# A Study on the Sign Inversion Behavior of Organic Magnetoresistance

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***Abstract*—We study the sign inversion behavior of organic magnetoresistance (OMR) in organic thin-film devices, to elucidate the mechanisms governing the well-known OMR phenomenon. From the combination of a percolation theory with a magnetic field modulated bipolaron mechanism, we derive a model that accounts for OMR sign inversion (OMRSI) behavior. It exhibits how an applied magnetic field acts together with other factors (temperature, bias, and film thickness) on the device current. Under the framework of space-charge-limited current, we reproduce two kinds of OMRSI behavior. In the end, we discuss the influence of hyperfine field on OMRSI lines.**

***Index Terms*—Hopping transport, organic magnetoresistance (OMR), percolation theory, space-charge-limited current (SCLC).**

IN NONMAGNETIC organic semiconductors, the large magnetic effect on current or resistance ($\Delta R(B)/R > 10\%$) at low magnetic field ($B < 10$ mT) and room temperature, which is dubbed as organic magnetoresistance (OMR) [1], [2], has potential applications in magnetic sensors and magnetically controlled optoelectronic devices [3], [4]. In organic light-emitting diodes (OLEDs), it has been found that the OMR can be both positive and negative, and temperature- and voltage-dependent OMR sign inversion (OMRSI) behavior has been assigned to a transition from a single-carrier regime to a double-carrier regime [5]. Because of intertwined spin and electrical transport properties, understanding the mechanisms of OMRSI may not only improve the properties of magnetic and electrical response but also help in the development of device applications.

To date, two kinds of OMRSI behavior have been experimentally observed, namely, bias-related OMRSI behavior and magnetic-related one. The former can be described as follows: at certain operating bias, the OMR increases (decreases) and saturates at a finite positive (negative) value with the increase in applied magnetic field, and the saturated value decreases from positive to negative [5] (from negative to positive [6]) as the operating bias increases. This behavior has been explained by several groups [7], [8]. The latter is comparatively complicated. It can be described as follows: at certain operating bias, the positive (negative) OMR increases (decreases) first and then decreases (increases) to negative (positive) values after reaching a finite maximum [9], [10] (minimum [11]) with the increase in applied magnetic field. Despite explanations that have been made by experimental researchers, the fundamental mechanisms governing these phenomena have not been well understood.

In this letter, we derive an OMR model that accounts for not only the bias-related but also the magnetic-related OMRSI behavior. It combines a percolation theory [12], [13] with a magnetic-modulated mechanism of bipolaron formation [7], [14], both of which describe a variable range hopping system with an exponential distribution of localized energy states [12], [14]. The electric field effect on OMRSI behavior is integrated by exploiting an effective temperature approach [15]. Under the framework of space-charge-limited current (SCLC), our model incorporates OMRSI sensitive factors [5], [9] such as thickness, operating bias, and temperature and reproduces typical experimental results [9], [11].

It was experimentally discovered that a unipolar (single-carrier) device had OMRSI behavior [10]; thus, we consider the magnetic effect on the transport of single carrier other than the course of carrier recombination. The carrier transport in organic devices can be described as the variable range hopping of charge carriers between localized states, which are randomly distributed in position and energy. We use an exponential density of state (DOS) as a good approximation of the tail states of real Gaussian distribution, which is written as $g(E) = (N_t/k_BT)\exp(E/k_BT_0)$ for $E < 0$ and $g(E) = 0$; otherwise, $N_t$ is the total number of states per unit volume, $T_0$ is a parameter related to the system disorder, $k_B$ is Boltzmann's constant, and $T$ is the temperature. Localized states, which have a deep energy level in the DOS, play an important role in the course of bipolaron formation. Because light elements composing organic materials are expected to lead to small spin–orbit coupling, we consider the influence of only local nuclei hyperfine field along with the applied magnetic field on the formation of bipolaron in organic materials.

