Macroscopic Quantum Tunneling in Quasi One-Dimensional Metals. I. Experiment

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A systematic program of experiments designed to test the tunneling theory of charge-density-wave conduction has been carried out over a wide temperature range below three different Peierls transitions in $NbSe_3$ and TaS_3. The results support the hypothesis that charge-density waves depin by quantum tunneling, and are in detailed and consistent agreement with predictions of the model described in the companion paper.

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Several inorganic linear-chain conductors, including $NbSe_3$ and TaS_3, exhibit nonlinear transport below their Peierls transitions.[1] This behavior is widely thought to result from Fröhlich conduction by moving charge-density waves (CDW's).[2] Early measurements in $NbSe_3$ showed that the dc I-E relation is well described by a function of the form

$$I_{\mathrm{CDW}}(E)=G_b(E-E_T)\exp(-E_0/E), \tag{1}$$

where E_T is a threshold field. The field-activated behavior suggested Zener tunneling, but this explanation was abandoned because the required energy gap was orders of magnitude smaller than kT. The tunneling approach was revived in a theory in which current flow within large phase-coherent regions (with at most one thermal degree of freedom) results from coherent tunneling of CDW electrons.[3]

For the past several years, the principal evidence for CDW tunneling has been the success of photon-assisted tunneling (PAT) theory[4] in accounting for the CDW response to ac and combined ac and dc fields. With use of only the measured dc I-V characteristic, a scaling parameter determined directly from experiment, and no other adjustable parameters, the model gives an excellent qualitative and semiquantitative account of the bias-dependent ac conductivity, direct mixing, harmonic mixing, and third-harmonic generation over the entire range 1 to 500 MHz of applied frequencies.[5] Two observations are considered particularly significant: (1) The induced-harmonic mixing and third-harmonic generation currents peak at output frequencies well below the classical "crossover" frequency in the ac conductivity; and (2) the small difference-frequency harmonic mixing response shows no internal phase shift, independent of dc bias and applied frequency. These results are predicted by the tunneling theory, but are in serious disagreement with classical overdamped-oscillator theories[6,7] of CDW motion.

We report here the results of a range of measurements in both TaS_3 and $NbSe_3$ that provide a quantitative test of a revised version of the tunneling theory presented in the companion paper II.[8] Two length scales enter the theory: the characteristic tunneling distance L_d, and the CDW electron mean free path length L. The tunneling distance determines the voltage EL_d which scales with a quantum of energy $\hbar\omega$, so that $e^*EL_d \leftrightarrow \hbar\omega$ where $e^*=(m_b/M_{\mathrm{F}})e$ represents an effective charge reduced by the ratio of the band mass to the Fröhlich mass. The mean free path L determines the limiting high-field conductance G_b. We show how the ratio L/L_d may be derived directly from experiment, and that values thus obtained are uniformly about $\frac{1}{3}$, as expected from the theory. The ratio $\omega_p/\sqrt{E_0}$ of the pinning frequency to the characteristic field is shown to be roughly constant, in accord with the weak-pinning model of Lee and Rice,[9] and with a magnitude that is consistent with the tunneling-theory predictions. The ratio $\hbar/e$ may be estimated from experiment, and is consistent with the accepted value.

In the tunneling theory, the dc I-E relation is predicted to have the form given in Eq. (1), where the characteristic field is given in II by the usual Zener expression

$$E_0=\pi(2E_\phi)^2/4\hbar e v_{\mathrm{F}}, \tag{2}$$

for tunneling across an energy gap

$$2E_\phi=(2v_{\mathrm{F}}/\pi c_0)\hbar\omega_p. \tag{3}$$

This gap corresponds to the energy required to create a soliton-antisoliton pair, where ω_p is the classical pinning frequency and $c_0=(m_b/M_{\mathrm{F}})^{1/2}v_{\mathrm{F}}$ is the phason velocity. As reported previously[10,11] and illustrated in Fig. 1, Eq. (1) describes the measured I-E data in both TaS_3 and $NbSe_3$ very accurately. Extensive measurements of the high-temperature ($59\ \mathrm{K} < T < 145\ \mathrm{K}$) CDW in $NbSe_3$, to be reported in detail elsewhere, show that the experimental data at all temperatures between 70 and 140 K and for fields between 2 and up to 200 times threshold can be fitted essentially exactly by the form of Eq. (1). These results appear to contradict the predictions obtained by Sneddon, Cross, and Fisher using a widely accepted classical model.[12]

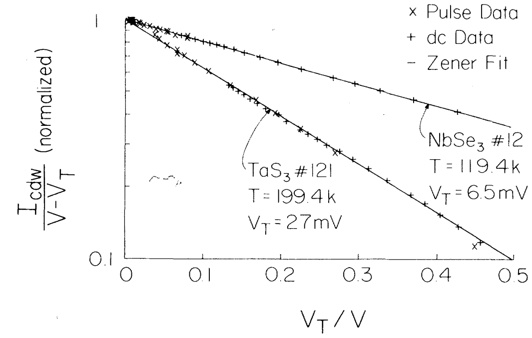

FIG. 1. Normalized I-V data for TaS_3 at 200 K between 2 and 30 times threshold, and for $NbSe_3$ at 120 K between 2 and 200 times threshold. The Zener fit is essentially exact over the entire measured range. The parameters E_0 and G_b are obtained from the slope and intercept, respectively, of the straight-line fit to the data.

