Aging dynamics in ferroelectric deuterated potassium dihydrogen phosphate

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(Received 17 June 2017; revised manuscript received 1 August 2017; published 18 September 2017)

Anomalously large dielectric aging is found in the high-susceptibility plateau ferroelectric regime of nominally ~95% deuterated potassium dihydrogen phosphate (DKDP). Much less aging is found in nondeuterated KDP throughout most of its plateau region. Optical images of the DKDP domain structure show no dramatic change during aging. Small changes in electric field restore the preaged susceptibility, but the previous aging almost recovers after returning to a respective aging field. Susceptibility vs field can show memory of at least two prior aging fields. Aging effects are not fully erased even by brief heating above the Curie point, indicating a role for diffusion of hydrogen to the domain walls, leaving changes in disorder that can survive temporary absence of domain walls. Asymmetrical nonlinear susceptibility develops for fields slightly above or below a prior aging field and during field sweeps, with the dependence of the second-harmonic magnitude on sweep rate giving a characteristic time comparable to the time for hydrogen to diffuse a domain-wall width.

DOI: 10.1103/PhysRevMaterials.1.044403

I. INTRODUCTION

KH_2PO_4 (KDP) [1] and its deuterated version, KD_2PO_4 (DKDP) [2], are commonly used nonlinear dielectrics, each with a ferroelectric (FE) phase. In KDP and DKDP, the FE phases show unusual plateaus in the real dielectric constant ε' over a temperature range below the Curie temperature, T_C, with the large susceptibility arising from a dense array of 180° domain walls [2–4]. The origins of the abrupt loss of susceptibility at the low-temperature edge of the plateau appear to be driven by either a phase transition or sharp crossover involving interactions among the domain walls [3,5], and probably pinning by interaction with disorder [3,5–7]. To better understand the cooperative behavior of domain walls in the plateau region, it is interesting to study dynamical symptoms such as aging effects—i.e., reduction in ε' over time under fixed conditions—that have been found in KDP [6]. Here we report that samples of typical, incompletely deuterated [2,8] commercial DKDP show unusually strong aging effects, much larger than found in KDP [6]. We present a variety of strong evidence that the principle mechanism for this giant aging involves diffusion of hydrogen to domain walls. Although this diffusion aging mechanism is irrelevant to the origin of the domain freezing at the low-T side of the plateau, the existence of this strongly time-dependent interaction between domain walls and disorder provides a probe for the roles of local pinning and interaction effects in the domain-wall freezing.

There are, broadly speaking, three main types of aging in disordered domain systems [9]. The first consists simply of domain growth, which reduces the domain-wall area and thus reduces the large component of ε' that comes from the domain walls. Another consists of gradual settling of domain walls into low free-energy configurations, stuck to underlying disorder. In typical cases, this settling consists of changes in domain-wall configurations to fit quenched disorder [6,9], but it can also result from changes in the disorder to fit a particular domain-wall configuration. The latter case is often found in magnetic aftereffects (e.g., [10]), and some ferroelectric systems (e.g., [11]), driven by the diffusion of mobile defects to domain walls. In addition to these simple, traditional domain aging mechanisms, there could also be more complicated aging typical of glasses and spin glasses, but with domains as the interacting ingredients rather than smaller units such as spins [9]. Since for KDP and DKDP (and other systems) interactions among the domain walls [12] are suspected to lead to a sort of cooperative glassy freezing [3,5,6], that would be a particularly interesting effect.

The distribution of H and D in partially deuterated KDP should be an important source of disorder, because T_C increases as a function of D concentration [2,4,8]. Therefore, in equilibrium, D should preferentially sit in the regions with good ferroelectric order, leaving H preferentially at the domain walls. In KDP, the deuterium concentration should be about the natural abundance, 0.016%, so that H-D disorder would be much less important than in our DKDP samples. Thus interaction between the domain walls and the large disorder due to incomplete deuteration is the obvious suspect for the cause of the large aging we shall describe, which is present in DKDP but not KDP.

This aging effect could occur either by domain-wall configuration adjustments or by relocation of H to domain walls. For partially deuterated KDP, it is known that the H-D distribution diffuses, with typical diffusion coefficients at room temperature on the order of 10^{-15} cm^2/s, varying as a function of D concentration [13]. Although we have found no studies of the temperature dependence of this rate, the diffusion was interpreted as being via tunneling, so extreme temperature dependences would not be expected [13].

We use a variety of techniques, ranging from optical imaging to behavior of ε' and nonlinear susceptibility under various field-temperature (E, T) histories, to probe the origins of what turns out to be anomalously large aging in DKDP. We shall first present evidence, based largely on simple photographic images and on the response of the aging to changes in electric field E, which unambiguously shows that the aging effect in DKDP is not due to domain growth. Then we shall present evidence, based primarily on memory after changes in E and after heating above T_C, to show that the aging involves degrees of freedom that can survive the absence of FE order, i.e., that it involves changes in the disorder itself. We shall present several lines of argument to show that the diffusion of H to

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domain walls is the dominant mechanism. Finally, we shall show some results on the time and temperature dependences of the aging, especially in response to abrupt quakes in the domain configuration, showing that minimization of the free energy of the local interaction of the domain walls and the disorder can compete with minimization of the free energy of the overall collective arrangement of the domains.

