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Flexoelectricity induced spatially modulated phases in ferroics and liquid crystals

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ABSTRACT

In the review we briefly analyze the state-of-art in the theory of flexoelectric phenomena and analyze how significantly the flexoelectric coupling can change the polar order parameter distribution in different ferroics and liquid crystals. The special attention in paid to the appearance of the spatially modulated phases induced by the flexocoupling in condensed and soft matter. Results of theoretical modeling performed in the framework of the Landau-Ginzburg-Devonshire formalism revealed that the general feature, inherent to both ferroics and liquid crystals, is the appearance of the spatially-modulated phases is taking place with increasing of the flexocoupling strength. We'd like to underline that theoretical and experimental study of flexoelectricity and related phenomena in nanosized and bulk ferroics, liquid crystals and related materials are very important for their advanced applications in nanoelectronics, memory devices and liquid crystals displays.

1. Flexoelectric effect in ferroics

The flexoelectric effect, first predicted theoretically by Mashkevich and Tolpygo [1] in 1957, exists in any matter (condensed or soft one), making the effect universal [2,3,4,5,6]. The static ***flexoelectric effect*** is an electric polarization generated in solids by a strain gradient and vice versa, whereas broadly known piezoelectricity assume homogeneous strain conditions. The induced strain is linearly proportional to the polarization gradient and, and the proportionality coefficients f, which are the components of the flexocoupling tensor, are fundamentally quite small, $f \sim e/a$, where e and a are respectively electronic charge and lattice constant [7]. Rigorously, the direct and converse static flexoelectric coupling constants f_{ijkl} were described with a fourth-rank tensor, as [2–6]:

$$P_i^{flexo} = f_{ijkl}\frac{\partial u_{jk}}{\partial x_l}u_{ij} = f_{ijkl}\frac{\partial P_k^{flexo}}{\partial x_l} \quad (1)$$

In these expressions u_{jk} and P_i^{flexo} are the tensor strain and polarization vector components, respectively. The physical picture of the flexoelectric effect in solids is shown in Figs. 1(a)–(c). When the geometric centers of positive and negative charges coincide, the net dipole moment of the unit cell is zero, and corresponding unstrained 2D structure of elementary charges is shown in Fig. 1(a). When each unit cell is uniformly tensiled and the tension gradually varies from one cell to another, the cations are displaced from the centre of the deformed unit cell and the strain gradient induces an uncompensated dipole moment via the flexocoupling mechanism [Fig. 1(b)]. The inhomogeneous deformation of the unit cell also produces a net dipole moment via the flexocoupling effect [Fig. 1(c)].

Unlike piezoelectricity, which exists only in noncentrosymmetric systems of 20 point groups, flexoelectricity occurs in all 32 crystalline point groups, because the strain gradients break inversion symmetry. Owing to the universal nature, flexoelectricity permanently attracts broad scientific interest, but its application potential in macromaterials is fundamentally limited due to the small strength f.

The flexoelectricity impact is of great importance in nanosized ferroics [8], for which the pronounced elastic strain and stress gradients are omnipresent near the surfaces, in thin films [9,10,11], at the topological defects, such as domain walls, and near the interfaces [10, 12,13,14]. Owing to the surface and interface effects, the

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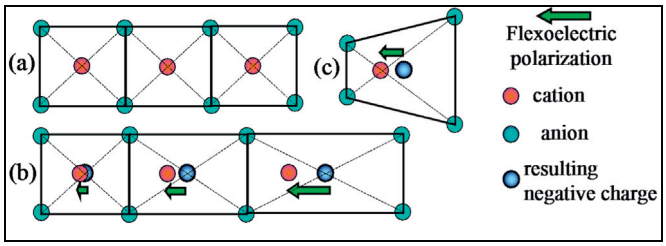

Fig. 1. Origin of flexoelectric effect in solids. **(a)** Unstrained 2D structure of elementary charges with zero net dipole moment. **(b)** Each unit cell is uniformly tensiled, but the tension gradually varies from one cell to another. An uncompensated dipole moment appears via the flexocoupling mechanism. **(c)** An inhomogeneous deformation of the unit cell produces a net dipole moment via the flexocoupling effect.
(Adapted from the papers [5, 11–13]).

