THE LUMINESCENCE OF DIAMOND—III

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1. THE ELECTRONIC EMISSION SPECTRA

AS was remarked in the first article of the series, the emission band at λ 4156 discovered by Ç. Ramaswamy in the year 1930 plays the leading role in the blue luminescence of diamond, while the band at λ 5038 studied later by Dr. Nayar and by Miss Mani plays an analogous role in respect of the green luminescence. These bands sharpen when the diamond is held at liquid air temperature and shift to λ 4152 and λ 5032 respectively. The λ 4152 emission also then appears resolved into a doublet, the width and separation of the components varying considerably with the specimen under study. In particular, the doublet is narrow for the diamonds which exhibit the blue luminescence feebly, a circumstance which is favourable for a satisfactory resolution of the associated vibrational spectrum into its discrete components. Absorption bands are also observed at λ4152 and λ 5032 in the spectrum of white light transmitted by the respective diamonds, the strength of such absorption varying *pari passu* with the intensity of the corresponding emission. Hence, one is justified in ascribing them to electronic transitions in the crystal lattice. Where there is an apparent lack of correspondence between the strength of the absorption and of the emission, there is evidence for the existence of self-reversal or other cause affecting the emission intensity.

The investigations of Dr. Nayar and of Miss Mani have also shown that λ 4152 and λ 5032 are by no means the only electronic transitions recorded in the luminescence spectra, though these stand out by reason of their special intensity and their association with vibrational transitions in the lattice. Lines

appearing strongly both in emission and absorption have been observed at λ 4189, 4197, 4206, 4907, 4959 and 5359. A fairly strong line at λ 5758 and numerous others which are less intense have also been recorded in the emission spectra of various diamonds but have not so far been detected in absorption. The electronic emission lines may be divided broadly into two groups, *viz.*, those that appear along with the emission at λ 4152 and the rest with that at λ 5032. They are observed respectively with the diamonds exhibiting these two types of luminescence.

The electronic line at λ 4156 present in the blue luminescence spectrum sharpens and increases in peak intensity when the diamond is cooled down. *Per contra*, it decreases in peak intensity when the diamond is heated up, until finally at 350° C. it merges into a continuous background and ceases to be visible. Its integrated intensity has been investigated by Chandrasekharan and found to remain unaltered over a wide range of temperature. Miss Mani's investigations have shown that the other electronic lines likewise shift towards smaller wave-lengths and sharpen when the diamond is cooled down to liquid air temperature The shift in wave numbers in the various cases is found to be of the same order of magnitude and roughly proportional to the respective frequencies.

2. The Electronic Absorption Spectra

The refractive indices of diamond fit very well into a dispersion formula containing two terms, the major term indicating an absorption at λ 1060, and the minor term with an absorption wave-length at λ 1750. The actually observed absorption in the ultra-violet, however, extends further towards greater wave-lengths. Diamonds of the non-luminescent type show a complete cut-off for wave-lengths less than λ 2250, while the best specimens of this class exhibit a complete transparency in the visible and near ultra-violet regions of the spectrum. Diamonds which exhibit luminescence, however, show a different behaviour. When the thickness of the plate is reduced sufficiently, the observed transmission extends down to λ 2250. There is, however, a strong absorption at greater wave-lengths, and indeed with the largest thicknesses, a complete cut-off is observed extending to λ 4152, and feebler absorption bands are noticed at even greater wave-lengths. These features are exhibited in Figs. 1 and 2 taken from a paper by K. G. Ramanathan.

In moderate thicknesses, however, blue-luminescent diamonds transmit wave-lengths greater than λ 3000 quite freely with the exception of certain absorption lines noticed in the region between λ 3500 and λ 3000, and the vibrational bands associated with the λ 4152 electronic transition.

