Multiple Aging Mechanisms in Ferroelectric Deuterated Potassium Dihydrogen Phosphate

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ABSTRACT

The anomalously large dielectric aging in ferroelectric partially deuterated potassium dihydrogen phosphate (DKDP) is found to have multiple distinct mechanisms. Two components cause decreases in dielectric response over a limited range of fields around the aging field. A large fraction of this aging occurs on time scales of ~1000s after a field change, as expected for a hydrogen/deuterium diffusion mechanism. A slower component can give almost complete loss of domain-wall dielectric response at the aging field after weeks of aging. There is also a particularly unusual aging in which the dielectric response increases with time after rapid cooling.
**Introduction**

The high-dielectric response plateau regime of the ferroelectric (FE) phase of KH$_2$PO$_4$ (KDP)$^1$, and partially deuterated KD$_{2x}$H$_{2(1-x)}$PO$_4$ (D$_x$KDP)$^2$-$^3$, has large dielectric susceptibility arising from a dense array of 180° domain walls.$^3$-$^5$ D$_x$KDP has been reported to show surprisingly large reduction in this dielectric response while aging, e.g. $\sim$40% reduction in response over 22 hours aging slightly below the Curie temperature, $T_C$. $^6$ In contrast, KDP itself shows less than $\sim$2% aging slightly below $T_C$. $^6$-$^8$ The large aging effect in D$_x$KDP has been attributed primarily to diffusion of H to domain walls$^6$, since the increase of $T_C$ with $x$. $^9$-$^11$ suggests that in equilibrium in D$_x$KDP sheets of higher H and lower D concentration should accumulate at domain walls, which lack full FE order. On the other hand, a closely related ferroelectric, RbH$_2$PO$_4$ (RDP), also shows giant aging effects for which such diffusion mechanisms are not considered to be a major source,$^8$ raising the question of whether multiple types of major ageing effects are present in D$_x$KDP. In this paper we show that the simple model of H diffusing to domain walls can account for the properties of only one component of the aging effect, and that at least two other major aging effects are also present. (For a fuller discussion of the different types of aging expected in ferroelectric systems, along with more extensive background references, see ref. $^8$.)

Here we show that there are very long-time aging components that can remove most of the domain-wall response at the aging field even at temperatures just a little below $T_C$, at least as extreme as what has been seen in RDP.$^8$ We show that the long-time tail of the aging does not fit the kinetics expected for the simple diffusion mechanism, and that the
kinetics of aging and of forgetting the aging effects differ for the long-time tail but not for the initial fast effect. The aging effects are found to be particularly huge for intermediate values of x in approximately the range where an anomaly in the entropy loss on forming the ferroelectric state has been reported. Finally, we show that under some conditions there is a highly anomalous upward aging, in which the dielectric response increases as a function of aging time.

Optical images of the domain structure show that the large aging cannot result from simple domain growth leading to loss of net domain-wall area, since that domain growth is not large. Several key lines of evidence led to the conclusion that the large aging comes from changes in the underlying disorder that pins the domain walls, rather than just in domain walls gradually finding well-pinned states on fixed disorder. The most significant is that aging at a particular electric field leaves a persistent hole near that field in plots of susceptibility vs. field, i.e. reduced susceptibility only for fields near the aging field. Reduction of susceptibility by domain-wall pinning to fixed disorder would, in contrast, produce a hole that would not persist after field changes large enough to move the walls far from their old positions. Some such persistence is, however, expected for alterations in the disorder, which would not immediately dissipate after the domain walls moved.