flexoelectric effect appears spontaneously near the surface of thin films and nanoparticles [15]; everywhere, where the electric polarization distribution is inhomogeneous. Notably, that the influence of flexoelectricity is important not only in thin ferroic films and nanoparticles, but also in their micro- and nanograined ceramics [16,17], where it should become competitive with surface piezoelectricity [18]. Despite the great importance of flexoelectricity, its tensorial components strength, estimated by Kogan [7] in early 1963, remained poorly known for most of ferroics [19], except for the experimental measurements [20,21,22] and ab initio calculations [23,24] of some components for ferroelectric perovskites, and fundamental limits on the coefficients upper bonds [25].

The direct and converse static flexoelectric effects, which lead to the appearance of polarization due to the strain gradient and vice versa [1], exist in a ferroic of arbitrary symmetry [8, 5, 6]. Corresponding tensorial Lifshitz invariant $\frac{f_{klij}}{2}\left(P_i\frac{\partial u_{kl}}{\partial x_j}-u_{kl}\frac{\partial P_i}{\partial x_j}\right)$ should be included to the free energy functional of all those ferroics, for which the polarization component (s) P_i is a primary order parameter. Using the way it was shown that the flexocoupling term in the form of Lifshitz invariant can induce thermodynamically stable incommensurate spatially modulated phase (**SMP**) in the temperature range between the disordered parent phase (**PP**) and long-range ordered homogeneous phase (**HP**) in many ferroics [26,27,28,29]. Note that the static flexoelectric effect is omnipresent from the symmetry theory considerations, and the earliest [1] and recent [23, 24, 30] microscopic calculations give nonzero values of flexoelectric coefficients f_{klij}. Also it becomes possible to define the static flexoelectric coefficients from direct experiments [21, 22, 31], as well as from the fitting of soft phonon spectra in ferroelectrics (see e.g. [32] and refs. therein).

Notably, that chirality, being the property of an object to be incompatible with its mirror image, can be strongly affected by the flexoelectric coupling. In particular, bichiral structure of ferroelectric domain walls can be driven by flexoelectric coupling [33] and chiral-achiral phase transitions at the walls becomes possible [34].

From considerations of the symmetry theory stating that all terms and invariants, which existence does not violate the symmetry of the system, are allowed, Kvasov and Tagantsev et al. [35] predicted the existence of a cross-term in the kinetic energy, $M_{ij}\frac{\partial P_i}{\partial t}\frac{\partial U_j}{\partial t}$, and named it dynamic flexoelectric effect (see reviews [3, 4] and refs therein). Here M_{ij} is the strength of dynamic flexoelectric coupling and U_i is elastic displacement. At present the situation with the magnitudes M_{ij} of dynamic flexoeffect is more complex and controversial that for the static one, because there are microscopic theories in which the effect is absent [36]. However, the Stengel result [36] contradicts to Kvasov and Tagantsev result [35], who evaluated the strength of the dynamic flexoelectric effect in $SrTiO_3$ from microscopic calculations and it appeared comparable to that of the static bulk flexoelectric effect. More discussion of the problem can be found in Refs [32, 37].

2. Impact of the flexocoupling on phonon spectra and spatially modulated phases in ferroics

Investigation of dynamic characteristics of phase transitions in ferroics, such as their soft phonon spectra, attracts great attention, being the source of valuable information for fundamental physical research and advanced applications [38]. For ferroelectrics the frequency ω_{TO} of transverse optic (**TO**) soft mode depends on temperature T, at that $\omega_{TO}(T_C)=0$ at transition temperature $T=T_C$ [39].

Basic experimental methods, which contain information about the soft modes and spatial modulation of the order parameter in ferroics (such as antiferroelectrics, proper and incipient ferroelectrics) are dielectric measurements [40], inelastic neutron scattering [39, 41,42,43,44,45], X-ray [26, 46,47,48], Raman [49] and Brillouin [46, 47, 50,51,52,53] scatterings and ultrasonic pulse-echo method [50, 52] allowing hypersound spectroscopic measurements. Scattering experiments proved that not only the TO mode softens substantially with decreasing temperature to freeze out at T_C in ferroics (such as ferroelectric perovskites), but also finite wave vector anomalies appear in the transverse acoustic (**TA**) mode for structural phase transitions [54,55,56].

