Phase front and domains during the paraelectric-ferroelectric transition in KD₂PO₄: Optical observation and dielectric contributions

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Observations of the phase front and the domains during the paraelectric-ferroelectric KD_2PO_4 phase have been performed in very good thermal homogeneity conditions (thermal gradient equal to 2×10^{-3} K mm⁻¹). Simultaneously, dielectric and loss constants have also been measured. The phase fronts exhibit a quasiplanar shape perpendicular to the *c* ferroelectric axis. The ferroelectric region is quasimonodomain when its *c* dimension is lower than 100 μ m. The dielectric constant is demonstrated as the sum of three contributions: a monodomain $\varepsilon'_{\text{mono}}$, a contribution of domains ε'_d proportional to $\varepsilon'_{\text{mono}}$ with a coefficient depending on the domain texture, and a contribution due to the existence of the phase front during the phase coexistence. [S0163-1829(99)10829-4]

I. INTRODUCTION

The KD_2PO_4 (DKDP) crystal, the deuterated isomorph of KH₂PO₄ (KDP) undergoes a first-order transition between a tetragonal paraelectric and paraelastic phase (42m) which is the high-temperature phase, and an orthorhombic ferroelectric and ferroelastic one (mm2). The polarization which is considered as the order parameter belongs to the B_2 representation as does the shear strain u_{xy} due to the piezoelectric behavior of DKDP. Moreover the shear strain appearance in the plane perpendicular to the ferroelectric axis c, it is possible to notice the values of normal lattice deformation with $u_{zz} = 6.5 \times 10^{-4}$ greater than u_{xx} and u_{yy} (about 1×10^{-4}). In the low-temperature phase the ferroelectric-ferroelastic domain structure exists with permissible walls¹ in (100) and (010) tetragonal planes. These domains are also mechanical twins and the importance of the mechanical energy in the domain structure KDP type crystals has long been known.² Similarly the linear dependence of the transition temperature with the deuteration degree changing from 121 to 228 K is known and explained.^{3,4}

The DKDP transition has been studied by means of classical macroscopic electric measurements. The double hysteresis loops, characteristic for first-order transitions, were observed above the phase transition temperature.⁵ The spontaneous polarization appears in leaps at the transition, reaching a value of about 4.2×10^{-2} C/m².⁶ A corresponding jump of the shear angle u_{xy} has been found, 24' (Ref. 7) or 33' (Ref. 8), by neutron studies. The character of the phase transition was also confirmed by calorimetric studies.^{9–11} The existence of a thermal hysteresis at the transition needs to be clarified. As in other ferroic crystals the properties of DKP family crystals are frequently described within the frame of Landau-Devonshire theory.^{12–15} In this approach the thermodynamical potential (for example the elastic Gibbs energy Φ) is written versus the polarization *P*

$$\Phi = \Phi_0 + \frac{A}{2}(T - T_0)P^2 - \frac{B}{4}P^4 + \frac{C}{6}P^6 + \cdots$$
 (1)

with A, B, and C positive constants in temperature. Three characteristic temperatures, important for the first-order transition, can be concluded from the above expression. T_0 , the lowest temperature for which the nonpolar phase can exist as a metastable state, $T^* = T_0 + B^2/4AC$, the highest temperature for which the zero field ferroelectric phase can exist metastably, and $T_c = T_0 + 3B^2/16AC$, the temperature at which both polar and nonpolar states correspond to the same Φ value. In the temperature range between T_0 and T^* the polar and nonpolar phases can exist. Then $B^2/4AC$ is the maximum magnitude of a possible thermal hysteresis of the phase transition. Taking into consideration the *A*, *B*, and *C* values given in the literature^{12,13} it can be concluded that the maximum range of the possible phase coexistence is of about 1° (much larger than for KH₂PO₄). However, $B^2/4AC$ is only the possible theoretical temperature range for the thermal hysteresis. While the thermal hysteresis has been observed by different authors, it is interesting that when the temperature was changed very slowly with a good thermal homogeneity for the crystal, this hysteresis could not be observed practically.¹⁵ The present paper will clarify this phenomenon.

