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Role of electron-hole pair formation in organic magnetoresistance

Sayani Majumdar,[1,2,*] Himadri S. Majumdar,[1] Harri Aarnio,[1] Dirk Vanderzande,[3] Reino Laiho,[2] and Ronald Österbacka[1]
[1]*Department of Physics and CoE for Functional Materials, Åbo Akademi University, Turku 20500, Finland*
[2]*Wihuri Physical Laboratory, University of Turku, Turku 20014, Finland*
[3]*Chemistry Division, Institute of Material Research, Universiteit Hasselt, B3590 Diepenbeek, Belgium*
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Magnetoelectrical measurements were performed on diodes and bulk heterojunction solar cell blends (BHSCs) to clarify the role of formation of Coulombically bound electron-hole (e-h) pairs on the magnetoresistance (MR) response in organic thin-film devices. BHSCs are suitable model systems because they effectively quench excitons but the probability of forming e-h pairs in them can be tuned over orders of magnitude by the choice of material and solvent in the blend. We have systematically varied the e-h recombination coefficients, which are directly proportional to the probability for the charge carriers to meet in space, and found that a reduced probability of electrons and holes meeting in space lead to the disappearance of the MR. Our results clearly show that MR is a direct consequence of the e-h pair formation. We also found that the MR line shape follows a power-law dependence of $B^{0.5}$ at higher fields.

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Organic magnetoresistance (OMAR) is a universal low-field magnetoresistance (MR) effect seen in organic diodes without magnetic electrodes.[1,2] Since the MR in organic materials is highest known among all nonmagnetic materials, this effect can readily be used for magnetic sensors and magnetically controlled optoelectronic devices. This phenomenon combined with cheap device manufacturing raises a natural interest within the applied physics community. The mechanism governing OMAR is actively debated and three different models have been proposed to explain the OMAR effect. They are the magnetic field-induced singlet triplet interconversion (MIST) model,[3] the triplet-exciton polaron quenching model,[4] and the bipolaron model.[5] The first two models have explained the OMAR effect to be due to the spin-dependent electron-hole (e-h) pair and, subsequent, exciton formation followed by exciton-exciton or exciton-charge interactions. The bipolaron model relies on the spin-dependent formation of double occupancy of a particular site, i.e., formation of bipolarons and subsequent enhancement or inhibition of carrier transport as the principal cause of OMAR. The main difference between the first two models and the bipolaron model is that the bipolaron model is a single-carrier model while the first two are dependent on singlet or triplet charge pair fusion and subsequent exciton formation, e.g., effectively a two-carrier process. Furthermore, Hu and Wu[6] showed that the OMAR in organic light emitting diodes (OLED) can be tuned between positive and negative values for the same device as explained using a double carrier process. They proposed that excited states in OLEDs either dissociate (singlets) or react (triplets) with charges to produce secondary charge carriers which modify the injection current accordingly to give either positive or negative MR. The magnetic field effect is caused by the interconversion between singlet and triplet states of the bound e-h pairs.

In low mobility materials ($\mu < 1$ cm^2/Vs), such as disordered organic materials, when the hopping distance is much shorter than the Coulomb radius $r_C = e^2/4\pi\varepsilon\varepsilon_0 kT$, where e is the electronic charge, $\varepsilon(\varepsilon_0)$ is the relative (absolute) permittivity, k is the Boltzmann constant, and T is the temperature, the recombination of free electrons and holes into Coulombically bound pairs follows the Langevin process.[7] The recombination coefficient is therefore proportional to the mobility and is described by the material-dependent Langevin-recombination coefficient $\beta_L = e(\mu_p + \mu_n)/\varepsilon\varepsilon_0$, where μ_p (μ_n) is the hole (electron) mobility. The Langevin recombination can, therefore, be seen as the upper limit for the recombination efficiency in disordered systems. In the Langevin process, the rate limiting step is determined by the *probability for the charge carriers to meet in space*, independent of the subsequent fate of the formed e-h pairs that can be either spin dependent or not. The formed e-h pairs either dissociate back to free charge carriers or form Coulomb pairs and/or excitons which later recombine either radiatively or nonradiatively, depending on their relative spin orientation and possible interfacial energy barriers in heterostructures. The Langevin process is a second-order process where the recombination rate R is proportional to the recombination coefficient β_L multiplied with the charge density ($R \propto \beta_L np$), where n and p are the electron and hole concentrations, respectively, i.e., square of the charge density.

