Transport by Charge-Density Waves in Linear-Chain Conductors

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I. Introduction

The remarkable nonlinear field and frequency-dependent conductivity of the transition metal trichaleogenides was observed first in $NbSe_3$ by Monceau, Ong, and Portis[1] at Berkeley in 1976. They found that resistivity peaks below Peierls transitions at 144 K and 59 K are largely wiped out at microwave frequencies and also with increasing electric fields. The following year, Sambongi et al.[2] at Hokkaido found a Peierls transition in TaS_3 at 220 K, below which the conductivity becomes thermally activated as in a semiconductor with a gap and exhibits similar effects. Further studies by several groups have found a number of other inorganic quasi-one-dimensional metals. Experimental investigation of these materials has yielded a rich variety of phenomena, still imperfectly understood. Thus a great deal remains to be done in both experiment and theory.

It is now generally recognized that the remarkable transport properties arise from the Fröhlich[3] mechanism of transport by moving charge-density waves (CDW's) formed below the Peierls transition temperature. The CDW's have a wave vector $Q = 2k_F$ in the chain direction such as to open up gaps at the quasi-one-dimensional Fermi surface (FS) at $\pm k_F$. Below a threshold field, E_T, the CDW is pinned to the lattice and the conductivity is ohmic. At higher fields the CDW begins to move with a nonlinear increase in current with field. Associated with the dc current is an oscillatory current or "narrow-band noise" with a fundamental frequency proportional to the drift velocity of the CDW and with a rich harmonic content.

Depinning also affects the frequency dependence of the ac conductivity, $\sigma(\omega)$. Many experiments have been carried out during the past two or three years on effects of ac fields up to the microwave range (9.8 GHz) and on detection and mixing involving combinations of ac and dc fields.

Complex hysteresis and memory effects have been observed with repeated pulses of dc voltages and with large amplitude ac. These effects appear to be particularly important when the voltage passes above threshold and then drops below. These observations indicate that pinning involves many metastable states of comparable energy. Some of these experiments will be discussed by J. Gill later in this symposium.

The theory of depinning is still subject to controversy and no one is yet able to explain all of the wide variety of phenomena that have been studied. Many of the qualitative features can be accounted for by an overdamped oscillator model.[4] It is assumed that in the absence of an electric field the CDW oscillates about the pinning positions at a characteristic frequency, ω_p, but that the relaxation time, τ is so short that $\omega_p\tau \ll 1$.

Other models[5] take into account the internal degrees of freedom of the CDW. It is assumed that as the CDW moves almost freely in high electric fields, the pinning forces from impurity pinning can be treated perturbatively. One then gets a series in inverse powers of E, the leading term in the correction to the conductivity $\sigma(E)$ being one in $E^{-1/2}$. Scaling and renormalization arguments have been used to determine the behavior near threshold. Both of these approaches are semi-classical and quantum effects enter only indirectly.

The density of carriers is such that the wavelength of the CDW is incommensurate with the lattice in $NbSe_3$ and in orthorhombic TaS_3 above 140 K, although the density is not far from the commensurate value of 1/2 electron per atom. Some models assume that the CDW is commensurate throughout most of the volume with the extra charges going into a lattice of solitons or discommensurations.[6]

Through a close interaction between theory[7] and experiment, my collaborators and I have been attempting to develop and verify a theory of depinning based on quantum tunneling of electrons through a small pinning gap over macroscopic distances. In this talk I will describe the tunneling theory as it has evolved and developed from this interaction. Although this morning's session is primarily theoretical, I also will describe some recent experiments by Miller et al.[8] at Illinois on rectification and harmonic mixing that give strong support to the tunneling model. In the time available, I will be able to give only the background of the tunneling theory together with predictions for experiments involving combined ac and dc fields.

Since other speakers will talk about semiclassical theoretical approaches, I will confine my discussion to the tunneling model, but will try to indicate areas where classical approaches may be appropriate and those where I believe quantum effects are essential.

