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Charge localization in organic conductors $(\mathrm{TM})_2\mathrm{X}$: The influence of anion ordering

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Abstract. An investigation of the different contributions leading to charge localization in a 1/2 or 1/4 filled band 1D conductor has been conducted through a study of transport properties in the solid solution $[(\mathrm{TMTSF})_{1-x}\ (\mathrm{TMTTF})_x]_2\mathrm{ReO}_4$. The existence of an ordering transition of the anions allows to identify two contributions to the electronic potential with wave vector $4k_F$. A dominant on-site $4k_F$ potential besides the bond contribution is revealed when Umklapp scattering is pertinent *via* the weakening of the localization arising at the $(0, 1/2, 1/2)$ anion ordering which is stabilized under pressure in the compound $[(\mathrm{TMTSF})_{0.5}\ (\mathrm{TMTTF})_{0.5}]_2\mathrm{ReO}_4$ *at variance* with the enhancement of localization observed in the homomolecular $(\mathrm{TMTTF})_2\mathrm{ReO}_4$ material.

PACS. 71.10.Pm Fermions in reduced dimensions (anyons, composite fermions, Luttinger liquid, etc.) – 74.70.Kn Organic superconductors

Organic conductors belonging to the $(\mathrm{TM})_2\mathrm{X}$ series where X denotes an anion such as Br^-, PF_6^-, ClO_4^- or ReO_4^- and TM means either the sulfur based or the selenium based donor molecule tetramethyltetra(thia/selena)fulvalene are important materials since they have provided the first case for superconductivity among organic conductors [1]. Due to the pronounced one-dimensional (1D) character of their electronic structure, they are also very interesting materials where the particular hall marks of 1D physics can be identified and studied in some details [2]. In a 1D conductor, collective modes associated either to spin or to charge fluctuations do not decay in time unlike ordinary quasiparticle excitations. These collective excitations become therefore the only long-lived low-lying excitations of the 1D Luttinger liquid. Furthermore, spin and charge modes are decoupled in a 1D conductor. If only chemical considerations are taken into account the highest occupied molecular orbital (HOMO) for each pair of TM molecules is populated with three electrons so that the band becomes quarter-filled in terms of holes with the Fermi wave vector $k_F = \pi/2a$ where a is the distance between anions along the stacking axis. However, structural analysis has revealed the existence of a non-uniform stacking of the molecules. There exists an alternation of the intermolecular distance which gives rise to a lattice dimerization and in turn to an alternation of the intrachain hopping integral, t_1 and t_2 [3]. The charge distribution acquires a modulation with the wavevector $2\pi/a$ which creates a new Brillouin zone at $k = \pm\pi/a$. This is a $4k_F$ bond potential due to the presence of anions in the structure. The bond alternation opens a gap $2\Delta_D = 2(t_1 - t_2)$ at $k = \pm\pi/a$ in a band $W = 2(t_1 + t_2)$ wide which becomes effectively half-filled.

The existence of Coulomb interactions in the 1D half-filled band conductor generates a correlation-induced charge localization (Mott-Hubbard charge localization) through Umklapp scattering g_3 of two carriers near the Fermi level with total momentum exchange $4k_F$ equal to a reciprocal lattice vector [4]. The resistivity is activated, $\rho(T) = \rho_0 \exp(\Delta_\rho/T)$, below a temperature $T_\rho \simeq 2\Delta_\rho/\pi$, while the spin sector remains unaffected by this localization. The Mott-Hubbard localization effects are more pertinent in conductors pertaining to the sulfur series than in the selenium one. They have been studied extensively in $(\mathrm{TMTTF})_2\mathrm{PF}_6$ and $(\mathrm{TMTTF})_2\mathrm{Br}$ with $T_\rho = 250$ and 100 K respectively [5].

