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Step-by-step first order antiferroelectric-paraelectric transition induced by frustration and electric field

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In this work we show analytically that even not too strong frustrating next neighbour interaction strongly affects first order antiferroelectric-paraelectric transition in an external electric field. We apply mean-field Landau theory. In the electric field a single phase transition at T_0 splits into a step-by-step staircase with a series of intermediate phases. Unexpectedly enough we found that the equilibrium structures of the phases differ substantially from structures formed at low temperature both without field and in field. Polarization of intermediate structures decreases with temperature in a stepwise manner. Similar step-by-step transitions can occur also in magnetic materials with frustrating interaction.

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Electrically or magnetically ordered frustrated systems (liquid crystals or solids) have always gained significant attention of researchers (see, e.g., monographs [1, 2]). However, in spite of relevant progress in this field, several problems remain open or at least not completely understood as it is clear from continuously growing number of original publications. In this work we study one of the oldest questions of such kind about the first order transition from antiferro- to para-phase (to be more specific in what follows we speak about uniaxial proper electric dipole ordering, however all results conceptually valid for any kind of antiferro-systems, including chiral liquid crystalline smectics and magnets). More than 60 years ago, C. Kittel [3] formulated a model of this transition, which includes a coupling between polarizations of two sublattices in antiferroelectrics. Since in most systems with antiferroelectric – paraelectric transition, it is a 1-st order phase transition, Kittel's theory has been applied to describe such a case by Okada [4]. In Kittel's model of antiferroelectric [3] with interaction only between nearest layers the system is represented by two alternating lattices labelled a and b with polarization P_a and P_b. Two order parameters namely polarization $Q \sim (P_a + P_b)$ and antipolarization $q \sim (-P_a + P_b)$ may be introduced [4]. Okada [4] used Kittel's theory for description of first-order transitions in field but also with interaction only between nearest layers. However in the majority of modern material science complex systems with dipole or quadrupole orderings, as a rule one may not restrict oneself to nearest neighbours coupling only. At least next to nearest neighbours have to be included. Moreover for many materials with antiferroordering one can expect the next neighbour coupling to be incompatible with the nearest neighbour interactions. Thus we face to so-called frustrating interactions.

Frustrating interactions can cause dramatic phenomena in structure of materials. They lead to formation of a manifold of unusual structures and transitions between them. Structure of electric polar and magnetic materials with frustrating interaction is known example of frustration phenomenon [5–18]. As an example to illustrate our findings we consider a polar material with layer structure. Interaction between nearest layers leads to formation of only two simple structures with ferroelectric (F) and antiferroelectric (AF) ordering having correspondingly parallel and antiparallel polarization $\mathbf{P}$ in nearest layers. Frustrating interaction favours opposite orientation of polarizations in next nearest layers which is incompatible both with ferroelectric and antiferroelectric structures [9, 17]. The relief of the frustration is formation of more complicated structures with spatial modulation in both the module and the orientation of polarization. However such behaviour is a rather rare phenomenon in solid and liquid crystalline materials. Most materials have only ferroelectric (F) or/and antiferroelectric (AF) phase. Frustrating interaction in most materials is too weak to form complicated structures. Okada [4] showed that interaction between nearest layers and external electric field can modify antiferroelectric (AF)–paraelectric (PE) transition with formation of a two-layer ferrielectric phase.

In this paper the peculiarities of the AF–PE transition in materials with frustrating interlayer interaction are studied. We show that near the temperature of the AF–PE phase transition in electric field frustrating interlayer interaction can realise in appearance of unusual structures which are not formed at low temperature. First order antiferroelectric–paraelectric transition splits in a series of transitions at which the polarization stepwisely decreases with temperature. The new structures are space modulated that is the order parameter changes from layer to layer.

