PHYSICAL REVIEW B VOLUME 29, NUMBER 8 15 APRIL 1984

Bipolaron transport in doped conjugated polymers

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(Received 7 October 1983)

Interchain hopping of bipolarons (doubly charged defects) is discussed as a mechanism for spinless conductivity in doped polyacetylene, doped poly(*p*-phenylene), and other doped polymers. It is shown that this mechanism can account for the observed dopant-concentration dependence of the conductivity in *trans*-polyacetylene and the observation of anomalously low magnetic susceptibilities in the highly conducting regime of several doped polymers.

I. INTRODUCTION

The discovery of relatively high conductivities in doped organic polymers[1] was surprising because almost all organic systems have rather low conductivities due to the large band gaps, strong electron-phonon coupling, and large site fluctuations which are characteristic of these materials.[2] The anomalous behavior of the magnetic susceptibility of doped polyacetylene[3] (i.e., appearance of a high-conductivity regime with low spin concentration) led to the novel idea that the mobile species responsible for conduction at low doping concentration is a charged spinless soliton.[4,5] The model of Su, Schrieffer, and Heeger,[4] improving on the earlier work of Pople and Walmsley,[6] used simple Hückel theory and elastic energy arguments.[7] In spite of the crudeness of the model, it seems to fit much of the optical, infrared, and magnetic data—particularly when polaron states (bound charged-soliton—neutral-antisoliton pairs) are included.[8,9] However, this description only works when there are degenerate ground states as in *trans*-polyacetylene, for only then are the solitons free to move independently. Thus, although the model describes *trans*-polyacetylene, there are many other organic polymer systems which show very much the same experimental results as polyacetylene (high conductivity, growing infrared and near-infrared absorption, and anomalous magnetic susceptibility), but which are unable to support topological solitons because they do not have degenerate ground-state structures. Although the list of such polymers is long [poly(*p*-phenylene), polypyrrole, polythiophene, poly(*p*-phenylene sulfide), etc.], we discuss a prototypical example, poly(*p*-phenylene) (PPP), in this paper.

We first review the experimental observations. When polyacetylene (PA) is doped with an electron acceptor such as AsF_5, the conductivity rises sharply with dopant concentration (C), and then saturates at a value ~ 1000 S/cm.[10] At the same time the optical absorption, which has an onset of 1.4 eV and a peak at 1.5 eV in the undoped *trans* material,[11] begins to grow in the "mid-gap" region (~ 0.7—1.0 eV).[12] The magnetic susceptibility shows a decrease of free spins initially upon doping and no normal metalliclike features until rather high doping levels ($C > 5\%$).[3] (The spin concentration is nonzero in the undoped *trans* material due to neutral solitons, or free radical defects, formed in the chain upon *cis-trans* isomerization.) As we pointed out above, these experimental results can be explained in principle by a model which ascribes the conductivity and optical absorption to spinless charged solitons, based on the degenerate ground-state structures in *trans*-PA. Because of this degeneracy, the positively charged species formed upon ionization can be split into two species, a charged spinless soliton and a neutral antisoliton with spin, each with an associated lattice distortion. In the PA structure there is (at least) one bound state of the neutral antisoliton and charged soliton, i.e., a polaron or radical ion which can contribute to the conductivity and optical absorption. However, two adjacent polarons are unstable with respect to forming two spinless charged solitons[8,9] (although there should be a concentration-dependent activation barrier[8]).

The experimental evidence in the PPP case is qualitatively the same as in PA with regard to conductivity,[13] optical absorption,[14] and spin properties.[15] This is surprising, since, as previously stressed, PPP and all other known examples of doped conducting polymers except *trans*-PA do not support free solitons because of the nondegenerate ground state.[8] The PPP structure analogous to the other ground state in *trans*-PA is the quinoidal structure which has significantly higher energy than the benzenoid structure. As a consequence, solitons in PPP are always bound in pairs. Thus upon doping, polarons are formed on the PPP chain—carrying spin as well as charge. However, our calculations[8] indicate that the most easily ionized electron in the system is the unpaired electron in the polaron; thus upon further ionization a spinless doubly charged species, a bipolaron, can be formed. In other words, in analogy to *trans*-PA, two polarons on a PPP chain are unstable with respect to forming a spinless defect, a bipolaron. The spatial extent of the PPP polaron—that is, the extent of the lattice distortion associated with the defect—is 4 to 5 rings; the extent of the bipolaron is similar.[8] The polaron and bipolaron structures in PPP can explain the new optical absorption upon doping[14] and the anomalous spin properties,[15] at least qualitatively. They also predict a relatively facile transport along a single chain because these structures, as in the charged soliton in polyacetylene, should have fairly high intrachain mobility (when the charge of the counterion is sufficiently screened).