Using the Landau-Ginzburg-Devonshire (**LGD**) theory [57,58,59], Morozovska et al. derived analytical expressions for the soft phonon modes frequency $\omega(k)$ dependence on the wave vector k and examined the conditions of the soft acoustic TA-modes appearance in ferroelectrics depending on the magnitude of the flexoelectric coefficient f and temperature T. If the magnitude of the flexoelectric coefficient f is equal to the temperature-dependent critical value $f_{cr}(T)$ at the temperature $T=T_{IC}$, $|f|=f_{cr}(T_{IC})$, then the TA-mode frequency tends to zero at $k\to k_0^{cr}$ according to the linear law $\omega(k\to k_0^{cr})\sim k-k_0^{cr}$ and, simultaneously, the ferroelectric polarization becomes spatially modulated. When the magnitude of the flexocoefficient is more than the critical value $|f|>f_{cr}(T)$ in a temperature range $T_C<T<T_{IC}$ lower than Curie temperature T_C, corresponding to the incommensurate phase, the TA-mode becomes zero for two wave vectors $k=k_{1,2}^{cr}$ according to the squire root law, $\omega(k\to k_{1,2}^{cr})\sim\sqrt{|k_{1,2}^{cr}-k|}$, and does not exist in the range of wave vectors $k_1^{cr}<k<k_2^{cr}$, where the incommensurate modulation exists. At fixed flexocoefficient f the transition into the incommensurate phase can appear at the temperature T_{IC} that depends on f. In addition we predicted the appearance of the "rippled" flexocoupling-induced incommensurate phase in the ferroics with initially commensurate phases only. The available experimental data on hypersound velocity in the solid solutions $Sn_2P_2(S,Se)_6$ [50] and neutron scattering in organic ferroelectric $(CH_3)_3NCH_2COO\cdot CaCl_2\cdot 2H_2O$ [44] are in a semi-quantitative agreement with the theoretical results [57–59]. For improvement and for quantification of the theory, it is necessary to measure the frequency dependence of the TA-modes in a uniaxial ferroelectric with a spatially modulated phase in the temperature interval near its appearance.

3. General formulation of Landau-Ginzburg-Devonshire formalism

LGD expansion of bulk (F_V) part of Helmholtz free energy F on the order parameter η and strain tensor components u_{ij} has the form:

$$F_v=\int_v d^3r\left(\begin{array}{c}\frac{a_{ij}(T)}{2}\eta_i\eta_j+\frac{a_{ijkl}(T)}{4}\eta_i\eta_j\eta_k\eta_l+\frac{a_{ijklmn}}{6}\eta_i\eta_j\eta_k\eta_l\eta_l\eta_m\eta_n-\eta_iE_i\\+\frac{g_{ijkl}}{2}\left(\frac{\partial\eta_i}{\partial x_j}\frac{\partial\eta_k}{\partial x_l}\right)+\frac{w_{ijkl}}{2}\left(\frac{\partial^2\eta_i}{\partial x_j{}^2}\frac{\partial^2\eta_k}{\partial x_l{}^2}\right)+\frac{h_{ijk}}{2}\eta_i^2\left(\frac{\partial\eta_j}{\partial x_k}\right)\\-\frac{f_{ijkl}}{2}\left(\eta_k\frac{\partial u_{ij}}{\partial x_l}-u_{ij}\frac{\partial\eta_k}{\partial x_l}\right)-q_{ijkl}u_{ij}\eta_k\eta_l+\frac{c_{ijkl}}{2}u_{ij}u_{kl}+\frac{v_{ijklmn}}{2}\left(\frac{\partial u_{ij}}{\partial x_m}\frac{\partial u_{kl}}{\partial x_n}\right)\end{array}\right)\tag{2a}$$

Coefficients $a_{ij}(T)$ explicitly depend on temperature T; a_{ijkl} is regarded temperature independent, a_{ijklmn} is a temperature independent and positively defined. Constants g_{ijkl} and v_{ijklmn} determine magnitude of the gradient energy. Higher gradient tensors w_{ijkl} and h_{ijk} are positively defined, q_{ijkl} is the bulk striction coefficients; c_{ijkl} are