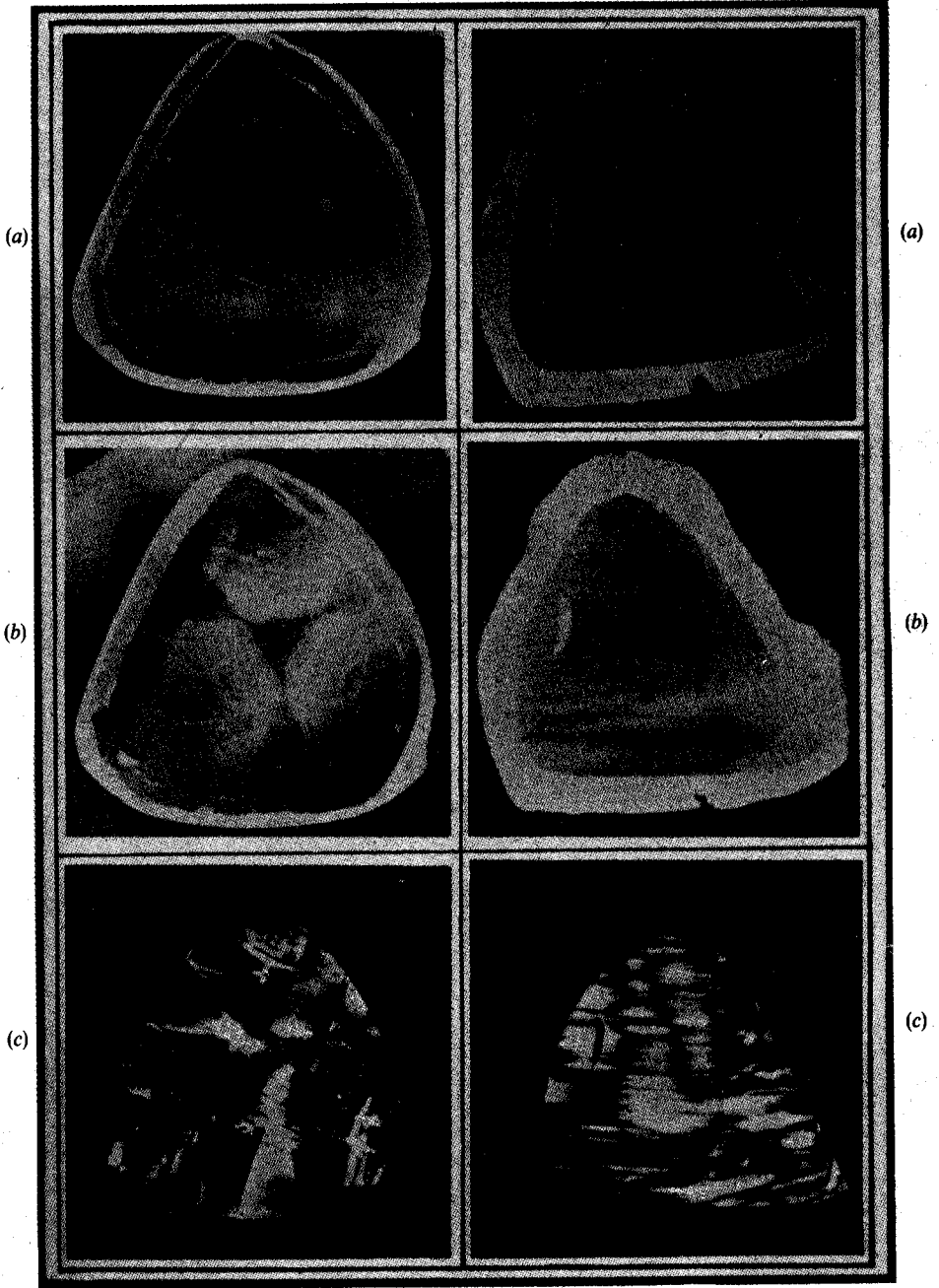


Figure 13

Plate VII

Figure 14

