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CHARGE DENSITY WAVE TRANSITION AND NONLINEAR CONDUCTIVITY IN NbS_3

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We report dc conductivity (σ) measurements on the linear chain compound NbS_3. The temperature dependence of σ indicates a phase transition at T_{MI} = 155 K with strong one-dimensional fluctuations above T_{MI}. Below T_{MI} the conductivity is strongly increasing with increasing electric field above a threshold field E_T, and is also strongly frequency dependent. We argue that the nonlinear conductivity is due to sliding charge density waves.

The transition metal trichalcogenides, MX_3, formed between the transition metal atoms Nb or Ta, and chalcogens S or Se form linear chain compounds where the transition metal atom is surrounded by trigonal chalcogen prisms. Phase transitions observed in $NbSe_3$[1] and TaS_3[2] are associated with the development of charge density waves (CDW's). The strong frequency[3] (ω) and electric field[4,5] (E) dependent transport phenomena observed in the CDW state are due to the dynamical response of the collective CDW mode.

In this communication we report dc conductivity (σ) measurements on the linear chain compound NbS_3. The temperature dependence of the low field conductivity shows a phase transition around T_{MI} = 155 K, with semiconducting behavior below T_{MI} and strong one-dimensional resistive fluctuations above T_{MI}. The conductivity is strongly non-ohmic below T_{MI}. These findings are closely analogous to those found in orthorhombic TaS_3,[6] and, together with electron diffraction observations,[7] suggest that the transition is associated with the development of a CDW state, and that the nonlinear conductivity is due to sliding charge density waves.

NbS_3 appears in two forms,[8] called type I and type II. The structure of type I was established recently,[9] and shows a pairing of Nb-Nb atoms along the chain direction. This form of NbS_3 is a semiconductor with large energy gap at high temperatures. The crystal structure of type II has not previously been established, but diffuse electron diffraction experiments[7,8] show one-dimensional diffuse lines at room temperature, and superlattice spots, indicative of a three-dimensional ordering, at low temperatures. The superstructure[7] occurs at a period close to 3 b_0 where b_0 is the lattice constant along the chain direction, but the question whether the CDW is commensurate or only near to commensurability, has not yet been established.

We have prepared the NbS_3 compound by direct reaction of the elements at 550°C and at 650°C. The sample prepared at 650°C has the published crystal structure phase I, and also the conductivity is that of semiconductor, in agreement with earlier observations.[10]

The NbS_3 compound prepared at 550°C is a new phase we call phase III. In this preparation the elements were first reacted to form NbS_2 at 850°C over one week. The sample was cooled to room temperature and ground to 100 mesh. Additional sulfur was added to bring the stoichiometry to NbS_3, and an additional amount of 10 mg of sulfur per cubic centimeter of tube volume was added to create a sulfur overpressure and to provide a mineralizing agent to encourage homogeneity. The new sample was sealed under vacuum and heated at 550°C for three weeks and then cooled over two days to 400°C. The sample was then quenched into room-temperature air from 400°C.

According to powder X-ray diffraction data, this phase is distinctively different from phases I and II reported earlier. In this phase the 001 reflections indicate a c axis very similar to the phase I, and it is likely that the a axis is also similar, but the monoclinic angle is increased to 98°-99°. We were not able to find the b axis based on our powder diffraction measurements.

The conductivity studies presented in this report are for the Form III of NbS_3. Typical crystal dimensions were 5mm × 10µm × 50µm, with the long dimension corresponding to the chain axis (b axis). Our measured conductivity is with respect to this axis. We have used a four-probe configuration in the dc measurements, with indium current leads ultrasonically soldered to the sample and voltage leads attached with silver paint. In order to avoid inhomogeneous stress within the sample, we have selected relatively short samples, with a uniform cross section, for our dc measurements. The conductivity and dielectric constant at 9.1 GHz were measured by the cavity perturbation method.[11]