In this paper we extended Kittel's [3] and Okada's [4] theories for frustrating interlayer interaction. We use the vector two-component order parameters ξ_i for each i-th layer which are more convenient to describe multilayer structures. In our calculations we employ the discrete phenomenological Landau theory of phase transitions [9, 11, 16, 17]. Expansion of the free energy [11, 19] $G = G_L + G_{IN} + G_E$ over the order parameter ξ_i includes conventional Landau terms G_L

$$G_L = \sum_i \left[\frac{1}{2}\alpha(T - T^*)\xi_i^2 + \frac{1}{4}b_0\xi_i^4 + \frac{1}{6}c_0\xi_i^6\right]. \qquad (1)$$

Negative sign of b_0 makes the transition first order [20]. Interlayer interactions G_{IN} are

$$G_{IN} = \frac{1}{2}a_1 \sum_i \xi_i\xi_{i+1} + \frac{1}{8}a_2 \sum_i \xi_i\xi_{i+2} + b[\xi_i \times \xi_{i+1}]^2. \qquad (2)$$

We consider materials with unique polar axis. The vector order parameter ξ_i is characterized by its modulus and orientation. In polar solid materials $\mathbf{P}_i$ can have only two opposite orientations and it may be considered as an Ising-like quantity proportional to the order parameter $\mathbf{P}_i = \xi_i P_0$. This case is mathematically simpler than chiral and polar liquid crystal smectics but both the qualitative physical results and the mathematical difficulties are already there.

The interaction with external electric field conjugated to the order parameter is $G_E = -\sum_i P_i E$. In polar smectic liquid crystals the situation is more complex [21]. Long axes of molecules are tilted by a polar angle θ_i with respect to layer normal z. Two-dimensional order parameter ξ_i is the projection of the nematic director $\mathbf{n}$ onto the layer plane. The azimuthal orientation of ξ_i is described by the angle φ_i. Layer polarization P_i is perpendicular to the plane of the tilt [21] and proportional to the order parameter $P_i = |\xi_i|P_0$. Interaction with the field can be written as $G_E = \sum_i |\xi_i|P_0 E \sin\varphi_i$. We will consider polar smectics in high field when the structures in electric field are planar. In this case $\sin\varphi_i$ factor can take only two values, namely ± 1.

Now let us discuss different terms in the free energy (1), (2) and their influence on the transition. Interaction between nearest layers (the first term in (2)) with negative a_1 favours parallel orientation of ξ_i in nearest layers (ferroelectric F phase). Antiparallel arrangement in nearest layers (antiferroelectric AF case) is favourable for positive a_1. The key new part of our analysis is the second term in (2). This frustrating interaction for $a_2 > 0$ favours antiparallel orientation of ξ_i in next nearest layers which is incompatible with both F and AF structures. Čepič et al. [9, 22] showed that in polar liquid crystals a_2 should be positive, that is this interaction can lead to frustration. As we will see this leads to an essential modification of the transition from the polar to paraelectric phase in an electric field. The third term in (2) is the potential barrier between ferroelectric and antiferroelectric ordering [22].

Let us now consider different structures which can form under combined action of frustration and electric field. To minimize the thermodynamic Landau potential we have to solve the system of equations $\partial G/\partial \xi_i = 0$. We need to consider structures with periodicity of two and three layers apart from the F phase.

For two-layer structures the derivative of the total free energy of the unit cell G_2 with respect to ξ_1 is

$$\partial G_2/\partial \xi_1 = \alpha(T - T^*)\xi_1 + b_0\xi_1^3 +$$

$$+ c_0\xi_1^5 + a_1\xi_2 + \frac{1}{4}a_2\xi_1 - EP_0 = 0. \qquad (3)$$

Index "2" in G_2 stands for the two-layer structure. Substituting ξ_2 from (3) into G, we obtain the dependence of the free energy G_2 on ξ_1 which allows to determine stable structures. Symmetry considerations show that in a three-layer structure two of the three layers should have equal order parameter $\xi_2 = \xi_3$. Similar to the two-layer structure, for the three-layer structures the dependence of energy G_3 on ξ_1 can be obtained.

Before considering the behaviour of antiferroelectric, it is appropriate to remind the characteristic features of the transformation of the F–PE transition in external field. Fig. 1a illustrates the known behaviour of the first order transition. Calculations were made employing the free energy G with $a_1 < 0$ when the ferroelectric phase is formed without field. Open points show the temperature dependence of spontaneous polarization without field. In field the transition shifts to higher temperature and field-induced polarization appears at high temperature. When the field increases the step in the transition decreases and at some field E_C the first order transition disappears. Above the critical field E_C a smooth decrease of the polarization with temperature takes place.

