PROPERTIES OF MOTT-PEIERLS INSULATING PHASE IN DEUTERATED COPPER-DCNQI SYSTEMS

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ABSTRACT:

We overview low frequency dielectric spectroscopy and non-linear dc electrical transport in single crystals of a member of copper-DCNQI charge-transfer salt with $N = 3$ commensurate charge density wave. Broad relaxation mode of moderate strength weakens and becomes narrower with decreasing temperature. Threshold electrical field diverges, concomitant with the slight increase of the non-ohmic conductivity effect. These features suggest that the entities responsible for the dielectric response are pairs of charged domain walls between metallic and insulating phases.

1. INTRODUCTION

In last three decades organic conductors attracted a special attention because of the immense diversity of ground states. One family of organic conductors, $Cu(2,5R_1R_2-DCNQI)_2$ (where DCNQI stands for dicyanoquinonediimine and R_1, R_2 = CH_3, CH_3O, Cl, Br, I etc.), is especially attractive because of its rich phase diagram, in which physical properties can be easily controlled by varying external (pressure, magnetic field) and internal (isotope substitution, doping) parameters (see for example review [1]). In the crystal of copper-DCNQI salt, one-dimensional DCNQI columns are interconnected to each other through the Cu ions, coordinated by four N atoms forming tetrahedron. Unlike in the other DCNQI salts, here the cation (copper) electrons of the highest occupied 3d orbital interact with DCNQI electrons of the highest occupied pπ orbital. As a result, room temperature (RT) longitudinal (along the *c*-axis) conductivity is enhanced to the order of 1000 $(\Omega cm)^{-1}$.

Physically intriguing case is related to $R_1 = R_2 = CH_3$ salt, in which either the application of even a small pressure or gradual deuteration change the ground state of the material. The undeuterated system $Cu(2,5(CH_3)_2-DCNQI)_2$ shows fully metallic behaviour throughout the whole temperature range, while the fully deuterated system $Cu(1,4D_2;2,5(CD_3)_2-DCNQI)_2$ shows one sharp entrance in the insulating state. Most interestingly, a range of partially deuterated systems, as well as the alloys between undeuterated and deuterated systems like $Cu[(2,5(CH_3)_2-DCNQI)_{0.70}(2,5(CD_3)_2-DCNQI)_{0.30}]_2$ (abbreviated as h_8/d_6 70%:30%) show both a sharp transition in the insulating state and a re-entrance back to the metallic state at low temperatures. These transitions are intimately connected to the formal valence of copper ions, which is somewhat smaller than +4/3 at RT, and varies slightly for different copper salts or different level of deuteration. The decrease of the temperature or the increase of the

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internal or external pressure results in the distortion of the coordination tetrahedron, which induces an extra charge transfer to DCNQI molecules. Eventually this structural change locks the Cu valence to exactly +4/3 with static charge ordering at the copper sites ($...Cu^{2+}Cu^{1+}Cu^{1+}...$). This effect is accompanied by the phase transition into the insulating state with the formation of the charge-density wave (CDW) in DCNQI chains along the c-axis. This was confirmed by the appearance of the three-fold superstructure with the strong intensity of the observed satellite spots [2]. However, it should be noted that although the dc conductivity measurements show an abrupt change in resistivity, the concomitant existence of a huge hysteresis, as well as the results obtained by ESR measurements [3] suggest that the insulating CDW and metallic phases coexist also near the phase transition. The observed phase transition, coined as the Mott-Peierls phase transition, is explained as a result of the Peierls transition with three-fold lattice distortion in the presence of strongly correlated Cu d-states [4]. In other words, in addition to electron-phonon interaction, strong electron-electron correlations and a three-dimensional coupling are shown to be necessary ingredients, which have to be taken into account to describe properly the observed phase diagram. In order to clarify the properties of the ground state near phase transition and better determine CDW dynamics, we have performed low frequency dielectric spectroscopy [5] and non-linear conductivity measurements [6], which are reviewed in this paper.

2. EXPERIMENTAL AND RESULTS

We report results obtained on h_8/d_6 70%:30% single crystals. All measured crystals have shown the same properties. Their room temperature conductivity was in the range 800-1200 $(\Omega cm)^{-1}$. The ohmic and non-ohmic resistivity have been measured in the four probe configuration using a standard dc technique or using two contact method and a Keithley 617 electrometer in V-I mode. The complex admittance ($G(\omega)$, $B(\omega)$) has been measured by a Hewlett Packard HP4284A impedance analyser (20Hz-1MHz) in the two probe configuration in the insulating state. 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 $G(\omega)$ at low frequencies, where $G(\omega)$ was independent of ω.