Bulk heterojunction solar cell blends (BHSCs) are formed by mixing a conjugated polymer donor and an acceptor molecule, typically a fullerene derivative 1-(3-methoxycarbonyl)propyl- 1 -phenyl - [6,6]-methanofullerene (PCBM). In BHSCs, whenever an exciton is created it dissociates very fast, typically within ~40 fs (Ref. 8) to form a Coulombically bound e-h pair at the donor-acceptor interface.[9] These e-h pairs can dissociate to free charges but the back transfer to an excitonic state is energetically unfavorable. The lifetime of such a Coulombically bound e-h pair depends on the energy offset between the donor and acceptor as well as the relative position and spin configuration and, in principle, the pair can stay bound for an extended period of time. However, in BHSCs made from regio-regular poly(3-hexylthiophene) (RRP3HT) mixed with PCBM in dichlorobenzene, the dissociation of the Coulombically bound e-h pairs is very effective and the probability for the charge carriers to meet in space (after photogeneration or injection) is drastically reduced. This is experimentally observed as a

greatly reduced bimolecular recombination coefficient by as much as 4 orders of magnitude compared to the Langevin-recombination coefficient, i.e., $\beta/\beta_L \sim 10^{-4}$.[10] The reason for this large reduction is not fully understood but the nanoscale morphology and, especially, the lamellar structure exhibited by RRP3HT seems to be very important parameters.[11,12] However, in BHSCs made from blends of poly[2-methoxy-5-(3′,7′-dimethyloctyloxyl)]-1,4-phenylene vinylene (MDMO-PPV) and PCBM, where the MDMO-PPV does not form two-dimensional (2D) lamellar structures, the e-h pair dissociation is only around 60% (Ref. 9) and the recombination is almost of Langevin type with $\beta/\beta_L \sim 0.5$,[10] even though the *excitons are fully quenched*. Since the probability for the e-h pair formation is proportional to the normalized recombination coefficient (β/β_L), we therefore find BHSCs, with different recombination coefficients, as an ideal test system to clarify whether OMAR is caused by the formation of e-h pairs (with subsequent spin-dependent recombination) or it is a single-carrier process. According to the bipolaron picture,[5] a reduced e-h pair formation probability would cause an increase in the bipolaron formation probability, while according to the excitonic models[3,4] we should observe a vanishing MR in *all solar cells* due to the quenching of the excitons.

The device structure used in the experiment for the diode is indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene)-poly(styrenesulphonate) (PEDOT:PSS) / RRP3HT / lithium fluoride (LiF)/Al and for the solar cells (ITO/PEDOT:PSS/RRP3HT: PCBM or MDMO-PPV:PCBM/LiF/Al). The ITO coated glass electrodes were coated with a very thin layer of PEDOT:PSS and annealed at 120 °C for 15 min. The π-conjugated polymer RRP3HT was spin coated from a chloroform or dichlorobenzene solution and annealed at 120 °C for 15 min. Finally the LiF and the aluminum electrode were vacuum evaporated to complete the device structure. For solar cells, a 1:1 blend of RRP3HT or MDMO-PPV and PCBM was used. The device preparation was done in a nitrogen-filled glove box and using anhydrous solutions. After fabrication, the devices were transferred in nitrogen atmosphere to a cryostat placed in between the pole pieces of an electromagnet capable of producing up to 300 mT magnetic field. The resistance of the device is then measured in dark by sending a constant current through the device and measuring the voltage drop across it in a varying magnetic field in the temperature range 100–300 K. If not mentioned otherwise, the MR was measured at a current >100 μA. For measuring the recombination coefficients, a 6 ns Nd:YAG laser operating in the second harmonic (532 nm) with the energy of 0.3 mJ per pulse is used. Integral mode of time of flight (TOF), charge extraction by linearly increasing voltage (CELIV), and double injection transients were used to measure the extracted charge carriers experimentally and from these measurements the β/β_L ratio was calculated.[10] The MR defined as