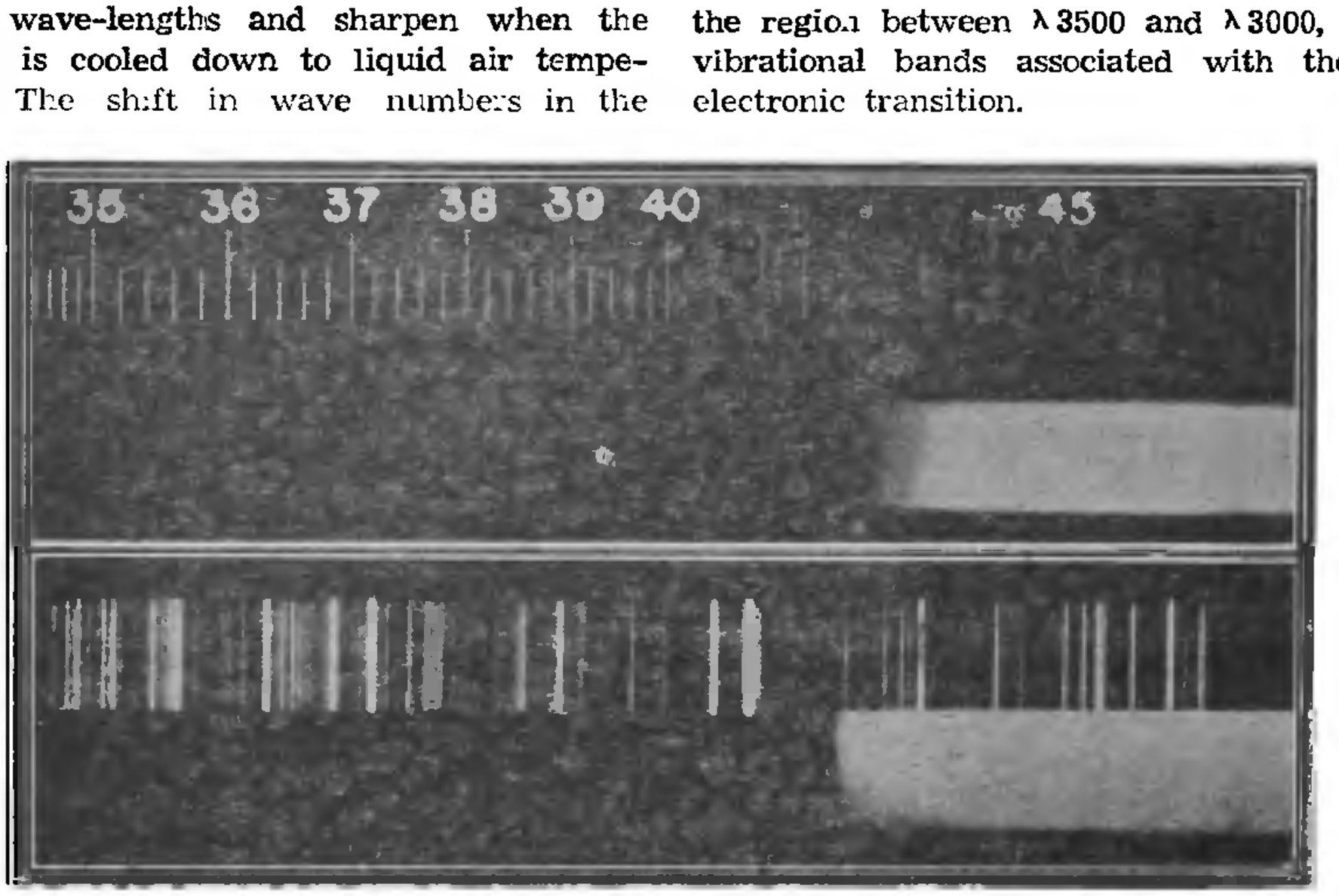

FIG. 1

Absorption of Visible Light by Thick Diamond: (*a*) At Room Temperature; (*b*) At Liquid Air Temperature.

Some 25 such absorption lines of the first kind can be seen in Fig. 3 which is reproduced from a paper by Dr. Nayar To record them successfully, it is necessary to hold the diamond at liquid air temperature and to adjust the thickness of diamond traversed as well as the photographic exposure suitably.

