# EFFECTS OF MAGNETIC FIELDS ON THE MUTUAL ANNIHILATION OF TRIPLET EXCITONS IN MOLECULAR CRYSTALS

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The intensity of triplet-exciton annihilation luminescence in anthracene crystals at room temperature increases in weak magnetic fields up to a maximum increase of 5% at 350 Oe. For stronger fields the intensity decreases, finally leveling off at 80% of the zero-field value for $H \gtrsim 5$ kOe. Sharp dips are found in the high-field intensity for field orientations at which a particular kind of level crossing occurs for pairs of triplet excitons. These effects result solely from field-induced changes in the rate constant for triplet-triplet annihilation.

We wish to report the discovery of some remarkable effects of magnetic fields on the intensity of fluorescence resulting from mutual annihilation of triplet excitons[1] (delayed fluorescence) in anthracene crystals at room temperature.

Experiments to measure the dependence of the intensity of delayed fluorescence on the magnitude and direction of a steady magnetic field were carried out on an anthracene crystal situated in the uniform field of an electromagnet. The crystal was irradiated with unpolarized red light with wavelengths longer than 5900 Å obtained by passing the steady focused light from a 150-W xenon lamp through two Corning C.S. 2-62 filters and heat-absorbing glass. Blue delayed fluorescence ($\lambda \approx 4400$ Å) from the crystal was led through a fiber-optics light guide and red-absorbing, blue transmitting filters (C.S. 5-56, 5-57, and 4-72) to a photomultiplier tube, the output of which was amplified and recorded by conventional means. In all cases, it was verified that the delayed fluorescence intensity was proportional to the square of the intensity of the incident light; this insured that the triplet-exciton population was controlled by monomolecular decay processes rather than by the bimolecular annihilation process.[1,2] The crystals were melt-grown[3] from highly purified natural anthracene. The effects of stray magnetic field on the xenon-lamp output and photomultiplier output were minimized by locating these devices more than 1 m away from the sample and by using appropriate magnetic shielding. Transmission of red light (with crystal) and blue light (without crystal) through the apparatus was established to be independent of magnetic field strength.

A typical result of a measurement at room temperature ($T \approx 295$°K) is shown in Fig. 1. In this case, an anthracene crystal (roughly $7 \times 9 \times 14$ mm$^3$ in size) which had been oriented with x rays was placed so that the magnetic field lay in the *ac* plane and the red light was incident normal to the *ac* plane. The triplet-exciton lifetime in this crystal was 15 msec. We distinguish two regions of the magnetic field effect. The low-field effect is an increase in delayed fluorescence which occurs in anthracene for field strengths between 0 and about 350 Oe. The high-field effect is a decrease in delayed fluorescence which occurs in anthracene for field strengths greater than this value. Qualitatively similar behavior was observed

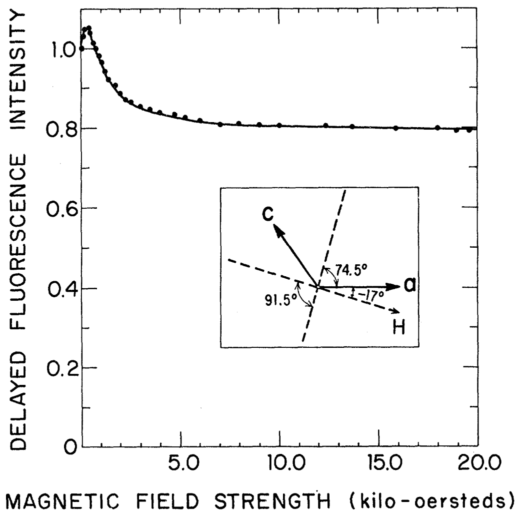

FIG. 1. The influence of a steady-state magnetic field on the delayed fluorescence intensity from an anthracene crystal (with 15 msec triplet lifetime) at room temperature. The magnetic field was applied in the *ac* plane of the crystal in the direction at −17° with respect to the *a* crystal axis as shown in the insert. The dashed lines in the insert indicate the field directions which produce the greatest diminution in delayed fluorescence intensity.

in other anthracene crystals having triplet lifetimes of 6, 16, 20, and 27 msec and in a 27-msec crystal at 77 and 4.2°K. In all cases seen so far, most of the change of delayed fluorescence intensity in the high-field effect occurs between 350 and 3000 Oe although the intensity continues to decrease as the field strength is raised; the maximum fields employed were 20 kOe at room temperature and 50 kOe at 4.2°K.

