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Domain-wall dynamics coupled to proton motion in a hydrogen-bonded organic ferroelectric

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Ferroelectric domain-wall motions associated with local proton rearrangement and collective proton relay have been revealed in hydrogen-bonded organic ferroelectrics, Phz-H_2ca [phenazine (Phz)-chloranilic-acid (H_2ca)], through dielectric measurements and piezoresponse force microscopy. The domain wall (DW) and thus protons therein are found to be so mobile as to migrate spontaneously, and this feature can be accounted for by the characteristic proton dynamics emergent in this material. Our findings indicate that incomplete proton transfer is a key to a mobile ferroelectric DW in hydrogen-bonded ferroelectrics.

Proton transport plays a major role in protonic conductors as fuel cells[1–3] and the transport of energy and charge in bioenergetics,[4] and it has been thus an important subject in condensed-matter physics and also in biochemistry. Hydrogen-bonded systems, such as ice,[5] imidazole,[6] and protein,[7] exhibit a considerable dc electrical conductivity due to proton transport, and soliton models incorporating kink-antikink asymmetry have often been used to describe the proton dynamics.[8] Proton dynamics also plays a key role in hydrogen-bonded ferroelectrics, in which not dc electrical conductivity but ac or transient electrical transport can occur. By applying electric fields, ferroelectric domain-wall (DW) motion is induced, which is accompanied inherently by local but collective rearrangement of the proton position.

For the investigation of such proton dynamics in hydrogen-bonded ferroelectrics, the model system has been KH_2PO_4 (better known as KDP).[9] In reality, however, the proton transfer in KDP occurs along a direction that is almost perpendicular to spontaneous polarization, and therefore the coupling between ferroelectric DW motion and proton transfer is not straightforward.[10–13] Recently, the arena of hydrogen-bonded ferroelectrics has opened up, that is, organic ferroelectrics.[14–16] In this Rapid Communication, we present the ferroelectric DW motions induced by collective proton transfer in one of the hydrogen-bonded organic ferroelectrics, Phz-H_2ca [co-crystal of phenazine (Phz) and chloranilic acid (H_2ca)],[17] in which the relation between proton displacement and polarization direction is straightforward. Through dielectric and real-space piezoresponse force microscope (PFM) measurements,[18] a variety of DW motions associated with proton rearrangement are identified without ambiguity: relaxation behavior and depinned creep behavior under ac electric fields, dielectric aging under zero dc electric field, and its rejuvenation by applications of strong ac electric fields. The mobile nature of a ferroelectric DW and thus the protons around it is understood from the viewpoint of characteristic proton dynamics emergent in the ferroelectric phase.

The schematic crystal structure of Phz-H_2ca (the space group being nonpolar $P2_1/n$ at room temperature) is shown in Figs. 1(a)–1(c).[17] The intermolecular hydrogen bonds (O−H···N), which play an essential role in the emergence of the ferroelectric phase, run along [110] in the $c = 0$ plane and along [$\bar{1}10$] in the $c = \frac{1}{2}$ plane, and they are crystallographically equivalent [Figs. 1(b) and 1(c)]. Upon the ferroelectric transition at T_c (∼253 K), a proton at one side of H_2ca shifts slightly toward the N atom of Phz but still stays chemically bonded to H_2ca even in the ferroelectric phase,[19] instead of the conventional site-to-site proton transfer between O and N atoms, while a proton on the other side remains strongly bonded to H_2ca. The proton displacement leads to local polarization along the hydrogen-displacement direction in each plane,[20] and the total macroscopic polarization P shows up along the b axis. As a result, the space group reduces to polar $P2_1$.[17] Note that between the $P\|+b$ and $P\|-b$ domains the proton showing displacement is on the opposite side in H_2ca: Therefore, ferroelectric DW motion is necessarily accompanied by proton motion, i.e., rearrangement of the proton position. The deuterated analog of Phz-H_2ca exhibits much higher T_c (∼304 K), further corroborating the significant role of the hydrogen bond in the present ferroelectricity.[21]

To investigate the proton dynamics coupled with DW motion in Phz-H_2ca, a complex dielectric constant $\epsilon^* = \epsilon_1 - i\epsilon_2$ was measured along the polarization axis (the b axis) in a wide frequency range from 30 mHz to 2 MHz, using an *LCR* meter (Agilent E4980A) and an impedance analyzer (Solartron 1260 with 1296 dielectric interfaces). The PFM measurements were done with a commercially available scanning probe microscope (Asylum MFP-3D).

