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LETTER TO THE EDITOR

Charge ordering phase transition in the quasi-one-dimensional conductor (TMTTF)$_2$AsF$_6$

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Abstract. Direct evidence of a new phase transition at $T_{CO} = 100.6$ K in the organic quasi-one-dimensional (TMTTF)$_2$AsF$_6$ salt has been obtained from conductivity and dielectric permittivity measurements. This phase transition is assigned to a charge-ordered state ($4k_F$ charge density wave of Wigner type) due to charge-induced electron–electron interactions.

Charge transfer salts formed of linear chains of organic molecules tetramethyltetrathiofulvalene (TMTTF) or tetramethyltetraselenafulvalene (TMTSF) with the general formula (TMTCF)$_2$X with C = Se, S and counterions X = Br, PF$_6$, AsF$_6$, ClO$_4$, etc, display a very rich variety of ground states such as metal, semiconductor, charge (CDW) and spin (CDW) density waves, antiferromagnetic (AF), spin-Peierls (SP), superconductivity (SC), . . . [1].

According to the type of counterions, by substitution of Se by S and varying the temperature, pressure and magnetic field, mutual transitions between these ground states can be realized [1]. For instance, it has been shown that at atmospheric pressure with decreasing temperature (TMTTF)$_2$X salts with X = Br, PF$_6$, AsF$_6$ turn from a metallic state at room temperature to a so-called charge localization state below $T_\rho \sim 200$ K, followed by a transition into a magnetic spin ordered state around 10 K, AF for Br and SP for PF$_6$ and AsF$_6$ [2,3]. Many of these transitions between ground states are accompanied by changes in structural factors, in magnetic and dielectric susceptibilities, in conductivity, etc, [1,4,5]. However, such behaviour is not always observed. For instance, for many compounds in the (TMTTF)$_2$X family their structure and magnetic susceptibility do not exhibit any change through their transition into a charge localization state (so-called structureless transitions [3,4]). Such a situation makes difficult the clear interpretation of the nature of phase transitions in these compounds.

It is known that the study of dielectric permittivity is one of the most direct methods for identifying a phase transition [6]. The magnitude of the real part of the dielectric permittivity $\epsilon'(T)$ usually shows a tendency for divergency near the critical temperature of the phase transition.

We present the results of measurements of the conductance G and of ϵ' for the quasi-one-dimensional conductor (TMTTF)$_2$AsF$_6$ in the wide temperature range between 10 and 300 K and for frequencies between 10^3 and 10^7 Hz. These data give strong evidence that (TMTTF)$_2$AsF$_6$ undergoes a new phase transition into a charge-ordered state at $T_{CO} = 100.6$ K, in spite of the absence of any structural variation.

We have studied several samples of $(TMTTF)_2AsF_6$ [7] prepared by a standard electrochemical procedure [8]. The results of measurements of these samples were qualitatively similar and we will present data only for one sample. This sample has a good regular cross-section of 7×10^{-5} cm^2 along the whole 3.3 mm length between electrical contacts. Its room temperature conductivity is about 20 Ω^{-1}cm^{-1}, close to the value published previously in [3]. Electrical contacts were prepared by evapourating gold pads on nearly the whole surface of the sample's ends, upon which thin annealed gold wires were afterwards attached using silver paste. The complex conductance $G(T, \omega)$ was measured using an impedance analyser HP 4192 A. The amplitude of the ac electric field applied to the sample was within its linear response and was typically around 10 mV cm^{-1}. As was previously mentioned, with decreasing temperature $(TMTTF)_2X$ crystals very often suffer cracks, and consequently, jumps in conductivity. Keeping the cooling rate below 0.2 K mn^{-1} diminishes considerably the occurrence of such cracks [9, 10]. In this regard, improvement was brought with our samples placed in a sealed cell in which a constant He gas pressure of 10 bars was applied during all temperature cycles.
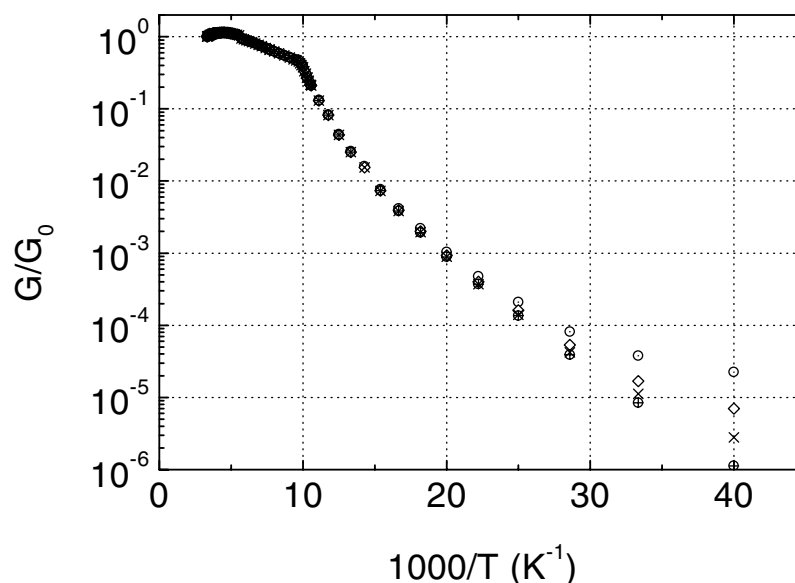

