Exploring organic magnetoresistance: an investigation of microscopic and device properties

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Exploring Organic Magnetoresistance
An investigation of microscopic and device properties

Proefschrift

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aan de Technische Universiteit Eindhoven
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voor een commissie aangewezen door het College
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Chapter 1

Introduction to organic spintronics

Abstract: In this chapter we introduce the field of organic spintronics. This field has generally been motivated by the drive to combine the low cost and ease of fabrication of organic semiconductor devices, with the nonvolatile nature of spintronics devices. Recently, a completely new spintronic effect unique to organic semiconductor devices, dubbed organic magnetoresistance (OMAR), has been discovered. OMAR is a large low field symmetric magnetoresistance (MR) present in completely non-magnetic organic devices at room temperature. These properties make OMAR promising for technological applications. However, OMAR remains a significant scientific puzzle since such a symmetric large room temperature effect cannot be explained by known MR mechanisms. The work in this thesis is motivated by the desire to determine the new physics responsible for the OMAR effect. In this chapter, we discuss the fundamental knowledge necessary for this study. We first discuss the basics of charge transport in organic semiconductors devices. Then we discuss some of the characteristic properties of OMAR. Finally, the scope of this thesis in terms of its contribution to the field of organic spintronics will be discussed.
Chapter 1. Introduction to organic spintronics

1.1 What is organic spintronics?

The fields of spintronics and organic electronics have been subjects of intense scientific inquiry over the last twenty years. Research in these fields has resulted in the development of many new technologies, and this research has also been responsible for both the Nobel Prize in chemistry in 2000 (conductive polymers) and the Nobel Prize in physics in 2007 (giant magnetoresistance). Spintronics research has lead to the development of the giant magnetoresistance (GMR) and tunnel magnetoresistance (TMR) [1]. GMR has vastly improved hard disk read heads which has been responsible for the exponential increase in data storage density over the past decade, while TMR has lead to magnetic random access memory (MRAM), which is a non-volatile RAM technology that allows for ‘instant on’ computing. Organic electronics research on the other hand has lead to the development of organic light emitting diodes (OLEDs), which are now being applied to make thinner and brighter displays, as well as organic field effect transistors (OFETs) whose low cost show promise for applications like radio frequency identification (RFID) and other ‘disposable electronics’ applications [2].

A major scientific interest in integrating spintronics with organic electronics is to realize long spin lifetimes. This is because organic semiconductor materials consist of low atomic mass elements resulting in low spin orbit scattering. Also, there would be technological benefits to using organic semiconductor materials in spintronic devices due to their low cost, ease of fabrication, and chemical tunability.

There are two approaches to achieve spintronics functionality in organic materials. The first is to use a ferromagnetic electrode to inject spins in the organic material. This has been done by fabricating organic spin valves, which are analogous to GMR sensors, but with organic materials instead of a metallic material as the nonmagnetic spacer. Recent experiments have shown that a GMR effect can be observed in such structures [6, 7]. The GMR effect is caused...
1.1. What is organic spintronics?

by a change in resistance due to a change in the mutual orientation of the magnetization of the two electrodes (fig. 1.2a). This demonstrates that it is possible to inject, transport, and then detect a nonequilibrium spin current in organic semiconductors materials. However, these results are controversial since the low mobility of organic semiconductors should make it very difficult to observe sizable MR, because of the so-called conductivity mismatch [8]. Also, hyperfine coupling to the nuclear spins should quickly cause the spins on the mobile charges to depolarize [9].

The second approach to achieve spintronics functionality is to apply magnetic fields to organic materials. Recently, a symmetric magnetoresistance effect has been shown in OLED type devices containing no magnetic materials [10]. A schematic magnetoresistance trace is shown in fig. 1.2b. The effect occurs at room temperature and can be quite significant at low magnetic fields (up to 10% at 10 mT [11]). This effect has been dubbed organic magnetoresistance (OMAR), and has been found in a wide variety of organic semiconducting small molecules and polymers. The large low-field room temperature magnetoresistance OMAR, combined with the low cost and ease of processing of organic semiconductor devices, makes OMAR interesting technologically. For example, OMAR could be used for magnetic pen input displays (Fig. 1.1), or large area magnetic field sensors. However, OMAR is even more intriguing from a scientific point of view since until recently there were no known MR mechanisms which can satisfactorily explain the properties of OMAR.

Until recently very little was known about this peculiar effect which has very few similarities to other magnetoresistance effects. Therefore, since OMAR is an entirely new effect and not an organic analogue of GMR sensors like organic spinvalves, we focus our studies on trying to better understand the mechanism(s) behind the observed effect. The primary goal of this thesis is to shed light on the new phenomenon(a) that is (are) responsible for organic magnetoresistance in order to better understand charge and spin transport properties in organic semiconductors, assist in the development of OMAR in future technology, and last but certainly not least, to satisfy intellectual curiosity.
1.2 Fundamentals of organic electronics

To have a basis in order to begin to understand the OMAR effect it is necessary to review the fundamentals of organic electronics. In this section we discuss the properties of $\pi$-conjugation, charge transport, energetic disorder, and charge injection in organic semiconductors.

1.2.1 $\pi$-conjugation

The electronic configuration of carbon in its ground state is $1s^22s^22p^2$. When carbon forms covalent bonds the $2s^22p^2$ valence electrons hybridize to form $sp$, $sp^2$, or $sp^3$ orbitals. In the case of $sp$ and $sp^3$ hybridization all the electrons are strongly localized resulting in extremely poor charge conduction. In the case of $sp^2$ hybridization two $p$ orbitals and one $s$-orbital hybridize to form three strongly localized $sp^2$ orbitals. This leaves the $p_z$ orbital, which is perpendicular to the coplaner $sp^2$ orbitals, unhybridized. When a chain of $sp^2$ hybridized carbons is constructed, two of the three $sp^2$ orbitals form strong $\sigma$-bonds with the neighboring carbons to form the chain, while the third $sp^2$ bond is bonded either to a hydrogen or a side group. The remaining $p_z$ orbital can overlap with the $p_z$ orbitals of the neighboring carbons along the chain, giving rise to a $\pi$-bond (see Fig. 1.3).

The $p_z$-electron can then delocalize itself across all the contiguous $\pi$ bonds in the molecule. Delocalization results in the conducting properties of these molecules. This is because there is one $p$-electron per atom, which can form its own band. As a result this should result in metallic behavior according to Bloch theory (assuming equidistant bond-lengths), since solids with half-filled shells have partially filled bands giving metallic transport [13]. However, a $\pi$-conjugated molecule with equidistant bond lengths is unstable. The instability results in the formation of the Peierls distortion. The Peierls distortion results from electrons wanting to localize between the carbon nuclei in order to screen their nuclear charges [14]. In order to accommodate this charge screening the chain of carbon atoms forms alternating single (long) and double bonds (short). This results in the simple metallic band being split into two sub-bands separated by an energy gap of 2-3 eV [15]. There is a completely filled valence band (the highest occupied molecular orbital, or HOMO) and an empty conduction band (lowest unoccupied molecular orbital, or LUMO). Since the energy gap is relatively small this results in semiconducting properties.
1.2.2 Charge conduction in $\pi$-conjugation systems

In organic materials, charges that are moving through a molecule cause distortion of the surrounding lattice due to Coulomb interactions with the nucleus. As the charge moves through the molecule it is accompanied by this lattice distortion. The charge and the accompanying distortion can be treated as a quasi-particle called a polaron, which has the spin of the accompanying electron or hole ($S = \frac{1}{2}$). Polarons can either be positively or negatively charged, and in the rest of this thesis positive polarons will be referred to as holes and negative polarons will be referred to as electrons.

For organic semiconductors band conduction only applies to single crystals of small molecules like pentacene or rubrene, which are difficult to process into devices. The most technologically relevant organic semiconductors are vapor deposited small molecules, and solution processed polymers, both of which are either polycrystalline or amorphous. In these materials band conduction does not apply because of energetic disorder in the HOMO and LUMO. The energetic disorder results from these materials having a disordered structure [16]. This can be caused by the irregular packing of molecules due to vapor deposition or spincoating. In the case of polymers, twists, kinks, and a distribution of polymer chain lengths also cause structural disorder [17]. Since the local energy levels are determined by the local structure and the conjugation length, structural disorder results in energetic disorder. The energetic disorder is usually approximated by a Gaussian density of states (DOS) with the standard deviation of the gaussian giving a characteristic energy width of $\sigma \sim 75 - 150$ meV [17].

This energetic disorder results in charges being localized on molecular sites. The mechanism for charges to move from one localized site to another is phonon-assisted tunneling or “hopping”. In this mechanism hops upward in energy are made possible by the absorption of phonons. The probability to hop from one energetic site to another is given by [18]:

$$p = \nu_0 \exp \left( -2\alpha R \right) \left\{ \begin{array}{ll} \exp \left( \frac{-\Delta E}{k_BT} \right) & \text{for } \Delta E > 0, \\ 1 & \text{for } \Delta E \leq 0. \end{array} \right. \tag{1.1}$$

Here, $\nu_0$ is the hopping attempt frequency, $\alpha$ is the inverse wave-function localization length, $R$ is the distance between the hopping sites, and $\Delta E$ is the energy difference between the sites. This mechanism is called “variable range hopping” since there is a tradeoff between long hops (small wavefunction overlap but large $\Delta E$), and short hops (small wave function overlap but large $\Delta E$). This expression makes it clear that disorder in the position and energy of hopping sites greatly effects the mobility of the charge carriers in the organic material.

1.2.3 Basics of organic devices

Most of the devices presented in this thesis are bipolar, meaning that both electrons and holes are injected into the device. To achieve good injection, the work functions of the electron injecting contact (cathode) and the hole injecting contact (anode) should match the respective LUMO and HOMO well. Ignoring the effect of interface dipoles, one could define the energetic barrier $\phi$ for electron charge injection as

$$\phi_e = \Phi_C - E_{LUMO}, \tag{1.2}$$

while for holes

$$\phi_h = E_{HOMO} - \Phi_A, \tag{1.3}$$
Figure 1.4: The process of charge hopping between localized sites with gaussian DOS with an energy width $\sigma$. Here an electron hops from one localized state to another with a distance $R$ and difference of energy of $\Delta E$.

where $\Phi_C$ and $\Phi_A$ are the workfunctions of the respective cathode and anode, while $E_{\text{LUMO}}$ and $E_{\text{HOMO}}$ are the energy difference between the vacuum level and the LUMO and HOMO respectively. The Fermi levels of the metal contacts are at the same potential when there is no external bias. This results in a potential across the organic semiconductor called the built-in potential, given by:

$$V_{\text{bi}} = \frac{\Phi_A - \Phi_C}{q},$$

where $q$ is the elementary charge. To get a significant charge injection $V_{\text{app}} > V_{\text{bi}}$ must hold, where $V_{\text{app}}$ is the applied voltage.

If $\phi$ is nonvanishing the injection will not be ohmic, and the injection step will limit the current. This is called injection limited transport. Historically, two approximations have been commonly used for injection limited transport, Fowler-Nordheim tunneling for large bias and low temperatures [19], and thermionic emission for higher temperatures and lower biases [20]. However, in actuality charge injection into organic semiconductors is very complicated and these simple macroscopic models are poor approximations. To properly model charge injection one must account for individual image charges, injection into the tail of the Gaussian DOS, and filamentary currents [21].

Once charge is injected into the material there are two contributions to the current. Charge carrier drift and charge carrier diffusion. Drift current results from charge carriers moving under the influence of an electric field, while the diffusive current is a result of carriers moving due to a charge concentration gradient. The current density is the sum of the drift and diffusion contributions. Therefore,

$$J = J_{\text{drift}} + J_{\text{diffusion}}. \quad (1.5)$$

This results in an electron current density of

$$J_e = q\mu_e n F + eD \frac{dn}{dx}, \quad (1.6)$$
and a hole current density of

$$J_p = q\mu_h p F - e D \frac{dp}{dx},$$

(1.7)

where $\mu_{e,h}$ is the charge carrier mobility where the subscripts $e$ and $h$ refer to the electron and hole respectively, $F$ is the electric field, $D$ is the diffusion coefficient, $x$ is the position and the charge density is given by $n$ for electrons and $p$ for holes. It should be noted that for injected charge carriers to undergo drift transport $V_{app} > V_{bi}$.

Organic semiconductors used in OLEDs and the devices we investigate are undoped, so all charge carriers must be injected into these devices. Since these materials have low mobilities, charges take a long time to transit the device, and therefore, at significant currents, charge carriers end up being very close to each other. This results in their mutual Coulomb interactions limiting the current, leading to the charge density being directly proportional to the bias, just like in a capacitor. Therefore, the current density is proportional to $V^2$. This phenomena is called space charge limited current (SCLC). For unipolar devices the expression for SCLC is given by [22]:

$$J = \frac{9}{8} \varepsilon \mu_e \varepsilon_0 \left( V - V_{bi} \right)^2,$$

(1.8)

where $\varepsilon_0$ is the permittivity constant, $\varepsilon_r$ is the dielectric constant of the material, and $d$ is the device thickness. Bipolar SCLC is given by [22]:

$$J = \frac{9}{8} \varepsilon \mu_p \mu_h \left( \mu_e + \mu_h \right) \left( V - V_{bi} \right)^2,$$

(1.9)

where $\mu_r$ is the recombination mobility, which is less than the mobility of the slowest carrier [i.e. $\mu_r < \min (\mu_e, \mu_h)$]. In the bipolar case Coulomb repulsion is reduced by the presence of oppositely charged carriers enhancing the current over the unipolar case by a factor $\sqrt{\frac{\min (\mu_e, \mu_h)}{\mu_r}}$.

In this thesis, we will specifically look at the behavior between unipolar SCLC (Eq. 1.8) and bipolar SCLC (Eq. 1.9), and we will see that this will give rise to unrecognized new phenomena.
1.3 Intro to OMAR

Organic magnetoresistance is the change in current when a magnetic field is applied to an organic device with no magnetic materials. It is an effect that is strong (up to 28 %\cite{23}) at room temperature and the characteristic fields needed to observe the effect are in the mT range. In this thesis we refer to this change in current caused by OMAR as the magnetoconductance, which is given by:

\[
MC(B) = \frac{I(B) - I(0)}{I(0)},
\]

(1.10)

Where \( B \) is the magnetic field, and \( I \) is the current through the device.

OMAR has been shown to have similar behavior in terms of \( MC(B) \) lineshapes over a wide range of material types, and exhibits two characteristic \( MC(B) \) lineshapes \cite{24}. A Lorentzian,

\[
MC(B) = MC_\infty \frac{B^2}{B^2 + B_0^2},
\]

(1.11)

and a more slowly saturating empirical “non-Lorentzian,”

\[
MC(B) = MC_\infty \frac{B^2}{(|B| + B_0)^2},
\]

(1.12)

where \( MC_\infty \) is the MC value at \( B = \infty \), and \( B_0 \) is the characteristic magnetic field. \( B_0 \) is the half width at half maximum in the case of the Lorentzian and the half width at quarter maximum in the case of the non-Lorentzian line shape (Fig. 1.6).

OMAR has been observed by Kalinowski et al. in 2003 where the authors observed that applying a magnetic field to a small molecule OLED type device, results in the current and the electroluminescence increasing \cite{10}. Francis et al. followed this work, with experiments that showed that semiconducting polymers can also show OMAR \cite{11}. At room temperature the polyfluorine based device they measured showed very large MCs at low magnetic fields.
1.3. Intro to OMAR

(~10% at 10 mT). These polyfluorine based devices were also the first devices that showed that OMAR could change sign as a function of the bias voltage. Later, it was also shown that the sign can be changed by changing the device temperature [24, 25]. The sign of OMAR is not only dependent on the operating conditions, but also the device structure such as the organic active layer thickness [26]. Resolving the mechanisms underlying this sign change is one of the key research issues in this thesis. To help understand this important phenomenon an in depth discussion of all the literature about this sign change will be presented in chapter 8.

OMAR has both been observed in devices that have been optimized for bipolar operation, and in devices that have been optimized for unipolar operation, which only inject one type of charge carrier (i.e. hole-only or electron-only devices). The bipolar devices show a relatively large increase in current with magnetic field (+MC), while the unipolar show a decrease in current with magnetic field (−MC) which is significantly smaller in magnitude [27]. These results show that the mechanism(s) that describe OMAR must be applicable for both unipolar and bipolar currents.

In principle, OMAR is interesting because it shows properties of both bulk and interface effects. In OLED type devices, the magnitude of OMAR has been shown to scale roughly linearly with thickness, showing that it is a bulk effect [24]. Also, in this type of device it has been shown that better workfunction matching of the electrodes to the HOMO and LUMO results in a larger OMAR, suggesting the interface does not play a major role in OMAR [11]. However, for devices consisting only of the doped polymer PEDOT:PSS as the active layer, the OMAR effect has been observed only if an injection limited contact is made by depositing a reactive metal on top of PEDOT:PSS [28]. Therefore, OMAR can also affect the injection of charge.

An intriguing property of OMAR is that “conditioning” greatly increases the magnitude of the OMAR effect [29]. Conditioning is the application of high current densities to the device for extended periods of time, which was shown to increase the amount of charge traps in the material [30]. It has also been shown that shining UV light on the device similarly induces traps in the device, also resulting in a significant increase in the magnitude of OMAR [30]. Interestingly, this process is partially reversible as some of the traps can be removed by annealing, resulting in the OMAR getting close to its original non-conditioned state [31].

1.3.1 Rejected models for OMAR

OMAR is interesting since it is one of the largest room temperature bulk magnetoresistance effects known in non-magnetic materials. Mermer et al. compared the effect to 4 known MR mechanisms for non-magnetic materials [24]. They determined the following. 1. The mobility of organic materials is too low for the effect to be explained by classical magnetoresistance. 2. The characteristic hopping distance in organic materials is too small for hopping magnetoresistance. 3. Magnetoresistance by e-e interactions can only occur at low temperatures. 4. Finally in weak (anti)localization there is a mobility dependence on the width of the MC(B) curve that is not present in OMAR. Therefore, with the discovery of OMAR the need arose to find new magnetoresistance mechanisms.

1.3.2 The role of spin in organic semiconductors

One major clue as to the origin of OMAR is that OMAR is drastically reduced when molecules containing a heavy atom are used [32–34]. This is likely due to spin orbit coupling, since
Figure 1.7: Schematic representation of the formation of different spin states of bipolarons or excitons from their precursor polarons of different spin polarizations. The spins are shown as vectors in a vertical magnetic field.

coupling of the spin angular momentum to the orbital angular momentum causes spin to cease being a good quantum number. These experiments demonstrate that spin dependent reactions are likely to be the cause of OMAR in organic semiconductors.

Spin is an important property in the charge transport of organic semiconductors. As stated earlier in section 1.2.2 the polarons responsible for charge transport have $S = \frac{1}{2}$. Therefore the property of spin becomes important once the formation of quasiparticles consisting of two charges (i.e. excitons or bipolarons) are considered. Two like charged polarons can combine to form bipolarons, while two oppositely charged polarons can combine to form excitons. The mutual orientation of the spins (i.e. triplet or singlet, figure 1.7) in both excitons and bipolarons is very important since these quasi-particles have much different properties depending on whether they have triplet ($S = 1, m_s = +1, 0, -1$) or singlet ($S = 0, m_s = 0$) character.

Bipolarons are doubly charged quasiparticles either consisting of two positive or two negative charges on a single molecular site. It may seem odd to think that two like charges can coexist on the same molecular site, because of the large Coulomb repulsion between the charges. However, charges also distort the lattice. By placing two charges on the same site the charges can share this lattice distortion, which significantly reduces the formation energy, $U$, of bipolarons. It has been found that $U \sim \sigma$ [35], so it is likely that bipolarons could form at molecular sites that are in the low energy tail of the gaussian DOS. Bipolarons are always spin singlet, because of the large exchange energy between the two charges when a triplet pair of charges is confined to a single molecular site [35, 36]. Therefore, the precursor polarons that form the bipolarons must be in a singlet configuration prior to bipolaron formation (Fig. 1.8).

In organic semiconductors, electrons and holes can meet at a molecule to form an excited state called an exciton. Coulomb energy is gained due to exciton formation, resulting in an optical gap which is 0.5 to 1 eV smaller than the electronic gap [37]. In these molecular Frenkel excitons the electrons and holes are geminate, i.e. they are located on the same molecule and typically on the same ligand. The spin of the precursor pairs is also important for excitons, not because they have different formation cross-sections, but because excited triplet and singlet excitons have vastly different properties. This is a result of the ground state ($S_0$) of the excitons having a singlet configuration. The different energy levels of the excitons and their transitions are outlined in Fig. 1.9. The singlet excited state ($S_1$) transition to $S_0$, $k_s$, is quantum mechanically allowed since spin is conserved. Therefore, these transitions are fast ($\sim 1 - 10$ ns) and efficiently giving rise to fluorescence [38]. The triplet excited state ($T_1$) transitions to $S_0$,
1.4. Mechanisms for OMAR

There are several mechanisms explaining OMAR based on different spin dependent transitions that are effected by the magnetic field [33, 40, 41]. Here, we discuss the three most prominent models. In all of the relevant models for OMAR it has been hypothesized that randomly oriented hyperfine fields, $B_{\text{HF}}$, from the nuclear spin of the hydrogen atoms induce spin mixing. This allows two separate charges that are initially in a triplet configuration to convert to a singlet configuration or vice versa. We see in figure 1.10(a) two polarons that are initially in a triplet configuration (solid arrows) can have a large degree of singlet character after precessing about their local hyperfine field (dashed arrows). If an external magnetic field, $B_{\text{ext}}$, much larger than $B_{\text{HF}}$ is applied, the effect of the randomly oriented $B_{\text{HF}}$ is quenched, and the spins coherently precess about a similar magnetic field. Thereby, the spin mixing is eliminated and $k_t$, are much slower since the triplet exciton transition to the singlet ground state is not allowed due to spin selection rules. Therefore, triplet excitons are long lived in the device ($100\mu s - 10\ s$) [38], since they undergo slow inefficient phosphorescent transitions. Another transition that is possible is between the excited excitonic states. This transition is called “intersystem crossing.” This is enabled by spin-orbit coupling weakening the spin conservation rules allowing a transition between the $S_1$ and $T_1$ with a rate of $k_{\text{ISC}}$. Since the $T_1$ state is lower than the $S_1$ state by 0.5 to 1.0 eV, the $T_1$ to $S_1$ transition is thermally activated [37].

Due to their long lifetime, triplet excitons can play an important role in the charge transport. Ern and Merrifield showed that triplets interact with paramagnetic centers (e.g. polarons), which can result in triplet polaron quenching, or triplet polaron charge scattering [39]. Both of these interactions result in a reduction of the mobility and hence a decrease in the current. Another reaction of triplet excitons is that free charges or the interface can dissociate the triplet excitons into their component electrons and holes, increasing the current in the device [26].

Figure 1.8: (color online) Diagram showing (a) the allowed formation of singlet bipolarons (BP$_S$), and (b) the energetically disallowed formation of triplet bipolarons (BP$_T$). The arrows solid (dashed) arrows represent the charge carriers before (after) bipolaron formation.
Figure 1.9: Diagram of the energy levels and transitions between the singlet state ($S_1$) triplet excited states ($T_1$) and the ground state ($S_0$).

Figure 1.10: (color online) Schematic representation of neighboring polarons initially in a triplet configuration. The spin states are shown before (solid arrows) and after (dashed arrows) precession about the local magnetic field. The situation for $B_{\text{ext}} = 0$ (a) and $B_{\text{ext}} \gg B_{\text{HF}}$ (b) are shown.

the original singlet or triplet configuration of the two spins remains (Fig. 1.10(b)).

This postulation that hyperfine fields are the root cause of OMAR has very recently been proven by Wang et al. [42]. The authors deuterated the organic semiconductor active layer, since deuterium has a significantly lower hyperfine field than hydrogen. They observed that deuteration significantly reduced the characteristic field width, $B_0$, of the MC($B$) traces, proving that internal hyperfine fields are responsible for the OMAR effect.

It is important to note that in photocurrent measurements [43] and delayed fluorescence measurements [44], several years prior to the work on OMAR, similar low-field room temperature magnetic field effects have been observed. Although not directly applicable to OMAR, both explain that their magnetic field effects are due to the presence of randomly oriented internal hyperfine fields.
1.4. Mechanisms for OMAR

1.4.1 Exciton mechanism

In the exciton mechanism the magnetic field acts to increase the intersystem crossing \( k_{\text{ISC}} \) between singlet excitons and triplet excitons [45], this results in a change in the current. According to Desai et al. increasing \( k_{\text{ISC}} \) should balance out the singlet-triplet exciton ratio. Thus, depending on the relative populations of triplet and singlet excitons the singlet-triplet ratio can increase or decrease. As discussed in Section 1.3.2, triplet excitons can play an important role in the charge transport due to their long lifetime. Therefore, by altering the singlet-triplet exciton ratio and changing the amount of triplet excitons in the device the current in the device should be affected.

