Theory of the ferroelectric phase in organic conductors: optics and physics of solitons.

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Abstract

Recently the ferroelectric anomaly (Nad, Monceau, et al) followed by the charge disproportionation (Brown, et al) have been discovered in $(TMTTF)_2X$ compounds. The corresponding theory of the combined Mott-Hubbard state describes both effects by interference of the build-in nonequivalence of bonds and the spontaneous one of sites. The state gives rise to three types of solitons: $\pi-$ solitons (holons) are observed via the activation energy Δ in the conductivity G; noninteger $\alpha-$ solitons (the FE domain walls) provide the frequency dispersion of the ferroelectric response; combined spin-charge solitons determine $G(T)$ below subsequent structural transitions of the tetramerisation. The photoconductivity gap 2Δ is determined by creations of soliton - antisoliton pairs. The optical edge lies well below, given by the collective ferroelectric mode which coexists with the combined electron-phonon resonance and the phonon antiresonance. The charge disproportionation and the ferroelectricity can exist hiddenly even in the Se subfamily giving rise to the unexplained yet low frequency optical peak, the enhanced pseudogap and traces of phonons activation.

I. COMBINED MOTT-HUBBARD STATE, CHARGE DISPROPORTIONATION AND FERROELECTRICITY.

The family of quasi one-dimensional organic superconductors (Bechgard - Fabre salts $(TMTSF)_2X$ and $(TMTTF)_2X$) demonstrates, at low temperatures, transitions to almost all known electronic phases [3]. At higher T_{ao}, usually there is also a set of weak structural transitions of the anion orderings (AOs) which are slight arrangements of chains of counterions X [4]. At even higher $T \approx T_0$, also other structureless transitions [5] were observed sometimes (in the TMTTF subfamily), but they could not be explained and later were left unattended with dramatic consequences for the whole field. Recently their mysterious nature has been elucidated by discoveries of the huge anomaly in the dielectric susceptibility ε [6, 7] and of the charge disproportionation (CD) seen by the NMR [8]. The new displacive instability and the usual orientational AOs seem to be independent, as proved by finding their sequence in the $(TMTTF)_2ReO_4$ [6]. The phase transition was interpreted [7] as the least expected one: to the Ferroelectric (FE) state, which is proved by the clear-cut fitting of the anomaly in $\varepsilon(T)$ to the Curie law. The FE transition is followed by a fast formation or a steep increase of the conductivity gap Δ but with no appearance of the spin gap. Hence we deal with a surprising FE version of the Mott-Hubbard state which usually is associated rather with magnetic orderings. The ferroelectricity was observed also in dielectrical mixed-stacks organic compounds showing the neutral-ionic transition (see [9] for a short review). Active experimental studies have been carried on during last two years, particularly by methods of the NMR and the ESR [10, 11]. (In references, we limit ourselves to studies relevant to the FE transition, leaving aside other cases of the CD.)

The FE transition in $(TMTTF)_2X$ is a very particular, bright manifestation of a more general phenomenon of the CD, which already has been predicted in [12] and now becomes recognized as a common feature of various organic and some other conductors, see [13]. The phenomenon unifies a variety of different concepts and observations, sometimes in quite unusual aspects or conjunctions. Among them are the ferroelectricity of good conductors, the instability towards the Mott-Hubbard state, the Wigner crystallization [14] in a dense electronic system, the ordered $4k_F$ density wave [15], a richness of physics of solitons, the interplay of structural and electronic phases [4, 16].

Already within the nonperturbed crystal structure the anions can provoke the dielectriza-

tion. In $(TMTCF)_2X$ they dimerize intermolecular distances, hence changing counting of the mean electronic occupation from 1/2 per molecule to 1 per their dimer. It originates [17] the small Umklapp scattering U_b which opens (according to Dzyaloshinskii & Larkin, Luther & Emery) the route to the Mott-Hubbard insulator. While the bonds are always dimerized, the molecules stay equivalent above T_0 which last symmetry is lifted by the CD. At $T < T_0$ the site inequivalence adds more to Δ which is formed now by joint effects of alternations of bonds and sites (remind also [18] and [19]). This change shows up as a kink in the conductivity $G(T)$ at T_0 which turns down to higher Δ saturating at low T. The steepness of G just below T_0 reflects the growth of the CD contribution to Δ which must be correlated with $\varepsilon^{-1} \sim T_0 - T$. None of these two types of dimerization change the unit cell of the zigzag stack which basically contains two molecules, hence $q_\parallel = 0$ ($\mathbf{q} = (q_\parallel, q_\perp)$ is the CD wave vector). But their sequence lifts the mirror and then the inversion symmetries which must lead to the on-stack electric polarization.

