and (210) reflections above the number permissible for the tetragonal system. At 46°K there is a discontinuous change in the relative intensities of the peaks present and the introduction of further well-defined peaks. No attempt has been made to index the two lower symmetry structures since a unique set of indices cannot be obtained from the powder-pattern data alone.

[7] It is interesting that the magnetic domains, which have also been observed, change their direction at the monoclinic transition such that they cross the structural domains at 45° angles in both ferromagnetic phases.

[8] Using a simple relaxation model and the peak value of the observed attenuation we estimate that $\tau = 2\times 10^{-8}$ sec. The compressional modulus also exhibits a discontinuity at this transition from which a change of +10% in the adiabatic compressibility (on cooling) is calculated.

[9] A. J. P. Meyer and P. Taglang, J. Phys. Radium 14, 82 (1953).

[10] A similar behavior has been found in UO_2 [O. G. Brandt and C. T. Walker, Phys. Rev. Letters 18, 11 (1967)].

[11] Since the antiferromagnetic state is not a single structural domain, it may not be possible to see, at the Curie point, the elastic anisotropy which favors the new distortions of the ferromagnetic state.

[12] C. P. Bean and D. S. Rodbell, Phys. Rev. 126, 104 (1962).

PHOTOCONDUCTIVITY IN ANTHRACENE CRYSTALS DUE TO EXCITATION OF TRIPLETS*

P. Holzman, R. Morris, and R. C. Jarnagin
Physics and Chemistry Departments, University of North Carolina, Chapel Hill, North Carolina

and

M. Silver
Army Research Office (Durham), Durham, North Carolina

(Received 13 July 1967)

Two separate pulse-light sources, the first capable of producing singlets from which triplets are obtained by intersystem crossing, the second producing primarily a photon flux, have been used to produce a photocurrent in anthracene. An enhanced photocurrent is produced by the second flash well after the first flash has terminated. The decay of this effect appears to be characteristic of the lifetime of the triplets. The enhanced photoconductivity is believed to be a result of a tandem excitation process involving the triplets as the intermediate state.

Ever since the first demonstration of multiexcitation phenomena in molecular crystals giving rise to a photocurrent from intense pulse light sources,[1] which was attributed to an exciton-exciton interaction,[2] several other multiexciton and photon processes have been reported. Pope[3] observed a photoemission proportional to I^2; Hasegawa,[4] using a Q-spoiled laser, observed a photocurrent proportional to I^4; Kepler[5] and Courtens[6] also using a Q-spoiled laser observed a current proportional to I^3; and Kawada and Jarnagin observed a delayed photocurrent proportional to I^2 in high dielectric constant solvents using a xenon flash.

These various effects have been interpreted in terms of exciton-exciton interactions due to the one-photon population of singlets[1,3] and two-photon population of singlets,[4] although these interpretations have been criticized by Schott,[7] Kepler,[5] and Courtens.[6]

The I^3 dependence has been attributed to a two-photon production of singlets and their subsequent photoionization. Finally, the delayed ionization[8] in high dielectric constant solvents is attributed to triplet-triplet interactions.

To make a more complete picture of possible multiexcitation effects, we have searched for and found what we believe to be the first observation of a triplet photoionization. The two xenon flash lamps of 10^{-5}-sec duration used were triggered to be fired with a preset but variable interval between them. The radiation from the lamp triggered first was filtered with four Corning 3-73 filters plus a 450-mμ low-pass Optics Technology filter. These filters had less than 1% transmission at 4210 Å and below. The absorption coefficient for anthracene[9] at this wavelength is about 30 cm^{-1} and the average absorption coefficient for the light used was between 2 and 3 cm^{-1} depending on crystal thickness. In a 2-mm crystal the spatial dependence of the concentration

