Domain-wall interaction in improper ferroelectric lock-in phases

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The polarization field relationship in the improper ferroelectric lock-in phase of purified Rb_2ZnCl_4 crystals is analyzed under quasistatic conditions. Domain walls are shown to interact in the same way as an ensemble of phase solitons. This justifies the application of soliton theory to derive information about the ratio $n = w/x_0$ between wall thickness and wall distance. Above $T' \approx 140$ K, n is found to increase with temperature and thermal hysteresis between cooling and heating data is observed. Apparently, x_0 increases via annihilation of antistripples on cooling until an equilibrium distance $x_0(T)$ is achieved, whereas it remains constant on heating. In addition, $w(T)$ seems to be an unambiguous increasing function of temperature. However, a completely different behavior is observed below T' where n is constant, indicating a freeze in of both x_0 and w. We suggest that this may indicate a transformation from rough domain walls above T' to flat walls at low temperatures. [S0163-1829(98)04317-3]

I. INTRODUCTION

Improper ferroelectric lock-in phases of Rb_2ZnCl_4 type A_2BX_4 crystals have attracted much interest due to their peculiar domain structure that follows from a regular lattice of phase solitons observed in the incommensurate (IC) phase slightly above the temperature T_L, where the incommensurate modulation vector locks into a commensurate value and the phase transition into the commensurate (C) phase takes place.[1–3] Close above T_L, quasicommensurate regions (quasidomains) with almost constant phase ϕ of the complex order parameter[4] are separated by the phase solitons in which the phase changes rapidly by $\phi = \pi/3$. In this way, a unique periodic sequence of six domain states characterized by discrete phase values $\phi = 0$, $\pi/3$, $2\pi/3$, π, $4\pi/3$, and $5\pi/3$ is created. Due to order-parameter coupling with polarization P_0, adjacent quasidomains have opposite sign of P_0.

The phase solitons are energetically unfavorable in the C phase and annihilate at T_L in a unique stripple process.[5,6] However, the monodomain ground state of the C phase is not obtained, but some solitons unable to create antistripples freeze in at T_L forming ferroelectric 180° domain walls.[7,8] Therefore, the domain structure of the C phase is built up by plane walls oriented exclusively in the same direction as the solitons of the IC phase, i.e., with normal vectors parallel to the crystallographic a axis. Moreover, the reduction of soliton density by antistripple annihilation below T_L preserves the sequence of six domain states in the lock-in phase.

Theoretical considerations predict that this sequence is retained even in external electric fields usually used in repolarization experiments.[9] Apparently, the nucleation or coalescence of domain walls, as it is observed in proper ferroelectrics in the initial and final stages of polarization reversal, respectively, does not occur in improper ferroelectric lock-in phases because this would require the rather unlike formation or annihilation, respectively, of stripples containing five domain states in the correct order. On the other hand, experiments in rectangular pulses indicate that the polarization reversal in these crystals takes place by sideways shifts of domain walls.[10] Thus ferroelectric domain walls in improper lock-in phases seem to respond in the same way to an electric field as phase solitons in the IC phase, i.e., pairs of domains (solitons) are created with an equilibrium distance given by the repulsive domain-wall (soliton) interaction.

The polarization reversal in improper ferroelectric lock-in phases seems to proceed in the simplest way possible in a ferroelectric system. Close below T_L, dynamic $P(E)$ hysteresis loops of purified Rb_2ZnCl_4 were described in a wide range of measuring frequencies treating sideways shifts of a field-independent number of plane 180° walls to be the only repolarization mechanism.[11] However, the correct treatment of the domain-wall interaction that provides the restoring force on a wall displaced due to the electric field remains an unsolved problem.

It was concluded from permittivity data[12] that the domain-wall interaction changes in Rb_2ZnCl_4 from an exponential to an oscillatory behavior on cooling below $T^* = 160$ K. In a real crystal, however, dielectric domain-wall contributions in weak fields are not exclusively caused by the motion of the wall as a whole, but other mechanisms related to the response of defect pinned walls may also contribute to the permittivity.[13,14] Therefore, the permittivity measured for a given bias field E_b is not necessarily the same as the slope $\epsilon_{diff} = \partial P/\partial E|_{E=E_b}$ of the $P(E)$ equilibrium curve given by the domain-wall interaction potential. On the other hand, Rb_2ZnCl_4-type improper ferroelectrics are known for the peculiar ''swan neck'' shape of quasistatic hysteresis loops that were recorded close below T_L.[15–18,11] Due to the unique repolarization mechanism, the domain walls are in a quasistatic experiment apparently always close to its equilibrium position given by the domain-wall interaction potential.

In this paper the polarization reversal of purified

Rb_2ZnCl_4 crystals is investigated under quasistatic conditions. From the experimental data, the domain-wall interaction potential is derived and conclusions about the temperature dependence of the domain-wall density in the lock-in phase are drawn. The paper is organized as follows. First, the polarization reversal at temperatures slightly below T_L is analyzed. It is shown that a master curve $P(E)$ can be derived from the quasistatic hysteresis loop, which obeys the same law as predicted by the phenomenological Landau theory for the soliton interaction in the IC phase. The field range is estimated in which the assumption of well-separated interacting domain walls is justified. In the second part, the influence of temperature on the quasistatic hysteresis loop is included. Hysteresis loops recorded in a wide temperature range 110 K$<T<T_L$ of the lock-in phase are analyzed in order to get information about changes of the domain structure due to temperature variation. The temperature dependence of model parameters is discussed with special emphasis on the thermal hysteresis during temperature cycling within the lock-in phase. It is shown that two temperature ranges $T>T^*$ and $T<T^*$, respectively, should be distinguished in the lock-in phase of Rb_2ZnCl_4. In the first range, the coercivity of quasistatic hysteresis loops is small and the temperature-dependent domain-wall density reveals a thermal hysteresis between the cooling and heating runs. On cooling below T^*, the coercive field starts to increase steeply and the domain-wall density freezes in. Apparently, the domain-wall–defect interaction changes at T^*, which may be connected with a transition between walls roughened by thermal fluctuations above T^* and essentially flat walls unable to create further antistripples below T^*.