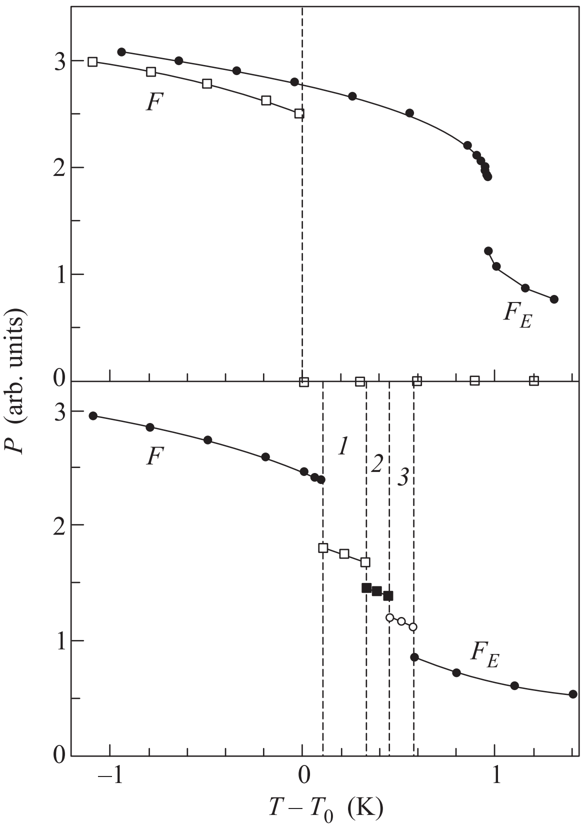

Fig. 1. (a) – Temperature dependence of polarization P in ferroelectric structure near the temperature of the first order transition: without electric field (open symbols) and in field $EP_0 = 1.4 \cdot 10^{-3}$ (solid symbols). T_0 is the temperature of the ferroelectric–paraelectric transition in absence of the field. (b) – Temperature dependence of polarization P in antiferroelectric material in electric field. The stepwise transition (a) is replaced by a staircase with step-by-step decrease of polarization (b). $EP_0 = 1.4 \cdot 10^{-3}$. Numbers *1*, *2*, *3* denote the regions with three-layer (F_{31}), two-layer (F_2), and three-layer (F_{32}) phases. $a_1 = -0.003$ in ferroelectric (a) and 0.003 in antiferroelectric (b). Other model parameters are: $\alpha = 0.01$, $b_0 = -0.5$, $c_0 = 6$, $a_2 = 0.004$, $b = 0.02$

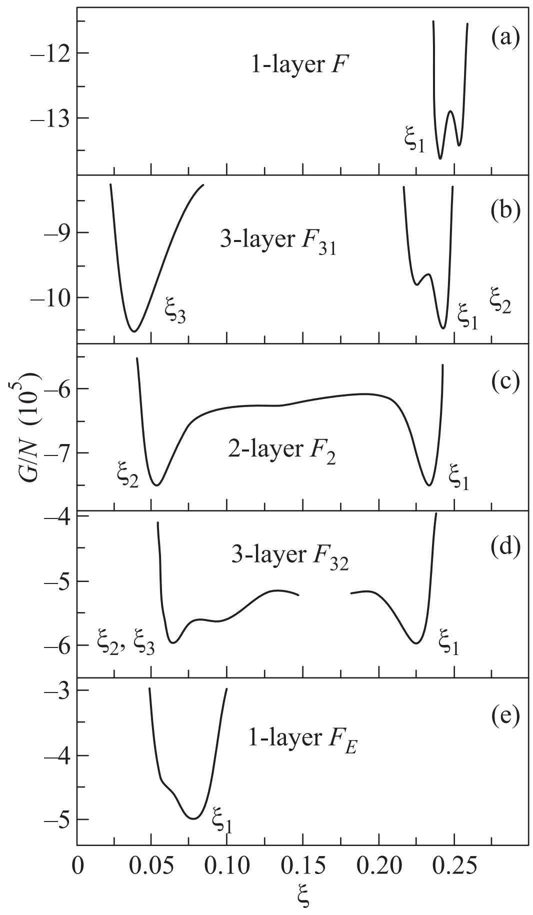

Fig. 2. Dependence of the free energy G/N on the order parameter for the ferroelectric F phase, $\Delta T = T - T_0 = 0.08$ K (a); three-layer F_{31} phase, $\Delta T = 0.22$ K (b); two-layer F_2 structure, $\Delta T = 0.39$ K (c); three-layer F_{32} structure, $\Delta T = 0.52$ K (d); and for the field-induced F_E structure, $\Delta T = 0.7$ K (e). Model parameters are the same as in Fig. 1b. N is the number of layers in the unit cell.

