MAGNETIC FIELD EFFECTS ON TRIPLET-EXCITON INTERACTION IN ANTHRACENE*

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Low-temperature triplet-exciton interaction, yielding delayed blue fluorescence, exhibits large magnetic field quenching. The observed effect differs, however, from that anticipated assuming thermalization and simple spin conservation. The quenching is concentration dependent, indicating that the magnetic field decreases exciton interaction probability.

When two triplet excitons mutually annihilate to yield singlet fluorescence, one expects magnetic field effects due to spin-conservation requirements. Johnson et al.[1] have reported room-temperature effects on triplet-exciton interaction which exhibit a maximum at a few hundred oersteds and a constant quenching of approximately 20% at fields greater than about 5 kOe. Merrifield[2] has interpreted these results in terms of a mutual-annihilation probability dependent on the fractional singlet character of the various possible exciton-pair states. Dipolar zero-field splitting and level-crossing resonances play key roles. In this paper we report an additional, much larger, effect at high magnetic fields and low temperatures.

Simple spin-conservation considerations suggest that it should be possible to quench the triplet-exciton interaction effectively by making the Zeeman splittings $\Delta E = g\mu_B H$ large with respect to kT. If only interactions of triplet pairs with total spin zero yield singlet fluorescence, then "condensation" into the lowest Zeeman substate should totally inhibit interaction. A spin-lattice relaxation time fast with respect to exciton lifetime is assumed. This calculated Boltzmann quenching is shown in Fig. 1. The interaction probability of an exciton pair with zero total spin is assumed constant with magnetic field. This calculation reflects only the relative populations of Zeeman substates.

Experiments were conducted in a superconducting magnet utilizing direct excitation of triplet states with red light. Alternative sources were He-Ne lasers at 6328 Å and a 900-W xenon lamp with a high-intensity Bausch and Lomb grating monochromator. The latter arrangement allowed measurement of the delayed fluorescence excitation spectrum and verification of the creation of triplets as the origin of observed signals. Sources and detectors were placed about $1\frac{1}{2}$ m from the magnet to avoid the influence of stray magnetic fields. Blue fluorescence was passed through a Lucite light pipe and a 10-cm cell of saturated copper-sulphate solution, and focused on the photocathode of an RCA-8645 photomultiplier placed in nested shells of magnetic shielding material. Susceptibility of the apparatus of less than 1% to strong magnetic fields was verified by passing low-level blue light through the system. A variable-speed chopping wheel allowed time-dependent measurements. The signal-to-noise ratio was enhanced by use of a computer of average transients.

Results of a quenching experiment with He-Ne laser excitation of a Harshaw crystal are shown in Fig. 2. Similar results were obtained using light from the xenon lamp with a maximum quenching of 50%. Low-field effects similar to those reported by Johnson et al.[1] were observed. They are not evident in Fig. 2 because of a persistent magnetic field of the order of 100-200 Oe (due to trapped flux) which prevented return to absolute zero after conditioning the superconducting magnet. The luminescence excitation spectrum was very similar to that previously reported[3] ex-

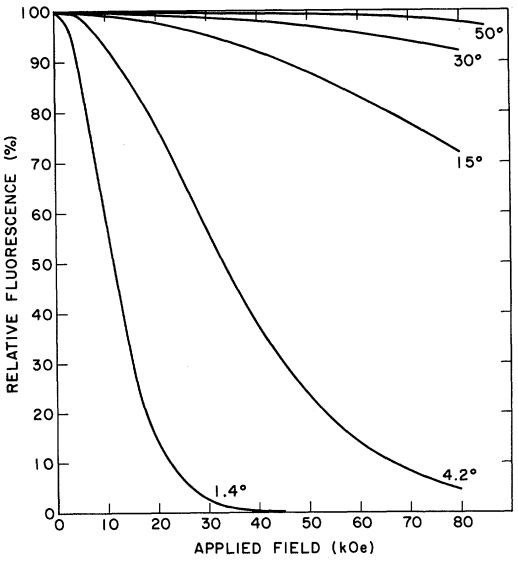

FIG. 1. Boltzmann magnetic field quenching calculated assuming spin conservation and fast spin-lattice relaxation.

