Temperature, electric-field, and carrier-density dependence of hopping magnetoresistivity in disordered organic semiconductors

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Based on the extended variable range hopping mechanism in a disordered energy landscape with a Gaussian density of states, we determine the dependence of the magnetoresistivity on temperature, carrier density, magnetic field, and electric field. Experimental electric-field and temperature characteristics in device based on organic semiconductors are excellently reproduced with this unified description of the magnetoresistivity. We further show that the spin transport indeed can be explained by the fact that magnetic field will decrease the density of transport states and similar to the decrease of carrier density without it. We finally demonstrate that magnetoresistivity is strongly dependent on the carrier density; by changing the carrier density in the hopping system, the magnetoresistivity can increase more than 500 times.

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I. INTRODUCTION

Organic semiconductors exhibit the characterization of a high disorder in morphology, chemical purity, and molecular structure, which differs in many regards from inorganic or purely carbon based-materials [1–4]. Recently, because of hyperfine interactions [5] and large room-temperature magnetoresistance (up to ∼20%) [6], organic spintronics have attracted more interest [7,8]. Generally, due to the existence of localized states and weak spin-orbital coupling, charge transport in organic semiconductors under the effect of magnetic field provides dramatically different phenomena from inorganic semiconductors or metals [7–10]. Organic magnetoresistance (MR) can date back to 1967 and a pronounced MR in organic devices has been frequently observed over the years [11–13], however several confusing phenomena and fundamental characteristics in organic MR have been only partially addressed until recently. For example, why do positive MR (+MR) and negative MR (−MR) traces display the line shape [14]? Do the spin correlations between same or oppositely charged carriers play a more important role [15,16]? Understanding the transport mechanism of charge carriers under the magnetic field is of crucial importance to design and synthesize better materials and further improve the MR of organic semiconductor devices.

The initial model explaining magnetic-field effects is the carrier-pair mechanism [17], which described field-induced changes of spin permutation symmetry. But this mechanism cannot explain organic semiconductors operating at the single carrier regimes. Recent works have proposed some theoretical descriptions of organic MR based on percolation theory. For example, Harmon *et al.* presented a model for organic MR to describe the effects of spin dynamics on hopping transport [15]. Then they extended the theory of MR to include exchange and dipolar couplings between polarons [16]. Recently, we have also developed a theory to interpret organic MR based on bipolaron-assisted transport mechanism [10]. However, these current theories only considered the effects of bipolaron formation, spin exchange, or spin-spin interactions on MR. Generally, organic devices usually work in a larger carrier density and high electric field. Therefore, it should be interesting to know how the electric field and carrier density affect the charge transport in organic spintronic devices. It is widely accepted that the charge transport in organic semiconductors depends on temperature T, electric field F, and charge-carrier density n [18–21]. The electric field has been observed to significantly affect spin transport in inorganic semiconductors [22]. Our previous work also has indicated that the electric field will significantly affect spin diffusion in disorder organic semiconductors [23]. On the other hand, the probability of bipolaron formation, spin exchange, and polaron hopping are closely related to temperature, electric-field, and carrier-density [24–26]. Thus these relative effects on charge transport should be taken into account when discussing the MR in organic spintronic devices. However, to the authors' knowledge the relationship between MR and T, F, and n is still lacking. The purpose of this work is to establish a unified theoretical description of the full T, F, and n dependence of MR, and to critically compare the results with experimental data and further analyze these effects on MR in organic spintronic devices.

II. THEORETICAL MODEL

It is well known that organic semiconductors display a higher degree of disorder, and charge (polaron) transport takes place mostly by hopping between localized states [27,28]. In the absence of magnetic field, one can consider hopping as a thermally assisted tunneling process and assume coupling to a system of acoustical phonons. The transition rate for a carrier moving from site i to site j is based on the Miller-Abrahams (MA) transition rate as follows [29,30]:

$$w_{ij} = \nu_0 \begin{cases} \exp\left(-2\alpha R_{ij} - \frac{E_j - E_i}{k_B T}\right), & E_j - E_i > 0 \\ \exp(-2\alpha R_{ij}), & E_j - E_i < 0 \end{cases}, \quad (1)$$