These latter salts contain anions whose symmetry (octahedral) does not disturb the inversion symmetry of the site where they are located. The situation is qualitatively different for anions such as ClO_4 or ReO_4 which are non centrosymmetric [6]. The oxygen atom of these tetrahedral anions can point towards S or Se atoms of one of the neighbouring TM molecules thus establishing a short anion-molecule contact. The many orientations of the anions which are possible in the structure allow at high temperature a restoration of the inversion symmetry on the average. However, these anions order at low temperature leading to a superstructure $\mathbf{q}_1 = (1/2,\ 1/2,\ 1/2)$

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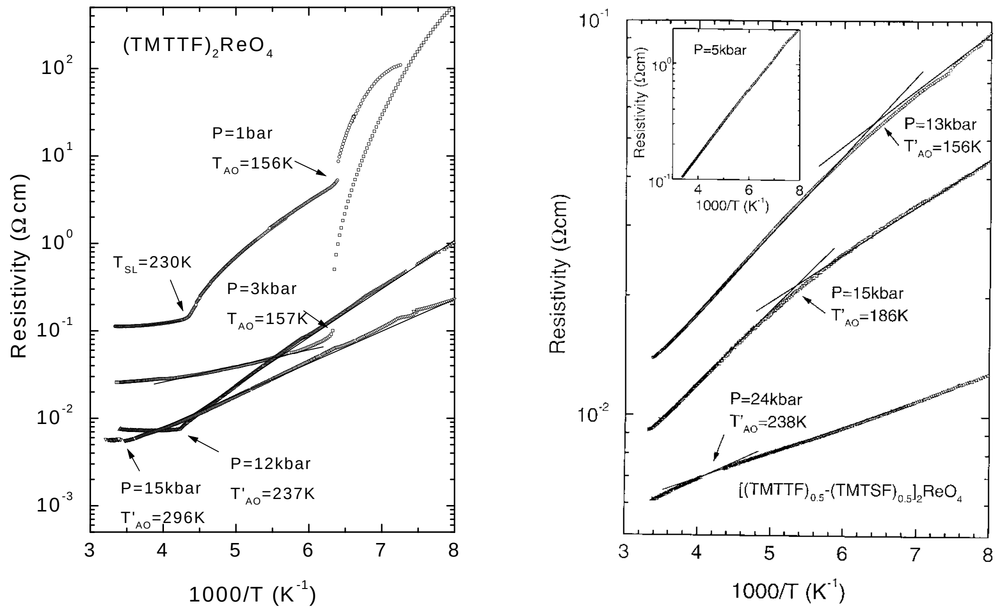

(a) (b)

Fig. 1. Resistivity data at different pressures plotted as ρ *versus* $1000/T$ in $(TMTTF)_2ReO_4$ (a) and $[(TMTSF)_{0.5}(TMTTF)_{0.5}]_2ReO_4$ (b).

in $(TMTTF)_2ReO_4$ and $(TMTTF)_2ClO_4$ at $T_{AO} = 154$ and 70 K respectively [6] . This $\mathbf{q}_1$ superstructure is accompanied by a $2k_F$ distortion of the organic stack which opens a gap at the Fermi level.

Such an anion ordering triggers in $(TMTSF)_2ReO_4$ a first order metal to insulator phase transition at $T_{AO} = 177$ K which is detected by transport [7] and NMR experiments [8]. However, structural studies have shown that the anion ordering reduced wave vector changes from $\mathbf{q}_1$ to $\mathbf{q}_2 = (0, 1/2, 1/2)$ under pressure. The two ordered phases coexist between 9 and 12 kbar and the $\mathbf{q}_2$ superstructure is completely established above 12 kbar [9]. This $\mathbf{q}_2$-ordering does not affect the electronic properties, the compound remaining metallic below the transition. The spin density wave ground state is replaced by a superconducting one above 9 kbar [10].

The present study has been motivated by an attempt to study the different possible sources for the $4k_F$ potential leading to localization in the presence of Coulomb repulsions in a 1/2 or 1/4 filled band 1D conductor. We shall see that the existence of an anion order under pressure allows to differentiate between on-site and bond contributions in the $4k_F$ potential.

Resistivity measurements were performed on needle shaped single crystals of typical dimensions $(2 \times 0.25 \times 0.1)\,\mathrm{mm}^3$ for $(TMTTF)_2ReO_4$ and $(2 \times 0.1 \times 0.05)\,\mathrm{mm}^3$ for $[(TMTSF)_{0.5}(TMTTF)_{0.5}]_2ReO_4$, using the four-contacts low-frequency lock-in technique. High pressure was provided in a clamped cell. Under ambient conditions, the a-axis conductivities were $\sigma_{RT} \simeq 10{-}20\,(\Omega\mathrm{cm})^{-1}$ and $\sigma_{RT} \simeq 2{-}4\,(\Omega\mathrm{cm})^{-1}$ respectively for the two studied compounds. In $(TMTTF)_2ReO_4$, σ increases linearly during pressurization with a pressure coefficient $\simeq +50\%\,\mathrm{kbar}^{-1}$, while the variation is much faster than linear in $[(TMTSF)_{0.5}\ (TMTTF)_{0.5}]_2ReO_4$ ($\sigma(20\,\mathrm{kbar})/\sigma(1\,\mathrm{bar}) \simeq 100$).

