MAGNETIC FIELD DEPENDENT CHARGE TRANSPORT STUDIES IN ORGANIC SEMICONDUCTING MATERIALS

DISSERTATION

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By
Jesse Martin, B.S.
Graduate Program in Physics

The Ohio State University
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Dissertation Committee:
Professor Arthur J. Epstein, Advisor
Professor Jay A. Gupta
Professor Michael A. Lisa
Professor David G. Stroud
Organic magnetoresistance is a phenomenon that is exhibited by many organic semiconductors. The resistance can change by more than 10% at room temperature and as little as 10 milli-Tesla (mT) applied magnetic field. The change can be either positive or negative, and is angle invariant with respect to magnetic field orientation. Several theories have been presented to account for this anomalous magnetoresistance, but thus far the magnetoresistance by interconversion of singlets and triplets (MIST) model has been the most successful in explaining the behavior. Despite all the research that has gone into this effect, very few reports have gone to fields above 1 Tesla (T). In this manuscript, several specific predictions made by the MIST mechanism will be tested including qualitative behaviors and a quantitative fitting. Studies have been performed up to 35 T to explore the high field behavior. It will be demonstrated that for the low field regime, the MIST model is in excellent agreement with experiment, but that the high field regime is caused by a separate mechanism, not described by any current theory.
To my wife, my helpmate and my support, Betsy.
First, I want to thank my advisor Dr. Epstein for the opportunity to study in his lab and for his continued support. The experiences I have gained here will last me a lifetime, and the education I have received has been invaluable. I wouldn’t be the man I am today had you not taken me into your research group.

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VITA

February 19, 1981 ......................... Born—Toledo, OH

June, 2004 ............................... B.S., The Ohio State University,
                                Columbus, Ohio

September, 2004 to December 2006 .......... GTA, The Ohio State University,
                                Columbus, Ohio

January, 2007 to present ................. GRA, The Ohio State University,
                                Columbus, Ohio

Publications


Fields of Study

Major Field: Physics

Studies in bulk magnetoresistance of organic semiconductors: Arthur J. Epstein
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Chapter 1
INTRODUCTION

Organic semiconductors (OSC’s) are among the most versatile materials available for study [1][2]. By standard chemistry techniques, many of their basic properties can be tuned. It is this ability to be customized combined with the option of solution processing and reel to reel printing that has led the industry to begin adopting OSC’s in many of its products, most notably in displays and solar cells. It is for these same reasons that many researchers have also turned to OSC’s for study. It is vital to understand the underlying physics that governs their properties to use these materials to their highest potential.

One area that seems particularly suited to the use of OSC’s is that of spintronics [3][4][5][6]. OSC’s exhibit long spin lifetimes due to the low weight elements from which they are composed. These low atomic weight elements have low spin orbit coupling, and spin orbit coupling is one of the main causes of spin relaxation. The primary means of reading and writing spins in spintronic devices is by through applied magnetic fields. It now becomes important to know how these applied fields impact the properties of OSC’s.

Many materials respond to an applied magnetic field with a change in conductance. There is a variety of mechanisms that can induce such a change, but the majority of them are small effects and can only be observed at low temperatures and large magnetic fields. Many OSC’s also exhibit various magneto-effects such as magnetic field dependent photocurrent [7][8], photoluminescence, and electroluminescence [9][10][11]. The one effect that has received the most attention though is organic magnetoresistance (OMAR) [12][13][14][15][16], but it differs from the inorganic semiconductors in that the effect can be a change of many...
percent at room temperature and small applied fields. There has been a number of theories presented to attempt to explain this phenomenon, but only the magnetoresistance by interconversion of singlets and triplets (MIST) theory has consistently been supported by the data. It is the purpose of this manuscript to explore specific facets of the MIST mechanism. In addition, most reports have focused on applied magnetic fields of less than 1 Tesla. In this dissertation data up to 35 Tesla shall be presented and analysed according to the dominant theories.

In the following chapter, background information necessary to understanding the data and the discussions that follow will be presented. The physics of light emitting diodes (LED), conduction in OSC’s, recombination, and recombination limited currents will be presented, as will spin statistics and the various models of organic magnetoresistance. It shall conclude with a discussion of the MIST mechanism.

Chapter 3 will cover the experimental methodology and procedures in detail, and how the data was handled for analysis and presentation. Certain characteristics of the data such as time dependent drift and a reproducible asymmetry shall also be presented.

Chapter 4 will explore predictions made by the MIST mechanism and how they relate to experimental studies.

Chapter 5 will present data in the high field regime. This data shall be analyzed and discussed in the context of the dominant theories.

Chapter 6 will be the conclusion. Consequences of the results shall be discussed and suggestions for future work that could shed additional light on the situation shall be presented.
Chapter 2
BACKGROUND

2.1 Organic light emitting diodes

Light emitting diodes (LED’s) are devices that produce photons by recombination of electrons and holes. The first LED’s used inorganic semiconductors as the active, luminescing layer, but organic LED’s (OLED’s) replace the inorganic with an organic semiconductor (OSC). All LED’s, whether organic or inorganic, rely upon recombination across an energy gap to produce photons. The magnitude of the energy gap determines the frequency of the emitted light. The frequency can be found by

\[ \Delta E = h \nu \] (2.1)

where \( \Delta E \) is the energy gap, \( h \) is Plank’s constant, and \( \nu \) is the frequency of the photon. OSC’s are a good choice for LED’s as they typically have energy gaps that lie between the ultraviolet to infrared range. Both charge carriers must be present for recombination to occur. Electrons must be injected into the conduction band from the cathode, and holes must be injected into the valence band from the anode. In OSC’s, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are analogous to the valence and conduction bands respectively.

2.1.1 Energy levels in organic semiconductors

Consider a hydrogen like atom. The nucleus forms a potential well for electrons and the electrons occupy discrete energy levels. As atoms come together to form polyatomic molecules,
the potentials and electron wave functions interact to form new energy levels. The deepest energy states are the core levels, and are localized to individual atoms. They tend to experience only small modifications from the bonding between the atoms. The valence states are higher in energy and experience significant modification from their initial state. The valence states allow the valence electrons to delocalize across multiple atoms.

One specific example of great importance in OSC’s is $\pi$-conjugation. The valence states of carbon are the single 2S state and the three 2P states. As carbon atoms draw near to each other, the valence states will hybridize into SP, SP$_2$, or SP$_3$ configurations. These new hybridized states take the shape of lobes (see figure 2.1). If the lobes overlap directly head on, this is known as a $\sigma$ bond. The two degenerate states will split, one shifted lower in energy (the bonding $\sigma$ state), and one shifted higher in energy (the anti-bonding $\sigma^*$ state).

In the case of SP$_2$ orbitals, the 2S state interacts with the 2P$_x$ and the 2P$_y$ states to form three coplanar lobes. One of these lobes will form the $\sigma$-bond between the two carbons. The 2P$_z$ orbital is spatially normal to the plane established by the SP$_2$ orbitals. Both 2P$_z$ orbitals from the two carbons will have an indirect overlap on the periphery of the orbitals above and below the plane of the SP$_2$ orbitals. This interaction leads to two new states, one shifted lower in energy (the bonding $\pi$ state), and one shifted higher in energy (the anti-bonding $\pi^*$ state).

The SP$_2$ hybridized states are very common in the carbon bonds of OSC. Consider the case of the polymer polyacetylene. It is composed of many carbons in the SP$_2$ configuration with hydrogens filling in the incomplete bonds of the carbons. The $\pi$ bonds will form a second bond between alternating adjacent pairs of carbons so that the structure of polyacetylene is alternating single and double bonds (see figure 2.2). This is called $\pi$-conjugation. The bonds can be either double-single-double-single and so on, or single-double-single-double and so on. One is labeled the A-phase, and the other the B-phase. The A- and B-phases are degenerate in energy, and can lead to a delocalization of unpaired charges along the chain. If a carbon atom becomes oxidized or reduced a change in the bonding occurs. The polyacetylene molecule, which previously tended to dimerize, will now have a distortion in it with A-phase on one side and B-phase on the other. The charge
Figure 2.1: Figure demonstrating the “new” orbitals created by SP$_2$ hybridization. Figure courtesy Prof. Grandinetti of OSU.
http://www.grandinetti.org/Teaching/Chem121/Lectures/Hybridization
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may move along the chain and will carry this distortion with it. The charge paired with the distortion is called a polaron. The Shu-Schrieffer-Heeger Hamiltonian\cite{17}, \cite{18} describes the motion of polarons along a $\pi$-conjugated system. If an electron is promoted from the HOMO to the LUMO, the hole and the electron may separate and become itinerant.

2.1.2 Charge transport in organic semiconductors

OSC’s are molecular materials as opposed to atomic materials. They are composed of discrete molecules that are van-der-Waals bonded to one another. The van-der-Waals bonding
leads to poor wave function overlap, and hence electrons are more or less localized to molecular sites. Itinerant charge carriers (electrons in the LUMO and holes in the HOMO) can hop from molecule to molecule via quantum mechanical tunneling. The mobility due to hopping transport is proportional to \( \exp \left( -\frac{E}{k_B T} \right) \) where \( E \) is an activation energy, \( k_B \) is Boltzmann’s constant, and \( T \) is the temperature. Hopping transport leads to low charge carrier mobilities. Additionally, most OSC’s are highly disordered, which leads to the presence of traps and scattering sites. OSC’s also typically have large band gaps \( \gtrsim 1.5 \text{ eV} \). This leads to few intrinsically free charges. The low charge carrier density combined with the low mobility leads to most OSC having high resistivities in the absence of doping.

