Density-wave defects and screening in quasi-1D conductors

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A nonlinear screening by one-electron excitations determines the length and energy scales of perturbations of the phase of density waves in quasi-1D conductors at low temperatures. A study is made of 2π phase solitons and phase perturbations of density waves caused by impurities. Metal islands may form at the center of a soliton and around impurities. © *1995 American Institute of Physics.*

An electronic crystal, i.e., a charge density wave or a spin density wave, forms at the temperature of the Peierls transition, T_P, in quasi-1D conductors.[1] The motion of the density wave gives rise to a collective conductivity mechanism. The properties of conductors with density waves at relatively high temperatures are basically understood. At low temperatures, in contrast, much is unclear, even in fields below the threshold for the creep of density waves. For example, the activation energy for conduction along chains decreases, while the activation energy for transverse conduction remains the same.[2] A sharp decrease in the thermal emf is observed. In certain materials, e.g., TaS_3 (Ref. 3) and $(NbSe_4)_{10/3}I$ (Ref. 4), the thermal emf in fact changes sign. No changes occur in the Hall constant[5,6] which would indicate a switch from an n-type conductivity to a p-type conductivity. The nature of the low-energy excitations at lower temperatures, where the glassy properties of density waves are manifested[7] and a hopping conductivity is observed,[8] is not completely clear. We do know that one-electron excitations are important at high temperatures, where they support a conductivity in weak fields and determine the elastic constants[9,10] and the friction[11,12] of density waves. It is believed that the electrons freeze as the temperature is lowered and play no role. It has been suggested[2,8,13,14] that the conductivity along the chains at low temperatures is determined by phase solitons with an energy well below the Peierls gap Δ. We show below that one-electron excitations must also be taken into consideration at low temperatures. Nonlinear effects in the screening, which are usually ignored, cause the screening by one-electron excitations to remain effective down to the lowest temperatures. In particular, defects of an electronic crystal (2π solitons) and of an ordinary crystal (impurities and pinning centers) lead to a pronounced curvature of the energy bands, so the Fermi energy may fall in a region of allowed one-electron states. Electronic excitations in the metal islands which form around defects in this manner can strongly influence kinetic and thermodynamic properties of conductors with density waves at low temperatures.

We consider smooth perturbations with length scales much larger than the correlation length $\xi = v/\Delta$, where v is the Fermi velocity. In this case the system can be described by equations which relate the phases $\varphi_n(x)$ and the electrostatic potentials $\Phi_n(x)$ on chains n,

$$\frac{\hbar v}{2}\frac{d\varphi_n}{dx} + \sum_m J_{nm}\sin(\varphi_m - \varphi_n) = e\frac{d\Phi}{dx}, \tag{1}$$

and the Poisson equation with the charge density on chain n,

$$\rho_n = -\frac{\kappa^2}{4\pi}\left[\frac{\hbar v}{2}\frac{d\varphi_n}{dx} + f(\mu_n)\right] + \frac{\varepsilon_\Delta}{4\pi}\frac{d^2}{dx^2}\left(\Phi_n - \frac{\hbar v}{2}\frac{d\varphi_n}{dx}\right). \tag{2}$$

Here $1/\kappa$ is the screening length in the metallic state, J_{nm} describes the interaction between chains, ε_Δ is the component of the dielectric constant due to the Peierls gap, and $\mu_n(x)$ is the local shift of the chemical potential, reckoned from the middle of the Peierls gap. At equilibrium, μ_n is determined from the condition that the electrochemical potential remain constant:

$$\mu_n - \Phi_n + \frac{\hbar v}{2}\frac{d\varphi}{dx} = \mu_e, \tag{3}$$

where $\mu_e \ll \Delta$ is the shift of the chemical potential in the ground state. This shift reflects the fact that either an n-type conductivity ($\mu_e > 0$) or a p-type conductivity ($\mu_e < 0$) is usually predominant in real conductors with density waves. The function $f(\mu)$ describes the contribution of one-electron excitations to the charge density, which is analogous to the contribution of electrons and holes in ordinary semiconductors:

$$f(\mu) = \int_\Delta^\infty d\epsilon \frac{\epsilon}{\sqrt{\epsilon^2 - \Delta^2}}[n_F(\epsilon - \mu) - n_F(\epsilon + \mu)], \tag{4}$$

where n_F is a Fermi distribution.

Equations (1)–(4) are identical for charge density waves and spin density waves. They are derived from the microscopic theory[9,10] in the semiclassical approximation. In the linear approximation in μ, and in the continuous limit with respect to n, they can be derived by varying a phase Hamiltonian.[15] The primary distinction between Eqs. (1)–(4) and the equations of Ref. 14, where phase solitons were studied in detail, is the incorporation of a nonlinear dependence on μ.

