

The effect of magnetic fields on photoprocesses in organic solids

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A review is presented of the present status of research on the influence of magnetic fields on photoprocesses in organic solids. This influence manifests itself in a change of the photoconductivity or luminescence of molecular crystals in weak magnetic fields at room temperatures ($\mu\text{H} \ll kT$). The magnetic effects on photoconductivity, luminescence, and photooxidation are considered together with a theoretical interpretation of these effects, based on allowance for the change of the eigenfunctions of the interacting paramagnetic particles in the Zeeman effect.

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1. INTRODUCTION

Studies of the semiconductor properties of organic solids have expanded considerably in recent years. These properties are seen in a broad class of substances which generally belong in their bonding type to the molecular compounds.^[1] Study of the mechanism of generation of free charges in these substances when acted on by light or penetrating radiation gives valuable information, not only for organic-semiconductor physics itself, but also for such branches of science as biology, radiation physics and chemistry, and photochemistry. The most widely studied phenomena are the optical and photoelectric properties of the molecular crystals of anthracene and tetracene, which occupy a place in the physics of organic solids analogous to that of germanium and silicon in the physics of inorganic semiconductors. Figure 1 shows a diagram of the energy levels of the excited and ionized states of anthracene and tetracene. Light absorption gives rise to singlet molecular excitations, which are called molecular excitons (or Frenkel excitons), which can migrate through the crystal. Singlet excitons are deactivated by emission of a quantum of light (fluorescence), by intercombination conversion to triplet molecular excitons, by interaction with impurities, by fission into a pair of triplet excitons, and by other processes. Triplet excitons can decay radiatively (phosphorescence) or without radiation, by quenching by impurities, by mutual annihilation, etc. The lifetime of triplet excitons is several orders of magnitude larger than for singlet excitons. This defines their essential role in processes of migration and conversion of energy in molecular crystals. Production of free charges in molecular crystals requires an energy considerably greater than the energy of excitons. Hence, ionization usually occurs by interaction of excitons with an impurity having a low ionization potential or elevated electron affinity, and also by interaction of excitons with one another. In addition to molecular excited states in molecular crystals, there can exist the so-called polar excited states, or charge-transfer states, which are formed by pairs of charges of opposite signs bound by Coulombic interaction. These states are an analog of the Wannier-Mott type of excitons in inorganic crystals. In one-component molecular crystals, they are usually called charge-transfer excitons. The charge-transfer states lie in energy below the bottom of the conduction band; the position of their lowest level corresponds to localization of an electron and a hole on adjacent molecules.¹⁾ The probability of conversion of a molecular excited state to a charge-transfer state is determined by the overlap of the molecular orbitals of adjacent molecules.

An estimate^[1] of this probability gives the value 10^{-5} . Therefore, polar excitations are practically not manifested in the absorption spectra of molecular crystals. However, their role as an intermediate stage in formation of free electrons and holes from molecular excitons remains substantial. We note that charge-transfer states can also be formed by excitation of impurity molecules (both direct, and by energy transfer from molecules of the crystal). Here a charge of one sign proves to be localized on the impurity.

The most widespread methods of studying absorption and conversion of radiation energy in molecular solids are based on studying luminescence and photoconductivity. The fundamental information on the features of excitation, ionization, energy transfer, and current-carrier transport has been gained with their aid. These features involve, first, the substantial role in these processes of the excited states and their interaction with impurities and with each other, and second, the low mobilities of the current carriers.

Essentially new possibilities of studying processes that accompany excitation of molecular solids have been opened up by the discovery in 1965 of the effect of a magnetic field on the photoconductivity of anthracene and tetracene.^[12] This study was the first in an entire series in which they found and studied the effect of magnetic fields on such non-equilibrium properties of molecular crystals as photoconductivity and luminescence. This was followed by discovery of magnetic effects on the fluorescence of anthracene excited by electron-hole recombination^[13] and singlet-triplet light absorption,^[14] on the fast fluorescence of tetracene,^[15] etc.

We should note that the well-known photomagnetic effects in inorganic semiconductors involve the effect of magnetic fields on the motion of the current carriers (see, e.g.,^[16]). However, it was shown in the very first studies that the effect of a magnetic field on the photoconductivity in organic semiconductors does not involve a change in the mobility of the current carriers upon application of a field.^[12, 17, 18] Actually, given the typical mobilities of current carriers in molecular crystals like anthracene, $u \lesssim 1 \text{ cm}^2/\text{V} \cdot \text{sec}$, the relative change in conductivity associated with deflection of the free charges in a magnetic field $H \approx 10^2 - 10^3$ oersteds amounts to only $\Delta\sigma/\sigma = u^2 H^2 \cdot 10^{-16} = 10^{-12} - 10^{-10}$. The experimental values of $\Delta\sigma/\sigma$ amount to $10^{-1} - 10^{-2}$. Moreover, when magnetic effects involve the effect of the magnetic field on the motion of the current carriers, the size of the effect depends on the relative orientation of the magnetic field and the electric field that is causing the directional

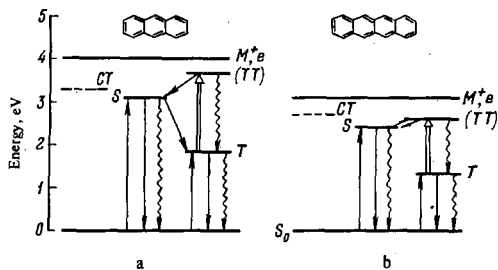


FIG. 1. Schematic diagram of energy levels for crystals of anthracene (a) and tetracene (b). S_0 is the ground state of the crystal; S and T are energy levels of singlet and triplet excitons; (TT) is an energy state formed upon collision of two triplet excitons; CT is the lowest level of charge-transfer states, their energy position not being defined exactly; M^+, e is the ionized state of the crystal; transitions to it result from interactions of excited states with one another and/or with impurities; these transitions are not shown in the diagram. The straight vertical arrows denote transitions between states that involve light absorption, fluorescence, and phosphorescence. The double arrows show triplet-triplet annihilation, and the wavy lines are radiationless transitions.

motion of the current carriers. There is no such dependence on the orientation of the fields in the magnetic effects on molecular crystals. It has also been shown that magnetic fields in molecular crystals do not alter the absorption of the exciting light,^[14,17,19] nor light-emission processes by singlet molecular excitons,^[14] nor the rate of monomolecular decay of excited triplet states.^[14]

It is important to note that the change in populations of the levels of paramagnetic states that are formed upon excitation, which involves their Zeeman splitting, cannot explain the effects observed with the fields that have been used (10^1 – 10^3 Oe). Since the size of this splitting μH (where μ is the Bohr magneton, and H is the magnetic field intensity) is much smaller than the thermal energy kT at room temperature, when $H = 10^1$ – 10^3 Oe, the relative change in the equilibrium populations of the Zeeman sublevels as defined by the ratio $\mu H/kT$ is only 10^{-2} – $10^{-4}\%$. This value is negligibly small in comparison with the experimentally observed variations in the photocurrent or intensity of fluorescence, which are as great as tens of percent.

One can explain the observed magnetic effects with the following general model. The energy of interaction of paramagnetic particles (or excitons) with an external magnetic field of intensity 10^1 – 10^3 Oe is comparable with the energy of spin-spin interaction at distances of the order of intermolecular distances. Hence we might expect in principle that the magnetic field affects spin-dependent processes in which this interaction is manifested. These processes can occur in systems having two particles of non-zero spin, e.g., an electron and a hole, two triplet excitons, a triplet and a radical, etc. If such a system cannot be characterized by its total spin, then an external magnetic field can mix its different spin substates. As we shall show below, it can alter the probabilities of transition of the system from one state to another. Since $\mu H \ll kT$, these changes will be observed only under the condition that the processes being treated occur within a time shorter than the relaxation time of the magnetic moments in the medium.

The number of studies on the effect of magnetic fields on the photoelectric and luminescent properties of molecular crystals and organic semiconductors is currently continuing to grow, and the set of studied problems and objects is expanding. However, the apparent paradox of

the effects that involves the fact that the thermal energy considerably exceeds the energy of magnetic interaction ($\mu H \ll kT$), and the variety of experimental approaches and interpretations applied by different investigators as yet limits widespread application of magnetic methods for studying non-equilibrium processes. Effects analogous to those described in this review have not yet been studied in inorganic semiconductors. However, in principle, they can occur in any medium where an interaction of paramagnetic particles occurs that determines any macroscopic property of the system.

2. EXPERIMENTAL DATA

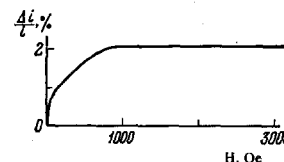
a) **Photoconductivity.** When crystals of condensed aromatic hydrocarbons are illuminated, photoconductivity arises that can have either a surface or a bulk nature, depending on the light-absorption conditions and the arrangement of electrodes on the specimen. In contrast to inorganic semiconductors, molecular crystals practically do not exhibit direct interband light absorption to give rise to free electrons and holes. Hence, the photocurrent is due to motion of charges that are formed by dissociation of molecular excitons. When electrodes are used that can inject electrons or holes into the specimen, the photoconductivity can involve release by light of charges captured in traps.

To characterize the change in photoconductivity in a magnetic field (the magnetic effect), people use the value of the relative change $\Delta i/i$ of the photocurrent. Different types of magnetic effects are discussed below.