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where v_0 is the attempt-to-jump frequency, α is the inverse localized length, R_{ij} is the hopping distance, E_i and E_j are the on-site energies at sites i and j, respectively, and k_B is the Boltzmann constant. When an electric field F is applied to the system, it will weaken the Coulomb barrier and hence reduce the thermal activation energies [20]. The transition rate with normalized energy ($\epsilon = E/k_BT$ and $r_{ij} = 2\alpha R_{ij}$) under the electric field is of the form [23,31]

$$w_{ij} = \begin{cases} v_0 \exp[-(1+\beta\cos\theta)r_{ij} - \epsilon_j + \epsilon_i + U], & \epsilon_j - \epsilon_i + U > -\beta r_{ij}\cos\theta \\ v_0 \exp(-r_{ij}), & \epsilon_j - \epsilon_i + U < -\beta r_{ij}\cos\theta \end{cases}, \tag{2}$$

where $\beta = qF/2\alpha k_BT$ comes from the difference of the energy due to a contribution $qFr_{ij}\cos\theta$ of electric field F (q is the elementary charge of the carrier and θ is the angle between the electric field and the hopping direction), U is the Hubbard energy. The variations in the on-site energy due to disorder are usually assumed to be Gaussian density of states (DOS), which holds for spin transport in disordered organic semiconductors as well [7,23],

$$g(E) = \frac{N_t}{\sqrt{2\pi}\sigma}\exp\left(-\frac{E^2}{2\sigma^2}\right), \tag{3}$$

where N_t is the total density of localized states and σ is the width of energetic disorder.

Then, let us consider the situation that a carrier with unit charge q (electron or hole) moves under the influence of an electric field, a site with energy ϵ_i in the hopping space; the most probable hop for a carrier on this site is to an empty site at a range R_{ij}, for which it needs the minimum energy. The conduction is a result of a long sequence of hops through this hopping space. In this situation, the average hopping range R_{nn} can be obtained following the approach used in our previous work [32] by solving the equation

$$B_c = \frac{1}{8\alpha^3}\int_0^{\pi}\sin\theta d\theta\int_0^{R_{nn}} 2\pi r^2 dr \times \int_{-\infty}^{R_{nn}+\epsilon_i - r(1+\beta\cos\theta)} \frac{g(\epsilon)}{1+\exp(\epsilon-\epsilon_f)}d\epsilon, \tag{4}$$

where $B_c = 2.8$ is the percolation criterion for a three-dimensional system and ϵ_f denotes the Fermi level.

Under the effect of magnetic field, both charge and spin motion are coupled, and three types of transport should be considered, as shown in Fig. 1(a): (i) spin exchange, (ii) polaron hopping toward an empty site, and (iii) polaron hopping toward a singly occupied site (i.e., bipolaron formation) with subsequent hopping including bipolaron motion and dissociation. Here we only consider MR deriving from the interaction between charge carriers of the same sign [10,15,16]. The first transport only exchanges the spin state of two adjacent sites and generates a net spin current, and hence does not contribute to MR for its zero charge current. The last two transports can carry charge current and hence contribute to MR. Figure 1(b) illustrates the diagram of variable range hopping (VRH) transport with the density of states under the effect of electric and magnetic field, where the current is carried by the hopping of polarons or bipolarons.

As described by Harmon, *et al.* [15], spin affects electronic transport in hopping transport through the Pauli exclusion principle, and faster spin-flip transitions coming from the hyperfine interaction open up "spin-blocked" pathways to become viable conduction channels, and external magnetic field suppresses this spin flip and changes the effective density of hopping sites, thus producing magnetoresistance. In the hopping space, it is most common for a polaron with arbitrary spin to hop to an unoccupied site. At the same time, there is a probability that a polaron may hop to a site singly occupied to form a singlet bipolaron, taking into account the probability of spin flips. Then, Eq. (4) is rewritten as

