Electronic excitations in the Peierls-Fröhlich state

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It is shown that the stationary electronic excitations in the Peierls state are tight-binding polarons with energy in the interior of the forbidden band, with large mass, and with anomalous charge. Within the framework of the Fröhlich model, the charge of any autolocalized state is equal to zero. An exact solution of the soliton type is obtained, with energy at the center of the forbidden band, with zero charge, and with spin 1/2.

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1. We show in the present paper that a specific strong interaction of excited electrons with deformations of the superstructure takes place in one-dimensional dielectrics of the Peierls type. For optical excitations, this interaction forms a pseudogap regardless of the presence of long-range order in the chain. Thermal excitations are deep autolocalized states with screened charge. The results can serve as a basis for the understanding of a number of characteristic properties of many quasi-one-dimensional substances, such as the strong smearing of the fundamental absorption edge, the so-called "pseudogap" (Refs. 1–3), the considerable difference between the mobility edge $\overline{\Delta}$ (Ref. 4), and the optical edge Δ_0 (Refs. 3 and 5), residual paramagnetic susceptibility, and others.

Consider a system of electrons interacting with phonons in a one-dimensional metallic chain. Let at $T = 0$ the system be in a state with a Peierls structural deformation,[1,2,6] characterized by an electron gap parameter $2\Delta_0$. The excited electron interacts with weak distortions of the superstructure

$$\Delta(x, t) = [\Delta_0 + \delta(x, t)] \exp\{i\phi(x, t)\}. \tag{1}$$

Near the edge of the band we have[8] the electron Hamiltonian ($E \approx \Delta_0$)

$$\mathcal{H} = \psi\left[\frac{p^2}{2m} + \Delta_0 + \delta + \frac{1}{2}\phi' + \frac{1}{2}\dot{\phi}\right]\psi \tag{2}$$

and a distortion energy

$$W_\phi + W_\delta = \int \frac{dx}{4\pi} v_F \left[\frac{\dot{\phi}^2}{u^2} + \phi'^2\right] + \int \frac{dx}{4\pi} \frac{v_F}{u^2} \frac{\delta^2 + \omega_0^2 \delta^2}{\Delta_0^2}, \tag{3}$$

where $m^* = \Delta_0/v_F^2$, $\omega_0/\Delta_0 \sim u/v_F = (m/M)^{1/2}$, m is the band mass of the electron, M is the mass of charge-density wave (CDW). A typical value is $m/M \lesssim 10^{-2}$. An important difference between the Peierls state and analogous three-dimensional systems, for example in metals with coinciding electron and hole Fermi surfaces, is the substitution $dx \leftrightarrows (p_F^2/\pi) d^3r$ in expression (3). As a result, the effects of electron–phonon

interaction in the three-dimensional case are small like $(\Delta_0/\epsilon_F)^2$, and in the two-dimensional case like (Δ_0/ϵ_F). In the one-dimensional case the interaction is not small, and there is only the adiabaticity parameter $(u/v_F)^2 \ll 1$ at $T < \omega_0$ and T/Δ_0 at $T > \omega_0$.

The electronic states that make up the fundamental absorption edge $2\Delta_0$ are determined in accordance with the Franck–Condon principle at a fixed spontaneous lattice configuration. It was shown in Ref. 7 that in such cases the thermal and quantum fluctuations of δ and ϕ can be regarded as a random potential with a distribution of the type of Gaussian white noise. As a result, the optical density of the states with an asymptote in the region of the gap was found to be in the form

$$n(\Delta_0 - \epsilon) \sim \epsilon^{1-\nu} \exp[-(\epsilon/\epsilon_1)^{\nu_1}], \tag{4}$$

where $\nu_1 = 3/2$ and $\epsilon_1/\Delta \sim (u/v_F)^{2/3}$ $(T < \omega_0)$. We see that $\epsilon_1/\omega_0 \sim (u/v_F)^{-1/3} \gg 1$, thus comfirming the correctness of the adiabatic approximation. The general conclusion is that the strong smearing of the fundamental edge in a Peierls dielectric is a specially pronounced Urbach phenomenon[8] and it is not specially connected with the absence of long-range order in the one-dimensional system.

