Ferroelectric Mott-Hubbard Phase of Organic $(TMTTF)_2X$ Conductors

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(Received 13 December 2000)

We present experimental evidence and a corresponding theory for the ferroelectric transition in the family of quasi-one-dimensional conductors $(TMTTF)_2X$. We interpret this new transition in the frame of the combined Mott-Hubbard state taking into account the double action of the spontaneous charge disproportionation on the TMTTF molecular stacks and of the X anionic potentials.

DOI: 10.1103/PhysRevLett.86.4080 PACS numbers: 71.30.+h, 71.27.+a, 71.45.Lr, 77.80.Bh

Low-dimensional electronic systems serve as a workshop on problems of strong correlations. The richest opportunities have been opened by the family of charge transfer salts M_2X formed of stacks of organic molecules tetramethyltetrathiofulvalene (M = TMTTF) or tetramethyltetraselenafulvalene (M = TMTSF) with anions $X = PF_6$, AsF_6, SbF_6, SCN, etc. as counterions. The ions occupy loose cavities delimited by the methyl groups of the organic molecules. These materials show almost all known electronic phases: a metal, a paramagnetic insulator, spin/charge density waves (SDW/CDW), a spin-Peierls state, and finally a superconducting state [1]. In parallel, there is a set of several different structural types due to anion ordering (AO) which are slight arrangements in X chains [2]. Their transition temperatures $T_a \approx 100-200$ K are much higher than that corresponding to electronic transitions occurring in the range of $T_c \approx 1-20$ K.

Very recently, in the already very rich phase diagram of these salts, a new phase transition has been discovered, being revealed by a huge anomaly in the low frequency dielectric constant ϵ' at $T_0 = 70$ K in $(TMTTF)_2PF_6$ and at 100 K in $(TMTTF)_2AsF_6$ [3]. Very soon NMR studies have proved [4] that the transitions at T_0 are related to charge disproportionation, also called charge ordering (CO), dividing molecules into two nonequivalent species. Previous reports on TMTTF salts with larger anions such as SbF_6 have suggested occurrence of a phase transition, sometimes called a "structureless" one, at a temperature of the scale of T_a. It shows itself in changes of the resistance [5] and the thermopower [6], in weak features in high frequency (~GHz) dielectric susceptibility [7]. However, x-ray investigations brought no observation of superlattice reflections [5] while some variation of intensity of Bragg reflections could actually have been noticed [16]. The NMR method allows us to identify the very fact of the CO via nonequivalence of molecular sites [4,8] but it cannot distinguish between the $\vec{q} = 0$ state and the known undulating ones [either along the stack such as the $4k_F$ (Wigner) condensation in $(DCNQI)_2Ag$ [8] or between stacks as in $(TMTTF)_2SCN$ [2]]. So, the identification of the nature of this "structureless" $\vec{q} = 0$ transition was still unsolved. We show hereafter that ϵ' in $(TMTTF)_2SbF_6$, as in the case of $(TMTTF)_2PF_6$ and $(TMTTF)_2AsF_6$, exhibits a huge divergence at $T_0 = 154$ K. Dielectric experiments are providing thus a unique access to the anomalous collective properties of this mysterious transition identifying the resulting state as a *never expected* ferroelectric (FE) one.

In the high temperature range $T > T_a, T_0$ the counterions already have a profound effect on the electronic properties: the anions dimerize the intermolecular spacing of the TMTTF molecules along the stacks. As a result, the conduction band is split into a filled lower band separated from a half-filled upper band by a dimerization gap, leading to Mott-Hubbard charge localization. The effects brought by the AOs with $\vec{q} \neq 0$ have been previously discussed (see [2,9], and references therein). The new effects of combined CO-AO with $\vec{q} = 0$ are the main topic of the present work.

Empirically one can see a systematic difference between the usual $\vec{q} \neq 0$ and $\vec{q} = 0$ transitions. The first ones have been always observed for noncentrosymmetric anions [10]; so, the orientational ordering for which a short contact interaction between the anion and the molecule is established was considered as the main mechanism, positional displacements being only the consequence of it. In a contrary manner to $\vec{q} \neq 0$ AOs, the $\vec{q} = 0$ ones are observed in systems with centrosymmetric anions. For such systems, we will present hereafter a possible universal mechanism only related to a positional instability. The remarkable fit of the anomaly in $\epsilon'(T)$ for the three centrosymmetric salts, $X = PF_6$, AsF_6, and SbF_6, to the Curie law suggests firmly the ferroelectric character of these phase transitions. We account for this FE state from the combined action of charge disproportionation and ionic displacements.

