The Impact of Discoveries of Ferroelectricity and Charge Disproportionation in Organic Conductors.

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Discoveries of the Ferroelectric anomaly (Nad, Monceau, et al) and of the related charge disproportionation (Brown et al) call for a revaluation of the phase diagram of the \((\text{TMTTF})_2X\) compounds and return the attention to the interplay of electronic and structural properties. We shall describe a concept of the Combined Mott-Hubbard state as the source for the ferroelectricity. We shall demonstrate the existence of two types of spinless solitons: \(\pi\)– solitons, the holons, are observed via the activated conductivity; the non-integer \(\alpha\)– solitons are responsible for the depolarization of the FE order. We propose that the (anti) ferroelectricity does exists hiddenly even in \(Se\) subfamily, giving rise to the unexplained yet optical peak. We remind then the abandoned theory by the author and Yakovenko for the universal phase diagram which we contrast with the recent one.

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I. INTRODUCTION. INTERPLAY OF ELECTRONIC AND STRUCTURAL PHASES.

The family \((TMTCF)_{2}X\), with \(C = T, S\), demonstrates almost all known electronic phases, see [3]. At higher temperatures \(T_{ao}\) there is also a set of weak structural transitions of "anion orderings" -AOs which are slight arrangements of chains of counterions X [4]. At even higher \(T \approx T_{0}\), another "structureless" transitions where observed sometimes [5] which origin stayed mysterious till now. Very recently their nature was elucidated by discoveries of the huge dielectric anomaly [6,7] and of the charge disproportionation seen by the NMR [8]. The phase transition has been interpreted [7] as the least expected one: to the Ferroelectric (FE) state. It is triggered by the uniform shift of ions yielding a macroscopic FE polarization which is gigantically amplified by the charge disproportionation at the molecular stack. The microscopic theory [7] for the "combined Mott-Hubbard state" was based on accounting for two orthogonal contributions, \(U_{b}\) and \(U_{s}\) to the Umklapp scattering coming from two symmetry breaking effects: the build in nonequivalence of bonds and the spontaneous nonequivalence of sites. This interference resembles the orthogonal mixing in the "combined Peierls state" [9] in conjugated polymers of the \((AB)_{x}\) type.

The FE transition in \(TMTTF - X\) is a very particular, as well as very bright, manifestation of the a more general phenomenon of the "charge disproportionation" or "charge ordering" which becomes recognized as a common feature of organic conductors (see the review [10] and other talks at this session). Similarly the earliest theoretical prediction [11] applies well to a common situation while the pronouncedly 1D electronic regime for the observed transition in \((TMTTF)_{2}X\) invokes particular difficulties as well as allows for a specially efficient treatment [7] which is also particularly suited for the FE transition.

The new events call for revaluation of studies in what was thought to be the abnormal metallic state [3] and return us to the old concept of the universal phase diagram [12,13] which was based upon effects of interference between electronic properties and fine symmetry changes due to the AOs or external fields. (See more in the Appendix.)
The usual $q \neq 0$ AOs were always observed for non centrosymmetric (NCS) ions, so that the orientational ordering, related to establishing short contacts of $O$ to $Se$ or $S$ atoms, was supposed to be a leading mechanism with positional displacements being its consequences only. But today we should think about a universal mechanism related to the displacive instability. These two orderings seem to be independent as it is supported by the latest finding of a sequence of the FE $q = 0$ and $q \neq 0$ transitions in $(TMTTF)_{2}ReO_{4}$ [6]. Already within the nonperturbed crystal structure the anions provoke the dielectrization. They dimerize intermolecular distances thus doubling the on-stack unit cell, hence changing the mean electronic occupation from 1/2 per molecule to 1 per their dimer. It originates [14] the small Umklapp scattering $U_{b}$ which opens (according to Dzyaloshinskii and Larkin, Luther and Emery) the route to the Mott-Hubbard insulator. (See [15] for a history introduction).

