PHYSICAL REVIEW B VOLUME 26, NUMBER 10 15 NOVEMBER 1982

Charge-density-wave transport in orthorhombic TaS_3. I. Nonlinear conductivity

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(Received 16 April 1982)

dc conductivity measurements are reported on the linear chain compound TaS_3 (orthorhombic form), which undergoes a phase transition to a charge-density-wave (CDW) state at $T_P = 215$ K. Strong resistive fluctuations, associated with the buildup of one-dimensional correlations, are observed above T_P. Below the transition nonlinear conductivity is observed when the electric field E is larger than a threshold field E_T. E_T is approximately 2 V/cm, and is weakly temperature dependent. The functional dependence of the conductivity σ on E is analyzed in terms of various models. A good agreement is found with Bardeen's tunneling model, which leads to a field-dependent conductivity $\sigma(E) \sim (1 - E_T/E)\exp(-E_0/E)$, but Fleming's empirical formula also provides a good fit to the data. The low-threshold field and the strong field dependence indicate small pinning energies and large coherence and correlation lengths. At low temperatures the coherent response of the CDW condensate is absent, and we argue that, because of the loss of coupling between the CDW segments, a disordered CDW state develops. These observations are compared with those made on a similar linear chain compound, $NbSe_3$.

I. INTRODUCTION

In a one-dimensional (1D) coupled electron-phonon system the ground state is characterized by a periodic lattice distortion and associated charge-density wave (CDW),[1]

$$\rho(x) = A\cos(2k_F x + \phi)\ , \tag{1}$$

where the amplitude A is related to the strength of the electron-phonon interaction, k_F is the Fermi wave vector, and ϕ is the phase of the wave. Depending on the band filling, the periodicity of the CDW can be commensurate or incommensurate with the underlying lattice. It has been suggested by Fröhlich[2] that an incommensurate CDW can move with respect to the lattice, resulting in a so-called sliding CDW. Sliding CDW's have not yet been observed at small dc electric field strengths because the CDW can be pinned by impurities, or—if it is commensurate with the lattice—by the lattice itself. A finite dc electric field, however, can depin the CDW if the dc field energy is larger than the pinning energy, and subsequently the CDW contributes to the measured dc conductivity. While a phase transition does not occur at finite temperatures in a truly 1D system, and at $T \neq 0$ the CDW's are not correlated on the neighboring chains and have a finite coherence length ξ_0, in a real system interchain interactions lead to a phase transition at finite temperature T_P. This transition, associated with the development of correlated CDW's is called the Peierls transition.[3] The nonlinear and frequency-dependent conductivity then reflects the three-dimensional (3D) CDW state.

Transition-metal trichalcogenides, MX_3, where M is the transition-metal atom and X = S, Se, or Te, have crystal structures composed of linear chains, with the transition-metal atoms surrounded by trigonal chalcogen prisms.[4] The chain structure leads to highly anisotropic electronic structure and consequently to quasi-one-dimensional transport properties. The trichalcogenides of group-IV transition metals (Ti, Zr, and Hf) are highly anisotropic band semiconductors, while most of the group-V trichalcogenides display metallic behavior at high temperatures. One member of this group, $NbSe_3$, has two phase transitions associated with the development of charge-density waves as determined by structural studies in the CDW phases.[5,6] The conductivity is highly nonlinear[7] and also strongly frequency dependent,[8] and the characteristic energies associated with the field and frequency dependence are orders of magnitude smaller than the thermal energy kT. This, together with the observation of narrow-band noise[9] is highly suggestive of a transport carried by the collectice CDW mode.

Another member of the group-V trichalcogenides, orthorhombic TaS_3, also shows a structural phase transition which is associated with the development of a CDW state.[10] The transition occurs at temperature $T_P=215$ K. Strong one-dimensional diffuse lines[11] with period $4c$ where c is the lattice constant along the chain direction are observed above T_P, while below T_P the CDW has the periodicity $0.5a^*$, $0.125b^*$, $0.25c^*$. The CDW is thus commensurate with the underlying lattice, although a slight deviation from commensurability cannot be ruled out at present. Also TaS_3 is more anisotropic[10] than $NbSe_3$, and therefore below the transition TaS_3 is semiconducting in contrast to $NbSe_3$ where only part of the Fermi surface is removed by the Peierls transition.

We have found[12,13] strongly nonlinear conductivity σ below T_P, which occurs at moderate electric field strengths. σ is also strongly frequency dependent,[14,15] and narrow-band noise is observed[16] in the nonlinear electric field region. In this paper we report our observations on the transport properties in the low electric field region, and on the detailed behavior of the conductivity in the nonlinear regime. We find that, in spite of the underlying structural differences between $NbSe_3$ and TaS_3, the nonlinear conductivities show similar field dependence below the Peierls transitions and warrant rather similar models. At low temperatures the coherent response of the CDW is broken, most probably by inhomogeneous electric fields which develop in the sample in the absence of normal electrons. We call this regime the disordered CDW region.

This paper is organized as follows. In Sec. II we describe our experimental methods, and in Sec. III our experimental data. In Sec. IV we analyze our experiments, which are in agreement with a temperature-dependent single-particle gap and impurity effects at low temperatures. The nonlinear conductivity can be described by tunneling formulas, and are in disagreement with simple classical models for CDW depinning. Preliminary findings on the nonlinear conductivity were published previously.[12,13] In Sec. V we compare the nonlinear behavior with that observed in $NbSe_3$. This is followed by the conclusion. Our experiments on the frequency-dependent conductivity are reported in the accompanying paper.[17] ac-dc coupling experiments and measurements on the narrow-band noise will be reported later.