Below $T_2 \sim 59$ K in $NbSe_3$, a second CDW is present which has a threshold field roughly 5–30 times smaller than that of the first CDW which forms below $T_1 \sim 145$ K. For fields at which the first CDW remains pinned, Eq. (1) provides an excellent fit to the experimental data on this lower transition as well.

A second prediction of the tunneling theory is that a scaling relation exists between the ac and dc conductivities. In the PAT theory for response to small-signal ac voltages, classical derivatives of the nonlinear dc I-V characteristic are replaced by quantum finite differences, in which $\hbar\omega$ is related to an effective voltage that combines with the dc voltage across the sample. For a sample of length L_s, this effective voltage is given by $V = \alpha\omega$, where

$$\alpha = (\hbar/e^*)(L_s/L_d) \sim 10^5(\hbar/e). \tag{4}$$

The PAT theory, modified to include the effects of internal CDW polarization,[13,14] predicts that the real part of the zero-bias ac conductivity is given by

$$\mathrm{Re}\,\sigma_{\mathrm{CDW}}(\omega) = I_{\mathrm{CDW}}(V_T + \alpha\omega)/\alpha\omega. \tag{5}$$

Thus, $\mathrm{Re}\,\sigma_{\mathrm{CDW}}(\omega)$ is expected to have the same form as a function of frequency as $I_{\mathrm{CDW}}(V)/(V - V_T)$ has as a function of dc voltage. This scaling relation is well obeyed in $NbSe_3$[10] and TaS_3[10,12] over a broad temperature range, although it does not seem to hold below 140 K in our TaS_3 samples where the effects of disorder are evident. The magnitude of the scaling parameter α experimentally obtained is consistent with theoretical estimates in II for e^* and L_d, as evidenced in the data reported below. Use of PAT theory is not specific to the model described in II; it is thought to be a general feature of all models based on quantum tunneling.

The tunneling model in II describes two length scales: an effective mean-free path for CDW electrons, $L = 2v_F\tau^*$, and the characteristic tunneling length, L_d. The ratio L/L_d can be inferred[15] directly from ac and dc conductivity together with narrow-band noise or interference measurements, all performed on the same sample. The limiting high-field conductance is given by

$$G_b = n_c N_{\mathrm{ch}} e e^* L/\pi\hbar L_s, \tag{6}$$

and the ratio of I_{CDW} to the noise frequency is

$$I_{\mathrm{CDW}}/\nu_n = n_c N_{\mathrm{ch}} e. \tag{7}$$

Here n_c is the condensed fraction of the carrier density and N_{ch} is the total number of chains in the cross section of the sample. The relation (7) implies that one electron passes per chain per cycle of ν_n. These expressions may be combined with Eq. (4) to yield the ratio of the two lengths,

$$\beta = 2\pi\alpha G_b/(I_{\mathrm{CDW}}/\nu_n) = 2L/L_d, \tag{8}$$

which is independent of the condensate fraction n_c.

A few comments on the experimental techniques used to obtain estimates for β are in order. First, the evaluation of α below T_2 in $NbSe_3$ is complicated by the presence of two CDW's. Fortunately, their frequency and voltage scales are sufficiently separated so that the scaling parameter for the low-temperature CDW may be estimated by comparing the low-field and low-frequency (5–20-MHz) conductivities. Second, measurements of the ratio I_{CDW}/ν_n in the expression for β give an estimate of the condensed carrier density. In $NbSe_3$, this ratio can be determined directly from the narrow-band noise spectrum. In TaS_3, the less coherent response necessitated the use of interference measurements. These consist of determination of the values of I_{CDW} at the peaks in dV/dI generated by locking of ν_n to an externally applied rf voltage. The ratio I_{CDW}/ν_n obtained in this manner increases with increasing rf amplitude, but saturates at large rf amplitudes. As discussed by Brown and Gruner,[16] this limiting ratio should best reflect the condensed carrier density, and was used in the calculation of β.

The experimental results used in the estimation of β are given in Table I. The value obtained is nearly independent of temperature and material, with $\beta \sim 0.6$ for TaS_3 and for both CDW's in $NbSe_3$. Note that the magnitude of the scaling parameter α varies by more than an order of magnitude over this data set. In the model of II, $L \sim c_0/\omega_p$ and $L_d \sim \pi c_0/\omega_p$, so that β is predicted to be approximately $2/\pi \sim 0.64$, in excellent agreement with the experimental result.