It was found that the magnitude of the high-field effect is a function of the direction of the magnetic field relative to the crystal axes. For the case where the magnetic field lies in the *ac* plane, it was found that there are two sharply defined directions, 91.5 deg apart, for which the magnetic field produced the greatest diminution of delayed-fluorescence intensity. These field directions were at −17° and +74.5° with respect to the *a*-crystal axis as shown in the insert of Figure 1. The dips at these field directions have a magnitude of 10% and an angular width at half-maximum of 15 deg. The delayed fluorescence intensity was insensitive to reversal of the sense of the magnetic field.

In principle, the magnetic field could be affecting the absorption coefficient $\alpha$ for the red light, the triplet lifetime $\tau$, the bimolecular annihilation rate constant $\gamma$, or even the fluorescence emission from singlet excitons after their formation by triplet-triplet annihilation. We eliminated the last possibility by demonstrating the absence of any magnetic field effect (for fields up to 20 kOe) on intensity of fluorescence from singlet excitons generated directly with uv light.

We demonstrated that magnetic fields effect $\gamma$ and do not influence $\alpha$ or $\tau$ in the experiments described above by employing pulsed-field techniques. The response of the delayed fluorescence intensity of an anthracene crystal with 27-msec triplet lifetime to a rectangular magnetic field pulse under steady-state illumination with red light is shown in Fig. 2. Both in the low-field (350-Oe pulse height) experiment [Fig. 2(a)] and in the high-field (2400-Oe pulse height) experiment [Fig. 2(b)], the time dependence of the delayed fluorescence follows the time dependence of the field. If either $\alpha$ or $\tau$ were affected by the magnetic field, the change in triplet population would take place with a response time characteristic of the triplet lifetime, and hence the change in delayed fluorescence would have a slow buildup and decay compared with the rapid risetime (2 msec) and falltime (<2 msec) of the field pulse.

Qualitatively similar results were obtained in pulsed-field experiments on a pyrene crystal. This suggests that the phenomena described above for anthracene are probably present in a variety of organic crystals in which triplet-triplet annihilation occurs.

Although at this point we are not able to provide a detailed explanation of our experimental observations, the physical factors which are involved seem fairly clear. In the first place, there must exist spin selection rules for triplet-triplet annihilation; to a first approximation only triplet pairs whose over-all spin state contains a singlet component are able to annihilate. The annihilation rate will thus depend on the detailed form of the spin wave functions, which in turn depend on an interplay between the zero-field splitting[4] and the Zeeman energy. The changes in delayed fluorescence intensity observed at low fields occur in the region where these two quantities are of comparable magnitude and hence where the spin wave functions are rapidly varying

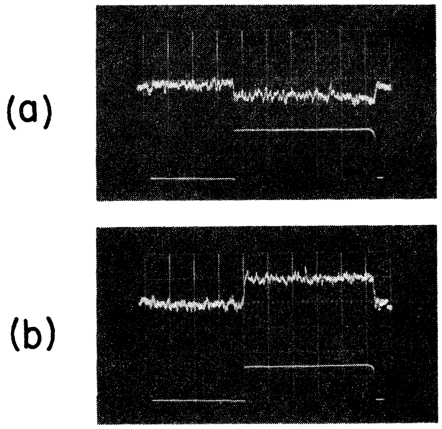

FIG. 2. Dual-beam-oscilloscope photographs showing effect of a pulsed magnetic field on delayed fluorescence at room temperature from an anthracene crystal with 27 msec triplet lifetime. The time scale was 10 msec/cm. In each photograph the upper trace shows the amplified photomultiplier signal (inverted) and the lower trace shows the current through the magnet coil. The 350-Oe pulse height (a) produces approximately a 5% increase in the delayed fluorescence, while the 2400-Oe pulse height (b) causes an 11% decrease in delayed fluorescence with a response which follows the field strength in the coil. For the sake of clarity, the photomultiplier outputs have been amplified and the zero-light-level signal would be completely off the top of the photographs.

functions of the field strength.

