Dielectric response of the charge ordered state in 
\( \theta-(\text{BEDT-TTF})_2\text{MZn(SCN)}_4 \) (M: Rb, Cs) compounds

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Abstract. We present results of measurements of conductivity and dielectric permittivity of the organic two-dimensional salts \( \theta-(\text{BEDT-TTF})_2\text{RBZn(SCN)}_4 \) and \( \theta-(\text{BEDT-TTF})_2\text{CSZn(SCN)}_4 \). A qualitative comparison between the dielectric response of these compounds is given with respect of the different nature of the charge order they exhibit.

1. Introduction

The metal-insulating transition due to electron localization is of a current interest, specifically in organic systems in which electron correlations are known to be important. In half-filled band, the insulating state is a Mott insulator where the electron is localized on each site due to the on-site Coulomb interaction, \( U \). However, many 1/4 filled band systems which should normally be metallic exhibit metal-insulator transitions. Over the last few years, it has been recognized that the effects of electron interactions are greatly enhanced by reducing dimensionality. Thus, in quasi-one-dimensional (1D) compounds, the crucial role of long range Coulomb interactions has been stressed in particular in the frame of the 1D extended Hubbard model. This model takes into account the magnitude of the on-site \( U \) and of the next-neighbouring \( V \) interactions relative to the mean kinetic energy determined by the energy band \( W = 4t \) (where \( t \) is the transfer integral between nearest-neighbor sites). It was shown within the mean field approximation \([1]\) that in 1D systems charge disproportionation (CD) can develop, the form of which depends on the magnitude of \( V \): at a value of \( V \) higher than some critical value \( V_c \), a \( 4k_F \) charge density wave (CDW) superstructure of Wigner type occurs.

The first experimental evidence of such a charge ordered state (CO) was obtained \([2]\) by means of NMR studies in the quasi-one-dimensional (DI-DCNQI)\(_2\text{Ag} \), where DI-DCNQI is 2,5-diiodo-N, N’-dicyanoquinonediimine. It was shown that, on decreasing temperature \( T \) below 200 K, the \(^{13}\)C NMR spectra are splitted, pointing the appearance of non-equivalent differently charged molecules along the molecular chains. These results were conﬁrmed \([3]\) by X-rays studies where X-ray diffraction patterns at 30 K have revealed the existence of \( 4k_F \) satellite reflections which correspond to the CO detected by NMR.

In the Fabre salts of \((\text{TMTTF})_2X \) formula where TMTTF is tetramethyltetraselenafulvalene and \( X \) a counteranion such as PF\(_6\), AsF\(_6\), ReO\(_4\), SbF\(_6\) ..., it was shown (for a review see \([4]\))
that at $T$ above the temperature range characteristic for magnetic spin ordering ($T \leq 20$ K) (TMTTF)$_2$X salts undergo a phase transition into a new charge ordered state at $T_{CO}= 70$ K for (TMTTF)$_2$PF$_6$, 100 K for (TMTTF)$_2$AsF$_6$ and 154 K for (TMTTF)$_2$SbF$_6$. These transitions have been revealed by the divergence at $T_{CO}$ of the low frequency real part of the dielectric constant. $^{13}$C NMR spectra have proved [5] that below $T_{CO}$ charge disproportionation occurs, dividing the TMTTF molecules within the unit cell into two non-equivalent species. The two-dimensional systems (BEDT-TTF)$_2$X with quarter filled bands should normally be in the metallic state. BEDT-TTF stands for bisethylenedithio-tetrathiafulvalene (alternatively abbreviated as ET) and X being a monovalent anion. However, in $\alpha$-(BEDT-TTF)$_2$I$_3$ [6; 7] and $\theta$-(BEDT-TTF)$_2$RbZn(SCN)$_4$ [8; 9] metal-insulator (MI) transitions were detected. In $\theta$-(BEDT-TTF)$_2$RbZn(SCN)$_4$ in the condition of slow cooling a first order MI transition was found around 190–200 K accompanied by the doubling of the unit cell along the c axis with a large displacement (about 0.2 A) of ET molecules [9–11]. The effect of both on-site and intersite Coulomb interactions on the electronic states in (ET)$_2$X compounds has been intensively studied [12; 13]. Charge ordered state with stripe-type were predicted to be stabilized. Different spatial charge patterns (horizontal, vertical or diagonal) were proposed depending on the balance between anisotropic transfer integrals in the donor plane and anisotropic intersite Coulomb interaction $V$ [12].

