A possible origin of anomalous properties of proper uniaxial ferroelectrics near the lock-in transition

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Abstract. A mechanism which may be responsible for the anomalies in the behaviour of type II ferroelectrics near the lock-in transition is considered. The state of the system is suggested to be quasistationary. The defects of the incommensurate modulation wave are found to play an important role and give additional contributions to the thermodynamic characteristics of the system.

1. Introduction

Proper uniaxial ferroelectrics with incommensurate (IC) phases are commonly classified as type II systems. Such a classification was introduced in [1] to emphasize the existence of the two different types of incommensurate-to-ferroelectric transition observed experimentally in ferroelectrics [2].

From a formal point of view, the main feature which characterizes these types is the presence (type I) or absence (type II) of the Lifshitz invariant in the expansion of the system thermodynamic potential [1]. The order parameter is usually considered to be two-component in the case of type I systems (Rb_2ZnCl_4, K_2SeO_4 and other compounds of the A_2BX_4 family [2]). For type II systems the order parameter is one-component and corresponds to spontaneous polarization oriented along some specific direction. Sodium nitrite $NaNO_2$ [2], thiourea $SC(NH_2)_2$ [2], BCCD [3] and $(Pb_ySn_{1-y})_2P_2(Se_xS_{1-x})_6$ solid solutions [4] belong to the group of type II ferroelectrics.

The properties of IC phases in type I and type II ferroelectrics are similar in the vicinity of the disordered-to-incommensurate transition. In particular, the spatial modulation of the order parameter is almost sinusoidal.

An essential distinction appears when approaching the transition from the IC phase into the ferroelectric state [1, 2]. In type I systems the dependence of the phase of the order parameter on the position transforms from sinusoidal into a stepwise one. A domain-like structure (soliton lattice) develops as the temperature decreases from T_I (the point of transition from the disordered phase into the incommensurate state) to the lock-in value T_c [1, 2]. A second-order lock-in phase transition can take place, at least in principle [5].

In contrast, in the case of type II ferroelectrics the squaring of the modulation wave profile is not observed at the low-temperature boundary of the IC phase [2, 3, 6]. The only exception is thiourea, for which a relatively large contribution of higher harmonics is found [7]. But

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even for thiourea the soliton lattice is not so developed as in the compounds of the A_2BX_4 family [8].

At the same time, in the proximity of the lock-in transition, proper uniaxial ferroelectrics demonstrate features typical of type I systems. A rise of the dielectric constant at low temperatures in the IC phase [9] and additional integrated satellite intensity [4] are examples of such anomalous properties.

For the systems with the Lifshitz invariant the above-mentioned phenomena are commonly explained on the basis of the soliton lattice concept (see, e.g., [10]). But in the case of proper ferroelectrics, as we have stated above, experimental data clearly point to the fact that the modulation wave is almost pure sinusoidal within the IC phase [2, 3, 6].

In principle, domain-like structures are theoretically possible for the systems with one-component order parameters $\varphi(x)$ [11]. But for the parameters of the thermodynamic potential found for certain compounds [12–14], the nonlinear states [11] are only metastable [15]. As for the equilibrium state, the contribution of higher harmonics to the modulation wave is estimated to be small [1, 16, 17].

Some anomalies, in particular the dielectric constant behaviour near T_c, may be explained by taking into consideration long-range elastic forces [13,17]. However, the elastic contribution is not sufficient to describe the temperature dependence of the order parameter and of the modulation wavenumber and the main thermodynamic characteristics simultaneously, e.g. in $Sn_2P_2Se_6$ [18].

The existence of some phenomena, such as the anomalous hysteresis [19], the memory effect [20] and the states of spin-glass type [21, 22] (see also [23]), shows that nonequilibrium processes are important for phase transitions in proper ferroelectrics.

The theory of stripple nucleation [24] is often used when considering anomalous hysteresis [25] and long-time relaxation of susceptibility [9]. In the case of type II ferroelectrics the problem is that the stripple nucleation [24] implies the existence of a soliton lattice.

The electronic mechanism is thought to be of importance when clarifying the memory effect in $Sn_2P_2Se_6$ [20]. However, such models are valid for semiconductors only.

The above-mentioned facts reveal that the properties of the IC phase near the lock-in transition, as well as the nature of this transition, are not fully understood for type II systems.

