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Aging of the field-induced asymmetry in a disordered ferroelectric

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Abstract. The isothermal aging of the asymmetry induced in the disordered dielectric crystal $KTa_{1-x}Nb_xO_3$ ($x = 0.027$) submitted to the biasing electric field $\boldsymbol{E}$, is investigated. To this end, the response of the complex dielectric constant to infinitesimal field changes $\delta\mathbf{E}$, applied to the sample after a variable aging delay, has been measured for different magnitudes of E and after different aging delays. Two different experimental procedures have been used: in both cases the response strongly depends on the time spent under field. For short aging delays, the response has a strong contribution proportional to δE and a weak quadratic contribution proportional to $(\delta E)^2$. As time elapses, the linear and the quadratic contributions age in opposite ways: the former decreases whereas the latter increases. This paradoxical behaviour is analyzed in the framework of a model which attributes aging and the related effects (rejuvenation, memory) to the evolution of polarization domain walls: the decrease of the linear contribution is related to the decrease of the total wall area, while the increase of the quadratic term is attributed to wall reconformations.

PACS. 61.43.-j Disordered solids – 77.22.Gm Dielectric loss and relaxation

1 Introduction

In many materials some properties or susceptibilities, such as the elastic or the dielectric constants, depend on the thermodynamic history of the studied sample. This means that the value of the physical parameter under study at a given instant is a function of the manner how the temperature, the applied field or any relevant parameter have varied in the past. However, several cases have to be distinguished.

For instance, in some compounds, particular chemical bonds may progressively be broken while other may be formed, therefore changing most properties of the material. This is chemical aging. It may occur in biological tissues or organic materials and it is often irreversible.

Another situation is the one of materials which contain some type of disorder and/or frustration which are put out of equilibrium by fast cooling (quenching) through a phase transition. In these materials, when all thermodynamic parameters are fixed (i.e. temperature, electric or magnetic fields...), as time elapses the sample tends towards equilibrium, as shown by the history dependent evolution of some susceptibility. This is physical aging. It is reversible by annealing the sample above the transition temperature. This is a very strong advantage for experimentalists since different out-of-equilibrium states can be easily studied, by simply changing the cooling procedure in several runs achieved on the same sample. Spin glasses [1–4] and disordered dielectric [5–9] are archetypes of these latter materials.

In the past few years, several series of experiments [5,10,11] performed on a family of disordered dielectrics have shown that some of these materials are very good candidates for an extensive study of aging. Indeed, under certain stoechiometric conditions, some of them undergo a phase transition at temperature T_{tr}, between the paraelectric phase ($T > T_{tr}$) and the disordered ferroelectric phase ($T < T_{tr}$) [12,13]. It was first observed that the time decrease of the dielectric constant at fixed temperature below T_{tr}, strongly depends on the cooling rate from the high temperature phase to the low temperature one [14]. In addition to this standard isothermal aging, more subtle phenomena were put in evidence: controlled temperature changes induce variations opposite to aging (rejuvenation) and restoration of aging after it has apparently vanished (memory). Moreover, since the low temperature phase is ferroelectric, even if disordered, it is expected that the biasing electric field modifies the

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conditions of aging. This has been experimentally confirmed [15,16].

However, the biasing field cannot be considered just as an additional parameter, playing a role analogous to the one played by the temperature. Actually, the electric field being a vector, it modifies the sample symmetry when applied, while a temperature change does not. Indeed, as more precisely described in the next section, the ferroelectric phase that occurs below T_{tr} is made up of randomly oriented ferroelectric domains. In absence of field the polarization averaged over all the sample volume is equal to zero; in that case a temperature change does not affect the probability distribution among the domains and does not induce a macroscopic polarization. On the contrary, the biasing field favors some domains and penalizes others, according to their own polarization. As a consequence, the macroscopic polarization is no longer null: the sample becomes polarized along the field and the system (sample + field) has the symmetry of a polar vector.

