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Temperature dependent sign change of the organic magnetoresistance effect

F. L. Bloom,^{a)} W. Wagemans, and B. Koopmans

Department of Applied Physics, Center for NanoMaterials and COBRA Research Institute, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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A sign change of the organic magnetoresistance 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 the 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 MRs show different characteristic field widths B_0 in the MR versus 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. © 2008 American Institute of Physics.

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Recently, there has been much interest in the magnetotransport 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 spin valve¹ and tunnel-magnetoresistance² 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 light-emitting-diode-type devices by Francis *et al.*³ and has been dubbed organic magnetoresistance (OMAR).

The OMAR effect can have MR values of 10% at relatively small magnetic fields of ~ 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 $MR(B)$ ($MR(B)=[R(B)-R(0)]/R(0)$, where R is the resistance and B is the magnetic field) have been identified and the characteristic width (B_0) is ~ 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 simulations⁸ and analytical modeling⁹ have been able to reproduce both the $MR(B)$ line shapes as well as the sign change of the OMAR effect.

In this paper, we look at the role temperature plays in OMAR. Specifically, we look at how the temperature affects the sign and the $MR(B)$ 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.

The devices were deposited on clean indium tin oxide patterned glass substrates. The substrates were first covered by spin coating a poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) 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) aluminum (Alq_3) by thermal evaporation in a high vacuum system (base pressure $\sim 10^{-7}$ 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 to a continuous flow liquid helium cryostat suspended between the poles of an electromagnet, where dc measurements were made by sourcing voltage and measuring current.

First, we measured several $MR(B)$ traces using a fixed 10 V bias at several different temperatures (Fig. 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

^{a)}Electronic mail: f.l.bloom@tue.nl.

FIG. 1. (Color online) MR vs magnetic field traces at 10 V bias for several different temperatures. The solid lines are fits to Eq. (1).

$$\text{MR}(B) = \text{MR}_\infty \left(\frac{B}{(|B| + B_0)} \right)^2, \quad (1)$$

where B_0 is the characteristic field width, and MR_∞ is the MR at infinite magnetic field. This empirical relationship was found by Mermer *et al.* to fit well to $\text{MR}(B)$ traces for Alq_3 and a wide variety of other organic semiconductors.⁴ The fits (solid lines in Fig. 1) show that Eq. (1) describes all the $\text{MR}(B)$ traces well and allows us to find the temperature dependence of both B_0 and MR_∞ . Due to the correspondence with Eq. (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 2(a) 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

FIG. 2. (a) MR_∞ vs T at 10 V. (b) B_0 vs T at 10 V; the filled squares represent +MR values while the open squares represent −MR values. Both the MR_∞ and B_0 values are a result of fitting the data in Fig. 1 to Eq. (1).

FIG. 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 $\text{MR}(B)$ was measured. The solid lines are fits of the data to a power law.

temperature dependence after the transition. The −MR data appear to saturate more slowly but also show 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 $\text{MR}(B)$ traces. By plotting B_0 versus temperature [Fig. 2(b)], 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 the −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. 3), we see that both the 100 K (+MR) and 240 K (−MR) traces are linear in the measured range, indicating power law behavior. This behavior is given by AV^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 $n_{240\text{ K}} = 13$, while $n_{100\text{ K}} = 7.1$. Therefore, it seems that some temperature dependent change in the charge transport results in a change in the sign of the MR. In another recent work, we proposed that this sign change is a result of the 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 $\text{Ir}(\text{PPy})_3$ 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 features 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. 2(b),

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 did 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, ~ 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 α hops into a neighboring singly occupied site β to form a bipolaron, and $r_{\alpha \rightarrow e}$ is the rate at which a carrier from α bypasses β by hopping over β into unoccupied sites in the environment. It has been shown in both Monte Carlo simulations⁸ and in analytical solutions of a two-site model⁹ 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 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 [$B_{\text{hf}} \approx 1$ mT (Ref. 4)], the relevant field scale in the bipolaron model.

In conclusion, we measured a temperature dependent sign change of OMAR in a Alq₃ based device. The distinct field widths of the +MR and –MR along with the abrupt change in MR sign suggest that the +MR and –MR are distinct effects and 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.

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