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THE LUMINESCENCE OF DIAMOND—IV

SIR C. V. RAMAN

1. STRUCTURE AND CRYSTAL SYMMETRY OF DIAMOND

THE clue to an understanding of the luminescence of diamond is to be sought for in the relationship between the spectroscopic properties of the material on the one hand and its crystal structure on the other. Of fundamental importance in this respect is a result which emerged from the Bangalore investigations, namely, that the diamonds which are the most perfect as indicated by their freedom from birefringence and by the low intensity and extreme sharpness of their X-ray reflections are those which most prominently exhibit the infra-red absorption of the first-order between 7μ and 14μ , and the series of sharply-defined absorption lines in the ultra-violet spectrum between $\lambda 2250$ and $\lambda 3500$. *Per contra*, the diamonds which do not manifest either the infra-red or the ultra-violet absorption in these regions are

those which exhibit the maximum of imperfections in their crystal structure, as indicated by the birefringence which they display and the intense and diffuse X-ray reflections which they give. These facts preclude us from ascribing the activity in infra-red and ultra-violet absorption present in one case and absent in the other to irregularities in crystal structure, and compel us to recognise that there is, in fact, a fundamental difference in structure between the two varieties of diamond. Spectroscopic theory enables us to specify the nature of such difference. If the electronic structure of diamond possesses centres of symmetry located at the points midway between every pair of neighbouring carbon atoms in the crystal lattice, the diamond would necessarily be infra-red inactive in the first-order vibration spectrum. But, if op

the other hand, such centres of symmetry are absent, the diamond would necessarily exhibit an infra-red activity of the first-order. Such a fundamental difference in electronic structure may be expected also to manifest itself in a notable difference in respect of ultra-violet absorption, as is indeed actually observed.

vity of crystals having a heteropolar constitution. It is also necessary to point out that the lower symmetry of the infra-red active diamond, whatever may be its origin, would not necessarily involve either piezo-electric or pyro-electric activity. The feebleness of the infra-red activity is itself also an indication