1) **The positive magnetic effect.** This effect was first found in studying anthracene and tetracene,^[12] and it consists in a steady-state increase in photocurrent upon applying a d.c. magnetic field to the specimen. The effect is observed in surface^[12,20-26] and bulk^[12,20,21,26-30] conductivity of thin films and in the surface photoconductivity of anthracene crystals.^[12,18,20,21] The size of the positive effect for all these cases amounts to 1–4% in fields of 1–2 Oe at room temperature. It does not depend on the relative orientation of the magnetic field and the specimen, on the intensity of the exciting light, nor on the voltage on the electrodes.^[12,18] Figure 2 shows a typical relation between $\Delta i/i$ and the magnetic field intensity H. As a rule, saturation of $\Delta i/i$ as a function of H sets in at fields of 200–1000 Oe. The positive magnetic effect has been studied in greatest detail in films of tetracene.

It has been shown in^[24,28,30] that the relative size of the positive magnetic effect in tetracene films does not depend on the wavelength of the light in the singlet-singlet absorption region. The size of $\Delta i/i$ declines, both as we approach the autoionization region,^[31] and at the long-wavelength absorption edge. Temperature-dependences of the positive effect have been studied in^[24,30]; $\Delta i/i$ rises with decreasing temperature, and at $T \approx 150^\circ\text{K}$ it attains a value of $\sim 13\%$ ^[24] (Fig. 3). The conductivity caused by electron irradiation of tetracene films also increases in a magnetic field;^[29] here the $\Delta i/i$ –H relation is the same as with photoexcitation.

FIG. 2. Relation of the relative increase $\Delta i/i$ in photocurrent in a polycrystalline tetracene film (thickness $\approx 10^4 \text{ \AA}$) to the magnetic field strength.^[23]



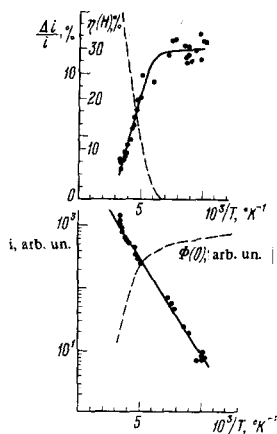


FIG. 3. Temperature-dependences of the photocurrent i and the fluorescence intensity Φ of a tetracene film and their relative increases $\Delta i/i$ and $\eta(H) = \Delta\Phi/\Phi$ brought about by saturation by the magnetic field. The solid lines are i and $\Delta i/i$, and the dotted lines are Φ and η . [24,68]

In the model^[20] currently used to explain the positive magnetic effect, the magnetic field affects the lifetime of a pair of interacting charges, or so-called charge-transfer exciton. According to^[20], the change in the mean lifetime of charge-transfer excitons in a magnetic field alters their probability of dissociation by an impurity, and hence it alters the rate of production of current carriers. Magnetically sensitive charge-transfer states can also be produced by excitation of impurity centers.^[30] The essential assumption in the model of^[20] is that the lifetimes for singlet and triplet charge-transfer states differ.

In principle, the photocurrent in a magnetic field could be increased also by "magnetically sensitive" processes involving molecular excitons such as triplet-triplet annihilation,^[14] interaction of a triplet exciton with a paramagnetic impurity,^[32] etc., which will be treated in greater detail in later sections. It has turned out to be possible to estimate their relative role in photoconductivity because each of the mechanisms gives rise to a specific dependence of the photocurrent on the magnetic field intensity. This approach has been applied in^[24,26] in studying the nature of the positive magnetic effect in tetracene. Study of the shape of the $\Delta i/i-H$ curves (see Fig. 2) and $\Delta\Phi/\Phi-H$ curves (see Fig. 3; Φ and $\Delta\Phi$ are the intensity of fluorescence and its variation in a magnetic field) showed that, in a surface-type cell, current carriers are not produced from the singlet excitations responsible for fluorescence, nor from doublet-triplet (TT) nor from triplet states.

A suitable method of studying different mechanisms of generation of current carriers and the nature of the positive magnetic effect is to study the changes of photoconductivity when a layer of an electron-acceptor is deposited on the surface of the specimen. This acceptor was chloranil in^[25,26]. Studies of the behavior of the surface photoconductivity of tetracene films in a magnetic field^[25,26] showed that the increase in photocurrent when chloranil is evaporated onto tetracene involves generation of free charges by interaction of triplet excitons with molecules of the acceptor. The electron affinity of chloranil (2.5 eV^[33]) makes possible hole-generation by tetracene triplet states. Interesting information under these conditions is furnished by studying the magnetic effect on the photocurrent^[25,26] (Fig. 4). This effect is a superposition of the positive effect with an effect that involves the variation of the concentration of triplet excitons in a magnetic field.^[34-36] One can vary the latter by varying the contribution of triplets to the mechanism

of generation of free charges by changing the spectral composition of the light, the temperature, etc.^[25,26]

One gets analogous results when oxygen instead of chloranil interacts with the surface of tetracene. As we know, photooxidation products are formed here, and they are centers for dissociation of molecular excitons. This increases the photocurrent by 1-2 orders of magnitude as compared with the "vacuum" value.^[37-39] The positive magnetic effect retains all its features in photooxidized specimens as well.^[40,41] "Thick" specimens ($d > l_T$, where l_T is the diffusion length of triplet excitons) show a decline in $\Delta i/i$ with increasing H .^[25,41] Apparently, it involves diffusion to the surface of triplets, whose concentration is reduced in fields $H > 500$ Oe.^[34-36]

In measurements of bulk conductivity of tetracene films, the positive magnetic effect at room temperature is masked by an effect involving variation in the magnetic field of the concentration of singlet molecular excitons^[26,30] (Fig. 5). This is caused by the fact that current carriers are generated at the electrodes under these conditions by diffusion to them of singlet excitons, which also give rise to fluorescence. However, the role of the process involving singlets decreases as the temperature is reduced, and the "pure" positive magnetic effect is again manifested.^[26,30]

The results given above show that superposed effects can always be separated. Here a positive magnetic effect is observed whenever generation of current carriers involves dissociation of excitons at an impurity. This effect cannot be associated with variations in a magnetic field of the concentration of molecular excitons or of the rate constants of their interactions with one another or with impurities.

Hence, we must seek possibilities of explaining the positive magnetic effect by magnetically sensitive processes that lead to ionization. Since magnetically sensitive photoconductivity sets in at the singlet-singlet absorption threshold, the appearance of free charges involves transfer of energy of singlet excitations to a center which this energy suffices to ionize. The hypothesis ascribing the magnetic effect to charge-transfer excitons^[20] assumes either that: 1) The energy transport itself to these centers results from capture of one of the

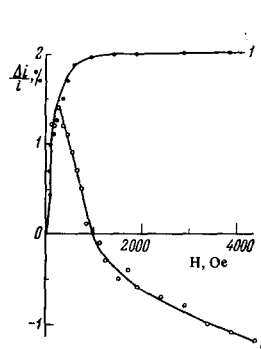


FIG. 4

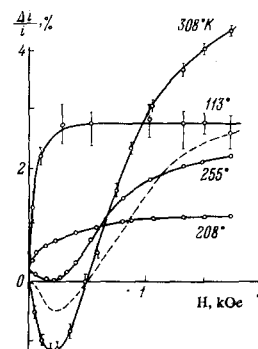


FIG. 5

FIG. 4. Relation of the relative increase $\Delta i/i$ in the photocurrent in a tetracene surface cell to the magnetic field intensity. 1—pure tetracene, 2—with chloranil evaporated onto the surface of the specimen. [26]

FIG. 5. The relations of the relative variations $\Delta i/i$ in the photocurrent to the magnetic field intensity found at different temperatures. Tetracene, sandwich-type cell. The dotted curve shows the variation in fluorescence intensity in a magnetic field at room temperature. [30]

charges of the exciton by the center, the exciton then dissociating; or 2) a charge-transfer state is formed at the impurity center. The latter assumption is favored by the magnetic sensitivity of the fluorescence of the excited complexes formed by tetracene and anthracene^[42] (see Sec. 2, Part b).

2) **The negative magnetic effect.** A new type of effect is observed in the bulk photoconductivity of single crystals: a decrease in the photocurrent when a magnetic field is applied.^[18,20,21,26,44-54] In anthracene at room temperature, $\Delta i/i$ can be as large as -15% in fields of 2 kOe. The negative magnetic effect is saturated at larger magnetic fields than the positive effect is: Fig. 6 shows a typical $\Delta i/i-H$ relationship. The value of $\Delta i/i$ depends sharply on the orientation of the magnetic field with respect to the crystallographic axes^[49,53,54] (Fig. 7). A feature of the negative magnetic effect is that it is observed only in the regions where the photocurrent depends quadratically on the voltage V applied to the specimen (Fig. 8) and sublinearly on the light intensity I : $i \sim V^2 I^m$, with $m < 1$ (Fig. 9).^[45] Transition to linear volt- and lux-ampere characteristics of the photocurrent is accompanied by a decrease in the size of $\Delta i/i$.^[45,47] This behavior of $\Delta i/i$ has helped in establishing the mechanism of the negative magnetic effect, which was originally ascribed to the effect of the magnetic field on the lifetime of charge-transfer excitons.^[18,20,21,44-49] However, further studies^[26,50,51,54] have shown that the negative magnetic effect on the photocurrent is due to the decrease in the magnetic field of the rate constant k_{TH} for interaction of triplet molecular excitons with captured charges.^[32] This interaction releases charges from deep traps into the conduction band, and increases the photocurrent.^[57] The photocurrent itself is limited here by the space charge of current carriers of the same sign that are injected into the specimen by the electrode, and their time of stay in the deep traps depends on the light intensity. A theory of these currents, which are called photoamplified, has been developed by Helfrich.^[57,58] Their behavior has been rather well studied experimentally (see, e.g.^[57-61]). Typical characteristics of photoamplified currents are a dependence on the voltage and the light intensity of the form $i \sim V^2 I^{1-(1/l)}$, where $l = T_c/T$, and T_c is the characteristic temperature of the depth distribution of the traps.^[57] The current carriers are injected into the bulk of the specimen with a special electrode or by light, which generates near the surface a considerable concentration of singlet excitons. The latter diffuse to the surface, and produce mobile holes at the boundary with the electrode.^[62,63] Current carriers are released from deep traps in the bulk of the crystal by photons or by molecular excitons that are generated by weakly-absorbed light or by the light of reabsorbed fluorescence.^[60,51,54,64,65] The rate of excitation of holes from the traps into the valence band by triplet molecular excitons considerably exceeds (at least by one order of magnitude) the corresponding rates for singlet excitons and photons, and it does not depend on the means of generating triplets in the bulk of the specimen.

