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Theory of Non-Ohmic Conduction from Charge-Density Waves in $NbSe_3$

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(Received 6 March 1979)

A theory of non-Ohmic conduction from depinning of charge-density waves by an electric field is presented. It is based on Zener-type tunneling of the charge-density waves across a gap at the Fermi surface that is determined by the pinning frequency. The theory applies to relatively pure specimens for which the pinning is due to approach to commensurability or cooperative action of impurities.

The remarkable transport properties of the quasi one-dimensional conductor $NbSe_3$ have attracted a great deal of interest. In the complex unit cell there are three chains of Nb atoms. Transport,[1,2] and x-ray[3] studies indicate two Peierls transitions to charge-density-wave states, one at $T_P = T_1 = 142$ K and one at $T_2 = 58$ K. Below the two transitions there are resistivity peaks from gaps opening up at the Fermi surface (FS). Hall data are consistent with a loss of 20% of the FS at T_1 and 60% of the remaining at T_2. The resistivity peaks are strongly frequency and field dependent. At microwave frequencies (9.6×10^9 Hz), the anomaly below T_2 is completely wiped out and that below T_1 nearly so. The non-Ohmic conductivity can be expressed in the form

$$\sigma = \sigma_a + \sigma_b \exp(-E_0/E), \tag{1}$$

where σ_a is the low-field conductivity and $\sigma_a + \sigma_b$ approximately that expected if the charge-density waves (CDW's) were not present.

The field E_0 is temperature dependent with a minimum of about 1.5 V/cm below T_1 and 0.1 V/cm below T_2. X-ray studies show that the CDW's are present with undiminished magnitudes in fields large enough to wipe out at least half of the resistivity anomalies.[3] The evidence is that the CDW's are weakly pinned and can be released to move freely by application of small electric fields. When moving, they transport carriers by the mechanism proposed by Fröhlich[4] and do not add to the resistivity. There is no evidence that they add to the conductivity which would be present in the absence of CDW's, although scattering by the $2k_F$ phonons which correspond to the state of macroscopic occupation in the CDW should be eliminated.

I propose here a simple theory based on Zener-type tunneling which relates the field E_0 with the frequency of the oscillations of the CDW about pinning positions, ω_P. Although based on a model of commensurability pinning, the theory could also apply to impurity pinning. The wavelength of an incommensurate CDW can always be expressed approximately as the ratio of two integers such that $N_W \lambda_W \simeq N_L a$, where N_W refers to the number of wavelengths, λ_W, of the CDW and N_L to the number of lattice periods, a, required to bring then into approximate coincidence. The pinning period is then $b = N_L a$, where a is the lattice period. It is presumed that the pinning sites are fixed relative to the crystal lattice. Although I discuss a one-dimensional model, it is presumed that there is a substantial coherence distance perpendicular to the chain direction.

A quite different theory for the field-dependent conductivity based on impurity pinning has been given by Lee and Rice.[5] Their prediction that E_0 should be proportional to the square of the impurity concentration, c_i, is in approximate agreement with data of Ong *et al.*[6] on the resistivity anomaly below T_2. The data show that E_0 approaches a limiting value as $c_i \to 0$, but this limit could be determined by impurities responsible for the residual resistivity. Impurity pinning will be discussed briefly later in this note.

As discussed by Fröhlich,[4] and for a more general model by Allender, Bray, and Bardeen,[7] a CDW may be characterized by macroscopic occupation of a phonon state of wave vector $2k_F$, where k_F is that of the quasi one-dimensional Fermi surface. When freely moving with a velocity v_s, the CDW is described by an exponential factor $\exp[2ik_F(x-v_st)]$, so that the frequency $\omega=2k_Fv_s$. The gaps at the FS of the electron distribution will then occur at $-k_F+\kappa$, $k_F+\kappa$, where $\kappa=m^*v_s$ and m^* is the electron band mass.

