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NON-LINEAR RESPONSE OF TRANSITION METAL TRI- AND TETRA-CHALCOGENIDES

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Abstract Electric field dependence of the d.c. electrical conductivity and of the fundamental frequency (i.e. the charge density wave velocity) for the transition metal tri- and tetrachalcogenides exhibiting CDW transport is compared to the tunneling model and to the classical collective pinning theory.

INTRODUCTION

Many of the chains which form the transition metal tri- and tetrachalcogenides, namely $NbSe_3$, NbS_3 type II, TaS_3 with the orthorhombic and the monoclinic unit cell, $(TaSe_4)_2I$ and $(NbSe_4)_{10}I_3$ distort themselves below the Peierls transition temperature.[1] All the distortion wave lengths and the associated charge density wave (CDW) of these compounds are incommensurate with the main lattice except for the orthorhombic TaS_3 for which the component along the chain axis locks to the commensurability of four atomic distances at $T_o' \sim 130$ K. Among this family, $NbSe_3$ is the unique compound undergoing a Peierls transition which remains metallic at low temperature. For all the other compounds the Peierls distortion is associated to a metal-semiconducting transition. These compounds exhibit non-linear transport properties at any temperature below the Peierls transition. This non-linearity has been ascribed to the Fröhlich conductivity resulting from the CDW motion when the latter is depinned by an electric field.

THEORETICAL MODELS

In general, the phase of the CDW is dependent on time and coordinates : $\phi(r,t)$. One group of theories consider that the sample under investigation is broken up into domains with finite sizes in which ϕ is independent of the position. The equation of motion of such a rigid CDW has been treated classically and with a quantum approach. The classical motion of the CDW taking into account deformations resulting from its interaction with impurities has also been studied. Another group of theories assigns some of the non-linear properties to the motion of local phase defects.

Rigid Motion of the CDW

Although the CDW interacts with impurities, it is assumed that its wave-vector is completely uniform. Consequently the CDW can be described with a unique dynamical variable : $\phi(t)$. When the inertial term is ignored, the classical equation of motion of the CDW is that of an overdamped oscillator.[2] Above the threshold field E_c, the current is the superposition of a continuous current and a modulation. The continuous current is $J=\sigma_a\left[E+\beta(E^2-E_c^2)^{1/2}\right]$ and the modulation has periodic components with frequencies which are multiple of the fundamental one, ω, such as :

$$\omega = \frac{1}{2}\left[\left(\frac{E}{E_c}\right)^2-1\right]^{1/2} \qquad (1)$$

At the threshold, dE/dJ has an infinitely negative value. However, experimentally dV/dI does not diverge at E_c which leads to think that the model with a unique domain is unrealistic. It has been shown that the divergence at E_c is suppressed when a distribution of threshold fields in a multidomain sample is considered.[3]

The same model treated quantically by Bardeen[4] leads to the following relationship between I and V :

$$I(E) = \sigma E = \sigma_a E + \sigma_b P(E) E \qquad (2)$$

with

$$P(E) = (1 - E_c/E)\exp(-E_o/E) \qquad (3)$$

where σ_a is the ohmic conductivity when $E \to 0$, $\sigma_a+\sigma_b$ the conductivity limit for $E \to \infty$. The activation field E_o can be expressed in terms of the threshold one such as :

$$E_o = kE_c \tag{4}$$

Typically $k \sim 1(2)$ for the upper (lower) CDW in $NbSe_3$, 5 for both forms of TaS_3, and $(TaSe_4)_2I$ and 9 for $(NbSe_4)_{10}I_3$.

