Charge-Density-Wave Transport in TaS_3

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We report the observation of strongly nonlinear conductivity with a sharp threshold field and a giant dielectric constant in the charge-density-wave state of TaS_3. We argue that these properties reflect the dynamical behavior of the charge-density-wave condensate, and compare the observed behavior with the properties of $NbSe_3$.

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In spite of recent efforts to search for charge transport carried by a collective mode called the charge-density wave (CDW), the only well-documented example for CDW motion is the linear-chain compound $NbSe_3$. The field[1,2]- and frequency[3]-dependent conductivity, together with the x-ray evidence[4] for CDW's, are in conflict with a single-particle conduction mechanism, and are interpreted in terms of CDW tunneling[5] or depinning.[6] Attempts to detect nonlinear conductivity in other CDW systems were either unsuccessful[7] or are the subject of other interpretations like disorder or hot-electron effects.

In this paper we report conductivity (σ) and dielectric-constant (ϵ) experiments in the linear-chain compound TaS_3. Diffuse x-ray studies[8] show a CDW with periodicity $4c_0$, where c_0 is the lattice constant along the chain direction, below the transition temperature $T_{MI} = 215$ K. The temperature dependence of the CDW order parameter was also established by Raman-spectroscopy studies.[9] We observe strongly nonlinear conductivity below T_{MI} with a well-defined threshold field E_T for the onset of nonlinearity. The CDW is also characterized by a giant dielectric constant which strongly depends on the frequency in the 10^6–10^8 Hz region. We discuss these findings in terms of recent models[5,6] proposed for the CDW dynamics, and point out the differences between $NbSe_3$ and TaS_3.

TaS_3 was prepared by reaction of the elements with excess sulfur at 650 °C for three weeks, with subsequent slow cooling for another three weeks to 400 °C. The typical dimensions of the crystals are 5 mm $\times 10$ μm $\times 1$ μm; the long dimension corresponds to the chain axis.[8] Powder x-ray diffraction shows an orthorhombic phase with lattice parameters reported earlier,[8] with no evidence for a second phase. We have used both two-probe and four-probe configurations for dc measurements. Contact resistances were found to be approximately 0.1 Ω, more than two orders of magnitude smaller than the room-temperature sample resistance, which varied between 16 and 100 Ω for different samples. Conductivity and dielectric constant results reported in this paper were performed on short samples to avoid inhomogeneous stress, with a two-probe configuration.

The low-field Ohmic dc conductivity is shown in Fig. 1 together with the derivative $d\sigma/dT$. The phase transition, as shown by the maximum of the derivative, is at $T_{MI} = 215$ K, and agrees with the CDW transition determined by Raman-spectroscopy,[9] and diffuse-x-ray studies.[8] Between 200 and 100 K, $\sigma(T)$ can well be described by an activated behavior with $\sigma(T) = A\exp-(\Delta/k_BT)$ with $\Delta = 740$ K. We associate the Ohmic conductivity with single-particle electrons excited across the Peierls-Fröhlich gap. Then the semiconducting behavior suggests that all electrons are condensed in the CDW mode. Below about 100 K the conductivity starts to flatten, probably due to residual disorder effects.[10] Measured over a temperature range larger than that shown in Fig. 1, $\sigma(T)$ agrees with that reported in Ref. 8. Figure 2 shows σ versus sample voltage at various temperatures both above and below T_{MI}. Heating effects were avoided by using both dc and pulse measurements with pulse widths as short as 0.5 μsec for large values of V. While σ is independent of V above the transition, the conductivity below T_{MI} is strongly nonlinear for electric fields above a threshold field V_T, and at high electric fields appears to approach the conductivity measured just above the phase transition. The sharp threshold persists between T_{MI} and 100 K. Below about 100 K, we do not find a sharp