Figure 1. Variation of the real part of the conductance G of $(TMTTF)_2AsF_6$ normalized to its value G_0 at room temperature as a function of the inverse temperature at frequencies (in kHz) 1 ($\oplus$), 10 ($\times$), 100 ($\diamondsuit$), 1000 ($\odot$).

Figure 1 shows the temperature dependence of the conductance G normalized to its value at 300 K as a function of the inverse temperature. With decreasing temperature, G first increases to a maximum at $T_\rho \simeq 230$ K (metallic type of conductivity) as previously reported in [3]. Below T_ρ, G decreases with a thermally activated behaviour down to 105 K with an activation energy $\Delta\rho = 175$ K. Near 100 K, we observe a sharp bend in the $G(1/T)$ variation while the temperature dependence of the logarithmic derivative d log G/d$(1/T)$ shows a sharp minimum at $T_{CO} = 100.6$ K. Below T_{CO}, G decreases very fast, practically without any frequency dispersion, down to $\simeq 70$ K. Below this temperature the conductance begins to become noticeably dependent on frequency, with a more pronounced dependence at lower T (figure 1). The $G(1/T)$ dependence measured at the lowest frequency (10^3 Hz) follows an Arrhenius type with an activation energy $\Delta \simeq 350$ K.
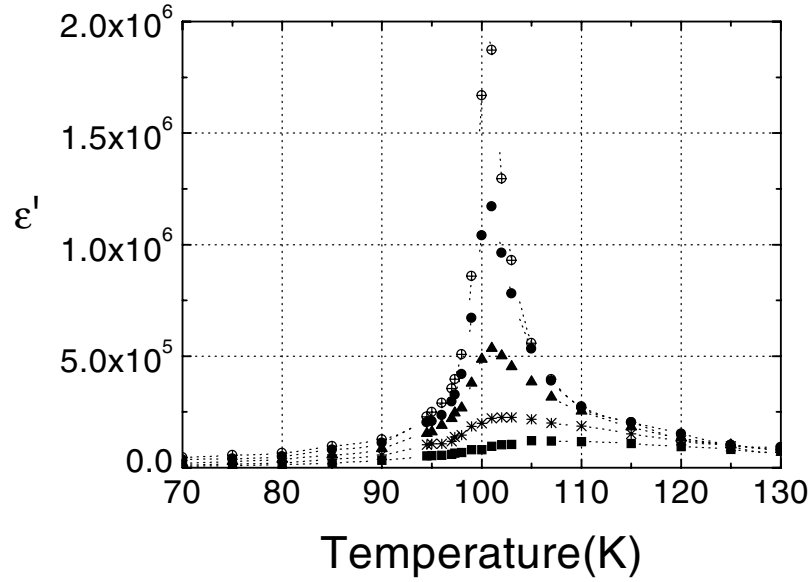
Figure 2. Temperature dependence of the real part of the dielectric permittivity ϵ' of $(TMTTF)_2AsF_6$ at frequencies: 100 kHz ($\oplus$), 300 kHz ($\bullet$), 1 MHz ($\blacktriangle$), 3 MHz ($*$), 10 MHz ($\blacksquare$).

Above T_ρ, the magnitude of the real part of the dielectric constant $\epsilon' = \mathrm{Im}\,\sigma(\omega)/\omega$ is below the resolution of our experimental setup. The appreciable growth of ϵ' begins only below T_ρ without visible frequency dependence down to $\simeq 140$ K. The most interesting frequency and temperature dependence of ϵ' is observed in a narrow temperature interval in the region of 100 K (figure 2). With decreasing T below about 130 K, we observed: (i) a considerable increasing of the frequency dispersion of ϵ'; (ii) a sharp growth of the magnitude of ϵ' with a tendency to diverge near $T \simeq 100$ K, characteristic for all frequencies under investigation, but more pronounced at low frequencies when ϵ' approaches the huge value of 2×10^6; and (iii) a very deep decrease of the ϵ' magnitude for temperatures below 100 K with a simultaneous decrease in frequency dispersion. Figure 2 shows data for frequencies at and above 10^5 Hz. Although measurements at lower frequencies show a still larger value of ϵ' near 100 K, however, scattering of experimental points became increasingly larger due to the effect of the finite orthogonality of the impedance analyser [11]. The temperature at which ϵ' is maximum does not depend on frequencies below 10^6 Hz within the accuracy of our measurements. At higher frequencies, the maxima move to higher temperatures.