The above-described mechanism of the negative magnetic effect permits us to understand the relationships between $\Delta i/i$ and V and I and their relation to the volt- and lux-ampere characteristics of the specimen. Figures 8 and 9 show typical shapes for these relationships. Transition to linear dependences of i on V and I involves

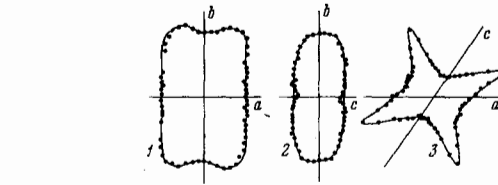
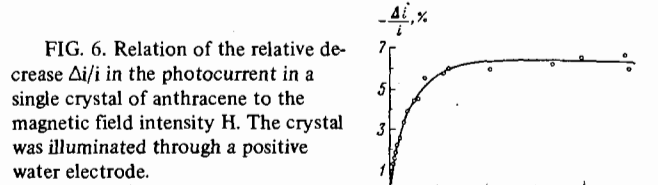


FIG. 7. Angular diagrams of the relative decrease $|\Delta i/i|$ in the photocurrent in a single crystal of anthracene in a magnetic field $H = 3000$ Oe. 1— H in the ab plane, 2—in the bc plane, 3—in the ac plane. The maximum value of $|\Delta i/i| = 13\%$.^[49]

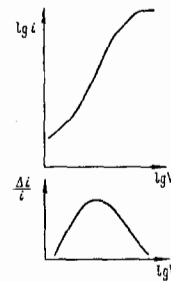


FIG. 8

FIG. 8. Typical relations of the photocurrent i in a single crystal of anthracene and its relative decrease $\Delta i/i$ in a magnetic field to the voltage V applied to the specimen. The magnetic effect is a maximum in the region $i \sim V^2$.

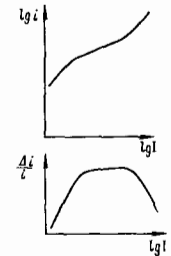


FIG. 9

FIG. 9. Typical relations of the photocurrent i in a single crystal of anthracene and its relative decrease $\Delta i/i$ in a magnetic field to the intensity I of the exciting light. The magnetic effect is a maximum in the region $i \sim I^m$, with $m < 1$.

loss of the limitation of current by the space charge. Here the photocurrent ceases to depend on k_{TH} , and this results in a decrease in $\Delta i/i$. We should especially distinguish the case of large light intensities,^[47,48] where the current limitation by the space charge of captured holes is partially eliminated by the considerable decrease in the lifetime of the current carriers in deep traps. For photoinjecting contacts, the number of current carriers that can be injected into the crystal depends on the light intensity. The number of injected charges is always proportional to the voltage applied to the specimen. Thus, we cannot separate the action of these factors when studying the relations of i and $\Delta i/i$ to the voltage and intensity.

The temperature-dependence of the negative magnetic effect in anthracene has been studied in^[48]. As long as the current remains limited by the space charge, the activation nature of the intercombination transition in anthracene^[66] should not affect the value of $\Delta i/i$. The decline in the size of the magnetic effect with increasing T cannot be explained by a single theory of photoamplified currents alone. Apparently it also arises from a decrease in the spin-lattice relaxation time that leads to an additional doublet-quartet mixing.

The above-described mechanism of the negative magnetic effect has been confirmed by studies of the kinetics

of the photocurrent when the crystal is excited by square-wave pulses of light of duration comparable with the lifetime of triplet excitons.^[26,51] Recording of the shapes of the photocurrent pulses graphically demonstrates the role in photoconductivity of dark injection, of photoinjection, and of bulk generation of triplet excitons.^[26,51] It makes no sense in this case to apply continuous excitation and to record the mean current,^[44] which permits one to study bimolecular processes. This is because the concentration of trapped holes does not depend on the light intensity, but is determined only by the voltage on the specimen. The decline in $\Delta i/i$ with decreasing τ that was observed in^[44] involves the decrease in mean light intensity with increase in the off-duty factor of the pulses.

An approximate expression for the size of the magnetic effect on the photoamplified current has the form

$$\frac{\Delta i}{i} \approx \left(1 - \frac{1}{l}\right) \frac{\Delta k_{T_h}}{k_{T_h}}, \quad (1)$$

Here Δk_{T_h} is the decrease in the rate constant for excitation of trapped charges by triplets in the magnetic field. The maximum value of $\Delta i/i$ that we have observed experimentally is 15%, where $1 - (1/l) = 0.5$. Consequently, the relative change in the rate constant for interaction of a triplet exciton with a trapped hole amounts to 30%.

3) **Sign-change effects.** A magnetic effect on the photocurrent is observed in tetracene in films^[26,27,30] and in single crystals^[54] that changes sign, depending on the magnetic field intensity (see Fig. 5). The effect depends on the relative orientation of the crystal and the magnetic field.^[54] It declines with decreasing temperature, and vanishes at $T \lesssim 200^\circ \text{K}$.^[30] In sandwich-type polycrystalline specimens, this effect is observed simultaneously with the positive effect described above, but they can be separated by using their differing temperature-dependences^[26,30] (see Fig. 5). This effect is observed in single crystals of tetracene excited with strongly absorbed light. When one uses excitation that is uniform throughout the bulk of the crystal, the effect is converted into the negative effect.^[54]

The described effects involve the change in the magnetic field of the steady-state concentration of excitons that dissociate to produce current carriers. For tetracene, these excitons are singlet molecular excitons, whose lifetime is determined by decay into two triplet excitons.^[67] The latter process is magnetically sensitive.^[68,69]

4) **Other magnetic effects.** A number of studies have reported observation of an effect of magnetic fields on photo- and dark conductivity of organic solids. However, they give no data that permit us to arrive at definite conclusions on the nature of these effects. Thus, in^[70] they observed an increase in the electrical conductivity of anthracene by 15–20% in magnetic fields of $\sim 8 \text{ kOe}$. The photoconductivity of copper phthalocyanine increased by 0.5–1.0% in fields of $\sim 8 \text{ kOe}$, with $\Delta i/i \sim H$.^[71] Increase in photo- and dark current in polynuclear aromatic compounds was observed in^[72]; as a rule, the size of the effects was 0.5–2.6% in 2-kOe fields. An increase in a 4-kOe magnetic field of the dark conductivity of solid nitrobenzene, accompanied by a symbatic increase in the dielectric constant, was observed in^[73a]. An increase of up to 1.5% was observed in^[73b] in the photoconductivity of thin, acicular crystals of tetrathio-tetracene in magnetic fields of $\sim 6 \text{ kOe}$.

b) **Luminescence.** 1) **Delayed fluorescence.** Soon after the effect of magnetic fields on photoconductivity had been discovered,^[12] observations also followed on such an effect on the delayed fluorescence (DF) of anthracene.^[13,14] The DF of molecular crystals arises from production of singlet molecular excitons when two triplet excitons collide: $T + T \rightarrow S + S_0$ (T and S are triplet and singlet excitons, and S_0 is the ground state of the molecule). The intensity of delayed fluorescence is proportional to the square of the concentration of triplet excitons: $I_d \sim \gamma n_T^2$. When the triplet excitons are generated by light (directly in the region of the S_0 - T transition or by using intercombination conversion from singlets), the relation of I_d to the intensity I of the exciting light can exhibit two regions. A quadratic region $I_d \rightarrow I^2$ is observed at low excitation levels where the lifetime of the triplets is determined by their monomolecular decay. At high n_T , the lifetime of the triplets is controlled by their mutual annihilation process, which leads to a linear dependence of I_d on I . Triplet excitons can also be generated by recombination of electrons and holes injected into the crystal. Delayed fluorescence is observed here, just as with photoexcitation.