In antiferroelectric without field the polarization of every layer shows behaviour similar to that in Fig. 1a. In non-zero external field a dramatic change of the transition takes place. Fig. 1b shows the behaviour of antiferroelectric with frustrating interaction for the same value of external field as in Fig. 1a. A single transition (Fig. 1a) transforms into a staircase with decreasing polarization. Fig. 2 shows the dependence of the energy on the order parameter for different states. In field at low temperature the antiferroelectric transforms into the ferroelectric structure. There is one global energy minimum (Fig. 2a) which corresponds to the ferroelectric (F) state with one-layer periodicity. All ξ_i are oriented in the same direction and have the same magnitude (Fig. 3a). At high temperature the dependence of the energy on ξ_i becomes more complicated. A dramatic change with respect to Fig. 1a is observed just above T_0, where T_0 is the temperature of the transition to the PE state without field. The continuous curve in Fig. 1a above T_0 is split into three separate curves (Fig. 1b) which represent the magnitude of polarization for different structures. In the first state (1) in Fig. 1b the dependence of G on ξ_i has two minima (Fig. 2b). The minimum with larger ξ_i is degenerate ($\xi_1 = \xi_2$ in Fig. 2b). Eventually, the three-layer structure F_{31} with $\xi_1 = \xi_2 \neq \xi_3$ is formed (Fig. 3b). In the next state (2) there are two non-degenerate minima with equal energy but with $\xi_1 \neq \xi_2$ (Fig. 2c). This is the two-layer structure F_2 with different values of ξ_i in the two-layer

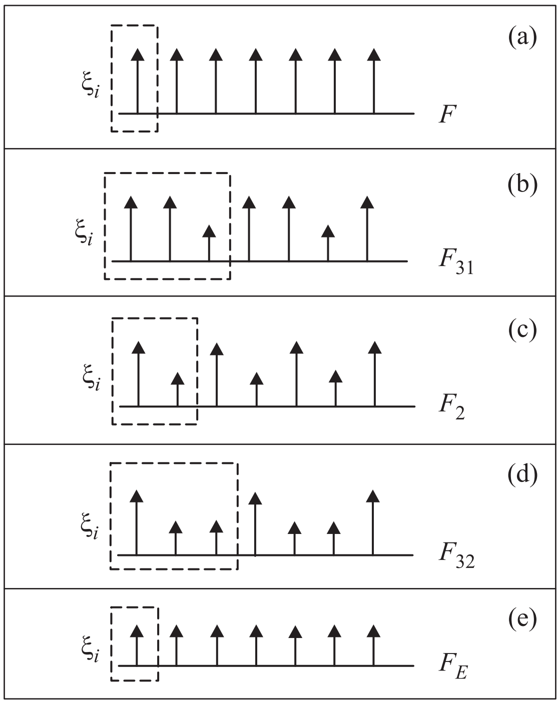

Fig. 3. Schematic representation of the polar structure in different phases. Dotted rectangles show the periodicity of the structures

unit cell. F_2 phase is the analogue of two-layer structure formed when there are no frustrations, i.e. only interlayer interaction between nearest layers takes place [4]. As in the F_{31} phase all ξ_i (and layer polarizations) are oriented in the same direction (Fig. 3c). The next $2 \rightarrow 3$ transition (Fig. 1b) leads again to formation of a three-layer structure (F_{32} in Fig. 3d). As in the F_{31} structure one energy minimum is degenerate ($\xi_2 = \xi_3$, Fig. 2d), however now unlike F_{31} the minimum with a smaller ξ_i is degenerate. At high field the three-layer F_{32} structure transforms into the F_E phase with a single energy minimum (Fig. 2e) and one-layer periodicity (Fig. 3e). This phase is similar to the high temperature field-induced ferroelectric structure F_E (Fig. 1a). All discussed transitions are of first-order.

