Magnetic effects on delayed fluorescence in naphthalene crystals at low and high triplet exciton densities

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(Received 30 December 1975)

We have measured the magnetic effects on the triplet exciton annihilation in naphthalene crystals at low and at high exciton densities. At high triplet densities the magnetic effects on delayed fluorescence intensity cannot be explained by the current theories on triplet exciton interactions in molecular solids. From the magnetic field anisotropy of the delayed fluorescence intensity at low triplet densities we conclude that in naphthalene the influence of spin-lattice relaxation on the kinematics of triplet exciton annihilation is not negligible. This implies that the exciton diffusion in this material is almost two dimensional, with the anisotropy of more than 1000 to 1.

I. INTRODUCTION

It is a well-known fact that in aromatic crystals the mutual annihilation of triplet excitons can lead to singlet excitons which decay with the emission of the so-called delayed fluorescence. Johnson *et al.*[1] discovered that the triplet annihilation process depends on the magnitude of a magnetic field and its direction relative to the crystallographic axes. This is the case even at room temperature and at low fields, where the Zeeman splitting of the triplet energy levels is much smaller than the thermal energy $k_B T$, so that spin polarization is negligible. The theoretical explanation of these effects has been given by Johnson and Merrifield[2] and in a more general form by Suna.[3] A qualitative model has been presented by Avakian.[4] These phenomena were subsequently reviewed by Merrifield[5] and by Swenberg and Geacintov.[6]

The validity of the above-mentioned theories[2,3] on triplet exciton annihilation has been so far verified in detail only in pure anthracene crystals and that only at low triplet densities. The experiments by Port[7] show that the magnetic field modulation of delayed fluorescence in naphthalene has some unexpected features. In the work presented here, the magnetic field effects on triplet annihilation in pure naphthalene are investigated at low and high triplet exciton densities. The experimental results are compared with Suna's theory. From this comparison it is obvious that in naphthalene the experimental findings cannot fully be interpreted with Suna's theory. The discrepancies and their explanations are discussed. In addition, Suna's theory is applied to high triplet exciton densities.

II. EXPERIMENTAL PROCEDURE

Naphthalene of scintillation grade purity was zone refined by circa 100 passes under N_2 atmosphere.

The crystals were grown from the melt by the Bridgman method in vacuum. The final samples of $2 \times 5 \times 5$ mm^3 size were obtained by cutting the ingots with a thread soaked in a solute and by cleaving the crystals along the *ab* plane. The triplet lifetime of the crystals used for the experiments was between 160 and 230 msec.

The experimental setup is shown in Fig. 1. The sample was placed between the pole pieces of a rotatable electromagnet. With the current-regulated power supply it was possible either to adjust the magnetic field at any fixed value up to 8 kG or to sweep the magnetic field strength between 0 and 8 kG. The triplet excitons were excited by the 476.2-nm line of a 1-W krypton laser or by the 476.5-nm line of a 0.5-W argon laser. For obtaining high triplet exciton densities the laser beam was focused onto the crystal by a lens. The delayed fluorescence light emitted from the crystal was deflected by 90° with a totally reflecting quartz prism, which was placed underneath the crystal. In this way the light emitted by the crystal could be separated from the exciting light. Finally the light was led through a 0.5-m-long quartz light guide, a focusing lens, and a suitable filter combination to a magnetically shielded photomultiplier (EMI 6256S).

In order to investigate the triplet annihilation in naphthalene two types of experiments were done: (a) Measurement of the delayed fluorescence intensity ϕ versus magnetic field strength B for several crystal orientations and for different triplet densities. (b) Measurement of the angular dependence of the delayed fluorescence in several given magnetic fields at different triplet densities.

The delayed fluorescence intensity was normalized by measuring

$$\Delta\phi(B) = [\phi(B) - \phi(0)]/\phi(0).$$

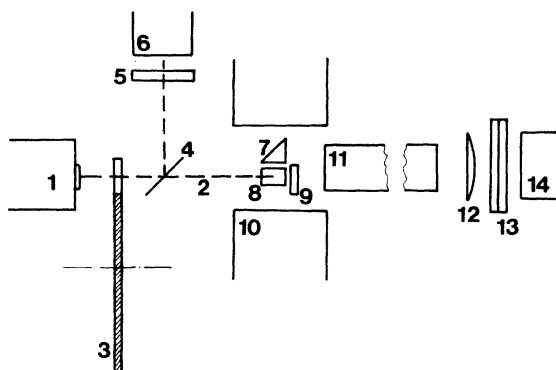For the intensity dependence on magnetic field

FIG. 1. Experimental apparatus. 1 laser, 2 light beam, 3 mechanical chopper, 4 beam splitter, 5 neutral density filter, 6 reference photomultiplier, 7 totally reflecting quartz prism, 8 naphthalene crystal, 9 shielding of the laser beam, 10 pole pieces of the rotatable electromagnet, 11 quartz light guide, 12 lens, 13 filters, 14 photomultiplier.

FIG. 2. Orientation of magnetic field B relative to the crystallographic axes a, b, c^*.

strength, case (a) above, the field was swept from 0 to 8 kG within a few minutes. The photomultiplier output was recorded with a signal averager. The linear sweep of the signal averager was used for driving the magnet power supply. In order to get good statistics an averaging over 16 to 128 sweep runs was necessary, depending on peak values of $\Delta\phi$ for a particular curve. The resolution reached in this way was about 10 G.