In this short review we will present our last results of the dielectric measurements on $\theta$-(BEDT-TTF)$_2$RbZn(SCN)$_4$ depending on the cooling conditions and on $\theta$-(BEDT-TTF)$_2$CsZn(SCN)$_4$ in order to establish better the nature of its ground state.

2. Charge order in $\theta$-(BEDT-TTF)$_2$RbZn(SCN)$_4$

$\theta$-(ET)$_2$RbZn(SCN)$_4$ is a layered material composed of conducting ET layers and insulating RbZn(SCN)$_4$ layers alternatively stacked along the b axis (interlayer direction). The packing pattern of the ET molecules in the conducting layer are disposed along a triangular lattice with one hole for every two molecules.

A drastic change in NMR lineshape in $\theta$-(BEDT-TTF)$_2$RbZn(SCN)$_4$ (RbZn salt, hereafter) [14; 15] was found below $T_{CO}$ with evidence of charge rich and charge poor sites. Raman spectroscopy on RbZn has revealed the split of the charge sensitive $\nu_2$ C=C stretching mode indicating a charge difference among ET molecules at non equivalent sites [16]. The charge distribution confirms the appearance of charge disproportionation (CD) below $T_{CO}$ with an average CD ratio $0.2 \sim 0.8$. From structural data performed at 90 K, the ionicitics of the ET molecules were estimated from the intramolecular bond-length distribution; "charge rich" and "charge poor" sites were found with ionicitics $0 \sim +0.2$ and $0.8 \sim +1.0$ and with a spatial pattern with hole rich and hole poor molecules aligned alternatively along the c-axis [10; 11]. In addition, it was shown that in RbZn a specific CD already appears well above $T_{CO}$ in the so-called metallic state [17–19]. This CD is associated with short-range slow charge fluctuations. The MI transition near 190 K can correspond to the formation of a 3D long-range ordering assisted by lattice dimerization along the c-axis.

Differences between rapid-cooled state (Q-state) and slow-cooled state (R-state) were found in susceptibility measurements, NMR, EPR and some transport properties [20; 21]. Diffuse scattering observed above $T_{CO}$—with $q = (1/3, k, 1/4)$—becomes weaker but still exists below $T_{CO}$ in the rapid-cooled state (at 4–5 K/min) [10]. That indicates that the Q-state may have the nature of the room temperature electronic state. But in the Q-state below $T_{CO}$ another diffuse rod of wave vector $\mathbf{q}_2 = (0, k, 1/2)$ was found to coexist. The modulation of $\mathbf{q}_2$ is also disordered in the interlayer direction (along b$^*$). After annealing at 180–190 K during around 12 hours to get the R-state, the diffuse rod $\mathbf{q}_2$ grows into a satellite reflection at c$^*/2$ resulting from the lattice dimerization.

We have performed ac conductivity measurements [22] with several cooling rates:
- slow cooling rate, typically 0.1–0.2 K/min during which the temperature was stabilized at each point and measurements within the whole frequency range performed. The ground state reached thus below $T_{CO}$ is the relaxed state (R-state),
- fast cooling rate between 9 and 10 K/min. In this case, the temperature was not stabilized and data were taken at an unique frequency, namely 1 MHz. The state at low temperature is the so-called quenched-state (Q-state),
- intermediate cooling rate, between 4 and 5 K/min, again without temperature stabilisation and measurements taken at frequency 1 MHz. We will call the state at low temperature reached in this condition the intermediate-state (I-state).

