TRANSPORT PROPERTIES OF CHARGE-DENSITY WAVE IN THE $(2,5(OCH_3)_2DCNQI)_2Li$

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ABSTRACT: *We have measured the behaviour of the organic conductor $(2,5(OCH_3)_2DCNQI)_2Li$ (abbreviated as DMeO-Li), where DCNQI stands for dicyanoquinonediimine, from the room temperature down to 4.2K. We have used standard high-precision DC methods and precision LCR meter (20Hz to 1MHz) to measure the DC resistivity and the complex AC conductivity, respectively. The complex conductivity has been then used to extract the dielectric function. The obtained results, in particular the non-ohmic I-V characteristics, the magnitude of the static dielectric constant ($\varepsilon_0 = 3\cdot 10^7$) and the characteristic relaxation time (τ_0) being much larger than that expected for the single-particle excitations, has unambiguously proved that measured features really belong to charge density wave (CDW) phase. The observed data have indicated that N=4 CDW is pinned by commensurability to the underlying lattice. This has been the first time that a commensurate case was observed. We have suggested that a coupling of the N=4 CDW to the coexisting N=2 CDW is the mechanism that yields to the dominant commensurate pinning. Since commensurate CDW theory is rather simple, the observed results are very instructive in sense they provide us a better insight into underlying processes concerning the formation and behaviour of CDWs.*

1. INTRODUCTION

In the last 25 years, a special attention is given to novel organic metals. At low temperatures they show series of unusual transport and magnetic properties. One of the new phases observed is a charge-density wave (CDW). This phase shows striking nonlinear and anisotropic electrical transport properties and a gigantic dielectric constant, which is at least 6 orders of magnitude larger than the one in standard semiconductors. Thus it is appropriate for possible future super-capacitors and other modern technology applications. The most exciting property of density waves is the possibility of the collective electrical transport, which otherwise exists only in the standard superconductors. In this study we concentrated at low-temperature state of DMeO-Li, in which two CDW phases with different orders (N=2 and N=4) coexist.

Lithium atoms give one electron to the two organic molecules and consequently a quarter filled conduction band is expected by the overlap of pπ DCNQI orbitals in the organic chains. Infrared measurements of Meneghetti *et al.* [1] have shown the existence of vibronic modes which might be associated with dimerized ($4k_F$ CDW) and tetramerized ($2k_F$ CDW) structure. The X-ray diffuse scattering measurements performed on $(2,5(CH_3)_2DCNQI)_2X$ compounds (abbreviated as DMe-X), where X is Li and Ag, have revealed that the phase transitions in the resistivity and the susceptibility appear concomitantly with new superstructures with a $4k_F$ and $2k_F$ wave vector, respectively [2,3]. In addition, these phase transitions were also observed in DMeO-Li [4]. On the basis of these results, it is generally accepted that two commensurate CDWs exist in the low-temperature state of all DMe-X and DMeO-X materials. In this paper we review our results concerning the single particle and collective (CDW) mode transport properties [3,5].

2. THEORY

Having the commensurate CDW, we expect a good correspondence to the model of a classical particle. In this model, starting from a single particle equation of motion we can relate parameters characterizing the response of pinned CDW with parameters describing the non-linear conduction associated with the sliding CDW condensate. The product of oscillator strength $\Delta\varepsilon$ and threshold field E_T, above which CDW starts to slide and carry the current, should be a constant

$$\Delta\varepsilon \cdot E_T = \frac{Ne}{\pi ab\varepsilon_0} \tag{1}$$

where N is the number of DCNQI molecules in the unit cell and a, b are the lattice constants. Additionally, we can obtain the expression, which relates the field (E) dependent conductivity σ_{CDW} with the mean relaxation time τ_0:

$$\sigma_{CDW} = \frac{Ne}{\pi ab\tau_0}\left(\frac{1}{E_T} - \frac{1}{E}\right) \tag{2}$$

3. EXPERIMENTAL AND RESULTS

The room temperature (RT) conductivity of the measured single crystals has been about $150 Scm^{-1}$. The ohmic and non-ohmic resistivity have been measured in the four probe configuration using a standard DC technique. The complex admittance (G(ω), B(ω)) has been measured by a Hewlett Packard HP4284A impedance analyzer (20Hz-1MHz) in the two probe configuration in the temperature range between 25K and 100K. Dielectric functions have been extracted from the conductivity using relations $\varepsilon'(\omega)=B(\omega)/\omega$, and $\varepsilon''(\omega)=(G(\omega)-G_0)/\omega$, where G_0 is DC conductivity obtained from measured G(ω) at low frequencies where G(ω) was independent of ω.