In the present paper we discuss a conjecture according to which the state of type II ferroelectrics is not truly equilibrium at the low-temperature boundary of the IC phase. The defects of the order parameter modulation wave, such as the spatial variation of the modulation amplitude and the change of initial phase (figures 1(a), 2(b)), are supposed to play an important role in the thermodynamics of these systems.

In the vicinity of the lock-in transition the defects of the polarization wave form a structure. Due to retarded temporal evolution, the states with the defect structure become quasistationary. The existence of a quasistationary structure of polarization wave defects is the reason for the additional contributions to the system characteristics (susceptibility, heat capacity etc). Under some conditions, e.g. for a strong influence of impurities, the density of wave defects is so large that the regular IC modulation is destroyed, and states similar to chaotic (amorphous) ones may occur.

The structure of the paper is as follows. In section 2 we formulate the one-dimensional Landau-type model used to describe the phase transitions in type II systems. Then, we reinvestigate the role of higher harmonics of the order parameter modulation wave. For type II ferroelectrics (excluding thiourea) the contribution of higher harmonics is found to be small. On the other hand, numerical analysis shows that there exist a lot of states in which, besides the fundamental IC modulation, subharmonics of the fundamental component are present (figures 1(b), 2(b)). In such states the amplitude and the wavenumber of the IC wave are
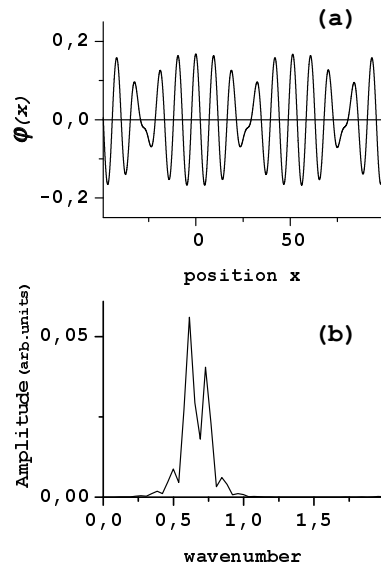
Figure 1. The spatial dependence of the order parameter $\varphi(x)$ (a) and the wavenumber spectrum (b) for the local minimum of the thermodynamic potential, $\varphi(0) = 0.168$, $\varphi''(0) = -0.072$, $\Phi \approx -0.000\,22$ (for the global minimum (model (3)) $\varphi(0) \approx 0.167$, $\varphi''(0) \approx -0.078$, $\Phi \approx -0.000\,34$). The material parameters are taken as for NaNO$_2$ [12], $q = 0.2$. The initial phase of the modulation wave $\varphi(x)$ differs by π in neighbouring domains.
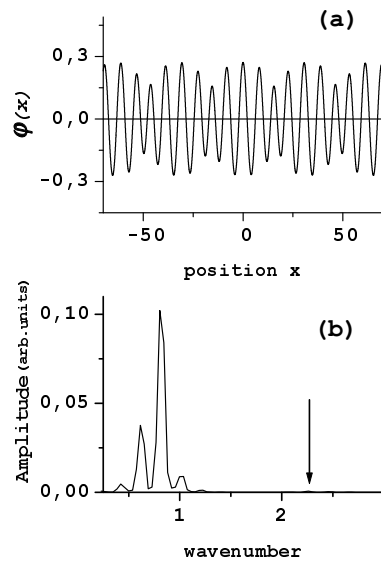

Figure 2. As figure 1, but for $q = 0.07$ and $\varphi(0) = 0.272$, $\varphi''(0) = -0.148$, $\Phi \approx -0.0023$ (for the global minimum (model (3)) $\varphi(0) \approx 0.354$, $\varphi''(0) \approx -0.124$, $\Phi \approx -0.0050$). The initial phase of the modulation wave does not change. The arrow indicates the small higher (third) harmonics.

relatively close to the equilibrium ones. These states are metastable and correspond to the local minima of the thermodynamic potential. Due to the existence of such local minima, the thermodynamic potential surface is very complex.

Possible consequences of the complex structure of the potential surface are considered qualitatively in section 3. Taking into account the results of studying the growth kinetics of IC domains [26–28], retarded temporal evolution of structural relaxation type is expected. The appearance of quasistationary states with the defects of the polarization wave is discussed.

In section 4, we evaluate the influence of phase defects on the system characteristics in the framework of a simple phenomenological model. In particular, the susceptibility may increase as $\chi^{-1} \sim (T - T_c + \Delta T)$, where ΔT is some constant, near the lock-in transition. The conclusions are presented in section 5.

