Macroscopic Quantum Tunneling in Quasi One-Dimensional Metals. II. Theory

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A consequence of photon-assisted-tunneling theory of charge-density waves in quasi one-dimensional metals is that the ac conductivity $\sigma(\omega) \simeq \sigma_b \exp(-\omega_s/\omega)$ scales with the dc current $I_{dc}(E)/(E-E_T) = \sigma_b \exp(-E_0/E)$. In a revised theory, $\omega_s = (c_0/v_F)\omega_p$, where c_0 is the phason velocity and ω_p the pinning frequency. Expressions are derived for ω_s and E_0. Relevant lengths are the Lee-Rice domain length, $L_d = \pi c_0/\omega_p$, the free path, $L \sim c_0/\omega_p$, and the current-current correlation length, $L_I \sim (v_F/c_0)L_d$.

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Remarkable transport properties observed in linear-chain metals such as $NbSe_3$ and TaS_3 that undergo Peierls transitions have been the subject of considerable study during the past few years.[1] The Fermi surface (FS) is quasi one dimensional with boundaries at $\pm k_F$ in the chain direction. Below a critical temperature, charge-density waves (CDW's) are formed with wave vector $2k_F$, from a combination of electron and ion motion, so as to open up a semiconducting gap at the FS with an increase in resistivity. Normally pinned by impurities to the lattice, the CDW gradually becomes depinned when a threshold field is exceeded and slides through the lattice, adding to the conductivity, as envisaged by Fröhlich.[2]

The way in which depinning occurs has been the subject of controversy between advocates of semiclassical approaches[3–5] and those favoring models in which quantum tunneling is an essential feature.[6] A theory based on macroscopic tunneling of electrons over large distances in space (~ 10 μm) through a very small pinning gap has been developed and refined through a close interaction between theory and experiment. Photon-assisted tunneling theory, developed for application to superconducting tunnel junctions,[7] gives good agreement with experiments on ac conductivity and on response to combinations of ac and dc voltages.[8] A modification of the theory, described in this Letter, gives good agreement not only with past data, but with experiments[9] designed to test quantitatively values of the parameters derived from microscopic theory.

Like a superconductor, the CDW state is a macroscopic quantum state. There is pairing of electrons and holes that differ by the wave vector $2k_F$, giving order in real space (the CDW) rather than momentum space. The CDW state also may be regarded as macroscopic occupation of phonons of wave vector $2k_F$. When moving uniformly with a drift velocity, v_d, the FS is at $-k_F+q$, k_F+q, where $mv_d = \hbar q$. The energy difference between opposite sides of the FS is the phonon energy, $\hbar\omega_d = 2\hbar k_F v_d$.

The Peierls gaps move with the boundaries of the FS and do not affect the current flow. The kinetic energy E_k of the ions in a moving CDW is much larger than that of the electrons alone; the total is $\frac{1}{2}(m+M_F)v_d^2$ per electron, where the Fröhlich mass,[2] M_F, is of the order of $10^3 m$. In the absence of pinning, the equation of motion is

$$m\, dv_d/dt = \hbar\, dq/dt = e^*E, \tag{1}$$

where $e^*/e = m/(m+M_F)$. With pinning, E is replaced by $EP(E)$, where $P(E)$ is the tunneling probability, $\exp(-E_0/E)$.

The field E is in (1) is the net field, $E = E_{appl} - E_{pol}$, the appiled field corrected for polarization effects.[10] Although very important for a complete picture of CDW motion, polarization effects are not included in the present discussion. The results are valid without correction only for $E_{appl} > \sim 2E_T$.

Following Fukuyama, Lee, and Rice,[11] pinning in $NbSe_3$ and TaS_3 is by impurity fluctuations. To minimize the pinning energy, the phase is adjusted in domains of length L_d and cross section $L_\perp^2 = (\xi_\perp/\xi_\parallel)^2 L_d^2$, where $\xi_\perp/\xi_\parallel$ is of the order of the anisotropy in conductivity. In the present model,[6] pinning is by self-trapped π solitons or phase kinks across which the phase changes by π. A phase change π corresponds to half a state, or, with both spins occupied, a charge e per chain or transverse wave vector. Typically there may be 10^5–10^6 chains, or independent $k_\perp$ values, per domain. The phase is coherent so that there is at most only one thermal degree of freedom for motion in the chain direction. To be stable, the total pinning energy in a domain should be large compared with $k_B T$.