To study the susceptibility of this system one must investigate its response to small variations of the static electric field $\boldsymbol{E}$. To this end, one should remember that the lower symmetry induced by the biasing field implies that the dielectric response to the small electric step algebraically added to $\boldsymbol{E}$ reads

$$\delta\varepsilon = \varepsilon(E+\delta E) - \varepsilon(E) = A(E)\,\delta E + \frac{1}{2}B(E)\,(\delta E)^2 + \ldots, \tag{1}$$

where all the coefficients of the odd terms, such as A, are equal to 0 for $E = 0$. For the sake of simplicity, time is omitted in (1) but, since the sample ages, both the complex coefficients A and B do depend on time and are therefore subject to aging. The main purpose of the present article is to study the time dependence of these coefficients or, equivalently, how the asymmetry induced by the field ages. A brief account of preliminary experiments achieved on $KTa_{1-x}Nb_xO_3$ has been already published [17]. We report here on new experiments performed on an extended aging duration, and following a new procedure. Moreover, the results are analyzed in terms of the so-called domain wall model. The long aging lapse makes possible a very precise determination of the time dependence of the two coefficients A and B. On the other hand, the comparison of the data obtained by the means of the two different procedures provides us with very useful information to refine the model which attributes the time-dependent part of the dielectric constant to the evolution of the polarization domain walls [18]. The article is organized as follows. The characteristics of the sample and the procedures used are first given. Then the data are reported and briefly commented. Finally, the domain wall model is presented and compared with our results.

2 Experimental details

At low temperatures, the pure potassium tantalate $KTaO_3$ has the cubic perovskite structure with the tantalum ions Ta^{5+} surrounded by the oxygen octahedral shell. As the temperature is lowered, the correlation between the displacements of the Ta^{5+} ions inside the oxygen shell increases, leading to a strong increase of the dielectric constant ε. However, as a consequence of quantum fluctuations, ε does not diverge, even at 0 K, and the ferroelectric transition is aborted. This is the reason why $KTaO_3$ is sometimes termed as "incipient" ferroelectric. Substituting a fraction x ($x \geq x_c \cong 0.008$) of tantalum ions Ta^{5+} by niobium ions Nb^{5+} allows the ferroelectric transition to occur at the temperature T_{tr} which, depending on x, is in the range 30–40 K. The lattice of the so constituted potassium niobotantalate $KTa_{1-x}Nb_xO_3$ has then the cubic symmetry [19]. Below T_{tr}, the two species exhibit very different dynamics. On the one hand, the Nb^{5+} ions are frozen in off-center positions and constitute electric dipoles located on random sites and oriented at random along one of the eight [111] directions inducing a local rhombohedral symmetry [13,19]. On the other hand, the Ta^{5+} ions take off-center positions too, but they are not completely frozen. Due to their mutual ferroelectric interactions, the dipoles attached to the Ta^{5+} ions tend to be all parallel. However, this trend towards a unique ferroelectric domain is hindered by the static random fields generated by the Nb^{5+} ions. As a first consequence, the sample is parceled into eight possible types of rhombohedral polar domains which are equally probable in absence of external electric field; the sample is hence macroscopically cubic, its dielectric constant is isotropic, and the total polarization is null. As a second consequence, the flip of a Ta^{5+} dipole from an orientation to another, leading to the motion of the domain walls, is strongly slowed down by the Nb^{5+} ions acting as random pinning sites; this is at the origin of aging.

In the sample used in this work, the transition occurs at $T_{tr} = 35$ K. According to the phase diagram [19], this corresponds to a niobium concentration $x = 0.027$. It was in the shape of a 0.877 mm thick plate, covered with thin chromium electrodes.

In the disordered dielectric crystals, aging and related phenomena strongly depend both on the thermal and on the electrical histories of the sample. Therefore, we measured the complex capacitance of the sample $C = C' - \mathrm{i}C''$ as a function of time, after both the temperature and the biasing electric field were changed in a controlled manner. We carried out two series of experiments, which are described below. The recorded data were then transformed into the dimensionless complex dielectric constant $\varepsilon = \varepsilon' - \mathrm{i}\,\varepsilon''$, by simply multiplying them by the geometrical factor $\alpha = 15.8\ \mathrm{pF}^{-1}$. The measurements were performed using an impedance analyzer (Hewlett-Packard 4192A) at the fixed frequency $f = 10$ kHz for which the accuracy is the best. This results from the balance between the magnitude of the phenomenon, which decreases if the frequency increases, and the characteristics of the impedance analyzer. The oscillating electric field applied to the sample had an amplitude of about $1.2\ \mathrm{kV\,m^{-1}}$.

