

THE PHOTO-CONDUCTIVITY OF DIAMOND

Part II. Theoretical Considerations

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1. *The Structure of Diamond*

ACCORDING to the theory put forward by Sir C. V. Raman (1944), the crystal structure of diamond has four possible variants; two of these, namely, Td I and Td II, have tetrahedral symmetry and the remaining two, namely, Oh I and Oh II, have the full or octahedral symmetry of the cubic system. The structure of any actual specimen of diamond is, in general, composite and includes more than one of the possible variants. Thus, in the non-fluorescent and ultra-violet transparent variety of diamonds, the Oh I and Oh II sub-types interpenetrate giving rise to lamellar twinning; the two sub-types are separated in the crystal by extended surfaces of discontinuity or laminations and the diamond is highly non-homogeneous. In the blue-fluorescent and ultra-violet opaque variety of diamond, the Td I and Td II sub-types are present, interpenetrating each other. As these two sub-types are not physically but only geometrically different, such interpenetration is irregular and occurs without any composition planes. Hence, diamonds of this class have a much higher degree of crystal perfection than those in which the Oh I and Oh II are mingled. Nevertheless, the interpenetration of the Td I and Td II does give rise to a non-homogeneity of the crystal which shows itself in the development of luminescence in diamonds of this class. The irregularities of crystal structure are of an entirely different type from those observed in the non-fluorescent diamonds, being in the present case closely connected with the intensity of the luminescence exhibited. The theory indicates further the possibility of the mixing up of the tetrahedral and octahedral types of structure in various ways. When there is an intimate mixing of tetrahedral and octahedral structures, the diamond gives a yellow luminescence and is of an intermediate type; the diamond in parts may exclusively be of the transparent type and in others it may be of the other variety; finally, in some cases a small quantity of a particular variety may be embedded in the bulk of the other variety. On account of these different

possibilities, the properties of diamond vary greatly from specimen to specimen.

These conclusions find unmistakable support in the experimental results contained in the various papers appearing in the present symposium. However, from our point of view we wish to draw attention to the results regarding the imperfection or mosaicity of structure of diamond obtained from the X-ray studies made at this Institute by R. S. Krishnan (1944), P. S. Hariharan (1944) and G. N. Ramachandran (1944). These studies show clearly that the mosaicity of the ultra-violet transparent variety of diamond is of a very high degree and varies not only from diamond to diamond but also from place to place in the same specimen. On the other hand, the mosaicity of structure of the blue fluorescent diamonds is comparatively low and increases with the intensity of blue fluorescence. The yellow fluorescent diamonds in this respect also are intermediate between these types.

2. *The Photo-Electrically Active Centres*

In view of the extremely small magnitude of the primary photo-electric current and the absence of any definite threshold frequency for its generation, it is hard to believe that the normal atoms of the crystal form the photo-electrons. Gudden and Pohl expressed the opinion that only a few "privileged atoms" are responsible for photo-conductivity. These atoms, which are probably those situated at slight irregularities, form the photo-electrically active centres, while the normal atoms of the lattice remain photo-electrically inactive. If these conceptions are correct, the greater the mosaicity of structure, the greater should be the photo-conductivity of the diamond. The high photo-conductivity of the highly imperfect ultra-violet transparent variety of diamond and the low photo-conductivity of the more perfect ultra-violet opaque variety thus becomes intelligible. A slight anomaly is presented by the weakly photo-conducting, strongly blue-fluorescent diamonds, namely, that in such diamonds higher mosaicity gives lower photo-conductivity. But this is not surprising in view of the fact that the mosaic structure revealed by the intensity of X-ray reflections being closely connected with the intensity of luminescence, it produces the luminescent centres and not the photo-electrically active centres. That the two are quite distinct in the present case is obvious from the fact that while a photo-electrically active centre is ionised by the absorption of a suitable quantum and the liberated electron is raised to the conduction level, the luminescence centre absorbs a quantum of radiation only to raise its electron to an intermediate level below the conduction band (production of an exciton). The dependence of the intensity of the 4152 absorption band on the intensity of

blue-fluorescence is a proof of this statement. Incidentally, since the absorbed energy is radiated again as luminescence energy, it is obvious that high intensity of fluorescence will only diminish the photo-conductivity. A close relationship between photo-conductivity and luminescence should be expected only in those solids where the mechanism of luminescence is analogous to that operating in the Lenard phosphors, *viz.*, when by the absorption of light energy, the electron is completely separated from the parent centre and is trapped at a distance from it, the luminescence occurring when the trapped electron comes back to the ionised centre.