It is possible to form single crystals with many OSC materials if the proper deposition techniques are observed and some OSC’s naturally form polycrystalline films. This leads to much higher mobilities in the bulk of the OSC. In these crystalline regions it is possible to get good wave function overlap between the molecules, which leads to increased delocalization. The transport in these crystalline regions can become band like, and in this way band transport can be exhibited by OSC’s.
<table>
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<td>α-6T</td>
<td>10⁻¹ (holes)</td>
<td>HOMO = 4.9</td>
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<tr>
<td>Alq₃</td>
<td>10⁻⁵ (electrons)</td>
<td>HOMO = 5.4</td>
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<tr>
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<td>10⁻⁵ (holes)</td>
<td>HOMO = 5.7</td>
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<tr>
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<td>10⁻⁵</td>
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<tr>
<td>RRP3HT</td>
<td>10⁻¹ (holes)</td>
<td>HOMO = 5.1</td>
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<tr>
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<td>10⁻⁵ (electrons)</td>
<td>HOMO = 5.3</td>
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<td>10⁻¹ (holes)</td>
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<tr>
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<td>1 (holes)</td>
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<tr>
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Table 2.1: Mobilities and HOMO/LUMO levels of common OSC’s. Numbers gathered from [19]

2.1.3 Energy alignment

Charge injection is important to the efficient function of an OLED. Maximum light output requires electrons and holes in equal number. Any extra charge carriers constitute wasted current. To first order, energy alignment at the interface is considered to propose good choices for cathode and anode materials. The goal is to align the work function of the electrode material with the appropriate charge transport states in the organic. The work function is the energy required to free an electron located at the Fermi level from the bulk of the metal. If the work function lies near or beneath the HOMO, then the barrier to hole injection will be small or non-existent, and it will be easy to inject mobile holes into the organic; likewise for electrons if the work function lies near or above the LUMO. Thus, a material with a large work function is desirable as the cathode, and a small work function as the anode.

In practice, interfacial energetics are much more complicated. Charge redistribution
can lead to band bending and dipoles at the interface while chemical reactions and defects caused by deposition of materials can create interfacial gap states. A very large body of work has been produced on the topic of organic interfaces with other materials, and it is beyond the scope of this work to describe it all, but there is one highly relevant technique to be touched upon: charge injection/blocking layers.

It is common practice to use a thin film of an intermediary material between the electrodes and the organic active layer\[21\]. The purpose of the film is to smooth the interface and protect the active layer from any of the previously mentioned interfacial effects. It is also the purpose to achieve more efficient charge injection and prevent the escape of non-recombined charge carriers so as to block any “leakage” current. By properly choosing the blocking/injection layers, ohmic or near-ohmic charge injection can be achieved. One common cathode layer is polyethylene dioxythiophene with polystyrene sulfinate PEDOT:PSS, although N,N-Bis(3-methylphenyl)-N,N-diphenylbenzidine (TPD) and copper phthalothiacyene (CuPc) are also common choices. It is less common to place a blocking/injection layer at the anode as typically efficient electron injection is easier to achieve than hole injection.

### 2.1.4 Charge transport regimes

Parmentor and Ruppel have analytically shown the solution to the space charge limited (SCL) regime\[22\]. Their solution

$$J = \left( \frac{3}{4} \right) \left[ \frac{2e\pi\mu_n\mu_p(\mu_n + \mu_p)}{\mu_R} \right]^{1/2} \frac{V^2}{L^3}, \quad (2.2)$$

where $J$ is the current density, $\epsilon$ is the relative dielectric constant of the medium, $\mu_n$ is the electron mobility, $\mu_p$ is the mobility of the holes, $\mu_R$ is the recombination mobility, $V$ is the applied voltage, and $L$ is the thickness of the OSC, shows that the current depends upon the inverse square root of the recombination mobility $\mu_R$. This $\mu_R$ is directly proportional to the bulk recombination coefficient $B$ by

$$\mu_R = \frac{eB}{2\epsilon}, \quad (2.3)$$
Thus, as the recombination decreases, the current density will increase. This is due to a back voltage that builds up in the bulk of the OSC due to a narrow recombination zone. As holes are injected on the anode side, and electrons are injected on the cathode side, they meet somewhere in the device. For high recombination, a narrow recombination zone will develop\cite{23}. A net positive charge will develop on the hole side, and a net negative charge will develop on the electron side. These built up charges lead to a back voltage that inhibits charge movement and charge injection. As $B$ decreases, $\mu_R$ decreases and the recombination zone broadens because the charges are able to travel further before recombining. This lessens the space charge and decreases the back voltage, allowing more current to flow.

In the opposite extreme the recombination zone now extends over the entire device, and there are electrons and holes everywhere leading to a net neutrality within the bulk of the OSC. There are now two contributions to the net current. They are a leakage current of electrons and holes that pass through the device and are removed at the opposing interfaces, and a recombination current of electrons and holes that meet and are removed by recombination. If $B$ increases, the current will increase as the recombination current grows in contribution. The current now takes the form\cite{24}

$$J = eBL[c(V)]^2.$$  

The function $c(V)$ describes the density of charge carriers. Note the linear dependence of $J$ on $B$. This is known as the recombination limited (RL) regime due to the direct linear dependence upon recombination.

### 2.2 Recombination

#### 2.2.1 Excitons and bound pairs

As two oppositely charged particles approach each other, they can become bound by the Coulomb force. The condition for them to become bound is the Coulomb potential must be greater than the thermal energy of the environment. This results in the separation
condition,

\[ r_c = \frac{e^2}{4\pi \epsilon k_B T}, \]  

(2.5)

where \( e \) is the elementary unit of charge, \( \epsilon \) is the dielectric constant of the material, \( k_B \) is Boltzmann’s constant, \( T \) is the temperature, and \( r_c \) is the Onsager radius. Any charge pair that is closer together than \( r_c \) is bound, and any pair with a separation further than \( r_c \) is unbound. These charge pairs have some probability to dissociate and become free charge carriers, and some probability to recombine. The recombination coefficient is given by

\[ B = b \left[ \frac{k}{k + q} \right], \]  

(2.6)

where \( b \) is the formation probability of bound pairs, \( k \) is the rate of recombination, and \( q \) is the rate of dissociation. The terms \( k \) and \( q \) depend upon the spin state of the bound charge pair.

### 2.2.2 Spin states

When two randomly oriented spin particles come into contact, their wave functions become entangled, and they will obtain a joint spin state\(^2\). In the case of spin-\(1/2\) particles, they can either form a singlet or a triplet state.

\[
| \downarrow \rangle + | \uparrow \rangle \implies \begin{cases} \frac{|\uparrow \downarrow\rangle - |\downarrow \uparrow\rangle}{\sqrt{2}} & S^2 = 0, S_z = 0, S_0 \\ |\uparrow \uparrow\rangle & S^2 = 1, S_z = 1, T_+ \\ |\downarrow \downarrow\rangle & S^2 = 1, S_z = -1, T_- \\ \frac{|\uparrow \downarrow\rangle + |\downarrow \uparrow\rangle}{\sqrt{2}} & S^2 = 1, S_z = 0, T_0 \end{cases}
\]

Each specific state has an equal chance to be formed. These states would be degenerate in energy if not for the exchange energy term in the spin Hamiltonian. The exchange energy is a cross term that is related to the probability that the two spins involved will exchange states. Since the strength of the exchange energy is due to the amount of overlap in the wave functions of the two charge carriers, it decays exponentially as the spins are separated.
Table 2.2: Spin State lifetime of some common OSC’s. Numbers gathered from [23].

<table>
<thead>
<tr>
<th>OSC</th>
<th>Singlet Lifetime (sec)</th>
<th>Triplet Lifetime (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracene (crystal)</td>
<td>$10^{-8}$</td>
<td>$10^{-2}$</td>
</tr>
<tr>
<td>Alq$_3$ (film)</td>
<td>$1.5 \times 10^{-8}$</td>
<td>$2.5 \times 10^{-5}$</td>
</tr>
<tr>
<td>Tetracene (crystal)</td>
<td>$2 \times 10^{-10}$</td>
<td>$10^{-5}$</td>
</tr>
<tr>
<td>TPD (film)</td>
<td>$10^{-9}$</td>
<td></td>
</tr>
</tbody>
</table>

from each other, of the form

$$J = J_0 \exp \left( \frac{-2r}{r_0} \right),$$

(2.7)

where $r$ is the separation between the charge carriers, $r_0$ is the minimum separation allowed (the Frenkel radius) and $J_0$ is the strength of the exchange energy at the Frenkel radius. The exchange energy is due to the Coulomb interaction and is expected to be of order 100 meV at the Frenkel radius. Thus, the singlet and triplet states are degenerate for well separated spin pairs, while for close pairs, the exchange energy causes the triplet state to be lower in energy.

Singlets are capable of direct radiative recombination (fluorescence). Triplets are incapable of direct radiative recombination, so they rely on secondary mechanisms to recombine (phosphorescence). The addition of secondary mechanisms takes longer, so the triplet states have longer lifetimes than do the singlets. Specifically, conversions within a spin manifold are called internal conversions, whereas a change of spin multiplicity is termed intersystem crossing. Internal conversion is a fast process, of order of the rate of nuclear vibrations [26].