We adopted a single cooling process for all the experiments reported here (Fig. 1a): after annealing above the transition temperature, the sample was rapidly cooled

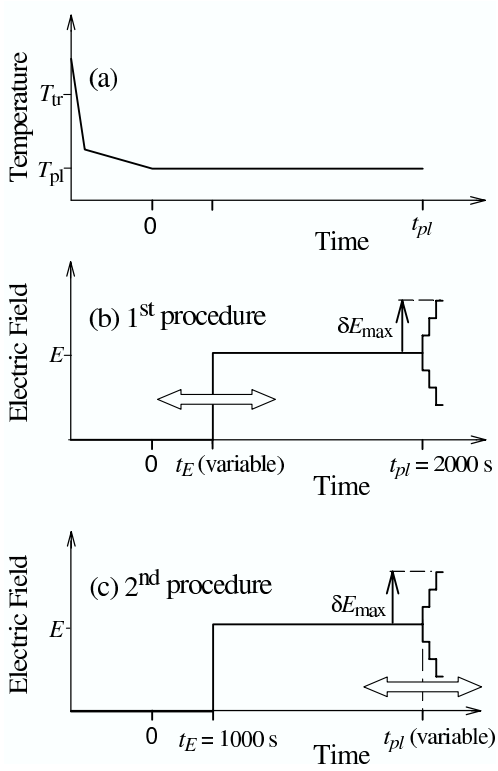

Fig. 1. Schematic representation of both temperature and electric histories of the sample. (a) For the sample used in these experiments, the transition temperature is $T_{tr} = 35$ K and the plateau temperature was fixed to 11.2 K; (b) first procedure: the plateau duration is fixed to $t_{pl} = 2000$ s and the biasing electric field is switched on at t_E varying from 0 to 2000 s; (c) second procedure: the switching time is fixed at $t_E = 1000$ s and the plateau duration t_{pl} varies from 0 to 10^4 s. For both procedures (b and c), E takes several values ranging from 0 to 7 kV m^{-1} and $\delta E_{\max} = 0.8$ kV m^{-1}. Actually, $\delta E_{\max}$is the result of seven elementary steps of about 0.11 kV m^{-1} each.

$\left(-4.3\ \mathrm{K\,min^{-1}}\right)$ across T_{tr} down to 18 K, where the cooling rate was reduced to -6 mK s^{-1}. This cooling rate was maintained during the lapse of time necessary for the temperature to reach the value $T_{pl} = 11.2$ K. The sample underwent then an isothermal evolution at the plateau temperature T_{pl} during a lapse of time t_{pl}.

At the date $t = t_E$ ($0 \leq t_E \leq t_{pl}$, the origin of times being the instant when the temperature reaches T_{pl}) a DC voltage, positive or negative, was applied across the sample; the amplitude of the corresponding biasing electric field **E** was always less than 7 kV m^{-1}.

At the outcome of this process (isothermal evolution at T_{pl} during t_{pl}, under the biasing electric field $\boldsymbol{E}$ during $t_{pl} - t_E$) we measured both the complex capacitance at 10 kHz of the sample, $C(t_{pl}, E)$, and its changes after infinitesimal increments (decrements) in the biasing electric field. The latter were obtained by increasing (decreasing) step by step the electric field from E to $E \pm \delta E_{\max}$. Each step had the amplitude $\delta E \approx 0.11$ kV m^{-1}, and the maximum value $\delta E_{\max}$ was about 0.8 kV m^{-1}; this is small enough to be considered as infinitesimal [20] and the corresponding changes in the dielectric constant coincide therefore with the derivative $(\partial\varepsilon/\partial E)(t_{pl}, E)$. The effects of an infinitesimal increase and of an infinitesimal decrease in E were recorded in two independent experiments and the sample was annealed above T_{tr} before each of these experiments. In other words, we measured separately the right hand side and the left hand side of the derivative $(\partial\varepsilon/\partial E)(t_{pl}, t_E)$. On the other hand, both ε and $(\partial\varepsilon/\partial E)$ were generally recorded in a duration short enough to guaranty that no measurable aging of the material occurs during the measurement process. Actually, this condition is not exactly fulfilled when the measurement of $(\partial\varepsilon/\partial E)$ takes place immediately after the biasing electric field is applied (i.e., for $t_E = t_{pl}$). Indeed, setting up an electric field in KTN induces rejuvenation, immediately followed by a fast evolution of the dielectric constant towards a new equilibrium state. Consequently the system rapidly ages and, although the measurement of $(\partial\varepsilon/\partial E)$ is completed in a few seconds, the aging occurring during this lapse of time significantly affects the results. In that case, we recorded the effects of aging, namely $\varepsilon(t \geq t_E, E)$, in an independent experiment and we subtracted the corresponding data from $\varepsilon\,(t \geq t_E, E + \delta E)$.

