PHYSICAL REVIEW B VOLUME 1, NUMBER 2 15 JANUARY 1970

Effects of Magnetic Fields on the Mutual Annihilation of Triplet Excitons in Anthracene Crystals

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(Received 11 September 1969)

Detailed measurements of the magnetic field dependence of the rate of mutual annihilation of triplet excitons in anthracene crystals at room temperature are presented. The field dependence consists of an increase at low fields, with a maximum at ca. 350 Oe, followed by a decrease at higher fields to less than the zero-field annihilation rate. For most field directions, a second maximum occurs at ca. 600 Oe. The amplitude of the field dependence is highly anisotropic. For fields >2000 Oe, resonances in the annihilation rate are found at $+76°$ and $-17°$ with respect to the *a* axis for fields in the *ac* plane and at $\pm 23.5°$ with respect to the *b* axis in the *ab* plane. For fields <500 Oe, a second set of resonances occurs at directions bisecting the high-field resonances and at intermediate fields the two sets coexist. These results are discussed in terms of a density-matrix description of the spin states of the interacting triplet pair and of the annihilation process. The field dependence is accounted for on the basis of the field dependence of the pair spin states together with the postulate that annihilation is spin-allowed. The observed resonances result from level crossings among the pair spin states. All of the structure in the field dependence and anisotropy data is satisfactorily reproduced by calculations based on the model, although complete quantitative agreement is not achieved.

I. INTRODUCTION

It has been known[1,2] for some time that a pair of triplet excitons in a molecular crystal may interact and annihilate to produce a singlet exciton which quickly disappears with the emission of a photon (delayed fluorescence). Recently, it was discovered[3] that the rate of this annihilation process is magnetic-field dependent at room temperature. The intensity of delayed fluorescence in anthracene crystals increases in low magnetic fields, reaching a maximum increase at ca. 350 Oe. Further increase in the field strength results in a decrease in delayed fluorescence intensity up to a field of ca. 5000 Oe, at which point the intensity has decreased to less than the zero-field value. Very little additional change takes place up to fields of 20 kOe. Measurements of the anisotropy of the magnetic effect at high-field strength shows sharp dips in the delayed fluorescence intensity for field orientations at which level crossings occur among the spin states of triplet-exciton pairs. It was shown by measurements with a pulsed magnetic field that these magnetic effects arise solely from field-induced changes in the rate constant for triplet-triplet annihilation.

More recently another set of resonances was observed[4] at low-field strength for field directions at which single-particle level-crossings occur. For a magnetic field lying in the *ac* plane of the anthracene crystal, there are two resonance directions (± senses for each) for fields >2000 Oe. At fields <500 Oe, two new resonances are found at directions which bisect the high-field resonance directions. At intermediate fields the high- and low-field resonances coexist. Following these findings, a theory of the dependence of the annihilation rate on the spin states of the interacting exciton pair was presented[5] which accounts for most of the observed magnetic effects. The basic idea of the theory is that the annihilation is proportional to the fractional singlet amplitude of the interacting exciton pair which is determined by an interplay between the Zeeman interaction and the triplet-exciton fine structure.

We report here the results of more detailed experimental studies of the magnetic field effect in the *ac* and *ab* planes of the anthracene crystal at room temperature and present a modified theory of the magnetic effects, which accounts for the observed features and gives good quantitative agreement with the data.

II. EXPERIMENTAL

The samples, with one exception, were crystals which had been grown in our laboratory. The one exception was a piece of "optical-quality" crystalline anthracene obtained from the Harshaw Chemical Co. Four samples were grown from the melt[6] and one from the vapor[7] from highly purified anthracene. The vapor-grown crystal was a plate roughly 7 mm o.d.×2 mm thick. One of the melt-grown crystals was a cleavage slice roughly 10 mm×15 mm and 1 mm thick. The other three melt-grown crystals and the Harshaw crystal were large; they had outside dimensions which ranged from 7 mm to 16 mm. The room-temperature triplet exciton lifetime was 15 msec for two of the large melt-grown crystals, 27 msec for the other, and 12 msec

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* Contribution No. 1607.

[1] R. G. Kepler, J. C. Caris, P. Avakian, and E. Abramson, Phys. Rev. Letters **10**, 400 (1963).

[2] S. Singh, W. J. Jones, W. Siebrand, B. P. Stoicheff, and W. G. Schneider, J. Chem. Phys. **42**, 330 (1965).

[3] R. C. Johnson, R. E. Merrifield, P. Avakian, and R. B. Flippen, Phys. Rev. Letters **19**, 285 (1967).

[4] R. C. Johnson and R. E. Merrifield, Bull. Am. Phys. Soc. **13**, 640 (1968).

[5] R. E. Merrifield, J. Chem. Phys. **48**, 4318 (1968).