As the ground state is nearly always a singlet state, the transition from excited singlet to ground singlet is an internal conversion while the triplet decay is an intersystem crossing. With intersystem crossing the triplets exchange spin with their environment, possibly through spin-orbit coupling or the randomly oriented hyperfine field, and convert into singlets. If the singlets are resonant with the triplets, this can be done quite readily and the triplets can convert into the short lived excited singlet.
2.3 Magnetoresistance

The bulk magnetoresistance exhibited by OSC’s is unique. Organic magnetoresistance (OMAR) can be either a positive change or negative one, and can invert between the two cases in a given sample as a function of temperature and applied voltage. OMAR can be of order 10 % at 300 K and 10 mT[27], and has been reported as large as 25 % without any magnetically ordered components in the device. Other characteristics include dependence upon applied electric field, sample thickness (independently from electric field), and temperature. There is no dependence on the orientation of the applied magnetic field. It has been shown that OMAR is only present when there is a bipolar current flowing through the device[28], [29], [30], despite some claims to the contrary. It has also been theorized that OMAR depends upon the randomly oriented internal hyperfine field[31],[32] based upon the size of the applied magnetic fields and angular independence, although there exist some publications that call this assumption into question[33][34]. There are currently four models which have come to the forefront. They are the bipolaron model, the exciton-polaron charge reaction model, the exciton-polaron mobility model, and the magnetoresistance by interconversion of singlets and triplets (MIST) model.

2.3.1 The bipolaron model

One of the earliest models to attempt to explain OMAR was the bipolaron model [35],[36],[37],[38]. This model claims that organic magnetoresistance is the result of spin-blocked hopping. As a charge carrier (polaron) hops from state to state, it may come upon a state that is partially filled. If the two charge carriers have identical spin, then they cannot both occupy the state due to the Pauli exclusion principle; however, if they have different spins, then they may both occupy the state, a bipolaron is formed, and there is no blockage to the movement of either charge carrier.

The charge carriers are expected to move with some hopping frequency, $\omega_{\text{hop}}$. The spins of the charge carrier are expected to precess with some frequency, $\omega_{\text{prec}}$. In the absence of an applied magnetic field, $\omega_{\text{prec}}$ should be the result of the internal, randomly oriented
hyperfine field, $\vec{H}_{hf}$. At each site, $\vec{H}_{hf}$ will be oriented in a different direction and of varying strengths. This induces a spin mixing element allowing random spin orientations to interact and creating the possibility of singlet bipolaron formation. As a magnetic field is applied, the spins precess about the new field orientation $\vec{H}_{total} = \vec{H}_{hf} + \vec{H}_{applied}$. This alters the probability of singlet bipolaron formation as the spins are no longer totally randomly oriented, which leads to increased spin-blocking.

With increased spin-blocking comes a reduction in $\omega_{hop}$ and a corresponding reduction in the charge carrier mobility. This reduction can lead to either positive or negative magneto-resistance depending upon the density of free electrons and holes and the branching ratio, a number that is introduced to describe the probability that a charge carrier will hop to the nearest neighbor partially filled site to form a bipolaron or by pass it to some other site. In a purely monopolar device, the MR will be positive due to the reduced mobility, but become negative with the onset of minority carriers. This is due to a reduction in the space charge as the minority charge density builds up from the reduced mobility. As the minority charge carrier density becomes comparable to the majority charge carrier density, the MR will be positive again due to the reduced mobility.[39]

There are two main problems with the bipolaron model. The first is that it is a monopole model, ignoring interactions between electrons and holes. It has been shown, however, that OMAR is only exhibited in the presence of a bipolar current [28], [29], [30]. OMAR is absent in materials that only support electron or hole conduction. Thus it can be concluded that OMAR is the result of interactions between both charge types.

The second problem is conceptual. The bipolaron model is a one dimensional model that assumes conduction is limited by bottleneck sites that can not be easily bypassed. For disordered small molecule OSC’s, such as tris(8-hydroxyquinoline) aluminum (Alq3), there are likely multiple near neighbor sites that could provide a path through the device. Additionally, for very pure Alq3 samples, typical resistivities are of order $10^{11} \, \Omega \cdot \text{cm}$ for intrinsic charge carriers, and $10^{8}-10^{9} \, \Omega \cdot \text{cm}$ under operational conditions after the onset of charge injection. If a monopole current density is considered, the typical distance between charge carriers can be estimated by finding the volume per charge carrier from the density
of charge carriers by using,

\[ \sigma = n\mu e, \]  

(2.8)

where \( \sigma \) is the conductivity of the material, \( n \) is the charge carrier density, \( e \) is the elementary charge, and \( \mu \) is the mobility of the charge carrier. For electrons in Alq3, the mobility is reported as being of order \( 10^{-5} \text{ cm}^2/\text{Vs} \). This leads to a radius of 10-100 nm. Assuming a typical molecular separation of several Angstroms, and Coulomb repulsion, it seems unlikely that electrons will form single site bipolarons as opposed to the less energetically costly option to remain separated. Even for polymers that constitute quasi-one dimensional materials, inter-chain hopping allows like charges to move around each other without the need for forming single site bipolarons. For these reasons, the bipolaron model will be ignored for the remainder of this paper, and only excitonic models will be considered.

2.3.2 Exciton-polaron charge reaction model

The exciton-polaron charge reaction model attributes OMAR to modification of the populations of singlet and triplet states and the resulting generation of secondary charge carriers\[40\]\[41\]\[42\]. When charge carriers meet in space, they can bind together to form neutral quasi-particles that no longer contribute to the current moving through the device. These quasi-particles can generate secondary charge carriers that increase the charge density in the device, and hence increase the current. The primary mechanisms considered are dissociation of singlets and charge reaction between triplets and free charge carriers. As a magnetic field is applied, the inter-system crossing rate is reduced due to a reduction in the energy gap between triplets and singlets making it less energetically favorable to convert. This tends to increase the number of singlets and decrease the number of triplets, though in some specific materials this is reversed due to the triplet having a higher energy. If the dissociation of singlets dominates the generation of charge carriers because of balanced charge injection, then the MR will be negative because of the increased contribution. If the charge reaction between triplets and polarons dominates the generation of secondary charge carriers, the result will be positive MR as the triplet populations decrease. This
tends to come from imbalanced charge injection with many free charges and some bound pairs. Additional processes are also considered such as exciton quenching, interface enhanced dissociation, triplet-triplet annihilation, and various other higher order processes.

2.3.3 Exciton-polaron mobility model

The exciton-polaron mobility model\[30\],\[43\],\[44\]\[33\] suggests that magneto-effects in OSC’s originate from interactions between free charge carriers and triplet states. If the triplet and the polaron have the same spin orientation, the free charge will be blocked from occupying the same site as the triplet. This leads to an effective scattering despite the triplet having zero netcharge. If the free charge and the triplet have opposite spin orientations, then they may occupy the same site. In this case, they may react, quenching the triplet and leaving just the free charge, or scatter off of each other leaving a triplet and a free charge. Both cases have some interaction time involved, and would represent a decrease in the free carrier mobility.

The magnetic field dependence comes from increased inter system crossing. This theory is founded on the idea that an applied magnetic field always increases the inter system crossing rate between singlets and triplets equally. If the device starts in a configuration with more singlets, then an increased magnetic field would enhance the triplet population, leading to an increase in the resistance. If the system starts in a configuration with more triplets, then the magnetic field leads to more singlets with a reduction in the resistance. Thickness dependence is attributed to diffusion length scales and disassociation at interfaces. Voltage dependence is explained with an increase in disassociation rate. In this way, the exciton-polaron mobility model attempts to explain positive and negative magnetoresistance.

2.3.4 MIST model

The MIST model attributes OMAR to a change in the bulk recombination coefficient as a function of applied magnetic field\[24\]. The magnetic field introduces Zeeman splitting for the spin states of the form

\[
Z = \mu_B g (\vec{S}_n + \vec{S}_p) \cdot \vec{H},
\]

(2.9)
where $\mu_B$ is the Bohr magneton, $g$ is the g-factor for electrons and holes, $\vec{S}$ is the spin of the electron or hole, and $\vec{H}$ is the applied magnetic field. The g-factor for electrons and holes is almost exactly the same in most OSC\textsuperscript{[45][46][47]}. For singlets and the $T_0$ triplet, the magnetic spin moment $S_z$ is equal to zero, and the Zeeman term is zero. For the $T_+$ and $T_-$ triplets, the magnetic spin moment is $\pm 1$ respectively, so the triplets are raised and lowered in energy respectively. This lifts the degeneracy between the $T_\pm$ triplets and the singlet states, hindering the inter system crossing as resonance is lost. This lengthens the average triplet lifetime by removing the primary recombination channel. The bulk recombination coefficient is a sum over the recombination coefficients of each spin state, with each spin state being weighted equally. As long as there is some small amount of spin mixing, the triplets will have lifetimes very similar to that of the singlet as they can change freely. If there is too much spin mixing\textsuperscript{[48]}, then the spin coherence is lost and there is no longer any meaning to the spin states as they are in constant flux. In this case, there will be no magnetoresistance. This is why the effect is only observed in low atomic weight materials, where spin-orbit coupling is negligible. In this way, recombination is always reduced by small applied magnetic fields.