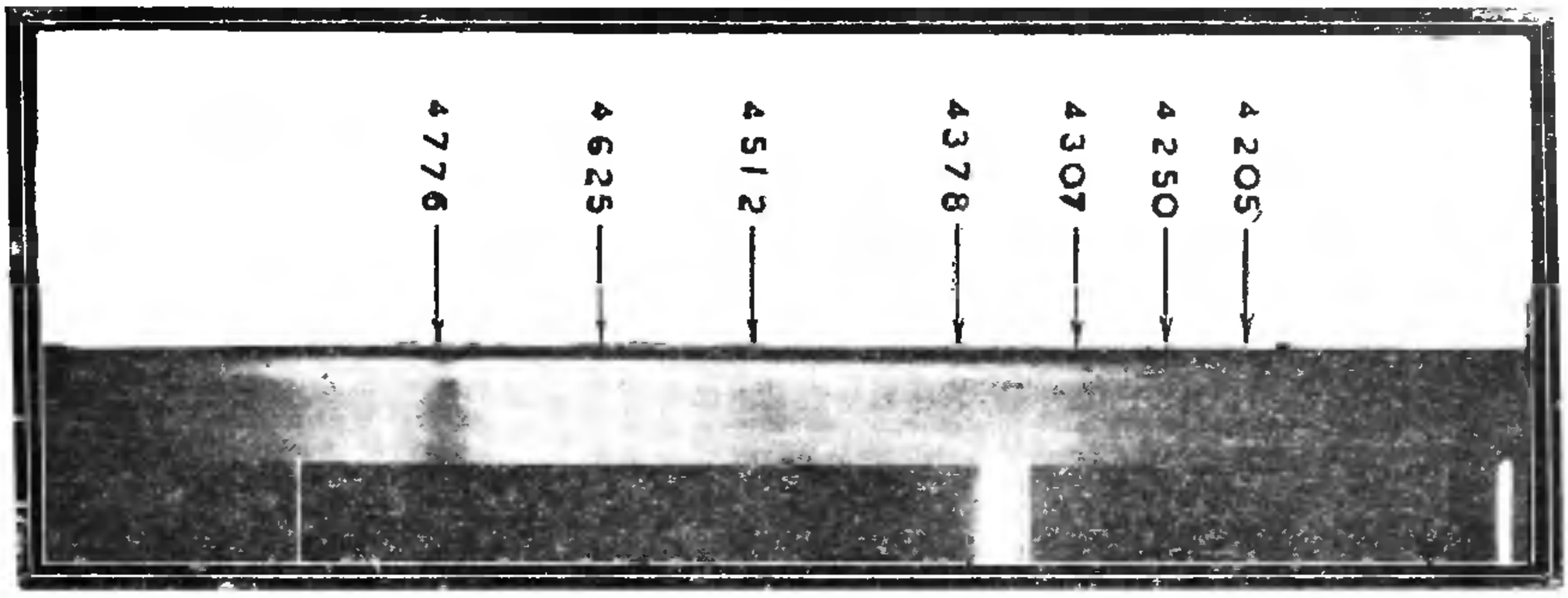

FIG. 2

Absorption of Visible Light by Thick Diamond under High Dispersion.

