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Low-frequency dielectric spectroscopy of commensurate density waves

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Abstract

We overview complex conductivity measurements (20Hz - 1MHz) in low-dimensional organic systems κ-(BEDT-TTF)$_2$-Cu[N(CN)$_2$]Cl, and deuterated Cu-DCNQI and its alloys, with commensurate density wave ground states. We discuss the obtained results in comparison with those for the incommensurate density waves, like in (TMTSF)$_2$PF$_6$, in which the phason relaxation in a disordered background dominates. We show that in the commensurate systems with a random domain structure charged domain walls provide a more appropriate description of the observed dielectric relaxation.

Keywords: transport measurements, organic conductors

1. Introduction

Density waves, both charge-density (CDW) and spin-density (SDW) waves, mostly studied so far are incommensurate with respect to the underlying lattice. The spatial variation of the DW phase in an incommensurate structure is referred to as a phason. A dynamical mode associated with this DW variation, also referred to as the phason, is theoretically gapless long wavelength excitation. However, in real crystals there is a small gap in the phason spectrum due to defects. The phason mode, as long as free-carrier excitations are present, couples to an applied DC and AC electric field and gives novel contributions to the electrical conductivity. The coupling to the former gives rise to a non-linear conduction of electrical current above a finite electric field (E_T) accompanied by narrow and broad band noise, whereas the coupling to the latter leads to a frequency dependent conductivity [1]. The dielectric response of the incommensurate DW at frequencies lower than 1MHz is produced by coupling to longitudinal screened phason mode [2]. The response is characterized by dielectric constants of the order $10^6 - 10^9$, and is broader than the Debye one which is expected for the system with a single degree of freedom [3–5]. This 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 DW in a random defect potential. The phason characteristic length scales inversely with DC threshold field [6] and is estimated to be about $L_{ph} \approx 25\mu$m in the SDW state of (TMTSF)$_2$PF$_6$ (abbreviated TM$_2$PF$_6$). Both the collective DC conduction and dielectric relaxation are strongly influenced by the free-carrier screening so that the response of incommensurate DW gradually slows down with temperature with the activation energy equal to the single-particle activation energy [4,5,7].

On the other hand, until recently not much was known about the collective charge dynamics of commensurate DW. Theoretically, a commensurate structure limits the spatial variation of DW to rather narrow localized regions, which are topologically equivalent to solitons in 1D or domain walls in $D \geq 2$. That is, in the case of commensurate domain structure, the phason excitations are frozen and replaced by solitons or domain walls, which are short wavelength excitations. In this paper, we focus on the dynamics of commensurate DW ground states studied by the low-frequency dielectric spectroscopy. We present two distinct examples: SDW state in a domain structure due to a ferromagnetic order of the layered system κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl (abbreviated κ-ET-Cl) and CDW state in a domain structure due to an overlap between CDW and metallic phases in the quasi-1D system Cu[(2,5(CD$_3$)$_2$-DCNQI] (abbreviated Cu-DCNQI d$_8$) [8,9]. We compare the observed response with that of incommensurate SDW in quasi-1D system TM$_2$PF$_6$, which represents the standard case of DW in

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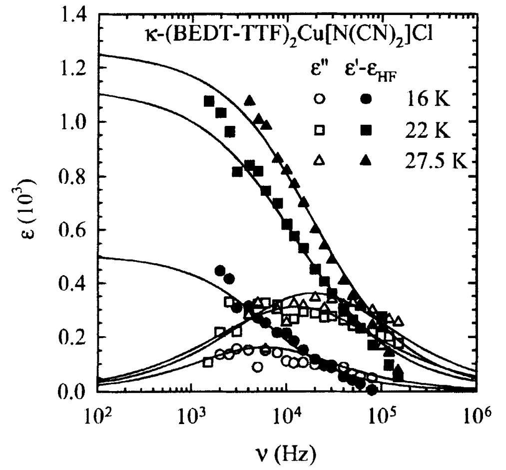

Fig. 1. Real and imaginary part of the dielectric function *versus* frequency at three selected temperatures.