The first information on phase coexistence in DKDP came from lattice deformations by neutron diffractometry.^{7,15} One of the authors¹⁶ suggests, with the intention of interpreting the measurements, that paraelectric and ferroelectric stripes perpendicular to the *c* ferroelectric axis alternate in the sample. The validity of this prediction was confirmed by direct optical observations along a tetragonal axis¹⁷ and by x-ray topography using a synchrotron radiation.^{18–21} As in both cases, the results are projections in a given direction therefore it was not possible to make any conclusion on the phase front shape. More recently the phase coexistence of DKDP has been systematically studied. Dielectric measure-

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ments and observations along the three tetragonal axes were simultaneously performed giving a good knowledge of the phase coexistence phenomena and of the phase front shape.²²⁻²⁴ The great importance of an external thermal gradient \mathbf{G}_e has been demonstrated: for G_e between 10^{-1} and $10^{-2} \,\mathrm{K\,mm^{-1}}$, the phase front shape and orientation change with \mathbf{G}_e orientation. When \mathbf{G}_e is parallel to the ferroelectric c axis the phase front is quasiplanar and near (001) plane.²⁵ When G_{e} is perpendicular to the c axis the phase front appears as a factory roof the section of which in a_1 (or a_2) tetragonal plane has a zig-zag shape.^{22,26} In all cases no part of the phase front makes an angle greater than 25° with the (001) plane except the particular case where the zig-zag height equals the sample thickness. Then the energies of the zig-zag edges can decrease by relaxation in the sample boudaries and their number increases.²⁷ When the angle α value between \mathbf{G}_{e} and the *c* axis changes between 0° and 90° of arc, the phase front orientation changes too with the appearance of the zig-zag shape for a critical α value (60° of arc with G_e equal 10^{-2} K mm⁻¹). A theoretical model explains these phenomena as a competition between the mechanical and chemical energies, with a quasinegligible effect of the electrostatic energy at zero applied electric field.²⁸ The interaction between the phase front shape and the domain textures has been sometimes observed as in dagger processes with notable G_e values²⁴ but the problem remains open. For example, the observation of quasimonodomain states in small volumes of the ferroelectric phase inside the paraelectric one requires confirmation.^{24,25}

Measurements of the dielectric constant ε'_c and the loss constant ε_c'' of the KDP family crystals have already been made versus different parameters: the amplitude and the frequency of the ac measuring field,²⁹⁻³¹ an external dc bias field in the c direction, 32,33 the irradiation conditions with γ rays and neutrons, the thermal history, etc. Optical observations of the domain texture performed simultaneously with dielectric measurements allowed us to demonstrate the domain contribution in the dielectric properties at low temperatures^{29,34,35} as nearer the transition temperature.^{33,36} This effect is known even if the variation law of this dielectric constant contribution of the domains versus the temperature must be clarified near the transition. Earlier studies during the phase coexistence of DKDP carried out under an external thermal gradient of about 0.2 K mm⁻¹ confirm this contribution of the domains in the dielectric properties^{25,26} and suggest also that the presence of the phase front in the crystal leads to an increase of its electric permittivity value.

In the present paper precise studies of the DKDP phase coexistence under a controlled thermal gradient of a value close to zero are presented. Dielectric measurements were performed simultaneously with optical observations of the domain structure and the phase front. They allow for a better understanding of the phase coexistence phenomena and a detailed discussion of the dielectric properties within this temperature region.

II. EXPERIMENTAL PROCEDURES

The DKDP crystals were grown by slow cooling of a supersaturated solution of KDP and heavy water. The observed transition at 218.6 K corresponds to a deuterion con-

centration of 90%. The weak tapering angle of the crystal (a few degrees of arc), the room temperature optical studies, and the dielectric properties lead to the conclusion of good crystal quality. The sample was cut with a wire saw. The orientations of sample faces were verified with x-ray Bragg diffraction (accuracy of a minute of arc) and each face was polished on a silk cloth with diamond paste. The sample dimensions were $a_1=5.5$ mm, $a_2=4.4$ mm, and c=7.4 mm. Semitransparent gold electrodes were evaporated on the *c* faces.