Although the above model seems to fit much of the experimental data and makes a nice connection between *trans*-PA and PPP (as well as all the other doped polymer systems), there remains the problem of interchain transport of the charged species, whether soliton, polaron, or bipolaron. This process is very likely to be the rate-determining step in the conductivity, especially in the PPP case where chains contain only a small number (~ 20) of monomer units.[13]

It is important to stress that any transport model based on polarons or electron hopping between soliton (or bipolaron) sites must show a corresponding magnetic susceptibility. Mele and Rice[16] have introduced disorder and three-dimensional effects into the one-dimensional soliton model and have calculated a finite density of states at the Fermi level for doped polyacetylene. Thus in this model an *electron* could hop between states produced by solitons pinned at dopant sites to yield observed conductivities. Although this model can deal with low spin concentration, it cannot treat truly spinless conduction. This idea has been developed further by Epstein *et al.*[17] via incorporation into a variable-range—hopping model which explains transport data for iodine-doped PA, but fails in other cases, notably AsF_5- and Na-doped PA, where the model appears to require a density of states at the Fermi level which is much too large.[10,18]

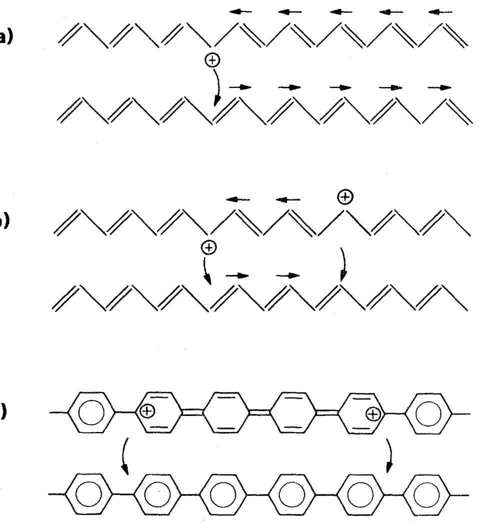

FIG. 1. (a) Interchain hopping of a soliton in *trans*-polyacetylene; arrows show required movements of carbon atoms. (b) Interchain hopping of bipolaron (two charged solitons) in *trans*-polyacetylene. (c) Interchain hopping of bipolaron in poly(*p*-phenylene).

Charged solitons and bipolarons carry no spin, and could therefore account for the vanishingly small magnetic susceptibilities observed in doped PA, doped PPP, and doped polypyrrole.[19] In this paper, we present a model for the spinless contribution to conductivity in PA and PPP based on bipolarons. It is important to emphasize that the model does not explicitly consider the dopant-ion array, and as in any other model involving charged solitons or bipolarons, transport would require screening of the dopant charges to overcome the Coulombic binding energy at the dopant site.

The paper is structured as follows. First, in Sec. II, we discuss interchain transport in *trans*-PA, a system with a degenerate ground state. In Sec. III we discuss PPP, a prototype for polymers without degenerate ground state. Conclusions are presented in Sec. IV.

II. INTERCHAIN HOPPING OF BIPOLARONS IN POLYACETYLENE

In polyacetylene, the problem of interchain transport can be distilled to the following. Consider two adjacent chains of *trans*-PA, one containing a charged soliton and the other defect free. Because the soliton and the ground-state structure have different equilibrium geometries, in order for the charged soliton to hop from one chain to the other, a large number of carbon atoms on each chain must relax to their new equilibrium positions, as depicted in Fig. 1. Although the process costs nothing in energy because all the energy lost on one chain is gained on the other, the potential barrier (activation energy) can be very large. However, it is also clear from this picture that a *pair* of solitons can jump from chain to chain with much smaller potential energy barrier, because then only a small number of carbon atoms on each chain (those between the two solitons) have to relax (see Fig. 1). This is the reason that Kivelson's model[20] for interchain charged-soliton transport requires a neutral soliton on one chain and a charged soliton on the other; the hopping process in that case would also have a small potential barrier. Note that Kivelson's theory is applicable only at low doping levels and basically deals with an extrinsic effect in that it requires the presence of the free neutral solitons created during the *cis-trans*—isomerization process.

