Evidence for Tunneling of Charge-Density Waves in TaS_3

J. H. Miller, Jr., J. Richard,[a] and J. R. Tucker
Department of Electrical Engineering and Coordinated Science Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

and

John Bardeen
Department of Physics, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801
(Received 23 May 1983)

The charge-density-wave contribution to ac and dc conductivity, rectification, and harmonic mixing has been measured on a single crystal of orthorhombic TaS_3. A modified tunneling theory based on the Zener model of charge-density-wave conduction provides a detailed and quantitative account of these experiments. This evidence strongly supports the hypothesis that macroscopic quantum effects are observed in the megahertz frequency region at temperatures as high as 200 K.

PACS numbers: 72.15.Nj

Nonlinear collective charge transport due to the motion of charge-density waves (CDW's) is observed in the inorganic "one-dimensional" metals $NbSe_3$[1] and TaS_3[2] below their Peierls transitions. A dc threshold field $E_T \sim 0.01$ to 1 V/cm is required in order to depin these CDW's from their equilibrium configuration.[3] The nonlinear ac conductivity resulting from CDW motion increases with applied frequency in the megahertz region, and eventually saturates at the limiting value observed for large dc fields.[4]

There has been controversy as to whether the depinning of CDW's can be described by classical models, or whether an explanation based on quantum tunneling is required. Simple overdamped oscillator models describe many qualitative features,[5] and classical theories which incorporate internal degrees of freedom have also been proposed.[6] A quantum theory,[7] based on Zener tunneling of the electron condensate through a small pinning gap, has been shown to give quantitative agreement with the nonlinear dc I-V characteristic. An extension of this theory utilizing the concept of photon-assisted tunneling[8] predicts a scaling relation between ac and dc conduction, and also the effects of combined ac and dc fields. In a previous series of experiments, Gruner *et al.*[9] and Zettl, Gruner, and Thompson[10] tested various aspects of this tunneling theory and found the predicted scaling relation to be accurately obeyed in both $NbSe_3$ and TaS_3. Serious discrepancies were found, however, for effects involving combined ac and dc fields.[9] Experiments reported here on TaS_3 have led to a revised form of the scaling relation between field and frequency that gives excellent quantitative agreement for ac-dc coupling effects, and removes the discrepancies with the original formulation of the theory. These results provide strong evidence in favor of the tunneling interpretation of CDW depinning.

The tunneling model gives an expression for the dc current of the form

$$I_{dc}(E) = I_N(E) + I_{CDW}(E) = G_a E + G_b(E - E_T)\exp(-E_0/E). \qquad (1)$$

Here E_T is the threshold field, G_a and G_b represent the Ohmic and CDW conductances, and E_0 is the characteristic field for Zener tunneling. The observed dc nonlinearity for fields $E > E_T$ above threshold is very accurately described by Eq. (1) in both $NbSe_3$ and TaS_3 out to the largest potentials $E \sim 100 E_T$ that can be experimentally applied.[9,10] Also, photon-assisted tunneling theory[8] may be adapted in this context to yield detailed predictions for the ac response of the CDW condensate, utilizing only the fit of Eq. (1) to the nonlinear dc I-V curve.

Experimental measurements of ac conductivity show no dependence on dc bias voltage V_0 in the range $-V_T < V_0 < +V_T$ below threshold. We believe that polarization effects in this region are decoupled from the tunneling currents induced by small-amplitude ac signals, and that the effective dc voltage is $V_0' = 0$ for $|V_0| < V_T$. According to this hypothesis, the relevant dc bias is $V_0' = V_0 - V_T$ for $V_0 > V_T$ and $V_0' = V_0 + V_T$ for $V_0 < -V_T$. The ac conductivity inferred from photon-assisted tunneling theory then becomes

$$\sigma(\omega, V_0) = \frac{I'(V_0' + \alpha\omega) - I'(V_0' - \alpha\omega)}{2\alpha\omega}, \qquad (2)$$

where $I'(V_0') = I_{CDW}(V_0)$ for $|V_0| > V_T$. With use of this revised interpretation, there is no sharp frequency threshold, and no change in the small-signal ac response for $|V_0| < V_T$, in agreement with experiment.

The frequency dependence of the ac conductivity in Eq. (2) for $V_0' = 0$ is predicted to scale with $V - V_T$ in the form $I_{CDW}(V)/(V - V_T)$, instead of with $I_{CDW}(V)/V$ as in the original version of the theory. This modified scaling between ac and dc response is illustrated in Fig. 1 for a crystal of orthorhombic TaS_3 whose threshold is $V_T = 32$ mV across a sample length $l \approx 0.5$ mm at $T = 190$ K. The scaling parameter is inferred to be $\alpha/2\pi = 0.7$ mV/MHz for this sample, consistent with microscopic estimates for tunneling across a 10-μm coherence length. The solid line in Fig. 1 is a theoretical fit to the dc data based on the Zener tunneling expression of Eq. (1) with $G_a = 0.56$ mmhos, $G_b = 2.50$ mmhos, and

$$E_0/E_T = 2.5 + 0.5E_T/(E - E_T). \tag{3}$$

The second term here is included *ad hoc* to eliminate singularities in the derivatives of Eq. (1) at $E = E_T$.