$$\%\mathrm{MR} = \frac{R_B - R_0}{R_0} \times 100 = \frac{\Delta R_B}{R_0} \times 100 \qquad (1)$$

in the RRP3HT-based diodes for a certain bias current at room temperature shows similar behavior as reported earlier.[2] Figure 1(a) shows %MR as a function of magnetic fields for different measuring currents at room temperature. Positive MR up to 16% was found at room temperature when measured with 100 μA. It has been generally accepted that the hyperfine field is responsible for the large OMAR response observed at low magnetic fields with MR line shapes of either Lorentzian $\%\mathrm{MR}(B) \sim B^2/(B_0^2+B^2)$ or a specific non-Lorentzian $\%\mathrm{MR}(B) \sim B^2/(|B|+B_0)^2$ type.[5] However, in our samples we always observe an additional effect at higher magnetic fields, namely, a power-law response with a distinct dependence of the measuring current. The line shape of the OMAR traces shows a crossover from a Lorentzian line shape at smaller magnetic fields and smaller current to a power-law fit with $B^{0.5}$ dependence. Figure 1(b) shows the fitting of different line shapes for a typical RRP3HT diode. For lower measuring current (1 μA), the line shape is a Lorentzian until 80 mT, while for higher measuring currents (100 μA) the deviation from a Lorentzian line shape occurs at an even lower field. The magnetic field value B', where the deviation occurs, decreases exponentially with increasing current.[13] Similar line shape of magnetoconductance was also observed earlier by Desai *et al.*[4] for Alq_3-based OLEDs where they found the OLED efficiency rising until B' although the OMAR effect increases until 300 mT. These observations suggest that there are two different phenomena

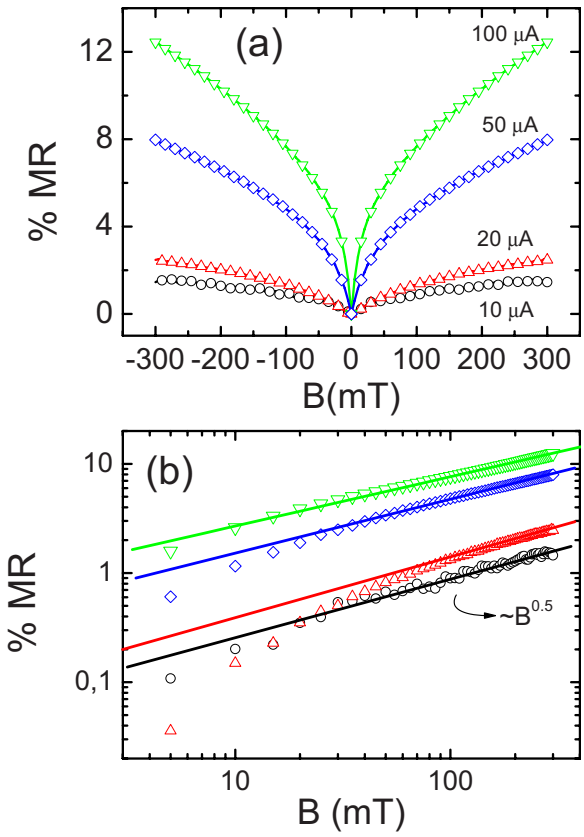

FIG. 1. (Color online) (a) %MR as a function of magnetic field of a typical RRP3HT diode device measured with 10, 20, 50, and 100 μA currents at room temperature. (b) %MR as a function of magnetic field for the same diode device for the same currents showing $\sqrt{B}$ dependence at higher magnetic fields with a deviation in lower magnetic field and lower driving currents.

