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CHARGE DENSITY WAVE TRANSPORT IN A NOVEL INORGANIC CHAIN COMPOUND, $(TaSe_4)_2I$

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We report the observation of nonlinear conductivity with a well-defined threshold electric field E_T, and frequency dependent ac conductivity, in a novel linear chain compound, $(TaSe_4)_2I$. The material undergoes a phase transition to a semiconducting phase at T ~ 260 K, and nonlinear and frequency dependent transport is observed below this temperature. We argue that the material is a new example of collective mode transport provided by a Peierls-Fröhlich charge density wave condensate.

Nonlinear and frequency dependent transport phenomena, observed in the linear chain compounds $NbSe_3$,[1] orthorhombic[2] and monochlinic[3] TaS_3, and in one form of NbS_3,[4] are due to collective response of a charge density wave (CDW) condensate. All of the above materials behave as anisotropic metals at room temperature, and at lower temperatures undergo phase transitions to insulating or semimetallic states where a periodic lattice distortion, along with an associated modulation of the electron charge density, occurs. The lattice distortion, together with the modulated charge density, is called the CDW. The frequency dependent response is due to the response of the CDW, which is pinned by impurities. The field dependent conductivity, which sets in when the applied electric field E exceeds a threshold field E_T, is due to the depinning and subsequent sliding motion of the CDW.

In spite of considerable experimental effort, CDW transport phenomena have been observed only in a small group of materials, the transition metal trichalcogenides of the group V transition metals. Moreover, without exception these materials occur in the form of very thin needles (with characteristic cross-sectional areas 10 μm × 10 μm, or less) making a wide range of experiments -- such as transport measurements perpendicular to the long axis, or optical studies -- exceedingly difficult or impossible.

In this paper we report the observation of highly nonlinear and frequency dependent transport phenomena in a compound prepared and characterized only recently.[5] While the material, $(TaSe_4)_2I$, is also a chain compound, its crystal structure is distinctively different from that of the trichalcogenide compounds. The crystals are huge when compared with those of the former group of compounds, and have typical cross sections of hexagonal form (dimensions larger than 1 mm per face of the hexagon) and exceptionally well developed smooth surfaces. The material shows a metal-insulator transition at 260 K, with nonlinear dc conduction below the phase transition. Although we do not have structural evidence for the periodic lattice distortion, the dependence of the conductivity σ on temperature, electric field E, and frequency ω demonstrates a CDW condensate response in this material.

Some crystals of $(TaSe_4)_2I$ were prepared from high purity starting materials. The stoichiometric mixture of the constituents was sealed in an evacuated quartz tube, and the reaction was performed in a gradient furnace with a typical temperature gradient of 10°C/cm. The crystals formed near the cold end of the tube and over the crystal growth region the temperature varied between 450 and 530°C. Within this temperature range we did not find strong dependence of the growth characteristics on the temperature. Large crystals of typical dimensions of 10 mm × 1 mm × 1 mm formed within a period of three days.

In contrast to the transition metal trichalcogenides, well defined crystallographic faces are evident in this compound, suggesting a hexagonal crystal structure. The crystals have a shiny, metallic luster just after preparation. This disappears over a period of approximately one week, most probably due to evaporation of iodine at the surface layer. While the material is in the form of well defined crystals -- suggesting substantial binding between the various chains -- it is relatively easy to split the specimens along the long (needle) direction, suggesting that the chains run parallel to the needle direction, as in other linear chain inorganic compounds.[1-4]

Dc resistivity measurements performed on crystals from different preparation batches showed identical temperature dependences, suggesting that variations of composition (often occurring in materials which contain halogen chains) do not occur in this compound.

We did not perform composition or x-ray analysis, but our resistivity data (see below) are in agreement with those reported by Rouxel, et al.[5]

Figure 1 shows the low field dc conductivity measured using a four probe sample mounting configuration, as the function of inverse temperature. Both continuous dc and low frequency ac lock-in techniques were used, with identical results. Due to some residual