The $(TMTTF)_2SbF_6$ crystals were prepared by a standard electrochemical procedure [11]. We present results on a sample with a regular cross section of 4×10^{-5} cm^2

 0031-9007/01/86(18)/4080(4)$15.00

and a length of 3 mm. Its room temperature conductivity was about 10 $\Omega^{-1}\,\mathrm{cm}^{-1}$ which is close to the value previously published [5]. The complex conductance $G(T)$ was measured in the frequency range 1 kHz–10 MHz using an impedance analyzer HP 4192A. The amplitude of the ac signal was typically 10 mV, within the linear response. With decreasing temperature, G increases continuously (metallic type of conductivity) to a maximum slightly above $T_0 = 154$ K. Below T_0, G sharply decreases following the thermally activated behavior with an activation energy $\Delta = 500$ K. From room temperature to about 200 K the magnitude of the ϵ' is relatively small (below our experimental resolution in this temperature range). With decreasing T below 200 K, we observed a sharp growth of the magnitude of ϵ' with a tendency to diverge near $T_0 = 154$ K, reaching the huge value of $\sim 10^6$ (at 100 kHz), and a very deep decrease of its magnitude below T_0. Figure 1 shows the temperature dependence of $1/\epsilon'$ in the $(\mathrm{TMTTF})_2X$ family with centrosymmetric anions PF_6, AsF_6 [3], and SbF_6. The generic features are very similar for the three compounds: the two branches above and below the appropriate T_0 are very close to be linear, i.e., to follow the Curie law $\epsilon' = A/|T - T_0|$. The slopes of these branches (i.e., the magnitudes of A) at $T < T_0$ are twice that at $T > T_0$, exactly as theoretically predicted in the description of a second order phase transition.

One can get simply a general idea of the hidden ordering in considering the joint effect of two sources to the dimerization, hence to the charge gap Δ. The *extrinsic* one is determined by the basic crystal structure and the *intrinsic* one is spontaneous being self-induced by the electronic subsystem. (This concept was already used in the theory of conducting polymers [12]). The gap $\Delta(W)$ appears as the consequence of both contributions to the umklapp scattering W. Without the CO, there is only the bond contribution W_b to the amplitude W from the built-in bond alternation. The CO adds the on-site contribution W_s from the nonequivalence of sites. The charge gap is a function of the total amplitude $W = \sqrt{W_s^2 + W_b^2}$ which results from the orthogonality of corresponding matrix elements of electronic scattering [12]. (Since the gap Δ is not a linear function of W, then the partial gaps do not add simply in quadrature as the components of W.) The energy change F_e of the electronic system due to both W_b and W_s depends only on the Δ and, consequently, on the total W. But the energy of lattice distortions depends only on the spontaneous site component W_s: $F_l = 1/2KW_s^2$. Thus the total energy can be written in terms of the total W as $F_{\mathrm{tot}} = F_e(W) + 1/2KW^2 - 1/2KW_b^2$. The ground state is determined by its minimum over W under the restriction $W > W_b$. The spontaneous W_s will appear if the two conditions are satisfied: (a) The energy has a minimum at some value $W = W_0$ and (b) W_b is not too big to meet the restriction $W_0 > W_b$. Since the value $W_0 = W_0(T)$ increases with decreasing temperature, there will be a phase transition at $W_0(T_0) = W_b$ provided that $W_0(0) > W_b$.

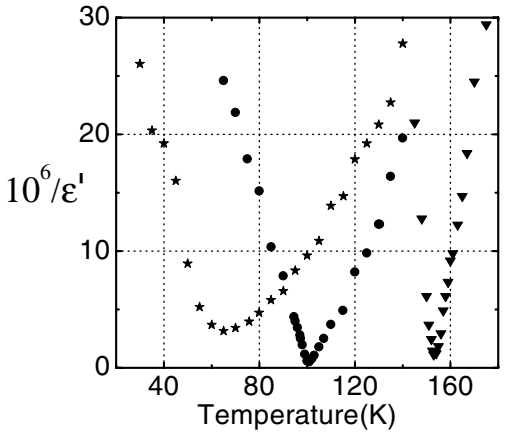

FIG. 1. Temperature dependence of the inverse of the real part of the dielectric permittivity ϵ' of $(\mathrm{TMTTF})_2X$ with $X = PF_6$ (stars), AsF_6 (circles), and SbF_6 (triangles) at the frequency of 100 Hz.