II. MATERIALS AND METHODS

DKDP crystals were obtained from United Crystals and KDP crystals were grown from water solution at the University of Illinois at Urbana-Champaign. For optics, the samples were polished using lapping disks with grit size down to 0.3 μm. Optical images, including digital movies, of the domain structure were obtained via polarized light microscopy using a Leica DM2700 microscope. Typical dimensions of the samples used for dielectric measurements were $\sim$1 mm thickness and $\sim$6.5 mm^2 area. Samples were made into capacitors by depositing a thin layer of Cr ($\sim$10 nm) followed by about 100 nm of Ag via thermal evaporation. Two different DKDP samples (called A and B) showed noticeably different aging properties despite being from the same supplier with no obvious macroscopic differences.

Most of our dielectric response measurements were made with applied ac voltage at 100 Hz, using a standard lock-in amplifier with a circuit that allowed dc voltage to be applied along with the ac voltage. Measurement of dielectric response for KDP is complicated by large nonlinear effects, attributed to weakly pinned domain walls [7] found at relatively low fields. Most of our measurements used 1 V rms or, for the second-order nonlinear response, 2 V rms—large enough to be well into the nonlinear regime in which several frequency-dependent features show up that are not apparent in the linear regime, and for which aging effects are particularly evident [7]. Broadband dielectric response data were taken using a QuadTech 7600 Plus LCR meter with a 1 V rms ac bias, and thus also well into the nonlinear regime. Although the response measured is therefore not, strictly speaking, the linear dielectric coefficient, we will still refer to the apparent coefficient determined from the current-voltage ratio as ε' for brevity.

III. RESULTS

A. Standard dielectric characterization

Figure 1 illustrates the voltage dependence of the response for DKDP, showing effects very similar to those reported for KDP [7]. Some of the kinetic features of the response are most evident in the nonlinear response, as previously reported [7].

All samples showed the usual FE transition with a plateau regime for ε', as shown in Fig. 2, in agreement with previous reports [2,3,5] that DKDP and KDP have very similar dynamical freezing at the low-T edge of the plateau. Thus the large aging we shall describe in our DKDP is not directly due to the shared physics of that dynamical freezing.

Analysis of the temperature dependence of the characteristic peak frequencies in $\varepsilon''(f,T)$ shown in Fig. 3 shows nearly ordinary Arrhenius behavior near the high-T end of the plateau and sharply non-Arrhenius behavior near the low-T end of the

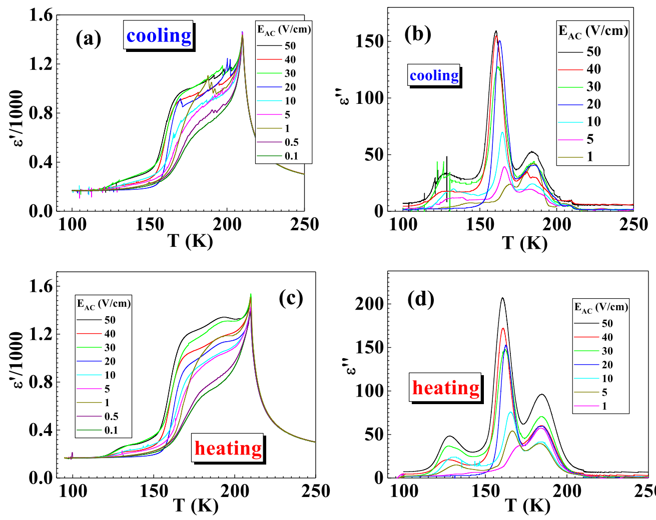

FIG. 1. DKDP dielectric susceptibility measured with different ac drive magnitudes. (a) (ε') and (b) (ε'') are measured during cooling at 4 K/min, and (c) and (d) during heating at 4 K/min. The ε'' panels omit data for 0.5 and 0.1 V/cm, which look just like the 1 V/cm data except with more instrumental noise. Digitation noise in the low-field traces has been smoothed. Sharp spikes appearing often in the DKDP cooling data and rarely in the heating data do not represent actual changes in ε', but are caused by spikes in the polarization current. Trianglelike steps, however, do represent changes in ε'. (The explanations of those effects are discussed later.) The rather complicated nonmonotonic dependences on ac field strength are interesting but will not be explored further here.

plateau, for which no plausible Arrhenius attempt rate could be used—again, similar to previous reports [3,5,12]. Previous work shows that the characteristic frequencies of these peaks in KDP are only very weakly dependent on ac field amplitude,

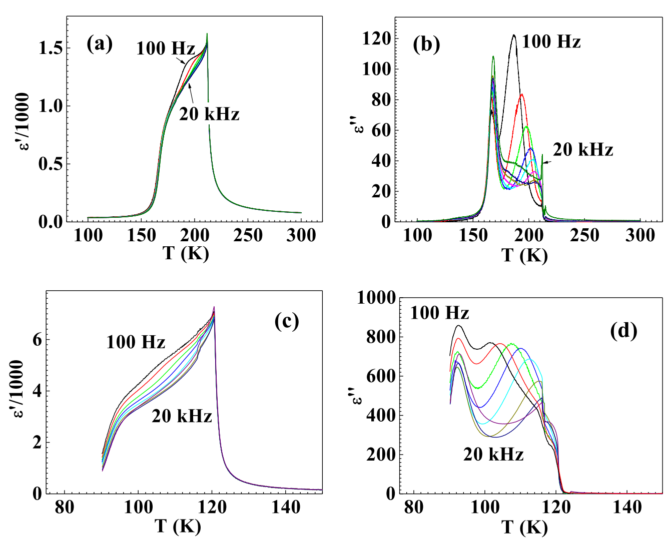

FIG. 2. Temperature dependences of the real and imaginary parts of dielectric susceptibility of DKDP sample B [(a),(b)] and KDP [(c),(d)] measured with 1 V rms ac drive at frequencies from 100 Hz to 20 KHz. Measurements were made upon cooling at 4 K/min.