$$B_c = \frac{1}{8\alpha^3}\int_0^{\pi}\sin\theta d\theta\int_0^{R_{nn}} 2\pi r^2 dr \left[\int_{-\infty}^{R_{nn}+\epsilon_i - r(1+\beta\cos\theta)} \frac{\frac{N_t}{\sqrt{2\pi}\sigma}\exp\left(-\frac{\epsilon^2}{2\sigma^2}\right)}{1+\exp(\epsilon-\epsilon_f)}d\epsilon + \int_{-\infty}^{R_{nn}+\epsilon_i - r(1+\beta\cos\theta)-U}\left(\frac{\frac{N_p}{4\sqrt{2\pi}\sigma}\exp\left(-\frac{\epsilon^2}{2\sigma^2}\right)}{1+\exp(\epsilon-\epsilon_f)} + \frac{\frac{3pN_p}{4\sqrt{2\pi}\sigma}\exp\left(-\frac{\epsilon^2}{2\sigma^2}\right)}{1+\exp(\epsilon-\epsilon_f)}\right)d\epsilon\right], \tag{5}$$

where N_t and N_p are the density of localized states for polarons and bipolarons, respectively. As described above, a polaron with arbitrary spin may hop to an unoccupied site; it may also hop to a site singly occupied with antiparallel spin, or that with parallel spin accompanying spin flips. The respective densities of these three types of sites correspond to the three parts in the last bracket of Eq. (5). In Eq. (5), the parameter p is the probability for the blockade to cease when the next hop is attempted as [16,23]

$$p = \frac{1}{3} - \frac{\int_0^{\infty}\exp(-t/\tau_h)\left[1 - \frac{a_{\text{eff}}{}^2t^2}{8}\left(1 + \frac{2\sin^2\omega_0 t/2}{(\omega_0 t/2)^2}\right)\right]dt}{3\tau_h}, \tag{6}$$

where $\tau_h = {w_{ij}}^{-1}$ is the hopping time, $\omega_0 = \gamma_e B\hat{Z}$ is the applied external magnetic field (γ_e is the gyromagnetic ratio

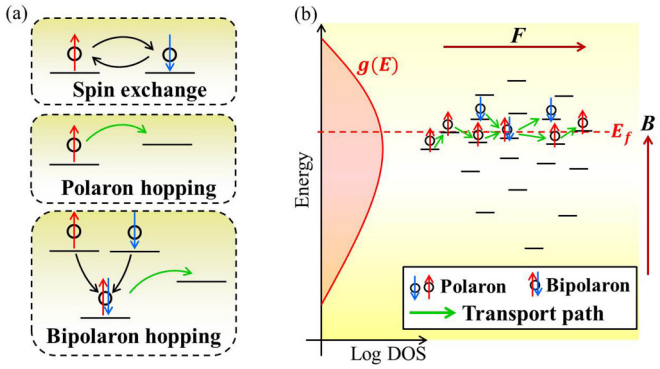

FIG. 1. (a) Three types of transport mode in organic spintronic devices, such as spin exchange, polaron hopping, and bipolaron hopping. (b) Diagram of variable range hopping (VRH) transport with the density of states under the effect of electric and magnetic field, where the current is carried by the hopping of polarons or bipolarons.

and $\hat{Z}$ is the magnetic direction), $a_{\rm eff}$ is the effective hyperfine coupling width due to all the nuclei at a site, and t is the time. The main difference between our work and Ref. [16] is that we introduce the Fermi level (corresponding to carrier density), energetic disorder, and electric field into this model. In the presence of an electric field, a particle with energy ϵ_i at a given site hops a distance R_{nn} in the hopping space, the average hopping distance along the electric field is $\overline{x_f}$ (the detailed derivation of $\overline{x_f}$ is in the Appendix). In the hopping space, the probability of all these hops is $\exp(-R_{nn})$; after knowing the average hopping distance, it is possible to say that the average rate of the transport is $v_0\overline{x_f}\exp(-R_{nn})$, hence, the mobility at energy ϵ_i is given as

$$\mu(\epsilon_i,B,F,T,\epsilon_f)=\frac{v_0\overline{x_f}\exp(-R_{nn})}{F}. \tag{7}$$

Then, the total resistivity of the hopping system is obtained from the mobility as

$$R(B,F,T,\epsilon_f)=\frac{1}{\sigma_{\rm con}(B)}=\frac{1}{\int_{-\infty}^{\infty}qg(\epsilon_i)\mu(\epsilon_i,B,F,T,\epsilon_f)k_BT/[1+\exp(\epsilon_i-\epsilon_f)]d\epsilon_i}. \tag{8}$$