The disordered organic system can be described under a percolation theory [12], [13], in which the conductance between sites $i$ and $j$ is written as $G_{ij} = G_0\exp(-s_{ij})$, where $G_0$ is a constant, $s_{ij} = -2\alpha R_{ij} - (|E_i| + |E_j| + |E_i - E_j|)/2k_BT$, $R_{ij}$ is the distance between the sites, $\alpha$ is the effective overlap parameter, and $E_i$ and $E_j$ are the respective energy

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levels. The critical percolation conductance $G_c$ is defined as the value of $G$ at which the first infinite cluster is formed. $G_c = G_0 \exp(-s_c)$ determines the device's conductivity; $s_c$ is the exponent of the critical percolation conductance. The onset of percolation is determined by calculating the critical average number of bonds per site: $r_N(G = G_c) = N_b/N_s$, where $N_b$ and $N_s$ are the total number of conducting bonds and possible connecting states per unit volume with fitting condition $s_c > s_{ij}$ and $s_c k_B T > |E - E_F|$, respectively. From the condition $s_c > s_{ij}$, we have the domain of site's energy in $g(E) : E_F < E < E_F + (s_c - 2\alpha R_{ij})k_B T$, and sites with energy in this area form first infinite cluster. In the presence of the electronic intrasite interaction $U$, there exist three electronic states for each Anderson localized state [14], namely, the unoccupied (UO) state, the singly occupied (SO, i.e., polaron) state, and the doubly occupied (DO, i.e., bipolaron) state. Then, the energy domain $E_F < E < E_F + (s_c - 2\alpha R_{ij})k_B T$ can be divided into two parts, namely, $E_F + (s_c - 2\alpha R_{ij})k_B T - U < E < E_F + (s_c - 2\alpha R_{ij})k_B T$ as the SO domain and $E_F < E < E_F + (s_c - 2\alpha R_{ij})k_B T - U$ as the DO domain. The DO domain with the penalty $U$ can accommodate two carriers with the same charge, and the first lower energy electron in this site is deeply trapped and seldom hops out; thus, the second electron hopping in must have a singlet spin configuration with respect to that of the first one [7]. With a triplet spin configuration, the path between two sites is temporarily blocked and disjunctive to the cluster. On the one hand, an applied magnetic field decreases the singlet probability of two spins, which causes blocking of transport (positive OMR). On the other hand, the magnetic field depresses the formation of bipolarons, which increases the population of polarons at the expense of bipolaron (negative OMR). The two competing components coexist as the origin of OMRSI behavior. With the consideration of spin flips induced by hyperfine field and an applied magnetic field $B$, the singlet probability $P(B)$ of two spins can be acquired. We adopt the formula given by Sheng *et al.* [2], [14] as $P(B) = P(0)B_0^2/(B^2 + B_0^2)$, where $B_0$ is a hyperfine-related parameter. For simplicity, we have $P(0) = 0.5$. As aforementioned, $N_s$ is the number of possible connecting states. It depends on the valence bond and has nothing to do with spin configurations. $N_b$ is the number of conducting bonds. It is obviously related to the spin configurations. Thus, we take the spin-flipped hopping into account in the SO-to-SO and SO-to-UO processes to infer $N_b$. To investigate the effect of electric field $F$ on OMRSI behavior, we replace temperature $T$ with an effective temperature $T_F = \{T_\beta + [\gamma e F/(\alpha k_B)]^\beta\}^{1/\beta}$, where $e$ is the electron charge, and $\beta$ and $\gamma$ are the fitting parameters [15]. Following Torricelli *et al.* [16], the polaron mobility in the presence of magnetic field turns out to be

$$\mu_p(B) = [A(B)]^\lambda \mu_{p0}(T, F) n_p(B)^{\lambda - 1} \tag{1}$$

where $\lambda = T_0/T_F$, $n$ is the carrier density, subscript $p$ is a notation of polarons, and $\mu_{p0}(T, F)$ is the polarons' mobility as a function of temperature $T$ and electric field $F$ [16]. The effect of magnetic field $B$ is embedded in the factor $A(B) = 1 + \exp(-U/k_B T_0)\ [P_{\rm SF}(B) - 1]$. Different from polarons, the bipolarons have a zero spin momentum. Therefore, their mobility may not be affected by magnetic field. In fact, little has been known about the bipolaron mobility in ordinary organic materials. We take an assumption of it in accordance with the nonmagnetic polaron mobility [12] under percolation theory as