3. *The Spectral Distribution Curves of Photo-Conductivity*

An atom situated at a lattice defect will have one or more of its bonds ruptured due to the presence of the discontinuity, the electron or electrons of which the valence bonds are broken being attached to the atom only loosely. This atom, which for all practical purposes, may be taken as a combined electron-positive charge system, will be ionised by absorption of a lower energy quantum than is necessary for a normal atom of the lattice and will constitute a photo-electrically active centre. The energy of the quantum necessary to ionise the centre will depend on the strength of the binding of the electron to the positive charge. This in turn will depend on the degree of the rupture of the bond and the environment of the centre. The discontinuity will not equally affect all the atoms situated at it; some will have their electrons more loosely bound than the others and so on. The centres would, therefore, not have a definite threshold frequency, and a long-wave-length tail in the spectral sensitivity curve would be an invariable accompaniment, the magnitude and the length of the tail depending on the mosaicity of the diamond. At the characteristic edge however, where the normal atoms of the lattice get ionised, the coefficient of absorption is so high that the whole phenomenon is confined to an extremely thin layer of the crystal. A high rate of absorption, therefore, naturally leads to a high rate of recombination and the two are probably so adjusted that before a liberated electron can move appreciably under an applied field, it recombines with the positive charge. The photo-conductivity, therefore, vanishes in the characteristic absorption region (Gurney and Mott, 1940). The spectral distribution curve of the transparent variety of diamond which has a pronounced long-wave-length tail, the photo-current dropping down at λ 2250 A.U., is thus clearly understood. The selective excitation of photo-conductivity for λ 2300 A.U. merely shows that the absorption of light is photo-electrically active in the volume of the crystal.

Sometimes, the normal atoms of the lattice absorb energy even in the region far removed from the characteristic absorption region and here also the

absorption is photo-electrically inactive. An interesting fact is then observed, namely, that though the quantity of absorbed energy is large, the observed photo-conductivity becomes less. The spectral distribution curve for photo-conductivity of the opaque variety of diamond shows a continuous rise in photo-conductivity upto λ 3400 A.U. but for wave-lengths between 3400–3000 A.U., the photo-current falls down in magnitude, showing a minimum at λ 3000. In the absorption spectra (Nayar, 1942), several absorption bands are observed in this region, clearly indicating that most of the energy absorbed is photo-electrically inactive and is spent only in raising the atoms to some higher levels. Even more interesting than this is the photo-conductivity of this variety of diamond in the region between λ 3000–2250 A.U. Although the diamond is practically opaque to these wave-lengths, the photo-conductivity does not fall down to zero but rises, showing a broad maximum and falling down to zero only at λ 2250 A.U. But the curious fact is that although the energy absorbed by this variety of diamond is far greater than absorbed by the transparent variety, the observed photo-conductivity is far smaller in the former case. The absorption is not photo-electrically inactive, since a considerable rise in the photo-conductivity is observed for these wave-lengths. The answer to this anomaly lies in the peculiar absorption characteristic of these diamonds. It is most probable that the characteristic absorption edge for these diamonds is also at λ 2250 A.U. and that absorption of the type where simultaneous ionisation and recombination occur as described previously, takes place only at this edge. For other wave-lengths in the region between λ 2250 A.U. and λ 3000 A.U., the absorption coefficient may not be very high and the absorbed energy is then confined to a thin though not to an extremely thin layer of the diamond. The recombination between the positively charged ion and the electron produced by absorption of light does take place but only after the electron has moved a short distance (short compared to the mean free path). The photo-current will be smaller than expected on the quantum equivalence law, yet it will always be observed, the magnitude depending on the distance the electrons travel before recombination.

In the intermediate type of diamonds where the octahedral and the tetrahedral types of structures get mixed up, the spectral distribution curve of photo-conductivity also takes an intermediate shape depending upon the extent to which the diamond approaches more closely the opaque or the transparent variety. The diamonds D2 and D22, whose special sensitive curves are figured by Robertson, Fox and Martin (1934), appear to be of this intermediate type, D2 approaching rather closely to the opaque variety in its behaviour both in the magnitude of the photo-current given by it and in

the presence of a subsidiary maximum at λ 3400 A.U. in the spectral sensitivity curve, which is quite analogous to that shown by their ultra-violet opaque diamonds D1 and D10.

4. *The Secondary Current*

The quantity of electricity that flows in the secondary current is so large that it is impossible to interpret it as a simple photo-electric effect. It is generally believed that this current is generated in the crystal on account of the reduction in the resistance of the crystal brought about by the flow of the primary photo-electric current. In ionic crystals, Tubandt (1920-21), Joffe (1928) and Gudden and Pohl (1926) maintain that the secondary currents are due to the conductivity being ionic, but as Hughes and Du Bridge (1932) remark, an alternative explanation is necessary in the case of crystals like diamond.