As far as $(TMTTF)_2ReO_4$ is concerned, the first order anion ordering is clearly visible at $T_{AO} = 156$ K in the charge sector through a jump of the resistance, Figure 1a. The temperature dependence of the resistivity reveals an additional anomaly at $T_{SL} = 230$ K, already observed in other experiments [11] which has been attributed to an increase of the $4k_F$ bond potential. The same "structureless" (SL) transition was identified in another large anion salt, $(TMTTF)_2SbF_6$, at 155 K [12].

Up to 6 kbar or so, the first order anion ordering is still observed at T_{AO} in the temperature domain 150–160 K. However significant modifications are observed above 7 kbar since the resistance instead of a jump undergoes a kink anomaly at a temperature which rises from 185 K at 7.5 kbar up to 296 K at 15 kbar, Figure 1a. The pressure dependence of the transition temperature T'_{AO} suggests, by analogy with the extensively studied behaviour of $(TMTSF)_2ReO_4$ [10,13], that the resistance kink anomaly is likely to be related to the ordering of the anions under pressure with wave vector $\mathbf{q}_2 = (0, 1/2, 1/2)$. The $\mathbf{q}_2$-ordering should have no drastic consequence on transport since the longitudinal energy dispersion is in turn not directly affected by such an ordering.

Furthermore, Figure 1a shows an activation of the resistance below T'_{AO} with an activation energy $\Delta_\rho \simeq 1100$ K at 9 kbar which is decreasing under pressure, Figure 2.

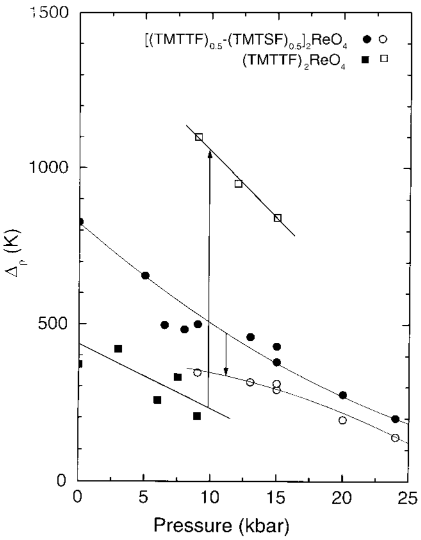

Fig. 2. Pressure dependence of the activation energy, Δ_ρ, of the resistivity in the high temperature disordered phase (filled symbols) and in the low temperature ordered phase (open symbols) for the two compounds.

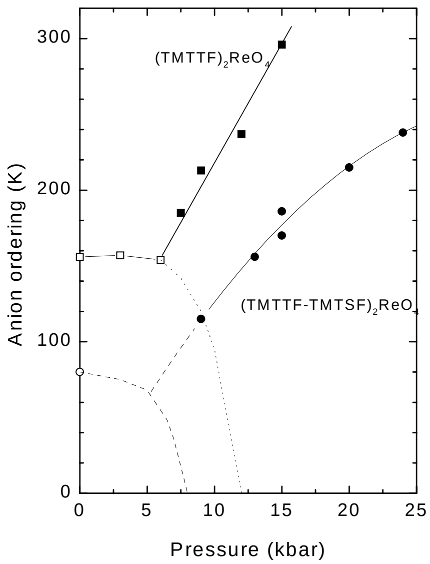

Fig. 3. Temperature-Pressure phase diagram of $(TMTTF)_2ReO_4$ and $[(TMTSF)_{0.5}(TMTTF)_{0.5}]_2ReO_4$ deduced from transport measurements. Open symbols correspond to $\mathbf{q}_1 = (1/2, 1/2, 1/2)$ anion ordering transition and filled symbols to $\mathbf{q}_2 = (0, 1/2, 1/2)$ transition. The dashed lines are arbitrarely drawn by analogy with phase diagrams of parent compounds in the same family.