If the device is in the SCL regime, then the MR will be negative. If the device is in the RL regime, the MR will be positive\textsuperscript{[49]}. The transition point is found by equating eqn.(2.2) with eqn.(2.4), the result being,

$$
\mu_c = \left( \frac{9\pi}{32} \right)^{1/3} (\mu_n + \mu_p) \left( 2 + \frac{\mu_n}{\mu_p} + \frac{\mu_p}{\mu_n} \right)^{-1/3} \left( \frac{eV}{ec(V)} \right)^{4/3} L^{-2/3}.
$$

(2.10)

If $\mu_R(H = 0) > \mu_c$, the magnetoresistance will be negative as the device is in the SCL regime, while if $\mu_R(H = 0) < \mu_c$, the magnetoresistance will be positive as the sample is in the RL regime. Changes in the applied voltage, the active layer thickness, and temperature (through the function $c(V)$) raise and lower $\mu_c$. Figure 2.4 provides qualitative sketches of the behavior of $\mu_c$ as a function of these variables.
Figure 2.4: Qualitative sketches of the behavior of $J$ and $\mu_c$ as predicted by the MIST model. Figure a) shows the dependence of the current density $J$ on the recombination mobility $\mu_R$ and the transition point $\mu_c$. Figure b) shows the dependence of $\mu_c$ on active layer thickness while c) and d) show the dependence on temperature and voltage, respectively. In c) is shown the temperature dependence. In d), $V_c$ is the critical voltage at which the behavior of $\mu_c$ changes.
Chapter 3

Experimental Processes

Samples were created in an organic light emitting diode geometry. The substrate is etched indium-tin-oxide (ITO) on glass. Chemical etching of the ITO layer was done by a solution of sulfuric acid. The ITO layer was then cleaned in several ultrasonication steps with detergent, DI water, acetone, and IPA. The final step was a UV ozone cleaning. A detailed description is presented in Table 3.1. These cleaning steps were performed in a class 1000 clean room to prevent defects from fine particulate. The substrates were then transferred to a low moisture glove box, which maintains a nitrogen atmosphere. In this glove box, a PEDOT:PSS layer was spin-coated at 2000 RPM for 30 seconds, and then annealed at 200 °C for 2 minutes. PEDOT:PSS was chosen as the cathode because it has a large workfunction of ~5 eV, the object being to promote hole injection. The substrates were moved through a vacuum airlock to another dry glove box that maintained an argon atmosphere. In this glove box the substrates were mounted in a high vacuum chamber for thermal deposition of the active OSC layer. Depositions were performed in the lower 10^{−6} Torr range and done at a slow rate so as to prevent thermal breakdown of the OSC and deposition of impurities. Accumulated layer thicknesses were monitored by a crystal monitor, and later verified by a Tencor Alpha-Step 500 surface profiler.

Some samples were prepared with gold films as the cathode, replacing the PEDOT:PSS. This was done to ensure that the PEDOT:PSS was not contributing to the MR. For the gold samples, glass substrates were cleaned according to Table 3.1 in the clean room. They were then transferred to a high vacuum chamber for e-beam sputtering of the gold film.
Table 3.1: Ultra sonication cleaning steps for OLED substrates.

<table>
<thead>
<tr>
<th>Step</th>
<th>Solution</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>K₂CO₃</td>
<td>5 min</td>
</tr>
<tr>
<td>2</td>
<td>Detergent</td>
<td>10 min</td>
</tr>
<tr>
<td>3</td>
<td>H₂O₂ NH₃ H₂O</td>
<td>10 min</td>
</tr>
<tr>
<td>4</td>
<td>DI H₂O</td>
<td>10 min</td>
</tr>
<tr>
<td>5</td>
<td>Isopropyl alcohol</td>
<td>5 min</td>
</tr>
<tr>
<td>6</td>
<td>Acetone</td>
<td>5 min</td>
</tr>
<tr>
<td>7</td>
<td>Isopropyl alcohol</td>
<td>rinse</td>
</tr>
<tr>
<td>8</td>
<td>UV Ozone</td>
<td>20 min</td>
</tr>
</tbody>
</table>

The deposition was performed in the upper 10⁻⁷ Torr range. The metal deposition vacuum chamber is in the same glove box as the organic deposition vacuum chamber so that during transfer the substrates were not exposed to ambient atmosphere.

The samples taken to the National High Magnetic Field Lab (NHMFL) in Tallahassee, Florida had CuPc as the cathode. CuPc has been shown to register no MR signal and is an excellent hole transporter. For these samples, the substrates were cleaned according to Table 3.1 and transferred to the organic deposition chamber in the glove box. 10 nm of CuPc were deposited as the cathode, and alpha sexithiophene (α-6T) was then deposited on top without breaking vacuum.

The poly 3-hexylthiophene (P3HT) samples with and without phenyl-C61-buryric acid methyl ester (PCBM) were supplied courtesy of Austin Carter.

All OSC’s were purchased as sublimation grade materials. They underwent a further in house thermal gradient sublimation step, and were reclaimed in a nitrogen atmosphere. At no time were the OSC’s allowed to come into contact with ambient atmosphere, so as to prevent doping from oxygen and moisture.

After the OSC layer, a 10 nm layer of calcium was deposited to act as the anode. Calcium was chosen because it has a relatively small workfunction of 2.87 eV, and because it is highly reactive. This causes the calcium particles to react with the OSC upon contact reducing the chance of penetration into the OSC, and improving electrical contact to the OSC. In addition, the calcium layer was deposited slowly, so as to further reduce the possibility
of penetration. The overall goal was to create as smooth an interface as possible. After the calcium, a capping layer of aluminum was deposited to protect the calcium layer. The aluminum layer was 80–150 nm in thickness.

Samples were stored in a freezer in the glove box, which was kept at \(-40{\degree}C\). All electrical wiring was done in the glove box and samples were transferred to testing apparatus in sealed containers such that they were never exposed to ambient atmosphere.

High magnetic field testing at OSU and temperature studies were conducted in a Quantum Design Physical Properties Measurement System (PPMS). The PPMS has a superconducting magnet capable of inducing an applied magnetic field of up to 9 Tesla (T). It has a temperature range of 2.5–350 K. The sample chamber is sealed and a soft vacuum is drawn (\(\sim 40\) Torr). The chamber is also light tight (no visible light can get to the sample). Two Keithley 2400’s were used to either bias at a constant voltage and measure the current, or bias at a constant current and measure the voltage. Labview was used to collect the data.

Low magnetic field studies were done between the coils of a resistive electromagnet. The tests were conducted in sealed chambers to prevent doping from exposure to ambient atmosphere. Two Keithley 2400’s were used as above.

Data taken at the NHMFL were collected in a resistive solenoid magnet capable of reaching fields up to 35 T. Samples were shipped to the NHMFL in sealed glass containers. They were wired in air under a flow of nitrogen gas as rapidly as possible so as to prevent accidental doping. The OLED geometry helps protect the active area from doping as the active area is capped by aluminum. Further more, the samples were extra thick (\(\sim 400\) nm) to minimize any impact of doping upon the bulk of the thickness. Additionally, research has shown that short term exposure has no impact upon the performance of \(\alpha\)-6T films in the OLED configuration\[50\].

Pure OSC are highly resistive due to HOMO-LUMO gaps in the visible spectrum. IV curves were taken of all samples, and all samples exhibited diode like curves with a linear region passing through zero and a knee at the turn on voltage (see figure 3.1). The linear region can be used to calculate the resistivity of the intrinsic charge carriers, while the region of voltage biasing larger than the turn on voltage is due to injected charge carriers. All
Figure 3.1: Typical current-voltage curve of an OLED used for OMAR studies.
samples had resistivities ranging from $10^{10} - 10^{12}\, \Omega\cdot\text{cm}$. The turn on voltage is a lower bound for which experiments may be performed, as magnetoresistance is not observed at voltages below it unless “light doping” was performed. The samples can not be biased at arbitrarily large voltages as high voltages can lead to current induced burn out, activation of electrochemical processes, and formation of metallic dendrites at interfaces from electro-migration. The voltage “window” is also temperature dependent as the lower bound shifts\[^{51}\]. Thus, there are finite voltage ranges over which data may be taken. The turn on voltage is sensitive to temperature due to thermal field emission, a process by which injection of charge carriers is phonon assisted.

Most samples suffer from time dependent drift in the electrical signal as seen in figure 3.2. Efforts to form a complete characterization of the drift have thus far been eluded. The principle difficulty in characterizing the drift comes from the variability of its nature. The drift can possess positive curvature, negative curvature, be linear, monotonic, non-monotonic, and have “wiggles” and discontinuous jumps. Some samples display less drift than others. Possible causes of the drift could be free ion motion, formation of metallic dendrites due to electro-migration at metal interfaces, electrochemical processes, and current induced burnout. The drift is largest when the samples are first biased. If the samples are allowed to rest for a period, the large initial drift will return. Drift correction was accomplished by means of recording the current at invariant magnetic field before and after the magnetic field sweep. A third order polynomial was used to fit this invariant field data to correct for the drift. Yet, after this drift correction, a characteristic and reproducible asymmetry about zero field persists as seen in figure 3.2. This asymmetry does not depend upon the sign of the field, but does depend upon the sweep direction, specifically increasing or decreasing field. The asymmetry is clear even before performing the drift correction. A possible explanation is a magnetically sensitive drift component that is not addressed in the aforementioned drift correction. The drift could be sensitive to the amount of current flowing through the device, and depend upon whether the sample was coming from a high current state or a low current state as dictated by the change in the magnetic field.

Data fitting, processing, and plotting were done using a combination of Origin, Excel,
Figure 3.2: Raw time dependent data for an Alq$_3$ device. The magnetic field was held constant from 0-600 seconds, 1850-2100 seconds, and 3350-3600 seconds. The time dependent drift begins by increasing the current and has positive curvature. The asymmetry about zero magnetic field is easily seen.
and GnuPlot.

The data points for figures 4.9, 4.10, and 4.11 were generated by averaging ±20 mT about the 200 mT point. Over this range, a linear approximation fits the data quite well. This was done to smooth out noisy data sets. The standard deviation of these points was taken as the error bars to account for the error from noise, but it should be noted that this will produce too large of an error bar as there is some slope to the data due to the magnetic field dependence.
Chapter 4
EXPLORING THE MIST MODEL

4.1 Extracted recombination mobility

Close examination of the MIST model produces a number of predictions that can be tested, even if only qualitatively. One claim made by the MIST model is that of the MR dependence upon $\mu_R$. According to the MIST model, it is the bulk recombination coefficient that is altered by the applied magnetic field. The current has a specified dependence upon $\mu_R$ which can be extracted and plotted versus magnetic field. If the MIST model is correct, then this extracted behavior will be the same for both positive and negative MR.