Several lines of evidence indicate that H-D diffusion is a major mechanism for the change in underlying disorder. First, there is the obvious contrast between D₃KDP and KDP, which shows little aging, especially when the temperature is not close to the
putative domain-wall-glass regime in which the domain-wall response is lost at low T.\textsuperscript{4,7,12,13} Second, the aging in D\textsubscript{x}KDP exhibits a characteristic time on the order of 100s, seen both in the dependence of second-harmonic generation on field-sweep-rate and in re-aging of susceptibility after small quakes in the domain configuration.\textsuperscript{6} This time scale is about what is expected based on H-D mutual diffusion rates of \(\sim10^{-15}\) cm\(^2\)/s\textsuperscript{14} and the domain-wall width of \(\sim2.5\) nm\textsuperscript{15}.

One possible reason, not previously explored, for large aging effects to be found in a commercial D\textsubscript{x}KDP sample but not home-grown KDP samples would be that some sorts of disorder other than the H-D distribution might be present in the commercial material. In this paper we report initial aging results on home-grown samples with a range of x and report some key detailed data on two such samples, showing that key features are not unique to the commercial D\textsubscript{x}KDP material but occur for other samples with x > 0.2.

The simplest aging picture for D\textsubscript{x}KDP would involve homogeneous diffusion of H to replace D at domain walls, since these walls lack FE order. The strong dependence of T\textsubscript{C} on x\textsuperscript{2,9-11} implies that the free energy difference between FE and paraelectric phases is a decreasing function of x. A close analogy exists to known aging mechanisms in ferromagnets (e.g.\textsuperscript{16}) and other ferroelectrics (e.g.\textsuperscript{17}), in which point-like defects diffuse to domain walls. One can roughly estimate the magnitude of the attraction of H to the domain walls if one makes the rough approximation that the domain wall environment is similar to the PE state, since the dependence of T\textsubscript{C} on x is known (dT\textsubscript{C}/dx = -100K)\textsuperscript{2,9-11}, as is the latent heat of the first-order PE-FE transition\textsuperscript{2,18,19} over a wide range of x. E.g.
at x=0.8 the latent heat is about 317 J/mole\textsuperscript{18}. The approximate value of the free-energy reduction as a single H (out of the two per chemical unit) in an FE region exchanges location with a D from a PE region is then \(~1.3\times10^{-23}\) J. That energy is less than a tenth of the thermal energy, \(k_B T\) (where \(k_B\) is Boltzmann’s constant and \(T\) is temperature), in the temperature range of interest. Thus if we assume that the free energy change of an H-D exchange between an FE region and a domain wall is similar to that of an exchange between an FE region and a PE region, one would expect that the equilibrium formation of an H-rich sheet at the domain walls would nearly follow a linearized Boltzmann distribution, and that the kinetics would be well approximated by a simple linearized diffusion process. Most importantly for our current experiments, one would expect that if the domain walls were moved via an applied electric field, the sheet formed at the original domain wall position on aging at the original field would diffuse away following the same kinetics with which it formed. We shall see that this similarity of aging and forgetting kinetics only holds for part of the aging effect.

We shall also show that the extremely large aging occurs for only some values of \(x\), suggesting that it may be connected with the formation of some order in the H-D arrangement. In particular, the most anomalous aging is found for \(x\) in the same range for which a large unexplained anomaly in the entropy loss in the ferroelectric transition has been reported\textsuperscript{2}.

We shall describe another surprising effect: upward aging. After rapid cooling the dielectric response grows over time rather than reduces, in sharp contrast to aging effects.
in a wide variety of disordered materials. Optical images of the domain structure in the rapidly cooled material will lead to a tentative explanation of its source.

Finally we shall discuss possible implications of the aging effects for the principle question remaining for KDP and related ferroelectrics- the origin of the rather abrupt freezing transition by which domain walls lose their mobility at low temperature. 3, 4, 12, 21