II. EXPERIMENT

The experiments were carried out on the same purified Rb_2ZnCl_4 crystal as was used in our previous papers.[18,19,11,20,21] The crystal is characterized by an anomalously small thermal hysteresis $\Delta T_L \approx 0.2$ K between heating and cooling curves $\epsilon(T)$ and a very high maximum permittivity $\epsilon_{max}>1000$ that was measured at a temperature T_{max} close below the lock-in transition temperature. Samples prepared from this crystal were thin plates with typical dimensions $3\times3\times0.5$ mm^3. Gold electrodes were evaporated onto the major faces.

The samples were mounted in a liquid-N_2 cryostat and brought to $T_L=194$ K with a cooling rate of 2 K/min. Within the lock-in phase, the temperature was changed with a small cooling/heating rate of 0.05 K/min. During this time, quasistatic hysteresis curves were recorded continuously. Since the frequency f_m of the triangular measuring field was in the range 0.005 Hz$<f_m<$10 Hz, the temperature stability during one cycle was $\Delta T \leqslant 0.1$ K.

The polarization field relationship at $f_m \geqslant 0.1$ Hz was investigated by means of a modified Sawyer-Tower circuit.[11] At low frequencies $f_m<0.1$ Hz, the sample current was integrated using a homemade choppered integration amplifier. The analogous integrator output was fed to a digital voltmeter, which was read out by a personal computer.

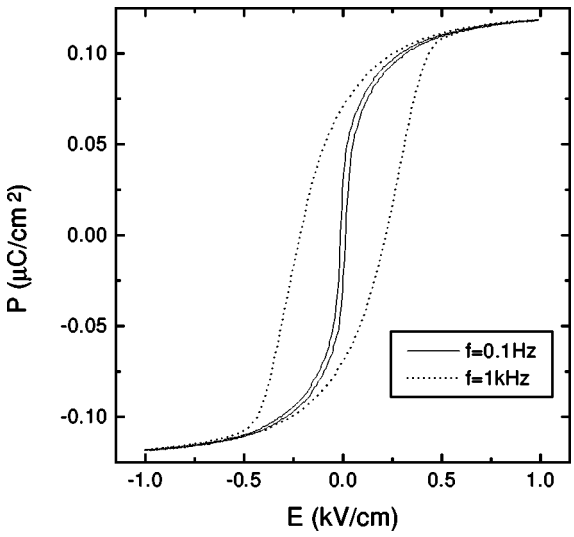

FIG. 1. Ferroelectric hysteresis loops measured in the C phase at $T=T_L-6$ K. The curves reflect the typical shape of hysteresis loops recorded in the quasistatic ($f=0.1$ Hz) and dynamic ($f=1$ kHz) regimes, respectively.

III. RESULTS AND DISCUSSION

A. Domain-wall interaction at $T=T_L-6$ K

First we present data obtained at a constant temperature $T=188$ K$=T_L-6$ K. Ferroelectric hysteresis loops recorded close below T_L at sufficiently low frequencies are characterized by an extremely small coercive field E_c in the order of 10 V/cm and a remanent polarization P_r not exceeding 30–50% of the saturation value (Fig. 1). The coercive field E_c shows a distinct frequency dependence (Fig. 2). With increasing measuring frequency, E_c is first nearly frequency independent but starts to increase if a characteristic frequency f_c is exceeded. Simultaneously, the swan neck shape of the loops is gradually lost and loops recorded at $f>f_c$

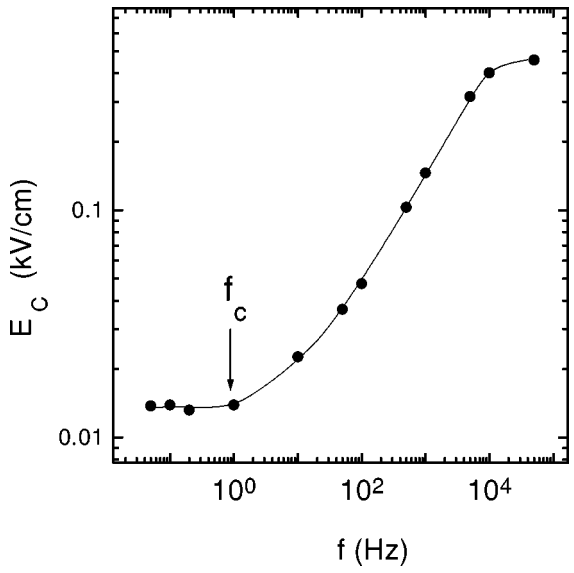

FIG. 2. Coercive field E_c of hysteresis loops recorded at $T=T_L-6$ K, dependent on the frequency f of the sinusoidal measuring field. The frequency f_c denotes the upper frequency limit of the quasistatic regime.

