

Time evolution of an incommensurate superstructure of a crystal near a structural phase transition to a homogeneous phase

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The time evolution of a soliton system in an incommensurate phase of a ferroelectric, which has undergone an abrupt transition to a nonequilibrium state, has been determined experimentally. The anomalous permittivity and the corresponding distance between solitons have a logarithmic time evolution. The law describing this evolution agrees qualitatively with the interpretation that the relaxation of the inhomogeneous system is a thermally activated process governed by metastability effects.

An incommensurate structure or incommensurate phase in a ferroelectric is a clear example of a degenerate inhomogeneous structure, and it is a case convenient for study. Included in the category of degenerate inhomogeneous systems are helical structures in magnetic materials, helical structures in liquid crystals, and Abrikosov vortices in superconductors. At temperatures close to the point of the transition to a commensurate polar phase, T_c , the superstructure of some crystals is similar to a ferroelectric domain structure with narrow walls (solitons) separating regions (quasidomains) in which the spontaneous polarization is oriented in mutually opposite directions.¹

Research on nonequilibrium phenomena in incommensurate phases of ferroelectrics is essentially still in its infancy.¹ In this letter we are reporting an experimental realization of a situation close to that analyzed theoretically in Ref. 2. We have determined the time evolution of the nonequilibrium incommensurate structure.

Let us begin by reviewing the basic results of Ref. 2. Near the temperature of the structural transition to a homogeneous phase, T_c , the specific free energy of the soliton system is

$$g = -\alpha \Delta T (1/l) + (1/l) V(1/l), \quad (1)$$

where l is the distance between solitons, $\Delta T = T - T_c > 0$, $\alpha > 0$, and $V(1/l) > 0$ is the soliton-soliton interaction energy. Above absolute zero, or in the presence of inhomogeneities, we have the following equality at large values of l (at low values of the soliton density $n = 1/l$):

$$V(1/l) = B(1/l)^\tau, \quad (2)$$

where $B > 0$ and $\tau > 1$. If the system is moved away from equilibrium, the driving force of the incipient relaxation is $F_d = -dg/dl$. In a defect-free crystal, the time evolution $l(t)$ should be described by the simple equation $dl/dt = -kdg/dl$ (k is a

kinetic coefficient). This equation presupposes that when an infinitely weak force arises, the system begins to relax at a rate proportional to this force.

In an inhomogeneous system, the situation is quite different. Metastable states are separated by energy barriers, and at absolute zero there is no motion of the system at all, provided that F_d does not exceed a certain threshold (the dry friction force or so-called pinning force F_{pin}). At a nonzero temperature the barriers are surmounted by a thermal-activation process, over times determined by an Arrhenius law. Pinning at these barriers becomes ineffective, and the force F_{pin} can be represented as a quantity which falls off with time. An expression for F_{pin} was derived in Ref. 2 (see also the papers cited in Ref. 2). It was assumed that the barrier energy is on the order of the energy of a characteristic fluctuation of the bending of a wall (with an amplitude $w \sim l$), caused by a nonuniformity of the defect distribution. In the 3D case we have, per 1 cm² of one soliton, $F_{\text{pin}} \simeq (T \ln \omega t)^{-(\tau+1)/2}$ (ω is a microscopic jump size). The system begins to move toward equilibrium under the condition

$$F_d = -dg/dl = F_{\text{pin}}/l, \quad (3)$$

and this condition continues to hold at all subsequent times.

In Ref. 2, an analysis of the relaxation of l toward the equilibrium value $n = 1/l = 0$ corresponding to the point of the phase transition, T_c , $\Delta T = T - T_c = 0$, led to a universal law $l(t) \simeq (T \ln \omega t)^{1/2}$. Experimentally, it is simpler to arrange conditions such that the relaxation occurs between states with different values of $n \neq 0$. Using (1) and (3) for this case, and assuming that the deviation of $|\Delta l| = |\bar{l} - l|$ from the equilibrium value \bar{l} is small ($|\Delta l|/\bar{l} \ll 1$), we can easily derive an expression for $\Delta l/\bar{l}$ or for the change in the anomalous dielectric susceptibility $\Delta\epsilon/\bar{\epsilon} \sim \Delta l/\bar{l}$ ($\bar{\epsilon}$ is the equilibrium value):

$$\Delta\epsilon/\bar{\epsilon} \sim \Delta l/\bar{l} \sim (T_c/\Delta T)^{2/\tau} (\ln \omega t)^{-(\tau+1)/2}. \quad (4)$$

Significantly, the equations for defect-free and defective crystals lead to different types of time evolution. If the deviation from equilibrium is small, the equation for a defect-free crystal leads to an exponential evolution, while the equation for a defective crystal leads to a logarithmic evolution. Our primary purpose in this study was to test this conclusion experimentally.

