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# Photoelectric Characterization of X-Ray Damage in Anthracene Crystals

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Most physical effects of moderate levels of ionizing radiation on aromatic organic crystals are not readily observable. Thus anthracene, with a total G-yield for X-rays of less than 1, can be used as a scintillation detector with no decrease of fluorescence efficiency except after extreme exposure to ionizing radiation. The electrical properties of anthracene crystals, however, are markedly affected by thermal neutron bombardment at exposures which are too weak to lower the fluorescence efficiency.[1, 2] The photocurrent excitation spectrum is altered and shifted to longer wavelengths, photocurrent gain is reduced, and the peaks in thermal-conduction "glow curves" are intensified.[1]

The photoconduction changes are attributed to the introduction of radiation-damaged sites as current-carrier traps.[3] The nature, whether physical or chemical, of these trapping sites and their stability has not been established. Pertinent information about the nature of the hole traps formed by ionizing radiation would be, for example, their stability and cross section, possibly enabling a distinction to be made between chemical impurities and physical defects.

By using transient photoconduction techniques,[4] we have observed directly carrier-trapping in anthracene crystals subjected to low doses of soft X-rays. From the derived hole lifetime and the efficiency of trap production, we can estimate the trap cross section. Comparison of these values with the results of annealing experiments indicate that the traps are probably chemical in nature. Twenty crystals were examined, subjected to doses from 0.8 to 6.4 Kr, which is a usual exposure for crystallographic diffraction studies. All the exposures introduced hole traps.

For examination in detail, an anthracene crystal was subjected to transient photocurrent measurements[4] after successive exposures. The crystal had been grown under nitrogen from zone-refined blue-violet-fluorescent-grade anthracene (Eastman X480). Transfer from the zone-refining tube to the crystal-growing tube was accomplished under a nitrogen atmosphere in a glove box. Since the photocurrent pulse-heights increased with light intensity and varied nearly linearly with applied electric field, it was accepted that the currents were not space-charge limited, and that in the decay of a pulse we were observing a depletion of free holes in the bulk of a crystal. Other evidence that the changes in the decay were not due to surface damage was that the crystal behaved the same whether the surface which had faced the X-ray source was illuminated during the flash photoconductivity measurement or whether the back side was. Further, stripping layers of anthracene from the surface of the irradiated crystal had no effect on the photocurrent pulses.

Irradiation was carried out with Copper K$\alpha$ rays (7 keV) from a General Electric CA7 tube, operated at 35 kV. The doses were determined by the change in optical density at 305 m$\mu$ of a similarly irradiated ferrous sulfate solution.[5]

For annealing, the crystal was wrapped in platinum foil and sealed into a pyrex ampoule with 1 atm dry prepurified nitrogen after having been evacuated to $10^{-6}$ torr. The crystal temperature was raised rapidly to 207° C, held for 7 days, and then cooled to room temperature at 1°/min. About 10 % of the crystal sublimed away. Another experiment was tried with a slow heating and cooling profile (heating 10°/hr to 160° C, holding 18 hr, cooling 5°/hr) using an oil bath for uniform heating. In this case no sublimation was noticed. Neither annealing treatment produced any change in the electrical properties of the crystals.

Over its first 30 $\mu$sec, within one carrier transit time, each pulse had a shape characterized by a decay time listed in Table 1. Observed over the time interval 30 to 100 $\mu$sec, however, which is after the carrier transit time, the pulses taken both before and after the first irradiation had the same decay constant, 56 μsec. The post-transit decay time is supposed to be determined mostly by the release of carriers from traps. After the second irradiation the currents beyond 30 μsec were too small to analyze.

Since none of the decay times vary with the dose after the first 800 rads, they cannot represent free carrier lifetimes limited by radiation induced traps, which would vary with the trap concentration $N_t$ by the relation

TABLE I Pulse Decay Times in an Irradiated Anthracene Crystal

| Dose (roentgens) | 0 | 800 | 1600 | 6400 |
|---|---|---|---|---|
| Decay time (μsec) | 384 | 24 | 20 | 20 |

$$\tau = \frac{1}{N_t S v} \tag{1}$$

where $S$ is the trap cross section and $v$ is the carrier thermal velocity. An alternative is that the current pulses are due to carriers being released from shallow traps and being distributed into the deeper-lying ones which were in the crystal before the irradiation. Then the 20-μsec decay time in Table 1 would represent the time spent in shallow traps which are emptied in 20 μsec. After this, the current is controlled by emptying of the previously-present deeper traps in 56 μsec. These trap-emptying times depend on the cross sections and energy levels of the traps but not on their concentrations.

The free-carrier lifetimes must then be less than 10 μsec in all the irradiated samples, since the first decay starts at most 10 μsec after the flash. The minimum cross section of the radiation-produced traps can be estimated from equation (1). As an example of how this might be done, we have used Weisz's yield data for trap production by X-rays, $7.4 \times 10^{-8}$ erg/trap.[3] (That this yield was the same for 120 kV X-rays and $^{60}$Co γ-rays suggests that variations in the source of the ionizing radiation might have only a small effect on the resulting traps.) The X-ray energies absorbed in our experiments were calculated from the mass absorption coefficient for Cu-K$\alpha$ radiation (5 cm$^2$ gm$^{-1}$) in anthracene.[6] Our 800-r dose ($2.4 \times 10^5$ erg/gm) then would produce $3.2 \times 10^{12}$ traps/gm, giving $N_t \sim 10^{12}$ cm$^{-3}$. Then with $v = 10^5$ cm/sec,[7] $S > 10^{-12}$ cm$^2$. It has not been determined whether the traps exist at a single energy level or whether they are distributed in energy, but this information would be available from thermal measurements as proposed by Weisz.[3] The density of traps at higher energy levels, which could shorten our transient photocurrents without being counted in the steady-state trapping experiments, might make the correct value of $N_t$ in equation (1) much higher than the one we used. The cross section, which from the present available data is almost 1000 times that of the anthracene unit cell, might then be materially reduced.

The cross sections of the traps produced by radiation might be expected to be unusually large. Studies in radiation chemistry have shown that radiation damage occurs in spurs,[8] which can be frozen in place in solids. The contents of a spur are expected to be a complex mixture of primary and successive reaction products, any of which might act as a hole-trapping center. The high local concentration of impurities within could make a whole spur act as a trap. Photocurrent measurement could then yield the diameter of the spur effective in hole trapping, which, from our preliminary result, might be as large as $10^{-6}$ cm, about 20 times the calculated average distance of the impurity molecules from the center of the spur.[8]

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