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Separating Positive and Negative Magnetoresistance in Organic Semiconductor Devices

F. L. Bloom,* W. Wagemans, M. Kemerink, and B. Koopmans

Department of Applied Physics, Center for NanoMaterials, and COBRA Research Institute, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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We study the transition between positive and negative organic magnetoresistance (OMAR) in tris-(8 hydroxyquinoline) aluminium (Alq_3), in order to identify the elementary mechanisms governing this phenomenon. We show how the sign of OMAR changes as function of the applied voltage and temperature. The transition from negative to positive magnetoresistance (MR) is found to be accompanied by an increase in slope of $\log(I)$ versus $\log(V)$. ac admittance measurements show this transition coincides with the onset of minority charge (hole) injection in the device. All these observations are consistent with two simultaneous contributions with opposite sign of MR, which may be assigned to holes and electrons having different magnetic field responses.

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There is broad interest in organic semiconductors because of their chemical tunability, low cost, and ease of processing. Magnetotransport in organic materials has started to be explored and both the spin valve [1] and tunnel-magnetoresistance effect [2] have been reported. Recently, an entirely new room temperature magnetoresistance (MR) has been observed in semiconducting organic materials by Francis *et al.* [3]. This magnetoresistance may be utilized for new applications in ''plastic'' electronics, since the effect is large (~10%) and requires relatively small magnetic fields. Understanding the mechanism of organic magnetoresistance (OMAR) may not only help in the development of future applications but may also improve the general understanding of charge transport in organic semiconductors and the role of spin, in particular.

Since the first report in 2004, OMAR has been reproduced by several other groups [4–6]. It has been found in many organic semiconductors having broadly varying properties; however, the observed behavior is surprisingly universal. Two characteristic line shapes of MR versus field were reported, where the MR as a function of magnetic field has been defined as $\mathrm{MR}(B) = [R(B) - R(0)]/R(0)$, where R is the resistance. The $\mathrm{MR}(B)$ curves were found to have typical field widths of the order of 10 mT [7]. For many devices both negative and positive magnetoresistance has been observed, displaying a transition which depends both on temperature and voltage [7]. The origin of this sign change has thus far not been established, neither experimentally nor theoretically. However, detailed understanding of the sign change could provide vital clues for further unraveling the origin of OMAR.

Three models have been proposed to explain the origin of OMAR. Two of them rely on magnetic field effects on excitons [4,5]. A third model relies on a magnetic field effect on bipolaron formation [8]. One distinguishable property between the excitonic models and the bipolaron model is that the excitonic models only work in bipolar devices while the bipolaron model predicts the effect to be present in electron-only and hole-only devices as well.

In this Letter, we investigate both the temperature and voltage dependence of the sign change. A correlation between the sign change and the onset of minority charge injection is found. We demonstrate that our observations cannot be explained by exciton models, but are consistent with a (bipolaron) model with two separate MR contributions where one may be assigned to majority carriers (electrons) and the other to minority carriers (holes).

We produced samples with two different molecules: (poly(2-methoxy-5-{3′, 7′-dimethyloctyloxy}-*p*-phenylenevinylene) (MDMO-PPV) and tris-(8-hydroxyquinoline) aluminum (Alq_3). The samples showed qualitatively similar features; however, here we present a coherent set of experimental results for a single Alq_3 device. The 4 mm × 4 mm devices were fabricated on cleaned indium tin oxide (ITO) patterned glass substrates. First, the substrates were covered by spin coating a poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) dispersion (H. C. Starck) after filtration using a 5 μm filter. Next, the samples were moved into a glovebox with a nitrogen atmosphere where in a high vacuum system (base pressure $\sim 10^{-7}$ mbar) 100 nm of 99.995% pure Alq_3 (Sigma-Aldrich) was evaporated. In a similar high vacuum system, within the same glovebox, 1 nm of LiF and 100 nm of Al were evaporated as the cathode. After fabrication, the samples were transported in nitrogen environment to a continuous flow liquid helium cryostat suspended between the poles of an electromagnet, where both dc measurements and ac admittance measurements were made.