II. EXPERIMENTAL

Orthorhombic TaS_3 was prepared by direct reaction of the elements with excess sulfur at 650 °C for three weeks, followed by slow cooling for another three weeks to 400 °C. Several preparations were performed by changing slightly the temperature of the reaction and also the reaction and cooling times, and conductivity experiments were performed on crystals obtained from the different preparation methods. Powder x-ray diffractions show an orthorhombic phase, as reported by Sambongi *et al.*,[10] and we have found no evidence for the monoclinic phase reported by Roucau *et al.*[18] As will be discussed later, our dc conductivity results also show a phase transition at $T_P=215$ K, in agreement with previous observations made on the orthorhombic phase of TaS_3.[19]

The dc conductivity measurements were performed by four-probe methods, but two-probe configurations were also used occasionally. The contact resistances were found to be 2 orders of magnitude smaller than the sample resistance at room temperature, and even smaller at low temperatures. The typical dimensions of the crystals are 5 mm$\times$10 μm$\times$1 μm, where the long dimension corresponds to the chain axis. While the current and voltage was measured by conventional digital voltmeters at high temperatures, in the low-temperature region a high impedance circuit was used to evaluate the conductivity. All conductivity measurements were performed along the chain axis, and no attempt has been made to measure the conductivity perpendicular to the chain axis. In spite of the relatively long samples available, for the conductivity measurements the spacing between the voltage leads was chosen to be as short as possible, usually less than 1 mm. We have found that the narrow-band noise spectrum (the purity of which depends strongly on sample quality) is more clear for short than for long samples, which most probably is due to a more homogeneous cross section for shorter samples.

The field-dependent conductivity was measured both by the dc method and by a pulse technique, the pulse method being used at higher electric fields to avoid sample heating effects. Rectangular pulses with pulse lengths as short as 0.5 μsec were used, and careful checks were made to ensure that heating was not responsible for the nonlinear conductivity. The differential conductivity dI/dV in the presence

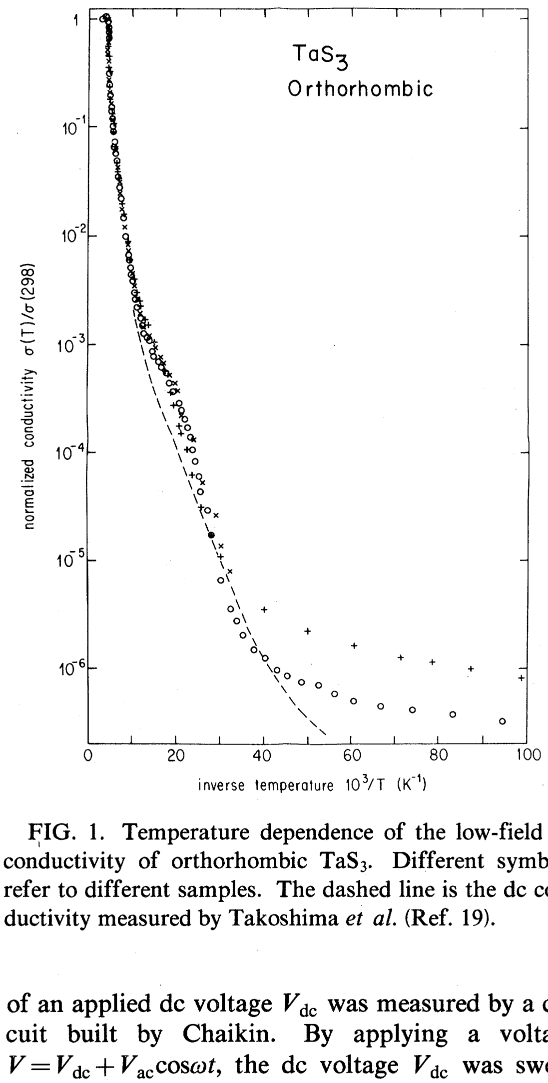

FIG. 1. Temperature dependence of the low-field dc conductivity of orthorhombic TaS_3. Different symbols refer to different samples. The dashed line is the dc conductivity measured by Takoshima *et al.* (Ref. 19).

of an applied dc voltage V_{dc} was measured by a circuit built by Chaikin. By applying a voltage $V=V_{dc}+V_{ac}\cos\omega t$, the dc voltage V_{dc} was swept between a positive and negative voltage over a large voltage interval while V_{ac} was kept at a small constant value. The in-phase component of the ac signal was recorded by a lock-in amplifier. Typical ranges for the dc voltage were ± 100 mV while V_{ac} was of the order of 1 mV. ω was typically $2\pi\times 10^3$ Hz. A ^{4}He gas-flow system was used to vary the temperature. The temperature stability was better than 0.1 K at every temperature.

III. EXPERIMENTAL RESULTS

The temperature dependence of the low-field dc conductivity σ, measured on crystals obtained from different preparation batches, is shown in Fig. 1. The dashed line is the dc conductivity result by Takoshima *et al.*,[19] also obtained on the orthorhombic form of TaS_3. The room-temperature dc conductivity, evaluated from the measured sample resistance and the dimensions of the crystals, is $2600\pm 500\ \Omega^{-1}\,\mathrm{cm}^{-1}$, also in agreement with previous studies.[10]

The overall behavior of the dc conductivity is the same as observed by others,[10,19] except for a small hump around 50 K observed in our samples. We do not know the origin of this behavior at present. It is different from the behavior expected for crystals which have a mixture of the orthorhombic and monoclinic form. Monoclinic TaS_3 has a phase transition at 160 K,[18] and corresponding humps in the conductivity are observed at this temperature on crystals containing both phases. The origin of the hump at 50 K may be due to a small amount of a yet-undetermined phase or to impurity states which give rise to an additional conductivity around this temperature. We have found no change in the nonlinear conductivity around this temperature region, and our I-V curves have a close similarity to those observed by Takoshima *et al.*[19] at low temperatures. We believe, therefore, that all the nonlinear behavior we are reporting in this paper is due to the orthorhombic phase of TaS_3.

The low-field dc conductivity between room temperature and 100 K is shown in Fig. 2; the inset shows the temperature derivative $d\sigma/dT$ in this temperature range. A peak of the temperature derivative is usually regarded as evidence for a phase transition in low dimensional conductors.[20] It occurs at 215 K in our orthorhombic TaS_3 samples, in excellent agreement with the observation of the phase transition by x-ray and Raman studies.[21,22] There is no jump in the conductivity, as

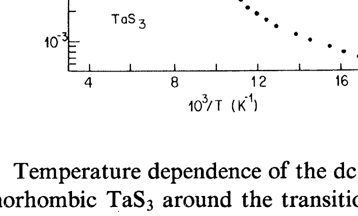

FIG. 2. Temperature dependence of the dc conductivity of orthorhombic TaS_3 around the transition temperature $T_P=215$ K. The inset shows the differential conductivity $d\sigma/dT$. The arrow in the inset identifies T_P.

