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PHOTOGENERATION OF FREE CARRIERS IN ORGANIC CRYSTALS VIA EXCITON-EXCITON INTERACTIONS*

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Although it has been suggested before[1] that the interactions between two excitons may be responsible for the photogeneration of free carriers in organic crystals, it is only recently that a theoretical calculation of this process has been made by Choi and Rice.[2] These very beautiful calculations were motivated by the results reported by Northrop and Simpson.[1] These experiments, however, cannot be unambiguously interpreted as being due to this bimolecular process since the current increased only linearly with intensity under uv excitation. Indeed, the transient current measurements of Kepler[3] rule out the possibility of free exciton-free exciton interactions when the crystals are excited with strongly absorbed light. Thus, until now there is no experimental evidence in the literature to support such a suggestion.

In this note, we wish to present some results which for the first time not only support the exciton-exciton theory, but also yield a bimolecular rate constant in good agreement with that calculated by Choi and Rice.[2]

We observe a current which increases with the square of the light intensity and also increases with temperature in the superlinear region. Bube[4] observed superlinear currents in CdSe and CdS and has attributed this effect to the action of different recombination centers. Our results cannot be so interpreted in any obvious way, because of our observed temperature dependence.

We have investigated transient photocurrents in the direction perpendicular to the *ab* plane in anthracene. Crystals obtained from the Harshaw Company as well as ultrapure Kodak crystals were used. The hole lifetime in all samples was greater than 100 microseconds. The crystals were cleaved in air and etched and polished using benzene. Blocking, electrolytic and pressed metal evaporated Vycor electrodes were employed. (The pressed electrodes were used to make temperature-dependent measurements.) The results were essentially independent of the electrode material. We used a dc applied voltage and excitation by a high-intensity microsecond flash of weakly absorbed light; i.e., light of wavelengths longer than 4150 Å. Only the light between 4150 Å and 4550 Å is involved, because the signal obtained from wavelengths longer than 4550 Å was reduced tenfold from that obtained from wavelengths longer than 4150 Å, while the intensity was reduced by only 30%. The transient pulse obtained from weakly absorbed excitation is quite different from that obtained from strongly absorbed light. These results are shown in Fig. 1. It is clear from the shape of these transients that with strongly absorbed light, carriers are generated at or near the illuminated surface while with high-intensity weakly absorbed light, carriers are generated approximately uniformly throughout the bulk, as well as at the surface of the sample. The bulk generation is inferred from

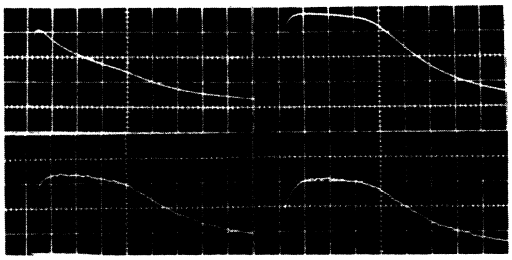

FIG. 1. Transient current pulses for high- and low-intensity, weakly and strongly absorbed light in a 1.45-mm anthracene crystal. 800 volts applied, 10 μsec/cm. Upper left: high-intensity weakly absorbed light, 5.6 μA/cm^2/cm; lower left: low-intensity weakly absorbed light, 0.24 μA/cm^2/cm; upper right: high-intensity strongly absorbed light, 5.6 μA/cm^2/cm; lower right: low-intensity strongly absorbed light, 0.24 μA/cm^2/cm. The uv intensities were adjusted to give the same size current pulses as those obtained from the weakly absorbed light.