2. States with subharmonics of the fundamental IC wave

Phase transitions in type II ferroelectrics can be described in the framework of the Landau theory. Following Ishibashi *et al* [16, 29] we write the thermodynamic potential in the form

$$\Phi = \Phi_0 \frac{1}{L} \int_0^L \left[(\varphi'')^2 - g(\varphi\varphi')^2 - \gamma(\varphi')^2 + q\varphi^2 + \frac{p}{2}\varphi^4 + \frac{1}{3}\varphi^6 - \varphi e \right] \mathrm{d}x. \tag{1}$$

Here $\varphi(x) = P_y(x)$ is the order parameter (the spontaneous polarization P oriented along the y-axis); $\varphi'(x) \equiv \partial\varphi/\partial x$. The order parameter is assumed to be modulated along the x-axis; the crystal length in this direction is equal to L. The material parameters g, γ, p do not depend on the temperature T, but $q = q_0(T - T_0)$, where q_0, T_0 are some constants. The external electric field is denoted by e.

In order to emphasize the physically relevant material parameters and simplify the analysis, the scale transformation of the order parameter $\varphi(x)$, the space coordinate x and the material parameters is performed in (1) (the factor Φ_0 appears due to this transformation) [15]. After the scale transformation, $\gamma = 1$. We retain the notation γ to trace the contribution of the invariant φ'^2 which provides stabilization of the IC phase. Hence, only three effective parameters vary in model (1): g, q, p.

The local part of the functional (1) corresponds to the standard expansion of the thermodynamic potential in the Landau theory of phase transitions. For some proper uniaxial ferroelectrics (sodium nitrite, $Sn_2P_2Se_6$), the direct (virtual) transition from the disordered phase into the commensurate state is expected to be of first order, i.e. the material parameter p is to be negative [4, 29]. In this case the invariant $\sim\varphi^6$ is required to provide the global system stability. For the compounds with $p > 0$, e.g. thiourea, the term $\sim\varphi^6$ may be omitted.

The order parameter $\varphi(x)$ is an extremum of the functional (1) and must satisfy the variational equation:

$$\varphi^{(IV)} + g(\varphi^2\varphi'' + \varphi\varphi'^2) + \gamma\varphi'' + q\varphi + p\varphi^3 + \varphi^5 = 0. \tag{2}$$

At high temperatures the ground state of the system (1) is disordered: $\varphi(x) = 0$ [16]. With decreasing temperature, the transition from the disordered state into the incommensurate phase takes place at the point $q = q_I = q(T_I) = \frac{1}{4}\gamma^2$, if the parameter $\gamma > 0$. The existence of a stable incommensurate state is a result of the competition and compromise between the gradient invariants $(\varphi'')^2$ and $(\varphi')^2$: if $\gamma > 0$ the term $(\varphi')^2$ favours the spatial modulation of the order parameter, and because $(\varphi'')^2$ the wavenumber b of the order parameter modulation wave is finite.

One of the most characteristic features of the IC phase is the dependence of the wavenumber b on the temperature. In model (1) this property is reproduced due to the invariant $(\varphi\varphi')^2$ [16, 17]. This term is also very important when describing the behaviour of the susceptibility at the low-temperature boundary of the IC phase [16]. Moreover, the nonlinear properties of the order parameter modulation strongly depend on the value of the coefficient at the invariant $(\varphi\varphi')^2$, i.e. on the value of the material parameter g [15].

In the proximity of the point q_I the order parameter modulation wave is almost sinusoidal [2]. As we have pointed out above, for most type II ferroelectrics the IC order parameter configuration differs faintly from the pure sinusoidal even in the close vicinity of the lock-in transition. That is why the one-harmonic approximation

$$\varphi(x) = a \sin[b(x + x_0)] \qquad (3)$$

is often used when describing the equilibrium distribution of the order parameter in the IC phase in type II ferroelectrics (see, for example, [12–14, 17]).

The one-harmonic model (3) reproduces fairly well a lot of properties of type II ferroelectrics. But in order to evaluate the deviation from the sinusoidal behaviour, a more general approach [15] is appropriate.

According to [15], for the systems (1) the equilibrium IC distribution of the order parameter $\varphi(x)$ can be approximated by

$$\varphi(x) = a \operatorname{sn}[b(x + x_0), k] \qquad (4)$$

where $\operatorname{sn}(x, k)$ is the Jacobi elliptic sine. Similarly to the case of (3), the model parameters a, b, k are to be defined with the aid of minimization of the thermodynamic potential (1) [15].