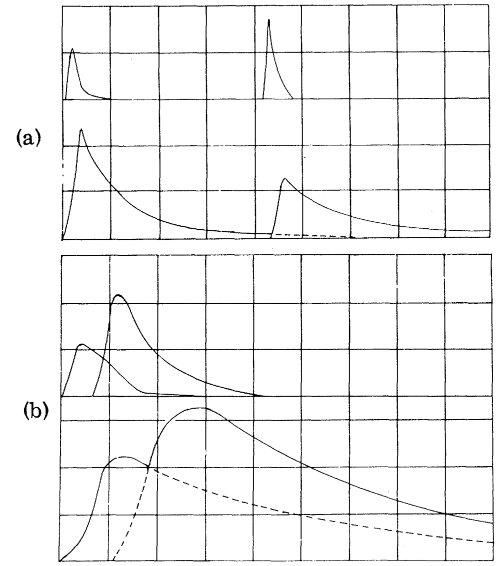

FIG. 1. Time sequence of pulsed photocurrent. (a) Photocurrent due to two flashes of light separated in time by about 200 μsec. The time scale was 50 μsec/cm and the current scale around 1 μA/cm. Upper two pulses represent light flash; lower pulses are the photocurrents. (b) Photocurrent due to two flashes of light separated in time by less than the pulse width of either lamp. The time scale was 10 μsec/cm and the current scale around 1 μA/cm. Upper pulses are the light flashes; lower pulses are the photocurrents.

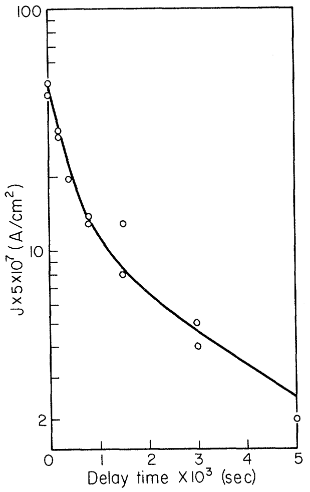

FIG. 2. Decay of second peak photocurrent as a function of delay time between first and second light pulse.

of triplets has been calculated for our incident radiation. The concentration varies by less than a factor of 2 from the illuminated to the back side. The radiation from the second lamp was filtered with a Corning 3-71 filter and a 550-mμ low-pass Optics Technology filter. The wavelength of the 10% transmission point on the short-wavelength edge was 4720 Å. All the crystals used had carrier lifetimes of greater than 200 μsec, and were around 1.5 mm thick. The applied voltage was 500 V and the voltage dependence of both photocurrents was linear as expected.

A typical set of photocurrents due to these two light flashes is shown in Figs. 1(a) and 1(b). No significant photocurrent due to the second flash was observed unless the first flash preceded the second. Figure 2 shows a semilog plot of the magnitude of the net photocurrent due to the second lamp as a function of delay time after the first flash. The resultant curve is characteristic of an initial bimolecular triplet decay which agrees with our estimate of the initial concentration of triplets and a subsequent monomolecular decay having a triplet lifetime of around 3-4 msec.

As can be seen by comparing the two photographs in Figs. 1(a) and 1(b), the increased photocurrent due to the second flash is not significantly larger when it overlaps the first flash. We have been able to overlap the light pulses such that at the start of the second flash, the singlet concentration has decreased to only $\frac{1}{3}$ of its peak value. At this time the triplet concentration is no more than 70 times larger than the singlet concentration. Because the magnitude of the signal can be accounted for by triplet photoionization, we conclude that the cross section for singlet photoionization cannot be larger than about 15 times the cross section for triplet photoionization. We have assumed that not more than 20 % of our signal is unaccounted for. We estimate the average triplet concentration to be around $10^{14}/\mathrm{cm}^3$ using $k_{ST}/k = 0.05$. The incident light intensity overlapping the singlet edge was $1.5\times10^{20}/\mathrm{cm}^2$ sec. An enhanced concentration of carriers of $3\times10^{9}/\mathrm{cm}^3$ was observed for a second-flash intensity of $5\times10^{21}/\mathrm{cm}^2$ sec giving a cross section for photoionization of the triplet of 4×10^{-21} cm². As stated above, the cross section for photoionization of the singlet cannot be larger than 15 times the triplet value and therefore must be less than 6×10^{-20} cm².

If it is assumed that photoionization of the singlet is responsible for the first pulse, then a cross section of 2×10^{-19} cm² would be required. However, this value is three times larger than the maximum possible according to our experiments in which the two light pulses overlap. Further, the magnitude of the first current pulse is proportional to the square of the light intensity of the first lamp which overlaps the singlet edge and not to the square of the total light intensity. Thus, it would appear that singlet-singlet interaction is responsible for most of the first current pulse under these flash conditions. We estimate a bimolecular rate constant of 8×10^{-11} cm^3/sec from the results reported here. This is about ten times larger than our previous value,[1] obtained using a mercury lamp. However, we have now made a much more careful estimate of the average absorption coefficient.