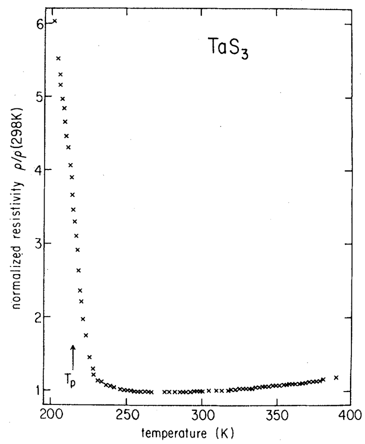

FIG. 3. Temperature dependence of the dc resistance of orthorhombic TaS_3 above the transition temperature. The transition at $T_P=215$ K is identified with an arrow.

would be expected for a first-order phase transition, and we conclude that the transition is of second order, although a weak first-order character cannot be ruled out. Careful measurements near to the transition showed no temperature hysteresis by cooling and heating (with a resolution better than 0.1 K), arguing against a first-order transition.

It is also evident from Figs. 1 and 2 that the low-field dc conductivity cannot be described by a single exponential behavior $\sigma(T)=\sigma_0\exp(-\Delta/kT)$ as expected for a semiconductor, but a progressive flattening is observed with decreasing temperature. This behavior is widely observed in various low-dimensional conductors. It may arise from a temperature-dependent gap $\Delta(T)$ which goes to zero at the transition temperature $T_P=215$ K. Indeed, a fit to $\sigma(T)$, assuming $\Delta(T)$ of the BCS form with $\Delta(T=0)=700$ K and $T_P=215$ K provides a good fit to the experimental data.[22] The other possibility is that residual disorder plays a progressively more important role in the conductivity at lower temperatures, and in the low-temperature region the conductivity is dominated by disorder effects.[23]

We also note that the low-field conductivity is nonmetallic above $T_P=215$ K. The high-temperature resistance, shown in Fig. 3, displays a metalliclike character (i.e., the resistivity increases with increasing temperature) only above about 300 K, while below this temperature the conductivity strongly decreases with decreasing temperature, and is at the phase transition approximately 5 times smaller than the room-temperature value.

The dc conductivity ($\sigma=I/V$), measured at various electric field strengths is shown in Fig. 4. The open circles refer to dc measurements, while the full points to pulse measurements. The conductivity is ohmic above the phase transition. Below 215 K the conductivity strongly increases with the applied voltage V, if V exceeds a threshold value V_T. Experiments on various samples with various lengths l give a threshold field $E_T=V_T/l$ approximately 2 V/cm below the phase transition. Around about 100 K the sharp threshold progressively starts to disappear, and at 73 K we do not observe a sharp

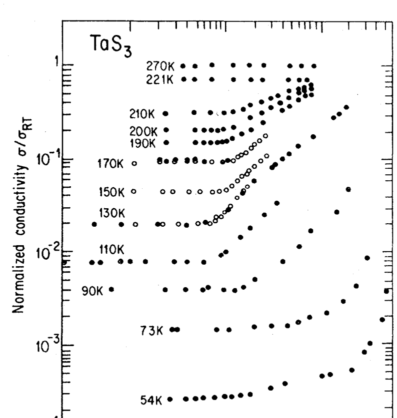

FIG. 4. Electric field dependence of the conductivity of orthorhombic TaS_3 at various temperatures: ○ dc measurements, ● pulse measurements. The sample length $l=0.4\pm0.1$ mm leading to $E_T=2.2$ V/cm below the transition.

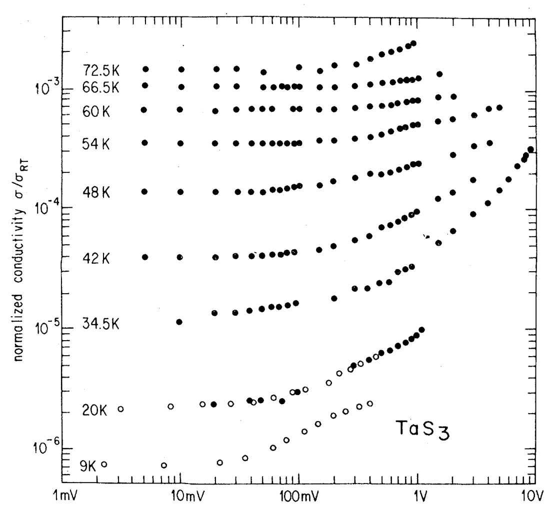

FIG. 5. Field dependence of the conductivity of orthorhombic TaS_3 at low temperatures. ○ dc measurements, ● pulse measurements. The sample length $l=0.4\pm0.1$ mm.

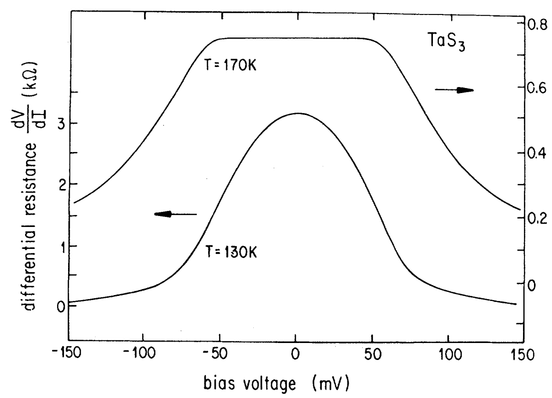

FIG. 6. Differential resistance dV/dI curves measured at two different temperatures in orthorhombic TaS_3. The sample length $l=0.5\pm0.1$ mm.

threshold for the onset of nonlinear conductivity. The temperature where the sharp threshold starts to be smeared varies slightly from sample to sample, and in some specimens we did not find a sharp threshold at temperatures as high as 130 K. In other cases the threshold persisted down to approximately 90 K. The nonlinear conductivity observed at low temperature using pulse methods is shown in Fig. 5. Our experiments are in general agreement with the observations by Takoshima *et al.*[19] In particular, the absence of a sharp threshold field and the more dominant nonlinear behavior with lowering temperatures is characteristic of both observations.