By a good fortune, the 3D pattern of the CD appears in two, anti-FE and FE, forms:
i) antiphase between stacks (found only for $X = SCN$), here $q_\perp \neq 0$ which allows for its structural identification [4];
ii) inphase, $\mathbf{q} = 0$ hence the structureless character, which is the macroscopic FE typically observed today [6].
Both types are the same paramagnetic insulators (the MI phase of [16]); also their CD shows up similarly in the NMR splitting [8].

While the earliest theoretical approach [12] applies well to a common situation [13], here the pronounced $1D$ electronic regime calls for a special treatment [7] which also must be well suited to describe the FE properties. It is done in terms of electronic phases φ and θ (defined as for the CDW order parameter $\sim \exp(i\varphi)\cos\theta$) such that φ'/π and θ'/π count local concentrations of the charge and the spin (see e.g. [20, 21] in [22]). Beyond the energies of charge and spin polarizations

$$\sim \hbar v_F (\varphi')^2 \text{ and } \sim \hbar v_F (\theta')^2, \tag{1}$$

there are also the commensurability energies originated by site and bond dimerizations (proportional to Umklapp amplitudes U_s and U_b). At presence of both of them, we arrive at the Hamiltonian for the combined Mott-Hubbard state [7]

$$H_U = -U_s \cos 2\varphi - U_b \sin 2\varphi = -U \cos(2\varphi - 2\alpha) , \ U = \sqrt{U_s^2 + U_b^2} , \ \tan 2\alpha = U_b/U_s$$

Quantum fluctuations renormalize U down to $U^*(\neq 0$ at $\gamma < 1)$ which determines the gap $\Delta \sim U^{1/(2-2\gamma)}$ as $U^* \sim \Delta^2/\hbar v_F$. The appearance of U_s is regulated by one parameter γ (the same as γ_ρ of [16] or K_ρ of our days) which depends on electronic interactions. The spontaneous CD $U_s \neq 0$ requires that $\gamma < 1/2$, far enough from $\gamma = 1$ for noninteracting electrons. The magnitude $|U_s|$ is determined by a competition between the electronic gain of energy and its loss $\sim U_s^2$ from the lattice deformation and charge redistribution. $3D$ ordering of signs $U_s = \pm|U_s|$ discriminates the FE and anti-FE states.

II. CONDUCTIVITY, SUSCEPTIBILITY AND OPTICS. SOLITONS, PHASONS AND PHONONS.

For a given U_s, the ground state is still doubly degenerate between $\varphi = \alpha$ and $\varphi = \alpha + \pi$ allowing for phase π solitons which are the charge e spinless particles (holons) observed in conductivity at both $T \gtrless T_0$. 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 α to $-\alpha$ or to $\pi - \alpha$. Hence the CD defect $U_s \Leftrightarrow -U_s$ requires for the phase soliton of the increment $\delta\varphi = -2\alpha$ or $\pi - 2\alpha$ which will concentrate the noninteger charge $q = -2\alpha/\pi$ or $1 - 2\alpha/\pi$. Below T_0, the α- solitons must be aggregated [23] into walls separating domains of opposite FE polarization; their motion might be responsible for the observed frequency dispersion of ε, which indeed is more pronounced bellow T_0 [6]. But at $T > T_0$ they may be seen as individual particles which possibility requires for a fluctuational $1D$ regime of growing CD. It seems to take place sometimes as demonstrated by the pronounced (while not singular in this case) raise of ε well above T_0 for the anti-FE case of the $X = SCN$. It signifies the growing single chain polarizability even before 3D interactions come to the game. But more typical cases exclude the fluctuational regime: Δ increases sharply below T_0 hence no pseudogap regime of the CD, also the pure Curie-Weiss law in ε extends widely around T_0 signifying the mean field are over $\pm 30K$.

Physics of soliton is particularly sensitive to a further symmetry lowering and a very fortunate example is the subsequent AO of the tetramerization in $(TMTTF)_2ReO_4$ [4, 6, 24]. The additional deformation exhorts upon electrons a $2k_F$ CDW type effect thus adding the energy

$$\sim U_{ao} \cos(\varphi - \beta) \cos\theta$$

(here the shift β, mixing of site and bond distortions, reflects the lack of the inversion symmetry below T_0). The U_{ao} term lifts the continuous $\theta-$ invariance thus opening at $T < T_{ao}$ the spin gap $\Delta_\sigma \sim U_{ao}^{2/3}$ as known for spin-Peierls transitions [21, 25]. Moreover it lifts even the discrete invariance $\varphi \to \varphi + \pi$ of H_U thus prohibiting the π solitons to exist alone; now their pairs will be confined by spin strings. But the joint invariance