Temperature dependent conductivity below 70 K is shown in Figure 1. It should be noted that the conductivity at 60 K is about the same as the RT conductivity due to the sample cracks that occurred between 80 K and 120 K, which decrease the conductivity by one order of magnitude. In the cooling cycle the sample undergoes two sharp phase transitions, metal-to-insulator (entry) at $T_{C1cool} \sim 46$ K and insulator-to-metal (re-entry) at $T_{C2cool} \sim 26$ K. Because of the huge hysteresis area, the entry $T_{C2warm} \sim 43$ K and the re-entry $T_{C1warm} \sim 55$ K temperatures in the warming cycle differ significantly from those in the cooling cycle. In order to obtain as large temperature range as possible for low frequency dielectric spectroscopy and non-linear conductivity measurements, we performed the following procedure. After the sample entered the insulating state at T_{C1cool}, it was further cooled to temperature just above T_{C2cool}. Measurements were then made in warming, until the sample entered the metallic phase at T_{C1warm}.

Figure 2 shows the field-dependent conductivity normalised to its ohmic value at few typical temperatures [5]. Above a certain threshold electrical field, E_T, conductivity starts to increase, since the additional, collective conducting channel opens. The
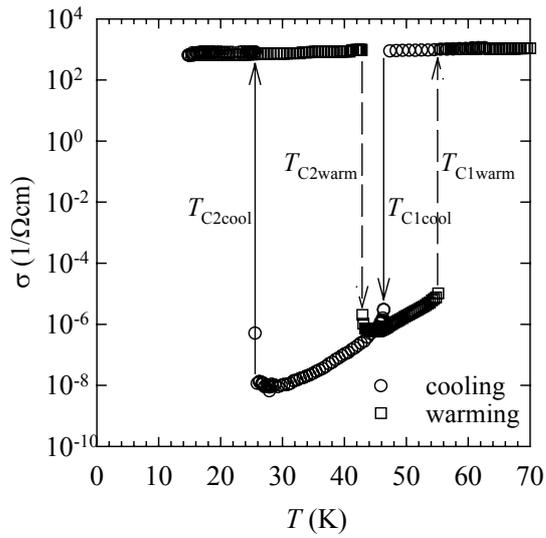
Figure 1: Conductivity versus temperature in cooling and warming cycle.
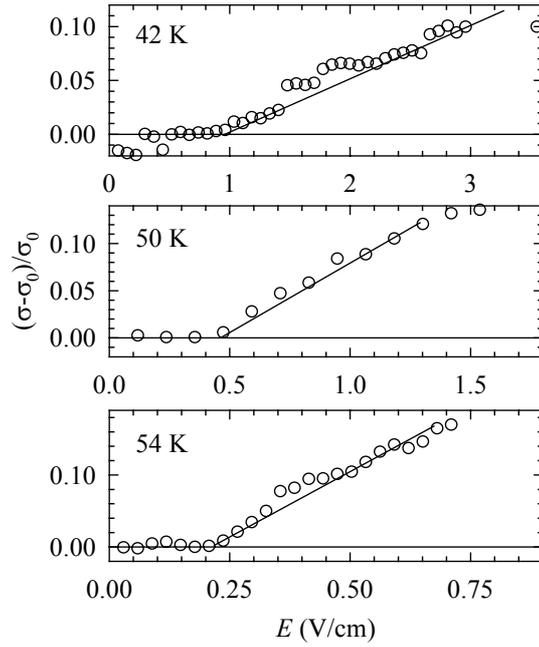
Figure 2: Non-ohmic conductivity normalized to its ohmic value versus electric field at few typical temperatures.
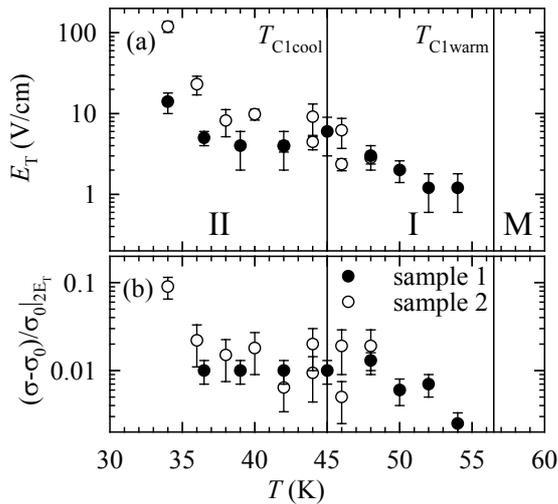
Figure 3: (a) threshold electrical field and (b) non-ohmic conductivity effect versus temperature. M, I and II denote metallic, hysteretic and insulating temperature range, respectively.

magnitude of non-ohmic conductivity, presented in Figure 3(a), is rather small and is of order of 1% of its ohmic conductivity in the broad temperature range, while it starts to increase at low temperatures. Despite the small effect, threshold field is clearly defined. In a broad temperature range, E_T is almost constant, while it diverges at low temperatures, as can be seen in Figure 3(b).