The approximation (4) allows us to describe not only the linear stage of the temperature evolution of the IC phase, but also the nonlinear features of the order parameter modulation [15]. In particular, the contribution of higher harmonics to the polarization wave can be estimated. For this purpose, one should calculate the equilibrium value of the elliptic modulus k [15]. Then, using the Fourier expansion of the elliptic sine [30], it is easy to find the ratio a_n/a_1, where a_1 and a_n are the amplitudes of the fundamental and the nth harmonic, respectively. For large values of k ($k \approx 1$), the fast Fourier transformation (FFT) of the modulation wave (4) can be used as well, because the formulae [30] are not strictly correct if $k \to 1$.

The results of such an investigation are summarized in table 1. They confirm the conclusions of [1, 16, 17]: although one may construct an abstract system for which the ratio a_3/a_1 is relatively large (the first row in table 1), in the real compounds, especially in $NaNO_2$ and $Sn_2P_2Se_6$, the role of higher harmonics is rather minor.

Table 1. The amplitudes of the higher harmonics of the IC modulation wave at the lock-in temperature T_c ($q_c = q(T_c)$, $k_c = k(T_c)$); $\varphi^6 = 0$ means that the φ^6-term is omitted; the superscripts 1–3 indicate parameters corresponding to $NaNO_2$ [12], $Sn_2P_2Se_6$ [13] and BCCD [14], respectively).

g	p	φ^6	q_c	k_c	a_3/a_1	a_5/a_1
-10.0	1.00	0	-0.212	0.965	0.136	0.0220
-1.0	1.00	0	-0.690	0.768	0.052	0.0029
0.0	1.00	0	-1.176	0.642	0.032	0.0011
-9.51[1]	-0.65	1	0.069	0.59	0.026	0.0007
-1.37[2]	-0.19	1	-0.225	0.706	0.041	0.0018
-8.00[3]	2.00	0	-0.365	0.887	0.086	0.0082

Hence, the soliton lattice concept is not appropriate when interpreting the anomalies in the behaviour of type II ferroelectrics near the lock-in transition, at least in the framework of model (4).

To obtain more information about the solutions of the variational equation (2), we have studied this equation numerically.

The fourth-order Runge–Kutta numerical procedure is used for solving equation (2). As long as we are searching for periodic solutions, it is reasonable to reduce the set of boundary

conditions $S = \{\varphi(0), \varphi'(0), \varphi''(0), \varphi'''(0)\}$ to a simple one: $S_0 = \{\varphi(0), 0.0, \varphi''(0), 0.0\}$ where $\varphi(0) \geqslant 0$, $\varphi''(0) \leqslant 0$ [31]. For the reduced set S_0 the solutions of (3) and (4) types appear with some nonzero phase shifts x_0. A spatially homogeneous solution $\varphi(x) = \text{constant}(x)$ corresponds to the case $\varphi''(0) = 0$.

Solving the variational equation (2), we also investigate the properties of the thermo-dynamic potential surface $\Phi(\varphi(0), \varphi''(0))$ at different temperatures.

A qualitative analysis of the results obtained shows the following.

There exists a valley of the potential minima in the potential surface $\Phi(\varphi(0), \varphi''(0))$. The thermodynamic potential changes abruptly within the boundaries of the valley [31]. A lot of local minima are located in the vicinity of the global minimum.

The global minimum of the thermodynamic potential Φ corresponds to the equilibrium state. This state may be approximately described by model (3) or more precisely by model (4).

In the states corresponding to the local minima (we consider the deepest of them) the spatial dependence of the order parameter $\varphi(x)$ is more complex (figures 1, 2).

At least two pairs of subharmonics with the wavenumbers $b \pm \omega$, $\omega \ll b$, are present in the wavenumber spectra (figures 1(b), 2(b)). The subharmonics are almost symmetrically located around the main component b. The amplitude of one of these subharmonics may be relatively large (figure 1(b)). It should be noted that the spectra with equal contributions of subharmonics $b \pm \omega$ are typical as well.

If ω is much less than b, the order parameter $\varphi(x)$ looks like a twice-modulated structure: the amplitude of the IC wave alters in the space with a period P which is much bigger than the IC one—$P \gg 2\pi/b$ (figures 1(a), 2(a)).