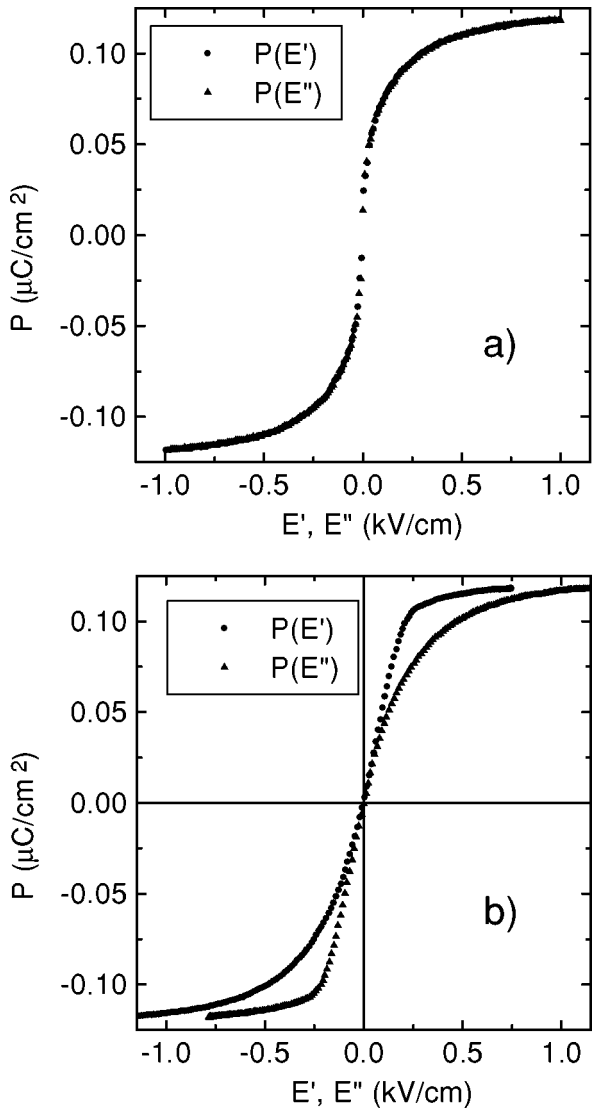

FIG. 3. (a) Master curve obtained from the quasistatic hysteresis loop by the transformation given in Eq. (3.1). (b) The same transformation applied to a dynamic hysteresis loop does not amount to an unambiguous $P(E)$ relationship.

have a more regular shape (see the dotted curve in Fig. 1). Apparently, f_c separates the range of high frequencies, where the coercivity $E_c^{dyn}(f,T)$ is given mainly by the dynamics of the wall, from the quasistatic frequency range, where the domain walls seem to be very close to its equilibrium position and the probably defect induced coercive field $E_c^{qs}(T)$ is small.

For a further analysis of the quasistatic hysteresis loop shown in Fig. 1, the two branches of the loop recorded for $dE/dt>0$ and $dE/dt<0$, respectively, were shifted parallel to the E axis according to the transformations

$$E'=E-E_c^{qs}, \quad E''=E+E_c^{qs}, \tag{3.1}$$

respectively. From the experimental data, a field $E_c^{qs}=12$ V/cm can be derived for which the resulting curves coincide with each other creating a ''master curve'' $P(E)$, i.e., an unambiguous, antisymmetric function of the electric field [Fig. 3(a)]. Note that the same transformation carried out on a dynamic hysteresis loop does not lead to an unambiguous $P(E)$ dependence [Fig. 3(b)]. It may be expected that the master curve reflects the $P(E)$ dependence of the ideal defect-free multidomain crystal and that the small hysteresis of the quasistatic hysteresis loop characterized by the quasistatic coercive field E_c^{qs} is caused by the domain-wall–defect interaction. In order to verify this hypothesis, we tried to describe the master curve with the model developed previously.[11] Assuming the polarization reversal in Rb_2ZnCl_4 to proceed exclusively by sideways shifts of a field-independent number of domain walls, we describe the behavior of a regular structure of planar 180° domain walls with an equilibrium domain-wall distance x_0. In an external electric field, domain walls are displaced by a distance Δx from their zero-field equilibrium position. The width x_+ of domains with a polarization parallel to E increases and the width x_- of oppositely oriented walls shrinks (Fig. 4). Consequently, the period of the domain structure $x_+ + x_- = 2x_0$ is doubled and the total polarization is

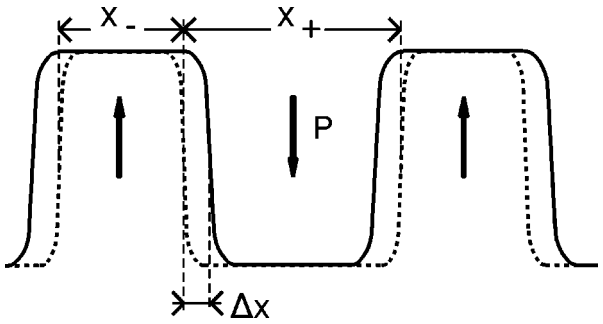

FIG. 4. Schematic representation of the soliton lattice of the IC phase slightly above T_L.

$$P=2P_0\frac{\Delta x}{x_0}, \tag{3.2}$$

where P_0 is the spontaneous polarization.

In equilibrium, i.e., for zero wall velocity, the wall displacement $\Delta x=(x_+-x_-)/4$ from its zero-field position is given by

$$\left.\frac{\partial G_{DW}}{\partial \Delta x}\right|_{\Delta x^{eq}}=0, \tag{3.3}$$

where $G_{DW}(\Delta x)$ is the potential energy of the wall. In what follows we will assume that the domain-wall interaction potential $G_{WW}(\Delta x)$ provides the major contribution to the potential energy of the wall and all other contributions to $G_{DW}(\Delta x)$ can be neglected. In other words, the restoring force F_{DW} acting on a wall displaced by the external field is treated in our model exclusively by the repulsive domain-wall interaction. However, no theory is available up to now for the domain-wall interaction in the ferroelectric phase. On the other hand, the soliton interaction in the IC phase can be described in the framework of the phenomenological Landau theory.[4,22]

In the soliton region close above T_L, the free-energy density of the crystal can be expressed in terms of soliton coordinates[23,9]

$$G=\frac{1}{x_+ + x_-}[-ab(T-T_L)+4b(e^{-x_+/w}+e^{-x_-/w}) + 1/2P_0E(x_- - x_+)]. \quad (3.4)$$

Here w denotes the soliton thickness and a and b are constant coefficients. This thermodynamic potential yields an interaction force per unit area

$$F_{DW}=-\frac{8b}{w}e^{-x_0/w}\sinh\left(\frac{2\Delta x}{w}\right) \quad (3.5)$$

between the phase solitons of the incommensurate phase.