I first consider the low-temperature limit, $T \ll T_P$, when few quasiparticles are excited across the Peierls gap. In this limit, the current density is nev_s, where n is the density of electrons. The increase in energy, including that associated with the motion of the ions in the CDW, is $\frac{1}{2}(m^*+M_F)v_s^2$ per electron, where $M_F \sim 10^3 m^*$ is the Fröhlich mass associated with ion motion.

When the CDW is pinned, there is no current flow so that $\langle v_s \rangle = 0$. There will, however, be oscillations in v_s at the pinning frequency, ω_p. If N_e is the number of electrons in coherent oscillations of the CDW between pinning sites, the average kinetic energy of the electrons is given by the zero-point energy, $\frac{1}{2}N_e m^* \langle v_s^2 \rangle = (\frac{1}{4})\hbar\omega_P$. An average κ may be defined by $\kappa_a^2 = (m^*/\hbar)^2 \langle v_s^2 \rangle$. Then $N_e \sim k_F/\kappa_a$, which gives $2\hbar v_F \kappa_a = \hbar\omega_P$.

These coherent oscillations are spread into a band of states centered near the FS, $\pm k_F$, as illustrated schematically in Fig. 1. In the absence of an electric field, the ground configuration corresponds to the filled band and there is no current flow. The upper band corresponds to antibonding states of the electrons in CDW oscillations. The diagram illustrates the configurations about which Peierls electron-hole pairing takes place and thus applies to CDW motion, not to quasiparticle excitations that require the Peierls gap.

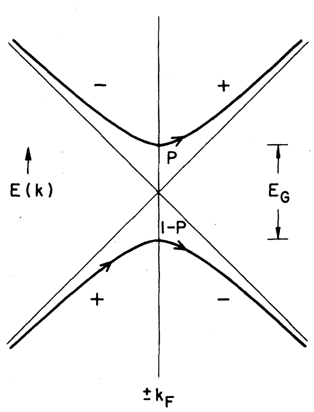

FIG. 1. Electron energies near the Fermi surface, $\pm k_F$, of a pinned charge-density wave. Quadrants marked + come from states near k_F, those marked − from states near $-k_F$. In an electric field there is a probability P that electrons reaching k_F tunnel to the next higher band and $1-P$ that they are reflected to $-k_F$ in the lower band.

In addition to the energy of the electrons, it is necessary to include the kinetic energy of lattice vibrations in the macroscopically occupied phonon state of wave vector $2k_F$ and frequency k_Fv_s. If $P_e = \hbar\kappa = m^*\langle v_s \rangle$ is the momentum per electron, the associated lattice momentum is $P_L = (M_F/m^*) \times P_e$.

In the absence of pinning, the equation of motion may be written

$$d(P_e+P_L)/dt + P_e/\tau = eE. \qquad (2)$$

Here τ is a relaxation time of the electrons for all scattering except to the $2k_F$ phonons in P_L. It is presumed that momentum is exchanged rapidly between P_e and P_L, but that P_L loses little momentum to other scattering processes, including $2k_F$ phonon umklapp scattering.[7] Equation (2) may be written in the form

$$\hbar\, d\kappa/dt + \hbar\kappa/\tau^* = e^*E, \qquad (3)$$

where

$$e^*/e = \tau/\tau^* = m^*/(m^*+M_F). \qquad (4)$$

In steady state $P_e = e\tau E$; and $\sigma_b = ne^2\tau/m^*$ is the conductivity associated with the CDW. In the absence of scattering, the k values of the occupied states in the energy band diagram move at a rate determined by $\hbar\, dk/dt = e^*E$.

Motion of k values of electrons in the filled band for the case of pinning does not change the occupancy and the current remains zero. Motion across the peak at k_F corresponds to reflection from k_F to $-k_F$. The CDW can, however, tunnel across the gap in exact analogy with Zener tunneling in a semiconductor. If one replaces e by e^*, one may use the usual Zener expression[8] for the probability, P, that an electron go from the lower band to the next higher when the k value reaches k_F:

$$P = \exp(-E_0/E), \qquad (5)$$

where

$$E_0 = \pi E_g^{\,2}/(4\hbar e^* v_F). \qquad (6)$$

The equation of motion for κ becomes

$$\hbar d\kappa/dt + \hbar\kappa/\tau^* = Pe^*E \quad (7)$$

and the contribution of the CDW to the conductivity is $\sigma_b \exp(-E_0/E)$ as in Eq. (1).