Our test samples were Rb_2ZnCl_4 crystals (space group $Pm\bar{c}n$), which undergo structural transitions at $T_i = 303$ K and $T_c \simeq 195.2$ K. The intermediate phase is incommensurate and modulated along the c (Z) axis. The low-temperature phase is a commensurate polar phase ($Pn2_1a$) with a spontaneous polarization along the b (Y) axis. The test crystals were bars with sides with dimensions of $3 \times 2.5 \times 3.5$ mm along the a , b , and c crystallographic axes, respectively.

An important factor in the experimental method used to study the evolution of the soliton system is the method used to abruptly drive the system to a nonequilibrium state. We suggest using a uniaxial stress for this purpose. This method has the advantage that it can create, essentially instantaneously, a soliton density n either higher or lower than its equilibrium value at any temperature T in the incommensurate phase, and this can be done without altering the symmetry of the crystal. In Rb_2ZnCl_4 crystals, according to the results we found in Ref. 3, a tensile stress σ_{yy} shifts the

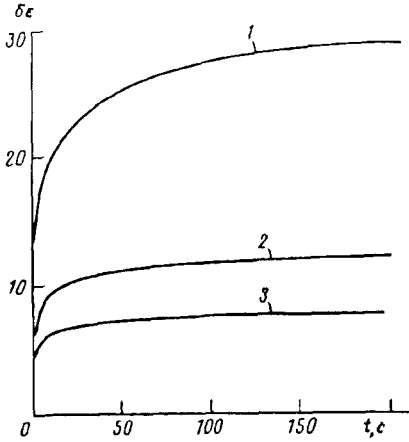


FIG. 1. Change in the permittivity, $\delta\epsilon = \epsilon - \epsilon_0$, of the incommensurate phase of an Rb_2ZnCl_4 crystal as a function of the time t after a transition of the crystal to a nonequilibrium state at $t=0$. (Here ϵ_0 is the permittivity at the time t ; $T_c = 195.2$ K.) 1) $\epsilon_0 = 145.79$, equilibrium value $\bar{\epsilon} = 345.0$, $\Delta T = 0.39$ K; 2) 104.30, 144.4, 0.62 K; 3) 77.43, 96.3, $\Delta T = T - T_c = 0.88$ K.

transition temperature T_c to a higher value; i.e., it reduces the interval $\Delta T = T - T_c$ and the equilibrium value of n . A stress σ_{xx} works in exactly the opposite way. The measurement procedure was thus as follows: The test crystal was cooled or heated to the desired temperature under a compressional stress $\sigma_{yy} = 5$ bar or $\sigma_{xx} = 5$ bar, respectively. The stress was then removed. As a result, an elevated density n was produced abruptly in the former case, and a depressed density in the latter. The evolution of the system was monitored by monitoring the changes in the n -dependent permittivity ϵ along the Y axis. The ϵ measurements were carried out with the help of a capacitance bridge at a frequency of 1 kHz; the results were recorded by a chart recorder. The error of the ϵ measurements was less than 0.1%, and the temperature was regulated within ~ 0.01 K.

At the time at which the stress σ was applied or removed, the sample temperature should change adiabatically by an amount δT , which is proportional to σ , because of the piezocalorimetric effect. As a result, the relaxation occurs isothermally only after a certain time t_0 , at which the equalization of the sample temperature and the cryostat temperature has reached completion. For this reason, we should use only the experimental data at $t > t_0$ in the analysis. It is convenient to rewrite Eq. (4) as

$$(\bar{\epsilon}/\Delta\epsilon)^\gamma \simeq F + G \ln(t/t_0), \quad (5)$$

where $\gamma = 2/(\tau + 1)$; we have a constant $F = (\bar{\epsilon}/\Delta\epsilon)^\gamma$ at $t = t_0$; and $G = D(\Delta T/T_c)^{2/\tau}$. For the test crystal at $\sigma = 5$ bar, estimates yield $\delta T < 0.01$ K and $t_0 \simeq 1$ s.

