

Electronic ferroelectricity in carbon based materials



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ABSTRACT

We review existing manifestations and prospects for ferroelectricity in electronically and optically active carbon-based materials. The focus point is the proposal for the electronic ferroelectricity in conjugated polymers from the family of substituted polyacetylenes. The attractive feature of synthetic organic ferroelectrics is a very high polarizability coming from redistribution of the electronic density, rather than from conventional displacements of ions. Next fortunate peculiarity is the symmetry determined predictable design of perspective materials. The macroscopic electric polarization follows ultimately from combination of two types of a microscopic symmetry breaking which are ubiquitous to quasi-1D electronic systems. The state supports anomalous quasi-particles—microscopic solitons, carrying non-integer electric charges, which here play the role of nano-scale nucleus of ferroelectric domain walls. Their spectroscopic features in optics can interfere with low-frequency ferroelectric repolarization providing new accesses and applications. In addition to already existing electronic ferroelectricity in organic crystals and donor–acceptor chains, we point to a class of conducting polymers and may be also to nano-ribbons of the graphene where such a state can be found. These proposals may lead to potential applications in modern intensive searches of carbon ferroelectrics.

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1. Introduction

Ferroelectricity is a phenomenon of spontaneous controllable electric polarizations in some, usually crystalline, solids [1]. Ferroelectric materials have a wide range of applications attracting related fundamental studies. They are used as active gate materials and electric RAM in microelectronics, as capacitors in portable WiFi communicators, electro-optical-acoustic modulators, electro-mechanical actuators and transducers, and ultrasound sensors in medical imaging [2–4]. For the last demand, flexible lightweight carbon ferroelectrics would be particularly welcomed.

Traditional ferroelectrics are inorganic materials, or crystals of inert organic molecules (e.g., Rochelle salt $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ or triglycine sulfate $(\text{NH}_2\text{CH}_2\text{COOH})_3 \cdot \text{H}_2\text{SO}_4$), but new organic families started to appear in 2000s [5–7]. Among other virtues like the lightness, organic materials are thought to be free from the processing difficulty of conventional ferroelectrics, like compatibility and contamination [8]. An obstacle to employing the new organic ferroelectrics was that the ferroelectric phase existed only

well below the room temperature—until the recent breakthrough [7].

Beyond organic crystals, old and new, there is also a special demand for plastic ferroelectrics, e.g. as sensors for the acoustic imaging, in shapeable actuators and capacitors, etc. Their important applications would be in medical imaging, because of a request for low weight material which acoustic impedance would be compatible with biological tissues. (Until now, this demand was satisfied by exploiting composite materials based on powders of ferroelectric oxides in a polymeric matrix which sensitivity is rather low.) The most exploited material is Poly(vinylidene fluoride) (PVDF) [9]. The advantage of all-polymeric ferroelectrics is that they are light, flexible, non toxic, unique as long stretching actuator. They are cheap to be produced being solvable in common organic solvents, so the active elements can be processed by a simple spin-casting. Still, polarizabilities of existing plastic ferroelectrics are rather low, providing the dielectric permittivity $\epsilon \sim 10$, in comparison with $\epsilon \sim 500$ in traditional inorganic ferroelectrics, hence a modest efficiency of devices.

The ferroelectric transition in PVDF and alike is driven by a cooperative ordering from *cis* to *trans* conformations of the polymeric chain, where chains' rotations give rise to opposite displacements of differently charged ligands—here the hydrogen

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and the fluorine, so in effect the electric polarization comes from ionic displacements as in inorganic materials.

The known purely polymeric ferroelectrics belong to the class of saturated polymers which do not possess the delocalized π -electrons, so the material is not active either electronically or optically. A synergy of all those properties can take place in π -conjugated synthetic carbon based materials like organic conductors and donor-acceptor chains or conducting polymers. The principle novelty is that in these materials the polarization comes from ordering of electrons rather than from displacements of ions, hence the nickname “electronic ferroelectricity” [10].

Beyond a set of principally new features, the responsive π -electronic systems can greatly enhance the dielectric permittivity ϵ . This expectation has already been confirmed in the family of organic conducting crystals (TMTTF)₂X—the Fabre salts: the background dielectric permittivity is $\epsilon \sim 10^3$ with astonishing rise to $\epsilon \sim 10^6$ at the phase transition. The high permittivity coexists with a low-activated conductivity while keeping the spin paramagnetism; altogether that gives rise to a new state of the “ferroelectric narrow-gap Mott semiconductor” [5,11–13]. The screening by remnant carriers eliminates the usual hysteresis which leads to fast repolarization. The frequency dependence of ϵ allows separating the critical relaxation within ferroelectric domains and sweeping of domain walls, to extract the critical slowing-down near the transition temperature and the low frequency absorption coming from the creep of domain walls [14]. Less conducting electronic ferroelectrics have been realized as organic donor-acceptor complexes with neutral-ionic transitions where the ferroelectricity [6,15,16] and its electronic nature [10] have been directly confirmed. Also, these materials became the objects of studies by advanced femto-second and tera-Hz optics [17–21].