Differential conductivity measurements performed in the presence of dc bias are particularly

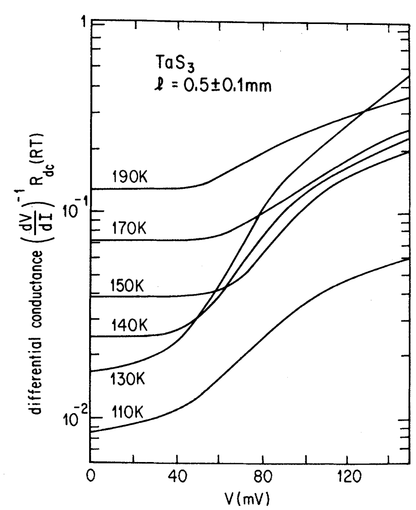

FIG. 7. Differential conductances of orthorhombic TaS_3 measured at various temperatures. The sample length l is given in the figure.

sensitive to the details of the nonlinear conductivity near the threshold value V_T. Actual dV/dI curves taken at two different temperatures are shown in Fig. 6. Curves, such as shown in Fig. 6, were used to evaluate the differential conductance $(dV/dI)^{-1}$. These curves, normalized to the low-field dc conductance measured at room temperature are shown in Fig. 7. Again, the sharp threshold is clearly observed at temperatures somewhat below T_P, but the threshold field disappears below 140 K, in agreement with the pulse conductivity measurements.

IV. DISCUSSION

In this section we discuss the experiments concerning both the low-field and nonlinear transport, and compare them with various models, suggested originally to describe the anomalous properties of $NbSe_3$. The dc low-field conductivity suggests that, depending on the temperature, different regions occur: Above room temperature we find a metallic conductivity. Below room temperature, but above $T_P=215$ K, the dc conductivity strongly decreases. Strong 1D diffuse lines are also observed in this temperature region.[11] We believe that this reflects the onset of 1D resistive fluctuations in this highly anisotropic material. Below T_P but above approximately 100 K we observe a sharp threshold field indicating that the CDW condensate responds to the external driving field in a coherent manner. We call this region the coherent CDW region. Finally, below approximately 100 K, where the low-field conductivity starts to flatten in the $\log\sigma$ vs $1/T$ representation, the coherent response of the CDW is broken, and we suggest that a disordered CDW state develops.

A. One-dimensional resistive fluctuations above T_P

Above about room temperature there is no evidence for 1D diffuse x-ray lines. Also, the resistivity increases with increasing temperature, characteristic of a metallic behavior. The mean free path in the one-dimensional tight-binding approximation is given by[1]

$$l=\frac{\sigma\pi\hbar}{2Ne^2c}\ , \tag{2}$$

where N is the carrier density and c is the lattice constant in the chain direction. Assuming that the carrier density is approximately the same as for

$NbSe_3$,[24] $N=10^2$ cm^{-3}, we obtain a mean free path $l \sim 10c$. At high temperature the resistivity can adequately be described by

$$\rho(T)=\rho_0+AT^5 , \tag{3}$$

with $\rho_0=3.2\times10^{-4}$ Ω cm and $A=2.9\times10^{-5}$ Ω cm K^{-5}. We do not believe that the high power observed represents a fundamental behavior. It is usually observed in highly anisotropic conductors which display a broad maximum in the conductivity. We also note that the conductivity is highly anisotropic,[19] $\sigma_\perp$, measured perpendicular to the chains, is approximately 100 times smaller than $\sigma_{||}$ measured parallel to the chains. Thus, the mean free path is less than one lattice constant in the direction perpendicular to the chains, leading to a genuine one-dimensional metallic behavior.

This strong anisotropy is responsible for the strongly one-dimensional character of TaS_3, and most probably for the onset of 1D fluctuations observed by x-ray studies well above the transition temperature. Diffuse x-ray lines with period $\lambda=4C$ start to be visible around room temperature with progressively increasing intensity with decreasing temperature.[11] The dc conductivity strongly decreases in this temperature range, and also a frequency-dependent conductivity and positive dielectric constant are observed.

Although both an increasing conductivity and increasing resistivity have been predicted theoretically in the 1D fluctuating region in 1D materials which show a Peierls transition,[20] we believe that the most likely explanation for the increasing resistivity is the opening of a pseudogap in the density of states, due to the development of the 1D correlations. The temperature dependence of the correlation length is given by[1]

$$\xi(T)=\frac{kT}{\epsilon_F}k_F^2\left[\frac{c}{f}\right] , \tag{4}$$

where ϵ_F is the Fermi energy and f is the band filling, and the reduction of the density of states $\widetilde{N}(0)/N(0)$ at the Fermi level is[25]

$$\frac{\widetilde{N}(0)}{N(0)}=\frac{\hbar v_F}{\Delta}\xi^{-1}(T) , \tag{5}$$

where v_F is the Fermi velocity and Δ the pseudogap. Thus the density of states is decreasing linearly with decreasing temperature. If the scattering processes would lead to a weakly temperature-dependent mean free path l, then the conductivity would decrease approximately 50% between 300 K and T_P. The observed large increase of the resistivity then suggest that additional effects, such as dynamical localization due to the fluctuating order parameter,[25] play an important role.

We believe that the observed frequency-dependent conductivity[17] and positive dielectric constant,[12] both of which become more pronounced if the temperature approaches T_P from above, argue for localization effects as the main source of the increasing resistance in the 1D fluctuating region.

B. Coherent CDW response below T_P

Below the Peierls transition temperature the response of the system to external driving forces is characterized by a field-dependent conductivity when the applied voltage exceeds a threshold voltage V_T, by a strongly frequency-dependent conductivity,[14,15,17] and by a giant dielectric constant.[12] The well-defined threshold field, and in particular the observation of narrow-band noise,[16] are highly suggestive of a coherent response of the CDW condensate, where the distribution of the various CDW segments is not important. Well-defined "noise" peaks, which reflect the time-dependent current or voltage fluctuations across the sample, would not be observable in various segments or domains responded individually.

We therefore analyze our experimental data in the light of theories which do not take into account the distribution for parameters, but will comment on these models in the conclusion section of the paper.