Classical Motion of a Deformable CDW

Dynamics of the CDW has been studied in the frame of the Fukuyama-Lee-Rice model in which the CDW is deformable to minimize its interaction with impurities. When the local distortions of the CDW are small i.e. when the velocity of the CDW is large, the impurity potential can be considered as a perturbation. In this approximation Sneddon et al.[5] have calculated the asymptotic behaviour of the conductivity. The deviation from the limit $E \to \infty$ follows the law :

$$j = \sigma_{E\to\infty}E - C\sqrt{E} \tag{5}$$

An extension of the same model in the hydrodynamic approximation has been made by Sneddon.[6] He has treated the problem of charge accumulation caused by the CDW distortions and their screening with the remaining normal electrons. For compounds in which the conductivity strongly decreases below T_c (such as TaS_3) this screening is strongly reduced which leads to long range interaction of the CDW with itself. The coefficient C in (5) is thus expected to increase rapidly when T is reduced below T_c and the conductivity will follow (5) on a relatively large range of E only in the vicinity of T_c.

Fisher[7] has solved the same problem in the vicinity of E_c in a regime in which the CDW distortions are quite large. He introduces a time-dependent mean field thermodynamic potential $\Phi(\phi_j,t)$, a function of the local phase, ϕ_j, of the CDW at site, j, and of time. In the static configuration, $E < E_c$, the potential Φ is multivalued with many minima and maxima which leads to metastable

states. When $E > E_c$ there is a unique state with long range order and an average phase $\overline{\Phi} = vt$. Fisher considers the CDW depinning in the frame of critical phenomena. He finds that, above E_c, the velocity of the CDW follows the law :

$$v \sim (E-E_c)^{3/2} \qquad (6)$$

Naturally, for $E >> E_c$, v is proportional to E. The power law coefficient, 3/2, in (6) is the consequence of collective pinning. If the number of impurities decreases and becomes a finite but small number, eventually one, the result for rigid CDW motion, $v \sim (E-E_c)^{1/2}$ as in (1), is recovered.

Numerical methods have been used by Sokoloff[8], Pietronero and Strässler.[9] When the size of the system increases, it is found that the curvature of v(E) has a definite tendency to become concave upwards, as expected in the thermodynamic limit, and that the singularity at the threshold is confined to a very narrow region.

EXPERIMENTAL RESULTS

We have measured the d.c. electrical conductivity and the fundamental frequency of the time-dependent voltage up to fields as high as 50 E_c in orthorhombic TaS_3 and $NbSe_3$ (to avoid heating problems, samples were immersed in cryogenic liquids) and the experimental data have been compared to the theoretical predictions expressed in (2), (5) and (6).

$NbSe_3$

In addition to the Bardeen expression (2) for the conductivity, Fleming[10] has found that the following empirical expression : $\sigma = \sigma_a + \sigma_b[(1-E_c/E)\exp(-E_o/E-E_c)]$, fitted very well his data obtained for $NbSe_3$ at T = 51 K and T = 125 K. Later, Sneddon et al.[5] have shown that the same data also fitted with an excellent accuracy their calculation (equat. 5). Figure 1 shows the variation of σ as a function of E for $NbSe_3$ at T = 125 K. The curve is the

Bardeen expression (2) with k = 1.03 and σ_b/σ_a = 0.26. The agreement between data and (2) is not perfect especially near $E/E_c \sim 15$ and in the limit of infinite electric fields in which the data lie above the theoretical variation. Such a behaviour has already been obtained by Oda and Ido.[11] Also, we have plotted the experimental data according to the calculations of Sneddon et al.[5] (equat. 5). In order to compare the results at different temperatures we have drawn the variation of the deviation of the conductivity from the limit $E \to \infty$ normalized to this limit conductivity as a function of $(E_c/E)^{1/2}$. Fig. 2 shows that for different temperatures the conductivity follows the $(E)^{-1/2}$ law over a very large scale in electric field, practically from $E \to \infty$ down to the threshold.

We have measured the fundamental frequency in the time-dependent voltage above E_c. Near the threshold $\nu = (E/E_c)^{\gamma}$ with γ = 1.07 at T = 137 K, 1.06 at T = 136 K, 1.08 at T = 129 K and 1.26 at T = 96 K.