The microscopic picture of new ferroelectric materials is based on coexisting symmetry lowering effects. The ground state degeneracy brings to life anomalous elementary excitations—the microscopic solitons, which carry non-integer electric charges and play the role of nucleus, at nano-scales, ferroelectric domain walls [22–26].

In this review, we discuss the carbon-based electronic ferroelectrics: from already established ferroelectricity in organic crystals and bimolecular donor-acceptor chains to its possible existence in conducting polymers and graphene nano-ribbons. We argue that a combination of two types of microscopic symmetry breaking in quasi-1D electronic systems should lead to a state with the macroscopic electric polarization. In addition to existing ferroelectricity in organic crystals [5,11] and donor-acceptor chains (see [10] and refs. therein), we indicate [27,28] a class of conducting polymers and may be also nano-ribbons of the graphene where such a ferroelectric state can be found.

The paper is organized as follows: In Section 2 we present the basic introduction to the ferroelectric state. In Section 3 we discuss the symmetry defined way to construct the ferroelectrics. In Section 4–6 we consider cases of the electronic ferroelectricity in conducting polymers, organic crystals and bi-molecular chains. In Section 7 we describe shortly a theory of the ground state and of elementary ferroelectric domain walls—solitons with noninteger charges. Section 8 is devoted to the summary, future road map, and conclusion.

2. Basic introduction to ferroelectricity

When an external electric field E is applied to a dielectric, positively/negatively charged species shift or rotate or align along/against the field. The density of induced dipole moment is called the polarization P which appears in several forms [1]:

- electronic polarization exists in all dielectrics as the electronic cloud deforms and shifts with respect to a nuclei, so an atom or a molecule acquires an induced dipole moment (Fig. 1, left)
- orientational polarization exists in substances built from asymmetric molecules, like SiO₂, H₂O or organic molecules having the preexisting dipole moment. Molecules reorient their dipoles aligning them to the field (Fig. 1, center)
- ionic polarization exists in all ionic solids—NaCl, MgO where weakly bound positive and negative ions shift in opposite directions (Fig. 1, right)

At low E , the induced dielectric polarization P is proportional to the field (Fig. 2, left). But at higher E , the polarization growth slows down (see Fig. 2); they are called the paraelectrics. In spite of the tendency to saturation, the polarization returns to zero if the electric field is switched off.

Some materials are able to generate the macroscopic polarization which happens spontaneously below a transition temperature T_{FE} . The local dipoles may be preformed, then the transition is called as the ordering type; otherwise it is called displacive. To be the ferroelectric, the polarization might be able of switching the direction following the applied electric field; if not, it is called the pyroelectric. From the crystallography point of view, a pyroelectric does not possess the inversion center of symmetry at any T , while the ferroelectric loses it only below T_{FE} .

Unlike pyroelectrics, in ferroelectrics the polarization direction can be switched by the applied electric field. In real time, the repolarization goes by expanding of favorable domains, hence by propagation of domain walls which can be pinned by lattice defects. Then the polarization depends not only on the present field but also on its history, yielding a hysteresis loop (Fig. 2, right). The value of P persistent at $E = 0$ is called the remnant polarization. The value of P extrapolated back from the saturation limit of high E is called the saturated polarization. Regions with different orientations of the polarization vector coexist below the saturation; they are called ferroelectric domains separated by domain walls. The reversed field required for removing the earlier polarization is called the coercive field. Further increase of the reverse field changes the polarization to the opposite, so the hysteresis loop is formed.

There is a common paradox of the ferroelectric state: the polarization works against the Coulomb energy. In traditional inorganic ferroelectrics (PZT—Pb(Zr_xTi_{1-x})O₃, SBT—SrBi₂Ta₂O₉, etc.) the ferroelectric polarization appears as a result of ions' displacements (Fig. 3, left).

In the polymer PVDF (Fig. 3, center) the polarization comes from cis-trans isomerization fitting to preferable angles of molecular bonds. In inert organic crystals there are molecular conformations (Fig. 3, right). In all these cases, one cannot make certain predictions about the ferroelectric instability without a thorough microscopic analysis.

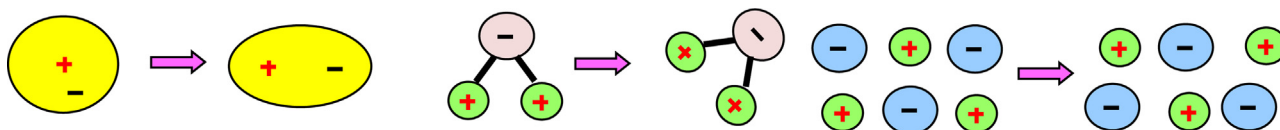


Fig. 1. Effects of the external electric field for cases of intra-molecular (left), orientational (center) and ionic displacive (right) polarizations.

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