Order-of-magnitude values for the transition in $NbSe_3$ below T_1 are $E_g \sim \hbar\omega_P \sim 2\times10^{-17}$ erg, $v_F \sim 10^8$ cm/sec, and $M_F/m^* \sim 10^3$. These values give $E_0 \sim 2$ V/cm, which is the order of magnitude of the minimum of the observed $E_0(T)$. Values of E_g and of E_0 for the lower transition are much smaller.

Note that while E_g is much less than k_BT, the energy involved in the coherent motion of the CDW is much larger. One must multiply not only by the factor M_F/m^*, but also by the number of coherent chains in the CDW. The probability P is for transmission of the entire CDW, which involves energies much larger than k_BT. Earlier attempts to account for Eq. (1) in terms of Zener tunneling failed because they considered electron tunneling, not CDW tunneling.

In certain limits, the same method may be applied to impurity pinning if it is known how the pinning frequency varies with the impurity concentration, c_i. In one limit, the CDW oscillations would be localized about the impurity sites and the frequencies would be independent of c_i, at least for small concentrations. The motion of the CDW in an applied field would then not be uniform and the model of Lee and Rice[5] based on formation and motion of dislocations in the CDW lattice might be valid. However, in another limit, impurities could determine the average wavelengths of the oscillations, the frequencies would be expected to be proportional to c_i, and E_0 would vary as c_i^2 as observed. One should be able to distinguish between the two models from analysis of measurements of the frequency dependence of the conductivity, $\sigma(\omega)$.

The experiments indicate that E_0 increases rapidly as $t = T/T_p \to 1$, roughly as $(1-t)^{-1/2}$. At first sight, one might expect that e^* in the denominator of (3) should be replaced by $\rho_s e^*$, where $\rho_s(t)$ is the superfluid fraction as reduced by quasiparticles excited across the Peierls gap, $2\Delta(t)$. The usual superfluid value for ρ_s, which varies as Δ^2 or $1-t$ near T_c, is based on taking $\hbar k$ rather than $mv_g = (m/\hbar)dE_q/dk$ for the quasiparticle momentum. Here $E_q = (\epsilon^2 + \Delta^2)^{1/2}$ is the quasiparticle energy. Lee and Rice[5] as well as Bariack and Overhauser[9] have shown that one should use the latter. This gives a superfluid fraction ρ_c, which varies as Δ rather than Δ^2 near T_c in agreement with observation. One may argue that the difference $\hbar k - mv_g$ is a superfluid backflow contribution and thus should be subject to pinning. When the CDW moves freely in an electric field, $v_s = v_n = e\tau E/m^*$ in the absence of phonon umklapp scattering.

In a discussion of branch or charge imbalance in a superconductor, Pethick and Smith[10] have defined superfluid fractions $\rho_s^{\,Q}$ and $\rho_n^{\,Q}$ and currents $J_s^{\,Q}$ and $J_n^{\,Q}$ which are separately conserved in the absence of energy relaxation and which reflect the difference between $\hbar k$ and mv_g. Thus $\rho_s^{\,Q}$ corresponds to ρ_c. The mathematics is similar for the two problems, although the physics is quite different.

Lee, Rice, and Cross[11] show that ρ_s applies in the static limit and ρ_c in the dynamic (high-frequency) limit. However, they point out that when the various relaxation processes are considered, no two-fluid model may be valid, and one must resort to the detailed Boltzmann equations.

Most of the work reported here was done at the University of Karlsruhe, where I was in residence under an award from the Alexander Humboldt Foundation. I am grateful for discussions there with Albert Schmid as well as to N. P. Ong, P. A. Lee, and T. M. Rice for communicating their results in advance of publication.

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