For slow cooling, below 200 K, the conductance $G$ decreases sharply by more than three orders of magnitude; after this jump the conductivity continues to decrease with a considerably larger activation energy $\Delta_{R-state} \approx 1900$ K. On heating the phase transition occurs at a temperature 5 K higher than on cooling [23]. These features are signatures of a first order phase transition. For fast cooling the conductance gradually decreases below 190 K without any sharp drop, indicating that the first order character of the transition which occurs in the slow cooling has been suppressed or at least has been largely reduced. The logarithmic derivative of the conductance exhibits however a broad peak around $T = 167$ K which may indicate that some features of the phase transition occurs yet at this temperature. The temperature dependence of the conductance at low temperature follows an activated behaviour with an activation energy $\Delta_{Q-state} \approx 320$ K (comparison between the Arrhenius plot of the conductance between slow cooling and fast cooling is shown in figure 2). The behaviour for intermediate cooling is between both for slow and fast cooling: still a relatively sharp jump of the conductance with a peak in the logarithmic derivative at 168 K and an activation energy at low temperature $\Delta_{I-state} \approx 800$ K.

In the temperature range 300–200 K, for the three cooling rates, log $G(1/T)$ dependence has practically a linear form and it corresponds to a thermo-activated variation of $G$ with an energy gap $\Delta \approx 200$ K.

The monotonous increase of the dielectric constant from room temperature down to the vicinity of the CO phase transition can be associated with the short-range charge inhomogeneity as detected by the broadening of the NMR spectra. That may also be connected to the observation
Figure 2. Comparison of the temperature variation of the real part of the dielectric permitivity of $\theta$-(BEDT-TTF)$_2$RbZn(SCN)$_4$ measured on cooling at a rate of 4–5 K/mn and on warming at the heating rate of 5 K/mn.

above $T_{CO}$ of diffuse planes and rods with $q = (1/4, k, 1/3)$ as revealed in x-rays measurements [10; 11]. As can be seen from figure 1, superposed to the background of the monotonous $\epsilon'$ growth, a peak of $\epsilon'$ appears [23] in the extreme vicinity of $T_{CO}$ which resembles the $\epsilon'(T)$ peak measured at the CO transition in (TMTTF)$_2X$ salts. For intermediate cooling, the sharp increase of $\epsilon'$, signature of the CO transition, occurs at a lower temperature, namely 175 K. Below $T_{CO}$ the dielectric constant decreases relatively fast down to 150 K (but much less than in the slow cooling conditions) and shows below a broad shoulder before decreasing to a value beyond our resolution at low temperature. For fast cooling there is no sign of any sharp divergence of $\epsilon'$. The temperature dependence of $\epsilon'$ exhibits just a very broad maximum around 150–200 K. For the three cooling rates between 200 K and room temperature, the $\epsilon'(T)$ dependence is similar.

Figure 2 shows a comparison of the temperature dependence of $\epsilon'(T)$ on cooling and on heating for intermediate cooling. It appears that when, below $T_{CO}$, the metastable state is melted and the original CO state is restored, $\epsilon'(T)$ drops to the value measured on slow cooling.

The low temperature (5–160 K) short range CO state, obtained at intermediate and fast cooling rates, is characterized by the same $\epsilon'(T)$ dependences on cooling and heating cycles, i.e. the short range CO state is fairly stable in this temperature range. All relaxation processes are accelerated in the temperature range 160–200 K where the maximum difference in the $\epsilon'$ magnitude is observed depending on the cooling rate. On heating, the abrupt increase of $\epsilon'$ occurs practically at the same temperature. Thus, on heating, all the metastable states formed at low temperature from cooling rates with different amplitudes are destabilized and the stable ground state formed on slow cooling becomes recovered in the temperature range of 160–190 K.