The charge density in a CDW may be written

$$\rho = \rho_0 + \rho_1 \cos[2k_F x + \phi(x,t)], \tag{2}$$

where $2k_F x$ is the phase of a uniform static CDW and $\phi(x,t)$ describes departures of the FS from $\pm k_F$. Space derivatives of ϕ give changes in electron density corresponding to changes in the magnitude, δk_F, of k_F, and time derivatives the displacement, q, of the FS, with $\omega_d = -\partial\phi/\partial t$.

We shall discuss the phase variations, $\phi_p(x)$, re-

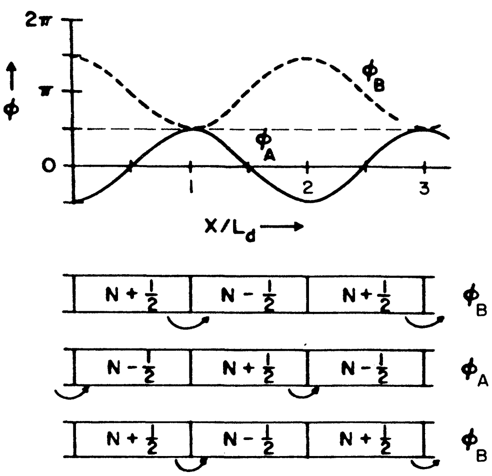

FIG. 1. The phase variations $\phi_A(x)$ and $\phi_B(x)$ that minimize impurity pinning energy. Tunneling steps are indicated below. Tunneling from ϕ_A to ϕ_B goes through the state $\phi=\phi_t=-\frac{1}{2}\pi$ at midgap (see text).

quired for pinning with use of an idealized model in which the pinning is periodic. There are two equivalent ground states that differ in the sign of the charge variation[6]:

$$\phi_A(x)=\tfrac{1}{2}\pi\cos(\pi x/L_d), \quad (3)$$

$$\phi_B=\pi-(\pi/2)\cos(\pi x/L_d)=\pi-\phi_A. \quad (4)$$

As illustrated in Fig. 1, both have the same phase (mod2π) at $x=0$ and for x an integral multiple of L_d. It is at these points that it is presumed in the model that the phase has the desired values to minimize the pinning energy. The phase variations ϕ_A and ϕ_B describe arrays of π solitons of alternating sign, each occupying a domain of length L_d. In terms of the pinning frequency $\nu_p=\omega_p/2\pi$,

$$L_d=\tfrac{1}{2}\lambda_p=\pi c_0/\omega_p, \quad (5)$$

where c_0 is the phason velocity, $v_F(m/M_F)^{1/2}$. More generally, ϕ_A is an aperiodic function in which L_d is a random variable.

When a current flows and the space average of the phase, $\phi_t=\langle\phi(x,t)\rangle$, decreases in time as $-\omega_d t$, the solutions alternate between the ϕ_A and ϕ_B states as shown in Fig. 1.[6] When $-\pi/2<-\phi_t<\pi/2$ (mod2π), ϕ_A has lowest energy; when $\pi/2<-\phi_t<3\pi/2$ (mod2π), ϕ_B has the lowest energy. Alternation between ϕ_A and ϕ_B states maintains a negative pinning energy. When ϕ_t is an odd multiple of $\frac{1}{2}\pi$, the amplitude of the space variation as well as the pinning energy vanishes.