We performed two series of experiments. First, the plateau duration t_{pl} was fixed to 2000 s, whereas the biasing electric field was switched on at the date $t = t_E$ varying in the range 0–2000 s (Fig. 1b). In the second series of experiments, t_E was maintained to 1000 s and the plateau duration varied in between 10^3 and 10^4 s (Fig. 1c). In both cases, the data recorded at $t = t_{pl}$ were analyzed in terms of the waiting time $t_{pl} - t_E$.

3 Results

Before we present our results, we recall that the dielectric constant being a complex quantity, the coefficients A and B in the expansion (1) are complex too. It is expected (and experimentally shown below) that the real parts A' and B' on the one hand, and the imaginary parts A'' and B'' on the other hand, have respectively the same behaviours. Therefore, as a shorthand, when we say that A (resp. B) has some property, we mean that A' and A'' (resp. B' and B'') possess the same property.

As an example of the response of KTN to a biasing electric field, we show in Figure 2 the dielectric constant (real part) as a function of time, after the sample has undergone the sequence of events summarized in Figure 1c. These experimental results correspond to $t_{pl} = 5000$ s, $t_E = 1000$ s, and $E = 3.4$ kV m^{-1}. Moreover, we show in the inset an expanded view of the data recorded at $t = t_{pl}$, for $\delta E_{\max} = 0.8$ kV m^{-1} (open circles) and $\delta E_{\max} = -0.8$ kV m^{-1} (open triangles). These latter data, recorded in two independent experiments, were then gathered in a single file corresponding to the "experimental derivative" $(\partial\varepsilon/\partial E)(t_{pl}, t_E)$. In Figure 3a are displayed the results for the fixed aging delay $t_{pl} - t_E = 1000$ s and for different magnitudes of the biasing electric field (sketch of Fig. 1b). We show also in Figure 3b the variations of

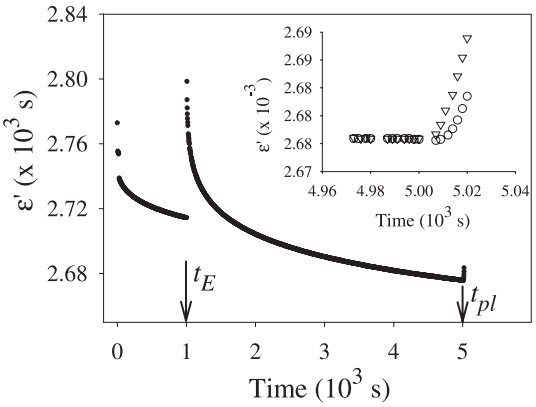

Fig. 2. Measured aging of the real part of the dielectric constant, using the experimental procedure 2 (Fig. 1c). The biasing electric field ($E = +3.4\ \mathrm{kV\,m^{-1}}$) is applied at $t_E = 1000$ s and the plateau duration is $t_{pl} = 5000$ s. Inset: expanded view of the data recorded at $t = t_{pl}$ for δE varying by steps of $+0.11$ kV m^{-1} (open circles) or -0.11 kV m^{-1} (open triangles).

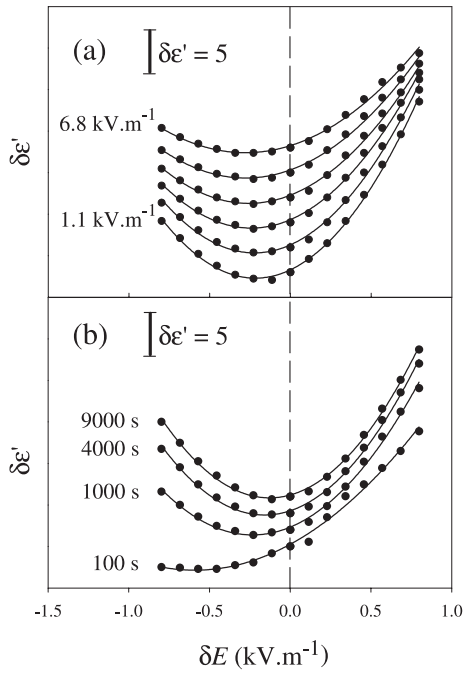

Fig. 3. Measured changes in the real part of the dielectric constant as a function of infinitesimal electric steps δE demonstrating the influence of the biasing electric field and of the delay on the experimental derivatives $(\partial\varepsilon/\partial E)$: (a) at the outcome of the aging procedure 1 (t_E variable, $t_{pl} = 2000$ s — Fig. 1b) for $t_{pl} - t_E = 1000$ s and for different values of the biasing electric field; (b) at the outcome of the aging procedure 2 ($t_E = 1000$ s, t_{pl} variable — Fig. 1c) for $E = 3.4\ \mathrm{kV\,m^{-1}}$ and for different values of the aging delay $t_{pl} - t_E$. The solid lines are the best fits to the data using (1) limited to second order in δE. For the sake of clarity, all the curves have been vertically shifted.

