Solid State Communications, Vol.39, pp.531-534.
Pergamon Press Ltd. 1981. Printed in Great Britain.

0038-1098/81/280531-04$02.00/0

HIGH FREQUENCY CONDUCTIVITY IN THE CHARGE DENSITY WAVE SEMICONDUCTOR TaS_3

C. M. Jackson, A. Zettl, and G. Grüner
Department of Physics, University of California, Los Angeles, California 90024

and

A. H. Thompson
Corporate Research Laboratory, Exxon Research and Engineering Co., Linden, New Jersey 07036

(Received 25 May 1981 by A. Zawadowski)

We report the observation of frequency dependent conductivity $\sigma(\omega)$ in the charge density wave (CDW) semiconductor TaS_3. Based on $\sigma(\omega)$ and other evidences, we suggest that three different temperature regions occur in this compound: 1-D fluctuating CDW region above T_{MI}, a coherent CDW state below T_{MI}, and a CDW glass state at low temperatures.

The linear chain compound TaS_3 undergoes a transition to a semiconducting phase at temperature T_{MI} = 215±5 K. Recent X-ray studies[1,2] show diffuse streaks above the transition with period 4c, where c is the lattice constant along the chain direction, while below T_{MI} a superlattice with period 2a × 8b × 4c is observed. Both observations reflect the development of a Peierls state below T_{MI}. The dc conductivity is strongly non-ohmic below the transition[3] with a sharp threshold field E_T down to about 100 K. Below this temperature the sharp threshold disappears and the conductivity increases smoothly with increasing electric field. We have also found a giant dielectric constant at radio frequencies (10-100 MHz)[3] and narrow-band noise,[4] below T_{MI}. These observations, similar to those for $NbSe_3$, are taken as evidence for the dynamical response of the charge density wave (CDW) condensate which develops below T_{MI}.

In this communication we report the observation of strongly frequency dependent conductivity in the CDW state of TaS_3. In contrast to the dc conductivity, which shows an activated behavior down to ∿ 100 K, the microwave conductivity remains high. Measurements at high radio frequencies yield a conductivity intermediate between those of dc and microwave. We argue that at low temperature the coherent CDW state is destroyed by disorder, leading to a charge density wave glass (CDWG) state.

The dc conductivity was measured by a conventional four-probe method. Measurements at high radio frequency (2.4 GHz) were performed with an HP 8754A network analyzer, using a two-probe configuration. The microwave (9.15 GHz) conductivity was measured using the cavity perturbation technique of Buravov and Shchegolev.[5] Typical sample dimensions were 2mm × 10μm × 2μm. The long dimensions correspond to the chain axis in TaS_3; all quantities measured and discussed here are with respect to this axis.

In the microwave measurements, the sample in a TE_{011} cylindrical cavity leads to a frequency shift δ and an absorption Δ. The conductivity σ and dielectric constant ε are given by

$$\sigma = \frac{\alpha}{N^2} \frac{(\Delta/2)^2}{(\Delta/2)^2 + (\alpha/N - \delta)^2} \tag{1}$$

$$\varepsilon - 1 = \frac{1}{N} \frac{\delta(\alpha/N - \delta) - (\Delta/2)^2}{(\Delta/2)^2 + (\alpha/N - \delta)^2} \tag{2}$$

where $\alpha = 2.1\ V_s/V_c$ is the filling factor, and V_s and V_c are respectively the sample and cavity volume. N is the depolarization factor, which for a cylindrical sample is given by[5]

$$N = \frac{3}{2} \frac{d^2}{L^2} \left(\ln \frac{4L}{d} - \frac{7}{3} \right) \tag{3}$$

where L is the sample length and d is the square root of the cross sectional area.