II. Background for tunneling model

Monceau *et al.*[1] found that the nonlinear dc current may be fitted approximately by

$$i_{dc} = \sigma_a E + \sigma_b E \exp[-E_o/E]. \tag{2.1}$$

This suggested tunneling through a pinning gap. However it was found that the tunneling probability is very small if the entire CDW tunnels as a massive object and that if electrons tunnel the gap required is much smaller than $k_B T$. The main purpose of my 1979 paper[7] was to show that a small pinning gap in a semiconductor model is possible if it applies only motion of electrons in the CDW condensate, not to excitations. Quasiparticle excitations are reduced by the much larger Peierls gap which does not affect motion of the condensate as a whole.

According to Fröhlich and the more general theory of Allender, Bray and Bardeen,[9] the charge density associated with a CDW moving with a velocity, v_d, may be described in a simple model by:

$$\rho = \rho_o + \rho_1 \cos[2k_F(x-v_d t)]. \tag{2.2}$$

The Peierls gaps appear at the boundaries of the moving FS, $k_F + q$, $-k_F + q$, where $\hbar q = mv_d$ and m is the band mass. Each v_d specifies a ground state (vacuum) for the system. The CDW may be regarded as coupled system of electrons and macroscopically occupied phonons of wave vector $2k_F$ and frequency $\omega_d = 2k_F v_d$ with independent degrees of freedom. The only degree of freedom of the electrons is for one or more to go from one side of the Fermi sea to the opposite, with a change in crystal momentum of $\pm\, 2k_F$ per electron transferred. But the phonons rapidly maintain an equilibrium value for the total momentum for the electrons, $P_e = (m/M_F)P_L$, where P_L is the momentum associated with the macroscopically occupied phonons and $M_F \sim 10^3 m$ is the Fröhlich mass.

To change v_d and thus the current by an electric field, the increase in momentum of the electrons from the field must be shared by the phonons. The equation of motion in the absence of pinning is per electron

$$d(P_L + P_e)/dt = (M_F + m)dv_d/dt = eE \tag{2.3}$$

or

$$\hbar dq/dt = e^* E\ , \tag{2.4}$$

where $e^* = me/(m + M_F) \sim 10^{-3}$ e. If v_d is changed to $v_d + \Delta v_d$, the Peierls gaps will appear at the new FS, $- k_F + q + \Delta q$, $k_F + q + \Delta q$.

In the model,[7] pinning is represented by a small pinning gap at the FS of magnitude $\hbar\omega_P$, where ω_P is a pinning frequency. Electrons are transferred across the gap by Zener tunneling. To account for the fact that electrons give up most of their momentum to the phonons, it is necessary to replace e by e^*. In the initial version of the theory, this was the only modification of the Zener theory, giving $E_o = \hbar\omega_P/2\xi_o e^*$, where $\xi_o = 2v_F/\pi\omega_P$ is the Pippard coherence distance. In the 1980 version,[7] with experimental evidence that $\omega_P/2\pi \sim 1.5\times10^7$ Hz in $NbSe_3$ below T_2, it was found necessary to replace $2\xi_o \sim 0.1$ cm by a much smaller distance L ~ 30 μm. The correlation length, L, for phase coherence is assumed to be analogous to the m.f.p. in the Pippard expression for acceleration of current in a superconductor.

In the Lee-Rice theory of pinning, the distance, L, is of the order of c_o/ω_P rather than v_F/ω_P. Wonneberger[11] extended the Caldeira-Leggett[12] theory that takes into account effects dissipation on tunneling to the problem of tunneling of electrons in the condensate of the CDW. He found that the effect of dissipation of momentum to the macroscopically occupied phoons is essentially to replace v_F by the phason velocity, $c_o = \sqrt{(m/M_F)}\, v_F$, giving values of L of the correct order of magnitude. It is thus likely that the length, L, for phase-coherence in $NbSe_3$ and TaS_3 is that given by the Lee-Rice theory. The length, L, is the maximum distance over which electrons can accumulate energy and momentum from the electric field. In other systems there is evidence that the pinning model of Barnes and Zawadowski,[13] based on analogy with Josephson tunneling, may be the most important.[14]