Now we are going to choose a microscopical description. Recall first a recent theoretical work [14] performed in the frame of a mean field approximation which has found that the CO can occur as the result of strong enough Coulomb interaction between electrons on nearest-neighbor sites. This model has been developed at $T = 0$ and it includes ultimately the spin ordering of the antiferromagnetic type which is characteristic for these systems at low $T \sim 10$ K. The phase transitions we observe occur at much higher $T \approx 100$–200 K and an appropriate approach is clearly needed. Hence, we shall consider the case of real 3D materials for, in our picture, the CO is stabilized by interaction with the 3D connected system of anions. At these high scales of T, Δ the electron subsystem still stays in the 1D regime, hence we shall use the bosonization procedure which is suitable for describing low energy and collective processes in 1D.

Let us consider a 1D electronic system with a mean occupation of $1/2$ electron per site (that is per molecule) with sites along the stack labeled as n at $x = na$. The low frequency long wave effects are described by the Hamiltonian for the phase φ in the charge channel which is separated from the Hamiltonian for the spin channel. We shall normalize the phase according to conventions for CDWs and SDWs which are $2k_F = \pi/2a$ modulations $\sim \cos[\pi/2n + \varphi(x) + \mathrm{const}]$. The $4k_F = \pi/a$ fluctuations of the charge density are $\rho_{4k_F} \sim (-1)^n \cos[2\varphi(x) + \mathrm{const}]$. For our crystals with two molecules per unit cell the $4k_F$ is projected to $q_x = 0$, then ρ_{4k_F} describes the charge disproportionation within the unit cell.

The Hamiltonian for φ (per site) can be written (see [15] for a review) as

$$H = \frac{\hbar}{4\pi\gamma}\left[\upsilon_\rho(\partial_x\varphi)^2 + \upsilon_\rho^{-1}(\partial_t\varphi)^2\right] - W\cos(2\varphi)\,. \tag{1}$$

Without interactions $v_\rho = v_F$ and $\gamma = 1$. Repulsive interactions reduce $\gamma < 1$ which value carries all necessary information: either about on-site/intersite interactions of the model [14] or about Coulomb interactions for the Wigner crystal (WC) scenario like in [8]. The umklapp scattering amplitude W of Luther and Emery or g_3 of Dzyaloshinskii and Larkin [15] is a feature of systems with one electron per unit cell. Normally W being of the order of the other interactions is not small; hence a big gap is opened in the charge $\varphi-$ channel, so that only gapless spin degrees of freedom are left for observations. But a specific feature of $(TMTCF)_2X$ crystals is that W is small and appears only as a secondary effect of the anionic sublattice, opening an intriguing crossover to "charge localization" [1] (to the Paramagnetic Insulator in earlier language of [9]).

The $4k_F$ susceptibility $\Pi_{4kf} \sim T^{4\gamma-2}$ is divergent only for strong enough interactions when $\gamma < 1/2$. For $\gamma > 1/2$ the umklapp term $\sim W$ is renormalized to zero and the system is a 1D metal, nowadays called the Luttinger Liquid. At the marginal line $\gamma = 1/2$, known in terms of bare interactions as the Luther-Emery line, $\Pi_{4kf} \sim \ln T^{-1}$ as for the Kohn anomaly leading to the Peierls instability [then the Hamiltonian is reduced to spinless fermions which actually are π solitons of (1), with the gap Δ]. At arbitrary $\gamma < 1/2$, W is renormalized to a finite value which we shall write as $W^* = a\hbar\omega_t^2/(8\pi\gamma v_\rho)$, $\hbar\omega_t \lesssim \Delta$. The frequency ω_t is a gap in the spectrum of linear phase excitations $\omega^2 = (v_\rho k)^2 + \omega_t^2$ and it enters, as a "transverse" frequency of the optical response, the expression for the dielectric susceptibility

$$\epsilon_\Delta = (\gamma v_\rho \omega_p^2)/(v_F \omega_t^2), \qquad \omega_p^2 = (8e^2 v_F)(\hbar s), \quad (2)$$

where ω_p is the plasma frequency of the parent metal and s is the area per stack. This contribution $\epsilon_\Delta \sim (\omega_p/\Delta)^2$ can be already very large as $\epsilon_\Delta \sim 10^{3-4}$, and it corresponds to the background upon which the anomaly at T_0 is developed. But ϵ_Δ is regular, showing only a dependence on Δ which starts to increase below T_0 without signs of decrease from above. These features would only add some upward kink in ϵ' below T_0, but cannot account for the observed anomaly.