Figure 1 shows experimental data on the relaxation of ϵ from a state with an elevated soliton density at three temperatures. The comparatively rapid change in ϵ occurs over a time $\sim 1-2$ min; thereafter the rate of change of ϵ is far lower. We observed the same time evolution of ϵ in the second case, i.e., with a depressed initial soliton density. It is simple to verify that while the initial deviations of ϵ from its equilibrium value are approximately the same in the two cases, and the relaxation is

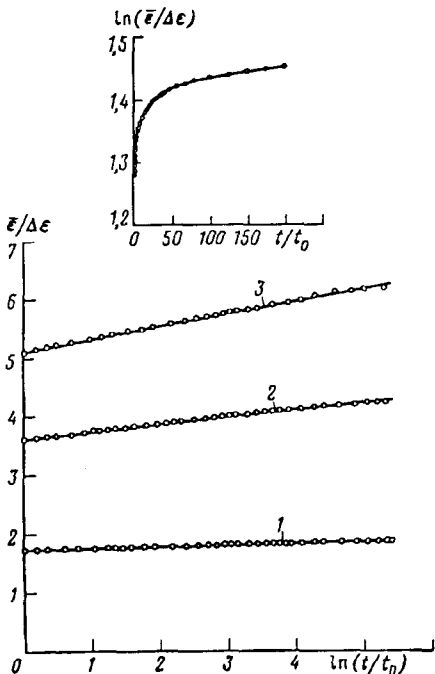


FIG. 2. $\bar{\epsilon}/\Delta\epsilon$ versus $\ln(t/t_0)$ for the incommensurate phase of the Rb_2ZnCl_4 crystal at various temperatures ($T_c = 195.2$ K, $\Delta\epsilon = \bar{\epsilon} - \epsilon$, $t_0 = 1$ s). 1) $\Delta T = T_c - T = 0.39$ K, $\bar{\epsilon} = 345$; 2) 0.62 K, 144.4; 3) 0.88 K, 96.3. The inset shows $\ln(\bar{\epsilon}/\Delta\epsilon)$ versus the time t for $\Delta T = 0.62$ K.

described by the same law, the equality $\bar{\epsilon} \simeq (\epsilon_1 + \epsilon_2)/2$ (ϵ_1 and ϵ_2 are the values of ϵ in the first and second cases) should hold at any instant, according to (5). In this manner we determined values of $\bar{\epsilon}$ for each temperature.

The results found on the time evolution of the soliton system are shown in Fig. 2. Here we have worked from the data in Fig. 1 to plot $\bar{\epsilon}/\Delta\epsilon$ versus $\ln(t/t_0)$ and also to plot $\ln(\bar{\epsilon}/\Delta\epsilon)$ versus t (in the inset). The former curves are straight lines, while the latter are very nonlinear (only one curve, for $\Delta T = 0.62$ K, is shown). The time evolution of ϵ thus also begins logarithmically, rather than exponentially, in accordance with (5); the exponent γ in (5) is 1.0 ± 0.1 . The exponent τ , which characterizes the soliton-soliton repulsion in (2), is then 1.0 ± 0.2 , close to the values calculated for τ for certain models of inhomogeneous systems.² The experimental estimate of τ is of course extremely crude, because of the several simplifying assumptions used in deriving (5). The value emerging from a more rigorous analysis may be significantly different.

It can also be seen in Fig. 2 that toward T_c the slope of the straight lines decreases ($G \simeq 0.2$ at $\Delta T \simeq 0.9$ K and $G \simeq 0.03$ at $\Delta T \simeq 0.4$ K). In other words, according to (5) the time scale of the relaxation of the system to a certain value $\bar{\epsilon}/\Delta\epsilon = \text{const}$, i.e., $t_p \sim \exp(\text{const}/G)$, increases, as expected. An arbitrary variation of $\bar{\epsilon}$ over a broad range in an analysis of the experimental data leads to substantial changes in the coefficients F and G , but it does not affect logarithmic law (5). We might add that just how close the soliton system approaches equilibrium at the end of the measurements varies with the temperature. The minimum values of $\Delta\epsilon/\bar{\epsilon}$ are 0.12 at $\Delta T = 0.88$ K

(curves 3), 0.19 at 0.62 K (curves 2), 0.49 at 0.39 K (curves 1). Even in the latter case (curves 1), in which the system is fairly far from equilibrium, the logarithmic law holds, within the measurement errors. The relative errors in the determination of $\bar{\epsilon}/\Delta\epsilon$ (Fig. 2) are less than 1%.

In summary, these experimental results show that upon a small deviation from equilibrium the anomalous permittivity and the soliton-soliton distance in the incommensurate phase of a ferroelectric which has been abruptly driven into a new non-equilibrium state begin to evolve logarithmically in time, not exponentially, as was assumed in Ref. 1. This conclusion agrees with the picture that the relaxation is a thermally activated process governed by metastability effects.²

On the other hand, we might expect that the simple logarithmic law will be disrupted when the soliton system relaxes from states far from equilibrium or over long times. In this case the relaxation may be influenced by a redistribution of defects by diffusion. That topic is of interest in its own right, but it was not taken up in the present study or in the theoretical paper by Kolomeiskii.² An analysis of the experimental data in this case could apparently reveal new information on the soliton interaction potential, on the critical behavior of solitons near the phase transition, and on the influence of various structural defects on the solitons.

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