The cryostat employed with a helium-gas exchange chamber allows optical observations and measurements along three perpendicular axes simultaneously with dielectric measurements. In the present case these three axes correspond to the tetragonal axes of the crystal. It has been demonstrated in a previous paper²⁶ that the sample boundary conditions have great importance for the temperature of the sample. It was noted that the thermal conductivity of DKDP is about 20 times higher than that of the helium gas and similar to the thermal conductivity of window glass. Detailed experimental studies showed the correlation between the thermal distribution inside the sample, the thermal boundary conditions, and the temperature rate.^{25,26} The results presented here have been obtained in the following conditions. The sample was hung in the helium gas chamber with the help of two thin copper wires which were also used for the electrical contacts. The *c* ferroelectric axis corresponded to an horizontal optical axis and was perpendicular to the thermal gradient G_e . The thermal gradient G_e in the helium gas chamber was controlled with an accuracy of 5 mK mm^{-1} with the help of two platinum resistors placed just above and below the sample. The temperature T reported further on is that of the low platinum resistor which was measured with a precision of 2×10^{-3} K. The dielectric measurements and optical observations of the phase front were done while cooling and heating rates were lower than $10^{-2} \,\mathrm{K \, min^{-1}}$. Only one complementary experiment corresponding to Fig. 7 was performed with other thermal conditions which are described in the text.

The sample capacity and dissipation factor were measured using an HP 4274 A impedance meter with a measuring field of 0.5 V cm⁻¹ in amplitude and 4 kHz in frequency allowing us to calculate ε'_c and ε''_c with a relative accuracy of 3 $\times 10^{-3}$ and 1×10^{-2} , respectively. As already described in a previous paper²⁴ the observations along the a_1 and a_2 axes allow us to rebuild the phase front shape while the observation along the *c* axis gives information on the domain texture. The diffraction of a laser beam propagating in the *c* direction³⁷ has also been used to detect the presence of the domains.

III. RESULTS

The results obtained simmultaneously concerning the phase front shape, the domain texture, and the dielectric ε'_c and ε''_c are presented for clarity successively. The correlations between the different phenomena are obviously noted.

A. Phase front

In the experimental conditions previously described as a very small thermal grandient G_e (equal to or lower than 5



FIG. 1. Evolution of the phase front during a DKDP phase transition in homogeneous thermal conditions ($G_i \sim 0.002 \text{ K mm}^{-1}$). Schematic illustration of the phase coexistence (PF or FP cycles) and photographs of the phase front in a section a_1 (FP cycle).

×10⁻³ K mm⁻¹), the evolution of the phase front shape is similar during a transition from the paraelectric to ferroelectric phase (PF) and for the ferroelectric to paraelectric phase (FP). When the transition begins the phase front appears at the same time in all the sample corners, which is schematically presented in Fig. 1(a). That proves the good thermal homogeneity of the sample. The corners are undoubtedly privileged places in the sample. First, the heat exchange between the sample and the surroundings is easier there. Secondly, in the sample corner a new phase is created with the minimum area of the phase front. Appearing nuclei join in such a way that from eight small phase fronts, two approximately flat fronts perpendicular to the *c* axis are created [Fig. 1(b)].

Those fronts move towards the sample center [Figs. 1(c) and 1(d)] where they form a wedge which disappears quickly [Fig. 1(e)]. Both fronts do not always move at the same speed. In the marginal cases only one front moves while the other remains still.



FIG. 2. Photographs during a PF transition of the phase fronts in a section a_1 and of the domain texture in a *c* section.

B. Domain structure

Existence and texture of the domains are others interesting phenomena worth studying. At the beginning of the PF phase transition only a few domain walls can be observed (Fig. 2). It has already been noticed that domains were not observable in the initial stage of the PF phase transition.^{24,25} But those observations have been made on a crystal under an external thermal gradient G_e equal to 0.2 K mm⁻¹. From the present experiment with a very small thermal gradient, G_e equal to 5×10^{-3} K mm⁻¹, which corresponds roughly to G_i equal to 2×10^{-3} K mm⁻¹ inside the crystal,²⁶ it can be concluded that the ferroelectric phase occupies a considerable volume of the sample whereas there are still only a few domains. Rapid formation of the domain structure begins when fronts meet in the sample center and the paraelectric phase stays only a dagger decreasing in height in the a_2 direction [Figs. 2(c)-2(e)]. At this moment, the creation of the domain wall traversing the whole sample in the c direction is possible. When phase fronts disappear there is a fairly dense domain texture which is dominated by one of the two domain species. Such a domain structure seems to be quite stable, but some arrangements happen in the temperature interval of a few degrees below the transition temperature as noted in KDP studies.33,36