First we measured the MR as a function of magnetic field at different temperatures and voltages. Figure 1 shows several MR (B) curves of the sample at 220 K and 300 K. The 7 V, 220 K positive MR (+MR) trace, and the 6 V 300 K negative MR (−MR) trace have a line shape that is the same as previously observed in literature [7]. These traces can be fitted with the empirical relationship:

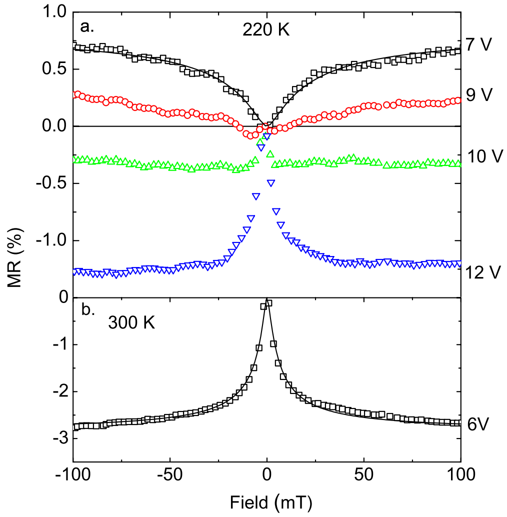

FIG. 1 (color online). (a) MR vs magnetic field curves at 220 K measured at different voltages. (b) MR vs magnetic field at 300 K. The solid lines are fits according to Eq. (1).

$$\mathrm{MR}\ (B) = \mathrm{MR}_\infty \left(\frac{B}{(|B| + B_0)} \right)^2, \qquad (1)$$

where B_0 is the characteristic field width, and MR_∞ is the MR at infinite B field [7]. In Fig. 1(a) we see that the sign of the MR changes from positive to negative between 9 V and 10 V, and (1) is not a good fit above 7 V. We also observe that the traces with +MR have a full width at half maximum (FWHM) of 41 mT which is significantly larger than the 11 mT FWHM of the −MR traces. Near the voltage where the MR switches sign there is an anomalous behavior, as shown by the local maximum at $B = 0$ mT for the 9 V trace. This behavior has also been observed by Mermer *et al.* [7]. However, the clear difference between the widths of the +MR and −MR features has not been previously reported.

The MR traces at 190 K and 240 K also showed a sign change from positive to negative MR with increasing voltage. In addition, all the traces had FWHMs similar to the 220 K data. The most noticeable change was that the transition voltage (V_{tr}) from +MR to −MR shifted to lower voltages as the temperature increased (inset in Fig. 3). The fact that V_{tr} is temperature dependent explains previous observations that the sign of the MR can change as a function of temperature.

At low voltages the log(I) versus log(V) plot is linear indicating a power law behavior with $I \propto V^6$ [Fig. 2(a)–2(c)], which is likely a signature of trap filling [9]. Investigation of the $I(V)$ characteristics near V_{tr} reveals an interesting trend. At all measured temperatures log(I) versus log(V) deviates from the power law and the slope increases at exactly V_{tr} (see vertical lines at $V = V_{tr}$ in Fig. 2).

To better understand what is happening at V_{tr} we did low frequency (212 Hz) admittance measurements using a lock-in technique. These measurements can reveal the presence of minority charge carriers (holes in Alq_3) by determining the differential capacitance (ΔC) [10]. In the case of space charge limited current (SCLC) the injected space charge necessarily lags behind the applied ac voltage modulation. Thus it gives a negative contribution, ΔC, to the total capacitance [10,11]. The onset of minority charge carrier injection causes a large increase in the amount of charge stored in the device due to charge compensation. This results in a large increase in ΔC, which may allow it to become larger than the geometric capacitance, thus causing the measured capacitance to become negative. This phenomenon is only observable at low frequencies, due to the low mobility of the minority charge carriers [10], and with weak electron-hole recombination since holes and electrons must be dispersed throughout the device [12].

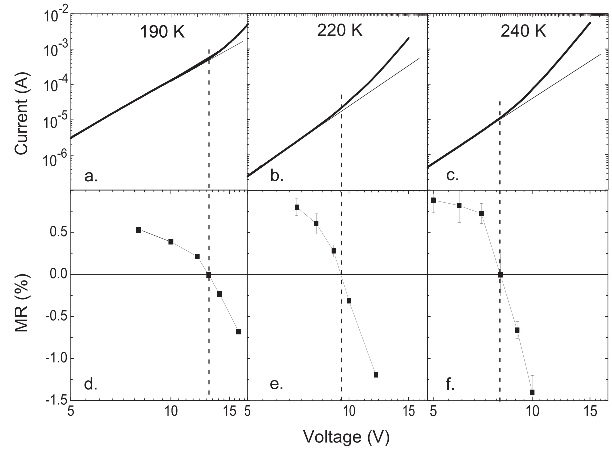

FIG. 2. (a)–(c) log(I) vs log(V) and (d)–(f) corresponding MR vs log (V) at 190 K, 220 K, and 240 K. The thin solid line represents a power law fit to the $I(V)$. The vertical dashed lines indicate the transition voltage V_{tr} where the MR switches from positive to negative.

In Fig. 3 the capacitance is plotted as a function of voltage at 190 K, 220 K, and 240 K. We observe that at a certain voltage the capacitance decreases, due to minority carrier injection, and it eventually becomes negative. Analogously, the minority charge injection also results in an increase of the slope of log(I) versus log(V) (Fig. 2) due to the increase in charge density with minority charge carrier injection.