[6] G. J. Sloan, Mol. Cryst. **1**, 153 (1966).

[7] G. J. Sloan, Mol. Cryst. **2**, 323 (1967).

for the Harshaw crystal. The triplet lifetime was 22.8 msec for the cleavage slice, and was about 2 msec for the vapor-grown plate. The crystals were oriented by x-ray and optical techniques. Anthracene crystals are monoclinic with an angular separation equal to 125° between *a* and *c* axes.[8] As is well known, anthracene commonly exhibits a mosaic structure when viewed near extinction between crossed polarizers.[9] If we use the nature of the extinction of light that is observed as the crystal is rotated in its *ab* plane between crossed polarizers as a rough measure of the degree of alignment of the grains of the crystal, then we can rank the crystal samples according to quality of structural alignment. In order of increasing quality, we rank the samples as follows: the two 15-msec crystals, the 27-msec crystal, the Harshaw crystal, the vapor-grown plate, and the cleavage slice. The mosaic structure was completely absent from the cleavage slice and vapor-grown plate and nearly absent from the Harshaw crystal. It turned out, as would be expected, that this same order is obtained if we rank the samples in order of increasing sharpness and narrowness of the level-crossing resonance line, i.e., increasing quality of structural alignment is associated with increasing sharpness and narrowness of resonance line. The results for all the samples are in substantial quantitative agreement, and we present only the experimental data for the cleavage slice as we believe that this exhibits a resonance line shape close to the intrinsic line shape for anthracene; the resonance line for the vapor-grown plate was identical and that for the Harshaw crystal very nearly the same.

Figure 1 is a schematic drawing of the experimental apparatus. Red light (5900–7900 Å) was filtered from the xenon lamp light by two Corning CS 2-62 red-transmitting, blue-absorbing filters and one Optics Technology KG-3 visible-transmitting, infrared-absorbing filter. This red light was made to fall on the anthracene sample. A short focal-length lens inside the sample chamber served to concentrate the red light on a small region of the crystal. The blue delayed fluorescence emitted from the sample was conducted along the 12-mm o.d. solid-glass clad-rod light guide and passed through the output filters to the photomultiplier tube (RCA-4517 with S-11 cathode). The output filters consisted of a stack of Corning blue-transmitting red-absorbing filters (one each of CS 5-56, 5-57, and 4-72). The photomultiplier current was detected by a picoammeter (Keithley 417) and recorded on the *Y* axis of an *X*-*Y* recorder (Hewlett-Packard 7001 AM).

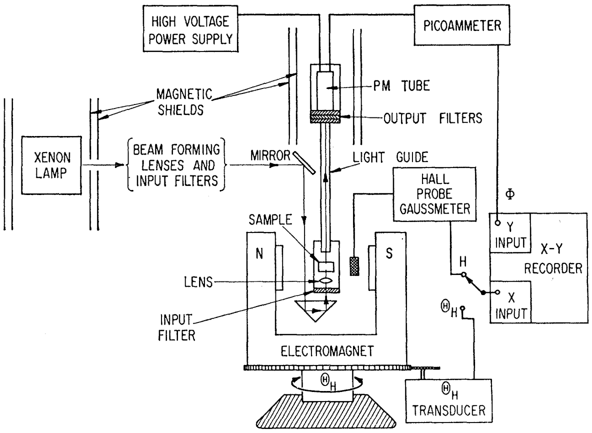

Fig. 1. Schematic drawing of the experimental apparatus.

Magnetic and electrostatic shielding of the photomultiplier tube was provided by the housing (Pacific Photometric Model 61). This housing was centered inside two concentric magnetic shields (made from 0.35-mm-thick sheets of Perfection Mica Conetic-AA magnetic shielding material). The 150-W xenon lamp (Hanovia 901C-1) was also centered inside two large concentric magnetic shields. The lamp was located at a 3-m and the photomultiplier tube at a 1-m distance from the electromagnet to further reduce the influence of the stray magnetic field. It was determined that the stray field could change the measured fluorescence intensity by no more than ±0.2%.

The delayed fluorescence intensity Φ (annihilation rate γ) depends on the magnetic field strength H and the angular position of the magnetic field Θ_H. The data was taken in the form of continuous curves on an X-Y graph. These were of two kinds: field dependence curves (at fixed Θ_H) and anisotropy curves (at fixed H). In both kinds the Y axis represented the magnitude of Φ. A field dependence curve was made by driving the X input of the recorder with a voltage from a Hall probe gaussmeter (Bell 610), which was linearly proportional to H. An anisotropy curve was made by driving the X input with a voltage from an angular transducer; changes in this voltage were linearly proportional to changes in Θ_H.