The FP phase transition behaves in a similar way. The paraelectric phase nuclei appear in the sample corners [Fig. 1(a)]. Fronts moving towards the sample center [as in Figs. 1(b)–1(d)] shorten the domain walls on both sides. As illustrated in Fig. 3, the disappearance of the domains can be observed when the phase fronts are at a distance of a few tens of micrometers. This optical observation has been confirmed also by studying the diffraction spectrum of a He-Ne



FIG. 3. Photographs during a FP transition of the phase fronts in a section a_1 and of the domain texture in a *c* section.

laser beam propagating along the c axis. This is clear evidence that the domains cannot exist when the ferroelectric region is too small.

C. Dielectric properties

As demonstrated previously, due to the geometry of the phase front, the temperature gradient inside the sample is very small. In these experimental conditions the reciprocal dielectric constant for the PF phase transition as a function of temperature is presented in Fig. 4(a). In the paraelectric



FIG. 4. Temperature variation during a PF transition of the reciprocal dielectric constant $\varepsilon_c'^{-1}$ and of the loss constant ε_c'' .



FIG. 5. Temperature variation of the reciprocal dielectric constant $\varepsilon_c^{\prime -1}$ during a PF-FP thermal cycle.

phase near the phase transition, the Curie-Weiss law is well fulfilled with a constant 4250 ± 30 K. When the phase front appears [temperature T_1 in Fig. 4(b)] the dielectric constant ε_c' increases rapidly reaching a value of the order of 10⁴. The maximum value of ε'_c depends on the dynamics of the domain structure creation and changes for successive PF phase transitions. The phase front withdrawal from the sample [at temperature T_2 in Fig. 4(b)] is signalized by the decreasing of ε_c' and a peak of ε_c'' . In the ferroelectric phase the variation of the reciprocal ε'_c versus the temperature is very regular except when the domain structure rearrangements occur. A domain rearrangement brings about first of all a rapid increase of ε'_{c} and then its slow decrease to a value lower than the one at the rearrangement beginning [see Fig. 4(a)]. Such rearrangements always happen at a few degrees below the transition temperature. This cannot be the case if the cooling does not go too deeply into the ferroelectric phase as in the example of Fig. 5. Then the temperature dependence of ε_c' obtained during cooling and heating is similar. However, ε'_{a} values during the cooling process are always greater than those during the heating one. Figure 5 gives an important result: temperatures at which the phase transitions begin are practically the same for PF cycle (T_1) and for FP cycle (T_2) , in relatively good agreement with Zeyen's result.¹⁵ It is difficult to comment in detail on the dielectric properties during the phase coexistence for the PF transition (Fig. 4). For the arrangements of the domain structure which happen at the same time the modification of the phase front shape complicate the phenomena. The situation is simpler during the FP transition. Then the domain structure rearrangements are not observed during heating if the crystal remained in the ferroelectric phase long enough. Figure 6 presents the variation of ε_c' and ε_c'' versus the temperature of a sample with a regular homogeneous domain structure (a structure containing only one domain wall orientation). The sample was left for 12 h at a temperature of 200 K. During heating, ε_c' changes monotonously in the ferroelectric phase to a temperature of T_2 when the phase front appears [marked (a) in Figs. 6 and 1]. From that moment the sudden increase of ε_c' and ε_c'' is observed. The dielectric and loss constants reach their maximum val-



FIG. 6. Temperature variation of ε'_c and ε''_c during a FP transition.

ues when both fronts come off the crystal surfaces [marked (b) in Figs. 6 and 1] and the loss constant ε_c'' decreases sharply just after that. A shifting of the phase fronts towards the sample center occurs, between (b) and (c) in Fig. 6 [(b) and (d) in Fig. 1]. That denotes that the length of the domain walls in the *c* direction decreases, and as a consequence the whole area of the domain wall decreases too. Between (c) and (d) in Fig. 6 in the narrow ferroelectric region a disappearance of the domains takes place as shown in Fig. 3. At (d) the phase front disappears which indicates the end of the phase transition. After the withdrawal of the phase front there is a rapid decrease of the ε_c' value and then it changes according to the Curie-Weiss law.