By spin statistics, injected charges form excitons with a singlet-triplet exciton ratio of 1:3. Therefore, in the case that charge is injected into the device, increasing \( k_{\text{ISC}} \) should lower the number of triplet excitons. According to the authors intersystem crossing results in a decrease in triplet density at room temperature since there is enough thermal energy to overcome the energy difference between \( T_1 \) and \( S_1 \) levels. This results in a decrease in the triplet exciton population which decrease in triplet polaron quenching and triplet polaron scattering, causing an increase in the current with magnetic field \((+\text{MC})\). Also, it is argued that in certain regimes triplet exciton dissociation plays a larger role then triplet polaron quenching. In this case the magnetic field induced reduction of the triplet exciton concentration results in a decrease in current with the magnetic field \((-\text{MC})\).

However, there are several objections to this model. The mechanism for how the magnetic field increases \( k_{\text{ISC}} \) is not described in this model, although it is suggested that random hyperfine fields may play a role. Also, the triplet exciton to singlet exciton transition is exponentially dependent on temperature (Fig. 1.9), and the triplet concentration (as well as the triplet lifetime) is highly temperature dependent [46]. However, the measured temperature dependence of OMAR is weak [24]. Finally, experiments show that the singlet-triplet ratio of excitons is unaffected by an applied magnetic field, suggesting that \( k_{\text{ISC}} \) is independent of magnetic field [47, 48].

1.4.2 e-h pair mechanisms

There are two different e-h pair mechanisms: one proposed by Hu et al. [41], and the other proposed by Prigodin et al. [33]. In these mechanisms the magnetic field acts to change the intersystem crossing between singlet and triplet e-h pairs instead of singlet and triplet excitons. e-h pairs are Coulombically bound pairs of electrons and holes. Unlike excitons, e-h pairs are nongeminate (i.e. the electrons and holes are on adjacent molecular sites), therefore the spacing between them is much greater than for excitons. This results in a significantly lower exchange energy between singlet and triplet e-h pair states \((1-10 \ \mu\text{eV} [41])\) than between singlet and triplet excitons \((0.5 - 1.5 \ \text{eV} [38])\). Therefore, magnetic field induced intersystem crossing in e-h pair states is argued to be much more likely than for excitonic states.

In the mechanism proposed by Hu et al. a magnetic field is considered to increase the intersystem crossing, which is induced by randomly oriented hyperfine fields [41]. The authors argue that singlet e-h pairs quickly dissociate into unbound electrons and holes due to their stronger ionic character, therefore there are many more triplet e-h pairs. Thus increasing the intersystem crossing with a magnetic field results in triplet e-h pairs being converted to singlet e-h pairs. As a result of this increase more e-h pairs are dissociated and a +MC should be observed. The model also considers that increasing the intersystem crossing decreases the
triplet e-h pair population, which in turn decreases the amount of triplet excitons this results in two competing effects. Therefore, there is a decrease in the triplet dissociation by free polarons, resulting in a $-MC$.

Another very similar e-h pair mechanism is proposed by Prigodin et al. [33]. In this mechanism the electron and hole are far enough apart such that the exchange interaction is negligible. Therefore, the triplet and singlet e-h pairs are degenerate and all the triplet levels ($T_{-1}, T_0, T_{+1}$) can interconvert to singlet electron-hole pairs. In this model singlet e-h pairs recombine to the ground state faster than triplets, therefore there is always an excess of triplet excitons and intersystem crossing results in triplet e-h pairs being converted to singlets e-h pairs. Therefore the intersystem crossing effectively increases the recombination since singlets e-h pairs recombine faster. By applying an external magnetic field the $T_{-1}$ and $T_{+1}$ e-h pair state are Zeeman split such that they are no longer degenerate with the singlet e-h pairs (Fig. 1.11). Therefore, only $T_0$ e-h pairs can recombine faster by converting to singlet e-h pairs via hyperfine field induced mixing, and subsequently recombine. This results in a decrease in recombination, decreasing $\mu_r$. Inspection of Eq. 1.9 shows this results in less recombination giving more dissociation and more current resulting in a $+MC$.

There are some inconsistencies with e-h pair based models when compared to the experiments. In devices where only one type of charge carrier has been injected and e-h pairs are not present, OMAR has been observed [27]. Also, these e-h pair based models would predict a linear increase in MC with EL efficiency and measurements show that this dependency is much weaker than a linear dependence [24].

### 1.4.3 Bipolaron mechanism

To form a bipolaron, a polaron must hop to a site with another polaron present, and as discussed in section 1.3.2, these polarons must have opposite spins. If the polarons have the same spin the
formation of bipolarons is blocked. At zero magnetic field, spin mixing from randomly oriented hyperfine fields will allow polaron pairs which are initially in a triplet configuration to mix into a singlet configuration, enabling bipolaron formation. An external magnetic field prevents spin mixing, thus polaron pairs which are initially triplet will remain so and this pair will not form a bipolaron.

The magnetic field effect on bipolaron formation affects the current since transport in OLED type devices occurs via a filamentary network of interconnecting paths [21]. This percolating behavior is due to the disordered energy landscape of the material. Therefore, the transport is highly one dimensional. Thus bipolaron formation can be a bottleneck if there are some low energy sites where quasi-trapped charges sit on the conducting path. In order for a charge to pass through these sites the conducting polaron must form an intermediate bipolaron with the immobilized polaron, before it can move further through the material. If these intermediate bipolarons cannot be formed, since the precursor polarons are in a triplet configuration, charge cannot pass through this site. This phenomena is called “spin blocking” and causes a decrease in the mobility which results in a decrease in the current. Hyperfine field induced spin mixing eliminates spin blocking, allowing for a larger current. Applying an external magnetic field allows for spin blocking to be retained, resulting in a $-\mu C$.

This model has been worked out both using a Monte Carlo approach [40], considering a large grid of lattice sites, and an analytical approach [49], considering two sites and the environment. Both models predict both the Lorentzian (Eq. 1.11) and the non-Lorentzian (Eq. 1.12) lineshape. The Monte Carlo based simulation shows that the OMAR magnitude is the largest when $\sigma \approx U$, which is the situation in which the bipolaron formation is best facilitated by the energetic disorder. Also, the simulated temperature dependence of OMAR is weak, just like observed experimentally. One should note that the bipolaron model also predicts a $+\mu C$ [40, 49] when including (long range) Coulomb repulsion. However, if bipolaron formation is a highly efficient process, this results in the formation of immobile bipolarons coming at the expense of mobile polarons resulting in a decrease in the mobility and a $-\mu C$. However, this effect is much weaker than the spin blocking effect.

Interestingly, spin blocking phenomena have also been observed in $^{13}$C carbon nanotube quantum dots [50] and the observed $\mu C(B)$ behavior is the same similar to OMAR. The effect is also based on the external field eliminating spin mixing enabled by the hyperfine field. In this case $^{13}$C provides the hyperfine field, and instead of bipolarons, doubly occupied quantum dots, which also have a much larger triplet energy than singlet energy, are the root cause. Therefore, in a much “cleaner” system this spin-blocking phenomena has been verified.

1.5 This thesis

In this thesis the goal is to determine the mechanisms which cause the unusual properties of OMAR. A strong emphasis is put on understanding the sign change of the OMAR effect in this thesis. Since this phenomena is difficult to understand within the context of the models presented in this chapter. Our experiments show that this sign change is coincident with the device going from unipolar to bipolar operation. Using macroscopic device modeling we show that this sign change can be an intrinsic property of the device physics and not the microscopic mechanism responsible for OMAR.

After this first introductory chapter dealing with the contemporary knowledge and notions regarding the OMAR effect (chapter 1), we cover the experimental methods used in this thesis
(chapter 2). Chapter 2 contains a detailed description of the methods used in sample fabrication and sample characterization.

In chapter 3 we investigate the sign change as a function of bias in Alq$_3$ based devices. We show that the positive and negative OMAR effects are due to two separate contributions to the OMAR response. Therefore the resulting lineshape is a superposition of these two contributions. We show that it is possible that the hole and electron channels may have different interactions with the magnetic field resulting in these two separate contributions.

Chapter 4 shows that this sign change can also occur due to a change in the temperature. We find that this temperature change resulting in the sign change in OMAR also results in a large change in the current-voltage characteristics. This indicates that a change in the charge transport is likely to be responsible for the change OMAR sign change.

We show conclusively using admittance and EL measurements that the sign change is a result of the device making a transition from unipolar to bipolar behavior in chapter 5. We see that right at the voltage where the sign changes the device makes a transition from unipolar diffusive transport to bipolar drift dominated transport.

In chapter 6 we develop a device model that describing the devices used in our experiments. Here, we show both numerically and analytically that in a device with an injection limited minority contact and an ohmic majority carrier contact that a decrease in the majority carrier mobility can result in an increase in the current. Therefore, we can show that when the magnetic field acts to decrease the mobility of both carriers, OMAR can change signs as a function of applied bias.

We go deeper into the details of the model described in chapter 6 in Chapter 7. We show that using the framework of space charge limited conductivity we can exactly solve the current as well as the magnetoconductance as a function of voltage. Using this model we show that the OMAR effect should become stronger when minority charge carrier injection becomes more inhibited and the recombination becomes weaker.

In chapter 8 we look at what has been observed in the literature regarding sign changes. Here we compare our results and interpretations to those that can be found in the literature. We show that by combining the microscopic bipolaron model with the macroscopic device model all the different types of sign changes that have been observed in the literature can be explained.

In chapter 9 we compare the electrically detected magnetic resonance(EDMR) response to OMAR response of the same device. We observe that the OMAR response and the EDMR response are highly correlated which indicates that OMAR is indeed due to spin-dependent recombination processes affecting the current. In the EDMR spectra we observe two distinct resonances, where one can be assigned to electron resonances and the other to the hole resonance. Interestingly we observe that the hole resonance inverts sign at exactly the same voltage at which OMAR inverts sign.

To determine exactly how the recombination strength affects OMAR we systematically doped Alq$_3$ with different amounts of a luminescent dye in chapter 10 to increase the recombination strength. We showed that increasing the recombination decreases the strength of the OMAR effect as predicted in the modeling done in Chapter 7. We also observed that the OMAR traces widened upon doping as well. This was speculated to be due to an increase in positional and energetic disorder.
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Chapter 2
Experimental Methods

Abstract: This chapter presents the experimental techniques used in this thesis. We discuss the properties of the materials, the sample fabrication techniques, and the different characterization methods used in this work. The emphasis in this chapter is on characterization since the sample fabrication and materials are relatively standard. The first technique we discuss is a novel method of measuring OMAR called the dIdB technique. Then we discuss other techniques from which we can gain insight about the OMAR effect. These methods are admittance spectroscopy, and electrically detected magnetic resonance (EDMR).
Figure 2.1: The molecular structure of (a) DCM, (b) Alq₃ and (c) MDMO-PPV.

2.1 Active layers

The two organic semiconductor active layers used in this thesis are tris-(8-hydroxyquinoline) aluminium (Alq₃, Fig. 2.1b.) and (poly(2-methoxy-5-{3',7'-dimethyloctyloxy}-p-phenylenevinylene) (MDMO-PPV, Fig. 2.1c.). Alq₃ is a semiconducting small molecule that is very commonly used as an electron transport material since it has a large electron mobility for organic semiconductors ($\approx 10^{-6}$ cm$^2$V$^{-1}$s$^{-1}$ [1]). Alq₃ is a poor hole transport material as the hole mobility is 2 orders of magnitude lower than the electron mobility [1]. MDMO-PPV is a semiconducting polymer commonly used in organic solar cells. It is a hole transport material and the hole mobility is $5 \times 10^{-6}$ cm$^2$V$^{-1}$s$^{-1}$. The electron mobility is much lower, but cannot be measured accurately since the electrons are highly trapped [2].

In chapter 10 we dope Alq₃ with the laser dye 4-(diacynamethylene)-2-methyl-6-(p-dimethylaminostyryl) (DCM, Fig. 2.1a.). This molecule is a common red laser dye, and is often used as recombination center in Alq₃ in order to achieve red emission due to its high fluorescence efficiency [3–5].

2.2 Sample Preparation

The samples are prepared on indium tin oxide (ITO) coated (coating thickness 130-160 nm) glass substrates (30 mm $\times$ 30 mm) which are prepatterned. ITO is a common anode used in OLEDs since it is transparent and has a high work function which allows for good energetic matching to the HOMO of the organic semiconductor active layer. Before applying the organic semiconductor active layers, the substrates are cleaned by ultrasonic cleaning in a detergent solution, and then rinsed for 20 min with deionized water, followed by another ultrasonic cleaning with isopropanol. To eliminate any remaining organic contamination the samples are then exposed to a 30 min UV/ozone treatment. Following this step a 60 nm layer of poly(3,4-ethylenedioxythiophene) with poly(stryrenesulfonate) dopant (PEDOT:PSS) is spin coated on the substrate. This layer is used in order to improve hole injection from the anode and to smooth
the ITO surface. To make devices with MDMO-PPV as the active layer a 5 mg/ml MDMO-
PPV:chlorobenzene solution is spin coated on top of the PEDOT:PSS. After spin coating all
further steps take place in dry nitrogen gloveboxes and the samples are never again exposed to
ambient conditions. To make devices with Alq₃ as the active layer, Alq₃ is thermally evaporated
in a high vacuum chamber (base pressure $5 \times 10^{-8}$ mbar) on top of the PEDOT:PSS coated
substrate. In this high vacuum chamber it is also possible to do coevaporation, this allows
for doping of the Alq₃ active layer, which is done in chapter 10. The metallic top electrodes
are then prepared by thermal evaporation in a different high vacuum set-up (base pressure
$1 \times 10^{-7}$ mbar). In this thesis three different cathodes were utilized. Ca(10 nm)/Al(100nm)
($\Phi = 2.9$ eV [6]) and LiF(1 nm)/Al(100 nm) ($\Phi = 3.1$ eV [7]) are low work function cathodes
which allow for good electron injection. When devices with only hole conduction are desired
a high work function cathode is used to prevent electron injection. To achieve this we used
Pd(10nm)/Au(50 nm) cathodes ($\Phi = 5.1$ eV [6]). These electrodes are patterned by shadow
masking, which results in devices with an active area of $3 \times 3$ mm. An example of a typical
device layout is shown in figure 2.2.

2.3 Measurement Set-up

After thermal evaporation of the cathodes the samples are transferred in a sealed container
from the fabrication glovebox to another dry nitrogen glovebox where the samples are char-
Figure 2.3: (a)(color online) Measurement setup showing the sample sitting between the poles of an electromagnet in a cryostat. (b) Electrical schematic used for making the dIdB measurements. (c) Principle of the dIdB measurement showing how measuring the current induced ∆I by an oscillating magnetic field ∆B can be used to measure the $\frac{dI}{dB}$. Figure taken from [15].

OMAR is typically measured by sweeping the field and measuring the current at a constant applied electrical bias [11–14]. However, there is a problem with using this simple method. The problem is that degradation and trapping effects cause the current not to be constant with time (see fig. 2.4). So when doing a typical OMAR measurement there are two contributions that can change the current. This results in a total change in the current of:

$$\Delta I(B, t) = \Delta I(B) + \Delta I(t),$$  \hspace{1cm} (2.1)
the $\Delta I(B)$ is the change in the current due to magnetic field effects (e.g. OMAR) and $\Delta I(t)$ is change in the current due to time-dependent effects. As seen in fig. 2.5b $\Delta I(t)$ can be large enough to significantly obscure $\Delta I(B)$ which occurs due to OMAR.

To eliminate $\Delta I(t)$ we developed a method to measure the derivative of the current with respect to the magnetic field (i.e. $dI/dB$). This is achieved by applying a static magnetic field superimposed with a small sinusoidal AC magnetic field ($B_{AC}$). Due to $I$ being a function of $B$, $B_{AC}$ induces an oscillating current, $I_{AC}$ (fig. 2.3c). This oscillating current is detected by measuring the voltage drop, $V_{AC}$, across a resistor in series with the sample ($R_s$)(fig. 2.3b). We note that $R_s$ is much less than the resistance of the sample so the relative voltage drop across $R_s$ is negligible compared to the voltage drop across the sample ($R_{sample}$). $V_{AC}$ is measured with a lock-in amplifier locked into the oscillation frequency of $B_{AC}$. Therefore, using Ohm’s law $I_{AC}$ can be determined by $\frac{V_{AC}}{R_s}$. By using a small enough value of $B_{AC}$ the relationship $\frac{I_{AC}}{B_{AC}} \approx \frac{dI}{dB}$ is valid. This approximation is valid only at low frequencies (i.e. $< 50$ Hz) [16]. Therefore, sweeping $B_{DC}$ allows one to obtain a very good approximation of $\frac{dI}{dB}(B)$. This can then be integrated to obtain $\Delta I(B)$(fig. 2.5). The magnetoconductance (MC) can then be determined by $\frac{\Delta I(B)}{I(0)}$, where $I(0)$ is the DC current with no applied magnetic field.

### 2.5 Admittance Spectroscopy

To look more carefully at the charge transport in organic semiconductors we utilized a technique called admittance spectroscopy. In this technique an ac voltage is applied to the sample, $v_{ac}$, and the real and the imaginary components of the current response, $i_{ac}$, are measured. The admittance is a function of the angular frequency, $\omega$, simply given by: $Y(\omega) = \frac{i_{ac}}{v_{ac}}$. The real and imaginary parts of the admittance are called the conductance [$G(\omega)$] and the susceptance [$B(\omega)$] respectively. It is much more common to express the imaginary term in terms of the
capacitance which is given by the relation \( C(\omega) = \frac{1}{\omega} B(\omega) \). Therefore,

\[
Y(\omega) = G(\omega) + iB(\omega) = G(\omega) + i\omega C(\omega).
\]

(2.2)

It has been shown that admittance measurements can be used to get insight on many phenomena such as charge trapping [17], the permittivity of the medium, energetic disorder [18], transit time effects [19], charge transport mechanism (\( i.e. \) drift or diffusion) [20], the presence of bipolar current [21], and space charge effects [22].

In this thesis, we are mostly interested in looking at space charge effects and examining the charge transport mechanism. These devices naturally have a significant capacitance since there are two metallic electrodes sandwiching the organic semiconductor which a poor conductor. This results in the device having a significant geometric capacitance \( C_{\text{geo}} \). Because of the low charge mobility of organic semiconductors current is flowing in the device, which causes space charge to build up. Space charge causes an inductive contribution to the admittance signal resulting in the measured capacitance being less than the geometric capacitance \( C_{\text{geo}} \). This inductive contribution is due to the finite time it takes to build up space charge in the device, this causes the current to lag behind the voltage stimulus. Thus space charge results in the measured capacitance being less than \( C_{\text{geo}} \). For unipolar SCLC the inductive space charge results in \( C = \frac{3}{4} C_{\text{geo}} \) [18]. Therefore, using admittance measurements it is possible to observe if the transport is indeed space charge limited. In a bipolar device there can be much more space charge since having both electrons and holes in the device reduces the Coloumb repulsion. Therefore, the space charge limitation is relaxed since the unlike charges compensate each other’s electric fields, allowing for a much greater charge density. The result of having this large amount of space charge is that the decrease in the capacitance \( (\Delta C) \) can be much larger than in the unipolar case. In fact \( |\Delta C| > C_{\text{geo}} \) and therefore the capacitance can in fact become negative [21]. Therefore, this method can also be used to check for the presence of bipolar space charge in the device.

Another property we utilize in this thesis is the ability to use admittance measurements, specifically \( C(V) \) measurements, to determine if the charge transport is dominated by drift or by diffusion. Diffusion of charge from the contacts results in higher charge densities near the contacts which results in an increase in the capacitance (fig. 2.6). Diffusion dominates when the electric fields in the device are small, such that drift from electric fields in the device is minimal. Therefore, there is a peak in the capacitance when the device is at a flat band condition which occurs at the voltage \( V_{FB} \). Van Mensfoort et al. showed that \( V_{FB} < V_{bi} \).
2.6. Electrically detected magnetic resonance

Electrically detected magnetic resonance (EDMR) is an electron paramagnetic resonance (EPR) technique. The principle of EPR is that microwave radiation causes a resonance between two spin states. The spin states are split in energy by the Zeeman effect by using an applied magnetic field. The Zeeman splitting energy is \( E_{\text{Zeeman}} = g\mu_b\mu_0H_0 \), where \( g \) is the gyromagnetic ratio, \( H_0 \) is the external magnetic field and \( \mu_b \) is the Bohr magneton and \( \mu_0 \) is the magnetic permittivity of free space. Once the Zeeman splitting energy becomes the same as the photon energy of the microwave radiation (i.e. \( E_{\text{Zeeman}} = h\nu_{mw} \) where \( \nu_{mw} \) is the frequency of the microwave radiation) the spins will resonate between the spin up and spin down states (fig. 2.8).

Unlike conventional EPR, which detects the absorption of microwave radiation at magnetic resonance, EDMR detects the change in current induced by the microwave radiation at magnetic resonance in an operating device fig. 2.12. Our undoped organic materials are not EPR-active prior to operation since there are no paramagnetic species in the material. Paramagnetic species are created only when excitons and polarons are created either by light or charge injection.
Figure 2.7: (color online) A simulation by van Mensfoort et al. showing the C(V) curves for different values of the injection barrier height $\Phi_1$ [20]. Note this simulation is shown for a unipolar device, but the same principles apply to bipolar devices as well.

Figure 2.8: (color online) A graph showing the principles of EPR between spin up ($P_\uparrow$) and spin down ($P_\downarrow$) polarons. The polaron levels are Zeeman split and brought into resonance with the microwave radiation $h\nu_{mw}$.
Since detection of current is much more sensitive than detection of microwaves, EDMR can be incredibly sensitive, much more sensitive than conventional EPR. In fact, single spins have been detected using this technique [23].

EDMR uses the fact that resonance between two spin states makes spin a bad quantum number (i.e. the spin of the particle or quasiparticle is ill defined). This can result in a change in current because the relative orientation of spins between two charges, or a charge and a triplet exciton can affect the current, as explained in section 1.3.2. It is of particular interest to note that the magnetic resonance condition causes a similar effect as the randomly oriented hyperfine fields in the material as discussed in 1.4. Since both magnetic resonance and the randomly oriented hyperfine fields cause spin decoherence, it has been argued that they should similarly affect the current. However, EDMR can provide more detailed information than OMAR, because the different spin and charge species in the device have different resonance characteristics. Two properties affect the characteristics of the resonance: the g-factor, which affects the magnetic field at which the resonance occurs, and the hyperfine field, which causes the broadening of the resonance. Thus by looking at the g-factor of the resonance EDMR may allow one to separate the different contributions from electrons and holes, whereas OMAR cannot differentiate between the g-factors of the different carriers.

In the remainder of the section, we first discuss polaron resonance, and then triplet exciton resonances. We will show that EDMR is a powerful tool to determine if OMAR is due to polaron-polaron interactions, triplet-polaron interactions or triplet-triplet interactions. In the last part we discuss the experimental setup and the alternative sample design necessary for these experiments.

As discussed in 1.3.2 polarons have a spin of \( S = 1/2 \), therefore it is possible to cause resonance between the \( P_{+1/2} \) and the \( P_{-1/2} \) states. In organic semiconductors the polarons have a g-factor very close to the free electron g-factor (i.e. \( g \approx 2 \)) due to the material’s low spin-orbit interaction. However, there are small spin orbit effects which result in very slight deviations from \( g = 2 \). These effects are different for electrons and holes since the electron and hole wavefunctions differ spatially. Thus, the electrons and holes may experience different spin-orbit effects and may have slightly different g-factors, and their resonances may be slightly shifted from each other. It has indeed been shown that electrons and holes can have very slightly different g-factors in EDMR [24] (Fig. 2.9). Therefore, it can be possible to determine what charge species is involved in the OMAR effect. Also electrons and holes have different resonance widths, indicating that the hyperfine coupling is different for the different types of charges [24].

EDMR also can be used to determine if triplet excitons play a role in OMAR. Triplet excitons have a spin of \( S = 1 \). Therefore, this results in triplet excitons having a \( g \approx 4 \) resonance, which occurs at half the field of the polaron resonance (Fig. 2.10) and is referred to as the half-field resonance. This is a typical experiment in EPR experiments in order to see the presence of any type of triplet state. What occurs at the half-field resonance is that the triplet exciton is resonated between \( T_{+1} \) and \( T_{-1} \) (Fig. 2.10). The half-field resonance can be used to determine if spin dependent process between triplet excitons, or triplet excitons and polarons play a role in OMAR.

Another indication of triplets in magnetic resonance experiments is the triplet powder pattern. The powder pattern is a resonance that results in shoulders split off from the main \( g = 2 \) polaron resonance. This resonance is from the microwave radiation flipping the spins between the \( T_0 \) and the \( T_{+1} \) or the \( T_{-1} \) state. The \( T_{+1} \) and the \( T_{-1} \) states are not equivalent to the \( T_0 \)
Figure 2.9: (color online) EDMR spectra of unipolar Alq₃ devices using a K-band (24 GHz) spectrometer. The different g-factors of the electron and hole only devices are shown on the x-axis of the figure. This figure was modified from [24].