I

II

III

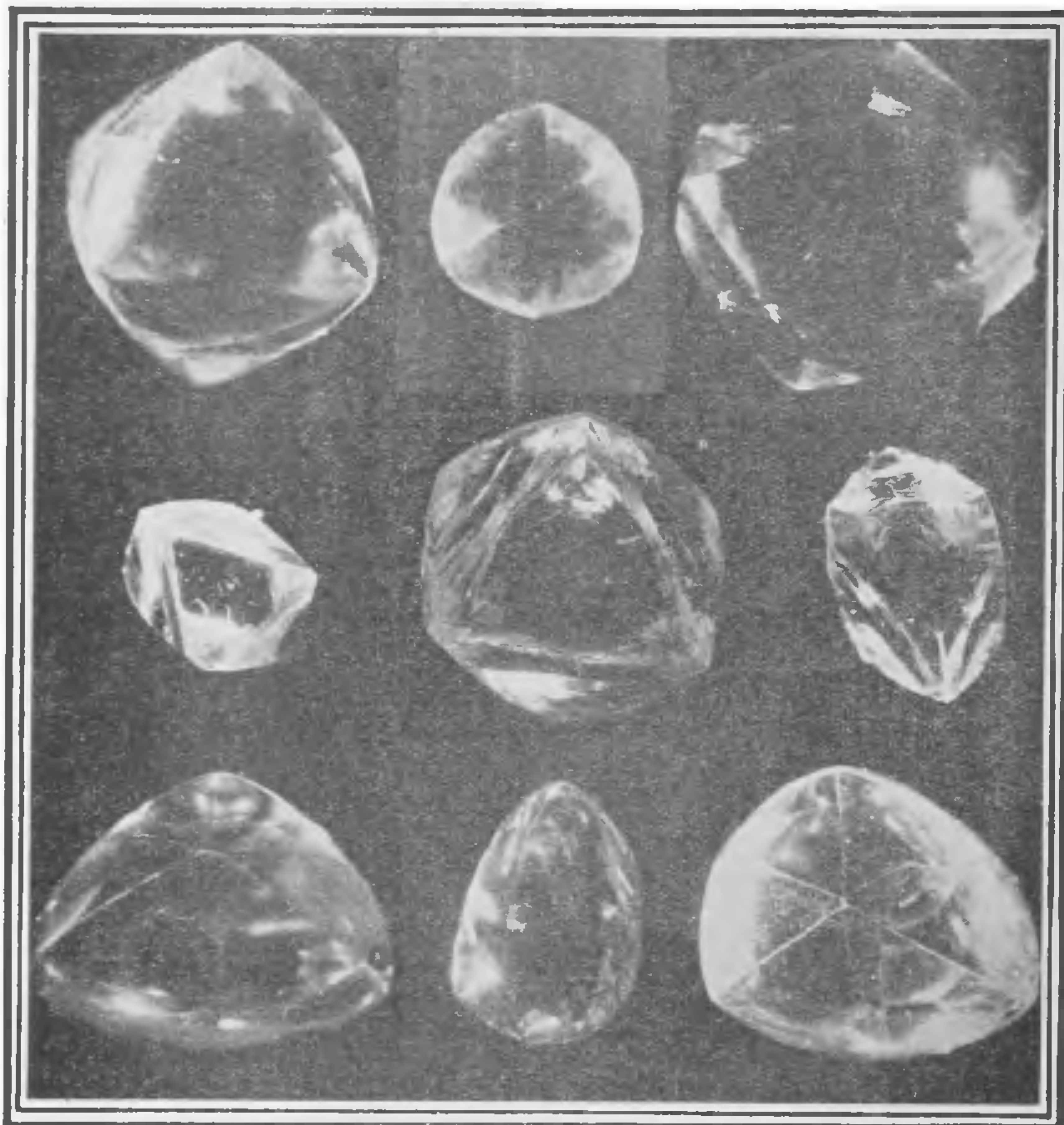


FIG. 1. Photographs of Diamond Crystals

Thus, spectroscopic theory leads us to recognise the existence of two varieties in the crystal structure of diamond possessing respectively tetrahedral and octahedral symmetry. It may be remarked that the infra-red activity present in one case and absent in the other is very feeble compared with the infra-red acti-

that the differences in structure between the tetrahedral and octahedral varieties when expressed in quantitative measure are very small. It is, therefore, not surprising that the two varieties of diamond make a very close approach to each other in many of their physical properties. Such similarity has another

important consequence. Since both structures belong to the cubic system, we should expect that their appearance side by side in the same specimen of diamond should be a very frequent occurrence. That this is indeed actually the case is shown by the frequency with which patterns of ultra-violet transparency are observed in cleavage plates of diamond, as already mentioned in an earlier article of the series. These patterns always exhibit a geometric character, the boundaries of separation between the opaque and transparent regions running parallel to the octahedral or dodecahedral planes in the crystal lattice. This is ocular evidence that we are concerned with a real difference in structure between the areas under consideration.

2. THE CRYSTAL FORMS OF DIAMOND

It is well known that crystals of the tetrahedral class in the cubic system frequently exhibit interpenetration twinning, as the result of which their external forms imitate or mimic octahedral symmetry. It follows that such interpenetration of the positive and negative tetrahedral forms should be commonly observable in crystals of diamond. This is fully borne out by experience. Indeed, from the very beginnings of crystallographic science, it had been noticed by mineralogists that the evidence presented by the crystal forms of diamond very definitely placed this substance in the tetrahedral class and indicated a strong disposition on its part to imitate octahedral symmetry by interpenetration twinning.

Fig. 1 reproduces photographs of nine crystals from the Bangalore collection which illustrate the tendency of diamond to exhibit pseudo-octahedral forms as the result of internal twinning. Five of the diamonds, *viz.*, A I, A II, C I, C II and C III are from Panna in Central India and have the rounded forms with smooth lustrous faces characteristic of the finest diamonds from that locality. They also show a feature which is highly characteristic of diamonds with curved surfaces, namely a pattern of sharp ridges which run along the six reflection planes of tetrahedral symmetry and divide the external area into 24 triangular areas (see for instance, A II, which is a nearly spherical diamond). A I, which is octahedral in its general shape, exhibits six sharp vertices where four ridges meet, while at each of its eight face-centres, six ridges meet: but the edges characteristic of a real octahedron are missing, being replaced by smoothly curved surfaces. On the other hand, the diamonds pictured in C I, C II and C III, have forms in which the features

characteristic of a hexakis-tetrahedron may be readily recognised, C I being the best example in this respect in the collection. The three diamonds reproduced as B I, B II, B III illustrate another typical form of diamond, *viz.*, octahedra with plane faces and grooved edges. B II (the central picture in Fig. 1) is a particularly fine example of this class from South Africa. It exhibits sharply-defined re-entrant edges which limit the faces of the octahedron and give them a hexagonal instead of a triangular outline. The form is very clearly a consequence of the interpenetration twinning of positive and negative hexakis-tetrahedra.

