THE PHOTO-CONDUCTIVITY OF DIAMOND

Part I. Experimental Results

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1. *Introduction*

AMONGST the many remarkable properties of diamond is that when illuminated by visible or ultra-violet radiation, it has a detectable electrical conductivity, while ordinarily it is an excellent insulator. This property of diamond which it shares with certain other highly refractive solids was discovered by Gudden and Pohl (1920) and was the subject of extended researches by them designed to elucidate the nature of the phenomenon. Under controlled conditions of illumination and applied voltages, Gudden and Pohl observed what they describe as the primary photo-electric current, which under appropriate conditions satisfied the quantum equivalence law, namely the release of one electron per absorbed quantum of radiation. With stronger or more prolonged illumination and larger applied voltages, what is known as a secondary current is produced. The action of red light in producing an extra current in previously illuminated diamond is another remarkable phenomenon studied by Gudden and Pohl.

Even in these earliest researches, it was clear that not all diamonds behaved alike. Gudden and Pohl found that the photo-conductivity was much more conspicuous with one specimen which was transparent to ultra-violet radiation upto λ 2300 A.U. than with two others which were opaque to wavelengths smaller than λ 3000 A.U. The spectral distribution of photo-conductivity was also different. In the former case the curve had a pronounced tail, the photo-current continuously rising with shorter wavelengths, while in the latter there was a maximum at approximately λ 3400 A.U. and a minimum at λ 3000 A.U. followed again by a rise in the photo-current for still smaller wavelengths. In their later work, Gudden and Pohl (1922) found a marked selective effect for incident light at λ 2260 A.U. Generally similar results have been observed by other workers, notably Robertson, Fox and Martin (1934). These authors found that the differences in ultra-violet transparency and photo-conductivity were accompanied by differences in the infra-red absorption spectrum, and they therefore suggested a formal recognition of the existence of two distinct types of diamond. But that such a classification is inadequate to explain the facts is evident even from their own observations. The spectral distribution curves of photo-conductivity reproduced in Fig. 13 on page 505 of their memoir for four ultra-violet transparent diamonds differ widely amongst themselves, indeed nearly as much as any one of them differs from the spectral distribution curves for the two ultra-violet opaque diamonds given in Fig. 12 on page 503 of the same paper. Both in respect of the actual magnitude of the photo-current and the shape of the spectral distribution curve, their six diamonds, D_{24}, D_{16}, D_{22}, D_2, D_1 and D_{10} evidently form a continuous sequence. The suggested classification of diamonds into two distinct types is therefore incapable of describing the facts in respect of photoconductivity in a satisfactory manner.

It is evident from what has been said that we cannot hope to understand the true nature and origin of photoconductivity in diamond unless we start with correct ideas regarding the crystal structure of the substance and its possible variations in different specimens. The introductory paper by Sir C. V. Raman of the present symposium (1944) deals with just these questions, and the results of that paper afford a fresh starting point for a consideration of the phenomena of photoconductivity and enable us to present an intelligible picture of the facts. In Part I of this paper, some observations by the author will be described which exhibit the wide range of variation of the phenomena amongst different specimens of diamond. The theoretical interpretation of the results will be considered in Part II.

2. *Experimental Arrangements*

The apparatus employed was a D.C. valve-bridge amplifier, the detailed working of which, with a circuit diagram, was described by Ananthakrishnan (1934). However, in the present case, the photo-electric cell of the set-up was replaced by a diamond holder. The latter was made of two brass rods which passed through two small ebonite pillars fixed on an ebonite base. The tips of the brass rods were made of lead which for its softness and stability was found to be more suitable than any other metal or graphite. The diamond could be tightly screwed between the two electrodes and good contact could be secured. The source of light was a quartz mercury arc of moderate intensity; the light from it was focussed on the diamond with a quartz lens. When required, the diamond could be illuminated simultaneously with red light from the opposite side, *viz.*, the white light from a 500-watt tungsten lamp filtered through a red glass. The high tension source was a set of dry batteries giving up to 250 volts. The same high tension set was used for the plate voltage of the amplifier as well as for applying a voltage to the diamond. The linearity of amplification was tested by measuring the photoconductivity of a specimen of diamond at different voltages (small compared to the saturation potential of the photo-current in diamond). The strict proportionality found between the applied voltage and the corresponding observed current showed the correct working of the amplifier.