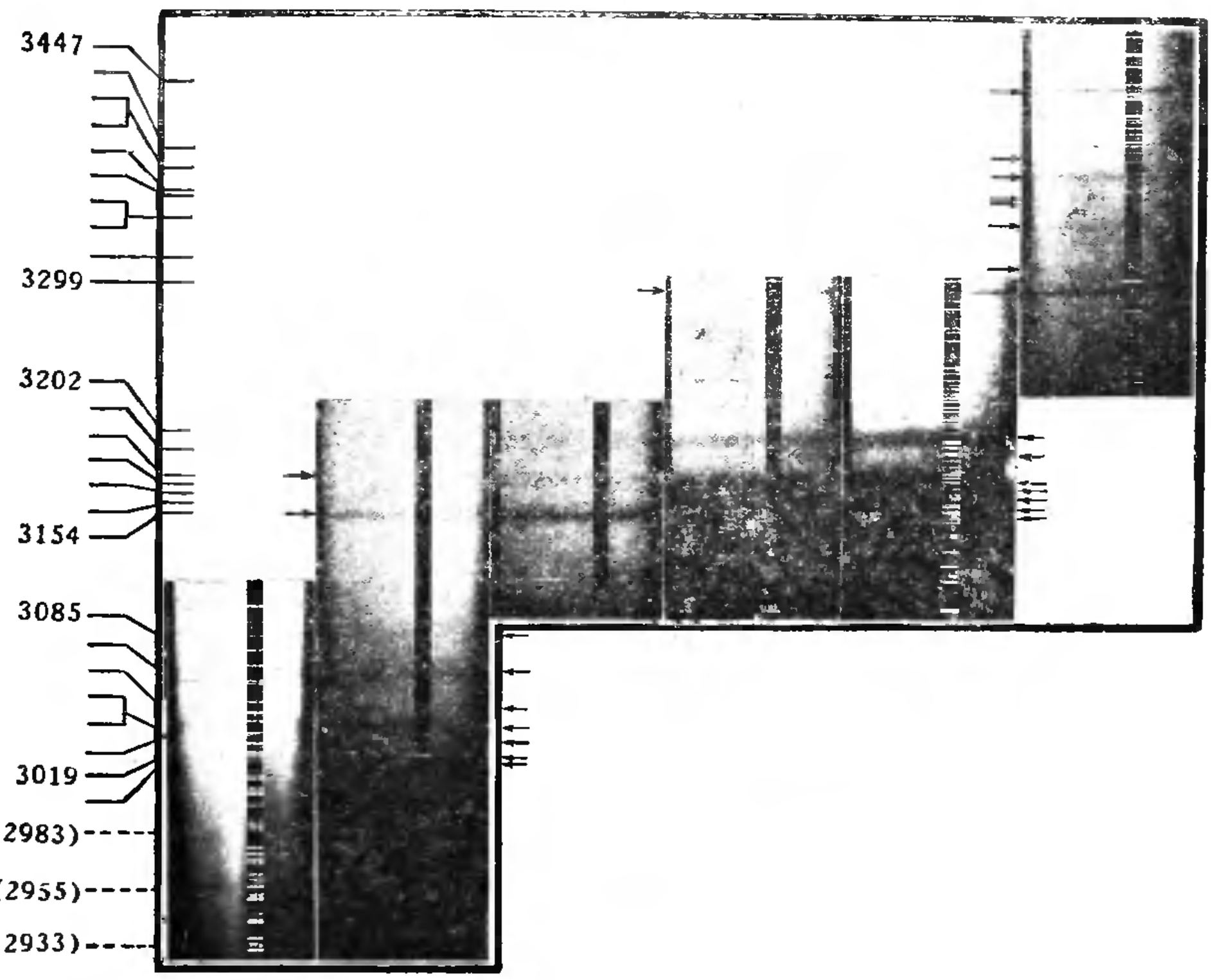

FIG. 3

Absorption Lines in the Ultra Violet.

Ordinarily, a diamond of the blue-luminescent class should be less than a millimeter thick to show any transmission for wave-lengths less than λ 3000. Very thin diamonds of the same variety exhibit a series of sharply-defined absorption lines in the wave-length region between λ 2370 and λ 2240. These are shown in Fig. 4 reproduced from a paper by K. G. Ramanathan.

It is noteworthy that a precisely similar set of absorption lines is observed also in the ultraviolet transmission of green-luminescent diamond, but can then be seen with moderate thicknesses of the material.