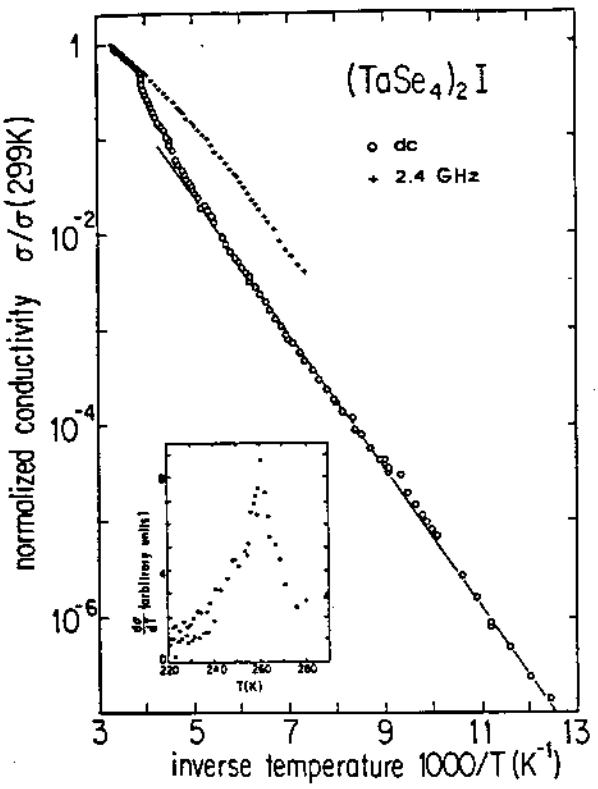

Fig. 1. Temperature dependence of the low field conductivity in $(TaSe_4)_2I$, measured at dc (0) and at 2.4 GHz (+). The full line is a fit to a semiconductor formula, Eq. (1), with an activation energy $\Delta/k_B = 3.1\times10^3$ K. The insert shows the derivative dσ/dT for the dc data.

iodine at the surface, conventional silver paint leads to contact resistances which occasionally may be in the 100 kΩ range. Freshly prepared samples or ultrasonically applied indium solder contacts were used to reduce the contact resistances to approximately 100 Ω at room temperature. A small hysteresis was usually found between cooling and heating. Whether this is associated with iodine ordering or stresses with the crystals is unclear, and is at present being investigated. It is evident that the material is a semiconductor over a broad temperature range, and the full line in Fig. 1 is the expression

$$\sigma(T) = \sigma_o \exp(-\Delta/2kT) \qquad (1)$$

with $\Delta = 3.3 \times 10^3$ K. A well defined hump in the conductivity, shown more clearly as a peak in the derivative of the conductivity dσ/dT in the inset of Fig. 1, gives strong indication of a phase transition at temperature $T_p \sim 260$ K. The overall behavior of σ(T) is similar to the transition metal trichalcogenide TaS_3[2] (orthorhombic form) where the peak in the temperature derivative of σ signals the occurrence of the Peierls transition as evidenced by x-ray studies.[2]

The large activation energy of $(TaSe_4)_2I$ as determined from Fig. 1 is somewhat surprising in the light of the transition temperature T_p. In the transition metal trichalcogenides the observed gap and T_p are well described[1,2] by the mean field BCS relation $\Delta = 3.52\ k_BT_p$, while here $\Delta \sim 13\ k_BT_p$. Large one dimensional fluctuations would decrease T_p and lead to a large Δ and small T_p, as observed here, but other effects -- such as a temperature dependent gap, which would show up only in a prefactor of Eq. (1) -- may also be of importance.

The room temperature conductivity of $(TaSe_4)_2I$ along the needle axis is $\sigma = 3.5 \times 10^2\ \Omega^{-1}\ cm^{-1}$, and is somewhat smaller than that obtained for the metallic trichalcogenides. Also, the temperature dependence of the conductivity near room temperature is "nonmetallic," i.e., σ decreases with decreasing temperature. Whether this behavior is due to one dimensional resistive fluctuations (as in TaS_3[6]), or due to a semimetallic behavior, remains to be seen.

While above T ~ 250 K the conductivity of $(TaSe_4)_2I$ shows an Ohmic behavior up to high applied dc electric fields (E ~ 300 V/cm), at lower temperatures σ is strongly nonlinear when the applied dc voltage V exceeds a threshold voltage V_T. Both pulsed and dc voltages were used to evaluate the electric field dependence of the conductivity. Figure 2a shows an I-V curve obtained by driving the sample from a continuous dc current source. Above approximately 120 mV the dc conductivity σ = I/V strongly increases with increasing V. While a sharp threshold field is not evident for the I-V curve, Fig. 2b shows σ = I/V versus the applied voltage measured by pulse

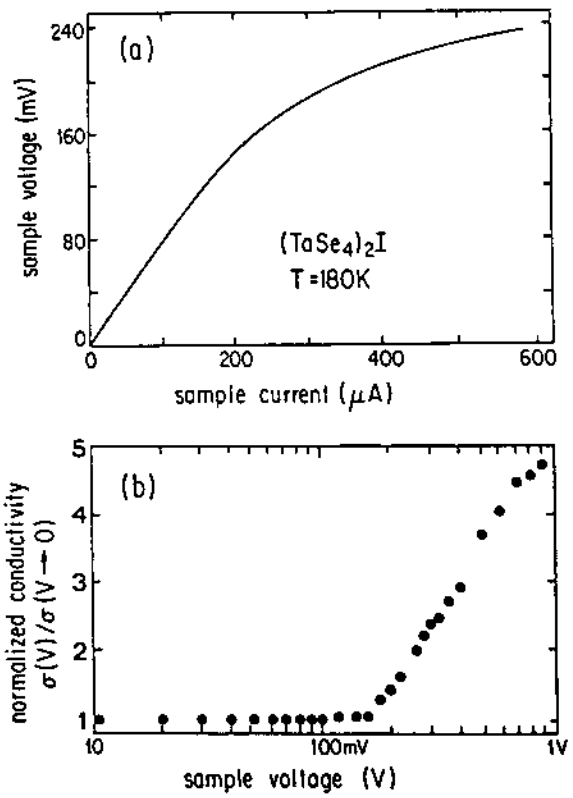

Fig. 2. Electric field dependence of the dc conductivity. The threshold electric field $E_T = V_T/\ell = 2V/cm$, where ℓ is the sample length.