For the anisotropy measurements, the magnetic field was periodically switched on and off in order to eliminate the errors due to fluctuation and drifts in the laser intensity and the measuring apparatus. Each particular value of $\Delta\phi$ was obtained by averaging over 1–200 cycles. Each cycle was of 20 sec duration and included two counting periods of 7.5 sec each. The zero value of the magnetic field was adjusted by using an auxiliary coil. The compensation was better than ± 3 G. It was also checked that there was no dependence of the zero-field value of the delayed fluorescence intensity on the mutual orientation of the crystal and the electromagnet.

The magnetic field could be rotated in any plane perpendicular to the crystallographic ab or ac plane. The orientation of the magnetic field B with respect to the crystallographic axes a,b,c^* is represented by the spherical angles ϑ and φ (see Fig. 2). The orientation of the crystal was determined with a polarization microscope. The error of the crystal orientation was smaller than 3 deg when the magnetic field was rotated in a plane perpendicular to the ab plane and smaller than 8 deg when it was rotated in the ab plane.

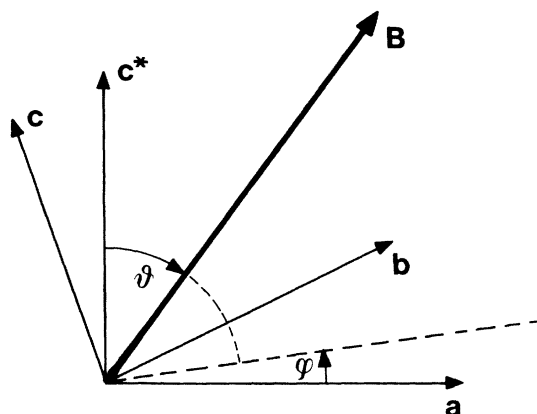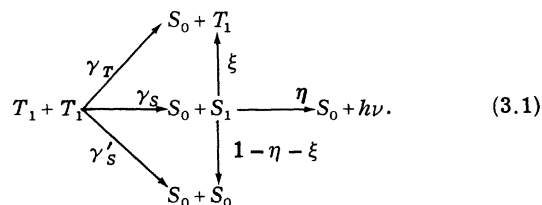At high densities the relative triplet exciton density was determined from the reduced triplet life-

time obtained by transient measurements. At low densities it was measured by using the dependence of the delayed fluorescence intensity on the intensity of the exciting light. The triplet lifetime was determined by transient measurements at low triplet exciton densities. All measurements were performed at room temperature.

III. CALCULATION OF MAGNETIC FIELD EFFECTS ON DELAYED FLUORESCENCE AT HIGH TRIPLET DENSITIES

We shall now examine the magnetic field effects on delayed fluorescence at high triplet densities. By "high triplet densities" we mean here the case in which the bimolecular decay rate dominates the reciprocal triplet lifetime β. The annihilation of two triplet excitons results either in a singlet or a triplet exciton. Owing to this branching the magnitude of the magnetic field effect on the delayed fluorescence depends on the triplet density.[8] For the calculation of the magnetic field effect at arbitrary triplet densities we shall employ the following kinetic scheme for triplet fusion, which is similar to that used by Groff et al.[8]

$$ T_1 + T_1 \begin{array}{c} \nearrow^{\gamma_T} S_0 + T_1 \\ \xleftarrow{\gamma_S} S_0 + S_1 \xrightarrow{\eta} S_0 + h\nu. \\ \searrow_{\gamma_S'} S_0 + S_0 \end{array} \quad \begin{array}{c} \uparrow \xi \\ \downarrow 1 - \eta - \xi \end{array} $$ (3.1)

γ_S, γ_S', and γ_T are annihilation rate constants leading to a singlet exciton S_1, a vibrationally excited ground state S_0, and a triplet exciton T_1, respectively. η is the fluorescence quantum yield, ξ and $1 - \eta - \xi$ are intersystem crossing and internal conversion rates, respectively. We further denote the triplet generation rate by α, and the monomo-

lecular decay rate by β. In the following we shall assume that the rates α, β, ξ, and η are independent of magnetic field[1,9] and of triplet density. In our experiments the triplet generation rate α is given by

$$\alpha = Ai, \tag{3.2}$$

where A is the $S_0 - T_1$ absorption coefficient and i is the intensity of the exciting light.

The kinetic scheme (3.1) implies the following equation for the triplet density n:

$$\dot{n} = \alpha - \beta n - (\gamma_T + \gamma_S + \gamma'_S)n^2 + \tfrac{1}{2}\gamma_T n^2 + \tfrac{1}{2}\xi\gamma_S n^2.$$

This equation can be rewritten

$$\dot{n} = \alpha - \beta n - \gamma_{\text{eff}} n^2, \tag{3.3}$$

where γ_{eff} is the effective bimolecular annihilation rate given by

$$\gamma_{\text{eff}} = \tfrac{1}{2}\gamma_T + (1 - \tfrac{1}{2}\xi)\gamma_S + \gamma'_S. \tag{3.4}$$

Knox and Swenberg[10] have shown that in anthracene γ'_S is negligible.

The measured delayed fluorescence intensity ϕ is given by

$$\phi = \tfrac{1}{2}G\eta\gamma_S n^2, \tag{3.5}$$

where G is the quantum yield of the measuring equipment (geometry factor, photomultiplier quantum yield, etc.).