As can be seen from figure 1, at temperatures below about 25 K, the normalized value G/G_0 decreases down to 10^{-6}, i.e below the resolution of our impedance analyser. Measurements at low T in the range of the SP phase transition [3] are underway using specific devices for low conductance samples.

As follows from our measurements and from data published earlier [3], $(TMTTF)_2AsF_6$ shows at room temperature a metallic type of conductivity. Below $T_\rho = 230$ K where the conductance reaches a maximum, G decreases following a thermally activated variation with a relatively small activation energy $\Delta\rho = 175$ K. This general behaviour of $(TMTTF)_2X$ samples with centrosymmetrical anions Br, PF$_6$ and AsF$_6$ is related to the small dimerization in the host molecular lattice resulting in the so-called charge localization [1]. This value of $\Delta\rho = 175$ K ranges between 100 K for Br salt [12], and 300 K in PF$_6$ salt [9, 10]. Quantitative estimates

of the charge gap were made in [13] for different values of the on-site Coulomb repulsion U and for the respective values of the intermolecular transfer integrals t_1 and t_2 along the stacks determined from quantum chemistry calculations [14]. In the case of the strong coupling limit, $U \gg t_1, t_2, 4t_1^2/t_2$, it was shown [13] that the charge gap is equal to the dimerization gap with a $1/U$ correction.

Neither magnetic spin susceptibility [1] nor x-ray diffuse scattering [3, 4] of $(TMTTF)_2AsF_6$ have revealed any variation in the temperature range around 100 K. However, an abrupt change in slope of the temperature dependence of the thermopower was reported around 95 K [15]. Therefore, our finding for the first time of very pronounced features in conductivity (figure 1) and dielectric constant (figure 2) shows unambiguously that $(TMTTF)_2AsF_6$ undergoes a phase transition in this temperature range. This phase transition is characterized by a sharp decrease of the conductance with a larger energy gap $\Delta = 350$ K at lower temperature and by a divergency of the dielectric permittivity ϵ' with a very large value above 10^6, close to the ϵ' magnitude measured for quasi-one-dimensional CDW and SDW systems [11, 12]. The growth of ϵ' above T_{CO} and its subsequent decrease below T_{CO} proceed with different rates, as can be seen in figure 3 where $(\epsilon')^{-1}(T)$ is drawn. The two branches above and below T_{CO} are very close to being linear, i.e to following the Curie law $\epsilon' \sim A/|T_{CO} - T|$. The slopes of these branches on the left and on the right are different, as typical for a second order phase transition near the transition temperature T_{CO} [6]. The crossing of the two branches yields very accurately the transition temperature, namely $T_{CO} = 100.6$ K.
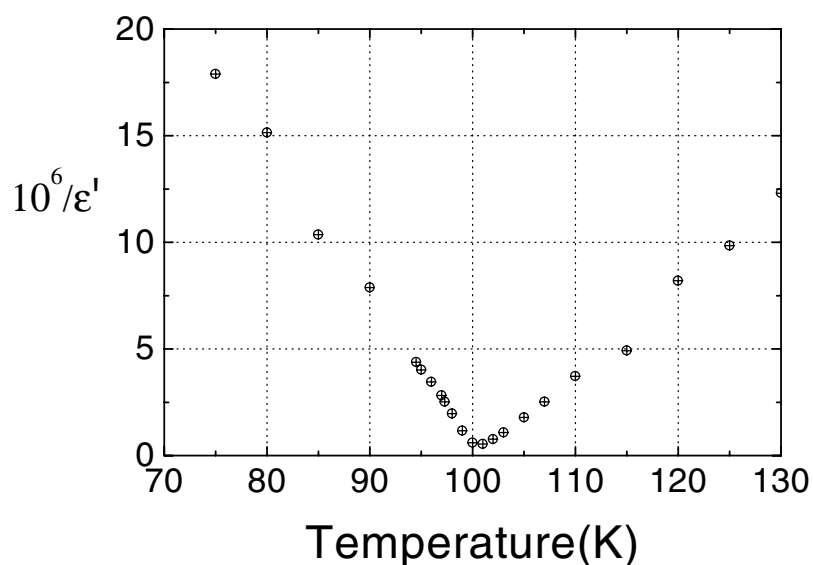

Figure 3. Temperature dependence of the inverse of the real part of the dielectric permittivity ϵ' of $(TMTTF)_2AsF_6$ ($\times 10^6$) at the frequency 100 kHz.

