Fast stage of the evolution of the nonequilibrium soliton structure of a dielectric

V. V. Gladkiĭ, V. A. Kirikov, and E. S. Ivanova
Institute of Crystallography, Russian Academy of Sciences, 117333 Moscow, Russia

(Submitted 10 June 1994)
Pis'ma Zh. Eksp. Teor. Fiz. **60**, No. 2, 109–113 (25 July 1994)

The evolution of a soliton structure after it has been abruptly driven into a state far from equilibrium is initially an accelerated process. The acceleration is greater, the greater the initial departure from equilibrium. Closer to equilibrium, deceleration causes the fast process to give way to a slow, thermal-activation process, as is characteristic of inhomogeneous systems. Distinctive features of the fast stage of the evolution and of its effect on the subsequent stages are identified. Experiments have been carried out by a dielectric method in the particular case of an Rb_2ZnCl_4 crystal, which is a ferroelectric with an incommensurate phase.

Narrow boundaries (solitons) separating domain-like regions with different values of certain thermodynamic properties (a soliton lattice) may form in the incommensurate phase of an insulator near a structural transition to a commensurate phase. As the temperature of this transition, T_c, is approached, the period of the soliton lattice, l, continuously grows.[1] The relaxation of l to its equilibrium value $\bar{l}$ in a real crystal is a slow process (~ 100 h). For this reason, over ordinary measurement times, ~ 1 h, the superstructure of the incommensurate phase is never at equilibrium and instead passes through several metastable states.[1]

In most of the corresponding experiments, measurements of the evolution of the incommensurate phase have begun at the time at which the crystal reaches a stable temperature, i.e., after $t \simeq 1$ h. Accordingly, only the slow part of the process has been studied.[1] In Ref. 2 we proposed a method for abruptly driving a soliton structure away from equilibrium, so that the fastest part of the evolution could be monitored. It was shown that up to times ~ 10 min, at modest initial deviations from equilibrium, the relaxation is a thermal-activation process. In the present letter we are reporting the observation of a different evolution mechanism: When there is a large initial excursion from equilibrium, the soliton structure begins to change in an accelerated manner. This change strongly influences the nature of the relaxation at all subsequent times (over longer times).

As a test sample we selected an Rb_2ZnCl_4 crystal with structural phase transitions at $T_i = 303$ K and $T_c = 195.2$ K (Ref. 1). The high-temperature phase has a symmetry space group $Pmcn$, while the low-temperature phase has a space group $Pn2_1a$, with spontaneous polarization along the b (Y) axis. The intermediate phase is incommensurate with spatial modulation along the c (Z) axis. Test samples were cut from the crystal in the form of rectangular bars with dimensions of $3 \times 2.5 \times 3.5$ mm, with edges oriented along the crystallographic a, b, and c axes.

0021-3640/94/020116-05$10.00

The nonequilibrium initial states of the soliton structure of the crystal were created abruptly, as in Ref. 2, by means of a uniaxial stress σ_{yy} or σ_{xx}. A compressional stress σ_{yy} shifts T_c toward a lower temperature, while σ_{xx} shifts it to a higher temperature. The meaning here is that a compression σ_{yy} increases (and σ_{xx} decreases) the temperature interval $\Delta T = T - T_c$ and the equilibrium value of the soliton density, $\bar{n} = 1/\bar{l}$. Extensions σ_{yy} and σ_{xx} change ΔT and the density $\bar{n}$ in the opposite direction.[2] To prevent the stress from affecting the soliton mobility and thus the evolution of the solitons, we carried out measurements of the time-varying processes only in mechanically free samples. The stress was used solely as a means to rapidly drive the structure into various nonequilibrium states. The measurement procedure accordingly included the following operations. The sample is first cooled under a stress $\sigma_{yy} > 0$ or heated under a stress $\sigma_{xx} > 0$ to a given temperature. The stress is then removed. As a result, the initial state of the sample immediately after the load is removed—removing the load is equivalent to stretching the sample—has an elevated soliton density n in the former case, and a lowered density in the latter, in comparison with the equilibrium value $\bar{n}$ and also in comparison with the value of n before the load is removed. The extent of the initial deviation of the soliton system from equilibrium ($\Delta n = |n - \bar{n}|$) is regulated by means of the stress: The duration is greater, the greater the stress σ_{yy} or σ_{xx} which compressed the sample before the measurements began.