The possibility of adiabatically treating quantum fluctuations of the displacements as a random potential is a distinctive feature of one-dimensional systems. In fact, a similar approach for a d-dimensional system would yield a formula of the type (4) with the quantities ν_1 and ϵ_1 generalized to

$$\nu_d = 2 - d/2, \quad (\epsilon_d/\Delta_0)^{2-d/2} \sim (\Delta_0/\epsilon_F)^{d-1}(\omega_0/\Delta_0),$$

whence

$$\epsilon_2/\omega_0 \sim \Delta_0/\epsilon_F, \quad \epsilon_3/\omega_0 \sim (\Delta_0/\epsilon_F)^4(\omega_0/\Delta_0). \tag{5}$$

It is seen from (5) that at $d = 3$ we have $\epsilon_3/\omega_0 \ll 1$ even in the absence of the small parameter of the static electron-lattice coupling, expressed in (5) in the form Δ_0/ϵ_F. Thus, the adiabaticity condition is satisfied at $d = 1$, is violated at $d = 2$, and at $d = 3$ the problem in the region of the smearing of the edge $\epsilon \sim \epsilon_3$ becomes in principle a dynamic problem (adiabaticity always takes place deep in the Urbach tail[8]).

3. A long-lived excited electron forms a static lattice distortion. It is seen from (4) and (5) that we have a typical polaron problem. It is known[9] that in the one-dimensional case the autolocalized state exists also for short-range interactions, just as in (4) and (5). Since the dynamic parameter u drops out of the problem in the case of a polaron at rest, the binding energy is $\epsilon_0 = \Delta_0 - \bar{\Delta} \sim \Delta_0$, i.e., we encounter a deep-level problem, which is beyond the scope of the approximation of (4) and (5). At any rate, if the quantum effects from the electrons of the occupied band $E < \Delta_0$ do not push out the polaron level into the continuum, it can be stated that the polaron dimension is $\sim \xi_0 = v_F/\Delta_0$, the mass is $m_p \sim m^* M/m$, and the coupling constant, defined in the polaron theory as $\alpha^2 \sim \epsilon_0/\omega_0$, is of the order of $\alpha \sim (M/m)^{1/4} \gg 1$.

In the approximation of (4), (5), and also in the Dirac two-band approximation (4), we encounter the problem of complete screening of the charge. An extremal solu-

tion for (4) and (5) yields

$$\phi'(x) = -\pi\psi^*(x)\,\psi(x)\,,\quad \phi(+\infty) - \phi(-\infty) = -\pi, \tag{6}$$

and it follows therefore from the phase properties[10] that in a deformed CDW there is induced a charge that screens completely the charge of the introduced electron. When the polaron moves with velocity $v < u$ we have $\phi(+\infty) - \phi(-\infty) = -\pi/(1 - v^2/u^2)$, i.e., a finite total charge $e^*(v) = ev^2/(1 - v^2/u^2)$ appears. The screening question can be resolved only by an exact investigation.

If states with $e^* = e^*(0) \neq 0$ exist, then the intensity I_p of their optical excitation can be estimated by interpolating the distribution (4). We obtain

$$I_p \sim \exp\{-(\epsilon_0/\epsilon_1)^{3/2}\} = \exp\{-c\,v_F/u\}, \quad c \sim 1\,. \tag{7}$$

Since $v_F/u \approx 10$, the polaron lines should be practically invisible, in agreement with the observed difference between Δ_0 and $\bar{\Delta}$. In analogy with (7), the probability of the pure electronic mechanism for the transition of the polaron between chains should be small. The transition of the polaron as a whole will depend on the transverse dispersion of the phonon modes ϕ_n.

At a finite temperature T, the polaron concentration $n = [(2m_pT)^{1/2}/\pi]\exp(-\bar{\Delta}/T)$ reaches a value ξ_0^{-1} at $(T/\Delta_0)^{1/2}\exp(-\bar{\Delta}/T) \sim v_F/u \gg 1$, i.e., at $T = T^* < \bar{\Delta}$. At $T > T^*$ the isolated-polaron approximation is not valid and the system goes over into the plasma regime.

The qualitative picture described in this section can pertain to real systems, where the Coulomb interaction of the electrons is also of importance. The correlation energy should prevent total screening of the charge.

