Theory of imbalanced electron-hole transport in conjugated polymers

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Electron-hole symmetry in conjugated polymers is found to exist in not only the band structure but also the defect levels caused by structure disorder. The commonly observed higher hole mobility is explained by (1) the compensation of the hole traps by the unintentional background p doping; and (2) the electron traps caused by oxidation. Higher electron mobility in N and O containing conjugated polymers is also explained. Carrier mobility is calculated as a function of doping condition and electric field. Balanced electron-hole transport is shown to be achievable by intentional n doping.

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I. INTRODUCTION

Conjugated polymers have emerged as a class of promising materials for optoelectronic applications.[1] One of the outstanding features of the highly electroluminescent (EL) conjugated polymers, with backbones containing exclusively carbon atoms (so-called p type), is that the hole mobility is in general several orders of magnitude larger than the electron mobility.[2,3] This imbalance causes unmatched electron-hole injection in polymer light-emitting diodes and is a major limit for their efficiency. This is quite surprising because the electron and hole effective masses differ by no more than a factor of 2 in *ab initio* calculations.[4] On the other hand, in the so-called n-type conjugated polymers, whose backbones contain oxygen or nitrogen atoms, the situation is reserved and the holes have a lower mobility than the electrons.[5] Microwave experiments demonstrated that the electron and hole mobilities are similar when the polymer chains are isolated in solution,[6] suggesting that the imbalance is related to the traps due to the structure defect levels in the films. However, as shown by the tight-binding calculation below, the structure disorder causes defect levels with electron-hole symmetry and cannot be the reason for the imbalance by itself. Little is known about how the symmetry is broken in transport.

In this work we propose that there are two origins for the imbalance in the carbon-backbone EL conjugated polymers, e.g., poly(p-phenylene vinylene) (PPV) and polyfluorene (PF). The first is the compensation of the hole traps due to structure defects by the background unintentional p doping, which generally occurs because of the relatively smaller electron-negativity (EN) of the polymer. Because the deepest traps are compensated first, a slight amount of compensation has a dramatic effect on the mobility. The second origin is that oxidation of the polymers causes electron traps but not hole traps. Oxygen has a lower on-site energy (higher EN) than the carbon, and causes a local potential well for the electrons but not for holes. In n-type polymers no traps are caused by oxidation because the energy of the bands of the O- and N- containing backbone is close to the energy of the addition oxygen. The asymmetric effect of oxidation is confirmed by tight-binding calculation for both p- and n-type polymers. The consequence of trap compensation by doping

on transport properties is studied in detail by calculating the carrier field-tunneling rate out of the traps, and the mobilities as functions of doping density and electric field. It is found that balanced electron-hole mobility can be achieved by tuning the intentional n doping, or equivalently Fermi level, for the p-type polymers.