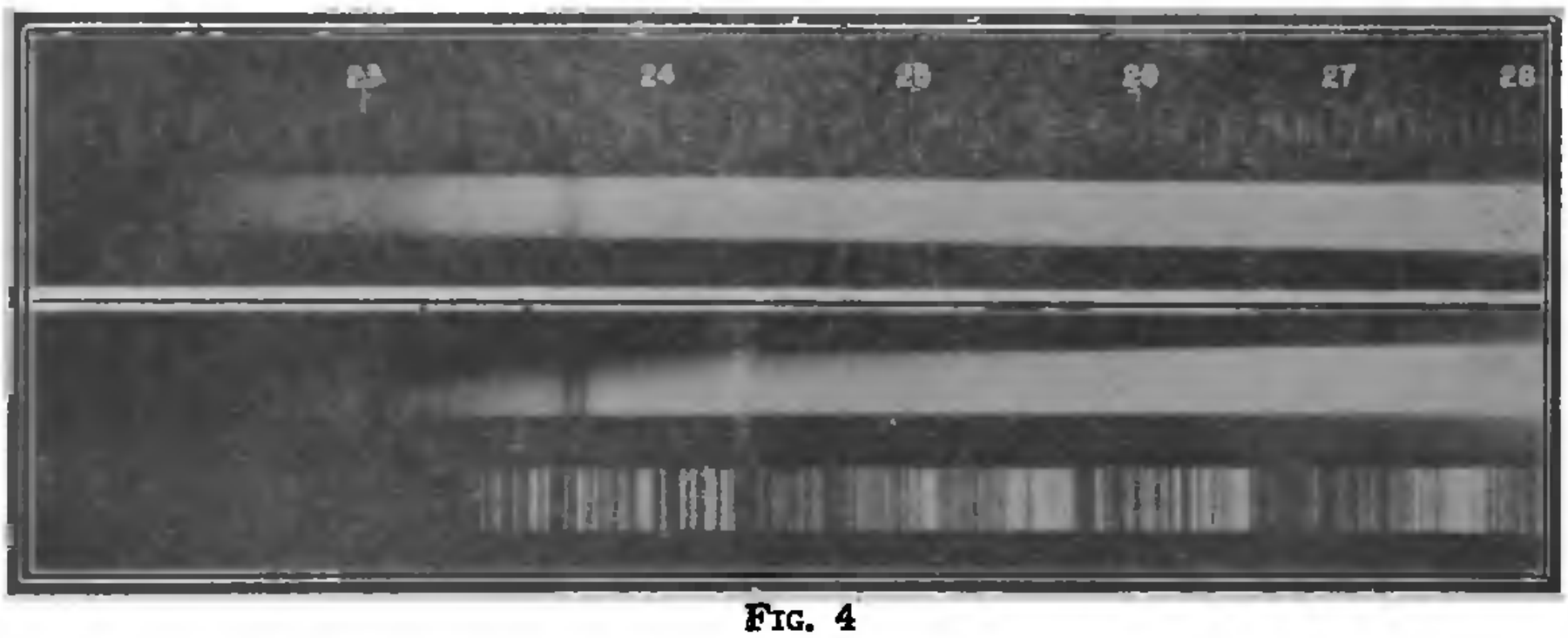

FIG. 4

Ultra-Violet Absorption Spectrum of Thin Blue-Fluorescent Diamond : (*a*) At Room Temperature and (*b*) Liquid Air Temperature.

It should be emphasised that the absorption spectra exhibited in Figs. 3 and 4 stand on a different footing from those mentioned in the preceding section and those shown in Figs. 1 and 2. They do not appear as emission lines, and their strength is not directly related to the intensity of luminescence. Indeed, the absorption lines seen in the vicinity of λ 3000 become weak and diffuse and the transparency extends further into the ultra-violet in the case of strongly blue-luminescent diamonds, as was first observed by Sunanda Bai.

3. THE INFRA-RED ACTIVITY OF DIAMOND

Polished cleavage plates are particularly suitable for quantitative studies on infra-red absorption. The results obtained by K. G. Ramanathan with a whole series of such plates are highly significant in relation to our present subject. No important differences are observed as between different diamonds in the infra-red activity in the spectral region between 1400 and 2800 cm.$^{-1}$ which covers the octaves and combinations of the fundamental vibration frequencies. There are, however, great differences in behaviour in the spectral region between 700 and 1400 cm.$^{-1}$ which covers the first-order vibration frequencies. The diamonds which are non-luminescent are completely transparent in the latter region. On the other hand, the non-birefringent and weakly blue-luminescent diamonds show a strong activity in the latter region, and the absorption-curves exhibit a series of peaks exhibiting a resolution of the vibration spectrum into distinct components (see Fig. 5). Green-luminescent diamonds show an inter-

