

Ferroelectricity: From organic conductors to conducting polymers

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ABSTRACT

We compare the ferroelectricity for two families of synthetic conductors: the experimentally found ferroelectricity in organic crystal like $(\text{TMTTF})_2\text{X}$ and a plausible ferroelectricity in specially designed polyene chains. The difference of the polymer with respect to the organic conductor is the reverse of the build-in (now the sites) and spontaneous (now the bonds) effects of dimerizations. The theory predicts the existence of solitons (dimerization kinks) with non-integer variable charges, both with and without the spin. With today's understanding, we see them as walls separating domains with opposite electric polarization. Their physics will serve to relate transient ferroelectric processes and the visible range optics.

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1. Introduction

The phenomenon of ferroelectricity refers to an ability of certain materials to develop a spontaneous electric polarization which may have several allowed directions, hence it can be altered by an external electric field. There are also two sister families: pyroelectrics where the polarization is persistent having only one allowed direction, and piezoelectrics which do not support a spontaneous polarization, but it appears under a strain. All three subfamilies have immense range of applications attracting related fundamental studies. The ferroelectric materials are the most universal: beyond their own virtues, they serve as pyroelectrics if treated by poled quenching, or as piezoelectrics if disordered.

The known microscopic mechanisms for the ferroelectric polarization are typically ionic: ion displacements from a centro-symmetric position in displacive ferroelectrics like most known $\text{PZT-Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$, ordering of ions among equivalent potential minima (order–disorder type of the ferroelectricity like in BaTiO_3), neutral–ionic transition where the charge disproportionation takes place among atoms in non-symmetric positions [1]. The contemporary discovery of ferroelectricity in organic conductors [2] has brought to life a new mechanism of the predominantly electronic origin, which opens new scales of the magnitude and rapidity of the effect.

Ferroelectricity is a rising demand in fundamental and applied solid state physics. Ferroelectrics are used in microelectronics as active gate materials, in capacitors, electro-optical-acoustic modulators, etc. There is a particular demand for plastic ferroelectrics, e.g. as a sensor for acoustic imaging in medicine and beyond, in shapeable capacitors, etc. Until now, this demand is satisfied by exploiting composite materials based on powders of ferroelectric oxides in a matrix of a conventional, non-conjugated polymer. A single example [3] of a purely polymeric FE is the saturated (that means not being active either electronically or optically) polymer poly(vinylidene fluoride) (PVDF). This material shows the ferroelectricity of a conformational origin as explained in Fig. 1.

2. Ferroelectricity in π -conjugated systems

Polarizabilities of existing plastic ferroelectrics are rather low, providing the dielectric permittivity $\varepsilon \sim 10$, hence resulting in a modest efficiency of devices. In synthetic conductors, like organic crystals or conducting polymers, the π -electronic systems can greatly enhance the dielectric permittivity. In this case, the major polarization comes from redistribution of electronic density, resulting in the amplification of dielectric permittivity ε by a factor of $(\omega_p/\Delta)^2 \sim 10^2$ (ω_p is the plasma frequency, Δ is the gap in the electronic spectrum).

The picture of the ferroelectricity implies the existence of a doubly degenerate ground state in the system. For quasi-one-dimensional conductors, the microscopic picture of the ferroelectricity is based on two coexisting symmetry lowering effects: the dimerization of bonds and the dimerization of sites,