II. BREAKING OF SYMMETRY IN DEFECTS

The band structure and trap position are calculated within the tight-binding model for PPV and PF. The chemical structures of the two polymers are shown in Fig. 1. The nearest-neighbor resonance integrals are also indicated. The values used for perfect polymer chains are $t_1=-2.2$ eV, $t_2=-3.0$ eV, and $t_3=-3.1$ eV for PPV; $t_1=-2.2$ eV, $t_3=-3.1$ eV, and $t_b=-3.0$ eV for PF. The t's are adjusted to fit the conduction and valance band structures obtained from more sophisticated methods.[4,7] The band structures have an exact electron-hole symmetry, with the Fermi level E_F located at zero energy (Fig. 1). The symmetry can be slightly broken if we introduce the small second nearest neighbor resonance integral.[8] Now we consider the structure defects which cause energy levels in the energy gap (carrier traps), neglecting ring distortions and considering a one-bond defect in one single repeat unit, with all other units remaining perfect. In practice a long chain with 50 units and periodic boundary condition is diagonalized. For PPV, defect levels can be caused only by the reduction of the double-bond resonance integral t_2 in the vinyl group[9] because local reduction of t_2 causes a smaller local vinyl double splitting which sets the band gap. Reduction of single bond t_1 does not cause any defect level.[9] For PF, defect level occurs only for increase of the bridge bond t_b because it causes larger splitting between the molecular orbitals of the two rings and pushes the levels closer to zero. No defect level occurs for t_b reduction. A t_b increase is less likely to happen compared with t_2 twist, so fewer traps are expected in PF.[10] In Fig. 1 the energy of the defect levels are shown as functions of the bond distortion. t_0 is the resonance integral for the bond in a perfect chain, while t is for the distorted bond, which is marked in the polymer chemical structures. For intrinsic polymers the defect levels are symmetrically placed around E_F. There is therefore a one-to-one correspondence between the electron
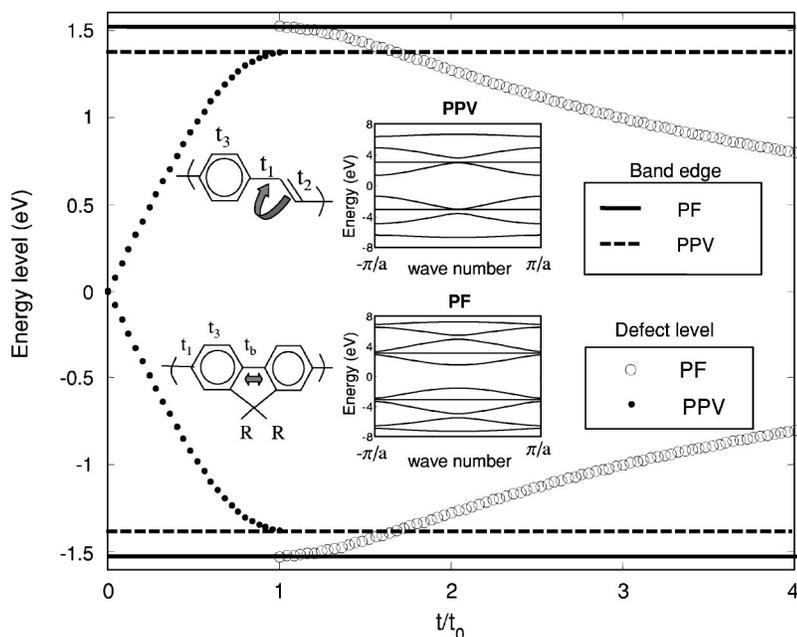
FIG. 1. The energy bands and defect levels for PPV and PF are shown. The defect levels are symmetric with respect to the Fermi level at zero energy. The distorted bonds are indicated in the chemical structures. t_0 is the resonance integral for the bond in a perfect chain. There is no defect level for t_1 increase (PPV) or t_b reduction (PF).

traps (above E_F) and hole traps (below E_F). We have considered many other defects for PPV and PF, including distortions in more than one bond, sp^3, and cross-links. None of them introduce asymmetric defect levels. This is consistent with the defect positions measured experimentally.[11] Structure defects in the film alone therefore cannot account for the great imbalance in carrier transport. We believe that imbalance is caused by the hole-trap compensation discussed below.

The highly electroluminescent polymers contain only carbon atoms in the π-backbone. Because the EN of carbon (2.5 eV) is smaller than the EN of other common atoms like nitrogen (3.0 eV), oxygen (3.5 eV), and chlorine (3.0 eV) in organic materials,[12] the electrons will transfer from the EL polymer to the nearby residual molecules in the film which contain N, O, and halogens. We believe that such a difference in EN and the resulting electron transfer is the reason for the prevalent unintentional background p doping. Such p doping introduces shallow empty acceptor levels just above the valence band, the electrons in the defect levels will drop into the empty acceptor levels such that the defect levels become empty and inactive for the holes. In other words the defect traps are compensated by the shallow acceptor levels [Fig. 2(a)]. If the residual molecule happens to be close to

the structure defect, it is also possible that the electron transfers directly from the defect level to the molecule without the intermediate step through the shallow level. Similar to the case of p doping, with n doping the electrons in the donor level can drop into the electron traps (empty defect levels) and make them inactive, i.e., the electron traps are compensated by the donor levels [Fig. 2(b)]. The inactivated hole traps can be reactivated by the additional n doping because the extra electrons can fill up the empty defect levels. One can therefore control the ratio between the active electron and hole traps by intentionally n doping a polymer film with an unintentional background p doping. Mobility ratio is changed accordingly. For the N and O containing polymers the EN of the backbone is larger than most residual molecules. So they are background n doped instead. Higher electron mobility results from compensation of electron traps.