ε', recorded under the field $E = 3.4$ kV m^{-1}, for different values of the aging delay $t_{pl} - t_E$ (sketch of Fig. 1c). We observed similar behaviour for the imaginary part ε''.

It is clear from Figure 3 that the variations of ε strongly depend both on the magnitude of E and on the time spent under field. Moreover, in both cases the variations are parabolic (see the solid lines in Fig. 3) and the expansion of the derivative $(\partial\varepsilon/\partial E)$ should therefore include a term proportional to $(\delta E)^2$. It is interesting to notice in Figure 3b that this B term evolves as time elapses since the variations, which exhibit a large linear component A for $t_{pl} - t_E = 100$ s, become almost quadratic when $t_{pl} - t_E = 9 \times 10^3$ s.

To quantify this behaviour, we have computed the best fit to the data recorded at the outcome either of the first (Fig. 1b) or of the second process (Fig. 1c), using the expansion given by (1), limited to second order in δE. We show in Figure 4 the variations of both A and B against the delay $t_{pl} - t_E$, for $E = 3.4\ \mathrm{kV\,m^{-1}}$. Immediately after the biasing electric field is applied, the linear coefficient A takes a finite value whereas the quadratic one B vanishing small. As time elapses, A monotonously decreases, whereas B rapidly increases. Note moreover that the aging of the coefficients A and B does not depend on the real age of the sample, given by t_{pl}, but depends only on the time spent under field. As already announced at the beginning of this section, whatever the sequence of events, both the real and the imaginary parts of each coefficient A or B undergoes similar behaviours. This is also attested by the best fits to the measured values of both $A'(t_{pl} - t_E)$ and $A''(t_{pl} - t_E)$ displayed in Figures 4a and 4b respectively as solid lines. Both these curves were computed assuming a power law of the form $A = A_0 - a\left[(t_{pl} - t_E) - t_0\right]^{\alpha}$; in both cases the best fits to the data where obtained with a single value of the exponent α. This clearly means that the same process is at work during the aging of the field-induced asymmetry of the real and the imaginary parts of the dielectric constant.

4 Discussion

From a microscopic viewpoint, aging in disordered ferroelectrics can be attributed to the slow evolution of the walls separating domains with different electric polarizations [21,22]. The first success of this model is that it satisfactorily describes the isothermal decrease (i.e. aging) of both the real and the imaginary parts of the dielectric constant $\varepsilon(t)$ as time elapses. Indeed in the framework of this model, the process responsible for the time-dependent dielectric properties is supposed to be located in the thin shell between two neighboring domains, the thickness of which is of the order of the lattice parameter a. Therefore, the effect on $\varepsilon(t)$ must vary as the wall area of a domain which is proportional to R^2, where R is the mean size of the domains, multiplied by the domain density $n(R)$ which is proportional toR^{-3}. The time-dependent part of the dielectric constant varies thus as R^{-1}. Since the mean size increases with time, one predicts that $\varepsilon(t)$ should decrease; this is the observed behaviour [23].