The temperature dependence of the dielectric response is shown in Fig. 1(d). A relatively large λ-shaped ϵ_1 peak is present, together with prominent dielectric dispersion below T_c (∼253 K). Note that the data were collected without dc electric fields E_{dc}, and hence the ferroelectric phase should be a multidomain state containing dielectric contributions from the DW motions. To identify the DW contributions, we measured ϵ_1 with the use of a dc bias (E_{dc}) of 170 V/cm, which will promote the formation of the monodomain state; the magnitude and dielectric dispersion both are found to be suppressed [Fig. 1(e)]. These features show evidence that ϵ_1 with a pronounced dielectric dispersion is attributed to the
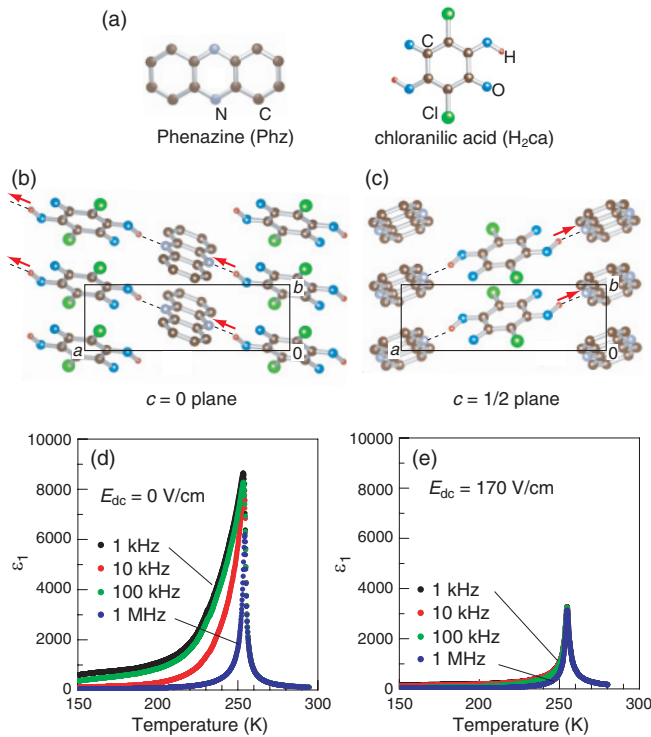
FIG. 1. (Color online) (a) Schematic illustrations of phenazine (Phz) and chloranilic acid (H_2ca) molecules. (b) and (c) Crystal structures of Phz-H_2ca projected in the $c = 0$ plane (b) and $c = \frac{1}{2}$ plane (c). Among hydrogen atoms, only hydrogen-bond-related ones are illustrated in (a)–(c). The arrows indicate the direction of proton displacement for the case of $P\|+b$. (d) and (e) Temperature dependence of dielectric constant under a zero dc electric field (d) and under a dc-electric-field bias of 170 V/cm. The data were obtained with an ac electric field of 14 V_{rms}/cm. The measurement frequency is from 1 kHz (the top curve) to 1 MHz (the bottom curve).
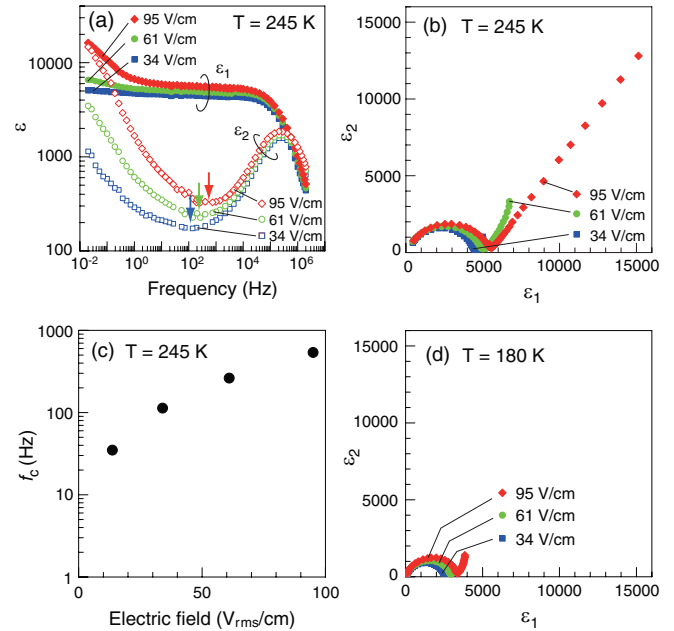