To help the discussion of the results an additional experiment has been carried out. The sample was put on a glass window near the platinum resistor. Furthermore the welds of a cupper-constantan thermocouple were glued with a silver paste on this platinum resistor and on the upper face of the sample. Then it was possible to measure the temperature evolution of the platinum resistor [curve (c)] and that of the crystal [curves (b) and (a) for PF and FP transitions, respectively, as shown in Fig. 7]. Even in the present case with a relatively high temperature rate (a few $10^{-2} \,\mathrm{K\,mm^{-1}}$), it clearly appears that the crystal temperature stays approximately constant during the phase coexistence. It is necessary to change the external temperature to bring thermal energy variation for the phase transformation. As during this time the temperature of the sample remains quasistable, a sharp change is observed when the phase front appears or disappears [Fig. 1(a) and 1(e) or (a) and (d) of Fig. 6]. Then it is easier to understand why during a FP transition the ε'_{c} value changes abruptly just after the phase front withdrawal [below (d) in curve $\varepsilon'_{c}(T)$ in Fig. 6]: the ε'_{c} jump is in agreement with the variation obtained by extrapolation of the paraelectric curve until the temperature of the phase front appearance [temperature T_2 of situation (a)].

IV. DISCUSSION

First let us explain the dielectric constant values already studied in DKDP crystals under notable thermal gradient



FIG. 7. The continuous line (c) corresponds to the temperature of the platinum resistor below the sample. Curves (a) and (b) give the temperature of the sample upper face during FP and PF transitions, respectively.

parallel²⁵ or perpendicular²⁶ to the *c*-ferroelectric axis. In the case presented the quality of the temperature homogeneity and the results allow the three following assumptions.

The thermal gradient in the crystal can be neglected. The main task of this paper was an observation of the phase transition (phase front and domain structure creation) as well as the measurement of the dielectric permittivity in the conditions near the thermal equilibrium of the crystal. The temperature gradient G_e in the helium gas exchange chamber was controlled and regulated. Its value did not exceed 0.005 K/mm. Taking into consideration the earlier discussion referring to the temperature distribution in the DKDP sample²⁶ one can assume that the thermal gradient in the central part of the sample was not larger than 0.002 K/mm. While changing the sample temperature with a rate of 10 mK/min it was observed that the phase front position was a temperature function rather than a time one. The phase front movement ceased when the temperature was stabilized in the phase coexistence region. One can suppose that in the described conditions of the experiment a sample efficaciously changed heat with the surrounding gas and at every moment was in the state close to the thermal equilibrium.

The phase transition begins at temperature T_c at which both phases are absolutely stable. This assumption has experimental confirmations. As earlier studies of DKDP crystals have already proved, the phase transition can undergo without thermal hysteresis.^{9,15,38} Some of our observations also confirm such a character of the phase transition. First, there is a slight difference between temperatures at which the transition begins, regardless of the phase transition direction. Secondly, a difference between T_0 (determined from the Curie-Weiss law) and T_c at which the phase transition starts remains constant. The difference can be considered as a hysteresis measure. If there is no thermal hysteresis of transition, then T_c denotes the phase equilibrium temperature hence $\Delta T = T_c - T_0 = 3B^2/16AC$. In all our experiments, regardless of the transition direction, the temperature difference was approximately stable and was equal to $\Delta T = (0.954 \pm 0.007)$ K. This means that if there is a thermal hysteresis of the phase transition, it is not higher than 0.01 K.

During phase coexistence the crystal remains at temperature T_c . It has been known from previous literature that the phase transition in DKDP crystal is an isothermal one.¹⁵ In Zeyen's experiment during the phase coexistence, the crystal temperature was constant at the same level T_c , upon cooling and heating, confirming the absence of thermal hysteresis. One can assume that the phase transitions (both PF and FP) begin at T_c and the crystal remains at that temperature until the end of the transition, despite the changes of external temperature as illustrated in Fig. 7. After the transition, the crystal reaches isotherm of the surroundings.

