# Low-frequency dielectric permittivity of (DI-DCNQI)$_2$Ag in the charge-ordered state

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**Abstract**
We report the results of measurements of the conductance and the low-frequency dielectric permittivity of the quasi-one-dimensional compound (DI-DCNQI)$_2$Ag. We analyse the physical nature of the phase transition occurring in this compound into a charge-ordered state and the formation of the appropriate energy gap. We compare the dielectric properties of (DI-DCNQI)$_2$Ag with those resulting from charge-ordered states recently reported in (TMTTF)$_2$X salts.

Studies of charge-ordered states (COS) in quasi-one-dimensional and quasi-two-dimensional compounds which are not connected with any structural lattice transition have recently aroused considerable interest (for a review, see [1]). One of the main physical reasons for the formation of a charge-ordered electronic superstructure is based on long-range Coulomb-correlated electronic interactions. The theoretical considerations performed in the frames of geology approach [2, 3] of Mott–Hubbard model [4–7] and of mean field theory [8] show that, under certain conditions, the formation of such a charge-ordered electronic superstructure of Wigner type or, in other words, a $4k_F$ charge density wave is favourable.

The first direct experimental evidence for the existence of such COS was obtained by means of NMR studies in the quasi-one-dimensional (DI-DCNQI)$_2$Ag (in short, DI-Ag) compound [9] (where DI-DCNQI is 2,5-diiodo-dicyanoquinonediimine). In this compound planar DCNQI molecules are uniformly stacked along the $c$-axis without visible dimerization at room temperature which corresponds to a quarter-filled band [1, 9]. It was shown that with decreasing temperature below 220 K, the $^{13}$C-NMR spectra are split, pointing out the appearance of non-equivalent, differently charged molecules along the molecular chains. This charge disproportionation saturates to $\sim$3 : 1 at temperatures below 130 K [9]. These results were confirmed by x-ray studies [10, 11]. X-ray diffraction patterns have revealed at 30 K the existence of $4k_F$ satellite reflections, which correspond well to the charge ordering

detected by NMR. Charge distribution has also been investigated by Raman vibrational spectroscopy [12].

Several studies of the temperature dependence of the conductivity $G$ and the dielectric permittivity $\varepsilon'$ at low frequencies have been fulfilled [13–15] for organic compounds belonging to another quasi-one-dimensional family, namely the $(TMTTF)_2X$ salts ($X = PF_6$, $AsF_6$, $SbF_6$, $ReO_4$ and $SCN$), which show a certain degree of dimerization of the molecular chains resulting in a half-filled band [1]. Anomalies in the $G(T)$ dependence and a Curie-type divergence of $\varepsilon'(T)$, similar to features corresponding to a second-order phase transition, were found in a temperature range below which the localized Mott–Hubbard state is well established and a charge gap opened. It was proposed that these transitions, where no lattice effects are detectable, correspond to a formation of electronic superstructures of Wigner type, analogous to that observed in DI-Ag. NMR measurements performed on the $X = PF_6$ and $AsF_6$ salts showed that the $^{13}C$-NMR spectra split below the same temperature $T_{CO}$ at which $\varepsilon'$ diverges and that this splitting saturates at 20 K below $T_{CO}$ [16]. These results are a confirmation of COS in $(TMTTF)_2X$ salts. Furthermore, from new experimental and theoretical investigations, the large polarization was found consistent with the breaking of an inversion symmetry of the unit cell, providing some evidence for a ferroelectric nature of these COS [15, 17].

It is well known that measurements of the temperature dependence of the dielectric permittivity is one of the most powerful techniques for studing a phase transition because, in the vicinity of it, $\varepsilon'(T)$ exhibits anomalies and divergence. A short description of the temperature dependence of the resistance and the spin susceptibility of DI-Ag were reported in [18]. For better understanding of a formation of COS in quasi-one-dimensional and quarter-filled conductors without inherent dimerization, we have carried out detailed measurements of the temperature dependence of the dielectric permittivity and of the conductance of DI-Ag in the wide frequency range between $10^3$ and $10^7$ Hz.

We have measured the complex conductance of three DI-Ag needle-like crystals prepared by the electrochemical reduction [19]. The characteristic length of these crystals was several mm and their mean cross-section was about $10^{-5}$ cm$^2$. Electrical contacts were prepared by evaporation of gold pads on the sample ends; thin gold wires were attached on these pads by silver paste. The complex conductance $G(T, \omega)$ was measured using the impedance analyser HP 4192A. The amplitude of the ac voltage applied to the sample was typically about 10 mV. The measurements were carried out by cooling the samples from room temperature down to liquid-helium temperature with a slow cooling rate of about 0.2 K min$^{-1}$. Throughout this temperature range we did not observe any jump ('cracks') in the sample resistance, at variance with measurements of $(TMTTF)_2X$ compounds. The obtained data being qualitatively similar for the three DI-Ag samples, we present below the data for one of them.

