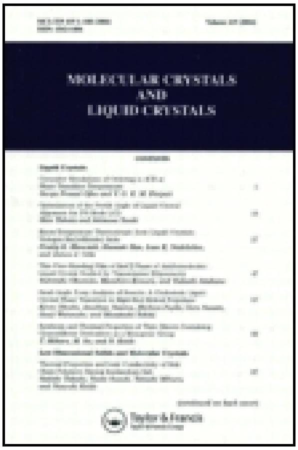

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Charge Density Wave Dynamics in $NbSe_3$ and TaS_3

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CHARGE DENSITY WAVE DYNAMICS IN $NbSe_3$ AND TaS_3

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I summarize recent experiments on the linear chain compounds $NbSe_3$ and TaS_3. In both materials, the charge density wave (CDW) state is characterized by a field (E) and frequency (ω) dependent response and noise. The ω dependent response is that of a strongly damped oscillator, the E dependence is in agreement with models based on CDW tunneling. Scaling properties and ac-dc coupling experiments are also summarized, and a short comparison is given with the predictions of various models.

1. INTRODUCTION

Charge density waves (CDW's) associated with the development of the Peierls-Frölich state are well documented through structural studies in various low dimensional conductors. The most thoroughly studied example is TTF-TCNQ and related organic linear chain compounds, and the linear chain compound KCP. The response of the collective mode, the CDW is drastically different from that expected for a single particle semiconductor, and is characterized by strongly frequency (ω) and field (E) dependent transport. These have been observed in TTF-TCNQ, but alternative explanations based on single particle effects and disorder induced localization have also been advanced to account for the experimental findings.[1]

I will discuss recent experiments on two linear chain compounds, $NbSe_3$ and TaS_3 (orthorhombic form), where phase transitions lead to a CDW ground state, and to strongly anomalous transport properties. These cannot be explained by single particle effects and provide the first direct evidence for a collective response of the CDW and for a sliding CDW conductivity.

Both $NbSe_3$ and TaS_3 form chain structure with the metal $(chalcogen)_3$ building blocks.[2] $NbSe_3$ shows two phase transitions, one at T_1 = 149 K, another at T_2 = 59 K; these reflect the independent development of two CDW's, both incommensurate with the underlying lattice, although the resulting periods q_1 = 0.244b* and q_2 = 0.26b* are close to a period 4b where b is the lattice parameter along the chain axis.[3] The phase transition occurs at T = 215 K in the orthorhombic form of TaS_3, and the CDW has a period $4c_0$ with c_0 the lattice constant along the chain direction, and is commensurate with the underlying lattice.[4] $NbSe_3$ appears to be more two dimensional than TaS_3: only part of the Fermi surface is removed due to the phase transition[5] in $NbSe_3$, while TaS_3 becomes a semiconductor below T_p. Also, one-dimensional (1D) fluctuations are not observed in $NbSe_3$ in the metallic phase above T_1, while diffuse 1D streaks are observed[4] in TaS_3 well above the transition temperature.

2. FREQUENCY DEPENDENT CONDUCTIVITY

In both $NbSe_3$ and TaS_3 the conductivity is strongly frequency dependent in the CDW states,[7,8] and also shows a large out of phase component. In Fig. 1 and Fig. 2, $Re\sigma(\omega)$ and $Im\sigma(\omega)$ are displayed,[9] for $NbSe_3$ below T_2 and for TaS_3 below T_{MI}. In both cases $Re\sigma(\omega)$ increases smoothly from the dc limit to a high frequency saturation, and $Im\sigma(\omega)$ shows a pronounced peak at frequencies, where $Re\sigma(\omega)$ has a strong frequency dependence. Unlike in KCP or TTF-TCNQ there is no evidence for a sharp peak in $Re\sigma(\omega)$ and for an accompanying zero crossing in $Im\sigma(\omega)$. The resulting dielectric constant $\varepsilon = Im\sigma(\omega)/\omega$ is huge, and for $\omega \to 0$ it is approximately 10^8 at T = 42 K in $NbSe_3$ and 10^7 in TaS_3 below the transition.

