Bipolaron-impurity complexes in quasi-1D semiconductors

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The interaction of bipolarons and Coulomb impurities in quasi-1D materials is analyzed. The bound state of a bipolaron at an impurity is asymmetric and degenerate in terms of the direction of the dipole moment. This circumstance gives rise to a low-frequency absorption and to a linear temperature dependence of the specific heat, $c(T)$. The results agree qualitatively with experimental data on doped polyacetylene.

1. Study of doped polymer semiconductors has shown that the primary nonintrinsic carriers in these materials are bipolarons. Conclusions regarding the existence of bipolarons follow from the experimentally established fact that there are no spin effects (no ESR signal or Knight shift in the NMR) anywhere before the metal-insulator transition.[1] Optical studies of polythiophene also indicate the electronic-level structure expected for bipolarons.[2] The experimental results agree with analytic and numerical calculations based on elementary models.[3–5] At low dopant concentrations, the existence of bipolarons leads to results not found in the standard picture. In the case of a bipolaron doping, all the impurities are typically charged: In the course of a doping, the number (N) of acceptors with charge e is twice the number of bipolarons, of charge[1)] $-2e$. At low temperatures, where all the bipolarons are basically localized at impurities, half of the impurities retain a charge e, while a complex of a bipolaron with an impurity has a charge of $-e$; i.e., each impurity now serves as both a donor and an acceptor.

In the present letter we examine the interaction of a bipolaron and Coulomb impurities in quasi-1D materials. We show that the state of a bipolaron at an impurity has a dipole moment and is doubly degenerate in terms of its direction along the axis of the chain. The Coulomb fields of the surrounding impurities lower the degeneracy, by analogy with the case of insulating glasses.[7] It thus becomes possible to explain the linear dependence[8] $c(T)$ and the low-frequency absorption[9] observed during the doping of polyacetylene. The observation of these properties in other polymers would serve as a test of the model-based theories of the structure of bipolarons.

2. For most quasi-1D semiconductors, the structure of the chain is approximately the same as the doubly degenerate structure observed in the chain of trans-polyacetylene. In this case, the bipolaron may be thought of as a bound state of two kinks of like charge (dimerization defects). A short-range repulsion and a Coulomb repulsion act between kinks, as does an attractive "confinement" with a constant force F (Refs. 3 and 5). The force F is the difference between the linear energy densities caused by the inexact degeneracy of the ground state on a single chain. In the case of trans-polyacetylene (in addition to the structure with a retarded rotation of the chains around their axis, which preserves individual solitons) and polymers of type $(AB)_x$, with a com-

plete crystalline ordering, the degeneracy is lifted by the interaction between chains,[5,9] while for other polymers (cis-polyacetylene, polyphenyl, polypyrrole, polythiophene, and polydiacetylene) the degeneracy is lifted by the structure of the chain itself.[3,5] Everywhere below we assume that the confinement is weak, and the internal structure of the kinds can be regarded as constant:

$$\alpha = F\xi_0/\Delta \ll 1 \qquad \xi_0 = \hbar v/\Delta . \tag{1}$$

The parameters Δ and v are determined from the electronic spectrum: $\epsilon(k) = \pm [\Delta^2 + (k\hbar v)^2]^{1/2}$. The bipolaron-impurity system is described by the Hamiltonian

$$\hat{H} = \frac{\hat{p}_1^2}{2M} + \frac{\hat{p}_2^2}{2M} + \frac{e^2}{\epsilon_\perp |x_2 - x_1|} + F|x_2 - x_1| + W_i + eE(x_2 + x_1) \tag{2}$$

where x_1 and x_2 are the coordinates of the centers of the bipolaron kinks, the fixed impurity is at the point $x = 0$,

$$W_i = 2\pi e \int_0^a r dr \int_{-\infty}^{\infty} \sum_{i=1}^{2} \rho(x - x_i) [\epsilon_\perp^2 \epsilon_\parallel (x^2/\epsilon_\parallel + r^2/\epsilon_\perp)]^{-1/2} \tag{3}$$

is the energy of the interaction of the bipolaron with the impurity, and the charge density distribution in the kink is

$$\rho(y) = -e(2\pi a^2 \xi_0)^{-1} \operatorname{ch}^{-2} y/\xi_0 . \tag{4}$$

For simplicity, we assume that the basis wave functions are distributed uniformly in a tube of radius a on the order of the distance between chains, and $\epsilon_\parallel$ and $\epsilon_\perp$ are the longitudinal and transverse dielectric constants.

