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Time-resolved spin processes in Alq_3 light-emitting diodes

F. Comandè and J.-Ph. Ansermet

Institute of Condensed Matter Physics, Station 3, École Polytechnique Fédérale de Lausanne–EPFL, CH-1015 Lausanne, Switzerland

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Using pulsed electroluminescence detected magnetic resonance (PELDMR), we study the dynamics of spin processes in Alq_3 based light-emitting diodes. The transitions induced by magnetic resonance are found to be much faster than the space charge reaction time that is measured by looking at the electroluminescence frequency response to an ac bias voltage. This observation excludes a change in the equilibrium space charge distributions as the cause of PELDMR, in favor of a change of the electron-hole recombination rate. At low temperatures the effect of electron spin resonance on the electroluminescence changes sign and lasts longer. The postpulse electroluminescence recovery is well fitted by a biexponential function characterized by two very different time scales, which are consistent with a detailed balance for the singlet and triplet states, in conformity with the electron-hole pair model.

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Spin-dependent processes in semiconductors are the key ingredient in many recent spintronics applications [1,2]. They are also believed to play a crucial role in determining the magnetic field response of organic semiconductors [3–5]. Nonetheless, the theoretical picture depicted so far remains diverse due to the large number of different processes that have been proven to affect the magnetic field response [6–10]. More specifically, it has been shown, by way of photoinduced absorption measurements, that the triplet/singlet exciton ratio can be affected by small magnetic fields in polymer thin films, in agreement with spin-dependent recombination models [11]. Moreover, using electrically detected magnetic resonance (EDMR), it has been shown that dye dopants in Alq_3 organic light-emitting diodes (OLEDs) affect the resonance g factor, suggesting charge trapping followed by recombination as the main mechanism in these devices [12]. On the other hand, a direct effect of magnetic field on mobility has been shown in Alq_3 by using time of flight measurements, as predicted by the bipolaron model [6,13]. Finally, there is also evidence of trap-induced magnetic field effects [14,15]. For this reason, new methods of investigation are required to discern the contributions of these different processes.

A possible approach is to study spin effects in the time domain. In the past, this was attempted mostly by using optically detected magnetic resonance (ODMR) of organic thin films as a function of frequency or time [16,17]. More recently, pulsed EDMR has been employed in organic solar cells to measure the intrinsic coherence time of spins in organic polymers and to study bipolaron formation [18,19]. Studies on actual OLEDs were performed by looking at the organic magnetoresistance (OMAR) frequency dependence [20,21]. In particular, the group of Wohlgenannt detected an intrinsic cutoff frequency for spin processes of 10 kHz in Alq_3 OLEDs. Recently, we proposed a way to explore spin dynamics in OLEDs by using pulsed electroluminescence detected magnetic resonance (PELDMR) [22]. PELDMR is particularly useful in systems such as OLEDs as it gives the opportunity to study spin processes while the device is operating, reproducing the same experimental conditions of most OMAR studies [3,4]. This differs from similar techniques that have been recently used, such as PEDMR and pulsed ODMR (PODMR), as in that case charges are excited via optical pumping, not electrically [18,19]. Because of this feature, they typically give very different results, as we know from continuous wave studies [23]. In our previous work we observed that the spin dynamics in Alq_3 LEDs is independent of bias voltage and performed numerical simulation to show that this is inconsistent with a change in charge mobility. Since then we performed complementary measurements on our samples, measuring the electroluminescence as a function of bias modulation frequency [24]. This method allowed us to estimate the effect of the space charge reaction time directly on the electroluminescence and confirm the conclusions reported in Ref. [22].

In this Rapid Communication, we move our analysis one step further by exploring spin-dependent dynamics at different temperatures. We show, by means of detailed balance equations, that our results are consistent with the electron-hole pair theory.

A diagram block of the PELDMR setup is reported in Fig. 1. This differs from the setup reported in Ref. [22] in the presence of an optical cryostat, cooled by a continuous flow of liquid helium. Also, a traveling wave tube microwave amplifier is used to amplify the microwave pulses. The electroluminescence produced by the sample is collected by a liquid-core light guide connected to the cryostat window and brought to a fast photomultiplier for detection. The signal is converted into a voltage using a fast transimpedance amplifier (50 MHz bandwidth). The acquisition is made by an universal 8 bit PCI-Express digitizer. This allowed us to achieve the high averaging rates necessary to extract the signal out of the noise (up to 10^6 averages). To synchronize all the setup components we use a programmable transistor-transistor logic (TTL) pulse generator card. The sample studied is a N,N-diphenyl-N,N-bis(1-naphthyl)-1,1-biphenyl-4,4-diamine (α-NPD 40 nm)/tris(8-hydroxyquinolinato)aluminum (Alq_3 60 nm) OLED with ITO/CuPc (Indium Tin Oxide/Copper (II) phthalocyanine) and LiF/Al electrodes. More details on the fabrication procedure can be found in Ref. [25].