The electric permittivity of a single domain crystal in an isothermal state can be calculated based on the Landau theory. Comparing calculated and measured values of ε'_c we can obtain some information about domain structure and phase front effect on the dielectric properties of the crystal.²⁵ In the paraelectric phase the reciprocal electric permittivity is a linear function of temperature (the Curie-Weiss law)

$$\frac{1}{\varepsilon_P'} = A(T - T_0). \tag{2}$$

For the studied crystal $A(=2.66\pm0.01)\times10^7$ Vm/CK has been found.

In the ferroelectric phase the electric permittivity changes with temperature according to the following equation:

$$\frac{1}{\varepsilon_F'}(T) = \frac{B^2}{C} - 4A(T - T_0) + \frac{B}{C}\sqrt{B^2 - 4AC(T - T_0)}$$
$$= 4A(T^* - T) + \frac{2A^{1/2}B}{C^{1/2}}(T^* - T)^{1/2}.$$
 (3)

Usually to trace that dependence we must know the values of *B* and *C* coefficients apart from values *A* and T_0 . Strictly speaking, we need $\Theta = B^2/C$ value because Eq. (3) can be written as follows:

$$\frac{1}{\varepsilon_{F}^{\prime}}(T) = \Theta^{2} - 4A(T - T_{0}) + \sqrt{\Theta^{2} - 4A\Theta(T - T_{0})}, \quad (4)$$

the Θ parameter can be found knowing phase transition temperature T_c and temperature T_0 as

$$\Theta = \frac{B^2}{C} = \frac{16}{3} A(T_c - T_0).$$
 (5)

This means that the electric permittivity for the ferroelectric phase can be calculated as a function of temperature when coefficient A_0 value and temperatures T_c and T_0 are known. The dependence is the following:

$$\frac{1}{\varepsilon_{F}'}(T) = \frac{16}{3}A(T_{c} - T_{0}) - 4A(T - T_{0}) + \sqrt{\left[\frac{16}{3}A(T_{c} - T_{0})\right]^{2} - \frac{64}{3}A^{2}(T_{c} - T_{0})(T - T_{0})}.$$
(6)



FIG. 8. Schematic illustration of phase fronts and domains in paraelectric (P) and ferroelectric phase (F) and during phase coexistence (PF or FP transitions).

As from the present measurements one has obtained $(T_c - T_0) = (0.954 \pm 0.007)$ K, thus $\Theta = (1.353 \pm 0.015) \times 10^8$ V m/C. This Θ value corresponds precisely to values with $B = 4.5 \times 10^{10}$ V m⁵/C³ and $C = 1.5 \times 10^{13}$ V m⁹/C⁵ known from previous studies.^{12,13}

Geometry of phase distribution during the phase coexistence is illustrated in Fig. 8. Taking as first approximation a model of plate capacitors, the electric permittivity of the sample can be written as follows:

$$\frac{1}{\varepsilon'} = \frac{V_F/V}{\varepsilon'_F} + \frac{V_P/V}{\varepsilon'_P},\tag{7}$$

where V_F , V_P denote volumes of ferroelectric and paraelectric phases and V is the total volume of the sample. ε'_F and ε'_P stand for permittivity of the ferroelectric and paraelectric phase at T_c , respectively,

$$\frac{1}{\varepsilon_F'} = \frac{1}{\varepsilon_F'(T_c)} = \frac{3}{4} \frac{B^2}{C} = 4A(T_c - T_0),$$
$$\frac{1}{\varepsilon_P'} = \frac{1}{\varepsilon_P'(T_c)} = \frac{3}{16} \frac{B^2}{C} = A(T_c - T_0).$$
(8)

At the constant rate of cooling or heating, volumes V_F and V_P change, more or less linearly with external temperature.²⁵ Hence T_1 denotes the border of phase coexistence from the paraelectric phase, and T_2 from the ferroelectric side thus

$$\frac{V_F}{V} = \frac{(T_1 - T)}{(T_1 - T_2)}, \quad \frac{V_P}{V} = \frac{(T - T_2)}{(T_1 - T_2)}, \quad (9)$$

and

$$\frac{1}{\varepsilon'}(T) = \frac{(T_1 - T)(1/\varepsilon'_F) + (T - T_2)(1/\varepsilon'_P)}{(T_1 - T_2)}.$$
 (10)

All parameters needed for the calculations are obtained from the present measurements: A and T_0 from temperature dependence of ε'_c in the paraelectric phase and T_c is a temperature at which the phase transition begins ($T_c = T_1$ for PF and $T_c = T_2$ for FP transitions).