Since the ferroelectric domain structure follows at T_L from the soliton lattice of the IC phase, it may be supposed that the domain-wall interaction force in the ferroelectric phase obeys the same law as given in Eq. (3.5) for the soliton interaction in the IC phase. In this way, the dynamic hysteresis loops of Rb_2ZnCl_4 close below T_L was described fairly well.[11] In the quasistatic frequency range, the wall velocity is very small and friction forces can be neglected, which leads to the nonlinear polarization-field relationship

$$P=a_1\ \mathrm{arcsinh}(a_2E). \quad (3.6)$$

The two coefficients a_1, a_2 given by

$$a_1=P_0w/x_0 \quad (3.7)$$

and

$$a_2=\frac{P_0w}{8b}e^{x_0/w}, \quad (3.8)$$

respectively, were used as free parameters to fit the master curve.

Equation (3.5) describes the interaction of well-separated phase solitons. In large fields, however, solitons will be brought together very closely and start to merge with each other. Therefore, it should be expected that the theory fails at a limiting field

$$E_{lim}=\frac{4b}{P_0w}\,(e^{-1}-e^{1-2x_0/w}), \quad (3.9)$$

for which the soliton coordinate x_- becomes equal to the soliton width w. In fact, the master curve can be fitted excellently according to Eq. (3.6) (Fig. 5) at low fields $E<300$ V/cm, whereas the extrapolation of the fits to larger fields deviates strongly from the experimental data. Estimating P_0 in Eq. (3.5) by the polarization value $P=0.125\ \mu\mathrm{C/cm}^2$ measured at $E=3$ kV/cm, we obtain from fits of experimental data obtained at $E<300$ V/cm the field $E_{lim}=0.34$ kV/cm as the upper field limit for which the master curve should be expected to obey Eq. (3.6). Clearly, this value is in good agreement with the field above which the experimental data deviate from the extrapolated fits (Fig. 5). In other words, the model provides, in addition to the description of the master curve $P(E)$ at low fields, also the correct value of the limiting field above which effects of soliton fusion become important. Apparently, Eq. (3.6) describes not just accidentally a certain part of the master curve, but domain walls in the improper ferroelectric lock-in phase can be treated by soliton theory in the same way as

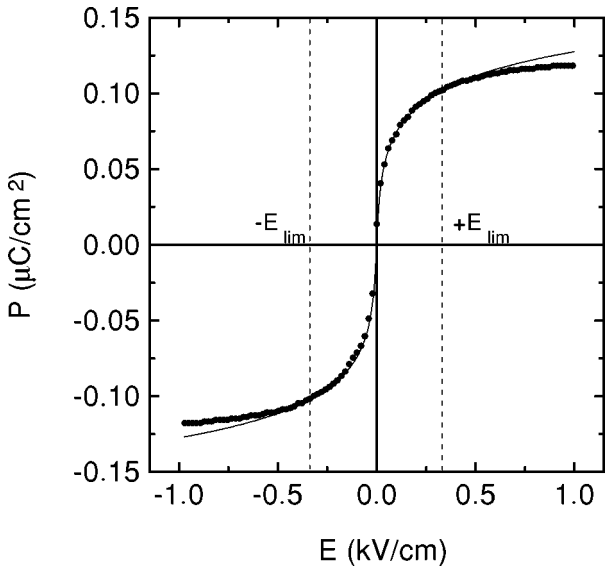

FIG. 5. Master curve derived from experimental data (full circles) and fit according to Eq. (3.6) (full line). The condition $x_- < w$ is fulfilled within the field range $|E|<E_{lim}$ indicated by dashed lines.

phase solitons in the IC phase. Consequently, the fitting parameter a_1 and a_2 contain physically meaningful information about the model parameters P_0, b, x_0, and w characterizing the thermodynamic equilibrium state of the lock-in phase and its ferroelectric domain structure, respectively.

B. Temperature dependence of the domain-wall interaction potential

The analysis of quasistatic hysteresis loops recorded at several temperatures provides information about the temperature dependence of the domain wall density $n=w/x_0$ and may help develop more understanding about the peculiar thermal hysteresis between cooling and heating data observed for the permittivity of purified Rb_2ZnCl_4 crystals.[3] However, even in purified Rb_2ZnCl_4, swan neck shape hysteresis loops that allow the construction of a master curve can be observed only in a limited temperature range below the IC-C transition temperature.[18,20] This can be attributed to the temperature-dependent viscosity coefficient β describing the friction force acting on a moving wall.[20] With decreasing temperature, β increases[20] and the low-frequency limit f_{lim} of the range of dynamic hysteresis loops decreases. In a quasistatic experiment carried out at a certain measuring frequency f_m, the swan neck shape of the hysteresis loops is therefore gradually lost if the crystal is cooled below a temperature T_{lim} with $f_{lim}(T_{lim})=f_m$. Within the frequency range $f_m>5\times10^{-3}$ Hz chosen in the present study, quasistatic hysteresis loops could be recorded for temperatures $175\ \mathrm{K}<T<T_L$. All master curves obtained within this temperature range were found to obey Eq. (3.6) in fields $E<E_{lim}$.

