THE RAMAN SPECTRUM OF DIAMOND

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1. *Introduction*

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

2. *Review of Previous Experimental Work*

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

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

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

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

3. *Experimental Technique*

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

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

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

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

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

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

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

4. *Results*

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

TABLE I

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

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

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

5. *Discussion of Results*

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

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

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

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

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

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

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

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

Summary

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

FIG. 1

FIG. 2

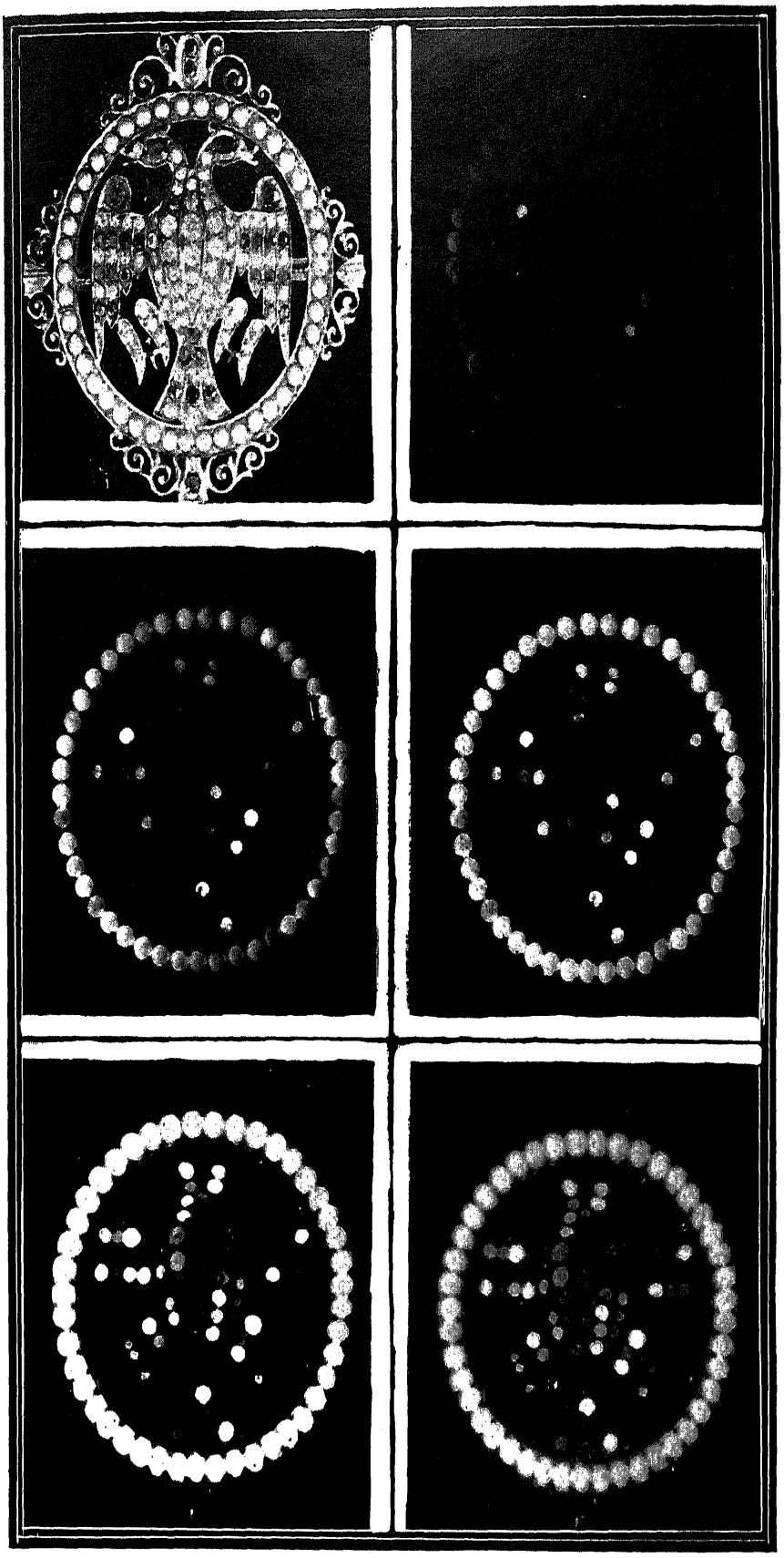


FIG. 3

FIG. 4

FIG. 5

FIG. 6

Luminescence of South African Diamonds

FIG. 1. Photograph in Daylight

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

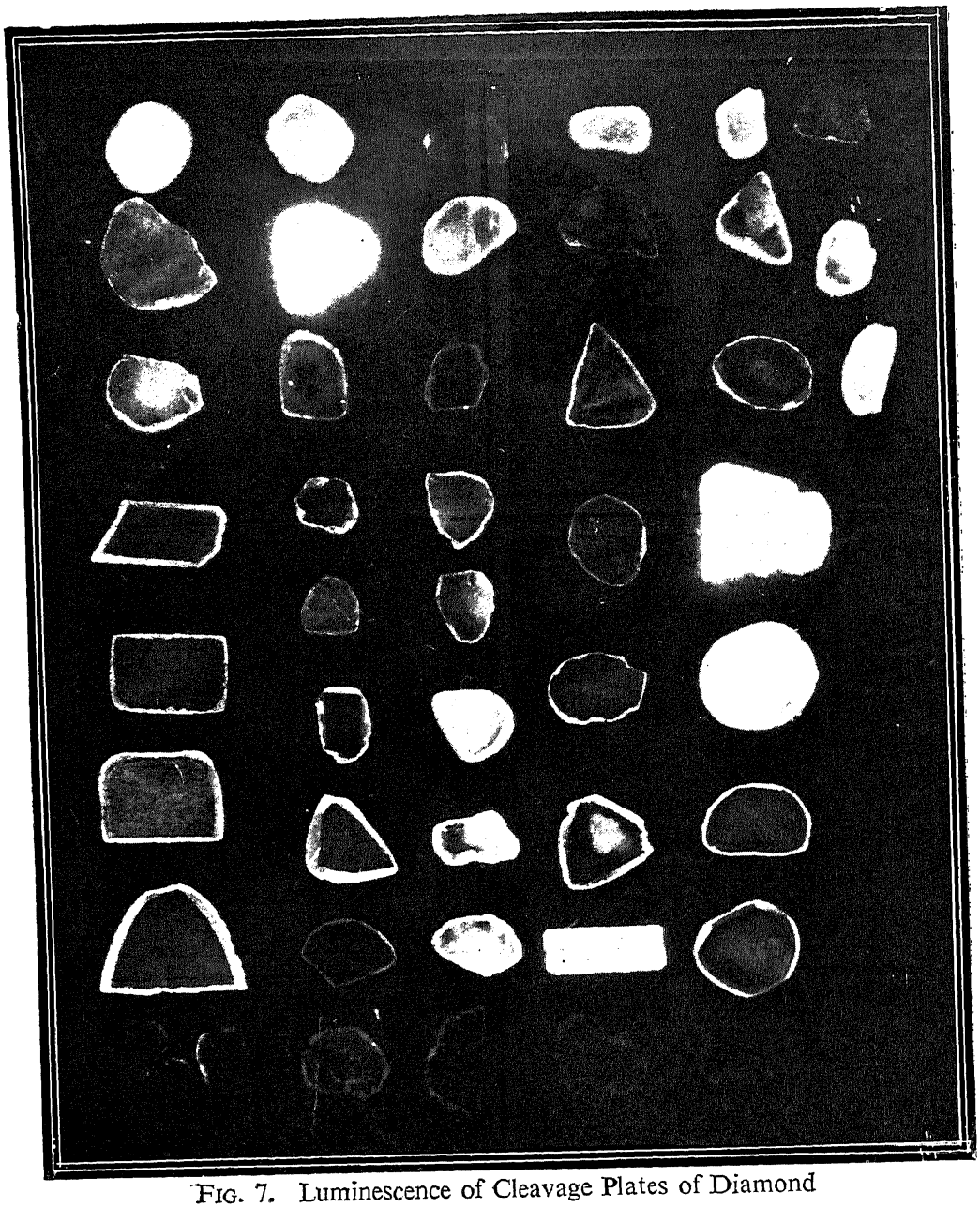


FIG. 7. Luminescence of Cleavage Plates of Diamond

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