It was found necessary, at least in some cases, that the diamond should be heated to a temperature of nearly 100° C. to remove any dark current due to moisture or previous excitation of the crystal. Since the applied voltage was small and the intensity of the mercury arc not very great, troubles due to secondary currents were mostly absent. An ordinary needle-galvanometer, therefore, served the purpose of measuring the photo-currents. However, a few diamonds which showed secondary effects on being illuminated for too long a time were examined by applying a smaller voltage to them. In each case, therefore, only the primary photo-electric current was measured.

The photo-conductivity of numerous diamonds from the personal collection of Sir C. V. Raman was measured, as far as possible under identical conditions. The crystals were either sandwiched between the electrodes so that the light entered through the edges of the plate (position A), or they were screwed tightly between them such that one of the broad faces alone could be illuminated (position B). Most of the diamonds studied were cleavage plates having a thickness of between half a millimetre and one millimetre, their linear dimensions varying between a few millimetres and one centimetre. Owing to the varying thickness and area of the plates, any comparison of the photo-currents obtained with them is necessarily only qualitative. Nevertheless, the variation in the magnitudes of the primary photo-currents observed in position A with different diamonds was so marked, that it could easily be recognised as due to an inherent property of the diamond and not to its varying dimensions. This becomes clearer on correlating the variations in photo-conductivity with the variations in other properties of the diamond.

3. *Photo-Currents under Ultra-Violet Irradiation*

Tables I, II and III give the values of the photo-currents of 36 diamonds arranged in the decreasing order of magnitude of the photo-currents observed in the position A. For all these measurements, the illumination was the total light of the quartz mercury arc and the applied voltage was

150 volts. The 36 diamonds have been grouped in three tables according to the magnitude of the photo-currents given by them in the position A. Table I refers to five diamonds giving high photo-currents of the order of 10^{-8} ampere; Table II to eleven diamonds which give moderate photo-currents of the order of 10^{-9} ampere and Table III to twenty diamonds giving small photo-currents of the order of 10^{-10} ampere. It will be noticed that the diamonds listed in the first two tables show higher photo-conductivity in the position A than in the position B, while under similar conditions, the diamonds appearing in the third table usually show slightly higher photo-conductivity in the position B than in position A.

Table I

Five diamonds exhibiting large photo-currents

Unit = 10^{-8} ampere

Diamond No.	Distance between electrodes in millimetres		Photo-current in the unit stated	
	Position A	Position B	Position A	Position B
208	0·62	3·4	7·0	1·0
227	2·10	3·1	3·0	1·5
39	1·12	4·9	2·5	0·5
57	0·75	..	[illegible]·0	..
206	0·63	3·9	[illegible]·0	0·5

Table II

Eleven diamonds exhibiting moderate photo-currents

Unit = 10^{-9} ampere

Diamond No.	Distance between electrodes in millimetres		Photo-current in the unit stated	
	Position A	Position B	Position A	Position B
201	0·53	3·5	5·2	0·9
207	0·94	3·8	5·0	2·0
48	0·82	5·4	5·0	0·8
209	0·71	4·3	4·0	1·8
200	0·74	4·7	4·8	0·6
47	2·50	2·5	1·8	1·8
199	0·68	3·6	1·6	1·3
202	0·72	2·7	1·5	1·8
198	0·59	4·2	1·4	1·0
195	0·60	5·9	1·4	0·7
49	2·40	2·4	1·1	1·1

TABLE III

Twenty diamonds exhibiting small photo-currents

Unit = 10^{-10} ampere

Diamond No.	Distance between electrodes in millimetres		Photo-current in the unit stated	
	Position A	Position B	Position A	Position B
31	0·96	4·2	9·6	8·8
36	0·76	5·8	8·7	12·0
210	0·64	4·7	8·0	0·8
180	0·48	5·5	7·6	3·2
45	0·68	4·7	7·6	9·6
197	0·88	3·1	5·6	8·8
53	0·78	4·0	5·2	2·5
196	0·62	2·6	4·8	2·4
188	0·71	4·7	4·8	2·4
221	0·68	5·1	4·0	11·0
211	0·55	4·3	4·0	4·0
187	0·52	5·4	4·0	4·4
171	0·67	3·5	4·0	1·2
224	1·52	7·4	4·0	2·8
41	1·10	4·7	3·6	1·8
34	1·20	7·2	3·2	1·8
40	2·70	..	3·2	..
181	0·60	4·6	2·0	4·0
184	0·81	3·1	2·8	0·8
38	0·85	7·0	1·6	4·0

4. *Photo-Conductivity in the Visible Spectrum*

Table IV gives the spectral sensitivity data of a few selected diamonds showing high or moderate photoconductivity for wavelengths lying in the visible region. The source of light was a 500-watt pointolite lamp and the various regions of the visible spectrum were isolated by means of suitable light filters. The observations were made only in the position A.

