Excitons, polarons, and bipolarons in conducting polymers

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A theory of the Peierls effect is proposed for systems with a nondegenerate ground state. The obtained results explain the difference between the optical properties of trans- and cis-polyacetylene and the nonparamagnetic nature of the majority current carriers in a broad class of polymers. The experimental identification of charged Bose particles and the possibility of superconductivity in lightly doped polymers are discussed.

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1. Experimental studies of conducting polymers[1] show that the kinetics of spin and charge excitations are brought about by different carriers which have the properties of strong-coupling polarons. These results can be explained in the context of the Peierls model. Theoretical studies[2–6] show that for incommensurable systems of the KSR type (class A) and for the polymer trans-$(CH)_x$ (class B) electron excitations are either by charged spinless (B) or by spin-carrying uncharged (A and B) solitons that separate domains with opposite signs $\pm\Delta_0$ of the dimerization parameter $\Delta(x)$. Because of the polaron effect,[2] these excitations have a lower energy than free electrons

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or holes. Experimental data[7] for polymers of polypyrrole, polyphenylene, and cis-$(CH)_x$ (class C) also show that the current carriers in these materials are spinless particles. As shown below, however, the existence of an isolated soliton (a domain wall)in these substances is impossible because of the absence of degeneracy of the ground state of the system. We present in this paper a theory of the equilibrium Peierls state and of the elementary excitations of class C systems.

2. The trans and cis modifications of $(CH)_x$ correspond to the simplest model of class B and C polymers. If the dimerization and the corresponding gap Δ_0 in the B case are the result of a spontaneous breakdown of symmetry as a result of interaction of π electrons with the lattice deformation (the Peierls effect), then an external dimerization will also occur in the C case due to the influence of the skeleton of the σ bonds. In this case the gap Δ is a combination of two sources: the external contribution Δ_e from the rigid polymer skeleton and the internal contribution Δ_i from the spontaneous deformation, which is stabilized by the interaction with the π electrons. By selecting $\Delta_e > 0$, we obtain $\Delta(x) = \Delta_e + e^{i\phi}\Delta_i(x)$, where ϕ is the phase shift between the matrix elements of the potentials Δ_i and Δ_e. The value $\phi = \text{const}$, like Δ_e, is determined by the atomic structure of the polymer. The energy functional of the system has the form

$$U\{\Delta\} = \sum_{E_\mu < \zeta} E_\mu\{\Delta(x)\} + \int dx \frac{\Delta_i^2(x)}{g^2},$$

where g is the interaction constant of the electrons with the deformation Δ_i, E_μ are the self-energies of the occupied states of the Dirac equation which describes the π electrons in the field of a dimerization potential $\Delta(x)$, and ζ is the Fermi level. We obtain for a homogeneous state $\Delta(x) = \text{const}$ and $|\Delta| = \bar{\Delta}$

$$U/L = (\bar{\Delta}^2/\pi v_F)[\lambda^{-1} - \ln(W/\bar{\Delta}) - 1/2] - \frac{2\Delta_e \cos\phi}{g^2}(\bar{\Delta}^2 - \Delta_e^2 \sin^2\phi)^{1/2} + \frac{\Delta_e^2}{g^2}\cos 2\phi, \quad (1)$$

where $\lambda = g^2/\pi v_F$ and W is an energy of the order of the width of a π band. In the equilibrium state $(\partial U/\partial\bar{\Delta})_{\Delta_e,\phi} = 0$ for $\bar{\Delta} = \bar{\Delta}_0$; hence,

$$(\bar{\Delta}_0^2/\Delta_e^2 - \sin^2\phi)^{1/2} \ln(\bar{\Delta}_0/\Delta_0) = (\cos\phi)/\lambda. \quad (2)$$

where $\Delta_0 = W\exp\{-1/\lambda\}$ is a gap in the limit $\Delta_e = 0$[trans-$(CH)_x$]. The absolute minimum of Eq. (1), according to Eq. (2), always lies at $\bar{\Delta}_0 > \Delta_0, \Delta_e \sin\phi$, and $\bar{\Delta}_0 > \Delta_e$ as long as $\Delta_0 \ll W$. In the limit $\phi = \pi/2$ $|\bar{\Delta}| = \max\{\Delta_e, \Delta_0\}$, i.e., $\Delta_i = \pm\sqrt{\Delta_0^2 - \Delta_e^2}$ for $\Delta_e < \Delta_0$, and spontaneous dimerization $\Delta_i = 0$ is absent for $\Delta_e > \Delta_0$. For $\phi \neq \pi/2$ the quantity $\Delta_i \neq 0$ always. In the cis-$(CH)_x$ case we can expect that both Δ_e and Δ_i arise primarily because of a change in the bond lengths, which corresponds to $\phi = 0$. In the $(CH)_x$ isomers $2\bar{\Delta}_0 \approx 2$ eV and $2\Delta_0 \approx 1.5$ eV, i.e., $\Delta_i/\Delta_e = 3/\lambda - 1 = 5$ in cis-$(CH)_x$ — the dimerization remains spontaneous for the most part. In general, we can see in Eq. (2) that $\Delta_i > \Delta_e$ for $\bar{\Delta}_0 < (\Delta_0 W)^{1/2}$, i.e., there is a wide region of parameters in

