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Stabilities of solitons, polarons and bipolarons in divalent-doped *trans*-polyacetylene

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Abstract. The stabilities of solitons, polarons and bipolarons in divalent-doped *trans*-polyacetylene have been studied by considering the impurity Coulomb confinement as well as the electron–electron interactions in the framework of the tight-binding Peierls–Hubbard model. It was found that transitions between bipolarons and solitons and between bipolarons and polarons will take place under certain conditions. The calculated values of the energy transitions agree well with the experimental results in the dilute Ca^{2+} -doped *trans*-polyacetylene material. The stability of excitations with respect to the impurity confinement and the electron–electron interactions have been discussed.

1. Introduction

It is well known that conjugated organic polymers can be doped to exhibit high electrical conductivities [1]. Because of the strong electron–lattice coupling of these materials, the transfer of charge from the dopant species to the polymers results in the creation of localized defects such as solitons, polarons and bipolarons in the chains. In the undegenerated ground-state conjugated polymers [2], bound pairs of topological defects stabilize the benzoid structure, resulting in the formation of soliton–antisoliton pairs or bipolarons charged doubly. In *trans*-polyacetylene, which exhibits a double degenerate ground state, the stable defects obtained are solitons or singly charged polarons. A doubly charged bipolaron could not exist in a steady state and would disintegrate into a soliton and an antisoliton which would separate from each other [3–6]. However, the optical absorption and electron paramagnetic resonance (EPR) data demonstrated that, even in doped *trans*-polyacetylene, the topological charged defects with divalent counter-ions are different from those with monovalent ions [7]. When polyacetylene was doped with monovalent counter-ions K^+ and Na^+ , the charged defects were topological solitons separating along the $(\text{CH})_x$ chains. The charged solitons were pinned to positions near the counter-cations. When doped with the divalent counter-ions Ca^{2+} and Eu^{2+} , however, the charged defects were conjectured to be soliton–antisoliton pairs or bipolarons charged doubly, which were created near the isolated divalent counter-cations on the $(\text{CH})_x$ chains. It is apparently inconsistent with the well known conclusion that in degenerate ground-state polymers the most stable excitation is a soliton. The formation of bipolarons shows that in the divalent doped *trans*-polyacetylene there is a different physical mechanism from that in undoped or monovalent-doped *trans*-polyacetylene. Recently, Phillipot *et al* [8], Harigaya *et al* [9], Stafström and Bredas [10] and Xie and Mei [11] have carried out a series of studies to investigate the impurity effect on monovalent-doped polyacetylene and predicted that even a weak interaction between π -electrons and the counter-ions can modify the energy bands. It also alters the creation energy and localization

of a soliton state. In their studies, only one single polyacetylene chain with monovalent doping was considered and the excess electron charges in the chain were supposed to be equal to the number of the impurity ions. In the divalent-doped polyacetylene, however, each impurity dopant will provide two electronic charges to the polyacetylene chains. In this case, it should be important to explain the properties of the divalent-doped polyacetylene: whether the two charges are confined to the counter-ion, leading to the formation of a doubly charged bound state, or whether they repel each other, leading to the formation of two singly charged states. In this paper, we present theoretical research on *trans*-polyacetylene doped with divalent donors. A system consisting of two neighbouring *trans*-(CH)_x chains are proposed to study the defect states in dilute divalent-doped case. By numerical iterations, the ground-state and non-linear excitations are obtained; then their stabilities with respect to the impurity counter-ions and electron-electron interactions are studied energetically.

2. Model and formula

When conjugated polymers are doped, the dopants are located between the chains and the charges will be transferred to the polymer chains from the dopants. Two possible situations could occur in the divalent-doping case: one is that the two electrons (holes) go into the same chain, and the other is that the counter-ion bridges two neighbouring chains and the charges go into two different chains, as illustrated in figure 1. The position of the impurity ions relative to a chain can be adjacent to a lattice site, usually called a 'site impurity', or to the middle of a bond, usually called a 'bond impurity'. In the bond-impurity case, the action of the impurity on π electrons can be renormalized to the following form:

$$H_{\text{IMP}}^{(j)} = -W(c_{n_j,s}^+ c_{m_j+1,s} + c_{m_j+1,s}^+ c_{m_j,s}) + \sum_{n_j,s} V(n_j) c_{n_j,s}^+ c_{n_j,s}. \quad (1)$$