The magnetic field was provided by an electromagnet with 10-cm o.d. cylindrical pole caps. A motor-controlled power supply allowed us to increase or decrease the magnet current smoothly and continuously at a chosen rate. This enabled us to change the field from some magnitude in one sense down through zero and up to some magnitude in the opposite sense. It was our practice to make field-dependence curves in this manner so that we could determine the delayed fluorescence intensity at zero field. The gaussmeter and recorder system were calibrated with a (2900±15)-Oe standard magnet and a zero-field chamber. We estimate that the maximum absolute error in the recorded magnitude of magnetic field strength was ±1%. We measured the stability of magnetic field strength of the electromagnet and found that it did not change at all at $H=3000$ Oe, -0.6% at 4000 Oe, and -0.8% at 5000 Oe over the period of time required to make an

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[8] J. M. Robertson, Rev. Mod. Phys. **30**, 155 (1958).

[9] F. R. Lipsett, Can. J. Phys. **35**, 284 (1957); G. C. Pimentel and A. L. McClellan, J. Chem. Phys. **20**, 270 (1952).

anisotropy curve. We measured the magnetic field homogeneity; the magnetic field strength varied by no more than 0.3% total over the region occupied by any of our samples. We measured the directional uniformity of the magnetic field and found that the field direction varied by no more than 0.3° total over the largest dimension of any sample.

The crystal was transferred from the x-ray goniometer head to a carefully aligned sample holder. The orientation of the crystal axes relative to the magnetic field was determined by use of a spirit level and by visual alignment of an edge of the sample holder with the plane surface of one of the magnet pole caps. We estimate that the maximum error in parallel alignment of a crystal plane with the plane of rotation of the magnetic field was $\pm 1°$. We also estimate that the maximum error in the angular position (Θ_H for $\mathbf{H}$ parallel to the axis) of a crystal axis was $\pm 1°$. The angular position Θ_H of any point on an anisotropy curve could be estimated with an accuracy of $\pm 0.5°$ though the accuracy of its position relative to that of a crystal axis was $\pm 1.5°$.

In all cases, it was verified that the delayed fluorescence intensity was proportional to the square of the intensity of the incident light. This ensured that the triplet-exciton population was controlled by monomolecular decay processes rather than by the bimolecular annihilation process.[1] Under these conditions the steady-state triplet population is independent of the value of the annihilation rate constant so that the delayed fluorescence intensity is directly proportional to this constant.

All experiments reported here have been done on crystals at room temperature ($T \approx 295°\mathrm{K}$).

III. THEORY OF EXCITON-EXCITON ANNIHILATION IN MAGNETIC FIELD

A. Model of Annihilation Process

The basic physical hypotheses which underlie the model of the annihilation process to be presented here are, first, that annihilation is spin-allowed, i.e., that it selects out only the singlet component of the nine spin states of a pair of interacting triplets and, second, that the magnetic field exerts its effects through its influence on the triplet-exciton spin states. We have employed the simplest possible model of the annihilation process which embodies these concepts.

The annihilation process will be discussed in terms of the mechanism

$$T+T \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (TT) \xrightarrow{k_2} S^*. \qquad (1)$$

The idea of this mechanism is simply that free, i.e., noninteracting, triplet excitons come together to form pairs which can either annihilate to yield an excited singlet or dissociate with the excitons returning to the reservoir. By a "pair" is meant simply two triplets which are close enough to interact; it is not meant to be implied that a pair is a stable entity or that it corresponds to any definite spatial configuration. This mechanism is clearly an oversimplification in that most of the details of the spatial correlation of the excitons brought about by annihilation are ignored by the simple division of excitons into "free" and "paired" varieties.

Since the lifetime of a pair is expected to be very short (comparable to the triplet-exciton jump time) compared to the spin-lattice relaxation time, one may expect interference among the pair spin states to be important. This means that a description of the pair purely in terms of the occupancies of the stationary states of the spin Hamiltonian (as was done implicitly in Ref. 5) will be inadequate and that instead one must employ the full density matrix[10] of the pair spin states. It will be seen in the following that an occupation-number description (i.e., a diagonal density matrix) is adequate when there are no near-degeneracies among the pair states and, in a certain sense, when exact degeneracies exist, but that the off-diagonal components of the density matrix become important in the vicinity of level crossings. Thus, the qualitative conclusions of Ref. 5 are correct, but the form of the theory given there is not adequate to describe the line shapes of the level-crossing resonances.

