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Memory effects in the vicinity of the incommensurate–commensurate phase transition in Rb_2ZnCl_4 single crystals

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Abstract. Memory effects have been studied in the vicinity of the incommensurate–commensurate phase transition in Rb_2ZnCl_4 single crystals. Properties in the incommensurate phase have been observed to depend critically on whether a crystal had been cooled or heated before the temperature is kept constant (thermal memory) or whether it had been subjected to stresses (mechanical memory) or to a static electric field (electric memory) previously. The crystal exhibits pronounced after-effects specific for incommensurate phases which can be understood in terms of soliton pinning on lattice inhomogeneities.

1. Introduction

Ferroelectrics with an incommensurate (I) phase are well known to exhibit pronounced memory effects [1, 2]. The properties of the incommensurate phase are critically influenced by stresses [3, 4]. Rb_2ZnCl_4 crystals undergo a structural phase transition, i.e. homogeneous → I polar phase ($D_{2h} \rightarrow C_{2v}$) transition, when cooled to 194.6 K. We have already reported the permittivity of the I phase of the ferroelectric Rb_2ZnCl_4 in a static electric field [5]. Perfect domain textures of the I phase have been explained very well by Janovec and Dvorak [6]. The commensurate (C) phase of the Rb_2ZnCl_4 has the space group D_{n2a} and the existence of the I phase is connected with the Lifshitz invariant [7].

In a previous paper [8], we reported the relaxation effects in the vicinity of the I–C phase transition in Rb_2ZnCl_4 crystals. It was felt that a study of memory effects in Rb_2ZnCl_4 crystals in the I phase may help us to understand the physical processes taking place in the crystal. With this aim in view, memory effects caused by external perturbations (thermal, electrical and mechanical) in the vicinity of the I–C phase transition in Rb_2ZnCl_4 crystals have been studied. The results of this investigation are reported here.

2. Experiment

Rectangular bars of the crystal Rb_2ZnCl_4 with edges parallel to the crystallographic axes (denoted for convenience as x, y and z) were used for measurements. The final

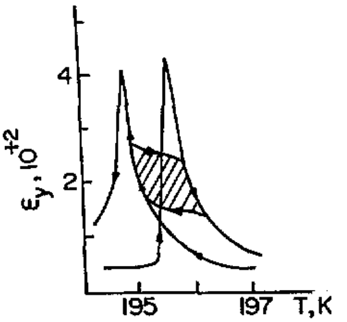

Figure 1. Temperature dependence of ε_y for Rb_2ZnCl_4. The range of the thermal hysteresis is $T_c^h - T_c^c = 1$ K.

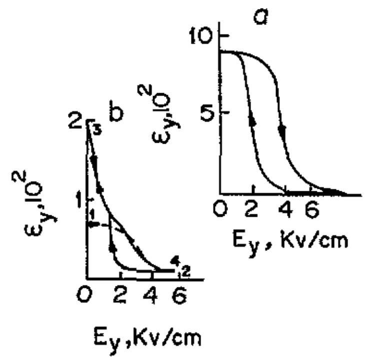

Figure 2. Dependences of (*a*) the static and (*b*) the dynamic values of permittivity ε_y on the polarizing static field E_y recorded in the I phase, $\Delta T = T - T_c =$ 1.8 and 1.26, respectively.

dimensions of the samples were 3 mm × 3 mm × 3 mm. Silver paste was applied as electrodes on two sides of the sample. Measurements in static fields were carried out using an electrometer and measurements in alternating fields were made by employing a conventional bridge method at a frequency of 1 kHz. The same samples were used for static and alternating fields. The field strength in both the cases had an intensity of $1\ \mathrm{V\,cm^{-1}}$.

3. Results and discussion

The temperature dependence of the permittivity ε_y is depicted in figure 1. From this figure we see that the transition temperatures T_c^c and T_c^h are 194.6 K and 195.62 K for cooling and heating, respectively. The range of hysteresis $T_c^h - T_c^c = 1$ K (shaded area). The temperature variations in ε_y during the cooling and the heating cycles were not identical in the full range of existence of the I phase.

The effects of the static and the dynamic electric field E_y on the permittivity ε_y at constant temperature are depicted in figures 2(*a*) and 2(*b*), respectively. The broken curve in figure 2(*b*) indicates the beginning of the cycle. The static or dynamic values of the permittivity ε_y are recorded in the range of existence of the I phase; $\Delta T = T - T_c =$ 1.8 and 1.26, respectively. The results on the permittivity of the I phase of ferroelectric Rb_2ZnCl_4 in a static electric field have already been reported by us [5]. We have now extended the work. It has been observed that, in Rb_2ZnCl_4 crystals in a zero field, ε_y attains a maximum at 194.6 K for cooling which then shifts on the application of E_y to higher temperatures. This maximum gradually decreases with inceasing E_y. Switching on and subsequently switching off E_y results in different changes in ε_y depending on whether the temperature was being decreased or increased before it is kept constant (*thermal memory*). It has also been concluded that

$$\Delta\varepsilon_y^r = 0 \qquad \text{when } T_c^h - T^h > 0.$$

Here $\Delta\varepsilon_y^r$ is the remanent value of ε_y and T_c^h is the transition temperature for heating. Since the remanent value of ε_y is finite (non-zero) between points 1 and 3 the crystal