It is clear from the previous experiments of Kepler[5] and Courtens[6] that singlet photoionization is important. We now have shown that triplet photoionization must also be considered. Thus, we are led to the conclusion that exciton-exciton and exciton-photoionization processes may all occur and the dominant one will depend upon the specific mode of excitation.

Finally, the maximum total energy involved with the photoionization of the triplets is less than 4.4 eV ($h\nu_{\max}=2.6+1.8$ eV triplet-state energy). Thus, the band gap must be less than 4.4 eV as previously proposed.[10]

---

*Work supported in part by the Advanced Research Projects Agency and the National Science Foundation.

[1] M. Silver, D. Olness, M. Swicord, and R. C. Jarnagin, Phys. Rev. Letters 10, 12 (1963).

[2] S. I. Choi and S. A. Rice, J. Chem. Phys. 38, 366 (1963).

[3] M. Pope, H. Kallmann, and J. Giachino, J. Chem. Phys. 42, 2540 (1965).

[4] K. Hasegawa and S. Yoshimira, Phys. Rev. Letters 14, 689 (1965).

[5] R. G. Kepler, Phys. Rev. Letters 18, 951 (1967).

[6] E. Courtens, A. Bergman, and J. Jortner, Phys. Rev. 156, 948 (1967).

[7] M. Schott, Phys. Letters 23, 92 (1966).

[8] A. Kawada and R. C. Jarnagin, J. Chem. Phys. 44, 1919 (1966).

[9] D. Hoesterey, private communication. This absorption curve was also used to interpret the results in Ref. 1.

[10] See, for example, G. Castro and J. F. Hornig, J. Chem. Phys. 42, 1459 (1965), or F. Chaiken and D. R. Kearns, J. Chem. Phys. 45, 3966 (1966).

TRANSITION TEMPERATURE OF Pb-In AND Pb-Tl ALLOYS*

T. M. Wu
Department of Physics and Condensed State Center, Case Western Reserve University, Cleveland, Ohio

(Received 28 June 1967)

The ratio between the energy-gap parameter at zero temperature, Δ_0, and the transition temperature, T_c, of a superconductor has been studied by many authors, both theoretically[1-3] and experimentally.[4-7] However, the theoretical calculations of this ratio $2\Delta_0/kT_c$ are all based on some kind of model for the phonon spectrum and the electron-phonon coupling constant. In this Letter we evaluate this ratio for Pb-In and Pb-Tl alloys using the empirical values of $\alpha^2(\omega)F(\omega)$ [where $\alpha(\omega)$ is the phonon coupling constant and $F(\omega)$ is the phonon density of states] and of the Coulomb pseudopotential U_C.[8,9] These quantities are calculated by inverting the gap equation using the experimental density of states and gap Δ_0 obtained from tunneling. The complex gap equations relating the gap function $\Delta(\omega)$ and the renormalization parameter $Z(\omega)$ to the phonon spectrum and the Coulomb interaction have been published by several authors.[10-12] We will not repeat them here.

This procedure allows calculation of the transition temperature of an alloy independent of any model of the phonon spectrum or electron-phonon coupling constant. The values of $\alpha^2(\omega)F(\omega)$ and U_C are obtained by inverting the gap equations to fit experimental values of Δ_0 and the electron density of states at zero temperature. Using these values, the gap and the renormalization equations are solved numerically at a number of temperatures. The transition temperatures given in Tables I and II for various Pb-Tl and Pb-In alloys are obtained via the procedure used by Swihart, Scalapino, and Wada,[2] i.e., linearly extrapolating the square of the gap at the gap edge, $\Delta_1^2(\omega=\Delta_1,T)$ (where Δ_1 is the real part of the gap function, $\Delta=\Delta_1+i\Delta_2$), versus temperature to the point where Δ_1 vanishes.

In Table I we see that both the gap Δ_0 and the ratio $2\Delta_0/kT_c$ of Pb-Tl alloys decrease with increasing Tl concentration, i.e., decreasing electron concentration. This decrease in-