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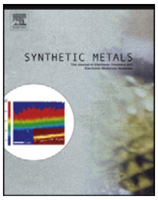

Magneto-conductance of π-conjugated polymer based unipolar and bipolar diodes

T.D. Nguyen[a], B.R. Gautam[a], E. Ehrenfreund[b], Z.V. Vardeny[a,*]

[a] Department of Physics, University of Utah, 115 S 1400 E, Salt Lake City, UT 84112, USA
[b] Department of Physics, Technion-Israel Institute of Technology, Haifa 32000, Israel

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ABSTRACT

The magnetoconductance (MC) of unipolar and bipolar organic diodes based on active layers made of the π-conjugated polymer DOO-PPV is presented in the range of magnetic field strength, B below about 100 mT, and for various polymer exchange isotopes. The MC(B) response is composed of two main regions: (i) a "sign-reversal" region for $|B| < 1–2$ mT, where MC(B) reverses its sign reaching a maximum absolute value $|\mathrm{MC}|_\mathrm{m}$ at $B = B_\mathrm{m}$; and (ii) a monotonic region for $|B| > 2$ mT, where MC(B) monotonically increases (decreases) for bipolar (unipolar) devices with an approximate Lorentzian line shape of width, ΔB. Similar behavior has been observed for the magneto-electroluminescence in bipolar devices. We found that MC(B) in both field regions is strongly isotope dependent; in particular both B_m and ΔB are larger for nuclei with larger hyperfine interaction (HFI) constant. The complete MC(B) response, including the novel sign-reversal component is explained by a model of spin-coupled pairs of either same or opposite charge polarons, in which the HFI is explicitly included in the electronic spin Hamiltonian.

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1. Introduction

The change in electrical conductance of organic diodes upon application of an external magnetic field, B (termed hereafter "organic magnetoconductance", MC) has been recently used to study the spin dynamics of the injected carriers [1–11]. MC is closely related to other magnetic field effects (MFE) such as field-induced changes in chemical and bio-chemical reaction yields, magneto-luminescence and magneto-phosphorescence, magneto-photoconductivity, and magneto-electroluminescence (MEL) in organic light emitting diodes. It has been generally accepted that the organic MFE originates from the field induced changes in the dynamics of long-lived loosely coupled polaron pairs (PP) in organic solids and devices [8,9]. In a recent paper, we have experimentally shown that the hyperfine interaction is responsible for the mixing of the spin sublevels of the PP species [12]. This was achieved by replacing protons with deuterons (D) in the π-conjugated polymer chains, where the D-polymer has smaller HFI constant, a_HFI. The obtained MEL(B) response was narrower in the D-polymer, in accordance with the reduced HFI constant. In addition, using high magnetic field resolution we showed that the MEL(B) response is composed of two regions: (i) a "sign-reversal" region at $|B| < 1–2$ mT, where MEL(B) reverses its sign reaching a maximum absolute value $|\mathrm{MEL}|_\mathrm{m}$ at $B = B_\mathrm{m}$, and (ii) a monotonic region at $|B| > \sim 2$ mT, where MEL(B) monotonically increases having an approximate Lorentzian line shape with half width at half maximum, ΔB. Both B_m and ΔB were found to be smaller for the D-polymer, in agreement with the smaller HFI constant. We explained the entire MEL(B) response, including the "normal" monotonic region, as well as the "sign reversal" region using a simple model Hamiltonian based on PP having HFI with few of the neighboring nuclear spins.

In this contribution we show that the sign reversal at very low fields reported earlier for the MEL(B) response is also observed in MC(B) in both bipolar and unipolar diodes. Namely, as $|B|$ decreases from $\sim$100 mT down to 1–2 mT, the monotonically decreasing (increasing) MC(B) changes from positive (negative) to negative (positive) in bipolar (unipolar) devices, forming a dip (peak) at B_m that scales with ΔB of the monotonic MC(B) response. We explain this ultra-small MFE (USMFE) component by extending the simple model Hamiltonian to include "spin pairs" (SP) of loosely bound polarons having HFI with several nuclear spins. The SP species are composed of either same charges (unipolar devices) or opposite charges (bipolar devices). In this model the intermixing between the hyperfine-split spin sublevels increases at very small B due to level-crossing at $B = 0$, thereby causing a MC sign reversal for both overall neutral and charged spin pairs.