The remanent polarization and coercive field, respectively, of dynamic hysteresis curves show in the whole lock-in phase the same frequency dependence and can be described by the same model of polarization reversal irrespective of the temperature range $T>175$ K or $T<175$ K considered.[20] Apparently, the unique repolarization mecha-

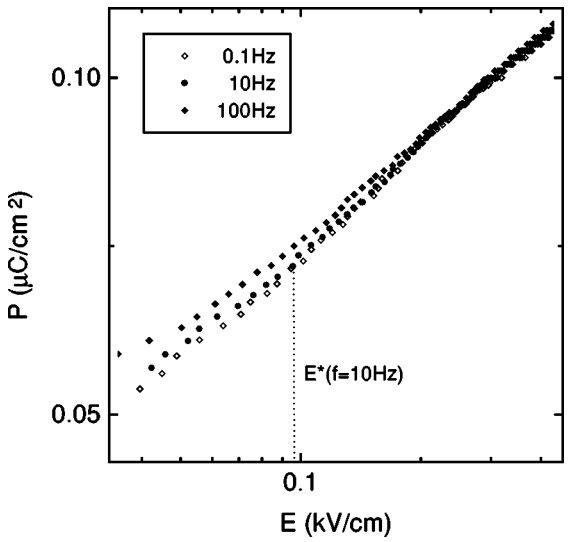

FIG. 6. $P(E)$ data taken at $T=T_L-6$ K from the quasistatic hysteresis loop ($f=0.1$ Hz) and two different dynamic hysteresis loops ($f=10$ and 100 Hz, respectively). For $E>E^*$, the loop recorded at $f=10$ Hz coincides with the quasistatic loop.

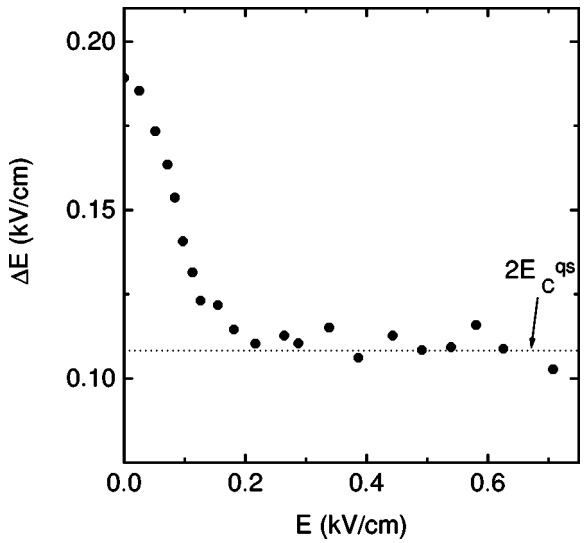

FIG. 7. Field dependence of the difference ΔE between the two branches of a dynamic hysteresis loop. In the high-field limit corresponding to the saturation range of the loop, $\Delta E/2$ corresponds to the coercive field E_c^{qs} of the quasistatic hysteresis loop.

nism effective immediately below T_L does not change on cooling below 175 K. Since frequencies necessary to obtain quasistatic hysteresis loops at low temperatures are not accessible in experiments, we propose a procedure to obtain information about the master curve from hysteresis loops measured in the dynamic regime at frequencies slightly above f_c. In Fig. 6 only that part of dynamic hysteresis loops measured close below T_L is shown, which was recorded for $0<E<E_{lim}$ and $dE/dt<0$. Clearly, for a given measuring frequency f_m, a field $E^*(f_m)$ can be found defining the lower limit of the field range $E^*(f_m)<E<E_{max}$ in which dynamic loops obtained at different frequencies coincide with each other and with the quasistatic loop. Within this field range, domain walls are apparently very close to its equilibrium positions given by the domain-wall interaction potential, i.e., this part of the dynamic hysteresis loop can be used to construct the master curve. Analyzing the difference $\Delta E=E_+-E_-$ between the two branches of the loop, i.e., between electric fields E_+ and E_-, which amount to the same polarization value for $dE/dt>0$ and $dE/dt<0$, respectively, the saturation value of $\Delta E(E)$ in high fields (Fig. 7) was assumed to be twice the coercive field E_c^{qs} of the quasistatic hysteresis loop. In this way, the temperature range in which information about the quasistatic $P(E)$ relationship of Rb_2ZnCl_4 was obtained could be expanded to low temperatures where a direct observation of quasistatic hysteresis loops is not possible.

The analysis of experimental data recorded at temperatures 120 K$<T<T_L$ revealed that the quasistatic $P(E)$ dependence in fields $E<E_{lim}$ can be fitted according to Eq. (3.6) in the whole temperature range investigated. The limiting field $E_{lim}(T)$ was found to decrease with increasing temperature (Fig. 8). Though the interaction potential is nonharmonic in the whole C phase, it gradually takes on a more boxlike shape on cooling down to $T^*\approx160$ K (Fig. 9), but does not change below T^*. This is caused mainly by the temperature dependence of the domain-wall density $n=w/x_0$, which will be discussed later. Due to the boxlike shape of the potential at low temperatures, the domain-wall interaction becomes important only if adjacent walls are close together and the domain-wall–defect interaction dominates in weak fields.

Slightly below T_L, the quasistatic coercive field $E_c^{qs}(T)$ depends only slightly on temperature, whereas it starts to increase steeply with decreasing temperature below $T^*\approx160$ K (Fig. 10). Note that the coercive field E_c^{dyn} of dynamic hysteresis loops shows thermal hysteresis between cooling and heating data,[21] which can be attributed to a corresponding hysteresis of the domain-wall density influencing the domain-wall interaction potential. However, no thermal hysteresis is found for $E_c^{qs}(T)$, indicating that coercivity of quasistatic loops is exclusively caused by the domain-wall defect interaction, which apparently increases strongly with decreasing temperature below T^*.

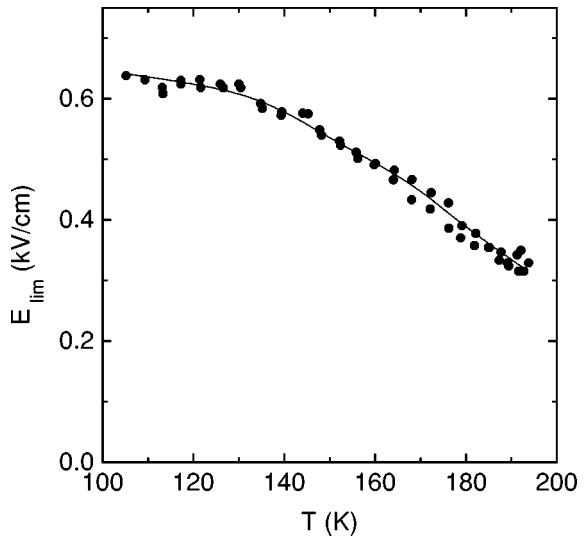

FIG. 8. Temperature dependence of the limiting field E_{lim} defined in Eq. (3.9).