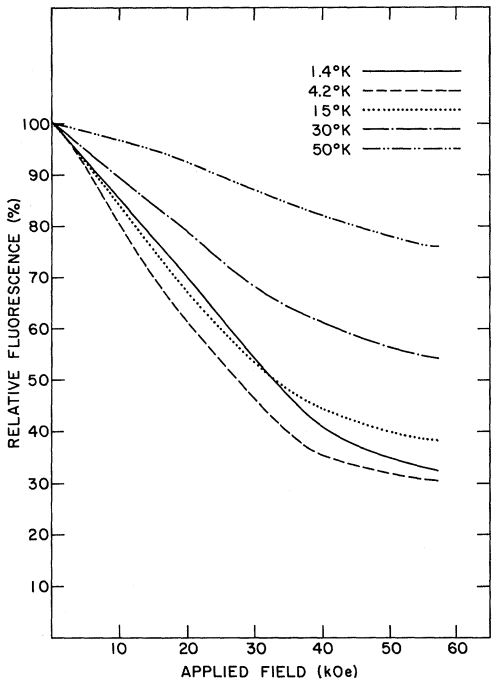

FIG. 2. Measured magnetic field quenching with 632.8-nm He-Ne laser excitation of Harshaw anthracene.

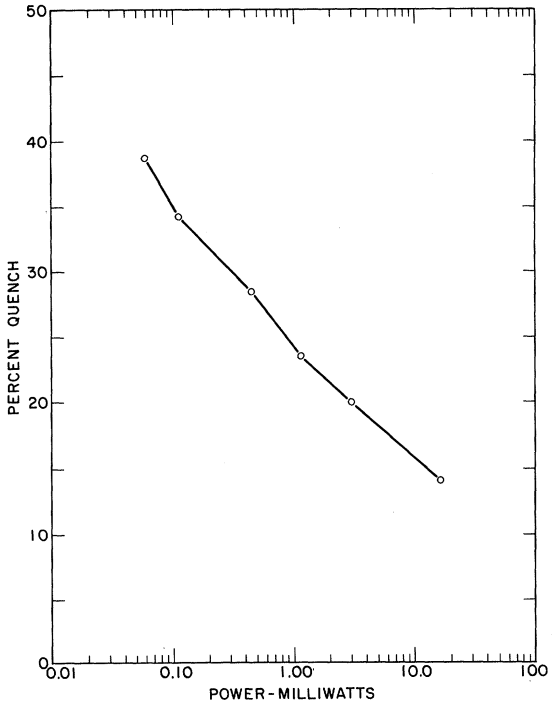

FIG. 3. Intensity dependence of magnetic field quenching of vapor-phase anthracene with xenon-lamp excitation. Dark-grown anthracene yields a similar result. The values shown are for magnetic field differences between the persistent value of a few hundred oersted and 57 kOe.

cept that low-temperature linewidths were narrower than could be measured in this apparatus (slit width corresponding to about 20 Å). The following experimental parameters were changed with no measurable modification of the magnetic field quenching: (1) crystal orientations with either $\vec{a}$ or $\vec{b}$ axis parallel to the magnetic field, (2) exciting light either perpendicular or parallel to magnetic field, and (3) circularly or linearly polarized exciting light. Unfortunately, the imperfect optical quality of the crystals and birefringence makes these experiments not completely conclusive.

Comparison of Figs. 1 and 2 shows that the Boltzmann model fails to predict the experimental results. In particular, the quenching as a function of magnetic field is much too slow at low temperatures.

The magnetic field quenching effect was intensity dependent. Figure 3 shows how it decreases with increasing input power, i.e., triplet concentration. Such an intensity dependence also contradicts the Boltzmann quenching model. In fact, a generalized calculation proves insensitive to intensity. The fact of strong intensity dependence is also evidence that the magnetic field does not alter the total triplet absorption coefficient α. This is also the case in the work of Johnson et al.[1] and of Clarke and Hochstrasser.[4]