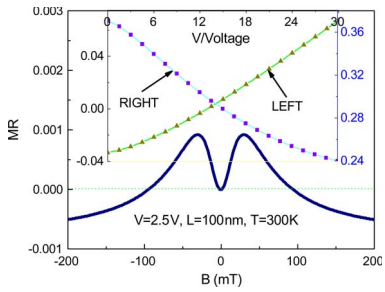


Fig. 1. (Main panel) Simulated OMRSI line for device ITO/PEDOT/$\alpha$-6T/Ca/Al. (Inset) Calculated bias-related OMRSI line.

$$\mu_{\rm bp}(B) = \mu_{\rm bp0}(T, F)\,[\eta(B) n_p(0)]^{\lambda - 1} \tag{2}$$

where the difference between $\mu_{p0}(T, F)$ and $\mu_{\rm bp0}(T, F)$ comes from different $\alpha$ of polarons and bipolarons, $\eta(B) = n_{\rm bp}(B)/n_p(B) = P(B)/p_d$ denotes the density ratio of bipolarons to polarons, and $p_d$ denotes the dissociation rate of bipolarons. Here, we suppose $\eta(0)$ and $p_d$ as constants at certain bias and temperature. Then, the SCLC equations that consist of both a polaron and a bipolaron term can be written as

$$J = (e n_p \mu_p + 2e n_{\rm bp} \mu_{\rm bp}) F(x) \tag{3}$$

$$dF(x)/dx = (e n_p + 2e n_{\rm bp})/(\varepsilon_0 \varepsilon_r), F(x) = -d\varphi(x)/dx. \tag{4}$$

Since $\mu_p$ and $\mu_{\rm bp}$ depend on the electric field, (4) cannot be directly solved. In order to work out an analytical expression of the current $J$, we replace the electric field in $\mu_p$ and $\mu_{\rm bp}$ with an effective electric field $F_{\rm eff}$. It is defined as the value of $F$ at which the most part of the charge transport takes place [16], i.e.,

$$F_{\rm eff} = (2T_0 + T)V/\left[2(T_0 + T)L\right]. \tag{5}$$

Then, we have the current density

$$J = f(B) J_0 \tag{6}$$

where all nonmagnetic factors are included in $J_0$, $f(B) = \{[A(B)]^\lambda + C[\eta(B)]^\lambda\}/[1 + 2\eta(B)]^\lambda$, and $C$ denotes the difference between $\alpha_{\rm bp}$ and $\alpha_p$. Substituting (6) into OMR definition $\mathrm{MR} = \Delta R(B)/R(0) = \Delta J(B)/J(B)$, we have

$$\mathrm{MR} = \left[f(0) - f(B)\right]/f(B). \tag{7}$$

Up to now, we have derived an MR expression that involves temperature, thickness, operating bias, and magnetic field. The ultimate OMR behavior is a comprehensive effect of all the physical quantities [5], [9]. The result can be applied to guide the design of such devices as OLEDs, magnetic storages, and sensors, in which the output light or the electrical signal are joint function of all the physical quantities.