Both the strong frequency dependence and the huge low frequency dielectric constants are in clear conflict with any interpretation in terms of single particle transport processes. The characteristic frequencies where σ is strongly ω dependent lead to energies $\hbar\omega$ of the order of 10^{-3} - 10^{-4} kT orders of magnitude smaller than the thermal energy. Alternatively, the dielectric constant ε, if interpreted in terms of a single particle contribution $\varepsilon = 1 + (\Omega_p^2/\Delta^2)$ where Ω_p is the plasma frequency, would lead to a gap Δ

FIGURE 1 Frequency dependent conductivity in $NbSe_3$ at T = 42 K. Both $\mathrm{Re}\sigma(\omega)$ and $\mathrm{Im}\sigma(\omega)$ are normalized to the dc conductivity measured at the same temperature.

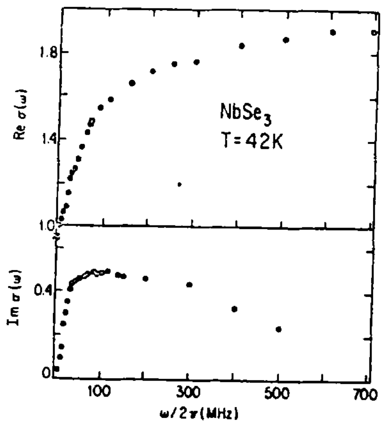
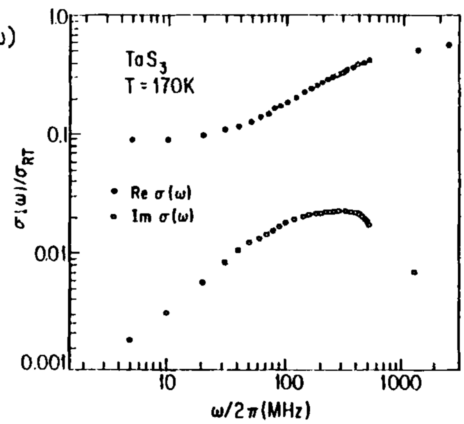


FIGURE 2 Frequency dependent conductivity in TaS_3 at T = 170 K. Both $\mathrm{Re}\sigma(\omega)$ and $\mathrm{Im}\sigma(\omega)$ are normalized to the room temperature dc conductivity.



again negligible compared to kT. The overall frequency dependence suggests a strongly damped response to the external ac excitation both in $NbSe_3$ and in TaS_3, if the response represents the contribution of the pinned mode. A description in terms of a classical oscillator

$$m\ddot{x} + \Gamma\dot{x} + kx = eEe^{i\omega t} \tag{1}$$

would suggest that the inertia term can be neglected and a system is strongly overdamped. An alternative explanation for $\sigma(\omega)$ based on the tunneling model[14] will be discussed later.

3. FIELD DEPENDENT CONDUCTIVITY

One of the early evidences for CDW transport in $NbSe_3$ was the observation of strongly increasing σ_{dc} with increasing electric field, observed for moderate field strengths.[11] It has later been shown[12] that in $NbSe_3$ nonlinear conductivity occurs only if the electric field E exceeds a threshold E_T, and beyond E_T, the experimental data can be fitted well with

$$\sigma(E) = [1 - (E_T/E)] \exp[-E_o/(E-E_T)] \quad , \qquad (2)$$

a formula suggestive for a tunneling phenomenon. E_T is of the order of 10^{-2} V/cm, depending strongly on the sample quality, suggestive for pinning by impurities. E_0 is approximately $2E_T$, and is again sample dependent. Nonlinear conductivity is also seen in TaS_3, $\sigma(E)$ is displayed[10] in Fig. 3. A sharp threshold exists from T_{MI} down to about 150 K; below this temperature the threshold field is smeared. This behavior is more clearly seen in the differential resistance measurements.[13] Detailed experiments show[13] that between T_{MI} and 150 K, the conductivity can be described by

