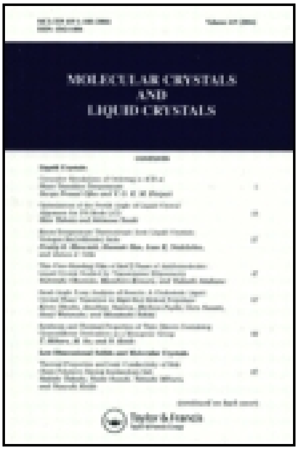

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Anisotropic Temperature Dependency of the Annihilation Rate of Triplet Excitons in Dibromo-Anthracene Pyromellic Dianhydride

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The magnetic field spin effect on photoluminescence of charge-transfer single crystal caused by annihilation of triplet excitons and controlled by Zeeman and zero-field splitting (ZFS) interactions is investigated. Phase transition related to reorientation of dibromo-anthracene molecules in the (x-y) plane of ZFS tensor of anthracene molecule is observed at T=205 K. When the temperature approaches the phase transition point at orientation of ZFS axis z parallel to the magnetic field the rate of spin-lattice relaxation dramatically increases and hence the magnitude of the magnetic field spin effect sharply drops down.

Keywords: triplet exciton; magnetic field spin effect; spin-lattice relaxation; phase transition

The photophysical processes in molecular crystals of charge-transfer complexes involve sophisticated set of the elementary acts: formation and transport of excitons, charge separation, dissociation and annihilation of the paramagnetic exited states [1-3]. In the present work the magnetic field spin effect (MFSE) is observed on the photoluminescence of charge-transfer single crystal of dibromoanthracene pyromellic dianhydride. The MFSE is due to the magnetic field (MF) controlled annihilation of the triplet excitons residing or hopping over DBA molecules: T + T ←→ [TT] → P, where T is the triplet exciton, P is the light-emitting product and [TT] is the spin-correlated contact pair of T-excitons [4-6]. The MFSE is defined as the relative change of luminescence intensity L in the external magnetic field H: $Y(H) = L^{-1}(dL/dH)$. The spin state of T-exciton is controlled by its spin Hamiltonian $H=H_Z+H_{ZFS}$, where H_Z is the Zeeman interaction with the external MF and H_{ZFS} is the zero-field splitting tensor of the molecule. Spin conservation requires the annihilation to proceed only when a given spin state of the TT pair has a component of singlet state. Changing the external MF alters the spin eigenstates of the pair, and therefore the total probability of recombination. Since ZFS tensor is rigidly connected with the principal axes of DBA molecule, and therefore with the crystalline axes, the MFSE is strongly dependent on the mutual orientation of the single crystal and the MF vector.

The synthesis and crystallographyc analysis of 9,10-dibromoanthracene 1,2:4,5-pyromellitic dianhydride (DBA-PMDA) single crystals was first carried out in L.Ya. Karpov Physico-Chemical Institute [7]. The represented experiments were started on crystals [7] and the most of the results were obtained on the crystals grown at "Crystallab", 3-rd Physical Institute, University of Stuttgart [8]. The crystals were illuminated by 320-500 nm radiation with intensity $10^{11} \div 10^{15}$ quants·s^{-1}·sm^{-2}. The fluorescence was detected in the range 550-670 nm. The single crystal was placed in the MF 0-100 mT and precise tuning of its orientation was carried out. MF modulation and lock-in detection were used to improve the accuracy of measurements.

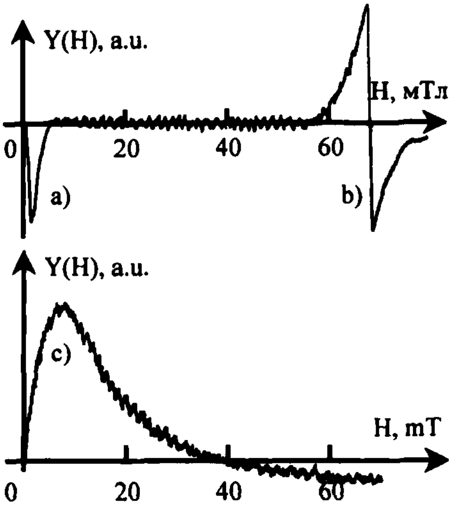

FIGURE 1 MFSE on photoluminescence of DBA-PMDA single crysrtal. a) negative effect, H || z; b) Z-resonance, H || z.; c) positive effect, H⊥z.

The following major results are obtained. The MFSE exhibits strong anisotropy with respect to crystal orientation in the MF. In the crystal orientation when H||z a pronounced resonance is observed at H=66,4 mT (Fig. 1b). At low fields 0-5 mT the sign of the MFSE in this orientation is negative (Fig. 1a) with the minimum at H=1,0±0,2 mT. In all other orientations the sign of MFSE in the region 0-20 mT is positive, no resonances are found and the MFSE maximum value is observed at much stronger fields, 6-10 mT.