Two different methods have been used in studying the effect of magnetic fields on fluorescence. The first method studies^[13,74,75] the recombination luminescence that arises upon double injection into the specimen of electrons and holes from specially prepared contacts.^[57,76,77] The second method consists in studying the effect of magnetic fields on the delayed fluorescence of anthracene under photoexcitation. Originally these studies were classified into two groups: study of delayed fluorescence in the regions where its intensity depends quadratically^[14,78-83] or linearly^[48,49,84] on the intensity of the exciting light. The interpretation of the effects differed in these regions. However, later studies^[85,86] led to the conclusion that the magnetic effect on the DF of anthracene is always due to the effect of the magnetic field on the rate constant γ for triplet-triplet annihilation. Figure 10 shows the relation of the magnetic effect on the DF of anthracene to the magnetic field intensity. We see that the DF intensity increases in weak fields ($H \lesssim 350 \text{ Oe}$), but declines in stronger fields. The anisotropy of this effect has been studied in^[14,49,78,80,86], and Fig. 11 shows its form. It was shown for the linear region of the I_d - I relation that the size of the magnetic effect practically does not vary over the temperature range 20–100°C.^[84] Its maximum value is of the order of 8%, and it does not depend on the quality of the crystal. Interestingly, the size of the magnetic effect increases twofold as we go from the linear to the quadratic region of the I_d - I relation.

Quenching by a magnetic field of the DF of anthracene at low temperatures (down to liquid-helium temperature) was studied in^[87]. This effect, which is manifest under conditions in which $\mu H \gtrsim kT$, involves unequal populations of the Zeeman sublevels of the triplet excitons. We note that even the low-temperature quenching cannot be explained fully by the change in the populations of the Zeeman sublevels alone.^[87,88]

The effect of magnetic fields on quenching of triplet excitons by radicals and other paramagnetic impurities has been studied by observations of DF in anthracene.^[32] Figure 12 shows the experimental dependences of the lifetime of triplets on the strength and direction of the magnetic field in an irradiated anthracene crystal, as taken from^[32]. It was shown^[32] that the effect is

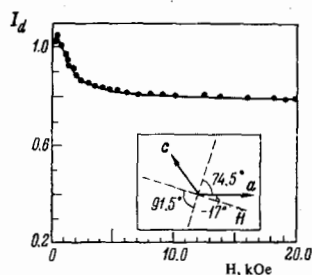


FIG. 10. Relations of the intensity of delayed fluorescence of an anthracene crystal to the magnetic field intensity H . Room temperature; magnetic field oriented in the ac plane as shown in the diagram. The dotted lines show the directions of H at which the size of the magnetic effect on the DF is a maximum. [14]

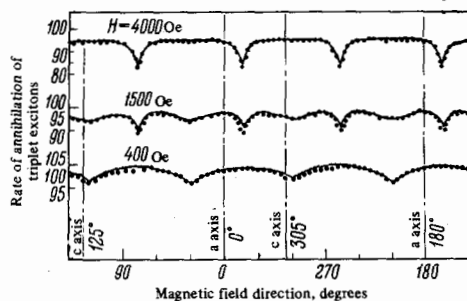


FIG. 11. Anisotropy of the relative variation in the rate constant γ for annihilation of triplet excitons in an anthracene crystal for strong (4000 Oe), weak (400 Oe), and intermediate (1500 Oe) magnetic fields H in the ac plane of the crystal. Solid lines—experimental curves; dots—calculated data. [80]

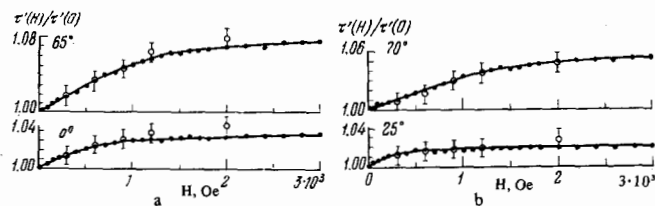


FIG. 12. A typical relation of the lifetime of triplet excitons $\tau'(H)$ (normalized with zero field) in an irradiated anthracene crystal to the magnetic field intensity H . a) Crystal cleaved in the ab plane, dose 4×10^3 rad; $\tau'(0) = 1.55 \times 10^{-3}$ sec; H in the ab plane at directions of 65° (resonance) and 0° with respect to the a axis; b) cleaved in the ac plane, dose 1×10^3 rad; $\tau'(0) = 4.95 \times 10^{-3}$ sec; H in the ac plane at directions of 70° (resonance) and 25° with respect to the a axis. The open circles are direct measurements of the lifetime, and the solid dots are from data on steady-state delayed fluorescence. [32]

due to the decrease in the magnetic field of the rate constant for quenching of triplet excitons by the paramagnetic centers produced upon irradiation.

The effect has also been studied of magnetic fields on the luminescence [89a] and DF of pyrene, [14, 89b] of *Chlorella*, [89c] and 9, 10-diphenylanthracene. [90]

In addition to annihilation of two "identical" triplet excitons, an effect has been found of magnetic fields on the interaction between a free triplet and a triplet captured by a specially introduced impurity. [91] These studies were conducted on anthracene crystals having tetracene as an impurity; the DF of the main substance and of the impurity were observed. It was proposed in [90] that the unusual behavior of the DF intensity of 9, 10-diphenylanthracene in a magnetic field involves the interaction between two triplets that differ in energy by about 1 cm^{-1} .

A considerable decrease (up to 75%) was found in [92] in the delayed fluorescence of anthracene photosensitized by rhodamine B when a magnetic field of 200–300 Oe was applied. The layer of rhodamine B adsorbed on the anthracene crystal, when excited by light of wavelength 680 nm, served as a source of triplets, whose annihilation in the anthracene gave rise to the observed fluorescence. The authors of [92] think that the magnetic effect is caused by the decrease in rate of generation of triplets. The latter are formed in the initial recombination of pairs of charges that had arisen at the surface by interaction of singlet-excited rhodamine B with the anthracene. The charge pairs are charge-transfer states whose probabilities of transition between singlet and triplet states depend on the magnetic field. To supplement the Zeeman term in the spin Hamiltonian, the authors also take account of the hyperfine interaction, which permits one to explain the magnetic effect even when the g factors of the electron and hole are equal. Taking account of the hyperfine interaction has the result that, when the singlet substate is occupied, application of a weak magnetic field that doesn't break the magnetic bond between the electron and the hole causes an increase in the probability of singlet-triplet transition. Stronger fields (above 10 Oe) decrease this probability.

Successful observations of the effect of magnetic fields on fluorescence of aromatic hydrocarbons in the solid phase have stimulated a search for analogous effects in liquids. [93–100] A change in a magnetic field of the DF of anthracene and pyrene dissolved in N,N -dimethylformamide and acetonitrile was observed in [93b, c]. Quenching by a magnetic field of the DF of anthracene dissolved in ethanol was studied in [94]. Use of a pulsed magnetic field made it possible to show that the observed effect, just as in a crystal, involves a decrease upon application of the field in the diffusional rate constant for interaction of two triplet excited molecules of anthracene to form singlet excited molecules. The lack of an increase of I_d in weak fields, which is characteristic of the solid phase, is ascribed to lack of ordered orientation of the interacting triplet molecules. An effect of a magnetic field has also been observed on quenching of triplet anthracene molecules in solution by cations of Würster's blue, [95] and on the electrochemiluminescence (ECL) of some derivatives of anthracene [96] and carbazole. [97a] In [97b, 98], an effect of a magnetic field was observed on the ECL of systems containing anthracene, tetracene, phenanthrene, 9, 10-diphenylanthracene, rubrene, 1, 3, 6, 8-tetraphenylpyrene, and fluoranthene dissolved in N,N -dimethylformamide. The increase in intensity of the ECL was as great as 27% in fields of ~ 7 kOe.

Bard, Faulkner, and their associates [96, 99] have used measurement of sensitivity to a magnetic field of the electrochemiluminescence of oxidation-reduction reactions in liquids as a method for estimating the energy liberated in recombination of ions (see also [97d]). Thus, when this energy suffices for creation of a singlet excitation upon recombination, and the ECL arises from its deactivation, there is no magnetic effect on the ECL. Direct production of a singlet is impossible for systems whose energy of recombination is small. Then recombination of ions gives only triplet excitations, whose annihilation gives rise to the ECL. Naturally, an effect of a magnetic field on the intensity of ECL is observed in these systems.

The DF in a magnetic field of 1,2-benzanthracene dissolved in ethyl alcohol has been studied in^[100]. In this substance, the delayed fluorescence and phosphorescence from the monomer and the dimer are spectrally well separated. This made it possible to study the magnetic effects for each of the emissions, and to establish the mechanism of production of the monomer and dimer delayed fluorescence. The dependences on H of the magnetic effects on the monomer and dimer DF differ. The results obtained in this study on partial polarization of fluorescence at low temperatures and on the relationships between the magnetic effect and the polarization are of interest.

2) **Fast fluorescence.** It was shown in^[101] that the fast component of the recombination luminescence of anthracene crystals that arises upon double injection of charges into the specimen is sensitive to a magnetic field. Here the magnetic effect on the delayed component of the luminescence behaves in the same way as in photoexcitation, and it is due to the effect of the field on the rate constant for annihilation of triplets that are formed by charge recombination.^[57] The anisotropies of the magnetic effects on the fast and delayed components of the recombination luminescence of anthracene are the same, while the signs of the effects are always opposite. The size of the effect on the fast component is about 30 times smaller than on the delayed component. Thus, e.g., $\Delta\Phi/\Phi \lesssim 0.8\%$ in fields of ~ 10 kOe.^[101] The authors of^[101] ascribe the sensitivity to a magnetic field of the fast component of the recombination luminescence of anthracene to the fact that recombination of electrons and holes gives rise to charge-transfer excitons, which can transform both into double-triplet (TT) states and into singlet molecular excitons. Here the relation of the magnetic effect on the fast component of the fluorescence to the orientation and intensity of the magnetic field should be the same as for the effect on the delayed component. The signs of these magnetic effects are opposite, and their relative values depend on the relation between the probabilities of transition of charge-transfer excitons to the singlet or to the double-triplet states.

