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LETTER TO THE EDITOR

Charge and anion ordering phase transitions in (TMTTF)₂X salt conductors

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Abstract

We report measurements of the low frequency conductivity and dielectric permittivity of quasi-one-dimensional organic (TMTTF)₂X salts with non-centrosymmetrical anions X = ReO₄ and SCN. We show that the 'structureless transition' at 227.5 K in (TMTTF)₂ReO₄ is due to charge ordering and has a ferroelectric character. The anion ordering transition strongly affects the dielectric response: it suppresses the polarizability in (TMTTF)₂ReO₄ and induces probably an antiferroelectric state in (TMTTF)₂SCN.

Intensive studies have shown that in the same family of (TMTCF)₂X organic quasi-one-dimensional salts, with C = Se or S and X = PF₆, SbF₆, ClO₄, ReO₄, SCN, etc. . .) a very rich variety of diverse ground states can be created as a function of temperature and pressure [1]. These states, such as metallic, charge and spin density waves, spin-Peierls, antiferromagnetic and superconductivity, very often show original features, which do not have direct well-known analogues in other systems.

In our previous publications [2–5] it was shown that at temperatures above the temperature range characteristic for magnetic spin ordering ($T > 20$ K) many members of the (TMTTF)₂X with centrosymmetrical anions undergo a phase transition into a new charge ordered state, namely at $T_0 = 70$ K in (TMTTF)₂PF₆ [2, 3], at 100 K in (TMTTF)₂AsF₆ [3, 4] and at 154 K in (TMTTF)₂SbF₆ [6]. These transitions have been revealed by the divergence at T_0 of the low frequency real part ϵ' of the dielectric constant [2–5]. NMR measurements on ¹³C have proved [6] that below the transition temperature for (TMTTF)₂PF₆ and (TMTTF)₂AsF₆ charge disproportionation or charge ordering (CO) occurs, dividing the TMTTF molecules within the unit cell into two non-equivalent species. One possible mechanism for this transition is that CO on the initially homogeneous charged molecular chains is due to electron–electron Coulomb correlated interactions, a CDW of a Wigner type, having thus a purely electronic origin without visible structural variations [7, 8]. On the other hand, in these (TMTTF)₂X salts with molecular and anion chains, the role of the anion sublattice is of great importance [9].

In a recent model [5], this transition has been explained as a combined effect of the charge disproportionation appearing in TMTTF molecules and the uniform shift of anions (transition at $q = 0$) 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 by the Curie law behaviour of $\epsilon'(T)$ of these compounds with $\epsilon' \sim A/|T_0 - T|$. The interplay between electronic correlations and lattice effects in this family of compounds has also been addressed in recent theoretical studies [10, 11].

However, in the centrosymmetrical cavities delimited by the (TMTTF) molecules non-centrosymmetrical anions are disordered at room temperature. With decreasing temperature, a structural transition due to anion ordering (AO) occurs with the appearance of a superstructure q_{AO} . This is the case for (TMTTF)₂SCN (the SCN anion has a linear form and a relative large dipole moment) with $T_{AO} = 169$ K [12, 13] and $q_{AO} = (0, \frac{1}{2}, \frac{1}{2})$ [14] and for (TMTTF)₂ReO₄ (ReO₄ has a tetrahedral symmetry). It was shown that the temperature dependence of the resistance and the thermopower of (TMTTF)₂ReO₄ show two anomalies near 225 K and 160 K [15]. In addition, the dielectric constant measured at 6.5 GHz presents also two not very pronounced anomalies near the same temperatures [16]. While the peculiarities near 160 K are due to anion ordering as revealed by x-ray studies [17] with $q_{AO} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, the anomalies near 225 K are not accompanied by observable structural variations [18] and correspond to a 'structureless transition'. Thus (TMTTF)₂ReO₄ presents a unique opportunity to study in the same compound the $q \neq 0$ and the charge ordering phase transition.

Hereafter we report on the dielectric response of the two transitions in (TMTTF)₂ReO₄ and make a comparison with the dielectric response in (TMTTF)₂SCN where a single $q \neq 0$ transition occurs. In the following, for simplicity, we will use the term AO for the $q \neq 0$ phase transition, and CO for the 'structureless transition', being aware that for this latter transition the centre of symmetry of molecules may, however, be broken ($q = 0$).