Figure 2.10: (color online) Diagram showing the $g \sim 4$ half-field triplet exciton resonance and the $g \sim 2$ polaron resonance.
state since there is a dipole-dipole interaction between the like oriented spins in these excitons that causes a finite energy difference between $T_{+1}$ and the $T_{-1}$ states and the $T_0$ state. This energy difference is called the zero field splitting ($E_{zfs}$), since prior to any external field being applied the energy levels are already split due to the dipole-dipole interaction (Fig. 2.11a.). This splitting causes $E_{mw}$ being resonant at fields A and B as defined in (Fig. 2.11). This results in shoulders split-off from the main $g \approx 2$ resonance in the EDMR spectra (Fig. 2.11b.). If this were observed in the EDMR spectra it would indicate that triplet excitons may play an important role in OMAR.

Finally, after having explained the different resonances that could be observable in EDMR we will describe the experimental setup. The EDMR spectra presented in this thesis are recorded with a X-band (9.4 GHz) Bruker ESP300E spectrometer equipped with a Varian magnet and a rectangular cavity. A constant voltage is applied to the device which is in series with a resistor ($R_s$), which is significantly less than the sample resistance ($R_{sample}$) (i.e. $R_s \ll R_{sample}$). Similarly as done in the dIdB measurements, the change in current due to magnetic resonance was detected by the ac voltage drop ($V_{LI}$) across a resistor ($R_s$) with a lock in amplifier (Fig. 2.12). From this the change in current that results from magnetic resonance can be determined ($\Delta I_{res}$). By knowing this along with the DC current ($I_{DC}$) the magnitude of the EDMR can be determined by $\frac{\Delta I_{res}}{I_{DC}}$.

In these experiments the sample architecture is slightly different due to the limited size of the microwave cavity. The cavity puts a restriction on the size of the sample to less than 5 mm wide. As a consequence, the 30 mm $\times$ 30 mm glass substrates we use for the OMAR measurements cannot be applied. Since the MDMO-PPV active layer we use was spin coated, it was not possible to precut the devices. The device’s small size would result in the spin coating process giving very large thickness inhomogeneities. The solution was to use ITO coated polyethylene terephthalate (PET) substrates, which can easily be cut to small sizes after processing with a pair of scissors. The substrates were first cut into 30 mm $\times$ 30 mm sizes after which the ITO electrodes were patterned by masking with scotch tape, and then etching with concentrated HCl. Next, the polymer layers are spin coated on the substrate, and the metals evaporated as described in section 2.2. After this the devices were cut out of the substrate into the approximate dimensions (4 mm $\times$ 15 mm).
Figure 2.12: Schematic of layout of the EDMR measurement setup. The sample is shown as a resistor and capacitor in parallel, which is inside a microwave cavity. The magnetic field is provided by the electromagnet, while the change in the current from magnetic resonance is determined by measuring the ac voltage drop across a series resistor with a lock in amplifier $V_{LI}$ at the microwave chopping frequency ($\omega_{\text{chop}}$).
Bibliography


Chapter 3

Separating positive and negative magnetoresistance

Abstract: We study the transition between positive and negative organic magnetoresistance (OMAR) in tris-(8-hydroxyquinoline) aluminium (Alq3), 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) vs. 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. ¹

Chapter 3. Separating positive and negative magnetoresistance

3.1 Introduction

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 spinvalve [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 vs. field were reported, where the MR as a function of magnetic field has been defined as $\text{MR}(B) = \left( R(B) - R(0) \right)/R(0)$, where $R$ is the resistance. The 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).

3.2 Experimental

We produced samples with two different molecules: (poly(2-methoxy-5-{3’,7’-dimethyloctyloxy}-p-phenylenevinylene) (MDMO-PPV), and tris-(8-hydroxyquinoline) aluminium (Alq3). The samples showed qualitatively similar features, however here we present a coherent set of experimental results for a single Alq3 device. The 4 mm x 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 ∼10$^{-6}$ mbar) 100 nm of 99.995% pure Alq3 (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.

### 3.3 Results and discussion

First we measured the MR as a function of magnetic field at different temperatures and voltages. Figure 3.1 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:

$$MR(B) = MR_{\infty} \left( \frac{B}{(|B| + B_0)} \right)^2,$$

where $B_0$ is the characteristic field width, which is 1/4 of the full width at half maximum (FWHM), and $MR_{\infty}$ is the MR at infinite $B$-field [7]. In figure 3.1a we see that the sign of the MR changes from positive to negative between 9 V and 10 V, and (3.1) is not a good fit above 7 V. We also observe that the traces with +MR have a 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. 3.3). 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($I$) vs. log($V$) plot is linear indicating a power law behavior with $I \propto V^6$ (fig. 3.2a-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($I$) vs. log($V$) deviates from the power law and the slope increases at exactly $V_{tr}$ (see vertical lines at $V = V_{tr}$ in fig. 3.2).

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 Alq3) by determining the differential capacitance ($\Delta C$) [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, $\Delta C$, 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 $\Delta C$, which may allow it to become larger than the geometric capacitance, thus causing the measured capacitance to become negative. This phenomena 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].

In figure 3.3 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 eventually becomes negative. Analogously, the minority charge injection also
results in an increase of the slope of $\log(I)$ vs $\log(V)$ (fig. 3.2) 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

Figure 3.1: (color online) (a) MR vs. magnetic field curves at 220K measured at different voltages. (b) MR vs. magnetic field at 300K. The solid lines are fits according to equation 3.1.

Figure 3.2: (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.
3.4 Modeling

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 3.2 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

![Figure 3.3: 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.](image-url)
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 $P_1(V) = A \cdot V^n / I_{tot}(V)$.

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:

$$MR(V) = P_1(V)MR_1 + (1 - P_1(V))MR_2.$$  (3.2)

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 equation 3.2 to the measured $MR(V)$ data. Figure 3.4a and b show 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 (3.1) 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 (figure 3.1b). 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 (figure 3.1a).

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.

**Figure 3.4:** (color online) Modeled $MR(V)$ and measured $MR(V)$ at 220 K (a) and 240 K (b). Modeled $MR(B)$ (lines) curves and measured $MR(B)$ (open squares) at different voltages (c).
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 (figure 3.4c). 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 equation (3.1), can easily be explained with a superposition of two MRs with behavior according to (3.1). 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.

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]:

$$J = \frac{9}{8} \varepsilon \sqrt{\frac{2\pi \mu_e \mu_h (\mu_e + \mu_h)}{\mu_r}} \cdot \frac{V^2}{L^3},$$  \hspace{1cm} (3.3)

where $\mu_e$, $\mu_h$, and $\mu_r$ are the respective electron, hole and recombination mobilities, $L$ is the thickness of the device and $\varepsilon$ 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 equation (3.3), 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:

$$\text{MR}(B) = -(C_e \frac{\Delta \mu_e}{\mu_e} + C_h \frac{\Delta \mu_h}{\mu_h}),$$ \hspace{1cm} (3.4)

where $\Delta \mu = \mu(B) - \mu(0)$, $C_e/h$ are prefactors that depend on details of the model, whereas 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 equation (3.2) 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 line width 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 $\mu_r$.
3.5 Conclusion

In conclusion, we performed 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.
Bibliography


Chapter 4

Temperature dependent sign change

Abstract: A sign change of the organic magnetoresistance (OMAR) effect is observed as a function of temperature. There is a large difference in the IV behavior when the sign of the magnetoresistance (MR) is positive compared to when sign of the MR is negative, pointing to the possibility that the sign change of the MR is due to a change in the charge transport mechanism. The positive and negative MR show different characteristic field widths $B_0$ in the MR vs. magnetic field curves. Also, the traces with positive MR show a clear temperature dependence of $B_0$ while no systematic dependence on temperature is seen in the traces with negative MR. This behavior can be qualitatively explained by the recently proposed bipolaron model. ¹

4.1 Introduction

Recently, there has been much interest in the magneto-transport of organic semiconductor devices [1–3]. This interest has been motivated by organic materials’ chemical tunability, predicted long spin coherence times, and ease of processing. New developments in the field include the successful fabrication of spinvalve [1] and tunnel-magnetoresistance [2] devices. Aside from these effects, which have been previously observed in other material systems, a completely new room temperature magnetoresistance (MR) was observed in 2004 in organic LED-type devices by Francis et al. [3] and has been dubbed OMAR (organic magnetoresistance).

The OMAR effect can have MR values of 10% at relatively small magnetic fields of $\sim 10$ mT without needing ferromagnetic contacts. The properties of: room temperature operation, large MR, and low required magnetic fields, may make OMAR devices desirable for magnetic field sensors. These sensors could become an important component for future use in “plastic” electronics.

The OMAR effect is also of great scientific interest since it has several interesting properties which make it unique compared to other magnetoresistive effects. The effect can be observed in organic semiconductor materials with vastly different properties and the effect is surprisingly universal. Two characteristic line-shapes of $\text{MR}(B) = (R(B) - R(0))/R(0)$, where $R$ is the resistance and $B$ is the magnetic field) have been identified and the characteristic width ($B_0$) is $\sim 5$ mT at room temperature for almost all organic semiconductor materials. Another interesting feature of OMAR is that the sign of the effect can change as a function of temperature and voltage [4]. This sign change has so far not been explained. However, we recently proposed that this sign change is a result of the device making a transition from unipolar to bipolar transport [5].

Besides interest in using these devices for applications, there are many unanswered fundamental questions as to the physical mechanisms responsible for this effect. There have been three recent models proposed to explain OMAR. Two of them are based on magnetic field effects on excitons [6, 7]. The third model attributes the effect to spin-blocking, via Pauli’s exclusion principle, frustrating the formation of doubly-occupied sites (bipolarons) [8, 9]. Recent Monte-Carlo simulations [9] and analytical modeling [8] have been able to reproduce both the $\text{MR}(B)$ line-shapes as well as the sign change of the OMAR effect.

In this chapter, we look at the role temperature plays in OMAR. Specifically, we look at how the temperature affects the sign and the $\text{MR}(B)$ line shape of OMAR. We relate this behavior to the bipolaron model in order to bring a better understanding of the mechanisms involved in this new field.

4.2 Experimental

The devices were deposited on clean indium tin oxide (ITO) patterned glass substrates. The substrates were first covered by spin coating a poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) dispersion to improve charge injection at the anode-active layer interface. Next, the samples were moved into a glovebox with a dry nitrogen environment to deposit 100 nm of the active layer tris-(8-hydroxyquinoline) aluminium ($\text{Alq}_3$) by thermal evaporation in a high vacuum system (base pressure $\sim 10^{-6}$ mbar). In a similar high vacuum system, within the same glovebox, 1 nm of LiF and 100 nm of Al were evaporated to form the cathode. After fabrication the samples were transported in a nitrogen environment.
4.3. Results and discussion

First, we measured several MR\((B)\) traces using a fixed 10 V bias at several different temperatures (fig. 4.1). The most striking feature is that the sign of the low temperature MR is positive while at high temperature the MR has a negative sign. All the MR\((B)\) traces were fitted to the equation:

\[
\text{MR}(B) = \text{MR}_\infty \left( \frac{B}{|B| + B_0} \right)^2,
\]

where \(B_0\) is the characteristic field width, and \(\text{MR}_\infty\) is the MR at infinite magnetic field. This empirical relationship was found by Mermer et al. to fit well to MR\((B)\) traces for Alq3 and a wide variety of other organic semiconductors [4]. The fits (solid lines in fig. 4.1) show that Eq. (4.1) describes all the MR\((B)\) traces well and allows us to find the temperature dependence of both \(B_0\) and \(\text{MR}_\infty\). Due to the correspondence with Eq. (4.1) it is likely that traces with a positive sign of MR (+MR) and the traces with a negative sign of MR (−MR) are from the same general mechanism.

Figure 4.2a shows that the change in sign of the MR occurs at a transition temperature of 188 K. The transition is very sharp and the +MR saturates immediately showing little temperature dependence after the transition. The −MR data appears to saturate more slowly, but also shows a large increase in magnitude near the transition temperature.

A distinguishing characteristic between the +MR and −MR traces is the difference in \(B_0\) of their corresponding MR\((B)\) traces. By plotting \(B_0\) vs. temperature (fig. 4.2b) we can see that there is an abrupt change in \(B_0\) as soon as the MR switches sign. From the concurrence of the sign change and the abrupt switch in the value of \(B_0\) one could conclude that the +MR and

![Figure 4.1](color online) MR vs. magnetic field traces at 10 V bias for several different temperatures. The solid lines are fits to equation (4.1).
the $-\text{MR}$ are two distinct effects. It is not the case that there is one temperature dependent curve for which $B_0$ and the magnitude gradually evolve as a function of temperature.

From the log($I$) vs. log($V$) characteristics (fig. 4.3) we see that both the 100 K (+MR) and 240 K ($-\text{MR}$) traces are linear in the measured range, indicating power law behavior. This behavior is given by $A \cdot V^n$, where $A$ is a constant and $n$ is the power law index. In the case of space charge limited current with traps, which is likely in the case where $n > 2$, the power law index can be determined by $n = T_t/T + 1$, where the energy depth of the trap is $kT_t$ [10], where $k$ is the Boltzmann constant. From this relationship we would expect that $n$ decreases with increasing temperature. What we observe is that $n$ increases when the temperature is raised. From fitting the measured $I(V)$ data we find $n_{240K} = 13$ while $n_{100K} = 7.1$. Therefore, it seems that some temperature dependent change in the charge transport results in a change in the sign of the MR. In other recent work we proposed that this sign change is a result of the

![Figure 4.2](image)

**Figure 4.2:** (a) $\text{MR}_\infty$ vs. $T$ at 10 V. (b) $B_0$ vs. $T$ at 10 V, the filled squares represent +MR values while the open squares represent $-\text{MR}$ values. Both the values $\text{MR}_\infty$ and $B_0$ are a result of fitting to the data in fig. 4.1 to equation (4.1).
device making a transition from unipolar to bipolar transport [5].

The field width of the +MR feature shows very interesting behavior. First of all, $B_0$ can be as large as 16 mT, which is larger than the 5 mT $B_0$ that has been observed in the literature for most organic semiconductors, including Alq$_3$. One exception is the molecule Ir(PPy)$_3$ which has shown a $B_0$ as large as 100 mT [11]. This has been explained by the large spin-orbit coupling present in the molecule. However, spin-orbit coupling cannot explain the large difference in widths between the +MR and −MR feature since the features coexist in the same material and the spin-orbit coupling is independent of temperature.

Besides the large $B_0$ of the +MR feature, there is another distinguishing characteristic of its behavior. From fig. 4.2b we can see that $B_0$ modestly increases as the temperature is decreased. This is an interesting observation since in almost all previously measured devices in literature $B_0$ has not shown any temperature dependence. Curiously, Sheng et al. observed that the large $B_0$ feature in Ir(PPy)$_3$ decreases in width as the temperature decreases [11], opposite to the dependence we observe, however they do not speculate on the origin of this effect. Therefore, it seems that the width of large $B_0$ features are more temperature sensitive than that of small $B_0$ features. It is worthy to note that the width does not scale with the thermal energy in the system $kT$, since the dependence of $B_0$ on $T$ does not change drastically even at very low temperatures, $\sim 2$ K.

This behavior of $B_0$ vs. $T$ seems to fit well in the context of the recently proposed bipolaron model [8, 9]. In this model it has been shown that $B_0$ is dependent on the “branching ratio”. This ratio is defined as $b = r_{\alpha\rightarrow\beta}/r_{\alpha\rightarrow e}$, where $r_{\alpha\rightarrow\beta}$ is the rate at which a carrier from a singly occupied site $\alpha$ hops into a neighboring singly occupied site $\beta$ to form a bipolaron, and $r_{\alpha\rightarrow e}$ is the rate at which a carrier from $\alpha$ bypasses $\beta$ by hopping over $\beta$ into unoccupied sites in the environment. It has been shown in both Monte-Carlo simulations [9] and in analytical solutions of a two-site model [8] that increasing $b$ results in $B_0$ increasing. Therefore, the more a carrier is forced to hop into another occupied site and form a bipolaron, the larger the

![Figure 4.3](image)

**Figure 4.3:** (color online) $I(V)$ at 100 K (+MR) and 240 K (−MR). The dashed line at 10 V shows the voltage at which the MR($B$) was measured. The solid lines are fits of the data to a power law
width of the MR feature. This qualitatively matches our temperature dependence of $B_0$. At lower temperatures, carriers are more likely to form bipolarons since carriers have less energy to hop into sites further away in the “environment”. Therefore, the carriers have to hop into neighboring singly occupied sites creating bipolarons and causing both $b$ and $B_0$ to increase. Finally, we note that upon decreasing $b$ (or increasing $T$), the models [8, 9] predict that below a certain value the linewidth saturates, and finally converges to a Lorentzian line shape with a width approximately equal to the hydrogen hyperfine field ($B_{hf} \approx 1 \text{ mT}$ [4]), the relevant field scale in the bipolaron model.

4.4 Conclusion

In conclusion, we measured a temperature dependent sign change of OMAR in an Alq$_3$ based device. The distinct field widths of the $+$MR and $-$MR along with the abrupt change in MR sign suggests that the $+$MR and $-$MR are distinct effects; not a single effect that evolves as a function of temperature. From the $IV$ characteristics it seems that the sign change is due to a temperature dependent change in the transport mechanism. The $B_0$ values of $+$MR were found to be a function of temperature, this temperature dependent behavior is in qualitative agreement with the recently proposed bipolaron model. To gain further insight in this field, a correlation between the measurable parameters in an operating device and the modeled physical parameters is necessary.
Bibliography


Chapter 5

Sign change at the onset of bipolar injection

Abstract: In this work we examine the transition between positive and negative organic magnetoresistance in poly(2-methoxy-5-{3',7'-dimethyloctyloxy}-p-phenylenevinylene) (MDMO-PPV) in order to understand how different regimes of charge transport affect the organic magnetoresistance (OMAR) effect. To characterize the charge transport in these devices we measured the current, low frequency differential capacitance, and electroluminescence efficiency as a function of voltage. These measurements show that the sign change of the magnetoresistance corresponds with a change from a unipolar diffusive transport below the built in voltage ($V_{bi}$) to a regime of bipolar drift transport above $V_{bi}$.\(^1\)

5.1 Introduction

Organic magnetoresistance (OMAR) is a room temperature magnetoresistance which has been observed in non-magnetic organic semiconductor materials contacted by non-magnetic electrodes, which can be as large as 10% at fields of 10 mT [1]. It has been observed that the magnetic field can act to both increase the current, positive magnetoconductance (“+MC”), and decrease the current, negative magnetoconductance (“−MC”), depending on the device thickness [2] or the operating conditions, such as voltage [1, 3] and temperature [1, 4].

The large magnitude at low magnetic fields, room temperature operation, and switchable sign of MC, not only makes these devices technologically interesting, but also scientifically interesting, since traditional magnetoresistance mechanisms fail to accommodate these properties. Recently, there have been several mechanisms proposed based on randomly oriented hydrogen hyperfine fields inducing spin mixing, which an external magnetic field acts to decrease. The spin mixing can induce singlet-triplet transitions of two-carrier states (i.e. excitons and bipolarons) or their precursor pairs. Bergeson et al. proposed that this can increase e-h pair dissociation which can have a +MC or −MC depending on the transport regime [5]. Hu et al. proposed there is a competition between increased e-h pair dissociation, which only has a +MC in their model, and charge induced triplet-exciton dissociation, −MC [6]. Desai et al. explain OMAR as a competition between triplet-exciton polaron quenching, +MC, and triplet-exciton dissociation at interfaces, −MC [2, 7]. Finally, Bobbert et al. explain that the change the spin mixing can change the current by altering the process of bipolaron formation of electrons and holes seperately which may have opposite signs [8].

It is clear from the models proposed above that understanding the sign change in OMAR is important for understanding its mechanism, and that these sign changes may be related to changes in the charge transport. Therefore, in this letter, we use current voltage (I(V)), electroluminescence (EL), and low frequency differential capacitance (C) measurements to determine the correspondence between the charge transport and the sign of OMAR. We find that exactly at the voltage where the transport changes from a unipolar diffusive transport to bipolar drift transport there is a sign change from −MC to +MC. This behavior can be most plausibly explained using the bipolaron model.

We fabricated 3 mm x 3 mm devices with the structure: glass/ITO/PEDOT:PSS (60 nm)/MDMO-PPV (80 nm)/Ca (10 nm)/Al (100 nm), where PEDOT:PSS is poly(3, 4-ethylenedioxythiophene) poly(styrenesulfonate), and MDMO-PPV is poly(2-methoxy-5-(3’', 7’’-dimethyoctyloxy)-p-phenylenevinylene). The polymer layers were fabricated by spin coating and after the this step the samples were only exposed to an atmosphere of dry nitrogen. We also prepared samples with LiF (1 nm)/Al (100 nm) contacts which showed the same behavior as the Ca/Al sample presented here. Magnetococonductance and low frequency differential capacitance measurements were made between the poles of an electromagnet in the dark at room temperature. To prevent measuring changes in the current not due to magnetic field effects (e.g. time dependent drift of the current), we measured the magnetococonductance using a lock-in amplifier to get the change in current induced by a small 27 Hz AC magnetic field on top of the DC magnetic field, resulting in $\frac{dI}{dB}(B)$. This is then integrated to obtain $(I(B) - I(0))$ vs. $B$. 
5.2 Results and discussion

First, we measured MC, given by $\frac{I(B) - I(0)}{I(0)}$, as a function of the magnetic field at several different voltages (Fig. 5.1). At low voltages the current decreases with increasing magnetic field, resulting in a $-MC$. Increasing the voltage results in the MC changing sign, giving $+MC$. The $MC(B)$ for both the $+MC$ and $-MC$ curves show good correspondence when fitted to (lines in Fig. 5.1):

$$MC(B) = MC_\infty \left( \frac{B}{(|B| + B_0)} \right)^2,$$

where $B_0$ is the characteristic field width and $MC_\infty$ is the MC at infinite $B$-field [1]. Equation 5.1 was first found empirically [1] and later shown to be consistent with analytical [9] and numerical treatments [8] of the bipolaron model. From the resulting fits we observe that $B_0$ is larger for the $-MC$ (3.0 mT) than for the $+MC$ (2.0-2.3 mT), consistent with our previous work on Alq$_3$ [3]. The most notable feature of the $MC_\infty$ behavior is the sign change at 1.7 V, which is referred to as the transition voltage, $V_{tr}$ (Fig. 5.2). As the voltage increases beyond the sign change, $MC_\infty$ shows a sharp increase in magnitude which is followed by a slow decay. This behavior has also previously been observed in Alq$_3$ devices [7].

To see if there are correlations between the sign of the MC and the charge transport we measured the current vs. voltage ($I(V)$) characteristics (Fig. 5.3a). From the $I(V)$ behavior we can see three distinct regions of charge transport. In the low voltage region (I) there is an ohmic leakage current. At 1.2 V there is an onset in the current which is the beginning of region II. In this region the current follows a power law dependence with a power law of $V^n$, with $n \sim 13$ (dashed line in Fig. 5.3a). Region III begins at 1.7 V where the current increases with voltage faster than the power law dependence of region II. Understanding the transition between region II and III is very important since the voltage at which it occurs ($V_{ii \rightarrow iii}$) is right

Figure 5.1: (color online) MC vs. $B$ for an ITO/PEDOT:PSS/MDMO-PPV (80nm)/Ca/Al sample at several different voltages. The open symbols represent the measured data and the solid lines are fits to Eq. 5.1.
at the voltage where the MC changes sign (i.e. $V_{\text{ii-iii}} = V_{\text{tr}}$).

Due to the good matching of the work functions of the ITO/PEDOT:PSS anode (5.1 eV) and the Ca cathode (2.9 eV) to the respective HOMO (5.3 eV) and LUMO (3.0 eV) of MDMO-PPV [10] one would expect bipolar injection. By measuring the EL current efficiency (Fig. 5.3a) we can quantify how balanced the electron and hole populations are in the device. Interestingly, the EL current efficiency is $\sim 0$ below $V_{\text{ii-iii}}$, indicating the current is likely to be highly unipolar in region II. At $V_{\text{ii-iii}}$ bipolar injection begins and there is an onset in the EL efficiency indicating that in region III the device starts to become bipolar. This results in charges of opposites sign being introduced into the device, reducing the Coulomb repulsion and relaxing the space charge limitation of the current. Therefore, the current increases beyond the power law dependence in region II. The onset of EL efficiency at the deviation from the power law behavior confirms our previous assertion in chapter 3 that this deviation is due to the device becoming bipolar.