B. Equation of Motion for Pair Density Matrix

On the basis of the processes represented in Eq. (1) one can write down in a fairly natural way an equation of motion for the density matrix of the pair spin states. This equation is most conveniently expressed initially in terms of a set of basis states which are eigenstates of the total spin of the pair. (Quantities expressed in this basis will be written with Greek indices with an index of zero corresponding to the singlet state.) In terms of these states the equation of motion is

$$\partial\rho_{\mu\nu}/\partial t = -i[\mathcal{H},\rho]_{\mu\nu} - k_{-1}\rho_{\mu\nu} - \tfrac{1}{2}k_2(\delta_{\mu,0}+\delta_{\nu,0})\rho_{\mu\nu} + (\tfrac{1}{9}k_1 n^2)\delta_{\mu\nu}, \qquad (2)$$

where $\mathcal{H}$ is the pair spin Hamiltonian, n is the concentration of free excitons, and the k's are the rate constants shown in Eq. (1). The terms on the right-hand side of Eq. (2) have the following meanings: The commutator describes the evolution of the density matrix brought about by the Hamiltonian; this term conserves the total pair population (given by $\mathrm{Tr}\rho$) but results in a coherent oscillation of the matrix elements. The second and third terms represent decay of the pair states by dissociation and annihilation, respectively, where it has been assumed that there are no selection rules for the first process but that annihilation destroys only those $\rho_{\mu\nu}$ which have a singlet component. The last term rep-

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[10] D. ter Haar, Rept. Progr. Phys. **24**, 304 (1961).

resents the formation of pairs from the free-exciton reservoir. The assumption that the source term in (2) is proportional to the unit matrix is equivalent to saying that all spin states of the free triplets are incoherently occupied with equal probability, i.e., that spin-lattice relaxation is complete among these states and that kT is large compared to the Zeeman and zero-field splittings. This is not a trivial assumption since it neglects any coherence in the source term which would result from repeated interactions of the same pair of excitons.

The pair spin Hamiltonian is taken to be simply the sum of two free-triplet spin Hamiltonians, i.e.,

$$\mathcal{H}=g\beta\mathbf{H}\cdot(\mathbf{S}_1+\mathbf{S}_2)+D(S_{z_1}{}^2+S_{z_2}{}^2) \\ +E(S_{x_1}{}^2+S_{x_2}{}^2-S_{y_1}{}^2-S_{y_2}{}^2), \quad (3)$$

where the first term represents the Zeeman interaction and the remaining terms describe the fine structure (or zero-field splitting) of the triplets. For triplet excitons the fine-structure tensor represents an average over the inequivalent molecules of the unit cell.[11]

The relation of the triplet-exciton annihilation rate constant γ to the density matrix can be seen by considering the equation of motion for $\mathrm{Tr}\rho=\sum_\nu \rho_{\nu\nu}$, which gives the rate of change of the total pair population. From Eq. (2) one finds that

$$\partial\,\mathrm{Tr}\rho/\partial t=-k_{-1}\,\mathrm{Tr}\rho-k_2\rho_{00}+k_1n^2. \quad (4)$$

The second term on the right-hand side of Eq. (4) gives the rate of destruction of pairs by annihilation and hence,

$$\gamma n^2=k_2\rho_{00}. \quad (5)$$

For explicit evaluation of the density matrix it is more convenient to express it in terms of a set of basis states which diagonalize the spin Hamiltonian $\mathcal{H}$ rather than states diagonalizing S^2. The relation between these two sets of states can be written

$$|n\rangle=\sum_\nu C_{n\nu}|\nu\rangle, \quad (6)$$

where italic indices are used to denote eigenstates of $\mathcal{H}$. Note that $C_{n0}=S_n$, the singlet amplitude of the nth pair state. Application of the transformation (6) to Eq. (2) yields for the equation of motion of ρ in the new basis

$$\partial\rho_{mn}/\partial t=-[i(E_m-E_n)+k_{-1}]\rho_{mn} \\ -\tfrac{1}{2}k_2\sum_l(S_m{}^*S_l\rho_{ln}+S_l{}^*S_n\rho_{ml})+(\tfrac{1}{9}k_1n^2)\delta_{mn}, \quad (7)$$

and for the annihilation rate

$$\gamma n^2=k_2\sum_{mn}S_mS_n{}^*\rho_{mn}. \quad (8)$$

In order to calculate γ, one wishes to find the solution of Eq. (7) for ρ_{mn} under steady-state conditions, i.e., for $\partial\rho_{mn}/\partial t=0$. It is convenient to express (7) in terms of the dimensionless quantities

$$\omega_{mn}=(E_m-E_n)/k_{-1}, \\ k=k_2/k_{-1}, \quad (9) \\ \alpha=k_1n^2/9k_{-1},$$

so that the steady-state equation for ρ becomes

$$(1+i\omega_{mn})\rho_{mn}=\alpha\delta_{mn}-\tfrac{1}{2}k\sum_l(S_m{}^*S_l\rho_{ln}+S_l{}^*S_n\rho_{ml}). \quad (10)$$