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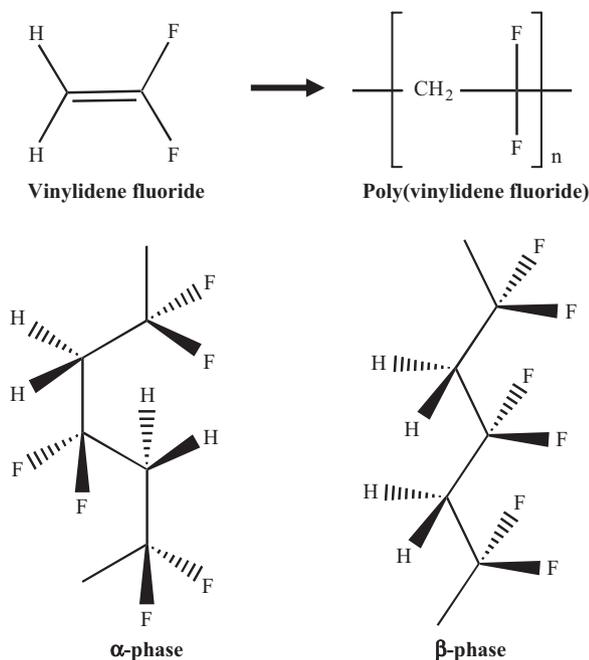


Fig. 1. Poly(vinylidene fluoride) PVDF [FEP]. The β -phase possesses an electric polarization transverse to the polymer backbone. Driving force for the ferroelectricity is the preference to the trans-conformation of the backbone which enforces the opposing placement of differently charged HH and FF units.

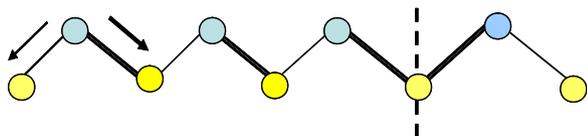


Fig. 2. Joint effect of site and bond dimerizations for the ferroelectric ground state. The arrows show dielectric moments of bonds: they do exist because of the site inequivalence and they are different in magnitudes because of inequivalence of bonds. Vertical line indicates the position of the soliton-ferroelectric domain wall.

see Fig. 2. The important requirement is that one of these two effects should be spontaneous.

The combination of the two effects removes the inversion and the mirror symmetry, eliminating the glide plane. Nevertheless, the doubly degenerate ground state is preserved, which immediately gives rise to the existence of solitons. We may consider solitons as ferroelectric domain walls separating domains with opposite electric polarization. A special experimental advantage follows that the ac electric field alternates polarization by moving charged solitons. Through solitons' spectral features in visible and IR ranges, it opens a special tool of electro-optical interference. In return, the physics of these exotic solitons will serve to describe transient processes in ferroelectric polymers.

3. Ferroelectricity in organic crystals

Ferroelectricity related to charge ordering was discovered in quasi-1D organic conductors (TMTTF)₂X [2], and expanded to layered compounds like δ -(EDT-TTFCONMe₂)₂Br [4]. Near the phase transition temperature (typically $T_c \sim 150$ K), the dielectric permittivity reaches a gigantic value $\epsilon \sim 10^6$ [2] or even more [4], and even well below T_c it is as high as $\epsilon \sim 10^3$. The effect coexists with the intrinsic conductivity, giving rise to a “ferroelectric narrow gap semiconductor” and leading to a fast re-polarization.

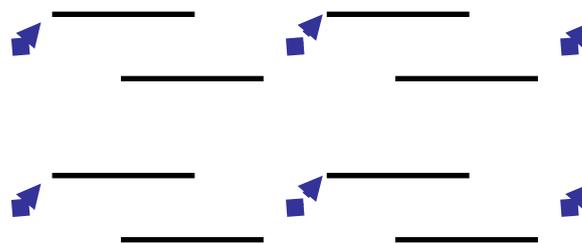


Fig. 3. (TMTTF)₂X compounds and their ferroelectric modification. Horizontal lines correspond to stacked TMTTF molecules (side view). Arrows show displacements of ions X (squares); they follow and stabilize the electronic charge disproportionation.

A microscopic picture of ferroelectricity in organic crystals [2,5] is based upon two coexisting symmetry lowering effects: the dimerization of bonds (which is build-in) and the dimerization of sites (which is a spontaneous symmetry breaking), leading to the Mott state, see Fig. 3. This state can be viewed and described as a Wigner crystal of electrons or equivalently as the $4k_F$ charge density wave $CDW_{4k_F} \sim \cos(2\varphi + \pi n)$ where n numbers the molecular sites.