As the voltage increases further the EL efficiency increases, this is likely due to better charge injection at the minority charge (electron) injecting contact, Ca. In this device, the difference between the work functions of the anode and cathode is 2.3 eV, which is close to $V_{\text{tr}}$. This suggests that the device is operating near the built-in voltage ($V_{\text{bi}}$). However, it is known that in organic devices injection barriers can vary by more than 1 eV from the vacuum level alignment at the interfaces [11]. Therefore, to accurately know ($V_{\text{bi}}$) it must be experimentally determined. We do so by utilizing low frequency differential capacitance measurements which detects the presence of diffused charge near the electrodes. Above $V = 0$, carrier diffusion gradually increases causing the observed increase in $C$ above the geometric capacitance ($C_{\text{geo}}$)(Fig. 5.3b), peaking just below $V_{\text{bi}}$ [12]. Simultaneously, the diffusion current exceeds the leakage current increases as a power law which in region II. As the voltage increases beyond $V_{\text{ii-iii}}$, the transport goes from diffusion to drift, and correspondingly $C$ decreases. As the voltage further increases in region III, $C$ decreases below $C_{\text{geo}}$ and even becomes negative as a result of the device becoming fully bipolar [13].

![Figure 5.2: MC$_\infty$ versus voltage obtained from fitting Eq. 5.1 to the data in Fig. 5.1. The vertical dotted line represents the transition voltage ($V_{\text{tr}}$) from negative to positive MC.](image)
From our results we can conclude that the transition from $-\text{MC}$ in region II to $+\text{MC}$ in region III occurs exactly at the transition from a dominately unipolar diffusive transport regime to a bipolar drift regime. It is interesting that we can observe OMAR in the diffusive transport regime, and as far as we know this is the first observation of OMAR in this regime of transport. We have previously observed sign changes in Alq$_3$ where we saw similar correspondence of the $I(V)$ deviating from power-law behavior and a sign change of the MC [chapter 3]. However, this transition occurred at voltages much larger than $V_{bi}$. So it is likely that the change in the sign of the MC in the present case is due to a transition from unipolar to bipolar transport and not from a transition from diffusion to drift transport.

There are two different models which could show a sign change as the transport transitions from dominately unipolar charge transport to bipolar transport. The work by Hu et al. proposes that there is a competition between triplet charge reaction ($-\text{MC}$) and singlet e-h pair dissociation ($+\text{MC}$) [6]. According to the authors, when the charge transport in the

Figure 5.3: (color online) (a) log$(I)$ (black), EL efficiency (red) and (b) low frequency (220 Hz) differential capacitance vs log$(V)$. The dashed green line in (a) represents a power law fit to the log$(I)$ vs. log$(V)$ in region II. The vertical dotted lines indicate the boundaries between regions I, II, and III.
device is unbalanced, the triplet exciton charge reaction dominates due to the relatively long triplet exciton lifetimes (note it is necessary for the device to be slightly bipolar in order to have enough triplet excitons to observe this effect). As the current becomes more balanced the singlet e-h pair dissociation becomes relatively more important and the MC changes sign. However, both the triplet-charge reaction and singlet e-h pair dissociation rely on the premise that the magnetic field can alter the singlet triplet exciton ratio. This is not observed either in charge induced absorption [14] or fluorescence-phosphorescence measurements [15]. Also, it would expected that if triplets played a role in the $-\text{MC}$ the $-\text{MC}$ effect should have significant temperature dependence due to the strong dependence of temperature on the triplet life time. Experiments show that the $-\text{MC}$ is only weakly effected by temperature [4].

The other model which could explain this behavior is the bipolaron model. This model is based on unipolar charge transport and electron and hole mobilities can be separately effected by the magnetic field. Therefore, below $V_{tr}$ the current is mostly unipolar and the majority carriers (holes) cause the MC. Above the transition voltage minority charge (electron) injection sets in and the minority charge carriers dominate the MC. It is possible for the minority charges to dominate the MC due to the compensation of space charge when the device becomes bipolar, since the sum of the relative mobility changes of electrons and holes determines the MC [chapter 3]. So in MDMO-PPV where electrons have a significantly lower mobility than holes, electrons can still dominate the MC. Also, Nguyen et al. have shown in almost unipolar devices that the minority charge carrier conduction may dominate the MC [16]. It has been shown in the bipolaron model that the sign of MC can be positive or negative [8, 9]. However, in the bipolaron model, it is not obvious as to why in this device electrons give $-\text{MC}$ and holes give $+\text{MC}$, while the opposite is true in Alq$_3$ [chapter 3]. We note that our data is consistent with earlier observations that MC observed in the unipolar regime is generally smaller than that observed in the bipolar regime [chapter 3]. This trend is not yet understood, and provides an interesting challenge for future research.

5.3 Conclusion

In conclusion, we show by EL, $I(V)$, and low frequency differential capacitance measurements, that the voltage at which the sign change occurs shows remarkable correspondence with the transition from unipolar to bipolar transport, confirming our previous assertion [chapter 3]. The best existing model to explain this correlation seems to be the bipolaron model. However, the nature of how electrons and holes are effected differently within this framework remains an outstanding question.
Bibliography


Chapter 6

Sign inversion of magnetoresistance in space-charge limited devices

Abstract: In this work, we explain the puzzling sign change of organic magnetoresistance in space charge limited devices by device physics. We prove analytically and numerically that in the case of bipolar conduction with an ohmic majority carrier and an injection limited minority carrier contact, a decrease in minority carrier mobility may give rise to an increase in the device current. It is shown that when the magnetic field acts to decrease the mobility of both carriers, a sign change in the magnetoconductivity as a function of applied bias may result. This modeled behavior is in agreement with experimental observations. \(^1\)

6.1 Introduction

Organic magnetoresistance (OMAR) is a magnetoresistance effect that has been observed in organic semiconductor devices without any magnetic materials [1, 2]. At room temperature the effect can cause a large (> 10%) magnetoconductance (MC), the relative change in conductance due to a magnetic field, at relatively low magnetic fields (∼10 mT) [2]. These properties combined with the chemical tunability and ease of processing of organic semiconductor materials, may make OMAR interesting for use in large area magnetic field sensing arrays.

So far, several mechanisms to explain OMAR have been introduced. All these mechanisms rely on random hyperfine fields inducing spin mixing, which an external magnetic field acts to decrease. This spin mixing can change the spin correlation between two-carrier states such as excitons and bipolarons or their precursor pairs, thus changing the singlet-triplet nature of these states. There are several mechanisms suggested on how this change in spin mixing can cause a change in current: it could change the recombination rate [3, 4], alter the process of triplet-exciton polaron quenching [5, 6], change dissociation of triplet-excitons by polarons [4] and electrodes [5, 6], and finally the spin mixing could alter the process of bipolaron formation [7, 8].

A crucial and puzzling property of OMAR is that the sign of the MC can depend on device thickness [5] as well as on operating conditions such as voltage [9–11] and temperature [9, 12]. Several groups have studied these sign changes, motivated by the notion that its further understanding may provide an essential key towards resolving the microscopic origin of OMAR. Different explanations for the sign change have been reported [3, 4, 6, 10, 11], and generally it has been thought the different signs OMAR correspond to differences in the microscopic mechanism at different device operating conditions.

In this Letter, we show that for bipolar devices operating under space-charge limited current (SCLC) conditions, an OMAR mechanism that causes magnetic contrast to both the hole and electron mobilities of the same sign, will cause a sign change in the MC as a function of applied bias. This sign change occurs at the transition between the unipolar (small electrical bias) and the bipolar (large bias) regime and is shown to be a natural consequence of the device physics. More specifically, it will be shown how a decrease in the minority charge carrier mobility, can lead to an increase in the total current. Although never noticed before, such a behavior should be more general for SCLC devices with one ohmic and one current-limiting contact, potentially having applications well beyond OMAR in organic devices.

Sign changes in OMAR have been previously observed when the device changes from unipolar to bipolar transport as a function of increasing voltage [10, 11, 13]. Here we examine a case where the majority carrier injection is ohmic and the minority carrier injection is injection limited. This is a common situation for bipolar devices at lower voltages, where the device is not yet fully bipolar. In this case the transition from unipolar to bipolar behavior is a result of the electric field at the minority carrier contact becoming large enough that minority charges start to be injected and the device becomes slightly bipolar. At this point, the injection of the minority charges dominates the resistance of the minority channel causing the minority charge injecting contact to act as a constant current source. The consequences of this effect are schematically illustrated in Fig. 6.1, where the mobility (µ) is represented by the arrows. Let us assume that by applying a magnetic field the minority charge carrier mobility decreases. Then the density of minority charges increases because the injected current in the minority channel is constant (Fig. 6.1b → Fig. 6.1c). The increase in the minority carrier density further compensates the Coulomb repulsion between the majority charges, causing the density of
the majority charges to increase. Since the more mobile majority carriers carry the bulk of
the current, an increase in their density increases the device current. Thus, the current can
respond oppositely to a change in minority carrier mobility. As such, the minority channel acts
as an internal gate that carries little current but significantly affects the charge density in the
current carrying majority channel.

6.2 Description: Analytical model

In order to understand the effect in a more quantitative way, we follow the analytical device
model of SCLC as introduced by Parmenter and Ruppel [14]. Their treatment leads to the well
known relationships for unipolar and bipolar SCLC. In order to treat the intermediate case
between unipolar and bipolar SCLC it is required to include a concrete functional dependence
for the minority charge carrier injection neither outlined in [14] nor [15]. Here we introduce the
main ingredients of the approach and some results as an example. A more detailed derivation
and thorough analysis is provided in chapter 7.

To derive the relationships for unipolar and bipolar SCLC, Parmenter and Ruppel solved
the coupled drift, Poisson, and the current continuity equations [14]. We follow their solution
of these equations but use specific boundary conditions: an ohmic majority carrier contact
at the cathode and an injection limited minority carrier contact at the anode. In this case
there is one parameter, the minority charge carrier current density at the anode (J_{amin}), for
which there is no solution. Therefore, we must explicitly model J_{amin} as a function of the
electric field at the anode, E_a. We found the general behavior, which we report on later, is
qualitatively independent of the type of injection model we choose, and both phenomenological
models with a certain onset electric field and more realistic injection models work well. Here

Figure 6.1: (color online) (a) Schematic band diagram of the modeled device. The device has
an ohmic electron (majority carrier) contact and injection limited hole (minority carrier) contact.
Diagrams showing the effect on the charge concentrations of the hole and electron channel as hole
mobility is decreased from panel (b) to (c) (μ is represented by the length of the arrows).
we chose a phenomenological function which reproduces the experimentally observed current voltage \([J(V)]\) behavior relatively well:

\[
J_{0,\text{min}} = J_0 \left( \exp \left( \frac{E_a}{E_0} \right) - 1 \right),
\]

(6.1)

where \(E_0\) determines how sharp the onset of the minority current is, and \(J_0\) is a constant prefactor. In all of our modeling we used weak recombination where the recombination mobility, \(\mu_r\), was modeled using Langevin-type recombination given by: \(\mu_r = L (\mu_e + \mu_h)\), where \(\mu_e\) and \(\mu_h\) are the respective electron and hole mobilities, and \(L \ll 1\) is a prefactor determining the strength of recombination.

Fig. 6.2a (red line) shows the modeled current density, \(J_{\text{mod}}\), as a function of voltage. We observe that at low voltage \(J_{\text{mod}}(V)\) can be described by unipolar SCLC (black line). When the voltage becomes large enough the injection limited anode begins to inject holes resulting in the current becoming larger than unipolar SCLC, similar to what we observed experimentally \([10]\). At higher voltages, \(J_{\text{mod}}(V)\) converges to bipolar SCLC (blue line) since the contact ceases to be injection limited due to the large \(E_a\).

### 6.3 Results: analytical model

To determine how a magnetic field effect on the mobility (magnetomobility) affects the overall device current we calculated \(J_{\text{mod}}\) with and without a magnetic field, the magnetic field is assumed to cause a voltage independent change of the mobility. From this we determined a “normalized MC”, which is defined as the relative change in the total current due to a relative change in mobility of a single charge carrier \(\frac{\Delta J}{J} / \frac{\Delta \mu_i}{\mu_i}\), where \(i = \text{“min” or “maj”}\) indicating the minority and majority carriers respectively. At the unipolar low voltage limit, magnetomobilities in the majority and minority channel obviously result in normalized MCs of 1 and 0 respectively (Fig 6.2b). At high voltage the charge transport converges to bipolar SCLC, which results in a normalized MC of 1/2 for both magnetomobilities in the majority and minority channel, since solving the equation for bipolar SCLC \([14]\) for the relative change in current due to a change in mobility in the case of weak Langevin-type recombination results in:

\[
\frac{\Delta J}{J} = \frac{1}{2} \left( \frac{\Delta \mu_{\text{min}}}{\mu_{\text{min}}} + \frac{\Delta \mu_{\text{maj}}}{\mu_{\text{maj}}} \right).
\]

In the intermediate voltage regime, when there is a magnetomobility in the minority channel, we see very interesting behavior. Initially, at the beginning of minority charge carrier injection, the normalized MC is negative, therefore increasing \(\mu_{\text{min}}\) results in a decrease in \(J\) for the reason outlined in Fig. 6.1. At high voltages where the anode is no longer injection limited the normalized MC converges to the expected bipolar behavior. In between we see that there is a local minimum in the MC\((V)\) followed by a sign change as a result of this transition away from injection limited behavior to bipolar SCLC. We also observe that increasing the mobility ratio, \(\frac{\mu_{\text{maj}}}{\mu_{\text{min}}}\), results in the normalized MC becoming more negative. \(\Delta \mu_{\text{min}}\) acts to change the current in the majority channel by increasing the majority carrier density, while the current in the injection limited minority channel remains constant. Therefore, the larger \(\frac{\mu_{\text{maj}}}{\mu_{\text{min}}}\) the more of the current is carried by the majority channel and the more negative the normalized MC.
6.4 Description: numerical model

To make a model of more realistic conditions, we solved the drift and diffusion equations numerically using the principles laid out by Malliaras and Scott [16]. We extended their approach to include trapping in the majority charge carrier (electron) channel.

The energetic distribution of traps was approximated with an exponential density of states below the LUMO (lowest unoccupied molecular orbital), $E_{\text{LUMO}}$. The trap density of states at

![Figure 6.2:](image)

**Figure 6.2:** (color online) (a) The analytically determined $J(V)$ with $\frac{\mu_{\text{maj}}}{\mu_{\text{min}}} = 2$, represented by “Model” (red). The upper and lower limit of the current is given by bipolar SCLC (blue) and unipolar SCLC (black) respectively. (b) The analytically determined normalized MC vs. voltage using different ratios of $\frac{\mu_{\text{maj}}}{\mu_{\text{min}}}$ in the case of a magnetomobility in the majority or minority channel. For all calculations $\frac{\mu_{\text{min}}}{\mu_{\text{r}}} = 40$. 

energy \( E \) for \( E < E_{\text{LUMO}} \) is given by:

\[
n_t(E) = \frac{N_t}{k_B T \cdot l} \cdot \exp \left( \frac{E - E_{\text{LUMO}}}{k_B T \cdot l} \right),
\]

where \( k_B \) is Boltzmann’s constant, \( T \) is the temperature, \( l \) is a dimensionless number, the product \( k_B T \cdot l \) is the characteristic trap energy, and \( N_t \) is the total density of trap states. In our calculations we used values of \( l = 5 \) and \( N_t = 2.5 \times 10^{18} \text{ cm}^{-3} \). The trapping time was set to 10 ms, while the detrapping was calculated according to the principles of detailed balance, which states:

\[
\frac{w_{12}}{w_{21}} = \exp \left( \frac{E_1 - E_2}{k_B T} \right),
\]

(6.3)

where \( w_{12} \) and \( w_{21} \) are the transition rates between the corresponding single particle energy levels \( E_1 \) and \( E_2 \). This results in trap filling according to Fermi-Dirac statistics. To insure the numerical stability of the calculation the first three \( k_B T \) intervals closest to the LUMO were ignored in the calculation. We verified that excluding these intervals leaves the final results unaffected. It should also be mentioned that the absolute value of the trapping time is irrelevant since we are analyzing the steady-state situation.

### 6.5 Results: numerical model

We modeled the device using an ohmic contact for the cathode, modeled by Boltzmann injection with a barrier height of 0.1 eV, and an injection limited anode, modeled by thermionic emission [17] with a barrier height of 0.8 eV. Fig. 6.3a shows the numerically calculated \( J(V) \). Here we observe, like in the analytical model, that at low voltages the \( J(V) \) follows a unipolar power law behavior (black line Fig. 6.3a, calculated with ohmic cathode and a blocking anode) with the power \( n \sim 4.5 \) (due to trapping [18]). We observe a deviation from the power law behavior once minority charge carrier injection begins, like observed experimentally [10, 13]. At high voltage the \( J(V) \) behavior saturates to bipolar behavior (blue line Fig. 6.3a, calculated with two ohmic contacts).

When there is a magnetomobility in the minority channel, the onset of MC occurs at the onset of minority charge injection and the normalized MC is negative at this onset (red line Fig. 6.3b). As the voltage increases there is a local minimum in the normalized MC. After this minimum the normalized MC then increases and eventually changes sign. This is the same qualitative normalized MC(\( V \)) behavior as in the analytical model. If we have magnetomobilities in both the minority and majority channels, which is possible in the bipolaron model for OMAR [7, 8], we see that the model would predict two sign changes (blue and green lines Fig. 6.3b). In single carrier devices it has been observed that OMAR has a stronger effect on the minority channel [11, 19], so the case where \( \frac{|\Delta \mu_{\text{maj}}/\mu_{\text{maj}}|}{|\Delta \mu_{\text{min}}/\mu_{\text{min}}|} \) (green line) would be more realistic.

One major difference between the numerical and analytical models is that the negative normalized MC from magnetomobilities in the minority channel is much larger in the numerical model. This is due to the presence of majority traps. As seen in Fig. 6.4, by removing the traps from the majority channel, the negative normalized becomes much smaller. The negative normalized MC results from changing the Coulomb repulsion in the majority channel by indirectly changing the minority carrier density via changing the minority charge carrier
mobility. Therefore, it seems reasonable that increasing the Coulomb repulsion by adding traps to the majority channel increases the strength of the negative normalized MC. If we look at how changing the $\frac{\mu_{\text{maj}}}{\mu_{\text{min}}}$ ratio affects the MC, it seems that the enhancement of the negative normalized MC due to trapping dominates the effect of the $\frac{\mu_{\text{maj}}}{\mu_{\text{min}}}$ ratio (Fig. 6.4 solid symbols). However, in the case without traps increasing the $\frac{\mu_{\text{maj}}}{\mu_{\text{min}}}$ ratio makes the normalized MC more negative (Fig. 6.4 open symbols), like in the analytical model.

**Figure 6.3:** (color online) (a) The numerically determined $J(V)$ of a device with traps in the majority channel and $\frac{\mu_{\text{maj}}}{\mu_{\text{min}}} = 2$, represented by “Model” (red). The upper and lower limit of the current is given by the “bipolar limit” (blue) and “unipolar limit” (black) line respectively. (b) The normalized MC vs. voltage in the case of magnetomobility in the majority (black) and minority (red) channels respectively. As well as for both channels combined, with $\frac{\Delta \mu_{\text{maj}}}{\mu_{\text{maj}}} = \frac{\Delta \mu_{\text{min}}}{\mu_{\text{min}}}$ (blue) and $5 \frac{\Delta \mu_{\text{maj}}}{\mu_{\text{maj}}} = \frac{\Delta \mu_{\text{min}}}{\mu_{\text{min}}}$ (green), normalized to $\frac{\Delta \mu_{\text{min}}}{\mu_{\text{min}}}$.
6.6 Discussion

The fact that the change in current reacts oppositely to a magnetomobility in the minority channel may be important in resolving apparent inconsistencies between experiments and the bipolaron model. The bipolaron model predicts both a positive magnetomobility ($\frac{d\mu}{d|H|} > 0$) and negative magnetomobility ($\frac{d\mu}{d|H|} < 0$) \cite{7, 8}. According to this model the maximum magnitude of the negative magnetomobility is larger than that of the positive magnetomobility. However, the largest MCs that have been observed are positive, which is inconsistent with the bipolaron model unless the current can react oppositely to the change in the mobility. By showing this with our models we can resolve this inconsistency.

More strongly, by using these models all the sign change behavior in literature can be explained when the magnetomobility is negative. Therefore, there is no need to ad-hoc assign different signs of magnetomobilities to different carriers or mechanisms. Two types of sign change behavior have been observed in literature. In one case, the MC changes from negative to positive with increasing voltage, which occurs at the transition between unipolar and bipolar behavior \cite{10, 11, 13}. The resulting lineshape is a superposition of two contributions of opposite sign and different field widths, which may be a result of separate magnetic field effects on electrons and holes \cite{10}. In the other case, the sign change occurs at high voltage and goes from positive MC to negative MC with increasing voltage, with a lineshape that remains unchanged (Fig. 4 in Ref. \cite{9}). This result is consistent with the high voltage sign change for a magnetomobility in the minority channel, which results from the minority contact becoming less injection limited as the voltage increases. To summarize, experimentally it has been observed that the MC is negative when the device is mostly unipolar, becomes positive when the device turns (injection limited) bipolar, and negative again when it is forced toward good bipolar injection.

![Figure 6.4:](image)

Figure 6.4: (color online) Numerically calculated normalized MC vs. voltage due to a magnetomobility in the minority channel for the case with (solid symbols) and without (open symbols) traps in the majority channel for different ratios of $\frac{\mu_{\text{maj}}}{\mu_{\text{min}}}$. The magnitude of the normalized MC for the calculations without trapping has been multiplied by a factor 4 to make these curves more visible.
If in our models negative magnetomobility for both carriers is assumed, the predicted signs of MC for the different transport regimes are exactly the same as experimentally observed.

Of course, observing both sign changes within a single device would provide conclusive experimental evidence that these models are applicable. However, observing the two sign changes in one device may be difficult since, as seen in Fig. 6.3, the numerical modeling shows these sign changes occur at currents that are separated by several orders of magnitude, so either the current density is too small to observe the low voltage sign change or the current density is too large to observe the high voltage sign change, resulting in device failure. However, it is common to observe a peak in the MC(V) \([6, 11, 13, 20]\), like we observe in the models (if one considers a negative magnetomobility) as the device becomes less injection limited. Moreover, we also observed that the second sign change is moved to higher voltages or even completely eliminated for a \(J_{\text{min}}(E_a)\) dependence that does not allow the device to fully saturate to bipolar SCLC at high voltages. This may explain why both sign changes have not been observed in a single device as well.

### 6.7 Conclusion

In conclusion, we have shown phenomenologically, analytically, and numerically, that by assigning a magnetic contrast of the *same* sign to the mobilities of electrons and holes, one can explain both the sign change in the MC as well as its magnitude. This provides strong evidence that the OMAR is an effect on the carrier mobility. The fact that the MC(V) behavior may be so strongly dependent on device physics and not on the microscopic mechanism highlights that the microscopic mechanism of OMAR need not change as a function of voltage. Finally, this device physics is not limited to OMAR in organic semiconductor devices, it should also be applicable to any SCLC device with one ohmic contact and one injection limited contact in which mobilities can be externally influenced.
Bibliography


Chapter 6. Sign inversion of magnetoresistance in space-charge limited devices
Chapter 7

Analytical Device Model

Abstract: In this chapter, we analytically solve the situation for space charge limited current (SCLC) for a device with an ohmic contact majority carrier contact and an injection limited minority carrier contact. We show how a magnetic field effect on the mobility or recombination would effect the current within the context of this model. We also look in depth at how the recombination strength as well as the injection affects both the $J(V)$ as well as the magnetoconductance. This analysis results in the surprising phenomenon in which a decrease in minority carrier mobility may give rise to an increase in the device current. We show that this effect is stronger when the minority charge injection is more inhibited and when the recombination is weak. This macroscopic device model in combination with the microscopic bipolaron model for organic magnetoresistance (OMAR) can explain all sign changes observed in OMAR experiments. However, the physics outlined in this chapter is applicable to any device which shows SCLC with one Ohmic contact and one injection limited contact in which the mobilities of the charge carriers within the device can be externally influenced. 1

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7.1 Introduction

Space charge limited current (SCLC) is a characteristic of devices with undoped low mobility materials, like undoped amorphous organic semiconductors. The phenomenon of SCLC has been thoroughly discussed and modeled in the 1950's in the work of Parmenter and Ruppel [1]. Until recently [2], SCLC has never been described at the transition between unipolar and bipolar behavior in a device with one ohmic and one injection limited contact. This transition is of particular interest since it has been reported that the sign of the of the organic magnetoresistance (OMAR) effect shows a sign change at this transition [3–6].