Now we consider the role of oxidation in the imbalance with a tight-binding model for the oxygen defect. We use poly (p-pyridyl vinylene) (PPyV, see Fig. 3) as a model system. The on-site energy ε_O and ε_N for O and N atoms are -2.2 and -1.3 eV, respectively.[13] They are roughly proportional to the EN differences with the carbon atom. In order to illustrate the key point that oxygen is effective in causing electron trap only for p-type polymers, ε_N is artificially adjusted to tune the EN of PPyV. For simplicity, two O atoms
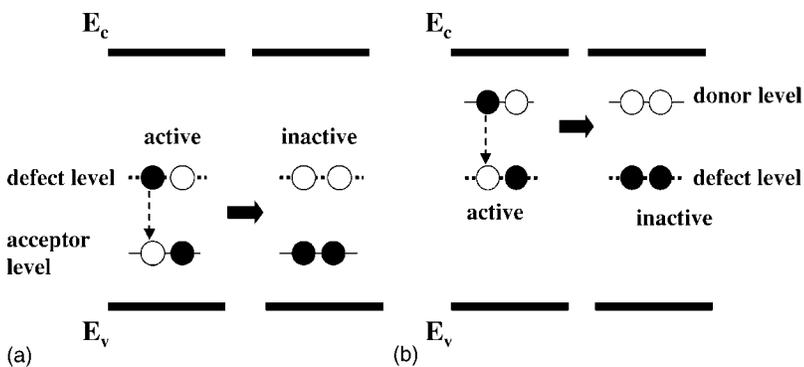

FIG. 2. (a) The hole trap (occupied defect level) is compensated by p doping. (b) The electron trap is compensated by n doping. Closed circles: occupied. Open circles: empty.
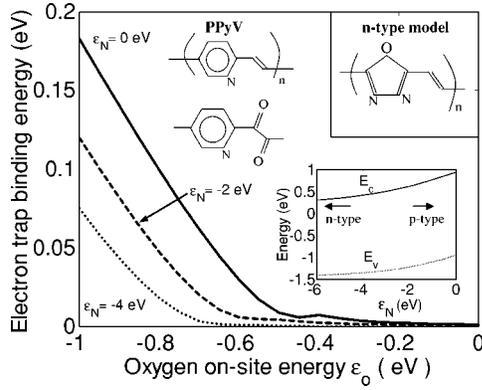
FIG. 3. The binding energy of the defect level of PPyV due to oxidation is plotted as a function of oxygen on-site energy ε_O for polymers with various electron negativity tuned by nitrogen on-site energy ε_N. The defect is deeper for less electronegative polymer (smaller $|\varepsilon_N|$, p type). The chemical structure of PPyV and the model n-type polymer are shown (see text).

are assumed to be attached symmetrically to one unit of PPyV in the oxidized form (Fig. 3) while other units remain perfect. ε_O is taken as a variable artificially as well. PPyV reduces to PPV as $\varepsilon_N = 0$. The resonance integral for the O–C bond is -2.2 eV,[13] and -1.4 eV for the N–C bond to fit the band gap of PPyV.[14] For fixed ε_N, a defect level emerges from the conduction band, with wave function localized around the oxygen atom if $|\varepsilon_O|$ exceeds a critical value (Fig. 3). The larger $|\varepsilon_O|$ is, the more electronegative the oxygen is relative to the backbone. So eventually the oxygen pulls an empty level off the tight-binding continuum which acts as an electron trap. Oxidation does not cause hole trap, even though it limits the motion of the free holes severely.[15] Because whether there is a trap is determined by the relative EN of the oxygen and the backbone, we artificially adjust the EN of the backbone by changing ε_N. As we increase $|\varepsilon_N|$ the backbone evolves from a p-type to an n-type polymer (increasingly electronegative). As expected the binding energy decreases as ε_N increases (and the EN difference between the backbone and the oxygen defect diminishes). A similar level appears for oxidized PF also. These results demonstrate that the oxidation of the p-type EL polymers is at least partially responsible for the dominance of electron traps and the breaking of the electron-hole symmetry. In reality we expect that oxidation and structure disorder coexist and both contribute to the electron traps. Their relative importance depends on the preparation of the particular sample. For the n-type polymers (large $|\varepsilon_N|$) there are shallower or no electron traps even if they are oxidized. The change of the conduction and valence band edges $E_{c,v}$ are shown as an inset in Fig. 3. Lower band edge implies a smaller electron injection barrier, another feature of n-type polymers. We also consider the oxidation of another hypothetical model n-type system poly(oxadiazole vinylene) (Fig. 3) and found that there is no defect level for $\varepsilon_O = -2.2$ eV and $\varepsilon_N = -1.3$ eV. Obviously the large amount of N and O in the backbone make the additional O insignificant. It is reported that there are many hole traps in the n-type polymers,[5] suggesting that those traps are exclusively due to uncompensated structure defects

since oxidation is not expected to cause traps.