Measuring the temperature dependence of the dielectric permittivity ϵ' is a powerful method for studying phase transitions because very often, in their vicinity, ϵ' presents an anomalous behaviour, even sometimes a divergency; the relaxation time also grows considerably and can reach 10^{-4} – 10^{-6} s [3, 19].

We have performed measurements of the temperature dependence of the complex conductance $G(T, \omega)$ using the impedance analyser HP 4192A in the frequency range 10^3 – 10^7 Hz. The amplitude of the a.c. voltage applied to the sample was typically 10 mV, within its linear response. We have studied two samples of (TMTTF)₂ReO₄ and (TMTTF)₂SCN, prepared by a standard electrochemical method [20]. These samples were single crystals with well defined facets. Their typical length was about 5 mm and their cross section about 5×10^{-5} cm². Electrical contacts were prepared by attaching thin gold wires with silver paste on gold pads evaporated on the sample's ends. In order to avoid the influence of the cooling rate on the results of measurements and to minimize possible 'cracks' with decreasing temperature, we have used a small cooling rate below 0.2 K min⁻¹ [2, 3]. In addition, our samples were placed in a sealed cell at a constant He gas pressure of 10 bars during all temperature cycles.

Figure 1 shows the dependence of the real part of the conductance G normalized to its magnitude G_0 at 295 K as a function of the inverse temperature for both (TMTTF)₂ReO₄ and (TMTTF)₂SCN compounds. The room temperature (295 K) conductivity of ReO₄ salt is about $20 \Omega^{-1} \text{ cm}^{-1}$ and that of SCN salt about $40 \Omega^{-1} \text{ cm}^{-1}$, values close to data in references [15, 16]. With decreasing temperature the conductance of both compounds increases first to a maximum at T_ρ (inset of figure 1), which corresponds to a metallic type of conductivity [1]. T_ρ is about 290 K for ReO₄ salt and about 265 K for SNC salt.

Below T_ρ the conductance of (TMTTF)₂ReO₄ salt decreases, following a thermally activated behaviour with an activation energy of $\Delta_1 = 800$ K. The $G(1/T)$ dependence shows a

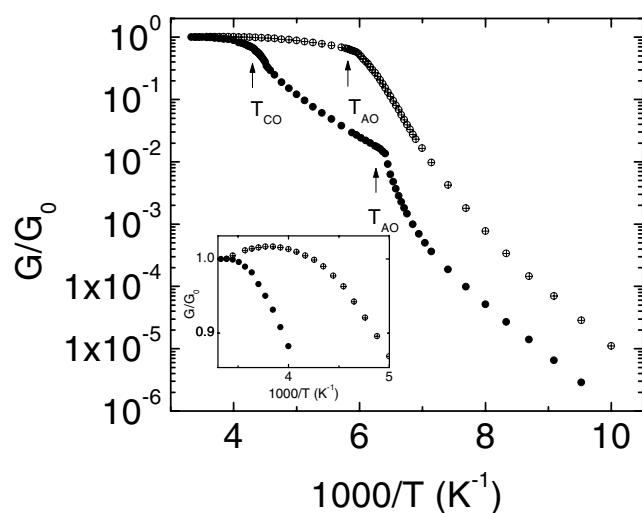


Figure 1. Variation of the real part of the conductance G normalized to its value G_0 at room temperature as a function of the inverse temperature at frequency 1 MHz for $(\text{TMTTF})_2\text{ReO}_4$ (\bullet) and $(\text{TMTTF})_2\text{SCN}$ (\oplus). The inset shows the temperature dependence of G/G_0 near its maximum.

sharp bend around 230 K, evolving gradually to a new thermally activated dependence (down to around 156 K) with a larger activation energy $\Delta_2 \simeq 1400$ K. Furthermore, at $T \simeq 155$ K a second sharp bend in the $G(1/T)$ dependence appears with the subsequent transition to another activated behaviour with $\Delta_3 \simeq 2000$ K. From room temperature down to 156 K, the conductance is frequency independent in the frequency range of 10^3 – 10^7 Hz investigated. An appreciable frequency dependence only appears at temperatures below the second transition ($T < 156$ K).