Note that, from Eq. (8), we only need to know those ρ_{mn} for which both S_m and S_n are nonvanishing. If there exists a subset of the pair eigenstates for which the S_n vanish, then inspection of Eq. (10) shows that the ρ_{mn} divide into three noncombining sets: those for which (i) both $|n\rangle$ and $|m\rangle$ have nonvanishing singlet amplitudes, (ii) one of these states has some singlet component and the other does not, and (iii) neither state has any singlet component. This situation arises in the present problem because the pair spin Hamiltonian (3) is invariant under exchange of the two triplets. As a consequence the pair eigenstates will be either even or odd under this operation. The even states will in general be singlet-quintet mixtures while the odd states will be pure triplets. It is thus possible to eliminate the three triplet-pair states at the outset and deal only with the six remaining singlet-quintet states.

Even with this simplification, solution of Eq. (10) for the ρ_{mn} is a problem for a computer. However, there are two limiting cases in which explicit solutions can be obtained. These are the case of no near-degeneracies among the pair states and the high-field limit in which only two states have singlet components.

C. Case of No Near-Degeneracies

If no two levels are close compared to their natural widths (given by k_{-1}), i.e., if $\omega_{mn}\gg 1$ for $m\neq n$, then it follows from Eq. (10) that the density matrix is approximately diagonal with elements given by

$$\rho_{nn}=\alpha/(1+k|S_n|^2). \quad (11)$$

This yields for the annihilation rate constant

$$\gamma=\tfrac{1}{9}k_1k\sum_n\frac{|S_n|^2}{1+k|S_n|^2}, \quad (12)$$

in agreement with the result obtained earlier in Ref. 5.

D. High-Field Limit: Level-Crossing Resonances

In the high-field limit, i.e., when the Zeeman splitting is much larger than the zero-field splitting so that the latter can be treated by first-order perturbation theory, the spin states become quantized along the applied field. In this basis, the singlet pair state is

$$|S\rangle=3^{-1/2}(|0,0\rangle-|+1,-1\rangle-|-1,+1\rangle), \quad (13)$$

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[11] H. Sternlicht and H. M. McConnell, J. Chem. Phys. 35, 1793 (1961).

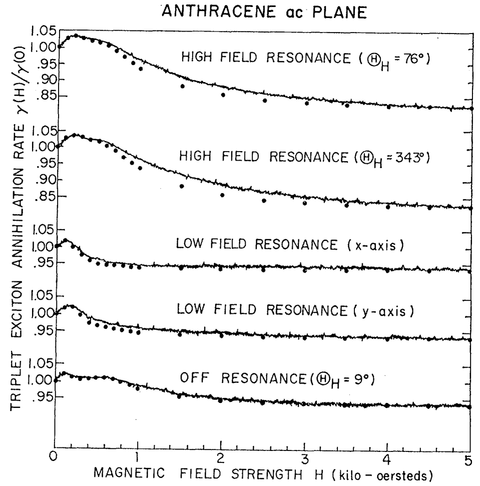

FIG. 2. Experimental measurements and theoretical calculations (dots) of the field dependence of the annihilation rate for several representative field directions Θ_H in the *ac* plane. The x and y axes are at $\Theta_H=29.5°$ and $299.5°$, respectively.

where the indices on the right-hand side refer to the spin quantum numbers of the individual triplets. Thus, there are only two (symmetric) eigenstates of the pair spin Hamiltonian (3) which have a singlet component. These will be designated

$$|0\rangle=|00\rangle,$$
$$|1\rangle=2^{-1/2}(|+1,-1\rangle+|-1,+1\rangle). \qquad (14)$$

The energies of these states are

$$E_0=2(D-E)\cos^2\alpha+2(D+E)\cos^2\beta,$$
$$E_1=D(1+\cos^2\gamma)+E(\cos^2\alpha-\cos^2\beta), \qquad (15)$$

where α, β, and γ are the angles made by $\mathbf{H}$ with the x, y, and z axes, respectively, of the fine-structure tensor, and the singlet amplitudes are

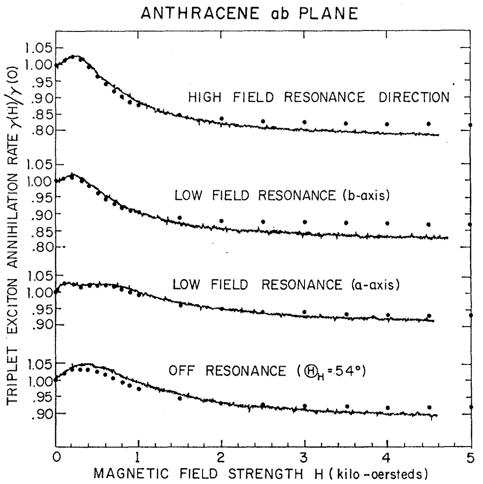

FIG. 3. Experimental measurements and theoretical calculations (dots) of the field dependence of the annihilation rate for several representative field directions Θ_H in the *ab* plane. The b axis is at $\Theta_H=0°$, and the high-field resonance direction at $\Theta_H=23.5°$.