What is the physical nature of this phase transition which, as was mentioned above, is not accompanied by any visible structural and magnetic modification near T_{CO}? We suggest the explanation based on the reconstruction of the electron energy spectrum due to pure electronic charge-induced correlation phenomena of the Wigner type. As was shown, electron–electron correlation phenomena play a leading part between many factors which determine the properties of $(TMTTF)_2X$ salts [1]. Due to dimerization, the system is effectively half-filled. In

this case, it was shown from the general theory of one-dimensional electron gas models [16,17] with Umklapp scattering that a one-site repulsion U will open a gap in the charge sector. Other models are based on various versions of the Hubbard model [13, 18–21] taking into account both interactions between electrons on the lattice sites (on-site interaction) and on the neighbouring sites (near-neighbour interaction). Using Monte Carlo techniques, it was shown that long range Coulomb near-neighbour interaction can produce a space charge modulation with a wave vector $4k_F$ (a $4k_F$ CDW) [18]. Analoguously it was recently shown that for a one-dimensional chain with or without dimerization a $4k_F$ CDW superstructure may occur with charge disproportionation for a large enough near-neighbour interaction [21]. We consider that the phase transition we found in $(TMTTF)_2AsF_6$ near 100 K is due to the formation of such a charge-ordered superstructure. Since in this temperature range the electron–phonon interaction is probably weaker than the electron–electron interaction, the formation of the $4k_F$ CDW superstructure is not accompanied by a modulation of the host lattice as in the case of a Peierls CDW. In these conditions the spin induced magnetic electron–electron interaction (which causes at low temperatures, typically around 10 K, a transition into a magnetic spin ordered state) is also weaker than the charge-induced one. This fact corresponds to the so-called spin–charge separation phenomena in one-dimensional conductors [1, 16], and it explains the absence near 100 K of any variation on the magnetic properties of this compound [1, 5].

Direct experimental evidence of charge disproportionation and charge ordering appeared recently [22] from NMR measurements on an analoguous quasi-one-dimensional material, namely $(DI-DCNQI)_2Ag$, a quarter-filled band conductor without dimerization. Our preliminary measurements of the dielectric permittivity on this compound show also a peak in the magnitude of ϵ' near the phase transition into the charge-ordered state [23].

Recent NMR studies [24] have also shown a charge redistribution of charge density between neighbouring sites of the molecular lattice, i.e a charge disproportionation near 100 K in $(TMTTF)_2AsF_6$ and at 65 K in $(TMTTF)_2PF_6$. For this latter compound this temperature agrees very well with our measurements of divergency of ϵ', which we reported earlier [9, 10].

The existence of a charge gap below T_ρ does not prevent the formation of a new charge-ordered state at a lower temperature T_{CO}. The magnitude of the energy gap below T_{CO} can be estimated as the sum of squares of the initial charge energy gap Δ_ρ and of the gap resulting from the charge ordering Δ_{CO} [4]; so, from the values we measured for $\Delta_\rho = 175$ K and $\Delta = 350$ K, we can estimate Δ_{CO} for $(TMTTF)_2AsF_6$ to be $\Delta_{CO} = \sqrt{\Delta^2 - \Delta_\rho^2} = 300$ K.

We ascribe the large value of the dielectric permittivity ϵ' near T_{CO} and its characteristic divergency proportional to $A/|T - T_{CO}|$ as resulting from the instability of the electron spectrum and from strong fluctuations of the order parameter (degree of charge ordering in the present case) which develop in a relatively wide temperature range near the phase transition. In this temperature range, the large ϵ' magnitude originates from the collective response of relatively large coherent charge-ordered domains weakly linked to the molecular lattice. With decreasing temperature below T_{CO}, interchain correlations and interchain interactions increase, both favouring the formation of a $4k_F$ commensurate charge superstructure with the result of a sharp decrease of ϵ'.

We have found in $(TMTTF)_2AsF_6$ a sharp decrease of the conductance and a divergency of the dielectric permittivity at $T_{CO} = 100.6$ K. These results give direct evidence of a phase transition, unknown up to now, in a new charge-ordered state ($4k_F$ CDW of Wigner type) due to charge induced electron–electron correlations.

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