In the case of $(\text{TMTTF})_2\text{SCN}$, with decreasing temperature below T_ρ , the thermally activated conductance decreases with an activation energy $\Delta_1 \simeq 500$ K down to 170 K, at which temperature a sharp bend in the $G(1/T)$ dependence is observed. Below 170 K, the measured new activation energy is $\Delta_3 \simeq 2000$ K. The frequency dependence of G is only measurable below 170 K. The temperature dependence of the dielectric permittivity $\epsilon' = \text{Im}\sigma(\omega)/\omega$ for ReO_4 and SCN salts is shown in figure 2 and figure 3. For $(\text{TMTTF})_2\text{ReO}_4$, the growth of ϵ' begins from room temperature and it diverges at 227.5 K, reaching the huge value of $\sim 5 \times 10^5$. Below 1 MHz, the magnitude of $\epsilon'(\omega, T)$ and the temperature of its maximum do not depend on frequency. However, at higher frequencies, the maximum value of ϵ' decreases and shifts to higher temperature (figure 2, curve at 10 MHz). Below 227.5 K the decrease of ϵ' is faster than its growth. Near 155 K, the temperature of the second transition, ϵ' , sharply decreases (close to a jump). The amplitude of this drop decreases with increasing frequency.

In $(\text{TMTTF})_2\text{SCN}$ the magnitude of ϵ' is considerably smaller than in ReO_4 salt and in the temperature range from room temperature down to ~ 240 K it is below the resolution of our measurements. Below 240 K, the ϵ' growth begins and its magnitude amounts to a maximum of $\sim 2 \times 10^4$ at $T \simeq 169$ K, the temperature corresponding to that of the sharp bend in the $G(1/T)$ dependence (figure 1). For a better comparison, we have drawn in figure 3 the $\epsilon'(T)$ dependences for ReO_4 and SCN salts on a semilogarithmic scale for the same frequency of 1 MHz. One can see firstly that the character of the first (at 227.5 K) and second (at 155 K) transitions in $(\text{TMTTF})_2\text{ReO}_4$ is different, secondly that in $(\text{TMTTF})_2\text{SCN}$ only one transition is observed below 169 K, and thirdly that the decrease of ϵ' in $(\text{TMTTF})_2\text{ReO}_4$ below 169 K occurs more slowly than that in $(\text{TMTTF})_2\text{ReO}_4$ below 155 K.

The divergency of ϵ' near 227.5 K in the ReO_4 salt compounds corresponds to the Curie law, $\epsilon' \simeq A/|T - T_{\text{CO}}|$ as shown in inset of figure 2 where $1/\epsilon'$ is plotted versus T in the temperature range of ± 20 K near the phase transition. Both branches of $1/\epsilon'(T)$ are almost

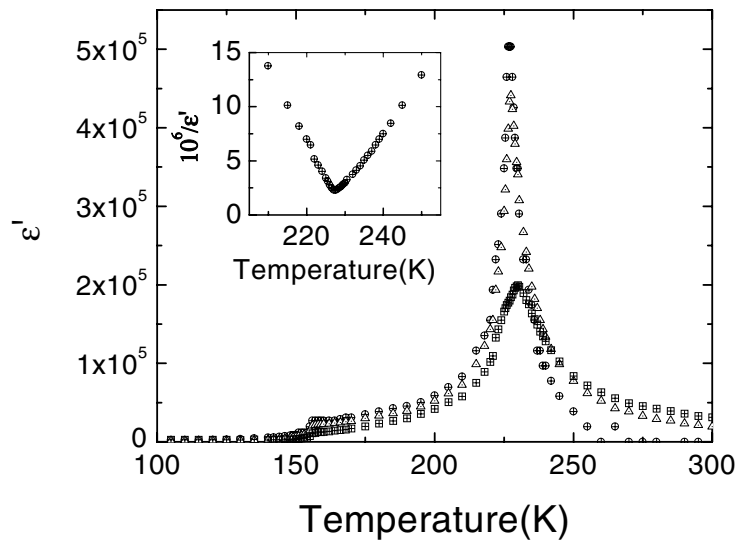


Figure 2. Temperature dependence of the dielectric permittivity ϵ' of $(\text{TMTTF})_2\text{ReO}_4$ at frequencies of 100 kHz (\oplus), 1 MHz (Δ) and 10 MHz (\boxplus). The inset shows the temperature dependence of $1/\epsilon'$ near T_{CO} .