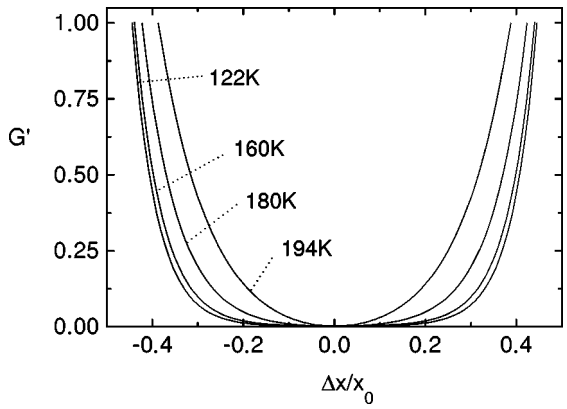

FIG. 9. Reduced domain-wall interaction potential $G' = G_{WW}(\Delta x)/G_{lim}$, determined from quasistatic hysteresis loops recorded at different temperatures of the C phase, dependent on the reduced domain-wall displacement $\Delta x/x_0$. The potential energy G' was related to the value $G_{lim}=G_{WW}[(x_0-w)/2]$ and the wall displacement Δx to the wall distance x_0.

The fitting parameters a_1 and a_2 defined in Eqs. (3.7) and (3.8) depend on P_0, which we have estimated by $P_0 \approx P(E_{sat})$, with $E_{sat}=3$ kV/cm$>E_{lim}$. The spontaneous polarization determined in this way is a continuous, monotonically decreasing function of temperature (Fig. 11) without any anomaly in the lock-in phase. This result agrees with previous findings of several authors[24,25] and does not change qualitatively if another value $E_{sat}>E_{lim}$ is chosen. The knowledge of $P_0(T)$ makes it possible to derive ratios b/w and w/x_0, respectively, from the fits of the experimental data. The ratio b/w (Fig. 12) exhibits a temperature dependence qualitatively similar to those of $P_0(T)$. Particularly, the model parameters b/w and P_0 are unambiguous functions of temperature.

A qualitatively different behavior was found for the domain-wall density $n=w/x_0$ (Fig. 13). For temperatures $T>T^*$, $n(T)$ increases with temperature and a pronounced thermal hysteresis is visible between heating and cooling run. However, the domain-wall density is almost temperature independent for $T<T^*$ and no thermal hysteresis can be detected in this temperature range. Since no thermal hysteresis of b/w was observed, the hysteresis of $n(T)=w/x_0$ at $T>T^*$ seems to be exclusively caused by $x_0(T)$.

The gradual decrease of $n(T)$ on cooling was observed also for nominally pure Rb_2ZnCl_4 crystals[26] and is in accordance with the assumption[25,3] that further antistripples create and annihilate in the lock-in phase. At $T=T_L$, the domain-wall density n_{pu} of the purified crystal presented in this study is approximately the same as the density n_{np} of a nominally pure crystal as it was derived from x-ray and dielectric data.[26] However, the ratio $n_{pu}/n_{np}\approx 10$ is obtained at $T=T_L-15$ K. In other words, n_{np} decreases on cooling much faster and amounts to a much smaller low-temperature saturation value. This indicates the crucial role of the defect density on the domain structure coarsening in Rb_2ZnCl_4.

On the other hand, x_0 is believed to remain constant in the subsequent heating run for domain nucleation in Rb_2ZnCl_4

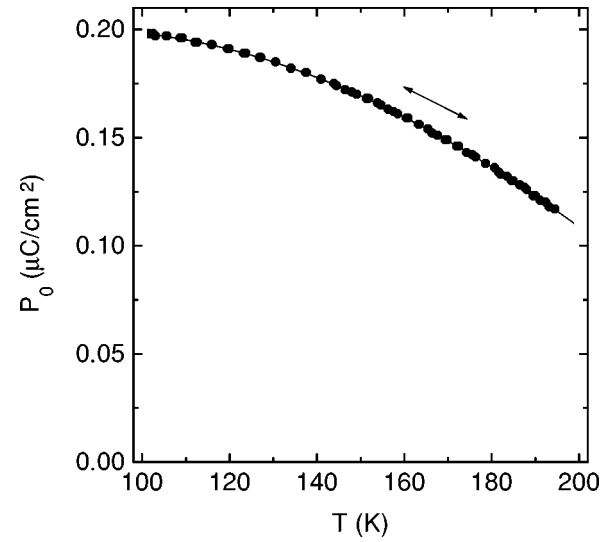

FIG. 11. Temperature dependence of the spontaneous polarization P_0 determined from the saturation value of polarization at $E=3$ kV/cm.

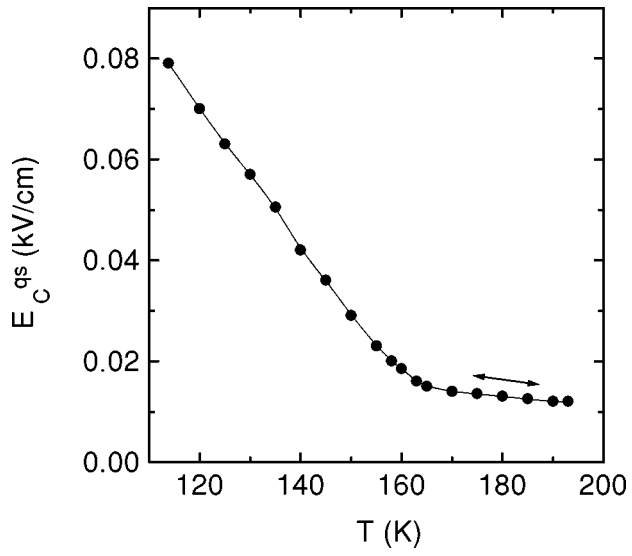

FIG. 10. Temperature dependence of the coercive field E_c^{qs} of quasistatic hysteresis loops.

