The effect of deuteration on the transition into a charge ordered state of $(TMTTF)_2X$ salts

LETTER TO THE EDITOR

The effect of deuteration on the transition into a charge ordered state of (TMTTF)$_2$X salts

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Abstract
From dielectric permittivity measurements, we show that deuteration yields a large increase of the transition temperature for the charge ordered state of (TMTTF)$_2$X (X = AsF$_6$, SbF$_6$, ReO$_4$) salts. We propose an explanation of this phenomenon, suggesting that deuteration induces a modification of the (TMTTF)$_2$X crystal unit cell.

It was recently shown from studies of dielectric permittivity [1–4], NMR [5, 6] and x-rays [7] that quasi-one-dimensional conductors of the (TMTTF)$_2$X family undergo a phase transition at T_{CO} into a charge superstructure—the charge ordered state (COS); this COS is observed in the temperature range between room temperature, where conductivity of metallic type predominates, and low temperature (about 20 K), where effects of magnetic ordering are seen. It is well known that the large variety of the states realized in (TMTTF)$_2$X salts results from the complexity of their crystal structure and from the many types of interaction inherent in these crystals: the interplay between such types of interaction as intrastack and interstack, electron–electron, electron–phonon interactions, interaction of molecular chains with anion chains, magnetic interactions, etc, govern the ground states of these crystals. Variation in factors such as the type of anion charge symmetry, temperature, magnetic field, pressure yields a change in the ratio between contributions of the above-mentioned interactions, thus providing the realization of various ground states.

According to theoretical [8–11] and experimental [1–7] results, the formation of a COS is currently considered in terms of the extended Hubbard model including correlated electron–electron on-site (U) and next neighbour intersite (V) interactions. However, the question of the effective factors providing the stability of COS is still an open and actively discussed question. As stated in some recent reports, the magnitude of the available next neighbouring interaction V is insufficient for the stabilization of the COS, and additional interactions such as electron–phonon [9, 11] interaction and that with anion chains [3, 10] have to be included. Thus, as

was shown in [3, 4], the shift of anion chains as a whole—a transition with a wavevector $q = 0$—can provide stability of the COS; the resulting breaking of the inversion symmetry centre of the two TMTTF molecules in the unit cell may yield the spontaneous dipole moment associated with the charge imbalance on the two molecules and consequently provide the ferroelectric properties measured in dielectric permittivity studies [3, 4]. Additionally, the anion type and the form of its charge symmetry (octahedron, tetrahedron etc) determine to a great extent the COS transition temperature T_{CO} and often the sequence of ground states with decreasing temperature (metallic, localization, COS, anion ordering, magnetic ordering) [2, 4]. The recent results on the effect of pressure on the ground states of $(TMTTF)_2SbF_6$ [12] are also interpreted in the framework of such suggestions. However, the question of the influence of others factors, for example the role of the amplitude of chain dimerization, needs to be better evaluated.

In addition to usual factors of action on a given crystal such as temperature and pressure, the exchange of hydrogen with deuterium in the methyl group of the TMTTF molecule has been used in the study of $(TMTTF)_2X$ compounds; it corresponds, in fact, to the study of an analogue of the isotopic effect. Indications of the increase of T_{CO} for AsF_6 and SbF_6 salts were obtained from measurements of the spin susceptibility [13]. It was also shown that the transition temperature in the spin–Peierls state at low temperature was decreased in deuterated AsF_6 salt [13]. Hereafter we report results of conductance and dielectric permittivity measurements for deuterated $(TMTTF)_2X$ samples with $X = AsF_6$, SbF_6 and ReO_4. The perdeuterio-TMTTF, TMTTF-d_{12}, was synthesized partially following the method of TMTSF-d_{12} after Wuld *et al* [14]. GC-MAS spectroscopy showed more than 97% deuteration. We have made measurements on single crystals with well defined facets and with length about 3 mm and cross section 10^{-4}–10^{-5} cm^2. Electrical contacts were prepared by attaching thin gold wires with silver paste on gold pads evaporated onto the sample ends. It should be noted that the absolute magnitude of the conductivity at room temperature of deuterated samples is smaller than that of hydrogenated ones. Measurements of real and imaginary parts of the complex conductance were carried out using the impedance analyser HP 4192A in the frequency range 10^3–10^7 Hz. The temperature regulation (cooling rate below 0.2 K min^{-1}) and the measurements of the conductance were carried out in an automatic regime under computer control.