A threshold field for nonlinear conduction may be accounted for by a finite L. In Zener tunneling, one must have $e^* E\ell = \hbar\omega_P$, where ℓ is the tunneling distance, so that if ℓ has a maximum value, L, there is a minimum threshold field, E_T, given by $e^* E_T L = \hbar\omega_P$. Simple density of states considerations for allowed transitions indicate that (2.1) should be replaced by:

$$i_{dc} = \sigma_a E + \sigma_b (E-E_T)\exp[-E_o/E] \qquad (2.5)$$

where E_o is of the same order as E_T. Empirically, with $E_o = \eta E_T$, it is found that $\eta \sim 1$-2 for $NbSe_3$ and ~ 2-5 for TaS_3. A somewhat similar expression, with E in the denominator of the exponential replaced by $E-E_T$, has been suggested on empirical grounds by Fleming. Both expressions give reasonably good fits to the observed data.

To calculate the acceleration of electrons from a value of $v_d > 0$ one may go to a frame of reference moving with velocity v_d. In this frame the Peierls gaps are at rest and the lattice and impurities with compensating charges move with a velocity $- v_d$. Since v_d is very small, at most of the order of a few cm/sec, the cost in energy for the motion of the compensating charges is negligible. The problem is then essentially the same as that for accleration from the lattice frame with $v_d = 0$ and the same pinning gap, $\hbar\omega_p$, must be overcome. Note that it is the macroscopic occupation of phonons that determines v_d. A change in v_d requires the cooperative effect of acceleration of the large number of electrons in a phase-coherent domain, one such as to change the average drift velocity of the electrons and the CDW.

One may regard the states of the entire system in a phase-coherent domain as defined by the total wave vector of both electrons and phonons, which must be an integral multiple of $Q = 2k_F$, or $K_{tot} = n \cdot 2k_F$ where n is an integer. The only degree of freedom is then n which in turn determines v_d. The total pinning energy in a domain is greater than thermal energy, $\frac{1}{2} k_B T$. It is believed that the macroscopically occupied phonons can be treated classically, but not the acceleration of the system by an electric field.

III. Effects of ac and combined ac and dc fields

The existence of a threshold field[15] suggested[7] that the voltage $V = EL$ across the phase-coherent distance L could be regarded as analogous to the voltage across a superconducting tunnel junction. Tucker[16] had extended the Tien-Gordon theory of photon-assisted tunneling in superconducting tunnel junctions to discuss the quantum limits of detection, mixing and related phenomena. For small signal ac, with $V = V_o + V_1 \cos \omega t$, Tucker finds that quantum effects replace classical derivatives with finite differences. The ac current due to a small applied V_1 is to replace the classical result

$$I_{ac} = V_1 \left\{ \frac{dI_{dc}(V)}{dV} \right\}_{V=V_o} \cos \omega t \tag{3.1}$$

by the finite difference

$$I_{ac}(\omega) = \frac{eV_1}{2\hbar\omega} \left\{ I_{dc}\left(V_o + \frac{\hbar\omega}{e}\right) - I_{dc}\left(V_o - \frac{\hbar\omega}{e}\right) \right\} \cos \omega t \ . \tag{3.2}$$

To apply to tunneling of electrons in the CDW problem, I first suggested[7] simply replacing e by $e^* \sim 10^{-3}e$ and taking $V_o = EL$. In the limit $V_o \to 0$, this gives a scaling relation between ac and dc conductivity if $\sigma_{dc}(E)$ is defined to be $I_{dc}(E)/E$ rather than dI_{dc}/dE:

$$\sigma_{ac}(\omega) = \sigma_{dc}(\hbar\omega/e^{*}L) \quad . \tag{3.3}$$

Experiments of Grüner and Zettl showed that this relation is obeyed very well for effective voltages $\hbar\omega/e^{*}$ above about twice threshold, but that there is no sharp threshold frequency for changes in $\sigma(\omega)$. The excess in the neighborhood of the threshold frequency, $\omega_T = e^{*}V_T/\hbar$ was attributed by absorption by the pinned mode centered at $\omega_P = \omega_T$.