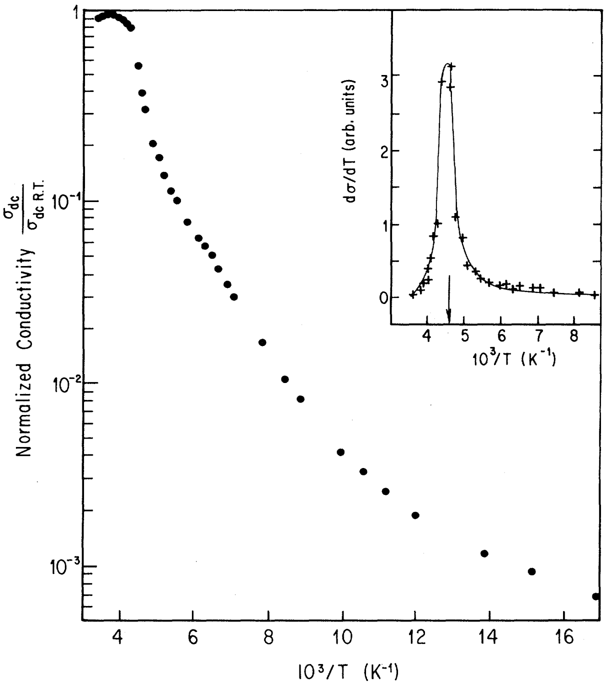

FIG. 1. Temperature dependence of the normalized conductivity of TaS_3. The inset show $d\sigma/dT$ near the transition T_{MI} =215 K. The average room temperature conductivity measured on several crystals is $\sigma = (2 \pm 0.5) \times 10^3\ \Omega^{-1}\ cm^{-1}$.

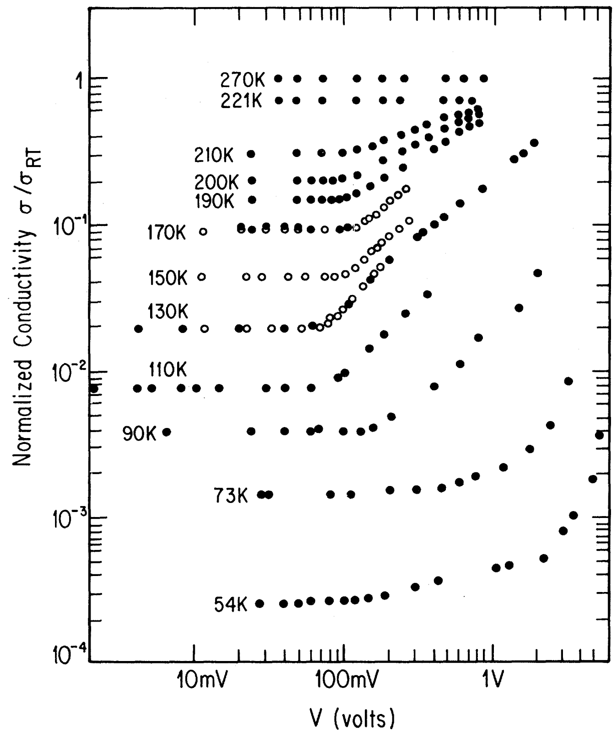

FIG. 2. Field dependence of the conductivity of TaS_3. Open circles, dc measurements, and closed circles, pulse measurement. The sample length l =0.4 mm leading to E_T =2.2 V/cm somewhat below the transition.