However, the results of^[102] force us to doubt the necessity of introducing charge-transfer excitons into the mechanism proposed in^[101]. In these studies, charge pairs were generated by ultraviolet light having energy quanta sufficient for exciting the higher singlet states, which have an appreciable probability of autoionization. Under these conditions, the fast component of the fluorescence depends on the magnetic field^[102] in the same way as in double injection.^[101] We note that when anthracene is excited with light having energy quanta close to the energy of the first excited state (i.e., when the probability of autoionization is exceedingly small), there is no magnetic effect on the fast component of the fluorescence.^[15, 102] The threshold energy for appearance of this effect equals the energy of the double-triplet state. Low-temperature measurements of the magnetic effect on the fast component of the fluorescence of anthracene and tetracene with photoexcitation showed that one cannot explain this effect by fission of charge-transfer excitons into two triplets, and the transition $S \rightarrow (TT)$ apparently occurs via the higher vibrational levels of the first electronic excited state.^[102] The authors of^[102] report that the sensitivity of the fast component of the fluorescence of anthracene to a magnetic field is greatest (+2.5% in a 4-kOe field) when the crystal is excited by electron bombardment.

In tetracene, a magnetic effect on the fast component of fluorescence was first observed in^[15]. Its size was as great as 30–40% in fields of 2000–3000 Oe^[68, 69] (Fig. 13). The effect on the fast component declines at lower temperatures, although the fluorescence intensity rises (see Fig. 3), while the magnetic effect on the DF increases. The anisotropy of the magnetic effects on the fast and slow components of the fluorescence of tetracene has been measured at different temperatures in^[35, 36]. Studies of magnetic effects on the fluorescence of tetracene have shown that the effect on the fast component involves the high probability of fission of a singlet into two triplets,^[34–36, 68, 69] as had previously been predicted.^[67] The temperature-dependences of the magnetic effects involve the activational nature of the transition $S + S_0 \rightarrow (TT)$.

A magnetic field can also affect the process of fission of a singlet exciton into two different triplet excitons.^[103] This conclusion follows from studying the fluorescence of tetracene crystals containing an impurity of pentacene.^[103]

The fast fluorescence observed upon exciting tetracene that had been deposited from a benzene solution onto the surface of an anthracene crystal was studied in^[42]. The excitation spectrum of this fluorescence matches the absorption spectrum of tetracene. However, the fluorescence spectrum itself differs from the fluorescence spectrum of a solid solution of tetracene in anthracene. Application of a magnetic field decreases the fluorescence intensity by 2% (Fig. 14). The relative size of the effect $|\Delta L/L|$ decreases slightly at lower temperatures (with an activation energy of 0.08 eV) and it depends on the orientation of the single crystal with respect to the magnetic field (Fig. 14). Since the fluorescence under study appears upon exciting tetracene, but it shows an anisotropy of the magnetic effect that involves the crystallographic axes of anthracene, it was assumed in^[42] that it arose from radiative singlet-singlet transition in excited complexes (exciplexes) formed on the surface of the anthracene. The exciplexes can exist in singlet and triplet states that differ little in energy, but which have differing lifetimes. Mixing of the

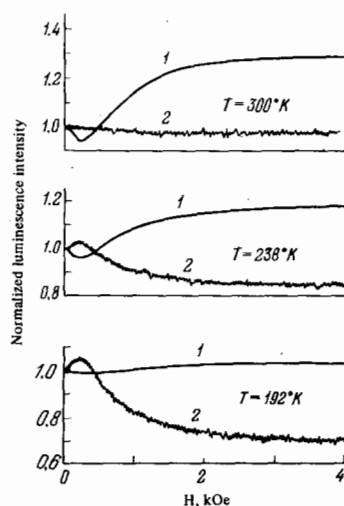


FIG. 13. Relations of the intensities of the fast (1) and delayed (2) components of the fluorescence of a tetracene crystal to the magnetic field intensity H. Field in the ab plane at a direction of -20° with respect to the b axis.^[35]

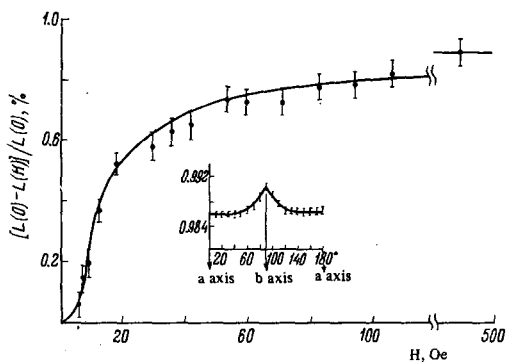


FIG. 14. Relation of the relative change in fluorescence intensity that arises upon excitation of tetracene on the surface of an anthracene crystal to the magnetic field strength. The anisotropy of the magnetic effect is shown (the ordinate is the relative fluorescence intensity in a field $H = 60$ Oe: $L(H)/L(0)$). [42]

wave functions of the singlet and triplet states causes the fluorescence intensity to decline.

A development of these studies is reported in [43a]. There, fluorescence spectra were studied when aromatic molecules (tetracene, rubrene, perylene, and coronene) deposited on the surfaces of molecular crystals (naphthalene, anthracene, pyrene, and stilbene) were excited by light. Quenching of fluorescence was observed for the following pairs: tetracene on naphthalene, rubrene on naphthalene, and rubrene on anthracene. The size of $\Delta L/L$ was as great as -12% . It was shown that the emission spectrum of the fluorescence has the shape of a broad, structureless band having maxima at 527, 567, and 577 nm for the above-cited pairs, respectively. Quenching by 30% of the fast fluorescence of excited complexes of rubrene with oxygen and other acceptors by magnetic fields of $\sim 10^2$ Oe was observed in [43b].

c) Photochemical processes. Triplet molecular excitons arise in the photooxidation of condensed aromatic hydrocarbons, in particular tetracene, when they react with oxygen in its ground (triplet) state. [104] This reaction produces tetracene molecules in the ground state and singlet oxygen (in the $^1\Delta_g$ state). [105] The primary products react with one another to form intermediate, unstable oxidation products, which can subsequently transform to stable products. The unstable photooxides are centers for dissociation of molecular (triplet) excitons. [1, 37-39, 41] Here charge carriers are produced, and this permits one to study the process of solid-state photooxidation by the method of surface photoconductivity.

An increase in the rate of photooxidation of tetracene in a magnetic field was observed in [40]. The interpretation of this effect is based on the effect of the magnetic field on the rate constant for interaction of the two triplets (of tetracene and oxygen) to produce a singlet product. [104, 105] This effect was studied in [60-63], etc., for the case of annihilation of two aromatic-hydrocarbon triplets. An essential feature of the magnetic effect on photooxidation is that one of the triplets (oxygen) is not excited, and it has two degenerate Zeeman sublevels. The shape of the relation of the observed effect to the magnetic field intensity (Fig. 15) permits one to distinguish it from effects involving the change in concentration of molecular excitons in tetracene in a magnetic field. [34-36]

In studying the initial stages of photooxidation in which the amount of products is negligibly small and the

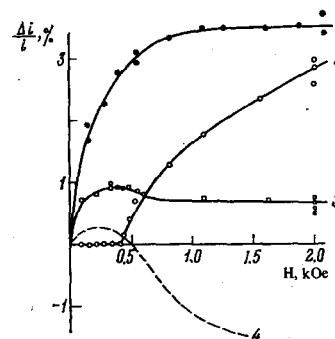


FIG. 15. Relation to the magnetic field strength of the following relative variations: 1-photocurrent in vacuo; 2-rate of photooxidation of tetracene; 3-photocurrent in a photooxidized specimen; and 4-relation to H of the concentration of triplet excitons. [41]

reverse process of their decomposition is not essential, it has been possible to show that the increase in the rate constant of photooxidation of tetracene in a magnetic field of ~ 2 kOe is $50 \pm 10\%$. [41] Under steady-state conditions, the increase in rate of photooxidation in fields of $H \sim 2$ kOe amounts to no more than $10^{-3}\%$ sec^{-1} . Such small values involve the almost complete reversibility (by light) of the photooxidation process. [41]

The study [106] was concerned with seeking an effect of magnetic fields on oxygen quenching of the phosphorescence of coronene, chrysene, and a,h-dibenzanthracene contained in polystyrene. To an accuracy of 1-2%, no effect of a 145-kOe field on the rate constant for quenching was observed. The authors of [106] developed a theory of the effect of a magnetic field on oxygen quenching of triplets of polynuclear hydrocarbons, and they discussed the possible reasons why they had not observed this effect within the limits of experimental accuracy.

Studies of the effect of oxygen on the magnetic sensitivity of the intensity of delayed fluorescence of anthracene and pyrene in solution were undertaken in [93C]. Introduction of oxygen into solutions of these substances in *N,N*-dimethylformamide changed both the sign and the shapes of the I_d-H relationships. There was no such effect when the solvent was acetonitrile. Since the oxygen in the solution quenched triplet states, the authors of [93C] think that they observed that the rate constant of this quenching reaction in the solution in *N,N*-dimethylformamide decreases in a magnetic field.