Correspondingly, the rectified current from the applied voltage $V = V_o + V_1 \cos \omega t$ is given by a finite difference second derivative.

$$\delta I_{dc} = \frac{1}{2} V_1^2 \{\frac{I_{dc}(V_o + \alpha\omega) - 2I(V_o) + \underset{\sim}{I}(V_o - \alpha\omega)}{(\alpha\omega)^2}\} \tag{3.4}$$

where $\alpha = \hbar/e^{*}$ for $V_o = EL$. Predicted photon-assisted tunneling expected for $V_o < V_T$, but $V_o + \alpha\omega > V_T$ was not observed in a series of careful experiments by Zettl and Grüner. Thus there was no adequate theory to predict effects of combined ac and dc fields.

About two years ago an experimental program was set up at Illinois under John Tucker to study rectification, mixing and other experiments to better understand coupling of ac and dc in linear-chain metals. John Miller joined the program as a graduate student and Jacques Richard is spending a year as a post-doctoral associate. In a series of experiments on samples of orthorhombia TaS_3 (provided by Grüner) Miller et al.[8] found no effect on any ac response when the dc bias was below threshold. Voltages $V_o < V_T$ polarize the CDW but do not affect the response to small amplitude ac fields. This suggested a modified form of scaling to voltages $V_o' = V_o - V_T$ above threshold (and $V_o' = V_o + V_T$ for $V_o < -V_T$). Voltages $-V_T < V_o < V_T$ correspond to $V_o' = 0$, indicating no change in the ac response when $|V_o| < V_T$.

This scaling applies only to small amplitude ac voltages. It is known that large amplitudes give a decrease in V_T and with an ac voltage of sufficiently large amplitude V_T goes to zero. Experiments with large amplitude ac will be discussed at this symposium by Zettl and Grüner[17] and are also underway by the Illinois group.

The revised scaling has been applied with success to ac conductivity, rectification and harmonic mixing. Harmonic mixing, first done on $NbSe_3$ in the microwave range by Seeger, Mayr and Philips,[17] given a dc current from mixing an applied second harmonic with the second harmonic generated from a nonlinear device by an applied signal at frequency ω. If a dc bias V_o is also applied, the total applied voltage is

$$V = V_o + V_1\cos(\omega_1 t + \phi) + V_2\cos\omega_2 t, \tag{3.5}$$

where for a dc response $\omega_2 = 2\omega_1$ or more generally there is response at $\omega_o = \omega_2 - 2\omega$. In harmonic mixing, it is a classical third derivative that is replaced by a quantum finite difference.

With $I'(V_o') = I_{dc}(V_o)$ and a scaling factor $\alpha = h/e^*$ if V_o represents a voltage across L or $\alpha = h\ell/e^*L$ if V_o is a voltage across a specimen of length ℓ, the revised scaling to V_o' gives the following finite difference expressions:

ac conductivity

$$I_{ac}(\omega) = \frac{V_1}{2\alpha\omega}\left\{I'(V_o'+\alpha\omega) - I'(V_o'-\alpha\omega)\right\}\cos\omega t \tag{3.6}$$

rectification

$$\Delta I_{dc} = \frac{V_1^2}{2(\alpha\omega)^2}\left\{I'(V_o'+\alpha\omega) - 2I'(V_o') + I(V_o'-\alpha\omega)\right\} \tag{3.7}$$

harmonic mixing

$$\delta I_{dc} = \frac{V_1^2 V_2}{16(\alpha\omega)^3}\left\{I'(V_o'+2\alpha\omega) - 2I'(V_o'+\alpha\omega) + 2I'(V_o'-\alpha\omega) - I'(V_o'-2\alpha\omega)\right\}\cos 2\phi\ . \tag{3.8}$$

Thus rectification and harmonic mixing can be determined from the dc characteristic and the scaling parameter α with no adjustable parameters.

