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LETTER TO THE EDITOR

Dielectric response in the charge-ordered θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ organic compound

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Abstract
We report measurements of low-frequency dielectric permittivity in two-dimensional θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ organic compound. The real part of the dielectric permittivity ε' exhibits a sharp peak in the extreme vicinity of the charge ordered phase transition at T_{CO}. The very low magnitude of ε' below T_{CO} results from the lattice dimerization asssociated with the charge ordered phase. We ascribe the temperature-dependent permittivity above T_{CO} to pre-existing charge inhomogeneities—charge disproportionation—as revealed previously by NMR measurements. A qualitative comparison between the dielectric response due to charge order in quasi-one-dimensional conductors and in this two-dimensional system is presented.

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 a 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 quarter-filled band systems, which should normally be metallic, exhibit metal–insulator transitions. The search for the origin of this has been generating intense activity recently. Over the last few years, it has been fully 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 through theoretical studies, 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-neighbour sites). In particular, it was shown within the mean-field approximation (Fukuyama and Seo 1997) that in 1D systems charge disproportionation (CD) can develop, the form of which depends considerably 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 (Hiraki and Kanoda 1998) by means of nuclear magnetic resonance (NMR) studies in the quasi-one-dimensional (DI-DCNQI)$_2$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 split, pointing to the appearance of non-equivalent differently charged molecules along the molecular chains. The CD saturates to nearly 3:1 at T below 130 K. These results were confirmed (Nogami *et al* 1999) by x-ray studies, where x-ray diffraction patterns at 30 K have revealed the existence of $4k_F$ satellite reflections which correspond well to the CO detected by NMR.

In the Fabre salts of formula (TMTTF)$_2$X, where TMTTF is tetramethyltetraselenafulvalene and X is a counteranion such as PF$_6$, AsF$_6$, ReO$_4$, SbF$_6$..., it was shown (Nad and Monceau 2006) that, at T above the temperature range characteristic for magnetic spin ordering ($T \leqslant 20$ K), (TMTTF)$_2$X salts undergo a phase transition into a new charge-ordered state at $T_{CO} = 70$ K for (TMTTF)$_2$PF$_6$, at 100 K for (TMTTF)$_2$AsF$_6$, and at 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 (Nad *et al* 1999). ^{13}C NMR spectra have proved (Chow *et al* 2000) that, below T_{CO}, charge disproportionation occurs, dividing the TMTTF molecules within the unit cell into two non-equivalent species. These CO transitions have a purely electronic origin without visible structural variation. The CO transitions in Fabre salts have been explained by a combined effect of the CD appearing in TMTTF molecules and the uniform shift of anions (a transition with a wavevector $q = 0$) 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 (Monceau *et al* 2001) by the Curie law of ε' of these compounds with $\varepsilon' = A/|T_{CO} - T|$.

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 is a monovalent anion. However, in α-(BEDT-TTF)$_2$I$_3$ (Bender *et al* 1984a, 1984b) and θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ (Mori *et al* 1995, 1998), metal–insulator (MI) transitions were detected without knowing their physical nature. In θ-(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 Å) of ET molecules (Mori *et al* 1998, Watanabe *et al* 2003, 2004).

The effect of both on-site and intersite Coulomb interactions on the electronic states in (ET)$_2$X compounds has been studied intensively (Seo 2000, Seo *et al* 2004). Charge-ordered states of stripe-type were predicted to be stable. 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 (Seo 2000).