3. Charge order in $\theta$-(BEDT-TTF)$_2$CsZn(SCN)$_4$

Following the classification of the $\theta$-(ET)$_2X$ salts according to their dihedral angle [9], $\theta$-(BEDT-TTF)$_2$CsZn(SCN)$_4$ with $\theta_d = 105^\circ$ is placed between compounds with respectively a CO ground state and a metallic one. It was already found [9] that the resistivity of CsZn salt changes little from room temperature down to 50 K, but grows sharply below 20 K; the magnetic susceptibility changes also little down to 20 K, showing a Curie type increase below 20 K. Near 20 K again a small jump in specific heat and entropy of CsZn salt have been also found [24]. One might think that these data could provide some evidence for the existence of a metal-insulator transition in CsZn salt near 20 K. The studies of infrared reflectance and Raman spectra show that no optical gap is observed in CsZn salt in the whole temperature range down to 10 K [25; 26].
The conductance $G$ of CsZn salt grows when the temperature decreases below room temperature. $G$ exhibits a maximum in the range 110–115 K. A further marked decrease of $G$ is observed near 20 K (figure 2a). Below this maximum, for all the CsZn samples we measured [33], we have observed that an hysteresis loop near 90 K with $\Delta T = 4–5$ K (figure 2b). This feature appears to be characteristic for a “diffuse” first order phase transition with a new charge distribution. A further marked decrease of $G$ is observed near 20 K. Below 20 K, the $G(T)$ dependence is rather similar to hopping type conductivity in a sample with disorder [34; 35].

The conductance $G$ of CsZn salt in the temperature range 4.3–20 K shows that the more accurate fit corresponds, indeed, to the relation $G \sim T^n$.
Figure 4. Variation of the logarithm of the conductance $G$ of $\theta$-(BEDT-TTF)$_2$CsZn(SCN)$_4$, normalized by its room temperature value $G_0$, as a function of logarithm of temperature in the range below 20 K.

Figure 5. a) Temperature dependences of the real part of dielectric permittivity $\epsilon'$ of $\theta$-(BEDT-TTF)$_2$CsZn(SCN)$_4$ at different frequencies indicated near the curves in MHz. b) Temperature dependence [36] of the real part $\epsilon'$ of (TMTTF)$_2$PF$_6$ at fixed frequencies (in kHz) top to bottom: 0.111, 0.5, 1.1, 2, 3, 5, 11, 30, 100, 300, 1000.

with $n = 2.9$ (see figure 4), i.e. it is very close to the theoretical value $n = 3$.

Figure 5a shows [33] the temperature dependences of the real part of the dielectric permittivity, $\epsilon'$, at various frequencies $10^4 - 10^7$ Hz. When $T$ is decreased below room temperature the magnitude of $\epsilon'$ begins to grow. Below 100 K, the $\epsilon'(T)$ curves show a maximum, $\epsilon'_m$, at some temperature $T_m$ dependent on frequency. With decreasing frequency this maximum shifts to lower temperatures and simultaneously the magnitude of $\epsilon'_m$ increases considerably up to large values in the order of magnitude of $10^6$. For temperatures below $T_m$ $\epsilon'$ decreases more rapidly than its growth above $T_m$. Such forms of $\epsilon'(T)$ dependences and their variation with
Figure 6. Comparison of the temperature dependence of $\epsilon'$ measured at 1 MHz for $\theta$-(BEDT-TTF)$_2$CsZn(SCN)$_4$ and fast cooled (9 K/mn) $\theta$-(BEDT-TTF)$_2$RbZn(SCN)$_4$.

frequency bear a strong resemblance to the known, so-called, slowing down behavior which is typical for various systems with certain degree of disorder [37]. In such a case, it is usually considered that, at $T_m$, the condition $\omega \tau \approx 1$ ($\omega = 2\pi f$, $\tau$ : relaxation time) is reached, at which the response of the sample begins to retard, i.e. it has not enough time to follow the more fast variation induced by the ac voltage, leading thus to the decrease of the $\epsilon'$ magnitude. $\log \tau$ ($\tau = 1/\omega$ is the relaxation rate) versus 1000/$T$ dependence is close to be linear, i.e. it can be well approximated by a thermo-activated type relation: $\tau = \tau_0 \exp(-\Delta/kT)$ with $\tau_0 \approx 10^{-9}$ s and $\Delta \approx 130$ K; that is in agreement with the theory for various glass states [38–40].