For positive MR, $I \propto B$, leading to $B \propto 1/R$, where $B$ is the bulk recombination coefficient and $R$ is the resistance. For negative MR, $I \propto B^{-1/2}$, which gives $B \propto R^2$. This behavior is only valid as long as $\mu_R$ is not equal to $\mu_c$. As $\mu_R$ approaches $\mu_c$, the SCL regime and the RL regime begin to mix, leading to a mixed behavior for the dependence of the current on $\mu_R$. With our current level of understanding, it is impossible to know how close $\mu_R$ is to $\mu_c$ without mapping out the transition through the inversion point; however, by plotting $\mu_R$ from multiple data sets that have demonstrated clear signs of positive and negative magnetoresistance, it becomes possible to say something of the general dependence of the current on $\mu_R$ in the different modes. Figure 4.1 shows the extracted $\mu_R$ data from a single $\alpha$-6T device that has exhibited both positive and negative MR. It is important to only compare extracted recombination mobilities from single devices so that differences in the devices have no impact on the comparison. A more illuminating way of presenting the data is to renormalize each figure to the value at a set field point (400 mT) and plot
Figure 4.1: Plotted above is the percentage change in the extracted recombination mobility, $\mu_R$, as a function of magnetic field. $\mu_R$ was extracted from a single $\alpha$-6T device that operated in both the positive and negative modes.
Figure 4.2: Data from 4.1 renormalized to the values at 400 mT and plotted on arbitrary units. Note the similarities in behavior.

to arbitrary units so as to rescale the data. This allows a qualitative comparison of the behaviors (figure 4.2). The very low portion (≤20 mT) of the data shows a sharp drop off followed by a lessening of the slope above 20 mT.

Figure 4.3 shows data from another α-6T device that operated in both the positive and negative MR mode. The noise level in this sample is significantly higher, but the center line of the two data sets display linear behavior until diverging at ∼100 mT. There is no reason why taking the inverse of one data set, and taking the squared value of another data set should produce the same behavior unless they originate from the same mechanism. If the extracted recombination mobilities had differed greatly in their dependence upon the
Figure 4.3: The extracted recombination mobility for an α-6T device studied at the NHMFL. The negative mode data and the positive mode data overlap completely up to just under 50 mT. At that point they begin to diverge. The data is quite noisy but it can be seen that from 0 mT to ±50 mT is a straight line.
magnetic field, this result would have been in conflict with the MIST mechanism. It would seem a great coincidence that the extracted \( \mu R \)'s have the same behavior unless the MIST mechanism is correct.

### 4.2 Fitting the data

According to the MIST model, at low applied magnetic fields the applied field is a perturbation to the internal randomly oriented hyperfine field. The magnetoresistance is defined as

\[
MR = \frac{R(H) - R(0)}{R(0)} = \frac{I(0)}{I(H)} - 1 = \frac{C[B(H) - B(0)]}{B(0)},
\]

where the scaling factor \( C \) is

\[
C = \left. \frac{d(\ln I(B))}{d(\ln B)} \right|_H.
\]

Eqn. (4.2) sets the magnitude and sign of the MR response to the magnetic field. An expansion of \( B \), the recombination coefficient, about the dimensionless parameter \( x = H/H_{hf} \), where \( H \) is the applied magnetic field and \( H_{hf} \) is the internal hyperfine field, gives a polynomial of even orders for small magnetic fields. Hence, for \( H << H_{hf} \) the magnetoresistance should behave like \( MR = a_1 x^2 + a_2 x^4 + \ldots \), where \( a_1 \) and \( a_2 \) are dimensionless scale parameters. This form also shows the angle independence of the MR as there are only even powers of applied magnetic field. Figure 4.4 is of data taken from an Alq_3 device in the range of -1.5 mT to 1.5 mT with a fit of the above form. As can be seen, the polynomial of even orders fits the data quite well.

In the limit of large applied magnetic field, the internal hyperfine field is a perturbation to the applied field and the expansion takes the form \( MR = c_1 x^2 + c_2 x^4 + \ldots \), where \( c_1 \) and \( c_2 \) are dimensionless scale parameters. The quick response displayed in the very small field limit and the strong dependence on \( H \) gives way to an apparent saturation as the applied field grows. Figure 4.5 shows data taken in the range of 100 mT to 250 mT with a fit of the above form. As can be seen, the polynomial of inverse even orders describes the data quite well. Data from another device fabricated with the non-conjugated polymer poly(vinylencarbazole) (PVK) as the active layer, is shown in figure 4.6 also with a fit of
Figure 4.4: A polynomial curve fit of the form $a_1H^2 + a_2H^4$ to the low field MR data of an Alq$_3$ device.
Figure 4.5: A fitting to Alq$_3$ data in the $H >> H_r f$ regime. The fit is of the form $MR = c_1/x^2 + c_2/x^4 \ldots$
Figure 4.6: A fitting to the PVK data in the $H \gg H_{hf}$ regime. The fit is of the form $MR = c_1/x^2 + c_2/x^4$. Data courtesy of Dr. Jeremy Bergeson.
Figure 4.7: Fittings to the α-6T data in the $H \gg H_h f$ regime. The fit requires the next highest term so the form is $c_1/x^2 + c_2/x^4 + c_3/x^6 \ldots$.

the above form. Again, the polynomial of inverse even orders describes the data quite well. For the following OSC’s it becomes necessary to add the next order term.

In figures 4.7 and 4.8 data is shown for devices made from α-6T and the poly(phenylene vinylene) (PPV) derivative “Super Yellow”. Both have curves overlayed representing fits to the forms $c_1/x^2 + c_2/x^4 + c_3/x^6$. It has been noted that an inverse square root of the absolute magnitude of the magnetic field seems to be an excellent fit as well, but such a fit is non-analytic because of the need of an absolute value. Also, it is not clear why these two
The fit requires the next highest term so the form is $c_1/x^2 + c_2/x^4 + c_3/x^6 \ldots$. Data courtesy of Dr. Jeremy Bergeson.
OSC’s should require extra fitting terms.

It should be noted that Alq$_3$ is a small molecule and that PVK is a non-conjugated polymer. This would lead to greater localization of the charge carriers located at any given site. On the other hand, PPV is a conjugated polymer, and $\alpha$-6T is a conjugated oligomer. It would seem that this structural difference may be the cause of the required higher term. It will be shown later that the so called saturation region is actually a transition region from low field behavior to high field behavior. It is speculated that the high field behavior is highly dependent upon the structural properties of the OSC and hence may be the origin of the difference in the transition. This point shall be elaborated upon in the final chapter.

4.3 Monotonic and non-monotonic voltage dependence

Studies of OMAR have revealed a variety of dependences upon the applied voltage in the magnitude of the MR at set applied magnetic field points and temperatures. Figures 4.9, 4.10 and 4.11 show data taken in PPV, PVK and Alq$_3$ devices.

Monotonic rises, falls, and non-monotonic behaviors are all observed. In addition, a transition from negative mode to positive mode, and back to negative mode as voltage is increased has been reported [39]. Such behaviors are predicted from the MIST model, and provide additional qualitative evidence that the MIST model is an accurate description of the mechanisms that lead to OMAR.

The scaling factor $C$ from eqn[4.2] sets the sign and magnitude of the MR response. For a given set of operational conditions ($V, L, T$), $\mu_c$ will have a given value as shown from eqn[2.4]. The recombination mobility at zero applied magnetic field will have a natural value dependent upon the material being studied. The relationship between $\mu_R$ and $\mu_c$ will establish the sign and size of $C$. If $\mu_c$ is greater than $\mu_R$, the sign will be positive, and the value will depend upon the slope of the current curve as a function of $\mu_R$ (see figure 2.4). Specifically, the slope of eqn [2.4] as established by $c(V)$. If the value of $\mu_c$ is reduced below that of $\mu_R$, the magnetoresistance will be negative and the value of $C$ will depend upon the relationship between $\mu_R$ and $\mu_{inf}$, the inflection point in the curve as the SCL.
Figure 4.9: The magnetoresistance exhibited at 200 mT by a PPV device as a function of voltage and temperature. A monotonic rise, fall, and non-monotonic behavior are shown. Data courtesy of Dr. Jeremy Bergeson.
Figure 4.10: The magnetoresistance exhibited at 200 mT by a PVK device as a function of voltage and temperature. A monotonic fall and a non-monotonic behavior are shown. Data courtesy of Dr. Jeremy Bergeson.
Figure 4.11: The magnetoresistance exhibited at 200 mT by an Alq₃ device as a function of voltage and temperature. A monotonic rise and non-monotonic behaviors are shown.
regime transitions into the RL regime. The current will undergo a maximum change at the
inflection point in the curve as this is the point of maximum slope.