The dependence of the magnetic field modulation of the delayed fluorescence on the triplet density can be easily explained by a qualitative argument: At low triplet densities, where the exciton lifetime is given by the monomolecular decay β, the intensity of delayed fluorescence is determined only by the annihilation rate γ_S. At high triplet densities, where the steady-state population n is determined primarily by the bimolecular annihilation rate γ_{eff}, which is, according to Eq. (3.4), a function of both γ_S and γ_T, the delayed fluorescence in a magnetic field is governed by the magnetic field dependence of both γ_S and γ_T. By using this dependence of magnetic field effects on triplet density, Groff et al.[8] have measured the ratio $\gamma_S/\gamma_T \approx \tfrac{1}{3}$ for anthracene. This result indicates that the matrix elements for fusion in the singlet and triplet channels must be nearly the same, since the measured ratio is close to the one expected from the statistical weights of the two channels. Furthermore, their results show that in the case of homofusion the fusion via the triplet channel is magnetic field independent, as expected from theoretical considerations[2,5]

In order to examine the influence of the triplet density n on the magnetic field effects, it is convenient to define an easily measurable and dimensionless quantity

$$\sigma = \gamma_{\text{eff}}\, n/\beta, \tag{3.6}$$

which is the ratio of the quadratic and linear terms in Eq. (3.3). Then we express the relative magnetic field dependence of the annihilation rates γ_S, γ'_S, and γ_T by the ratios

$$p(B) = \frac{\gamma_S(B)}{\gamma_S(0)} = \frac{\gamma'_S(B)}{\gamma'_S(0)}, \quad q(B) = \frac{\gamma_T(B)}{\gamma_T(0)}. \tag{3.7}$$

Here we have assumed that γ_S and γ'_S have the same magnetic field dependence. The stationary case of Eq. (3.3) is

$$\gamma_{\text{eff}}\, n^2 + \beta n - \alpha = 0. \tag{3.8}$$

With the definition (3.6) one can rewrite Eq. (3.8) for $B = 0$ as

$$\alpha = \beta n(0)[1 + \sigma(0)]. \tag{3.9}$$

By solving Eq. (3.8), which represents a quadratic equation for n, we obtain

$$n(B) = \{[\beta^2 + 4\alpha\gamma_{\text{eff}}(B)]^{1/2} - \beta\}/2\gamma_{\text{eff}}(B). \tag{3.10}$$

Using Eq. (3.9) we eliminate α from Eq. (3.10). Then we express the ratio $\phi(B)/\phi(0)$ using Eq. (3.5) and eliminate $n(0)$ on the right-hand side of this ratio with the help of Eq. (3.6). In this way we obtain

$$\frac{\phi(B)}{\phi(0)} = p(B)\left(\frac{\{1 + 4r(B)\sigma(0)[1 + \sigma(0)]\}^{1/2} - 1}{2r(B)\sigma(0)}\right)^2,$$
$$\tag{3.11}$$

where

$$r(B) = \gamma_{\text{eff}}(B)/\gamma_{\text{eff}}(0). \tag{3.12}$$

The expression (3.11) shows that at high densities the low-density ratio p is multiplied by a concentration dependent factor. As shown in earlier works,[2,5] for high magnetic fields $p < 1$. At low fields this ratio can be greater than one ($p > 1$). From Eqs. (3.7), (3.4), and (3.12) it is obvious for $q = 1$ that $p > 1$ implies $r > 1$, and that $p < 1$ implies $r < 1$.

If γ_T, γ_S, and γ'_S are independent of triplet density, the following consequences can be deduced from Eq. (3.11):

(a) $\phi(B)/\phi(0)$ is a monotonically decreasing or increasing function of $n \sim \sigma(0)$ for $r > 1$ or $r < 1$, respectively.

(b) In the high-density limit, where $\sigma(0) \gg 1$, the ratio $\phi(B)/\phi(0)$ is given by a simple approximation

$$\phi(B)/\phi(0) \approx p/r. \tag{3.13}$$

(c) If γ_T is independent of magnetic field, the following inequality is valid at arbitrary triplet

density and at high fields B:

$$p < \phi(B)/\phi(0) < p/r < 1. \tag{3.14}$$

(d) In the low-density limit, where $\sigma(0) \ll 1$, we have

$$\phi(B)/\phi(0) \approx p < 1.$$

If we keep the magnetic field B constant and increase the triplet density n, then the ratio $\phi(B)/\phi(0)$ increases monotonically and reaches the limiting value p/r. It is interesting to note that always $p/r < 1$, even in the high-density limit.

In order that $\phi(B)/\phi(0) > 1$ at high densities, as we have measured in naphthalene, it is necessary that γ_T is magnetic field dependent and

$$p > q. \tag{3.15}$$

On the other hand, if for some value of magnetic field B the ratio $\phi(B)/\phi(0)$ is greater than 1, then this ratio decreases monotonically with increasing triplet density and all that has been said about the high-field case (3.14) can be used for this case, provided that all inequalities are reversed.

So far we have not discussed in detail the annihilation rates γ_S and γ_T. For this purpose the triplet annihilation has to be treated more carefully. According to Ref. 3 the mutual annihilation of triplet excitons is described by a hierarchic system of matrix equations. In this system the equation for the one-particle density matrix contains terms with the two-particle density matrix. The equation for the two-particle density matrix contains terms with the three-particle density matrix, etc. If the higher-order terms in each equation are neglected, the first two lowest-order equations form a closed system from which the two-particle density matrix can be calculated. From the two-particle density matrix one can determine the annihilation rates γ_S and γ_T. The higher-order terms in the hierarchic system of equations can be neglected as long as the bimolecular decay rate $\gamma_{\text{eff}} n$ is much smaller than the monomolecular decay rate β, that is at low triplet densities.

