On the nature of the conductivity of quasi-one-dimensional systems in the Peierls phase with period doubling

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A model of a Peierls dielectric with a small concentration of free carriers in the conduction band is constructed in the average-field approximation. This model is used as the basis for analyzing the conductivity mechanism of polyacetylene.

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As a result of the discovery of the anomalous properties of polyacetylene $(CH)_x$ (see Ref. 1 and the papers cited there and also Ref. 2), an interest has arisen in the study of the Peierls transition with a doubled period in quasi-one-dimensional chains.[1,3,4] A unique feature of this transition is the absence of a charge density wave (CDW)[5] below the transition point. Because of this, the behavior of such a system in external fields has a purely semiconductor nature.[2] However, even a slight doping of polyacetylene drastically alters its properties; the authors[1,3,4] attributed this to the appearance of charged solitons (domain walls) in the Peierls lattice. (The possibility of the formation of such polaron states in the Peierls phase was first investigated in Ref. 6.) For a detailed analysis of the dynamics of these soliton states, it is of considerable interest to construct a simple model of a Peierls dielectric (PD) with a small concentration of free carriers in the conduction band.

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As is known, the Peierls transition in one-dimensional metals with one conduction electron per atom can occur into one of two energy-degenerate phases that differ in the configuration of the Peierls lattice relative to the original lattice ($u_n = \pm(-1)^n u_0$, where u_n is the displacement of the nth atom and u_0 is the macroscopic displacement of the lattice ions).[1)]

The electron spectrum in these configurations is defined by the standard expression (see, for example, Ref. 7)

$$E(k) = \operatorname{sgn}\epsilon(k)\sqrt{\Delta_0^2 + \epsilon^2(k)}, \quad \epsilon(k) = -W\cos ka, \tag{1}$$

where Δ_0 is the energy gap of a homogeneous PD, related to u_0 by the expression $\Delta_0^2 = \pi g^2 W \kappa u_0^2$. Here W is the width of the PD conduction band, g is the electron-lattice coupling constant, κ is the lattice elasticity coefficient, and a is the period of the original lattice. According to Eq. (1), a "free" electron in the conduction band ($p = k - k_F \ll k_F$), ignoring the polarization of the Peierls lattice (PL), has the relativistic form of the dispersion law $E^2(p) = \Delta_0^2 + v_F^2 p^2$ (v_F is the Fermi velocity).

Our goal is to describe phenomenologically the dynamics of a system consisting of the PL and the "free" carriers interacting with it. In the average-field approximation, assuming that the displacement u is a weakly varying (over a distance of order a) function of the coordinates and taking into account the dispersion law of the bare electrons (1), we have for the energy density of the investigated system

$$H = N^*\left\{\frac{1}{2}c_0^2\left(\frac{d\phi}{dx}\right)^2 + \frac{\Omega^2}{4}(\phi^2 - f^2)^2\right\} + \bar{\Psi}\{v_F\sigma_1\frac{d}{dx} + g^*\phi\}\Psi. \tag{2}$$

Here ϕ is a dimensionless scalar field related to Δ by the relation $\phi^2 = \Delta^2/\pi g^2 W^2$, $f = \phi(\Delta_0)$, $\Omega^2 = \omega_A^2/2f^2$, ω_A is the activation frequency of the small amplitude fluctuations of the order parameter (optical phonons[5]), c_0 is their phase velocity, and $N^* = 8\epsilon_0/\omega_A^2 f^2$, where ϵ_0 is the difference in the energy densities of the system in the metallic and Peierls phase. The wave functions $\Psi(\bar{\Psi} = \Psi^*\sigma_3)$ of the conduction electrons are normalized to unity, σ_i are the Pauli matrices, and $g^* = (\sqrt{\pi})gW$.[2)] In the phenomenological approach the constants Δ_0, ω_A, c_0, ϵ_0 are arbitrary (determined from an experiment). Therefore, the energy functional (2) can be used to describe the electron states of any quasi-one-dimensional system with a real, scalar order parameter. Keeping this in mind, we shall obtain general formulas with arbitrary model constants, and finally we shall discuss the results for a PD, using the parameters obtained in the microscopic theory (see, for example, Ref. 7).

The equations of motion, corresponding to Eq. (2), has two, qualitatively different exact solutions (compare with Refs. 8, 9): 1) a domain wall (kink) that links the two degenerate phases of the PL, and an electron localized on it.

$$\phi = f\operatorname{th}\left(\frac{\omega_A}{2c_0}x\right), \quad \Psi = \left(\frac{\omega_A}{c_0}\right)^{1/2} 2^{-(1+\alpha)/2}\left\{\operatorname{sech}\left(\frac{\omega_A}{2c_0}x\right)\right\}^{\alpha}\begin{pmatrix}1\\1\end{pmatrix} \tag{3}$$

$\alpha = 2c_0\Delta_0/v_F\omega_A$. The energy of the state is $E_s = \alpha(16/3)\epsilon_0 c_0/\omega_A$. We obtain from Eq.