The OMAR effect causes a relative change in the conductivity due to a magnetic field, which is referred to as the magnetoconductance (MC), in organic semiconductor devices. OMAR has several interesting properties: it can be large (up to 30\%[7]) at room temperature, it does not require the use of any magnetic materials, and interestingly the sign of the effect can change as a function of the bias voltage [3–6, 8]. The OMAR effect has been the subject of much scientific inquiry since no known MR effect has been able to describe the properties of OMAR [9]. However, the recent consensus within the field is that the microscopic mechanism responsible for OMAR is due to spin-mixing induced by randomly oriented hyperfine fields in the material [10–13]. The MC is caused by the applied external magnetic suppressing the effect of the randomly oriented hyperfine fields, thus causing the spin mixing to decrease. It is believed that the spin mixing can affect the current by changing either the mobility of the carriers or their rate of recombination. However, to understand how a microscopic effect, which can affect the mobility or recombination, changes the current it is necessary to understand the relevant device physics governing the macroscopic properties of the device.

The sign change in OMAR as a function of applied bias is of particular research interest, since understanding this peculiar property may provide essential keys to extract the exact nature of the OMAR effect. Several groups have studied the sign change and have given different explanations in order to account for it. Some groups have suggested the microscopic mechanism itself changes as a function of voltage, [5, 6, 14] while others have proposed that a change in conduction mechanism results in the sign change [8]. Like in our previous work [2], we will show that it is possible for the sign change to be a result of device physics, therefore no change in conduction mechanism is necessary. However we extend our previous work by showing this result is completely analytically treatable in the framework of SCLC. This analytical treatment makes it easier to take a comprehensive look at how the recombination strength, and charge injection affect the sign inversion.

In this chapter, we specifically look at the transition from unipolar SCLC to bipolar SCLC. We model the situation of a space charge limited (SCL) device with one ohmic contact and one current limited contact as a function of the applied bias. We show how a magnetic field effect on the mobility or recombination would effect the current within the context of this model. This modeling reveals intriguing new device physics which shows that in certain situations a decrease in the mobility can cause an increase in the current. We show that in concert with a microscopic mechanism for OMAR in which an applied magnetic field decreases the mobility (e.g. the bipolaron model [10]) all the experimentally observed sign change behavior can be explained. It is important to note that although our discussion focuses on OMAR in organic semiconductor devices, this model framework can be applied more generally to any device that shows SCLC for which the mobilities of the charge carriers within the device can be externally influenced.
7.2 ‘Normalized MC’

We start our analysis by defining the magnetomobility as the relative change in charge mobility \(\mu_i\), further the magnetorecombination is the relative in the recombination strength, which is expressed in terms of the of the recombination mobility \(\mu_r\). The magnetorecombination and magnetomobility can be expressed by the equation:

\[
\Delta \mu_i / \mu_i \equiv \frac{\mu_i [B] - \mu_i [0]}{\mu_i [0]},
\]

(7.1)

at applied field \(B\) and for a mobility of a certain type, \(i = e, h, r\). Furthermore, we introduce the concept of normalized magnetoconductance \((NMC)\), defined as the ratio of the magnetoconductance of the whole device and the magnetomobility for that mobility-type:

\[
NMC_i \equiv \frac{\Delta I}{I} \frac{\Delta \mu_i}{\mu_i} \approx \left( \frac{\partial I}{\partial \mu_i} \right) / \left( \frac{I}{\mu_i} \right).
\]

(7.2)

The last approximation in terms of partial derivatives is useful when an explicit expression for the total current in terms of \(\mu_e, \mu_h, \mu_r\) is available, such as will turn out to be the case in some limits of SCL devices. Using this notation, it is easily seen that the MC of a SCL device can be written as a sum of the electron, hole, and recombination NMC:

\[
MC = \frac{\Delta I}{I} = \frac{1}{I} \left( \frac{\partial I}{\partial \mu_e} \Delta \mu_e + \frac{\partial I}{\partial \mu_h} \Delta \mu_h + \frac{\partial I}{\partial \mu_r} \Delta \mu_r \right)
= \frac{\Delta \mu_e}{\mu_e} NMC_e + \frac{\Delta \mu_h}{\mu_h} NMC_h + \frac{\Delta \mu_r}{\mu_r} NMC_r,
\]

(7.3)

in the limit of relatively small magnetomobilities or magnetorecombination, \(|\Delta \mu_i / \mu_i| \ll 1\). For strictly single-carrier (unipolar) devices one obtains as a trivial relation for that carrier:

\[
NMC_{e,h} = 1,
\]

(7.4)

this means that an increase/decrease of the electron (hole) mobility by a certain percentage leads to a change of the current by the same percentage. In the present section, we address the case of bipolar devices, in which non-trivial and quite surprising deviations from this trivial behavior occur—even leading to sign changes and negative values of NMC in specific cases. Although only very recently such behavior has been addressed for the first time [2], the behavior is thought to be very generic, and intrinsic for bipolar SCL devices.

7.3 Analytical approach

In order to put this effect on a more quantitative footing, we follow the analytical approach as introduced by Parmenter and Ruppel [1], but extend it to derive the behavior in the intermediate regime, right at the onset of minority-carrier injection, not treated explicitly in [1]. Following [1], we make three approximations: (i) the diffusion current is neglected, (ii) thermal equilibrium carrier densities are neglected, and (iii) traps are neglected. As to (iii), it allows for an elegant analytical treatment of the problem capturing the relevant physics, but traps can be included in a numerical device model [2], as briefly discussed at the end of this chapter.
We consider a planar device of thickness \( d \) and dielectric constant \( \epsilon \), ranging from \( x = 0 \) (cathode) to \( x = d \) (anode), with local densities of electrons and holes \( (n \text{ and } p) \), respectively, and with mobilities \( (\mu_e \text{ and } \mu_h) \), respectively) independent of the densities and (local) electrical field \( E \). Based on the foregoing approximations, the task is to find the current density:

\[
J = (n\mu_e + p\mu_h)eE,
\]

subject to Poisson’s law

\[
\frac{dE}{dx} = \frac{e}{\epsilon \epsilon_0} (n - p),
\]

while fulfilling the continuity equation

\[
-\mu_e \frac{d(nE)}{dx} = \mu_h \frac{d(pE)}{dx} = \frac{2enp\mu_r}{\epsilon \epsilon_0}.
\]

For the simple case of a single-carrier device (e.g., \( p = 0 \)) this set of equations leads to the well-known SCL behavior, with the current density proportional to the square of the applied voltage,

\[
J = \frac{9}{8} \epsilon \epsilon_0 \mu_M V^2 d^3.
\]

In order to derive a corresponding relation for a bipolar device, one may introduce a dimensionless parameter \( D^2 \):

\[
D \equiv J_e/J = en\mu_e E/J,
\]

representing at any point \( x \) the fraction of the total current carried by electrons. Integrating Eqs. (7.5) through (7.7) then leads to an expression for the total voltage over the device [1]

\[
V = \int_0^d Edx = \sqrt{\frac{2Jd^3}{\nu_e \nu_h \mu_r \epsilon \epsilon_0} \int_{D_a}^{D_c} \int_{D_a}^{D_c} D^{2\nu_e-1} (1 - D)^{2\nu_h-1} dD\frac{D_c^{\nu_e-1}(1 - D)^{\nu_h-1} dD}{f_{D_a}^{D_c} D^{\nu_e-1}(1 - D)^{\nu_h-1} dD}},
\]

where \( D_a = D(x = 0), D_c = D(x = d) \). Furthermore, for the sake of a compact notation, mobilities relative to the recombination mobility have been defined, \( \nu_e = \mu_e/\mu_r \) and \( \nu_h = \mu_h/\mu_r \). The latter quantities are usually larger than unity, particularly in the case of weak Langevin-type recombination, in which case

\[
\mu_r = L(\mu_e + \mu_h),
\]

with \( L \) a prefactor (\( L \ll 1 \) for weak recombination).

Equation 7.10 is easily rewritten to get an expression for the current density as a function of applied bias

\[
J = \left( \frac{\nu_e \nu_h \mu_r \epsilon \epsilon_0 V^2}{2d^3} \right) \left[ \int_{D_a}^{D_c} D^{\nu_e-1}(1 - D)^{\nu_h-1} dD \right]^3 \left[ \int_{D_a}^{D_c} D^{2\nu_e-1}(1 - D)^{2\nu_h-1} dD \right]^2.
\]

Equation (7.12) provides a compact solution to the problem, once the boundary conditions \( (D_a \text{ and } D_c) \) are unambiguously defined. In Ref. [1] it was conjectured that in order to minimize
the voltage over the device, $D_a$ should be minimized and $D_c$ maximized under the constraint of a maximum (injection-limited) value $J_{sc}$ for the electron current at the cathode, and a similar $J_{sa}$ for the hole current at the anode. In the case of two non-saturated blocking contacts (i.e. Ohmic contacts; $J < J_{sa}$ and $J < J_{sc}$), one obtains $D_a = 0$ and $D_c = 1$. This situation represents a pure hole current at the anode and a pure electron current at the cathode. In that case, and under the approximation $\nu_e \gg 1$ and $\nu_h \gg 1$, Parmenter and Ruppel derived Eq. 7.8

$$\mu_{\text{eff}} = \frac{2}{3} \sqrt{\frac{2\pi}{2\pi} \frac{\mu_e \mu_h}{\mu_r} (\mu_e + \mu_h)}.$$  

(7.13)

Thus one obtains the same functional dependence on $V$ as compared to unipolar SCL devices (Eq. (7.8)), but with a current that is enhanced roughly by the square root of the ratio of the slower carrier mobility to the recombination mobility. For Langevin recombination (Eq. (7.11)), the result simplifies to

$$\mu_{\text{eff}} = \frac{2}{3} \sqrt{\frac{2\pi}{2\pi} \frac{\mu_e \mu_h}{L}}.$$  

(7.14)

The above results allow for an analysis of the resulting magnetoconductance effects in pure bipolar transport for a magnetic field effect on the mobility. In the case of Langevin recombination, using Eqs. (7.8) and (7.14), and adopting the concept of magnetomobilities, leads to

$$\frac{\Delta I}{I} = C \left( \frac{\Delta \mu_e}{\mu_e} + \frac{\Delta \mu_h}{\mu_h} \right),$$  

(7.15)

with $C = 1/2$. Similarly, assuming a constant $\mu_r$ that is not a function of $\mu_e$ and $\mu_h$ (instead of Langevin recombination), one finds the same expression with $C = 1$. Thus, in the present case of two Ohmic contacts only the relative magnetomobilities matter. As a consequence, even in cases where the total current is entirely dominated by one type of carrier, with respect to the magnetoconductance the role of minority and majority carriers is balanced:

$$\text{NMC}_e = \text{NMC}_h = C.$$  

(7.16)

We can similarly analyze how a magnetic field effect on the recombination affects the magnetoconductance in pure bipolar transport. This results in a relationship between the magnetoconductance and the magnetoconductivity given by:

$$\frac{\Delta I}{I} = -\frac{1}{2} \frac{\Delta \mu_r}{\mu_r}.$$  

(7.17)

This relationship does not depend on the type of recombination.

After having discussed the well-known case of two Ohmic contacts, we address the intermediate case with only one Ohmic contact (without loss of generality assumed to be the cathode) and the other contact (the anode) being injection limited. In this case there is one parameter, the (saturated) minority-carrier current at the anode ($J_{sa}$), which is not fully specified yet. Note: in the rest of the chapter holes will be the injection limited minority carrier and the electrons the Ohmically injected majority carrier. It also should be taken into account that $J_{sa}$, and thereby $D_a = 1 - J_{sa}/J$, will in general be a function of the local field at the anode, $E_a = E(d)$. To include this boundary condition quantitatively, one needs to introduce an explicit dependence of the injection current on the local field, $J_{sa}[E_a]$. Neither in Ref. [1],
nor in Ref. [15], such an analysis has been done, whereby the exotic behavior of NMC in the intermediate situation remained unobserved.

Here, we continue by rewriting the integral expression for $E_a$ from Ref. [1] in terms of incomplete Bessel functions,

$$\beta_z[a, b] = \int_0^z t^{a-1} (1 - t)^{b-1} dt, \quad (7.18)$$

$$\beta_z[a, b] = \int_0^z t^{a-1} (1 - t)^{b-1} dt. \quad (7.19)$$

Using the identity $\beta_z[a, b] = \beta_1[a, b] - \beta_{1-z}[b, a]$ leads to

$$E_a = \sqrt{\frac{2Jd}{\nu_e\nu_h\mu_e\epsilon_0}} \frac{D_a^{\nu_e/2}(1 - D_a)^{\nu_h/2}}{\sqrt{\beta_1 - D_a[\nu_h, \nu_e]}}. \quad (7.20)$$

Having compact expressions for $E_a$ [Eq. (7.20)] and $J$ [Eq. (7.12)], the final solution, $J[V]$, is obtained by solving $J$, $J_{sa}$ and $E_a$ from

$$E_a = E_a^{SCLC}[J_{sa}, J], \quad (7.21)$$

$$J = J^{SCLC}[J_{sa}, V], \quad (7.22)$$

$$J_{sa} = J_{sa}^{model}[E_a], \quad (7.23)$$

for any arbitrary value of $V$. The superscript ‘SCLC’ refers to using the functional form in terms of indicated parameters according to the theory of SCL current, while the label ‘model’ refers to a certain model for the functional dependence of the injection current at the anode, which is a function of the electric field at the anode. The function $J_{sa}^{model}(E_a)$ specifies the so-far failing boundary condition that is needed to solve the set of equations.

In order to continue our analytical treatment of the problem, we use the similarity of Eqs. 7.12 and 7.8 and some specific properties of the beta functions to derive

$$\mu_{eff} = \frac{4}{9} \nu_e \nu_h \mu_e \beta_{J_{sa}/J}(\nu_h, \nu_e)^3 \beta_{1-J_{sa}/J}(3\nu_h/2, 3\nu_e/2)^2. \quad (7.24)$$

Next, we introduce a factor $P$:

$$P = \frac{J - J_e}{J} = \frac{\mu_{eff} - \mu_e}{\mu_{eff}}, \quad (7.25)$$

which describes the fraction of the total current that is in excess of the power law expansion of the current in the low bias (unipolar) regime. Figure 7.1(a) shows the dependence of $P$ on $J_{sa}/J$ for different combinations of $\nu_e$ and $\nu_h$. Thereby, we see that in the limit $\nu_e \gg 1$ and $\nu_h \gg 1$, $P$ converges exactly to a simple graph that is linear below a critical value of $J_{sa}$ and constant above. Interestingly, the slope of $P(J_{sa}/J)$ at small $J_{sa}$ can be calculated analytically for arbitrary $\nu_e$ and $\nu_h$ (according to Eq. 7.24), with the result

$$\frac{dP}{d(J_{sa}/J)} = \frac{3\nu_h(\nu_e + \nu_h)}{(1 + \nu_h)(2 + 3\nu_h)}. \quad (7.26)$$
7.3. Analytical approach

Since the value of $P$ for $J_{sa}/J \gg 1$, i.e. within the complete bipolar regime is predicted by Eq. 7.13, we have thus obtained a fully analytical expression for $P$ in the limiting case. As a last step, this expression is used to obtain an analytical expression for the current density $J$ as a function of $J_{sa}$, by inverting Eq. 7.25

$$
\nu_{\text{eff}} = \begin{cases} 
\nu_e \left( 1 - \frac{J_{sa}}{J} \cdot \frac{3 \nu_h (\nu_e + \nu_h)}{(1 + \nu_h)(2 + 3 \nu_h)} \right)^{-1} & \text{if } J_{sa} < J_{sat} \\
\frac{2}{3} \sqrt{2 \pi (\nu_e \nu_h (\nu_e + \nu_h))} & \text{if } J_{sa} > J_{sat} \end{cases}
$$

(7.27)

where $J_{sat}$ is simply defined by the crossing point of the two line segments in Fig. 7.1(b); for small enough $\nu_h/\nu_e$ it is given by $J_{sa} = \nu_h/\nu_e$.

In a similar way we continue our analysis of $E_a$ as described by Eq. 7.20. Without direct proof, from inspection of results [Fig. 7.1(c)], we found this equation to take a particularly simple form in the specific limit of large $\nu_e$ and $\nu_h$:

$$
E_a = \sqrt{\frac{2 J d}{\nu_e \nu_h \mu_e e_0}} \sqrt{1 - \frac{J_{sa}}{J_{sat}}}.
$$

(7.28)

In passing, we note that both Eqs. 7.27 and 7.28 are not only exact in the limit $\nu_e \to \infty \land \nu_h \to \infty$, they also provide an exact solution in the limit of infinitesimally small $J_{sa}$ for arbitrary $\nu_e$ and $\nu_h$. Thereby, the equations provide an exact treatment of the device right after the onset of minority-carrier injection.

After having obtained approximate solutions for $J[J_{sa}]$ and $E_a[J_{sa}]$ in terms of $\nu_e$ and $\nu_h$, we have prepared ourselves to solve Eqs. 7.21 to 7.23. Numerically one can do so for any function $J_{sa}^{\text{model}}[E_a]$, which should have the property that for low fields the injected minority-carrier current is absent or extremely small, while this current becomes significant above a certain threshold field. Since results for different models are qualitatively similar, we concentrate here on three examples:

$$
J_{sa}^{\text{model}}[E_a] = 0 \text{ for } E_a < E_0 \text{ else } J_{sa}^{\text{model}}[E_a] = \infty,
$$

(7.29)

$$
J_{sa}^{\text{model}}[E_a] = 0 \text{ for } E_a < E_0 \text{ else } J_{sa}^{\text{model}}[E_a] = J_0 \left( \frac{E_a - E_0}{SE_0} \right)^2,
$$

(7.30)

$$
J_{sa}^{\text{model}}[E_a] = J_0 \exp \left[ \frac{-(1 + S)}{S} \right] \left( \exp \left[ \frac{E_a}{SE_0} \right] - 1 \right),
$$

(7.31)

where $E_0$ is the threshold field, and $J_0 = \frac{1}{2} e_0 \mu_e E_0^2 / d$ is the single-carrier current right at the threshold field. Furthermore, $S$ is a dimensionless parameter that controls the sharpness of the onset, defined such that $J_{sa}[(1 + S)E_0] = J_0$. Note that Eq. (7.29), describing an ideal on/off switch, is just a limiting case of Eq. (7.30) for $S \to 0$ and needs no separate treatment (Fig. 7.2 black line). Equation (7.30), where $J_{sa}$ has a quadratic dependence on $E_a - E_0$, is of particular interest because it provides the opportunity to fully solve the problem analytically in the limit $\nu_e \gg 1$ and $\nu_h \gg 1$ [16] (Fig. 7.2 solid lines). The third case, Eq. (7.31) where $J_{sa}$ has an exponential dependence on $E_a - E_0$, was introduced in Ref. [2]. This case is not analytically solvable, but is of interest because it results in a smooth onset of the minority-carrier injection which is more in line with experimental results (Fig. 7.2 dashed lines).

The solution corresponding to Eq. (7.30) can be written in a compact form

$$
J = J_0 \left( \frac{V^2}{V_0^2} + \frac{\Delta \mu_\infty \Delta V^2}{\mu_e V_0^2} + \frac{4 \Delta \mu_\infty^2 - 2 \Delta \mu_\infty \sqrt{2 \Delta \mu_\infty^2 + D_0 \Delta \mu_\infty \Delta V^2}}{D_0 \mu_e V^2} \right),
$$

(7.32)
where $V_0 = \frac{2E_0}{3}$ is the onset voltage, (with $\mu_{\text{eff}}$ is the effective mobility for the device),
$\Delta \mu_\infty = \mu_\infty - \mu_e$, $\Delta V^2 = V^2 - V_0^2$ and $D_0 = (d^2 \mu_{\text{eff}}/dV^2)_{V_0}$ is the second derivative of $\mu_{\text{eff}}$

**Figure 7.1:** The exact calculations (red dotted lines) and approximations (black solid lines) for $P(J_{sa})$ (a), $\nu_{\text{eff}}(J_{sa})$ (b), and $E_a(J_{sa})$ (c). The approximations are given by Eq. 7.26 (a), Eq. 7.27 (b), and Eq. 7.28 (c). The respective $[\mu_e, \mu_h]$ for panel (a) is given by $[2000, 1000]$ (1), $[50, 25]$ (2), and $[10, 5]$. While for panel (b) the values are $[3000, 1000]$ (1), $[400, 200]$ (2), and $[70, 50]$ (3). Finally in panel (c) the mobilities are $[4000, 2000]$ (1), $[600, 300]$ (2), $[200, 100]$. 
at $V = V_0$. In order to explore the resulting (organic) magnetoresistance, one can either analytically take the partial derivatives of the total current and use the right-hand side of Eq. 7.2, or use the middle term in Eq. 7.2 and perform calculations of $J$ for two values of $\mu_i$ (differing by a value $\Delta \mu_i$).

### 7.4 Results and discussion

In this section we will first discuss the general results of the device model. In this discussion we will cover how model parameters such as $L$ and $S$, effect the $J[V]$, and how $\Delta \mu_i/\mu_i$ effects NMC$_i$. Next, the results of this modeling will be compared to experimental OMAR results. From these comparisons we can get some insight as to which microscopic models that describe OMAR may be valid.

Some results, assuming Langevin recombination, are sketched in Fig. 7.3. Panel (a) shows the current versus voltage for different values of $S$, and keeping $\mu_e/\mu_h = 10$ and $L = 0.001$ fixed. For these parameters, there is a $\sim 12$-fold increase of the current between the unipolar and pure bipolar regime. Below and well above $V_0$ a $V^2$ behavior is observed. It is seen, however, that for finite values of $S$ the pure bipolar regime ($\mu_\infty = \mu_{\text{eff,bip}}$ according to Eq. (7.13); black dashed line) is never reached, and the current saturates to a $V^2$ behavior described by $\mu_\infty < \mu_{\text{eff}, \text{bip}}$ (colored dotted lines). Such a saturation to a constant $\mu_\infty < \mu_{\text{eff,bip}}$ is characteristic for the quadratic $(E_a - E_0)^2$ behavior in $J_{sa}[E_a]$. This saturation occurs at lower and lower values of $\mu_\infty$ relative to $\mu_{\text{eff,bip}}$ (i.e. $\mu_\infty/\mu_{\text{eff,bip}}$ decreases), while saturation is postponed to larger voltages, as $S$ increases. This saturation behavior leads to a constant value of $J_{sa}/J$ for $V \to \infty$, where both $J_{sa}$ and $J$ converge to a quadratic dependence. Because of this behavior, $S$ will be further denoted as the saturation parameter. For $S \gg 1$ the increase of the current after the minority-

![Figure 7.2](image_url)

**Figure 7.2:** The dependence of minority charge carrier (hole) injection at the anode as a function of local field at the anode, $E_a$. The black line represents a perfect on/off switch (Eq. (7.29) and Eq. (7.30) with S=0). The $E_a/E_0$ vs $J_{sa}/J_0$ dependence is shown for $S = 1$ (blue) and $S = 5$ (red). The injection models represented by Eq. (7.30) and Eq. (7.31) are represented by dashed and solid lines respectively.
carrier injection vanishes completely. Note that only for $S = 0$ (not shown), the situation corresponding to an ideal switch, the complete bipolar regime is reached: $\mu_\infty = \mu_{\text{eff,bip}}$.

Figure 7.3(b) shows, for the same parameters, the development of $NMC_e$ (dashed lines) and $NMC_h$ (solid lines) as a function of $V$. For intermediate values of $S$ (e.g., $S = 0.2$) $NMC_h$ becomes negative right after minority-carrier injection, fully confirming our qualitative predictions about the sign change. For increasing voltage, however, $NMC_h$ passes a minimum, after which it rises to a value close to the limiting value known for the pure bipolar regime, $NMC_h = 0.5$ [Eq. (7.16)]. For a high enough saturation parameter $S$ (i.e., $S = 0.2, 2$; green and blue solid lines respectively), the negative region of $NMC_h$ becomes more pronounced and the

Figure 7.3: Results for the current density $J[V]$ and the normalized magnetoconductance $NMC[V]$ for different saturation parameters $S$, while fixing $\mu_e/\mu_h = 10$ and $L = 10^{-3}$. (a) $J[V]/J_0$ for $S = 0.02$ (red), 0.2 (orange), 0.7 (green) and 2 (blue). The black solid line represents the extrapolation of the single-carrier current, the black dashed line represents the pure bipolar limit, and the colored dotted lines represent the large-bias saturation currents for the corresponding values of $S$. $NMC_e$ [(b) solid lines], $NMC_h$ [(b) dashed lines] and (c) $NMC_r$ [(c) solid lines], using the same color code as in (a).
current reaches its asymptote before the minimum in NMC$_h$ is reached. As a consequence, the upturn to positive values is suppressed, and NMC$_h$ saturates at a negative value for $V \rightarrow \infty$. In the opposite regime of a very low $S$ (i.e. $S = 0.02$, red solid line), we observe a complete quenching of the negative region of NMC$_h$. We note that in that case, the anode should be considered a constant field source rather than a constant current source, whereas we needed the latter in our intuitive explanation of the sign reversal.