Measurements of Miller et al.[8] of rectification and harmonic mixing as a function dc bias in TaS_3 at 190 K are in reasonable quantitative agreement with experiment. Finite amplitude ac signals were required to over-ride the broad-band and "narrow-band" noise throughout the entire range. The ac voltages applied across a specimen of length $\ell = 0.5$ mm were 5 mV for rectification and $V_1 = 11$ mV and $V_2 = 15$ mV for harmonic mixing as compared with a threshold voltage of 32 mV. This tends to broaden the peaks of the measured signals. It was found that agreement between theory and experiment is improved with smaller amplitude signals; for example a large narrow peak near threshold of the theoretical harmonic mixing curve for $\omega_1/2\pi = 2$ MHz can be reproduced in height and breadth by careful measurements with small amplitudes.

The major discrepancy is that the theory predicts a harmonic mixing signal for $V_o' = 0$ or $V_o < V_T$ which is not found experimentally. However, it was found that if the frequency difference $\omega_o = \omega_2 - 2\omega$ is increased to 2-3 MHz, a frequency small compared with other frequencies in the problem, the expected signal is recovered, as shown in Fig. 1. It is believed that the problem is connected with the response of the CDW when biased below threshold.

The overdamped oscillator model predicts a harmonic mixing signal of the same order of magnitude that also decreases as ω^{-3} at high frequencies, but predicts a phase shift of $\frac{1}{2}\pi$ from a signal varying a $\cos 2\phi$ for $\omega \ll \omega_c$ to $\cos\left(2\phi + \frac{1}{2}\pi\right)$ for $\omega \gg \omega_c$, where $\omega_c = \omega_p^2\tau$ is the "cross-over" frequency and τ is a relation time such that $\omega_p\tau \ll 1$. It is estimated from $\sigma(\omega)$ that $\omega_c/2\pi$ should be of order 100 MHz for TaS_3 at 190 K. Measurements up to 500 MHz, shown in Figs. 2 and 3, indicate no phase shift greater than $\sim 10°$ in conformity with the tunneling model.

It is believed that these measurements give strong evidence in favor of the quantum model. With essentially only the scaling parameter, α, as an adjustable parameter, one can account for a variety of rectification and mixing experiments with small amplitude ac signals. The value of α is of reasonable order of magnitude. For TaS_3 at 190 K, α = 0.7 mV/MHz, where the voltage is that across a specimen of length ℓ = 0.5 mm. The pinning frequency $\omega_p/2\pi$ = 45 MHz, if estimated from the threshold voltage of 32 mV, or more than twice as large if estimated from $E_o \sim 3E_T$. In view of the uncertainties in the parameters involved, these estimates give values of α of the correct order of magnitude. Thus the theory is self-consistent. The experiments and theoretical interpretations imply macroscopic quantum effects from frequencies in the megahertz range at temperatures as high as 200 K.