If the sample is highly conducting, then the shift δ is equal to δ_0, where

$$\delta_0 = \frac{\alpha}{N} = 1.4 \frac{L^3}{V_c} \left(\ln \frac{4L}{d} - \frac{7}{3} \right)^{-1} . \tag{4}$$

Here δ depends only on the sample dimensions and the cavity volume. In the limit of a highly conducting sample, only the conductivity can be calculated. Figure 1 shows the measured δ and Δ as as function of temperature. Within experimental accuracy, δ is independent of temperature at high temperatures while in the same temperature range the dc conductivity is large, suggesting that is given by Eq. (4). Additional evidence for the "metallic" limit is that if N is calculated from the room temperature δ, then N agrees well with that calculated from Eq. (3), as shown in Table 1. This agrees with the highly conducting limit of a skin effect analysis.[6] We have assumed, therefore, that $\delta = \delta_0$ above 140 K, and calculated the conductivity with this assumption.[7] Figure 2a shows the normalized conductivities for dc, 2.4 GHz, and 9.15 GHz. We note that the detailed form of the conductivity depends on the above as-

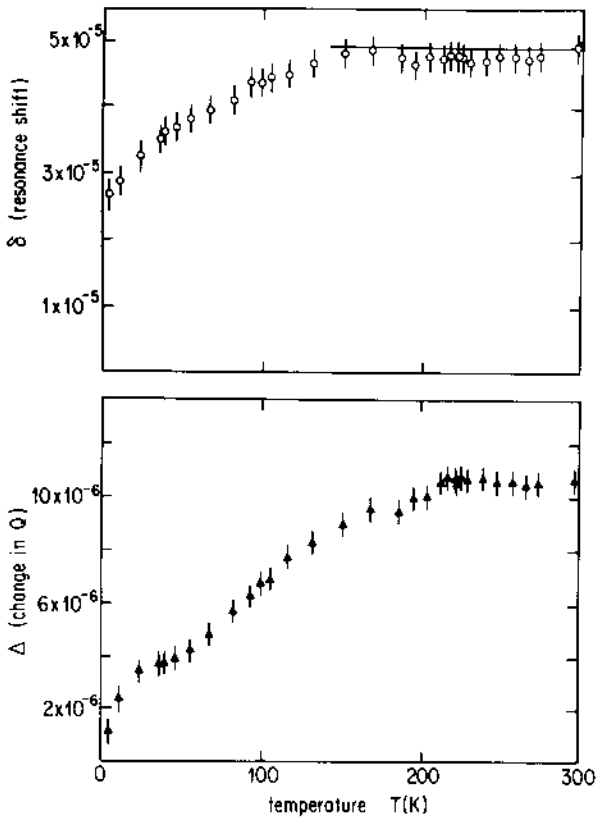

Figure 1. Cavity shift and absorption as a function of temperature in TaS_3. The solid horizontal line is the maximum shift.

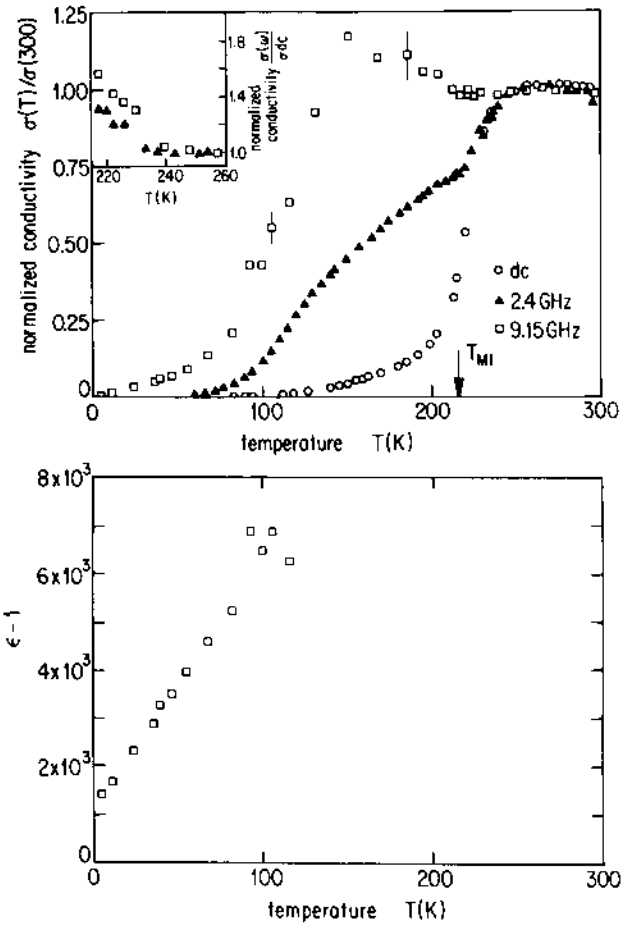

Figure 2. (a) The normalized dc conductivity, σ(2.4 GHz), σ(9.14 GHz) of TaS_3. The insert shows σ(ω) normalized to the dc conductivity above the transition. (b) Microwave dielectric constant versus temperature.

sumptions. A finite deviation between the measured δ_0 and the actual δ_0 would lead to a normalized microwave conductivity somewhat lower than shown in Fig. 2a. The dielectric constant below 140 K is shown in Fig. 2b.