We monitored the evolution of the soliton structure by monitoring the changes in the anomalous electric susceptibility ϵ along the Y axis; this constant is a monotonic function of n (Ref. 1). The faces of the samples perpendicular to the Y axis were coated with a silver paste for the ϵ measurements. The changes in ϵ were measured with a capacitance bridge at 1 kHz and a chart recorder. The error of the ϵ measurements was no worse than 0.1%; the temperature was regulated within 0.01 K. The sample was left at room temperature for a day (with $\sigma_{yy} = \sigma_{xx} = 0$) before each measurement. The results of the ϵ measurements exhibited a satisfactory reproducibility. The width of the temperature hysteresis in the values of ϵ of the test samples in the incommensurate phase—this width is a measure of the number of defects in the crystal[1]—is 0.3 K

Figure 1 shows the results of measurements of the evolution of ϵ of an Rb_2ZnCl_4 crystal from various initial equilibrium states. We know[1] that the susceptibility ϵ increases with decreasing soliton density n. Accordingly, ϵ increases with the time for initial states with an elevated value of n (Fig. 1a), while it decreases for states with a depressed value of n (Fig. 1b). We see that the fastest changes in ϵ occur in a time $t \simeq 0.2$ s. Over this t interval, the rate of change of ϵ progressively increases and then goes through a maximum; i.e., the change in ϵ initially occurs in an accelerated manner and then slows down.

An important point is that the $\epsilon(t)$ curves for the initial states with elevated and depressed n are qualitatively different. In the former case, the $\epsilon(t)$ curves intersect (Fig. 1a); i.e., the soliton structure passes through identical states more rapidly, the further the initial state from equilibrium. For the latter states, these curves do not intersect (Fig. 1b).

When the stress σ is removed at the time $t = 0$, the crystal temperature should, in general, vary adiabatically by an amount $\delta T = \kappa T/c \times \Delta\sigma$ because of the piezocaloric effect. Here κ is the thermal expansion coefficient, c is the specific heat (per 1 cm^3), and $\Delta\sigma$ is the change in stress. Estimates for Rb_2ZnCl_4 based on data on κ and c in Ref. 1