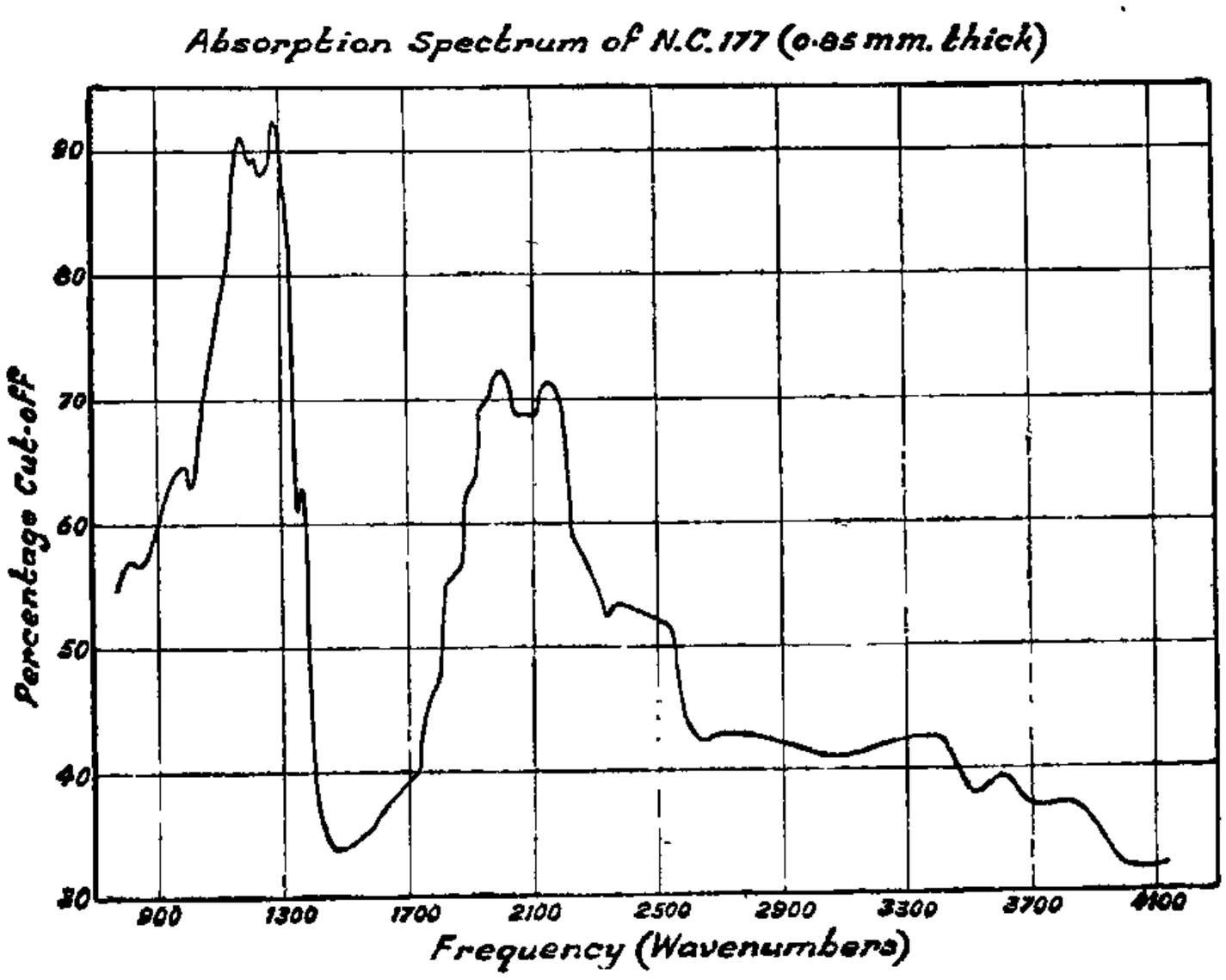

FIG. 5

Infra-Red Absorption Spectrum of Blue-Fluorescent Diamond.

mediate behaviour, such as would result from passage successively through two plates of appropriate thickness belonging respectively to the active and non-active types (see Fig. 6). *Strongly* blue–luminescent diamonds are found to exhibit an infra-red activity which is distinctly less than in the case of diamonds with a weak luminescence. The character of the absorption-curve also shows minor variations accompanying the changes in the colour and intensity of the luminescence.