TABLE IV

Five diamonds with large or moderate photo-conductivity

Diamond No.	Applied voltage	Photo-current in amperes					
		White light	Red	Yellow	Yellow-green	Blue	Blue-violet
	Volts						
57	120	$4{\cdot}0\times10^{-8}$	$2{\cdot}7\times19^{-9}$	$1{\cdot}5\times10^{-9}$	$9{\cdot}0\times10^{-9}$	$1{\cdot}2\times10^{-8}$	$1{\cdot}0\times10^{-9}$
39	120	$7{\cdot}6\times10^{-9}$	$2{\cdot}0\times10^{-10}$	$1{\cdot}4\times10^{-10}$	$1{\cdot}5\times10^{-9}$	$1{\cdot}0\times10^{-9}$	$6{\cdot}0\times10^{-10}$
206	220	$4{\cdot}2\times10^{-9}$	$8{\cdot}0\times10^{-11}$	$4{\cdot}0\times10^{-11}$	$3{\cdot}2\times10^{-10}$	$7{\cdot}6\times10^{-10}$	$4{\cdot}4\times10^{-10}$
48	220	$1{\cdot}6\times10^{-9}$	..	..	$1{\cdot}2\times10^{-10}$	$2{\cdot}8\times10^{-10}$	$1{\cdot}6\times10^{-10}$
56	220	$8{\cdot}4\times10^{-10}$	..	..	$1{\cdot}6\times10^{-10}$	$8{\cdot}0\times10^{-11}$	$6{\cdot}0\times10^{-11}$

Table V gives the data for four weakly photo-conducting diamonds. The readings were taken both for the positions A and B, the source of light being the 500-watt pointolite lamp without any filters.

TABLE V

Four diamonds with small photoconductivity

Diamond No.	Applied voltage	Photo-current in amperes	
		Position A	Position B
	Volts		
36	150	$4{\cdot}4\times10^{-10}$	$1{\cdot}2\times10^{-10}$
31	150	$4{\cdot}0\times10^{-10}$	$1{\cdot}2\times10^{-10}$
224	150	$3{\cdot}2\times10^{-10}$	$4{\cdot}0\times10^{-10}$
221	150	$1{\cdot}6\times10^{-10}$	..

It will be noticed that with these diamonds, white light gives a higher photo-current in the position A.

5. *The Effect of Red Light*

Ordinarily, no photo-conductivity is produced even with strong illumination by red or infra-red light. A very interesting phenomenon, however, arises when the diamond is illuminated simultaneously by strong red or infra-red light and by light of a shorter wave-length which excites photo-conductivity. It is then noticed that the photo-current given by the shorter wave-length light is greatly enhanced by the presence of the red light, increasing under suitable conditions to double its original value. The extra current produced by red light in the manner stated above is known as the positive primary, ersatz or substitution current. This effect was demonstrated by Gudden and Pohl as early as 1924 and it is of interest to study its variation in different diamonds. Table VI gives the data for the red light effect with some eighteen diamonds. It will be seen that it is conspicuously shown by the strongly and moderately photo-conducting diamonds, but is scarcely noticeable or altogether absent in the weakly photoconducting ones.

6. *Secondary Current Phenomena*

The primary photo-electric current which is observed when the crystal is illuminated for a short time starts or falls down to zero instantaneously with the imposition or cutting off of the irradiating light. But if the crystal is illuminated for too long a time, the current begins to increase and finally reaches a steady maximum value which is often several times the initial value