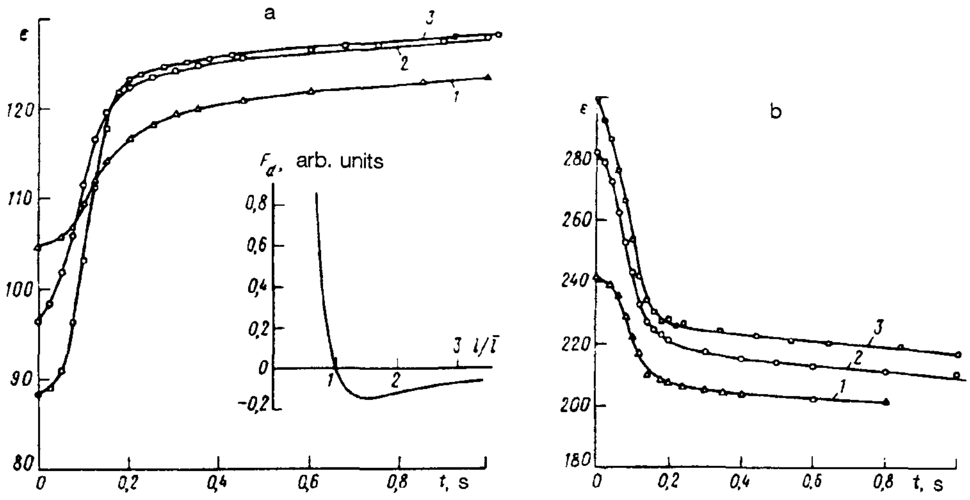

FIG. 1. Time evolution of the anomalous electric susceptibility ϵ of an Rb_2ZnCl_4 crystal for various initial nonequilibrium states with either elevated (a) or depressed (b) soliton densities. $T_c = 195.4$, $T = 195.8$ K, $\Delta T = T - T_c = 0.4$ K. The equilibrium value of the susceptibility is either $\bar{\epsilon} = 143.3$ (a) or 152.3 (b). The compressional stress σ_{yy} (a) or σ_{zz} (b), which induces the initial nonequilibrium state, is 10, 15, or 20 bar (curves 1–3, respectively). The inset shows the driving force of the relaxation, F_d, found from Eq. (1) as a function of the period of the soliton structure, $l/\bar{l}$, where $\bar{l}$ is the equilibrium value.

yield $\delta T \simeq 0.01-0.02$ K. The change in ϵ corresponding to δT found experimentally is so small (0.2–0.4) that it does not affect the $\epsilon(t)$ curves in Fig. 1. Accordingly, the evolution of ϵ should be assumed to be an essentially isothermal process over the entire time interval.

It was found experimentally in Ref. 2 that, upon a small initial deviation of the soliton system in Rb_2ZnCl_4 from equilibrium, the susceptibility ϵ varies logarithmically in time between $t_0 = 1$ s and $t \simeq 10$ min:

$$\bar{\epsilon}/\Delta\epsilon \simeq F + G\log(t/t_0), \tag{1}$$

where $\Delta\epsilon = |\bar{\epsilon} - \epsilon|$, $\bar{\epsilon}$ is the equilibrium value, $t_0 = 1$ s, and F and G are constants.

Law (1) agrees with the idea, developed in Ref. 3, that the relaxation of the inhomogeneous system is a thermal-activation process governed by metastability effects. This law can be easily derived[2,3] under the following assumptions. First, the specific free energy g of the soliton system near T_c, where the soliton density $n = 1/l$ is small, is

$$g = -\alpha\Delta T(1/l) + B(1/l)^2. \tag{2}$$

Here $\Delta T = T - T_c > 0$, $\alpha > 0$, and $B > 0$. The first term is the soliton–soliton attraction energy, and the second is the corresponding repulsion energy. Second, the initial deviation of the system from equilibrium is small, so the driving force $F_d = -dg/dl$ of the beginning relaxation does not exceed a certain threshold value (the dry-friction force or so-called pinning force). Here we have $\Delta\epsilon/\bar{\epsilon} \sim \Delta l/\bar{l} \ll 1$ $(\Delta l = |\bar{l} - l|)$.

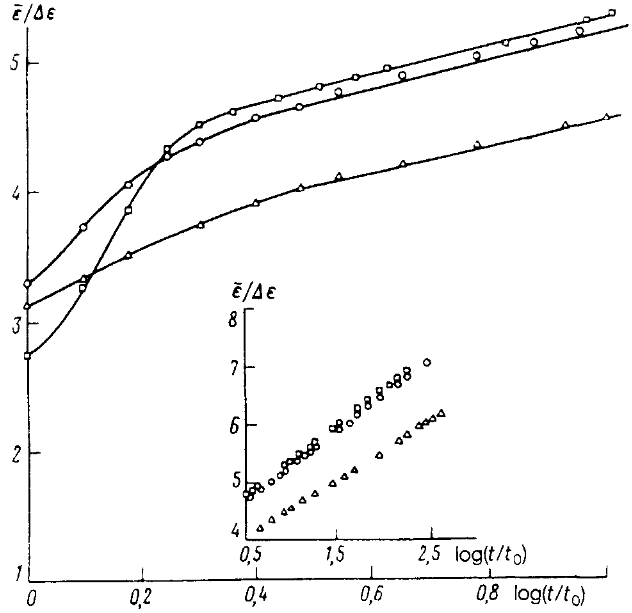

FIG. 2. Plot of $\bar{\epsilon}/\Delta\epsilon$ versus $\log(t/t_0)$ according to the data in Fig. 1a. $t_0=0.1$ s. 1, 2, 3—The same meaning as in Fig. 1a. The inset shows the same plot over the time interval 0.3–60 s.