In Fig. 9(a) the experiment results are compared with the values obtained from the above equations (ε'_{mono}). At temperature T_1 , both ε' (measured) and ε'_{mono} change abruptly. It can be explained by a rapid change of the crystal temperature from $T_2 = T_c$ to T_1 which is the actual temperature in the chamber. It seems to prove the hypothesis about the isothermal character of the phase transition. Figure 9(b) represents the difference ($\varepsilon' - \varepsilon'_{mono}$) which can be treated as a contri-



FIG. 9. (a) Temperature variation of the measured ε'_c and the calculated monodomain value ε'_{mono} (continuous line) during a FP transition. (b) Temperature variation of the difference $\varepsilon'_c - \varepsilon'_{mono}$. T_2 and T_1 are the temperatures where the phase fronts appear and disappear, respectively.

bution of the domain structure and the phase front existence to the electric permittivity. Figure 10 shows how the electric permittivity should change if in the phase coexistence region ε'_F were the same as measured at temperature T_2 . The solid line in Fig. 10(a) represents permittivity taking into account the contribution of the domain structure $(\varepsilon'_{mono} + \varepsilon'_d)$. Figure 10(b) reflects the difference $\varepsilon' - (\varepsilon'_{mono} + \varepsilon'_d)$, showing distinctly that permittivity in the phase coexistence region is higher than could be expected.

At this stage it is difficult to form unique interpretation. However comments are possible. First let us discuss the ε'_c values in the ferroelectric phase. It is generally accepted that in a case of a single domain state, the dielectric constant ε'_{α} is well described by Eq. (3). Furthermore, it has already been suggested to add an additional term ε_d which is the domain structure contribution.³³ This term depends on the density of the domain walls^{2,33,36,39} and clearly on temperature as illustrated in Fig. 9. It has been well known for a long time that the domain contribution ε'_d is always greater during a cooling cycle than during a heating one:^{33,34} the density of the domain walls is greater in the cooling cycle. In addition, this property has been used to obtain regular domain textures at a given temperature with different domain wall density using different temperature cycles.³⁴ But if this result is well known, what is the dependence between ε'_d and the density of domain walls? Because during the FP cycle the domain structure has not undergone visible changes, ε'_d variation



FIG. 10. (a) Comparison between the $\varepsilon'_c(T)$ curve and the calculated curve $\varepsilon'_{mono} + \varepsilon'_d$ versus *T*. (b) Calculated contribution in the dielectric constant of the phase front existence versus *T* during a FP transition.

with temperature in Fig. 9(b) does not result from change in domain structure geometry. The ratio between the measured ε'_c and ε'_{mono} calculated according to the Landau theory is presented in Fig. 11. It is natural that the ratio in the paraelectric phase equals 1. This simply means that the Curie-Weiss law is fulfilled. However, unexpectedly, for the FP cycle in the ferroelectric phase, the ratio is practically constant having the value 3.8. One can expect that the value of $\varepsilon'_c / \varepsilon'_{mono}$ depends on domain structure geometry, which is confirmed by the results presented in Fig. 12. In this case of the PF cycle, the results of Fig. 4 are used. Again $\varepsilon'_c / \varepsilon'_{mono}$ is



FIG. 11. Temperature variation of the ratio $\varepsilon'_c / \varepsilon'_{mono}$ during a FP transition.



FIG. 12. Temperature variations of the ratio $\varepsilon'_c / \varepsilon'_{mono}$ during a PF transition.

practically constant in the region of a few degrees below the phase transition where great domain structure arrangements are not observed. When a notable rearrangement happens as near 210 K, an abrupt increase of ε'_c occurs but with time it decreases and $\varepsilon'_c / \varepsilon'_{mono}$ reaches a new quasiconstant value lower that the value of the beginning. The rearrangements of the domain texture always correspond to a decrease of the domain wall density. It is now possible to describe the known decrease of ε'_c versus temperature with the following expression:

$$\varepsilon_{c}' = \Lambda \times \varepsilon_{\text{mono}}'$$
$$\varepsilon_{c}' = \varepsilon_{\text{mono}}' + \varepsilon_{d}'$$
(11)

with

$$\varepsilon_d' = (\Lambda - 1)\varepsilon_{\text{mono}}, \qquad (12)$$

where the coefficient Λ grows with the domain wall density.