3. Let us consider classically equilibrium configurations for Hamiltonian (2). Under condition (1), the distances between the centers of kinks are much larger than the length of the charge distribution in a kink, ξ_0. Under these conditions, the Coulomb interaction between kinds far from an impurity can be described as for point charges, and the size of a free-polaron (the distance between the centers of the kinks forming the bipolaron) is

$$\xi_1 = (e^2/\epsilon_\perp F)^{1/2} = \xi_0(\delta/\alpha\epsilon_\perp)^{1/2} \gg \xi_0; \quad \delta = e^2/\hbar v \sim 1. \tag{5}$$

For a bipolaron localized at an impurity, we find from (2), using condition (1), that the most favorable configuration is that in which one of the kinks is found directly at an impurity, with a small displacement, neutralizing the charge of the impurity, while the other is distant. The size of the bipolaron in this case is

$$l \approx x_2^{(0)} = \left(\frac{2}{3}\xi_0^2 e^2/\epsilon_\perp F\right)^{1/4} \sim \xi_0(\delta/\alpha\epsilon_\perp)^{1/4} \gg \xi_0 . \tag{6}$$

The bound state of a bipolaron at an impurity is evidently asymmetric in terms of charge distribution, and it is degenerate in terms of the direction of the dipole moment

along the axis of the chain. (An axisymmetric polaron was found in Ref. 10 in the 3D case.)

4. The degeneracy of the state of a bipolaron at an impurity is lifted by tunneling and external fields, primarily the Coulomb fields of the surrounding impurities. Even at low temperatures, all the impurities are charged, so that electric field fluctuations are clearly important. For the tunneling integral between two states of the bipolaron at an impurity we find the following rough estimate:

$$t \sim \exp\left[-(MF)^{1/2}(\xi_0\xi_1)^{3/4}\hbar^{-1}\right].$$

Accordingly, a bipolaron localized at an impurity is a two-level system. Using results from the theory of two-level systems (Ref. 7, for example), we find $c(T)$,

$$c(T) = \frac{Ne^2l}{T^2}\int_{-\infty}^{\infty} dEE^2P(E)\mathrm{ch}^{-2}(eEl/kT) \tag{7}$$

the absorption coefficient for a low-frequency electromagnetic field, $\alpha(\omega)$,

$$\alpha(\omega) = \frac{32\pi^2NeL}{c}\,\frac{\omega t^2}{(\hbar\omega)^2+t^2}\tanh\frac{\hbar\omega}{2kT}\,P\left(\frac{\hbar\omega}{2el}\right) \tag{8}$$

and the relaxation time τ,

$$\tau^{-1} = \frac{16}{3}\,\frac{t^2(el)^2}{c^3\hbar^4}\int_{-\infty}^{\infty} eEl\coth\frac{eEl}{kT}P(E)dE. \tag{9}$$

Here $P(E)$ is the distribution function of the electric fields. For an uncorrelated impurity charge distribution, for example, we would have

$$P(E) = \frac{1}{\pi E_0}\int_0^{\infty} dt\cos(tE/E_0)\exp(-t^{3/2})$$
$$E_0 = 2.6eN^{2/3}/(\epsilon_\parallel^2\epsilon_\perp)^{1/3}\ ;\quad P(0) = 0.9/\pi E_0\,. \tag{10}$$

In the expression for $c(T)$, values $eEl \lesssim kT$ are important. Experimentally, a linear behavior $c(T)$ is observed at $N = 4$ mole % and $1\ \mathrm{K} < T < 10\ \mathrm{K}$ (Ref. 8), corresponding to typical values $eEl \leqslant 10^{-22}$ J. From Ref. 10 we find $eE_0l \sim 2.8\times10^{-20}$ J; i.e., in (7) we can set $P(E) \approx P(0)$. We then have

$$c(T) = (0.15\,\pi Nk^2/eE_0l)\,T = \gamma T\,;\qquad \gamma = 0.07\ \mathrm{mJ/deg^2} \tag{11}$$

The experimental value is[8] $\gamma = 0.05\ \mathrm{mJ/deg^2}$. The value found for γ from (11) should be larger than the experimental value, since some of the material is in an amorphous state, where there is no confinement acting between kinks, and the bipolarons decay into free kinks. The agreement with a linear behavior $c(T)$ indicates that the hopping integrals are very small, and the numerical agreement indicates that the impurities are distributed uniformly. This result may imply that they are basically neutral at room temperature, where the equilibrium impurity distribution is formed.

Using $t \leqslant 1$ K, we find the upper estimate $\alpha(\omega) < 5\times10^3\ \mathrm{cm}^{-1}$. The results on the

absorption could hardly be interpreted in any unambiguous way since there are also other absorption mechanisms, e.g., the hopping conductivity of bipolarons between impurities. More significant would be the observation of the nonlinear and relaxation processes which are characteristic of two-level systems. It is important to bear in mind that the results will depend on the thermal history of the sample because of the high impurity mobility. At a relatively high temperature, the impurities will be ionized, and Coulomb correlations will be important in their distribution, while at intermediate temperatures the impurities will be distributed as neutral particles. When a sample is held at a low temperature, complexes of a bipolaron and two impurities will form; they may then coalesce into walls which pass through filaments.[11]

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[1)]An analogous situation has been examined in the Éfros model for a Coulomb gap.[6]

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