Various models were proposed to account for the nonlinear conductivity observed in $NbSe_3$. Most of these are based on the original suggestion by Fröhlich that sliding CDW's may contribute to the conductivity. The unified feature of these models is that they assume that the CDW is pinned by impurities or by the underlying lattice, and at low electric fields transport is carried by the normal electrons present. In TaS_3 low-field semiconducting behavior is then due to the thermally excited single-particle states as argued before. Although a pinned CDW is characterized both by amplitude and phase fluctuations, amplitude fluctuations require a higher energy.[25] Consequently, only the phase fluctuations are considered in models which attempt to account for the nonlinear phenomena. For a weakly pinned CDW moderate electric fields may overcome the pinning energies, leading to a motion of the CDW as a whole.

Two models were proposed recently to account for the field- and frequency-dependent conductivity

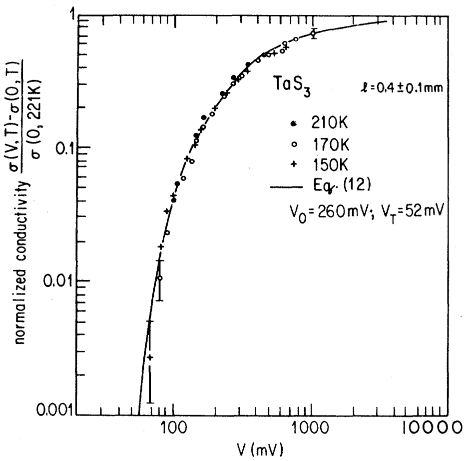

FIG. 8. Field dependence of the nonlinear conductivity $\sigma(V)-\sigma(V=0)$ at three different temperatures for orthorhombic TaS_3. The full line is Eq. (12) with parameters given in the figure.

in detail. The first model[27,28] treats the CDW as a classical particle moving in a periodic potential with period determined by the period of the CDW. Another model, proposed by Bardeen[29,30] suggests that tunneling over macroscopic distances is responsible for the unusual transport phenomena. In both models, because of the large number of electrons condensed in the CDW state, the temperature does not play a role, and both rely on $T=0$ treatment of the problem.

Direct evidence for this assumption is produced in Fig. 8 where the nonlinear part of the conductivity $\sigma(V)-\sigma(V=0)$ is plotted at different temperatures. It is evident from Fig. 8 that while the ohmic conductivity (measured below threshold) is strongly temperature dependent, the nonlinear part of the conductivity is independent of temperature. In other words, the total conductivity can be decomposed as

$$\sigma(T,E)=\sigma(T)+\sigma(E)\ , \tag{6}$$

with the first part representing the ohmic and the second the nonohmic part of the conductivity. The decomposition given by Eq. (6) strongly suggests that two different transport processes are responsible for $\sigma(T,E)$. The temperature-dependent ohmic part is due to single-particle excitations across the (single-particle) gap Δ, as discussed before, while the field-dependent part $\sigma(E)$ is due to the CDW condensate.

In the classical model,[27,28] the frequency-dependent conductivity $\sigma(\omega)$ reflects the response of the particle in a periodic potential. According to frequency-dependent conductivity measurements,[15] the response of the CDW to external ac fields is strongly overdamped. Accordingly, the equation of motion for large-amplitude dc driving fields is given (for a sinusoidal periodic potential) by

$$\frac{1}{\tau}\frac{dx}{dt}+\frac{\omega_0^2}{Q}\sin Qx=\frac{eE}{m}\ , \tag{7}$$

where m and e are the mass and charge of the CDW, $\omega_0^2=k/m$, where k is the restoring force, $1/\tau=\gamma/m$, with γ the friction coefficient, and $Q=2\pi/\lambda$, where λ is the CDW wavelength. The dc conductivity is given by

$$\sigma(E)=\begin{cases}0, & E<E_T \\ \dfrac{ne^2\tau}{m}\left[1-\left[\dfrac{E_T}{E}\right]^2\right]^{1/2}, & E\geq E_T\end{cases} \tag{8}$$

The model gives a sharp threshold field E_T for the onset of nonlinearity. The differential conductivity dI/dV is given by

$$\frac{dI}{dV}\frac{1}{\sigma(E\to\infty)}=\frac{E}{(E^2-E_T^2)^{1/2}}\ , \tag{9}$$

which diverges at the threshold field E_T.

In the tunneling model[29,30] coherent tunneling of CDW's over macroscopic distances is responsible for the nonlinear transport. The tunneling probability is given by

$$P(E)=\begin{cases}0, & E<E_T \\ A\left[1-\dfrac{E_T}{E}\right]\exp\left[\dfrac{-E_0}{E}\right], & E\geq E_T\end{cases} \tag{10}$$

where A is a constant of proportionality and the characteristic field E_0 is given by an expression similar to that for the (single-particle) Zener tunneling,

$$E_0=\frac{\pi\varepsilon_g^2}{4\hbar e^* v_F}=\frac{\varepsilon_g}{2\xi_0 e^*}\ , \tag{11}$$

where ε_g is the pinning gap, $e^*/e=m/M_F$ is the ratio of the band mass to the Fröhlich mass, and ξ_0 is the coherence distance. The threshold field is given by $e^*E_TL=\varepsilon_g$ where L is a correlation distance over which the electric field is applied to lead to the nonlinear conductivity. The tunneling probability given by Eq. (10) leads to

$$\sigma(E)=A\left[1-\frac{E_T}{E}\right]\exp\left[\frac{-E_0}{E}\right], \qquad (12)$$

and to the differential conductivity,

$$\frac{dI}{dV}\frac{1}{\sigma(E\to\infty)}=\left[1+\frac{E_0(E-E_T)}{E^2}\right]\exp\left[\frac{-E_0}{E}\right]. \qquad (13)$$

Expression (13) is similar to that suggested by Fleming[9] on experimental grounds to account for the nonlinear conductivity observed in $NbSe_3$:

$$\sigma(E)=A\left[1-\frac{E_T}{E}\right]\exp\left[\frac{-E_0}{E-E_T}\right]. \qquad (14)$$