The period of the current oscillations is π in phase as $\phi_A\rightarrow\phi_B\rightarrow\phi_A\rightarrow$ so that the frequency of the oscillations in "narrow band noise"[12] is $\omega_n=2\omega_d$. With both spins occupied, a charge e flows in each chain per cycle of ν_n.[13]

In the Fukuyama-Lee-Rice theory,[11] the length L_d is optimized by minimizing the sum of increase in E_k required to give the phase variation (ϕ_A or ϕ_B), varying as L_d^{-2} per electron, and the negative potential energy from impurity fluctuations, proportional to the square root of the number of impurities in a domain, $N_i^{1/2}$, or $L_d^{-3/2}$ per electron. At the minimum, the total energy is $-\frac{1}{3}$ the increase in E_k. The impurities open up a small pinning gap at the FS, which, unlike the Peierls gaps, is fixed to the lattice and so impedes current flow. Variations of the FS in space and time are the same as those of a model without Peierls gaps if appropriate account is taken of the Fröhlich mass.

The magnitude of the gap may be estimated by calculation of the increase in E_k arising from the density variations associated with $\phi_A(x)$ and equation of $-\frac{1}{3}$ of it to the pinning energy for a simple band model with a gap $E_g=2\Delta$ at the FS. In the band model, the energy per electron is

$$W_{\text{pin}}=-(\pi/2k_F)\tfrac{1}{2}N(0)\Delta^2=-E_g^2/16E_F. \quad (6)$$

Here $2k_F/\pi$ is the density of electrons per unit length per chain and $N(0)=(\pi\hbar v_F)^{-1}$ is the density of states at the FS. This procedure gives a value for Δ very close to $E_\phi=\pi^{-1}v_F\hbar\omega_p/c_0$, the soliton energy, and suggests that the gap is close to that required to produce a soliton-antisoliton pair. Thus Δ is taken equal to E_ϕ.

When ϕ_A is the ground state it describes the state at the top of the filled band with energy $\epsilon=-\Delta$ given by the linear combination

$$\psi=\tfrac{1}{2}\sqrt{2}[\exp(ik_F x+\tfrac{1}{2}i\phi)+\exp(-ik_F x-\tfrac{1}{2}i\phi)] \quad (7)$$

with $\phi=\phi_A$. The pinning energy arises from Friedel oscillations[14] around the impurity sites. When $0<-\phi_t<\pi/2$ the lowest state in the higher band is that for $\phi=\phi_A-\pi$. When $\pi/2<-\phi_t<3\pi/2$ the ground state is ϕ_B and the higher band is $\phi_B-\pi=-\phi_A$. With ϕ_B the ground state, the CDW is displaced by π in phase or by $\lambda_{\text{CDW}}/2$. When $\epsilon=0$ (midgap) $-\phi_t=\pi/2$ and there is no E_k from space variations and no pinning energy. The amplitude of the wave function for $\epsilon=0$ decays in space as $\exp(-\kappa_m x)$, with $\hbar v_F\kappa_m=\Delta$. Tunneling is required to go from $\phi_A\rightarrow\phi_B\rightarrow\phi_A$ states (Fig. 1) so as to maintain a negative pinning energy.

The Zener tunneling probability[15] is given by $\exp(-2\kappa_a d)$, where $\kappa_a=\langle\kappa\rangle$ and d is the tunneling distance such that $eEd=2\Delta$. The usual Zener expression is obtained with $\kappa_a = (\pi/4)\kappa_m$. With $\Delta = E_\phi = (v_F/c_0)\hbar\omega_p/\pi$,

$$E_0 = \frac{\pi}{4}\frac{(2E_\phi)^2}{\hbar v_F e} = \frac{(\hbar\omega_p)^2}{\pi\hbar v_F e^*}. \tag{8}$$

This expression differs from Maki's expression[16] for E_0 for creation of a soliton-antisoliton pair in an electric field in that v_F replaces the phason velocity, c_0, in the denominator. For $v_F >> c_0$, an expression similar to (8) should be valid.[17] Arguments that led to c_0 in the denominator are faulty.[18]