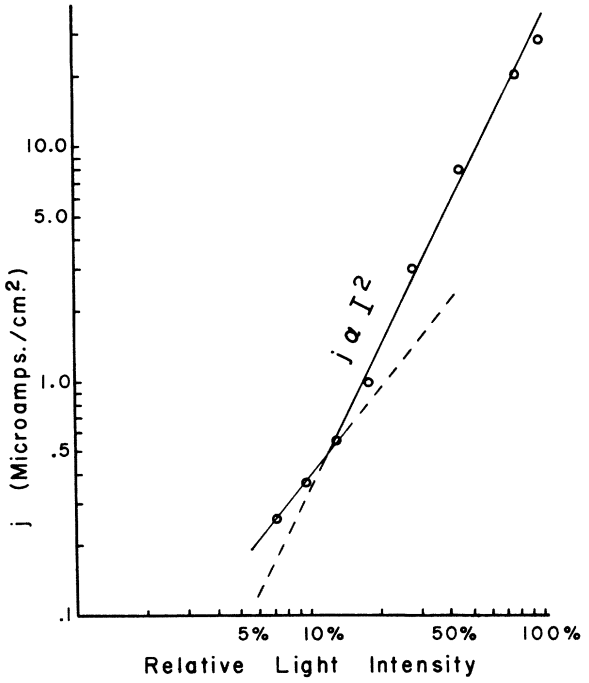

FIG. 2. Current density versus incident light intensity for weakly absorbed light for 1000 volts applied. 100% intensity represents a total of 10^{16} photons/pulse/cm^2.

the decaying nature of the pulse. This decay is not due to trapping, for if it were, the current pulses from low-intensity weakly absorbed light and uv excitation would also show such a sharp decay. Because the rate of decay of the current pulse increases with intensity of the weakly absorbed light, we also conclude that the bulk generation increases more rapidly with intensity than the surface generation.

The current obtained from the weakly absorbed light increases as the square of the intensity, at least in the high-intensity region. These results are shown in Fig. 2. With uv excitation and for currents less than the space-charge-limited value, we observe a linear dependence in agreement with Kepler.[3] At low intensity of weakly absorbed light, where the current approaches a linear dependence upon light intensity, the primary source of carriers is the surface, i.e., the pulse resembles the one obtained from uv excitation (see Fig. 1).

From our data on the currents in the square-law region, we can calculate a bimolecular rate constant. From the size of our current pulses, their initial decay, and the known mobilities of the carriers,[3] the calculated density of carriers at 100% light intensity is approximately 1.2×10^{10} carriers/cm^3. Our 100% intensity flash contains 10^{16} photons/cm^2 in the 4150Å-4550Å range. The light pulse can be approximated by $I_0\exp(-t/\tau)$, where $\tau\approx2$ μsec. Under these flash conditions, the total number of carriers per cm^3 generated is given by

$$n_c = \tfrac{1}{2}\alpha f_0^{\,2} t_f^{\,2}\tau, \qquad (1)$$

where $f_0 = I_0/x_0$, x_0 is the absorption depth of the light, t_f is the exciton lifetime, and α is the bimolecular rate constant. The absorption depth[5] is about 2 cm and t_f is 2×10^{-8} sec.[6] This yields a value of $\alpha\approx5\times10^{-12}$. If one considers the accuracy of our intensity measurements (which are good to an order of magnitude), the accuracy of the values of t_f and x_0, and the accuracy of Choi's and Rice's[7] calculation, our result is remarkably close to the 2.6×10^{-12} value they calculated.

One final remark should be made regarding the surface or near-surface generation of carriers. This must be an inherently linear process (or possibly a free exciton-metastable or trapped exciton interaction) rather than a free exciton-free exciton interaction plus recombination of free carriers. If recombination of free carriers were involved, then the quantum efficiency would be less at the surface than in the bulk. Consequently, with weakly absorbed light we would never see surface generation larger than bulk generation.

