Tunneling mechanism for the conductivity of quasi-1D conductors with a charge density wave at low temperatures

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Experiments are reported on the conductivity of quasi-1D conductors with a charge density wave. The results show that at temperatures below a certain characteristic T_0, and in electric fields below a certain threshold, the primary conductivity mechanism is a tunneling of collective excitations of a charge density wave, i.e., phase solitons.

As the temperature of many quasi-1D conductors is lowered below a critical T_P, a Peierls instability gives rise to a superstructure and a corresponding modulation of the charge density: a charge density wave.[1,2] The properties of quasi-1D conductors with charge density waves at temperatures $T_P/2 < T < T_P$ have been studied extensively and can, in general, be described satisfactorily by the existing theories.[1,2] In particular, it has been shown that a charge density wave in a real crystal is pinned by impurities and defects, and in weak electric fields the conductivity σ_1 is determined by electron–hole excitations across a Peierls gap Δ. In an electric field above a threshold E_T, the charge density wave goes into motion, the conductivity increases in a nonlinear fashion, and narrow-band oscillations are generated.

At low temperatures, $T \ll T_P$ (at about $T < 30$ K for typical quasi-1D conductor TaS_3), however, the properties of the charge density wave change substantially. The curve of $\log \sigma_1(1/T)$ is not an activation law with an activation energy Δ. Its slope decreases significantly, and the curve can be described well by $\sigma_1 \propto \exp(-T_1/T)^a$ with $a = 1/2$ and $T_1 \simeq 400$ K (Ref. 3). The ac conductivity is described by $\sigma_{ac} \propto \omega^\beta$ with $\beta = 0.7$ (Ref. 4). Each of these expressions corresponds to a hopping conductivity with a variable hopping length.[5] In the same temperature region we see a maximum on the temperature dependence of the dielectric constant, $\epsilon'(T)$, whose position and height depend on the frequency.[6] There are also several anomalies in the behavior of the heat capacity[7] and the ESR.[8] The $\sigma(E)$ dependence changes. However, the rather complicated behavior of the conductivity as a function of the electric field, $\sigma(E)$, at $E < E_T$ has not been studied in detail in this temperature region, nor have the physical mechanisms responsible for this conductivity been analyzed.

In this letter we are reporting data on the conductivity of quasi-1D conductors with a charge density wave at low temperatures in electric fields $E < E_T$. We also offer a qualitative analysis, which indicates that tunneling becomes one of the primary mechanisms for conductivity when the temperature is lowered below a certain value T_0.

The measurements were carried out on thin crystalline samples of orthorhombic

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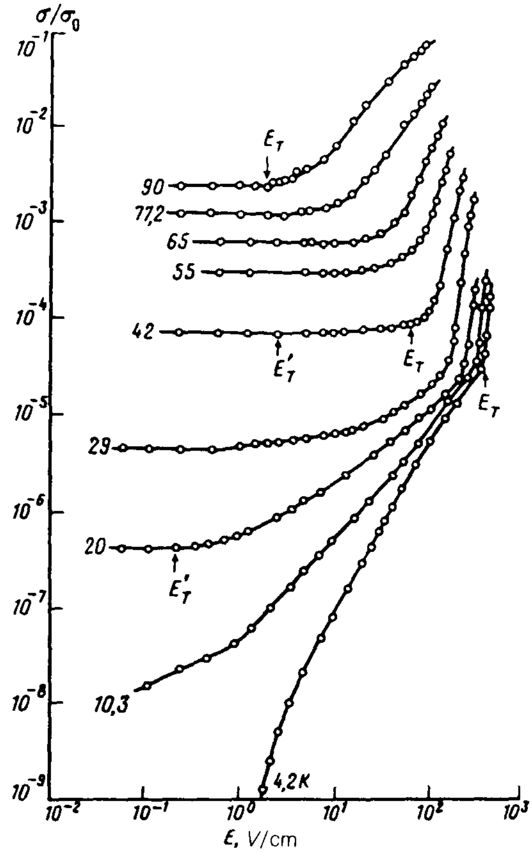

FIG. 1. Conductivity of an o-TaS_3 sample, divided by its value at room temperature, σ_0, versus the electric field at various temperatures (the curve labels).