Within the spatial range in which the modulation wave amplitude is almost constant, the characteristics of the twice-modulated structure are close to the equilibrium ones. In particular, this is true for the value of the thermodynamic potential (per unit of length, of course). In order to calculate the correct value of the thermodynamic potential, the spatial alteration of the wave amplitude should be taken into account.

Hence, the regions where the modulation wave amplitude changes significantly are similar to discommensurations. In fact, they separate the domains of almost equilibrium IC modulation. In some cases the phase of modulation wave differs by π in the neighbouring domains (figure 1(a)).

If the periods of both modulations (fundamental and additional) are of the same order (i.e. $\omega \sim b$), then irregular states appear (figure 3). The density of discommensurations is too large, and the domains of IC phase are destroyed. It is known that the states with a large number of domain walls are a form of the chaotic state [32].

The values of the thermodynamic potential for the equilibrium state Φ_0, for the twice-modulated structure Φ_ω and for the chaotic state Φ_{chaos}, are related as $\Phi_0 < \Phi_\omega < \Phi_{chaos}$.

A remarkable feature of the twice-modulated structures is their numerical stability. The numerical uncertainties are not essential if the length l of the numerical integration is less than some critical value l_c (for $l > l_c$ the solution becomes unstable, i.e. its amplitude increases infinitely). For the states with subharmonics, the value of l_c is 10^2–10^5 times larger than the critical length for the equilibrium state.

Twice-modulated structures have also been found in the framework of the chain model for thiourea [33]. According to [33], the nodes (discommensurations) appear due to the Umklapp terms in the free energy expansion. The Umklapp terms, which stabilize the higher-order commensurate phases of $C_{1/7}$ type, generate a finite number of subharmonics of the fundamental component. The states with nodes are metastable [33].
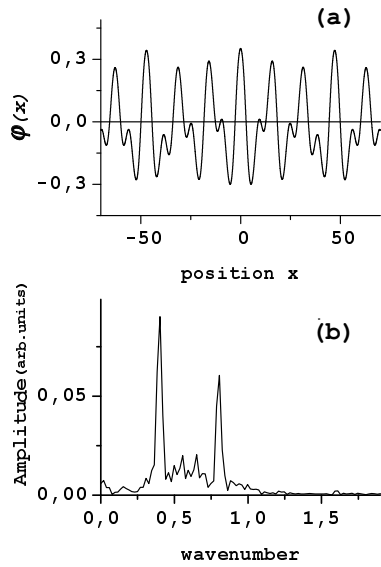
Note that the Umklapp terms are absent in model (1).

Figure 3. As figure 2, but for $\varphi(0) = 0.352$, $\varphi''(0) = -0.096$, $\Phi \approx -0.0019$. The state is nearly irregular.

3. Quasistationary states as a possible origin of anomalous properties of type II ferroelectrics

In order to clarify the role of the metastable states described in the preceding section, our stationary consideration should be supplemented by investigation of the growth kinetics of the IC structure. Such a study has been carried out numerically in [26–28].

In [26–28] model (1) is generalized by adding the gradient term $(\partial\varphi/\partial z)^2$ with a large positive coefficient (the latter is required to simulate the strong system anisotropy). Due to such a generalization, two-dimensional nuclei of the IC phase are also taken into account. The two-dimensional nuclei cost less energy than the one-dimensional ones, and their appearance is more probable.

The analysis of the results obtained in [26–28] and the ones considered in the preceding section shows that the following qualitative description of the IC phase in type II ferroelectrics is possible.

Quenching from the disordered state to the IC phase or a change of temperature in the IC phase puts the system into a nonequilibrium state.

Throughout the sample, relaxation starts. The amplitude of the order parameter and the wavenumber of the modulation wave relax exponentially quickly to the almost equilibrium values [26, 27]. The time for the amplitude relaxation seems to be of the same order as the time for the order parameter relaxation in the disordered and commensurate phases (cf. [9]).

However, the polarization wave $\varphi(x) = af(bx + x_0)$ is characterized not only by its amplitude a and its wavenumber b but also by the initial phase x_0. In the absence of the mechanisms which may fix the initial phase throughout the sample, x_0 is different at various positions.

As a consequence, at the end of an early stage of relaxation a foam of clusters (domains) of the IC phase appears [26]. Within the boundaries of the clusters the initial phase x_0 changes, and the polarization wave defects occur. In the space $\Phi(\varphi(0), \varphi''(0))$ the system moves into the valley of the thermodynamic potential minima.