threshold field; this is most probably related to the flattening off of the conductivity, and may reflect the effect of residual disorder. We associate the threshold field with the onset of strong increase of σ with V in this region. Our experimental results in this temperature range agree with those found by Takoshima *et al.*[11] The temperature dependence of V_T is shown in Fig. 3. With the sample length l = 0.4 mm, the threshold field E_T = 2.2 V/cm just below the transition. Measurements on samples of different length l established that E_T is independent of l and E_T given here is accurate within a factor of 2. We also note that because of the progressively larger conductivity for $V \rightarrow 0$, the field-dependent part of σ becomes progressively weaker near T_{MI}, but the functional form of $\sigma(V)$ appears to be independent of the temperature. This behavior is shown in the lower part of Fig. 3, where $\sigma(3V_T)/\sigma(V_T)$ is displayed as a function of temperature. The dielectric constant was measured by a radio-frequency bridge technique,[3] where the sample (represented by a parallel resistance and capacitance) is balanced by a variable resistance and capacitance. The temperature dependence of ϵ is shown in the inset of Fig. 3. It is obtained with use of the relation $\epsilon = 2\pi RC\sigma$, where R and C are the sample resistance and capacitance and σ the conductivity. The dielectric constant is zero above T_{MI} and is extremely high in the CDW state. It is also strongly frequency dependent, and accompanied by a strongly frequency-dependent conductivity for small ac amplitudes. Detailed experiments on $\sigma(\omega)$ and $\epsilon(\omega)$ will be reported later.[12]

We now discuss these results. Both the presence of a sharp threshold field[2] and a giant dielectric constant[3] (which is also frequency dependent) are also observed in $NbSe_3$ and are regarded as convincing evidence of a pinned collective mode, which becomes depinned at high dc electric fields. Also, the threshold remains sharp even at high temperatures, which leads to a lower limit for the length L of the CDW segments. The usual argument that the energy supplied by the electric field acting over the CDW length L must be larger than the thermal energy in order to observe a sharp threshold

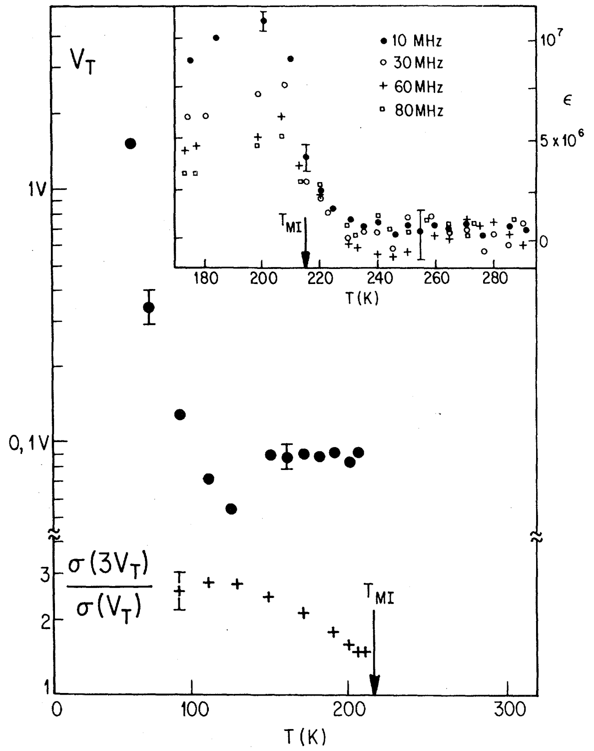

FIG. 3. Temperature dependence of V_T and conductivity increase at $3V_T$. The inset shows the dielectric constant measured at various frequencies.

leads to $L > k_B T(eE)^{-1} \sim 5\times10^{-3}$ cm or 1.5×10^5 lattice constants, below T_{MI}.

Two models were proposed recently to account for the nonlinear and frequency-dependent conductivity due to the CDW condensate. One describes the nonlinear conductivity in terms of collective CDW tunneling.[5] The other model[6] treats the CDW as a classical object moving in a periodic potential under the influence of an electric field. In the tunneling model[5] the nonlinear conductivity is given by