Therefore, in the absence of free neutral solitons, a pair of charged solitons (which, by analogy with PPP, we will refer to as a bipolaron) will be the most likely structure to hop from one chain to another. Since the number of free neutral solitons in *trans*-PA is expected to decrease to essentially zero at moderate doping levels, the conductivity in PA should be dominated by interchain hopping of charged solitons pairs (bipolarons) even at rather low conductivities. Note that a bipolaron in *trans*-PA is not a stable entity. Instead, two charged solitons would show uncorrelated motion and, in fact, would repel each other (even ignoring the Coulombic repulsion) unless confinement energy is a dominant factor.[21,22] Nevertheless, a bipolaron in *trans*-PA provides an interesting vehicle for interchain transport.

In order to estimate the concentration dependence of the interchain hopping of two (charged) solitons a distance l carbon—carbon bonds apart on a *trans*-PA chain, we write the probability of a hop as

$$P(l)=aX_{12}(l)\Phi_1(l)\Phi_2(l+2)\ . \tag{2.1}$$

The factor $X_{12}(l)$ is the Franck-Condon factor (or square of the vibrational overlap) for the jump, a is the square of the electronic transfer integral, $\Phi_1(l)$ is the probability of finding a second charged soliton a distance l from the first on a single chain (chain 1), and $\Phi_2(l+2)$ is the probability of finding a structure consisting of $l+2$ carbon—carbon bonds on a neighboring chain (chain 2). We are making two assumptions here: (a) the probabilities for chains 1 and 2 are independent of one another, and (b) interchain jumps which would result in positive charges next to one another are forbidden (hence, the $l+2$ term in Φ_2). Assumption (a) is a gross oversimplification, but one which is difficult to remove. Assumption (b) infers some interaction between (positive) solitons which we believe is important. The factor $X_{12}(l)$ can be expected to decrease monotonically with l; we will assume that the functional form of X_{12} is

$$X_{12}(l)\propto\exp(-fl)\ . \tag{2.2}$$

In order to proceed, we must estimate $\Phi_1(l)$ and $\Phi_2(l)$. For simplicity, we will consider only two limiting cases. The first is when two charged solitons on a chain do not interact at all. This case is unrealistic, but instructive. The second case is when the charged solitons on a chain interact in such a way that the distribution of intersoliton distances is a peaked function (Gaussian). In the *absence* of any intrachain soliton interaction, we have

$$\Phi_1(l)=\Phi_1^{(0)}(l)=C(1-C)^{l-1}\ , \tag{2.3}$$

where C is the probability of finding the charged soliton on a site, taken to be equal to the concentration of positive charges (assumed equal to the concentration of the dopant on a per carbon atom basis). Note that we have

$$\sum_{l=1}\Phi_l(l)=1\ . \tag{2.4}$$

In PA, there are some restrictions on l due to the bonding sequence; we neglect them here for simplicity.

The expression for $\Phi_2(l)$ can be found from that for $\Phi_1(l)$, since the probability of having at least $l+2$ consecutive noncharged sites is the total probability of having a separation larger than $l+2$ between charges, that is,

$$\Phi_2(l+2)=\sum_{m=l+3}\Phi_1(m)\ , \tag{2.5a}$$

$$\Phi_2^{(0)}(l+2)=C\sum_{m=l+3}(1-C)^{m-1}=(1-C)^{l+2}\ . \tag{2.5b}$$

We then find for the hopping probability [from Eq. (2.1)],

$$P^{(0)}(l)=e^{-fl}C(1-C)^{l+2} \tag{2.6}$$

and the spinless contribution to the conductivity will be

$$\sigma_{++}(0)=AC\sum_{l=1}^{\infty}P(l)=\frac{AC^2(1-C)}{1-e^{-f}(1-C)^2}\ , \tag{2.7}$$

where A is a temperature-dependent factor containing the electronic transfer integral, etc. Note that the conductivity will be proportional to C^2 at low C, and will saturate at some concentration depending only slightly on f ($C_{\text{sat}}\sim 0.6$ for all f). This model has many of the elements necessary to obtain the correct limiting behavior, but because it does not allow for the Coulomb repulsion between charged solitons [except in so far as $\Phi_2(l)$ begins with $l=l+2$], $\Phi_1(l)$ is overestimated at small l, and the model is not useful for calculational purposes.