It is interesting to compare the transport properties of $(TMTTF)_2ReO_4$ with those of the recently synthesised solid solution $[(TMTSF)_{1-x}$ $(TMTTF)_x]_2ReO_4$ [14]. The structure analysis has shown that the $x = 0.5$ compound, namely (S–Se)ReO_4 is actually a long range ordered crystal exhibiting an alternation of TMTSF and TMTTF molecules along the three crystallographic directions *a*, *b* and *c*. This molecular alternation breaks the inversion symmetry preexisting between molecules within a stack when they are of the same nature. Their on-site energies (energy of the HOMO level) become inequivalent and the $4k_F$ potential seen by the electrons acquires a component coming from the difference in on-site energies.This new compound provides a unique situation to study the role played by a $4k_F$ site contribution on the Mott-Hubbard localization. This contribution is absent in the disordered state of homomolecular $(TM)_2X$ salts [6]. Since extrema of the potentials are located on the molecular sites and shifted by a quarter of a wavelenght for on-site and bond potentials respectively, the on-site potential adds in quadrature to the bond potential leading to an enhancement of the localization gap $2\Delta_\rho$. The existence of such a $4k_F$ site potential has been invoked to explain the conductivity of (S–Se)ReO_4 being about five times smaller than the conductivity of the parent compound (S–S)ReO_4 with a localization gap about two times larger. As shown in Figure 2 from the analysis of the temperature dependent resistance in the non ordered phase, Figure 1b, Δ_ρ is a monotonously decreasing function on pressure in both (S–S)ReO_4 and (S–Se)ReO_4 due to the pressure induced decrease of the dimerization (and bond potential).

At ambient pressure, the anion $\mathbf{q}_1$-ordering has been identified at $T_{AO} = 82$ K not only through its consequence on the transport which is already strongly localized at low temperature but also *via* a concomitant drop of the susceptibility [15].

Although the resistance of (S–Se)ReO_4 exhibits a localized character over the whole pressure regime up to 24 kbar a close look at its temperature dependence reveals the existence of a kink anomaly at a pressure dependent temperature T'_{AO}, see Figure 1b. This kink anomaly is related to a well defined change in the transport activation. Moving through T'_{AO} the activation energy decreases by about 30%. It is tempting to ascribe it after a comparison with the (S–S)ReO_4 and (Se–Se)ReO_4 phase diagrams to the onset of anion ordering $\mathbf{q}_2$, Figure 3.

Figure 2 shows the most important result of this study, namely an increase and decrease of the localization gap $2\Delta_\rho$ going from non-ordered to $\mathbf{q}_2$-ordered phases of (S–S)ReO_4 and (S–Se)ReO_4 respectively. In order to explain the opposite effects of anion ordering on the localization in the two compounds we present in Figure 4 the structural changes induced by anion ordering on the organic stacks. The $(a,\ c - b)$ plane has been chosen as it is the plane containing the shortest contacts between the anions and the molecules along the $a + c - b$ direction. As long as a homomolecular compound is concerned, the $\mathbf{q}_2$-ordering establishes alternatively short and long contacts between anions and molecules (sulfur atoms) in a given stack, all neighbouring stacks being equivalent (Fig. 4, left). The effect of ordering is the creation of a $4k_F$ site potential leading in turn to an increase of the localization gap, as it is observed in the (S–S)ReO_4 compound. As far as the (S–Se)ReO_4 compound is concerned, assuming that the same $\mathbf{q}_2$ anion ordering is favoured by the preexisting (0, 1/2, 1/2) molecular ordering, short contacts between anions and either all sulfur or all selenium atoms are established (Fig. 4, right). Again, all neighbouring stacks are equivalent although we cannot decide which type of molecule

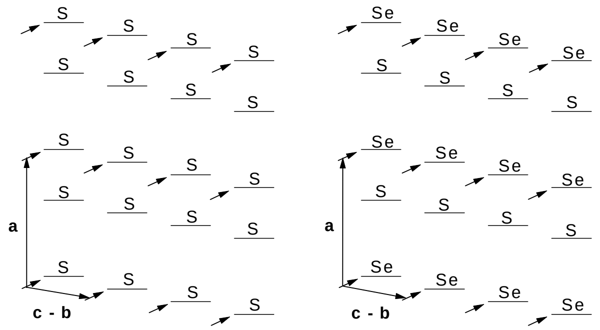

Fig. 4. Schematic representation of the organic stacks in the *(a, c-b)* plane for the $\mathbf{q}_2$-ordered phase of $(\mathrm{TMTTF})_2\mathrm{ReO}_4$ (left) and $[(\mathrm{TMTSF})_{0.5}(\mathrm{TMTTF})_{0.5}]_2\mathrm{ReO}_4$ (right) (Se (S) is for a TMTSF (TMTTF) molecule). The arrows indicate the short contact interaction between anions and molecules. The bond alternation has been exagerated for the clarity of the figure.