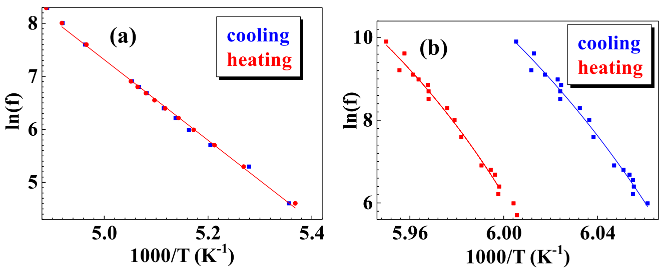

FIG. 3. Natural logarithm of the frequency vs the temperature at which the ε'' peak is found. These measurements were made using fixed frequency and swept T. The results in this range are close to those obtained using fixed T and swept f. (a) shows that the frequency dependence of the peak temperatures near T_C nearly follows an Arrhenius law with an attempt rate of 10^{20} Hz—mildly unphysical, indicating gradual growth of barriers on cooling. (b) shows that the peak near 165 K departs from the Arrhenius form, showing distinct curvature with an apparent Vogel-Fulcher temperature near 160 K. The attempt rates are reasonable—roughly 10^{10} Hz—but very sensitive to the Vogel-Fulcher parameter. An Arrhenius fit would require an extremely unphysical attempt rate, above 10^{160} Hz.

so that the non-Arrhenius freezing is not an artifact of looking at the nonlinear response [7].

B. Basic aging effects

The basic pattern of gradual reduction in ε' vs time under fixed conditions is illustrated in Fig. 4, which shows ε' aging vs time for DKDP at $E = 0$ at several temperatures. (The initial oscillations are due to the temperature controller.) Very substantial aging is found throughout the plateau region.

Figure 5 contrasts the large aging in DKDP within the plateau region with the smaller aging in KDP. The DKDP aging is largest in the upper range of the plateau, but the smaller KDP aging is largest at the lower end, indicating that a different mechanism is present in DKDP. Figure 5(a) also hints at a surprising result: the fractional rate at which ε' decreases in DKDP not only depends on the sample and on T_{aging}, but it

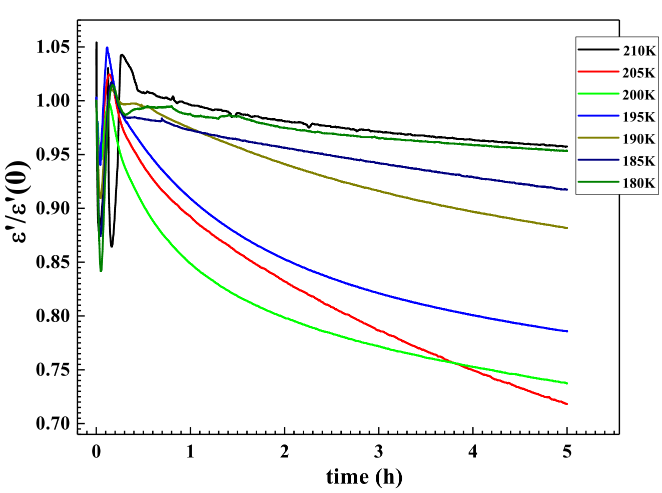

FIG. 4. Aging in $\varepsilon'(t)$ for a few temperatures for DKDP. Oscillations in the first half hour are due to the temperature controller.

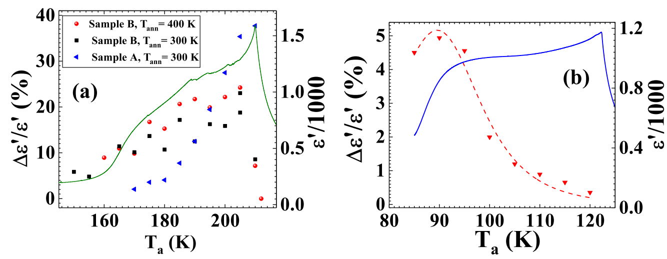

FIG. 5. These data points show the fractional reduction in ε' in the 5 h after reaching the temperature shown on cooling for (a) two DKDP samples, and (b) a KDP sample, with the lines serving as a reminder of $\varepsilon'(t)$. No aging is found above T_C. The aging fraction in DKDP depends on the sample and somewhat on the annealing temperature between runs.

also seems to be somewhat larger on aging runs preceded by annealing at 400 K rather than 300 K.

It is evident that the large aging in DKDP in the central and upper parts of the plateau cannot be a direct effect of the physics shared with KDP, which shows much smaller aging throughout most of its plateau region. The most obvious difference relevant to effects measured far from T_C is the additional disorder from the H impurities in DKDP. The difference of the DKDP aging after between-run anneals to 300 and 400 K (well above T_C) suggests that some ingredient other than domain walls and fixed disorder may be involved, since all domain-wall effects should completely reset near T_C and since fixed disorder does not anneal. The H/D distribution is the obvious candidate for disorder that can change configuration at temperatures above or below T_C.