The intensity dependence is to be expected if the magnetic field influences the bimolecular interaction coefficient γ, since the delayed fluorescence signal φ is given by $\varphi = \frac{1}{2}\gamma n^2$, where n is the triplet concentration. The steady-state triplet concentration is determined by $\alpha I = \beta n + \gamma n^2$, where αI is the generation rate and β^{-1} is the triplet lifetime. At low intensities $\varphi = \frac{1}{2}\gamma(\alpha I/\beta)^2$. At high intensities $\varphi = \frac{1}{2}\alpha I$, which is independent of γ. The general solution is

$$\varphi = \frac{\beta^2}{4\gamma}\left[1 + \frac{2\gamma\alpha I}{\beta^2} - \left(1 + \frac{4\gamma\alpha I}{\beta^2}\right)^{1/2}\right].$$

Intensity-dependent quenching implies that one is operating in the transition regime between monomolecular and bimolecular kinetics. This is substantiated by the double logarithmic graphs of fluorescence intensity as a function of input power. In order to fit these curves at the measured absolute input power level, the value of γ required is of the order of 100 times larger than that measured at room temperature. The refinement of this simple kinetic model to include the

effect of interaction of free and trapped excitons does not alter the requirement for low-temperature enhanced interaction. This "enhancement factor" for free-trapped interaction is consistent with the previous work on phosphorescence.[5]

Low-temperature chopped-light experiments show much slower rise times than decay times. The rise time evidently is a measure of the build-up of a trapped exciton population, while the decay represents the trapping of free excitons. A variety of crystals was studied: vapor-phase grown, Harshaw, and grown from the melt in the absence of light. Room-temperature lifetimes ranged from 2 to 40 msec. All lifetimes increased at low temperatures, but not sufficiently to account for the low-temperature enhanced interaction. These was no magnetic field effect on rise or decay times. This is evidence that β is constant as a function of magnetic field.

These results may be summarized as follows: The Boltzmann model is contradicted both by the low-temperature magnetic field dependence and by the intensity dependence. Neither the total absorption coefficient α nor the lifetime β is a function of magnetic field. Sensitivity of the interaction γ to magnetic field is indicated by the intensity dependence.

This does not explain the failure of the Boltzmann model. There must be errors in one or both of the assumptions: (1) that spin-lattice relaxation is fast with respect to exciton lifetime, or (2) that spin is conserved in the reaction $T+T \rightarrow S$. If the first assumption were incorrect, one might expect spin polarization to result from preferential absorption into one of the Zeeman states.[4] In some crystal orientations this nonthermal population could be altered in a microwave field at the paramagnetic resonance condition.[6] An experiment at 35 GHz with static and microwave magnetic fields parallel showed no effect (other than heating the sample).

A gamma-irradiation experiment was performed with the expectation that the introduction of paramagnetic defects might increase the rate of spin-lattice relaxation. The room-temperature fluorescence φ is reduced by irradiation with a few hundred rad, as observed by Weisz et al.[7] This decrease is associated with shorter room-temperature lifetimes. Surprisingly, the low-temperature fluorescence is not substantially influenced by radiation doses of 60 000 rad. At 2.2×10^6 rad the crystal turns straw brown and there are in excess of 10^{16} free radicals/cm^3 detectable by EPR. At this damage level the fluorescence excitation spectrum indicates that many of the excitons are created at or near defect sites. Still the small decrease of fluorescence intensity is probably due to reabsorption rather than to any fundamental change in triplet exciton behavior. Low-temperature lifetimes are made longer by irradiation and the magnetic field quenching is consequently smaller for a given input power level. If the radiation damage speeded a normally slow spin-lattice relaxation, the Boltzmann model would predict the opposite effect, i.e., a larger magnetic field quenching.

In view of these results, viz., that the low-temperature exciton-exciton interaction is insensitive to resonant microwaves or radiation damage, one questions the original assumption of spin conservation in the $T+T \rightarrow S$ reaction. If there is a spin reservoir (the trap, for example), spin considerations may not be a restriction on interaction.

Since γ is affected by the magnetic field, it seems likely that the mechanism of quenching must involve either (1) reduced probability for creation of the singlet state from two excitons which are close enough to annihilate, or (2) reduced exciton-exciton interaction due to a change of transport properties. In the low-temperature experiment in which most of the excitons are trapped and the interaction is predominantly the free-trapped variety, it can be shown that φ is independent of transport properties. This is a consequence of compensating effects in the trapping probability, which controls free-exciton concentration, and in the probability that a free exciton will hunt out a trapped exciton. Thus, the magnetic field must influence interaction rather than transport.