The main task of the late relaxation stage is to adjust the initial phase x_0 throughout the sample. The growth of the cluster size takes place. This process is similar to cellular

structure coarsening [34]. In particular, the analysis [26, 27] reveals that the number $N(t)$ of polarization wave defects ('phase defects' in the terms of [26, 27]) obeys the temporal dependence $N(t) \sim t^{-0.56}$. This result is close to the law $\rho(t) \sim t^{-1/2}$ of the relaxation of the cell interface density [34] (see also [35]).

Thus, a typical feature of the late stage of relaxation is its long-duration character. This conclusion is in agreement with experimental data (see, e.g., [9]).

In the space $\Phi(\varphi(0), \varphi''(0))$ the system slowly moves from one local minimum of the thermodynamic potential to another.

The rate of relaxation changes with decreasing temperature. Close to the disordered-to-incommensurate transition the gradient (nonlocal) gain of the thermodynamic potential (1) is dominant. The adjustment of the initial phase x_0 is strong. In the terms of the cellular coarsening theory [34], the mobility of the cell interface is large. As a consequence, the resultant quasistationary state contains a few phase defects (see figure 1 in [26]). Their existence only slightly modifies the system characteristics.

Another situation is realized at the low-temperature boundary of the IC phase. Here the local part of the thermodynamic potential is the main one. The mobility of cluster boundaries diminishes, and the relaxation is critically slowed down [26]. The density of the modulation wave defects is relatively large during the duration of the experiment, and additional gains of the susceptibility, heat capacity etc are observed (see, e.g., [4]).

Impurities can significantly retard the processes of cellular coarsening [34,35]. Due to the influence of impurities, the number of phase defects can become so substantial that the regular IC structure will be destroyed. In this case the system state is chaotic. States resembling spin glasses are observed in $(Pb_y Sn_{1-y})_2 P_2 (Se_x S_{1-x})_6$ solid solutions, especially when $y > 0.2$ and $x < 0.8$ [21,22]. A fast cooling may also lead to the appearance of irregular structures [23,28]. It should be noted that the existence of chaotic states may attest that the relaxation processes in type II ferroelectrics are similar to the structural relaxation in amorphous solids [35,36]. In other words, hierarchically subordinated ensembles of clusters should be considered. Power, logarithmic and even double-logarithmic temporal dependences may occur in this case [36]. This means that, in fact, the relaxation stops far from the true equilibrium state.

To some extent, the processes of the late stage are similar to the relaxation of the soliton lattice in the ferroelectrics of the $A_2 BX_4$ family [24, 25]. A phase defect annihilation is analogous to nucleation of the IC stripple. The distinction is that the soliton energy is negative in the IC phase, whereas the energy of the phase defect is always positive (a true equilibrium state has no phase defects). From this point of view, the phase defect is closer to the domain wall in the ferroelectric state.

In the case of nucleation, the appearance of a stripple or antistripple requires some energy [24]. This leads to hysteresis [25].

The elimination of the phase defect requires some energy as well. But in contrast to the soliton lattice case, the phase defects may exist at any temperature within the IC phase (with varying density, of course). That is one of the reasons for the anomalously wide temperature range of the dielectric constant hysteresis. The impurities will enlarge the hysteresis range, slowing down the relaxation of the phase defect structure (cf. [19]).

4. The 1D model of the quasistationary state

At least two-dimensional models should be used when describing the relaxation processes [26–28]. At the same time, a 1D model can be meaningful in a qualitative analysis of the resultant quasistationary state.

Let us consider a system in which the density of phase defects is so large that one may speak of a phase defect structure, and simultaneously small enough that the state is still regular (not chaotic). Due to the strong system anisotropy, the clusters are extended predominantly along the direction perpendicular to the axis of the order parameter modulation. Then model (1) is believed to be appropriate.

At first, we clarify a possible origin for the subharmonics (figures 1(b), 2(b)).