The decrease in capacitance shifts to higher voltages when the temperature decreases, in a similar fashion as the temperature dependence of V_{tr} (inset in Fig. 3). The shift in the injection voltage of minority carrier injection with temperature is most likely due to hopping injection of holes at the anode-Alq_3 interface [13].

Concluding so far, the noticeable threefold correlation of (i) the sign change, (ii) the change in $I(V)$ behavior, and (iii) the onset of minority charge injection, shows that the sign change of the MR is a result of a transition from unipolar to bipolar conduction. The observation of MR in

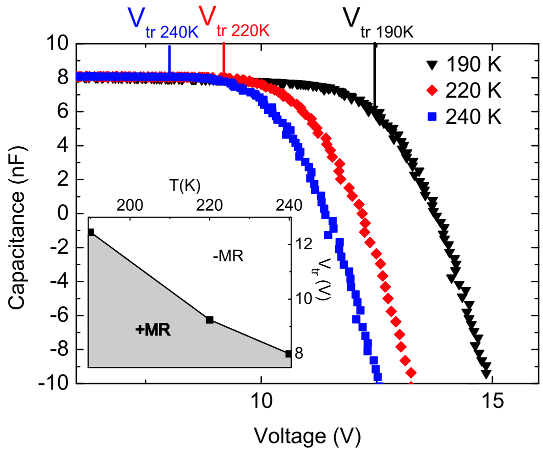

FIG. 3 (color online). Capacitance vs voltage at different temperatures measured with a 50 mV, 212 Hz ac excitation. The inset shows the transition voltage (V_{tr}) vs temperature.

these devices at operating voltages where they are unipolar is in disagreement with two recent models which explain OMAR via an excitonic effect [4,5], since bipolar currents are necessary to create excitons.

To further understand the sign change we performed simple modeling. There are two possible scenarios that can be used to describe the sign change. (1) The mechanism responsible for the MR has a continuously varying amplitude and FWHM as a function of voltage. (2) There are two contributions to the MR of opposite sign, which may have different but fixed FWHMs, coexisting in the device; the resulting line shape and amplitude are due to a superposition of these effects. First we try to explain the bias dependence of both the magnitude of the MR and the line shape by using a superposition of two MR effects (scenario 2); later our experimental results will be shown to be inconsistent with scenario 1.

Figure 2 shows that when the $I(V)$ exhibits power law behavior, the MR is positive and with the deviation from this power law the MR starts decreasing resulting in the MR eventually becoming negative. From this attribute we assume that the total current is a superposition of two contributions $I_{tot} = I_1 + I_2$. The current from the power law behavior, which is responsible for the positive MR, is defined as I_1, which is found by fitting the $I(V)$ to $I_1 = A \cdot V^n$. The other current, I_2, is the current in excess of the power law and is assigned a negative MR. The proportion of the current exhibiting power law behavior can be given as a function of voltage by the relation $P_1(V) = AV^n/I_{tot}(V)$.

If one fixed value of MR is assigned to the power law regime (MR_1) and another MR is assigned to the excess current (MR_2), it is possible to determine MR(V) from $P_1(V)$ via the relationship:

$$MR(V) = P_1(V)MR_1 + [1 - P_1(V)]MR_2. \quad (2)$$

We stress that assuming MR_1 and MR_2 to be independent of V is an empirical approach, but we will later discuss further justification. By calculating P_1 from the $I(V)$ curve MR_1 and MR_2 can be found by fitting Eq. (2) to the measured MR(V) data. Figure 4(a) and 4(b) shows the result for 220 K and 240 K. The values $MR_1 = 0.8\%$ and $MR_2 = -3.7\%$ give excellent fits at 220 K. Likewise, good fits were obtained for 190 K and 240 K.

After having fitted the MR(V), we can similarly model the MR(B) line shapes with two separate parallel MR contributions of opposite sign. MR(B) fits to (1) were made to MR traces that exhibited completely positive or negative behavior in order to find B_0 for each sign of MR. The fit for the −MR field width, using data taken at 300 K with a bias of 6 V, gave $B_0 = 2.8$ mT [Fig. 1(b)]. The +MR field width was obtained from a fit to data measured at 220 K with a 7 V bias, which results in $B_0 = 10.3$ mT [Fig. 1(a)].

From the analysis of MR(V) we know the magnitudes of the MRs and the relative proportions of +MR and −MR. Therefore, we can calculate the MR(B) curves at several voltages without any further free parameters. The correspondence of the model to the measurements can be seen by plotting the modeled MR(B) with the measured MR(B) data [Fig. 4(c)]. The correlation between the model and the data is excellent with the model even reproducing the small anomalous bump around 0 mT present in the 9 V trace.