semiconductor polymers in which the spontaneous Peierls dimerization Δ_i is equal to or greater than the external effect Δ_e.

Inhomogeneous autolocalized states, which are stationary charge carriers and (or) spin carriers, are also extremes of the functional (1); they can be determined by using the methods described elsewhere.[4,8] $\nu = \nu_e + \nu_h = 0$, 1, and 2 for a small number of trapped fermions (electrons ν_e and holes ν_h); the exact solution for $\Delta_i(x)$ has the form

$$\Delta_i(x) = \delta_\infty \{1 - \operatorname{th}\alpha [\operatorname{th}(x/\xi + \alpha/2) - \operatorname{th}(x/\xi - \alpha/2)]\} - \Delta_e \cos\phi$$

$$\delta_\infty = (\bar{\Delta}^2 - \Delta_e^2 \sin^2\phi)^{1/2}, \quad \xi = \xi_\infty \operatorname{cth}\alpha, \quad \xi_\infty = v_F/\delta_\infty, \tag{3}$$

where α is an arbitrary parameter. For $\alpha \ll 1 \xi \approx \xi_\infty/\alpha \gg \xi_\infty$, $(\Delta_i - \delta_\infty)/\delta_\infty \approx -2\alpha^2\left[1 + \cosh\frac{2\alpha x}{\xi}\right]^{-1}$, and Eq. (4) describes a shallow polaron. For $\alpha \gg 1, \xi \approx \xi_\infty$ and Eq. (4) has the form of two domain walls at a distance $a = \xi_\infty \alpha$. The energy of the local states is $\pm E_b = \pm(\bar{\Delta}^2 \sin^2\phi + \delta_\infty^2 \cosh^{-2}\alpha)^{1/2}$; their occupation numbers are $\nu_+ = \nu_e, \nu_- = 2 - \nu_h$, and $\nu_e + \nu_h = 2 + \nu_+ - \nu_- = \nu$. The total excitation energy is

$$E_\nu = \frac{4}{\pi}\bar{\Delta}\left[\left\{\frac{\pi}{4}\nu\cos\beta + \sin\beta - \beta\cos\beta\right\} + \gamma\{a - \operatorname{th}\alpha\}\right], \tag{4}$$

where

$$\cos\beta = (\sin^2\phi + \delta_\infty^2/\bar{\Delta}^2 \operatorname{ch}^2\alpha)^{1/2}; \quad \gamma = \Delta_e \cos\phi/\lambda\bar{\Delta}.$$

$E_\nu(\alpha)$ reaches a minimum $E_\nu = E_\nu(\alpha_\nu)$ at $\alpha = \alpha_\nu$, which is determined from the equation

$$(\delta_\infty^2/\bar{\Delta}^2 - \sin^2\beta)(\nu - (4/\pi)\beta) = 4\gamma(\delta_\infty/\bar{\Delta})\sin\beta\cos\beta. \tag{5}$$

The excitation charge and the dipole moment are (for $\phi = 0, P_\nu = 0$)

$$e^* = (\nu_e - \nu_h)e; \quad P_\nu(\alpha) = (e\xi_\infty\alpha)[2\beta/\pi - \nu]\frac{2\delta_\infty(\bar{\Delta}^2 - \delta_\infty^2)}{\bar{\Delta}^2 \sin 2\beta}. \tag{6}$$

The $E_\nu(\alpha)$ terms are represented by the solid lines in Fig. 1 in the limit $\gamma = 0$ (class B). The dashed line represents the plot of the additional term $E_c(\alpha) \sim \gamma$ in Eq. (4), which is different from zero for class-C systems when $\phi \neq \pi/2$. If $\gamma \ll 1$, the $\alpha_2 \gg 1$ and the excitation can be regarded as a bound state of two domain walls. In this case $E_2(\alpha) \approx \mathcal{F}a$, where $\mathcal{F} = 4\gamma\bar{\Delta}/\pi\xi_\infty$ is the distance-independent gravitational force between the walls. According to Eq. (6), the charges of the remote walls are equal to $(\nu_e - 2\beta_\infty/\pi)e$ and $-(\nu_h - 2\beta_\infty/\pi)e$, where $\sin\beta_\infty = \delta_\infty/\bar{\Delta}_0$, in agreement with the results of Ref. 4.