FIG. 2. (Color online) (a) Frequency dependence of complex dielectric constants, $\epsilon^* = \epsilon_1 - i\epsilon_2$, measured at 245 K with various magnitudes of ac electric fields. Solid and open symbols represent ϵ_1 and ϵ_2, respectively. Arrows indicate local ϵ_2 minima, which we define as the dynamical transition frequency f_c between the relaxation and creep regimes (see the text). (b) Cole-Cole representation of the data shown in (a). (c) ac-electric-field dependence of f_c, below which the creep regime sets in. (d) Cole-Cole representation of the dielectric spectra at 180 K.

DW motions, namely, the rearrangement of protons. In this context, the frequency-dependent nature below T_c can be readily understood as follows: At low frequencies (e.g., at 1 kHz) DW motion accompanying proton rearrangement can follow the oscillating external electric fields E_{ac} and thus can contribute to ϵ^*, while at high frequencies (e.g., 1 MHz) the DWs cannot follow E_{ac} and thus become silent. In fact, ϵ_1 at 1 MHz under 170 V/cm [Fig. 1(d)] is nearly the same as that under zero electric field [Fig. 1(e)] except for the immediate vicinity of T_c. This indicates little dielectric contribution from the DW motion at 1 MHz. In the paraelectric phase, where the ferroelectric DWs are absent, ϵ_1 is reasonably frequency independent in the present frequency window (10^3–10^6 Hz).

As suggested by recent experiments[22] and theories,[23,24] DW motions induced by an ac driving force may exhibit various kinds of kinetics depending on the driving force magnitudes, frequencies, and temperatures. To get further insight into the DW motion involved, we looked into the dielectric spectra, i.e., the frequency dependence of ϵ_1 and ϵ_2. Figure 2 shows a typical dielectric spectra below T_c measured with various magnitudes of E_{ac}. For clarity, we refer to the dielectric spectra at 95 V_{rms}/cm, in which two characteristic frequencies are clearly visible: (i) Around 300 kHz, ϵ_1 exhibits a marked change together with the ϵ_2 peak and (ii) below ~500 Hz ϵ_2

shows a significant increase with lowering frequency. These two dynamical regimes become more evident by adopting the Cole-Cole representation,[25] as shown in Fig. 2(b), where the dielectric spectra reduce to a flattened semicircle and an inclined straight line. The present Cole-Cole profile can be well accounted for by the recently proposed universal scheme of DW dynamics.[26] The flattened semicircular part is the "relaxation" regime and points to the polydispersive response of DW segments that are shorter than the Larkin pinning length, which is the shortest length scale of the weakly pinned DW.[27] In the relaxation regime, each DW segment oscillates locally without net DW displacement.[28] The linear part in Fig. 2(b) is the "creep" regime, which refers to a thermally assisted field-driven motion of DW. From the viewpoint of proton dynamics, the relaxation motion corresponds to a local rearrangement of protons, while the creep motion corresponds to a cooperative, sequential displacement of the proton on a mesoscopic length scale, i.e., proton relay. At low temperatures (e.g., at 180 K), the same Cole-Cole profile with a reduced magnitude is observed [Fig. 2(d)], reflecting the diminished dielectric dispersion in Fig. 1(d).