4. For the Fröhlich model we can formulate the problem exactly. Any stationary state of a system with wave functions

$$\bar{\psi}_\nu(x, t) = (\psi_\nu^+(y),\ \psi_\nu^-(y))\exp(-iE_\nu t)\,,\quad y = x - ut$$

and with deformation $\Delta(x,t) = \Delta(y)$ is described in the adiabatic limit $u/v_F \ll 1$ by a system of self-consistent equations

$$\frac{v^2}{g^2\bar{\omega}^2}\,\frac{d^2}{dy^2}\Delta(y) + \frac{\Delta(y)}{g^2} + \sum_\nu \psi_\nu^+(y)\,\psi_\nu^{-*}(y) = 0\,. \tag{8a}$$

$$i(v_F + v)\frac{d}{dy}\psi_\nu^-(y) - E_\nu\psi_\nu^-(y) + \Delta^*(y)\,\psi_\nu^+(y) = 0, \tag{8b}$$

$$i(v_F - v)\frac{d}{dy}\psi_\nu^*(y) + E_\nu\psi_\nu^*(y) - \Delta(y)\psi_\nu^-(y) = 0, \tag{9}$$

The subscript ν numbers both the states of the continuous spectrum $\nu = k$ and the autolocalized states ν_0. We multiply (9) by $\Delta^*(y)$ and take the imaginary part. Using (8a,b) we obtain the following relations for the densities

$$\rho_{\pm} = \sum_{\nu} \psi_{\nu}^{\pm}(y)\,\psi_{\nu}^{\pm}(y),$$

$$i[v_F \mp v]\frac{d\rho_{\pm}}{dy} = \frac{v^2}{g^2\bar{\omega}^2}\left[\Delta^* \frac{d^2\Delta}{dy^2} - \Delta\frac{d^2\Delta^*}{dy^2}\right]. \tag{10}$$

Putting $\Delta(y) = |\Delta(y)|\exp\{i\phi(y)\}$, we find that the inhomogeneous part of the total density $\delta\rho(y)$ is always equal to

$$\delta\rho = \delta\rho_+ + \delta\rho_- = \frac{1}{\pi}\,\frac{v^2/u^2}{1 - v^2/v_F^2}\left|\frac{\Delta(y)}{\Delta_0}\right|^2\frac{d\phi}{dy}. \tag{11}$$

Consequently, just as in the approximation (2) and (3), the charge of the immobile polarons is $e^*(0) = 0$.

At $v = 0$ we can indicate one exact solution of Eqs. (8) and (9). Accurate to the phase $\Delta(x) = \Delta_0 \tanh(x)\xi_0$, $\xi_0 = v_F/\Delta_0$ we have $\psi_\nu^{\pm} = (v_\nu \pm V_\nu)(1 \mp i)/2$ and we obtain from (8a,b) one bound state $\nu_0 = 0$:

$$E_0 = 0,\ V_0 = 0,\ v_0 = 1/[\sqrt{2}\,\mathrm{ch}(x/\xi_0)] \tag{12}$$

and continuum states $\nu = k$:

$$E_k = -\sqrt{\Delta_0^2 + k^2 v_F^2},\quad V_k = \frac{1}{\sqrt{2}}e^{iku},\quad v_k = \frac{-1}{\sqrt{2L}}\,\frac{kv_F + i\Delta(x)}{\sqrt{k^2 v_F^2 + \Delta_0^2}}\,e^{iky}. \tag{13}$$

The solutions (12) and (13) satisfy condition (9) identically for a single occupation of ν_0. The energy density, accurate to $(v/u)^2$, is

$$w(x) = \sum_{\nu} E_\nu \bar{\psi}_\nu^* \bar{\psi}_\nu + \frac{|\Delta|^2}{g^2} + \frac{v^2}{2g^2\bar{\omega}^2}\,\frac{d|\Delta|^2}{dy}. \tag{14}$$

Substituting (12) and (13) in (14) we find that the total energy is $W_p = 0$, and the mass is $m_p = \Delta/\pi u^2$, owing to the gain in the lattice energy. We thus obtain a stationary autolocalized activationless $W_p = 0$ and uncharged $e^* = 0$ state of the system. It manifests itself via a lattice deformation $\propto \tanh(x/\xi_0)$ and a localized spin $\frac{1}{2}$. This state exists without changes also in the case of a half-filled band, when account is taken of umklapp processes. Consequently, the result $e^* = 0$ is not connected with the Frohlich effect. In the system of chains with the ordering temperature T_c the jump of the phase of the gap relaxes over distances $R_c \sim T_c/v_F$. For a system with oppositely charged filaments, the single-electron charge of the polaron is then restored. We obtain also $W_p \sim T_c$. Allowance for the zero-point oscillations of the lattice makes a contribution $W_p \sim \omega_0$.

Deductions common to all real systems are the following: $\Delta_0 - \bar{\Delta} \sim \Delta_0$, the edge $\bar{\Delta}(W_p)$ cannot be observed optically, and the mass $m_p \gg m^*$. As a result of the latter, the metallic regime sets in already at $T \ll \bar{\Delta}$.

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