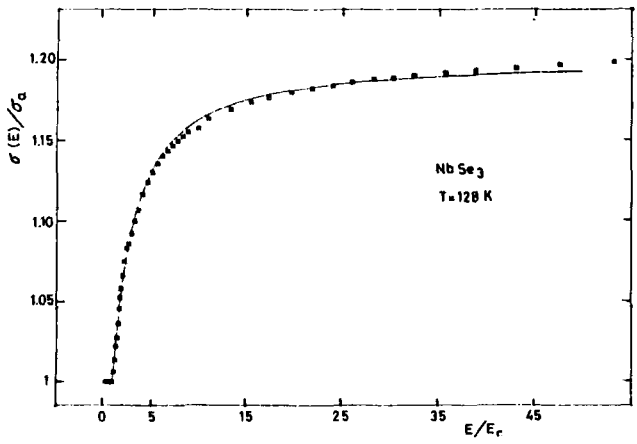

FIGURE 1 Electric field dependence of the conductivity of $NbSe_3$ at T=128 K. The curve is the Bardeen expression (equation 2).

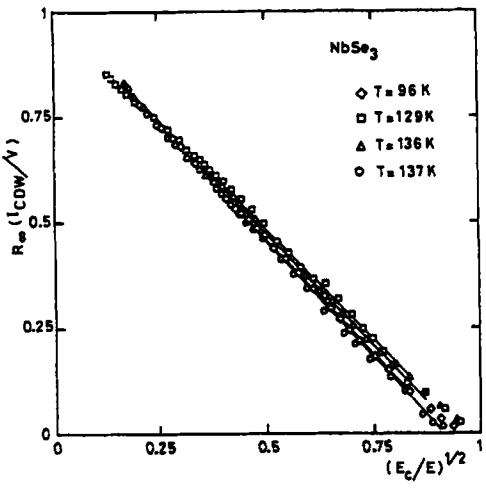

FIGURE 2 Electric field variation of the conductivity of $NbSe_3$ (normalized to the infinite electric field limit). Equat. 5 predicts a straight line as experimentally found.

TaS_3

Figure 3 shows the variation of σ as a function of E up to E/E_c= 40 for orthorhombic TaS_3 at different temperatures. Again the curves are the theoretical expression given by Bardeen (equat. 2).

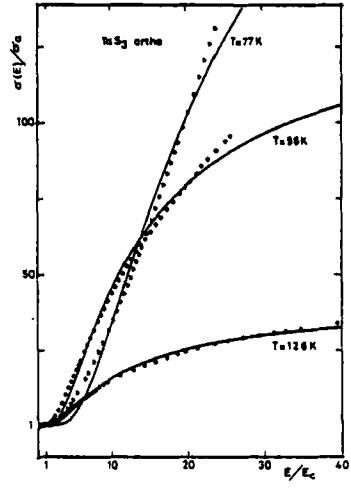

FIGURE 3 Electric field variation of the conductivity of orthorhombic TaS_3 at different temperatures. The curves are the best fits to the Bardeen equation (3).

It has to be recalled that there are only two parameters in these fits : the coefficient k and the ratio σ_b/σ_a. While k is equal to around 5 for temperatures between 150 K and the Peierls transition temperature (215 K) the best fits in Figure 3 are for k=10 and σ_b/σ_a = 40 at T = 126 K, k = 10 and σ_b/σ_a = 140 at T = 96 K and k = 12 and σ_b/σ_a = 300 at T = 77 K. However, the agreement between data and theoretical predictions is not good and it can be seen that in the limit of high electric fields the Bardeen expression lies always below the experimental data. Improvement in the fit can be obtained if a third parameter is introduced : in this way we have tried the following expression

$$\sigma = \sigma_a + \sigma_b\left[(1-E/E_c)\ \exp(-E_o/E)^{\alpha}\right] \qquad (7)$$

With α as an adjustable parameter an excellent agreement between experimental data and (7) is found with $\alpha \sim 0.8$ at T = 126 K, α = 0.5 at T = 90 K and $\alpha \sim 0.2$ at T = 77 K.