Our dielectric spectroscopy unveils the dynamical phase transition between the relaxation and creep regimes as a function of driving frequency, consistent with what was theoretically predicted by Nattermann *et al.*[23] The critical frequency of dynamical transition f_c can be estimated from the intersection point between the linear and semicircular parts in the Cole-Cole plots or, equivalently, from the local minimum

of the ϵ_2 dielectric spectra. Insights obtained from a set of dielectric spectra under various E_{ac} state that the f_c depends on the amplitude of E_{ac} [see the arrows in Fig. 2(a)]: Larger E_{ac} results in higher f_c, as shown in Fig. 2(c). This tendency can be interpreted in terms of the E_{ac}-dependent pinning barrier, as described in the following. Given that the required time t_c for DWs (or, equivalently, protons) to jump over the pinning barrier Δ is described by $t_c \sim \exp\{\Delta(E_{ac})/k_B T\}$, the creep motion cannot set in for high frequencies such that $f t_c > 1$. Hence, f_c separating between local relaxation and mesoscopic creep regimes is given as[23,29]

$$f_c \sim \exp\{-\Delta(E_{ac})/k_B T\}, \qquad (1)$$

which correlates the E_{ac} dependence of f_c with that of Δ. In the case of Phz-H$_2$ca, the extrapolation of f_c in Fig. 2(c) suggests that f_c may not be vanishingly small but finite in the limit of infinitesimal E_{ac}. If this is the case, Δ will remain finite under a zero electric field as well and hence DW migrations toward a more stable state may occur via thermal activation.

To see the temporally changing DW configuration, the real-space observation, e.g., via PFM measurements,[18] would be informative. Because of the crystal habit of Phz-H$_2$ca, only the in-plane PFM measurements on the as-grown bc plane are feasible, where the polarization ($\|b$) lies in the plane. The typical surface topography and PFM phase images are shown in Fig. 3(a) and Figs. 3(b) and 3(c), respectively. Two kinds of color contrasts in the phase images point to an electric polarization P that is either parallel or antiparallel to the b axis. The consecutive phase images with a 113-min time interval [Figs. 3(b) and 3(c)] clearly demonstrate that the DW configuration evolves with time even without dc electric fields, in accord with the inference from our dielectric data. Through such spontaneous DW migration, relatively small domains present in Fig. 3(b) are found to eventually merge and then form winding, stringlike domain patterns, which are roughly parallel to the polarization axis [Fig. 3(c)].

Observed time evolutions of the PFM image may suggest the time-dependent nature of the dielectric properties as well. To confirm this, we investigated the time evolution of ϵ_1 at 250 K. The data were recorded at 100 kHz (i.e., deep in the relaxation regime) after the temperature was stabilized (± 20 mK) at the target temperature. As shown in Fig. 4, a temporal decay of ϵ_1 (i.e., dielectric aging) is observed as

FIG. 4. Time evolution of dielectric constant at 250 K. The measurement of ϵ_1 was done with E_{ac} of 14 V_{rms}/cm at 100 kHz. During the experiment, we applied a 10-Hz ac electric field of 580 V_{rms}/cm at this temperature at arbitrary intervals (indicated by arrows in the figure), which is larger than the coercive field.

expected. A remarkable finding here is that by the application of E_{ac} higher than the coercive field (indicated by arrows in Fig. 4) the aged dielectric response retrieves high ϵ_1 (hereafter we call this behavior *rejuvenation*) and then the aging follows again. Having established that the dielectric responses reflect the DW motion, the dielectric aging and rejuvenation should be associated with a change in the DW mobility and/or the DW density. Although it is difficult to draw a definite conclusion because of a lack of information about the DW configuration in the bulk, we can postulate from the PFM results and E_{ac} dependence of f_c that the DWs themselves could seek for a more stable configuration by means of spontaneous migrations. With this assumption, it is concluded that the DWs are getting trapped by a built-in potential landscape during the aging and, consequently, the DW mobility becomes diminished. This scenario is somewhat different from the prevailing mechanism of dielectric aging, where mobile charged defects and/or rotatable defect dipoles stabilize the preexisting domain pattern, which is supposed to be static.[30–32] The application of strong E_{ac}, on the other hand, presumably releases the DWs from the well-trapped configurations, leaving relatively free DWs; thus the rejuvenation, i.e., recovery of a large dielectric response, is achieved.[33]