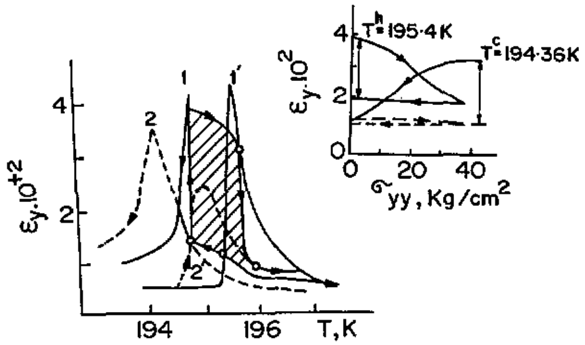

Figure 3. Temperature dependence of ε_y under the mechanical stress for Rb_2ZnCl_4: point 1, $\sigma_{yy} = 0$; point 2, $\sigma_{yy} = 30$ kg cm^{-2}. The inset shows the change in ε_{yy} at the constant temperatures $T^c = 194.36$ K and $T^h = 195.4$ K due to stress σ_{yy}.

exhibits an electrical memory. In other words $\Delta\varepsilon_y^r \neq 0$ when $T_c^c - T^c < 0$ (electrical memory). From figure 2(*b*), the value of $\Delta\varepsilon_y^r$ has been found to be 1.3×10^2 (between points 1 and 3).

The influence of the mechanical stress σ (stress component σ_{yy}) on the temperature dependence of permittivity ε_y is presented in figure 3. Since a significant difference is observed between the loading and unloading cycles, hysteresis behaviour is established. This is indicated by the shaded area in figure 3. It is further observed that the stress components σ_{zz} and σ_{xx} (where *z* is the direction of structure modulation and *y* is parallel to the spontaneous polarization) either do not shift the phase transition temperature T_c or shift it to higher T_c', i.e. $T_c' - T_c \geqslant 0$, respectively, but σ_{yy} on the contrary shifts T_c to lower T_c', i.e. $(T_c' - T_c) < 0$. The change in ε_y at a constant temperature due to the stress σ_{xx} (and σ_{yz}) occurs only after cooling while the change due to stress σ_{yy} occurs only after heating the crystal ($\Delta\varepsilon_y^r$ being revealed after the stresses are reduced to zero; mechanical memory). This mechanical memory effect is shown in the inset in figure 3. We have estimated the value $(\Delta\varepsilon_{yy}/\varepsilon_{yy})_{max} = \pm 3.8$ when $\sigma_{xx} = 30$ kg cm^{-2} and $(\Delta\varepsilon_{yy}/\varepsilon_{yy})_{max} = \pm 2.0$ when $\sigma_{yy} = 30$ kg cm^{-2}.

The after-effect (memory) phenomena observed in the region of the I phase of a ferroelectric are the features which distinguish this phase from the conventional C phase. When a Rb_2ZnCl_4 crystal is subjected to an external perturbation (thermal, electrical or mechanical), it exhibits a transition to a metastable state which is the result of pinning of a modified soliton structure by lattice inhomogeneities [9]. It is important to note that such external perturbations alter actively as long as the change is in one direction (an increase or a decrease in soliton density N_s). If the perturbation tends to alter the sign of the increase ΔN_s, the soliton structure resists the change and the crystal remains for a long time in the previous state [10]. An analysis of the experimental results shows that the reason for the different responses from crystal in these two cases is the different degrees of non-equilibrium of the states of the crystal created by external perturbations. In the former case, an external perturbation enhances a non-equilibrium state, the rate of change in N_s with time is high and the effects can be detected readily. In the latter case, the perturbation reduces non-equilibrium, the rate of change in N_s decreases strongly and the value of N_s remains almost constant for a long time.

In particular, the compression σ_{yy} seeks to drive the crystal to a new equilibrium state with higher N_s in the I phase. Thus, after the crystal has been cooled when it is in the metastable state with N_s^m greater than N_s^0 for the equilibrium state at the same temperature ($N_s^m > N_s^0$), the application of σ_{yy} decreases the deviation in the N_s^m-value from that in the new equilibrium state $(N_s^0)'$ for $\sigma_{yy} \neq 0$, i.e. $(N_s^0)' - N_s^m < N_s^0 - N_s^m$. On the contrary, after the crystal has been heated where N_s^m is smaller than the equilibrium value N_s^0 at the same temperature ($N_s^m < N_s^0$), the application of σ_{yy} increases the deviation, $(N_s^0)' - N_s^m > N_s^0 - N_s^m$. Naturally, in the second case when the deviation of the crystal state from the equilibrium state is greater, the relaxation process and the variation in the crystal properties are more pronounced and can be easily detected.

From the above it is clear that all the memory effects in the I phase have the same origin. These can be attributed to soliton pinning of lattice inhomogeneities.

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