Figure 1 shows the temperature dependences of the real part of the conductance G, normalized by its room temperature value G_0, for $(TMTTF-d_{12})_2AsF_6$ and $(TMTTF-d_{12})_2SbF_6$ (inset in figure 1) with the appropriate dependences in non-deuterated samples [2]. As can be seen from figure 1 these dependences $(G/G_0)(1/T)$ are qualitatively similar for H and D samples of the AsF_6 salt. However, the effect of deuteration yields (a) a whole shift of the $G(1/T)$ curve towards the high temperature range, (b) an increase of the temperature at which $G(1/T)$ shows a bump which corresponds to the temperature of the phase transition in COS, T_{CO}, (c) an increase of the temperature, T_ρ, from 230 to 250 K where the conductance is maximum. Below T_{CO} both $(G/G_0)(1/T)$ dependences, of deuterated and non-deuterated samples, are parallel down to 30 K, the minimum temperature at which our experiments were performed. The thermoactivated decrease of the conductance below T_{CO} is associated with the formation of an energy gap Δ_{CO} as a result of the COS transition [1, 2]. The parallelism of the $G(1/T)$ dependences of $(TMTTF-d_{12})_2AsF_6$ and $(TMTTF)_2AsF_6$ samples at low temperature indicates the approximate equality of their energy gap within the accuracy of our measurements.

In the case of the $(TMTTF-d_{12})_2SbF_6$ sample the $(G/G_0)(1/T)$ curve is also qualitatively similar to the appropriate curve for the non-deuterated sample with a shift to the higher temperature range (inset in figure 1). As is known, in the SbF_6 salt the $G(1/T)$ dependence does not exhibit any maximum at T_ρ before the transition into the COS at T_{CO} [4]. Probably this fact can be associated with the small dimerization of the molecular chains in SbF_6 salt and
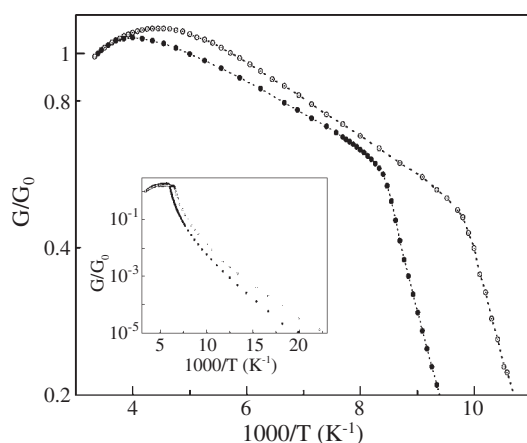
Figure 1. Arrhenius plot of the conductance G of $(TMTTF)_2AsF_6$, normalized by its room temperature magnitude G_0, at frequency 1 kHz for deuterated (●) and non-deuterated forms (⊙). The inset shows the analogous G/G_0 dependences for deuterated (●) and non-deuterated (⊙) $(TMTTF)_2SbF_6$.
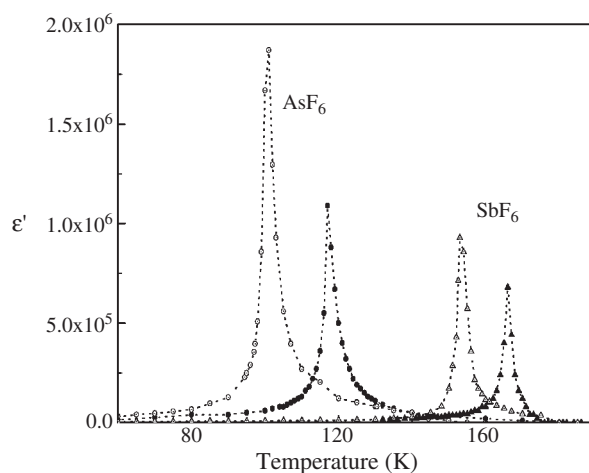

Figure 2. Temperature dependences of the real part of the dielectric permittivity ϵ' at frequency 100 kHz; $(TMTTF)_2AsF_6$: deuterated (●) and non-deuterated (⊙); $(TMTTF)_2SbF_6$: deuterated (▲) and non-deuterated (△).

with the abrupt decrease of G at T_{CO} before the development of charge localization occurring normally at T_ρ. As can be seen from the inset in figure 1 the slope at low temperature of the $(G/G_0)(1/T)$ curve for the deuterated sample is slightly larger than that for the non-deuterated one. That corresponds to a small increase of Δ_{CO} up to 660 K in comparison with 550 K for the non-deuterated sample [2, 4].

