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V. Ern [a] & A. R. McGhie [a b]

[a] Central Research Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware, 19898

[b] Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pa, 19104

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Quenching of Triplet Excitons in Anthracene Crystals by Internal Beta-Irradiation

V. ERN and A. R. McGHIE†

Central Research Department‡
E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898

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Abstract—We wish to report effects of bulk irradiation of anthracene by low energy electrons, tritium β-particles, on triplet exciton lifetime in anthracene crystals doped with small concentrations of randomly tritiated carbazole.

A series of anthracene crystals were grown in a Bridgman oven at 1 mm/hr from the melt containing initial dopant concentrations ranging from 1 to 5×10^3 ppm of tritiated carbazole (New England Nuclear) of specific activity 2 μc/mg. The radiochemical purity of the tritiated carbazole was better than 98% as determined by thin layer chromatography and liquid scintillation counting. The starting anthracene was highly prepurified[1] with triplet exciton lifetimes in the range 20–25 msec.[2] This material was zone refined again in a combination tube[1] immediately prior to doping and all handling was carried out under nitrogen. After growth, the crystals were cooled to room temperature at approximately 3 °C/hr and removed from the glass crystal growing tubes by HF etching. The absolute concentration of carbazole and its distribution along the crystalline ingots (typically 10 cm long) was determined by standard liquid scintillation counting techniques on sections cut from the ingot. Triplet exciton lifetimes τ in the samples were measured from the time dependence of delayed fluorescence due to triplet-triplet exciton annihilation by techniques described elsewhere.[3] The change in triplet exciton lifetime due to internal

† Present address: Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pa. 19104.

‡ Contribution No. 1772.

β-particle irradiation was followed in time up to a year after crystal growth by repetitive measurements at suitably chosen time intervals ranging from one to several weeks depending on the tritium disintegration rate in the sample. Triplet lifetimes in the freshly grown crystals varied only from 22.5 msec to 17.5 msec in going from 1 ppm to 5×10^2 ppm carbazole. This indicates that carbazole itself does not significantly contribute to the triplet exciton quenching in anthracene crystals.

In all the radioactively doped samples the triplet exciton monomolecular decay rate constant β ($= 1/\tau$) was found to increase linearly in time, and at a rate proportional to the radioactive carbazole concentration in the crystal. Figure 1 illustrates the observed effect for an anthracene crystal containing a tritium concentration of 9 μc/gm. The change in triplet decay rate constant $\Delta\beta$ after a

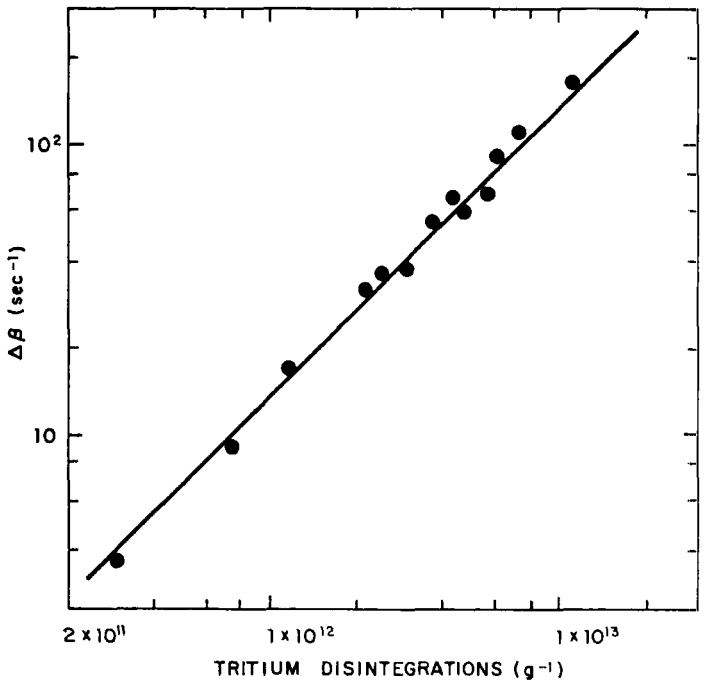

Figure 1. Change of triplet exciton decay rate constant ($\Delta\beta$) in anthracene due to internal irradiation by tritium β-particles as a function of accumulated number of disintegrations per gram (N_d). Anthracene crystal containing 9 μc/gm tritium introduced by doping with randomly tritiated carbazole.

