EUROPHYSICS LETTERS 20 April 1997

Europhys. Lett., **38** (3), pp. 219-224 (1997)

Low-frequency dielectric response of charge-density wave pinned by commensurability in $(2,5(OCH_3)_2DCNQI)_2Li$

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(received 28 November 1996; accepted in final form 15 March 1997)

PACS. 71.45Lr – Charge-density-wave systems.
PACS. 72.15Nj – Collective modes (e.g., in one-dimensional conductors).

Abstract. – We have used complex conductivity measurements between 20 Hz and 1 MHz to probe the dielectric response in the low-temperature phase of the $(2,5(OCH_3)_2DCNQI)_2Li$ organic conductor. The observed data reveal the existence of the relaxation process which is well described by a Debye-like expression for an overdamped response of a system with a single degree of freedom. Both the static dielectric constant ($\varepsilon_0 = 3 \times 10^7$) and the characteristic relaxation time (τ_0) are much larger than that expected for single-particle excitations. τ_0 is thermally activated in a manner similar to the dc conductivity. We attribute the observed relaxation to $N = 4$ charge density wave pinned by commensurability to the underlying lattice.

Since 1987 an important amount of research has been devoted to a novel class of charge-transfer salts $(2,5R_1R_2DCNQI)_2X$, where DCNQI stands for dicyanoquinonediimine. R_1 and R_2 stand for CH_3, OCH_3, Cl, Br and X for an inorganic cation like Li, Ag, Cu etc. [1]. The mixed-valence copper salts have been so far the most studied, due to the possibility to control easily, by varying external (pressure, magnetic field) and internal (isotope substitution, doping) parameters, unique physical properties inside an extremely rich phase diagram [2], [3]. On the other hand, silver and lithium atoms give one electron to two organic molecules and consequently a quarter filled conduction band is expected by the overlap of $p\pi$ DCNQI orbitals on the organic chains. Infrared measurements of Meneghetti *et al.* [4] 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 only on $(2,5(CH_3)_2DCNQI)_2Ag$ compound (abbreviated as DMe-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 [5]. On the basis of these results, it is generally accepted that a charge-density wave (CDW) exists in the low-temperature state of all non-copper materials. However, the collective mode properties of the charge-density wave in this state are still unknown.

Generally, it is now well established that below their respective phase transitions (Peierls and spin-density wave: SDW) collective modes of CDW and SDW, incommensurate with the underlying lattice, can slide above a finite threshold field ($E_{\rm T}$) so contributing to the electrical conductivity [6]. Such a motion gives dc current which depends on the applied field in a nonlinear manner and a periodic, but nonsinusoidal time-dependent current (commonly called conduction narrow-band noise in the Fourier space). Below $E_{\rm T}$ CDW cannot move due to the pinning to randomly distributed defects in the underlying lattice. The response of the incommensurate CDW to an external low-frequency ac field is broader than the one expected for the system with a single degree of freedom and is strongly influenced by the single-particle screening. The former feature reflects a distribution of relaxation times associated with a single process due to a distribution of metastable states around the equilibrium position. These metastable states correspond to local changes of the phase of the pinned CDW in the random defect potential. On the other hand, not much is known about the collective-mode properties of commensurate CDW. Theoretically, one should expect a large threshold field and a little contribution to the collective conduction which scales with the order of commensurability (N) [7], [8]. Indeed, for $N = 2$ as in transpolyacetylene the commensurability pinning is too strong so that CDW is completely locked to the underlying lattice. In TTF-TCNQ under pressure a drastic increase in $E_{\rm T}$ at $N = 3$ is detected [9]. Finally, in $({\rm Per})_2{\rm M}({\rm mnt})$ with M = Au or Pt, $N = 4$ CDW is believed to be established below about 10 K [10]. Threshold fields are found to be in the range of 0.1–1 V/cm and transport due to CDW sliding was demonstrated by narrow-band noise measurements. The impurity pinning is proposed to be the dominant mechanism overcoming the $N = 4$ commensurability pinning. However, a detailed temperature dependence study of $E_{\rm T}$ and nonlinear contribution to the conductivity is still missing. Moreover, no attempts to probe features of the dielectric response of the pinned commensurate CDW have been reported until now.