We can also examine how a magnetic field effect on the recombination (magnetorecombination) affects the MC. In this section we calculated the magnetorecombination by using a relative change in the Langevin recombination prefactor (i.e. $\frac{\Delta J}{J} = \frac{\Delta \mu_r}{\mu_r}$). Figure 7.3(c) shows how different values of $S$ would influence NMC$_r$. We see that for low values of $S$ [e.g. $S = 0.02$ (red solid line)] that NMC$_r$ quickly saturates to NMC$_r = -1/2$ (the case for pure bipolar SCLC). Making minority charge carrier injection more difficult by increasing the value of $S$ results in NMC$_r$ decreasing. This happens because current is less sensitive to changes in the recombination the more unbalanced the electron and hole populations. Also, since $\frac{\mu_{\infty}}{\mu_{\text{eff,bip}}}$ decreases as $S$ increases this means the populations of electrons and holes are become more unbalanced as $S$ increases. Therefore, the higher the value of $S$ the lower the magnitude of the saturation value for NMC$_r$, as observed in Fig. 7.3(c).

It is possible to examine how $J$ is affected by changing the recombination as well [Fig. 7.4(a)]. This was done by calculating $J$ for different values of $L$ while fixing $\mu_e/\mu_h = 10$ and $S = 0.7$. The model shows that the lower the value of $L$, the larger the enhancement of the current after the onset of minority charge carrier injection, which occurs above $V_0$ (Fig. 7.4(a) solid lines). This is because the lower the value of $L$ the higher the value of $J_{\text{bip}}$ [Fig. 7.4(a) dashed lines] as expected from Eq. (7.8) and Eq. (7.14)]. However, since $J_{\text{bip}}$ is greatly enhanced when $L$ is very low the anode cannot source enough current for $J$ to saturate to $J_{\text{bip}}$. Therefore, $\frac{\mu_{\infty}}{\mu_{\text{eff,bip}}}$ decreases as $L$ decreases. This results in the anode becoming a progressively better constant current source as $L$ decreases.

As a result of the contact becoming a better constant current source, we observe that as $L$ decreases NMC$_h$ decreases as well. In Fig. 7.4(b) we see that for a large value of $L$ no negative NMC$_h$ is observed at all (e.g., $L = 0.1$, blue solid lines), thus the contact is acting more like a constant field source. When reducing $L$ a negative region develops ($L = 10^{-2}$, green solid lines), which is getting more pronounced upon further reduction ($L = 10^{-3}, 10^{-6}$; orange and red solid lines respectively), while the upturn is delayed towards higher voltages and is completely eliminated for low enough values of $L$ (i.e. $L = 10^{-6}$, red solid line).

The fact that the anode cannot source enough current to reach $J_{\text{bip}}$ when $L$ is low also means that the current is more unipolar as $L$ decreases. This explains why NMC$_r$ decreases as $L$ decreases since the more unipolar the current is the less sensitive a device is to a change in recombination, as seen in Fig. 7.4(c).

As an example of a boundary condition that does not allow for a fully analytical treatment, we briefly compare results using the exponential $J_{\text{sa}}^\text{model}[E_a]$ of Eq. (7.31). Fig. 7.5(c),(d) shows results for $S = 0.1$ and $\mu_e/\mu_h = 2$ [2]. Clearly, this model for $J_{\text{sa}}^\text{model}[E_a]$ results in a more gradual onset of minority charge carrier (hole) injection, as expected. A region with negative NMC$_h$ is again obtained around the onset. For comparison, results for the analytically solvable injection model using identical parameters are displayed in Fig. 7.5(a),(b). Although detailed dependencies discussed before depend in a subtle way on the injection function, we find that the specific trend of a negative NMC$_h$ at the onset of hole injection is a general property and is not specific to a special injection function.
Although the foregoing analysis unambiguously demonstrates the occurrence of a negative $NMC_h$ for an ideal, drift-limited SCL device without traps, one may wonder whether this behavior also exists in realistic devices with a finite density of traps, and when carrier diffusion is no longer neglected. In Ref. [2] we did explicit device modeling for such a device including traps. In that work, the drift and diffusion equations were solved numerically using the principles laid out by Malliaras and Scott [17], extending the approach to include trapping in the majority charge-carrier (electron) channel. For more details of this modeling we refer to Ref. [2]. Qualitatively, the numerical modelling shows the same behavior as the analytical model presented here. However, by placing traps in the electron channel the $NMC_h$ is much more strongly negative at the same values of $L$. At $L = 0.01$ the numerical model shows $NMC_h$

\[ \text{Figure 7.4: Results for } J[V] \text{ and } \text{NMC}[V] \text{ for different Langevin factors } L, \text{ while fixing } \mu_e/\mu_h = 10 \text{ and } S = 0.7. \text{ (a) } J[V]/J_0 \text{ for } L = 0.1 \text{ (blue), } 10^{-2} \text{ (green), } 10^{-3} \text{ (orange) and } 10^{-6} \text{ (red). The black solid line represents the extrapolation of the single-carrier current, while the colored dotted lines represent the bipolar current limit for the corresponding values of } L. \text{ NMC}_e \text{ [(b) dashed lines], NMC}_h \text{ [(b) solid lines] and NMC}_r \text{ [(c)solid lines], using the same color code as in (a).} \]
can be as low as $-0.7$, without traps this value is only $-0.09$, identical to the analytical model presented here with $L = 0.01$ (Fig. 7.4(b) orange solid line). Therefore, in realistic devices with traps the sign inversion due to the anode acting like a constant current source is stronger, so this sign inversion effect not only is present in realistic devices, but is actually a more important effect since traps make $NMC_h$ more negative.

Now that we have presented the general properties of the device modeling we can apply the model results explicitly to situations that may describe the OMAR effect. From this analysis we can determine how different microscopic mechanisms would change the current in our devices according to our device model. By so doing we get an idea of the mechanism behind the OMAR effect.

Experimentally, it has been observed that below the onset of minority charge injection, when the device is unipolar, the device shows a negative MC ($-MC$) \cite{3–5}. The MC in the unipolar region cannot be due to recombination effects, therefore it is likely due to a magnetomobility effect. The question in the OMAR community is whether the observed positive MC ($+MC$), above the onset of minority charge carrier injection, is due to a magnetorecombination effect or a magnetomobility effect. To answer this question it is important to understand the prevailing microscopic models which describe OMAR either as a magnetomobility effect or a magnetorecombination effect.

The most developed model which describes OMAR as an effect on the charge carrier mobility is the bipolaron model \cite{10, 11}. This model is based on the magnetic field dependent formation of doubly charged bipolarons. The two charges comprising a bipolaron have a large exchange interaction due to the charges being on the same site in the material, therefore these two charges are necessarily in a singlet configuration. In this model the spin mixing is induced by the spin precession around randomly oriented hyperfine fields in the material. This allows two separate

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7.5.png}
\caption{Results for $J[V]$ and NMC$[V]$ for the quadratic (a,b) and exponential (c,d) injection models, which are given by Eq.(7.30) and Eq.(7.31) respectively, fixing $\mu_e/\mu_h = 2$, $L = 0.0125$ and $S = 0.1$. In (a,c) the red line indicates the modeled $J[V]$ while the black solid line represents the extrapolation of the single-carrier current, and the black dashed line represents the bipolar current limit. In (b,d) NMC$_e$ is represented by red dashed lines while NMC$_h$ is represented by red solid lines.}
\end{figure}
charges that are initially in a triplet configuration to convert to a singlet configuration, thus allowing them to form a bipolaron. If an external magnetic field that is much larger than the hyperfine fields is applied, the spins coherently precess about the external magnetic field, thereby the spin mixing is eliminated, which decreases the rate of bipolaron formation. Since charges flows through these bipolaron sites, hindering the formation of bipolarons blocks the current flow. This causes what is called ‘spin blocking’ resulting in a decrease in the mobility with magnetic field (i.e. negative magnetomobility). It is important to note that if bipolaron formation becomes a highly efficient process, that it is possible to get a positive magnetomobility since the formation of immobile bipolarons grows at the expense of mobile polarons. Thus by preventing the formation of bipolarons, by applying an external magnetic field, polarons can completely transit the device without being immobilized due to bipolaron formation. This is called ‘reduced polaron capture’ and results in a positive magnetomobility.

The fact that in this device model a change in current reacts oppositely to a magnetomobility in the minority channel may be important in resolving apparent inconsistencies between experiments and the bipolaron model. The bipolaron model predicts both a positive magnetomobility \( \frac{d\mu}{d|H|} > 0 \) from spin blocking and negative magnetomobility \( \frac{d\mu}{d|H|} < 0 \) from reduced polaron capture \([10, 11]\). According to this model the maximum magnitude of the negative magnetomobility due to spin blocking is larger than that of the positive magnetomobility due to reduced polaron capture. However, the largest MCs that have been observed are positive \([7]\), which is inconsistent with the bipolaron model unless the current can react oppositely to the

**Figure 7.6:** (color online) (a) The modeled MC\([V]\) dependence for negative magnetomobilities (due to spin blocking) in both the electron and hole channels of the device, with \( \frac{\Delta \mu_h}{\mu_h} = \frac{\Delta \mu_e}{\mu_e} \) (red open circles) and \( \frac{\Delta \mu_h}{\mu_h} = 10 \frac{\Delta \mu_e}{\mu_e} \) (light blue and green solid lines) both normalized to \( \frac{\Delta \mu_h}{\mu_h} \). The values of \( L = 10^{-3} \) (red open squares and light blue solid lines) or \( L = 10^{-6} \) (light green solid line) while the \( S \) was fixed at \( S = 0.7 \). The dashed lines are fits according to Eq. 7.33 to the modeled curves. (b) Experimental MC\([V]\) curve at a measuring field of 83 mT of an ITO/PEDOT:PSS/MDMO-PPV/LiF/Al device.
change in the mobility. By showing this with our model we can resolve this inconsistency.

In Fig. 7.6(a), we see how MC[\(V\)] would look for a magnetomobility in both the electron and hole channels. These graphs can be made by combining the data from NMC\(_e\) and NMC\(_h\) for a given set of parameters according to Eq. 7.3. Here we assume a negative magnetomobility for both carrier types (i.e. spin blocking in the bipolaron model) since this is consistent with the observation of \(-\mu_c\) in unipolar electron-only and hole-only devices [5]. In Fig. 7.6 we show the cases where \(\Delta \mu_h = \Delta \mu_e\) (red open squares) and \(\Delta \mu_h = 10 \Delta \mu_e\) (light blue and light green solid lines), but the case where \(\Delta \mu_h = 10 \Delta \mu_e\) is more realistic since it has been found that in single carrier devices that OMAR is stronger in the minority channel [5]. We can see that by using our analytical device model it is possible to well replicate the experimental results in Fig. 7.6(b), which shows the MC(\(V\)) behavior for a bipolar MDMO-PPV device. At low biases prior to minority charge carrier injection a small \(-\mu_c\) is observed. After minority charge carrier injection begins the MC changes sign and as the voltage increases the MC decreases further and then goes through a local maximum (a very commonly observed feature of OMAR [3, 5, 18, 19]) and decreases further as the voltage increases. The model shows exactly the same MC[\(V\)] behavior in the same transport regimes as observed experimentally [3, 5]. Furthermore, it is shown in Figs. 7.3 and 7.4, that if hole injection at the anode is better or the recombination is higher, the model would predict another sign change from \(+\mu_c\) to \(-\mu_c\) at high voltages. This high voltage sign change may have been experimentally observed previously [9, 20], however this sign change has never been observed with the lower voltage sign change that is coincident with minority charge carrier injection. Therefore, by using this model and assuming that OMAR is a magnetic field effect on the charge mobility all the sign change behavior in literature can be explained by using a negative magnetomobility for both carriers. Therefore, there is no need to ad-hoc assign different signs of magnetomobilities to different carriers or mechanisms.

In chapter 3 we had introduced an empirical relationship in order to determine the MC[\(V\)] behavior based on the \(J[\(V\)]\) behavior [4]. This relationship was given by:

\[
MC[\(V\)] = (1 - P[\(V\)])MC_1 + P[\(V\)]MC_2. \tag{7.33}
\]

where \(P[\(V\)]\) is the fraction of the that current in excess of the unipolar power law dependence (see Eq. 7.25). If we use this relation to fit the traces constructed in Fig. 7.6 we see that it describes the modeled MC[\(V\)] behavior well up until the point where there is a local minimum in the MC due to the contact becoming less injection limited (dashed blue line calculated with \(MC_1 = -0.10\) and \(MC_2 = 0.65\)). If we choose parameters such that the anode always remains a constant current source (solid light green line in Fig. 7.6) a fit using Eq. 7.33 is almost a perfect description of the modeled MC[\(V\)] (dashed green line calculated with \(MC_1 = -0.10\) and \(MC_2 = 0.80\)). Therefore, the empirical relationship determined in our previous work [4] is compatible with this device modeling when the contact is acting like a constant current source.

Spin mixing from randomly oriented hyperfine fields could also cause a magnetic field dependence on the recombination rate [8, 12]. In this model the spin correlations of electron-hole (e-h) pairs cause the magnetorecombination. These e-h pairs are spatially separated such that they are close enough for them to be Coulombically bound yet far enough away such that exchange interactions are negligible. In the case where there is no applied magnetic field, singlet e-h and triplet e-h pairs are degenerate in energy, this allows spin precession around the randomly oriented hyperfine fields to cause spin mixing resulting in singlet-triplet interconversion.
Applying a magnetic field Zeeman splits the triplet states such that the $m = \pm 1$ triplet states are no longer energetically degenerate with the singlet state, therefore the $m = \pm 1$ triplet states can no longer interconvert with the singlet state. This results in more long lived triplet e-h pairs which recombine at a much lower rate than the singlet e-h pairs, therefore these triplet e-h pairs have a finite chance of dissociating back into mobile charges. Therefore, the recombination decreases resulting in a negative magnetorecombination. Since recombination eliminates mobile charges a negative magnetorecombination effect always causes an increase in the current in the case of SCLC.

The magnetorecombination effect described above has lead to suggestions that the $+MC$ observed after minority charge carrier injection could be due to the negative magnetorecombination effect [5]. However, we can see by examining Figs. 7.3c. and 7.4c that there is no local maximum in the MC$[V]$, unlike the case when a negative magnetomobility is considered. As we stated earlier this local maximum is common feature of OMAR. Also, a magnetorecombination effect cannot describe the high voltage sign change from $+MC$ to $-MC$ with increasing voltage. This does not rule out that a microscopic mechanism that causes the magnetorecombination has a voltage dependence which could explain these features. However, the voltage dependence of the models that explain OMAR as a magnetic field effect on the recombination have not yet been worked out.

If we look at Fig. 7.4(b) and Fig. 7.4(c) we see that the model predicts that as the recombination strength (given by $L$) increases that MC should increase if OMAR is due to a magnetorecombination effect and decrease if OMAR is due to a magnetomobility effect. We have recently completed experiments that explore how increasing the recombination should affect the MC chapter 10. We increased the recombination strength by doping the active layer with a dye molecule whose energetic levels reside within the HOMO-LUMO gap of the host. With increasing dopant concentration the recombination strength increased while the magnitude of the MC decreased. So these results are also best described if we consider OMAR to be due to a magnetic field effect on the charge mobility.

Therefore, we have shown that within the context of this simple device model the experimentally observed OMAR behavior can be best described by a microscopic mechanism which causes a decrease in the mobility with magnetic field.

### 7.5 Conclusion

In conclusion, we have modeled how a magnetomobility effect and a magnetorecombination effect should affect the current in a device where one contact is Ohmic and the other is injection limited. It was shown that a negative NMC due to a magnetomobility of the minority carriers should be a quite common feature for SCL devices above the onset of minority carrier injection. In realistic devices with traps, this effect may be even stronger than predicted than for the analytically solvable ideal devices. Within the context of this model the experimentally observed OMAR behavior would be best described by a microscopic mechanism which decreases the mobility. Although this chapter focused on OMAR in organic devices the physics outlined in this chapter should be applicable to any device which shows SCLC with one Ohmic contact and one injection limited contact where the mobilities of the charge carriers within the device can be externally influenced.

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Bibliography


Abstract: In this section we make a comprehensive summary of the experiments showing sign changes in as well as the explanations for these sign changes in literature. We make a comparison of our models and experimental results with those of literature. We show that by combining the microscopic bipolaron model with the macroscopic device model all the sign changes that have been observed in literature can be explained.\footnote{published as part of the chapter ‘Magnetoresistance and Spin Transport in Organic Semiconductor Devices’ by M. Wohlgenannt, P.A. Bobbert, B. Koopmans, and F.L. Bloom in Organic Electronics edited by Z.V. Vardeny}
8.1 Introduction

As mentioned in 1.3, it has been observed that one property of OMAR is that the sign of the MC can change depending on device operating conditions such as temperature [1, 2] and voltage [3–6]. The sign of OMAR can also be changed by the structure of the device, such as the active layer thickness [7], or the injecting electrodes [5, 8]. The sign change is puzzling because it is non-trivial to explain why the sign of the MC changes within the currently proposed models for OMAR. Therefore, understanding why the sign of OMAR can change should shed light on the mechanism(s) responsible for OMAR. In this chapter we will discuss the different types of sign changes that have been observed, and how they have been explained within the context of the proposed microscopic mechanisms of OMAR.

8.2 Unipolar-to-Bipolar Sign Change

There have been several observations of OMAR changing sign when a change in the operating conditions of the device causes a transition from (mostly) unipolar to bipolar conduction [3–5] (these experimental observations are discussed in greater detail in 5). The (mostly) unipolar regime always corresponds to the current decreasing with magnetic field (negative MC) and the bipolar regime corresponds to the current increasing with magnetic field (positive MC) (fig. 8.1. It has also been observed that the negative and positive MC(B) have different line widths, $B_0$, and the resulting line shape at the transition from negative to positive MC is a superposition of the negative and positive MC component [4]. Several different explanations for this sign change have been proposed within the context of the microscopic models previously discussed and they fit into three separate categories.

![Figure 8.1: Magnetoconductance vs. Voltage for an ITO/PEDOT:PSS/MEH-PPV/Ca/Al device. Figure adapted from [5]](image)
The first category applies to unipolar models. It has been proposed that OMAR is an effect acting on the charge-carrier mobility. If the magnetic field alters the charge-carrier mobility, it could affect the mobilities of electrons and holes in opposite ways (increasing the mobility of one carrier while decreasing the mobility of the other). This is possible in the bipolaron model for magnetoresistance [9]. Also, Rolfe et al. suggested that electrons and holes could scatter differently from triplet excitons, causing the magnetic field to increase the mobility of holes and decrease the mobility of electrons [10]. What is postulated is that when the device is unipolar, the charge carrier transporting the charge has a small negative magnetomobility, giving a small negative MC, while the other charge carrier has a large positive magnetomobility, which dominates the total OMAR response when the device is bipolar, resulting in a large positive MC [4]. However, in the context of these models, it is not understood why electrons and holes would have different signs of the magnetomobility.

The second category explains the sign change using two microscopic mechanisms: one microscopic mechanism explains the negative MC in the regime of (mostly) unipolar transport, and a separate mechanism explains the positive MC in the regime of bipolar transport. Hu et al. propose that OMAR is a result of a competition between the triplet exciton-charge reaction and the electron-hole recombination [8] (both are described in 1.4). The authors propose that in the mostly unipolar regime the triplet exciton-charge reaction dominates, resulting in a negative MC. In the bipolar regime the electron-hole recombination mechanism dominates, resulting in a positive MC. According to the authors, when the charge transport in the device is mostly unipolar, the triplet exciton-charge reaction dominates, due to the relatively long triplet exciton lifetimes (note that it is necessary for the device to be slightly bipolar in order to have enough triplet excitons to obtain this effect). As the current becomes more bipolar the electron-hole recombination mechanism becomes relatively more important and the MC changes sign. Both the triplet exciton-charge reaction and the electron-hole recombination mechanism rely on the premise that the magnetic field can alter the ratio between singlet and triplet excitons. This is not observed either in charge-induced absorption [11] or fluorescence-phosphorescence measurements [12]. Also, it would be expected that if triplet excitons cause the negative MC, this effect should have a significant temperature-dependence, due to the strong influence of temperature on the triplet exciton lifetime. However, experiments show that the negative MC is only weakly affected by temperature [2].

Wang et al. studied how OMAR in 2-methoxy-5-(2'-ethylhexyloxy) 1,4-phenylene vinylene (MEH-PPV) is effected by blending it with PCBM [5]. It is well known from work on organic solar cells that the resulting blend phase-separates into MEH-PPV-rich and PCBM-rich phases. This results in the holes and electrons being transported separately in the MEH-PPV and PCBM, respectively. The motivation of the authors to make this blend was that the resulting separation of the electrons and holes greatly reduces electron-hole interactions, and bimolecular recombination is therefore greatly suppressed. In their experiments on the unblended MEH-PPV they observed the typical negative MC in the unipolar regime and the positive MC in the bipolar regime [5]. When a blend of 1:1 MEH-PPV:PCBM was made, in order to decrease the effects of charge recombination, the positive MC in the bipolar regime was quenched, while the negative MC in the unipolar regime remained. From this the authors concluded that the negative MC observed in the unipolar regime is caused by the magnetic-field effect on bipolaron formation [9], and that the positive MC observed in the bipolar regime must due to the magnetic-field effect on electron-hole recombination, since this recombination is strongly reduced in the blend. However, adding PCBM to MEH-PPV does not only affect recombination,
it also vastly changes the charge-carrier mobilities. The electron mobility in the blend is many orders of magnitude higher, due to the lower energetic disorder for electrons in the PCBM. In this case the bipolaron model would also predict that the positive MC should decrease because the MC decreases with decreasing disorder in the bipolaron model [9].

(3) The third category explains the sign change by device physics. It is shown in chapter 6 that decreasing the minority carrier mobility can result in an increase in the current. Using this framework the sign change can then be explained if the magnetic field only acts to decrease the mobilities of the charge carriers. Therefore, when the device is unipolar this results in a negative MC, and once the device starts to inject minority carriers and becomes injection-limited bipolar the sign changes to a positive MC, because the current reacts oppositely to the decrease in minority carrier mobility [13]. As a consequence, it is not necessary to assume that the mobilities of electrons and holes have an opposite response to the magnetic field.

### 8.3 High-Voltage Sign Change

Another sign change that has been observed is one that occurs at high voltages, where as a function of increasing voltage the sign changes from positive to negative MC. The line shape of the MC($B$) curves is almost the same for both signs of the magnetoconductance and the magnetitudes of the positive and negative MC are fairly similar [14] (fig. 8.2). Since the line shape of the positive and negative MC is the same, this sign change is likely to be solely due to device physics, and one does not need two different contributions to OMAR to explain the results.

The model by Bergeson et al. can explain this high-voltage sign change within the context of the electron-hole pair model [6] (see 1.4). They argue that the current can react in opposite ways

![Figure 8.2: Magnetoconductance traces for an ITO/polyflourene(60 nm)/Ca device. Figure adapted from [14]](image-url)
to changes in the rate of charge recombination, depending on the operating conditions of the device. In the bipolar SCLC regime (Eq. (7.8)) a decrease of the recombination mobility $\mu_0$ leads to a further interpenetration of charge densities of opposite sign, resulting in a decrease of the space charge and an increase in the current. In this case $J \propto \mu_0^{-1/2}$, see Eq. (7.13)). The authors claim that the charge densities of either sign cannot keep increasing as the recombination decreases, because of several factors, like dielectric relaxation. The authors assume that for very weak recombination the current increases with the recombination mobility as $J \propto \mu_0$. Therefore the electron-hole pair mechanism, in which an increasing magnetic field reduces the recombination rate (i.e. $\mu_0$ decreases), gives a positive MC in the SCLC regime and a negative MC in the regime of very weak recombination. The authors claim that at low voltages the devices show SCLC behavior, yielding a positive MC, whereas they claim that with increasing voltage the charge density becomes too high for SCLC conditions and the device will follow the behavior of very weak recombination, resulting in a negative MC.

The high-voltage sign change can also be explained by a unipolar OMAR mechanism affecting the charge mobility in the devices. It is shown in chapter 6 that if there is a magnetomobility in the minority channel, a sign change from negative to positive MC can be induced by forcing the minority charge injecting contact from injection-limited to Ohmic behavior by increasing the voltage. This happens at relatively high voltages, and only requires a magnetomobility in the minority channel, so only one line width would be observed. Hence, a unipolar OMAR mechanism may also explain this sign change.

### 8.4 Sign Change with Changing Device Thickness

It has also been observed by Desai et al. that the sign of the MC can be changed by changing the thickness of the device [7]. In this experiment they observed in devices with an Alq$_3$ active layer that samples with a large thickness exhibit a positive MC, while if the thickness decreases below a critical thickness, the device exhibits a negative MC (fig. 8.3). They attributed the different signs to different reactions involving triplet excitons, which depend on the device thickness. At large thicknesses the authors claim that triplet exciton-polaron quenching dominates, resulting in a positive MC. They claim that that as the thickness of the Alq$_3$ layer decreases, it is more likely that a triplet exciton can diffuse to the cathode, which would result in the triplet exciton dissociating into a positive and negative polaron, resulting in a negative MC. The authors point to the fact that when 20 nm thick exciton blocking layer of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) is grown on top of the Alq$_3$, only a positive MC is observed. Therefore, by not allowing the triplet exciton to go to the cathode to dissociate, they claim that there can no longer be any triplet exciton dissociation and thus no negative MC.