time interval Δt is a linear function of the accumulated number of tritium disintegrations per gram, $N_d = n_d \Delta t$. The disintegration rate n_d, measured by liquid scintillation counting, can be considered constant during the β-irradiation since the tritium half-life ($\sim$12.3 years) is much longer than the time scale of the measurements. A least-squares fit of the measurements on several crystals gives an average increase in triplet exciton quenching rate of 13.5 sec^{-1} per 10^{12} tritium disintegrations per gram of anthracene. In terms of the energy absorbed by the crystal this corresponds to 1.5×10^{-3} sec^{-1} for 1 erg of β-particle energy absorbed per gram of material.[4] This value is slightly larger, by a factor of four, than the change in triplet exciton quenching rate found by Weisz *et al.*[5] for ^{60}Co γ-ray irradiation of anthracene at dose rates nearly 10^6 times larger than the present rates of irradiation with β-particles.

It is expected that β-particles will introduce paramagnetic triplet exciton quenching centers, i.e., trapped charge carriers and free radicals, in the crystal and, therefore, yield a system with a magnetic field-dependent triplet lifetime.[3] All β-irradiated samples showed a magnetic field dependence of lifetime consistent with a triplet-doublet interaction.[3] Minimum triplet lifetimes were found at zero field with the field-dependence saturating at high fields where the Zeeman splitting becomes large compared with the zero-field splitting. The high field values were found anisotropic with broad maxima near $-20°$ and $75°$ with respect to the crystal a axis for H lying in the ac plane and near $\pm 20°$ with respect to the b axis when H was in the ab plane. Figure 2 illustrates the anisotropy as well as the field dependence for the on- (20° to b) and off- (a axis) resonance directions in the ab plane of a crystal exposed to 9×10^{12} tritium disintegrations.

The magnitude of the observed magnetic field effects (e.g., maximum $\tau(H)/\tau(0)$ of $\sim$1.08 and of $\sim$1.03 for the on- and off-resonance directions, respectively) is the same as that found for high energy x-irradiated anthracene.[3] This indicates that similar distributions of triplet exciton quenching centers are being formed by both types of radiation. This is further corroborated by the fact that thermal annealing of the β-particle irradiated samples at 120 °C, under conditions identical to those used by Levinson *et al.*[6] for ^{60}Co γ-irradiated anthracene, gave a degree of annealing[7] of the triplet exciton