On slow cooling the resistance of samples has displayed a steady but not significant decrease down to about 130K ($R(RT)/R_{min}=2$), followed by a broad and shallow minimum and a final increase below about 100K. The $4k_F$ and $2k_F$ CDW phase transitions appear at about T_{C1}~60K and T_{C2}~50K, respectively [4]. Here we concentrate on the temperature region below T_{C2}~50K (full points in Fig. 1.). Between 50K and 25K the conductivity follows a typical semiconductor (Arrhenius) behaviour. Below 25K conductivity decrease starts to saturate. Then the leading conduction mechanism might be associated to carriers localized on randomly distributed impurities and described by Mott's variable-range hopping formula

$$\sigma = \sigma_0 e^{-\left(\frac{E_0}{k_B T}\right)^{\frac{1}{1+d}}} \qquad (3)$$

where d is the dimensionality of hopping, $E_0=16\alpha^3/n_i(E_F)$, $n_i(E_F)$ the energy-volume density of carriers on Fermi surface, while α describes the space length of the wave function of localized states. As we see in Fig. 1, Eq. (3) perfectly describes the temperature dependence of the conductivity in this temperature domain with d=3.

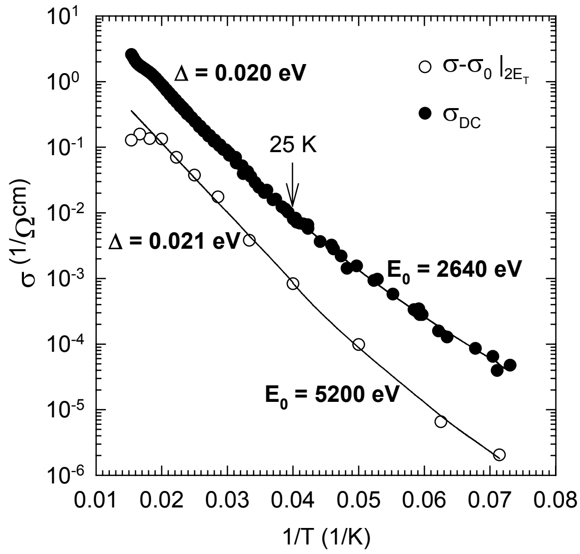

Fig. 1. Ohmic conductivity (full points) and non-ohmic conductivity at twice the threshold field (open points).

Fig. 2. shows the field-dependent conductivity normalized to its ohmic value at a few selected temperatures. Note that the onset of the nonlinear conductivity becomes much sharper below 25K. Further note that a weak, but observable non-linear contribution exists even above 50K, in the region of CDW fluctuations. We have started to observe these effects below 75K when $2k_F$ fluctuations start to grow up [4]. The non-linear contribution reaches maximum and starts to weaken below 25K, concomitantly with a strong increase of the threshold field, as shown in Fig. 3.

The collective and single particle conductivities are closely related. As shown in Fig. 1., they both obey the same temperature dependence in the temperature range from 50K down to 14K: above 25K following Arrhenius and below 25K variable range hopping temperature dependence. The change of the behavior below 25K might be related with the fact that the free-carrier screening becomes negligible. One could expect that the latter happens once the electrical density becomes smaller than the one electron per Lee-Rice domain L_{CDW}. We have estimated L_{CDW} from [6] and have got 25K for the crossover temperature.

In order to probe the intrinsic (linear) relaxation of CDW about its equilibrium state, we have employed AC signal levels in the range between 0.07 and 0.70 of the threshold voltage and we have always obtained essentially the same result. The real part of the

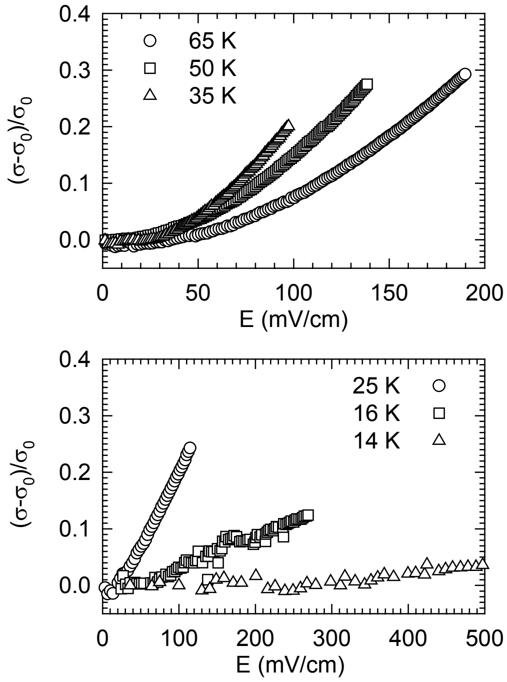

Fig. 2. Non-ohmic conductivity vs. field at a few selected temperatures.