The phase φ is to be determined by minimizing the energy of the CDW. Two types of dimerization give rise to two sources for commensurability, hence to two contributions U_s , U_b to Umklapp interactions between the CDW and the underlying lattice

$$U_U = -U_s \cos 2\varphi - U_b \sin 2\varphi = -U \cos(2\varphi - 2\alpha),$$

$$U = (U_b^2 + U_s^2)^{1/2}, \quad \tan 2\alpha = U_s/U_b.$$

The site's addition $U_s \neq 0$ originates the ferroelectric ground state if the same α is chosen for all stacks. Spontaneous U_s itself can change the sign between different domains of the ferroelectric displacements. Then the electronic system should also adjust its state from α to $-\alpha$. Hence, the domain boundary $U_s \leftrightarrow -U_s$ will concentrate the non-integer charge $q = -2\alpha/\pi$ per chain. These α -solitons form a gas of quasi-particles at $T > T_0$ and organize themselves in plane domain walls at $T < T_0$. Beyond the ferroelectricity, the material is a spinless semiconductor: or at given U_s , the ground state is still doubly degenerate between $\varphi = \alpha$ and $\varphi = \alpha + \pi$; it allows for phase $\pm\pi$ -solitons—the holons with the charges $\pm e$.

4. Design for a ferroelectric conjugated polymers

In perspectives of applications, crystalline organic materials may be too fragile, also their transition temperatures to the ferroelectric state are still in the cryogenic range. So it is tempting to find a similar effect in more robust and technological materials like conjugated polymers.

Major activity in physics and applications of conjugated polymers has been centering on their ability to emit light in the optical range of about 2 eV (see e.g. Ref. [6] and references therein). These optically active materials are already close to applications and even commercialized. If one succeeds using their fast π -electrons to perform also the ferroelectricity, it will be possible to use the transient ferroelectric processes to monitor the visible range optics and vice versa.

A secure guess is to look for the so-called (AB)_x polymer—see Fig. 1, proposed theoretically in early 1980s [7,8]. Indeed, the first member of this potentially vast family of “di-substituted polyacetylenes” has already been synthesized [9], studied for non-linear optical properties [10], but not tested yet for the low-frequency response which could have recovered the ferroelectricity.

The virgin polyacetylene $(\text{CH})_x$ [11] possesses the spontaneous bond dimerization originated by the Peierls effect. Schematically, the dimerization is pictured usually as the alternation of single and double bonds, suggesting the π -electrons are hybridized mainly at the double bonds where the distance between carbon atoms is shorter. The modified polyacetylene is obtained by changing some or all of hydrogen atoms by other side groups (curiously, just such a scheme was suggested by W. Little as a proposal for a high-temperature superconductor). The $(\text{AB})_x$ skeleton is achieved if the side groups (radicals R_1 and R_2) alternate giving rise to a polymer with the formula $(\text{CR}_1\text{CR}_2)_x$. A simple example is given by the $(\text{CHCF})_x$ polymer, where every second hydrogen is substituted by the fluorine; its synthesis was vaguely mentioned in early 1980s; the contemporary example is described below.

In any case, the build-in non-equivalence of sites appears along the polymeric chain. The difference with respect to $(\text{TMTTF})_2\text{X}$ is the reverse of the build-in (now the sites) and spontaneous (now the bonds) effects of dimerization. There is a joint effect of two contributions to the dimerization gap $\Delta = (\Delta_{\text{ex}}^2 + \Delta_{\text{in}}^2)^{1/2}$, where the extrinsic part Δ_{ex} comes from the build-in site dimerization and the intrinsic part Δ_{in} comes from the spontaneous bond dimerization—the remnant of the Peierls effect.