3. THE ORIGIN OF THE BLUE LUMINESCENCE

The existence of interpenetration twinning in the tetrahedral type of diamond which is demonstrated by the study of its crystal forms allows us to offer an intelligible explanation of the observed association of blue luminescence with this particular variety of diamond. Every boundary within the crystal at which the positive and negative tetrahedral structures meet is a discontinuity in the crystal structure. The finer the subdivision of the entire volume of the crystal between the two interpenetrating structures, the more numerous would be the possible centres of luminescence brought into existence thereby. The interpenetration of the positive and negative tetrahedral forms thus furnishes a mechanism for the production of luminescence centres in greater or less number and, therefore also for a highly variable intensity of emission as between different specimens or within the volume of any given diamond, as is actually observed.

If the blue luminescence arises in the manner stated above, it follows that an increased intensity of luminescence would necessarily mean an increase in the lack of perfect homogeneity in the lattice structure of the crystal. In other words, the more intense the luminescence which a diamond displays, the less perfect would it be as a crystal. This consequence was actually foreseen by the present writer before X-ray studies confirmed its reality. In particular, an investigation by Dr. G. N. Ramachandran established the existence of a quantitative relationship between fluorescence intensity and the characters of the X-ray reflections by the lattice planes of the crystal, *viz.*, their intensity and their angular range.

A further consequence of the idea that interpenetration of the positive and negative tetrahedral forms is the origin of the blue luminescence may also be pointed out. If the subdivision of the crystal by such interpenetration

tration is carried far enough, we should expect the behaviour of the diamond to be noticeably altered as the result of the juxtaposition of the oppositely directed tetrahedral structures at their boundaries of separation. In particular, a diamond which exhibits an intense blue luminescence may be expected to differ noticeably in its behaviour in respect of infra-red and ultra-violet absorption from a diamond which shows only a weak luminescence. This, again, has actually been observed. One finds a distinct weakening of the infra-red activity characteristic of the tetrahedral type of structure in the more strongly blue-luminescent diamonds; simultaneously, the sharp absorption lines in the ultra-violet between $\lambda 2250$ and $\lambda 3500$ tend to become weaker and the diamond as a whole becomes more transparent to that region of the spectrum.

octahedral or dodecahedral planes in the crystal. The use of a Babinet compensator in addition reveals that the lamellæ present in the diamond are alternately under tension and compression. It thereby becomes evident that the birefringence arises from the co-existence in the same specimen of two sub-species both having octahedral structures but of slightly different lattice spacings (see Fig. 2).

As already remarked, intergrowths of the octahedral and tetrahedral species of diamond are exceedingly common. Cleavage plates in which there are such intergrowths invariably exhibit birefringence. They also exhibit bands of green luminescence. It is evident that when diamond of the non-luminescent or octahedral type and of the blue-luminescent or tetrahedral type are present side by side in the same specimen, the boundaries between them would re-