Gupta and Hammond [107a] found that in solutions an application of a magnetic field of ~ 9 kOe decreases the initial quantum yields of photoisomerization of stilbenes and perylenes (acceptors) when sensitized by ketones (donors). Excitation of acceptor molecules A to the triplet state $^3A^*$ causes them to isomerize, while non-sensitized photoisomerization is not sensitive to a magnetic field. It was proposed in [107a] that a magnetic field can affect the ratio between the paths of decay of triplet excited complexes $^3(DA)^*$ to the molecules D and A or to D and $^3A^*$. We note that the excited complexes are charge-transfer states, and the mechanism of magnetic sensitivity of such states implies a change in the ratio of rates of decay of the complexes by different paths in a magnetic field. [20, 42] A theoretical interpretation of the results of [107a] based on *S-T* mixing in the exciplex induced by the magnetic field has also been proposed in [107b].

It is also known that fields of ~ 85 Oe accelerate *cis-trans*-butene isomerization sensitized by iodine. [108]

This is associated with the effect of the magnetic field on predissociation of molecular iodine.

In [109], they observed an effect of a 15 000-Oe field on the ratio of yields of products of intracell radical recombination and bulk recombination of radicals. They studied the reaction of pentafluorobenzyl chloride with *n*-butyl lithium in *n*-hexane. The authors ascribe the observed effect to the influence of the magnetic field on the probability of an S-T transition in the radical pair, with account taken of the hyperfine interaction.

There are a number of reviews (see, e.g., [110]) that discuss attempts to detect an effect of magnetic fields on the rates of chemical reactions. It is outside the scope of this review to describe these attempts. We note only the studies [111-114] on the effect of magnetic fields on the rate of para-ortho-hydrogen conversion catalyzed by rare earths.

3. THEORETICAL MODELS

Interpretation of magnetic effects in different photo-processes is currently based on taking account of the change in the eigenfunctions of the interacting paramagnetic particles in the presence of a Zeeman effect. Theoretical models based on the sensitivity to a magnetic field of the conditions of motion of charges [55, 70, 115] have not been experimentally confirmed, and they will not be discussed in this review.

a) **Electron-positive charge systems. Charge-transfer states.** The positive magnetic effect on the photocurrent has been explained by mixing in the magnetic field of singlet and triplet charge-transfer states formed by an electron and a hole bound by Coulombic interaction. [20] The charge-transfer exciton is considered to be an intermediate stage in the process of ionization of molecular excited states.

It is assumed in interpreting the positive magnetic effect that charge-transfer states are produced from singlet molecular excitons. Since the positive magnetic effect occurs over a spectral range from the singlet-singlet absorption threshold to the autoionization threshold, we must assume that the energy of the first excited singlet state (3.15 eV in anthracene, and 2.4 eV in tetracene) suffices for producing the charge-transfer state.

The current carriers arise from ionization of an impurity. Hence the charge-transfer state can be produced near a charged impurity center. We should note that excited charge-transfer complexes (exciplexes) that are formed by interaction of molecules, one of which is excited, should also show the magnetic properties of charge-transfer states. The formation of such excited complexes has been studied experimentally in solutions (see, e.g. [116]) and in crystals. [117]

The model proposed in [20] to describe the positive magnetic effect was based on analogy between a charge-transfer exciton and a positronium atom. For positronium atoms, we know that their lifetime until annihilation decreases substantially in a magnetic field, owing to partial conversion of the ortho-states of positronium to the more short-lived para-state. [118] We can also expect an analogous effect for excitons or for excited charge-transfer complexes. In fact, they can have two states with differing orientations of the spins of the electron and the hole, or para- and ortho-states, in which the ortho-state is triply degenerate with respect to projection of the magnetic moment *m*. This degeneracy is re-

moved in a magnetic field, and it becomes possible to mix the wave functions of the ortho- (with *m* = 0) and para-states. If we assume that the lifetimes of the "pure" states differ, then this alters their lifetimes in the mixed state. Hence, it changes their probabilities of dissociation. A detailed calculation of the effect of a magnetic field on the populations of the ortho- and para-states of charge-transfer excitons has been performed in [20, 23]. We shall give here only the fundamental results of this calculation.

The ortho- and para- charge-transfer states can be described by the ψ -functions $\psi_{1,\pm 1}$, $\psi_{1,0}$ and $\psi_{0,0}$ which are the solutions of the Schrödinger equation with the potential $U(r) = -e^2/\epsilon r$, where ϵ is the dielectric constant of the medium. The subscripts of the ψ -functions denote the total magnetic moment and the projection of the magnetic moment, respectively.

The energy levels of the ortho- and para-states differ from one another by the amount of energy ΔW of the spin-spin and exchange interactions.

The magnetic field causes a Zeeman effect on the ortho-state by removing the degeneracy with respect to the magnetic quantum number *m*. Moreover, the para-state and the ortho-state with *m* = 0 become mixed in the magnetic field. In the magnetic field, the functions $\psi_{1,0}$ and $\psi_{0,0}$ are replaced by the functions

$$\begin{aligned} u_{1,0} &= \frac{1}{\sqrt{1+a^2}} \psi_{1,0} + \frac{a}{\sqrt{1+a^2}} \psi_{0,0}, \\ u_{0,0} &= \frac{1}{\sqrt{1+a^2}} \psi_{0,0} - \frac{a}{\sqrt{1+a^2}} \psi_{1,0}, \end{aligned} \quad (2)$$

where $a = \Delta g \mu H / \Delta W$. [3] Here Δg is the difference between the *g* factors of the electron and the positive charge. In order that a magnetic effect should exist, it is essential that this difference should not be zero.

If the rate of filling of the state $\psi_{1,0}$ is *A* in the absence of a magnetic field, and that of the state $\psi_{0,0}$ is *B*, then in the presence of a field, the corresponding rates of filling of the states $u_{1,0}$ and $u_{0,0}$ will be $A' = A(1-x^2) + Bx^2$, and $B' = Ax^2 + B(1-x^2)$. Here *x* denotes the quantity $a/(1+a^2)^{1/2}$. When the magnetic field is turned on (*x* > 0), the lifetimes of the para- and ortho-states (τ_p and τ_o) will change:

$$\begin{aligned} \frac{1}{\tau_p} &= \frac{1}{\tau_p} (1-x^2) + \frac{1}{\tau_o} x^2, \\ \frac{1}{\tau_o} &= \frac{1}{\tau_p} x^2 + \frac{1}{\tau_o} (1-x^2). \end{aligned} \quad (3)$$

The concentrations n_{u_1} and n_{u_0} of filled $u_{1,0}$ and $u_{0,0}$ states will be determined by the equations

$$\begin{aligned} \frac{dn_{u_1}}{dt} &= A(1-x^2) + Bx^2 - \frac{n_{u_1}(1-x^2)}{\tau_o} - \frac{n_{u_1}x^2}{\tau_p}, \\ \frac{dn_{u_0}}{dt} &= Ax^2 + B(1-x^2) - \frac{n_{u_0}(1-x^2)}{\tau_p} - \frac{n_{u_0}x^2}{\tau_o}. \end{aligned} \quad (4)$$

Equations (4) permit us to calculate the change in the steady-state total populations of charge-transfer states having *m* = 0: [3]

$$\Delta n = n_{\psi_0} x^2 \frac{(1-\eta)}{(\xi+x^2)}; \quad (5)$$

Here $\eta = n_{\psi_1}/n_{\psi_0}$ is the ratio of the steady-state concentrations of ortho- (with *m* = 0) and para-states of the excitons in the absence of a magnetic field; $\xi = \tau_p'/\tau_o'$.

We assume that $\xi \ll 1$. Equation (5) implies that

$$\Delta n = 0, \text{ if } \eta = 1; \Delta n < 0, \text{ if } \eta > 1; \Delta n > 0, \text{ if } \eta < 1.$$

The change in a magnetic field of the lifetimes of the charge-transfer states must lead to a change in their

diffusion distances and probabilities of energy transfer, while the change in the populations of these states alters the rate of generation of current carriers. In particular, in singlet-singlet excitation, $\eta < 1$ and $\Delta n > 0$. Hence, application of a magnetic field will increase the photocurrent. The relationship between the increase in photocurrent $\Delta i \sim \Delta n$ and the magnetic field described by Eq. (5) is saturated at $x^2 \sim \xi$. When $\xi < 1$, saturation can be observed when $\Delta g\mu H \ll \Delta W$.

In the study of fluorescence of excited charge-transfer complexes, the effect of the magnetic field has been attributed to the change in population of the singlet (or para-) state of the exciplex.^[42] The fluorescence intensity L is determined by the rate G of production of singlet excited states of the complex and by the distribution of the singlet component over the different spin states

$$L = \sum_i G f_i \tau_i \frac{f_i}{\tau_i}; \quad (6)$$

Here f_i is the fraction of the singlet component in the i -th spin state, τ_i is the overall lifetime of the i -th state, $G \cdot f_i$ is the rate of population of the i -th state owing to singlet-singlet transition, and f_i / τ_i is the probability of radiative transition in the i th state. In the absence of a magnetic field, only one state is singlet: $\tau_1' = \tau_1$, $f_1 = 1$, and $L = G$. In a magnetic field:

$$\frac{\Delta L}{L} = - \frac{x^2}{(\tau_1/\tau_3) + x^2} \frac{\tau_1}{\tau_3}; \quad (7)$$

The model of a charge-transfer exciton^[20] as applied to excited complexes formed from different molecules permits us to describe the experimental data involving quenching of fluorescence by weak magnetic fields ($H \sim 10$ Oe), and the saturation of the effect with increasing H . The observed anisotropy of the magnetic effect was ascribed in^[42] to anisotropy of the Zeeman interaction when the spin is coupled with the axis of the exciplex.