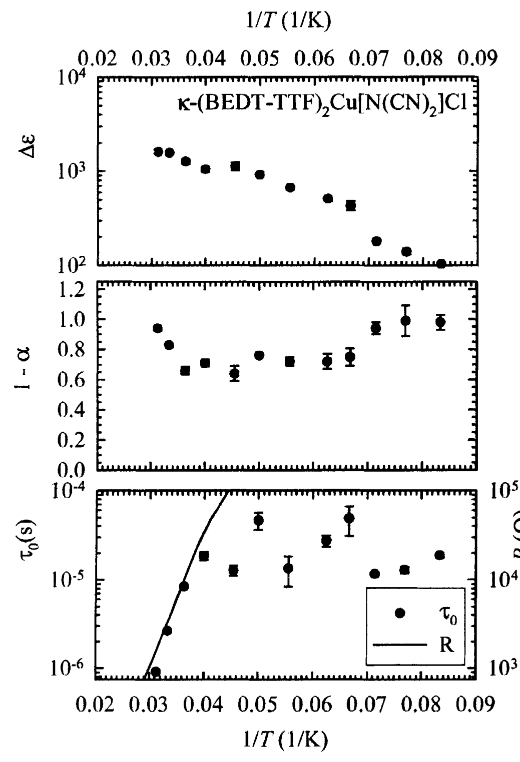

Fig. 2. Relaxation parameters *versus* inverse temperature.

an incommensurate structure due to a random impurity potential [4,5].

2. Results

First, we show the dielectric response of a commensurate SDW established in κ-ET-Cl. Due to very strong on-site Coulomb interactions, the DC resistivity increases gradually below room temperature. An antiferromagnetic order of localized spins, which are canted

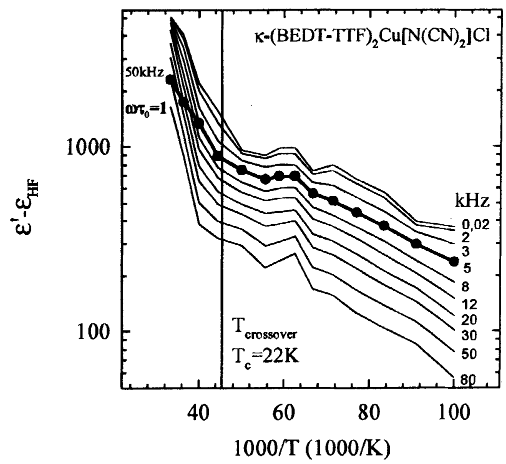

Fig. 3. Real part of the dielectric function *versus* inverse temperature at a few selected frequencies.

by an angle of 0.06 degrees from the easy axis is established at $T_C = 22$K. The magnetic moment amounts to $0.4 - 1\mu_B$/molecule [10], which is much larger than the value of $0.08\mu_B$/molecule observed in the case of SDW in TM_2PF_6 formed by itinerant spins [11]. The low temperature state is, therefore, a weak ferromagnetic state divided in domains with equivalent spin configurations. Figure 1 shows frequency domain plots of the real and imaginary part of the dielectric function at three selected temperatures. The full lines in Figure 1 correspond to the calculated fits to the Havriliak-Negami (HN) function

$$\varepsilon_{HN}(\omega) - \varepsilon_{HF} = \frac{\Delta\varepsilon}{1 + (i\omega\tau_0)^{1-\alpha}}, \quad (1)$$

which represents an empirical generalization of the Debye relaxation. The three parameters, dielectric strength ($\Delta\varepsilon$), width of the relaxation time distribution $(1 - \alpha)$ and mean relaxation time (τ_0), which fully characterize the dielectric relaxation, as a function of inverse temperature are shown in Figure 2. DC resistance (R) is also shown for comparison. The observed features of the relaxation process confirm the origin of this relaxation as an intrinsic property of the weak ferromagnetic state. The relaxation might be attributed to the activation between different metastable states, which correspond to local changes of the spin configurations. The feature that $\Delta\varepsilon$ is of the order of 10^3 and that it decreases with decreasing temperature indicates that a charged domain wall pair, and not the phason, is the relaxation entity. The feature $(1 - \alpha) \approx 0.75$ indicates a random ferromagnetic domain structure in the temperature range 13 K $< T < T_C$. The observation that below 13 K mode narrows, that is $(1 - \alpha)$ approaches 1, reveals a progressive restoration of a regular ferromagnetic domain structure at low temperatures. In the fluctuation region above T_C, τ_0 is activated with the single particle activation energy $\Delta \approx \Delta_{fc} \approx 150$K showing the free-carrier screening is effective. However, below T_C the temperature in-