While bonds are dimerized, the molecules stay equivalent above $T_{0}$. The adventure of the NMR was a clear detection [8] for appearance at $T_{0}$ of the site nonequivalence as a sign of the charge disproportionation. But it brought the same observation both for the structureless transitions and for the AO already known as a very rare structure of the type $q_{2} = (0, 1/2, 1/2)$ in $(TMTTF)_{2}SCN$ where the site inequivalence was already known from the structural studies, see [4]. What is the difference then between the $q_{2}$ and the ”structureless” transitions? A clear cut fitting of the anomaly in $\epsilon(T)$ to the Curie law [6] suggests that we are dealing with the least expected case of the Ferroelectric -FE phase. Even more curiously, it is the FE version of the Mott-Hubbard state which usually is associated rather with magnetic orderings. The $q_{2}$ transition showed already the common polarization along a single stack but alternating in perpendicular directions which is the anti-FE ordering. For the ”structureless” transition all displacements must be identical $q = 0$, both along and among the chains/stacks, thus leading fortunately to the FE state. The polar displacement give rise also to the joint effect of the build-in and the spontaneous contributions to the dimerization, due to alternations of bonds and sites. (Both contributions can be of the build in type in the particular case of the $(TMTSF)_{0.5}(TMTTF)_{0.5}$ mixture [16].)
II. THE COMBINED MOTT-HUBBARD STATE AND THE FERROELECTRICITY.

The charge gap $\Delta = \Delta(U)$ appears as interference of two contributions to the Umklapp scattering: site $U_s$ and bond $U_b$, and it is a function of the total amplitude $U = \sqrt{U_s^2 + U_b^2}$.

The electronic energy $F_e$ depends only on $\Delta$ that is on the total $U$. But the energy $F_i$ of ionic displacements and of the related molecular distortions depends only on the spontaneous site component $U_s$: $F_i = 1/2KU_s^2$. The total energy $F_{tot} = F_e(U) + 1/2KU^2 - 1/2KU_b^2$ must be minimal over $U$ under the restriction $U > U_b$. The ground state will change if the minimum appears at some $U = U_0 > U_b$. Since $U_0 = U_0(T)$ increases with decreasing $T$, there will be a phase transition at $T = T_0$ such that $U_0(T_0) = U_b$.

Forms of the Umklapp energy $H$ can be derived from the symmetry alone [7]. The non-dimerized system allows only for $\sim U_4 \cos 4\varphi$, which usually is negligibly small as demonstrated by common 4-fold commensurate CDWs. The site and bond dimerizations originate $H^s_U = -U_s \cos 2\varphi$ and $H^b_U = -U_b \sin 2\varphi$ correspondingly. At presence of both types of dimerization the nonlinear Hamiltonian becomes

$$H_U = -U_s \cos 2\varphi - U_b \sin 2\varphi = -U \cos(2\varphi - 2\alpha), \quad \tan 2\alpha = U_b/U_s$$

For a given $U_s$, the ground state is still doubly degenerate between $\varphi = \alpha$ and $\varphi = \alpha + \pi$ which allows for phase $\pi$ solitons which are the charge $e$ spinless particles, the holons, observed in conductivity. Also $U_s$ itself can change the sign between different domains of ionic displacements. Then the electronic system must also adjust its ground state from $\alpha$ to $-\alpha$ or to $\pi - \alpha$, whichever is closer. Hence the domain boundary $U_s \leftrightarrow -U_s$ requires for the phase soliton of the increment $\delta\varphi = -2\alpha$ or $\pi - 2\alpha$ which will concentrate the non-integer charge $q = -2\alpha/\pi$ or $1 - 2\alpha/\pi$ per chain. While the 3D coupled ionic displacements are described by the MF approach, the electronic degrees of freedom must be treated exactly at given $U_s$ as described in [7]. The total Umklapp value is renormalized from $U$ to $U^*(U) \sim \Delta^2 = \Delta^2(U)$.

There are three contributions to the electronic polarizability:

1. Ionic displacements would already lead to the macroscopic polarization, like in usual
ferroelectrics, but alone they cannot explain the observed gigantic magnitude of the effect. Their contribution was estimated [7] as $\epsilon_i \sim 10^1 T_0 / |T - T_0|$ which is by $10^{-3}$ below the experimental value $\epsilon \approx 2.5 \times 10^4 T_0 / (T - T_0)$.

2. *Intergap electronic polarizability* is regular at $T_0$: $\epsilon_\Delta \sim \omega_p^2 / \omega_i^2$ where $\omega_p$ is the plasma frequency of the parent metal. This value can be as large as $\sim 10^4$ which corresponds indeed to the background upon which the anomaly at $T_0$ is developed.