It is the value of $\mu_c$ that is altered by the parameters of voltage, thickness, and temper-

ture, and $\mu_{inf}$ is altered in the same manner, increasing when $\mu_c$ increases and decreasing
along with $\mu_c$. As $\mu_{inf}$ moves about $\mu_R$, a change in the magnitude of the response is
expected. Figure 2.4 provides cartoon sketches of the dependence of $\mu_c$ ($\mu_{inf}$) on voltage,

thickness and temperature. Of particular interest is the dependence on voltage. For small
$V$, $\mu_{inf}$ will increase until $V$ reaches the critical voltage, $V_c$. At $V_c$, $\mu_{inf}$ will decrease. This
information can be used to interpret the results from figures 4.9, 4.10, and 4.11. Consider
a device in the negative mode, such as the data presented. When $\mu_{inf}$ approaches $\mu_R$, an
increase in the magnitude of the signal would be expected. This could result either from
$\mu_R > \mu_{inf}$, $V < V_c$ or $\mu_R < \mu_{inf}$, $V > V_c$. A reduction in the signal would result from
$\mu_{inf}$ moving away from $\mu_R$. Non-monotonic behaviors come from two sources: $\mu_{inf}$ passing
through $\mu_R$ and $V$ passing through $V_c$.

The exciton-polaron charge reaction model could explain this behavior through by con-

sidering different charge injection schemes. By allowing the charge injection to be altered
in different voltage regimes, the balance between holes and electrons is changed. It is this
balance that would determine whether or not the system is dominated by the contribution
from singlet dissociation, or triplet-charge annihilation. Considering such specific scenarios
as a spectrum of interfacial gap states that alter the charge injection, and field assisted
dissociation of excitons, it is possible to concoct a variety of ways to inject non-monotonic
behaviors into the model. Ultimately, the variety of possible scenarios along with the diffi-
culty to distinguish one scenario from another makes it difficult to verify the exciton-polaron
charge reaction model.

The exciton-polaron mobility model could follow a similar path to explaining such behv-

iors as it also depends upon the relation between the triplet states and free charge carriers.

Ultimately, the MIST model is attractive because it does not need to include any ad
hoc features to explain this voltage dependence. It is already built into the model.

The report of inversion from negative to positive to negative also supports the MIST
model. As the voltage is increased, $\mu_c$ increases until $V$ reaches $V_c$, at which point, $\mu_c$ will decrease. This would allow $\mu_c$ to pass through $\mu_R$ twice, producing a negative to positive to negative response. The MIST model disallows a switch from positive to negative to positive with increasing voltage, as that would require $\mu_c$ to decrease then increase, then decrease. If such a behavior was ever confirmed, it would provide evidence against the MIST model.
Chapter 5
HIGH MAGNETIC FIELD MAGNETORESISTANCE

5.1 High field magnetoresistance in Alq3

5.1.1 Data taken at 300 K

In figure 5.1 is shown MR data collected for Alq3 samples in the negative MR mode that are 100 nm and 200 nm thick at various voltage biases with PEDOT:PSS as the hole injecting layer. Also displayed are data for a 200 nm thick device with gold replacing the PEDOT:PSS at various biases. All data in figure 5.1 were taken at 300 K. A non-monotonic transition from low field behavior to high field behavior occurs around 500 mT.

The high field (above 1 T) response reverses the OMAR behavior with a positive increase, recovering towards the zero field value. The shape of the high field MR remains qualitatively similar despite changes in thickness and voltage biases. It seems to be related to the magnitude of the low field behavior as data sets with smaller responses in the low field also have smaller responses in the high field. Thus it seems to depend upon voltage and film thickness in the same manner as does the low field portion.

The MR response is also unchanged when PEDOT:PSS is replaced by gold; thus the high field recovery is due solely to the Alq3 OSC’s response to the magnetic field. If we look to the models to describe this response, it is seen that the MIST model has a natural extension that could account for this behavior.

As charges are injected from either side, they form charge pairs. In the steady state
Figure 5.1: Data shown for a set of Alq$_3$ devices taken at 300K. Device A1 is has an active layer thickness of 100 nm, device A2 has an active layer thickness of 200 nm, and device B2 has an active layer thickness of 200 nm. A1 and A2 use PEDOT:PSS as the anode and B2 uses gold as the anode. The high field portion ($\geq 1$ T) is of the same order as the low field portion and they have similar dependencies on voltage and thickness.
solution, these charge pairs will follow a Boltzmann distribution as a function of separation. The exchange energy has a strong dependence upon the distance separating the charge pairs of the form

\[ J = J_0 \exp \left( \frac{-2r}{r_0} \right), \]  

(5.1)

where \( r_0 \) is the Frenkel radius, \( r \) is the separation between the charge pairs, and \( J_0 \) is the energy at the Frenkel radius which is expected to be of order 100 meV. In the absence of a magnetic field, the exchange energy lifts the degeneracy of the triplet and singlet states. An applied magnetic field adds the Zeeman splitting term

\[ Z = \mu_B g (\vec{S}_n + \vec{S}_p) \cdot \vec{H}, \]  

(5.2)

to the spin Hamiltonian, and for large magnetic fields, induces degeneracy between the raised triplet state and the singlet state. The degeneracy exists for those charge pairs for which the Zeeman splitting is comparable to the exchange energy as determined by the distance separating the charge pair.

The degenerate pairs are allowed to switch between the two states by means of spin mixing\(^{[24]}\), possibly from the random internal hyperfine field, although some publications suggest it is due to other mechanisms. The more degenerate charge pairs that exist, the larger the influence upon the recombination coefficient of the system as the triplet recombination coefficient is expected to be of the form \( B_T = NB_S \), where \( B_{T,S} \) is the recombination coefficient of raised singlet and raised triplet, and \( N \) is the number of degenerate bound pairs. Figure\(^{[5.2]}\) is a schematic representation of the induced degeneracy. Also depicted is the expected behavior for a population distribution weighted towards tightly bound charge pairs. As can be seen, it roughly resembles the actual behavior. The specific behavior is dependent upon the morphology of the OSC, as this will have an impact upon the distribution of bound charge pairs as a function of separation. Thus, it is expected that different materials will have different high field behaviors.

The exciton-polaron charge reaction model predicts a monotonic continuation of the MR behavior or a trend towards saturation depending upon whether the distribution of states
Figure 5.2: A schematic representation of the Zeeman induced degeneracy in the exchange energy between the raised triplet and the singlet. The point of degeneracy corresponds to a specific charge pair separation, $r$. Some percentage of charge pairs will be at this separation as dictated by the population distribution, which is morphology dependent. If the population is weighted towards tightly bound pairs, then the induced degeneracy will experience a net increase as the magnetic field is increased. Lower right shows the expected behavior for a population that follows a Boltzmann type distribution. About the crossing point, the hyperfine mechanism will dictate $\delta r$, the spread about the crossing point that allows spin transitions.
follows a Boltzmann type distribution, or a Gaussian distribution, respectively. This model assumes that it is always the case that an applied magnetic field will cause an increase in the singlet population, and thus there would be no change in behavior from the low field to the high field.

The exciton-polaron mobility model assumes that an applied magnetic field increases the conversion rate between triplets and singlets equally and that it always increases the conversion rate. As the device is in the dark and all charge pairs are formed from injected charge carriers, the increase in interconversion leads to an increase in the singlet population as there are three times more triplets than singlets. Unless some new mechanism is introduced, the exciton-polaron mobility model assumes a trend towards saturation as a steady state is reached.

A plot of the high field data versus the natural log of the magnitude of the magnetic field reveals a linear behavior above 1.3 T (see figure 5.3). This empirical fit produces a mean slope of $0.81 \pm 0.29$ across all samples measured. The origin of this dependence upon the natural log of $\mathbf{H}$ is unknown as attempts to extract this behavior from any model have thus far been unsuccessful. The dependence upon the magnitude of the magnetic field is oddly non-analytic, but can be understood by considering the Zeeman splitting term. The magnetic field gets dotted into the total spin of the bound charge pair. When the magnetic field is positive, it raises the +1 spin triplet and this is the spin state that becomes degenerate with the singlet. When the magnetic field is negative, the -1 spin triplet is raised and becomes degenerate with the singlet state. The negatives cancel, leading to an apparent dependence upon the magnitude of the applied magnetic field.

5.1.2 Freezing out of the high field MR

Data taken at 200 K (see figures 5.4,5.5) show a reduction in the high field response. The signal above 1 T does not recover as much as is seen in the room temperature data. A semi-log plot reveals that the linear dependence upon $\ln B$ has been lost as there is now some curvature in the data (see figures 5.6,5.7).

The freezing out of the high field MR is even more pronounced at 100 K (see figure 5.8)
Figure 5.3: The data from 5.1 plotted versus the natural log of the absolute value of magnetic field. The MR shows a linear behavior in this semi-log plot. The mean slope across many devices is $0.81 \pm 0.29$. The value 9.5 converts to 1.3 T and the value 11.5 converts to 10 T.
Figure 5.4: Data taken from an Alq3 device with an active layer of 200 nm held at 200K. The high field MR (≥1 T) shows signs of quenching at the lowered temperature.
Figure 5.5: Data taken from an Alq$_3$ device with an active layer of 100 nm held at 200K. The high field MR ($\geq$1 T) shows signs of quenching at the lowered temperature.
Figure 5.6: A semi-log plot of data taken at 200K for the Alq$_3$ device shown in figure 5.4. The linear behavior has been lost and some curvature has been induced in the high field region. The value 9.5 converts to 1.3 T and the value 11.5 converts to 10 T.
Figure 5.7: A semi-log plot of data taken at 200K for the Alq₃ device shown in figure 5.5. The linear behavior has been lost and some curvature has been induced in the high field region. The value 9.5 converts to 1.3 T and the value 11.5 converts to 10 T.
Figure 5.8: Data is shown for a pair of Alq₃ devices held at 100K. Device b has an active layer thickness of 200 nm, and device h has an active layer of 100 nm. Note the voltage dependence and the reduction in the freezing out of the high field response.

as the high field response seems to have been completely frozen out. A semi-log plot clearly shows that there is no recovery, only a continued drop off in some devices or a leveling off in others (see figure 5.9). Figure 5.10 shows a comparison of characteristic MR curves from each temperature.