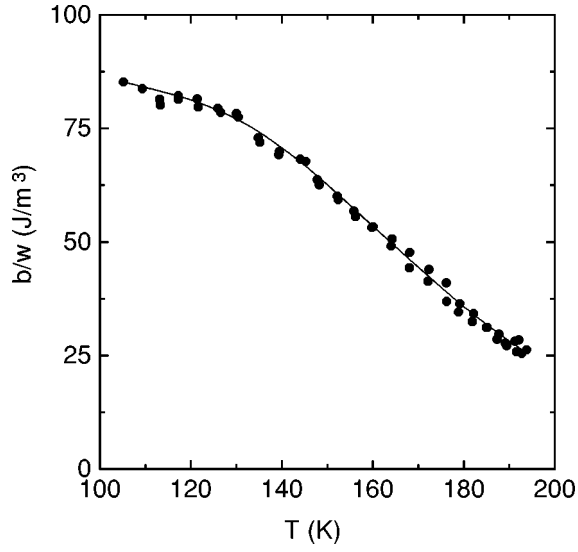

FIG. 12. Temperature dependence of the ratio of model parameters b/w.

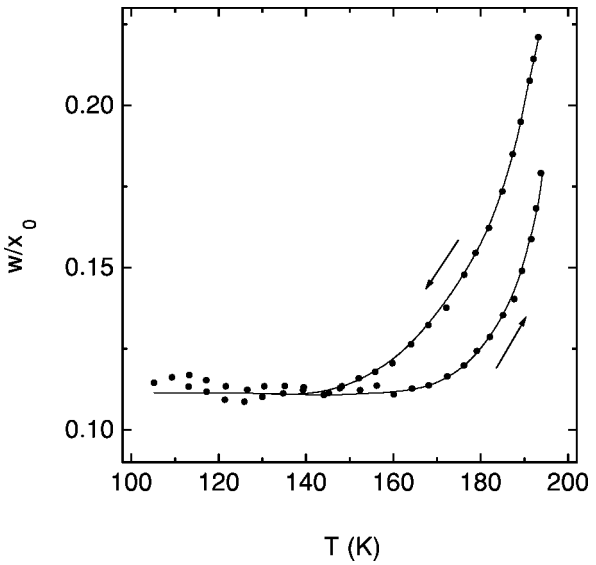

FIG. 13. Temperature dependence of model parameters w/x_0 corresponding to the domain-wall density n.

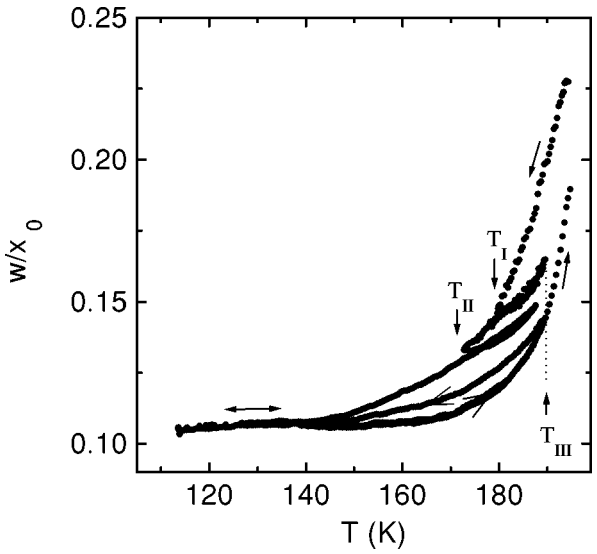

FIG. 14. Behavior of the domain-wall density during temperature cycling within the ferroelectric lock-in phase.

requires the creation of energetically unfavorable stripples containing five domain states in the proper sequence.[5] However, our fits indicate an increase of $n(T)$ on heating (Fig. 13), which is similar to the result obtained from permittivity data of purified crystals.[3,19] One possible explanation for the increase of $n(T)$ not discussed up to now may be a temperature-dependent wall thickness $w(T)$. Theoretical considerations predict a relationship $w(P_0)$ (Refs. 9 and 27) and thus an implicit temperature dependence $w(T)$. Moreover, thermal fluctuations of the local domain-wall position lead to small curvatures of the wall increasing its surface.[26] For nominally pure Rb_2ZnCl_4, a ratio $r=\sigma_x/w=1.8$ between wall roughness σ_x and thickness was derived at $T=T_L$,[26] indicating that domain walls in Rb_2ZnCl_4 are rough at least slightly below T_L, which may reduce the wall-defect interaction considerably.[28]

Whereas the behavior of $n(T)$ at $T>140$ K may be related to an unambiguous, monotonically increasing function $w(T)$ and to stripple annihilations taking place exclusively on cooling, the situation changes at $T<140$ K, where the coarsening of the domain structure on cooling apparently stops and the domain-wall density freezes in at approximately 40% of the value observed at T_L. Moreover, the wall thickness apparently becomes also temperature independent at $T<140$ K. This is obviously not related to the order-parameter modulus ρ_0, which influences the wall thickness $w(\rho_0)$ but does not show any anomaly within the lock-in phase as it can be concluded from the temperature dependence $P_0(T)$ (Fig. 11). On the other hand, it may be related to the anomaly of $E_c^{qs}(T)$ at the slightly higher temperature T^*, which we interpret as an indication for a gradual increase of the defect domain-wall interaction on cooling below T^*.