(TMTTF or TMTSF) has the closest contact with the anions. However, in order to explain a drop of the localization energy at the $\mathbf{q}_2$-ordering transition, the $4k_F$ potential thus created must compensate the preexisting site potential related to the alternation of organic molecules. Moreover, if bond potentials were modified at the anion ordering, the variations induced on the localization gap should have the same sign if not the same amplitude in both homomolecular and heteromolecular compounds.

The $\mathbf{q}_2$ anion superstructure is also present in the sulfur compound $(\mathrm{TMTTF})_2\mathrm{SCN}$ below 160 K at ambient pressure and under pressure up to 15 kbar. An increase of the resistivity has been observed in the ordered phase [16] which could be attributed to an enhancement of the localization energy as in the (S–S)ReO_4 compound. In conclusion, the study of transport properties under pressure of $(\mathrm{TMTTF})_2\mathrm{ReO}_4$ and $[(\mathrm{TMTSF})_{0.5}(\mathrm{TMTTF})_{0.5}]_2\mathrm{ReO}_4$ shows that in the presence of the $(0, 1/2, 1/2)$ anion ordering the 1D Mott-Hubbard localization is enhanced in the former compound while it is weakened in the latter. Opposite effects of anion ordering could be related to the modulation of the site energy existing for the ordered solid solution.

We may try to compare the data in Figure 2 with the estimate of the charge gap which has been made within the dimerized Hubbard model of a 1D chain at quarter filling [17,18]. Analytical results have been obtained in limits which are likely to be applicable to the compounds studied in the present work, namely the strong coupling limit as far as the Coulomb repulsion is concerned. According to the data in Figure 2 the decrease of the activation energy accompanying the onset of the $\mathbf{q}_2$-ordering in $[(\mathrm{TMTSF})_{0.5}(\mathrm{TMTTF})_{0.5}]_2\mathrm{ReO}_4$ amounts to about 150 K at 9 kbar. Following the previous heuristic argument for the influence of the $\mathbf{q}_2$-ordering on the $4k_F$ on-site localization we can say that 150 K is a lower limit estimate of the on-site activation energy. This latter energy might be larger since as mentionned above, site and bond potentials add in quadrature. The strong U limit of the model taking into account only the alternation of the on-site energies leads to $\Delta_c = 2\Delta_\rho = 2\varepsilon_0(1 - ct/U)$ where $2\varepsilon_0$ can be related to the difference in redox potential between TMTTF and TMTSF molecules ($2\varepsilon_0 = 130$ meV for TTF and TSF molecules [19]), c is a tabulated parameter [18] and t is the intrachain overlap integral taken from quantum chemistry calculations [20]. For this latter parameter, we have taken the average of the overlap integrals t_1 and t_2 for both TMTTF and TMTSF molecules in the PF_6 salt under ambient conditions, *i.e.* $t = 173\,\mathrm{meV}$. Since $2\varepsilon_0/t = 0.75$, Table III in reference [18] gives $c = 4.56$ and therefore $2\Delta_\rho = 27\,\mathrm{meV}$ leads to $U = 998\,\mathrm{meV}$. This value of the Coulomb repulsion not only justifies the strong U limit but is also in fair agreement with the derivation from NMR measurements performed on the parent compound $(\mathrm{TMTTF})_2\mathrm{PF}_6$ [21]. Figure 2 suggests also that the bond contribution to the activation energy is at most 350 K in the heteromolecular compound at 9 kbar. This value is not far from the data in $(\mathrm{TMTTF})_2\mathrm{ReO}_4$ ($\simeq 250$ K) and $(\mathrm{TMTTF})_2\mathrm{PF}_6$ ($\simeq 300$ K) at the same pressure. The comparison between theory and experimental data can be at best qualitative. A significant improvement will consist in taking into consideration in the Hubbard calculation the simultaneous existence of on-site and bond contributions to the localization gap.

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