In the absence of excited particles (the bottom curve $\nu = 0$), the domain walls attract each other even at $\gamma = 0$, so that the gap becomes homogeneous $\Delta(x) \equiv \bar{\Delta}_0$ if the finite length of the chain or the chemical impurities do not impose antisymmetrical

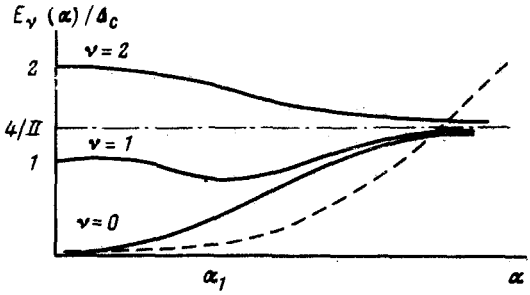

FIG. 1.

boundary conditions.[4,6] A polaron state with $\alpha_1 = \text{arc coth}\,(2^{1/2})$, $E_b = 2^{-1/2}\bar{\Delta}$, and $E_1 = 2^{3/2}\pi^{-1}\bar{\Delta} \approx 0.9\bar{\Delta}$ for $\gamma = 0$ is formed for an isolated fermion (the middle curve $\nu = 1$). Its properties do not change from class B ($\gamma = 0$) to class C. In contrast to the isolated domain walls for class B, the polaron carries both a charge $\pm e$ and a spin 1/2. Two domain walls, which repel each other at $\gamma = 0$, are formed for a pair of fermions $e + e$, $e + h$, and $h + h$ (the top curve $\nu = 2$). However, a bound state with $\alpha = \alpha_2(\gamma)$, which is determined from Eq. (5) is formed when $\gamma \neq 0$. We note that, according to Eq. (2), we cannot have $\gamma \gg 1$. For $\gamma \sim 1$ the role of Coulomb repulsion $U_Q \sim e^2/\epsilon\xi$ increases, where ϵ is the low-frequency dielectric constant, whereas $E_2 \approx \bar{\Delta}\,\xi_\infty^2/4\xi^2$. A crude estimate gives $E_2 > U_Q$ for $\gamma e^2/\epsilon v_F < 1$. In the opposite case, the neutral pair $\nu_e = \nu_h = 1$ is a Mott exciton and the charged pair (bipolaron $\nu_e = 2$ and $\nu_h = 0$ or $\nu_e = 0$ and $\nu_h = 2$) breaks up into two polarons ($\nu = 2$)$\rightarrow$2($\nu = 1$).

The obtained results make it possible to interpret many experimental data: the long photoresponse time[9] in trans-$(CH)_x$ is explained by the formation of domain walls in a time $\tau \sim \omega_{ph}^{-1} \sim 10^{-13}$ sec, which subsequently fly apart. The potential barrier of the repelling walls prevents intersection of the e and h localization regions which delays their recombination. The exponential increase of photoconductivity in the region of 1.1 eV to 1.5 eV is attributable to the fluctuational Urbach absorption[2] in the range of the production threshold of separated domain walls [$(4/\pi)\bar{\Delta}_0 \approx 1.0$ eV] to the production of free e-h pairs. The absence of detectable photoconductivity[9] and, on the other hand, the presence of luminescence[10] in cis-$(CH)_x$ are in agreement with the nonescape principle. A strong electron-phonon interaction has been observed in Raman scattering experiments near $2\bar{\Delta}_0$.[10]

The production of strong-coupling polarons can be observed from the suppression of their direct optical excitation and from the strong diffusion anisotropy, which can be detected from the NMR data for the spin component (polarons with $\nu = 1$). The absence of photoconductivity when a pronounced absorption peak is present may indicate that the e-h pairs are antolocalized. The increase of conductivity as a result of doping or injection without an increase of the paramagnetic response in class-C systems may indicate that e-e (or h-h) bipolarons are produced. Since bipolarons are spinless $s = 0$, charged $e^* = \pm 2e$ particles, their gas with a concentration $c \ll \xi_\infty^{-1}$ can become superconducting. The transition temperature T_c can be estimated by using the results of Ref. 11: $T_c/\delta_\infty \sim c\xi_\infty \left(\frac{\omega_i}{\delta_\infty}\right)^{2-2b}\left(\frac{\omega_\perp}{\delta_\infty}\right)^b$, where ω_i is the frequency of a

phonon corresponding to the deformation $\Delta_i, w_\perp$ is the frequency of bipolaron transitions between the filaments, and $b \approx 2/3$.

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