In systems with quasi-two-dimensional exciton diffusion β is replaced by the effective monomolecular decay rate[3]

$$\beta_{\text{eff}} = \tfrac{1}{2}\beta + \psi_c^* + (\tfrac{1}{4}\beta^2 + \beta\psi_c^*)^{1/2}, \tag{3.16}$$

where ψ_c^* is the out-of-plane hopping rate. For systems with $\beta \ll \beta_{\text{eff}}$ it is then possible to use Suna's theory[3] as long as

$$\gamma_{\text{eff}} \, n \ll \beta_{\text{eff}} \tag{3.17}$$

even at high triplet densities, that is for $\beta \ll \gamma_{\text{eff}} \, n$. In this case the magnetic field effects on the delayed fluorescence intensity can be calculated ac-

cording to Eq. (3.11). In Sec. IV we shall discuss the validity of the condition (3.17) in naphthalene crystals together with the experimental data.

IV. COMPARISON OF THE EXPERIMENTAL RESULTS WITH SUNA'S THEORY

We shall now compare our experimental data with Suna's theory[3] and with the calculations in Sec. III. In the following $\Delta\phi$ will denote the relative change of the delayed fluorescence intensity in the magnetic field B:

$$\Delta\phi(B) = [\phi(B) - \phi(0)]/\phi(0). \tag{4.1}$$

Figures 3(a)–3(c) show the anisotropy of delayed fluorescence intensity of naphthalene with the magnetic field rotated in the ac plane at 8, 1.75, and 0.4 kG, respectively. All three measurements were performed at a medium triplet exciton density for which $\sigma \approx 1$. We verified that the anisotropy of $\Delta\phi$ between 180° and 360° is the same as between 0 and 180° as is required by crystal symmetry.

The high-field (8 kG) resonance peak at $\vartheta \approx 113.4°$ is shown in detail in Fig. 4 for three different triplet densities. For naphthalene as a whole the anisotropy in the ac plane is quite similar to that observed in anthracene.[2] In Fig. 3 the high-field resonances at $\vartheta \approx 23.0°$ and $\vartheta \approx 113.4°$ can clearly be distinguished from the two low-field resonances at $\vartheta \approx 67.5°$ and $\vartheta \approx 157.5°$. However, there are some unexpected differences compared to anthracene: in naphthalene the two low-field resonances in Fig. 3 are of different shape, and for high fields [Fig. 3(a)] they are not symmetrical with respect to the x and y axes of the crystal fine-structure tensor. By rotating the crystal about all three crystallographic axes by an angle equal to plus or minus the error of crystal orientation we found that crystal misorientation within the error limits cannot be the reason for this asymmetry. As seen in Fig. 3(a) both low-field resonances are still present at fields as high as 8 kG.

With increasing triplet exciton density the anisotropy curves are shifted as a whole to higher values of the relative intensity change $\Delta\phi(B)$. As shown in Fig. 4, the off-resonance value of $\Delta\phi$ becomes even positive at high densities, whereas the shape and angular position of the resonances are practically unchanged. Such a behavior is in contrast with Eq. (3.11).

The angle $2\vartheta_0$ between the two resonance directions in the ac plane ($\varphi = 0°$) has been measured to a high accuracy of about 0.15°. According to Johnson and Merrifield[2] the ratio D^*/E^* of the exciton fine-structure tensor is given by

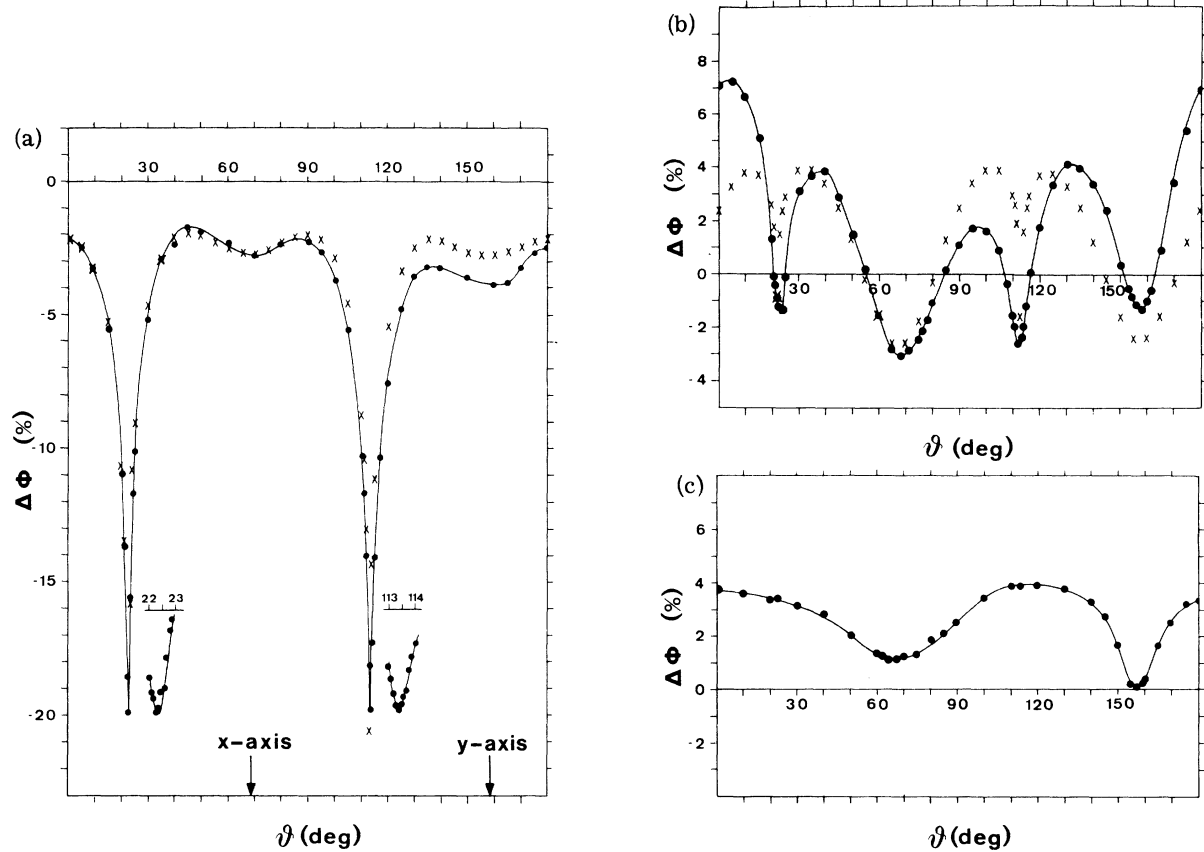$$\cos 2\vartheta_0 = D^*/3E^*. \tag{4.2}$$