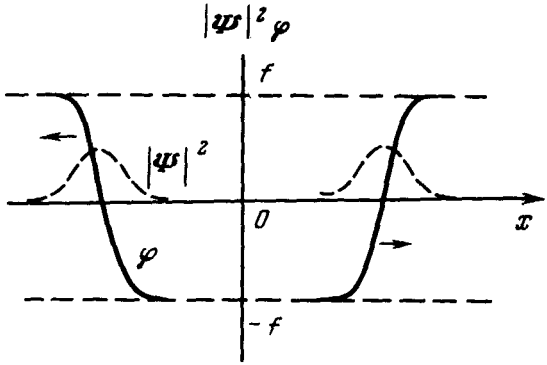

FIG. 1

(3) a similar solution for the antikink by replacing $f \to -f$ and $\begin{pmatrix}1\\1\end{pmatrix} \to \begin{pmatrix}i\\-i\end{pmatrix}$. The wave function Ψ(3) describes the filling of a level at the center of the forbidden band ($E = 0$); 2) A bound kink-antikink state with a localized electron [the analog of a large-radius polaron, whose explicit expression can be obtained for $\alpha = 1$ (Ref. 8), in the microscopic theory of a PD [7] $\alpha = 2/\sqrt{3}$].

$$\phi = f\left\{1 - \frac{k^2 v_F^2}{\Delta_0 E}\,\mathrm{sech}\,[k(x + x_0)]\,\mathrm{sech}\,[k(x - x_0)]\right\}, \tag{4}$$

$$\Psi = e^{-iEt}\sqrt{\frac{k}{8}}\begin{pmatrix}\mathrm{sech}\,[k(x - x_0)] + \mathrm{sech}\,[k(x + x_0)]\\ \mathrm{sech}\,[k(x - x_0)] - \mathrm{sech}\,[k(x + x_0)]\end{pmatrix}, \tag{5}$$

where

$$E^2 = \Delta_0^2 - k^2 v_F^2; \quad \mathrm{th}\,2kx_0 = \frac{kv_F}{\Delta_0}; \quad k\sqrt{\Delta_0^2 - k^2 v_F^2} = \frac{\Delta_0^4}{16 v_F^2 \epsilon_0}. \tag{6}$$

The energy of the states (4) and (5), which is related to the kink energy (3), is a function of the parameter $\gamma = \Delta_0/2E_s$

$$\frac{E_b}{E_s} = \left\{\left(1 + \frac{2}{3}\gamma\right)^{3/2}\left(1 - \frac{2}{3}\gamma\right)^{3/2}\right\}. \tag{7}$$

The value γ defines the ratio of the minimum energy of a "free" electron in the conduction band ($E = \Delta_0$) to the energy of the most strongly bound electron-lattice states ($E = 0$). It is physically clear that at $\gamma \ll 1$ the electron polarizes the lattice slightly and alters negligibly the energy gap. At $\gamma \lesssim 1$ the gap distortion is of the order of its equilibrium value. When $1 < \gamma < 3/2$, the "polaron" phase (4) and (5), which is metastable, decays by tunneling to the kink-antikink state (see Fig. 1). At $\gamma > 3/2$ the "polaron" states are missing.

Using the macroscopic values of the energy functional (2), we have $E_s = (8/3\pi\sqrt{3})\Delta_0$, $\gamma \gtrsim 1$. Therefore, by disregarding the metastable states we can say that doping of the $(CH)_x$-type PD is necessarily accompanied by a severe lattice distortion, and the free charges are always bound at the kinks and antikinks.

Thus far we were discussing the states of a single, "surplus" electron in the PL. A soliton lattice, whose period can be related to the concentration,[4] can be produced in the PD, if the concentration of doped electrons is sufficiently high. In fact, at $\gamma > 1$ the kink and antikink always repel each other at distances $x_0 \gg v_F/\Delta_0$. This is essentially the reason for metastability of the polaron solutions.

The simplest, exact periodic solution for displacement of the PL ions and for the electron wave function has the form

$$\phi = f\sqrt{\frac{2k^2}{1+k^2}}\, sn(\gamma; k); \qquad \Psi = c(k)\{dn(\gamma; k) + kcn(\gamma; k)\}^{\alpha}, \tag{8}$$

where *sny*, *cny*, and *dny* are the elliptic functions of the modulus k, $\gamma = x\omega_A/c_0\sqrt{2(1+k^2)}$, and $c(k)$ is a normalization constant determined from the equation

$$\int_0^{D(k)} \Psi^* \Psi\, dx = 1; \qquad D(k) = 4K(k)\sqrt{2(1+k^2)}\,\frac{c_0}{\omega_A} \tag{9}$$

[$K(k)$ is a complete first-order elliptic integral.] The periodic solution ϕ (8) was used in Ref. 4 to determine the critical concentration of impurity atoms at which the transition of the PD to the metallic phase occurs. We note that, disregarding the fermions, this unstable[12] solution can be stabilized for $\gamma > 1$ according to the dynamics of the doped charges in the Peierls lattice described above.

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[1)]We note that a lattice doubling is energetically advantageous[7] for a concentration ζ of conduction electrons per atom close to unity $|1-\zeta| \lesssim \Delta/W$. The "excess" electrons in this case enter the conduction band.
[2)]It is of interest to note that the examined model has been investigated by many authors[8,9] in connection with the quark-confinement problem; the microscopic theory of the electronic states in a PD [6,10] turned out to be similar to the Gross-Neveau field model.[11]

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