After defining the MR as $\mathrm{MR}=\frac{[R(B,F,T,\epsilon_f)-R(0,F,T,\epsilon_f)]}{R(0,F,T,\epsilon_f)}$, based on Eq. (8) one can write the final MR as

$$\mathrm{MR}=\frac{\int_{-\infty}^{\infty}qg(\epsilon_i)\mu(\epsilon_i,0,F,T,\epsilon_f)k_BT/[1+\exp(\epsilon_i-\epsilon_f)]d\epsilon_i}{\int_{-\infty}^{\infty}qg(\epsilon_i)\mu(\epsilon_i,B,F,T,\epsilon_f)k_BT/[1+\exp(\epsilon_i-\epsilon_f)]d\epsilon_i}-1. \tag{9}$$

III. RESULTS AND DISCUSSION

In Fig. 2, we display the comparison between the theoretical calculation and experimental data for magnetic-field dependence of MR at different electric fields (voltage). This dependence shows a striking similarity to the B dependence found by the empirical relation $\mathrm{MR}\propto B^2/(B^2+B_0^2)$ [25], that is, MR increases with $|B|$ and saturates at high external magnetic field. The parameters used for the calculation here are $N_t=N_p=1\times10^{28}\,\mathrm{m}^{-3}$, $E_f/\sigma=6.5$, $\alpha^{-1}=1$ Å, $v_0=1\times10^{10}\ \mathrm{s}^{-1}$, $\gamma_e=2.1\times10^8\,\mathrm{ns}^{-1}\mathrm{mT}^{-1}$, $U=0.5\,\mathrm{eV}$, and

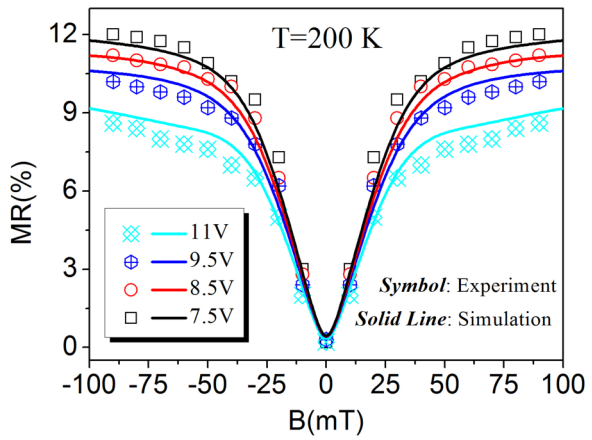

FIG. 2. Magnetic field dependence of magnetoresistance (MR) at various voltages. Symbols: experimental data from Ref. [37]. Lines: fits using the theoretical model given by Eq. (9).

$a_{\rm eff}/v_0=1.5$. These parameters are typical ones for organic semiconductors [16,33]. Currently, the physical origin for MR saturation is attributed to the decrease in hyperfine interaction induced spin mixing with the Zeeman split energy levels [34]. The saturation should occur when $B\gg a_{\rm eff}$ [16]. Here, using our model, we can understand this mechanism in the language of equilibrium energy. The conduction occurs when the ratio of bond density and site density reaches the bonding criterion B_c. Hyperfine interaction induced spin flip increases the possible hopping destinations, corresponding to bond density. External magnetic field suppresses this effect and thus decreases the bond density. The decrease of bond density will result in the decrease of site density required for percolation path forms, i.e., the decrease of the Fermi level. Therefore the influence of magnetic field can be seen as decreasing the Fermi level of the hopping system. The value of MR can be regarded as proportional to the conductivity ratio, i.e., $\mathrm{MR}=\sigma_{\rm con}(B=0)/\sigma_{\rm con}(B)-1$. With the increase of B, corresponding to the decrease of the Fermi level, it has been well known that the conductivity of the hopping system will decrease with Fermi level decreasing, thus the MR will increase. However, when the Fermi level is decreased to the so-called equilibrium energy [35], the conductivity will keep a constant, so MR will saturate finally. The critical carrier concentration, above which the mobility will increase, is $n_c=\frac{N_{\rm total}}{2}\exp[-(\epsilon_T-\epsilon_f)]$ when ϵ_f is below the so-called equilibrium energy $\epsilon_\infty=-(\frac{\sigma}{k_BT})^2$ [35,36], where ϵ_T is the transport energy. Under the influence of magnetic field, the total density of localized states $N_{\rm total}$ is simply rewritten as $N_t+N_p/4+3pN_p/4$. In this situation,