$$\varphi \to \varphi + \pi \ , \ \theta \to \theta + \pi$$

is still present giving rise to *combined topological solitons* [26] (cf. [21]). Here they are composed by the charge e core (with $\delta\varphi = \pi$ within the length $\xi_\rho \sim \hbar v_F / \Delta$) which is supplemented by longer spin $1/2$ tails of the $\theta-$ soliton ($\delta\theta = \pi$ within the length $\xi_\sigma \sim \hbar v_F / \Delta_\sigma \gg \xi_\rho$). These complexes of two topologically bound solitons are the carriers seen at $T < T_{ao}$ at the conductivity plot for the $X = ReO_4$, see the plot in [24]. Similar effects should take place below intrinsically electronic transitions, particularly close can be the spin-Peierls one for $X = PF_6$. But there the physics of solitons will be shadowed by $3D$ electronic correlations which are not present yet for the high T_{ao} of $X = ReO_4$.

Contrary to a common interpretation, e.g. [27, 28, 29], the optical absorption edge is not a two particle gap $E_g \neq 2\Delta$ but rather the collective mode gaped at $\omega_t \approx \pi\gamma\Delta < 2\Delta$. (Here and below we simplify some relations as for $\gamma \ll 1$, see [20].) The spectral region between ω_t and 2Δ is filled by a sequence of quantum breathers, bound states of two solitons. The regime changes qualitatively: from the essentially quantum side $1/2 < \gamma < 1$ with $E_g = 2\Delta$ to the quasi classical low γ scheme, just at the borderline for the CD instability $\gamma = 1/2$ which is not quite recognized in existing interpretations of optical data. (E.g. the resent extensive studies were all performed for the case equivalent to $\gamma > 1/2$, in our notations, and cannot be applied to the $(TMTTF)_2X$ as it was supposed [27].) Notice also that while the condition $\gamma < 1/2$ follows ultimately from the observed CD instability, the condition $\gamma < 1/8$ for the extreme suppression of charge fluctuations [28] is not necessary, see more discussion below.

Since Δ is already well known and ω_t is measurable, then we can access the basic microscopic parameter γ. It is already clear that ω_t is much below 2Δ, hence γ is rather small, but the exact determination of ω_t is complicated by phonon lines present in the same region [28, 29]. But these very lines provide another, earlier unattended indication for the CD. Their already noticed [29] surprisingly high intensity in $TMTTF$ may be due to the just

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lack of the inversion symmetry lifted by the CD. (Oppositely, poorly resolved but still strong sometimes, phonon lines in $TMTSF$ [29] tell in favor of a fluctuational regime of the CD in accordance with the pseudogap, rather than a true gap, in electronic optical transitions.)

To respond to current needs of experimental analysis in optics we shall present, without derivations, the formula for the mixed electron-phonon contribution to the dielectric response function valid at $T \geq T_0$:

$$\varepsilon(\omega)/\varepsilon_\infty = 1 + \frac{(\omega_p^*/\omega_t)^2(1 - (\omega/\omega_0)^2)}{(1 - (\omega/\omega_0)^2)(1 - (\omega/\omega_t)^2) - Z} \quad , \quad Z = \left(\frac{\omega_{cr}}{\omega_t}\right)^{2-4\gamma} \leq 1 \qquad (2)$$

Here ω_p^* is the renormalized metallic plasma frequency, ω_0 is the bare frequency of a molecular vibration associated to the CD, $\omega_{cr}(T)$ is the critical value of the optical gap $\omega_t(T)$ below which the spontaneous CD takes place. Near the criticality $Z(T_0) = 1$ we see here the *Fano antiresonance* at ω_0, the *combined electron-phonon resonance* at

$$\omega_{0t}^2 \approx \omega_0^2 + \omega_t^2$$

and finally the *FE soft mode* at

$$\omega_{fe}^2 \approx \frac{(1 - Z)}{\omega_0^{-2} + \omega_t^{-2}}.$$

Being overdamped near T_0, this mode must grow in frequency at $T < T_0$ following the order parameter, that is as $\sim \varepsilon^{-1/2}$, to become finally comparable with ω_{0t}. Near T_0 the two modes share the total weight ω_p^{*2} in the ratio $(\omega_t/\omega_0)^2$ which is also the experimentally accessible parameter.

With reasonable suggestions on dependences $\omega_t(T)$ and $\omega_{cr}(T)$ we find the critical singularity at $\omega = 0$ as $\varepsilon(T) = A|T/T_0 - 1|^{-1}$. It develops upon the already big gapful contribution $A \sim (\omega_p^*/\omega_t)^2 \sim 10^3$ in a reasonable agreement with experimental values $\epsilon \sim 10^4 T_0/(T - T_0)$. It confirms that the FE polarization comes mainly from the electronic system, even if the corresponding displacements of ions are very important to choose and stabilize the long range $3D$ order.