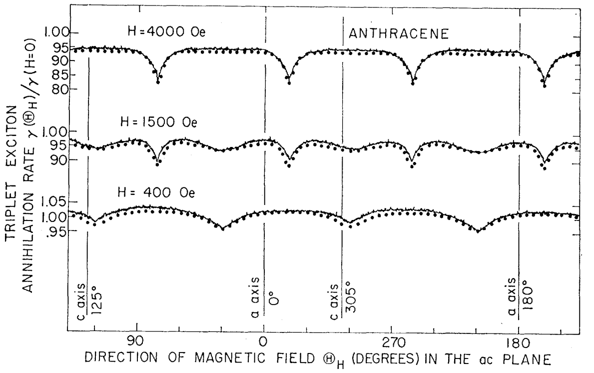

FIG. 4. Experimental measurements and theoretical calculations (dots) of the anisotropy of the annihilation rate in the *ac* plane for three magnetic field strengths. The high-field resonances are evident at 4000 Oe and the low-field resonances at 400 Oe. At 1500 Oe, both sets of resonances coexist. The low-field resonance directions are the directions of the x and y principal axes of the fine-structure tensor.

$$S_0=3^{-1/2}, \quad S_1=(\tfrac{2}{3})^{1/2}. \qquad (16)$$

Solution of Eq. (10) for the steady-state 2×2 density matrix formed from these states involves straightforward but tedious algebra. The result for the annihilation rate is

$$\gamma(\omega)=\gamma(\infty)-\frac{\gamma(\infty)-\gamma(0)}{1+\omega^2/\Delta^2}, \qquad (17)$$

where $\omega=(E_0-E_1)/k_{-1}$, and $\gamma(0)$ and $\gamma(\infty)$, the rates exactly at resonance and far from resonance, respectively, are given by

$$\gamma(0)=\tfrac{1}{9}k_1[k/(1+k)], \qquad (18)$$

$$\gamma(\infty)=\tfrac{1}{9}k_1k\left(\frac{\frac{1}{3}}{1+\frac{1}{3}k}+\frac{\frac{2}{3}}{1+\frac{2}{3}k}\right). \qquad (19)$$

The width Δ is given by

$$\Delta^2=\frac{(1+k)(1+\frac{1}{2}k)^2}{(1+\frac{1}{3}k)(1+\frac{2}{3}k)}. \qquad (20)$$

Note that Eq. (18) for $\gamma(0)$ could have been obtained from Eq. (12) using (13) as the basis state. [The other linearly independent combination of the states (14) is a pure quintet.] Similarly, $\gamma(\infty)$ can be obtained from (12) using (14) as basis states. This illustrates the remark made earlier that a description in terms of a diagonal density matrix and the consequent expression (12) for γ is valid whenever there are no near-degeneracies and when exact degeneracies exist. Of course, the full density-matrix description is required to derive the line-shape function given by Eq. (17).

IV. EXPERIMENTAL RESULTS: COMPARISON WITH THEORY

Experimental measurements of the field dependence of the annihilation rate for several representative field directions in the *ac* plane are shown in Fig. 2. Figure 3 gives similar results for the *ab* plane. The experimental results are shown by the solid lines in these figures and in all cases have been normalized to $\gamma(0)$, the zero-field value. The principal qualitative features of the field dependence of γ are an increase at low fields, a maximum at about 200 Oe, and a decrease at higher fields to a value below that at zero field. In most directions a second maximum or a shoulder appears around 600 Oe. There exist particular field directions for which the high-field decrease in γ is markedly enhanced. This is shown in more detail in Figs. 4 and 5, which show measurements of the anisotropy of the magnetic effect for three different field strengths as the field is rotated in the *ac* and *ab* planes of the crystal, respectively. The high-field resonances appear quite clearly at 4000 Oe. At 300 or 400 Oe a set of resonances appears at directions which exactly bisect the high-field resonance directions. At intermediate fields, the two sets of resonances coexist.

In order to perform quantitative calculations on the basis of the theory presented in Sec. III, it is necessary to fix the values of four parameters. These are the fine-structure splitting parameters D and E of Eq. (3) and the rate constants k_{-1} and k_2 appearing in Eq. (2). The rate constant k_1 is not required as it is eliminated by the normalization of the experimental data. In addition to values for these parameters, the directions of the principal axes of the fine-structure tensor are also required. Because of the monoclinic symmetry of the anthracene crystal, the b axis of the crystal will be a principal axis of the averaged fine-structure tensor which we shall choose as the z axis. The x and y axes thus lie in the *ac* plane, but their orientation within this plane is not determined by symmetry and depends on the specific values of the fine-structure parameters.