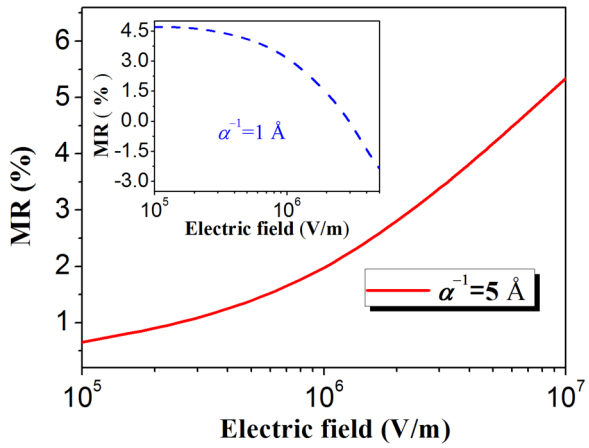

FIG. 3. Electric-field dependence of MR for a larger localization length of $a^{-1} = 5$ Å. Inset: for a smaller localization length of $a^{-1} = 1$ Å.

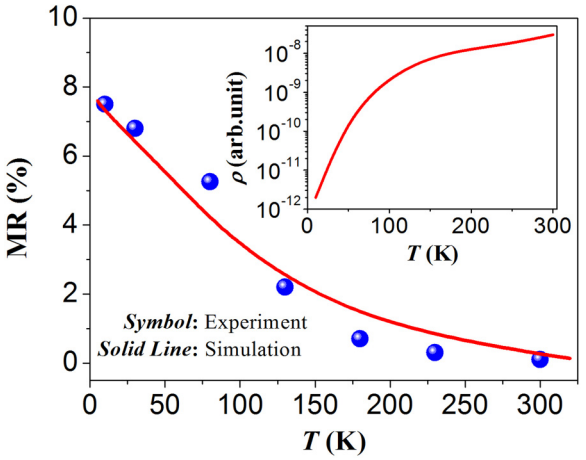

FIG. 4. Temperature dependence of MR. Symbol: experimental data from Ref. [41]. Solid line: fits using the theoretical model given by Eq. (9). Inset: temperature dependence of magnetic resistivity.

$n_c = \frac{N_t+N_p/4+3pN_p/4}{2}\exp\ (-\{\epsilon_T - [\epsilon_f + \ln(\frac{N_t+N_p/4+3pN_p/4}{N_t})]\})$, where one can see that the increase of B will lead to the decrease of p and if $\epsilon_f + \ln(\frac{N_t+\frac{N_p}{4}+\frac{3pN_p}{4}}{N_t}) = \epsilon_\infty$, the mobility will stay constant and MR will saturate.

Another interesting property in Fig. 2 is that the MR will decrease with the increase of electric field. However, this is not a general rule. For a larger localization length, MR will increase with electric field, as shown in Fig. 3. The negative MR will also appear at a larger electric field, as shown in the inset in Fig. 3. Actually, both decrease and increase of MR with electric field have been observed by experiments [34,38]. The physical reason has been attributed to the different injection efficiency [15]. Basically, the charge hopping conductivity $\sigma_{\rm con}$ can be described by phenomenological Gill equation as [39]

$$\sigma_{\rm con} \propto \exp\left[-\frac{E_a - \beta_0\sqrt{F}}{k_B}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right], \qquad (10)$$

where T^* is the "Gill temperature," E_a is the zero-field activation energy, and β_0 is the constant. Both electric field and carrier density will change T^*, and T^* will increase with $q\alpha^{-1}F$ and decrease with carrier density. As pointed above, the MR can be described as

$$\begin{aligned} {\rm MR} &= \frac{\sigma_{\rm con}(B=0)}{\sigma_{\rm con}(B)} - 1 \\ &= \exp\left[\frac{\beta_0\sqrt{F} - E_a}{k_B}\left(\frac{1}{T^*(B)} - \frac{1}{T^*(B=0)}\right)\right] - 1. \end{aligned} \qquad (11)$$

If the localization length α^{-1} is small, the influence of $q\alpha^{-1}F$ is very weak, due to the effect from magnetic field being similar to the decrease of carrier density, $T^*(B) > T^*(B=0)$, therefore, MR will decrease with electric field. However, with the increase of α^{-1}, the influence of $q\alpha^{-1}F$ becomes dominant; MR reasonably increases with electric field.