**Materials and Methods**

Highly deuterated DKDP crystals were obtained from United Crystals. Other D$_x$KPD crystals were grown by us from water/heavy water solutions, by gradually reducing the solution temperature. We grew D$_x$KDP crystals by cooling KDP-DKDP solutions, prepared to be saturated at 80°C, starting from 90°C at 1K per hour with no seed. We checked the value of x using our measured T$_C$’s. We use $x=(T_C - 122K)/107$ K ±0.02 for a calibration curve, a consensus reached in several careful studies in which x of the crystal itself was measured independently, using several different techniques.9-11 Since the commercial crystals had T$_C$=211 K, they actually had x=0.83 ±0.02, despite their nominally higher specified x of 0.95. (The supplier confirmed that 0.83 is a plausible value.)
Samples were made into capacitors with the c-axis orthogonal to the contact surfaces by cutting with a diamond saw and lightly polishing. Contacts were made by depositing a thin layer of Cr (~10nm) followed by about 100nm of Ag via thermal evaporation. Sample thicknesses ranged from 0.7 mm to 1.2 mm, with contact areas of ~ 6.5 mm$^2$. Optical samples were polished using lapping discs with grit size down to 0.3 µm. Deposited electrodes for the optical samples were offset laterally ~1mm to allow unobstructed view of a region between the electrodes, so that for these samples the applied fields were not parallel to the c-axis. Digitized optical images of the domain structure, including movies taken after field changes, were obtained via polarized light microscopy using a Leica DM2700 microscope.

Our dielectric response measurements were made via a standard lock-in amplifier with applied ac voltage at 100Hz, along with adjustable dc voltage up to ±100 V in one set-up or ±400 V in another. The dielectric response of KDP and D$_3$KDP is highly non-linear even at low fields, due to weakly pinned domain walls. Since some of the interesting features of the response are most evident in the non-linear regime, most of our measurements were made with 1 V rms ac voltages, corresponding to ~10 V/cm ac fields. We did, however, run some checks of the aging at much lower ac fields, finding qualitatively similar results. For brevity we will refer to the dimensionless polarization/field ratio as $\varepsilon'$, although $\varepsilon'$ formally should only refer to the low-field limit of that ratio. We approximately removed a baseline due to background stray capacitance, measured by fitting $\varepsilon'$(T) well above $T_C$ to a Curie-Weiss law.
Several experimental protocols allowed separating the effects of aging at different fields. In one, after cooling at \( E=0 \) and then aging at a field of one sign the field was switched to opposite sign, in order to move the domain walls from the positions at which they had already had a chance to age. Then as the sample aged at the new field brief several-second excursions were made to the original field, to track how the response there forgot the effects of the prior aging. In a related protocol, after aging at an initial field the field was steadily swept over a range including the aging field, tracking both how the response at the initial field forgot its aging and how the response at a range of other fields aged. In a combined protocol, the sweeps were begun only after the measurements of multiple excursions back to the initial aging field.

In some protocols, we cooled the sample very rapidly (>10K/min), with the initial intent to follow a shorter time scale of initial aging. We found instead qualitatively different behavior, *upward* aging of the response, and tracked its time course after stopping cooling at several different temperatures in the plateau regime.

**Results**

Fig. 1 shows the in-phase and out-of-phase dielectric response for samples of two materials described in this paper. The results are very similar to those previously reported on materials of this sort, e.g. \(^{13}\).
Fig. 1. The in-phase and out-of phase response at 100 HZ with an applied ac voltage of 1V rms is shown as a function of temperature for a commercial sample with x=0.83 (panels (a) and (c) and a home-grown sample with x= 0.33 (panels(b) and (d)).

Fig. 2 shows two stills from a digital movie of the domain structure in a commercial taken at 193 K, after cooling through T_c at ~4K/min. Several important results are apparent. The domain structure consists of parallel sheets, as expected. These sheets are not, however, highly regular but show variations in thickness. As the sample ages the number of domain walls shows negligible decrease on the time scale of ~ 1 hour over which the susceptibility decreases by ~ 20%. In the movie, one can see that occasional localized rearrangements of the domain structure occur for several hours. These images,
clearer than the ones in our previous paper,\textsuperscript{6} confirm that simple domain growth is not a significant source of aging, but they do indicate that changes in domain configuration can continue for a long time.