The real nature of the MI phase transition in θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ has only recently been determined by NMR (Miyagawa *et al* 2000, Chiba *et al* 2001a, 2001b) as being due to charge ordering. A drastic change in NMR line-shape was found below T_{CO}, with evidence of charge-rich and charge-poor sites. Raman spectroscopy on θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ has revealed the split of the charge-sensitive ν_2 C=C stretching mode, indicating a charge difference among ET molecules at non-equivalent sites (Yamamoto *et al* 2002). The charge distribution confirms the appearance of charge disproportionation (CD) below T_{CO} with an average CD ratio 0.2–0.8. The loss of inversion in the insulating phase, as concluded from the selection rule, suggests that the charge is ordered along horizontal stripes. For θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$, from structural data performed at 90 K, the ionicities of the
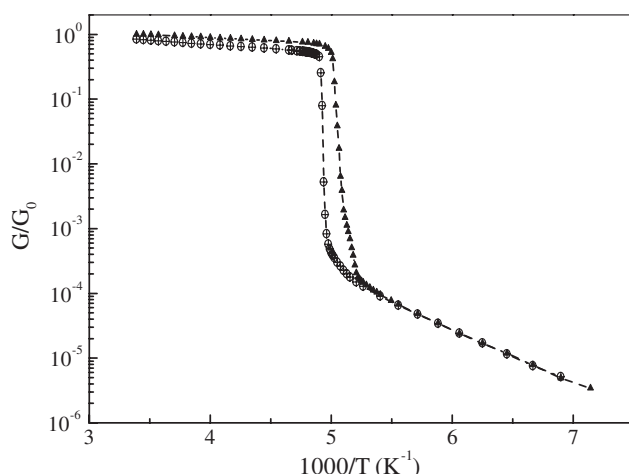
Figure 1. Dependences of the conductance G (at a frequency of 1 kHz) of θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ for slow cooling (triangle) and heating (circles) at a rate of 0.1 K min^{-1}, normalized by its value G_o at room temperature as a function of the inverse temperature.

ET molecules were estimated from the intramolecular bond-length distribution; 'charge-rich' and 'charge-poor' sites were found with ionicities of 0 to +0.2 and 0.8 to +1.0 and with a spatial pattern with hole-rich and hole-poor molecules aligned alternatively along the c-axis (Watanabe *et al* 2003, 2004). This CO and its spatial pattern also agree with reflectance spectra and polarized Raman and infrared spectroscopy (Wojciechowski *et al* 2003).

However, it was shown that, in θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$, a specific CD already appears well above T_{CO} in the so-called metallic state (Takahashi *et al* 2004, Chiba *et al* 2003, 2004). 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.

Dielectric permittivity is known to be one of the most direct methods for identifying a phase transition. Following our previous work (Nad and Monceau 2006) on charge ordering on quasi-one-dimensional conductors of Fabre salts (TMTTF)$_2$X and in (DI-DCNDI)$_2$Ag (Nad *et al* 2004), we have undertaken measurements of the low-frequency dielectric response of the charge-ordered state in θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ compound. Hereafter we report our preliminary results performed on this compound.

Electrical contacts were prepared by gold pads on the surface of the sample on which thin gold wires were attached afterwards with silver paste. We have carried out the measurements of the complex conductance $G(T, \omega)$ using an HP 4192A impedance analyser in the frequency range 10^3–10^7 Hz and in the temperature range 4.2–295 K. The amplitude of the ac voltage field applied to the sample along the c-axis was within the linear response and typically 30 mV cm^{-1}. Because the conductivity of this compound is relatively large (about 10 S cm^{-1}), we selected samples with minimum cross-section (about 10^{-4} cm^2) and maximum length (several millimetres) in order to get samples with a maximum resistance mostly suitable for measurements using our impedance analyser. The temperature regulation (a cooling rate about 0.1 K min^{-1}) and the measurement of the complex conductance were carried out using an automatic regime under computer control. The resolution of our dielectric set-up is estimated to about 5×10^3 at room temperature and 10^3 below T_{CO}.