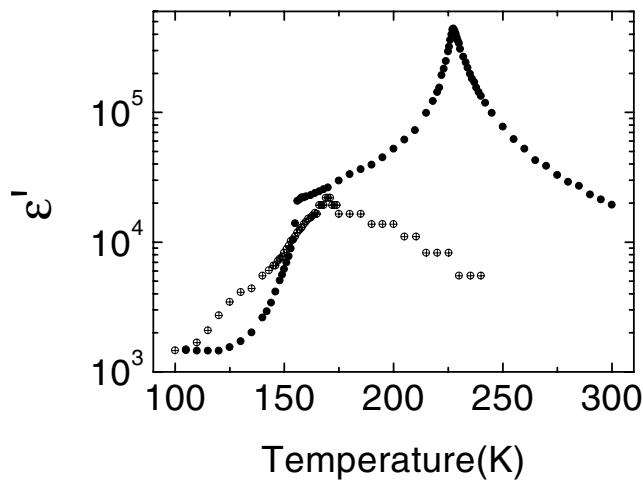


Figure 3. Temperature dependence of the dielectric permittivity on a semilogarithmic scale at frequency of 1 MHz: $(\text{TMTTF})_2\text{ReO}_4$ (\bullet), $(\text{TMTTF})_2\text{SCN}$ (\oplus).

linear with the Curie constant $A = 4.7 \times 10^5$ above the transition and 7×10^5 below it.

From the present results and those published earlier on centrosymmetrical anions [1, 4–6, 18], we can suggest the following scenario of the low temperature physical modifications of the $(\text{TMTTF})_2\text{X}$ salts with non-centrosymmetrical anions $\text{X} = \text{ReO}_4$ and SCN . The structure of $(\text{TMTTF})_2\text{X}$ salts is already dimerized at room temperature ($4k_{\text{F}}$ superstructure), resulting in different distances d_1 and d_2 between TMTTF molecules along chains [18]. This dimerization has the character of a so-called bond dimerization while the charges on the sites of the molecular sublattice remain identical. The bond dimerization leads to the formation of an energy gap (or pseudogap) in the electron spectrum and consequently to charge localization below T_{ρ} . That is seen in the flat maximum in the $G(1/T)$ dependence and the following approximate activated decrease of G with the activation energy Δ_1 , while $\epsilon'(T)$ does not show

any anomaly near T_ρ (figure 2). Such a behaviour is probably general for all $(\text{TMTTF})_2\text{X}$ salts, independently of the anion symmetry [2–5, 18], the difference between them being observed only in the magnitudes of T_ρ and Δ_1 .

As can be seen from the present work in $(\text{TMTTF})_2\text{ReO}_4$, we have observed two transitions with a different type of $\epsilon'(T)$ dependence. The first transition near $T_{\text{CO}} = 227.5$ K is characterized by a pronounced bend in the $G(1/T)$ dependence with a change in the activation energy (figure 1) and by the divergency of ϵ' reaching a huge value and following the Curie law. Furthermore the transition does not exhibit any evident structural modification [18]. We consider this transition in $(\text{TMTTF})_2\text{ReO}_4$ to be similar to the structureless transitions in salts with centrosymmetrical anions, i.e. charge disproportionation on adjacent TMTTF molecules and uniform shift of anions yielding a ferroelectric character [4,6]. As a result of CO, an energy gap Δ_{CO} opens and adds in quadrature to the dimerized gap $\Delta_1 \simeq 800$ K that already exists below T_ρ , i.e. $\Delta_2^2 = \Delta_1^2 + \Delta_{\text{CO}}^2$ and hence $\Delta_{\text{CO}} \simeq 1100$ K. The CO electronic superstructure is characterized by the same $4k_{\text{F}}$ wave vector as the dimerized superstructure [18], thus contributing only to some enhancement of the intensity of the Bragg peak of the dimerized superstructure without the appearance of new reflections.

It was shown that at room temperature the ReO_4 anions are dynamically disordered about a centre of symmetry [17]. ReO_4 anions have a tetrahedral symmetry intermediate between that of centrosymmetrical octahedral anions (AsF_6 , SbF_6) and that of anisotropic noncentrosymmetrical linear anions SCN. Therefore, it is very likely that this disorder does not destroy the CO yet reduces the magnitude of the maximum of ϵ' by nearly one order of magnitude in comparison with centrosymmetric anions [3–5]. Thus, the phase transition in $(\text{TMTTF})_2\text{ReO}_4$ near T_{CO} has rather the character of a diffuse ferroelectric transition of second order. That may explain the ratio of 1.5 of the Curie constants above and below T_{CO} and not 2 as expected for a simple mean field theory as we observed in $(\text{TMTTF})_2\text{AsF}_6$, $(\text{TMTTF})_2\text{PF}_6$ and $(\text{TMTTF})_2\text{SbF}_6$ [3–5].