The variation of the conductance $G$ measured at 1 kHz, normalized to its magnitude $G_o$ at 295 K, as a function of the inverse temperature is plotted in figure 1. The conductance of DI-Ag is continuously decreasing from room temperature down to liquid-helium temperature. The $G(1/T)$ dependence does not show any maximum as usually observed in compounds of the $(TMTTF)_2X$ family [1, 14, 15]. The temperature dependence of the logarithmic derivative $\mathrm{d}(\log(G/G_o))/\mathrm{d}(1000/T)$ is also shown in figure 1. Two pecularities indicating a change in the slope of $G(1/T)$ are visible: a narrow minimum near $T_1 = 200$ K and a broad minimum near $T_2 = 75$ K. Below $T_1$, the $G(1/T)$ dependence corresponds closely to a thermal activation behaviour with an activation energy of about 440 K. Below $T_2$, the slope of $G(1/T)$ dependence reaches nearly the same value as that in the temperature range between 200 and 100 K and thus the same activation energy of around 440 K. It
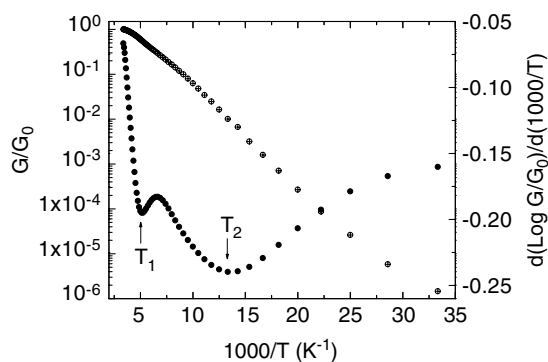
**Figure 1.** Variation of the real part of the conductance $G$ of (DI-DCNQI)$_2$Ag measured at frequency 1 MHz normalized to its value at room temperature $G_o$ ($\otimes$) and of the logarithmic derivative $d(\log G/G_o)/d(1/T)$ ($\bullet$) as a function of the inverse temperature.
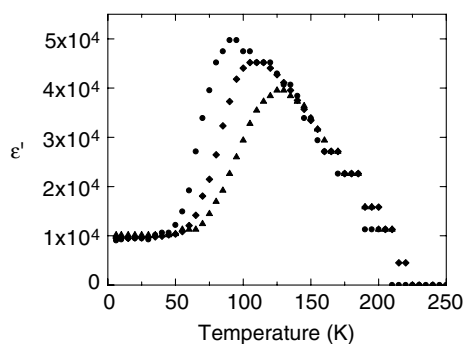


**Figure 2.** Temperature dependence of the dielectric permittivity of (DI-DCNQI)$_2$Ag measured at frequencies 100 kz ($\bullet$), 1 MHz ($\blacklozenge$) and 5 MHz ($\blacktriangle$).

should be noted that below 140 K the conductance begins to be slighty dependent on frequency.

The temperature dependence of the real part of the dielectric permittivity $\varepsilon' = \text{Im}\,\sigma/\omega$ is shown in figure 2 at frequencies of 100 kHz, 1 and 5 MHz. The growth of $\varepsilon'$ (above the resolution of our measurements) becomes noticeable only at temperatures below around 220 K. With decreasing temperature, the magnitude of $\varepsilon'$ continues to increase and is independent of frequency down to 140 K. For lower temperatures, $\varepsilon'$ reaches a maximum at a temperature depending on frequency: with decreasing frequency the magnitude of the maximum of $\varepsilon'$ increases and its position in the temperature scale is shifted to lower temperature. Such a variation resembles the slowing down behaviour typical of relaxation phenomena. Below 50 K, the magnitude of $\varepsilon'$ approaches the background level determined by the resolution of our measurements in this temperature range.

According to previous results [9, 18], the following scenario of the variation of successive states in DI-Ag with decreasing temperature can be proposed. DI-Ag is a paramagnetic insulator below room temperature at ambient pressure. In (TMTTF)$_2$X compounds, the conductance first increases when temperature is decreased below room temperature and shows a maximum around 200 K before decreasing at lower temperatures. The so-called charge

localization due to bond dimerization inherent to $(TMTTF)_2X$ compounds is considered as the physical reason for such a $G(T)$ dependence. However, there is no inherent dimerization in DI-Ag [18].