Table I. Comparison of depolarization factors calculated from the geometric size of the sample to the depolarization factor calculated from the room temperature shift δ_0.

sample	length (L)	diameter (d)	N_{geom}	N_{shift}
1	2.3 mm	0.038 mm	1.3×10^{-3}	1.4×10^{-3}
2	1.7 mm	0.025 mm	1.0×10^{-3}	8.5×10^{-4}
3	2.6 mm	0.013 mm	9.0×10^{-5}	1.9×10^{-4}

Figure 3 shows the conductivity in a log σ vs. 1/T representation. We note that the conductivity is frequency dependent even above T_{MI} = 215 K (this is more clearly seen in the insert of Fig. 2a). Below T_{MI}, but above approximately 100 K, the dc conductivity shows an activated behavior with an activation energy of about 740 K.[3] The high radio frequency conductivity shows a change in slope at T_{MI}, with an activation energy below T_{MI} much smaller than that of the dc measurement. The microwave conductivity is "metallic" in this region, i.e., it increases with decreasing temperature. Below 100 K the dc conductivity can be described by a fractional power law, $\sigma = \sigma_0 \exp(T_0/T)^{1/m}$ with $m \sim 3$.

We believe that while disorder seems to play an insignificant role between 100 and 215 K, transport at low temperatures is dominated by strong disorder effects. In light of X-ray evidences[1,2] for a CDW below T_{MI}, we argue that just below the transition a coherent CDW state devel-

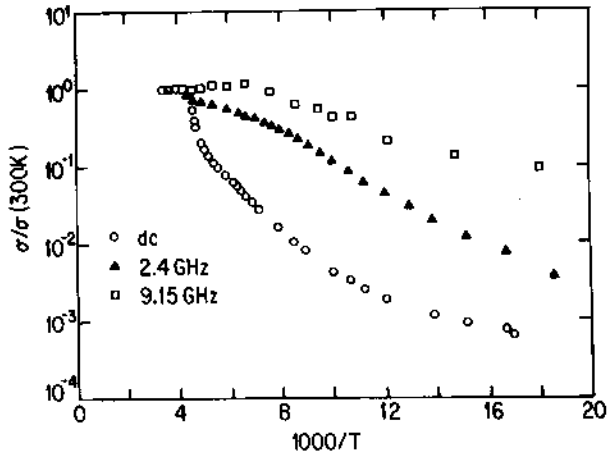

Figure 3. The normalized σ_{dc}, σ(2.4 GHz), and σ(9.14 GHz) versus inverse temperature.

ops, but that at low temperatures impurities destroy this coherence. This destructions leads to a strongly disordered CDW state, which we call the charge density wave glass (CDWG) state. Above T_{MI}, on the other hand, one dimensional fluctuations seem to dominate the transport properties. We discuss below the evidence for these suggestions, and the characteristic features of the three CDW regions.

1. Fluctuating conductivity above the transition

The dc conductivity σ_{dc} has a maximum at 270 K and then strongly decreases with decreasing temperature. We also observe a pronounced frequency dependent conductivity in this region (see the insert of Fig. 2a). Diffuse X-ray studies[1] show the presence of 1-D streaks between room temperature and T_{MI}. We suggest, therefore, that the decreasing dc conductivity and $\sigma(\omega)$ reflect one-dimensional resistive fluctuations in this temperature region. While various models[8] appropriate to this temperature region can lead to either an increasing conductivity or an increasing resistivity, the increasing resistivity and frequency dependent conductivity found here suggest that the CDW's are pinned even above T_{MI}, and can be depinned at high frequencies. The behavior of σ_{dc} reflects the formation of a pseudogap in this fluctuating region.