In Fig. 2, we report the postpulse relaxation to equilibrium at different temperatures. We observed a strong effect of temperature on the tuning of the resonator. Therefore, the effective power on the sample during the pulse is not the same when the temperature is changed. At 294 K, the voltage applied

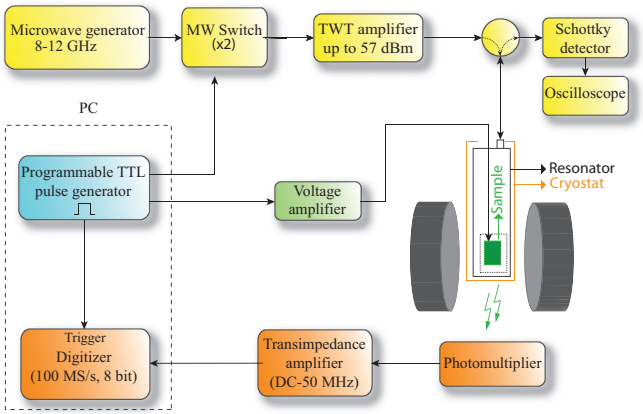

FIG. 1. (Color online) Circuit scheme of the PELDMR setup. The yellow branch provides the microwave excitation and the orange branch allows for optical detection. Here the green is used to distinguish the OLED power circuit. All these different circuits are synchronized by a programmable TTL generator (in blue).

on the sample is 4.7 V. This bias voltage was increased with decreasing temperature in order to keep the light emission constant. Similarly to what was already shown by Li and coworkers using continuous wave ELDMR, at low temperature the resonance changes sign, resulting in an enhancement of the electroluminescence [23]. Contrary to bias voltage [22], temperature has a net effect on the resonance dynamics. The time needed to restore the electroluminescence equilibrium increases with decreasing temperature. The curves in Fig. 2 cannot be described by a single exponential. So we used a biexponential function to describe our data (in red in Fig. 2). The time constants obtained from the fits are reported in Table I. From the table it is clear that upon lowering temperature we increase both characteristic time constants of the recovery.

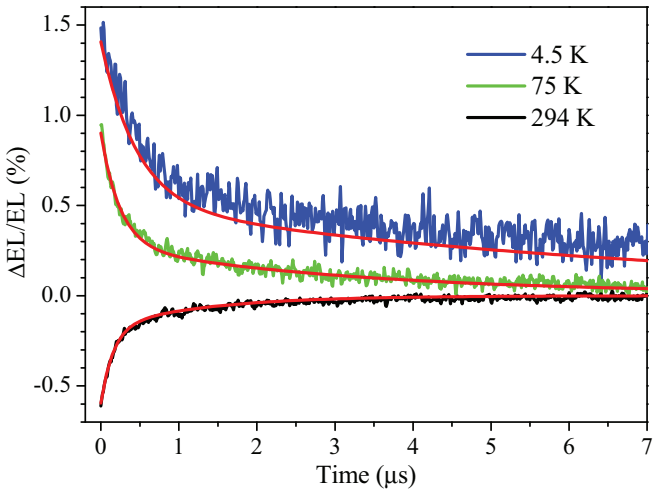

FIG. 2. (Color online) Postpulse electroluminescence recovery at different temperatures. The bias voltage is gradually increased to keep the light emission constant. A double exponential function (in red) is used to fit the three curves. Best fit recovery times are reported for each curve in Table I.

TABLE I. Recovery time constants t_1 and t_2 obtained from the biexponential best fits in Fig. 2. The $\lambda_\pm$ values are their inverses.

T (K)	t_1 (ns)	t_2 (μs)	λ_+ (MHz)	λ_- (MHz)
294	158	1.28	6.33	0.781
77	240	3.15	4.17	0.317
4.5	457	7.08	2.19	0.141