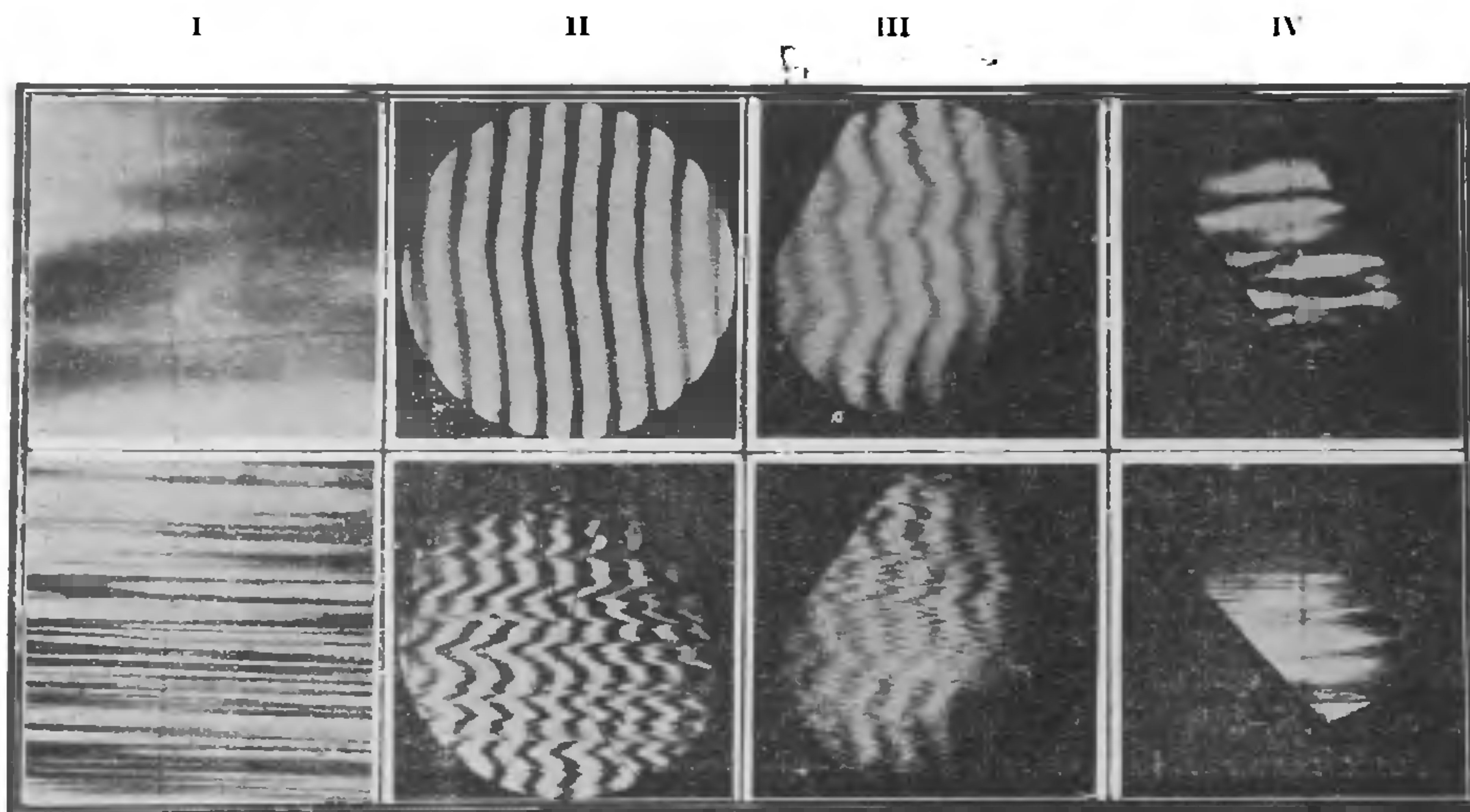


FIG. 2. Birefringence of Diamond as seen in the polarising microscope on the Federov stage: A as viewed normally, and B as viewed under tilt: I and IV without compensator, and II and III with it.

4. THE ORIGIN OF THE GREEN LUMINESCENCE

One need not be surprised that the diamonds having an octahedral symmetry of structure are not luminescent under ultra-violet irradiation. For, they are transparent to radiations of wave-length greater than $\lambda 2250$, and if there is no absorption, there can be no re-emission. The origin of the birefringence exhibited by such diamonds becomes clear when a cleavage plate of the same is examined under a polarising microscope provided with a Federov stage. It is then found that the birefringence is due to a lamellar structure running parallel to the

present discontinuities of crystal structure. Since absorption of ultra-violet radiation can occur in the vicinity of such boundaries, there is clearly a possibility of their functioning as centres of luminescence. There is ample experimental evidence to show that the green type of luminescence arises in this way. In the first place, one can understand on this basis why both the blue and green types of luminescence usually appear together, though in varying ratios of intensity. One can also understand why the green luminescence exhibits a banded structure and why there is a perfect

correspondence between such structure and the birefringence pattern observed in the same diamonds. Then again, it is found that when a cleavage plate of diamond showing the banded green luminescence is tilted one way or another, the birefringence and luminescence bands both sharpen in one position and both become diffuse in the other position, showing that they have a common orientation in the crystal. See Fig. 3 in which A and B represent the same cleavage plate photographed in two different directions relative to its surface. I represents the green luminescence bands and II the birefringence.

thus affording support to the hypothesis that both the green luminescence and birefringence arise from local variations in crystal structure. We may further remark that the explanation given above for the origin of green luminescence is supported by the observation that the patterns of ultra-violet transparency exhibit a close correspondence with such luminescence. The X-ray topographs also show a great intensity of X-ray reflection along the bands of green luminescence.