Figure 6 shows the domain structure during aging at $T = 200\ K$, directly visualized by polarized light microscopy. Over most of the sample, the approximate domain size is unchanged, and there are only small motions of the domain

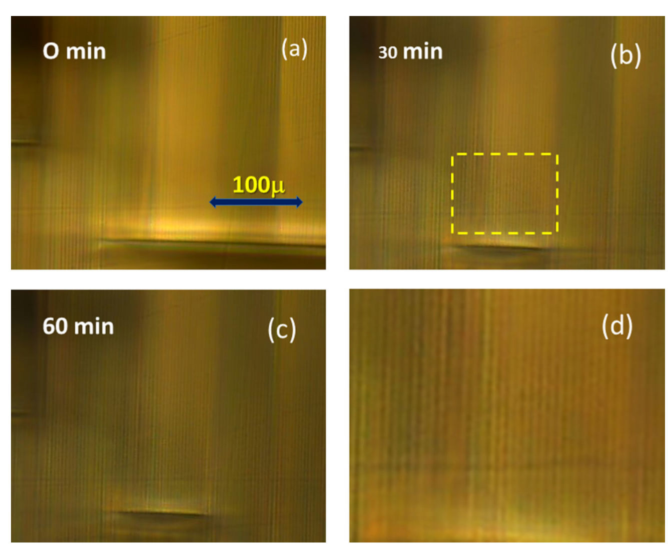

FIG. 6. Evolution of the domain pattern during aging in a DKDP sample at 200 K, viewed by polarized light microscopy. Panel (d) shows a blowup of the marked region from panel (b), in which the near-vertical stripes representing the main domain structure are clearly visible.

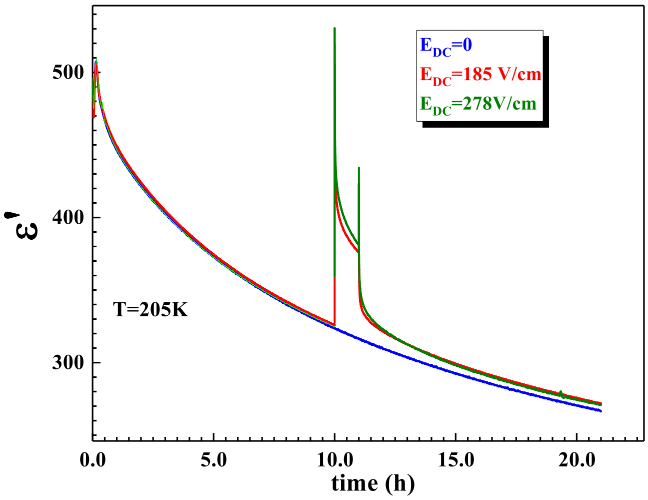

FIG. 7. Aging of ε' for 21 h at $T = 205$ K (a), with $E = 0$, and with 1 h interruptions of dc fields of 185 and 278 V/cm, respectively.

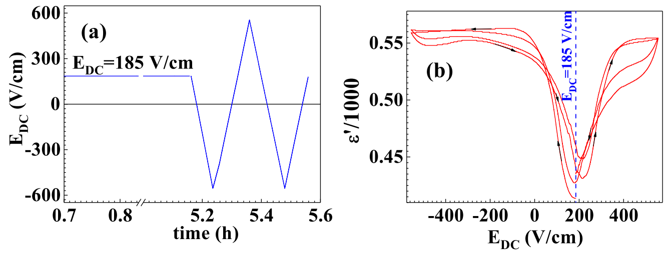

FIG. 8. (a) shows the dc bias protocol for the "hole-burning" experiment, with $T = 202$ K. (b) shows the $\varepsilon'(E)$ measured during the field-sweep parts of the protocol, after aging at $E_{dc} = 185$ V/cm.

walls. In one anomalous region (lower part of the picture) the domain structure changes substantially. Since the approximate aging behavior is similar in each sample and involves huge fractional changes in ε', we believe that the anomalous regions are not needed to understand its crudest qualitative features. We shall, however, see relatively large variability between samples and on repeated thermal cycles. Large defects in the domain pattern are likely to be involved in those effects. The lack of dramatic change in the domain pattern over most of the sample thus rules out domain growth as a primary mechanism of the large aging effect found in DKDP.

The domain contrast appears by eye to slightly increase on aging, a result we hesitated to report until a keen-eyed referee also noticed it. This contrast sharpening suggests a gradual change in the local potential seen by the domain walls, consistent with either H accumulation at the walls or with detailed adjustment of the walls to fixed disorder.

C. Aging and changes in *E* field

If the aging consists of detailed settling of domain walls onto quenched disorder, one would expect to be able to erase its effects by moving nearly all the domain walls off of their initially favored positions by applying a large enough change in E. After resetting E to the initial value, the aging should start over again from the beginning. If, on the other hand, the aging primarily consists of changes in disorder via H diffusing to domain walls, simply moving the domain walls would not immediately erase the H sheets that formed during aging, although they would gradually diffuse away. Thus resetting E to the initial value would allow the walls to settle back to those sheets, letting the aging resume from roughly its previous value. Aging in complicated glassy systems, such as spin glasses [14] and dielectric glasses [15] can also show memory of prior aging fields [9].

Figure. 7 shows the response of the aging after changes in E, most notably rejuvenation after sufficient change in E. Despite the rejuvenation after changing E, most of the memory of aging is restored fairly quickly after resetting to the initial value of E. This pattern contrasts sharply with expectations for an aging mechanism involving detailed settling of domain walls on quenched disorder; yet it is consistent with aging due to H diffusion or with aging of a glass of interacting domain walls.