Figure 1 shows the low field conductivity plotted in a 1/T representation. The insert shows the derivative dσ/dT. The peak in the derivative indicates a broad phase transition near T_{MI} = 155 K. Between about 150 and 100 K, the conductivity follows a semiconducting behavior, and can be well described by $\sigma=\sigma_0\exp(-\Delta/K_BT)$, Δ = 1770 K. We associate the transition at T_{MI} with the formation of a charge density wave state. The semiconducting behavior below T_{MI} then indicates that all electrons are condensed in the CDW state, and the finite (and ohmic) low field conductivity reflects normal electrons excited into the conduction band across the Peierls-Frölich gap Δ. Between room temperature and 155 K the conductivity, σ, decreases with decreasing temperature, although an activated behavior is not observed. Electron diffraction studies[7] have observed diffuse lines at room temperature which developed into sharp spots upon cooling. We therefore suggest that the decreasing σ is associated with the development of a pseudogap in this temperature region. Below 100 K the conductivity flattens slightly. This may be the result of residual disorder effects.[12]

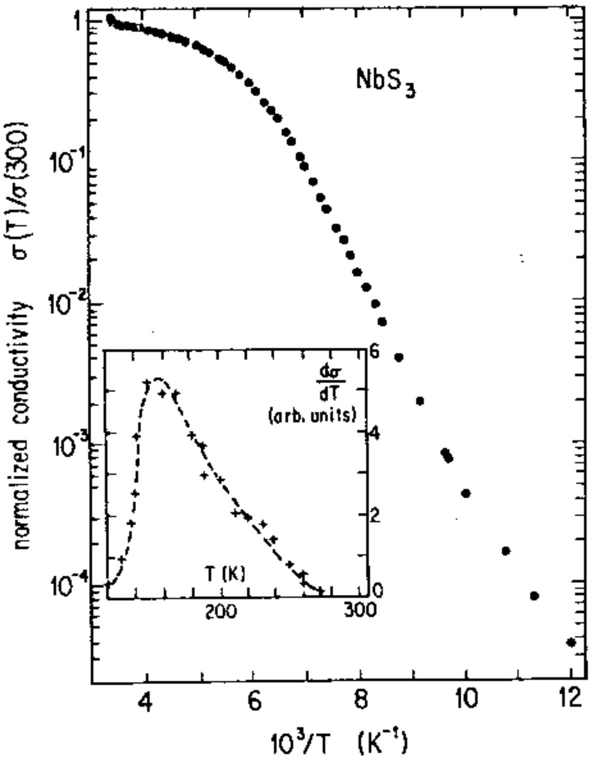

Fig. 1. Normalized low field dc conductivity σ for NbS_3. The insert shows the derivative dσ/dT.

The microwave conductivity and dielectric constant are presented in Fig. 2. While at room temperature σ is independent of frequency, at lower temperatures (but standing well above T_{MI}) a dispersion is found. The large microwave conductivity and dielectric constant are characteristic of weakly pinned charge density wave systems.

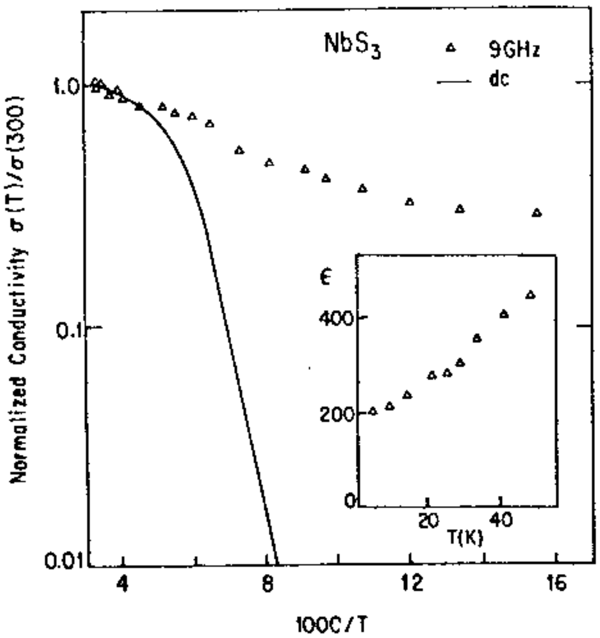

Fig. 2. Normalized dc conductivity (solid line) and microwave conductivity (Δ) vs 1/T. The insert shows the low temperature dielectric constant.