TaS_3 (o-TaS_3) and monoclinic TaS_3 (m-TaS_3). Electrometers with a high input resistance ($\approx 10^{16}$ Ω) were used to measure the conductivity and current-voltage characteristics in weak electric fields ($E < E_T$) and at low temperatures. In strong electric fields, the measurements were carried out by a pulsed technique with a pulsed two-channel integrator.[10]

Figure 1 shows the conductivity σ of an o-TaS_3 sample versus the electric field at temperatures $T < T_P/2$ ($T_P = 220$ K for o-TaS_3). At $T = 90$ K, the $\sigma(E)$ dependence has the shape typical of the entire temperature range $T_P/2 < T < T_P$. In fields below E_T the conductivity remains constant; at $E > E_T$ a nonlinear conductivity appears, due to the motion of a charge density wave. As the temperature is lowered, the $\sigma(E)$ curve begins to change. In the nonlinear region, $E < E_T$, the curve becomes less convex upward; it approaches a power law at 70–80 K. The region of the transition between the ohmic and nonlinear regions widens, and two threshold fields, E'_T and E_T, appear on the $\sigma(E)$ curve (Fig. 1; Ref. 3). Initially ($T = 40$ K) there is a slight deviation from an ohmic behavior at $E > E'_T$, and there is a progressive increase in σ. Below 30 K, the increase in σ between E'_T and E_T becomes progressively more substantial. The value of E'_T decreases in proportion to T (Ref. 10), while E_T increases:

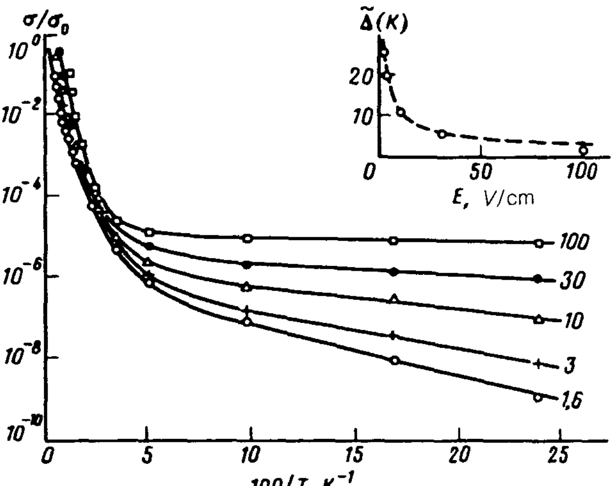

FIG. 2. Temperature dependence of the conductivity of an o-TaS_3 sample in various electric fields (the curve labels).

$E_T \propto \exp(-T_0/T)$ with $T_0=20$ K for o-TaS_3 and $T_0=25$ K for m-TaS_3 (Ref. 10).

At $T<20$ K the resistance of the samples in a weak field becomes very high (10^{13}–10^{14} Ω) and thus difficult to measure. For this reason, it is usually not possible to reach the linear, ohmic part of the current-voltage characteristic at $T<20$ K. At $T=4.2$ K, the conductivity increases by several orders of magnitude, starting at the weakest fields, and the $\sigma(E)$ curve becomes convex upward (Fig. 1). At $E<E_T$, however, a narrow-band generation is observed. This generation is associated with a motion of the charge density wave as a whole.[11] At $E\approx E_T$ there is an abrupt change in slope on the $\sigma(E)$ curve; at the same time, a narrow-band generation with a frequency which depends linearly on the current of the charge density wave appears.[1,2,12]

Figure 2 shows the temperature dependence of the conductivity, $\sigma(1/T)$, for various fields E for the same o-TaS_3 sample. We see that at $T<30$ K, for all E, there is a transition to a more gently sloping nonlinear region on the curves of $\log \sigma(1/T)$. The slope of these curves decreases with increasing E and as E approaches E_T. If we treat the parts of the $\log \sigma(1/T)$ curves at $T<10$ K as approximately linear, and if we think of their slope as corresponding to an "average" activation energy $\tilde{\Delta}$, then we can plot $\tilde{\Delta}$ versus E (see the inset in Fig. 2). In our case, this dependence is $\tilde{\Delta} \propto E^{-\gamma}$ with $\gamma=1/2$. Similar curves of $\sigma(1/T)$ for o-TaS_3 can be found from results we reported earlier on $\sigma(E)$ curves for various values of T to 4.2 K (Refs. 3,10). We replot these results as curves of $\sigma(1/T)$ for various values of E. Qualitatively the same results were recently found for quasi-1D $(TMTSF)_2PF_6$ conductors with a spin density wave[9] and also for o-TaS_3 samples with a very small cross section at temperatures to 2 K (Ref. 12). The $\sigma(1/T)$ curves which we found for other typical quasi-1D conductors–