One can predict approximately how large a change in E should be required for rejuvenation if the aging is due to local interactions with disorder, since motion of a domain wall by one domain-wall width would largely remove it from the locally favored positions, e.g., from the sheet of H. Figure 8 shows ε' and ε'' as a function of E on E sweeps taken after aging at 185 V/cm at 202 K. These show a clear hole in ε' with a characteristic full width at half maximum of about 200 V/cm. There is also a somewhat narrower peak in $\varepsilon''(E)$. As discussed below, that width does correspond approximately to the field change needed to move domain walls about one domain-wall width. As we shall discuss, this characteristic rejuvenation field would be surprisingly large for aging due to a complex glass of interacting domains.

Some hysteresis appears in the position of the aging hole, depending on the sign of dE/dt. An effect of this sort is expected in an H-diffusion picture, since the recent history of the domain-wall positions not only creates new inhomogeneities of H, but can also drag old ones around. We have not attempted to calculate the magnitude or even the sign of that effect.

Figure 9 shows $\varepsilon'(E)$ data similar to Fig. 8, but taken after aging 10 h at 185 V/cm and then 10 h at 370 V/cm. Two clear holes appear, so the system can remember at least two different E fields. Once again, this result is difficult to explain in a picture of detailed domain-wall adjustment to fixed disorder. This result is, however, compatible with aging creating sheets of enhanced H concentration, since two sets of sheets can coexist. It is also compatible with complex glassy aging, which can maintain memories of multiple past conditions [9].

The dependence of ε' on E after aging implies a nonzero second derivative of polarization, P, with respect to E, which would lead to a second-harmonic generation whose sign would depend on the sign of the change in E after aging. Figure 10 shows this effect. There is also an offset in the second-harmonic generation coefficient depending on the sign of the sweep of $E(t)$. This effect is not obtainable from simply taking the derivative with respect to E of the ε' shown in Fig. 8. It is nonetheless expected, because in addition to the deliberate long-time aging, there is an ongoing short-time aging that leaves each domain wall in an asymmetrical potential as E is

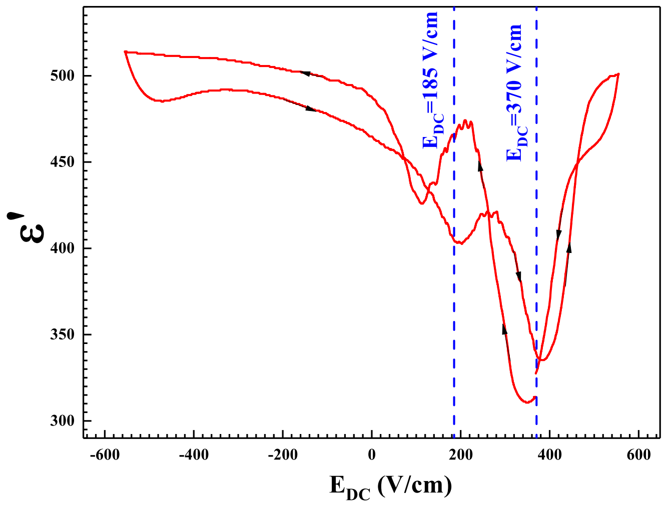

FIG. 9. Aging in ε' at 202 K with $E_{dc} = 185$ V/cm for 10 h followed by $E_{dc} = 370$ V/cm for 10 h, then measured by scanning E_{dc} as shown in Fig. 8.

swept over time, with the sign of the asymmetry depending on the direction of the sweep.

The sweep-dependent second-harmonic generation should show a nonmonotonic sweep rate dependence. Very fast sweeps should develop very little aging effect, and thus very little second harmonic. Very slow sweeps should leave the domain walls sitting near the symmetrical bottom of the aged potential minimum, and thus again give little second harmonic. The maximum should occur when the field moves the domain wall about one width per time for the aging to get well underway. In a simplified picture of aging via hydrogen diffusion with a Gaussian spatial pattern, $e^{-x^2/2w^2}$, of interactions between H and the wall and weak enough to

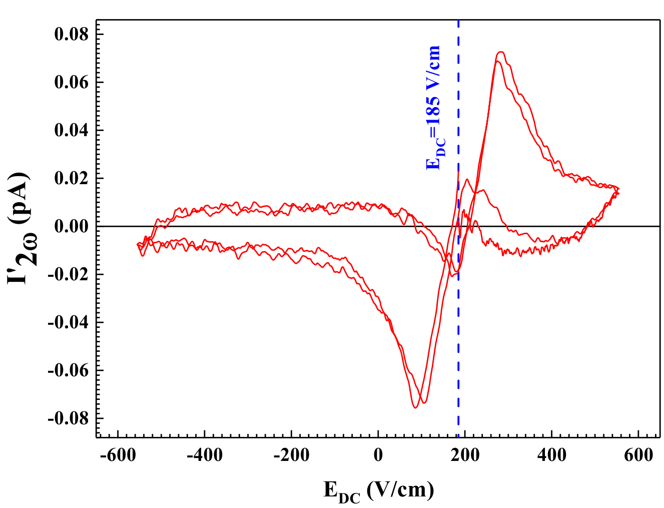

FIG. 10. Second-harmonic current component in the dc bias hole-burning experiment of Fig. 8. The two similar traces were taken consecutively, as shown in the protocol of Fig. 8(a). Positive sign here means positive current maxima at the maxima of dV^2/dt of the fundamental ac voltage drive, as would be produced by an instantaneous quadratic response. The out-of-phase second-harmonic current was much smaller.