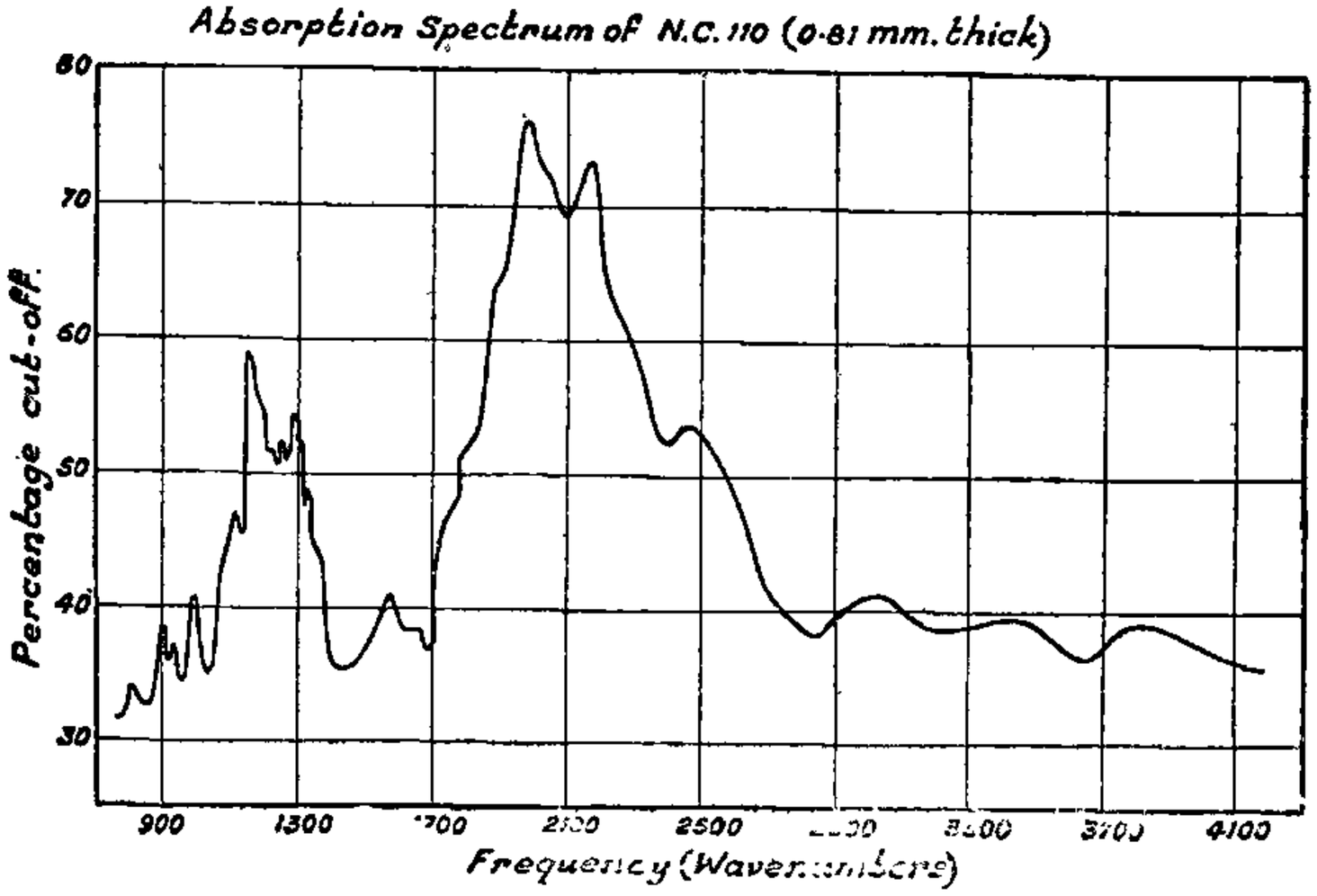

FIG. 6

Infra-Red Absorption Spectrum of Green-Fluorescent Diamond.