In this letter we report the results of our experiments on dc and frequency-dependent conductivity in the low-temperature state of $(2,5({\rm OCH}_3)_2{\rm DCNQI})_2{\rm Li}$ material (abbreviated as DMeO-Li). We show that the observed data give direct evidence for a collective mode contribution to the dielectric properties which might be attributed to the commensurate CDW with dominant commensurability pinning.

Three high-quality single crystals of DMeO-Li were studied with lengths of 0.1–0.5 cm and cross-sections in the range of $1\text{–}2.5 \times 10^{-5}\ {\rm cm}^2$. All three samples exhibited qualitatively the same behaviour. The room temperature (RT) conductivity was about $150\ {\rm Scm}^{-1}$. The ohmic resistivity was measured in the four-probe configuration using a standard dc technique. The complex admittance ($G(\omega)$, $B(\omega)$) was measured by a Hewlett Packard HP4284A impedance analyzer (20 Hz–1 MHz) in the two-probe configuration in the temperature range between 25 K and 100 K where contact resistances were negligible in comparison to the sample resistance. Dielectric functions were 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 $G(\omega)$ at low frequencies where $G(\omega)$ was independent of ω.

On slow cooling the resistance of samples displayed already observed behaviour [11]. Namely, a steady but not significant decrease down to about 130 K ($R({\rm RT})/R_{\rm min} = 2$), followed by a broad and shallow minimum and a final increase below about 100 K. As a detailed resistance behaviour below 100 K has never been published, we present in fig. 1 the logarithm of low-field resistance as a function of inverse temperature. Two features have to be noted. An anomaly centered at 60 K followed by a sudden change in slope at 48 K (see inset of fig. 1). The estimated activation energy above 60 K and below 48 K is about 120 K and 300 K, respectively.

In order to probe the intrinsic (linear) relaxation of an incommensurate CDW, *i.e.* about

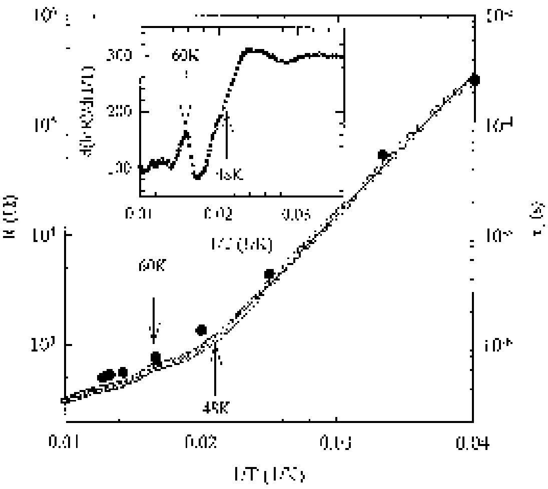

Fig. 1

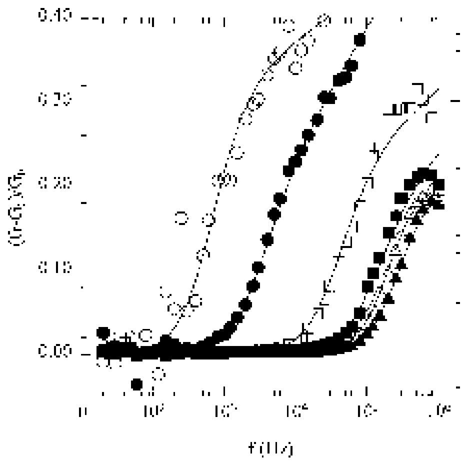

Fig. 2

Fig. 1. – Logarithm of resistance (R, open points) and of mean relaxation time (τ_0, full points) *vs.* inverse temperature for a $(2,5(CH_3O)_2DCNQI)_2Li$ crystal. Full lines show the fits to Arrhenius form. Inset shows the logarithmic derivative of resistance *vs.* inverse temperature for the same sample.