If the temperature is close to T_I ($T \approx T_I$) the amplitude of the order parameter is small ($a \ll 1$) [15]. Hence, the variational equation (2) can be linearized:

$$\varphi^{IV} + \gamma \varphi'' + q\varphi = 0. \tag{5}$$

The periodical solutions of equation (5) acquire the form

$$\varphi(x) = a_1 \cos(b_1 x + \alpha_1) + a_2 \cos(b_2 x + \alpha_2) \tag{6}$$

where the wavenumbers $b_{1,2}$ satisfy the equations

$$b^4 - \gamma b^2 + q = 0 \tag{7}$$

and

$$b_{1,2}^2 = b_0^2 [1 \pm (1 - q/q_I)^{1/2}] \tag{8}$$

$$b_0^2 = \frac{1}{2}\gamma. \tag{9}$$

The wavenumber b_0 minimizes the thermodynamic potential (1) for the one-harmonic model (3):

$$\Phi = \frac{1}{2}a^2(b^4 - \gamma b^2 + q) + \frac{3}{16}a^4 \tag{10}$$

where, for simplicity, we set $g = 0$ and neglect the φ^6-term (the latter means that the parameter p is considered to be positive: $p > 0$ [16]).

At the point $T = T_I$ the wavenumbers b_1, b_2 and b_0 are equal to each other. The correlation length

$$\xi = \frac{2\pi}{b_1 - b_2} \approx \frac{2\pi}{b_0}(1 - q/q_I)^{-1/2} \overset{q \to q_I}{\to} \infty \tag{11}$$

is infinite, and there exists only one periodic solution (3), (9) (in fact, it exists formally because its amplitude is equal to zero at $T = T_I$ [16]).

If $T \leqslant T_I$ then $\xi < \infty$, and a set of periodic solutions appears. In addition to the fundamental harmonic (3), (9), the subharmonics

$$b_{1,2} \approx b_0 \pm \frac{1}{2}b_0(1 - q/q_I)^{1/2} \equiv b_0 \pm \omega$$

occur. For the solution (3), (9), the thermodynamic potential is negative: $\Phi_0 < 0$ [16] (this is the global minimum if the amplitude a takes its equilibrium value as well). For the subharmonics (6), (8), the potential is positive: $\Phi \geqslant 0$ (cf. (7) and (10)). In the states in which both the relatively large fundamental component and subharmonics are present, the thermodynamic potential Φ_ω takes an intermediate value: $\Phi_0 < \Phi_\omega < 0$ (local minima).

Strictly speaking, the solutions (6), (8) are exact only at the point $T = T_I$. But it seems plausible that equation (2) possesses analogous solutions, too.

Now let us evaluate the influence of subharmonics on the system thermodynamic characteristics.

In order to calculate the contribution of subharmonics in a 'pure' form, we consider a simple situation when the order parameter has the following spatial dependence (compare figure 1(a) in the present paper with figure 2(a) in [33] and figure 2 in [26]):

$$\varphi(x) = \frac{1}{2}a\cos(b-\omega)x + \frac{1}{2}a\cos(b+\omega)x + p_0 = a\cos\omega x\cos bx + p_0 \tag{12}$$

where $L^{-1} \ll \omega \ll b$ (L is the crystal length); $p_0 = \text{constant}(x)$ simulates the influence of the electric field e.

Integrating the thermodynamic potential (1) with respect to the order parameter (12), we suggest for simplicity that the wavenumbers ω and b are commensurate: $m\omega = nb$, where m, n are some integers. We also omit the φ^6-invariant in (1) ($p > 0$).

Then the minimization of the thermodynamic potential with respect to a, b, p_0 yields (for the case $g = 0$)

$$a^2 = \frac{16}{9p}(q_I - q + \Delta(\omega)) \approx \frac{4}{3}a_0^2 \qquad\qquad a_0^2 = \frac{4}{3p}(q_I - q) \tag{13}$$

$$b^2 = \frac{1}{2}\gamma - 3\omega^2 = b_0^2 - 3\omega^2 \qquad\qquad b_0^2 = \frac{1}{2}\gamma \tag{14}$$

$$\Phi = -\frac{2}{9p}(q_I - q + \Delta(\omega))^2 \approx \frac{2}{3}\Phi_0 \qquad\qquad \Phi_0 = -\frac{1}{3p}(q_I - q)^2 \tag{15}$$

$$\chi^{-1} = \frac{8}{3}q_I - \frac{2}{3}q + \frac{8}{3}\Delta(\omega) \approx 2q_0\left(\frac{4}{3}T_I - \frac{1}{3}T - T_0\right) \qquad \chi_0^{-1} = 2q_0(2T_I - T - T_0). \tag{16}$$

Here

$$\chi = \lim_{e \to 0}\frac{\mathrm{d}p_0}{\mathrm{d}e}$$

is the susceptibility and $\Delta(\omega) = 8\omega^4 - 2\gamma\omega^2 \approx -4b_0^2\omega^2$. The expressions for the amplitude a, the wavenumber b and the thermodynamic potential Φ are given for the case $e = 0$. The equilibrium (for model (3)) a_0, b_0, Φ_0 and χ_0^{-1} are written out for comparison.