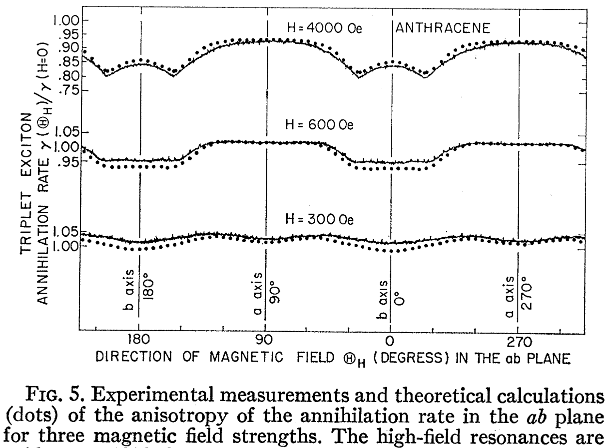

FIG. 5. Experimental measurements and theoretical calculations (dots) of the anisotropy of the annihilation rate in the *ab* plane for three magnetic field strengths. The high-field resonances are evident at 4000 Oe and the low-field resonances at 300 Oe. At 600 Oe both sets of resonances coexist. The b axis is the z principal axis of the fine-structure tensor.

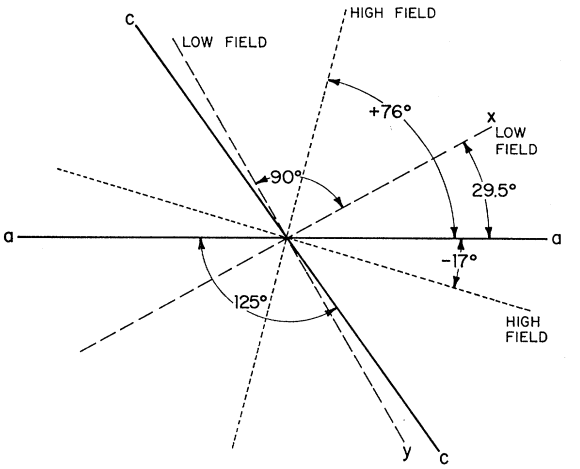

FIG. 6. Resonance directions of the magnetic field in the *ac* plane of anthracene where the high- and low-field level-crossing resonances occur.

The positions of the high-field resonances depend only on the ratio D/E, whose value can thus be fixed immediately. The resonance condition [cf. Eq. (15)] is $E_0=E_1$. If the field is in the *ac* plane so that $\cos\gamma=0$ and $\cos\beta=\sin\alpha$, the angle α_0, at which resonance occurs, is determined by

$$\cos 2\alpha_0=D/3E. \tag{21}$$

The resonances will thus occur at angles at $\pm\alpha_0$ (with respect to the x axis) and their angular separation is $2\alpha_0$. Taking the experimental value of the separation to be 93°±1° yields $D/E=-0.16\pm0.05$. This may be compared with a value of -0.18 ± 0.04 obtained for this same ratio by ESR measurements.[12] The high-field

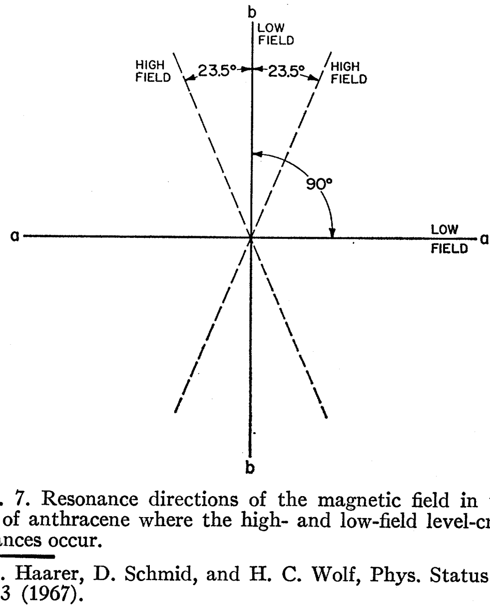

FIG. 7. Resonance directions of the magnetic field in the *ab* plane of anthracene where the high- and low-field level-crossing resonances occur.

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[12] D. Haarer, D. Schmid, and H. C. Wolf, Phys. Status Solidi 23, 633 (1967).

resonance measurements also determine the orientation of the x and y axes with respect to the crystallographic a axis, since the x axis bisects the two high-field resonances. Experimentally these lie at $+76°$ and $-17°$ with respect to the a axis, and hence the x axis is at $+29.5°\pm1.5°$ as shown in Fig. 6. (The ESR measurements[12] place the x axis at $+27.4°$ with respect to a.)