The differential conductivity corresponding to Eq. (14) is

$$\frac{dI}{dV}\frac{1}{\sigma(E\to\infty)}=\left[1-\frac{E_0(E-E_T)}{(E-E_T)^2}\right]\exp\left[\frac{-E_0}{E-E_T}\right]. \qquad (15)$$

Although Eqs. (8), (12), and (14) lead to nonlinear conductivity only if the electric field exceeds a threshold field E_T, and all lead to a saturation of $\sigma(E)$ at high electric fields, they differ in important features. The most clear-cut difference shows up in the differential conductivity dI/dV near threshold. Figure 9 shows dI/dV, normalized to the $E\to\infty$ conductivity, calculated for the classical model with a sinusoidal potential, for the tunneling model, and for Fleming's empirical formula. In the latter two

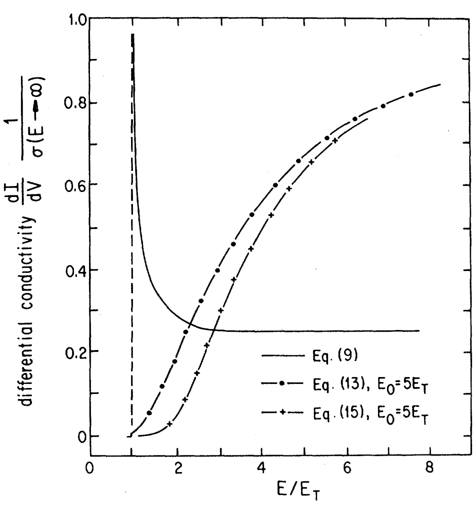

FIG. 9. Differential conductivity calculated from the various proposed forms of the nonlinear conductivity (see text).

cases we have assumed that $E_0=5E_T$ (see below). The divergence of the differential conductivity at E_T is the general feature of the classical description.[31] A singularity of the form

$$(E^2-E_T^2)^{1/2} \qquad (16)$$

is obtained for any periodic regular potential $V(x)$ for which $[dV(x)/(dx)]$ is finite, and singular behavior is also observed for a parabolic potential.[25] Also a description in terms of an electronic analog, the relaxation oscillator,[32] leads to a divergent differential conductivity. Comparing Fig. 9 with the experimentally observed behavior displayed in Fig. 6, it is evident that a classical description does not lead to the appropriate detailed behavior of the nonlinear conductivity near threshold $E\sim E_T$.

The singularity obtained in the classical model can be removed by assuming that thermal fluctuations lead to a smearing of the sharp onset of the nonlinear conductivity.[33] The classical equation is the same as that which describes the I-V characteristics of Josephson junctions, and a finite temperature treatment of the resistively coupled Josephson junction[33] leads to a thermal smearing of the sharp I-V characteristics. We have, however, shown before that finite temperature effects do not play an important role; the onset of nonlinearity is sharp at all temperatures below T_P. The assumption that there is a distribution of CDW segments, each of which responds individually to the external dc field, leads to Eq. (14) for a particular assumption on the distribution of parameters which characterize the response of the CDW's.[34] This model, however, cannot explain in its present form the appearance of sharp noise peaks which are observed in the nonlinear region.

We proceed therefore with a detailed comparison of our experimental results with the predictions of the tunneling model, although we note that our data can be adequately analyzed also in terms of Fleming's empirical formula.

The full line of Fig. 8 is Eq. (12) fitted to the experimental points. This fit, together with the measured sample length, leads to $E_T=1.3$ V/cm and $E_0=6.5$ V/cm$=5E_T$, and $A=0.8\sigma_{RT}$. The differential conductivity measured on a different sample can also be fitted with the tunneling formula. Such a fit is shown in Fig. 10, where the full line is Eq. (13) with $E_T=1.05$ V/cm, $E_0=5.2$ V/cm, and $A=0.8\sigma_{RT}$, the same relation between E_0 and E_T as used before to fit the conductivity data. Figure 8 together with Fig. 10 shows that a tunneling formalism leads to an excellent fit to the experimental-

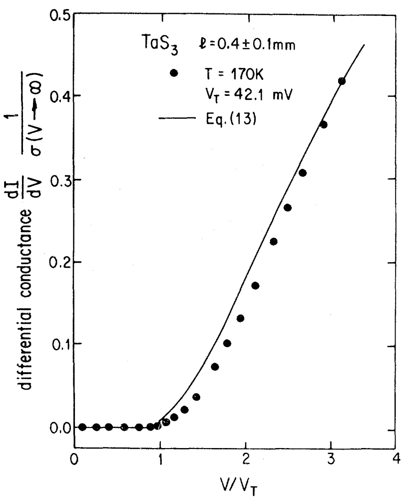

FIG. 10. Differential conductivity measured in orthorhombic TaS_3 at 170 K. The full line is a fit to the prediction of the tunneling model, Eq. (13), with parameters given in the text. The sample length is given in the figure.

ly found field dependence over a broad electric field range. An equally good fit is obtained by using the empirical expression, Eqs. (14) and (15), which differs only slightly from the formula proposed by Bardeen. We note that similar good fits are attained for $NbSe_3$ in both CDW phases,[35] the main differences being that for $NbSe_3$, $E_0 \sim E_T$ or $E_0 \sim 2E_T$ provide appropriate fits.

The parameters E_0 and E_T obtained from the fit to the experimental data can be used to evaluate the gap ϵ_g, across which the CDW has to tunnel, and the correlation length L and coherence length ξ_0. Equation (8) leads to

$$\epsilon_g = \left[\frac{4\hbar e^* v_F}{\pi} \right]^{1/2} = \left[\frac{4\hbar e m v_F}{M\pi} \right]^{1/2}, \tag{17}$$

and with $m/M_F \sim 10^{-3}$ and $v_F = 10^7$ cm/sec characteristic for a narrow-band material with bandwidth $D \sim 1$ eV, we obtain $\epsilon_g = 2\times10^{-17}$ ergs or $\epsilon_g = 0.11$ K, orders of magnitude smaller than the single-particle gap $\Delta = 700$ K. The correlation length L can be evaluated from $e^* E_T L = \epsilon_g$, and we obtain $L = 8\times10^{-3}$ cm. The coherence length ξ_0 is obtained from the relation $E_0 = E_T[1 + L/(2\xi_0)]$ and we obtain $\xi_0 = 10^{-3}$ cm. Similar enormous length scales are observed in both CDW phases of $NbSe_3$.[35]