### 8.5 Discussion

The simplest explanation for the sign change discussed in the previous section is that the minority- and majority-charge transport have different responses to the magnetic field, which may have opposite signs. Since the sign change occurs at the onset of minority charge-carrier injection, one could assume that OMAR in the unipolar regime is dominated by the magnetic-field response of the majority carriers, while in the bipolar regime the response is dominated by the minority carriers. It may seem odd that in the bipolar regime the magnetic-field response
can be dominated by the minority carriers, since due to their low mobility their contribution to the charge transport is negligible. However, we have shown in the case of bipolar SCLC (Eq. (7.8)) in chapter 6 that it is the relative mobility change of each carrier that determines the change in current (Eq. (7.3)). This is due to the oppositely charged carriers compensating the Coulomb repulsion in the device. Therefore, a magnetic-field response of the mobility of the slow minority charges can dominate the response of the MC in the bipolar regime. Also, it has been shown experimentally in unipolar devices that OMAR is significantly stronger in the minority channel than in the majority channel [5, 15], so in the bipolar regime it is likely that the response of the minority channel dominates.

The bipolaron model shows that the line width of OMAR is strongly influenced by (carrier-dependent) material parameters [9], and as such could indeed be different for electrons and holes. This could explain why the positive and negative MC have different line widths. It is well-known that the wave functions of electrons and holes of organic semiconductors are spatially different, which may result in electrons and holes experiencing different hyperfine interactions with the nuclear spin of the hydrogen atoms. In electrically detected magnetic-resonance experiments the broadening of the resonance is attributed to the random hyperfine fields experienced by the charge carriers. It has been observed in Alq3 that the electrons have a significantly broader resonance than the holes [16], indicating that electrons experience a stronger hyperfine fields. Since in all the models proposed for OMAR the line width of the MC(B) scales with the hyperfine field this may explain why we observe a wider MC(B) in the (mostly) unipolar regime as compared to the bipolar regime. This matches well with our experiments on Alq3, which indicate that the magnetic-field response is dominated by electrons in the unipolar regime and by holes in the bipolar regime. However, it should be noted that in the bipolaron model the line width is not only determined by the hyperfine fields, but also by

![Figure 8.3: Magnetoconductance measured at 290 mT vs. Alq3 thickness (d). The structure of the devices is ITO/TPD(50 nm)/Alq3(d)/LiF/Al. This figure has been adapted from [7].](image-url)
other parameters [9, 17].

The fact that the current reacts oppositely to a magnetomobility in the minority channel may be important in resolving apparent inconsistencies between experiments and the bipolaron model. The bipolaron model predicts both a positive magnetomobility ($d\mu/d|B| > 0$) and negative magnetomobility ($d\mu/d|B| < 0$) [9, 17]. According to this model the maximum magnitude of the negative magnetomobility is larger than that of the positive magnetomobility. However, the largest MCs that have been observed are positive, which is inconsistent with the bipolaron model, unless the current can react oppositely to the change in the mobility. That this can be the case has been shown in detail in chapter 6 and this may therefore resolve this inconsistency.

More strongly, by using the device models outlined in chapter 6, the sign-change behavior in literature can be explained with a universal negative magnetomobility for both the minority and majority charge carriers. Therefore, there is no need for an ad-hoc assignment of different signs of magnetomobility to different carriers or mechanisms. Two types of sign-change behavior have been observed in literature. In one case the MC changes from negative to positive with increasing voltage, which occurs at the transition between unipolar and bipolar behavior [3–5]. The resulting line shape is a superposition of two contributions of opposite sign and different field widths, which may be a result of separate magnetic-field effects on electrons and holes [4]. In the other case, the sign change occurs at high voltage and goes from positive MC to negative MC with increasing voltage, with a line shape that remains unchanged (Fig. 4 in Ref. [14]). This result is consistent with the high-voltage sign change for a magnetomobility in the minority channel, which results from the minority contact becoming less injection-limited as the voltage increases [13].

To summarize, it has been experimentally observed that the MC is negative when the device is mostly unipolar, becoming positive when the device turns (injection-limited) bipolar, and negative again when it is forced toward good bipolar injection. We model the case where both carriers have a negative magnetomobility and the relative magnetomobilities of the carriers are given by $5\Delta\mu_{\text{maj}}/\mu_{\text{maj}} = \Delta\mu_{\text{min}}/\mu_{\text{min}}$. This ratio has been chosen since OMAR has been shown to have a much stronger effect on the minority channel [5, 15], i.e. $|\Delta\mu_{\text{maj}}/\mu_{\text{maj}}| < |\Delta\mu_{\text{min}}/\mu_{\text{min}}|$. The results of the model are shown in Fig. 8.4. The model predicts exactly the same signs of MC for the different transport regimes as experimentally observed. In both the model and experiment we observe a negative MC when the device is mostly unipolar, then the MC becomes positive when the device turns (injection-limited) bipolar, and finally the MC turns negative again when the device is forced towards good bipolar injection.

Of course, observing both sign changes within a single device would provide conclusive experimental evidence that these device models are in fact applicable. However, observing the two sign changes in one device may be difficult, since, as seen in Fig. 8.4, the numerical modeling shows that these sign changes occur at currents that are separated by several orders of magnitude, so either the current density is too small to observe the low-voltage sign change or the current density is too large to observe the high-voltage sign change, resulting in device failure. However, it is common to observe a peak in the MC($V$) [3, 5, 18, 19], like we observe in the device models (if one considers a negative magnetomobility) when the device becomes less injection-limited. Moreover, we also observed that the second sign change is moved to higher voltages or even completely eliminated for a $J_{\text{amin}}(E_a)$ dependence that does not allow the device to fully saturate to bipolar SCLC at high voltages (Fig. 7.4). This may also explain why both sign changes have not been observed in a single device.
Concluding at this stage, a clear correlation between the sign change in OMAR and the onset of minority carrier injection was observed. Using the treatments outlined in chapter 6 we showed that by assigning a magnetic contrast of the same sign to the mobilities of electrons and holes, one can explain both the sign change in the MC as well as its magnitude. This provides strong evidence that OMAR is an effect acting on the charge-carrier mobility.

![Figure 8.4:](image)

**Figure 8.4:** (a) Numerically determined $J(V)$ of a device with traps in the majority channel and $\mu_{\text{maj}}/\mu_{\text{min}} = 2$, represented by ‘Model’ (red). The upper and lower limits of the current are given by the ‘bipolar limit’ (blue) and ‘unipolar limit’ (black) line, respectively. (b) Normalized MC vs. voltage in the case of magnetomobility in both the electron and hole channels combined, with $5\Delta\mu_{\text{maj}}/\mu_{\text{maj}} = \Delta\mu_{\text{min}}/\mu_{\text{min}}$. 
Bibliography


Chapter 9

Comparing EDMR and OMAR Sign changes

Abstract: In this chapter we explore the relationship between EDMR and OMAR. We observe that the behavior of electrically detected magnetic resonance (EDMR) and organic magnetoresistance (OMAR) is highly correlated, confirming the notion that OMAR is due to spin-dependent decoherence affecting the current. In bipolar devices we see both a sign change in the EDMR response and OMAR response at the same voltage. In these bipolar devices we observe two distinct resonance features in the EDMR spectra with different g-factors and widths. By comparison to the EDMR in unipolar devices we can assign one resonance feature to holes and the other to electrons. Interestingly, when the device is bipolar we observe that the resonances are of opposite sign. These resonance properties are best described when the EDMR and consequently OMAR is explained by spin-dependent bipolaron formation.\textsuperscript{1}

\textsuperscript{1}to be published as 'Comparing OMAR and EDMR sign changes' by F.L. Bloom, H. Moons, E. Goovaerts, and B. Koopmans.
9.1 Introduction

As discussed in chapter 2.6 EDMR can be a good way of determining spin dependent processes in OLEDs. We have already seen in chapters 3 and 10 that utilizing the results from EDMR experiments in literature can help in the interpretation of our OMAR experiments and open a window on the physical phenomenon responsible for OMAR. We have used these experiments to support our assertion that electrons and holes were responsible for the opposite signs of OMAR in Alq3 (Chapter 3) because EDMR experiments showed that electrons and holes have different resonance widths [1]. These experiments also support our assertion and that the dye molecules trap charges in Alq3 (Chapter 10) since dye doped Alq3 shows a broadening of the EDMR signal when compared to pristine Alq3 [2]. But so far no systematic study has been done comparing OMAR directly to EDMR in the same devices. In this chapter we will describe experiments where we analyze the sign change in MDMO-PPV devices using both EDMR and magnetoresistance measurements.

Sign changes have also been observed previously in EDMR. In the work of Li et al. the authors observe a sign change in ITO/CuPc/TPD/Alq3/AlOx/Al OLEDs, where CuPc is copper phthalocyanine and TPD is N,N'-diphenyl-N,N'-bis(3-methylphenyl)-(1,1'biphenyl)-4,4'-diamine. In this work a narrow current-enhancing resonance is observed at low temperatures and a broader current-quenching resonance at high temperatures is observed (Fig. 9.1). From Fig. 9.1 it is obvious that the spectra cannot be explained by a single resonance feature, and the authors say it can be explained by a combination of a broad quenching resonance and a narrow enhancing resonance. In Chapter 2.6 the hypothesis is that EDMR should be similar to OMAR since both phenomena are due to spin mixing. Only the origins of the spin mixing are different: OMAR coming from spin precession about random hyperfine fields, and EDMR from magnetic resonance. Therefore, the \( B = 0 \) situation in OMAR should be similar to the \( B = B_{\text{res}} \) (\( B_{\text{res}} \) is the field at magnetic resonance) situation in EDMR, since this is where spin mixing in EDMR and OMAR is maximum. Based on this conjecture the \(+MC\) (\(-MC\)) in OMAR would be equivalent to a quenching (enhancing) resonance in EDMR since in both cases the current increases (decreases) the further the applied magnetic field is from the \( B \)-field at which spin mixing is maximized. If we consider this we find similar trends as to what was observed in our OMAR measurements in Alq3 in chapter 4, where we see a \(+MC\) at high temperatures and a \(-MC\) at low temperatures. So the temperature dependent sign change in our OMAR study seems to be highly correlated with the EDMR experiments of Li et al..

Interestingly, it has been argued by both Li et al. [3] and Graeff et al. [1] that bipolarons play a major role in the observed EDMR resonances. However, unlike the bipolaron model of Bobbert et al. [4] the authors of these papers have considered that bipolarons play a bigger role at the interface, while Bobbert et al. are concerned with how bipolaron formation affects hopping in the bulk. The authors of [1, 3] consider the importance of interface bipolarons since it has been shown there is a high density of bipolarons at the interface [5]. In their models the magnetic resonance results in an increase in bipolaron formation, just like the random hyperfine fields in the bipolaron model, because it randomizes the spin allowing two polarons with a parallel configuration to convert to an antiparallel configuration and form a bipolaron. This has been postulated to cause both an enhancing [1] as well as a quenching resonance [3].

Graeff et al. [1] argue that enhancing formation of doubly charged bipolarons at the interface would increase the band bending at that interface and enhance the charge injection from that interface, causing an enhancing resonance. The authors observe enhancing resonances for
unipolar devices. This agrees with this assertion since the only possible spin-dependent process in unipolar devices is bipolaron formation.

However, there are arguments in other literature that bipolaron formation should cause a quenching resonance in bipolar OLEDs [3, 6]. The authors argue that the formation of less mobile bipolarons reduces the population of mobile polarons which results in the current decreasing at magnetic resonance. This argument seems to be more in line with theoretical assertions that bipolarons at the interface should reduce the current [7], but is not in line with the observation by Graeff et al. that unipolar devices have an enhancing resonance.

There are other spin-dependent processes that can affect the current in EDMR just like in OMAR. Many studies show that magnetic resonance increases the polaron recombination rate [8, 9]. This is due to the larger formation cross section of singlet excitons compared to the triplet excitons [10](i.e. $\sigma_s > \sigma_t$). The reaction rate between spin parallel pairs ($R_P$) is proportional to $2\sigma_t$ whereas the reaction between antiparallel spin pairs ($R_{AP}$) is proportional to $\sigma_s + \sigma_t$. This results in $R_{AP} > R_P$. Therefore, when the device is off resonance there is a buildup of parallel polaron pairs in the device. Magnetic resonance makes $R_{AP} = R_P$, as a result more polaron pairs can recombine via the fast recombining singlet exciton channel, which has been shown to increase the electroluminescence of the devices [3].

Interestingly, in operating devices the polaron wave function can be distorted due to the electric fields in the device. This results in the g-factor being anisotropic as well as dependent on the applied bias. This can be observed by comparing EDMR measurements made with the field applied parallel and perpendicular to the electric field. As seen in fig. 9.2 the g-factor increases when the magnetic field is applied parallel to the electric field. Graeff et al. speculate that this observed g-factor anisotropy is due to the processes which cause EDMR occurring at the interfaces where the electric fields are particularly large. This supports their assertion that bipolaron formation occurs at the electrode/organic semiconductor interface.

At present no one has yet done a direct comparison between OMAR and EDMR, which is interesting considering their many potential similarities. In this chapter we use these two

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**Figure 9.1:** X-Band spin-1/2 EDMR spectra of an ITO/CuPc/TPD/Alq$_3$/AlO$_x$/Al OLED. Figure adapted from [3].
complimentary techniques to determine the nature of the spin-dependent process that affect the current. Specifically we look at the sign change behavior in order to gain more knowledge on what specific spin-dependent processes are responsible for each sign of OMAR or EDMR.

### 9.2 Methods

In this chapter we used ITO/PEDOT:PSS/MDMO-PPV/LiF/Al devices which are made on polyethylene terathalate substrates, since they are easier to process. The fabrication of these samples is described in detail in chapter 2.6. The samples were measured both for OMAR and EDMR. To measure EDMR samples were placed in the microwave cavity of an X-band (9 GHz) electron paramagnetic resonance (EPR) setup. The samples were measured at a constant bias as provided by a Keithley 2400 source meter. The change in current was measured by a lockin-amplifier locked in to the microwave chopping frequency. The measurement technique is described in detail in 2.6.

### 9.3 Results and Discussion

First the OMAR response was measured using the modulation method described in 2.4. Results are shown in Fig. 9.3a for several values of bias voltage. Thus we find a $+\text{MC}$ at low bias and a $-\text{MC}$ at high bias, with sign change occurring at $\approx 2.0 \text{ V}$. This is the same behavior that we observed previously where we attributed the sign change to the device going from unipolar to bipolar behavior [11]. Thereby, we confirm that this batch of samples, grown on plastic substrates for the EDMR measurements, behave qualitatively similar to the previous devices on glass substrates.
Next, we performed the EDMR measurements, for the same voltages at which we measured OMAR (Fig. 9.3b.). The EDMR spectra clearly display a single enhancing resonance at the lowest voltages of 1.6 V and 1.8 V. Upon increasing the voltage we see that the EDMR response becomes more complicated. At 2.0 V the overall response is still enhancing, however the line shape is becoming asymmetric. At 2.4 V a strong quenching resonance is present but there appears to be another resonance at a higher-g (lower B-field) that is enhancing. At 2.8 V it becomes very apparent that this is indeed the case as the high-g enhancing resonance becomes much stronger.

In comparing the OMAR response to the EDMR response one notices several interesting correlations. At lower voltages, when there is a $-\Delta C$, one observes a single enhancing resonance in the EDMR signal. In contrast, at higher voltages, when there is a $+\Delta C$, there appears to be two resonances, a high-g enhancing resonance, and a low-g quenching resonance. In the intermediate case where the OMAR is weak one sees that the EDMR signal is also very weak. So by comparing the OMAR and EDMR signals we conclude that their behavior is highly correlated. This confirms the widely accepted assertion that OMAR is due to spin-dependent processes affecting the current.

To further explore the roots of the different EDMR resonances we applied fits to the EDMR curves 9.4. At 1.6 V and 1.8 V, we see that a single enhancing resonance describes the data well. However, at higher voltages we see that a single resonance is no longer sufficient to explain the data. Therefore, we attempted to fit all the data to two separate resonances fixing the g-values and fixing the width while letting the amplitude vary with voltage. The results are shown in fig. 9.4 and are labeled ‘two peak fit’, which fit the experimental data very well. Spectra at low voltages are dominated by a single Lorentzian resonance at $g = 2.00255$ with a full width at half maximum (FWHM) of 0.76 mT. At high voltages another resonance appears. It is a broad enhancing resonance at $g = 2.00318$ and can be fit by a gaussian with a FWHM of 1.73 mT. Interestingly, the narrow Lorentzian resonance at $g = 2.00255$ switches sign and becomes quenching. If we look at the EDMR spectra we see that once the OMAR changes sign at 2.0 V two things happen in the EDMR spectra. There is the appearance of the broad high-g resonance and the narrow low-g resonance changing sign. As the voltage increases further, the
Figure 9.4: The result of fitting the measured EDMR spectra with two separate resonances of where the g-values and FWHM remained are the same for all the voltages

low-g resonance becomes more strongly quenching and the broad high-g resonance becomes more prominent.

This finding is very interesting because we had shown that the sign change in these devices was coincident with the device going from unipolar to bipolar operation [11]. Using EDMR we show that at this sign change the EDMR response goes from a single resonance to two resonances with the resonance that is present during unipolar operation of the device changing sign. We had previously conjectured that this sign change was the result of the magnetic responses of the mobilities of electrons and holes being different. One now may may shed further light on this scenario, because it might resolve the role of electron and hole by their different g-factor.

To further disentangle the contribution of the different carriers we made unipolar electron and hole-only devices-only. The electron-only devices consisted of Al/LiF/MDMO-PPV/LiF/Al. The hole-only devices consisted of ITO/PEDOT:PSS/MDMO-PPV/Pd/Au. Similarly to the bipolar devices above we measured both the OMAR response as well as the EDMR signal as represented in figs. 9.5 and 9.6. In fig. 9.5 we see that these unipolar devices have a much smaller OMAR response than the bipolar devices, and both show a $-MC$ in line with what would be expected from the bipolaron model of OMAR [4]. If we look at the EDMR signal (Fig. 9.6) we see that there are enhancing resonances for both the electron and hole-only sample. This is what has been reported for unipolar devices in EDMR before, and this has also been assigned to spin-dependent formation of bipolarons [1]. If we fit these resonances we see that the electron-only device can be described by a gaussian with $g = 2.00318$ and a FWHM of 1.59 mT while the hole-only resonance can be described by a Lorentzian with $g = 2.00255$ and FWHM = 0.76 mT. It should be noted that the EDMR response and OMAR response of these unipolar devices were not strongly affected by the applied bias.

If we compare the resonances in the unipolar devices with the resonances in the bipolar device (table 9.1) we see that the FWHM and g-factor of the hole-only resonance corresponds well with the FWHM and g-factor of the bipolar low-g narrow resonance, while the FWHM of
Figure 9.5: OMAR response of an (a) Al/LiF/MDMO-PPV/LiF/Al electron-only device at 1 V and an (b) ITO/Pedot:PSS/MDMO-PPV/Pd/Au hole-only device at 0.75 V.

Figure 9.6: EDMR response and corresponding fits to an (a) Al/LiF/MDMO-PPV/LiF/Al electron-only device at 1 V and an (b) ITO/Pedot:PSS/MDMO-PPV/Pd/Au hole only device at 0.75 V.
Chapter 9. EDMR sign change

the electron-only device corresponds well to the FWHM of the broad high-g bipolar resonance. However, the corresponding g-factor does not correspond well. This could be due to different electric fields in the bipolar and unipolar devices as it has been shown that the g-factor can shift depending on the local electric field [1].

Table 9.1: g-values and FWHM-values

<table>
<thead>
<tr>
<th>device</th>
<th>$g_{\text{hole}}$</th>
<th>FWHM$_{\text{hole}}$</th>
<th>$g_{\text{elec}}$</th>
<th>FWHM$_{\text{elec}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>unipolar</td>
<td>2.00268</td>
<td>0.76 mT</td>
<td>2.00268</td>
<td>1.59 mT</td>
</tr>
<tr>
<td>bipolar</td>
<td>2.00255</td>
<td>0.76 mT</td>
<td>2.00318</td>
<td>1.73 mT</td>
</tr>
</tbody>
</table>

Based on this analysis, we assign the narrow low-g resonance to excitation of hole spins while the broad high-g resonance is assigned to the excitation of electron spins. The difference in the g-factors between electrons and holes in the bipolar device is not completely unexpected since the wavefunctions of electrons and holes differ spatially and therefore they experience different spin-orbit coupling [1]. This may result in electrons and holes having different g-factors.

The fact that at high bias the electron and hole resonance are of opposite signs seems to rule out spin-dependent e-h recombination as the source of the EDMR resonance and therefore of OMAR. If spin-dependent e-h recombination resulted in the EDMR signal one would expect that resonating the electron spin or resonating the hole spin would result in the same sign of the EDMR response, since the e-h recombination would be affected in the same way no matter which polaron species is in resonance. It could be that electron and holes scatter differently with triplet excitons as described by Rolfe et al. [12], but like in several other experiments we did not observe any half-field resonances, so it is unlikely that triplet excitons play a role in the EDMR or the OMAR [1–3]. The foregoing analysis would only leave spin-dependent bipolaron formation as the mechanism that dominates the OMAR and EDMR response.

In the latter scenario, at low biases hole conduction dominates resulting in the $-MC$ in OMAR and a single enhancing EDMR signal. At higher biases we see that the broad enhancing resonance starts, which is likely due to the onset of electron injection. This results in the hole resonance changing from enhancing to quenching, and the OMAR changing from $+MC$ to $-MC$.

The key question is why does the hole resonance change sign at the onset of electron injection? From the unipolar devices it seems that spin dependent bipolaron formation only results in a $-MC$ and an enhancing resonance. Thus bipolaron formation likely results in the mobility of the charge carriers decreasing as the magnetic field increases in the case of OMAR, or in the case of EDMR as the applied field gets further off resonance. Previously we had come up with a model where the change in mobility can be opposite to the change in current [13]. This could explain why the hole resonance changes sign. This model is valid when one of the contacts is injection limited, and the other ohmic. We proved using this model that a decrease in the mobility of the injection limited charge carrier could cause the device current to increase. However, we observe that the hole resonance is the first one apparent in the device, so the hole injecting contact (ITO/PEDOT:PSS) has better injection than the electron injecting contact (LiF/Al). Since the resonance of the less injection limited contact changes sign, this model does not explain why the hole resonance changes sign at the onset of electron injection. Therefore, there must be another reason related to the device physics which could result in this sign change.
9.4 Conclusion

In conclusion, we demonstrated that the EDMR response and OMAR response of a device are highly correlated and are likely due to the same spin-dependent processes. We showed that there are two resonances of opposite sign and different g-values. This seems to rule out spin-dependent e-h formation as the source of the EDMR and OMAR. However, although our results can be partly explained by a combination of the bipolaron model and our previous device modeling, the exact physics that results in the sign change of the EDMR response and OMAR response cannot not be determined at this moment. Further investigation is needed to understand the precise phenomena governing this sign change.
Bibliography


Chapter 10
The effect of luminescent dye doping on organic magnetoresistance

Abstract: We report on the effect of doping organic devices with luminescent dye molecules on the organic magnetoresistance effect. The addition of the dye 4-(diacynomethylene)-2-methyl-6-(p-dimethylaninostyryl) (DCM) adds recombination in the tris-(8-hydroxyquinoline) aluminium (Alq₃) host material, causing an increase in the recombination strength. Our experiments show that the presence of the dye decreases the magnitude of the OMAR effect, while it increases the width of the OMAR feature. The reduction of the MC with increasing recombination strength is consistent with an OMAR mechanism where the magnetic field acts to change the charge mobility. Furthermore, the widening of the MC(B) traces is speculated to be due to an increase in energetic and positional disorder upon doping.¹

10.1 Introduction

Organic magnetoresistance (OMAR) is a magnetoresistive (MR) effect that has been found in non-magnetic devices consisting of either semiconducting small molecules or semiconducting polymers [1–3]. OMAR is of technological interest because it combines the low cost and ease of fabrication of organic semiconductor devices with a room temperature magnetoresistive effect, which can be large (> 25%) at reasonable magnetic fields (≈ 80 mT) [4]. The OMAR effect is also highly interesting scientifically, since no previously known MR mechanisms could account for such a large low-field effect at low temperature without magnetic materials.