Figure 2 shows the temperature dependences of the real part of the dielectric permittivity ϵ' for deuterated and non-deuterated $(TMTTF)_2AsF_6$ and $(TMTTF)_2SbF_6$ samples. All these curves exhibit a pronounced peak at the temperature of the COS phase transition where the dielectric constant shows a divergence [1–4]. As can be seen from figure 2 the effect of deuteration leads to a considerable shift of the peaks in $\epsilon'(T)$ curves to higher temperatures,
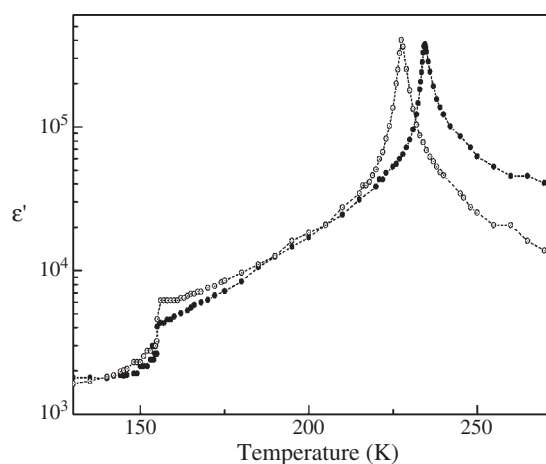
Figure 3. Temperature dependences of the real part of the dielectric permittivity ϵ' of $(TMTTF)_2ReO_4$ at frequency 1 MHz for deuterated ($\bullet$) and non-deuterated forms ($\odot$).

by 16 K for AsF_6 salt and by 13 K for SbF_6 salt. In addition, the magnitudes of the ϵ' maxima decrease. In other respects the forms of the $\epsilon'(T)$ dependences near T_{CO} for both deuterated AsF_6 and SbF_6 salts are well described by a Curie law $1/\epsilon'(T) \sim |T - T_{CO}|$, analogously to non-deuterated samples [2]. The frequency dependences of the $\epsilon'(T)$ curves do not appreciably change as a result of deuteration for either AsF_6 or SbF_6 salts.

The variations of the temperature dependence of the dielectric permittivity ϵ' for $(TMTTF)_2ReO_4$ occurring as a result of deuteration are shown in figure 3 on a semi-logarithmic scale, for better visibility of the low temperature part of the $\epsilon'(T)$ curves. For this salt we also observed a shift of the $\epsilon'(T)$ peak, corresponding to the COS transition [2, 4], to higher temperature by 7 K. The form of the $\epsilon'(T)$ dependence near T_{CO} for deuterated ReO_4 salt is similar to that for the non-deuterated one, but with a slightly smaller amplitude of the maximum of the peak in ϵ'. The second anomaly in the temperature dependence of ϵ' for $(TMTTF)_2ReO_4$ salt is observed near the temperature $T_{AO} \approx 155$ K which corresponds to the anion ordering transition with the wavevector $q = (1/2, 1/2, 1/2)$ [2, 4]. Below T_{AO}, ϵ' sharply decreases. As can be seen from figure 3 the $\epsilon'(T)$ dependences for deuterated and non-deuterated ReO_4 salts in the T_{AO} temperature range are qualitatively similar. However, unlike the case for the phase transition into the COS state, the transition into the AO state in the deuterated ReO_4 salt occurs at practically the same temperature T_{AO} as in the non-deuterated one.

From all above-mentioned data it follows that deuteration does not have a qualitative effect on the sequence and the kinds of the phase transitions in $(TMTTF)_2X$ ($X = AsF_6$, SbF_6 and ReO_4); however, the quantitative characteristics of these transitions are changed. As seen in figure 1, deuteration yields a shift of the whole $G(1/T)$ curve to higher temperatures, i.e. to a simultaneous increase of T_{CO} and T_ρ. This may signify that deuteration influences the bond dimerization, which determines T_ρ, as well as electron correlation effects, which determines T_{CO}, while it does not influence the anion ordering transition (because T_{AO} does not change).