We may expect that the same irregularities in the crystal structure which give rise to the production of the photo-electrically active centres also serve as good trapping centres for the liberated electrons. In crystals with repeated twinings, tablets of compressed powders and some glasses, which may be regarded as the collection of tiny crystals welded together, the primary photo-electric current is largely suppressed and only a high secondary current is observed, except when the intensity of light is low and the applied voltage is small. The facts that even when the primary photo-electric current is large, time is required for the development of the secondary current, and that flaws and irregularities of structure help its production show that the trapping of electrons along the surfaces of discontinuity is responsible for the secondary current. If the discontinuity is such that it extends from one end of the crystal to the other even along irregular paths, in due course of time, due to the trapping of the electrons, a sort of "conducting channel" will be formed from one electrode to the other. The trapped electrons can deliver the charge from one place to the next close by, even if they are not free in the same sense as in the metallic conductors. All the trapped electrons are not equally free to move in the channel; those trapped in the vacant lattice points or at other obstacles are held more firmly than those which are in the middle of the channel. The electrons are attracted to the anode and at the same time they enter the crystal from the cathode, delivering charge from one place to the other in the manner stated above. The net result is a flow of electrons belonging to the metallic electrodes. Also, it is easy to see that due to the surplus of the electrons, all the positive ions left in the crystal would be neutralised in due course of time. Further, it is also clear that time would always be required for establishing and destroying

the "conducting channels" in the crystal and that the secondary current would always develop or decay with a time lag. It would develop more promptly if the primary photo-electric current be large and also if the thickness of the crystal between the electrodes be small. In the latter case, many more channels bridging over the electrodes can be formed, and it is due to these reasons that the secondary current is produced more easily in the diamond in the position A. It will also be seen that when all the conducting channels are established, the secondary current would reach a steady maximum value.

The absence of the secondary current in the opaque variety of diamond is due to the absence of the extended surfaces of discontinuity and the small magnitude of the primary photo-electric current.

5. Relation between I_r and I_d

It is well known that when electrical charges are left behind in the crystal (the activated crystal), the absorption curve broadens towards the longer wave-lengths (Gudden and Pohl, 1925) and consequently the photo-electric effect for longer wave-lengths increases. From the picture given already for the production of the secondary current, it can be visualised that the trapped electrons will produce a similar effect on the atoms situated in the neighbourhood. This happens because the active centre which is more of a combined electron-positive charge system than an actual atom, is further influenced by the presence of the charge in its vicinity. If the trapped charge is an electron, it will attract the positive charge and repel the electron of the centre, producing a further instability in the centre. Again, if the trapped electron comes quite close to an active centre, the instability produced in the latter may be so great that it can now lose its electron even by the absorption of a quantum of red light. Any other active centre which is not close to the electron or which itself is not much affected by the discontinuity would not so much be influenced; only by absorption of a higher energy quantum than that of red light could such a centre be deprived of its electron. In short, the photo-conductivity of the crystal for longer wave-lengths would increase and on illumination by a long-wave-length light say, red light, it would give an increased current I_r . Since this increase is due to the presence of the trapped electrons, I_r must have a close dependence on their number. Again, as the dark current I_d (*i.e.*, decaying secondary current) depends on the number of the conducting channels and the latter on the number of the trapped electrons, a linear relation $I_r = KI_d$ obviously follows. But not all the trapped electrons are capable of contributing to the dark current, for unless they are so arranged that a chain of them along the

channels from one end of the crystal to the other is created, their irregular distribution would not be of any help. But such electrons influence their neighbours as well as the electrons taking part in the production of the secondary current. Clearly, therefore, I_r is due to the sum of two currents, one produced by the presence of the electrons for the dark current and the other by the rest of the trapped electrons.

If, at any instant, N be the number of trapped electrons of which n_1 are responsible for the dark current and n_2 are irregularly distributed, we must have

$$I_d = xn, \text{ where } x \text{ is a constant.}$$

But $I_r = K'y(n_1 + n_2)$ where K' depends on the intensity of red light and y depends on the number of centres per trapped electron which will be ionised by absorption of red light. Therefore,

$$\begin{aligned} I_r &= K'y \left(\frac{I_d}{x} + n_2 \right) = K' \frac{y}{x} (I_d + n_2x) \\ &= K (I_d + n_2x) = K (I_d + a), \end{aligned}$$

where a depends on the degree of activation. It will be seen that this relation is the same as that obtained by Robertson, Fox and Martin (*loc. cit.*).

Now, when the trapped electrons are ejected out of the channels by an absorption of energy (or by thermal agitation) sufficiently large to overcome the potential barrier presented by the boundaries of the channel, the diamond would come back to its normal state. Not all but a great majority of these electrons would have the same potential barrier to overcome and, hence, although there would be no definite frequency necessary for bringing back the diamond to its original state, there would be an optimum frequency required for this purpose. Probably this corresponds to $\lambda 2800$ A.U. Red light being unable to eject the electrons from their trapped position would continue to excite a constant current.