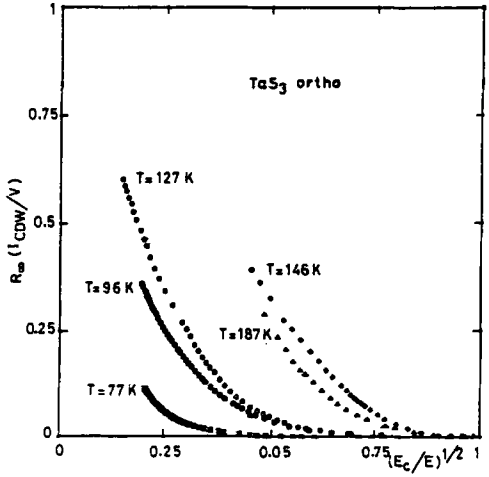

FIGURE 4 Electric field variation of the orthorhombic TaS_3 (normalized to the infinite electric field limit according to equation (5))

FIGURE 4 shows the same data as in Figure 3 but plotted according to the Sneddon et al. calculation (equat. 5). In this plot the conductivity for $E \to \infty$ has been taken to be the conductivity at the Peierls transition. Contrarly to $NbSe_3$ (see Figure 2) there is no linear variation of σ as a function of $E^{-1/2}$. As a function of temperature the results drawn in Figure 4 are qualitatively in agreement with the Sneddon calculations[6] which take into account the long range interaction of the CDW with itself leading to a decrease of the coefficient C in (5) when T is lowered.

The a.c. voltage generated above E_c is very easily detected by Fourier analysis in orthorhombic TaS_3. ν is linear with J_{CDW}, the current carried by the CDW : at T = 127 K for ν = 500 MHz, $J_{CDW} \sim 3\ 10^4\ Acm^{-2}$. At high velocity, ν is linear with $(E-E_c)$. The variation of ν as a function of $E-E_c$ near the threshold is drawn in Figure 5 at different temperatures. The curves are

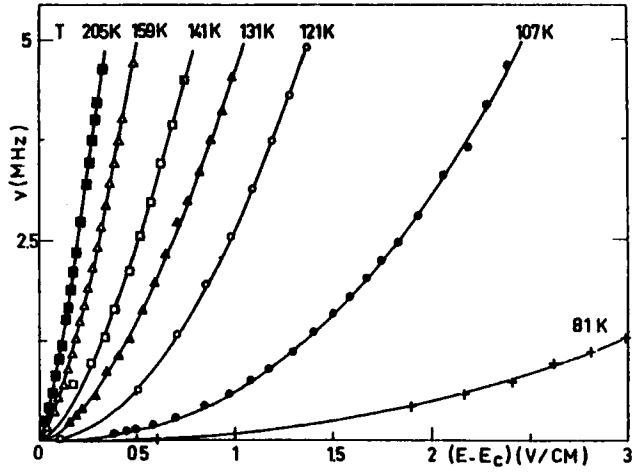

FIGURE 5 Variation of the fundamental frequency (or the CDW velocity) as a function of $(E-E_c)$ for orthorhombic TaS_3. The curves are the best fits of equation 6.

$(E-E_c)^{\gamma}$. For 205 K < T < 130 K, γ is approximately equal to 1.5 (1.33 at T = 205 K, 1.45 at T = 159 K, 1.44 at T = 141 K, 1.63 at T = 131 K) but its value is 2 at T = 121 K and 2.3 at T = 107 K and 81 K.

CONCLUSIONS

In the vicinity of the threshold the electrical conductivity can be fitted by several functional forms but however the classical collective pinning theory accounts for the electric field dependence of the conductivity and of the CDW velocity. Qualitative agreement with the Sneddon calculations has been found in particular the long range interaction of the CDW with itself when the CDW ground state is insulating. The confirmation of the tunneling model has to searched for in the joint ac + dc experiments as reported in these proceedings by Seeger et al.[12].

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