Figure 1 shows an Arrhenius plot of the real part of the conductance G, normalized by its magnitude G_o at room temperature. On cooling in the temperature range 300–200 K, the conductance decreases, i.e. it demonstrates a non-metallic character of conductivity. As can be seen from figure 1, in this temperature range, the $\log G(1/T)$ dependence has practically
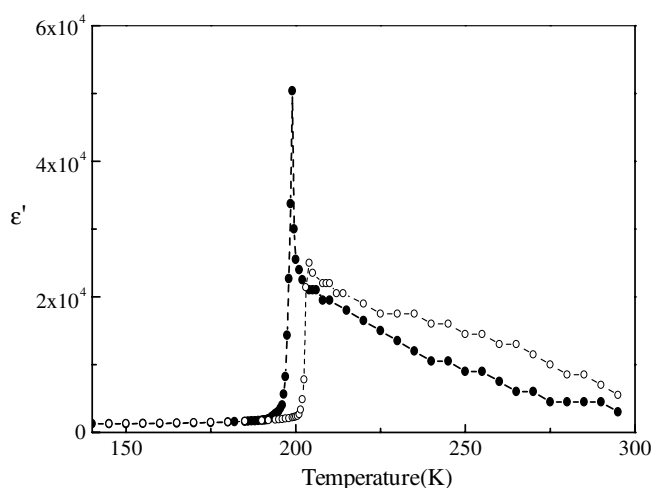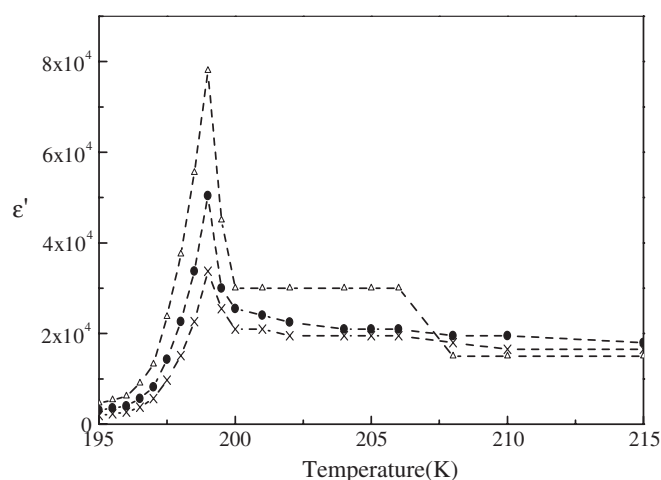
Figure 2. Temperature dependences of the real part of the dielectric permittivity ε' of θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ at a frequency of 1 MHz for cooling (full circles) and heating (empty circles) at a rate of 0.1 K min^{-1}.

a linear form and it corresponds to a thermo-activated variation of G with an energy gap $\Delta_1 \approx 200$ K. Below 200 K, the conductance decreases sharply by more than three orders of magnitude, and after this jump the conductivity continues to decrease with a considerably larger activation energy $\Delta_2 \approx 1900$ K. On heating, the insulator–metal transition occurs at a higher temperature than on cooling.

The temperature dependence of the real part of the dielectric permittivity $\varepsilon'(T)$ at 1 MHz is drawn in figure 2. On cooling, $\varepsilon'(T)$ shows smooth monotonic growth, beginning from room temperature. But, near the temperature of the phase transition at T_{CO}, ε' exhibits very sharp, close to divergent, growth in a very narrow temperature range. Just below T_{CO}, a jump-like decrease of ε' occurs to a very small magnitude. On heating, the jump of ε' is observed at a temperature about 5 K higher than on cooling. So, the characters of $G(T)$ and $\varepsilon'(T)$ dependences are typical for a first-order phase transition, as observed previously using other techniques (Mori *et al* 1998, Watanabe *et al* 2003, 2004, Wojciechowski *et al* 2003). It should be noted that the maximum value of ε' is not very large: it is smaller by more than one order of magnitude with respect to the appropriate maximum ε' value in 1D compounds of the (TMTTF)$_2$X family (Nad and Monceau 2006). In particular, because of the relatively small ε' value in θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$, sufficient accuracy in measurements can be achieved only at frequencies higher than 0.1 MHz.

Figure 3 shows the temperature dependence of ε' in the temperature range close to T_{CO} at three frequencies 0.1, 1 and 3 MHz. Positions of the $\varepsilon'(T)$ maxima coincide practically for all these frequencies, while the magnitude of the $\varepsilon'(T)$ peak increases with decreasing frequency. The variation of $\varepsilon'(T)$ out of the temperature range near the phase transition is weakly frequency dependent.