Non-Luminescent

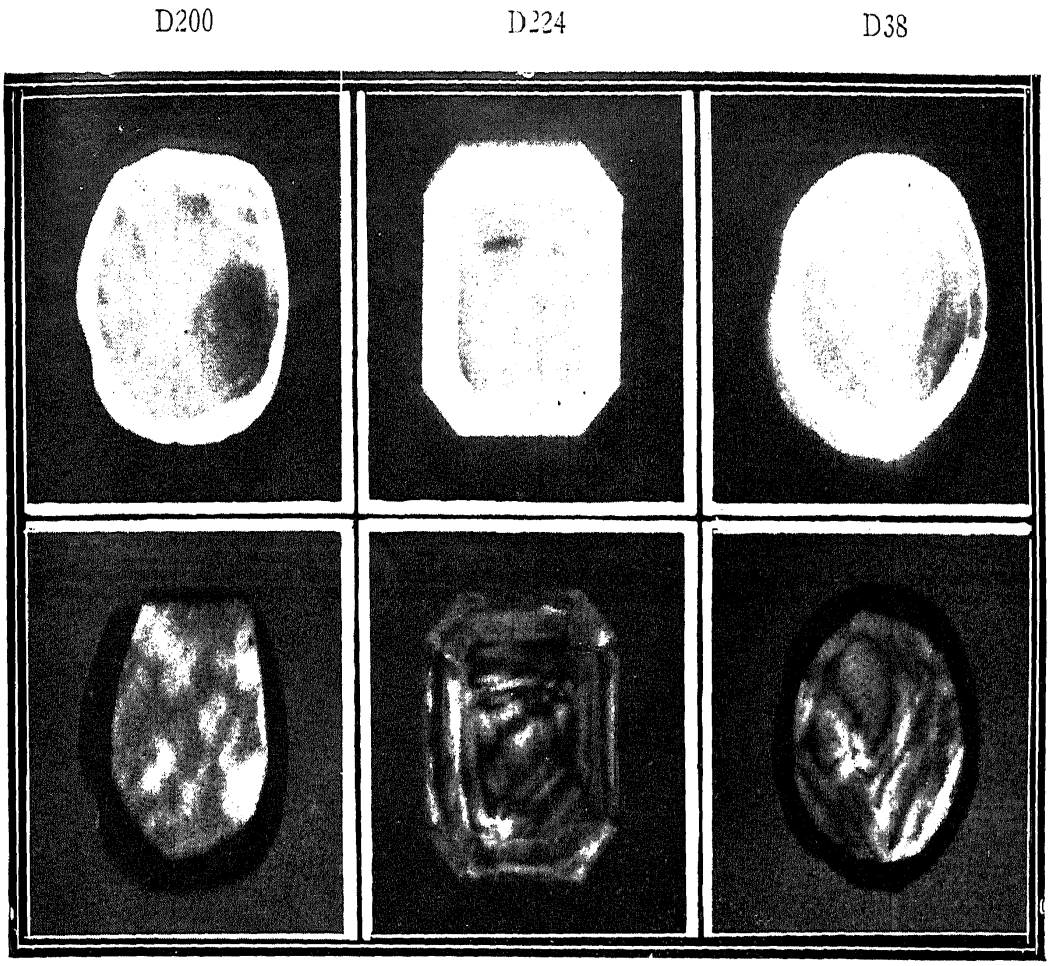


FIG. 8. Comparison of Luminescence and Birefringence Patterns

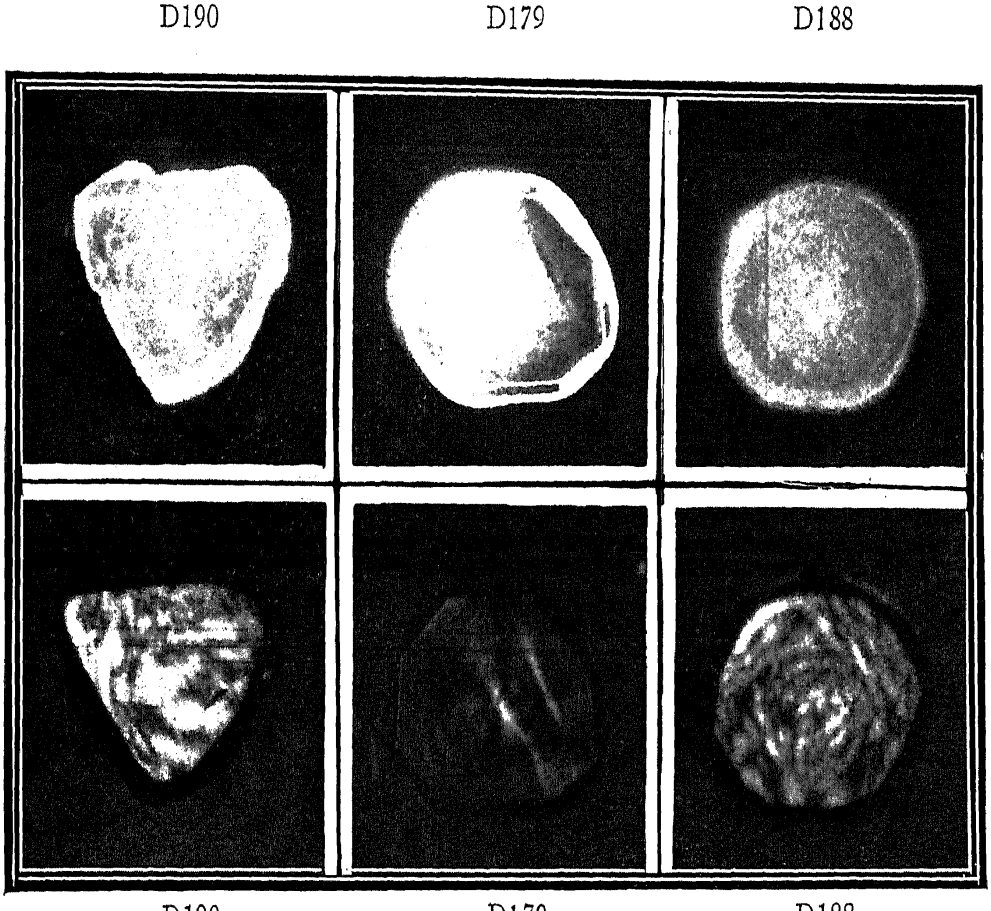


FIG. 9. Comparison of Luminescence and Birefringence Patterns

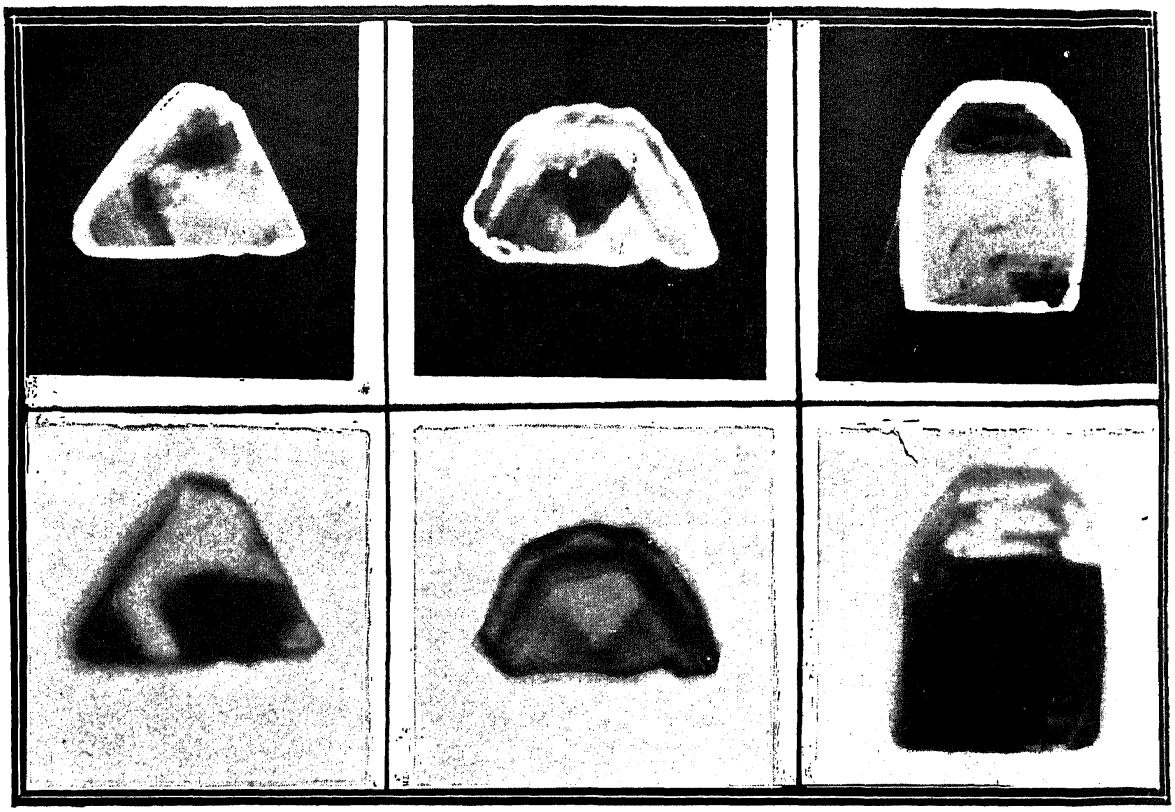


FIG. 10. Comparison of Luminescence and Ultra-Violet Transparency Patterns

FIG. 11
50 K.V. 10 minutes

FIG. 12
56 K.V. 30 minutes

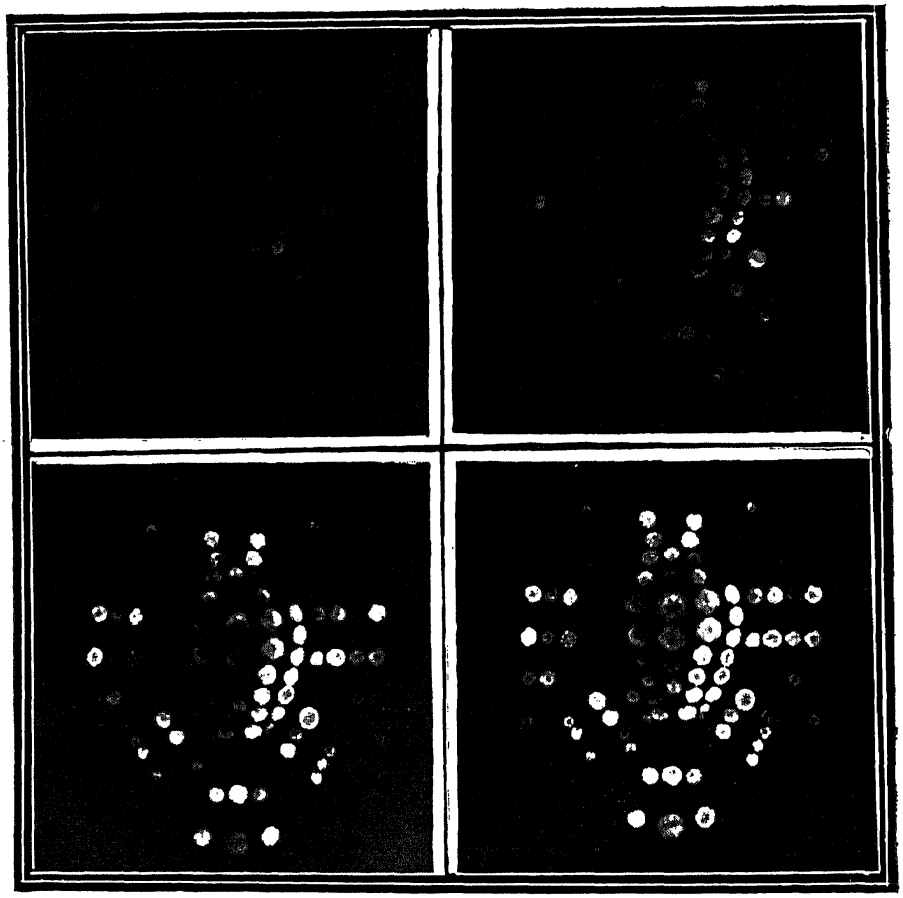
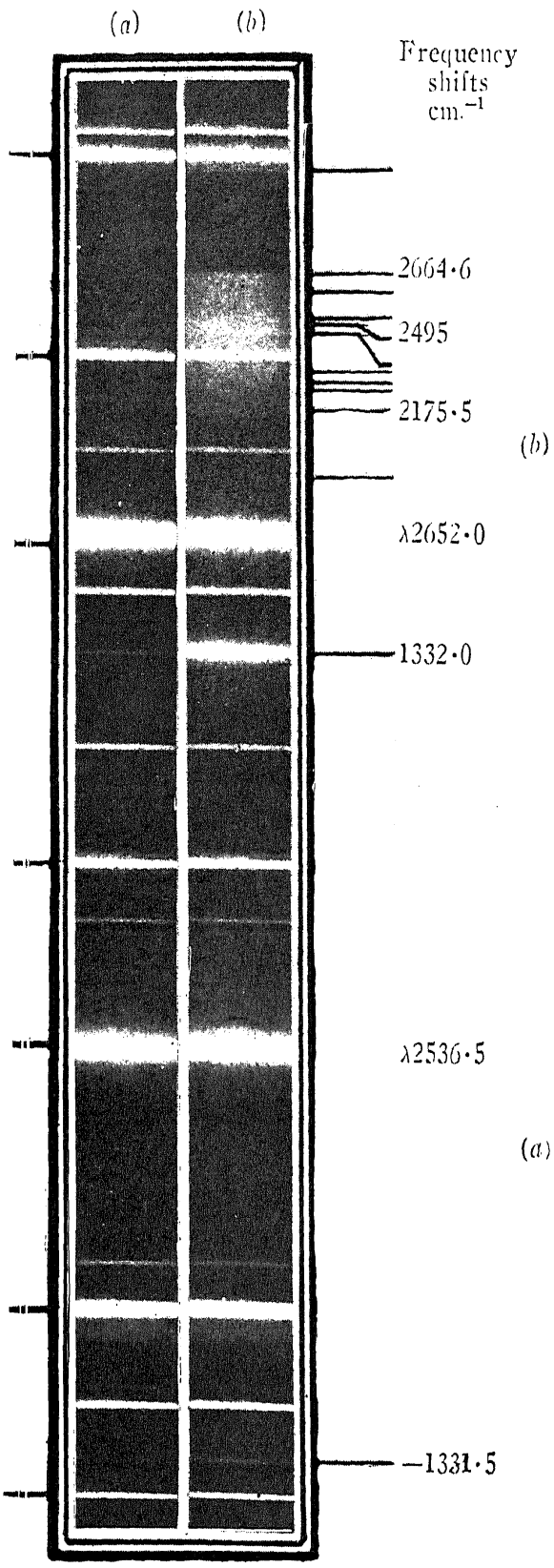