The second transition in $(\text{TMTTF})_2\text{ReO}_4$ near $T_{\text{AO}} = 155$ K (figures 1 and 2) is different in nature from the first. It corresponds to the formation of the pronounced superstructure with wave vector ($\mathbf{q} = \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) due to ReO_4 anion ordering, leading to a considerable deformation of the organic stacks [17]. The strong spatially modulated potential resulting from the anion ordering probably suppresses the CO superstructure and consequently the magnitude of ϵ' decreases sharply. It was also shown that the EPR susceptibility goes to zero below T_{AO} while it was unaffected near T_{CO} [15]. The opening at T_{AO} of the energy gap Δ_{AO} adds in quadrature to the gap Δ_2 existing at $T > T_{\text{AO}}$ and that results in the activation energy $\Delta_3 \simeq 2000$ K experimentally observed below T_{AO} (figure 1). From this value one can evaluate $\Delta_{\text{AO}} = \sqrt{\Delta_3^2 - \Delta_2^2} \simeq 1400$ K. As seen from figure 3 the $\epsilon'(T)$ dependence near T_{AO} is very different to that near T_{CO} : there is no divergency of ϵ' and at $T < T_{\text{AO}}$, ϵ' decreases very fast (practically a jump-like variation), resembling a first-order transition as observed in x-ray studies [17].

In the case of $(\text{TMTTF})_2\text{SCN}$, we have only observed one transition at $T_{\text{AO}} = 169$ K which corresponds to anion ordering with $\mathbf{q} = (0, \frac{1}{2}, \frac{1}{2})$ [14, 18]. The absence of any features related to a CO transition in the temperature range above T_{AO} and the small value of ϵ' near T_{AO} can result from the influence of the large disorder induced by the strong anisotropic noncentrosymmetrical linear SCN anions. The AO gap adds in quadrature to the dimerized gap $\Delta_1 \simeq 500$ K opened below T_ρ ; its magnitude can be deduced from the $\Delta_3 \simeq 2000$ K activation energy measured below T_{AO} , such as $\Delta_3^2 = \Delta_1^2 + \Delta_{\text{CO}}^2$ leading to $\Delta_{\text{AO}} \simeq 1900$ K. $\epsilon'(T)$ shows a maximum near T_{AO} (but 25 times smaller than the maximum ϵ' value in ReO_4 salt) (figure 3) and its temperature dependence cannot be described by a Curie law. As there is no anomaly in the paramagnetic susceptibility near T_{AO} (an antiferromagnetic ground state

occurs below 7 K [14]) and consequently no opening of a gap in the magnetic excitations, the AO in the SCN salt differ from the AO transition in $(\text{TMTTF})_2\text{ReO}_4$ and is more similar to the CO transition in this latter salt. However, due to the finite transverse component of q , each anion chain can move in the opposite direction to neighbouring chains, yielding an antiferroelectric (AFE) character to the phase transition.

In conclusion, we have shown that a ferroelectric transition in the charge gap state of $(\text{TMTTF})_2\text{X}$ salts occurs not only for centrosymmetrical anions like PF_6 [3], AsF_6 [4], SbF_6 [5], but also for the octahedral ReO_4 anion. It was shown that near 227.5 K the real part of the dielectric constant, ϵ' , reaches a maximum magnitude of 2×10^5 . Anion ordering transitions which occur for non-centrosymmetrical salts have a specific effect depending on the distortion wave vector. In the case of $(\text{TMTTF})_2\text{ReO}_4$, the anion ordering transition at $T_{\text{AO}} = 155$ K with a wave vector $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ totally destabilizes the ferroelectric state, ϵ' jumping sharply to a very low value. On the other hand, the particular wave vector $(0, \frac{1}{2}, \frac{1}{2})$ of the anion ordering transition in $(\text{TMTTF})_2\text{SCN}$ yields an antiferroelectric character of this transition. These results are a clear demonstration of the combined effect in these one-dimensional organic salts of Coulomb interactions coupled to anionic potentials.

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