The full quantitative implementation requires to resolve for divergence (triple for the $TMTTF$!) in reported values [28, 29] of such a basic, and usually robust, parameter as the plasma frequency. The uncertainty could be simply an artifact of inadequate parametrizations of $\varepsilon(\omega)$ at the scale ω_{0t} (the right form (2) was never exploited). But more fundamentally, it can be also a signature of the strong renormalization $\omega_p^* \ll \omega_p$ which could have developed while the probe frequency decreases from the bare scale $\omega_p > 1eV$ to the scale

$\omega_t, \omega_0 \sim 10^{-2} eV$. Remind the full (kinetic $\sim C_{kin}$ and potential $\sim C_{pot}$) energy of elastic deformations (1) for the charge phase φ:

$$\frac{\hbar v_F}{4\pi} \left\{ (\partial_t \varphi)^2 C_{kin}/v_F^2 + (\partial_x \varphi)^2 C_{pot} \right\} \equiv \frac{1}{4\pi\gamma} \left\{ (\partial_t \varphi)^2 / v_\rho + (\partial_x \varphi)^2 v_\rho \right\}$$

$$\gamma = \frac{1}{C_{pot}C_{kin}} \ , \ \frac{\omega_p^*}{\omega_p} = \left(\gamma \frac{v_\rho}{v_F} \right)^{1/2} = \frac{1}{C_{kin}} \ , \ \frac{v_\rho}{v_F} = \frac{C_{pot}}{C_{kin}}$$

We see that the lowering of ω_p^* singles out the effect of the effective mass enhancement $C_{kin} > 1$ which is due to coupling of the phase mode with acoustic phonons [30]. (Another factor for reduction of the parameter γ, the Coulomb hardening $C_{pot} > 1$ acts upon γ and velocity v_ρ [31] but cancels in their product which gives ω_p^*.) The mass enhancement will not be effective above acoustic, or any other $q = 0$, frequencies ω_a (actually $C_{kin} = C_{kin}(0)$ is a function of ω: $C_{kin}(\omega) = C_{kin}(0)\omega_a^2/(\omega_a^2 + \omega^2)$. It explains the difference in extracting values of ω_p^* from very high and from intermediate frequency ranges.) If true, then the CD state resembles another Wigner crystal: electrons on the He surface, see [32], where selftrapped electrons gain the effective mass from surface deformations - the riplons.

III.   PERSPECTIVES AND CONCLUSIONS: THE $TMTSF$ FATE.

Compounds of the $TMTSF$ subfamily are highly conductive which today does not allow for low frequency experiments. Nevertheless the transition may be their, just being hidden or existing in a fluctuational regime like for stripes in High-T_c cuprates [33]. (The fluctuational regime of the CD was already observed in layered organic conductors [34].) The signature of the FE CD state may have been already seen in optical experiments [28, 35]. Indeed the Drude like peak appearing within the pseudogap can be interpreted now as the optically active mode of the FE polarization; the joint lattice mass will naturally explain its, surprisingly otherwise, low weight. Even the optical pseudogap itself [28, 35], being unexpectedly big for $TMTSF$ compounds with their less pronounced dimerization of bonds, can be largely due to the hidden spontaneous dimerization of sites. Recall also the above mentioned optical activation of intramolecular phonons [29].

A popular interpretation (see [28]) for optics of $TMTSF$ compounds neglects even the existent dimerization of bonds and relies upon the generic 4- fold commensurability effects originating higher order (8 particles) Umklapp processes. They give rise to the energy

$\sim U_4 \cos 4\varphi$ which stabilization would require for ultra strong $e - e$ repulsion corresponding to $\gamma < 1/8$ in compare to our moderate constraint $\gamma < 1/2$. While not excluded in principle, this mechanism does not work in $TMTTF$, already because this scenario does not invoke any CD instability. Moreover, the experiment shows that even small increments of the dimerization, just below the IInd order transition at T_0, immediately transfer to the activation energy, hence the domination of the two-fold commensurability.

Optical experiments will probably be elucidated when addressed to members of the $(TMTTF)_2X$ family, showing the CD, with a particularly reduced value of the associated gap (below typical molecular vibrations - down to the scale of the pseudogap in $(TMTSF)_2X$).

We conclude that the world of organic metals becomes polarized and disproportionated. New events call for a revision (see more in [36]) of the existing picture (see [37]) and suggest new experimental and theoretical goals. Further integrated studies are necessary.

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