The degeneracy between $\varphi = 0$ and $\varphi = \pi$ corresponds to the displacement of the electronic system by just one lattice position x. Hence the $\pm\pi$ soliton just adds/removes one electron in real space. The elementary excitations registered as charge carriers are these solitons. Their activation energy $\Delta \sim \omega_t$ is determined from our results for G as, e.g., $\Delta \approx 500$ K for SbF_6. At finite concentration of solitons as normal carriers $\sim \rho n$ coming either as thermal excitations or via incommensurability, there is an additional contribution to the low frequency complex ϵ which we can write in a Drude form $\epsilon_n = -\rho_n \omega_p^2/(\omega^2 + i\omega/\tau_n)$. The latter can be assigned to the observed conductivity [3].

The scaling relations for the gap Δ and for the electronic free energy F_e read (in units of E_F) $F_e \sim -\Delta^2 \sim -W^\zeta$ with $\zeta = 1/(1-\gamma)$. So the instability condition is $\zeta < 2$ that is $\gamma < 1/2$. Indeed, this condition is satisfied, the value W can appear spontaneously: the gain of the F_e is higher than the loss $\sim KW^2$ of energy due to spontaneous deformations which originate the potential W. The minimum is achieved at $W = W_0 \sim K^\beta$ with $\beta^{-1} = 2 - \zeta = (1-2\gamma)/(1-\gamma)$.

For our particular system it is, by principle, important to notice the two sources giving rise to the weak twofold commensurability, that is the two contributions to the umklapp interaction. The nondimerized system with 1/2 electron per site has a symmetry $x \to x + a$ and $x \to -x$ which corresponds to phase transformations $\varphi \to \varphi + \pi/2$ and $\varphi \to -\varphi$. Thus the lowest order invariant contribution to the Hamiltonian is $\sim W_4 \cos 4\varphi$, which is usually negligibly small as studies of CDW have shown. It is small as coming from umklapp interaction of 8 particles, half of them staying far away from the Fermi energy; but also it is renormalized as $\sim W_4^{4\zeta}$ so that super low values $\gamma < 1/8$ are required for its stabilization. For the site dimerization the symmetry $x \to x + a$ is broken while the symmetries $x \to x + 2a$ and $x \to -x$ are preserved. The Hamiltonian, invariant under the corresponding transformations of φ: $\varphi \to \varphi + \pi$ and $\varphi \to -\varphi$ is $H_W^s = -W_s \cos 2\varphi$. The bond dimerization preserves the symmetries $x \to x + 2a$ and $x \to a - x$ (reflection with respect to the bond center). Hence the invariance is required with respect to $\varphi \to \varphi + \pi$ and $\varphi \to \pi/2 - \varphi$ leading to $H_W^b = -W_b \sin 2\varphi$.

Altogether the nonlinear Hamiltonian becomes

$$H_W = -W_s \cos 2\varphi - W_b \sin 2\varphi = -W \cos(2\varphi - 2\alpha);$$
$$W = \sqrt{W_b^2 + W_s^2}, \qquad \tan 2\alpha = W_b/W_s.$$

The CO modulation is $\rho_{co} \sim \cos(\pi x/a + 2\alpha) = (-1)^n W_s/\sqrt{W_s^2 + W_b^2}$. For a given W_s the ground state is doubly degenerate between $\varphi = \alpha$ and $\varphi = \alpha + \pi$, which still allows for phase π solitons. Moreover W_s itself can change its sign between different domains of anionic displacements. Then the electronic system must also adjust its ground state from α to $-\alpha$ or to $\pi - \alpha$, whichever is closer. Thus, at the domain boundary, a phase soliton of $\delta\varphi = -2\alpha$ or $\pi - 2\alpha$ will be placed carrying a noninteger charge $q = -2\alpha/\pi$ or $1 - 2\alpha/\pi$ per chain. This is nothing but the electric polarization at the boundary between opposite FE domains.