Solving these equations in the general case is extremely difficult, especially since this solution depends on the particular crystal structure and electronic structure of the material, i.e., the arrangement of the chains and the form of J_{nm}. Here we solve the problem analytically in two models: at $T = 0$ in a model with an interaction between nearest chains forming a square lattice, replacing the sines in (1) by a sawtooth function; and in a single-chain model[16] in which the interaction of the chains is described by a self-consistent field. The results found in these models are qualitatively the same and are confirmed by numerical calculations.[17] We also make use of a discrete Laplacian in the

Poisson equation for directions perpendicular to the chains. It can be shown that this simplification, like the replacement of the sine by a sawtooth function, leads to no more than numerical changes in the results.

We begin with the model of an interaction between nearest neighbors. We introduce the notation $J_{n,n+1}=\alpha\hbar v/2d^2$, where d^2 is the area per chain, and the quantity $\alpha\ll 1$ describes the anisotropy of the crystal. This quantity can be estimated from the anisotropy of the conductivity. We introduce dimensionless variables in which the coordinate x and the energy are expressed in units of $\ell=d/\sqrt{\alpha}$ and $T_0=\hbar v\sqrt{\alpha}/2d$, respectively ($k_B=1$). These units were introduced in Ref. 14, where they determined the length and energy of a soliton. The scale value T_0 is on the order of T_P, so we have $\delta=\Delta/T_0\gg 1$ and $\ell\gg\xi$. We introduce the dimensionless parameter $\zeta=1/(\kappa d)^2\equiv\hbar v/8e^2$, which describes the ratio of the Fermi energy to the Coulomb energy. For typical values $v=2\times 10^7$ cm/s, we would have $\zeta\approx 10^{-2}$.

In terms of dimensionless variables, the equations are

$$\sum_i \sin(\varphi_{n+i}-\varphi_n)=\frac{d\mu_n}{dx}, \tag{5}$$

$$\frac{d\varphi_n}{dx}=-f(\mu_n)+\zeta\left[\sum_i(\Phi_{n+i}-\Phi_n)+\alpha\frac{d^2\Phi_n}{dx^2}+\alpha\varepsilon_\Delta\frac{d^2\mu_n}{dx^2}\right], \tag{6}$$

$$\mu_e=\mu_n-\Phi_n+d\varphi_n/dx, \tag{7}$$

where the summation over i includes neighboring chains. Replacing the sine in (5) by the sawtooth function $s(\varphi)=2\arctan(\tan\varphi)$ makes it possible to solve the equations exactly through discrete Fourier transforms, with a switch from the chain numbers n to $\mathbf{k}$ ($-\pi/2<k_x$, $k_y<\pi/2$): $\Phi(\mathbf{k})=\Sigma_n\Phi_n\exp(-i\mathbf{k}\cdot\mathbf{n})$. As a result, the only nonlinearity remaining in the equations is in the function $f(\mu)$, which describes the contribution of electrons and holes to the charge density. At $T=0$ this contribution arises only where μ reaches the edge of the gap. This event occurs only at the central chain. We write a solution for the case in which corrections on the order of $\alpha\varepsilon_\Delta\zeta=2/3\delta^2\ll 1$ are ignored. The nature of the solution is determined by the parameter $p=\sqrt{\zeta}(\delta\pm\mu_e)/\pi$. For values $p>1$ μ does not reach the edge of the gap, and the solution is

$$\mu(\mathbf{k},x)=\mu_e\delta(\mathbf{k})\mp\frac{\pi}{\sqrt{\zeta}}e^{-\sqrt{\zeta}\hat{k}^2|x|},\quad \varphi(\mathbf{k},x)=\pi[1+(1-e^{-\sqrt{\zeta}\hat{k}^2|x|})\operatorname{sign}x],$$

where $\hat{k}^2=4-2\cos k_x-2\cos k_y$. The energy of the soliton, calculated as the sum of the elastic energy of the density wave and the Coulomb energy generated by charge (2), is $W=\pi/\sqrt{\zeta}$ in this case or, in dimensional units, $W=\sqrt{\alpha}\omega_p$, where ω_p is the plasma frequency. For values $p>1$, the energy W is lower than the energy of a one-electron excitation. At $p=1$, these energies are comparable, and $\mu_0(0)$ reaches the edge of the gap. The length of the soliton is $\sim 1/\sqrt{\zeta}\gg 1$, and the decay of the perturbation over distances $x\gg 1/\sqrt{\zeta}$ is the same as that found in Ref. 14: $\mu_n=\mp(1/4\zeta|x|)\exp[-n^2/4\zeta|x|]$.