2. Coherent CDW state below the transition

Both X-ray and conductivity experiments show a sharp phase transition at T_{MI}. As impurities or intrinsic disorder would smear a sharp CDW transition[9,10] (observed in other cases, the most notable example being the linear chain compound KCP),[11] we conclude that disorder plays a negligible role at high temperatures. Below T_{MI} the dc conductivity is nonlinear above a well-defined threshold field E_T. A similar nonlinearity is found in $NbSe_3$.[12] Also, narrow band noise is observed[4] below T_{MI} with the noise frequency f_n proportional to the excess current I_{CDW} carried by the charge density wave. Both observations strongly suggest that a distribution of CDW segments does not occur between T_{MI} and $\sim$ 100 K. A distribution of CDW segments would imply a distribution of pinning forces and thus a smearing of the sharp threshold field. If f_n is related to I_{CDW} using a simple phenomenological model[13] where the noise is caused by drifting CDW's, one obtains $f_n = \mu_d/\lambda$, where μ_d is the drift mobility of the CDW and λ is the characteristic distance determining the noise frequency. The total current due to the CDW is given by $I_{CDW} = \mu_d ne$, where n is the number of drifting CDW segments. Then $f_n = I_{CDW}(ne\lambda)^{-1}$. This linear relation between f_n and I_{CDW} demonstrates that the number of drifting CDW's is independent of the applied voltage, i.e., the CDW condensate displays a coherent response with respect to the dc excitation.

The dynamical response of the CDW condensate in $NbSe_3$ can be described by an overdamped harmonic oscillator, which gives

$$\sigma(\omega) = \frac{ne^2\tau}{m} \frac{(\omega/\omega_{c.o.})^2}{1 + (\omega/\omega_{c.o.})^2} \qquad (5)$$

with the frictional force, τ, the mass of the CDW condensate, m, and $\omega_{c.o.} = \omega_0^2\tau$ where ω_0 is the pinning frequency. A tunneling model[14] also describes the smooth increase of $\sigma(\omega)$ with increasing frequency, and σ saturates at high frequencies and at high electric fields. The increasing microwave conductivity with decreasing temperature then suggests that τ increases with decreasing temperature as in another material,[15] $NbSe_3$. The pinning frequency ω_0 can be expressed as $\omega_0^2 = k/m$, where k is the CDW restoring force constant. Any phase-locking of uncorrelated CDW's at the transition is not expected to affect the value of k. However, the condensate mass m increases below T_{MI} due to the greater CDW coherence. The associated decrease in ω_0^2 then leads to a sudden change in slope for $\sigma(\omega)$ at the transition temperature (see Fig. 2), and also a sharp lowering of the dc threshold field just below the transition, as observed.[3] A detailed comparison with the tunneling model will be presented elsewhere.

3. Charge density wave glass state at low temperatures

Below about 100 K the sharp threshold of the nonlinear conductivity disappears.[3,16] Instead we observe a smoothly increasing σ_{dc} with increasing applied voltage. Also, the low field dc conductivity becomes nonexponential below this temperature. The fractional power law $\sigma_{dc}(V\to 0) = \sigma_0 \exp(T_0/T)^{1/m}$ was previously interpreted[17] in terms of variable-range hopping of a strongly disordered semiconductor. While σ_{dc} most probably reflects single particle transport processes, disorder also leads to the breakup of the coherent CDW state.[9,10] This results in a distribution of CDW segments, with the subsequent distribution and also increase of restoring forces. One would consequently expect a smearing of the response to a dc electric field, and thus an absence of a sharp threshold field, as is observed. Such a progressive CDW localization also results in a frequency response which is shifted to pro-

gressively higher frequencies with decreasing temperatures, and subsequently to a high frequency conductivity which decreases with decreasing temperature, as observed. The dielectric constant, shown in Fig. 2b, is also suggestive of a progressive CDW localization with decreasing temperature. The dielectric constant is given by $\varepsilon = \Omega_p^2/\omega_p^2$ where $\Omega_p^2 = 4\pi ne^2/m$ is the plasma frequency of the collective mode, for $\omega < \omega_p$.

We believe that the strong decrease of the ε with decreasing temperature indicates an increase of ω_0^2 with decreasing temperature, although detailed frequency dependence measurements would be needed to confirm this assertion. We also note that both the dc and the microwave conductivities and ε show a behavior closely analogous to the CDW compound KCP,[18] where disorder plays an important role in a wide temperature range.