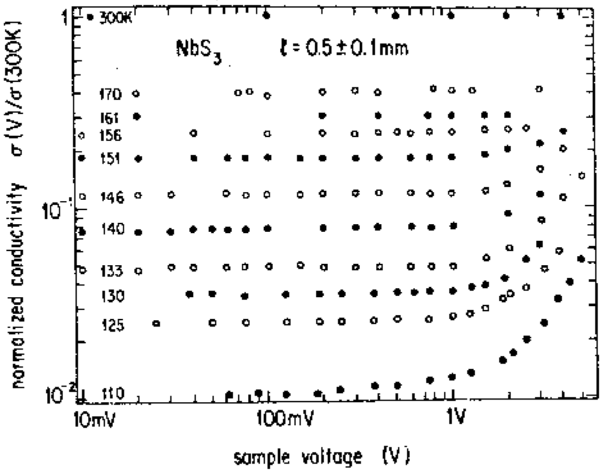

Fig. 3. Field dependent conductivity σ(V) for NbS_3 at selected temperatures. σ is independent of V above T_{MI} = 155 K. The sample length ℓ is given on the figure.

Figure 3 shows σ versus applied sample voltage (V) at selected temperatures both above and below T_{MI}. We have avoided sample heating effects by using a pulsed technique, with typical pulse widths of 10 μs. Above T_{MI} σ is independent of V, while below T_{MI} σ is strongly nonlinear above a well-defined threshold value V_T. Below V_T ohmic conduction is observed. Between T_{MI} and 125 K the threshold field is approximately independent of temperature. With the measured sample length ℓ = 0.5 mm, the observed threshold V_T = 1 V corresponds to a threshold field E_T = 20 V/cm. Measurements on different samples of different lengths indicate that E_T is independent of ℓ. At temperatures below 125 K the threshold for the onset of nonlinear conduction becomes less well-defined. Such a smearing of E_T is most likely due to the small number of normal conduction electrons present in NbS_3 at low temperatures. This allows for inhomogeneities in the internal electric field, and a consequent distribution of field energies within the sample.

We interpret the nonlinear conductivity as due to sliding charge density waves. The existence of a sharp threshold electric field for the onset of nonlinear conduction suggests that the CDW is pinned at low electric field strengths, and can become depinned at high electric field strengths. Similar nonlinear conductivity with a sharp threshold field is also observed in both $NbSe_3$[4] and TaS_3,[6] and is regarded there as strong evidence for conduction due to moving CDW's.

It is appropriate to comment on the overall similarity of σ measured for NbS_3 and σ measured for orthorhombic TaS_3. TaS_3 undergoes a Peierls transition[6] to an insulating CDW state at T_P = 215 K, and the low field conductivity for TaS_3 also shows strong resistive fluctuations,[3] with σ decreasing with decreasing temperature, and diffuse one-dimensional streaks[2] present in the X-ray diffraction pattern. In both materials the measured microwave conductivity is high down to low temperatures. The electric field dependent conductivity $\sigma(V)$ for TaS_3[6] at temperatures below T_P follows in general the same form of $\sigma(V)$ for NbS_3 presented here, with a smearing of the sharp threshold field below 100 K also seen in TaS_3. Between 200 K and 150 K the threshold field for TaS_3 is approximately 2 V/cm[6], one order of magnitude smaller than that for NbS_3. The stronger pinning results in a smaller dielectric constant in NbS_3. Although the CDW in TaS_3 is commensurate[2] with the underlying lattice, the effective pinning mechanism for TaS_3 is unclear. Nevertheless, the larger threshold field observed in NbS_3, which represents a greater CDW pinning force, could reflect a different pinning mechanism or a more important role played by impurities. Impurities could not only lead to a larger E_T for NbS_3, but could also smear a sharp transition to the CDW state.[13] Indeed, as evidenced by the width of the derivative peak in Fig. 1, the transition for NbS_3 is quite broad, in strong contrast to the sharp transition[6] observed in TaS_3.

In conclusion, the low field dc conductivity of the linear chain compound NbS_3 (type III) indicates a phase transition to an insulating CDW state approximately at T_{MI} = 155 K. Below T_{MI} the nonlinear and frequency dependent conductivity is interpreted as due to sliding charge density waves.

It appears that in transition metal trichalcogenides with multiple crystallographic phases, the appearance of charge density wave transitions and collective transport phenomena are closely related.

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