3. *Collective electronic contribution*. can be estimated roughly, see more in [7], as a product of above two, $\epsilon_{el} \sim \epsilon_i \epsilon_\Delta$ which provides both the correct $T$ dependence and the right order of magnitude of the effect. We see that the anomalous diverging polarizability is coming from the electronic system, even if the instability is triggered by the ions which stabilize the long range 3D FE order.

III. DISCUSSION, PERSPECTIVES AND CONCLUSIONS.

By now the revaluation concerns only the TMTTF subfamily which usually, by the temperature $T_0$, is already in the Mott-Hubbard regime. The TMTSF compounds are highly conductive which today does not allow for these difficult experiments. Nevertheless the transition may be their, just being hidden or existing in a fluctuational regime like for stripes in High-$T_c$ cuprates. When it is confirmed, then the whole analyses [3] of intriguing abnormal metallic state will be revised as it already should be done for the TMTTF case. Probably the signature of the FE charge ordered state is already seen in optical experiments [17]. Indeed the Drude peak with a surprisingly low oscillation strength appearing within the pseudogap can be interpreted now as the optically active mode of the FE polarization; the joint lattice mass will naturally explain the low weight. Vice versa, the FE mode must exist in TMTTF compounds where it is probably located below the optically accessible range of frequencies. Even the optical pseudogap itself [17], being unexpectedly big for TMTSF compounds with their less pronounced dimerization of bonds, can be enlarged by the spontaneous dimerization of sites as it was seen explicitly in TMTTF compounds.
More generally, there are two conflicting philosophies for these magnificent materials:

A. The picture of [3] implies that the sequence of electronic phases follows a smooth variation of basic parameters reducible to the effective pressure, see Fig. 5 in [3]. The majority of compounds with NCS anions were abandoned, presumably their AOs were thought to exhort ill defined or undesirable complications. The advantages are appealing:

a) Concentration on simplest examples avoiding structural effects;
b) Generality in a common frame of strongly correlated systems driven mostly by basic parameters;
c) Extensive use of experiments under pressure and by the NMR.

But there is also another side of the medal:

1) Concentration on only simplest examples avoiding the rich information [4] on correlation of electronic and structural properties;
2) Necessity to introduce the case of the NCS anion ClO$_4$ to demonstrate the appearance of the superconductivity under pressure (The logic of the "effective pressure" demands to show for this compound only the nonrelaxed phase with the SDW state rather than the relaxed phase where the superconductivity appears only after the particular structural transition of the AO.);
3) Accent upon pressure as a universal parameter and missing the NMR splitting.
4) Ignoring the "structureless" transitions which are typical just for these selected compounds with centrosymmetric anions. (The wide temperature range of the Curie anomaly in $\epsilon(T)$ tells that the developing of the charge disproportionation seen as the FE affects a broad temperature region.)

B. The specific picture developed in [12–14,18] suggested the synthesis of structural and electronic phase transitions with the accent upon compounds with AOs. It extends naturally to new observations on charge disproportionation and ferroelectricity. Its main statements are the following (see [12] and Ch.6 of [13] for applications):

a) Displacive, rather than orientational, mechanisms are driving the AOs (the Ernshaw instability of separated charges);
b) Each fine structural change exerts a symmetrically defined effect which triggers a particular electronic state;
c) 1D "g-ological" phase diagram of the LL results in 2D, 3D phase transitions only with the backup of special symmetry lowering effects;
d) Main proof for the 1D physics of the Mott transitions is given by the $q_2$ structure of the $(TMTTF)_2SCN$. (Today it is seen as the charge disproportionation with the anti FE arrangement.)
e) Superconductivity appears only if the system is drawn away from the half filling thus avoiding the Mott insulator state. It happens in the relaxed phase of the $(TMTSF)_2ClO_4$ thanks to the unique $q_3$ type AO leading to inequivalence of chains (This is a purely defined case of what today is called the "internal doping". Its magnitude, i.e. the "interchain charge disproportionation", was exactly determined from data on fast magnetic oscillations [18].)
But there are major difficulties of this picture as well.
1. In applications to Se compounds there are common problems of any quasi 1D approach confronting the success of the band picture for the FISDWs (and vice versa!).
2. There are cases of the superconducting state without observation of the particular $q_3$ type of the AO. (Nevertheless, the recent views on independent AOs allows to suggest that the $q_3$ structure is still their, at least in local or dynamic form without the long range order. Low $T$ structural studies of, particularly, $(TMTSF)_2PF_6$ are required.)