Of the momentum, $2\hbar k_F$, and energy, $2E_\phi$, added by transfer of an electron across the gap, nearly all goes rapidly to macroscopically occupied phonons; only a fraction $m/M_F = e^*/e$ remains with the electrons. An effective energy difference for electrons between adjacent domains with a voltage difference EL_d is e^*EL_d, the energy electrons would pick up if the CDW were accelerated freely in the field, E. The scaling relation is

$$e^*EL_d \leftrightarrow \hbar\omega, \tag{9}$$

in which e^*L_d is determined from E_0. The scaling for the ac conductivity is $E_0/E \rightarrow \omega_s/\omega$, so that $\sigma(\omega) = \sigma_b \exp(-\omega_s/\omega)$ with

$$\hbar\omega_s = e^*E_0L_d = (c_0/v_F)\hbar\omega_p. \tag{10}$$

In earlier versions of the theory,[6] consistent with Maki's expression for E_0, ω_s was taken equal to ω_p, with estimated values for ω_p smaller than in the present theory by a factor of $(c_0/v_F)^{1/2}$.

From (8) and (10), the following relations are found for the pinning frequency, ω_p, and the scaling frequency, ω_s, in terms of E_0:

$$\omega_p^2 = \pi\hbar v_F e^* E_0,$$
$$\omega_s^2 = [m/(m+M_F)]\pi\hbar v_F e^* E_0. \tag{11}$$

For $e^*/e = 10^{-3}$ and $v_F = 2.5\times10^7$ cm/sec, values appropriate for $NbSe_3$ and TaS_3, $\omega_s/2\pi = 57\sqrt{E_0}$ MHz, where E_0 is in volts per centimeter, in agreement with experimental results in I.

There is a further rapid relaxation of the momentum and energy gained by the CDW from the field to the lattice. A tunnel event, creation of a pair of charges, $+e$ and $-e$ moving in opposite directions, gives a phase change π over a mean free path in each direction or a distance $L = 2v_F\tau^*$, a phase-phase correlation length of order c_0/ω_p. The CDW current per chain is

$$e\,\partial n_T/\partial t = (ee^*EL/\pi\hbar)P(E), \tag{12}$$

where $\partial n_T/\partial t$ is the rate at which tunnel events occur. Probability amplitudes for different $k_\perp$ values in a phase-coherent region add coherently (Ref. 19), to give for the current in a sample with N_{ch} chains

$$I_{CDW} = n_c N_{ch} ee^* ELP(E)/\pi\hbar, \tag{13}$$

where n_c is the condensate fraction, proportional to $[1-(T/T_P)^2]^{1/2}$ near the Peierls transition temperature, T_P.

The current-current correlation length, the distance in the chain direction over which tunnel events are coherent, is $L_I = (v_F/c_0)L_d$, related to the displacement q in k space corresponding to the addition of ω_s to ω_d to the electrons in L_I. Tunneling events in L_I are coherent. When $\omega_d < \omega_p$ tunneling is from one ground state, ϕ_A, to the other, ϕ_B, as illustrated in Fig. 1.

As shown in I, the expressions derived for the scaling relation (9), the relations between ω_s and ω_p and E_0, and the ratio of the lengths, $L/L_d \sim \pi^{-1}$ are in good quantitative agreement with experiments. This agreement shows that the agreement of earlier experiments with photon-assisted tunneling theory is more than phenomenological and is soundly based on microscopic theory. Extensions of the theory that take into account disorder in phase-coherent domains and the many metastable configurations possible should be able to account for phenomena near threshold not covered by the present treatment. Since the total pinning energy in domains of volume $\propto L^3$ is proportional to L, at high temperatures regions of large L are stable and effects of metastable states are a minimum.

I am greatly indebted to John Tucker and his first student, John Miller, who initiated an experimental program at Illinois in 1982 to study the possible application of photon-assisted-tunneling theory to CDW transport to show that it does, indeed, successfully account for a wide range of CDW phenomena. They also contributed importantly to the theory and suggested novel experiments. I have also worked closely with George Grüner and his associates, including Alex Zettl, now at Berkeley, and with Karl Seeger and his students, who did the first work on harmonic mixing at microwave frequencies, I am also grateful to Tucker's newer students Greg Lyons and Rob Thorne, as well as R. M. Fleming, A. J. Leggett, K. Maki, G. Mozurkewich, P. Monceau, N. P. Ong, J. Richard, W. Wonneberger, and A. Zawadowski.

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[19]See Bardeen and Tucker, Ref. 6, p. 155.