A decrease in thermal diffusive separation could be the cause of this quenching. As the temperature drops, there is insufficient thermal energy to separate the tightly bound pairs. Recombination becomes dominant for all spin states. The low field regime is only altered by a small amount as well separated pairs can still separate due to the weakness of the
Figure 5.9: A semi-log plot of the Alq$_3$ data taken at 100K. Note the complete freezing out of the high field behavior. The value 9.5 converts to 1.3 T and the value 11.5 converts to 10 T.
Figure 5.10: Comparison of data taken at several different temperatures. Note the freezing out of the high field response as the temperature decreases.
Coulomb binding at long ranges.

Another possible means is the recombination of charge pairs before they can draw close to one another. The charge mobilities have a strong dependence on the temperature, and as the thermal energy drops, phonon assisted hoping is quenched. The recombination rate has only a weak temperature dependence, so would remain relatively constant. If the charges are recombining before they can become tightly bound, then this would lead to a reduction in the high field response. However, one would expect a relative increase in the low field portion, especially since the Onzager radius has increased. The fact that the low field portion also reduces seems to contradict this unless the other temperature dependences are stronger. If \( \mu_R \) is approaching \( \mu_c \), then the scaling function \( \Psi(4.2) \) goes to zero, reducing the magnitude of the response.

The exciton-polaron charge reaction model predicts that a decrease in thermal energy would decrease the number of secondary charges generated as the thermal energy of the free charge carriers is diminished. This would lead to a lower chance of breaking the bound pairs apart. Additionally, the thermal dissociation of singlets would decrease. This leads to a reduced sensitivity to the magnetic field as fewer secondary charges are generated. It is unclear why this thermal dependence would be more pronounced for the high field than the low field.

The exciton-polaron mobility model predicts that decreased temperature leads to a reduced magnetic field response, as well. As the thermal energy reduces, the mobility of polarons decreases, leading to longer transit times. The recombination of singlets and triplets remains relatively constant, so the triplet states would vanish on a short time scale after forming, compared to the movement of the polarons. Thus, the free charges have a reduced chance of interacting with triplet states.

### 5.2 High field magnetoresistance in \( \alpha \text{-}6\text{T} \)

Figures 5.11 and 5.12 show the MR behavior of \( \alpha \text{-}6\text{T} \) as a function of temperature. The asymmetry is particularly pronounced in \( \alpha \text{-}6\text{T} \) devices. When the low field portion is in the
Figure 5.11: An α-6T device at various temperatures. After the inversion from negative mode to positive mode, the high field portion of all data sets is a reduction in the resistance. The high field portion from the positive mode data seems to be going to the same value as the negative mode data.
Figure 5.12: An α-6T device at various temperatures. The data displays a pronounced asymmetry. The positive mode data has a less abrupt turnover on the negative magnetic field side, and is non-monotonic on the positive magnetic field side.
negative MR mode, the high field portion continues to change in the same direction as low field data. The difference in behavior between Alq\textsubscript{3} and α-6T could be due to differences in charge pair distributions as a function of charge separation and hence exchange energy. The high field response should map out the charge pair distribution according to the MIST model. It is known that Alq\textsubscript{3} tends to be highly disordered with little long range order, while α-6T tends toward a polycrystalline nature. This difference in morphology would lead to different charge pair distributions. In contrast, the monotonic behavior lends support to the exciton-polaron charge reaction model which predicts a monotonic behavior with increasing field. The exciton-polaron mobility model expects a saturation, and is thus contradicted.

At 200 K, one side seems to exhibit a rise before turning negative again. This apparent rise is possibly due to the asymmetry previously mentioned. At 100 K, both devices exhibited positive MR. The high field portion reverses from that of the low field. Some of the data displays a monotonic change, while some is non-monotonic. This difference could be due to the local degree of order exhibited for each device. If the devices are in different crystal phases, they would display different high field behaviors. None the less, the high field response from the positive mode does reverse behavior from the low field response, which is different from the negative mode behavior. The MIST model would expect the positive mode and the negative mode to behave the same way, either both reversing at the transition or both following a monotonic trend. Figures 5.11 and 5.12 also show that the high field response trends toward the same behavior regardless of what the low field is doing. This would seem to suggest that the low field and high field responses are decoupled and due to separate mechanisms.

In contrast to this is data taken at the NHMFL on α-6T devices (see figure 5.13). A comparison of the data over low field ranges shows a very similar response at different scales (figure 5.14). The difference in scale is predicted by the MIST model. The devices taken to the NHMFL were ∼400 nm thick as compared to the samples characterized at OSU. According the MIST model, as the thickness is increased, \( \mu_c \) will decrease, and since these devices are in the negative mode, this will move \( \mu_{inf} \) away from \( \mu_R \), putting \( \mu_R \) on a more shallow portion of the slope. However, the high field portions diverge dramatically as shown.
Figure 5.13: Data taken from an $\alpha$-6T device at the NHMFL over the range of -35 T to 35 T. The sample was biased at 100 $\mu$Amps. The high field MR ($\geq$1 T) has lost the behavior shown by $\alpha$-6T samples studied at OSU, and resembles that of Alq$_3$. 
Figure 5.14: Data shown is a comparison between an $\alpha$-6T device studied at OSU and an $\alpha$-6T device studied at the NHMFL over low field ranges. The behaviors are the same but of different magnitudes.
in figure 5.15. The response seems quite similar to that of Alq$_3$, although at a different scale. This difference in the high field portion could be due to differences in crystal structure between the two sets of samples. The samples characterized at the NHMFL were deposited quite rapidly ($\sim 6.5$ Å/sec) as opposed to the OSU samples which were deposited much slower ($\sim 1.5$ Å/sec). The faster rate of deposition makes $\alpha$-6T films more disordered, making them more like Alq$_3$\cite{52}.

In figure 5.16 data is shown for an $\alpha$-6T device in the positive MR mode. Despite being in the positive mode, the very high field response is the same as that for the negative MR mode, simply off set by the amounts that the two samples had risen or fallen in the low
Figure 5.16: Very high field data from the NHMFL is shown for an $\alpha$-6T device. The curves display both positive and negative mode OMAR. Despite the difference in low field behavior, the high and very high field behavior is the same.
Figure 5.17: Data is shown for a set of devices with pure P3HT as the active layer and PCBM added in as a percentage by weight. The device with 1 % PCBM shows a negligible change, but the device with 35 % PCBM shows a significant change.

field portion. This similarity between the data sets at high fields seems to add credence to the suggestion that the high field is governed by a separate mechanism than the low field.

5.3 Recombination quenching in P3HT

Figure 5.17 shows data from a set of devices with P3HT as the active layer. P3HT is a common OSC for organic photovoltaics (OPV) and lends itself to a large leakage current, so it is not surprising that it is in the positive magnetoresistance mode. As the magnetic field transitions from the low field regime to the high field regime, the MR also goes through a
reversal in behavior, returning towards zero. Shown in the figure is a sample composed of pure P3HT, and samples that have had PCBM added to them, 1 % by weight and 35 % by weight, respectively. In OPV, PCBM is added to aid in charge pair separation, thus decreasing the total recombination rate. These samples were not annealed, so as to prevent phase separation and maintain an even dispersion of PCBM throughout the device. The magnitude at which the transition from low to high field response occurs shows a slight decrease for the 1 % sample, and displays a marked decrease for the 35 % sample. It should be noted for the 1 % sample that the high field portion is also reduced, suggesting that the reduction in low field response is due to other device characteristics.

OLED’s have two contributions to the current flowing through the device. One is the leakage current from electrons and holes that pass through the OSC and are removed at the interfaces, and the other is the recombination current due to electrons and holes that meet, and are removed by recombining. In the positive mode, the leakage current is much larger than the recombination current. The MIST model attributes the MR response to a diminished recombination current. The purpose of adding PCBM to the OSC is to enhance the leakage current and quench the recombination current. As the recombination current is reduced, any change in the recombination current has a smaller contribution to the change in the overall current, thus quenching the low field MR. This result can also be explained by both exciton-polaron models. These models rely upon the interaction between excitons and free charges. As the exciton population is quenched by the PCBM, there are fewer excitons to interact with the free charges, thus decreasing the effect.

In contrast, the high field response in the 35 % device is unchanged in either shape or total change over the course of the sweep. This implies that the high field response is a separate effect from that of the low field MR. An extensive analysis is provided in the final chapter.
Chapter 6
CONCLUSION

6.1 Summary and extended analysis

The results from magnetoresistance studies have been presented and analyzed in the context of the most current and probable theories. In chapter 4, predictions from the MIST mechanism regarding low field ($\leq 500$ mT) behavior were explored.

The MIST model predicts that OMAR is the result of the magnetic field changing the bulk recombination coefficient. It also gives a specific dependence of the current on the recombination coefficient that depends on whether the device is in the positive mode or the negative mode. In negative mode, the recombination coefficient is proportional to the square of the resistance. In the positive mode, the recombination coefficient is proportional to the inverse of the resistance. By extracting the recombination coefficient from the data, normalizing, and plotting versus magnetic field, it is found that the behaviors are qualitatively very similar. That the square of one data set should have the same behavior as the inverse of a different data set would be quite a coincidence unless they are both derived from the same underlying mechanism.

The magnitude of the low field response shows a strange dependence on the voltage as it is sometimes monotonically increasing in magnitude, sometimes monotonically decreasing in magnitude, and sometimes non-monotonic. It is shown that the MIST mechanism not only predicts this but demands this type of behavior. Other reports of transitions from negative mode to positive mode and back to negative mode again also agree with the behavior that the MIST model prescribes. While this is one more piece of qualitative support
for the MIST mechanism, it is found that neither exciton-polaron model is contradicted by such trends provided the proper initial conditions are assumed.