Fig. 2 shows two stills from a digital movie of the domain structure in a commercial $x=0.83$ sample taken at 193 K, at about 1.5 min and 53 min after cooling through $T_C$ at $\sim$4K/min.
Our previous results\textsuperscript{6} described aging of the effective susceptibility taken with 1V rms ac voltages, giving ac fields of roughly 10V/cm rms. Since the non-linear susceptibility and the linear susceptibility can show qualitatively different behavior\textsuperscript{13}, we checked whether the aging of the linear susceptibility measured at very small ac fields resembled that measured at large fields. As shown in Fig. 3, it was qualitatively similar but not quantitatively identical. Thus most of our aging results, taken at larger fields, should be taken to give only the qualitative behavior of the linear response.

Fig. 3 shows aging taken at small ac fields. The lowest ac field is within the range of almost completely linear response.\textsuperscript{13}
In order to check the functional form of the loss of susceptibility we measured the aging over very long times. Fig. 4 shows very long-time aging of $\varepsilon'$ taken at $T=200\text{K}$ over 11 days for a sample of the commercial D$_x$KDP. Similar results, with an even more prominent long-time tail of the decay, were found on a 15.8 day run using a dry-ice bath at $\sim195\text{K}$ rather than a cryostat, although with some glitches at points where the dry-ice was re-filled. The long-time tail of the aging was surprisingly large, with $\varepsilon'$ dropping to $\sim13\%$ of the initial value after 11 days.

![Graph showing aging of ε’(t) for a commercial x=0.83 sample, 0.87 mm thick at 200K.](image)

Fig. 4. $\varepsilon'(t)$ is shown for a commercial x=0.83 sample, 0.87 mm thick, at 200K.

Occasional glitches in $T$ show up as transient changes in $\varepsilon'(t)$. 
A simple linearized diffusion model in which H accumulates at a Gaussian-shaped potential at domain walls gives an excess binding free energy of the wall that is proportional to \(1 - \left(1 + \frac{t}{\tau}\right)^{-1/2}\), where \(t\) is the elapsed time since the H distribution was uniform and \(\tau\) is a characteristic diffusion time, roughly the square of the domain wall width divided by the diffusion constant. The \(t^{-1/2}\) tail of this form is insensitive to the shape assumed for the domain wall potential, simply reflecting the form of the diffusion process in one-dimension. In the simplest model the linear susceptibility would fall off inversely with the curvature of the pinning potential. The H-binding contribution to the curvature would increase as \(\left(1 - \left(1 + \frac{t}{\tau}\right)^{-3/2}\right)\). The actual form of the curve does not come close to fitting a \(t^{-3/2}\) tail.

If one assumes instead a model in which the reduction of the non-linear susceptibility due to the increase in pinning potential is proportional to the increased pinning potential rather than to its curvature, one obtains a \(t^{-1/2}\) tail:

\[
\text{Eq. (1)} \quad \varepsilon(t) = \varepsilon(\infty) + \left(\varepsilon(0) - \varepsilon(\infty)\right)\left(1 + \frac{t}{\tau}\right)^{-1/2}.
\]
This form can fit the long-time tail for \( t > 5 \) hr, but only by using \( \tau \approx 30,000 \) s and thus missing most of the initial decay, as shown in Fig. 5.

Fig. 5. shows the fitting of the long-time tail of the aging shown in Fig. 4 to Eq. 1.

The inset shows the initial decay, faster than that given by the fitting form.

A similar form with the diffusion exponent \( 1/2 \) replaced with a best-fit exponent \( p = 0.32 \pm 0.02 \) does an even better job of fitting the long-time aging tail, but at the expense of
implying a negative final value for $\varepsilon'$. Although this fit produces negligible residuals in the tail, it still misses most of the decay in the first hour.