However, it is unlikely that the condition $p>1$ would hold in typical conductors with density waves, because of the values $\zeta \simeq 0.01$, and δ would hardly exceed 10 [values $\Delta T_P \sim 3-5$ are typical; the highest value, in $(NbSe_4)_{10/3}I$, is[1] 6.9]. We would therefore expect typical values $p<1$ and thus the formation of metal islands at the center of a soliton. In this case the solution would be found by joining at the point with $|\mu|=\delta$. As a result, we find that the phase changes by $2\pi(1-p)$ within an island, and the length of an island is

$$l_m = 2(\pi p/6\delta)^{1/3} \int_1^{1/p} dx (x^2-1)^{-1/3}. \tag{8}$$

At values $p \ll 1$ we have $l_m = (1/3)(\pi/6\delta)^{1/3}$. At the center of a soliton we have $\mu_0(0) = \mp[\delta + (9\pi^4/2\delta)^{1/3}(1-p^2)^{2/3}]$. The penetration of μ into the region of allowed one-electron states results in a slight local suppression of the gap: $[\delta(0)-\delta(\infty)]/\delta \sim \delta^{-2/3}$. The quantity μ exceeds the local value of δ, but it does not reach the unperturbed size of the gap. The perturbation of the phase and the potential at chains with $n \neq 0$ is small. As in the absence of a metal island, it falls off slowly, extending to many chains.

The elastic energy of the density wave and the Coulomb energy, both associated with phase perturbations, contribute to the energy of the soliton. There is also a contribution from the increase in energy due to the suppression of the gap at the metal island. We can calculate the first of these contributions by means of the standard formulas (Ref. 14, for example). The second contribution is determined under the condition $|\mu|>\Delta$ by the energy density $W_\Delta = (|\mu|\sqrt{\mu^2-\Delta^2}-\Delta^2)/\pi v$, as is easily shown. As a result, for the contribution of the region outside the metal island we find

$$W_\zeta = p(\delta \pm \mu_e). \tag{9}$$

The basic contribution of the metal island to the energy comes from the elastic energy of the density wave (the first term) and the decrease in the gap:

$$W_M = (6\pi^2\delta)^{1/3} \int_1^{1/p} (x^2-1)^{1/3} dx + 2\delta(1-p). \tag{10}$$

As mentioned earlier, Eqs. (1) and (2) are semiclassical, so their use requires justification at points with $|\mu| \approx \Delta(x) < \Delta(\infty)$. A complete solution on the basis of the microscopic theory can be constructed easily in the limit of a small island, $1-p \ll 1$. In this case the retarded Green's function is found by joining the semiclassical solution with the solution describing a chord soliton.[18] From the condition for self-consistency of the phase we conclude[19] that the level of the chemical potential should pass through a localized state at the center of the soliton. As a result, the phase at the central chain varies slowly away from the center of the soliton, while at the center, where μ reaches the edge of the gap, it changes by an amount $2\theta = 2\pi(1-p)$ over a distance $\xi/\sin\theta$. The energy of the soliton is the same as that in (9), (10) in the limit $p \to 1$.

At $T=0$ the energy of the soliton is thus lower than the energy of one-electron excitations if $p>1$, while it is higher under the condition for the formation of a metal island: $p<1$.

The condition for the formation of a metal island at nonzero temperatures can be found directly from (5), (6). To find it, we multiply the left and right sides of these equations, integrate over x from $-\infty$ to x, and sum over n. As a result, we find the relation between the values of the potentials and phases at the point x and at infinity:

$$\sum_{n,i}\left[\frac{\zeta}{2}[\mu_{n+i}(x)-\mu_n(x)]^2+\int_0^{\mu_n(x)}f(\mu)d\mu-2\sin^2\frac{\varphi_{n+i}(x)-\varphi_n(x)}{2}\right]=0. \qquad (11)$$

Let us apply this equality to the center of the soliton. Ignoring $\mu_{n\neq 0}\ll\mu_0$ (and, for brevity, μ_e), we find that μ reaches the edge of the gap under the condition

$$A=\zeta\delta^2+\pi^2\sqrt{2\delta}\tau^{3/2}/24<4. \qquad (12)$$

Here $\tau=T/T_0$. For $\tau=0$, expression (12) differs from the condition $p=1$ found in a model with a sawtooth force, in that π is replaced by 2. As was mentioned above, since ζ is small at $\tau=0$ we would expect condition (12) to hold, while at temperatures $\tau>\tau_M\approx 2(9/\delta)^{1/3}(1-\delta^2\zeta/4)^{2/3}$ the screening by electrons excited thermally across the gap becomes effective, and the shift of μ does not reach δ.