The real part of the conductivity normalised to the dc value $(G(\omega)-G_0)/G_0$ as a function of frequency at a few typical temperatures is shown in Figure 4 [6]. Above the phase transition temperature a frequency independent conductivity is found. The initial analysis of the dielectric function was performed by the inspection of Cole-Cole plots, which are presented in Figure 5. The intersection of the arcs with ε' axis at high and
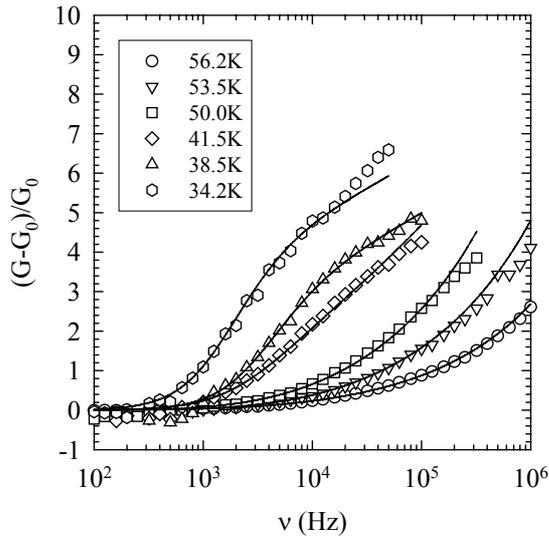
Figure 4: Real part of conductivity normalised to the dc value versus frequency at few typical temperatures. Full lines are fits to HN form.

Figure 5: Cole-Cole plots of the dielectric response at three representative temperatures. Full lines are fits to HN form.

Figure 7: (a) relaxation strength, (b) shape parameter and (c) mean relaxation time versus inverse temperature. M, I and II denote metallic, hysteretic and insulating temperature range, respectively.
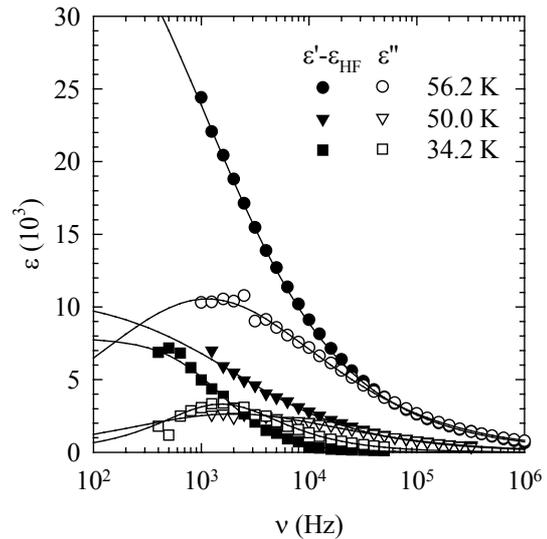
Figure 6: Frequency dependence of real and imaginary parts of the dielectric function at three representative temperatures. Full lines are fits to HN form.

low ε' values, corresponding to low and high frequencies, indicates the values of the static dielectric constant ε_0 and the high frequency dielectric constant ε_{HF}, respectively. The value of the relaxation strength $\Delta\varepsilon = \varepsilon_0 - \varepsilon_{HF}$ is moderate, of the order of 10^4. Finally, Figure 6 shows frequency domain plots of the real and imaginary part of the dielectric function at three representative temperatures.

Detailed analysis of the collective mode was made in terms of the complex dielectric function $\varepsilon(\omega)$ given by a generalisation of the Debye expression known as the phenomenological Havriliak-Negami (HN) function [7]

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

where $\beta = 1$ for symmetrical cases. τ_0 and $1-\alpha$ are the mean relaxation time and the shape parameter, which describes the symmetric broadening of the relaxation time distribution function, respectively.

The full lines in Figures 4, 5 and 6 correspond to the calculated fits. The fit parameters as a function of inverse temperature are shown in Figure 7. The mean relaxation time τ_0 is constant within the error bar and is too long to be attributed to free carriers. Therefore, we are led to identify the origin of this relaxation as an intrinsic property of the insulating state. The relaxation strength $\Delta\varepsilon$ decreases with temperature for one order of magnitude between 56.5 K and 34.2 K. The width of the relaxation time distribution expressed by the $(1-\alpha)$ parameter is about 0.6 at high temperatures. However, the mode narrows with decreasing temperature and already below 45 K it is almost Debye-like, i.e. $(1-\alpha) \sim 1$.