Recently, there have been several microscopic models introduced to explain the OMAR effect. These models are all based on the principle that spin mixing is induced by spin precession about randomly oriented hydrogen hyperfine fields within the material. This spin mixing can cause polaron pairs to undergo transitions between singlet and triplet spin configurations. The role of the external magnetic field is to overrule the effect from the random hyperfine fields, causing the spins to rotate coherently about the same magnetic field. Therefore, the polaron pairs maintain their initial singlet or triplet character. It has been postulated that this spin mixing can change the singlet-triplet nature of charged polaron pairs with like (unlike) charges, which can affect the formation rate of bipolarons [5] (excitons [6]). This in turn changes the charge mobility (recombination) altering the current in the device. It has also been speculated that this spin mixing could alter the current in the device by increasing the number of triplet-excitons which could increase either triplet-exciton polaron quenching, or triplet-exciton dissociation [7].

Device models have been recently introduced to observe how changing the macroscopic parameters, such as the mobility and charge recombination would effect the current in a space charge limited current (SCLC) device [8, 9]. These models are interesting for investigating the OMAR effect since there is a debate in the field whether the mechanism responsible for OMAR is due to a magnetic field effect on the mobility (magnetomobility), or a magnetic field effect on the charge recombination (magnetorecombination).

In this work we systematically change the charge recombination by doping the organic active layer with different concentrations of a luminescent dye. By using knowledge obtained from the device modeling aim at discriminating between different microscopic scenarios. More specifically aim to determine if the changes in OMAR due to the dye doping can be better explained by a magnetomobility or a magnetorecombination effect. Our experiments show that the presence of the dye decreases the magnitude of the OMAR effect, while it increases the width of the OMAR feature. The decrease in OMAR can be explained by recently developed device models where OMAR is considered to be a magnetomobility effect. The increase in the width of OMAR is speculated to be due to the increase in energetic and positional disorder upon dye doping.

10.2 Experimental

In this doping experiment we used tris-(8-hydroxyquinoline) aluminium (Alq₃) as the host molecule and the red laser dye 4-(diacyanomethylene)-2-methyl-6-(p-dimethylaminostyryl) (DCM) as the dopant. From the inset in figure 10.1b we can see that DCM acts as a midgap dopant with its HOMO (5.6 eV) and LUMO (3.4 eV) lying within the energy gap of Alq₃ (HOMO = 5.8 eV, LUMO = 3.0 eV) [10]. The 3 x 3 mm devices were fabricated on indium
tin oxide (ITO) covered glass substrates. The substrates were solvent cleaned and then treated for 30 min in a UV-ozone photoreactor. Next, 60 nm of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) dispersion (H.C. Starck) was spin coated on the substrate. Following this step the samples were only handled in a dry nitrogen glovebox environment and were never again exposed to the ambient atmosphere. The next step was to evaporate the Alq$_3$:DCM active layer by thermal evaporation in a high vacuum system (base pressure $< 10^{-7}$ mbar). The film doping was accomplished by coevaporating the Alq$_3$ and the DCM from two separate sources, which were monitored independently by separate quartz crystal thickness monitors. The rate of Alq$_3$ evaporation was $\sim 1$ Å/s and the overall film thickness was 100 nm for all the samples. The concentration of dopants was determined by the ratio of the growth rates of Alq$_3$ and DCM resulting in a certain concentration of DCM in volume percent (vol.%). This is a different method of doping than utilized in previous experiments on Alq$_3$:DCM. In those experiments evaporation took place from a single source containing a mixture of the DCM and Alq$_3$ powders [10, 11]. In those cases the concentration was varied by changing the mass ratio of the powders in the mixture, giving a concentration in weight percent (wt.%) of the powder. However, it is likely that the concentration in the powder is not similar to the concentration in the film due to the large difference in evaporation temperatures for Alq$_3$ ($\sim 190$ °C) and DCM ($\sim 140$ °C). Therefore, we consider coevaporation to be a better method in order to achieve a reliable doping concentration. After the evaporation of the active layer, 1 nm of LiF and 100 nm of Al were thermally evaporated in another evaporation chamber (base pressure $< 5 \cdot 10^{-7}$ mbar) to form the cathode. This results in a total device stack of ITO/PEDOT:PSS(60 nm)/Alq$_3$:DCM(100 nm)/LiF(1 nm)/Al(100 nm).

The samples were characterized by electroluminescence (EL) measurements as well as magnetotransport measurements. The EL measurements were performed using an Avantes AVS USB 2000 spectrometer. Magnetoconductance measurements were made between the poles of an electromagnet in the dark at room temperature. To prevent measuring changes in the current not from the magnetic field, such as any time dependent drift of the current, we used a lock-in amplifier to measure the change in current induced by a small 27 Hz AC magnetic field on top of the DC magnetic field, resulting in $\frac{dI}{dB}(B)$, where $I$ is the current and $B$ is the magnetic field. This modulated magnetic field measurement can be used to determine $\text{MC}(B)$. This technique also significantly reduces the noise in the measurements allowing us to more precisely observe subtle changes in OMAR that result from dye doping. The details of this this measurement technique have been described in detail by Wagemans et al. [12].

## 10.3 Results and discussion

In Fig. 10.2 we see how DCM doping affects the EL spectrum. We observe that upon doping with the lowest concentration of DCM (0.8 vol. %) the short wavelength peak $\sim 525$ nm, due to luminescence from the Alq$_3$ molecules, is completely eliminated. This proves that even at the lowest doping concentration all the recombination occurs on the DCM molecules. This is in contrast to previous experiments on Alq$_3$:DCM which do still show some spectral features of Alq$_3$ after DCM doping [11]. It is possible that our samples are more homogenous since they were prepared by coevaporation, eliminating Alq$_3$ rich areas where recombination would still take place on the Alq$_3$ molecular sites. Another feature observed is that the peak emission wavelength ($\lambda_{\text{peak}}$) is red shifted from the expected DCM peak of 579 nm (as determined
from the HOMO-LUMO gap) and red shifts further as the DCM concentration increases (inset Fig. 10.2). This red-shift is related to the polarity of the environment surrounding the DCM molecule. It has been observed before that polar solvents can red-shift the photoluminescence spectrum of DCM solutions [13]. Since DCM has a very large excited state dipole (26.3 D [13]) and Alq_3 has a small ground state dipole moment of (7.1 D [14]) increasing the DCM doping concentration creates a more polar environment, causing the red shift to increase with increasing DCM concentration. This same behavior has been observed in similar doping systems (e.g. Alq_3:DCM2 [15]).

In order to see if the recombination strength was increased we measured the EL current efficiency (EL intensity per unit current) as a function of dopant concentration (Fig. 10.3). Here we initially see a large increase in efficiency as a result of doping, but this begins to decrease as a function of increasing DCM concentration. Without the dye molecules recombination takes place on the host Alq_3 molecules which are surrounded by other Alq_3 molecules, this causes the formation of excimer states which are excited states delocalized on several molecules. These excimer states have a lower binding energy than the exciton state and provide more channels for non-radiative decay, so charge recombination on these sites is more likely to be non-luminscent.

![Figure 10.1](image.png)

**Figure 10.1:** (a) The molecular structure of DCM. (b) The energetic levels of the host (Alq_3) and the dopant (DCM).
At low dye concentrations the DCM molecules are isolated, therefore they do not form excimer states so recombination on these sites causes a higher luminescence efficiency. In these devices

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure10.2.png}
\caption{The EL spectrum for various doping levels of DCM. $\lambda_{DCM}$ is the wavelength given by the HOMO-LUMO gap of isolated DCM molecules. The inset shows the peak wavelength ($\lambda_{\text{peak}}$) vs. DCM concentration determined from the spectrum shown in the graph.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure10.3.png}
\caption{The EL efficiency vs. DCM concentration measured at a current density of 22 A/m$^2$.}
\end{figure}
the luminescent singlet excitons can be generated in the Alq$_3$ and then diffuse to a DCM site (exciton diffusion length $6 \pm 2$ nm in Alq$_3$ [16]). When these excitons arrive at the DCM site they are transferred non-radiatively to a DCM dopant by the Förster resonant energy transfer or the Dexter charge transfer process. Recombination on DCM is much more luminescently efficient due to the dye molecules being spatially isolated from each other in the Alq$_3$ host matrix. After the excitons are transferred to the dye they decay and luminesce immediately since excitons have an extremely short lifetime on DCM [17].

Charges can also directly recombine on the DCM molecules, forming excitons on the DCM itself. This occurs because DCM acts to trap both electrons and holes since the HOMO (LUMO) is higher (lower) than the HOMO (LUMO) of Alq$_3$ [10]. Therefore, charges will get trapped on the DCM molecules and will be immobilized, they will remain on the DCM site until a charge of opposite sign is trapped by the DCM causing exciton formation and charge recombination to take place. If the charges are of opposite spin a singlet exciton is formed on the DCM which immediately undergoes radiatively decay emitting a photon. Due to this charge trapping, less charge can transit the device without recombining and the recombination efficiency increases. Castro et al. showed in a very similar guest-host system Alq$_3$ DCM-TPA, where DCM-TPA is 4-(dicyanomethylene)-2-methyl-6-2-[(4-diphenylamino)-phenyl]ethyl-4H-pyran, that charge trapping on the dye site is the dominate mode of charge recombination [18]. Direct recombination on the dye molecules is the most relevant process for the device physics we discuss later. This is because direct recombination results in an increase in the overall recombination rate reducing the number of mobile charges. The Förster resonant energy transfer process and the Dexter charge transfer processes result in only increasing the luminescent recombination leaving the overall recombination rate unchanged.

These processes explain why initially, upon doping, there is a large increase in the EL efficiency. However, beyond 0.8 vol.% DCM the efficiency begins to drop off again. This occurs because the dye molecules get too close together as the dopant concentration increases. This problem becomes compounded due to the fact that DCM is prone to aggregating because of attractive dipole-dipole interactions. This aggregation causes DCM excimer states, resulting in an increase in non-radiative recombination, this well known phenomenon is called ‘dye self quenching’. However, it is likely that that the overall recombination strength increases with the increase in DCM concentration above 0.8 vol.% due to the larger number of DCM trapping sites, but this recombination becomes more non-radiative due to dye self-quenching. Therefore, the measured EL efficiency decreases.

Now that the effect of the dye on the recombination is now characterized we can look at the magnetotransport properties of the samples. In order to measure how DCM doping affects OMAR we measured the magnetoconductance (MC), which is defined as $MC(B) = \frac{\Delta I(B)/I(0)}{B^2}$ as a function of magnetic field, at several voltages, for many different concentrations of DCM. An example of these measurements is shown in Fig. 10.4. The data (open squares) fits well to the empirically found ‘non-Lorentzian’ (solid lines) given by:

$$MC(B) = MC_\infty \frac{B^2}{(|B| + B_0)^2},$$

where $B_0$ is the half-width at quarter maximum, and $MC_\infty$ is the MC at infinite B-field [19]. The MC($B$) dependence in Eq. 10.1 has been found to result from random hyperfine fields in the material altering the spin dependent formation rates of both biopolars and excitons [20, 21]. We also see that as a result of doping both $MC_\infty$ decreases significantly and $B_0$ becomes larger.
when DCM is added to the system. In the following paragraphs these phenomena will be discussed in greater detail.

In Fig 10.5a we see that the presence of DCM significantly decreases MC$_\infty$. The initial decrease in MC$_\infty$ upon doping is the most dramatic, with the lowest attainable concentration (0.8 vol.%) decreasing MC$_\infty$ by a factor 6 at 8 V, as compared to the undoped sample. Further increasing the concentration of DCM systematically decreases MC$_\infty$ in almost the whole range of measured voltages.

This is more apparent if we plot the dimensionless parameter $\alpha$ vs. concentration, where $\alpha$ is given by:

$$\alpha = \frac{MC_{\infty}(0 \text{ vol%}) - MC_{\infty}(x \text{ vol%})}{MC_{\infty}(0 \text{ vol%})}$$

The larger the value $\alpha$ the more the MC$_\infty$ is lowered by the DCM doping. Figure 10.6 shows that the MC$_\infty$ monotonically decreases as the DCM concentration increases. Also, this effect is stronger at lower biases. This is because in the non DCM doped sample there is a local maximum in the MC at 9 V (fig. 10.5a.). We have seen this local maximum in device models in which the minority charge carrier contact is injection limited and the majority charge carrier contact has Ohmic injection [22]. This model is applicable to the present device since the workfunction of the minority charge injecting (anode) contact, ITO/PEDOT:PSS (5.1 eV), is substantially above the HOMO of Alq$_3$ resulting in an injection limited contact with a nominal injection barrier of 0.7 eV. In contrast the workfunction of the majority charge injecting contact

![Figure 10.4](image)

**Figure 10.4:** The measured (open squares) and fitted (solid lines) MC($B$) dependence at 10 V for a device an Alq$_3$ (black) only device and an Alq$_3$:DCM device with 11 vol% (red) DCM. The dashed line show the values of $B_0$ and MC$_\infty$ as determined by fits to Eq. 10.1
(cathode) LiF/Al (3.1 eV [23]) matches well to the LUMO of Alq₃ giving a nominal injection barrier of only 0.1 eV, therefore, the behavior of this contact has a more ohmic character.

The monotonic increase in $\alpha$ as a function of voltage may be a direct result of the increase in recombination due to dye doping. In another work we modeled how changing the recombination strength in a device with an injection limited minority contact and an ohmic majority carrier contact would effect the MC [8]. In the device model we modeled OMAR as either a magnetic field effect on the mobility (magnetomobility) or as a magnetic field effect on the recombination (magnetorecombination). As a function of increasing recombination strength, the model predicted that the MC should decrease if OMAR was due to a magnetomobility effect, and increase if OMAR was due to a magnetorecombination effect (see fig. 7.4).

The models show that increasing the recombination makes the injection limited anode less injection limited and less like a constant current source [8]. The more the contact acts like a constant current source the stronger the MC if OMAR is a magnetomobility effect. A magnetorecombination effect would give the opposite results since the injection becomes better with increased recombination. Therefore the injection limited contact becomes more ohmic and the the magnetorecombination effect becomes stronger since changes in the recombination have the strongest effect for completely balanced charge injection. Therefore, our results are more consistent with the model if OMAR is considered to be a magnetomobility effect, such as described by the bipolaron model [5]. More specifically the results are most consistent with a decrease in the mobility of the minority charge carriers with increasing $B$(holes in Alq₃).

It should be noted that traps that only trap one type of charge carrier don’t increase the charge carrier recombination. Since these charge carriers remain trapped they increase the space charge in the device, which we have shown increases the magnetoconductance [22].

One feature we observed is that $B₀$ increases substantially with dye doping. Here, the behavior with concentration is different than that of MC∞. Initially upon doping MC∞ (see Fig. 10.5) changes drastically, while $B₀$ changes incrementally as doping increases. So qualitatively it could be argued that these changes are not due to the same effects. We note this because changes in $B₀$ cannot be related to effects due to device physics, since the models show that the relative change in current scales linearly with the relative change in mobility or recombination when these changes are relatively small, which is the case here. Therefore, what is happening to $B₀$ must be due to the presence of the DCM molecules altering the microscopic mechanism that causes the magnetomobility or magnetorecombination responsible for the OMAR effect. This increase in $B₀$ can be explained in two different ways. First, Bobbert et al. proposed that for both bipolarons and e-h pairs an increase in the ‘branching ratio’ can increase the width of the MC($B$) feature [20]. The branching ratio is the ratio of the bipolaron (e-h pair) formation rate and the rate at which charges can hop around another charge and avoid bipolaron (e-h pair) formation. Thus, forcing the formation of bipolarons (e-h pairs) can cause an increase in the branching ratio resulting in an increase in $B₀$. It has been found that the positional and energetic disorder increase with increasing DCM dopant concentration in Alq₃ [24]. This is likely to increase the branching ratio since the more disordered the material is, the less likely charges are going to hop around another charge that lies in its current path. This is verified by the fact that the current becomes more filamentary as the disorder increases [25]. However, the calculation for how the branching ratio dependents on disorder for bipolaron or e-h pair formation has never been done. The second way the widening of the MC($B$) could occur may be due to an increased hyperfine field upon the doping of Alq₃ with DCM. In most models explaining OMAR the hyperfine field is responsible for spin mixing,
therefore increasing the magnitude of the hyperfine field results in an increased width of the MC$(B)$ curve and increasing $B_0$. It has been observed in Alq$_3$:DCM-TPA that doping results in a larger width of the EDMR spectra which is most likely due to higher hyperfine fields the polaron experiences when located on the dye molecule [18]. It is very likely that this could be similar for DCM due to its similarity to DCM:TPA.

Another interesting feature is that $B_0$ decreases as a function of voltage in the doped samples.

![Figure 10.5: The dependence of $MC_\infty$ (a) and $B_0$ (b) on the bias voltage for different concentrations of DCM.](image)

The values of $MC_\infty$ and $B_0$ have been determined by fitting the data according to Eq. 10.1.
This decrease is more pronounced with increasing DCM concentration. It can be speculated that this voltage dependence of $B_0$ could be due to the strongly charge density dependent mobility in dye doped organic semiconductor systems [26]. Higher biases will result in larger charge concentrations, and these charges will fill up the low energy sites from the dye. This will result in a substantially increased mobility since the low lying dopant states are completely filled and no longer act to trap charges. Therefore the DCM plays less and less of a role in the charge conduction as the bias increases. Since it is obvious that the presence of the dye molecules causes an increase in $B_0$, reducing the dye molecules role in the conduction process should reduce their influence on $B_0$, causing $B_0$ to decrease.

10.4 Conclusion

In conclusion, we have found that by increasing the recombination by dye doping the magneto-conductance decreases and the field width, $B_0$, becomes larger. The reduction of the MC with increasing recombination strength is consistent with an OMAR mechanism where the magnetic field acts to change the charge carrier mobility, which we have shown previously by device modeling. The increase in $B_0$ may be due to the increased energetic and positional disorder that occurs upon dye doping.

Figure 10.6: The reduction of MC due to DCM doping, $\alpha$ vs. DCM concentration for different bias voltages. $\alpha$ is determined by Eq. 10.2
Bibliography


Conclusions and Outlook

In conclusion, our work has shown that the mechanism(s) responsible for OMAR must allow for at least two separate components of opposite sign. A $-\text{MC}$ component which dominates during unipolar operation and a $+\text{MC}$ component which dominates during bipolar operation. This results in a sign change from $-\text{MC}$ to $+\text{MC}$ at the onset of bipolar injection in the device (Chapter 3 and 5). Therefore, the mechanism behind OMAR cannot be completely explained by an e-h pair based model since these models are only valid during bipolar operation. Therefore, a model that allows for a unipolar MC, such as the bipolaron model, must be valid.

Our work shows that more experimental evidence seems to be consistent with the bipolaron model. The weak temperature dependence we observe (Chapter 4) as well as the broadening of the MC traces upon dye doping (chapter 10) are consistent with what has been theoretically predicted for the bipolaron model. Also, in EDMR measurements (chapter 9) we see that it is likely that the two separate components of OMAR are from separate contributions affecting the electron current and the other from hole current independently, this would be consistent with bipolaron formation causing separate effects on the hole and the electron mobilities. Thus, the bipolaron model is a likely candidate to explain OMAR.

Using a macroscopic device model we show that a unipolar OMAR mechanism which could effect the charge mobilities of both the electrons and holes (like the bipolaron mechanism) could cause the sign change at the onset of bipolar injection (Chapter 6 and 7). This is a natural result of device physics if a device has an ohmic majority charge carrier contact and an injection limited minority charge carrier contact. This device model was consistent with all the sign change behavior as a function of bias that is observed in literature. The model also predicts that the MC should become less negative with increasing recombination and this was observed experimentally by using a dye to increase the recombination (chapter 10). Our modeling shows that a unipolar MC effect that affects the charge mobility can explain the observed changes in the MC($V$) behavior.

In summary, our research shows that OMAR is due to an effect which affects the charge mobility of both electrons and holes. The changing behavior of the MC as a function of bias is a result of device physics, and not due to the microscopic mechanism changing as a function of bias.

In the future further exploration of OMAR using EDMR would be highly useful. As shown in chapter 9 we show that EDMR and OMAR are intimately linked. With EDMR one cannot only see differences in resonances which show different polaron types involved in spin dependent processes, but by doing a thorough chopping frequency dependence one can determine the different lifetimes of the separate resonances as well. Thereby it may be possible to determine if indeed the minority charge carrier that dominates the bipolar response of OMAR.
Summary

Exploring Organic Magnetoresistance: An investigation of microscopic and device properties

Recently there has been much interest in combining the fields of organic electronics and spintronics. This has been motivated by the fact that low atomic mass of organic materials are predicted to have long spin lifetimes. Also, spintronic devices could benefit from the chemical tunability, ease of fabrication, and mechanical flexibility of organic semiconductors. The nascent field of organic spintronics has already presented many new phenomena which must be explained with novel physics, here we explore one of these phenomena, organic magnetoresistance (OMAR).

OMAR is a room temperature spintronic effect in organic devices without any magnetic materials. OMAR is a large change in resistance (up to 25%) at low magnetic fields (20mT). OMAR represents a scientific puzzle since no traditional magnetoresistance mechanisms can explain the combination of properties listed above. Another one of the remarkable properties of OMAR is that the sign of the MR can change based on operating conditions of the device, like temperature and voltage. In this dissertation we focused in particular on resolving the origin of the sign change since understanding this unique property should be a major step in unraveling the microscopic origin of OMAR.

We have explored the properties of the sign change experimentally with bipolar semiconducting small molecule and polymer devices, in which we observed sign changes as functions of voltage and temperature. These devices showed a strong correlation between the sign change and the onset of minority charge carrier injection and we could describe the lineshape and MR(V) behavior as a superposition of two MR effects of opposite sign. From this work we concluded the separate MR effects were from the mobilities of holes and electrons having different responses to magnetic fields, which is best described by the bipolaron model for OMAR.

To test this conclusion, we employed analytical and numerical device models assigning separate magnetomobilities to holes and electrons. The models show, counter-intuitively, that in the case when the minority charge carrier contact is injection limited, a decrease in minority charge carrier mobility increases the current. This is a result of the minority carrier contact acting like a constant current source, and of the compensation of the majority carrier space charge by the oppositely charged minority carriers. We show that these models describe the observed MR(V) behavior very well, and if one assumes the magnetic field acts to reduce the mobility of electrons and holes, we observe that our models can reproduce all the sign changes observed in literature. The device model also predicts how different device parameters affect the observed MR, to test its predictions we performed experiments in which we increased the charge recombination by dye doping the organic active layer, we also observed how changing the charge injection by altering the organic semiconductor/ metal contacts experimentally compared with
the device model.

The fact that the current can increase when the minority carrier mobility decreases may explain the fact that in experiments the magnitude of the negative MR features has been much larger than the positive MR features, even though, microscopically, the bipolaron model predicts the opposite. Therefore, the presence of both signs of magnetoresistance may be related only to the device physics and not to the microscopic mechanism which causes OMAR.
Publication List

Related to this thesis:

*Comparing OMAR and EDMR sign changes*
*In preparation.*

*The effect of luminescent dye doping on the organic magnetoresistance effect*
F.L. Bloom, J.M. Veerhoek, W. Wagemans, and B. Koopmans
*In preparation.*

*Modeling magnetoresistance behavior in space-charge limited devices with one injection limited contact*
F.L. Bloom, W. Wagemans, M. Kemerink, and B. Koopmans
*In preparation.*

*Spin in organics, a new route to spintronics*
B. Koopmans, W. Wagemans, F. L. Bloom, P. A. Bobbert, M. Kemerink, and M. Wohlgenannt
*Submitted.*

*Separating the photocurrent and injected-current contributions to the organic magnetoresistance*
W. Wagemans, W.J. Engelen, F. L. Bloom, B. Koopmans

*Magnetoresistance and Spin Transport in Organic Semiconductor Devices*
M. Wohlgenannt, P.A. Bobbert, B. Koopmans, and F. L. Bloom
Chapter in Organic Spintronics ed. Z.V. Vardeney

*Sign inversion of magnetoresistance in injection limited organic devices*
F.L. Bloom, W. Wagemans, M. Kemerink, and B. Koopmans

*Correspondence of the sign change in organic magnetoresistance with the onset of bipolar charge transport*
F.L. Bloom, W. Wagemans, M. Kemerink, and B. Koopmans
Temperature dependent sign change of the organic magnetoresistance effect
F.L. Bloom, W. Wagemans, and B. Koopmans

A two site bipolaron model for organic magnetoresistance
W. Wagemans, F.L. Bloom, and B. Koopmans

Separating positive and negative magnetoresistance in organic semiconductor devices
F.L. Bloom, W. Wagemans, and B. Koopmans

Other publications:

Extremely large magnetoresistance in boron-doped silicon

Impact on interface crystallization on inelastic tunneling in Al/AlOx/CoFeB

Optical anisotropy of cyclopentene terminated GaAs(001) surfaces
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Molecular enhancement of ferromagnetism in GaAs/GaMnAs heterostructures

Tunneling through MnAs particles at a GaAs p(+)n(+) junction
F.L. Bloom, A.C. Young, R.C. Myers, E.R. Brown, A.C. Gossard, and E.G. Gwinn

Molecular Crystals and Liquid Crystals

Effect of dispersing aid on electrical and mechanical behavior of carbon black filled latex
Curriculum Vitae

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