FIG. 3. (a) Relative change $\Delta\phi = [\phi(B) - \phi(0)]/\phi(0)$ of delayed fluorescence intensity as a function of the magnetic field orientation ϑ in the ac plane of a naphthalene crystal at a high field of $B = 8$ kG. Relative triplet density is approximately $\sigma \approx 1$. Points: experimental data; crosses: calculated according to Suna's theory with $\lambda_s = 2 \times 10^{11}$ sec^{-1} and $\psi_c* = 1.5 \times 10^5$ sec^{-1}. (b) Delayed fluorescence $\Delta\phi$ measured as a function of the magnetic field orientation ϑ in the ac plane of a naphthalene crystal for medium field $B = 1.75$ kG. Relative triplet density is approximately $\sigma \approx 1$. Points: experimental data; crosses: calculated for $\lambda_s = 2 \times 10^{10}$ sec^{-1} and $\psi_c* = 7 \times 10^5$ sec^{-1}. (c) Measured delayed fluorescence $\Delta\phi$ as a function of the magnetic field orientation ϑ in the ac plane of a naphthalene crystal for a low field of $B = 0.4$ kG. Relative triplet density is approximately $\sigma \approx 1$.

With $\vartheta_0 = 91.1° \pm 0.15°$ this yields

$$D*/E* = -0.058 \pm 0.003,$$

which agrees well with the value

$$D*/E* = -0.059 \pm 0.004$$

obtained by Haarer and Wolf[11] with EPR measurements.

We also calculated $\gamma_s(B)$ with the aid of Suna's theory. The lattice structure of naphthalene,[12] the fine-structure tensor,[11] and the two components D_{aa} and D_{bb} of the diffusion tensor[13] of naphthalene were taken as known quantities. The spin relaxation of the triplet excitons was neglected.

$\gamma_s(B)$ was then determined for the out-of-plane hopping rate ψ_c* and the nearest-neighbor annihilation rate constant λ_s in the singlet channel as parameters. As we can write Eq. (4.1) in the form

$$\Delta\phi = c\gamma_s(B) - 1, \tag{4.3}$$

where c is a constant and independent of B, we get $\Delta\phi$ in arbitrary units. Thus the shift of the whole resonance curve towards higher values of $\Delta\phi$ with increasing triplet density is approximately taken into account as a free adjustable parameter.

As shown in Fig. 3(a), the best correspondence between the calculated and the experimental values at high fields is obtained with $\lambda_s = 2 \times 10^{11}$ sec^{-1} and $\psi_c* = 1.5 \times 10^5$ sec^{-1}. The value of λ_s is almost the same as in anthracene,[3] but ψ_c* is extremely small. It is five orders of magnitude smaller than the hopping rate in the ab plane. This means that the triplet exciton diffusion in naphthalene is practically two dimensional. However, since the quality of the fit is not very sensitive to changes in λ_s and ψ_c*, and since the width of the high-field res-
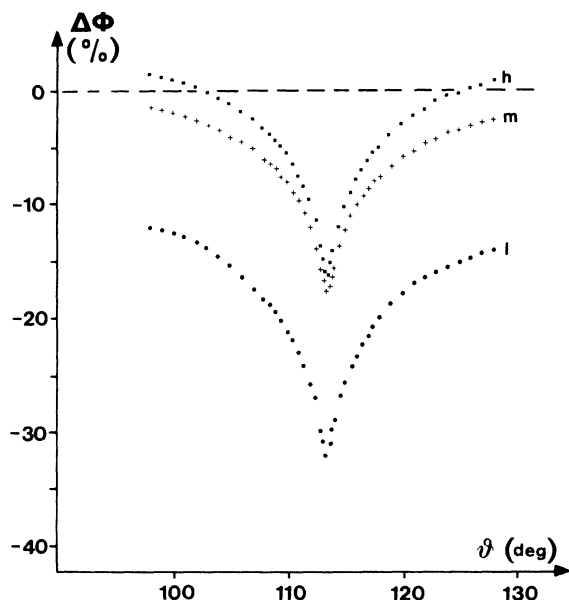
FIG. 4. Detailed line shape of the high-field resonance at $\vartheta = 113.4$ deg in the ac plane of naphthalene measured at three different exciton densities. h: high density with $\sigma \approx 20$, m: medium density with $\sigma \approx 2$, l: low density with $\sigma \approx 0.1$. Magnetic field is $B = 8$ kG.

onances depends strongly on the crystal quality, the error may be quite large. According to Port[7] the linewidth varies between 5 and 10 deg. The resonance curve represented in Fig. 3(a) has a width of approximately 5 deg. Therefore, we expect that in this case the error caused by the crystal imperfections is small. Another source of error is the neglection of the spin relaxation, which will be discussed later.