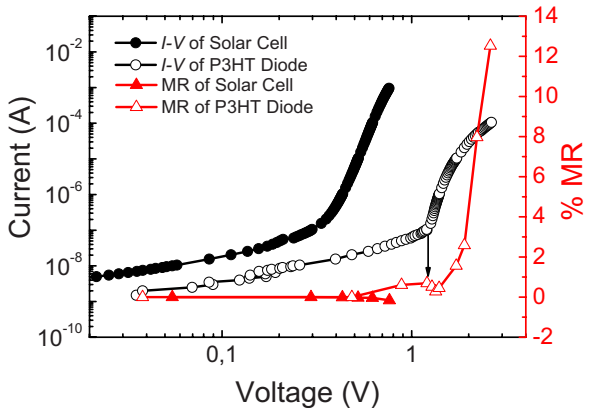

FIG. 2. (Color online) *I-V* characteristics (circle) and %MR (triangle) as a function of voltage in a typical RRP3HT diode (open symbols) and a RRP3HT:PCBM solar cell (filled symbol) showing vanishing MR due to a reduced probability of forming e-h pairs.

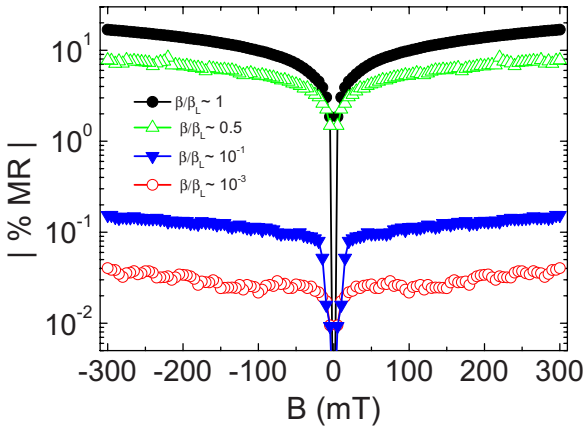

FIG. 3. (Color online) %MR as a function of magnetic field (B) in different devices with varying β/β_L ratio in a RRP3HT diode (●), in a RRP3HT:PCBM BHSC (○) made from dicholorobenzene, in a RRP3HT:PCBM BHSC (▼) made from chloroform, and in a MDMO-PPV:PCBM BHSC (△).

which govern the spin dynamics of the charge carriers in the diode devices and the entire line shape cannot be fitted to a single function. The MR line shape in organic semiconductors is not necessarily universal and varies depending on operating conditions of the device. The dependence of MR on the square root of B at higher magnetic fields (%MR $\sim B^{0.5}$) is a well-known phenomenon in colossal magnetoresistance materials and is indicative of a highly disordered electronic system with strong electron-electron interaction effects.[14] Presence of low-field and high-field components of MR has also been suggested in a recent article.[15] The low-field component is suggested to be due to the magnetic field change in the spin sublevels mixing via the hyperfine interaction in polaron pair species. The high-field component is suggested to be due to changes in spin sublevel mixing of charge-transfer states caused by a "Δg mechanism." However, further detailed temperature, high magnetic field, material, and thickness-dependent study of the OMAR line shapes are needed to clarify the two components.

Figure 2 shows the current-voltage and %MR-voltage characteristics for both a typical diode and BHSC measured between 0 and 5 V bias in the dark and at room temperature. The MR increases rapidly beyond the threshold voltage (V_{th}) of the RRP3HT diode (marked by the arrow in the figure) but for the BHSCs negligible MR is observed—almost 3 orders lower in magnitude compared to the RRP3HT devices. In these BHSCs we have measured $\beta/\beta_L \sim 10^{-3}$. Thus, by reducing the probability of e-h pair formation in good solar cells, we have observed a dramatic decrease in the MR value. This observation is in good agreement with Lee *et al.*,[16] who found similar behavior in light-induced MR response on P3HT/PCBM solar cells, except only at open-circuit voltage.

To further investigate the dependence of e-h recombination on the MR response, we prepared BHSC devices with varying β/β_L ratios and measured their magnetotransport properties. Figure 3 shows the maximum observable MR as a function of magnetic field for different devices exhibiting different β/β_L ratios. The solar cells from RRP3HT:PCBM blend in dichlorobenzene have $\beta/\beta_L \sim 10^{-3}$ and showed the smallest MR—around 10^{-2}%. For BHSCs made from RRP3HT:PCBM blends in chloroform, the β/β_L ratio is $\sim 10^{-1}$ with a MR response of 0.2% and for MDMO-PPV:PCBM devices $\beta/\beta_L \sim 0.5$ (Ref. 10) showing almost as high MR response as the RRP3HT device alone. This means that even though excitons are completely quenched in all the BHSCs, we see an increase in the OMAR response when the