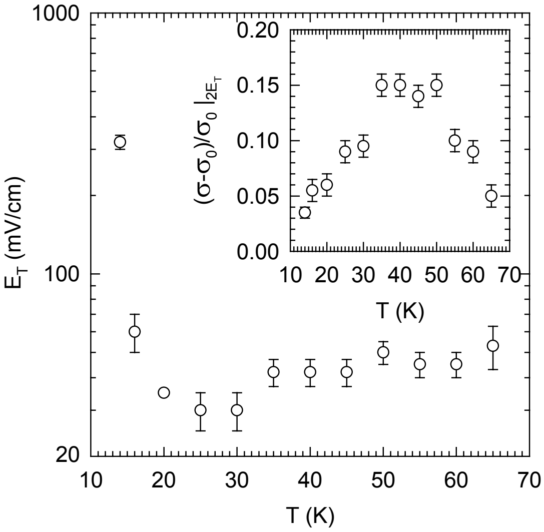

Fig. 3. Threshold field and non-ohmic conductivity at twice the threshold field, normalized to its ohmic value (Inset).

conductivity normalized to the dc value $(\sigma(\omega)-\sigma_0)/\sigma_0$ as a function of frequency at a few selected temperatures between 30K and 65K is shown in Fig. 4. Note that an enhanced AC conductivity grows in importance and starts at lower frequencies as the temperature lowers. This behavior becomes markedly emphasized once the temperature crosses below 50K. Detailed analysis of the pinned CDW response was made in terms of the complex dielectric function $\varepsilon(\omega)$ given by a generalization of the Debye expression known as the phenomenological Havriliak-Negami (HN) function

$$\varepsilon(\omega)-\varepsilon_{HF}=\Delta\varepsilon\frac{1}{\left[1+(i\omega\tau_0)^{1-\alpha}\right]^{\beta}} \qquad (4)$$

where $\beta=1$ for symmetrical cases. The HN formulation has been widely used to describe the non-Debye character of the relaxation processes in disordered systems including CDWs [7]. $\Delta\varepsilon = \varepsilon_0 - \varepsilon_{HF}$ is the oscillator strength, ε_0 is the static dielectric constant ($\omega \ll 1/\tau_0$) and ε_{HF} is the high frequency dielectric constant ($\omega \gg 1/\tau_0$). τ_0 and α are the mean relaxation time and the shape parameter which describes the symmetric broadening of the relaxation time distribution function, respectively.

Fig. 5. shows frequency domain plots of $\varepsilon'(\nu)$ and $\varepsilon''(\nu)$ at a number of selected temperatures covering the whole temperature range investigated. Note that $\varepsilon'(\nu)$ and $\varepsilon''(\nu)$ curves move toward lower peak frequencies ($\nu_0=\omega_0/2\pi=1/2\pi\tau_0$) with decreasing temperature without significant change in the shape and the peak amplitude. The full lines in Fig. 4. and Fig. 5. correspond to the calculated fits according to Eq. (4). Since ε_{HF} is negligibly small compared to ε_0, the fits were insensitive to it and it was therefore set to zero. We get $\Delta\varepsilon = \varepsilon_0 - \varepsilon_{HF} \approx \varepsilon_0 = (3 \pm 0.4)\cdot 10^7$ and $1 - \alpha = 0.94 \pm 0.07$. The huge zero frequency dielectric constant of the order of 10^7 is typical for CDWs. The value of

$1-\alpha \approx 1$ is characteristic of a single relaxation process with a characteristic (single) relaxation time widely known as the Debye process.

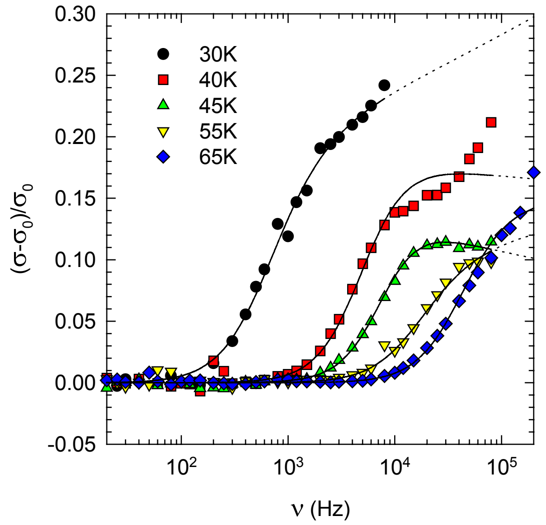

Fig. 4. Real part of the conductivity normalized to the dc value ($(\sigma-\sigma_0)/\sigma_0$) versus frequency for the temperature range between 65K and 30K. Full lines are fits to HN form.