We finish to say that new events call for a substantial revision of the contemporary picture of the most intriguing family of organic metals and for further efforts to integrate various approaches to their studies.
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IV. APPENDIX: HISTORY EXCURSIONS.

The recent events call again for a unifying picture of electronic and structural effects which returns us to suggestions already made about two decades ago. Below we quote from publications written in early-mid 80’ which views usually have been ignored by now.

Extracts from [12]. For more details see Ch.6 in [13].

... We suggest a general model for the phase diagram of the Bechgaard salts in a way that the variation of electronic states is mainly determined by the crystal symmetry changes. a complicated phase diagram PD includes the states: Metal M, insulator I, Peierls insulator CDW, magnetic (paramagnetic) insulator MI (PI), antiferromagnetic AF insulator SDW, field induced SDW, superconductivity SC of singlet or, not excluded yet, triplet types.

... 1D divergent susceptibilities give rise to observable phenomena only if the pair coherence is preserved in the course of the interchain tunneling. In the gapless regime it can be maintained by proper interchain electronic phase shifts which can appear due to some symmetry changes. There are alternating or random potentials for superconductivity and high magnetic fields for SDW.

... This theory permits us to suggest a general model for the phase diagram of the Bechgaard salts in a way that the variation of electronic states is mainly determined by the crystal symmetry changes. The variation of phases follows the change of an anion type $X$, anion structure, pressure, temperature, magnetic field.

... We suggest a simple general model where details of the PD are uniquely determined by the anion structure changes. Experimental data show us the following correlation between the anionic structure (characterized by the wave vector $\vec{q}$) and the state of the electronic system.
1. Unperturbed structure. Bonds are dimerized. PD: M→MI→SDW.

The last two phases are clearly separated only in \(TMTTF\) subfamily.

2. \(\vec{q}_2 = (0, 1/2, 1/2)\). The molecules are not equivalent. PD: M→MI→SDW (or CDW = Spin-Peierls). \(T_{MI}\) and \(T_{SDW}\) are well separated \((X = SCN: T_{MI} = 160K\) while \(T_{SDW} = 7K)\)

3. \(\vec{q}_3 = (0, 1/2, 0)\). The neighboring stacks are not equivalent. PD: M→SC→FISDW.

4. \(\vec{q}_4 = (1/2, 1/2, 1/2)\). The tetramerization. PD: M→I transition being driven externally by the AO.

The rare case 2. helps us to fix the model for the whole family: a strongly correlated 1D state with the separation of charge- and spin degrees of freedom. The typical case 1. qualitatively corresponds to the same model while the separation is less pronounced and interpretation may be controversial.

The most important for appearance of the SC is the case 3.: the alternating potentials lead to some redistribution of the charge between the two types of stacks, hence their system is driven from the two fold commensurability which removes the Umklapp scattering, destroys the Mott-Hubbard effect and stabilizes the conducting state down to lower temperatures where the SC can appear.

**Extracts from [14].**

Here are some extracts from [14] which itself was an extension of earlier observations on effects of counterions in charge transfer CDWs of the KCP type [19].

...we propose an alternative explanation of \((TMTSF)_2PF_6\), based on the fact that this material possesses a weak dimerization gap \(\Delta\). This gap is due to the environment of the given chain, which, unlike the chain itself, does not posses a screw symmetry along the chain axis. Without the effect of the environment the band is quarter-filled. The environment (\(PF_6\), etc.) opens a small gap \(\Delta\) in the middle of this band which therefore becomes half-filled.
Hence also small are the corresponding constant for the Umklapp scattering: \( g_3 \sim g_1 \Delta / E_F \).

The effect of \( g_3 \) appears only below sufficiently low temperature \( T_3 \sim E_F g^{1/2} (g_3/g)^{1/g} \),

\[ g = 2g_2 - g_1. \]

...Assuming the pressure suppresses \( g_3 \) and with it \( T_3 \), the Josephson coupling \( J \) of superconducting fluctuation will finally overcome the Umklapp scattering. This interpretation explains the observations in \((TMTSF)_2PF_6\) as a result of competition of the two small (off-chain) parameters, \( g_3 \) and \( J \), rather than as a result of the accidental cancellation of the large coupling constants \( 2g_2 \) and \( g_1 \).

... In this way there appears a region in the phase diagram where the superconductivity exists in absence of \( g_3 \), but where the CDW is introduced by \( g_3 \).

... A closer examination of the model shows that it is the triplet superconductivity.