2. Experimental

We report MC measurements in organic diodes based on active layers made of the π-conjugated polymer 2-methoxy-5-(2′-dioctyloxy) [DOO-PPV]. Three isotope enriched DOO-PPV

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[*] Corresponding author. Tel.: +1 801 581 8372.
E-mail address: val@physics.utah.edu (Z.V. Vardeny).

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were used: H-DOO-PPV (fully protonated-hydrogen), D-DOO-PPV (deuterated-hydrogen rich), and C13-DOO-PPV (^{13}C-carbon rich). The three isotope rich DOO-PPV polymers have different a_{HFI} since skeletal protons (nuclear spin $I = 1/2$, nuclear g-factor $g_P = 5.59$) are replaced by deuterium ($I = 1$, $g_D = 0.857$) in D-DOO-PPV (causing smaller a_{HFI}); whereas some of the ^{12}C nuclei ($I = 0$, no HFI) in the C13-rich polymers are replaced by ^{13}C nuclei ($I = 1/2$, $g_{C13} = 1.406$, having substantial a_{HFI}), thus increasing the effect of the HFI. We also measured MEL with very similar responses (not shown here).

The devices used were 5 mm^2 diodes, where the organic spacers were deposited on a hole transport layer: poly(3,4-ethylenedioxythiophene) [PEDOT]–poly(styrene sulphonate) [PSS]. For the bipolar devices we capped the bilayer structure with a transparent anode: indium tin oxide [ITO], and a cathode: calcium (protected by aluminum film). We also fabricated unipolar devices: the hole-unipolar device was in the form of ITO/PEDOT-PSS/DOO-PPV/Au; whereas the electron-unipolar device was Al/LiF (~2 nm)/DOO-PPV/Ca/Al. The organic diodes were transferred to a cryostat that was placed in between the two poles of an electromagnet producing magnetic fields up to ~300 mT. The devices were driven at constant bias, V using a Keithley 236 apparatus; and the current, I was measured while sweeping B. MC(B) is defined by the relation $MC \equiv [I(B) - I(0)]/I(0)$.

3. Results and discussion

Fig. 1(a) shows the MC(B) response of several bipolar diodes for $|B| < 50$ mT at room temperature and $V > V_{BI}$, where V_{BI} is the device built-in potential at which both positive and negative charges are injected into the active layer [7]. For $|B| > 2$ mT, MC(B) is positive, monotonically increasing reaching a saturation level, MC_{max} at large B. This is the normal MC(B) response of which width ΔB increases from 2.8 mT for D-DOO-PPV, to 6.2 mT for H-DOO-PPV, to 9.1 mT for ^{13}C-DOO-PPV (see Fig. 1(c)). The correlation of ΔB with the HFI strength in the three DOO-PPV polymers proves that the HFI plays very significant role in determining the MC response in polymeric organic diodes [12]. The USMFE observed earlier in MEL(B) [12] is shown here for the MC(B) response in Fig. 1(b): starting from $B = 0$, MC(B) is first negative reaching a minimum, MC_{min} at $B = B_m$, where it starts increasing, reverses its sign and increases thereafter. We found that B_m is isotope dependent. The USMFE response component shows up in MC(B) responses of most organic devices that we have measured. When we plot B_m vs. ΔB for the three DOO-PPV isotopes (Figs. 1(c)), it appears that B_m increases with ΔB (i.e. larger a_{HFI}).

The USMFE response is not limited to bipolar devices. In Fig. 2(a) and (b) we show MC responses of hole-only DOO-PPV diodes; similar responses were also measured for MEH-PPV devices for both hole-only and electron-only unipolar diodes [13]. The monotonic, high-field MC component in unipolar devices is negative (Fig. 2(a)) [10], and thus the USMFE response here appears as 'negative-to-positive' sign reversal with a pronounced maximum at B_m. Fig. 2(b) shows that $B_m \sim 0.15$ mT for the H-DOO-PPV hole-only device, whereas $B_m \sim 0.4$ mT for the C13-DOO-PPV hole-only device. Importantly, the width ΔB in MEH-PPV is smaller by a factor of three in the hole-only device compared to the electron-only device [13]; this is consistent with smaller a_{HFI} for holes than for electrons, in agreement with recent measurements using transient spin response [14]. We therefore conclude that B_m increases with ΔB (and consequently with a_{HFI}) in unipolar devices as in bipolar devices.