The tunneling-theory expressions may be used to calculate parameters of the model from experimentally measured quantities. Some of these parameters are given for $NbSe_3$ and TaS_3 at selected temperatures in

TABLE I. Tunneling-theory parameters derived from ac and dc conductivity and narrow-band noise or interference measurements, all performed on single samples of TaS_3 and $NbSe_3$. For sample TaS_3 No. 120, $L_s = 1.4$ mm, and $E_T(200\ K) = 380$ mV/cm; and for $NbSe_3$ No. 10, $L_s = 0.7$ mm, $E_T(120\ K) = 70$ mV/cm, and $E_T(49.1\ K) = 6.4$ mV/cm. The quantity β, which is twice the ratio of the mean free path to the tunneling length, is predicted to be ~ 0.64.

Sample	T (K)	G_b (ms)	E_0 (mV/cm)	$2\pi\alpha$ (mV/MHz)	$\frac{I_{CDW}}{\nu_n}$ (μA/MHz)	β
TaS_3	208.9	2.37	1380	3.35	13.4	0.59
No. 120	200.2	2.50	1520	3.51	15.0	0.59
	184.5	2.50	1990	4.10	16.1	0.64
	169.5	2.34	2510	4.72	17.3	0.64
	154.5	2.09	2960	6.00	18.7	0.67
	139.4	1.66	2930	8.00	20.0	0.66
$NbSe_3$	127.5	5.48	200	0.66	6.99	0.52
No. 10	120.0	9.12	227	0.82	9.35	0.80
	100.0	9.57	205	0.82	10.2	0.76
	79.6	11.4	535	1.40	7.19	2.20
	53.3	21.0	10.5	0.13	4.75	0.58
	49.1	35.9	9.2	0.13	8.45	0.56
	43.4	37.2	14.9	0.18	9.08	0.74

Table II. These calculations reflect modifications to the theory from previous versions, as described in II. In particular, the pinning frequency ω_p and the scale frequency ω_s are no longer taken to be equal, but are related by $\omega_s = (c_0/v_F)\omega_p$. Thus ω_s is now loosely identified with the classical "crossover frequency" and is typically tens of megahertz, while ω_p is on the order of a gigahertz. The values listed in Table II for the pinning frequency are comparable to those inferred by Sridhar, Reagor, and Gruner[17] from the rolloff of the ac conductivity at millimeter-wave frequencies with use of the overdamped-oscillator model, except below T_2 where two CDW's are present.

TABLE II. Tunneling-theory parameters at selected temperatures for TaS_3 and $NbSe_3$, derived from the data in Table I. The ratio $\omega_s/2\pi\sqrt{E_0}$ is predicted to be 57 MHz $(\mathrm{V/cm})^{-1/2}$.

	TaS_3 No. 120 184.5 K	$NbSe_3$ No. 10 120.0 K	49.1 K
$\omega_s/2\pi$ (MHz)	67	19	4.8
$\omega_p/2\pi$ (GHz)	2.3	0.59	0.15
L_d (μm)	1.6	3.4	22
$\omega_s/2\pi\sqrt{E_0}$ [MHz$(\mathrm{cm/V})^{1/2}$]	48	39	51
$\frac{(\hbar/e)_{\mathrm{expt}}}{0.658\times10^{-15}\ \mathrm{V\ s}}$	1.4	2.0	1.2
M_F/m_b	1200	1400	1100

The quantities ω_s, ω_p, and E_0 all depend on impurity concentration and thus are sample dependent. However, the experimental measurements may be combined to yield ratios which are predicted to depend only on k_F, M_F, and m_b. One such quantity is

$$\omega_s/2\pi\sqrt{E_0} = (e v_F/4\pi\hbar)^{1/2}(m_b/M_F). \tag{9}$$

Use of $v_F = 2.5\times10^7$ cm/s and $M_F/m_b = 1000$ for both TaS_3 and $NbSe_3$ yields $\omega_s/2\pi\sqrt{E_0} \approx 57$ MHz$(\mathrm{V/cm})^{-1/2}$. This theoretical prediction is in excellent agreement with the experimentally deduced values listed in Table II for both TaS_3 and $NbSe_3$. Alternatively, these estimates for v_F and M_F/m_b may be combined with the measured values of ω_s and E_0 in Eq. (9) to infer from experiment the value of $\hbar/e$. Since M_F/m_b is not accurately known and the estimate for $\hbar/e$ depends upon $(M_F/m_b)^2$, the magnitude of $\hbar/e$ obtained in this way is likely to be accurate to within a factor of 2 at best. The experimentally derived values for $\hbar/e$ in Table II are thus consistent with the accepted value in both TaS_3 and $NbSe_3$. Table II also gives estimates of M_F/m_b obtained from Eq. (9) with use of the correct value of $\hbar/e$.

The ability to estimate $\hbar/e$ directly from experiment helps confirm that quantum tunneling is responsible for acceleration of CDW electrons in an electric field.

The quantum tunneling theory gives the correct form for the dc I-V relation. It correctly predicts the nonlinear coupled ac-dc response of the CDW system throughout the megahertz frequency region. Values for L/L_d, M_F/m_b, and several other parameters inferred from experimental data with use of the tunneling theory are consistent with each other and with predicted or generally accepted values. The great diversity of experimental results explained by the tunneling theory is convincing evidence that the dynamics of charge-density waves in quasi one-dimensional metals represent macroscopic quantum effects in a new range of temperature and frequency.

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