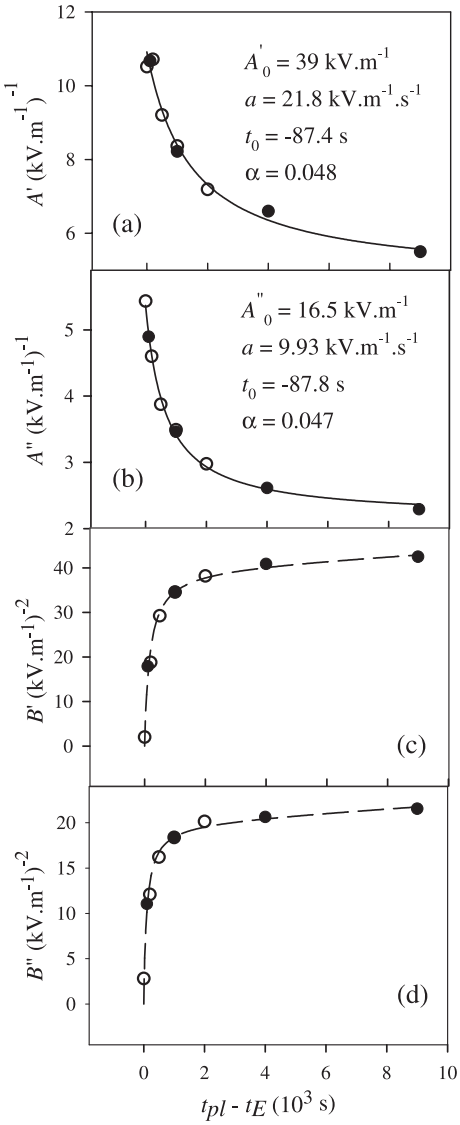

Fig. 4. Variations of the linear coefficient A ((a) real part, (b) imaginary part) and of the quadratic coefficient B ((c) real part, (d) imaginary part) as a function of the aging delay $t_{pl} - t_E$, for $E = 3.4$ kV m^{-1}. The data were deduced from the fits displayed as solid lines in Figure 3. The open circles are for the first procedure (Fig. 1b), whereas the full circles correspond to the second procedure (Fig. 1c). The solid lines (a and b) are the best fits to the data using $A = A_0 - a\left[(t_{pl} - t_E) - t_0\right]^{\alpha}$. The dashed lines (c and d) are guides for the eyes.

Since the material under study is ferroelectric, one must take into account the role of the applied electric field. Although there are eight possible directions of polarization in KTN, we oversimplify the model and consider only two types of domains, one with the polarization parallel to the biasing field and the other antiparallel. The biasing electric field has opposite effects on them: those with their polarization parallel to the field are favored and they grow while the others necessarily slim. It is expected that this simplified view retains the essential features.

When $E = 0$, the wall contribution to the dielectric constant is given by:

$$\varepsilon(0) = K\, n(R,0)\; R^2, \tag{2}$$

where $n(R,0)$ is the total density of domains in absence of field. In that case, $n(R,0)$ can be split into two equal populations, namely $n_+(R,0) = \frac{1}{2} n(R,0)$ and $n_-(R,0) = \frac{1}{2} n(R,0)$, corresponding respectively to the two opposite polarizations which have equal probabilities when $E = 0$.

When the field $\boldsymbol{E}$ is applied, it modifies both the sizes and the density of domains. Let $R_+(E) > R_+(0) = R$ and $R_-(E) < R_-(0) = R$ be the typical sizes of the domains respectively parallel and antiparallel to the field, and $n_+(R_+, E)$ and $n_-(R_-, E)$ their densities. These quantities are related by the volume constraint

$$n_+(R_+, E)\; R_+^3 + n_-(R_-, E)\; R_-^3 = 1. \tag{3}$$

Then the walls contribution to the dielectric constant reads:

$$\varepsilon(E) = K\left(n_+(R_+, E)\; R_+^2 + n_-(R_-, E)\; R_-^2\right). \tag{4}$$

As for the volume contribution, it is not affected by the field since the oscillating response of the domain cores is not dependent on the polarization.

Both the size and the density of the domains being scalar, they must be functions of scalar quantities built with the electric field. Among them, the simplest are the scalar product of the field by the dipolar momentum p of a domain and the scalar product of the field by itself (in a one-dimensional model they read respectively pE and E^2). However, since the two domain populations are equal before the field is applied, the term pE cancels by the sum over all the domains; therefore, it may be omited in the calculation of even rank tensors such as the dielectric constant. Consequently, we assume the forms $R_\pm(E) = R\left(1 \pm \alpha_\pm E^2\right)$ for the two domain sizes, where α_+ and α_- are two positive constants but not necessarily equal. We assume moreover that $n_+(R_+, E)$ has the form $n_+(R_+, E) = \frac{1}{2} n(R,0)\;\left(1 - \beta_+ E^2\right)$, where β_+ is a positive constant; (3) imposes then $n_-(R_-, E) = \left(1 - n_+(R_+, E)\; R_+^3\right) \cdot R_-^{-3}$.