We have found no reasonable simple functional form that will fit both the long-time tail and the fast initial decay, with the residuals always indicating an extra initial fast component. We shall see via more complicated experimental protocols that the initial component is qualitatively different from the slower part, with only the initial decay showing the reversibility expected for the H diffusion effect.

Since the large aging involves changes in the underlying pinning potential, not just in the domain configuration $^6$, it is important to check that it is not a special feature of possible defects in one brand of commercial crystal. In our home-grown samples, we found large aging in all samples with $x > 0.2$ but not in samples with smaller $x$. The aging was particularly huge for samples with $x = 0.3-0.5$, as illustrated in Fig. 6.
Fig. 6 Aging of $\varepsilon'$ is shown for a commercial $x=0.83$ sample with thickness 0.60 mm (1) and a home-grown $x=0.33$ sample (2) with thickness 1.22 mm at temperatures of 0.92 $T_c$ and 0.9 $T_c$ respectively. Each sample was cooled in zero field to the aging temperature and then the dc field of about 350V/cm was applied. $\varepsilon'(0)$ here refers to the value before the field change.

All these aging effects change $\varepsilon'$ only over a range of E around the aging field. Fig. 7 shows very broad field sweeps taken immediately after aging a commercial sample for 1
hour at 200 K. At fields ~ 3000 V/cm away from the aging field, the effects on $\varepsilon'$ become small. The shift in hole position toward more negative fields after a positive field excursions is a hysteretic effect found in all the sweep data. Qualitatively similar behavior was found in a sample with $x=0.46$ at $T=155$ K, but with the width of the hole reduced by about a factor of four.

![Graph of $\varepsilon'$ vs. $E$](image)

**Fig. 7.** $\varepsilon'$ vs. $E$ taken at 200K after aging a commercial sample at $E=0$ for 1 hour.

The sweep rate was $\sim 3$ V/cm-s.
Since the long-time tail of the aging kinetics appears incompatible with a simple H-D diffusion model, supporting the likelihood of multiple aging mechanisms, we looked for other possible difference in the kinetics or field dependence of the short-time and long-time components. We ran a series of experiments to check not only the kinetics of the initial aging but also the kinetics with which it was forgotten when the field was changed.

To check the time evolution of ε’ (E,t) over a range of E, we used continuous field sweeps over ±1140 V/cm after initial aging for 11 days at 200K and E=0 V/cm. The sweeping took place over the course of 15 hours with each individual scan taking ~62 minutes. A representative sampling of the field-increasing part of the scans is shown in Fig. 8, with early time scans sampled more densely to exhibit the more rapid short time behavior. During the continuous sweep ε’ continues to decrease for fields out in the wings of the initial hole, even as it increases near the original aging field, i.e. forgets the aging effects.
Fig. 8 shows a sampling of the scans following the 11 day aging experiment at $T=200$ K. Here each scan took 6 minutes.

Figure 9 illustrates that time dependence of $\varepsilon'$ in the hole, partway up the wings, and at the edge of the sweep range.
Fig 9 shows the $\varepsilon'(t)$ during the sweeps is shown at the minimum value, at 420 V/cm, and at 1150 V/cm.

The field-decreasing sweeps are similar to the ones shown in Fig. 8, but with the $\varepsilon'$ (E) holes shifted to negative E rather than positive E. That hysteresis, in which the minimum $\varepsilon'$ occurs shortly after E passes through the $E_{\text{aging}}$, is found consistently. The effect is much larger than would be produced by the lock-in response time and thus reflects the physics of the domain wall pinning. The hysteresis is expected, if the domain
wall positions are not unique functions of E, but lag behind their equilibrium positions due to partial pinning by disorder.\textsuperscript{8}

The general conclusion from the sweep experiments is that the initial aging hole is lost during the field sweeps, while an additional much less sharply field-dependent aging forms. These results point toward the formation of reduced $\varepsilon'$ around any E at which the sample is found, whether sitting at a fixed value or being swept.