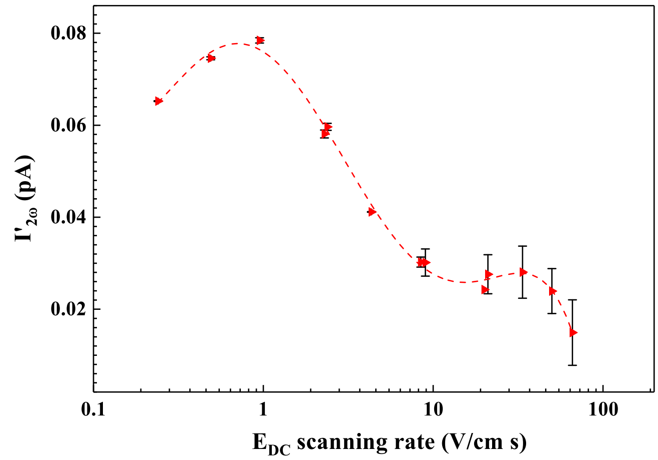

FIG. 11. Difference in second-harmonic component in-phase with the time derivative of the squared polarization between positive-going and negative-going field sweeps as a function of field-sweep rate. In each case, the sample was cooled to 202 K in a field of 1200 V/cm to keep the resulting aging hole away from the sweep range of -1000 V/cm to $+1000$ V/cm. This produced a large range of fields for which the results, like those in Fig. 10 around -300 V/cm, give a field-independent offset between the two sweep directions. Data from -400 V/cm to $+400$ V/cm, well within the range for which the results showed no systematic dependence on field, were averaged. Results show averages from several sweeps, with single-sigma error bars estimated from the between-sweep differences. For the slower sweep rates, error bars were comparable to the thickness of the points. The dashed line is just a guide for the eyes.

linearize the Boltzmann distribution of H, it is not hard to calculate an analytical expression for the dependence of the second harmonic on sweep rate; and it does indeed peak very close to a rate equal to the H diffusion constant divided by the domain-wall width, w.

Figure 11 shows how the second-harmonic generation depends on sweep rate, expressed in V/cm s. The maximum occurs for a rate of about 1 V/cm s. Since the voltage change needed to sweep through a half-width of a memory hole here is roughly 100 V/cm, this implies a characteristic time of $\sim$100 s. Given the domain-wall half-width, known from x-ray scattering to be $\sim$2.5 nm [16], that would imply an H diffusion constant of $\sim 6 \times 10^{-16}$ cm^2/s, remarkably close to the literature value [13] of $\sim 10^{-15}$ cm^2/s taken at somewhat higher T.

D. Memory and rejuvenation after temperature changes and on domain quakes

Thus far we have eliminated simple domain growth and domain-wall settling to quenched disorder as the primary mechanisms of the large aging in DKDP. We have not definitively ruled out aging of the interacting domain-wall glass, although the dependence of the aging rate on high-T annealing protocol would not be easy to explain in such a picture, and the characteristic rejuvenation field scale points toward local interactions of domain walls and disorder. Such glassy aging is well known to be erased by small heating above the aging temperature [9]. Here we show that the aging

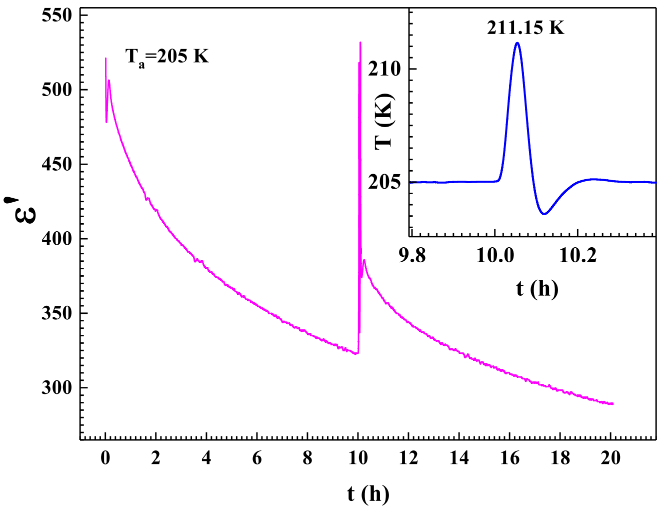

FIG. 12. Aging at 205 K interrupted by a temperature excursion to 211.15 K. As in these results, a significant portion of the aging from the first 10 h survived heating above T_C in similar trials, using maximum temperatures of up to 216.5 K. In each such trial, ε' itself showed that the sample was heated above the peak at T_C, serving as a direct local thermometer.

not only survives small heating, but it even partly survives heating above T_C, which would totally erase any domain-wall configuration effects.

Figure 12 shows aging similar to that of Fig. 6, but with a brief interruption after 10 h to a heated temperature of 211.15 K—just above T_C. Remarkably, this heating leaves the aging effect largely in place, indicating that something other than the domain walls themselves must carry the memory. This is a particularly strong piece of evidence pointing to the formation of H sheets stabilizing domain walls, since such sheets would only gradually diffuse away above T_C. The partial loss of memory probably indicates that when a new set of domains form, they only partially follow the pattern of the previous set, despite the preexisting H sheets.

The data shown thus far point to a relatively simple electric aftereffect picture of the aging, in which domain walls become decorated with diffusing H, forming potential wells. We now discuss more complicated results on rejuvenation, pointing to a competition between minimizing the free energy of the global domain-wall configuration—whose freezing gives the loss of susceptibility at the low-T edge of the plateau [3,5,6]-and minimizing the free energy of short-range interactions between the domain walls and disorder.