Further experiments will be necessary to obtain the dependence between the ration $\varepsilon'_c/\varepsilon'_{mono}$ and the density of domains. For example, dielectric measurements may be simultaneously performed with diffraction of a laser beam to attempt the mean domain width.^{36,37,40,41} Small electrical hysteresis cycles at a given temperature will be useful to ensure that the observed domain texture is the equilibrium one.³⁶ In the same way thermal cycles may be used to obtain similar results.³⁴ To conclude, quantitative information is obtained on the domain structure contribution in ε'_c near the

transition. It was already clearly demonstrated in the KDP family crystals that at low temperatures below freezing, ε'_d and the corresponding losses ε''_d were proportional to the total domain wall area. That proved that there is no lateral interaction of the domain walls at this temperature range.³⁴ The domain freezing corresponds to a region where the domain tips begin to move longitudinally.²⁹ For the above temperature the natural domain texture is not often the equilibrium one. The reason is that during the cooling, the thermal energy variation is not sufficient to create domain rearrangement. Then, small thermal or electric hysteresis cycles allow the simplification of the domain texture with the decrease of ε_c' and ε_c'' values. Domains are in strong lateral interactions and as consequence great permittivity values at zero field as show by the thermal noise method. Collective phenomena between domains have been experimentally demonstrated³⁶ such as the nonlinear response in dielectric²⁹ and piezoelectric responses. The present results concern a temperature range near the transition where domain rearrangements are easier. The study should be continued to obtain the correlation between the domain texture (density, arrangement) and the ε_c' and ε_c'' constants.

The Fig. 10 result is obtained with hypothesis a ε'_F value during the phase coexistence equal to $\varepsilon'_F(T_c)$ given by the relation (8). Our experimental results are in agreement with the hypothesis of a quasiconstant temperature T_c in the crystal during the transition obviously when the temperature rate is small (lower than 10^{-2} K min⁻¹). But it is open to discussion that the ε'_d contribution should be the same for a given sample volume at the temperature T_c in both situations F and FP of Fig. 8: in F the limits of the domains in a section (c) are the sample electrodes and in FP these limits are the phase fronts. It can be suggested that the pinning of the quasidislocations inside the wall is not the same with possible differences in the domain density and in the lateral motions of the domain walls under an ac electric field. Furthermore phase fronts can be regions with space charges electric response of which is difficult to predict. To progress on these problems, experiments are actually performed to detect the possible interaction between domains and phase fronts, and between the phase fronts themselves. The action of a small dc electric field on the phase front by different optical methods is also studied in these good thermal conditions. One can see that the phase front at the microscopic level is an open problem. But the result demonstrated in the present paper is clear: the existence of the phase front inside the sample creates a special contribution in the permittivity value which can be added to the monodomain contribution (ε_F' or ε_P') and the extrapolated domain contribution ε'_d for ferroelectric regions.

V. CONCLUSION

Optical observations of phase fronts and domains during the DKDP phase coexistence with a high homogeneity in the sample temperature have been performed. They demonstrate that usually the transition happens with the help of the creation and motion of two quasiplanar phase fronts only almost perpendicular to the *c*-ferroelectric axis. The ferroelectric region remains quasimonodomain if the distance between a phase front and the *c* sample boundary or between the phase fronts themselves is lower than a few tens of micrometers. In the other cases, domains appear in the ferroelectric region often with walls parallel to one of both permissible orientations (100 or 010). The dielectric constant ε'_c can be considered as the sum of three contributions: the contribution of a monodomain sample (ε'_P or ε'_F), the contribution of the do-

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mains ε'_d , as observed in the ferroelectric phase at lower temperatures, and the contribution due to the phase front existence during the phase coexistence. The ε'_d contribution follows in the temperature range of a few degrees below T_c a simple law of variation versus the temperature $\varepsilon'_d = (\Lambda - 1)\varepsilon'_F$ with Λ function of the domain texture. Λ decreases with decreasing density of domains.

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