techniques. Ohmic behavior is found up to V = 160 mV = V_T, while beyond this the conductivity strongly increases with increasing voltage. The threshold electric field, calculated from the known sample length ℓ, is $E_T = V_T/\ell \sim 2V/cm$ at this temperature. Measurement on various samples of different lengths showed that E_T is independent of the length of the specimens and is an inherent property of the compound. The threshold voltage and $\sigma(V)$ were also measured at various temperatures, and Fig. 3 shows V_T as a function of temperature. V_T decreases with increasing temperature, below the phase transition T_P = 260 K, and nonlinear behavior is not observed above T_P.

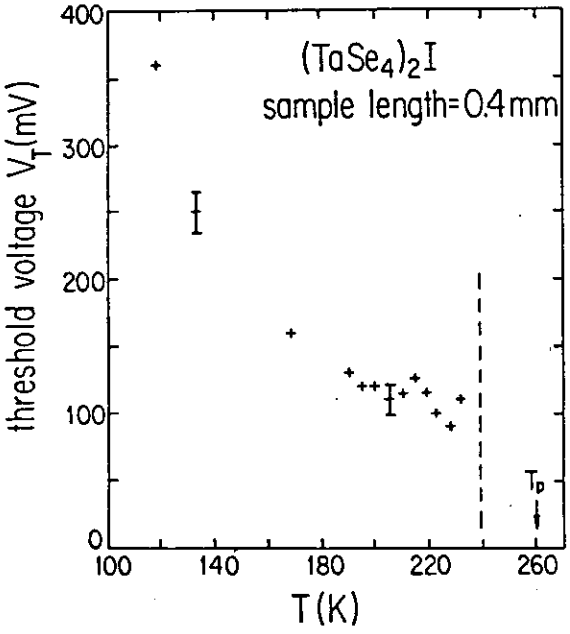

Fig. 3. Temperature dependence of the threshold electric field E_T. The dotted line indicates the temperature above which no nonlinear conduction was observed up to high electric field values.

The normalized conductivity of $(TaSe_4)_2I$, measured at $\omega/2\pi$ = 2.4 GHz (performed with an HP 8754A Network Analyzer using a small amplitude ac excitation) is shown along with the low-field dc conductivity in Fig. 1. For these two probe ac measurements, evaporated gold contacts were used, with contact resistances typically less than 1 Ohm. Figure 1 shows that no frequency dependence of σ is observed above T_P = 260 K, while below the transition a strong ω dependence is evident, and at 140 K $\sigma(\omega/2\pi = 2.4\ GHz)$ exceeds the dc value by more than one order of magnitude. The strong ω dependence of the conductivity is quite similar to that observed in NbS_3[4] orthorhombic TaS_3.[6]

As we have mentioned, there is no clear structural evidence that the phase transition observed at T_P = 260 K is associated with a periodic lattice distortion. However, the observations of frequency dependent and nonlinear conductivity with a sharp threshold field, which displays a characteristic temperature dependence, are strong indications that $(TaSe_4)_2I$ is a new compound which displays charge density wave transport phenomena. Such behavior is observed in all compounds with CDW ground states which also display collective CDW conduction, i.e., $NbSe_3$,[1] orthorhombic[2] TaS_3 and NbS_3.[4] Moreover, the overall functional form of $\sigma(E)$ observed in $(TaSe_4)_2I$ is also similar to that found in the transition metal trichalcogenides.[1-4] The temperature dependence of the threshold field (the increasing E_T with increasing temperature) is again similar to observations in these compounds. The magnitude of the threshold field -- approximately 2V/cm just below the phase transition -- is comparable to that found in moderately pure TaS_3[2] (orthorhombic form), and much smaller than that found in NbS_3.[4]

While it is clear that more detailed transport experiments, together with structural studies, are required to establish the detailed nature of the transport mechanism, we believe that the experiments reported here provide strong evidence for charge transport carried by a collective mode. Collective CDW transport therefore does not seem to be confined to a narrow group of compounds such as transition metal chalcogenides. The relatively large samples are also well suited to studies of anisotropic effects, optical properties, etc. It is expected that other compounds of this group, such as compounds with Cl and Br, may show CDW transport phenomena. Studies of this group, together with the recently studied[7] blue bronze $K_{0.33}MoO_3$, may also provide important information on the interplay of crystal binding, multiple phases, phase transitions, and collective transport phenomena.

More detailed experiments on the frequency dependent response and on other transport coefficients, together with x-ray studies, will be reported later.

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