$$\sigma(T_1E) = \sigma(T) + \sigma(E) \qquad (3)$$

where the first term in the right hand side is the ohmic contribution, the second represents the field dependent contribution. A good fit to $\sigma(E)$ is provided by tunneling formula[14] proposed by Bardeen

$$\sigma(E) = [1 - (E_T/E)] \exp(-E_o/E_T) \qquad (4)$$

with E_0 = 6.5 V/cm and E_T = 1.3 V/cm. Equation (4) is shown by the full line in Fig. 4, where $\sigma(T,E) - \sigma(T)$, evaluated at various temperatures is displayed. It is clear from Fig. 4 that Eq. (4) provides an appropriate description of the experimental data. Detailed differential conductance measurements lead also a good agreement with Eq. (4), at electric fields somewhat above the threshold field E_T.

The small electric field strengths required for the nonlinear conductivity strongly support a collective transport mechanism. Assuming that the energy provided by the dc field over a distance ℓ must be larger than kT, leads to the condition $eE_T\ell > kT$. With $kT \sim 10^{-2}$ eV and with $E_T \sim 10^{-2}$ V/cm for $NbSe_3$ below T_2, and 1 V below T_1 and $E_T \sim$ 1 V/cm for TaS_3, one arrives at a characteristic length ℓ, orders of magnitude larger than the lattice constants.

FIGURE 3 $\sigma(E)$ in TaS_3. Open circles: dc measurements. Full circles: pulse measurements. Ref. 10.

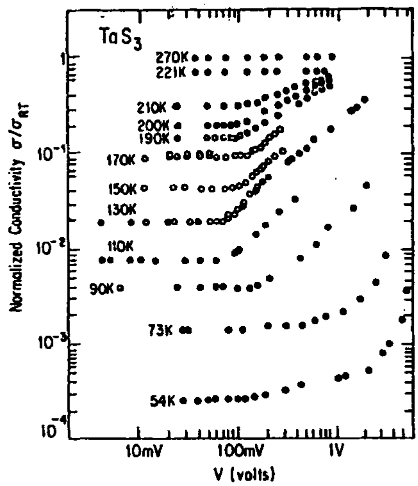
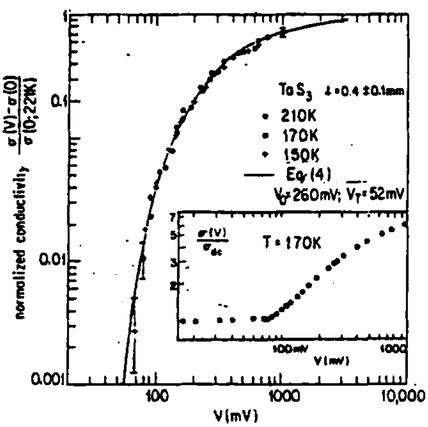


FIGURE 4 Nonlinear conductivity, $\sigma(E) - \sigma(0)$ at various temperatures. The full line is Eq. (4) with parameters given on the Figure. Ref. 13.



4. NARROW BAND NOISE

One of the most unusual phenomena in $NbSe_3$ and TaS_3 is the observation of narrow band "noise" in the nonlinear conductivity region.[12] A typical noise spectrum[15] observed in $NbSe_3$ is shown in Fig. 5. It is characterized by a strong fundamental, indicated by an arrow and several harmonics at frequencies which are multiple integers of the fundamental frequency f_n. We believe that more complicated patterns, observed by others[16,17] and also by us,[15,18] represent inhomogeneous current distributions. Experiments performed

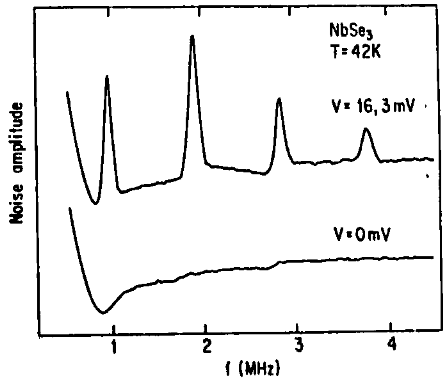


FIGURE 5 Narrow band noise spectrum in $NbSe_3$ below T_2. Ref. 15.