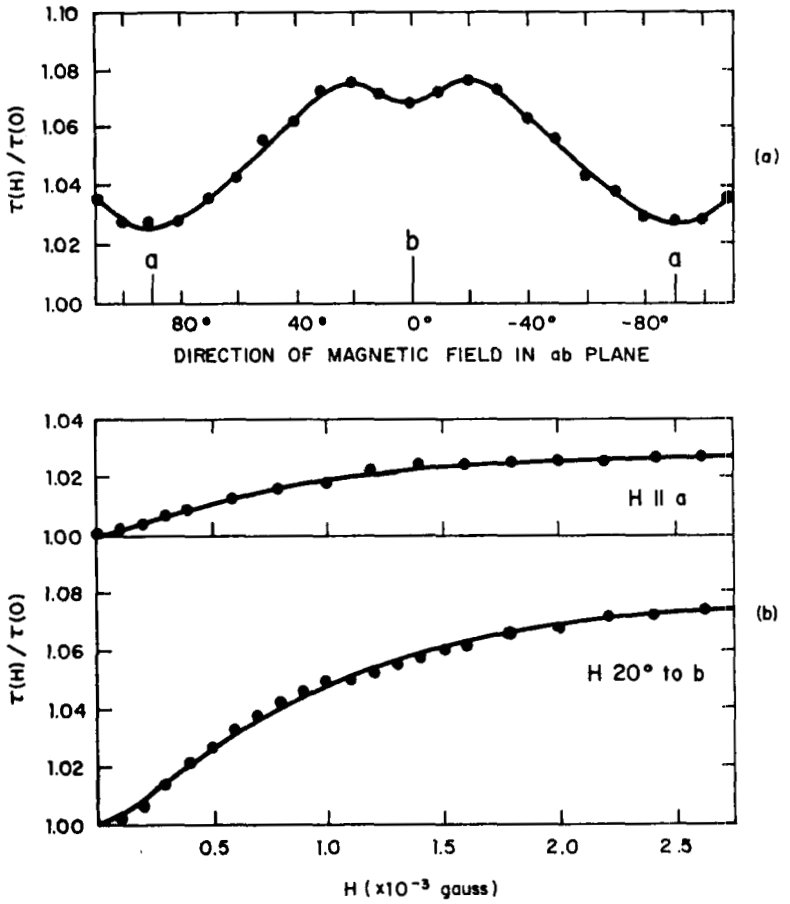

Figure 2. Magnetic field dependence of the normalized to zero-field triplet exciton lifetime, $\tau(H)/\tau(O)$, in the *ab* plane of an anthracene crystal exposed internally to 9×10^{12} tritium disintegrations per gram. $\tau(O) = 5.35$ msec. (a) high-field anisotropy, $H = 3.0 \times 10^3$ gauss; (b) dependence for H along the off- (*a* axis) and on- (20° to *b*) resonance directions.

quenching rate similar (~59%) to that observed with γ-irradiated crystals (~55%).[6] The just annealed samples still showed a reduced (by a factor of ~2) magnetic field effect on triplet exciton lifetime. This indicates that not all of the paramagnetic quenching centers are removed by the annealing.[8] It has been recently shown that charge carrier trapping centers are introduced by irradiation[9,10] and that triplet excitons in anthracene are effectively quenched by

trapped charge carriers[11] via a magnetic field dependent interaction.[12] This gives support to an earlier suggestion[6] that trapped charge carriers are the thermally annealed triplet exciton quenching centers. The remaining paramagnetic species are possibly either deeper, not annealable traps or free radicals produced in this case by radiation damage due to the β-particles and by ^{3}He abstraction after tritium disintegration.[13] Recent work indicates that no appreciable free radical recombination will take place below 160 °C.[14,15]

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4. The maximum energy of the tritium β-ray spectrum is $\sim$18 KeV with an average energy $\bar{E}_\beta = 5.7$ KeV. (See, for example, *Radiation Dosimetry*, G. J. Hine and G. L. Brownell, eds., Academic Press, Inc., New York, 1956, pp. 694–704.) The maximum penetration depth of tritium beta-particles in anthracene is of the order of a few microns.
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7. The degree of annealing is defined as $(\beta-\beta')/(\beta-\beta_0)$ where β_0 and β are the triplet exciton decay rates before and after irradiation, respectively, and β' the rate after annealing the irradiated sample.
8. In general, one can have $\beta(H) = \beta_0 + \Sigma_d \gamma_d N_d + \Sigma_p \gamma_p(H) N_p$, where β_0 is the triplet exciton quenching rate before irradiation, and where γ_d and $\gamma_p(H)$ are the interaction rate constants of triplet excitons with the diamagnetic and paramagnetic quenching centers introduced in concentrations N_d and N_p, respectively, by the irradiation. The sums are taken over the possible types of centers. Present results indicate a simple situation in which only paramagnetic centers of similar interaction rate constants with triplet excitons are being introduced by the irradiation, that is, $\beta(H) \approx \beta_0 + \gamma_p(H)N$. In this case, as observed here, one has $(\beta(H) - \beta'(H))/(\beta(O) - \beta'(O)) \approx (\beta(H) - \beta_0)/(\beta(O) - \beta_0)$, where the primed quantities refer to the values of the decay rate constants after annealing.
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