6. The Effect of Red Light

This phenomenon has been explained by Gudden and Pohl by suggesting that the positive charges left behind in the crystal as a result of the removal of the electrons by the primary photo-electric current are released by the absorption of red light. A more specific theory of the effect of red light again has been put forward by Gudden and Pohl (1926) which suggests that due to the presence of the positive charges, a temporary photo-electric effect by longer wave-lengths becomes possible. Electrons are separated from the active centres until the accumulated charge builds up to a maximum value. At this stage, a sort of rearrangement (or local recrystallisation) takes place, whereby the location of the positive charges slips

towards the space element adjacent on the side next to the cathode. The commonly accepted view to-day is that not the positive charges but their locations slip towards the cathode (Hughes, 1936).

The principal effect of red light in producing the positive primary current should be the same as for the production of I_p , already discussed, the difference arising only due to the fact that the charges left behind in the crystals are positive charges, and not electrons. A particular space-element of the surface of discontinuity, after the separation of the primary photo-electric current, will have accumulated a large positive charge and will have formed what is called an excitation centre. Now, the total effect of the excitation centre will be so great on the neighbouring active centres that they can be ionised by the absorption of red light even if they are not quite close to it. The liberated electrons will travel to the anode under the external applied field and will be caught by the excitation centre, turning the latter into neutral centres. The location of the excitation centre will thus slip continuously towards the cathode by a repetition of this process (Fig. 1).

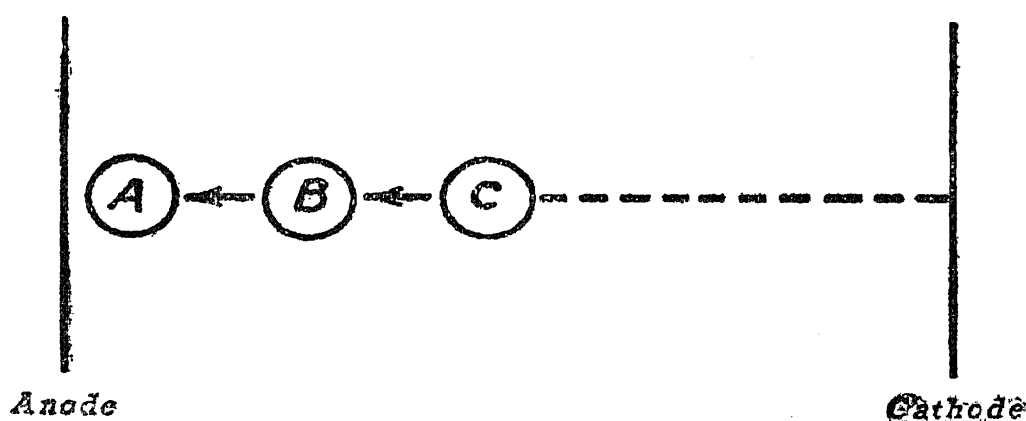


FIG. 1

It is easy to see that no electrons on the side towards the anode of the excitation centre can be released by red light after the excitation centre has begun to travel. For, as soon as the photo-electric effect in the centres (B) adjacent to the excitation centre (A) take place, A shifts to B. The liberated electrons have not time enough to reach the previous excitation centre A which still remains positively charged. The excitation centre at B, therefore, cannot release any positive charges from A and by continuation of the above process travels to C and so on.

It is easy to see now that as long as the active centres lie in the neighbourhood of the excitation centre so that by the presence of the latter a temporary photo-electric effect by red light is possible in them, the effect of red light will be observed. But as soon as this condition breaks down, the excitation centre can no longer slip towards the cathode, for the influence of

the positive charges on the normal atoms will be negligible. In the opaque variety of diamonds where there are only a very few centres and these are distributed in an irregular way, no positive primary current will be observed.

In conclusion, the author wishes to express his grateful thanks to Sir C. V. Raman, Kt., F.R.S., N.L., with whom he has had many useful discussions on the topics dealt with in this paper.

7. Summary

The variations in the photo-conductivity of diamond have been explained in this paper on the basis of the variations in the structure of the crystal, evidence for the existence of which is forthcoming from other directions, especially the study of the X-ray reflection intensities. Assuming that the non-homogeneities and irregularities in the crystal produce the photo-electrically active centres, the differences in the magnitudes of the photo-currents given by the different types of diamonds are explained. Various other observed facts regarding photo-conductivity also become intelligible, *viz.*, the spectral distribution curves of photo-conductivity, the absence of a definite threshold frequency, the effect of red light, and the production of a secondary current. The differences between the spectral distribution curves for the ultra-violet opaque and transparent types of diamond, and in particular the rising of the curve for wavelengths below 3000 A.U. are explained. A theoretical relation is also derived connecting the magnitude of the dark current and that of the current produced on excitation by red light.

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