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EXCESS CURRENTS IN ELECTRON TUNNELING BETWEEN SUPERCONDUCTORS*

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In carrying out current-voltage (I-V) measurements on Al-Al, Sn-Sn, Pb-Pb, Sn-Pb, and Sn-Tl superconductor-metal oxide-superconductor tunnel junctions,[1] we have observed striking, polarity-independent deviations from the usual I-V curves associated with single particle tunneling (hereafter referred to as SPT).[2-5] These deviations are in the form of excess currents which we believe are due to additional tunneling mechanisms rather than to energy gap anisotropy or to density-of-states effects.[6] Three forms of excess currents were distinguishable at voltages $V < \Delta_a(T) + \Delta_b(T)$ [where V is the applied voltage times the electronic charge and $\Delta(T)$ is one half the energy gap of the superconductor at the operating temperature, T]: (1) an excess current characterized by a sharp temperature-independent jump at $V = \Delta(T)$ for identical superconductors (S-S), and $V = \Delta_a(T)$ and $V = \Delta_b(T)$ for two different superconductors (S_a-S_b); (2) a temperature-independent excess current which has an exponential dependence on applied voltage; and (3) an excess current which has a strong dependence on temperature as well as an approximately exponential dependence on applied voltage.

Typical I-V curves for Pb-Pb, Sn-Tl, and Al-Al tunnel junctions are shown in Fig. 1 together with the corresponding theoretical SPT curves. (Curves for Sn-Sn are similar to those for Pb-Pb, while curves for Sn-Pb are similar to those for Sn-Tl). For Pb-Pb, we note the presence of an excess current jump at $V = \Delta_{Pb}(T)$ with the extra current increasing rapidly at larger biases. The portion of the curve for $V < \Delta_{Pb}(T)$ is essentially what is expected for SPT. For

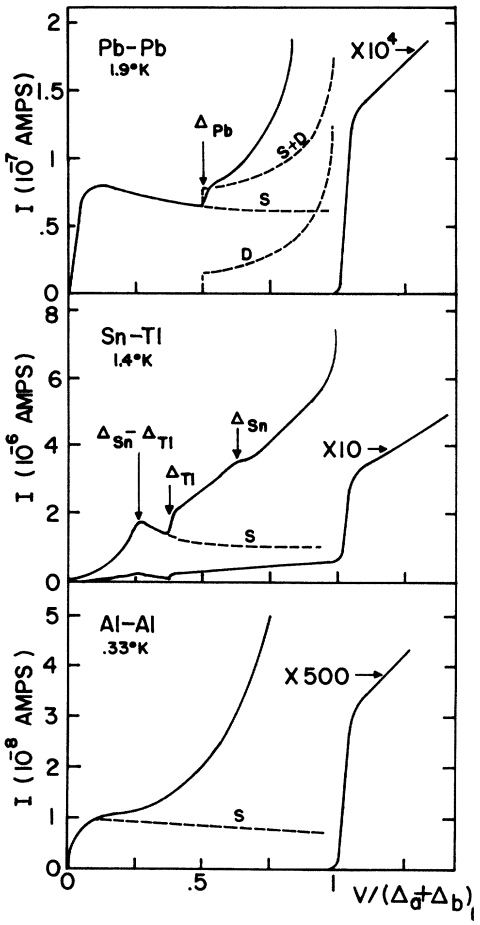
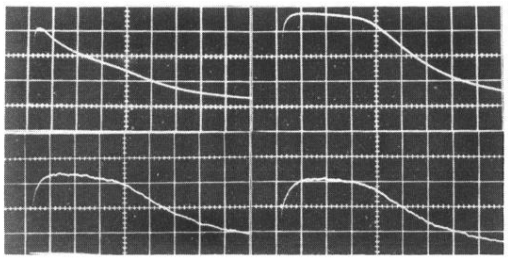


FIG. 1. Current-voltage curves for Pb-Pb, Sn-Tl, and Al-Al. The solid lines represent the experimental data and the dashed lines marked S represent theoretical SPT curves. For Pb-Pb, the theoretical DPT curve, marked D, and the sum of the SPT and DPT curves, marked $S+D$, are shown also.



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