The first term is the transfer integral between site m_j and $m_j + 1$ caused by the dopant ion which is located in the middle of this bond within the j th chain, and the second term the effective Coulomb binding of the counter-cation to π electrons in this chain. In the site-impurity case, only the second term is very important. In the donor-doping case, the counter-ion shows long-range confinement for π electrons. Here, a screening potential was adopted for the impurity potential [9]:

$$V(n_j) = \Theta \frac{-Ze^2}{\epsilon[(n_j - m_j - \frac{1}{2})^2 c^2 + \gamma d_j^2]^{1/2}} \exp(-\beta|n_j - m_j - \frac{1}{2}|) \quad (2)$$

where e is the magnitude of the unit charge, Z is the valence charge of the dopant, ϵ is the dielectric constant in the perpendicular direction with respect to the chains of polyacetylene materials, γ is the ratio of the dielectric constant in the parallel direction to that in the perpendicular direction (ϵ), c is the lattice constant of the undimerized chain, d_j is the perpendicular distance of the counter-ion away from the j th chain, and β is the potential screening factor along the chains. A factor Θ was introduced to take into account the degree of confinement of the counter-cation. Here we consider only the n-type doping (donor) case. Therefore, the effective potential is attractive.

Then, the Hamiltonian employed to study the doped double-chain *trans*-(CH)_x system, contains the following terms:

$$H = \sum_j (H_{\text{SSH}}^{(j)} + H_{\text{IMP}}^{(j)} + H_{e-e}^{(j)}). \quad (3)$$

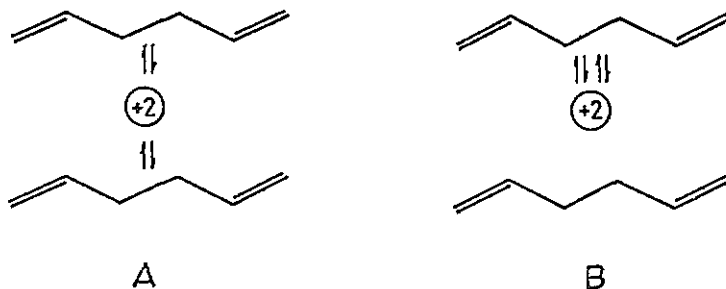


Figure 1. Possible charge transfers when *trans*-polyacetylene is doped with a divalent donor counter-cation. The doped two electron charges could be either, in case A, shared by each chain or, in case B, localized on a single chain.

Here, $H_{SSH}^{(j)}$ is the well known SSH Hamiltonian including the terms describing the π -electron hopping and the σ -bond repulsion energy within the j th chain ($j = 1, 2$) [3]:

$$H_{SSH}^{(j)} = - \sum_{n_j, s} [t_0 - \alpha(u_{n_j+1} - u_{n_j})] (c_{n_j+1, s}^+ c_{n_j, s} + c_{n_j, s}^+ c_{n_j+1, s}) + \frac{1}{2} K \sum_{n_j} (u_{n_j+1} - u_{n_j})^2 \quad (4)$$

where t_0 is the nearest-neighbour transfer integral of the undimerized chain, α is the electron-phonon coupling strength due to the modulation of the lattice, u_n is the displacement of the n th (CH) unit, $c_{n_j, s}^+$ and $c_{n_j, s}$ are the creation and annihilation operators, respectively, of an electron with spin s at site n_j , and K is the force constant between adjacent units. H_{e-e} in equation (3) represents the electron-electron interactions; it is important in the n -type doping case. Here a simple Hubbard form was adopted:

$$H_{e-e}^{(j)} = \frac{1}{2} U \sum_{n_j, s} c_{n_j, s}^+ c_{n_j, s} c_{n_j, -s}^+ c_{n_j, -s}. \quad (5)$$

The electron-electron interaction term was simply treated in the unrestricted Hartree-Fock approximation. The validity of this approximation has been discussed in [12]. In our model, the interchain coupling has been neglected. As we mainly concentrate on the stability of the localized excitations in divalent-doped polyacetylene, the local confinement of the impurity ions should be more important. The effect of interchain coupling on excitations is interesting and possibly quite important. For example, the delocalization (spread over more than one chain) of a polaron as a function of the coupling strength has been studied recently [13, 14].