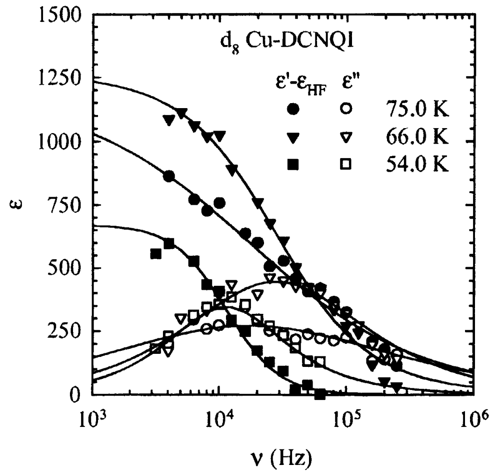

Fig. 4. Real and imaginary part of the dielectric function *versus* frequency at three selected temperatures.

dependent behaviour of τ_0 indicates a substantial reduction of the free-carrier screening in the ground state. Indeed, the free-carrier density below T_C, estimated from the resistance increase between room temperature and T_C and allowing the electron to move inside a 2D plane, turns out to be smaller than the one electron per domain wall characteristic length $L_{wall} \approx 0.1 - 1\mu m$. The latter might be also obtained from the theoretical expression which relates L and E_T [6,12]. These two distinct dissipation regimes (above and below T_C, which coincides with the crossover temperature T_{CO}) are reflected in the behaviour of ε' (see Figure 3):

$$\varepsilon'(T) \propto \varepsilon' e^{-\frac{\Delta}{T}}. \tag{2}$$

At $T > T_{CO}$ and $T < T_{CO}$ DW dynamics is governed by free-carrier activation energy $\Delta_{fc} \approx 150\mathrm{K}$ and by low energy barriers $\Delta \approx 50\mathrm{K}$, respectively.

As a second case, we show the dielectric response of a commensurate $N = 3$ CDW established in the deuterated Cu-DCNQI d_8 system. Compared with conventional organic metals, the novel electronic states have emerged associated with the hybridization between π-orbitals of DCNQI molecule and d-orbitals of Cu ions [13]. The metal-insulator phase transition is a result of the Peierls transition with three-fold lattice distortion in the presence of strongly correlated Cu d-states. In an insulating state the π-d hybridization is disconnected and $N = 3$ CDW is formed in the organic network. The former explains the discontinuous nature of the phase transition followed by large hysteresis effects. Figure 4 shows frequency domain plots of the real and imaginary part of the dielectric function at three selected temperatures. The parameters $\Delta\varepsilon$, $(1 - \alpha)$ and τ_0 as a function of inverse temperature are shown in Figure 5. On the basis of similar consideration procedure we conclude that the observed relaxation is due to charged domain wall pairs in a random domain structure that gradually restructures in to a regular structure at enough low temperatures. Again, no influence of the free-carrier screening is detected below $T_{CO} = T_C = 80\mathrm{K}$. In the hysteresis region the system consists of metallic domains in the insulating, CDW ordered background, whereas at enough low temperatures the regular $N = 3$ CDW structure is established in the whole bulk of the crystal. The temperature behaviour of ε' at several selected frequencies is shown in Figure 6. In the hysteretic region we estimate the size of domain wall to be $L_{wall} \approx 0.1 - 1\mu m$ [9,14]. The relaxation governed by low energy barriers smaller than 50 K at low frequencies might be attributed to these

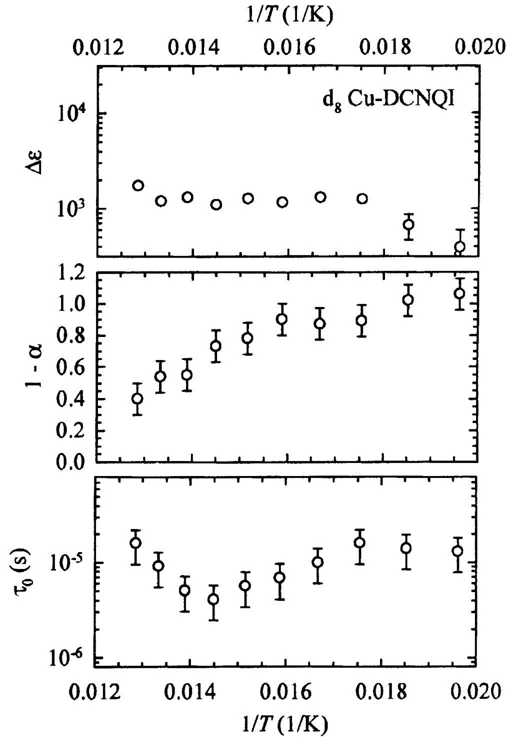

Fig. 5. Relaxation parameters *versus* inverse temperature.