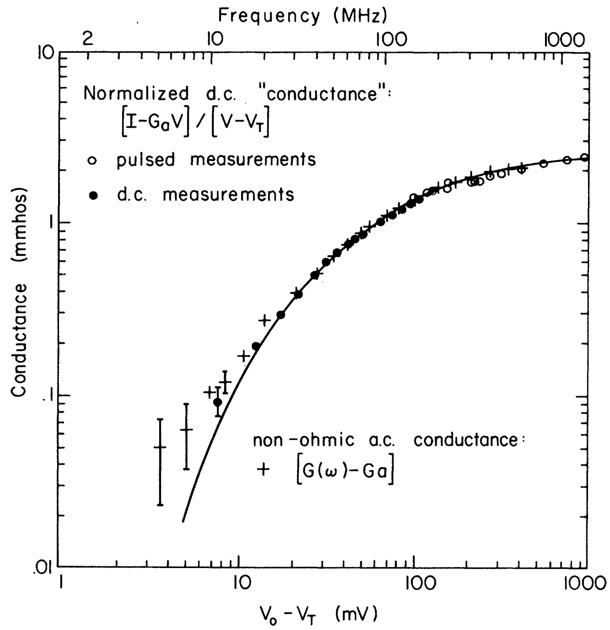

FIG. 1. Comparison of nonlinear dc and ac conductance for a crystal of orthorhombic TaS_3 at $T = 190$ K, according to the scaling relation derived from Eq. (2). The solid line is a theoretical fit of the dc data to Eq. (1).

The data of Fig. 1 can be utilized to predict the complete ac response on the basis of photon-assisted tunneling theory. The nonlinear ac conductivity measured as a function of both frequency and applied dc bias is found to be in excellent quantitative agreement with Eq. (2). Much more sensitive tests of CDW dynamics can, however, be carried out in the form of mixing experiments. A dc field may be combined with the output from two frequency-locked signal generators to apply a voltage across the sample of the form

$$V(t) = V_0 + V_1 \cos(\omega_1 t + \varphi) + V_2 \cos(\omega_2 t). \tag{4}$$

Rectification due to the CDW nonlinearity may then be probed by setting $V_1 = V_2 \ll V_T$ and choosing a small difference frequency $\omega_0 = \omega_1 - \omega_2$ suitable for lock-in detection. Under these conditions, the magnitude of the time-dependent rectification signal $\Delta I_0 \cos(\omega_0 t + \varphi)$ is predicted to be

$$\Delta I_0 = \frac{1}{2} V_1^2 \left[\frac{I'(V_0' + \alpha\omega) - 2I'(V_0') + I'(V_0' - \alpha\omega)}{(\alpha\omega)^2} \right], \tag{5}$$

where $\omega = \omega_1 \approx \omega_2$. The expression in square brackets is seen to approach the second derivative of the dc I-V characteristic for $\alpha\omega \ll V_T$. In Fig. 2, experimental rectification measurements are compared with the tunneling result of Eq. (5) for the sample characterized in Fig. 1. The theoretical curves are generated with use of the fit to the nonlinear dc I-V characteristic described previously, together with the ac amplitude $V_1 = 5$ mV applied in these experiments. Note that both scales in Fig. 2 are absolute, and that there are no adjustable parameters.

Harmonic mixing experiments, again taken on the same TaS_3 sample during the same experimental run, are illustrated in Fig. 3. In this case, the applied signal in Eq. (4) is adjusted so that the output frequency $\omega_0 = 2\omega_1 - \omega_2$ due to harmonic mixing is detected by the lock-in amplifier. A frequency doubler together with a double-balanced mixer was used to synthesize the reference frequency, and a Schottky diode mounted in place of the sample provided an absolute phase calibration. The tunneling-theory prediction for the magnitude of the harmonic mixing signal $\Delta I_0 \cos(\omega_0 t + 2\varphi)$ is given by

$$\Delta I_0 = \frac{1}{8} V_1^2 V_2 \left[\frac{I'(V_0' + 2\alpha\omega) - 2I'(V_0' + \alpha\omega) + 2I'(V_0' - \alpha\omega) - I'(V_0' - 2\alpha\omega)}{(\alpha\omega)^2 (2\alpha\omega)} \right], \tag{6}$$