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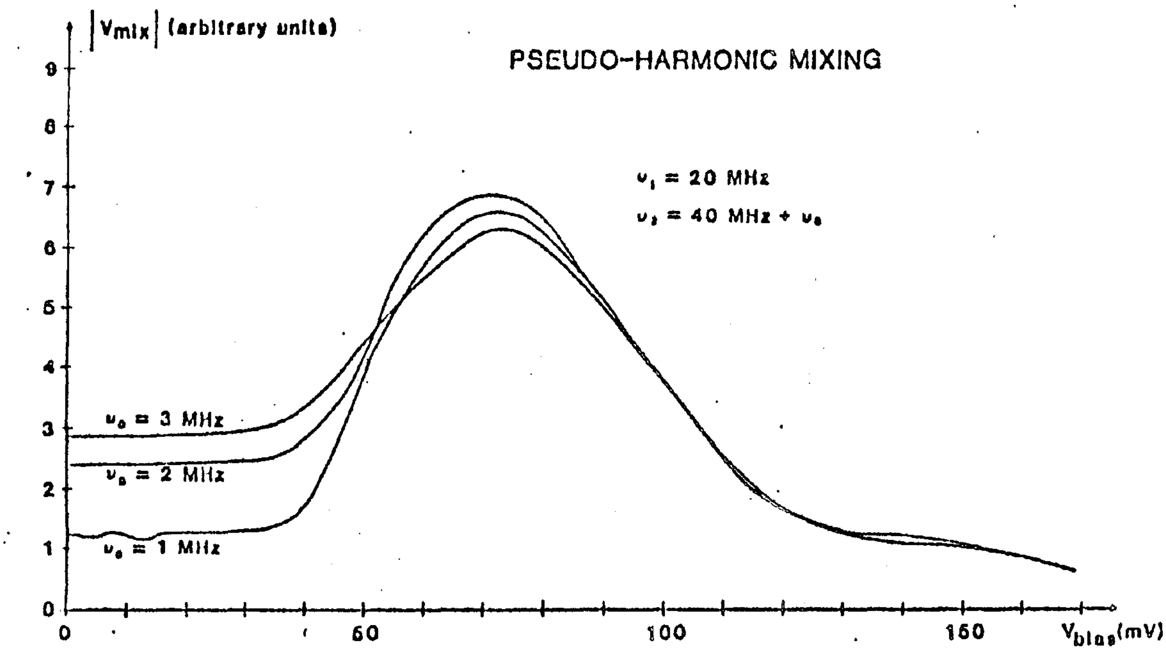

Fig. 1. Harmonic mixing in TaS_3 at 190 K for frequencies $\nu_o = \nu_2 - 2\nu_1$ approach theoretical for zero bias as ν_o increases to 2-3 MHz. Note that varying ν_o makes no difference at high bias. (From J. H. Miller, J. R. Tucker et al. (to be published).)