In our attempt at explaining the T_{CO} increase induced by deuteration, we are led to consider the following facts. First, as follows from structural studies, the volume of the unit cell W and the length of the unit cell a increase along the anion sequence: Br, PF_6, AsF_6, SbF_6 (see in table 1 the structural data taken from [7, 15–17]). It has to be noted that the anion volume itself increases following the same sequence; that probably determines the appropriate growth of the

Table 1. Room temperature structural and electrical data for (TMTTF)$_2$X.

Anion X	a (Å)	W (Å^3)	σ_0 (Ω^{-1} cm^{-1})	T_{CO} (K)
Br	7.03	616	100	28
PF$_6$	7.136	672	40	70
AsF$_6$	7.175	698	20	101
SbF$_6$	7.183	707	10	153

unit cell [15]. Second, as can be seen from table 1, the magnitude of the conductivity at room temperature decreases when considering the same anion sequence; that has to be correlated with the growth of a and of the unit cell volume [16]. Third, the COS transition temperature, T_{CO}, increases with the a and W growth. Fourth, the application of pressure yields the decrease of T_ρ and T_{CO} [6, 12, 19] and most probably also the decrease of a.

A qualitative phenomenological explanation of these experimental facts may be based on a simple assumption, namely that the distance R between the TMTTF molecules is an important factor, which determines both the conductivity and the charge ordering phenomena for these molecular stacks. Indeed, this distance R determines the degree of overlap of orbitals of the TMTTF molecules along the chains and it is natural that, when R increases, the overlap decreases and the conductivity falls [15, 20]. Taking into account these considerations as well as the already mentioned fact of the decrease of the room temperature conductivity σ_0 with the growth of R in the sequence of anions (table 1), we assume that the decrease of σ_0 which we have observed in deuterated AsF$_6$ and SbF$_6$ samples can be ascribed to the growth of R induced by deuteration.

In accordance with [2–4], the phenomenon of charge ordering may be most naturally explained on the basis of the extended Hubbard model taking into account Coulomb correlated electron interactions on TMTTF chains. The magnitude of these interactions is governed by the ratio V/t [8–11], where V is the potential of the next neighbouring interaction and $t = (1/2)(t_1 + t_2)$ is some effective intrachain transfer integral, with t_1 the transfer integral within dimers and t_2 the transfer integral between dimers. Usually the difference between t_1 and t_2 is not very large and it decreases with decreasing temperature [22]. The interchain transfer integrals are about one order of magnitude smaller than the intrachain ones and they can be neglected [22].

The interaction of molecular chains with anion chains is probably not a decisive factor for formation of the CO state, although the shift of anion chains with regard to molecular chains is the factor which ensures the stability of the CO state. As can be seen from figure 3, deuteration does not lead to any change of the transition temperature T_{AO} into the anion ordered state, i.e. it can hardly have an influence on the anion interaction and on the anion ordering. On the other hand, deuteration leads to a considerable increase of the transition temperature T_{CO} on entering the charge ordered state on molecular chains, i.e. it has an influence on the interactions within these chains. That favours our suggestion that long range Coulomb correlated interactions along molecular chains are the driving force for the CO transition.

In the simplest case, the magnitude of V, determined by long range Coulomb interactions, is proportional to $1/R$, while the magnitude of t, determined by orbital overlap, is proportional to $1/\exp R$ [22]. As was shown in recent theoretical studies [20–23], the magnitude of V/t in the (TMTTF)$_2$X family is large enough for the development of COS, and V/t grows with increase of R under certain conditions. It is natural to suggest that, since the V/t magnitude determines the possibility of the transition into the COS [8–11], so for a larger magnitude of V/t the phase transition into the COS will occur at higher temperatures. This suggestion
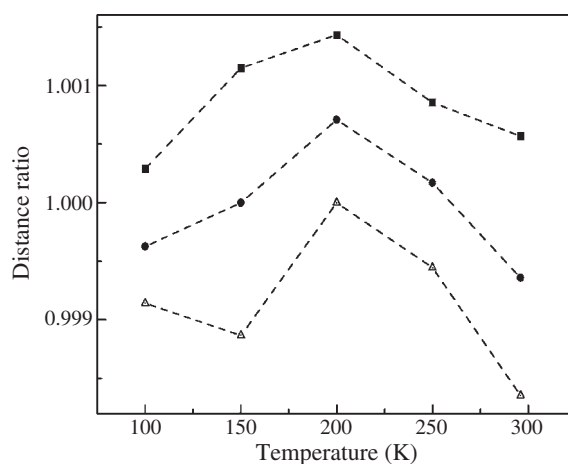
Figure 4. Variation with temperature of the ratio of the lengths of dimers in deuterated (B_D) and non-deuterated (B_H) (TMTTF)$_2$SbF$_6$ (■), the ratio A_D/A_H of the lengths in deuterated and non-deuterated samples (△) and the ratio of the unit cell lengths, a, in deuterated (a_D) and non-deuterated (a_H) samples (●).