In order to test the model, we simulated two experimental results. One is shown in Fig. 1 for OLED structure ITO/PEDOT/$\alpha$-6T/Ca/Al. The referenced experiment is chosen from [9], where the OMR was measured at a bias of 2.5 V and room temperature with a 100-nm organic layer. Under these conditions, the OMRSI investigation can help understanding the mechanism of the OLED and favor modulation to its

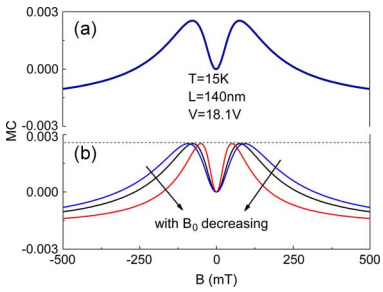


Fig. 2. (a) Simulated MC sign inversion line for device ITO/CuPc/NPB (60 nm)/BCP (80 nm)/LiF/Al. (b) Simulated influence of hyperfine field on MC versus $B$.

performance. In the main panel of Fig. 1, the MR versus $B$ is accordingly calculated with $U \approx 0.05$ eV, as suggested in [4]; $T_0 = 323.5$ K; $\alpha^{-1} = 1.8 \times 10^{-10}$ m; $\beta = 1.55$; $\gamma = 1.2$; and $P_d = 20.35\%$ according to [15] and [16]. It reproduces the magnetic-related OMRSI behavior of the experimental result. For other conditions, the structure may be used in magnetic-controlled sensors, where large MR favors the device sensitivity. We can regulate the MRs by adjusting the parameters, as shown in the inset in Fig. 1. The MR can either increase (left) or decrease (right) with bias increasing from 0 to 30 V, and the left line increasing from negative to positive is a typical bias-related OMRSI behavior in organic semiconductors.

The other is shown in Fig. 2 for device structure ITO/CuPc/NPB (60 nm)/BCP (80 nm)/LiF/Al. The referenced experiment is chosen from [1], where MC (relative change rate of current induced from magnetic field) was measured under a bias of 18.1 V and a temperature of 15 K. For the convenience of comparison, we calculate MR and turn it equivalently into MC. The MCs versus $B$ are calculated with $U \approx 0.05$ eV, $T_0 = 578.5$ K, $\alpha^{-1} = 2.2 \times 10^{-10}$ m, $\beta = 1.58$, $\gamma = 1.801$, and $P_d \approx 15\%$ [15], [16]. $B_0$ is a hyperfine-related parameter. For $B_0 = 55$ mT, our theoretical result is shown in Fig. 2(a). It also reproduces the magnetic-related OMRSI behavior of the experimental result [11]. We indicate the magnetic field corresponding to the MC maximum as $B_m$. Fig. 2(b) shows effects of $B_0$ on MC. Decreasing $B_0$ from 55 to 25 mT, the MC maximum remains unchanged, which has not been reported as far as we know, whereas $B_m$ dwindles with decreasing $B_0$, which is in accordance with [10].

It is noteworthy that the MR line in Fig. 1 (MR with maximum) and the MC line in Fig. 2 (be equivalent to MR with minimum) recreate the two typical OMRSI phenomena, as aforementioned. Until now, we have reproduced both OMRSI phenomena with one model. In case we reference the model in the device design, once the material and the device structure are setted, we can confirm the variation trend of the device output signal and, particularly, the fine feature at low magnetic field. This will be beneficial to the stability control of the operating area.

It should be noted that the magnitude of the predicted OMR effect appears to be smaller than usual. We suppose that is a joint effect of two opposite but interdependent primary mechanisms, namely, blocked transport from decreased singlets (causing positive OMR) and increased population of polarons (causing negative OMR). In this letter, we focus on the sign-inversion domain of OMRs, in which the two competing components coexist, and the MRs approach to zero. We may give prominence to one of the competing components by changing parameters in our model to achieve large MR. As shown in Fig. 1, the MRs can be larger than 30% at $B < 100$ mT. This is necessary for improvement in the device sensitivity.

To conclude, in this letter, we have presented a model accounting for the OMRSI behavior under the SCLC framework. Using this model, we have reproduced both the bias- and magnetic-related OMRSI behavior being in accordance with reported experimental results. Because of including such parameters as temperature, thickness, and operating bias, this model would be helpful in device design and stability control of operating performance.

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