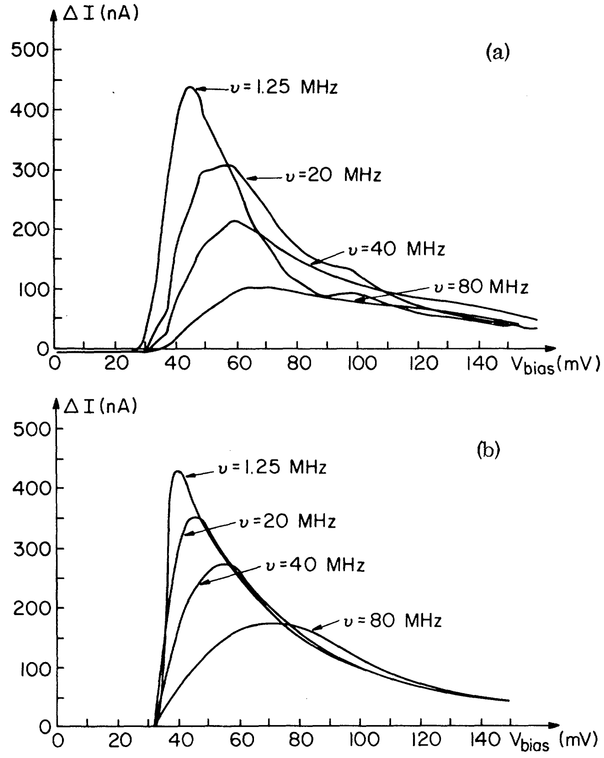

FIG. 2. (a) Rectification vs dc bias and frequency for a crystal of orthorhombic TaS_3 at $T = 190$ K. (b) Predictions of the tunneling model from Eq. (5) and the fit to the dc I-V data shown in Fig. 1.

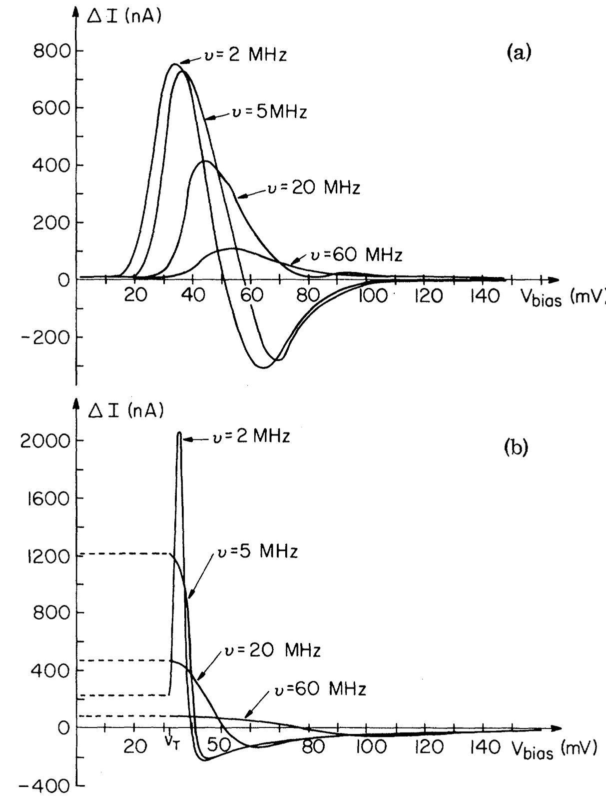

FIG. 3. (a) Zero-phase harmonic mixing signal vs dc bias and frequency for a crystal of orthorhombic TaS_3 at $T = 190$ K. (b) Predictions of the tunneling model from Eq. (6) and the fit to the dc I-V data shown in Fig. 1.

where $\omega = \omega_1 \approx \omega_2/2$. The theoretical curves in Fig. 3 are generated by inserting the fit to the dc I-V characteristic into this expression. The dashed portion of the theory curves indicates that a bias-independent harmonic-mixing current is expected for $V_0 < V_T$ below threshold. This behavior is indeed observed for large output frequencies $\omega_0 \gtrsim 1$ MHz. The experimental harmonic-mixing results for $\omega_0 = 1$ kHz shown here are seen to vanish for $V_0 < V_T$, while the behavior above threshold is in good semiquantitative agreement with the theory. Finite ac amplitudes $V_1 = 11$ mV and $V_2 = 15$ mV were required to characterize the response over the entire range of parameters. This causes some apparent rounding of the sharp peaks in the mixing signal at low frequencies, and agreement with theory in this region is substantially improved by using smaller applied ac amplitudes. Previous measurements of harmonic mixing in $NbSe_3$ at microwave frequencies by Seeger, Mayr, and Phillip[11] are also in general agreement with the tunneling theory.