III. DEFECTS AND MOBILITY

So far we have considered only a single trap. The mobility is determined by the trap distribution and E_F, which is controlled by doping. In order to make quantitative predictions on the relation between carrier mobilities and doping, we need the carrier escape rate from the trap as a function of applied electric field F and trap binding energy ε_T. The phonon-assisted field tunneling from a point defect level in inorganic crystalline semiconductors is studied by Makram-Ebeid and Lannoo.[16] Even though conjugated polymer film is not a crystal, this theory can be applied because tunneling is a process which occurs within a conjugation segment with local one-dimensional periodicity and energy bands. The immediate final state of the tunneling is an extended intrasegment wave function as in inorganic semiconductors. Inter-chain hopping occurs only afterwards as subsequent independent processes and will be discussed later. The tunneling rate W from the trap is

$$W = \frac{2\pi}{\hbar} A\upsilon_b \sum_f |\langle \psi_b \chi_b| - eFz | \psi_f \chi_f \rangle|^2 \delta(E_f - E_b), \quad (1)$$

where $A\upsilon$ denotes the thermal average. b and f indicate bound and free states, respectively. $\psi_{b,f}$ is the single-electron wave function and $\chi_{b,f}$ is the lattice wave function. $\psi_{b,f}\chi_{b,f}$ are the Born-Oppenheimer products. The field F is applied along the z direction. In terms of the binding energy ε_T the escape rate can be written as[16]

$$W = \sum_{m=-\infty}^{\infty} W_m P(\varepsilon_T + m\hbar\omega), \quad \text{with}$$

$$P(\varepsilon) = (F/2\hbar)(\hbar^2/2m^*)^{1/2}\exp[-4/3(2m^*/\hbar)^{1/2}(\varepsilon^{3/2}/F)],$$

$$W_m = \{\exp(-2\eta/\sqrt{2S})[(1+\eta/\sqrt{2S})/(1-\eta/\sqrt{2S})]\}^m$$

$$\times W_m^0[S(1-\eta^2/2S)], \quad \text{and}$$

$$W_m^0(S) = \exp[m\hbar\omega/2kT - S\coth(\hbar\omega/2kT)]$$

$$\times I_m[S/\sinh(\hbar\omega/2kT)].$$

I_m is the Bessel function. m is the difference between the phonon numbers of the final and initial states. η is $-2(2S)^{1/2}\hbar\omega/\varepsilon_T$. k is the Boltzman constant, and T is temperature. $\hbar\omega = 0.17$ eV is the optical phonon energy. The effective mass m^* is obtained from the band structures. The resonance integral of the distorted bond is expressed as $t(x) = t|_{x=0}(1+\alpha x)$. t is the resonance for the empty distorted bond which determines ε_T. x is the bond length change. $\alpha = 4.1$ eV/Å (Ref. 17) is the effective electron-phonon coupling constant. The dimensionless lattice coordinate Q is defined by $x = \sqrt{\hbar/(M\omega)}Q$, where M is the carbon atom mass.[18] Using Fig. 1 and $t(x)$ the defect electronic energy can be expressed as a function of Q. When the defect is occupied
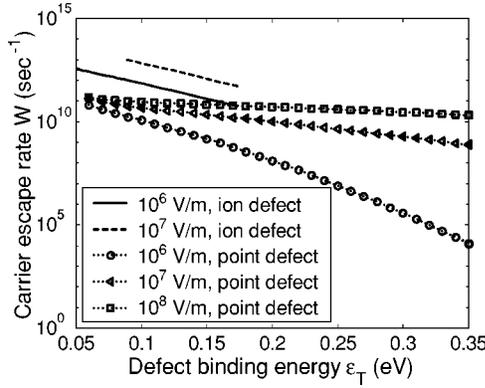
FIG. 4. The escape rate W out of the trap is plotted as a function of the trap binding energy ε_T. The rate for shallow ionic defect due to doping is also shown. The electric field F is indicated.