It is interesting that the low-temperature exciton interaction is not inhibited by radiation damage. Under the conditions of these experiments, the probability that a free exciton will encounter a defect site before it sees another exciton is about 10^5:1. The simplest interpretation is that there is a large number of shallow traps in the crystals prior to irradiation and that the additional radiation-produced defects represent a small relative modification. The interaction must involve two different species, i.e., free and trapped excitons, as evidenced by the different lifetimes calculated from rise and decay curves in chopped-light experiments. The large exciton-interaction probability under these conditions may indicate that long-range effects are operative. Such a low-temperature enhanced "effective volume"

has been suggested by Knox and Swenberg.[8]

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TITANIUM-DOPED TUNNELING BARRIERS IN A MAGNETIC FIELD

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Both a giant resistance peak and a small conductance peak have been observed in a single tunnel junction. The conductance peak splits into two peaks in a magnetic field indicating that it is similar to the conductance peaks seen previously.

In a single tunnel junction we have observed effects at zero voltage which hitherto have only been seen in quite different junctions. There is a small conductance (G) peak of the type that has been seen in Ta–Ta-oxide–Al junctions[1,2] in which the peak height increases as the temperature is lowered and which, in a magnetic field, splits into two peaks.[3] Also, there is a giant resistance (R) peak of the sort that was first seen in Cr–Cr-oxide–Al junctions.[2] This strongly suggests that the two effects which have been considered as separate phenomena are simply two manifestations of a single underlying effect of the magnetic impurities.

The samples were of Ti-doped Al-Al_2O_3-Ag junctions in which we have previously reported giant-resistivity behavior.[4] Rather less[5] Ti was used which has the effect of decreasing and broadening the giant resistance as reported by Mezei for Cr.[6] The differential resistance at 77, 20, and 1.8°K is shown in Fig. 1. The junctions were shown to be tunneling in all cases by observing the superconducting Al gap at 1°K.

At higher temperatures the resistance peak is clearly evident with no sign of the conductance peak which becomes superimposed on the resistance peak at the lowest temperatures. The curve at 1.8°K is similar to that found by Mezei for Cr dopings except that our results are symmetrical about $V=0$. The resistance peak is similar to those seen before in Ti-doped junctions except that the half-width which at 77°K is 50 mV only decreases to 25 mV at 4.2°K, compared with the reduction from typically 35 to 10 mV that we previously observed, and the peak height increases by a factor of 1.6 compared with the order of magnitude increase we had previously.

The conductance peak is similar to that mea-

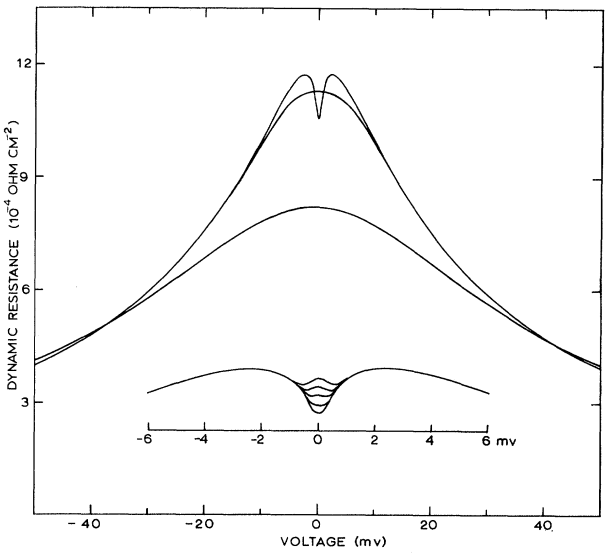

FIG. 1. The differential resistance is shown as a function of voltage at 77, 20, and 1.8°K in ascending order, for the Ti-doped junction. Inset shows how the conductance peak decreases and splits in a magnetic field. The curves in ascending order are for 0, 17, 25, 34, and 42 kG, respectively.