3. DISCUSSION

The non-linear conductivity and dielectric relaxation appear in the insulating state. The magnitude of non-ohmic conductivity is constant in the broad temperature range, and starts to increase at low temperatures, concomitantly with the increase of the threshold field. This behaviour is somewhat surprising. That is, the increase of threshold field suggests that the sliding mechanism starts to freeze below 45 K. In that case one would expect concomitant decrease of non-ohmic conductivity as reported in commensurate charge density wave system, as in the case of $N = 4$ CDW of DCNQI-Li system [8]. Therefore, our experimental results suggest that density wave sliding is replaced by a new mechanism of collective conduction.

Further confirmation of a new mechanism is given by behaviour of the parameters of the dielectric relaxation. Namely, the relaxation strength is of the order of 10^4 and decreases on lowering the temperature, which is in contradiction with the behaviour in the density wave systems in which a phason is a relaxation entity, as for example in Bechgaard salts [9]. We propose a charged domain wall pair excitations from the $N = 3$ charge density wave, pinned by commensurability to the underlying lattice, as the relaxation entity. At temperatures below the hysteretic region (that is, below 45 K), the observed Debye form of relaxation indicates, in the framework of the uniform pinning (single-particle) model, that a commensurate pinning of CDW is established on the long

range scale. On the other hand, in the hysteretic temperature range (above 45 K) the insulating CDW phase exists only on the short range scale, since the nucleation of the metallic phase starts to grow up. Macroscopically, the system may be described as consisting of insulating (CDW ordered) and metallic domains with a high degree of randomness. Then, dynamically correlated CDW clusters would yield to a broad relaxation, as observed experimentally. This picture is in agreement with results obtained by ESR measurements suggesting the coexistence of the insulating CDW and metallic phases [3]. It should be also noted that qualitatively the same behaviour was observed in commensurate spin density wave of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl, in which charged domain wall pair in the ferromagnetic domain structure is proposed as the relaxation entity [10,11]. Note that a common aspect of these two systems is a domain wall structure of spin/charge density wave ground state. Finally, we comment behaviour of relaxation time. Since it is time-independent within the error bar, in contrast to activated behaviour of dc conductivity in the same temperature range, this shows that free electrons screening is not effective.

CONCLUSION

We identify broad relaxation as the intrinsic property of the $N = 3$ commensurate charge density wave below the Peierls-Mott phase transition and suggest that metallic islands act as charged domain walls in the random domain commensurate structure. We interpret the Debye relaxation observed at lower temperatures to be the manifestation of the $N = 3$ CDW long-range order established outside the hysteretic region. The unusual behaviour of non-ohmic conductivity in temperature range, where free electrons screening is not effective, confirms the existence of a new collective mechanism, which might be either attributed to thermal excitations or to tunnelling of charge domain walls.

REFERENCES

[1] R. Kato, *Bull. Chem. Soc. Jpn.* **73** (2000) 515.

[2] A. Kobayashi, R. Kato, H. Kobayashi, T. Mori, H. Inokuchi, *Solid State Commun* **64** (1987) 45A.

[3] D. Gómez, J.U. von Schütz, H. C. Wolf, S. Hünig, *J. Phys. I France* **6** (1996) 1655.

[4] T. Ogawa and Y. Suzumura, *Phys. Rev. B* **53** (1996) 7085.

[5] M. Pinterič, T. Vuletić, M. Lončarić, S. Tomić, J.U. von Schütz, *Eur. Phys. J. B* **16** (2000) 487.

[6] T. Vuletić, M. Pinterič, M. Lončarić, S. Tomić, J.U. von Schütz, *Synth. Met.* **120** (2001) 1001.

[7] R.J. Cava, R.M. Fleming, R.G. Dunn, E.A. Rietman, *Phys. Rev. B* **31** (1985) 8325.

[8] M. Pinterič, N. Biškup, S. Tomić, J.U. von Schütz, *Synth. Metals* **103** (1999) 2185.

[9] T. Vuletić, D. Herman, N. Biškup, M. Pinterič, A. Omerzu, S. Tomić, M. Nagasawa, *J. Phys. IV* **9** (1999) Pr10-275.

[10] M. Pinterič, M. Miljak, N. Biškup, O. Milat, I. Aviani, S. Tomić, D. Schweitzer, W. Strunz, I. Heinen, *Eur. Phys. J. B* **11** (1999) 217.

[11] M. Pinterič, N. Biškup, S. Tomić, D. Schweitzer, W. Strunz, I. Heinen, Proceedings of 35th International Conference on Microelectronics, Devices and Materials, Ljubljana, Slovenia (1999) 83.