With a small deviation from the equilibrium configuration u_{n_j} , the self-consistent condition for the lattice can be derived [10] by minimizing the total energy of the system:

$$E = \sum_{\mu, s} \epsilon_{\mu, s} - \frac{1}{2} U \sum_{j, n_j, s} X_{n_j, s} X_{n_j, -s} + \frac{1}{\pi \lambda} \sum_{j, n_j} (\phi_{n_j} + \phi_{n_j+1})^2 \quad (6)$$

where $\epsilon_{\mu, s}$ is the electronic eigenvalue and $X_{n_j, s}$ is the charge distribution of electrons with spin s in the j th chain; the prime indicates a sum over the occupied states. The dimensionless order parameter ϕ_{n_j} and the coupling factor λ have been introduced as

$$\phi_{n_j} = (-1)^{n_j} \frac{\alpha}{t_0} u_{n_j} \quad \lambda = \frac{2\alpha^2}{\pi K t_0}. \quad (7)$$

The energy is measured in units of t_0 .

3. Results and discussion

We performed calculations on *trans*-(CH)_x chains containing $N_1 = N_2 = 100$ (CH) units, with typical parameters $t_0 = 2.5$ eV, $\alpha = 4.2$ eV Å⁻¹, $K = 18.7$ eV Å⁻² and $c = 1.22$ Å [2], corresponding to $\lambda = 0.24$, and for the divalent impurity potential with $Z = 2$, $e^2 = 14.3$ eV Å, $\epsilon = 2.5$, $\lambda = 5.0$, $d_1 = d_2 = 2.0$ Å, $\beta = 0.5$ and $W = 1.25$ eV. The criterion for terminating the optimization is that the total energy difference between two successive iterations is less than 10^{-5} .

First, the equilibrium lattice configurations were iterated, with a full impurity potential $\Theta = 1$ and electron–electron interaction strength $U = 0.4t_0$, for case A and case B (shown in figure 1). In case A, a divalent donor provides two electrons to two (CH)_x chains, i.e. each chain has one excess electron. The calculations gave a singly charged polaron state in each chain. The static configuration was shown in figure 2. The total energy of the double-chain system is $E_A = 2E_{p-1} = -264.606t_0$. In case B, both the two electrons of the divalent donor are transferred to one of the two chains; the other chain remains neutral. In case B, a confined kink–antikink pair or a bipolaron state forms steadily in the charged chain. It is doubly charged and bound to the position near the counter-ion. In contrast, the neutral chain still has a dimerization structure except for small distortions of a few sites near to the counter-ion due to the impurity effects, as shown in figure 2. The total energy in this case is $E_B = E_{p-2} + E_0 = -132.598 + (-132.926) = -265.524t_0$. It is apparent that the inequality

$$E_B < E_A \quad (8)$$

holds. This means that in *trans*-polyacetylene doped with divalent impurities, a pair of electron charges are confined in one of the two chains, favouring the formation of a bound state. It is energetically more advantageous than the situation when two charges are shared by the two chains under the given typical parameters here.

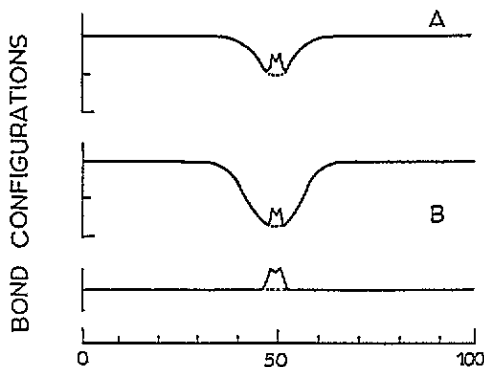


Figure 2. Bond configurations $\phi_n + \phi_{n+1}$ of *trans*-(CH)_x for a singly charged chain (A)—formation of a polaron—and for doubly and neutrally charged chains (B)—formation of a bipolaron in the doubly charged chain and small distortions in the neutral chain.