The diamonds which show the first-order infra–red activity most strongly are those which make the nearest approach to ideal perfection of crystal structure as shown by their freedom from birefringence and their X–ray behaviour. *Per contra*, the diamonds which do not show the first-order activity are those which exhibit the largest departure from ideality as indicated by such tests. In these circumstances, it is clearly not possible to ascribe the infra-red activity exhibited by the former class of diamonds to structural imperfections or other accidental circumstances. We are, in fact, compelled to recognize that the difference in behaviour connotes a fundamental difference in crystal structure. The nature of such difference follows from well-established spectroscopic principles, according to which the absence or presence of first-order infra–red activity in a crystal of the cubic class depends on whether the structure of the crystal does or does not possess centres of symmetry. In other words, the observed behaviour in respect of infra-red activity indicates that the electronic structure of the non-luminescent diamond has the highest or Oh type of symmetry, while the electronic structure of the blue-luminescent diamonds possesses only the lower or Td type of symmetry.

4. THE ORIGIN OF THE LUMINESCENCE

The experimental facts already described do not permit us to accept the belief formerly entertained that the luminescence of diamond arises from the presence of chemical impurities. They also serve to exclude the alternative hypothesis that the luminescence is activated by extraneous impurities. As early as 1941, Dr. Nayar suggested that the origin of the blue luminescence studied by him should be sought for in the departure of the crystal structure from ideal perfection. While this suggestion contains an element of truth, the results of subsequent investigations with a wider range of material show that it is not by itself sufficient to cover the facts. It does not, for instance, explain why diamonds which, as judged by optical and X-ray tests, show structural imperfections of the crystal in the highest degree, are precisely those which are non-luminescent. Neither does it account for the green type of luminescence and for the relationship between luminescence and birefringence which has been so clearly established. We are thus forced to look a little deeper to reach a clear understanding of the array of facts revealed by the Bangalore investigations.

(To be continued)

DR. M. S. KRISHNAN

SCIENTISTS all over India will welcome the news of the appointment of Dr. M. S. Krishnan, M A., Ph D., A.R.C.S., F.N.I., as Director of the Geological Survey of India. Dr. Krishnan is the first Indian to become the Head of this important Department of the Government of India.

Born in 1898 at Maharajpuram, Tanjore District, Dr. Krishnan has had a brilliant academic career. After taking his Honours degree in Geology with distinction from the Madras Presidency College in 1919, he worked as a Demonstrator for two years in the same college. He then went to the Imperial College of Science and Technology, and in 1923, was awarded the Ph.D. degree of the London University.

Dr. Krishnan joined the Geological Survey of India in 1924 as an Assistant Superintendent and did a considerable amount of field work in the Orissa States of Gangpur, Keonjhar, etc. Later, under his direction, many mineral deposits were investigated, and systematic geological mapping commenced in several districts of the Madras Presidency.

From 1933 to 1935, he was Professor of Geology at the Presidency College, Calcutta, which post he held along with that of the Curator (now styled Petrologist) in the Geological Survey.

In 1935, he went to Great Britain, United States of America, and Canada, and visited several important centres of Mining and Geology. On his return in 1936, he was appointed a Member of the Coal Mining Committee constituted by the Government of India.

Dr. Krishnan became a Superintending Geologist in 1945, and in 1946 visited England as an Official Delegate to the Royal Society Empire Scientific Conference. In 1947, he was deputed to Europe and America to make a special study of the methods of investigation of rare earth minerals. In 1949, he attended, at Lake Success, the United Nations Scientific Conference on the Conservation and Utilisation of Resources as a Member of the Indian Delegation.

He was President of the Geology Section of the Indian Science Congress in 1935. He is a Fellow or Member of many learned societies of the world, chief among which are the Indian Academy of Sciences, National Institute of Sciences of India, National Academy of Sciences of India, Mining, Geological and Metallurgical Institute of India, Geological, Mining and Metallurgical Society of India, Indian Society of Soil Science, Indian Ceramic Society, Geological Society of London. American Institute of Mining and Metallurgical Engineers, Canadian Institute of Mining and Metallurgy, Society of Economic Geologists of America, and Mineralogical Societies of America, England, France, Germany and Switzerland.

Dr. Krishnan has published numerous valuable papers on the mineralogy, petrology and economic geology of many parts of India.

The Geological Survey of India has just completed one hundred years of its life, and it is most fitting that at the beginning of the second century, its activities should be guided by such an eminent geologist as Dr. Krishnan who combines wide administrative and organisational experience with intense love for original research. We wish him a very successful tenure of office.