One conclusion emerges directly from the sweep data. The results seem incompatible with a simple model in which the domain walls are modeled as rigid objects described by a one-dimensional position, with uniform response to electric fields, with aging simple due to a potential well from H accumulation at the wall position. In such a model, a field application sufficient to move the walls by several wall thicknesses would pull the walls out of the wells and eliminate the aging effects. The tails of the hole extend somewhat beyond 1000 V/cm from the aging field for the x=0.83 samples. The polarization change for a ~1000 V/cm field corresponds to ~1% of the saturation polarization, corresponding to domain wall motion of ~0.5% of the domain-wall spacing. Based on the optical images, that would be ~20 nm displacement, which is more than four times the domain-wall thickness measured by X-ray methods.\textsuperscript{15} A picture of simple potential wells for a 1-D position fails in another even more basic regard. The effect would depend on the second derivative of the potential, which would have an integral of zero over the large sweep range. The aging effect does not come close to integrating to zero over this range, since there are at most very small positive tails to the negative hole. Together with the
prominent hysteretic effect on the position of the minimum in $\varepsilon'$, these results point toward a model in which flexible domain walls develop some strongly pinned regions $^7,8$ allowing partial memory of the aging to persist for larger field excursions.

Judging the kinetics by which the aging at the initial field is lost is complicated in sweep experiments by the new aging at fields in the sweep range, which includes the initial field. To simplify the interpretation of the forgetting kinetics, we aged the sample at one field, then switched to another. Brief excursions (9s each) back to the original field then allowed tracking the kinetics with which the aging effects at that original field were forgotten, complicated only by the superposition of aging effects at a single distinct new field.

In the experiment illustrated in Fig. 10, we aged a commercial sample at $E= -2174\text{V/cm}$ for 21 hours at $T=202\text{K}$, then switched the field to $E= +2174\text{V/cm}$. Fig. 10 shows $\varepsilon'$ (t) at both the new field and the original one. Qualitatively similar behavior was found after
shorter initial aging times and also on an $x=0.46$ sample.

Fig. 10 shows the aging at the new voltage (300V) and the recovery from the initial 21-hour aging at the original voltage (-300V) as a function of time.

The aging at the new field shows no new features, but the forgetting kinetics at the old field are revealing. In the first hour after the field switch, $\varepsilon'$ at the original field increases by approximately the same amount that $\varepsilon'$ at the new field decreases. This fast component of the effect is this reversible, as would be expected for simple linear diffusion kinetics. Over the next 80 hours, however, $\varepsilon'$ at the original field barely
increases at all, while $\varepsilon'$ at the new field decreases by more than a factor of two. $\varepsilon'$ at the original field does not return to its initial pre-aged value. The new field is so far from the old field that the tail of the aging hole at the new field cannot account for any significant fraction of that discrepancy. Thus the long-time aging does not show the reversibility of the short-time aging, a qualitative distinction.

In some protocols the samples were cooled rapidly (>10K/min) through $T_c$ to the target temperature. As shown in Fig. 11 for target temperatures in the range 170K to 195K for a commercial sample $\varepsilon'$ increased initially after reaching the target temperature. At lower or higher temperatures the effect was not noticeable. From the time course of the upward aging at intermediate temperatures, it is clear that it has a strongly $T$-dependent rate. Above the range where upward aging is evident, it simply seems to be too fast to see, and below that range it is too slow to see. $\varepsilon'(t)$ after the temperature stabilized could be fit fairly well with the sum of a rising exponential and a falling exponential, without too much uncertainty in the characteristic times of the rising time constant. The rise-times show an Arrhenius-like temperature dependence, with an attempt rate on the order of roughly $10^{15}$ Hz, although with uncertainty due to not knowing a proper functional form for the downward aging background.
Fig. 11. Aging behavior at a range of temperatures of a commercial x=0.83 sample after rapid cooling, exhibiting upward aging on strongly T-dependent times. The initial oscillations for times under 0.5 hr are caused by temperature oscillations.