The simplest picture of H-rich sheets forming at domain walls predicts that the aging effects would persist under temperature changes, unless those changes caused the domain-wall positions to move (similar to field changes). Figure 13(a) shows the behavior of $\varepsilon'(T)$ upon further cooling and then heating of sample A after a 5-h aging pause at 205 K during the initial cooling. Under these conditions, there is substantial thermal rejuvenation, i.e., loss of the effects of aging, upon cooling a few kelvin below the aging temperature, similar to that found in KDP measured at low ac fields [6]. This loss is not recovered upon reheating to the aging temperature [6], which contrasts with the behavior of spin glasses [9] and some cubic

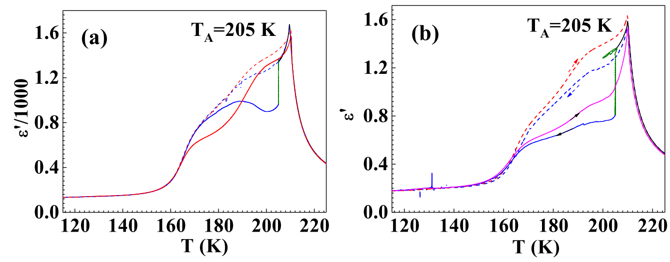

FIG. 13. (a) shows ε' on a temperature sweep of sample A with a 5-h pause for aging at 205 K during cooling, compared to a reference without a pause. The sweep rate is 4 K/min. The dashed lines represent the reference susceptibility obtained while cooling (blue) and heating (red) with no aging. (b) shows ε' on a T-sweep of sample B with a 20-h pause for aging at 205 K during cooling, compared to a reference without a pause. The sweep rate is 4 K/min. The smaller upward steps on cooling are real, not instrumental artifacts. Random-sign spikes at low temperature are from spikes in I_P, not actual changes in ε'.

relaxor ferroelectrics [17] showing holelike memory effects of past aging temperatures, similar to the memories of past fields shown in Figs. 8–10. Thus, for sample A, it appears that cooling irreversibly shifts the domain-wall positions, just as Mueller *et al.* had concluded from aging experiments on KDP [6].

Figure 13(b), in contrast, shows a similar experiment on sample B, which gives little or no thermal rejuvenation. Here, unlike previous reports on the smaller aging of KDP [6], most of the effect of aging persists throughout the plateau regime and remains upon reheating to the aging temperature and even above, as seen in the comparison of the after-aging curve with the no-aging reference curves. We suspect that such sample differences are connected with large-scale defects in the domain structure, as seen in the optical images. This result confirms a previous speculation of Mueller *et al.* [6] that detailed aging properties might turn out to be quite sample dependent.

The rejuvenation after a large-scale domain-wall reconfiguration can be seen particularly clearly when that rearrangement occurs in abrupt quakes. Direct measurement of the current generated by the capacitor, $I_P(t)$, almost always shows a remarkable noise effect during cooling, consisting of large random-sign current spikes. An example run showing such spikes is shown in Fig. 14. (These current spikes give

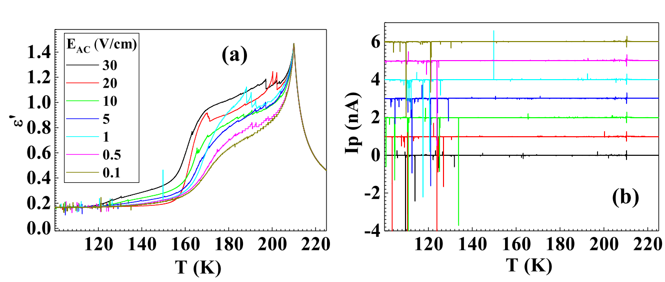

FIG. 14. (a) Steps in ε' and (b) spikes in I_P upon cooling at several different ac bias voltages. (Apparent random-sign spikes in ε' are artifacts produced by the spikes in I_P.)

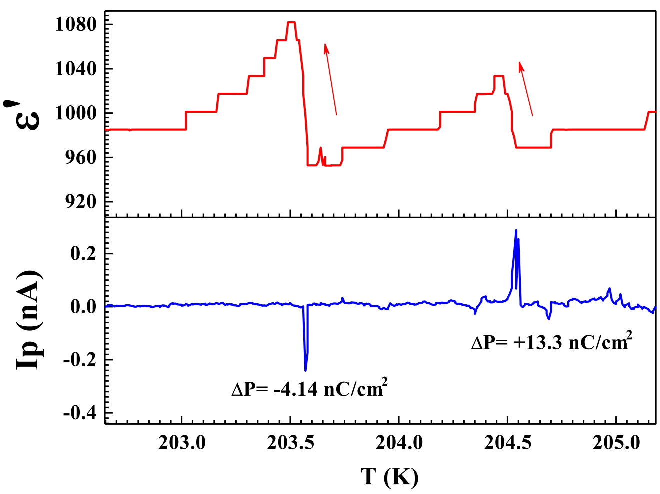

FIG. 15. Random-sign I_P spikes found on cooling are accompanied by upward steps in ε'.

random effects in the lock-in output used in the susceptibility measurements, accounting for the spikes in Fig. 1.) The change in polarization of the largest spikes exceeds 1% of the saturation polarization of the sample. Any such current spikes from polarization changes would have to be accompanied by domain-wall reconfiguration. If the aging consists of detailed local mutual adjustment of domain walls and disorder to maximize pinning, the domain walls involved in any current spike should rejuvenate. A detailed examination of the change in ε' during $I_P(t)$ spikes, as shown in Fig. 15, shows just such rejuvenation regardless of the sign of the spikes.