A further result which supports the tunneling theory is the absence of an internal phase shift in harmonic mixing. In general, the time dependence of the harmonic mixing signal will be given by $\cos(\omega_0 t + 2\varphi - \psi)$. The tunneling theory predicts that $\psi = 0$ under all conditions, while classical models are expected to yield nonzero phase shift at high frequencies. For large applied frequencies $\alpha\omega \gg V_0', V_T$, Eq. (6) becomes

$$\Delta I(t) = \frac{\eta}{8}\left(\frac{V_1}{V_T}\right)^2\left(\frac{\omega_T}{\omega}\right)^3 G_b V_2 \cos(\omega_0 t + 2\varphi), \quad (7)$$

where $\eta = E_0/E_T$ and $\omega_T = V_T/\alpha$. A straightforward calculation using the classical overdamped oscillator model[5] with a sine-Gordon potential gives

$$\Delta I_0(t) = \frac{1}{8}\left(\frac{V_1}{V_T}\right)^2\left(\frac{\omega_c}{\omega}\right)^3 G_a V_2 \cos(\omega_0 t + 2\varphi - \tfrac{1}{2}\pi) \quad (8)$$

for frequencies $\omega \gg \omega_c = \omega_0^2\tau$ large compared to the classical "crossover" frequency. The phase shift in the overdamped limit is expected to increase from $\psi=0$ for $\omega \ll \omega_c$ to $\psi=\pi/2$ for $\omega \gg \omega_c$.[12] Applied frequencies as high as $\nu_1=500$ MHz and $\nu_2=1$ GHz have been mixed in a second crystal of TaS_3 whose classical crossover frequency is $\nu_c \approx 80$ MHz. A phase shift $\psi=0\pm10°$ is observed, and the absence of any measurable quadrature component is therefore additional strong evidence for a quantum interpretation of CDW depinning in a regime where $h\nu \sim 10^{-6}kT$.

The crystals used in these experiments were provided by George Gruner and Alex Zettl at the University of California at Los Angeles, along with much valuable advice and discussion. The harmonic-mixing experiments were inspired by the work of K. Seeger and his collaborators at Vienna, and we thank A. R. Kerr of the National Aeronautics and Space Administration Institute for Space Studies for expert guidance on rf measurement techniques. This research was supported by the U. S. Joint Services Electronics Program (U. S. Army, U. S. Navy, and U. S. Air Force) under Contract No. N00014-C-79-0424, and by the National Science Foundation through Grant No. ECS 81-20038. One of us (J.H.M.) is a recipient of a General Electric Foundation predoctoral fellowship.

---

[a]Permanent address: Centre de Recherches sur les Trés Basses Températures, Centre National de la Recherche Scientifique, B. P. 166X, F-38042 Grenoble, France.

[1]P. Monceau, N. P. Ong, A. M. Portis, A. Meerschaut, and J. Rouxel, Phys. Rev. Lett. 37, 602 (1976).

[2]T. Takoshima, M. Ido, K. Tsutsumi, and T. Sambongi, Solid State Commun. 35, 911 (1980); A. H. Thompson, A. Zettl, and G. Gruner, Phys. Rev. Lett. 47, 64 (1981).

[3]R. M. Fleming and C. C. Grimes, Phys. Rev. Lett. 42, 1423 (1979).

[4]N. P. Ong and P. Monceau, Phys. Rev. B 16, 3443 (1977); G. Gruner, L. C. Tippie, J. Sanny, W. G. Clark, and N. P. Ong, Phys. Rev. Lett. 45, 935 (1980).

[5]G. Gruner, A. Zawadowski, and P. M. Chaikin, Phys. Rev. Lett. 46, 511 (1981); P. Monceau, J. Richard, and M. Renard, Phys. Rev. B 25, 931 (1982).

[6]L. Sneddon, M. C. Cross, and D. S. Fisher, Phys. Rev. Lett. 49, 292 (1982); D. S. Fisher, Phys. Rev. Lett. 50, 1486 (1983); R. A. Klemm and J. R. Schrieffer, Phys. Rev. Lett. 51, 47 (1983).

[7]J. Bardeen, Phys. Rev. Lett. 42, 1498 (1979), and 45, 1978 (1980).

[8]J. R. Tucker, IEEE J. Quantum Electron. 15, 1234 (1979).

[9]G. Gruner, A. Zettl, W. G. Clark, and J. Bardeen, Phys. Rev. B 24, 7247 (1981).

[10]A. Zettl, G. Gruner, and A. H. Thompson, Phys. Rev. B 26, 5760 (1982).

[11]K. Seeger, W. Mayr, and A. Phillip, Solid State Commun. 43, 113 (1982).

[12]K. Seeger, *Semiconductor Physics* (Springer-Verlag, New York, 1973), p. 414.