Why are such highly mobile and even spontaneously migrating DWs realized in this material? We may trace the possible origin to the characteristic proton dynamics that is emergent in the ferroelectric phase. Previous neutron diffraction studies revealed that a proton of H$_2$ca is not transferred completely to the N atom of Phz but is still located near the center of the N and O atoms, with a significantly elongated thermal ellipsoid.[19] Such a "partial proton transfer" is an aspect not seen in the other hydrogen-bonded ferroelectrics, suggesting that protons are confined not in a well-defined double-minima potential but rather in a single-minimum-like potential. From a viewpoint of the fluctuation-dissipation theorem, intensive fluctuations in proton locations should correspond to a high sensitivity to external perturbations, reasonably endowing the ferroelectric DW accompanied by proton rearrangement with a mobile nature.

To summarize, we have carried out dielectric and PFM measurements on the hydrogen-bonded organic ferroelectrics
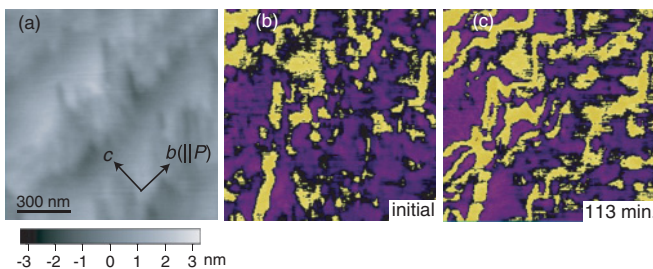

FIG. 3. (Color online) Surface topography (a) and unprocessed, as-measured PFM phase images [(b) and (c)] of the bc plane measured at 250 K. The two phase images were taken in the same area with a time interval of 113 min. The different color contrast in the phase images represents the different polarization direction, which is either parallel or antiparallel to the b axis.
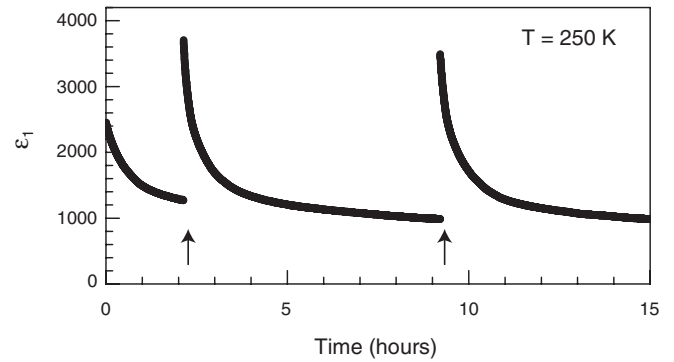
Phz-H$_2$ca and identified a variety of DW motions, such as relaxation (local proton rearrangement), creep (collective proton relay), aging, and rejuvenation. The DW is found to be quite mobile, and this is ascribed to the intensive proton fluctuations inherent in the ferroelectric phase of this material. Our results demonstrate that partial proton transfer can host mobile ferroelectric DWs in hydrogen-bonded ferroelectrics.

[1] A. I. Baranov, L. A. Shuvalov, and N. M. Shchagina, Pis'ma Zh. Eksp. Teor. Fiz. **36**, 381 (1982) [JETP Lett. **36**, 459 (1982)].

[2] S. M. Haile, D. A. Boysen, C. R. I. Chisholm, and R. B. Merle, Nature (London) **410**, 910 (2001).

[3] M. Sadakiyo, T. Yamada, and H. Kitagawa, J. Am. Chem. Soc. **131**, 9906 (2009).

[4] A. C. Scott, Phys. Rep. **217**, 1 (1992).

[5] P. V. Hobbs, *Ice Physics* (Clarendon, Oxford, UK, 1974).

[6] A. Kawada, A. R. McGhie, and M. M. Labes, J. Chem. Phys. **52**, 3121 (1970).

[7] J. F. Nagle, M. Mille, and H. J. Morowitz, J. Chem. Phys. **72**, 3959 (1980).