Figure 16 shows a warming run in the temperature range for which spikes had been densest during cooling. Very few spikes in $I_P(t)$ and no large steps in $\varepsilon'(t)$ are found. The contrast between the many quakes on cooling and the very few on warming was consistent on all runs. Although quakes were more evident in sample B than in sample A, they are not unique features of any particular sample. Similar ones appear in records on entirely different samples taken many years ago in our laboratory.

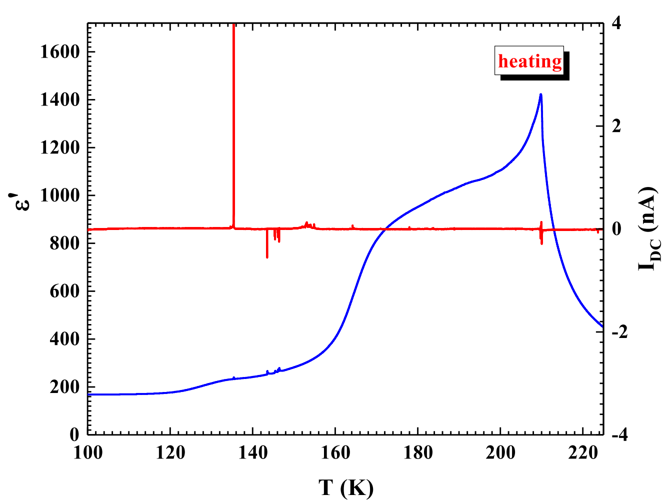

FIG. 16. A record of I_P, similar to that of Fig. 14, but taken during heating. ε' is shown for the same sweep with E_{ac}10 V/cm.

IV. DISCUSSION

The large aging in DKDP can be accounted for by a simple picture of H diffusion to the domain walls, creating free-energy wells. The ability of the system to retain memory of prior aging fields even after much larger field excursions is consistent with the main mechanism being the formation of H-rich sheets, and seems incompatible with a model of detailed domain-wall adjustment to fixed disorder. The persistence of memory even after heating to above T_C is dramatic evidence supporting the same conclusion, since such memory requires the formation of some pattern that persists even in the absence of ferroelectric domains. It also rules out domain-wall glass aging effects, although those remain a plausible mechanism for the smaller aging in KDP.

The key quantitative feature, the characteristic field scale for rejuvenation, is consistent with pictures of aging driven by local adjustments of the domain walls and the disorder. The polarization change for a ~200 V/cm field corresponds to ~0.2% of the saturation polarization, corresponding to domain-wall motion of ~0.1% of the domain-wall spacing. Based on the optical images, that would be ~5 nm displacement, which is comparable to the domain-wall thickness measured by x-ray methods [16].

For complex glassy systems, the characteristic field width of the memory holes is typically comparable to or much less than the thermal energy scale divided by the dipole moment of the individual constituents (e.g., spins) [14] or two-level systems in glassy dielectrics [15]. The field hole width here would imply a dipole moment of the glass constituents corresponding to the moment of a region with volume $\sim 10^{-18}$ cm^3, which seems far too small to be compatible with any sort of domain-glass aging effect in a material with visible domains whose smallest dimension is several microns.

The H-diffusion picture implies a characteristic time comparable to the time for H to diffuse a domain-wall width. The nonmonotonic dependence of the second-harmonic generation on voltage sweep rate gives a characteristic time in just the range expected given the known domain-wall thickness and approximately known diffusion rate. There is no particular reason to expect a time in this range for other aging pictures.

The noisy domain-quake effects shed light on the relation between short-range disorder and long-range interaction effects. Domain quakes occur almost exclusively upon cooling. As the strength of the cooperative domain-wall interaction term grows, walls jump from local minima to new global minima, restarting the process of developing local aging minima. The response of ε' to a quake thus represents rejuvenation of part of the sample. Upon warming, in contrast, the strength of the cooperative interaction terms weakens, so domain walls that are in some metastable global minimum remain in the same global minimum, developing deeper local minima without interruption. Our conclusion, based on stochastic quakes, that the domain walls readjust their configuration on cooling but stay nearly fixed upon heating is essentially the same as that reached by Mueller *et al.* [6] based on the difference between the average true linear $\varepsilon'(T)$ (measured at low ac voltage) taken on very slow cooling and heating.

The aging, rejuvenation, and noise effects also shed light on the physics of the dielectric freezing at the low-T edge of the plateau. Below ∼165 K, prior aging has very little effect on ε', although above ∼160 K there is still a large ε' associated with the plateau. Since after sufficient aging time the aging effect mostly retraces upon subsequent warming, the inhomogeneities in the H distribution remain below 165 K, even though they have little effect on ε' there. It seems that at low T, the interaction responsible for the strongly non-Arrhenius freezing is strong enough so that the domain-wall dynamics in that temperature range are nearly independent of the strength of the local pinning, at least within the substantial range of variation of local pinning strength caused by aging. Direct measurements of aging effects in the suspected domain-wall glass might be possible in the low-T edge of the plateau in plain KDP, where D diffusion effects are negligible.

ACKNOWLEDGMENTS

R.H. and S.F.C. were supported by Research Experiences for Undergraduate grants NSF PHY-13-59126 and PHY-16-59598, respectively. We thank Alexei Grinberg for technical help with the $2f$ measurements, and Michael Coumans, Minyang Tian, Arnulf Taylor, and Zongyuan Wang for help in doing aging experiments and data analysis on KDP.

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