Finally we note that the high-field conductivity $\sigma(E \rightarrow \infty)$ is close to the conductivity which is measured above the Peierls transition. A fit to Bardeen's tunneling formula leads to $\sigma(E \rightarrow \infty) = 0.8\sigma(300\ \text{K})$, suggesting strongly that the contribution of sliding CDW's to the conductivity is comparable to the conductivity due to the normal electrons in the absence of CDW formation. A similar situation is obtained in $NbSe_3$, where the resistivity peaks associated with the development of CDW's are removed by applying a large electric field. Arguments of why this is the case have been presented by Bardeen[30] and by Gorkov and Dolgov.[36]

C. Disordered CDW state at low temperatures

Below about 130–100 K (depending on the crystals measured) there is no evidence for a sharp threshold field for the onset of nonlinear conductivity and also the sharp noise peaks disappear below this temperature.[16] We believe that this is evidence for the lack of coherent CDW response, and the various CDW domains in the sample respond incoherently to the external driving force. Because of the absence of long-range coherence we call this state the disordered CDW state. The conductivity is still highly nonlinear in this temperature region at small electric field strengths, and it certainly reflects the response of various CDW segments. One could account for the observed nonlinear conductivity by assuming a distribution of internal electric fields or by a distribution of characteristic energies which represent the CDW response to external perturbations. Such a distribution would lead to the disappearance of the sharp threshold field and of the narrow-band noise peaks.

The origin of the coupling between various CDW regions which leads to a coherent response at high temperatures, but which is not effective at low temperatures, is not clear. The most trivial explanation for this behavior is that thermally excited electrons tend to homogenize the electric field inside the sample, and in the absence of normal electrons large electric fields may build up at grain boundaries, dislocations, impurities, etc. This effect would tend to be a natural source of the distribution of driving fields inside the specimen. Another effect is that normal electrons may provide a (yet unknown) coupling between the various CDW segments and thus provide a phase-coherent state which extends throughout the whole sample. Still another coupling mechanism may be provided by phonons at high temperatures, and then the synchronization of the CDW segments is through the underlying lattice. We are not aware, however, of any discussion of these phenomena.

V. COMPARISON OF TaS_3 AND $NbSe_3$

In this section we compare the nonlinear behavior found in orthorhombic TaS_3 to that observed in another linear-chain compound, $NbSe_3$, which shows CDW transport phenomena: nonlinear[7] and frequency-dependent[8] conductivity, and narrow-band noise.[9]

While both $NbSe_3$ and orthorhombic TaS_3 are composed of MX_3 chains with rather similar geometrical configuration, there are two important differences between orthorhombic TaS_3 and $NbSe_3$. First, TaS_3 is more anisotropic than $NbSe_3$. The anisotropy of the conductivity in $NbSe_3$ is approximately ten, about an order of magnitude smaller than in TaS_3.[19] This difference in dimensionality is further supported by the fact that the whole Fermi surface is destroyed in TaS_3 by the CDW formation, while a sizable fraction of electrons remain uncondensed in $NbSe_3$ at both transitions. This leads to a semiconducting behavior in TaS_3, while the resistivity remains small in both CDW phases in $NbSe_3$. Also, strong one-dimensional fluctuations are observed in TaS_3 above the transition. These are absent in $NbSe_3$.[5]

The overall similarity of the nonlinear response in $NbSe_3$ and TaS_3 then demonstrates that the dimensionality of the underlying electronic structure does not play an important role. The related question of the effect of the uncondensed electrons in the observed parameters in question is more subtle. First, the presence of normal electrons leads to homogeneous electric fields inside the sample, an effect certainly required for a coherent CDW response. In the absence of normal electrons, large inhomogeneous electric fields could build up at different regions in the sample, leading to a distribution of driving fields, and consequently, to a distribution in the response to external fields. While in $NbSe_3$ the uncondensed electrons lead to homogeneous fields inside the sample, in TaS_3 normal electrons excited across the single-particle gap may give rise to this same feature. This homogenizing effect may be responsible for the observed coherent response somewhat below T_P and the noncoherent response well below T_P. Also, for a complete description of CDW response, most probably both the normal and uncondensed electrons should be included by taking into account that two channels, provided by the normal and by the condensed electrons, participate in the charge transport.

The other important difference between $NbSe_3$ and TaS_3 is in the observed periodicity of the CDW. In $NbSe_3$ two phase transitions are observed, one at $T_1=149$ K and another at $T_2=59$ K. Both are associated with the development of an incommensurate CDW.[5] Below T_1 the period of the CDW parallel to the chains $q=0.243$, and below T_2, $q=0.259$. Although both are close to commensurability four (i.e., $q=0.25$), the nonlinear response is due to an incommensurate CDW which is pinned by the residual impurities. Impurity pinning was also directly demonstrated by experiments performed on doped[37] and irradiated materials.[38] According to recent x-ray observations,[11] orthorhombic TaS_3 has a commensurate CDW, $q=0.25\pm0.01$, although a slight derivation from commensurability cannot be ruled out at present. If subsequent high-resolution x-ray studies confirm the commensurate CDW, then pinning of impurities and pinning by commensurability lead to rather similar responses to external perturbations. Indeed, expressions (12) and (14) provide a good description of the nonohmic conductivity both in $NbSe_3$ and TaS_3 with the only difference being that in TaS_3 $E_0 \sim 5E_T$ and in both phases of $NbSe_3$, $E_0 \sim E_T$ or $E_0 \sim 2E_T$ provides an appropriate fit.

In $NbSe_3$ both E_0 and E_T display a characteristic temperature dependence.[9,39] Both diverge at the phase transitions T_1 and T_2 and have a minimum somewhat below the transition temperature, then increase with decreasing temperature. In contrast to this, E_0 and E_T are independent of the temperature in the region where a coherent CDW response is observed in TaS_3. This difference may be due to the presence of normal electrons in $NbSe_3$ and may be related to the temperature dependence of the ohmic conductivity. No model is available at present which takes this effect into account.