The lack of data on the difference of g factors of the positive and negative ions forming the complex currently prevents us from calculating the energy difference between the singlet and triplet states of the complex.

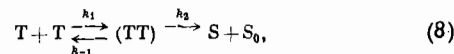
A calculation was recently performed in^[107b] of the probability of singlet-triplet conversion in an external magnetic field for excited charge-transfer complexes, using the time-dependent perturbation theory. This calculation graphically shows how the spins that form the singlet state of the complex precess in the external magnetic field with differing frequencies for spins having different g factors, and this gives rise to a triplet component with a probability proportional to the difference of Zeeman frequencies.

In addition to the Zeeman interaction (for differing g factors of the electron and the hole), mixing of singlet and triplet states can also arise from the hyperfine interaction. Taking account of interaction between the spins of the electron and the hole must lead to a change in the probability of S-T transition, even when the g factors of the interacting particles are equal. Such a mechanism of the effect of a magnetic field was first treated theoretically for radical pairs in^[119] where it was associated with the problem of chemical polarization of nuclei and electrons. This mechanism has been used in^[92] (for charge-transfer states) and in^[109] (for radical pairs in a chemical reaction) for interpreting the experimental data discussed in this review.

b) Triplet-triplet annihilation and fission of singlet excitons. The effect of a magnetic field on the delayed

fluorescence of anthracene arises from the magnetic sensitivity of the constant γ for triplet-triplet annihilation.^[14] A theory of this phenomenon has been developed, based on the experimental data of Johnson and Merrifield.^[79,80,80]

Annihilation of triplets is described by the following process:



Here k_1 , k_{-1} , and k_2 are the rate constants for collisions, for backward scattering, and for formation of singlets, respectively. We assume that free excitons do not interact with one another until they form a pair (TT). We also assume that the lifetime of such a contact pair is appreciably shorter than the spin-lattice relaxation time. Hence, spin interaction of the two triplets in the (TT) state becomes substantial. We must use the density matrix^[120] of pair spin states to describe such a system.

When there is no degeneracy of close-lying levels, one can show^[80] that one can apply an approximate calculation based on the populations of the steady states of the spin Hamiltonian of the pair, which is equal to the sum of the spin Hamiltonians of the free triplets:

$$\mathcal{H} = g\beta H(S_1 + S_2) + D(S_{z1}^2 + S_{z2}^2) + E(S_{x1}^2 + S_{x2}^2 - S_{y1}^2 - S_{y2}^2). \quad (9)$$

Further treatment will be carried out for this approximate model.

A contact pair of two triplets has nine spin substates, which comprise a singlet, a triplet, and a quintuplet. As we have noted, the populations of all the substates are the same at room temperature. The rate of formation of each substate is $k_1 n^2/9$. The scattering process does not depend on the spin. In contrast, the rule of spin conservation is essential in annihilation. The rate of annihilation for the i th spin substate can be written in the form $k_2 S_i^2$, where $S_i = \langle S | \psi_i \rangle$ is the amplitude of the singlet component in this state. Then the probability of annihilation for the i th substate is $k_2 S_i^2 / (k_{-1} + k_2 S_i^2)$. We can get the overall rate constant γ for annihilation by summing the probabilities over all states:

$$\gamma = \frac{k_1}{9} \sum \frac{k_2 S_i^2}{k_{-1} + k_2 S_i^2}. \quad (10)$$

Equation (10) implies that γ increases with increasing number of states that contain a portion of the singlet component.

A magnetic field can alter the distribution of the singlet component over the states. The spin Hamiltonian of (9) consists of two parts, which describe: 1) the Zeeman splitting, and 2) the zero-field splitting. When $H = 0$, the eigenstates of the Hamiltonian correspond to the principal values of the zero-field dipole tensor H_0 . It has been shown^[79,80] that in this case only three spin states will have a singlet component in a single crystal of anthracene. Adding an external field $H < H_0$ causes an additional mixing of the states that correspond to H_0 and a redistribution of singlet character over a larger number of states. That is, it increases γ . In the strong-field limit ($H > H_0$), the Zeeman splitting considerably exceeds the zero-field splitting, and the latter must be treated as a perturbation. Under these conditions, the spin states are quantized along the external field, and only two states remain that have singlet character, or fewer than in zero field. Thus, the value of γ must decline in strong fields, and hence also the intensity of fluorescence will decline. The $\gamma(H)$ relationship calculated by this theory^[79,80,121,122] agrees well with experiment (see Fig. 10).

Since we are dealing with crystals, the size of the Zeeman splitting should depend on the direction of the magnetic field with respect to the axes of the dipole tensor (or the crystallographic axes). For some directions, the levels of different states that have singlet character ($|0, 0\rangle$ and $|+\ -\rangle$) will cross. This will give rise to an additional degeneracy and to a corresponding decrease in γ , i.e., an anisotropic magnetic effect will be observed. This also holds for weak fields when the field is oriented along the principal axes of the dipole tensor, and the Zeeman and zero-field splittings are comparable. Here also one observes satisfactory agreement with experiment.

Suna^[121] has made a more exact calculation of the annihilation process, with account taken of the kinematics of the triplet excitons. The calculation took approximate account of the two-dimensional nature of the diffusion of triplets in anthracene.

These discussions were originally applied by the authors only to the case in which the intensity of delayed fluorescence depends quadratically on the intensity of the exciting light. Under these conditions, it is not essential what products besides singlets arise from triplet-triplet annihilation. It was subsequently shown^[85] that this model also holds when I_d is linearly dependent on I , if we take account of the fact that there is a triplet channel in annihilation: $T + T \rightarrow T + S_0$. The authors of^[85] concluded that the rate constant of this TT-annihilation channel does not depend on the magnetic field. They also estimated that 0.22 ± 0.01 of the collisions in triplet annihilation give rise to singlets.

The theory developed for anthracene has also been successfully applied for interpreting the magnetic sensitivity of such phenomena as TT-annihilation and its inverse process, singlet fission in tetracene,^[34-36] collision of two "non-equivalent" triplets,^[91] and fission of a singlet into two different triplets in mixed crystals.^[108]

A theory has also been developed for triplet-triplet annihilation in liquid solutions,^[94] which has the feature of taking account of arbitrary orientation of the colliding triplet molecules of anthracene. This feature has the result that γ declines monotonically with increasing magnetic field intensity.

c) Interaction of a triplet with a paramagnetic impurity. A decrease in a magnetic field of the rate constant for quenching of triplet molecular excitons in anthracene by paramagnetic centers was found in^[32], and they proposed an interpretation of this phenomenon. Let us examine the fundamental assumptions of the model described in^[32].

When a triplet exciton T (of spin $S = 1$) collides with a radical R or other paramagnetic particle (of spin $S = 1/2$), the triplet can undergo scattering, which does not depend on the spin, or quenching. The quenching process involves transition from an initial spin state that is a mixture of a doublet and a quartet to a pure doublet final state:



The rate k_l of transition of each of the six l th initial substates to the final state will depend on its amplitude of the doublet component:

$$k_l = k(|D_l^+|^2 + |D_l^-|^2),$$

Here $D_l^\pm = \langle \psi_l |^2 \psi_{\pm 1/2} \rangle$ is the amplitude of the doublet component $M_S = \pm 1/2$ in the initial state. If we denote

the rate of scattering by k' , then the probability of quenching of the initial l -th substate can be written as $k_l/(k' + k_l)$, and the overall rate of quenching of excitons by the paramagnetic impurity will be

$$Q = \frac{1}{6} A \sum_{l=1}^6 \frac{k_l}{k' + k_l}, \quad (12)$$

Here A is the total rate of exciton-radical collisions. The value of Q will be a maximum when $|D_l^+|^2 + |D_l^-|^2 = 1/3$ for all l , i.e., when the distribution of doublet amplitude over all six substates is uniform; a minimum will be observed for complete separation of the doublet and the quartet.^[32]

If we write the spin Hamiltonian for a triplet exciton as:^[123]

$$\mathcal{H} = g\beta H S_x + DS_z^2 + E(S_x^2 - S_y^2), \quad (13)$$

where the first term describes the Zeeman interaction, and the rest describe the zero-field splitting, we can determine the eigenfunctions of (13) in zero field,^[124] and show that the rate of quenching will be a maximum under these conditions.

In the strong-field limit, the Zeeman energy considerably exceeds the zero-field splitting, and all the spin states are quantized along the external field direction. Here the doublet component is distributed over four initial substates, and this decreases Q ^[32] (see Fig. 12). We can find from Eq. (13) the energy difference between the states $|0, \pm 1/2\rangle$ and $|\pm 1, \pm 1/2\rangle$ for the strong-field case:

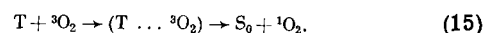
$$E(0, \pm \frac{1}{2}) - E(\pm 1, \mp \frac{1}{2}) = \frac{1}{2} D(1 - 3 \cos^2 \gamma) + \frac{3}{2} E(\cos^2 \beta - \cos^2 \alpha). \quad (14)$$

We see that this difference depends on the angles α , β , and γ between the direction of the magnetic field H and the axes x , y , and z of the zero-field splitting tensor. The difference (14) can vanish for certain field orientations, and this will correspond to the minimum value of Q for the given H . By using the values of the parameters for the zero-field splitting,^[125] we can calculate the anisotropy of quenching of triplets by radicals, which is analogous to the anisotropy found in TT-annihilation.^[14] Qualitative agreement of calculation with experiment was shown in^[32].