In the high-field region, i.e., where the Zeeman energy is large compared with the zero-field splitting, the spin wave functions become quantized along the magnetic field and no longer depend on the field strength. However, in this region the zero-field splitting still manifests itself as an anisotropy in the energies of the magnetic levels. In particular, for an arbitrary field orientation the energy of a pair of triplets, each having $M_S=0$, will not be equal to that of a pair having $M_S=+1$ and $-1$, respectively, these being the only pair states which have a singlet component. However, there exist particular field directions for which these two energies are equal. It is particularly simple to calculate these directions when the magnetic field lies in the *ac* plane, since the two differently oriented molecules in the anthracene unit cell are related to each other by a glide reflection in this plane,[5] and hence the energies of the magnetic sublevels of a triplet are the same for either kind of molecule. The triplet energies in the high-field limit were calculated with values of the zero-field splitting parameters $D$ and $E$ of 0.072 $\text{cm}^{-1}$ and $-0.007$ $\text{cm}^{-1}$, respectively.[6,7] The calculated field directions, defined as in Fig. 1, for which $2E_0=E_{+1}+E_{-1}$, are $-20°$ and $+74°$, in good agreement with the experimental observations. The observed high-field anisotropy is thus intimately related to the occurrence of this particular type of level crossing and may represent a level-crossing resonance[8] or, perhaps more likely, a so-called "anticrossing" resonance.[9]

We wish to acknowledge the invaluable assistance of Dr. G. J. Sloan who provided us with the crystals with which these experiments were conducted.

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[2] If the annihilation process controls the triplet-exciton population, then a change in only the annihilation rate will not change the delayed fluorescence intensity. The triplet population will adjust itself to the new steady-state situation under the same incident light intensity (same triplet creation rate) to give the same delayed-fluorescence intensity.

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# DENSITY OF He$^4$ NEAR THE CRITICAL POINT

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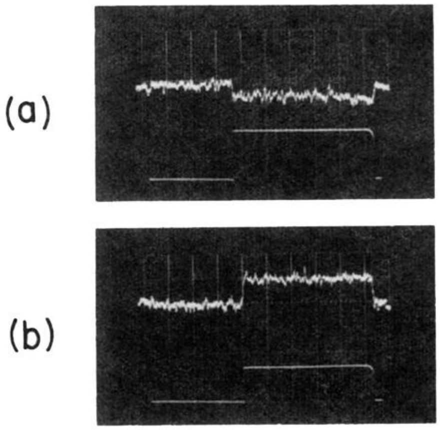
The density of He$^4$ has been measured along five isotherms near the critical point. Using a modified form of the power-law expression $|P-P_c| \propto |\rho-\rho_c|^\delta$ for the critical isotherm, we find $3.8 \leq \delta \leq 4.1$. Assuming that the specific heat follows a relation $C_v \propto |T-T_c|^{-\alpha'}$ and that the density of the coexistence curve behaves as $|\rho-\rho_c| \propto (T_c-T)^\beta$, previous measurements for $\alpha'$ and $\beta$ allow us to test Griffith's inequality $\beta(\delta+1)+\alpha' \geq 2$. We obtain a maximum value for $\beta(\delta+1)+\alpha'$ of 1.9.

It is known experimentally that a real gas-liquid system at its critical point exhibits behavior that is significantly different from that of a "classical" system such as a van der Waals gas. Recent attempts have been made to describe the behavior of various singular quantities in terms of a simple power law. In this scheme, the densities of the gas or liquid phases, when in equilibrium with each other, are given by the expression $|\rho-\rho_c| \propto (T_c-T)^\beta$, where $\rho_c$ is the critical density, and $T_c$ is the critical temperature. Similarly, the pressure of the fluid along the critical isotherm is related to the density by $|P-P_c| \propto |\rho-\rho_c|^\delta$, where $P_c$ is the critical pressure, and, finally, the specific heat along a path of constant critical



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