[8] A. V. Savin and A. V. Zolotaryuk, Phys. Rev. A **44**, 8167 (1991).

[9] M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Oxford University Press, New York, 1977).

[10] E. Nakamura and K. Kuramoto, J. Phys. Soc. Jpn. **57**, 2182 (1988).

[11] B.-G. Kim and J.-J. Kim, Phys. Rev. B **59**, 13509 (1999).

[12] V. Mueller, Y. Shchur, H. Beige, A. Fuith, and S. Stepanow, Europhys. Lett. B **57**, 107 (2002).

[13] V. Mueller, Y. Shchur, H. Beige, S. Mattauch, J. Glinnemann, and G. Heger, Phys. Rev. B **65**, 134102 (2002).

[14] S. Horiuchi, Y. Tokunaga, G. Giovannetti, S. Picozzi, H. Itoh, R. Shimano, R. Kumai, and Y. Tokura, Nature (London) **463**, 789 (2010).

[15] S. Horiuchi and Y. Tokura, Nat. Mater. **7**, 357 (2008).

[16] S. Horiuchi, R. Kumai, and Y. Tokura, Adv. Mater. **23**, 2098 (2011).

[17] S. Horiuchi, F. Ishii, R. Kumai, Y. Okimoto, H. Tachibana, N. Nagaosa, and Y. Tokura, Nat. Mater. **4**, 163 (2005).

[18] S. V. Kalinin, A. N. Morozovska, L. Q. Chen, and B. J. Rodriguez, Rep. Prog. Phys. **73**, 056502 (2010).

[19] R. Kumai, S. Horiuchi, H. Sagayama, T. Arima, M. Watanabe, Y. Noda, and Y. Tokura, J. Am. Chem. Soc. **129**, 12920 (2007).

[20] F. Ishii, N. Nagaosa, Y. Tokura, and K. Terakura, Phys. Rev. B **73**, 212105 (2006).

[21] S. Horiuchi, R. Kumai, and Y. Tokura, J. Am. Chem. Soc. **137**, 5010 (2005).

[22] Th. Braun, W. Kleemann, J. Dec, and P. A. Thomas, Phys. Rev. Lett. **94**, 117601 (2005).

[23] T. Nattermann, V. Pokrovsky, and V. M. Vinokur, Phys. Rev. Lett. **87**, 197005 (2001).

[24] A. Glatz, T. Nattermann, and V. Pokrovsky, Phys. Rev. Lett. **90**, 047201 (2003).

[25] AK. Jonscher, *Dielectric Relaxation in Solids* (Chelsea Dielectrics, London, 1983).

[26] W. Kleemann, Annu. Rev. Mater. Res. **37**, 415 (2007).

[27] A. I. Larkin and Yu. N. Ovchinnikov, J. Low Temp. Phys. **34**, 409 (1979).

[28] T. Nattermann, Y. Shapir, and I. Vilfan, Phys. Rev. B **42**, 8577 (1990).

[29] A. A. Fedorenko, V. Mueller, and S. Stepanow, Phys. Rev. B **70**, 224104 (2004).

[30] U. Robels and G. Arlt, J. Appl. Phys. **73**, 3454 (1993).

[31] L. X. Zhang and X. Ren, Phys. Rev. B **73**, 094121 (2006).

[32] Y. A. Genenko and D. C. Lupascu, Phys. Rev. B **75**, 184107 (2007).

[33] One may expect that the application of strong E_{ac} should produce the monodomain state and hence the dielectric response would decrease further rather than retrieve high ϵ_1. However, Phz-H$_2$ca does not, in this case; in the *P*-*E* hysteresis loop of Phz-H$_2$ca, the remnant polarization at a zero electric field is only ∼50% of the spontaneous polarization (Ref. 17). This indicates that the so-called backswitching occurs when the external electric fields are released to zero (Ref. 34). Thus, even if strong E_{ac} has been applied, the multidomain state is recovered, and the domain boundaries are not yet well trapped.

[34] S. Kim, V. Gopalan, K. Kitamura, and Y. Furukawa, J. Appl. Phys. **90**, 2949 (2001).