The electron-hole pair (EHP) model offers a mechanism to explain magnetic field effects, which involves spin-dependent recombination and can be a valid candidate to explain our data [7]. In an EHP, the intercharge distance (r) is larger than the exciton one. As a consequence, the exchange constant $J(r)$ is small, causing triplet and singlet states to be very close in energy. The effect of an external magnetic field is to remove partially this degeneracy by splitting the triplet states. This has an effect on the mixing between triplet and singlet states [7]. In particular, if the Zeeman energy splitting is larger than the spin mixing interaction energy, the mixing between $T_{+1,-1}$ and S,T_0 is quenched [7]. In the case of a high magnetic field, the spin mixing term can be treated as a perturbation compared to the Zeeman term. Spin transitions between $T_{+1,-1}$ and S,T_0 occur owing to the interaction between the spin degree of freedom and the lattice vibrations [26,27]. In the case of very small magnetic fields, spin mixing terms mix completely the singlet and triplet states. This is important if we look at how an EHP evolves [7]. There are two possible outcomes: recombination into an exciton or dissociation in free polarons. In the case of recombination, the spin state of the exciton will be the same as that of the EHP. On the other hand, dissociation results in the generation of free polarons that cause, in turn, an increase in the current. It has been shown that the rate constants for dissociation and recombination depend on whether the pair is in a triplet or singlet state [28,29]. This implies a different evolution for the populations of triplet and singlet EHP. In the case of small or no magnetic field, spin mixing compensates (or partially compensates) this difference. On the other hand, when a large magnetic field is applied, only the T_0 and the S_0 states will still mix efficiently, while the $T_{1,-1}$ populations will evolve to different equilibrium values, according to their dissociation and recombination rates. Through this mechanism it is possible to tune the overall dissociation and recombination, affecting current and light emission, respectively. According to this model, the effect of magnetic resonance is to restore partially the mixing between the $T_{+1,-1}$ states and S,T_0, as it occurs at zero magnetic field.

In the picture we draw so far, we considered the exchange interaction to be small compared with the Zeeman splitting. A large exchange interaction would shift considerably the singlet EHP energy state with respect to the triplet and would result in two distinguished spin 1/2 magnetic resonance peaks [30]. This is not observed in our samples.

As in Refs. [7,30], we can describe the dynamics of our spin system in the postpulse recovery using the following rate equations:

$$\dot{n}_S = -k_S n_S - q_S n_S + \frac{G}{4} + k_{\mathrm{mix}}(n_0 - n_S) - \left(n_S - \frac{n_{\mathrm{tot}}}{Z}\right)\frac{1}{T_1}, \quad (1)$$

$$\dot{n}_0 = -k_T n_0 - q_T n_0 + \frac{G}{4} + k_{\rm mix}(n_S - n_0) - \left(n_0 - \frac{n_{\rm tot}}{Z}\right)\frac{1}{T_1}, \tag{2}$$

$$\dot{n}_{+1} = -k_T n_{+1} - q_T n_{+1} + \frac{G}{4} - \left(n_{+1} - n_{\rm tot}\frac{e^{\frac{E_Z}{K_B T}}}{Z}\right)\frac{1}{T_1}, \tag{3}$$

$$\dot{n}_{-1} = -k_T n_{-1} - q_T n_{-1} + \frac{G}{4} - \left(n_{-1} - n_{\rm tot}\frac{e^{\frac{-E_Z}{K_B T}}}{Z}\right)\frac{1}{T_1}, \tag{4}$$

where Z is the Boltzmann partition function,

$$Z = 2 + e^{-E_Z/K_B T} + e^{E_Z/K_B T}, \tag{5}$$

and

$$n_{\rm tot} = n_S + n_{+1} + n_{-1} + n_0. \tag{6}$$

n_S and $n_{+1,0,-1}$ correspond to the populations of the various spin states, singlet and triplet, respectively. The quantities $k_{S,T}$ and $q_{S,T}$ represent the recombination and destruction rates for singlet and triplet EHP, and G is the overall generation rate, which is assumed to be spin independent. $k_{\rm mix}$ is the mixing rate between the S and the T_0 states, which is not expected to change in the presence of an external magnetic field. The T_1 introduce the relaxation towards the Boltzmann distribution. Several papers in the literature have estimated electrons T_1 times in Alq$_3$ of the order of 10 μs, for magnetic fields of hundreds of mT [31–33]. Since the dynamic features we observe in our PELDMR traces occur in much shorter time scales, we assume these terms to be negligible. Under this approximation the evolution of the $T_{+1,-1}$ states proceeds independently from S and T_0. This allows us to solve for $n_S(t)$ and $n_0(t)$, obtaining

$$n_S(t) = C_1 e^{-\lambda_+ t} + C_2 e^{-\lambda_- t} + \frac{G(d_T + k_{\rm mix})}{4\left(d_T d_S - k_{\rm mix}^2\right)}, \tag{7}$$

$$n_0(t) = -C_1\frac{\lambda_+ - d_S}{k_{\rm mix}}e^{-\lambda_+ t} - C_2\frac{\lambda_- - d_S}{k_{\rm mix}}e^{-\lambda_- t} + \frac{G(d_S + k_{\rm mix})}{4\left(d_T d_S - k_{\rm mix}^2\right)}, \tag{8}$$