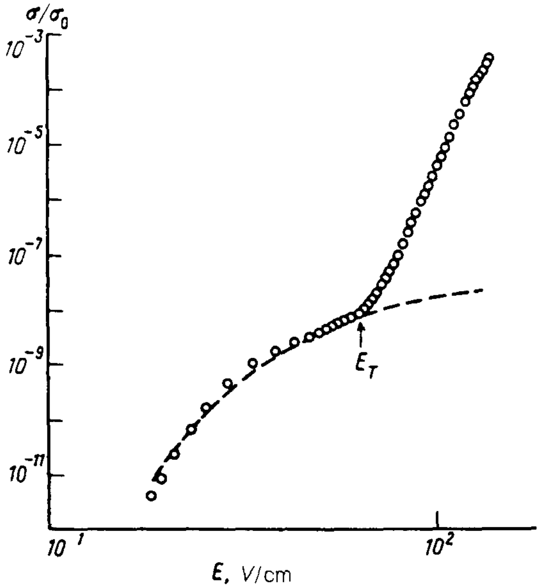

FIG. 3. Conductivity of an m-TaS_3 sample versus the electric field at 4.2 K. The dashed curve is a plot of $\sigma/\sigma_0 \propto E_0/E \exp(-E_0/E)$ with $E_0 = 210$ V/cm.

monoclinic m-TaS_3 and blue bronze, $K_{0.3}MoO_3$—have a similar shape.

The electric-field dependence of the conductivity of the m-TaS_3 sample (at fields both above and below the threshold E_T) is shown in Fig. 3 at a fixed low temperature, 4.2 K (Ref. 13). This figure also compares the experimental $\sigma/\sigma_0(E)$ curve at $E < E_T$ with the theoretical function $\sigma/\sigma_0 \propto (E_0/E)\exp(-E_0/E)^{\delta}$, which is analogous to the function $I/I_0 \propto \exp(-E_0/E)$ used in Ref. 9 to describe the current-voltage characteristic of a quasi-1D conductor with a spin density wave. Our experimental behavior agrees best (but not completely) with the theoretical behavior at $E < E_T$ with the values $\delta = 1$ and $E_0 = 210$ V/cm.

In interpreting the data we should note that at temperatures below 30 K there are substantial changes in the properties of quasi-1D conductors with a charge density wave. For example, there is a transition from an activation-law conductivity to a hopping conductivity,[3,4] and the dielectric susceptibility measured at low frequencies diverges.[6] At these temperatures, the concentration of electron–hole excitations across the Peierls gap becomes negligible, and kinetic phenomena in the conductor are determined primarily by the charge density wave and its collective excitations: solitons and dislocations.[3,4,10,11,14–16] At $T \ll T_P$ the charge density wave tends to become coherent at distances as great as possible both along and across the axis of highest conductivity. In real crystals, however, the potentials of randomly distributed impurities and defects cause substantial local deformations of the charge density wave, particularly at low temperatures, where these potentials are not screened by free carriers. Taking the existing theoretical models[14–16] into account, one might suggest[6] that the ground state of the charge density wave at temperatures below a certain T_0 is a superstructure in which strong pinning centers are frozen and that the phase of the charge density wave changes rapidly, over a small distance ($\sim 10^{-5}$ cm), by amounts of $\pm 2\pi m$. In other words, phase solitons form: quasiparticles with a definite charge and an effective mass. At $E < E_T$, at which the charge density wave as a whole is not moving, the dielectric susceptibility and the conductivity of the conductor are determined by the polarization and by whether these solitons can move. In general, on the other hand, this state is in many ways an analog of the glassy state in such materials as spin glasses[17] and orientation glasses.[18]

The experimental results show that the primary mechanism for the conductivity in such a state of a charge density wave is a hopping of solitons between impurity centers separated by various distances.[3,4] The detachment of a pinned 2π soliton from an impurity center results from an instantaneous local disruption of the order parameter of the charge density wave and a change of 2π in the phase difference. In other words, this is a phase slippage.[19–24] This process can be thought of as a transition between two potential minima with an energy barrier roughly equal (in this case) to the condensation energy per electron,[10] $T_0 = 20–25$ K. At $T < T_0$, a tunneling through this barrier becomes predominant in a weak electric field. In the course of phase slippage, the order parameter of the charge density wave is disrupted in a minimum volume corresponding to a unit cell of the superlattice of the charge density wave. Since a unit cell usually contains something on the order of ten electrons, the phase slippage apparently corresponds to a macroscopic quantum tunneling.[10,25,26]