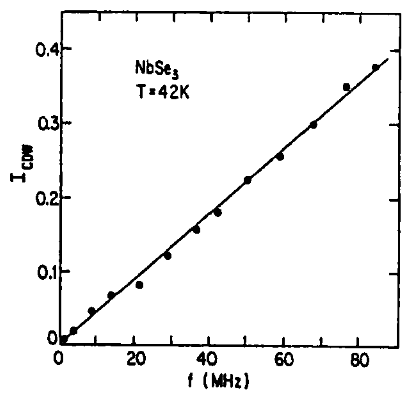


FIGURE 6 The fundamental of the noise frequency versus CDW current in $NbSe_3$. Ref. 15.

at various dc current levels show that

$$f_n \sim I_{CDW} \tag{5}$$

where $I_{CDW} = I(V) - I(V,\text{ohmic})$ is the contribution due to the moving CDW. This relation is shown for $NbSe_3$,[16,15] in Fig. 6 in TaS_3[17] a similar relation is observed. A simple argument[16,19] leads to Eq. (5). Assuming that the noise frequency is due to a characteristic displacement λ of the CDW, then $f_n = \mu_{CDW}/\lambda$ where μ_{CDW} is the drift velocity of the CDW. The CDW current is then given by $I_{CDW} = ne\mu_{CDW}$ where n is the number of electrons in the CDW state. Then $f_n = I_{CDW}/ne$. With $n = 10^{21}$ cm^{-1} both for $NbSe_3$ and TaS_3, and assuming that all electrons are condensed in the CDW state in TaS_3 and approximately 40% of the electrons are condensed in $NbSe_3$ one obtains $\lambda = 8$ Å[17] and 14 Å[15,19] in TaS_3 and $NbSe_3$. Both are in good agreement with the CDW periods observed by X-rays.[3,4] We conclude, therefore, that the narrow band noise is associated with the displacement of the CDW by one period λ.

5. AC-DC COUPLINGS

With a conductivity which is both nonlinear and frequency dependent various combinations of ac and dc driving field $E = E_{dc} + E_{ac} \cos \omega t$ can be applied to study the fine details of the pinning and subsequent notion of the CDW.

We have searched for photon assisted tunneling[14] under circumstances when $eV + \hbar\omega > eV_T$ but $V_{dc} + V_{ac} < V_T$ where eV is the energy supplied by the dc field. No photon assisted tunneling was observed in $NbSe_3$ or in TaS_3 down to signal levels one or two orders of magnitude smaller than that calculated for single particle tunneling.[14] dc conductivity, however, can be induced by an ac field of sufficient amplitude.[18,13] When $\omega \to 0$, $V_{dc} + V_{ac} > V_T$ leads to an excess dc conductivity. Due to the strongly damped response of the CDW condensate, however, progressively larger ac fields are required for inducing dc conductivity, simply because the response cannot follow the excitation for strongly damped systems. Assuming that a dc conductivity results if a displacement of the CDW due to an ac driving force exceeds a critical value X_{crit}, one obtains $E^{ac}_{crit}(\omega) = E^{ac}_{crit}(0)$ $[1 + (\omega/\omega_0{}^2\tau)^2]^{1/2}$ for an overdamped oscillator. Thus, E^{ac}_{crit} strongly increases with increasing ω as observed both in $NbSe_3$[20] and in TaS_3.[9]

Another type of experiment, where the low frequency ac polarization is measured in the presence of dc field, confirms that even for $V > V_T$ the motion of the CDW is not completely free. For a free sliding, one expects zero dielectric constant. When the conductivity is due to a sequence of sliding, pinning and sliding, etc., then a finite polarization can develop during the period when the CDW is pinned. This results in a finite dielectric constant even in the nonlinear conductivity region. One expects that the time period when the CDW is pinned, smoothly decreases with increasing electric field; this leads to an increasing conductivity and decreasing low frequency dielectric constant. $\sigma(V)$ and $\varepsilon(V)$ measured on the same TaS_3 sample is shown in Fig. 7, similar relation between $\sigma(V)$ and $\varepsilon(V)$ was found in $NbSe_3$. The slowly decreasing ε is in agreement with the previous arguments about pinning and depinning of the CDW.