If we define the creation energy, ϵ_d of a topological excitation as

$$\epsilon_d = E_d - E_0 \quad (9)$$

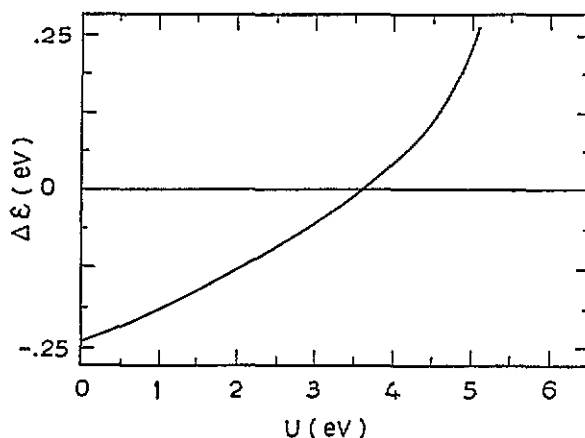


Figure 3. Dependences of the energy difference $\Delta\epsilon$ on electron-electron interactions at a given impurity confinement $\Theta = 1$.

then we obtain the creation energy $\epsilon_{p-1} = 1.53$ eV for a polaron and $\epsilon_{p-2} = 2.94$ eV for a bipolaron under the given parameters. So the important relations

$$\epsilon_{p-1} < \epsilon_{p-2} < 2\epsilon_{p-1} \quad (10)$$

between polaron and bipolaron hold even in *trans*-polyacetylene. The formation of one bipolaron is energetically more favourable than the formation of two independent polarons. Inequality (10) is well known in other quasi-one-dimensional conducting polymers such as polyparaphenylene, polythiophene, polyaniline and polypyrrole, where the ground state is non-degenerate. In these systems [2], the kink and antikink associated with the bipolaron are confined by the quinoid structure. Here in divalent-doped *trans*-polyacetylene which has a degenerate ground state, the Coulomb potential of the counter cation acted in a confining manner to bind a charged kink-antikink pair together.

It is expected that whether a bipolaron or a pair of polarons is more favourable in divalent-doped *trans*-(CH)_x is related to the competition between impurity confinement and electron-electron repulsion. Therefore, we studied the stability of excitations by calculating the energy difference between a bipolaron and a pair of polarons:

$$\Delta\epsilon = E_B - E_A = (E_{p-2} + E_0) - 2E_{p-1} = (E_{p-2} - E_0) - 2(E_{p-1} - E_0) = \epsilon_{p-2} - 2\epsilon_{p-1} \quad (11)$$

as a function of the electron-electron Hubbard term U and the impurity potential factor Θ .

The calculated results show that each excitation can exist in the steady state under certain circumstances. Beyond these conditions, a transition between bipolarons and solitons or between bipolarons and polarons can take place. Figure 3 shows the dependence of the energy difference $\Delta\epsilon$ on the electron-electron interaction U at a given impurity confinement $\Theta = 1$. We can see that a demarcation point exists at about $U_c = 1.48t_0$. When $U < U_c$, i.e. when the electron-electron interactions are relatively weak compared with the impurity confinement, bipolarons are stable; when $U > U_c$, which corresponds to a relatively stronger electron-electron interactions, it is difficult to confine two electrons together; so bipolarons will become unstable, and instead the formation of singly charged polarons will be easy energetically.

At a given electron–electron interaction energy $U = 0.4t_0$, the effect of the impurity potential on $\Delta\epsilon$ is shown in figure 4. Three energy ranges were predicted. From the related lattice configurations in these ranges we know that they correspond to the soliton, bipolaron and polaron states. When the impurity confinement is non-existent or weak ($\Theta < \Theta_c(\text{KK-BP})$), solitons are the most energetically favourable. This has been extensively studied in the impurity-free SSH model over the last decade. With increase in the degree of confinement, it was found that the impurity confinement could overcome the internal repulsions between charged solitons and antisolitons, and the free soliton states are no longer stable; a bound kink–antikink pair, i.e. a doubly charged bipolaron, would form. This is an elemental excitation stabilized by the impurity counter-cations in divalent-doped *trans*-(CH)_x that has not been mentioned previously. The differences between the optical absorptions of polyacetylene doped with Ca²⁺ versus Na⁺ and Eu²⁺ versus Na⁺ counter-cations showed that [7], in the dilute divalent-doping cases, three peaks were observed; two of them are above and below the middle of the gap respectively, and the other is the interband transition. For Ca²⁺ doping, the corresponding positions of the peaks were observed at about 0.6, 1.2 and 2.0 eV. Here the possible energy transitions associated with the bipolarons has been calculated with the electron–electron interaction energy $U = 2.0$ eV and impurity confinement $\Theta = 1$. The calculations gave three transition energies; they are 0.52, 1.67 and 1.95 eV. The theoretical values agree well with the above experimental data.