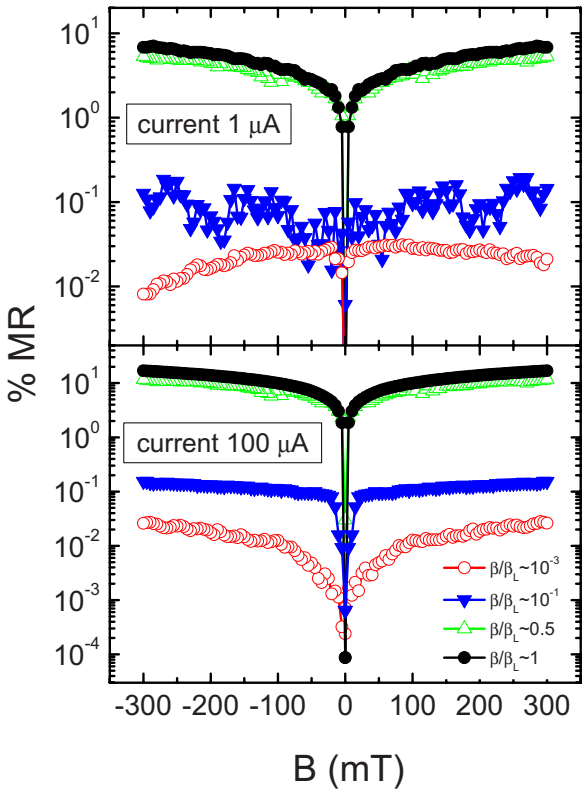

FIG. 4. (Color online) %MR as a function of magnetic field (B) in different devices with varying β/β_L ratio for bias current of (a) 1 μA and (b) 100 μA. The %MR ratio between various materials remains the same even when the bias current is increased by 100 times, underlining the role of recombination coefficient, i.e., e-h pair formation and not the recombination rate, in the OMAR phenomenon.

probability to form e-h pairs is increased, as seen in the MDMO-PPV/PCBM devices.

In Figs. 4(a) and 4(b) we plot the MR for two different bias currents in the samples with different recombination coefficient. Two order different current densities imply four orders difference in the recombination rate (R) due to the proportionality with square of carrier density (as shown previously). It is clear from the figures that it is not the recombination rate but the recombination coefficient which is influencing the MR response of different materials.

The mechanism for the OMAR from Coulombically bound carriers is still debatable. While Frankevich *et al.*[17] and Hu and Wu[6] concluded that spin mixing of singlet and triplet e-h pairs under magnetic field is possible, recent results from McCamey *et al.*[18] showed that spin mixing in the bound polaron pair state is highly improbable. However, from our experiment with BHSCs, since the excitons are quenched in *all* solar cells, we conclude that excitons are not necessarily the reason for the MR effect. MDMO-PPV/PCBM solar cells show a large MR response in spite of having no excitonic effects, but only charge pairs (as proven in Ref. 9 in this Rapid Communication). Together with our results, it means that the OMAR is a direct consequence of the e-h pair *formation process* (with subsequent spin-dependent recombination).

In conclusion, we have used BHSC to clarify the role of formation of Coulombically bound e-h pairs on the MR effect. BHSCs are a good model system since the excitons are effectively quenched. By systematically varying the probability for e-h pairs to meet in space, as observed by the experimentally measured recombination coefficient, we found that a reduced probability for electrons and holes to meet in space lead to a vanishing MR. The MR increases with increasing probability of e-h pair formation, as observed in BHSCs from MDMO-PPV:PCBM blends, even though the excitons are fully quenched in disagreement with the exciton models. We also found that the MR line shape in RRP3HT diodes shows two components: one Lorentzian at low fields and one component that follow a power-law dependence of $B^{0.5}$ at higher fields with a bias-current-dependent crossover. The recently proposed model of trions (a bipolaron stabilized by an opposite charge on another segment) needs to be investigated carefully in this context.[19]

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*Corresponding author; sayani.majumdar@utu.fi

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