The domain images taken after rapid cooling show many patches of domain sheets rotated 90° from each other, i.e. some along the a-axis and some along the b-axis, as seen in Fig. 12. Unlike the ordinary downward aging, the upward aging involves the annealing of these patchy domains.
Fig. 12. A patchy domain pattern formed after rapid cooling (~30K/min) of a commercial sample through the transition to roughly 130 K.

Discussion

Perhaps the least expected result here is the upward aging found after fast cooling. Its mechanism appears not to be closely related to the other effects. This patchwork domain structure appears to reduce the domain-wall dielectric response, compared to that obtained from large parallel sheets. Initial annealing after quick cooling is dominated by the growth of the parallel-sheet structure. This novel upward aging appears to have little connection with the other aging mechanisms.
The most striking feature of the downward aging is that over periods of many days at temperatures a little below $T_C$ the dielectric response falls to almost to the same level as found in the low temperature regime with frozen domain walls. RBD may show about as large an effect, although it has not been followed for quite as long. Although there have been several ideas for why the domain-wall response is lost at the low-$T$ end of the plateau region, none would imply that a similar loss of response would occur over time at a much higher temperature. The magnitude of this aging varies substantially between materials with different compositions, although not between different samples taken from a single preparation. The most anomalous results were found for with $0.3 < x < 0.5$.

This downward aging consists of at least two components. Both components give holes in the $\varepsilon'$ vs. $E$ plots, with the hole centered near the aging field. That result confirms that modification in the underlying pinning potential is required, not just adjustment of domain walls to a fixed potential.

One major component of downward aging remains consistent with an H-D diffusion effect giving an enhancement of $H$ along the domain walls. This component of the hole in $\varepsilon'(E)$ mostly forms on times shorter than $\sim 1$ hr and then is forgotten on a roughly similar time scale after the field is changed.
A second component of the downward aging also gives a hole in $\varepsilon'(E)$, but with time scales of formation extending out to many days. Unlike the first component, however, the forgetting kinetics and the aging kinetics for this component are not similar. Some of the long-time aging does not recover at all on the time scale of our experiments. An effect of this sort could be expected for defect rearrangements that involve both large activation barriers and large free-energy differences between the aged state and the initial state. That combination can lead to relatively fast forward kinetics but slow reverse kinetics.

Understanding of the aging mechanisms is far from complete. The presence of deuterium seems to be essential for these large downward aging effects close to $T_C$ in D$_x$KDP, although obviously not in RDP$^8$. A simple model of sheets of domain-wall attracting H–rich regions forming fits only the faster downward aging components. The other component appears to require local modifications of disorder in ways that create strong binding sites for domain walls.

Aging at any field value lowers subsequent response at that field regardless of aging at other fields. Such an effect cannot be modeled by a simple domain-wall binding potential as a function of a one-dimensional variable representing domain-wall position. Obviously, one cannot simultaneously have holes in the potential as a function of position at all positions in such a model. The results point toward a different type of model, in which strong binding sites gradually form within each domain wall.

The detailed microscopic nature of those binding sites is beyond the scope of this paper.
Deuterium appears to play a key role even in the long-time aging in this material. Perhaps the most intriguing result is that for x of about 0.35 to 0.5, the aging is extremely large, even compared to the commercial x=−0.83 material. A very prominent anomaly in the entropy loss on forming the FE phase (including both the latent heat and some component from the heat capacity) has been reported at about the same x. That raises the possibility that the domain walls are binding to distinct H-D ordered patterns that form for some x in the FE state.

The binding of the domain walls to disorder grows very substantially on aging just below $T_C$ in partially deuterated material. Yet the temperature at which the domain walls freeze (the bottom of the plateau) is very weakly sensitive to that aging. That supports the picture of the domain-wall freezing as a sort of collective glassy crossover, in which the temperature scale is set by the stiffness of the domain walls and the interaction potential between them more than by the strength of the pinning potential.

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