For intermediate fields only a qualitative agreement is obtained with the same set of parameters. Also with other values of λ_s and $\psi_c{}^*$ the correspondence is not much better, as it is shown in Fig. 3(b). This is most probably due to the neglection of the spin relaxation in our calculation.

The spin relaxation could not be considered in the fit, because the spin relaxation rates are known neither theoretically nor experimentally. The simplest way to take the spin relaxation into account is by replacing the effective decay rate β_{eff} by a new decay rate $\beta_{\text{eff}} + \zeta$, where ζ is the average spin relaxation rate.[3] However, the experimental value of ζ is not known, since ζ is a quantity which is different from the relaxation rates[11] measured with EPR. On the other hand, the theoretical calculation[3] of ζ which is based on the hopping between the inequivalent molecules is not applicable. It has been shown by Reineker[14] that for anthracene this leads to values significantly different from the experimental data.[11] For the magnetic field rotated

in the ac plane the differences are up to 70%. For naphthalene crystals the discrepancies are even larger.[11] To our knowledge there is no quantitative explanation for this behavior. However, for a qualitative discussion of the triplet decay rate β_{eff} $+ \zeta$ we shall approximate ζ by the spin-lattice relaxation rate $1/T_1$ measured by Haarer and Wolf.[11] Since in naphthalene $1/T_1$ is of the order of 10^7 sec^{-1}, which is much larger than the value of β_{eff} $\approx \psi_c{}^*$ obtained in our fit, the spin relaxation may not be neglected.

In the ac plane the relaxation rate $1/T_1$ has a minimum for the magnetic field pointing in the direction of the y axis of the crystal fine-structure tensor.[11] According to Eqs. (40) and (45) in Ref. 3 the low-field resonances become deeper with decreasing triplet decay rate $\beta_{\text{eff}} + \zeta$. This explains why the low-field resonance in Fig. 3(a) in the direction of the y axis is deeper than that at the x axis. The asymmetry of the low-field resonances in Fig. 3(a) could be explained in the same way by including the anisotropy of the spin relaxation.

This additional off-resonance anisotropy caused by the spin relaxation indicates that ζ must be at least of the order of $\psi_c{}^*$. Thus we have an approximate upper limit to $\psi_c{}^*$, which is of the order of 10^7 sec^{-1}. According to Eq. (23) of Ref. 3 this means that the anisotropy of the exciton diffusion in naphthalene is $D_c{}^*{}_c{}^*/D_{aa} \lesssim 10^{-3}$. The theoretical value given by Tiberghien and Delacote[15] $D_c{}^*{}_c{}^*/D_{aa}$ $= 4 \times 10^{-4}$, which is in agreement with our result. This indicates that the triplet diffusion in naphthalene is almost two dimensional.

The positions of the high-field resonances are in agreement with the resonance directions calculated from Eq. (1) in Ref. 16, with the exciton fine-structure tensor from Ref. 11. However, for some directions of the magnetic field in the ab plane or nearly parallel to the ab plane the width of the resonances is much larger than predicted by Suna's theory,[3] as shown in Figs. 5 and 6.

In the measurements of Haarer and Wolf[11] the EPR linewidth becomes, for some orientations of the magnetic field in the ab plane, so large that the determination of relaxation rates is extremely difficult. We assume that for these orientations the spin-relaxation rate is of the order of the exciton hopping rate between the nonequivalent molecules ($\approx 10^{11}$ sec^{-1}). For such large relaxation rates the approximations made by Suna[3] are no longer valid. After each jump the excitonic spin-wave-function relaxes towards the value given by the spin Hamiltonian of the molecule on which the exciton is located, rather than having the value given by the averaged crystal Hamiltonian. In this case the fusion between two excitons may be regarded as a kind of heterofusion and therefore the
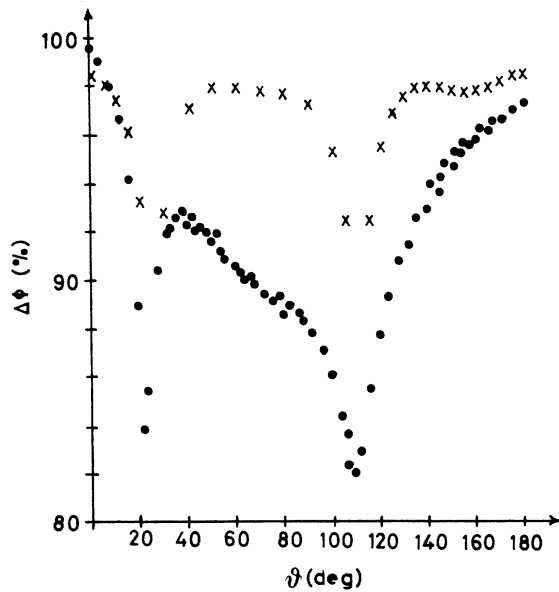
FIG. 5. Delayed fluorescence intensity $\Delta\phi$ as a function of the magnetic field orientation ϑ in the plane φ = 30 deg. Magnetic field is B = 8 kG and the relative triplet density is approximately $\sigma \approx 1$. Points: experimental data from Ref. 17; crosses: calculated for λ_s = 2×10^{11} sec^{-1} and $\psi_c *= 1.5 \times 10^5$ sec^{-1}.