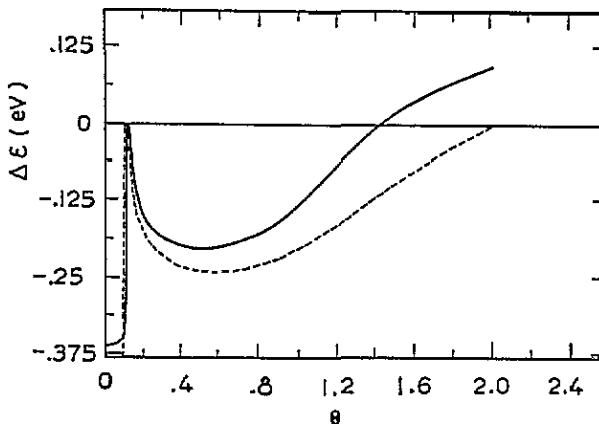


Figure 4. Dependences of the energy difference $\Delta\epsilon$ on the impurity confinement Θ at electron–electron interaction energies $U = 1.0$ eV (---) and $U = 2.0$ eV (—).

For higher confinement of the impurity potentials, the electrons would be strongly confined by the counter-cation, but the electron–electron repulsion energy would be increasing much more rapidly than the increase in the bonding energy; this will lead to an increase in the energy of a bipolaron. Then an unstable bipolaron will translate into a pair of singly charged polarons (figure 4).

A bipolaron could exist in quite a wide range of impurity confinements. At $U = 2.0$ eV, the calculations gave the transition points $\Theta_c(\text{KK-BP}) = 0.15$ between solitons and bipolarons and $\Theta_c(\text{BP-SP}) = 1.45$ between bipolarons and polarons. In real divalent-doped materials, because the confinement strengths of the impurity are not constant but have a distribution as the distances of the doped ions to the chains are variable; therefore, the doping processes would lead to the formation of solitons and polarons as well as

bipolarons depending upon the confinement of the impurity in local areas. In addition, the calculated results predicted that $\Theta_c(\text{KK-BP})$ changes little with the electron–electron interactions (see figure 4); this means that the soliton–bipolaron transition is caused mainly by the doped counter-ions. In contrast, $\Theta_c(\text{BP-SP})$ would change greatly with the electron–electron interaction energy U ; so the bipolaron–polaron transition is sensitive both to the doped counter-ions and to the electron–electron interactions. Figure 5 is a phase diagram on a Θ – U plane, which summarizes our calculated results. Regions I, II and III correspond to the stable soliton, bipolaron and polaron states, respectively.

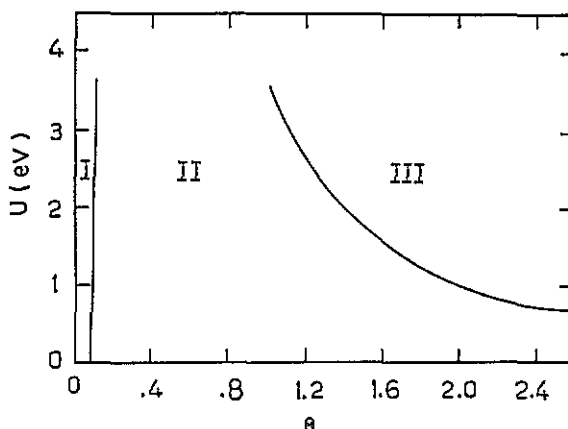


Figure 5. Phase diagram of the stability of non-linear excitations in the Θ – U plane. Regions I, II and III correspond to stable soliton, bipolaron and polaron states, respectively.

4. Conclusion

In doped *trans*-polyacetylene, owing to the strong electron–lattice coupling present in the material, the transfer of charges from the dopant to the polymer chain would lead to the formation of self-localized defects or excitations. It has been predicted that the kind of excitations (solitons, polarons or bipolarons) that will occur depends essentially upon the competition between impurity confinement and electron–electron repulsion. We found that bipolaron excitations could form in divalent-doped *trans*-polyacetylene under certain conditions. When the confinement is weak, the bipolaron would disintegrate into a soliton and a antisoliton as obtained in the SSH model. When the confinement is very strong, the bipolaron would disintegrate into two singly charged polarons. The energy transitions associated with the bipolarons calculated here agree well with the experimental results for Ca^{2+} -doped *trans*-polyacetylene. Finally, a phase diagram concerning the non-linear excitations in divalent-doped *trans*-polyacetylene has been given.

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