5. CONCLUDING REMARKS

The foregoing account of the subject has been confined to statements of fact and to inter-

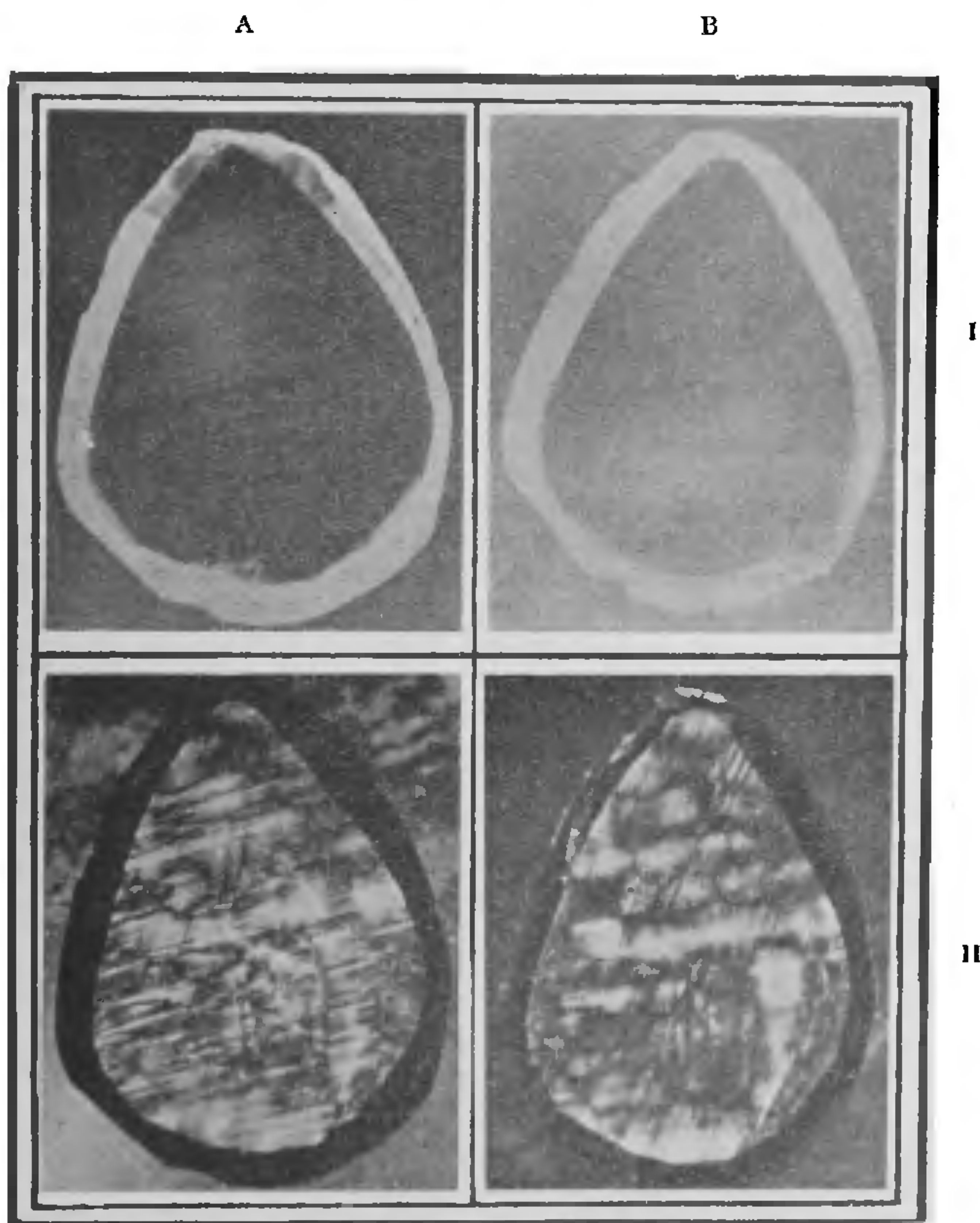


FIG. 3. Showing Effect of Tilting on Birefringence and Luminescence

From measurements of the tilt of the plate necessary to give the maximum sharpness to the bands, it is readily shown that we are concerned with layers running parallel to the octahedral or dodecahedral planes in the crystal,