Recently, transport properties of DI-Ag under pressure have been reported [20]. It was shown that the temperature dependence of the conductivity exhibits a maximum, i.e. the form of $G(T)$ dependence of DI-Ag under a moderate pressure becomes qualitatively similar to the appropriate dependence in $(TMTTF)_2X$ compounds at ambient pressure. It can then be suggested that in DI-Ag at ambient pressure the maximum of $G(T)$ may occur at a temperature higher than 300 K, indicating the formation of the so-called Mott–Hubbard localization in a quarter-filled system without dimerization [21].

Below 220 K, several features have been observed: a minimum in the temperature dependence of the logarithmic derivative of the conductance (figure 1), the growth of $\varepsilon'$ (figure 2), the splitting of NMR spectra [9] as well as the appearence of satellite reflections at $0.5c^*$ [10, 11]. All these features are associated with the onset of a phase transition into a COS with a $4k_F$ electronic superstructure. The development of this superstructure is attributed to long-range Coulomb interactions and electron–electron correlation phenomena of Wigner crystal type [8–11]. However, the process of formation of such a state is spread on a relatively large temperature range. The intensity of the $0.5c^*$ superlattice reflections increases gradually from 200 K [10] and the charge superstructure with the charge disproportionation 3 : 1 is only completed below 130 K [9]. It is in the same temperature range between 200 and 130 K that, as seen in figure 2, $\varepsilon'$ progressively grows and reaches a maximum depending on frequency. In this temperature range, the superlattice which corresponds to well developed COS remain however soft enough and capable of being easily polarized, which determines the $\varepsilon'$ magnitude. These results show that the COS phase transition takes place in a wide temperature range (about 100 K) or indicate the diffuse character of the phase transition. In contrast, as shown by NMR studies [16] in $(TMTTF)_2X$ compounds (X = $PF_6$ and $AsF_6$) the temperature range of the appropriate phase transition is considerably narrower—about 20 K. Accordingly, the $\varepsilon'$ dependence is sharper, very close to the Curie law corresponding to a typical second-order phase transition [14, 15].

Below 130 K, in the temperature range where the $4k_F$ electronic superstructure is well formed, some changes in the electronic properties have been observed. As seen in figure 1 the logarithmic derivative of the conductance shows a broad minimum, i.e. the slope of the $G(1/T)$ dependence first increases before approaching at lower temperatures the same value measured between 200 and 100 K indicating an energy gap (or rather a pseudo-gap) of nearly 440 K. Such a behaviour can be explained if one considers the fact that, after completion of the CO superstructure at about 130 K, this $4k_F$ superstucture when the temperature is decreased becomes more and more rigid, approaching the real 'static' superstucture of an electronic crystal. One possible origin for the increase of the CO superstructure, due to a decrease of screening effects by free charge carriers, is their concentration being strongly reduced at lower temperatures. That corresponds probably to the transformation of the pseudo-gap into a more well-formed gap with a decrease in the broadening of its edge. While at higher temperatures, say around 130 K, the edge of the energy gap is washed away, allowing many possible states for electrons to move on the bottom to the conduction band, at lower temperatures the edge of the energy gap becomes sharper and many states accessible earlier for electron motion are now excluded in the process of charge transport with the result of a decrease in mobility and conductivity [22].

The frequency dependence of $\varepsilon'$ favours also an increase in the rigidity of the superstructure (figure 2). The observed growth of the maximum amplitude of $\varepsilon'$ and its shift to lower temperatures when the frequency is decreased are typical of a slowing down behaviour and the

development of relaxation processes with growing relaxation time. Around 50 K, the rigidity of the COS becomes very large and the magnitude of $\varepsilon'$ decreases sharply.

In summary we have shown that the dielectric permittivity of (DI-DCNQI)$_2$Ag increases below 220 K, the temperature at which a new charge-ordered state with charge disproportionation occurs as previously demonstrated by NMR and x-ray studies. The increase in the permittivity reflects the polarizibility of the growing (soft) $4k_F$ superstructure. But, at lower temperatures (below 140 K), the charge-ordered state becomes rigid as seen by the frequency dependence and the slowing down behaviour of the dielectric permittivity.

On the one hand, the maximum on the $\varepsilon'(T)$ dependence is additional evidence of the existence of the charge-ordering transition in the quasi-one-dimensional compound DI-Ag, similar to the same type of transition in (TMTTF)$_2$X, in spite of the absence of an inherent dimerization and the realization of a quarter-filled band in the former compound. On the other hand, in DI-Ag, the maximum value of $\varepsilon'$ is more than an order of magnitude smaller than in (TMTTF)$_2$X compounds, which can indicate a considerable role for the dimerization of the molecular chains as well as the loss of the inversion symmetry of the unit cell involved in charge-ordering phenomena.

## Acknowledgments

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