FIG. 13
70 K.V. 30 minutes

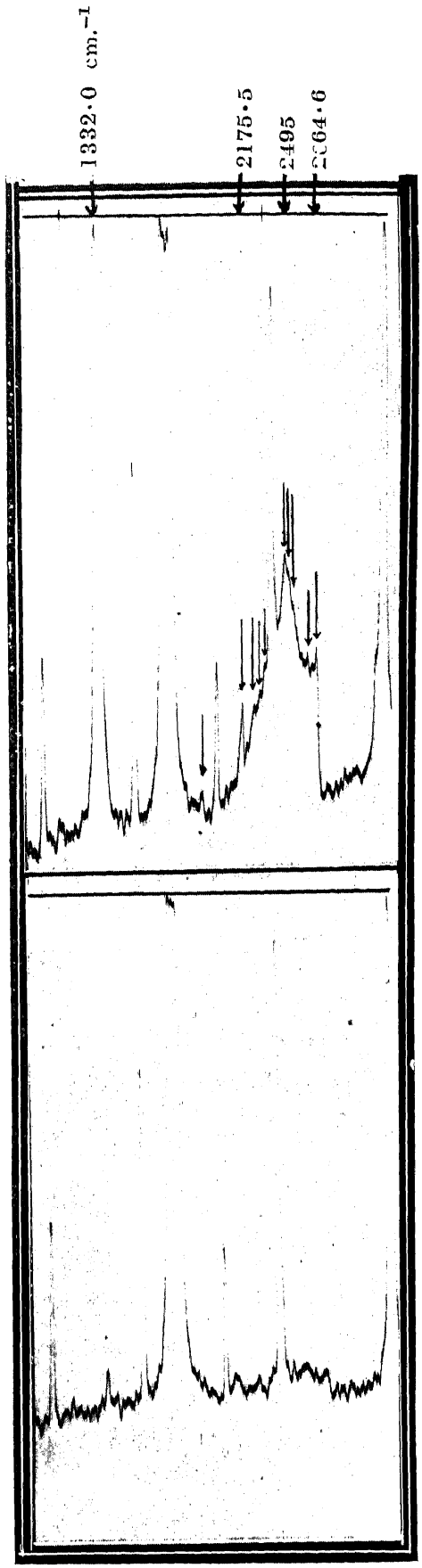
FIG. 14
70 K.V. 60 minutes

Luminescence of Diamonds under X-Rays with Increasing Exposures



(a) Mercury Spectrum
(b) Raman Spectrum

FIG. 1



Microphotometric Record

(a) Mercury Spectrum
(b) Raman Spectrum

FIG. 2

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