The theory developed in^[32] has also been applied successfully to interpret the negative magnetic effect on the photocurrent (see Sec. 2, Part a).

d) Interaction of triplets of aromatic hydrocarbons with oxygen. Kearns and Stone^[126] have treated theoretically the effect of spin-spin interactions on the quenching by oxygen of the triplet state of molecules. By using a method analogous to that applied by Merrifield,^[79, 80] these authors showed that, in a condensed phase, one can expect a change in a magnetic field of the rate constants of quenching processes of triplets of aromatic molecules by oxygen and by NO.

Following discovery of the effect of a magnetic field on the rate of photooxidation of tetracene,^[40] a theoretical model of this phenomenon has appeared.^[127] It is based on the magnetic sensitivity of the rate constant γ of the following process, which is one of the initial stages of oxidation:



The calculation was performed for the anthracene molecule. Its results do not depend on the state in which the

singlet oxygen was produced ($^1\Delta_g$ or $^1\Sigma_g$). The spin Hamiltonian of the contact pair (T^3O_2) has the form: [127]

$$\mathcal{H} = g_1\beta H \hat{S}_1 + \hat{S}_1 D \hat{S}_1 + g_2\beta H \hat{S}_2 + D_2 \left(\hat{S}_z^2 - \frac{2}{3} \right), \quad (16)$$

Here D_1 and D_2 are the zero-field splitting tensors, and the subscripts 1 and 2 refer to the aromatic hydrocarbon and to oxygen, respectively. The z direction is taken along the axis of O_2 .

Some features of the calculation involve the marked difference between the zero-field splitting values (~ 300 Oe for anthracene, [125] and ~ 30 Oe for oxygen [128]) and the two-fold degeneracy of the levels of oxygen in zero field arising from the axial symmetry of O_2 . The entire range of H values can be divided into three regions:

1) **Weak fields:** $0 \leq H \leq 10^2$ Oe. The value of γ slowly increases with increasing H, owing to removal of degeneracy (at $H = 0$, six of the nine spin substates of the contact pair are pairwise degenerate).

2) **Intermediate fields:** 10^3 Oe $\leq H \leq 10^4$ Oe. The change in γ when the magnetic field is turned on remains constant. The theory predicts an anisotropy that depends substantially on the position of the oxygen molecule in the crystal, since $D_{O_2} \gg D_{\text{aromat}}$. The anisotropy of the magnetic effect on γ has been calculated for the case in which the axis of the O_2 molecule is oriented along the short axis of the anthracene molecule (see Fig. 1 in [127]). The possible increase in γ over the stated range of H was also estimated, and it can be as large as 70%, depending on the value of the ratio $k = k_S/k_{-1}$ (k_S is the rate constant for annihilation to give a singlet product, and k_{-1} is the rate constant for backward scattering).

The effect of a magnetic field on γ over the range $0 < H < 10^4$ Oe is not determined by the change in the distribution of the singlet component, as was shown in [126], but by the removal of degeneracy of the levels that have singlet character.

3) **Strong fields:** $H > 10^5$ Oe. The Zeeman interaction is much larger than the zero-field interaction, both in O_2 and in the triplet of the aromatic hydrocarbon. This decreases the number of states that contain a singlet component. The value of γ is less than in the absence of an external magnetic field.

The shape of the expected $\gamma(H)$ relationship is given in [127], and it agrees satisfactorily with the existing experimental data. [40, 41]

A theory of the effect of a magnetic field on the rate constant for interaction of oxygen with triplet-excited molecules of polynuclear aromatic hydrocarbons has also been developed in [106]. They compare the cases of zero external field and of very large external fields that appreciably exceed the zero field of the oxygen molecule. In addition to the spin-spin interaction in the contact pair formed by the triplet molecules of oxygen and the hydrocarbon, they also take account of charge-transfer interaction. They treat the different relationships among the energy values of these interactions.

4. CONCLUSIONS AND PROSPECTS

This review has treated the fundamental results of studying the effect of magnetic fields on photoprocesses in organic solids. We can now say that these studies have

opened up a new field of investigation that is closely associated with a wide circle of scientific disciplines.

It has become possible to study in detail the behavior of systems in which spin-spin interaction is essential. A magnetic field affects the course of the non-equilibrium process involving two paramagnetic particles; the time of contact or of reaction of these particles must be considerably shorter than the relaxation time of their magnetic moments. In this regard, the conditions for observing an effect of a magnetic field resemble the conditions for observing chemical polarization of nuclei and electrons. [129, 4] We shall emphasize again one fact that we deem to be highly untrivial: this involves weak magnetic fields at room temperature, where the size of the Zeeman splitting is much smaller than kT. Studies of magnetic effects are not only of independent interest, but they also give extensive information on the behavior of excited and ionized states in molecular solids. As an example, it suffices to cite such results as elucidation of the mechanism of photoamplified currents: study of the dynamics of triplet excitons; determining the parameters of the zero-field splitting tensor in crystals at triplet concentrations much smaller than when the EPR method is used; discovery of the fission of singlet excitons into two "different" triplets and annihilation of these triplets in mixed crystals; and refinement of the mechanism of photooxidation, etc.

The conditions that are necessary for observing an effect of magnetic fields on photoprocesses permit us to speak of the possibility of considerably extending the number of objects in which one can observe such an effect, and to use for study processes involving excited states. As we see it, this is one of the paths of development of the magnetic method.

The second path is to study the mechanism of magnetic sensitivity in cases not yet well enough clarified, and to seek new magnetic effects and new magnetically sensitive processes. It seems to us expedient here to distinguish a number of aspects.

The positive magnetic effect on the photocurrent that is manifested in fields of the order of 10^2 Oe has not been studied fully enough. Elucidation of this problem must make a substantial contribution to understanding such processes as ionization and energy transfer in solids. Observation of a positive magnetic effect on currents resulting from electron bombardment in tetracene films is also highly noteworthy. [29] Further studies along this line can be useful in elucidating the nature of radiative transitions in molecular systems in a condensed phase.

We may hope that studies of charge-transfer states will be expanded by using magnetic methods in aromatic substances. [5] Substantial prospects are involved here with the effect of weak magnetic fields on the fluorescence of excited complexes. [42, 43]

We should expect to observe an effect of magnetic fields on the interaction of triplet molecular excitons with trapped electrons analogous to that which occurs with trapped holes (see Sec. 2, Part a, and Sec. 3, Part c). It would be interesting to observe a magnetic effect on the interaction of triplets with free charges.

Studies on the effect of magnetic fields on photoprocesses in liquids seem very promising. They may prove in the future to be a powerful instrument for studying mechanisms of photochemical reactions in solutions.

One of the most interesting fields of application of the magnetic method promises to be to study the interaction of aromatic hydrocarbons with oxygen. Only the first results have yet been obtained here, but they permit us to make optimistic prognoses. Thus, observation of acceleration by a field of the photochemical reaction of photooxidation of tetracene^[40] gives us grounds for assuming that other photooxidation reactions also will be magnetically sensitive. An effect of magnetic fields on the interaction of triplets of aromatic hydrocarbons with oxygen should also be observed by the method of delayed fluorescence. We should also expect magnetic effects on the interaction of oxygen with other paramagnetic particles in organic systems. It would be interesting to study the effect of magnetic fields on the interaction of aromatic hydrocarbons with NO.^[126] Processes of oxygen quenching of excitations in solutions of aromatic hydrocarbons are very important. Apparently, here also the magnetic method would be extremely useful (see^[93c]). We may hope that studies of the effect of magnetic fields on photooxidation reactions will contribute toward solving such an important problem as photosynthesis.

Perhaps studies of magnetic effects on relatively simple model systems will later open up physical approaches to the problems of magnetobiology, where, as we know,^[131] weak magnetic fields affect many processes that occur in living cells and organisms.

¹⁾The energy of these states has been calculated in anthracene; [¹] experimental searches have been undertaken for features in absorption spectra that could be ascribed to transitions from the ground singlet state to charge-transfer states. [^{2,3}] However, no reliable spectroscopic data have been obtained on these transitions in anthracene. [⁴⁻⁷] Apparently, this involves their low probability. [^{3,8-11}]

²⁾An explanation was proposed in [⁵⁵] for the negative magnetic effect, based on the effect of the magnetic field on motion of current carriers when the latter are distributed exponentially through the thickness of the specimen. [⁵⁶] However, this model does not take into account the experimental data that size of the magnetic effect is independent of the relative orientation of the electric and magnetic fields, and it does not give the right order of magnitude of the size of the effect.

³⁾The magnetic field does not mix the states with $m = \pm 1$ and $m = 0$.

⁴⁾The generality of these studies has been acknowledged quite recently (see, e.g. [^{92,107b}]).

⁵⁾A highly promising method of studying charge-transfer states in molecular crystals is also to measure the Stark effect. [¹³⁰]

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