Next, we want to discuss the temperature dependence of MR. Figure 4 shows the comparison between the calculation and experimental data for the temperature dependence of MR. The parameters used for calculation here are $N_t = N_p = 2\times10^{28}$ m^{-3}, $F = 4.5\times10^5$ V/m, $\alpha^{-1} = 8$ Å, $E_f/\sigma = 2.1$, and the other parameters are the same as those in Fig. 2. It is clear here that even the magnetic resistance will increase with temperature (as shown in inset in Fig. 4), and the value of MR will decrease with increasing temperature. The physical explanation is the same as discussed above; the hopping conductivity for the medium carrier-density regime can also be simplified as [40] $\sigma_{\rm con} \propto \exp(\frac{qE_f}{k_BT})$, then ${\rm MR} = \frac{\sigma_{\rm con}(B=0)}{\sigma_{\rm con}(B)} - 1 = \exp(\frac{qE_f(B=0)-qE_f(B)}{k_BT}) - 1$, due to the influence from B being the same as the decrease of the Fermi level, so the MR will decrease with the increase of temperature.

In what follows, we want to discuss the carrier-density dependence of the MR in detail. It is widely known that the hopping transport properties are strongly dependent on the carrier density, but the experimental research for such an issue has been very scarce. Using the same parameters as those in Fig. 2, we plot the carrier-density dependence of MR in Fig. 5. Very strikingly, the MR will increase the carrier density steeply after passing a peak value. It will decrease to zero eventually.

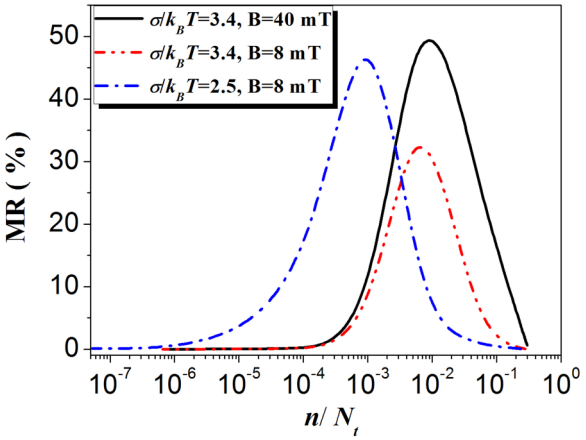

FIG. 5. Carrier-density dependence of MR for different temperatures and magnetic field.

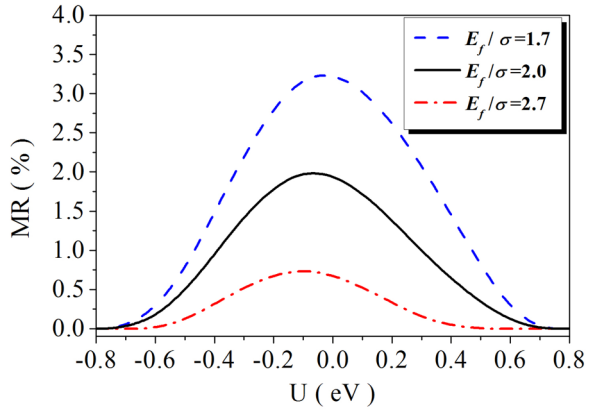

FIG. 6. MR as a function of Hubbard energy for different disorder parametric in the normalized Fermi level E_f/σ.