Though it is well known that a number of quantities related to the polarization dynamics in Rb_2ZnCl_4, such as the coercive field of dynamic hysteresis loops,[29,20] the switching time in rectangular pulses,[10] and the relaxation time of dielectric dispersion,[19] show anomalies at T^* similar to those of $E_c^{qs}(T)$, the mechanism causing the anomaly is still unknown. Since approximately the same T^* was reported for purified and nominally pure crystals, the mechanism apparently does not depend sensitively on defect concentration. The interpretation of the present data leads us to the assumption that this anomaly may have something to do with the wall thickness, which is apparently temperature dependent at higher temperatures, whereas it seems to be constant for $T<T^*$. We suggest, therefore, that this anomaly may be related to a special type of roughening transition[30] of the domain walls in Rb_2ZnCl_4. Ferroelectric domain walls are considered to be candidates for the occurrence of roughening transitions due to competition between thermal fluctuations and pinning on the discrete lattice.[31] The reason that no roughening transition was reported up to now in ferroelectrics may be attributed to the fact that domain walls of many ferroelectric systems are, apparently in contrast to the solitonlike walls in Rb_2ZnCl_4, very thin and continuum theory is not applicable.[32] We are aware that the available model has to be refined in order to describe the anomal behavior at T^* properly. However, the idea of a transition from a smooth wall at $T<T^*$ to a wall with increasing roughness at $T>T^*$ would qualitatively explain both the small coercivity at $T>T^*$ (due to the reduced domain-wall–defect interaction of a rough wall) and the monotonic increase of $w/x_0(T)$ (due to the increase of the apparent width of the wall roughened by thermal fluctuations). In any case, more experimental work including light- and neutron-scattering experiments is required to verify this hypothesis.

Finally, we present data obtained during cycling of temperature within the lock-in phase (Fig. 14). First, the cooling run was interrupted at the temperature T_I where a domain-wall density $n_I(T_I)$ was obtained (Fig. 14). After that, the sample was heated up to a temperature T_{III} where a density $n_I'(T_{III})>n_I(T_I)$ was observed. The cycle was completed by cooling the sample again to T_I and the cooling run was continued. Note that initial and final domain-wall densities at T_I are almost identical and w/x_0 is an unambiguous function of temperature within the whole temperature cycle $T_I \rightarrow T_{III} \rightarrow T_I$. A similar result was observed for the temperature

cycle $T_{II} \rightarrow T_{III} \rightarrow T_{II}$ (Fig. 14). We conclude that x_0 increases on cooling, but remains constant within the temperature cycles $T_I \rightarrow T_{III} \rightarrow T_I$ and $T_{II} \rightarrow T_{III} \rightarrow T_{II}$, respectively, where the temperature dependence $n(T)$ is apparently given exclusively by $w(T)$. In other words, there seems to be an ''equilibrium'' domain-wall distance $x_0^{eq}(T)$ in Rb_2ZnCl_4 that is a decreasing function of temperature.

The coarsening of the domain structure on cooling after a temperature step ΔT, which takes place versus accidental annihilations of stripples, proceeds in purified Rb_2ZnCl_4 apparently on shorter time scales than the variation of temperature chosen in our experiments, which were carried out with a cooling/heating rate of $\Delta T/\Delta t = 0.2$ K/min. The equilibrium wall distance $x_0(T)$ may be related to the ''cutoff'' distance x_0^{max}, above which nucleation of antistripples stops, as it was observed in $NaNO_2$.[33] On the other hand, an additional attractive domain-wall interaction decreasing logarithmically with x_0 was predicted, taking into account thermal fluctuations of the domain wall.[34] The competition between the domain-wall attraction, wall surface energy, and exponential wall repulsion may indeed lead to a shallow energy minimum at a finite x_0^{eq}, which unfortunately could not be detected in our experiments because it is probably masked by wall-defect interaction.

Whereas the behavior discussed up to now is compatible with dielectric data reported by Unruh and Levstik,[24] a different result was found on the temperature cycle $T_{III} \rightarrow T_{IV} = 110\ \text{K} \rightarrow T_{III}$, which may be related to antistripples created at low temperatures that are unable to annihilate and serve as nuclei for the formation of new domain walls on heating.

IV. CONCLUSIONS

We have shown that quasistatic hysteresis curves of Rb_2ZnCl_4 differ in symmetry from curves measured under dynamic conditions, which allows an easy distinction between both types of curves. From the quasistatic hysteresis loop, a master curve $P(E)$ can be derived that carries information about the domain-wall interaction potential. The master curve was described quantitatively assuming that sideways shifts of a field-independent number of domain walls is the only repolarization mechanism and that the repulsive interaction force between domain walls in the ferroelectric C phase and between phase solitons in the IC phase, respectively, is qualitatively the same. Thus the peculiar swan neck shape of quasistatic hysteresis curves in Rb_2ZnCl_4 was shown to reflect the unique mechanism of polarization reversal in improper ferroelectric lock-in phases.

Analyzing hysteresis curves recorded in a wide temperature range of the lock-in phase, it was shown that all model parameters influencing the domain-wall interaction potential except w/x_0 are unambiguous functions of temperature. On the other hand, w/x_0 exhibits a pronounced thermal hysteresis between cooling and heating at temperatures $140\ \text{K} < T < T_L$. This can be attributed to the annihilation of antistripples during cooling, which apparently stops at $T = 140$ K, where w/x_0 freezes in. On heating, w/x_0 starts to increase above the temperature $T^* \approx 160$ K, where additionally an anomaly of the coercive field of quasistatic hysteresis loops was observed. We suggest that this behavior may be attributed to a roughening transition of domain walls in Rb_2ZnCl_4. Above T^*, thermal fluctuations may increase the apparent width of the domain wall and weaken the wall-defect interaction.

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