The dielectric permittivity results that we have presently obtained on the CO of the 2D θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ compounds show differences when compared with those previously reported concerning 1D Fabre salts (Nad and Monceau 2006). In the latter, the CO phase transition is a second-order phase transition with the Curie law dependence of the $\varepsilon'(T)$ variation near T_{CO}. We have proposed that the charge disproportionation is stabilized by the shift of anion chains with a wavevector $q = 0$, thus yielding a ferroelectric character to the low-temperature charge-ordered phase (Monceau *et al* 2001). No structure change has yet been determined at the CO transitions, which consequently were called 'structureless transition', although the ferroelectric character should imply the loss of the inversion centre

Figure 3. Temperature dependence of the real part of the dielectric permittivity ε' of θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ at frequencies of 0.1 (triangles), 1 (circles) and 3 (crosses) MHz at a slow cooling rate 0.1 K min^{-1} in the restricted temperature range in the vicinity of the charge-ordered phase transition.

and the change of the space group from P_{1-} to P_1. On the other hand, charge ordering in θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ is associated with a first-order structural transition with a dimerization along the stacking chains.

The monotonous increase in the dielectric constant from room temperature down to the vicinity of the CO phase transition can be associated with short-range charge inhomogenity, as detected by the broadening of the NMR spectra. This may also be connected to the observation above T_{CO} of diffuse planes and rods with $q = (1/4, k, 1/3)$, as revealed in x-ray measurements (Watanabe *et al* 2003, 2004). Measurements (Inagaki *et al* 2003) of the out-of-plane dielectric constant have been analysed with a Debye-type relaxation even above T_{CO}, suggesting that insulating and metalic phases coexist in the 'metallic' state. The thermo-activated character of conductivity in the temperature range above T_{CO} with an activation energy equal to 200 K (figure 1) may indicate that the so-called 'metallic' state corresponds rather to a semiconducting state with a narrow energy gap, which is of the order of magnitude of the temperature under investigation.

As can be seen from figure 3, superposed to the background of the monotonous ε' growth, a peak of ε' appears in the extreme vicinity of T_{CO} which resembles the $\varepsilon'(T)$ peak measured at the CO transition in (TMTTF)$_2$X salts. At the CO transition in θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$, the space group changes from orthorhombic $I222$ to $P2_12_12_1$, yielding breaking of some inversion centre, thus allowing the possibility of a ferroelectric character to the CO phase transition.

The jump to a very low value of the dielectric permittivity ε' below T_{CO} is associated with the formation of the lattice superstructure and with the opening of a new large energy gap Δ_2. The behaviour below T_{CO} can be analysed in the light of that observed in (TMTTF)$_2$ReO$_4$ or (TMTTF)$_2$BF$_4$ below the temperature where anion ordering occurs (Nad and Monceau 2006). In (TMTTF)$_2$ReO$_4$, ε', which exhibits a sharp peak at the CO phase transition at T_{CO}, decreases sharply below the AO ordering (Nad *et al* 2001) at $T_{AO} = 154$ K. The wavevector associated with the AO ordering is $q = (1/2; 1/2; 1/2)$. This means that the polarizability is decreased strongly by the dimerization along the chains. The situation is very similar to that in θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ with the dimerization below T_{CO} along the c-axis, the direction where the ac field is applied.

In conclusion, we have measured the dielectric response due to charge ordering in the two-dimensional θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ compound. The CO phase transition is first order

and manifests itself by a strong lattice distortion involving a dimerization along the c-axis of large magnitude. In the case of one-dimensional Fabre salts, the stabilization of the charge disproportionation developed at the CO phase transition occurs through the shift of anion chains with a wavevector $q = 0$, which may indicate that the interchain interaction and the electron–phonon interaction in these 1D lattices are relatively weak, allowing relative motion of anion chains with respect to molecular TMTTF chains. In the case of θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$, the formation of the 2c superstructure and the opening of a very large gap at $T < T_{CO}$ may result in the fact that charge ordering cannot be stabilized by a shift of anions as in (TMTTF)$_2$X salts. One may consider that, on the one hand, the smaller mobility of anion chains within the 2D lattice and, on the other hand, a relatively strong electron–phonon interaction in 2D compared to 1D compounds yield the stabilization of charge ordering through the formation of a 2c superstructure.

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