As long as the field δE is small (that is to say $\alpha_\pm \cdot (\delta E)^2 \ll 1$, and $\beta_+ \cdot (\delta E)^2 \ll 1$) the wall contribution to the dielectric constant reads

$$\varepsilon(\delta E) = K\, n(R,0)\; R^2 \times \left\{1 + \left[(\alpha_+ - \alpha_-) - \frac{1}{2}(\beta_+ - \beta_-)\right]\; (\delta E)^2\right\}, \tag{5}$$

where β_- verifies $3(\alpha_+ - \alpha_-) - (\beta_+ - \beta_-) = 0$. Using now the volume constraint (3) and the walls contribution (2) for $E = 0$, one finds:

$$\varepsilon(\delta E) = \varepsilon(0) + \frac{1}{2} B(0)\; (\delta E)^2, \tag{6}$$

where the coefficient $B(0)$ is defined by $B(0) = -\varepsilon(0)\;(\alpha_+ - \alpha_-)$.

Equation (6) clearly demonstrates that the weak field adds a quadratic contribution to the dielectric constant, as experimentally observed. Note moreover that the model does not determine the sign of the coefficient $B(0)$ but our experimental results show that it is positive.

Let us now examine how (4) is modified when a weak field δE is algebraically added to the strong field E. If δE is small enough, $\varepsilon(E+\delta E)$ can be expanded to second order in δE, namely $\varepsilon(E+\delta E) = \varepsilon(E) + A(E)\ \delta E + \frac{1}{2}B(E)\ (\delta E)^2$. The field dependence of both coefficients A and B are easily deduced from (2) and from the definitions of $R_\pm$ and of $n_\pm$. We found:

$$A(E) = \varepsilon(0)\left[\left(1+\alpha_+E^2\right)\left(2\alpha_+ - \beta_+ - 3\alpha_+\beta_+E^2\right) + \left(1-\alpha_-E^2\right)\left(\beta_- - 2\alpha_- - 3\alpha_-\beta_-E^2\right)\right] E. \quad (7)$$

$A(E)$ is an odd function of E. A trite but tedious calculation shows that $B(E)$ is an even function of E. These two results agree with symmetry considerations and they were actually observed in our experiments.

This simple model for aging characterizes the domains with a single parameter, the mean size R. It captures the main features of aging but more subtle phenomena, such as the behaviours of both A and B as time elapses or rejuvenation and memory, are beyond the possibilities of this simplified version. In order to explain these experimental facts some improvements of the model have to be done which imply that new degrees of freedom play a role.

Indeed, due to the pinning sites generated by the Nb^{5+} ions, a domain wall is a rough surface that permanently modifies through thermally activated local reconformations. This means that parts of the surface may occupy two (or several) positions and go from one to another by jumps over an energy barrier, the magnitude of which depends on the size. The characteristic time of equilibration for a reconformation of area $l \times l$, with $a < l < R$ is $\tau = \tau_\infty \exp\left(\Gamma\, l/a\, k_B T\right)$ where Γ is a characteristic energy [16]. Consequently, all the reconformations of size smaller than $l(t_a) = a\, k_B T\, \Gamma^{-1} \ln(t_a/t_\infty)$ are in thermal equilibrium at the temperature T after the aging time t_a [22].

If now a weak biasing field is applied to the system, those reconformations with $l \leq l(t_a)$ that were equilibrated are suddenly pushed out of equilibrium and contribute anew to ε which therefore increases. Indeed, whatever the perturbation, (a weak field step as well as a weak temperature step) changes the domain frontiers. Since many walls are pushed into new places, they become young: their reconformations are not equilibrated. Consequently, the dielectric constant, which has decreased before the perturbation is applied, becomes larger and the more the sample has aged the more the perturbation is efficient to rejuvenate it. Moreover, since the strong field E completely disturbs the domains, the initial isothermal aging (before $t = t_{pl}$) is erased and is not relevant.

In the preceding discussion the time did not appear explicitly since our purpose was only to describe the immediate response to the weak field δE which occurs within a very short time (a few seconds) on the aging scale. Indeed, our experiments show that both the coefficients A and B depend on time. Therefore they must read $A(E,t)$ and $B(E,t)$ where, for simplicity, the plateau temperature T_{pl} is not written. In fact, an important point still has to be explained: how aging modifies these field effects and, more precisely, why the coefficient $A(E)$ decreases as the time elapses, while the coefficient $B(E)$ increases.