The latter tunneling has been studied fairly well for the case of the decay of metastable states in systems with Josephson junctions.[25,26] The tunneling of a soliton through a potential barrier V set up by a strong pinning center was examined theoretically in Ref. 20 for the case of a charge density wave. The nature of this calculation (in terms of a tunneling probability $\exp A$, where A is an action) corresponds to the case of macroscopic quantum tunneling. This calculation can apparently be used for a qualitative analysis of the results we have found. It was shown in Ref. 20 that in the limit $T \to 0$ the resistivity of a quasi-1D conductor with randomly distributed impurity centers obeys $\rho \propto \exp(E_0/E)$, where the characteristic field E_0 is determined by the impurity potential V, the average distance between impurities, and the effective mass of a soliton. An estimate of E_0 based on the results of Ref. 20 for o-TaS_3 yields $E_0 \sim 10^2$ V/cm.

It can be seen from Fig. 3 that the experimental $\sigma/\sigma_0(E)$ dependence at $T = 4.2$ K can be approximated fairly well by $\sigma/\sigma_0 \propto \exp(-E_0/E)$, which corresponds to the behavior derived in Ref. 20. In this case we find $E_0 = 210$ V/cm. This value is very close to the value characteristic of the motion of a charge density wave in a strong field, which is governed by phase slippage under the influence of this field.[10,11,23] A similar correspondence between the experimental E dependence of the conductivity and the tunneling formula has been found in quasi-1D conductors with spin density waves at low temperatures.[9] This circumstance seems to suggest a qualitative similarity between the properties of spin and charge density waves in a glassy state which forms at low temperatures.

It is pertinent to note that at low temperatures quantum fluctuations (zero-point vibrations) can also play a significant role in the conductivity of charge and spin density waves. Since the 1D superlattice of a charge (or spin) density wave is "soft," the vibrations of its sites around their displaced equilibrium position are fairly large in amplitude (on the order of the displacement itself[27]). Although the amplitude of these vibrations is considerably smaller than the lattice constant of the superlattice, they seem to still be capable of causing a substantial blurring of the singularity in the density of states near the edge of the Peierls gap,[28] and at a sufficiently low temperature can lead to quantum-diffusion effects.[29]

A tunneling mechanism for the conductivity is also indicated by the temperature dependence of the conductivity at $T < 30$ K. In a weak field, the $\log \sigma(1/T)$ dependence is not linear (i.e., an activation law). It is described well by $\sigma \propto \exp(-T_1/T)^{\alpha}$ with $\alpha = 1/2$, which corresponds to a 1D hopping conductivity with a variable hopping length, which underlies the tunneling. As the field at which $\sigma(1/T)$ is measured is raised, this dependence becomes progressively smoother (Fig. 2), while remaining noticeably nonlinear. However, the number of temperature points in Fig. 2 is insufficient to draw correct conclusions about the magnitude of the power α or its E dependence. More-detailed measurements are necessary. Nevertheless, the "average" slope $\tilde{\Delta}$ of the approximately linear parts of the $\log \sigma(1/T)$ plot decreases with increasing E, roughly in proportion to $E^{-\gamma}$ with $\gamma = 1/2$ (see the inset in Fig. 2). This change in $\sigma(1/T)$ with increasing E agrees qualitatively with the proposition that a tunneling mechanism plays a governing role in the conductivity. In a first approximation in which we ignore the changes in the shape of the barrier with increasing E, there is an increase in the slope of the potential relief corresponding to metastable states of solitons, and the tunneling probability increases. This increase corresponds to a decrease in the "average activation energy" on the $\sigma(1/T)$ curve. As E approaches E_T, the effective barrier shrinks significantly, and processes of a thermal activation across the barrier as the result of thermodynamic fluctuations become significant in the conductivity. At $E > E_T$, the motion of the preexisting solitons and dislocations frozen in the charge density wave is joined by a regular process in which new solitons form and move, as a result of the strong field-induced deformation of the charge density wave near contacts and strong pinning centers.[10,11] This situation corresponds to a sharp increase in the conductivity and to the appearance of periodic oscillations at $E > E_T$.

We can thus draw a conclusion from the set of results presented here [in particular, the change in $\sigma(1/T)$ with increasing E and the correspondence between the shape of the $\sigma(E)$ curve at low temperatures, $T < 20$ K, and a tunneling mechanism] and data obtained previously. This conclusion is that the electrical conductivity of quasi-1D conductors with charge density waves, at temperatures below a characteristic T_0 ($T_0 \simeq 20$ K for TaS_3), and in fields below a threshold, results from a macroscopic quantum tunneling of solitons. This result also indicates common features in the conductivity mechanisms of quasi-1D conductors with charge and spin density waves at low temperatures.

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