agrees well with the T_{CO} increase concomitant with the growth of R in the anion sequence Br, PF$_6$, AsF$_6$, SbF$_6$ (table 1).

In order to determine the change of the distances between TMTTF molecules along molecular chains due to effect of deuteration, we have carried out structural studies of (TMTTF-d$_{12}$)$_2$SbF$_6$ and hydrogenated (TMTTF)$_2$SbF$_6$ samples at several temperatures from room temperature down to 100 K [13]. As is well known, the molecular chains in (TMTTF)$_2$X salts are slightly dimerized, i.e. the distances between neighbouring TMTTF molecules are not equal: with B the distance within the dimer, the distance A between dimers is slightly larger than B. Figure 4 shows the temperature dependences of the ratio of the dimer length in the deuterated sample, B_D, to the appropriate length in a non-deuterated sample, B_H, as well as the ratio A_D/A_H and the ratio of the unit cell lengths a in D and H samples: a_D/a_H. As can be seen from figure 4, deuteration does indeed leads to an increase of the dimer length B throughout the temperature range. Relative growth of a is also observed in the temperature range 200–150 K. As far as the distance between dimers, A, is concerned, A_D for the deuterated sample is smaller than the value A_H for the hydrogenated one except in the temperature range around 200 K, where A_D and A_H are equal. The result of these measurements indicates a decrease of dimerization (B/A) in deuterated samples. Figure 4 shows that these ratios are not monotonically temperature dependent. The dimer length B and the length of the unit cell a increase in the temperature range near 200 K, i.e. in the same temperature range where the charge ordered state appears in SbF$_6$ salt. It seems to us that these data confirm qualitatively the above-mentioned phenomenological picture. However, the reality appears more complicated and cannot be reduced to a simple growth of all parameters of the unit cell with deuteration. A deeper theoretical analysis is clearly needed, taking into account, for example, the variation of dimerization of molecular chains. Nevertheless, it appears most likely that the increase of T_{CO} that we measured in deuterated (TMTTF)$_2$AsF$_6$, (TMTTF)$_2$SbF$_6$ and (TMTTF)$_2$ReO$_4$ samples can be associated with the growth of the ratio V/t due to the increase of the distance between TMTTF molecules along their molecular chains.

Isotopic substitution also has a great effect on the transition into other ground states which occur in 1D and 2D organic compounds. For example, deuteration yields an increase of the

superconducting critical temperature of the 2D organic compound κ-$(ET)_2Cu(NCS)_2$ (ET is the organic molecule bis(ethylenedithio)-tetrathiafulvalene; see [24] and references therein). Simultaneously it was shown from angle-dependent magnetoresistance measurements that the warping of the Fermi surface is increased and that the interlayer transfer integral decreases [25]. However, it should be noted that in other 2D organic compounds such as κ-$(ET)_2Cu[N(CN)_2]Br$, the superconducting T_c decreases with deuteration [25]. Additionally, as indicated above for $(TMTTF)_2AsF_6$ [13] and also found from neutron scattering experiments on $(TMTTF)_2PF_6$ [26], the spin–Peierls transition temperature in these compounds decreases with deuteration. Thus, the effect of isotopic substitution depends on a subtle interplay between the various interactions which govern this transition.

In summary, from dielectric susceptibility measurements, we have found that deuteration of $(TMTTF)_2X$ salts $(X = AsF_6, SbF_6$ and $ReO_4)$ yields an increase of the characteristic temperatures for charge localization, T_ρ, and for charge ordering, T_{CO}, while the temperature of the anion ordering transition, T_{AO}, does not change. We tentatively explain these effects, considering the evolution of parameters for salts with different anions X, in terms of an increase of the distance between TMTTF molecules along the molecular chains induced by deuteration

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