To clearly understand the effect of Hubbard energy on MR, we then calculate the MR at different Hubbard energies. Figure 6 shows MR as a function of Hubbard energy for different disorder parametric in the normalized Fermi level E_f/σ. The parameters used for calculation here are $F = 10^5$ V/m, $\alpha^{-1} = 8$ Å, and the other parameters are the same as those in Fig. 2 One can see that the calculated MR decreases with raising E_f/σ. Otherwise, it is obvious that the MR effect will reach the maximum around $U = 0$. In the $U > 0$ regime MR shows the decreasing trend, while showing the opposite result as U becomes negative. This result is consistent with our previous work [10].

Finally, we want to discuss the physical origin for MR under the effect of magnetic field. The schematic picture is plotted in Fig. 7. As we discussed above, the magnetic field affecting the charge transport can be regarded as the Fermi level decreasing (corresponding to carrier density decreasing). We have also pointed out that the hopping conductivity is strongly dependent on carrier density. The typical carrier-density dependence of the hopping mobility is as the blue line in Fig. 7 [42]. The mobility is a constant at the low-density regime, while it increases as a power law as soon as the Fermi level approaches

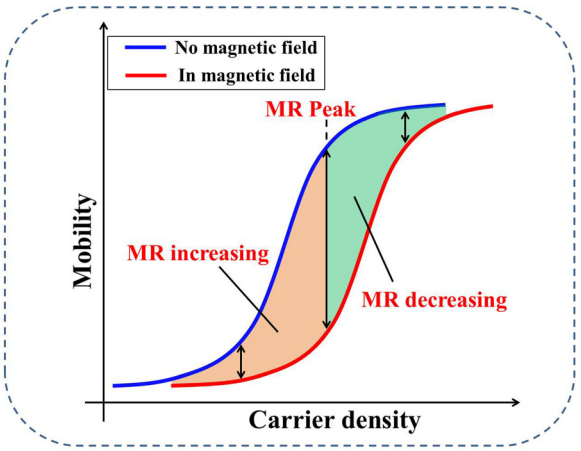

FIG. 7. Schematic explanation for carrier-density dependence of MR.

the equilibrium energy, and saturates at the very high-density regime. Since the influence from the magnetic field is similar to the carrier density decreasing, the blue line will shift right to the red line, which is presented as the density dependence of mobility under the magnetic field B. So the MR will increase with carrier density at first, and reach the peak where the mobility of the red line starts to increase. After that, the MR decreases to zero.

IV. CONCLUSION

The good fit we obtain with the experimental data of MR strongly suggests that the underlying dependence of the MR on temperature, carrier density, and electric field in these materials is correctly described by extending the variable range hopping model presented in this work, at least in the regime of temperature, electric field, and magnetic field considered here. Another important conclusion is that the influence of magnetic field on charge transport, can be effectively explained by the fact that the magnetic field decreasing the hopping density can be seen as decreasing the total localized density of states or staying the same in the total localized states, as well as decreasing the Fermi level of this hopping system. We can define this Fermi level as magnetic Fermi level $E_f(B)$, which is usually smaller than the original Fermi level. Moreover, a markedly larger MR value can be obtained if we find the proper carrier density in the hopping system, according to our calculations here, which simulate the experimental research on this issue. We should, however, also point out that the spin-orbit coupling is not discussed here. Intuitively, spin-orbital coupling provides another channel of spin flip, and thus tends to hinder the hyperfine effect and decrease MR. In a rough approximation, this effect can be included in the expression of probability for the blockade to cease [Eq. (6)]. However, the dependence of this effect on various parameters, particularly external electric and magnetic fields, is nontrivial and deserves further study.

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APPENDIX

In the presence of an electric and magnetic field, polarons and bipolarons are more possible hops along the field direction and, concomitantly, there will be a net spatial displacement. Summing up the jump trajectories for an initial energy ϵ_i, the average real forward hopping distance along the electric

field, $\overline{x_f}$, is given as

$$\overline{x_f}(\epsilon_i, B, F, T, \epsilon_f) = \frac{\overline{x_f}'(\epsilon_i, B, F, T, \epsilon_f)}{2\alpha}, \tag{A1}$$

where $\overline{x_f}'(\epsilon_i, B, F, T, \epsilon_f)$ is the normalized average forward hopping distance of polarons and bipolarons given as