In order to include Coulomb repulsion between charged solitons, at least qualitatively, we perform the calculation in the case that Coulomb repulsion makes $\Phi_1(l)$ strongly peaked [in contrast to $\Phi_1^{(0)}(l)$]. For example, if we take a Gaussian of width d centered at $\langle l\rangle$ for the distribution of nearest intersoliton distances, we obtain

$$\Phi_1(l)=N^{-1}\exp[-(l-\langle l\rangle)^2/d^2]\ , \tag{2.8a}$$

with the normalization factor N given by

$$N=\sum_{l=1}^{\infty}\exp[-(l-\langle l\rangle)^2/d^2]\ . \tag{2.8b}$$

Now, $\Phi_1(l)$, $\Phi_2(l)$, and $\sigma_{++}(l)$ can be computed, and in Fig. 2 we plot σ_{++} vs C for $\langle l\rangle=1/C$ and representative values of d (equal to $\langle l\rangle/4$ and $\langle l\rangle/2$) and f (equal to 0.05 and 0.1). The experimental data are a composite of

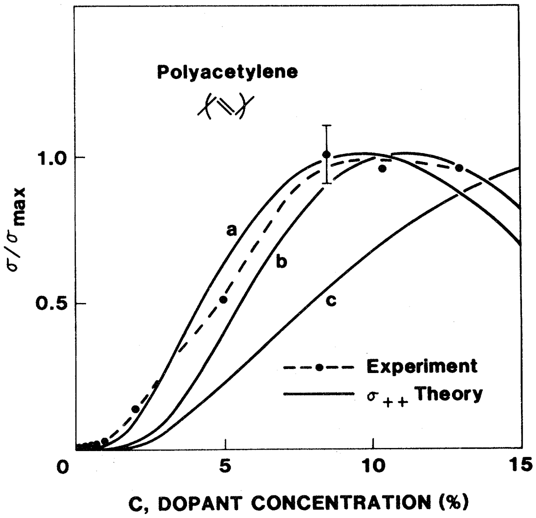

FIG. 2. Normalized conductivity vs dopant concentration C for polyacetylene. Experimental data are taken from Refs. 10 and 23. The theoretical curves describe the bipolaron contribution to the conductivity according to the model described in this paper. Curve a: $d=\langle l\rangle/4$ and $f=0.05$; curve b: $d=\langle l\rangle/4$ and $f=0.10$; and curve c: $d=\langle l\rangle/2$ and $f=0.10$, where $\langle l\rangle$ is the average distance between solitons (equal to $1/C$), d is the width of the soliton distribution, and f is the parameter for the Franck-Condon factor.

Moses *et al.*[10] at low doping levels and Park *et al.*[23] at high ($>5\%$) doping levels. The "spinless-conductivity" regime is the region up to about 7% doping levels, where the magnetic susceptibility rises dramatically.[3] In agreement with experiment, σ_{++} shows a rapid rise at small C and a saturation with intermediate C. The calculations are quite sensitive to the width of the soliton distribution, as could be expected within this model, and less sensitive to modest changes in the Franck-Condon factor. At high values of C, σ_{++} decreases in our model due to the lack of a suitable landing place on chain 2 for the bipolaron. Recall that we are only calculating the spinless contribution to the conductivity. Conductivity with spin commences at the 7% doping level, at which point there probably is overlap between the soliton band and the valence band of the polymers and facile generation of carriers with spin.[8,24]

III. INTERCHAIN HOPPING OF BIPOLARONS IN POLYPARAPHENYLENE

In the case of PPP or any other nondegenerate ground-state polymer, spinless conductivity has to be based on bipolarons. There is some experimental indication of the existence of bipolarons in AsF$_5$-doped PPP (Ref. 14) as well as in highly conducting polypyrrole.[19,25,26] In nondegenerate ground-state systems, the two charged solitons making up the bipolaron are at a fixed distance ($l=L$) from each other and their motion is strongly correlated. Of course, the distance may fluctuate slightly; however, this will not be important in our discussion and can be ignored. We assume that the bipolarons on the chain can be thought of as rods of length L on a line; thus $\Phi_1(l)$ is a δ function,

$$\Phi_1(l)=\delta_{l,L} \ . \qquad (3.1)$$

In order for the second chain to accept the bipolaron, this second chain must not have another bipolaron whose center is within $(L+1)/2$ units on either side of center of the bipolaron on the first chain. Thus, for noncorrelated bipolarons,

$$\Phi_2^{(0)}(l)=(1-c_b L)^{L+2} \ , \qquad (3.2)$$

where C_b is the concentration of bipolarons (equal to $C/2$ at intermediate to high C). We obtain