The double degeneracy of the ground state is preserved, giving rise to three different topological solitons—bond dimerization kinks, see Fig. 4. But unlike the standard polyacetylene chain, all the three types of solitons carry variable, non-integer charges [6,7]. So, for this combined Peierls state, there is no total spin–charge separation, contrary to traditional 1D Peierls and Hubbard models. Thus, the earlier neutral spin-carrying soliton, $S = 1/2$, acquires the charge $Q_s = e(2/\pi)\tan^{-1}(\Delta_{\text{ex}}/\Delta)$. The spinless solitons ($S = 0$) change their charges according to $Q_{\pm} = Q_s \pm e$.

There is an important constraint for the Δ_{in} to be spontaneously generated: the already existing Δ_{ex} should not exceed the optimal Peierls gap Δ_0 : $\Delta_{\text{in}} = (\Delta_0^2 - \Delta_{\text{ex}}^2)^{1/2}$. That calls for a serious chemistry precaution: to keep a sufficiently small difference of the side groups R_1 and R_2 .

The only known existing di-substituted polyacetylene has been synthesized a decade ago [9]. Later on it attracted an attention in view of very promising applications as a light emitting material, even the lasing effect has been demonstrated [10]. The detailed optical characterization [10] provides an indirect proof for presence of the spontaneous bonds dimerization via spectral signatures of solitons. An “accidental” origin of the success to get the Peierls effect comes from a truly weak difference of alternating radicals: they are the phenyl rings which differ only by a side group attached most distantly from the carbon backbone bearing the π -electrons. Then the build-in site dimerization gap is small and the system is provoked to add the bond dimerization contribution to the gap. There was no check for the ferroelectricity yet: it seems plausible to be tried and realistic to be discovered.

Notice finally, that the theory guides definitely only towards a single chain polarization. The bulk arrangement may be also anti-ferroelectric—still interesting for high ϵ while lacking the manipulability. An empirical reason for the optimism is that among many members of the $(\text{TMTTF})_2\text{X}$ family only one with $\text{X} = \text{SCN}$ shows the anti-ferroelectric interstack ordering; others show the ferroelectric response.

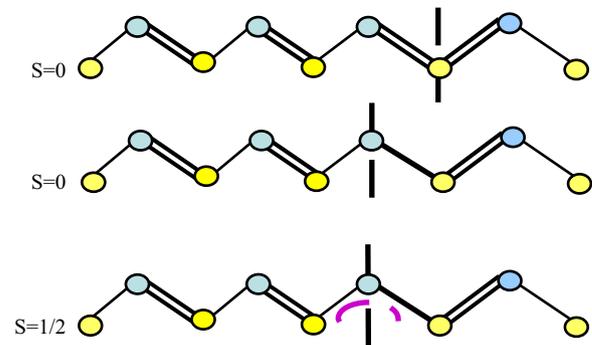


Fig. 4. Three types of topological solitons in $(\text{AB})_x$ polymeric chain.

5. Conclusions

π -Conjugated systems can support the electronic ferroelectricity. The effect is registered and interpreted in two families of organic crystalline conductors (quasi 1D and quasi 2D). The mechanism is well understood as combined collective effects of Mott or Peierls types. The design is symmetrically defined and can be previewed. An example of a “must be ferroelectric” polyene has been already obtained and a presence of the spontaneous dimerization seems to be confirmed. Cases of low-temperature ferroelectric phases should not be overlooked for the beginning.

Conductivity and/or optical activity of π -conjugated systems will add more functionality to their ferroelectric states. Polarizability of polymeric chains can allow manipulating their morphology (e.g. hybrids of conducting polymers and liquid crystals [12]). The Su–Schrieffer–Heeger solitons of *trans*- $(\text{CH})_x$ will serve duties of re-polarization walls and their studies will add to reconciliation of applied and fundamental physics of polymers.

Acknowledgments

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