6. MODELS

Various models were proposed to account for the experimental observations summarized before. Most of these theories consider only phase fluctuations, the CDW moves as a rigid entity, in accordance with X-ray observations in the presence of a dc electric field.[3] These models will be discussed by Professor Bardeen at this conference, and therefore I only briefly summarize their relevance to the experiments reported here.

Lee and Rice[21] consider impurity pinning of the CDW, which is treated phenomenologically. This treatment leads to a sharp threshold field, in agreement with experiments, but no attempt is made to account for the detailed form of the conductivity.

A description in terms of a classical treatment[18] of the CDW motion incorporates the overdamped response of the CDW with respect to a low amplitude ac excitation. The nonlinear dc conductivity results from a motion of CDW in a periodic potential tilted by the electric field. The model leads to a sharp threshold field E_T and strongly nonlinear I-V characteristics, and accounts for the observation of narrow band noise. The description, however, does not reproduce the fine details of the depinning and subsequent motion. The depinning occurs when the restoring force goes to zero; this leads to a divergent dielectric constant at E_T. Also the differential conductance dI/dV diverges at E_T. Neither of these have been observed,[9] suggesting that depinning is more complicated than that described, or that the treatment of the CDW as a classical object is not appropriate. Equations (2) and (4), which have been used extensively to analyze the experiments on $NbSe_3$ and TaS_3, strongly suggest a formalism in terms of a tunneling process, and the small electric fields suggest a tunneling process across gaps much smaller than kT. A coherent tunneling of CDW's across small pinning gaps leads to[14]

$$E_o = \varepsilon_g / 2\xi_o e^* \tag{5}$$

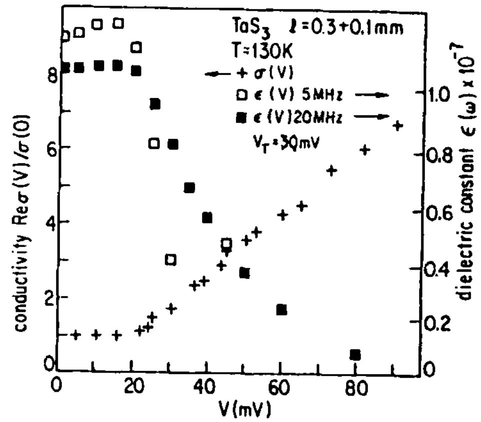


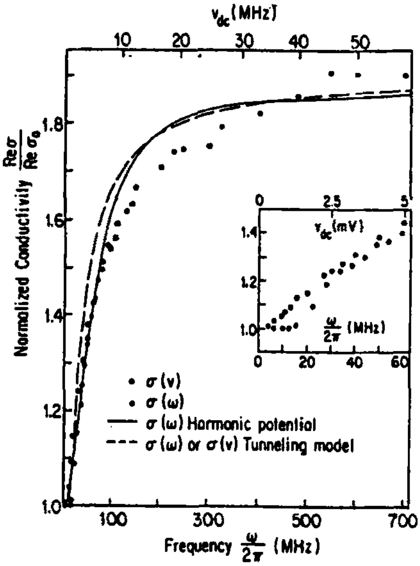
FIGURE 7 σ(V) and ε(V) in TaS . The frequency $\omega/2\pi$ of the dielectric constant measurements is shown in the Figure.

where $e^*/e = m/M_F$ is the ratio of the band mass to the Frölich mass, $\xi_0 = 2hV_F/\pi\varepsilon_g$ is the coherence distance. Tunneling is only possible when the potential drop along the correlation length L is larger than ε_g, and thus $e^*LE_T = \varepsilon_g$. The tunneling probability $P(E) = (1 - E_T/E)\exp(-E_0/E_T)$ leads to the expression (4). The observed values E_0 and E_T can then be used to evaluate ε_g, and with $m/M_F \sim 10^{-3}$ one arrives at ε_g values in the millidegree region. The field dependent conductivity can be related to σ(ω), and one obtains[14]