the total energy is the sum of the electronic energy and the lattice energy $(1/2)\hbar\omega Q^2$. The equilibrium lattice coordinate Q^* is located at the minimum of the total energy. The Huang-Rys factor S is $Q^{*2}/2$. The point defect escape rate W is plotted in Fig. 4. The rate drops several orders of magnitude as the binding energy ε_T increases. So the existence of a few deeper levels can have a dramatically large effect on the overall transport. The ionized acceptor/donor may also cause shallow traps for the carriers which are self-localized as polarons. For the polarons the escape rate out of the shallow ionic potential is given by[19] $W_{\mathrm{ion}}=\omega_p/2\pi\exp(-\varepsilon_T+e_f/kT)$ where $e_f=2\sqrt{e^3F/\kappa}$. $\kappa=8$ is the dielectric constant. ε_T is the barrier of the averaged ionic Coulomb potential experienced by a polaron. ω_p is the oscillation frequency of the polaron around the bottom of the averaged potential well. The rates are shown in Fig. 4. The vertical distance between the ion and the backbone is taken as 2 Å, about half the interchain distance.[20] The barrier disappears for a typical field around 10^8 V/m in a light-emitting diode. So the ionic defects can hardly trap the carriers and are neglected in the calculation of mobilities.

For structure defects the trap distribution is taken as exponential: $\rho_t(\varepsilon)=(x_t/\sigma_t)\exp[(\varepsilon-E_c)/\sigma_t]$ for electrons and $\rho_t(\varepsilon)=(x_t/\sigma_t)\exp[(E_v-\varepsilon)/\sigma_t]$ for holes. For oxidation the electron traps have a δ distribution: $\rho_t(\varepsilon)=x_t\delta[\varepsilon-(E_c-\sigma_t)]$. ε is the trap energy. The dimensionless trap density x_t is the averaged number of traps per repeat unit. For both electron and hole the trap density of states is cut off at the midgap. In conjugated polymers the electric transport is due to the carrier hopping among conjugation segments with variable energy. Without the traps the carriers are in the form of polarons in the segments, and the polaron hopping mobility follows the Poole-Frenkel law[2] $\mu_{\mathrm{PF}}=\mu_0\exp(\gamma\sqrt{F})$. In the presence of the point defects in the segments the carriers have to tunnel out of the traps into the free carrier continuum in order to form a mobile polaron and contribute to the hopping transport. The fraction of the carriers in the traps must be taken into account in the calculation of the overall mobility μ, which can be determined as follows. Assume n_T and n_F are the density of trapped and free carriers (mobile polarons), respectively. The total carrier density n_{tot} is n_T+n_F. The particle current j can be expressed as $j=n_{\mathrm{tot}}\mu F=n_F\mu_{\mathrm{PF}}F$, which implies
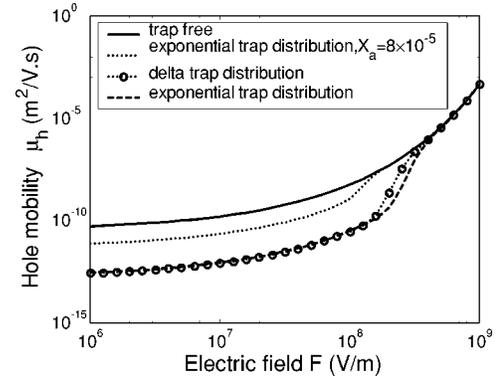

FIG. 5. The effect of traps and their compensations on the hole mobility μ_h are shown. Solid line: no trap; dashed line: exponential traps without doping; dotted line: exponential traps with p doping; and dot-circle line: δ traps without doping. $\sigma_t=0.13$ eV for exponential and $\sigma_t=0.5$ eV for δ distribution.