The mean field approach appears appropriate for anionic displacements: critical fluctuations are suppressed by well-pronounced 3D correlations, as inferred from the perfect Curie-like anomaly in ϵ' (Fig. 1) as well as from x-ray studies on known AOs [2]. For electrons quantum fluctuations must be treated exactly as it has been sketched above for the Hamiltonian (1). The angle α is invariant and only the total gap value is subject to the renormalization

from W to $W^*(W) \sim \Delta^2$. Finally, the total energy, as a function of the mean phase $\bar{\varphi}$ and W_s at given W_b, is

$$F \sim -\Delta^2\left(\frac{W_s}{W}\cos 2\bar{\varphi} + \frac{W_b}{W}\sin 2\bar{\varphi}\right) + \frac{K}{2}W_s^2 - \frac{e}{\pi}E\bar{\varphi},$$

which includes contributions from electrons, the lattice, and the external electric field E. At $W_b > W_{cr} \sim K^{1/\beta}$ this energy has only one minimum at $W_s = 0$, $\bar{\varphi} = \pi/4$ (modulo π) but this point becomes unstable at $W_b = W_{cr}$ *from which the anomaly in* ϵ *originates.* At $W_b < W_{cr}$ this minimum is split in two ones which appear, first closely, at $2\bar{\varphi} = 2\bar{\varphi}_\pm = \pi/2 \pm 2\delta\bar{\varphi}$, $W_s = W_b \tan 2\delta\bar{\varphi}_0$. The resulting ground state will be FE if the same $\bar{\varphi}_\pm$ is chosen for all stacks (our case), while the state is antiferroelectric if the sign of $\bar{\varphi}_\pm$ alternates [the case of $(TMTTF)_2SCN$, see references in [2,9]]. Above the CO instability the minimization yields

$$\bar{\varphi} = \pm\frac{\pi}{4} - \frac{eE}{W_b - W^{cr}}, \qquad W_s = \frac{E/2\pi}{W_b/W^{cr} - 1},$$

$$\epsilon' = \frac{4e^2/s}{W_b - W^{cr}}.$$

In writing ϵ' we recall that $e\varphi/s\pi$ is the electronic polarization which equals ϵE. We come back to the formula (2) but with a modified denominator: $\omega_t^2 \to \omega_t^2 - \omega_{cr}^2$. Thus $\epsilon \to \infty$ at the transition point $W_b = W^{cr}$ which is the joint electron-ion instability. Importantly, the value of Δ is related to the bare value of ω_t which stays finite, hence the "normal" carriers (the π solitons) are always gapful.

In short, we have supposed above that instead of changing T one lets the parameters K, W_{cr}, or W_b be varied at $T = 0$. Actually all of them are functions of T and the transition temperature T_0 is determined by $W_b(T_0) = W_b^{cr}(T_0)$. Expanding around T_0 we recover the experimental observation $\epsilon^{-1} \sim T - T_0$ and we need only to understand why the Curie law extends over a rather broad region of $\delta T = T - T_0 \approx 30$ K. Clearly the expansion is valid when δT is small in comparison with the lowest energy scales which are the ionic cage energy $\sim 10^2$ K [2] and $\Delta \sim 10^2$ K. It seems that relative to these scales the expansion within $\sim 10^1$ K is well assured. Remarkably we arrive even at the right magnitude of the observed effect: $\epsilon \sim 10^4 T_0/(T - T_0)$.

In conclusion, we have shown that $(TMTTF)_2X$ salts with centrosymmetric anions $X = PF_6$, AsF_6, and SbF_6 undergo a phase transition at which the dielectric constant shows a huge divergent peak. The ferroelectric character of this phase transition is demonstrated by the Curie law behavior of $\epsilon'(T)$ of the three compounds. These results also bring the nature of the so-called structureless transition of the $(TMTTF)_2SbF_6$. The transition has been explained by the combined action of the uniform shift of anions with respect to the oppositely charged organic stacks and of the charge disproportionation appearing in each TMTTF molecule yielding thus a macroscopic ferroelectric polarization. Our approach provides a physically transparent phenomenological interpretation in terms of strongly fluctuating $4k_F$ density wave, i.e., a local Wigner crystal, subjected to a weak twofold commensurability potential. Up to now these FE transitions concern only the salts based on TMTTF molecules for which T_0 is already in the regime of Mott Hubbard charge localization state. The salts based on TMTSF are less 1D and are metallic in this temperature range which precludes dielectric measurements. Nevertheless, the same type of FE transition may exist, just being hidden or existing only in a fluctuating regime. If such a fact would be confirmed by future experiments, then the whole analysis of intriguing abnormal properties in the metallic state should be revised, as it already needs to be made (see also [4]) for the paramagnetic insulator phase of TMTTF salts with CS anions as demonstrated by the present work.

We would like to thank C. Carcel and J. M. Fabre for providing us the samples. Part of this work was supported by the Russian Fund of Basic Research (Grant No. N99-02-17364) and the twinning research program (Grant No. N98-02-22061) between CRTBT-CNRS and IRE-RAS.

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