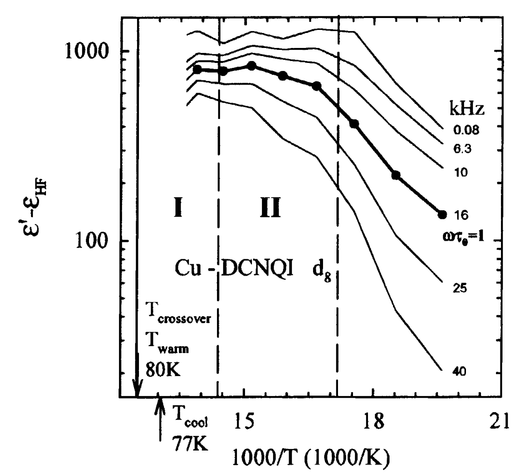

Fig. 6. Real part of the dielectric function *versus* inverse temperature at a few selected frequencies.

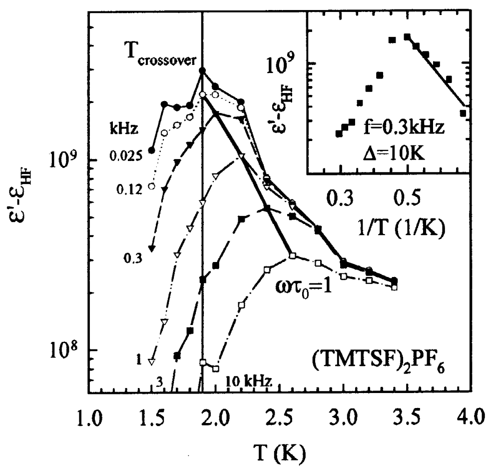

Fig. 7. Real part of the dielectric function *versus* temperature at a few selected frequencies.

entities. Conversely, at low temperatures, the dynamics is governed by high energies close to the free-carrier one $\Delta \approx \Delta_{fc} \approx 500$K. The latter indicates that another kind of relaxation entities of much smaller size (probably of the order of 0.001 μm, since the length-scale of $N = 3$ superstructure is 3c $\approx$ 0.001 μm) dominates the relaxation when the regular commensurate structure is established.

Finally, in Figure 7 we show for comparison ε' *versus* temperature in the incommensurate SDW state of TM_2PF_6. In this case ε' starts to decrease with temperature below $\omega\tau_0 = 1$ line. However, only at $T < T_{CO}$, which is estimated to be 1.9 K [4], the relaxation starts to be governed by energy barriers Δ, which are lower than the free-carrier activation energy $\Delta_{fc} \approx 20$K (see Inset of Figure 7).

3. Conclusion

In the case of DW in incommensurate structure (SDW in TM_2PF_6), DW responds to the outer AC perturbation field by its long wavelength phason excitations, and the interaction with free-carriers yields the dominant dissipation. The dielectric constant is huge of the order of $10^6 - 10^9$. At temperatures at which the screening is effective (at $T > T_{CO}$) the dynamics of DW system is governed by the free-carrier activation energy. Conversely, at $T < T_{CO}$ the system is brought into metastable states with low energy barriers. The characteristic length of the relaxation entity is about 25 μm, and its associated activation energy is about 10 K. At temperatures where the mean relaxation time of DW is longer than the duration of AC perturbation, the DW ceases gradually to be able to follow the AC perturbation and dielectric function decreases.

Two other examples of DW dielectric relaxation in κ-ET-Cl and in Cu-DCNQI d_8, are distinct in the following aspects. First aspect is the commensurate domain structure, that is the DW system is divided into distinct but energetically equivalent states. In κ-ET-Cl material, this aspect is brought in by the ferromagnetic order, whereas in Cu-DCNQI d_8 compound, it comes from the coexistence of the CDW insulating and metallic phases. In both cases, DW responds to the outer AC perturbation field by its short-wavelength domain wall excitations whose associated dielectric constant is of the order of 10^3. The second distinct aspect is a negligibly small number of free-carriers below T_C, so that the screening is ineffective in the whole temperature-frequency window. Energy barriers of the metastable states associated with short-wavelength excitations scale inversely with the size of these objects. For the objects of the estimated size of the order of 0.1 - 1 μm and 0.001 μm, we found the energy barriers of about 50 K and 500 K, respectively.

Acknowledgments

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