TABLE VI

Effect of red light

Diamond No.	Photo-current in amperes			
	Hg. Arc	Hg. Arc + Red light	Red light alone	Extra current due to red light
208	$7{\cdot}0\times10^{-8}$	$10{\cdot}0\times10^{-8}$	$2{\cdot}4\times10^{-10}$	$3{\cdot}0\times10^{-8}$
39	$2{\cdot}5\times10^{-8}$	$4{\cdot}2\times10^{-8}$	$2{\cdot}0\times10^{-10}$	$1{\cdot}7\times10^{-8}$
206	$2{\cdot}0\times10^{-8}$	$2{\cdot}8\times10^{-8}$	$8{\cdot}0\times10^{-11}$	$8{\cdot}0\times10^{-9}$
207	$5{\cdot}0\times10^{-9}$	$7{\cdot}4\times10^{-9}$	nil	$2{\cdot}4\times10^{-9}$
201	$5{\cdot}2\times10^{-9}$	$7{\cdot}8\times10^{-9}$	nil	$2{\cdot}6\times10^{-9}$
200	$4{\cdot}8\times10^{-9}$	$6{\cdot}8\times10^{-9}$	nil	$2{\cdot}0\times10^{-9}$
209	$4{\cdot}0\times10^{-9}$	$4{\cdot}4\times10^{-9}$	nil	$4{\cdot}0\times10^{-10}$
199	$1{\cdot}6\times10^{-9}$	$2{\cdot}0\times10^{-9}$	nil	$4{\cdot}0\times10^{-10}$
195	$1{\cdot}4\times10^{-9}$	$2{\cdot}2\times10^{-9}$	nil	$8{\cdot}0\times10^{-10}$
198	$1{\cdot}4\times10^{-9}$	$1{\cdot}9\times10^{-9}$	nil	$5{\cdot}0\times10^{-10}$
210	$8{\cdot}0\times10^{-10}$	$9{\cdot}6\times10^{-10}$	nil	$1{\cdot}6\times10^{-10}$
180	$7{\cdot}6\times10^{-10}$	$8{\cdot}0\times10^{-10}$	nil	$4{\cdot}0\times10^{-11}$
36	$8{\cdot}7\times10^{-10}$	$8{\cdot}7\times10^{-10}$	nil	nil
221	$4{\cdot}0\times10^{-10}$	$4{\cdot}0\times10^{-10}$	nil	nil
31	$9{\cdot}6\times10^{-10}$	$9{\cdot}6\times10^{-10}$	nil	nil
45	$7{\cdot}6\times10^{-10}$	$7{\cdot}6\times10^{-10}$	nil	nil
224	$4{\cdot}0\times10^{-10}$	$4{\cdot}0\times10^{-10}$	nil	nil
184	$2{\cdot}8\times10^{-10}$	$2{\cdot}8\times10^{-10}$	nil	nil

of the primary photo-electric current. If the light is now cut off, this increased current, unlike the primary photo-electric current, does not fall down instantaneously but decays with a considerable time-lag. This current which starts as well as decays with a time-lag is known as the secondary current. High applied voltages and strong intensity of light help the production of the secondary current.

In the present case although high voltages were not applied, yet on continued illumination for a long time some diamonds did show secondary currents, the magnitudes of which were in some cases 3 to 5 times the initial or primary photo-electric current. On sufficiently lowering the applied voltage, no diamond showed the secondary current. The diamonds which gave the secondary currents are those listed in Table I and a few others, namely D202, D199, and D195, appearing in Table II. None of the diamonds appearing in Table III gives any secondary current. It should also be remarked that secondary currents developed much more promptly in the position A than in B. In fact D202, D199, D195 did not show any secondary currents in the position B.

As mentioned above, the secondary current persisted even after the illumination was cut off and as a result of this a " dark current " in other words, a current without illumination was observed. A diamond in this state when exposed to light of a longer wave-length gave a current which was much larger than that obtained when this radiation was imposed on the normal diamond. With red light, this increased current showed a close relationship with the dark current and decayed in a manner similar to the latter, finally coming to a constant value which was still higher than that produced by red light in the normal diamond (Fig. 1, curves I and II). A somewhat similar effect has been described by Robertson, Fox and Martin (*loc. cit.*)