FIG. 6. Delayed fluorescence intensity $\Delta\phi$ as a function of the magnetic field orientation φ in the ab plane of a naphthalene crystal. Magnetic field is B = 8 kG. h: high triplet density $(\sigma \approx 10)$, m: medium triplet density $(\sigma \approx 1)$. Points: experimental data; crosses: calculated for λ_s = 2×10^{11} sec^{-1} and $\psi_c *= 1.5 \times 10^5$ sec^{-1}.

resonance minimum is smeared out.

Figures 7(a)–7(d) show the field dependence of the delayed fluorescence intensity as it is measured for certain magnetic field directions in the ac plane. The magnetic field dependence of $\Delta\phi$ is almost the same in both high-field resonance directions. In Fig. 7(a) one of them at ϑ = 113.4° is displayed. The measurements for the two low-field resonance directions are presented in Figs. 7(b) and 7(c). Finally, Fig. 7(d) shows the magnetic field dependence of $\Delta\phi$ in an off-resonance direction (ϑ = 130°). For each of these orientations the field dependence was measured at three different triplet exciton densities. The original experimental points are shown for medium density. For experimental reasons the measurements for high and low densities had a different scale on the $\Delta\phi$ axes. Therefore, only fitted curves, which had been brought to scale, are shown for high and low densities. The standard deviations of a single measured point from the fitted curve at high and low densities are also shown in Figs. 7(a) to 7(d). At low magnetic fields the three curves coincide.

We can see that, similarly as in Figs. 4 and 6, $\Delta\phi$ is shifted to higher values with increasing triplet density. The magnitude of this shift is approximately proportional to the magnetic field strength.

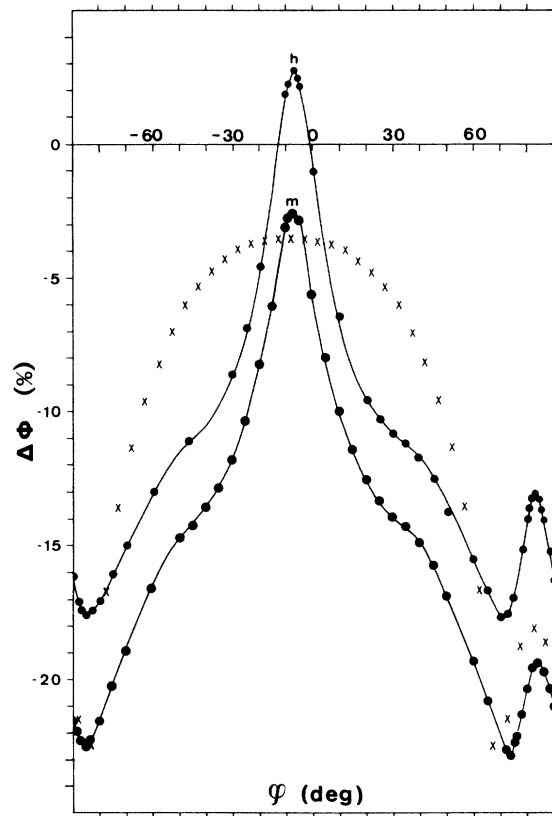The striking change of sign of $\Delta\phi$ from negative

to positive values at high triplet densities [see Fig. 7(d) for B above 3 kG, Fig. 4 for $\vartheta \approx 100$ and 130°, and Fig. 6 for $\varphi \approx 0°$] contradicts the results of Sec. III and therefore cannot be explained by the current theories.[2,3] This behavior is certainly not caused by the magnetic field dependence of γ_T due to spin relaxation. According to Eq. (55b) of Ref. 3 this dependence is weak and has the wrong sign to explain this behavior, since the condition (3.14) is not fulfilled. We estimated that the rise in temperature within the crystal caused by the laser beam during the high-density experiments is of the order of mK which is negligible.