$$\sigma(\omega) = \sigma_{dc}(h\omega/e^*) \tag{6}$$

and thus the σ(E) and σ(ω) can be scaled together with appropriate normalized ω and E values. Indeed, σ(ω) and σ(E), measured over a broad frequency and field range, displays the same universal behavior in $NbSe_3$ both below T_1 and below T_2 and in TaS_3 below T_{M1}. Figure 8 shows σ(ω) and σ(E) in $NbSe_3$ with the ω and E axes chosen to demonstrate the validity of Eq. (6). Similar scaling has been observed at the higher temperature DCW state of $NbSe_3$ and in TaS_3. It is evident from Fig. 8 that the scaling relation suggested by the tunneling model is confirmed by the experiments, except at field and frequency values near E_T (see the insert of Fig. 8). There is a sharp threshold for the onset of

FIGURE 8 $\sigma(\omega)$ and $\sigma(E)$ in $NbSe_3$ at T = 42 K. Ref. 23.



dc nonlinearity, but the frequency dependence starts at $\omega \to 0$. This suggests that there is another contribution coming from the response of the pinned mode, as described by Lee, Rice, and Anderson.[22] A phenomenological description leads to a dielectric constant

$$\varepsilon_p(\omega) = \Omega_p^2/(\omega_T^2 - \omega^2 - i\Gamma\omega) \tag{7}$$

where $\Omega_p = 4\pi ne^2/M$, $\hbar\omega_T$ is the pinning energy, and Γ the damping constant. $\sigma_p(\omega) = [\omega \text{ Im } \varepsilon(\omega)]/4\pi$, and the resulting ac conductivity is given by

$$\sigma_{ac}(\omega) = \sigma_p(\omega) + \sigma_{tun}(\omega) \tag{8}$$

with $\sigma_{tun}(\omega)$ given by Eqs. (4) and (6). Equation (8) gives an excellent description of $\sigma(\omega)$ in the whole measured frequency range[23] both in $NbSe_3$ and TaS_3, with gap values of the order of 10^{-17} - 10^{-19} ergs, in agreement with the gaps obtained from $\sigma(E)$ alone. Also, the low frequency dielectric constant given by $\varepsilon(\omega \to 0) = \Omega_p^2/\omega_T^2$ in this model and accounts well for the measured values both in $NbSe_3$ and TaS_3.

A detailed account of the experiments in terms of the model, together with the resulting value for ε_g coherence length and correlation distance L, will be reported elsewhere.[23] I also note that the analysis leads to a strongly damped oscillator response, $\sigma_p(\omega)$, and therefore the model also accounts for the increasing ac amplitude required to lead to a dc conductivity, with increasing frequency, in agreement with the experiments described before.

7. CONCLUSIONS

$NbSe_3$ and TaS_3 represent probably the most well documented examples for collective response of charge density waves to external dc and ac driving fields. The nonlinear conductivity strongly suggests a tunneling process, the pinned mode is characterized by weak pinning and strong damping. Although a satisfactory description is available to account for the broad variety of phenomena in the presence of dc and/or ac fields, the underlying microscopic description is still lacking. Unresolved questions include the nature of the damping forces and the microscopic evaluation of the magnitude of the sliding CDW conductivity (which appears to have a magnitude close to that of the normal electrons), and the details of the dynamics at intermediate electric field strength.

Also, all parameters, like E_T, E_0, etc., display a characteristic, and yet unexplained, temperature dependence in $NbSe_3$, while in TaS_3 the sharp threshold disappears at lower temperatures. The latter may be due to the increased role of impurities (which are not screened by the conduction electrons because of the small number of carriers available) at low temperatures; this can lead to a charge density wave glass state. Also, while I have focused only on phenomena occurring in the Peierls-Frölich state, strong precursor effects, reflecting one dimensional resistive fluctuations occur in TaS_3.[8]

We also expect that $NbSe_3$ and TaS_3 are not the only compounds where collective transport, carried by the charge density wave, can be observed, and similar compounds may provide further examples for the unusual phenomena reported here.

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