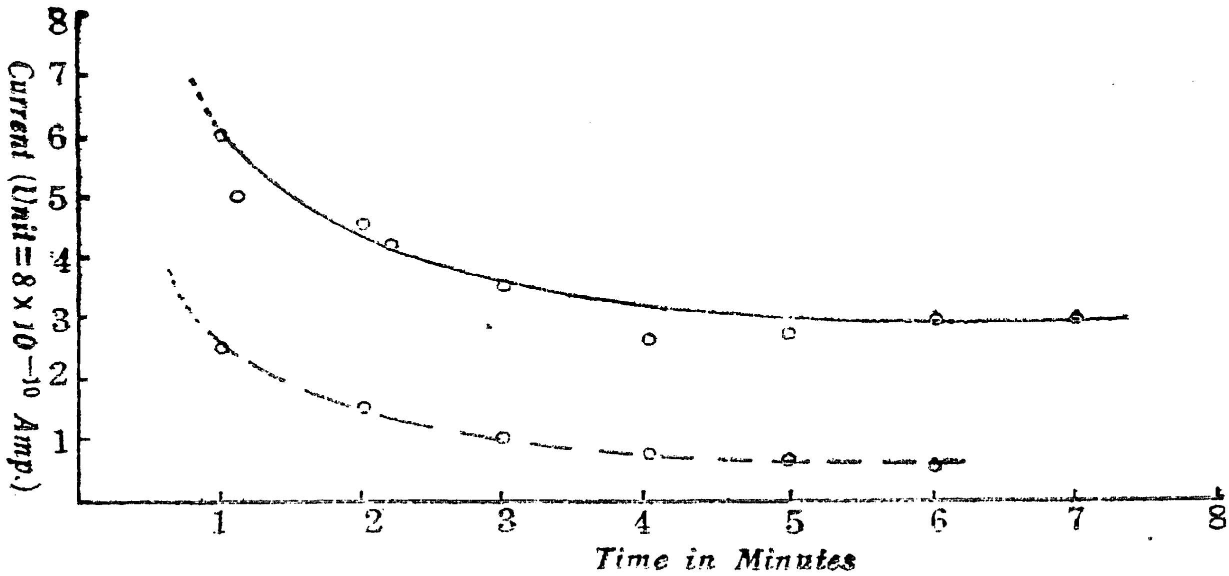

FIG. 1. Relation between I_r and I_d

- - - - - Curve showing the decay of I_d with time

——— Curve showing the decay of I_r with time

7. *Relation to Other Optical Properties*

The remarkable variations in photo-conductivity described above admit of being correlated with other properties of the specimens, namely (*a*) their transparency to the radiations exciting photoconductivity, (*b*) their absorption spectra, and (*c*) their luminescence. These latter properties have been studied extensively and are being reported on in other papers appearing in the symposium (Sunanda Bai, 1944; Rendall, 1944; Mani, 1944). It has accordingly been easy to establish the relationships between them and photoconductivity.

The division of the 36 diamonds into three groups (Tables I, II and III) according to the magnitude of the photo-currents developed under ultra-violet irradiation, also practically represents their classification according to their degree of transparency to the 2537 radiation of the quartz mercury arc. The diamonds appearing in Table I are transparent to those radiations, those in Table II are partially transparent in greater or less degree, while those in Table III are practically opaque to those radiations. The absorption spectra of the diamonds appearing in the three Tables also differ widely. The diamonds in Table I have a transmission extending up to λ 2250 A.U. in the ultra-violet and even beyond. Nearly all the diamonds in Table II show a similar transmission, but this is much weaker and there are several absorption bands in the region of wave-lengths greater than λ 2250. The diamonds in Table III show strong absorption bands in the region between λ 3000 and λ 2800 A.U. and a practically complete extinction at shorter wavelengths. The diamonds in Table III may also be subdivided into two classes, those nearer the top of the table which are more or less completely transparent in the visible spectrum, and those nearer the bottom which show strong absorption bands in that region. A classification is also possible on the basis of the luminescence properties. The five diamonds listed in Table I are non-luminescent. Of the eleven diamonds in Table II D207 is non-luminescent, while the luminescence of all the others is very weak with the exception of the three yellow diamonds D200, D201 and D202. The twenty diamonds appearing in Table III are moderately or strongly luminescent. Those nearer the top of the table have relatively small intensities, while those near the bottom, especially D187, D224, D41, D34, D40 and D38 exhibit very intense luminescence. There is, thus, a clear inverse correlation between photoconductivity and luminescence in the diamonds studied.

In conclusion, the author wishes to express his indebtedness to Prof. Sir C. V. Raman for suggesting the problem and for guidance during the course of the work.

8. *Summary*

The photo-conductivity of 36 diamonds, mostly in the form of polished cleavage plates, has been studied. They may be roughly classified into three groups showing respectively high, moderate or weak photo-conductivity. But there is no sharply defined demarkation between these groups and it is therefore not possible to make a clear-cut division of diamonds into two distinct types on the basis of their photoconductivity as proposed by Robertson, Fox and Martin.

The diamonds which are highly photo-conducting under ultra-violet irradiation are also those which give high photo-conductivity with visible light. They also exhibit the well-known red light effect and give rise on continued illumination to a secondary current which persists when such

illumination is cut off. A diamond in this state gives a larger current when illuminated by red light, and the magnitude of this is quantitatively related to that part of the secondary current which persists even without illumination. The weakly photo-conducting diamonds do not give these effects. The correlations which exist between photo-conductivity, ultra-violet transparency, spectral transmission curves and the intensity of luminescence of the diamond are pointed out.

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