The anomalous line shapes, which do not to fit either to a Lorentzian or Eq. (1), can easily be explained with a superposition of two MRs with behavior according to (1). Only the relative contributions of the MRs and no other properties have to change with voltage. Scenario 1 is not applicable, as a single line shape with varying width cannot account for the anomalous line shapes.

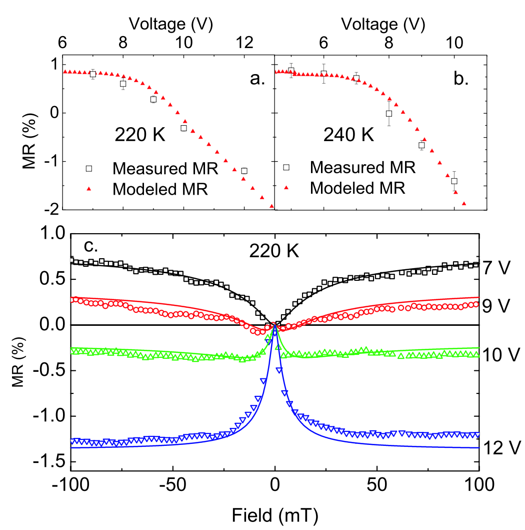

FIG. 4 (color online). Modeled MR(V) and measured MR(V) at 220 K (a) and 240 K (b). Modeled MR(B) (lines) curves and measured MR(B) (□) at different voltages (c).

The simplest explanation for the two separate MRs is that the electron and hole channels have different responses to the magnetic field, which may have opposite signs. Despite the fact that hole mobility in Alq_3 is much lower than the electron mobility, changes in the hole mobility can significantly affect the current by using the fact that in this Alq_3 device electrons and holes recombine weakly, as concluded from the admittance experiments. Thus, throughout the device the holes act to compensate the electrons' Coulomb repulsion. Therefore, changing the hole mobility changes the electron density. This can be shown using the equation for the current density of a two carrier SCLC [14]:

$$J = \frac{9}{8}\varepsilon\sqrt{\frac{2\pi\mu_e\mu_h(\mu_e + \mu_h)}{\mu_r}}\frac{V^2}{L^3}, \quad (3)$$

where μ_e, μ_h, and μ_r are the respective electron, hole, and recombination mobilities, L is the thickness of the device, and ϵ is the dielectric permittivity. This relation is for SCLC without traps, but is thought to hold for devices with traps, such as the one examined here, as well [14]. As a consequence of Eq. (3), a magnetic field dependence of the hole mobility can lead to a significant magnetoresistance even if hole transport provides a negligible contribution to the current. In the bipolar regime this leads to a magnetoresistance of the general form:

$$\mathrm{MR}\,(B) = -\left(C_e\frac{\Delta\mu_e}{\mu_e} + C_h\frac{\Delta\mu_h}{\mu_h}\right), \quad (4)$$

where $\Delta\mu = \mu(B) - \mu(0)$, $C_{e/h}$ are prefactors that depend on details of the model, whereas $\mathrm{MR}(B) = -\Delta\mu_e/\mu_e$ in the single-carrier regime. Extending the analysis of the bipolar SCLC regime as discussed in [14], we found that in certain limits Eq. (2) can be derived in an exact way, and MR_1 and MR_2 can be assigned to the single-carrier and bipolar regime, respectively, further justifying our empirical approach. Recent theoretical work has shown that both the sign as well as the linewidth of OMAR are strongly depending on (carrier dependent) materials parameters [8], and as such could indeed be different for electrons and holes. Similar trends for electron and hole linewidths in Alq_3 have been observed by electrically detected magnetic resonance [15] and one might speculate on a common origin. A more detailed microscopic interpretation of our results goes well beyond the scope of our Letter and will be an issue of future work. Finally, we emphasize that exciton based models cannot accommodate two separate effects since there is only one mobility channel that the magnetic field can affect, namely μ_r.

In conclusion, we performed $\mathrm{MR}(B)$, $I(V)$, and $C(V)$ measurements at different voltages and temperatures. A clear correlation between the sign change in OMAR and the onset of minority carrier (hole) injection was observed. Results can be modeled by separate OMAR contributions of opposite signs, which may be due to different magnetic response of the mobility of holes and electrons. These results support the recently proposed bipolaron model. Although this work is important in the understanding of the mechanism of the sign change, the microscopic origin of the opposite MRs and different B_0 of electrons and holes is still unclear. To resolve this issue, more dedicated experiments on specifically engineered samples and further development of theoretical models will be necessary.

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*f.l.bloom@tue.nl

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