4. Discussion
It has been suggested from previous NMR measurements [26; 41] that the ground state of fast cooled RbZn resembles the behavior of CsZn near 20 K. However recent NMR as well as Raman spectra indicate that at low temperature the charge modulation in CsZn is negligible or very weak. At variance, in fast cooled RbZn, short range CO domains exist with large amplitude between charge rich and charge poor sites. Our measurements show unquestionably that the ground states between fast cooled RbZn and CsZn are totally different. The difference between both compounds is very well demonstrated in the dielectric response as shown in figure 6. In fast cooled RbZn, the temperature dependence of $\epsilon'$ shows only a broad maximum with a small amplitude without any structure. At the opposite, $\epsilon'(T)$ exhibit the characteristic behavior of a glassy system, previously observed either in charge density waves [42] and in spin density waves [36], namely in the Bechgaard salts (TMTSF)$_2$X (see figure 5b for comparison). Thus, the data we have obtained [33] provide strong arguments for the assumption that the low temperature ground state of CsZn salt represents a combination of frustrated domains which, with decreasing temperature, are frozen into a glass-like short-range charge ordered state.

The CO transitions in Fabre salts have been explained by a combined effect of the charge disproportionation appearing in TMTTF molecules and the uniform shift of anions (transition with a wave vector $q$ =0) with respect to the oppositely charged organic chains. The resulting breaking of the centre of symmetry between adjacent molecules induces the ferroelectric character of this transition as revealed [43] by the Curie law of $\epsilon'$ of these compounds with $\epsilon' \propto A/[T_{CO} - T]$. As can be seen from figure 1 in $\theta$-(BEDT-TTF)$_2$RbZn(SCN)$_4$ superposed to the background of the monotonous $\epsilon'$ growth a peak of $\epsilon'$ appears in the extreme vicinity of $T_{CO}$ which resembles the $\epsilon'(T)$ peak measured at the CO transition in (TMTTF)$_2$X salts. At
the CO transition in $\theta$-(BEDT-TTF)$_2$RbZn(SCN)$_4$ the space group changes from orthorhombic I222 to P2$_1$2$_1$2$_1$ yielding the breaking of inversion center as concluded from the selection rule in Raman measurements [44], allowing thus the possibility of a ferroelectric character to the CO phase transition. A CO transition occurs also in $\alpha$-(BEDT-TTF)$_2$I$_3$ [6; 7]. By optical second harmonic generation, a ferroelectric polarization has been detected below the CO phase transition with observation of ferroelectric domains [44]. Our preliminary results of dielectric response in this compound shows also a sharp peak at the CO transition as in the RbZn salt, which may result from the ferroelectric character of the charge order.

5. Conclusions
Charge ordered state (COS) develops in many 1D and 2D organic compounds. The driven force for the formation of COS is strong electron-electron interactions. However, for stabilization of COS in electronic systems the reorganization of anion and molecular sublattices is necessary. In 1D organic compounds of the (TMTTF)$_2$X family the stabilization is realized by a shift of the anion sublattice as a whole, leading to the ferroelectric nature of the COS.

In 2D organic compounds of the $\theta$-(BEDT-TTF)$_2$X family, where the interaction between electron and lattice subsystems is stronger, the stabilization of COS takes place below a temperature $T_{CO}$ by the formation of a lattice superstructure with doubling of the unit cell period as observed in $\theta$-(BEDT-TTF)$_2$RbZn(SCN)$_4$ in slow cooling conditions. The temperature dependence of the real part of the dielectric permittivity $\epsilon'$ demonstrates the tendency to divergence when approaching $T_{CO}$ from above and a sharp downfall of $\epsilon'$ below $T_{CO}$. At very fast cooling a mixed lattice structure with a partly developed 2c superstructure is frozen at low temperature in some metastable state and consequently the maximum in the $\epsilon'(T)$ dependence is suppressed.

In the case of the $\theta$-(BEDT-TTF)$_2$CsZn(SCN)$_4$ compound the competition between two different superstructures is observed in the whole temperature range. The COS cannot be stabilized like in the case of the RbZn salt; COS with a short range order exists only in a limited part of the sample (domains) while on the long range scale the sample stays in a disordered state. This state is very similar to a glassy state. Indeed, the $\epsilon'(T,f)$ dependences show the features characteristic to a slowing down behaviour which is typical for glassy states.

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