$$\sigma(E) = A(1 - E_T/E)\exp(-E_0/E), \quad E > E_T, \tag{1}$$

with $E_0 = \pi\epsilon_g^{\,2}/4\pi e^* V_F$, where ϵ_g is the pinning gap, e^* is the effective charge of the CDW, and V_F the Fermi velocity. E_T is determined by the length of the CDW through $e^* E_T L = \epsilon_g$. $\sigma(E)$ can be fitted well with Eq. (1) with $E_T = 2.2$ V/cm and $E_0 = 11$ V/cm, at temperatures below T_{MI} but above 150 K. Then with $e^*/e = m/M_F = \frac{1}{500}$, where M_F and m are the Fröhlich mass[5] and band mass, and with $V_F = 10^7$ cm/sec, we obtain $\epsilon_g = 2.1\times10^{-17}$ erg and $L = 3\times10^{-3}$ cm, respectively. The dielectric constant is given by $\epsilon(\omega\to0) = 4\pi n_s e^2/m^*\omega_p$, with n_s the number of condensed electrons, and $\omega_p = \epsilon_g/\hbar$ is the gap frequency. The number of electrons is not known in TaS_3 from independent measurements. For the present we will simply assume that n is the same as that, for $NbSe_3$, $n = 0.95\times10^{21}$ electrons/cm^3 (for a discussion of n in $NbSe_3$, see Ref. 6). As TaS_3 is semiconducting below the transition, we assume that all electrons are condensed in the CDW state. Then from $\epsilon = 10^7$ we obtain $\omega_p = 5.7\times10^{11}$ sec^{-1} and $\epsilon_g = 0.57\times10^{-17}$ erg, in good agreement with the estimate based on the nonlinear conductivity.

In the classical description of CDW depinning[6] the threshold field is given by (for a sinusoidal periodic potential) $E_T = (\lambda/2\pi)m\omega_0^{\,2}/e$ where λ is the CDW period, and $\epsilon(\omega\to0) = \pi\hbar e^2/m\omega_0^{\,2}$. The two parameters can be combined to obtain

$$ne\lambda = \tfrac{1}{2}E_T\,\epsilon(\omega\to0)\,; \tag{2}$$

with the measured values $E_T = 2.2$ V/cm and $\epsilon(\omega\to0) = 10^7$, we obtain $\lambda = 8$ Å in good agreement with the CDW period $\lambda = 4c_0 = 13.3$ Å obtained from x-ray studies.[8] We conclude, therefore, that both the tunneling model and the classical description account well for the nonlinear conductivity and dielectric constant. We note that a similar analysis, performed for $NbSe_3$, also gives results consistent with the predictions of both models.[5,6]

We have also observed[16] narrow-band noise with several harmonics in the nonlinear conductivity regime and a noise frequency which is proportional to the current due to the sliding CDW. This feature, also observed in $NbSe_3$, provides additional evidence for a sliding CDW.

The strong similarities of the nonlinear conductivity and dielectric constant found in $NbSe_3$ and TaS_3 are surprising in the light of structural differences of the two compounds. $NbSe_3$ has an incommensurate CDW[4] which is most probably pinned by impurities, while in TaS_3 the CDW has a period $4c_0$ and is commensurate with the underlying lattice.[8] This would suggest pinning by the lattice potential in TaS_3, i.e., a commensurability pinning. Pinning by impurities, however, cannot be ruled out at present. Also $NbSe_3$ has a substantial two-dimensional character and only part of the Fermi surface is removed. TaS_3 is more anisotropic leading to a complete destruction of the Fermi surface by the CDW formation and a semiconducting state below the transition. These differences may show up in the detailed field- and frequency-dependent response of the CDW condensate. Such experiments may also lead to a distinction between models[5,6] which account for field- and frequency-dependent CDW transport, and could clarify the relative role of commensurability and impurities in determining the dynamical response of the CDW condensate.

The measurement of various transport properties, in the Ohmic regime below T_{MI}, together with a detailed investigation of the CDW dynamics and measurements on doped samples are expected to clarify the unusual properties of this compound. We are at present engaged in the experimental investigation of these phenomena.

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[12]σ is independent of the frequency up to 1 GHz above T_{MI}, and shows a strong frequency dependence below T_{MI}. In contrast to $\sigma(E)$, however, we do not find a sharp threshold frequency for the onset of $\sigma(\omega)$. Detailed experiments on $\sigma(\omega)$ and $\epsilon(\omega)$ will be reported elsewhere (C. Jackson, A. Zettl, G. Grüner, and A. H. Thompson, to be published).

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