As follows from the formulae (13)–(16), the additional modulation of the order parameter $\varphi(x)$, caused by the contribution of the subharmonics and expressed in (12) by means of the factor $\cos\omega x$, changes the thermodynamic characteristics of the system. In particular, the slope of the inverse susceptibility becomes smaller. Note again that generally the relationship (16) is assumed to be possible in the vicinity of the lock-in transition and $\chi^{-1} \to \chi_0^{-1}$ when $T \to T_I$.

The invariant $(\varphi\varphi')^2$ is essential when describing the susceptibility behaviour [16, 17]. Assuming that $g \neq 0$ ($g < 0$ [15]) and that the amplitude a is relatively small (cf. [16]), one can obtain

$$\chi^{-1} \approx \frac{8}{3}q_I - \frac{2}{3}q + \frac{4g\gamma}{3(3p-g\gamma)}(q_I - q) = q_0\left(\sigma - \frac{2}{3}\right)(T - T_c + \Delta T) \tag{17}$$

where

$$\sigma = -\frac{4}{3}g\gamma(3p - g\gamma)^{-1}$$

$$\Delta T = \left(\sigma - \frac{2}{3}\right)^{-1}\left[\left(\frac{8}{3} - \sigma\right)\Delta T_I - 2\Delta T_0\right]$$

$$\Delta T_n = T_n - T_c$$

$$n = I, 0.$$

If $\Delta T / T_c \ll 1$ and $\sigma - \frac{2}{3} > 0$, then the relationship (17) acquires a form similar to the Curie–Weiss law. Such a susceptibility behaviour ($\chi \sim (T - T_c)^{-1}$) is typical of type II ferroelectrics in the proximity of the lock-in transition [9, 13]. Note that in deriving (17) we do not take into account the second harmonic of the modulation wave. The second harmonic is important for reproducing the susceptibility rise near T_c if the state of the system is regarded as true equilibrium (e.g. in the framework of model (3)) [16, 17].

5. Conclusions

In the present paper we have considered a mechanism which may be responsible for the anomalies in the behaviour of type II ferroelectrics in the proximity of the lock-in transition.

Near T_c the states of type II ferroelectrics are suggested to be quasistationary. In addition to the fundamental IC modulation of the order parameter, there exists a structure of modulation wave defects. The reason for such a behaviour is the retarded temporal evolution of the system in the late stages of relaxation. To some extent, the phase defects are similar to domain walls or discommensurations. The defect structure gives additional contributions to the system characteristics (susceptibility, heat capacity etc). If the density of phase defects is very large (e.g. due to a strong influence of impurities), chaotic states occur.

The phase defects are thought to exist in the systems of type I as well. But their role might be minor in this case. In fact, in such systems the anisotropy invariant (the Umklapp term of relatively low order) is a powerful tool for controlling the phase of the order parameter [1]. The soliton lattice appears just due to the anisotropy invariant. This term is a part of the local gain of the thermodynamic potential and its role increases with decrease of the temperature down to T_c.

An analogous mechanism is absent in the case of type II ferroelectrics. The adjustment of the phase of the modulation wave is favoured by the nonlocal (gradient terms in (1)) interactions only. But the role of the gradient gain is relatively faint at the low-temperature boundary of the IC phase [26].

A one-dimensional model may be useful when describing the quasistationary states in type II ferroelectrics. In particular, the increase of susceptibility is predicted near the lock-in transition. The reason for the susceptibility rise is a contribution of the subharmonics of the fundamental component of the modulation wave.

The integrated description of the temporal evolution and stationary properties of the IC phase in type II ferroelectrics seems to be possible in the framework of the field supersymmetric formulation of the phase transition theory [35]. This approach gives possibilities for explaining the existence of two stages of the relaxation, the appearance of retarded evolution of the structural relaxation type and the dependence of system characteristics on the rate of cooling and on the sample history. In particular, the recent investigation performed with the aid of the generating functional method shows that the mean value of the order parameter fluctuations may be nonzero in the most probable state of thermodynamic systems [37].

Acknowledgments

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