As a consistency check, the above value for D/E can be used to calculate the expected high-field resonance directions in the ab plane. The predicted directions are at $\beta=23.2°$, which may be compared with the experimental values of $\beta=23.5°$. The resonance directions in the ab plane are shown in Fig. 7.

An approximate value for the parameter $k=k_2/k_{-1}$ can be obtained from the high-field value of $\gamma(H)/\gamma(0)$ in a direction off of resonance. The value obtained will be approximate since we will assume that Eq. (12) is a valid approximation under these conditions as well as at zero field. This amounts to the assumption that $k_{-1}\ll E$, which, as will be shown shortly, is reasonably well fulfilled. We choose to determine the value of k from measurements in an off-resonance direction rather than on-resonance as was done in Ref. 5, since the experimental results in such directions should be relatively immune to possible field inhomogeneity or crystalline imperfections which would serve to broaden and reduce the apparent magnitudes of the resonances and, in addition, any inadequacies in the theory would be expected to show up most strongly at the resonances.

To calculate $\gamma(0)$ from Eq. (12), we require the zero-field eigenfunctions of the single-particle fine-structure Hamiltonian, which are[13]

$$\begin{aligned}|x\rangle&=2^{-1/2}(|-1\rangle-|+1\rangle)\,,\\|y\rangle&=i2^{-1/2}(|-1\rangle+|+1\rangle)\,,\\|z\rangle&=|0\rangle\,,\end{aligned}\tag{22}$$

where the axis of quantization is the z axis of the fine-structure tensor. In terms of these single-particle states the singlet-pair state is

$$|S\rangle=3^{-1/2}(|xx\rangle+|yy\rangle+|zz\rangle)\,.\tag{23}$$

Hence, at zero field, there are three pair states which have equal nonvanishing singlet amplitudes. Equation (12) then gives for the zero-field annihilation rate

$$\gamma(0)=\tfrac{1}{9}k_1k/(1+\tfrac{1}{3}k)\,.\tag{24}$$

Combining this with Eq. (19) for the high-field, off-resonance value of γ gives

$$\gamma_{\mathrm{off}}(\infty)/\gamma(0)=[1+(4/9)k]/(1+\tfrac{2}{3}k)\,.\tag{25}$$

The experimental value for this ratio is 0.930 ± 0.005, which gives $k=0.40\pm0.04$.

Having determined the ratios D/E and k_2/k_{-1}, we now need the absolute value of one member of each ratio. These have been obtained by calculating field-dependence curves from the solution of Eq. (10) and adjusting E and k_{-1} empirically to give the best fit to the experimental data. The width of the calculated high-field resonance line is quite sensitive to the value of k_{-1}, which was therefore adjusted to give the experimental line width. The value of E was found from the position of the low-field peak in the field-dependence curves (Figs. 2 and 3); the field value at which this peak occurs varies linearly with E.

The parameter values which result from this curve-fitting procedure are the following:

$$\begin{aligned}&D=-56\pm10\ \mathrm{Oe}\,, && E=350\pm30\ \mathrm{Oe}\,,\\&k_{-1}=(2.8\pm0.3)\times10^9\ \mathrm{sec}^{-1}\,, && k_2=(1.1\pm0.1)\times10^9\ \mathrm{sec}^{-1}\,.\end{aligned}$$

For comparison, the ESR values of D and E are -62 ± 15 Oe and 350 ± 20 Oe, respectively.[12] Even though the condition $k_{-1}\ll E$ is not too well fulfilled, it was found that the value 0.4 for k, determined from use of the approximate solution (12), still gives the best fit to the data when the exact solutions to Eq. (10) are used.

The results of the calculations with these values of the parameters are shown along with the experimental results in Figs. 2–5. The qualitative agreement is quite satisfactory in that the structure in the field-dependence curves, such as the existence of double maxima at low fields, as well as the structure in the anisotropy data, is satisfactorily reproduced. It is particularly satisfying that the existence of this structure does not depend on the particular values assigned to the parameters. Variations in the parameter values merely alter the amplitudes of the field effects.

As indicated by the errors assigned to the parameters above, variation by ±10% produces about an equally good quantitative fit to the experimental data. It was not possible to find a set of values which would yield complete quantitative agreement within experimental error. This is doubtless a result of the oversimplified model employed. A more elaborate theory of the annihilation process in which the spatial as well as the spin degrees of freedom of the triplet exciton are taken into account and which yields considerably improved quantitative agreement with the magnetic field data has recently been developed by Suna.[14]

ACKNOWLEDGMENTS

We express our appreciation to Dr. A. Suna for many helpful discussions and to Dr. G. J. Sloan for the crystals which he provided.

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