The evolution of a system of solitons which develops with acceleration obviously cannot be described by a simple kinetic equation of the form $dl/dt=-kdg/dl$. It is also easy to see that the changes in ϵ in the course of such an evolution do not obey logarithmic law (1). This point is seen most vividly for initial nonequilibrium states with an elevated soliton density ($l/\bar{l}<1$; Fig. 1a). In this case the solitons "repel each other," and the driving force $F_d=-dg/dl\sim(\bar{l}/l)^3-(\bar{l}/l)^2$, found from Eq. (2), can reach particularly large values (see the inset in Fig. 1a). Figure 2 shows plots of $\bar{\epsilon}/\Delta\epsilon$ versus $\log(t/t_0)$ found from the data on $\epsilon(t)$ in Fig. 1a at $t_0=0.1$ s. We see that these plots become linear, i.e., that Eq. (1) holds, only at a time $t\simeq0.3$ s; the experimental points corresponding to the fastest initial stage of the process deviate substantially from straight lines. The slope of these lines gives us the coefficient $G\simeq0.1$ in (1); the result agrees, within the experimental errors, with the value of this coefficient at a close temperature for a small deviation of the system from equilibrium.[2] The curves of $\bar{\epsilon}/\Delta\epsilon$ versus $\log(t/t_0)$ for the initial nonequilibrium states with a depressed soliton density ($l/\bar{l}>1$), found from the data in Fig. 1b, have a shape like that in Fig. 2, but, in contrast with the former case, the indications of a rapid first stage of the evolution of the structure are not as apparent. The curves here, like the $\epsilon(t)$ curves in Fig. 1b, do not intersect; they approach straight lines in a shorter time (~0.1 s; these straight lines are not shown in the figures).

The evolution of a soliton system, which has been abruptly driven into a state far from equilibrium, can thus be pictured as follows. The system moves toward equilibrium in an accelerated manner as long as the driving force F_d, which decreases as equilibrium is approached, exceeds the dry-friction (pinning) force F_{pin}. The rate reaches a maximum in the case $F_d=F_{\text{pin}}$. At $F_d<F_{\text{pin}}$, the motion of the system slows down, and the subsequent evolution is a thermal-activation process described by Eq. (1). The greater the initial deviation from equilibrium, the faster the system goes through specific states, and

the closer the system lies to the equilibrium after the accelerated motion comes to an end, and the slow thermal-activation process begins. In this regard, the behavior of the soliton system is reminiscent of the polarization reversal of the domain structure in a ferroelectric.[4] It is possible that the specific mechanisms for these two processes are also similar: a slow nucleation of regions with new parameters,[1,4] which can be observed upon small deviations from equilibrium, and a rapid movement of a region of an inhomogeneity (a domain wall[4] or a soliton) in the case of large deviations.

The fast initial stage of the change in the nonequilibrium system of solitons thus has a strong influence on the relaxation at subsequent times. This fast stage must be taken into account in research on such processes in all inhomogeneous systems analogous to incommensurate phases. We might add that an analysis of experimental data in the time interval in which the soliton system is changing in an accelerated manner may provide information on the relation between the constants characterizing the interaction of the solitons and on the dry-friction (pinning) coefficient, which depends primarily on the defect concentration in the crystal.

This study had financial support from the Russian Fund for Fundamental Research (Project 93-02-14163).

[1] H. Z. Cummins, Phys. Rep. **185**, 211 (1990).
[2] V. V. Gladkiĭ *et al.*, JETP Lett. **58**, 603 (1993).
[3] E. B. Kolomeĭskiĭ, Zh. Eksp. Teor. Fiz. **99**, 562 (1991) [Sov. Phys. JETP **72**, 314 (1991)].
[4] M. E. Lines and A. M. Glass *Principles and Applications of Ferroelectrics and Related Materials* (Oxford Univ. Press, New York, 1977).

Translated by D. Parsons