Fig. 2 allows to follow the formation of different phases. In the one-layer F structure apart from the absolute energy minimum (Fig. 2a) there is a metastable one at higher ξ. This metastable state corresponds to the three-layer structure. Upon increasing temperature the metastable minimum is shifted to lower ξ and becomes deeper. At the $F \rightarrow F_{31}$ transition two minima become equal and then the minimum at higher ξ becomes stable. Analogous behaviour occurs at the $F_E \rightarrow F_{31}$ transition (Fig. 2e). The shoulder of $G(\xi)$ near the minimum transforms at decreasing temperature into a minimum corresponding to the three-layer structure. This structure becomes stable at lower temperature (Fig. 2d).

Fig. 4 shows the temperature dependence of the order parameters ξ_i in different structures. In the F_{31}, F_2,

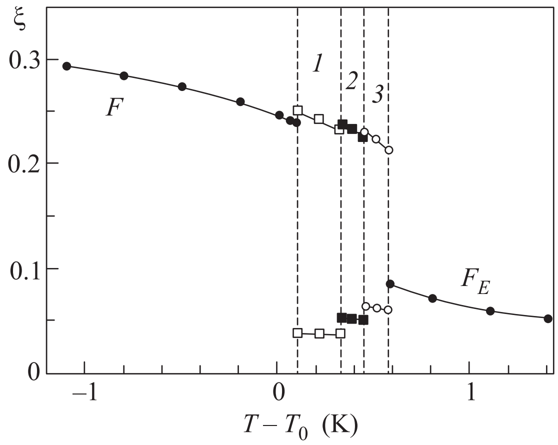

Fig. 4. Temperature dependence of the order parameters ξ_i in one-layer ferroelectric F, three-layer F_{31} (*1*), two-layer F_2 (*2*), three-layer F_{32} (*3*), and field-induced F_E structures. Model parameters are the same as in Fig. 1b

and F_{32} phases ξ strongly changes from layer to layer. ξ_i is split in two branches with low and high values of ξ_i. The low-lying branch is related with the existence of the F_E phase, the high-lying branch is due to the F phase. The competition between interlayer interaction and electric field leads to stabilization of the branches at the same temperature and formation of multilayer structures. Two branches explain also the stepwise decrease in the polarization and the values of steps. In the F phase all layers have high values of ξ. In the F_{31} phase only two layers have high values of ξ. In the F_2 phase one layer has high ξ value, and the other one has low ξ. In F_{32} structure already two layers have low ξ.

So, combination of the two states in electric field (F and F_E with high and low ξ_i) and existence of interlayer interaction favouring antiparallel orientation of ξ_i leads to formation of intermediate (compromise) phases (F_{31}, F_2, F_{32}). In these compromise structures both states (with low and high ξ) are realized within multilayer structures. Stepwise change of polarization can be observed in precise dielectric measurements near the first order transition. Diffraction technique can detect the multilayer structures.

In summary, interlayer interaction can dramatically modify the behaviour of the first order antiferroelectric–paraelectric transition in electric field. Previous formulations of the models for the first order antiferroelectric–paraelectric phase transition do not lead to the structures and phase sequences found in our work. A single transition known from the simple model is split into a multistep transition with ferrielectric three-layer, two-layer and again three-layer structures. Polarization decreases with temperature in a step-wise manner. The discovery of multilayer phases in polar liquid crystals [7, 14, 22, 23] unambiguously points the existence and relevance of the frustrating interaction between next nearest layers. Moreover in liquid crystals the frustrating interaction is strong enough, otherwise formation of new multilayer structures would be forbidden. This suggests that the predicted effects can be also observed in other polar materials. We anticipate analogous behaviour in magnetic systems. Namely such behaviour can occur for example in metamagnetics (with easy axis) in which interaction between layers favours a change of spin direction from one layer to the next and frustration plays an important role. We hope that our new theoretical predictions can be tested experimentally. Magnetometric or dielectric methods could be useful to measure the ferro part of the polarization and corresponding susceptibility. Antiferro-characteristics might be probed by various scattering techniques.

We report here only a brief summary of our results and leave more detailed analysis for a future work. In particular we did not touch any interface, domain structures, defects, surface effects and other system non-uniformities. However, any theoretical model which takes all these elements into consideration as realistically as it is possible, would be extremely complicated and would not lead to qualitatively new results.

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