Also, in $NbSe_3$, the threshold field is approximately 1 order of magnitude smaller below T_1 and 2 orders of magnitude smaller below T_2 than in TaS_3. According to the tunneling model, this leads to a larger correlation length L and coherence length ξ_0, and consequently to a smaller gap for the CDW transport. This may reflect the difference between impurity and commensurability pinning, or—if TaS_3 is also incommensurate—less impurities in the $NbSe_3$ sample than in TaS_3. Experiments in carefully purified TaS_3 samples, and also doped or irradiated materials, could clarify this point.

VI. CONCLUSION

The CDW formation in the highly anisotropic band-conductor orthorhombic TaS_3 leads to a broad variety of phenomena associated with the response of the collective CDW mode. Above the Peierls transition at $T_P = 215$ K one-dimensional CDW correlations lead to resistive fluctuations. The gradual opening of a pseudogap, together with dynamical localization, leads to a strong increase of the dc resistivity. Although the conductivity is frequency dependent[14] and a positive dielectric constant[12] is observed in this temperature region, the conductivity is ohmic up to high electric field strengths, and there is no evidence for a collective response in the dc transport properties.

Below the Peierls transition the development of the 3D-ordered CDW state leads to strongly nonlinear response, rather similar to that observed in both CDW phases of $NbSe_3$. The observation of a sharp threshold field together with the narrow-band noise strongly suggests that coherence extends throughout the whole sample, and even though the CDW segments may have a finite coherence length the various segments are coupled together. The situation may be similar to coupled Josephson junctions,[40] where even weak coupling leads to a coherent response. Owing to the inherent nonlinearity of the problem such coupling is natural, although the mechanism of the coupling (whether it is provided by the uncondensed electrons, or by phonons) is not clear at present.

The observation that the field-dependent conductivity is independent of the temperature somewhat below T_P provides direct evidence that thermally excited collective modes (such as thermally excited solitons) do not play an important role in the CDW dynamics. It also argues against models such as the finite-temperature treatment[33] of the classical model. In this model the singularity obtained at $T=0$ is removed at finite temperatures, and the differential conductivity smoothly increases with increasing electric field as observed. This would lead to a progressively sharper increase of dI/dV with decreasing temperature, a feature not observed in our experimental data. A random noise term, included in Eq. (7) may remove the singularity and lead to the required smooth increase of the differential conductivity above threshold. As mentioned before, this term, however, should not be related to temperature-induced fluctuations. We also note that the classical model, with the inclusion of distribution of CDW parameters, also removes this singularity.[34] This model, however, has some difficulties to account for the observed narrow-band noise peaks. The detailed form of the nonlinear conductivity therefore argues for a description in terms of a tunneling process, and the small characteristic fields E_0 and E_T then lead to very long-length scales of the order of a few micrometers.

The main features of the nonlinear conductivity in TaS_3 and in $NbSe_3$ appear to be similar, in spite of the large differences in the anisotropy of the band structure and the presence of normal (uncondensed) electrons in $NbSe_3$ in the CDW states. We conclude that the normal electrons do not affect the field dependence itself, but may determine the temperature dependence of parameters such as E_0 and E_T which characterize the observed field dependence.

Perhaps the most important unresolved question is the commensurability of the CDW in TaS_3. If subsequent structural studies confirm the recent observation that the CDW is commensurate with the underlying lattice, then commensurability and impurity pinning play similar roles and only the average pinning energy and coherence length are the important parameters in the problem. If, however, the CDW is only close to commensurability, then the rather similar response of $NbSe_3$ and TaS_3 to external driving forces is not surprising.

It appears that, due to the extremely weak interactions between chains, various crystallographic phases may be obtained, depending on the details of the preparation procedure. A mixture of the orthorhombic and monoclinic phase can be obtained even within one needle.[41] The temperature dependence of the dc resistivity of our orthorhombic TaS_3 is slightly different from that measured by Takoshima *et al.*[19] and recently the same group found nonlinear conductivities which are similar to ours but with larger threshold fields.[42] There is also a disagreement between the resistivities of the monoclinic form found by Ido *et al.*[42] and Roucau *et al.*[18] While we did not find differences between the various preparation batches, and we have performed field- and frequency-dependent transport and noise measurements on the same samples to arrive at a consistent picture of CDW transport phenomena, these studies should be complemented with structural studies on the same samples.

It has also been suggested recently that at temperatures below 100 K thermally activated solitons determine the low-field dc conductivity in TaS_3.[19] This is based on the observation that the temperature dependence of the conductivity over a wide temperature range can be resolved into two activated behaviors.[19] The high-temperature slope, which corresponds to a larger activation energy, is thought to represent the contribution of thermally excited single-particle states. The low-temperature slope, which can be represented by an activation energy approximately one-third of the high-temperature activation energy, is claimed to represent soliton excitations. We do not find clear evidence for this behavior, but this may be due to the anomaly found near to 50 K in our samples. While we believe that the overall nonexponential form of the conductivity is due to residual disorder effects, further studies are necessary to clarify this point.

We also mention that while we have analyzed our experimental findings in terms of models which describe the CDW transport as a displacement of the CDW as a whole, it has also been suggested that the CDW may be distorted, and therefore can be represented by regions where commensurate CDW segments are separated by discommensurations, which may be described as solitons. In contrast to solitons in commensurate CDW systems, the discommensurations are not thermally excited. Therefore, this suggestion is not *a priori* in disagreement with the temperature-independent $\sigma(E)$ as found in TaS_3. These models,[43,44] however, have not been worked out in detail, and it remains to be seen whether they describe the main features of the nonlinear transport in $NbSe_3$ and in TaS_3.

ACKNOWLEDGMENTS

We thank J. Bardeen, B. Horowitz, M. Weger, W. G. Clark, and T. Holstein for helpful discussions on CDW transport phenomena. Useful correspondence with P. Monceau and T. Sambongi are also acknowledged. The x-ray analysis of our samples was performed by Sofinya and A. Jacobsen. This research was partially supported by NSF Grant No. DMR-81-03085. Part of this work was completed when two of us (A.Z. and G.G.) were visitors at the Exxon Research and Engineering Company. One of us (A.Z.) also acknowledges support from an IBM fellowship.

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