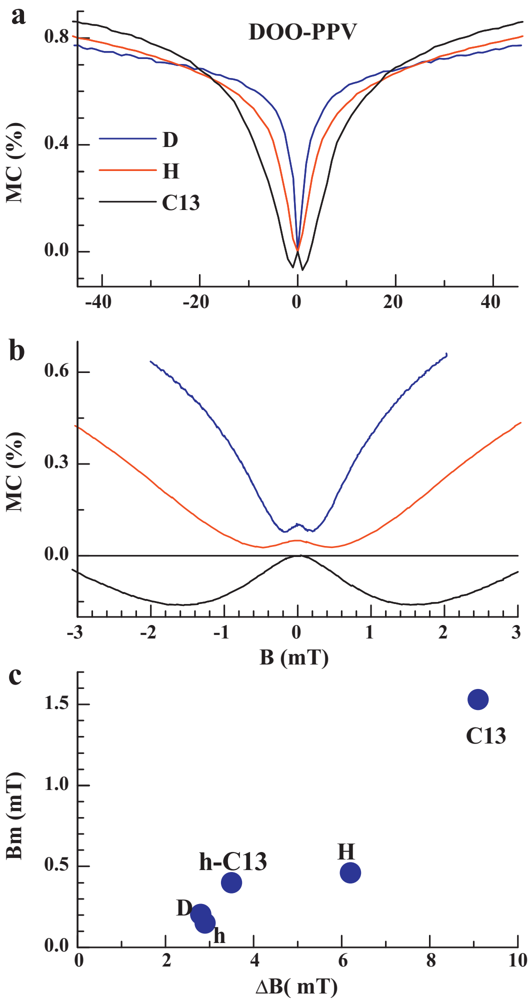

Fig. 1. Magnetoconductance (MC) response vs. field, B in bipolar organic diodes based on three isotopes of DOO-PPV polymers, namely: H-, D- and C13-DOO-PPV. Panel (a) shows MC(B) for $|B| < 50$ mT, panel (b) shows the MC(B) measured with high field resolution, for $|B| < 3$ mT (some MC responses are shifted vertically for clarity). MC_{max} is the saturation MC value at large B. ΔB is the HWHM for the normal MC(B) response shown in (a); B_m is the field at which the MC response in (b) reaches a minimum. Panel (c) summarizes B_m vs. ΔB for the MC(B) responses shown in (a), as well as the USMFE response of hole-only H- and C13-DOO-PPV shown in Fig. 2.

In order to explain the MC(B) in the organics, it has been generally assumed that some of the injected spin 1/2 carriers form weakly bound SP in either singlet $(SP)_S$ or triplet $(SP)_T$ spin configuration. At $B = 0$, the singlet and triplet intermix due to the hyperfine interaction. As B increases, the intermixing between the two spin configurations decreases due to the increased Zeeman splitting, thereby affecting their respective populations; this leads to a monotonous $MC_M(B)$ response [8,9]. However, in the presence of exchange interaction, $J \neq 0$ a new $MC_{LC}(B)$ component emerges at $B \approx B_{LC} = J$, where a singlet–triplet level-crossing (LC) occurs giving rise to excess spin intermixing between the singlet and triplet SP manifolds. The $MC_{LC}(B)$ component has therefore an opposite sign with respect to the more regular $MC_M(B)$ response, which results in a strong MC(B) modulation at $B = B_{LC}$ [15]. Recognizing the high degree of level degeneracy at $B = 0$ of a pair of charge carriers interacting with neighboring nuclei, we explain the USMFE response as due to a LC response at $B = 0$; this model is viable even for $J = 0$.

Our model is based on the time evolution of the SP spin sublevels in a magnetic field. For bipolar devices the SP species is the polaron-pair, whereas for unipolar devices the SP species is a π-dimer (i.e. bi-radical, or bipolaron [6,9]). The spin Hamiltonian, H, includes exchange interaction, HFI and Zeeman terms: $H = H_{Zeeman} + H_{HFI} + H_{ex}$; where $H_{HFI} = g\mu_B\sum_{i=1}^{2}\sum_{j=1}^{N_i}[S_i \cdot$