In conclusion we suggest, on the basis of the behavior of the dc conductivity and the nonlinear and frequency dependent response, that in TaS_3 the coherent response of the CDW condensate somewhat below T_{MI} is followed at low temperatures by a response characteristic of a strongly disordered CDW state. The mechanism which may lead to strong disorder effects at low temperatures, with coherent CDW response at higher temperatures, is unclear. We note, however, that in TaS_3 the CDW is commensurate with the underlying lattice.[2] This may result in both commensurability and impurity pinning, with the different pinning mechanisms playing different roles at different temperatures. Also, TaS_3 is more anisotropic than is $NbSe_3$, which results in the complete destruction of the Fermi surface in TaS_3 at the transition temperature. This may lead to disorder effects much more evident than in $NbSe_3$. Detailed studies on samples with various amounts of impurities should clarify the relative role of disorder and commensurability in the transport properties of this compound. Independent measurements of the microwave conductivity on TaS_3 have been reported recently[19] with results in broad agreement with those reported here.

We acknowledge many conversations with P. M. Chaikin, W. G. Clark, and T. Holstein. The microwave conductivity equipment was built with A Janossy. We also wish to thank W. P. Ong for communicating the progress of work on TaS_3. This work was supported by a grant from the UCLA Academic Senate Research Committee.

REFERENCES

1. SAMBONGI, T., TSUTSUMI, T., SHIOZAKI, Y., YAMAMOTO, M., YAMAYA, K., and ABE, Y., Solid State Commun. 22, 279 (1977).
2. TSUTSUMI, K., SAMBONGI, T., KAGOSHIMA, S., and ISHIGURO, T., J. Phys. Soc. Japan 44, 1735 (1978).
3. THOMPSON, A. H., ZETTL, A., and GRÜNER, G., Phys. Rev. Lett. (submitted for publication).
4. GRÜNER, G., ZETTL, A., CLARK, W.G., and THOMPSON, A.H., Phys. Rev. B, June 15 (1980).
5. BURAVOV, L. I., and SHCHEGOLEV, I.F., Prib. i Tekh. Eksper. 14, 171 (1971); Instrum. Exp. Tech. (USSR) 14, 528 (1971).
6. ONG, N. P., J. Appl. Phys. 48, 2935 (1977).
7. We remark that due to the fibrous morphology of TaS_3, the calculated absolute (i.e., unnormalized) microwave conductivity is smaller than the true value. We find $\sigma \sim 10^2\ (\Omega\ \mathrm{cm})^{-1}$ at microwave frequencies at 300 K in contrast to the value reported in Refs. 1 and 2 of about $10^3\ (\Omega\ \mathrm{cm})^{-1}$. This difference, however, does not affect the overall temperature dependence of σ (9.15 GHz).
8. For a review, see THOMAS, G. A., in The Physics and Chemistry of Low Dimensional Solids, L. Alcácer, Ed. (D. Reidel Publ. Co., Holland, 1980), p. 31.
9. BULAEVSKII, L. N., and SADOVSKII, M. V., Fiz. Tverd. Tela 16, 1159 (1974).
10. SHAM, L. J., and PATTON, B. R., Phys. Rev. B 13, 3151 (1976).
11. ZELLER, H. R., in Low-Dimensional Cooperative Phenomena, H. J. Keller, Ed. (Plenum Press, New York, 1975).
12. FLEMING, R. M., and GRIMES, C. C., Phys. Rev. Lett. 12, 1423 (1979).
13. GRÜNER, G., ZAWADOWSKI, A., and CHAIKIN, P. M., Phys. Rev. Lett. 46, 511 (1981).
14. BARDEEN, J., Phys. Rev. Lett. 45, 1978 (1980).
15. GRÜNER, G., TIPPIE, L. C., SANNY, J., CLARK, W. G., and ONG, N. P., Phys. Rev. Lett. 45, 935 (1980).
16. TAKOSHIMA, T., IDO, M., TSUTSUMI, K., and SAMBONGI, T., Solid State Commun. 35, 911 (1980).
17. TSANG, J. C., HERMAN, C., and SHAFER, M. W., Phys. Rev. Lett. 40, 1528 (1978).
18. SHCHEGOLEV, I. F., Phys. Stat. Sol. A9, 12 (1972).
19. VERMA, G., ECKERT, J. C., ONG, N. P., KHANNA, S. K., and SOMANO, R. B., Bull. Am. Phys. Soc. 26, KK4, 449 (1981).