$$\mu=\frac{1}{1+\dfrac{n_T}{n_F}}\mu_{\mathrm{PF}}. \qquad (2)$$

The ratio n_T/n_F between trapped and free carriers can be obtained from the transition rates. Let $W_{1(2)}$ be the transition rate from a free band state (trap) to a trap (free) state. W_2 can be decomposed as $W_2=W_2^{th}+W_2^f$, where W_2^{th} is the thermal activation rate and W_2^f is the field tunneling rate defined in Eq. (1). For electrons without field we have $W_2^{th}/W_1=e^{-\beta(E_c-\varepsilon)}$ in equilibrium. $1/\beta$ is kT. The ratio between the trapping and escaping rates is therefore $W_2/W_1=e^{-\beta(E_c-\varepsilon)}[1+(W_2^f/W_2^{th})]=e^{-\beta(E_c-\varepsilon)}\xi$, where $\xi\equiv1+(W_2^f/W_2^{th})$. W_2^{th} can be approximated as $\omega/2\pi e^{-\beta(E_c-\varepsilon)}$, where ω is the optical phonon energy.[19] Including the Pauli exclusion principle in detailed balance, the occupation probability g_T and $g_F=g(E_c)$ for trap and free states are related by $g(\varepsilon)W_2[1-g(E_c)]=g(E_c)W_1[1-g(\varepsilon)]$. The relation can be reorganized as $g(\varepsilon)=\{[1-g(E_c)]W_2/[g(E_c)W_1]+1\}^{-1}$. Assuming $E_c-E_F\gg1/\beta$, the occupation probability $g(E_c)$ for the free state is approximated by the Boltzmann factor $e^{-\beta(E_c-E_F)}$. The defect occupation probability becomes $g_T(\varepsilon)=[1+\xi e^{\beta(\varepsilon-E_F)}]^{-1}$. The Fermi distribution is recovered if there is no field ($\xi=1$). The density of trapped electron n_T is $\int_{-\infty}^{E_c}g_T(\varepsilon)\rho_t(\varepsilon)d\varepsilon$. The total density of free carrier n_F is X_cg_F. $X_c=N_c\upsilon$, where N_c is the effective band density of state and υ is the unit cell volume. The trapping ratio in Eq. (2) is finally expressed as

$$\frac{n_T}{n_F}=\frac{1}{X_c}\int_{-\infty}^{E_c}\frac{g_T(\varepsilon)}{g_F}\rho_t(\varepsilon)d\varepsilon. \qquad (3)$$

Equation (3) is substituted into Eq. (2) to obtain the mobility μ as a function of F and E_F. For holes the integral is from E_v to ∞.

In Fig. 5 we plot the hole mobility μ_h against electric field F for some trap density x_t. $\gamma=5.2\times10^{-4}$ (m/V)$^{1/2}$, $N_c=2.5\times10^{19}$ cm^{-3}, and $\upsilon=2.7\times10^{-22}$ cm^3. As $x_t=0$, μ_h follows the usual Poole-Frenkel form. For finite x_t the mobility is significantly suppressed in the lower field region without

background p doping ($E_F=0$). As F increases the field tunneling rate out of the trap becomes larger than the thermal activation rate. The thermal equilibrium is broken and the carrier population in the traps start to be depleted. μ_h becomes identical to the trap-free value as F further increases. The transition from the trap-dominated to free mobility is more abrupt for the δ distribution than the exponential distribution as expected. In fact this difference can be used to tell whether the predominant traps are due to structure disorder or oxidation. As the polymer is p doped the deep hole traps are compensated and the mobility increases. There is a two orders of magnitude increase of μ_h for doping as slight as $x_a=8\times10^{-5}$. In Fig. 6 we plot the electron and hole mobilities μ_e and μ_h as functions of intentional n doping x_d for a fixed unintentional p doping x_a. As x_d increases the deep hole traps are reactivated and μ_h drops. Eventually the electron traps start to be filled (inactivated) by the doping and μ_e starts to rise. There is a near mirror symmetry of the two curves around $x_d=x_a$. For a given material with fixed structure disorder, the ratio between μ_e and μ_h is therefore not a constant but can be continuously tuned by doping. EL efficiency can be improved by balancing the carrier injection if either chemical or electrochemical n doping can be made practical for the polymers like PPV and PF.

IV. CONCLUSION

It is shown that the electron-hole symmetry exists in the trap levels for conjugated polymers with structure defects. The oxygen defects and the background p doping which
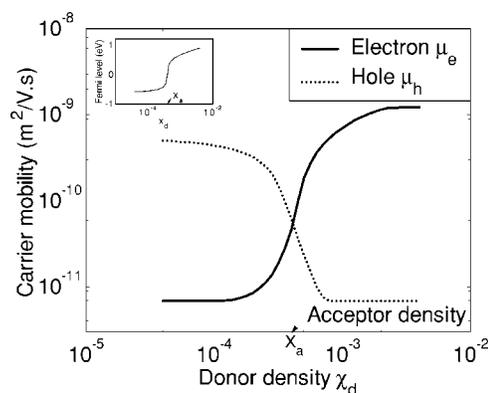

FIG. 6. The carrier mobilities μ_e and μ_h, plotted as functions of the n-doping density x_d, are shown to have a near mirror symmetry with respect to the background p-doping density x_a. The compensated hole traps are reactivated while the electron traps are compensated as x_d crosses x_a. The Fermi level E_F is also shown.

compensates the hole traps are the origins for the imbalanced electron-hole transport. Equal electron and hole mobilities can be achieved by intentional n doping.

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