The most surprising result is the unusual temperature dependence of the MFSE when H||z (Fig.2). Unlike other orientations, in this case the sharp decrease of the MFSE magnitude is observed at T=205 K, the minimum value being at least 100 times less than that at room temperature. At all other orientations the MFSE temperature dependencies are monotonous and much less steep.

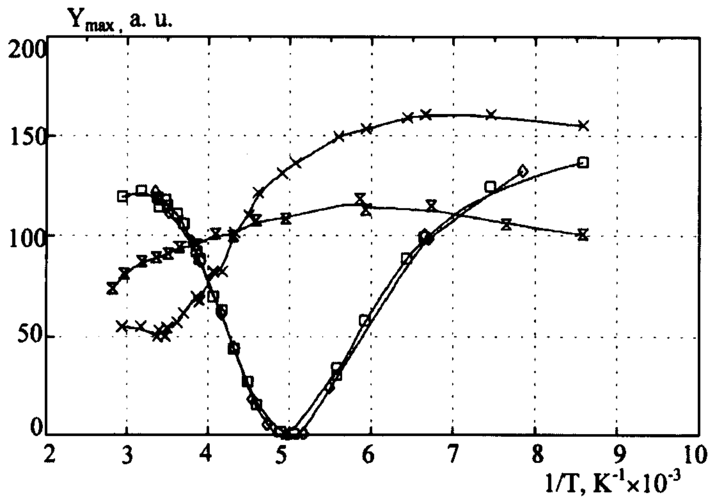

FIGURE 2 Temperature dependencies of the maximum magnitude of the MFSE: (×) - H || z, Z-resonance; (□) - H || z, low-field resonance; (◊) – direction of H is close, but not coinciding with z, low-field resonance; (⧖) - H ⊥ z, low-field resonance.

The shape and sign of the MFSE in the case H||z can be clearly understood from the analysis of eigenstates of the T-excitons determined by the ZFS and Zeeman interaqction. In the basis of ZFS principal states $|x\rangle, |y\rangle$ and $|z\rangle$: $H_{ZFS} = D(S_z^2 - \frac{1}{3}S^2) + E(S_x^2 - S_y^2)$, where D and E are the ZFS parameters. The recombination rate for any given state of the pair is proportional to the singlet component of this state. In the particular case H||z the calculation shows that in the most realistic limit of short lifetime of the contact pair the annihilation rate constant $k_a \propto \frac{1}{3} + \frac{2}{3}\left[1 + (g\beta H/E)^2\right]^{-1}$, and the MFSE, i.e. the MF-dependent part of the luminescence intensity L is given by:

$$Y_{\parallel}(H) = \frac{1}{L_{\parallel}}\frac{dL_{\parallel}}{dH} \approx \frac{1}{L_0}\frac{d}{dH}(\delta L_{\parallel}) \propto -\frac{H}{\left[1+(g\beta H/E)^2\right]^2},$$

where $g\beta H$ is the Zeeman energy and E is the ZFS parameter. The minimum of this dependency is achieved at $H = H_{min} = E/\sqrt{3}$.

Experimental value $H_{max} \approx 1\,mT$ gives the estimation E ≈ 1,7 mT. The estimated value is essentially smaller than that observed in the crystals of pure anthracene: E ≈ 9 mT [1]. This difference may be explained by the presence of heavy Br atoms having strong spin-orbit coupling ~ 0.5 eV. There are two mechanisms of ZFS formation (3): 1) as a result of magnetic dipole interaction of spins constituting the triplet exciton and 2) due to the combined effect of the exchange interaction J in a pair of electrons which form the triplet pair and anisotropic Zeeman interaction responsible for high Δg value. For example the following estimations exist for the D parameter: $D(1) \sim -(g\beta)^2/r^3$ and $D(2) \sim (\Delta g/g)^2 J$, where r is the average distance between the electrons forming the pair. In the absence of heavy atoms the second mechanism is negligible due to the small Δg. In this case, however, the Δg may become big enough, so the two mechanisms can compete and the resulting E can become much smaller than that in pure anthracene.

The proposed explanation of the abnormal temperature dependency of the MFSE magnitude at H||z is based on the spin-lattice relaxation (SLR). It is known [4-6] that analogous charge-transfer crystals undergo a phase transition at T ≈ 200 K which consists in reorientation of molecules in x-y plane. The hopping of T-excitons over molecules which differ in azimuth angle as well as molecular librations induce strong fluctuation of the spin Hamiltonian and subsequently induce transitions between $|x\rangle$ and $|y\rangle$ states. When H is parallel to z the SLR can be substantial compared to the coherent interactions. When the system approaches the phase transition, the SLR rate increases dramatically thus suppressing the evident MFSE [8, 9].

This approach also explains the fact that the effect of phase transition is only seen at H||z. Indeed, in all other orientation the characteristic frequencies of coherent interactions are of the order of D (in frequency units) and the SLR rate is limited to $w_r(\max) \approx E$. Besides, the SLR of this type mixes only $|x\rangle$ and $|y\rangle$ states of the T-excitons. When H||z the MFSE is determined by transitions between exactly these states, in all other orientations the MFSE arises from transitions between other states having essential component of $|z\rangle$.

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