Fig. 2. – Real part of the conductivity normalized to the dc value ($(G - G_0)/G_0$) *vs.* frequency for a temperature range between 70 K and 25 K: 70 K (full triangles), 60 K (open triangles), 50 K (full squares), 40 K (open squares), 30 K (full points) and 25 K (open points). Full lines are fits to the HN form.

its equilibrium state, one has to employ small ac signal levels of the order of 10% of the threshold voltage for the nonohmic conduction [12]. As for commensurate CDW no data are available, we have first looked for possible nonohmic effects. We have found an increase of the low-field conductivity above $E_T \approx 40$ mV/cm which corresponds to 7 mV for the sample investigated in the most details. For the employed ac signal levels in the range beween 0.07 and 0.70 of the threshold voltage we have always obtained essentially the same result. The real part of the conductivity normalized to the dc value $(G(\omega) - G_0)/G_0$ as a function of frequency at a few selected temperatures between 25 K and 70 K is shown in fig. 2. Note that an enhanced ac conductivity grows in importance and starts at lower frequencies as the temperature lowers. This behaviour becomes markedly emphasized once the temperature crosses below 50 K. 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

$$\varepsilon(\omega) - \varepsilon_{\mathrm{HF}} = \Delta\varepsilon \frac{1}{[1 + (i\omega\tau_0)^{1-\alpha}]} . \tag{1}$$

The HN formulation has been widely used to describe the non-Debye character of the relaxation processes in disordered systems including incommensurate CDWs [6], [12]. $\Delta\varepsilon = \varepsilon_0 - \varepsilon_{\mathrm{HF}}$ is the strength of the relaxation process, ε_0 is the static dielectric constant ($\omega \ll 1/\tau_0$) and $\varepsilon_{\mathrm{HF}}$ 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. Initial analysis of $\varepsilon(\omega)$ was performed by inspection of Cole-Cole plots which are presented in fig. 3. The intersection of the arcs with ε' axis at high and low ε' values, corresponding to low and high frequencies, indicates the values of

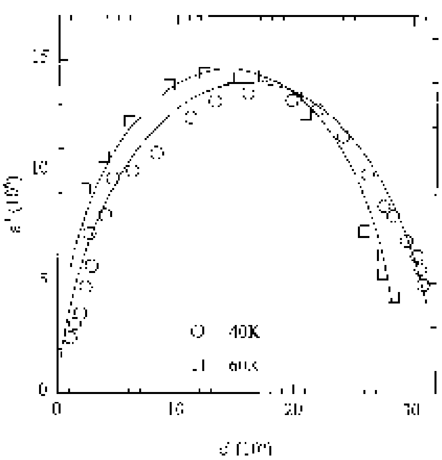

Fig. 3

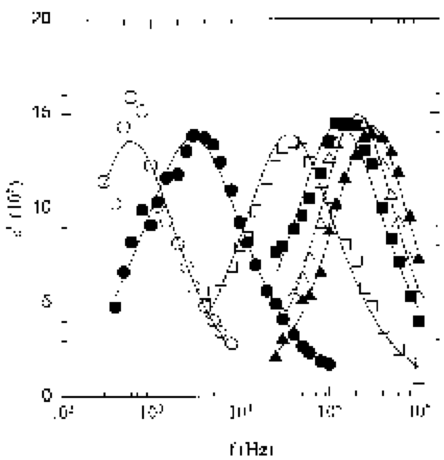

Fig. 4

Fig. 3. – Cole-Cole plots of the dielectric response at two selected temperatures. Full lines are from fits to the HN form.

Fig. 4. – Imaginary part of the dielectric function (ε'') *vs.* frequency for a temperature range between 75 K and 25 K: 75 K (full triangles), 60 K (open triangles), 50 K (full squares), 40 K (open squares), 30 K (full points) and 25 K (open points). Full lines are from fits to the HN form.