Curve fittings to the data confirm the MIST model predicted behavior in both Alq3 and PVK in the saturation regime, and for Alq3 in the very low field limit. Curve fittings to the conjugated polymer PPV and the conjugated oligomer α-6T require an additional higher order term. It is initially preposed that as the saturation regime is actually a transition phase from low field behavior to high field (≥1 T) behavior, and as the high field regime is predicted to be dependent on the morphology of the OSC, perhaps the extra term is the result of competition between the two regimes. High field studies reported in chapter 5, however, contradict this preposal. Another possibility is that of the strength of the hyperfine field in each material. The hyperfine field is the result of randomly oriented nuclear spins, primarily from hydrogen in OSC’s. When a charge carrier wave function is able to sample more hydrogens, the hyperfine field it experiences goes down as the statistical variation decreases. A charge carrier on an Alq3 molecule is localized to a single quinolate group, and “sees” 6 hydrogens. Likewise, a charge carrier in a film of PVK is localized to a single carbazole unit, and experiences 8 hydrogens. There are 12 hydrogens per α-6T oligomer and with the delocalization due to polycrystalline regions, a charge carrier can be influenced by even more. A PPV mono-unit has 8 hydrogens, but with the spread of the charge carrier wave function over multiple units, many more hydrogens contribute to the local random hyperfine field. The result is that a smaller hyperfine field is expected in α-6T and PPV than in Alq3 and PVK. The smaller perturbation may need more terms to fit the data. Neither exciton-polaron model has generated quantitative predictions of the MR dependence on magnetic field.

It is also shown that the low field MR magnitude is reduced by decreasing the contribution from the recombination current for P3HT devices operating in the positive mode. This result supports the MIST model but not the exciton polaron models. The exciton-polaron charge reaction model should be enhanced due to increased secondary charge pair generation. The inclusion of PCBM will encourage the formation of excimers (excitons formed across different species of molecules). Excimers are slower to recombine and thus more likely
to break apart. This leads to a reduction in the recombination current and an enhanced generation of secondary charge pairs. As the leakage current is now of greater contribution to the overall current, the exciton-polaron charge reaction model predicts a larger change.

Excimers will still form singlet and triplet states, and thus there are still triplets for the polarons to interact with. There are two possible scenarios. If the dissociation rate is increased more than the recombination rate is decreased, then triplets will have shorter lifetimes and will be rapidly quenched, thus reducing the polaron scattering rate. If the recombination rate is reduced more than the dissociation rate is increased, this will lead to longer lifetimes and the triplet population will be greater, producing an increase in the effect.

In the specific case of P3HT with PCBM, the holes on the P3HT have high mobilities while the electrons on PCBM have low mobilities. The most likely result is that the holes can easily be broken away from the electrons by thermal or electric field assisted dissociation. However, the exciton-polaron mobility model attributes positive MR with a reduction in the singlet population and an increase in the triplet population. This data was taken in the dark, and the current is the result of injected charges. This would lead to the formation of more triplet states, and would lead to an increase in singlet population with magnetic field. This is a contradiction to the exciton-polaron model.

In chapter 5 high field studies of various OSC’s are reported. High field MR from Alq3 was found to have a positive increase in resistance as opposed to the negative MR at low field. The size of the effects were of very similar magnitude, and the high field MR was also found to share the same voltage and device dependencies as the low field MR, with both increasing and decreasing in magnitude together. This relationship between the magnitudes of high and low field behavior was also seen in α-6T devices. This initially suggested that the two regimes were related.

The MIST model does make predictions regarding the high field regime. Increased Zeeman splitting leads to degeneracy between the singlet states and one of the triplet states at a particular separation. This altered degeneracy leads to a change in the bulk recombination coefficient which alters the charge transport properties of the device. If the distribution of charge pairs as a function of separation is weighted towards more closely
bound pairs, then the degeneracy increases with increasing field, leading to an enhanced recombination coefficient. Alq$_3$ tends to form disordered films and it is assumed that a Boltzmann distribution describes the steady state population. This would lead to more tightly bound pairs than loosely bound pairs. The result would be an increase in the recombination coefficient at high fields in contrast to the reduced recombination coefficient at low fields. This would explain the negative low field behavior and the positive high field behavior.

This concept is initially supported by the high field results found in $\alpha$-6T. For $\alpha$-6T samples prepared by slow deposition, which is expected to lead to increased crystallinity, the high field results are different from those of Alq$_3$. The change in morphology would be expected to lead to different charge pair populations as a function of separation. Specifically, the increased crystallinity combined with the elongated conjugated path ways should lead to increased delocalization of the charges and increased separation between them. If the charge pair population is weighted towards well separated charge pairs, increased magnetic field would give a decreased degeneracy as fewer and fewer triplets populate the degenerate states. This would give a negative change in resistance for the high field MR as is observed.

When $\alpha$-6T is deposited rapidly, the high field MR becomes very similar to that of Alq$_3$. Rapid deposition of $\alpha$-6T leads to more disordered films. These results demonstrate that the high field MR is dependent on the morphology of the OSC, just as the MIST mechanism suggests.

However, further review of the data supports the idea that the high field MR is caused by a mechanism distinct from that of the low field. Although the low field portion of the P3HT data supports the MIST mechanism, the high field results suggest there is a decoupling of the two regimes as increased PCBM concentration had no impact on the high field MR. In both the $\alpha$-6T data taken at OSU and NHMFL, the high field data shows the same behavior regardless of whether the low field portion is negative or positive. Also, the data from the Alq$_3$ devices shows the high field MR to be quenched as temperature is reduced, but the low field portion shows only a modest reduction. Looking at the complete set of data, it seems clear that the high field and low field MR are not from the same source.
All the data reported for the low field is in excellent agreement with and support for
the MIST model. It would seem that the MIST model is the most complete and accurate
theory for describing the low field magnetoresistance.

In contrast a new theory must be sought for the high field MR. The high field MR is
dependent on the morphology of the OSC film. It is a phonon assisted process as it falls
off with temperature. It is not dependent on the recombination current in the device. It
can be positive or negative. It is dependent on the thickness of the active film and the
applied voltage. The theory that accounts for high field MR must take all of these factors
into consideration.

6.2 Possible future studies

There is strong indication that the MIST mechanism is a good theoretical starting point
for low field OMAR, but there have yet to be any conclusive results that definitively prove
one model or another. Additionally work must also be done to ascertain the origin of the
high field OMAR. Some possible future experiments are presented in the following.

The most obvious follow up work involves studies on the dependence of the high field
OMAR on the degree of order in the film. Films with varying sizes of crystalline regions
ranging from very small to single crystal films could be characterized with X-ray diffraction
and then measured in high field to determine the response and the transition point between
the two regimes already noted. Temperature dependence studies could be incorporated into
this work.

An interesting class of materials to study would be diamines. These diamines consists of
a single phenyl unit with two amine units on either side of the molecule. Additional phenyl
units can be added to lengthen the molecule, either as fused rings, or bridged by a carbon σ-
bond. This class of materials could be used to study the dependence of OMAR on molecular
morphology without inclusion of new elements. Diamines could also be incorporated into
the crystallinity studies mentioned above.

Organic light emitting transistors (OLET’s) are transistor devices that emit light [53] [54] [55].
Microscopic viewing reveals a narrow light emissive region that corresponds to the recombination region in space charge limited OLED’s. If magnetic studies were done on such devices, it would allow direct imaging of the influence of the magnetic field on the recombination zone. Such an experiment would provide indisputable evidence for or against the MIST model. It could also shed light on the high field behavior for if the high field MR is the result of a magneto-mobility mechanism, the location of the emissive region should move with application of the magnetic field[56].

Another way to explore the low field MR would be with spin OLED’s[57][58]. The concept behind spin OLED’s is that the efficiency can be altered by injecting non-randomized spins. This leads to a modification of spin state populations. If anti-parallel spins are injected, 50 % of the spin states formed will be singlets, and 50 % will be $T_0$ triplets. Neither are influenced energetically by a magnetic field, so no MR should be observed according to models that rely on Zeeman splitting. If parallel spins are injected, then 50 % of the spin states will be $T_+$ triplets and 50 % will be $T_-$ triplets. The response to the magnetic field should be quite large according to Zeeman splitting models as all of the spin states are now coupled to an applied magnetic field.

Such an experiment would be limited to magnetic fields less than the coercive field of the soft magnet. This is not a real problem though as OMAR is pronounced at low fields. Additionally, the magnetic field should be aligned to the magnetization axis of the magnetic electrodes. This would prevent, or at least minimize precession, which would act to mix the spins. A final consideration would be for the film to be less than or of the order of the spin diffusion length so as to maintain spin coherence.

A final possible experiment would be the dependence on area versus perimeter. It has been demonstrated that OPV devices are very sensitive to the amount of perimeter present[59]. The electric field is enhanced at the perimeter due to edge effects. This enhanced electric field increases field assisted dissociation in the region near the perimeter. This could provide additional evidence for the dependence of the low field on bound charge pairs, and help determine the mechanism behind the high field magnetoresistance.
6.3 Closing remarks

In this manuscript, the results from magnetic field dependent charge transport studies have been presented. It is found that the MIST mechanism is well supported for the low field MR. It is also found that the high field MR is not an extension of the low field effect, but requires a separate theory. While the MIST model thus far provides the best description of low field OMAR, more work is needed to prove one model over any other. It is necessary to study the high field response to figure out what the cause is of high field OMAR.
Bibliography