$$\overline{x_f}'(\epsilon_i, B, F, T, \epsilon_f) = \frac{I_1 + I_2}{I_3 + I_4}, \tag{A2}$$

where

$$I_1 = \int_0^{\pi} d\theta \sin\theta \left\{ \int_{\epsilon_i - \beta R_{nn}\cos\theta}^{\epsilon_i + R_{nn}} d\epsilon \left[\frac{N_t}{\sqrt{2\pi}\sigma} \exp\left(-\frac{\epsilon^2}{2\sigma^2} \right) [1 - f(\epsilon)] \right] \left(\frac{R_{nn} - \epsilon + \epsilon_i}{1 + \beta\cos\theta} \right)^3 \right.$$
$$\left. + \int_{\epsilon_i - \beta R_{nn}\cos\theta - U}^{\epsilon_i + R_{nn} - U} \left[\frac{\left(\frac{N_p}{4} + \frac{3pN_p}{4}\right)}{\sqrt{2\pi}\sigma} \exp\left(-\frac{\epsilon^2}{2\sigma^2} \right) [1 - f(\epsilon)] \right] \left(\frac{R_{nn} - \epsilon + \epsilon_i - U}{1 + \beta\cos\theta} \right)^3 \right\} \times \cos\theta,$$

$$I_2 = \int_0^{\pi} d\theta \sin\theta \left\{ \int_{-\infty}^{\epsilon_i - \beta R_{nn}\cos\theta} d\epsilon \left[\frac{N_t}{\sqrt{2\pi}\sigma} \exp\left(-\frac{\epsilon^2}{2\sigma^2} \right) [1 - f(\epsilon)] \right] \right.$$
$$\left. + \int_{-\infty}^{\epsilon_i - \beta R_{nn}\cos\theta - U} \left[\frac{\left(\frac{N_p}{4} + \frac{3pN_p}{4}\right)}{\sqrt{2\pi}\sigma} \exp\left(-\frac{\epsilon^2}{2\sigma^2} \right) [1 - f(\epsilon)] \right] \right\} {R_{nn}}^3 \times \cos\theta,$$

$$I_3 = \int_0^{\pi} d\theta \sin\theta \left\{ \int_{\epsilon_i - \beta R_{nn}\cos\theta}^{\epsilon_i + R_{nn}} d\epsilon \left[\frac{N_t}{\sqrt{2\pi}\sigma} \exp\left(-\frac{\epsilon^2}{2\sigma^2} \right) [1 - f(\epsilon)] \right] \left(\frac{R_{nn} - \epsilon + \epsilon_i}{1 + \beta\cos\theta} \right)^2 \right.$$
$$\left. + \int_{\epsilon_i - \beta R_{nn}\cos\theta - U}^{\epsilon_i + R_{nn} - U} \left[\frac{\left(\frac{N_p}{4} + \frac{3pN_p}{4}\right)}{\sqrt{2\pi}\sigma} \exp\left(-\frac{\epsilon^2}{2\sigma^2} \right) [1 - f(\epsilon)] \right] \left(\frac{R_{nn} - \epsilon + \epsilon_i - U}{1 + \beta\cos\theta} \right)^2 \right\} \times \cos\theta,$$

$$I_4 = \int_0^{\pi} d\theta \sin\theta \left\{ \int_{-\infty}^{\epsilon_i - \beta R_{nn}\cos\theta} d\epsilon \left[\frac{N_t}{\sqrt{2\pi}\sigma} \exp\left(-\frac{\epsilon^2}{2\sigma^2} \right) [1 - f(\epsilon)] \right] \right.$$
$$\left. + \int_{-\infty}^{\epsilon_i - \beta R_{nn}\cos\theta - U} \left[\frac{\left(\frac{N_p}{4} + \frac{3pN_p}{4}\right)}{\sqrt{2\pi}\sigma} \exp\left(-\frac{\epsilon^2}{2\sigma^2} \right) [1 - f(\epsilon)] \right] \right\} {R_{nn}}^2 \times \cos\theta,$$

where $f(\epsilon) = \frac{1}{1+\exp(\epsilon - \epsilon_f)}$ is the Fermi-Dirac distribution and $1 - f(\epsilon)$ is the probability that the final site is empty.

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