We consider first the very short times. This means that the weak increase δE is applied immediately (i.e. within a few seconds) after the strong field E. During this very short lapse the domain walls have not enough time to evolve. Therefore it is equivalent to apply $E+\delta E$ in one step or E shortly followed by δE in two consecutive steps. In the first case the derivatives can be calculated from the curve $\varepsilon(E)$ and the result is the "mathematical derivatives". In the second case the first two "experimental derivatives" $A(E,0)$ and $B(E,0)$ are provided. From the preceding argument, they coincide with the two corresponding "mathematical derivatives". For the value $\delta E_{\max}$ used in the experiments described above we have $B(E,0)\ \delta E_{\max} \ll A(E,0)$ (see figure 4). This means that at the very beginning of aging in the field E, the variation of ε is practically linear with δE and (1) reduces to:

$$\varepsilon(E+\delta E, 0) \cong \varepsilon(E,0) + A(E,0)\ \delta E. \quad (8)$$

Then, the variation $\delta\varepsilon$ is dominated by the displacement of the domain walls, independently of their detailed shape, because the reconformations of the walls pass from an out-of-equilibrium state to another (statistically equivalent) out-of-equilibrium state.

We turn now towards longer times, taking into account the evolution of the domain walls, in order to explain why the real and the imaginary parts of A decrease while they increase for B (see Fig. 4). If we assume that the coefficients $\alpha_\pm$ and $\beta_\pm$ appearing in (7) are only weakly time-dependent, the quantity $A(E,t)$ must vary, in a first approximation, as $\varepsilon(0,t)$. This explains why it decreases with time. This result is obtained because the model for $A(E)$ takes into account only the changes which occur in the mean characteristics of the domains (their size and their density) and not in the fine structure of their walls.

This fine structure, to which rejuvenation is attributed, is responsible for the behaviour of the coefficient $B(E)$. When the field δE is applied, forces are induced on the walls which bring them into new positions where the reconformations are no longer in equilibrium. Then the walls are young and they provide a larger contribution to ε. Therefore, the coefficient $B(E)$ measures rejuvenation. This effect possesses two properties: (*i*) The fields δE and $-\delta E$ act in opposite directions, but in both cases the walls become younger; consequently, the effect is an even function of δE; (*ii*) the longer the lapse of time t, the more reconformations are equilibrated and the more reconformations are pushed out-of-equilibrium by δE; therefore, the coefficient B is an increasing function of $t = t_{pl} - t_E$. It is worthwhile to notice that an analogous effect was observed with temperature jumps [11]: both δT and $-\delta T$ induce rejuvenation increasing with aging.

5 Conclusion

The isothermal AC dielectric constant of a KTN sample has been measured at 10 kHz as a function of time when DC biasing fields were applied. These new experiments performed over a large time scale provide us with a very accurate characteristic time of aging and allow to show that a unique microscopic process is at the origin of the aging of the asymmetry of both the real and the imaginary parts of the dielectric constant (see Fig. 4).

The similarity of the data obtained according to two different procedures (corresponding to two different sample histories) shows that the field $\boldsymbol{E}$ erases the anterior aging. This is a strong argument in favor of the domain wall model since the field displaces the aged walls towards new positions where they are younger. Moreover, both the coefficients $A(E,t)$ and $B(E,t)$ of the expansion (1) age, but in opposite — and somewhat — paradoxical ways. The domain walls model allows also to explain this behaviour. Just as the biasing field, the small field δE induces a shift and a subsequent rejuvenation of the walls. The term $A(E,t)\ \delta E$ is attributed to the variation of the total area of the domain walls, through their average characteristics (mean size and mean density) as they are changed by δE; consequently, it decreases approximately as $\varepsilon(E,t)$. On the other hand, the term $^1\!/_2 B(E,t)\ (\delta E)^2$ is related to the rejuvenation of the walls which are driven onto new positions, whatever is the sign of δE, where they are put out of local equilibrium; therefore, it increases the dielectric constant.

All these results reinforce the appropriateness of the domain walls model to the description of aging in disordered ferroelectric phases. They also make clear why the term $A(E,t)\ \delta E$, which characterizes the polar symmetry induced by the field E, and the term $^1\!/_2 B(E,t)\ (\delta E)^2$ vary in opposite manners.

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23. This simple calculation of the wall contribution to the dielectric constant implies that the walls are sufficiently regular. If they were fractal, the result (decreasing of the wall contribution when the domain size increases) would be still valid as long as the dimensionality of the surface is $2+\eta$ with $\eta < 1$ (the regular case corresponds to $\eta = 0$)