$$\sigma_{++}^{(0)} \propto C_b(1-C_b L)^{L+2} X_{1,2}(L) \ . \qquad (3.3)$$

This function will peak at $C_b \sim [L(L+3)]^{-1}$, which for PPP, where $L \sim 5$ (Fig. 3), implies $C \sim 5\%$. In order to understand the effect of Coulomb repulsion on the conductivity, we must model the distribution of separations of bipolarons on a single chain. This is a difficult problem in general, but in the limit of strong Coulomb repulsion the bipolarons will be very nearly equally spaced, and for $C_b > (2L)^{-1} \sim 0.1$ (or $C > 0.2$) there will no longer be room for the bipolaron to jump without moving many bipolarons. At $C_b = L^{-1} \sim 0.2$ ($C \sim 0.4$), there will be no room at all for the next bipolaron. Thus repulsion will tend to cut off the bipolaron contribution at concentrations above the peak in the conductivity unless a correlated motion of bipolarons is possible. The approximate calculation of Eq. (3.3) is therefore expected to be a reasonable approximation for $C \sim 0.15$. Unfortunately, there are no experimental data available for σ vs C in PPP due to the gross inhomogeneity of the doping process.[13] It should be stressed, however, that a behavior consistent with the qualitative model presented in Fig. 3 is found upon oxidation of polypyrrole.[27] At early stages of oxidation, conductivity increases dramatically, whereas the optical absorption due to bipolarons remains small, indicating an initial superlinear evolution of conductivity with respect to bipolaron concentration. At higher oxidation levels, the conductivity levels off while the bipolaron absorption bands get broader and more intense.

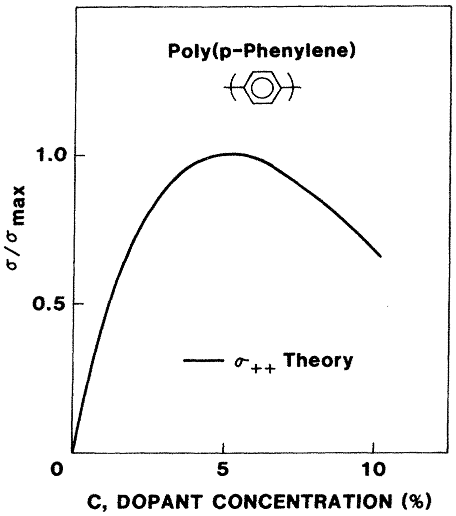

FIG. 3. Normalized conductivity vs dopant concentration for poly(p-phenylene).

IV. SUMMARY

We have presented a model for electrical transport of general applicability to doped conjugated polymers. The model is based on bipolarons, doubly charged (dication or dianion) defect states formed by combination of two polarons or by ionization of a polaron. For polymers with nondegenerate ground states such as poly(p-phenylene), the bipolaron-transport model is, in our opinion, the only model which will yield truly spinless conduction in the doped-polymer system. We have demonstrated in this paper that bipolaron transport can be applied to *trans*-polyacetylene, and that this model yields results for conductivity versus doping level which are in qualitative agreement with experimental observations. We emphasize the qualitative features of our transport model, since there are a number of aspects of the problem which are undoubtedly important, but which have not been included in the model. We have considered only bipolaron conductivity in doped-polymer films. At higher doping levels the mechanism of conductivity changes from bipolaron to another mechanism with more conventional metallic characteristics. We have not attempted to describe this transition from spinless carriers to carriers with spin. In addition, we have assumed in our bipolaron model that the relevant matrix elements (and Franck-Condon factors) do not change with concentration; if they do, we will not have computed the entire concentration dependence of the conductivity. Screening effects due to the dopant-ion array should also contribute importantly to the concentration dependence.

More study is needed in order to understand the complete implications of the bipolaron-transport model. However, it is clear that bipolarons are important in the description of transport in doped-polymer systems, especially since recent experimental results on PPP (Refs. 14 and 15) and polypyrrole (Refs. 19 and 25) are quite consistent with this description.

ACKNOWLEDGMENTS

One of us (R.R.C.) is very grateful to the Facultés Universitaires Notre-Dame de la Paix for the support that made his stay in Namur, where this work was completed, possible. We also thank D. Boudreaux for helpful comments and suggestions. Another of us (J.L.B.) was supported by the Belgian National Science Foundation.

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