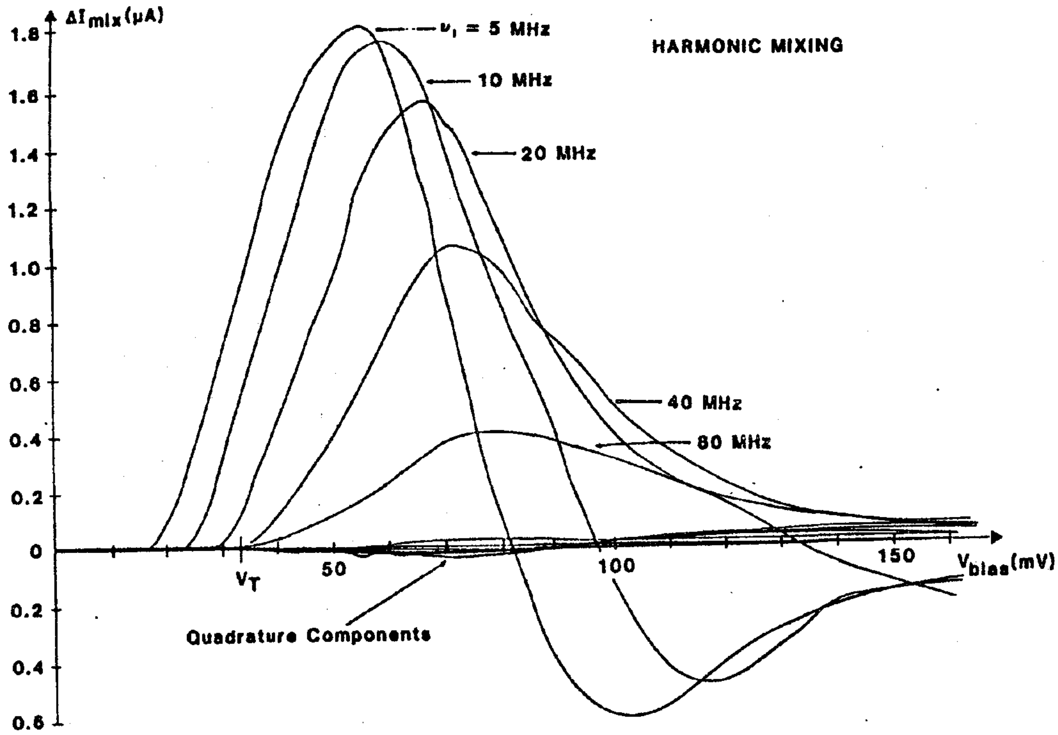

Fig. 2. In phase, $h_s \cos\Psi$, and quadrature component, $h_s \sin\Psi$, of harmonic mixing signal, $h_s \cos(2\phi+\Psi)$, in TaS_3 at 190K, at various fundamental frequencies, ν_1. The shift in threshold results from use of finite amplitude rather than infinitesimal applied ac voltages. (From J. H. Miller, J. R. Tucker, et al. (to be published).)

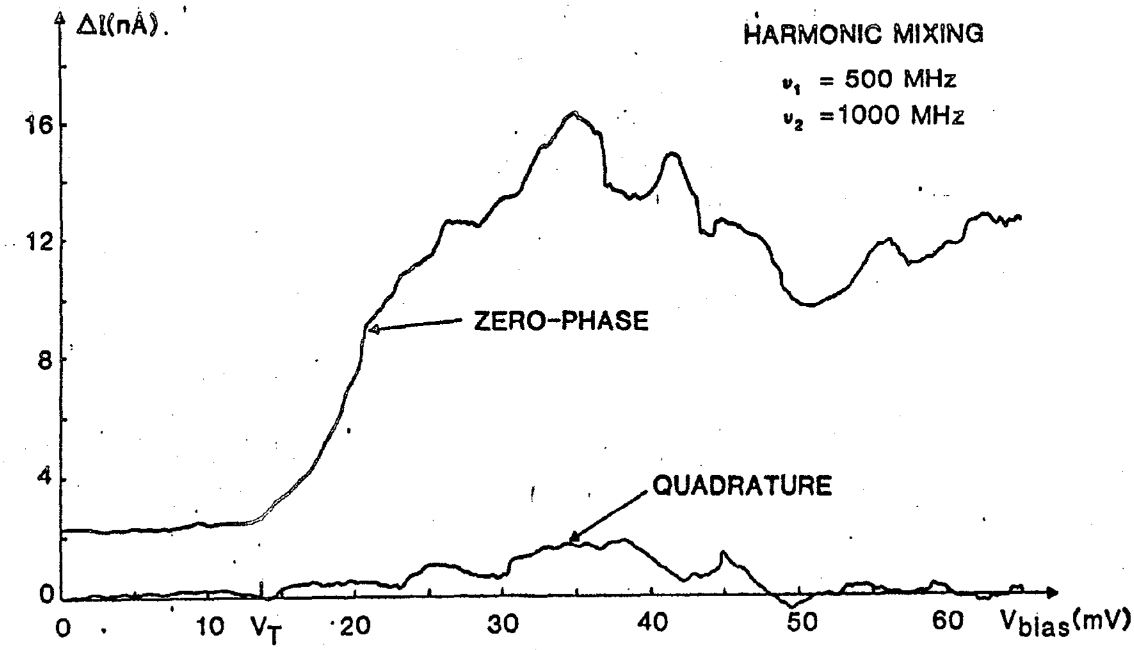

Fig. 3. In phase, $h_s\cos\Psi$, and quadrature component, $h_s\sin\Psi$, of harmonic mixing signal, $h_s\cos(2\phi+\Psi)$ in TaS_3 at 190 K for a fundamental frequency ν_1 = 500 MHz, well above the "cross-over" frequency of the over-damped oscillator model. (From J. H. Miller, J. R. Tucker, et al. (to be published).)