We turn now to the perturbation of the phase caused by impurities. We assume that at $n=0$ and $x=0$ there is a point charge, equal to the charge of an electron, which is described by adding a term $\pi\delta(x)\delta_{n,o}$ to (6), where $\delta(x)$ is the Dirac δ-function. In this case the solution of the equations consists of pieces of a soliton attached to the impurity, and the condition for the formation of a metal island around an impurity becomes $A<2$.

We now consider a neutral pinning center, described in the standard way by a term $\propto \delta(x-x_i)\sin(\varphi_n-2k_Fx_i)$, in the equation for the phase. We consider the case of strong pinning, in which the value of $\varphi(x_i)$ is set by the impurity. Again, the solution is either an entire soliton, localized at the impurity, or pieces of a soliton attached to the impurity. The condition for the formation of a metal island in the first case is the same as (12). In the second case, we find, using (11), $A<4\sin^2[\varphi(x_i)/2]$. Since $\varphi(x_i)$ is a random number, this condition is the same as (12) in order of magnitude. We note, however, that the standard model of a pinning center which we have used is overly crude, since it ignores the perturbation of the modulation of the order parameter near an impurity,[20] and it leads to an abrupt change in the derivative of the phase (and thus of the potential) at the impurity.

To study the form of the soliton at nonzero temperatures, we use the single-chain model which has been used previously[16] for the case of a long-range interaction between chains. Since the perturbations of the phase and the potential in the soliton are small at all chains except the central one, according to the solution for $T=0$ and also according to numerical calculations,[17] this model is also a good approximation for an interaction between nearest chains. Discarding the small terms and the functions with $n\neq 0$ from (1) and (2), we find

$$4\sin\varphi=-\frac{d\mu}{dx},\quad \frac{d\varphi}{dx}=-4\zeta\mu-f(\mu). \qquad (13)$$

At $T=0$ the results found with the help of (13) differ from (8)–(10) only by numerical factors. As the temperature is raised, there is an increase in the density of one-

electron excitations. They screen the charge more effectively, leading to a decrease in the shift of the chemical potential. At $\tau > \tau_M$, it may not reach δ. At sufficiently low temperatures, with $1-N_s=\sqrt{2\pi\delta/\tau}\exp(-\delta/\tau) < 4\zeta$, far from the center, where we have $|\mu| < \mu_\zeta = \tau \ln [4\zeta/(1-N_s)\tau^2]$, the decay of the perturbation is governed by the parameter ζ (μ_ζ is calculated at a logarithmic accuracy). The contribution of this region to the energy is

$$W_\zeta = (\sqrt{\zeta}/\pi)(\mu_\zeta \mp \mu_e)^2. \tag{14}$$

Near the center of the soliton, with $\mu^2 > \mu_\zeta^2$, there are many thermally excited electrons, and the quasineutrality condition holds. This region expands with increasing temperature, and at $1-N_s > 4\zeta$ it extends to all distances. The shape of the soliton is similar to the solution for a soliton wall at a discommensuration:[19]

$$\varphi = 2\arctan\left[\sqrt{1+\frac{4}{\tau^2(1-N_s)}}\sinh(4x\sqrt{1-N_s})\right] - \pi.$$

At $\tau(1-N_s) \ll 1$ the soliton energy can be estimated from $W \approx 2(\tau^2+1)/\tau$, while at $\tau(1-N_s) \gg 1$ it can be estimated from $W \approx 8/\sqrt{1-N_s}$.

At low temperatures the screening of the charge generated by the perturbation of the phase of the density wave thus leads to large shifts of the chemical potential away from the middle of the gap. The magnitude of the shift is set by the large characteristic lengths, so metal regions may be formed not only by solitons or impurities but also by other irregularities, e.g., contacts. The energy of a soliton increases with decreasing temperature. It depends on the sign of its charge. According to (9), (10), and (14), the energy of a soliton is lower than the energy of a soliton whose charge has the sign opposite that of the majority one-electron charge carriers. Accordingly, when there is a change in the conductivity mechanism from a one-electron mechanism to a soliton mechanism (or if the conductivity begins to be determined by a creep of a density wave, which can be described by the motion of solitons between pinning centers[16]), there should be a change in the sign of the majority charge carriers. This change in sign can explain the observed change in the sign of the thermal emf. The formation of metal islands around impurities at low temperatures may set the stage for a hopping conductivity and may explain the formation of excitations with a low energy.

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