with

$$\lambda_\pm = d_S + d_T \pm \sqrt{(d_S - d_T)^2 + 4k_{\rm mix}^2}, \tag{9}$$

where

$$d_{S,T} = k_{S,T} + q_{S,T} + k_{\rm mix}. \tag{10}$$

Here, the constants C_1 and C_2 depend on the starting $n_{S,i}$ and $n_{0,i}$ populations. The recovery predicted by the rate equations is biexponential. This agrees well with our data at all temperatures. Also the increase of the recovery time with temperature suggests a decrease of recombination, destruction, and mixing rates, which is reasonable.

We have seen that the short time scale of PELDMR allowed us to rule out mobility as the cause of the spin-dependent electroluminescence. Nonetheless, we do not exclude the possibility of spin-dependent mobility in Alq$_3$ OLED. Possibly, since the materials used to prepare the devices we studied are highly purified, spin-dependent mobility such as trap-assisted mobility may be small in our samples.

We also investigated the chance that the double exponential recovery could have its origin in the presence of other organic materials in our device. In fact, it is possible that part of the spin-dependent recombination occurs in a layer different than Alq$_3$, creating excitons that are then transferred through diffusion or direct transfer to the emissive layer. In particular, CuPc has recently been proposed as a viable candidate material for organic spintronics devices due to the very long T_1 and T_2 times [34]. Nonetheless, an effect of the latter can be excluded due to the CuPc band gap being much smaller than Alq$_3$, making exciton transfer impossible. On the other hand, α-NPD excitons could in principle be converted in Alq$_3$ excitons and affect the sample electroluminescence. Nonetheless, charge recombination in the hole transport layer is strongly limited by the very low density of electrons that are blocked at the interface with Alq$_3$ [25,36]. This statement is further supported by the absence of blue α-NPD emission in the OLED electroluminescence. Additionally, the presence of multiple spin-dependent recombination processes would cause multiple biexponential recoveries in our PELDMR signal that are not observed, not even at longer times (we explored up to 1 ms at room temperature).

To complete our analysis, we want to discuss the change in sign that it is observed when the temperature is decreased from the point of view of spin-dependent recombination. From the rate equations it can be deduced that a quenching in the electroluminescence due to magnetic resonance mixing is obtained for

$$k_T + q_T > k_S + q_S. \tag{11}$$

Vice versa the enhancing of the electroluminescence at low temperature requires

$$k_T + q_T < k_S + q_S. \tag{12}$$

In other words, at room temperature the equilibrium population of singlet EHP is larger than triplet, while at low temperature the latter are dominant. An explanation for this behavior may come from the different temperature dependencies of recombination and dissociation coefficients. For instance, let us assume that, due to the singlet EHP higher energy, $q_S > q_T$, as it was found in polymer devices [18]. At room temperature, this would imply k_T to be larger than k_S and recombination to be dominant over dissociation, so as to fulfill relation (11). At low temperature instead, due to relation (12), dissociation would then be dominant over recombination. In a first approximation both recombination and dissociation are expected to be thermally activated processes and therefore exponentially dependent on temperature. Nonetheless, for low temperature measurements, the bias voltage we apply to induce the electroluminescence is much higher, and this has been proven to enhance dissociation [37]. Moreover, the interaction of EHP with polarons and excitons should also be taken into account. Ultimately, the $\lambda_\pm$ values reported in Table I and Eq. (9) suggest that the $k_{S,T}$ and $q_{S,T}$ coefficients are decreasing sublinearly with temperature, confirming that the hypothesis of an exponential dependence of dissociation and recombination on temperature is oversimplified.

To conclude, the hypothesis we made of $q_S > q_T$ is supported by magnetic resonance studies on similar Alq_3 samples, where the ELDMR and EDMR signals vary accordingly when decreasing the temperature [23]. This can occur, in agreement with the rate equations (1)–(4), only if the dissociation rate for singlet EHPs is higher than the triplet. Continuous wave EDMR measurements at room temperature on our samples have shown similar results [24].

To summarize, we explored the dynamics of the electroluminescence changes induced by high powermicrowave pulses as a function of temperature. At low temperatures the resonance changes sign, resulting in an electroluminescence enhancement. Also the time response changes significantly, with low temperature signals lasting longer. The postpulse electroluminescence recovery to equilibrium is well fitted by a biexponential function, characterized by very different time scales. By a detailed balance we demonstrated that this is consistent with the electron-hole pair model.

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