ε_0 and $\varepsilon_{\mathrm{HF}}$, respectively. The huge zero-frequency dielectric constant of the order of 10^7 is typical for CDWs. In the observed Cole-Cole plots all points at all frequencies fall on a single semicircle with its centre on the ε' axis and of radius close to $(\varepsilon_0 - \varepsilon_{\mathrm{HF}})/2$. These features are characteristic of a single relaxation process with a characteristic (single) relaxation time widely known as the Debye process. Figure 4 shows frequency domain plots of $\varepsilon''(f)$ at a number of selected temperatures covering the whole temperature range investigated. Note that $\varepsilon''(f)$ curves move toward lower peak frequencies ($f_0 = \omega_0/2\pi = 1/2\pi\tau_0$) with decreasing temperature without significant change in the shape and the peak amplitude. The full lines in fig. 2, 3 and 4 correspond to the calculated fits according to eq. (1). Since $\varepsilon_{\mathrm{HF}}$ is negligibly small compared to ε_0, the fits were insensitive to it and it was therefore set to zero. We get $\Delta\varepsilon = \varepsilon_0 - \varepsilon_{\mathrm{HF}} = \varepsilon_0 = (30. \pm 4) \times 10^7$ and $1 - \alpha = 0.94 \pm 0.07$. The third fit parameter τ_0 as a function of inverse temperature is shown as full points in fig. 1. The characteristic relaxation time τ_0 presents Arrhenius type of the behaviour $\tau_0 = \tau_{00} \exp[\Delta/T]$ with different slopes above 60 K and below 50 K. The best fit to data is obtained with $\tau_{00} = 7.5 \times 10^{-8}$ s and 4.1×10^{-9} s, and $\Delta = 111$ K and 268 K above 60 K and below 50 K, respectively.

Our dielectric response data have identified the following features of the relaxation process which takes place below 75 K. The shape of the spectra is symmetric around the characteristic relaxation time. The width is close to the one expected for the Debye process and does not change with temperature. The relaxation strength is of the order of 10^7 and is also temperature independent. The characteristic relaxation time is thermally activated with activation energies close to the free-carrier ones. Moreover, it also indicates the break in the slope at 50 K as dc resistivity does. The attempt relaxation time is about 1 ns and therefore too long to be attributed to free carriers [13]. This time should correspond to the microscopic relaxation time of CDW phase mode. The observed features confirm the origin of this relaxation as an intrinsic property of a CDW state. They identify the phason mode pinned by commensurability to the underlying lattice as the relaxation entity and its interaction with free carriers as the dissipation mechanism. Namely, a lack of substantial broadening usually observed for CDW pinned by impurities indicates a very narrow distribution of activation energies belonging to energy barriers of metastable states. These metastable states correspond to local changes of the phase of the pinned CDW. It is important to note that at temperatures as high as 80 K, thermal fluctuations might be sufficient to hide the existence of the metastable minima. However, the width of CDW response does not become appreciably larger even at temperature as low as 25 K where the influence of thermal fluctuations can certainly be excluded. Finally, the fact that the energy scale for the barrier heights is close to the free-carrier activation energy found in dc resistivity indicates the crucial influence of the free-carrier screening on the CDW dielectric relaxation.

Now, we comment more in detail our statement that the observed dielectric response comes from the CDW phason mode pinned by commensurability. Theoretically, one should distinguish $N = 2$ commensurability from $N \geq 3$ cases. For $N = 2$ CDW, the order parameter is real (*i.e.* it has only amplitude and no phase) and a particular dynamics due to amplitude deformations is expected. $N \geq 3$ CDW has a complex order parameter and, in contrast to incommensurate CDW, there are well-defined energetically most favourable positions in the underlying lattice at which it is pinned. Consequently, the pinning energy depends on the phase of the order parameter which determines the relative position of the CDW and the lattice. The importance of this term, *i.e.* the dependence of the pinning energy on phase, strongly diminishes with increasing N, as first suggested by Lee, Rice and Anderson [7]. Further, the dynamics of the $N \geq 3$ CDW is rather well described in the uniform pinning (single-particle) model [6]. This model starts with the equation of motion for a particle moving in a periodic pinning potential and in the low-frequency, overdamped limit predicts a Debye form of the relaxation response. Experimentally, the impurity pinning (*i.e.* the pinning of CDW to randomly distributed impurities) appears to be the dominant pinning mechanism for $N = 4$ CDW, which usually prevails over the commensurability one. This conclusion can be inferred from the observed value and temperature behaviour of threshold field and the low-frequency dielectric response [14].