pretations of the same based on well-established principles and therefore of a compelling nature. There are other aspects of the subject which are of interest but being of a somewhat speculative character have not been touched upon

here. For instance, what is the exact nature of the difference in the electronic structures exhibiting respectively tetrahedral and octahedral symmetry? Why are there two subspecies of octahedral symmetry, as is evident from the lamellar structure and birefringence of non-luminescent diamond? We have also not dealt with various other important issues which arise from the facts under consideration. What

is the scheme of electronic energy levels in diamond which give rise to the observed emission and absorption spectra? Why are the transitions between them allowed in some cases and forbidden in others? Unless we are in a position to answer such questions, we cannot claim to have fully understood either the structure of diamond or the many fascinating phenomena which it displays.

HUMAN BIOLOGY AND SOCIAL WELFARE

IN his Presidential Address to the Section of Anthropology and Archæology at the 38th Session of the Indian Science Congress, Bangalore, 1951, Dr. Sarkar makes out a case for the role of human biology in the process of building up the welfare state. He lays emphasis on the numerous gaps in our knowledge of the fundamental problems of the science due to long neglect. In many parts of India there is no compulsory registration of births, marriages and deaths. The work of the geneticist and the social and civic legislator is thus made difficult by the absence of adequate information and scientific knowledge which could be collected easily by scientific bodies and hospitals. Case reports and clinical data of common diseases such as tuberculosis, venereal diseases, etc., are entirely lacking. A central body could classify and publish such data if collected by the institutions concerned. A system of universal finger printing would settle out of court all disputed cases of identity and prevent frauds and forgeries. Population problems have been tackled so far by alarmist economists and not by sound biologists. Dr. Sarkar is of the view that there is no fear of over-population. The ban on widow marriage in Bengal is depleting the population of the food growers of the country.

Though the work done so far on the menarcheal age of women in India is not conclusive, there are indications to show that the menarcheal age is going down especially in those communities whose socio-economic con-

ditions are better. The Age of Consent Committee's findings in this respect are not satisfactory.

Dr. Sarkar regrets that in no case of disputed paternity have the law courts called in at any time for expert scientific opinion. Drawing up a parallel between the varied aspects of family life in India and the United States, Dr. Sarkar finds that there are many common characteristics of the modern family in both the countries such as urbanization, secularization and a trend to companionship. The only feature in which America differs from India is in the high divorce rate in America with its basic instability of the family, a feature which will become characteristic of India as well on the passing of the Hindu Code Bill. Dr. Sarkar deprecates such legislation as divorce laws in the absence of factual and statistical studies of genetic and sociological problems. A national commission on marriage, he says, should precede the Hindu Code Bill.

Even the much maligned caste system with its group endogamy and clan exogamy has been productive of beneficial results in India, says Dr. Sarkar. Of the sixteen Bengalis who were Presidents of the Indian National Congress, nine have been Kayasthas who are cited as an example of the Galton-Pearson ideal of national eugenics—a dominant fertility of the fitter stocks. Social legislation, says Dr. Sarkar, should be broad-based on this biological axiom.

C. J. JAYADEV.

ARCHIVES OF BIOCHEMISTRY AND BIOPHYSICS

IN view of the ever-increasing use of physical methods in problems of biochemistry—especially in borderline fields, Academic Press announces the intended widening of the scope of its journal, *Archives of Biochemistry*. In addition to established biochemical topics, the Editors will consider manuscripts in the fields of virus research, radiation effects on living matter, macromolecular biology and chemistry,

studies of the application of radioactive indicators, and physics of biological systems.

Beginning with Volume XXXI, Number 1, March 1951, the title of *Archives of Biochemistry* will be changed to *Archives of Biochemistry and Biophysics* to indicate more accurately the new scope of the journal. The Editorial Board has also been enlarged; Drs. E. Newton Harvey, E. C. Pollard, and R. W. G. Wyckoff have accepted an invitation to serve.