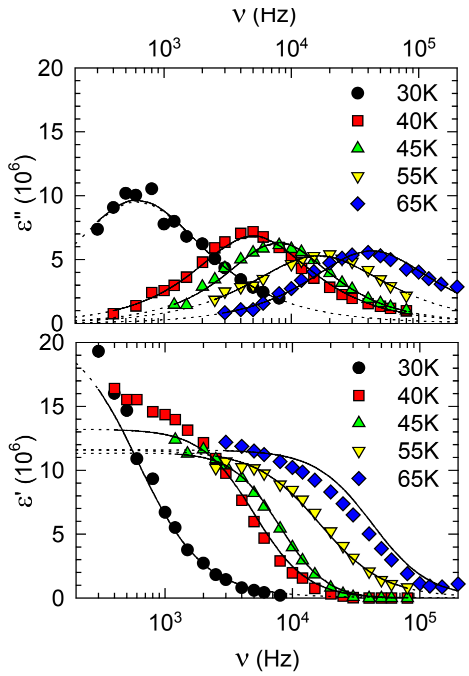

Fig. 5. Imaginary (ε'') and real (ε') part of the dielectric function versus frequency for temperature range between 65K and 30K. Full lines are from fits to HN form.

The third fit parameter τ_0^{EXP} as a function of inverse temperature is shown as full points in Fig. 6. The characteristic relaxation time τ_0 presents Arrhenius type of the behavior. The best fit to data is obtained with Δ=0.019 eV. We can test Eq. (2) comparing experimentally obtained τ_0^{EXP} and τ_0^{THE} calculated from the nonlinear conductivity from

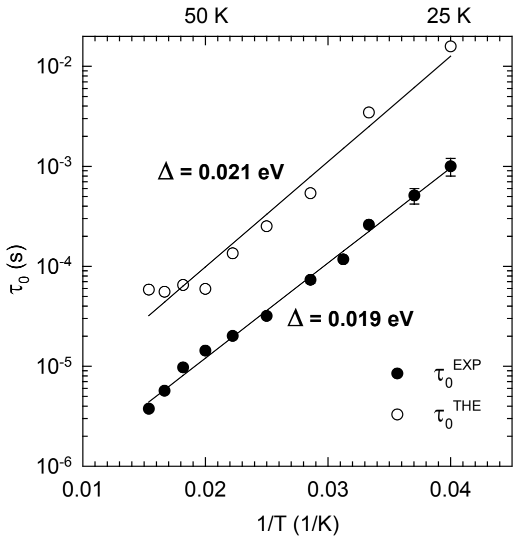

Fig. 6. Experimentally obtained (full dots) and theoretically calculated from non-ohmic contribution data (empty dots) values for relaxation times.

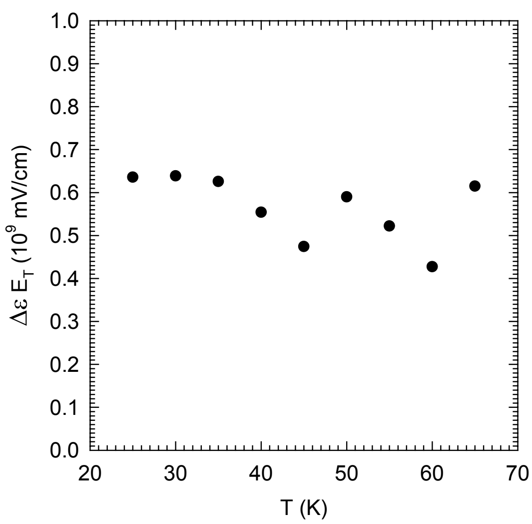

Fig. 7. The product of the oscilator strength and the threshold field.

Eq. (2). As shown in Fig. 6., their activation fits perfectly. The factor of 10 in amplitudes might be due to the fact that the model does not take into account the existence of free charge carriers.

The product $\Delta\varepsilon \cdot E_T$ (Fig. 7) has a narrow spectrum of values $(5.4 \pm 1.1)10^7$ V/m and therefore obeys qualitatively Eq. (1). However, the theoretical value of the product is two orders of magnitude bigger than the observed one. Below 25K, this product is not constant any more.

4. CONCLUSION

In the low-temperature N=4 CDW state, single particle transport is thermally activated down to 25K. In addition, there is a collective conduction channel above the finite electrical field E_T due to the sliding of N=4 CDW. Below E_T, this CDW is pinned to the background lattice by commensurate potential due to the presence of N=2 CDW and its relaxation is well described by the Debye-like expression for an overdamped response of a system with a single degree of freedom.

Below 25K both conduction channels freeze out. The single particle transport mechanism is asserted to the variable range hopping, while the low temperature CDW transport mechanism remains unclear at the moment. Further studies are under the way to clarify the latter point.

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