So far it is difficult to say whether the condition (3.17) is fulfilled for naphthalene. However, it is unlikely that the out-of-plane hopping rate $\psi_c *$ is smaller than the bimolecular decay rate $\gamma_{\text{eff}} n$, which was always less than 100 sec^{-1} in our experiments. In this case the condition (3.17) is fulfilled and consequently the higher-order terms in Suna's theory can be neglected.
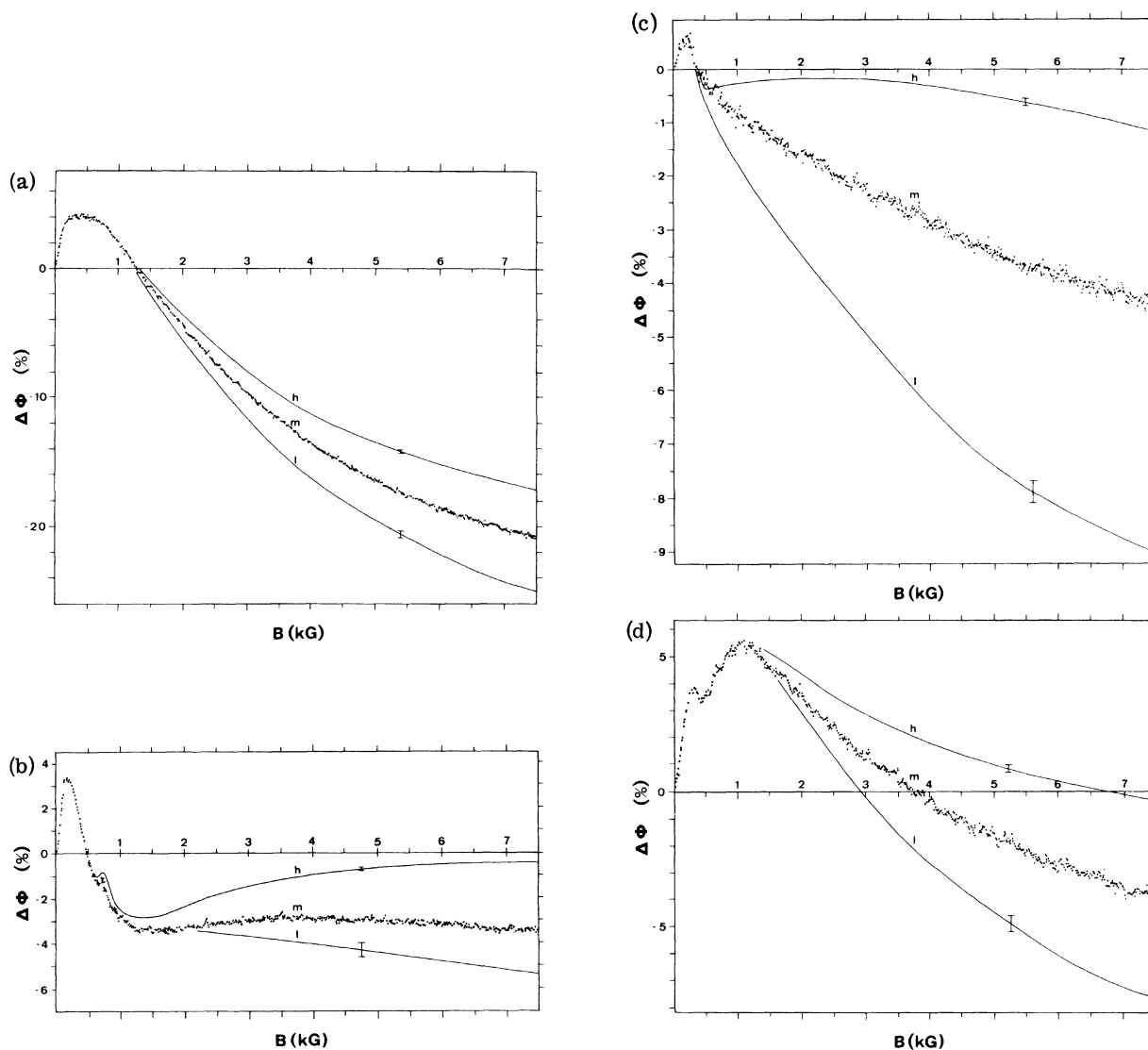
FIG. 7. (a) Relative change $\Delta\phi$ of delayed fluorescence as a function of the magnetic field strength B, measured in the direction $\vartheta = 113.4$ deg (high-field resonance) in the crystallographic ac plane of naphthalene, h: high triplet density ($\sigma \approx 10$), m: medium triplet density ($\sigma \approx 1$), l: low triplet density ($\sigma \approx 0.1$). (b) Relative change $\Delta\phi$ of delayed fluorescence as a function of the magnetic field strength B, measured in the direction $\vartheta = 67.5$ deg (low-field resonance) in the crystallographic ac plane of naphthalene, h: high triplet density ($\sigma \approx 10$), m: medium triplet density ($\sigma \approx 1$), l: low triplet density ($\sigma \approx 0.1$). (c) Relative change $\Delta\phi$ of delayed fluorescence as a function of the magnetic field strength B, measured in the direction $\vartheta = 157.5$ deg (low-field resonance) in the crystallographic ac plane of naphthalene, h: high triplet density ($\sigma \approx 10$), m: medium triplet density ($\sigma \approx 1$), l: low triplet density ($\sigma \approx 0.1$). (d) Relative change $\Delta\phi$ of delayed fluorescence as a function of the magnetic field strength B, measured in the direction $\vartheta = 130$ deg (off resonance) in the crystallographic ac plane of naphthalene, h: high triplet density ($\sigma \approx 10$), m: medium triplet density ($\sigma \approx 1$), l: low triplet density ($\sigma \approx 0.1$).

V. CONCLUSIONS

We have shown that the magnetic effects on de-layed fluorescence intensity in naphthalene crystals cannot be fully explained by the existing theories.[2,3] With increasing triplet density the relative change $\Delta\phi(B)$ of fluorescence intensity is shifted from negative towards positive values in a greater extent than predicted. However, from a semiqualitative comparison of Suna's theory with the experimental results at low triplet densities we conclude that in naphthalene the influence of spin-lattice relaxation on the kinematics of triplet exciton annihilation is not negligible. As a consequence of this an upper limit for the triplet exciton diffusion in the c^* direction is obtained: $D_{c^*c^*} \lesssim 10^{-3} D_{aa}$.

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