As far as DMe-Li and DMeO-Li systems are concerned, they are special since in their low-temperature state two CDW with the order of comensurability $N = 2$ and $N = 4$ coexist. Namely, our recent X-ray diffuse scattering data on the former compound have revealed the existence of weak diffuse planes at the wave vector $0.5c^*$ and $0.25c^*$ which correspond to quasi-1D $4k_F$ and $2k_F$ scatterings, respectively. They start to be visible at RT and 100 K, and transform into satellite reflections below about $T_{c1} = 50$–60 K and $T_{c2} = 45$–50 K, respectively. Although we are lacking at the moment X-ray data on DMeO-Li material, we believe that they should be essentially the same in particular as far as the assignment of the diffuse scattering is concerned. Note that our dielectric relaxation data on DMeO-Li correspond surprisingly well to X-ray data obtained on DMe-Li material. In particular, we start to observe a dielectric relaxation mode below about 80 K, with a sizeable shift in frequency of the associated peak below about 50 K, only. Moreover, we consider that DMe-Li and DMeO-Li systems are essentially the same as far as the physical properties of the electron gas are concerned. Our statement is based on the following. First, the charge (spin) density is known to be centered at NCN positions of DCNQI, and is barely influenced by the choice of CH_3 or OCH_3 group [11]. Second, the spin-orbit coupling is of the same strength in both DMe-Li and DMeO-Li materials as deduced from the ESR linewidth and relaxation rate measurements [11]. Finally, the temperature dependence of dc conductivity and ESR susceptibility is essentially the same in both lithium materials indicating the existence of phase transitions in the temperature range between 60 K and 45 K. Therefore, we are tempted to associate the anomaly at 60 K and the break in the slope at 48 K, visible in dc resistivity, with the $4k_F$ and $2k_F$ phase transitions, respectively.

Therefore, we have evidence that $N = 2$ and $N = 4$ CDW coexist in the low-temperature state of DMeO-Li material. Based on the arguments given above, the $4k_{\mathrm{F}}$ CDW ($N = 2$) cannot be responsible for the observed response. Consequently, we associate the dielectric response with the $2k_{\mathrm{F}}$ CDW ($N = 4$) pinned to the underlying lattice. In the framework of the single-particle model, we can estimate the pinning frequency ω_{p} from the measured dc threshold field. Taking into account $E_{\mathrm{T}} \approx 40$ mV/cm and assuming $m^* \approx 10^3\ m_{\mathrm{e}}$ for the condensate mass, we obtain $\omega_{\mathrm{p}} \approx 10$ GHz, a value usually observed for CDW [9]. Then, two possible mechanisms which yield the $N = 4$ commensurability pinning to prevail over the impurity pinning might be envisaged. The first and simplest possibility is that the DMeO-Li material is an extremely pure material, not encountered until now. Although we cannot completely discard this possibility, we do not consider it very likely. Instead, we propose that the $N = 4$ commensurability potential is reinforced in the second order by the presence of $N = 2$ CDW.

In conclusion, our low-frequency dielectric measurements in the low-temperature state of DMeO-Li have identified, for the first time, a Debye-like relaxation of the charge-density wave phase mode with Arrhenius-like decay determined by the resistive dissipation. The $2k_{\mathrm{F}}$ ($N = 4$) CDW pinned by commensurability to the lattice is proposed to be at the origin of the observed relaxation. A coupling of the $2k_{\mathrm{F}}$ ($N = 4$) CDW to the coexisting $4k_{\mathrm{F}}$ ($N = 2$) CDW is suggested as the mechanism which yields to the dominant commensurability pinning. To our knowledge this might be the first opportunity to study experimentally a theoretically intriguing problem of two CDWs with different orders of commensurability. Further combined detailed X-ray and dielectric response experiments, as well as theoretical calculations, are under way to elucidate our proposal.

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We acknowledge stimulating discussions with A. Bjelis and K. Maki. This work was partially supported by the Croatia-Germany bilateral collaboration project, ref. KRO-020-95.

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