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Large-scale Domain Engineering in Two-Dimensional Ferroelectric CuInP₂S₆ via Giant Flexoelectric Effect

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Abstract: Room-temperature ferroelectricity in two-dimensional materials offer a potential route for developing atomic-scale functional devices beyond Moore's law. However, as a key for the technology implementations of ferroelectrics in electronics, the controllable generation of uniform domains remains challenging in two-dimensional ferroelectrics at current stage because domain engineering through an external electric field at 2D limit inevitably leads to large leakage current and material break-down. Here, we demonstrate a voltage-free method, the flexoelectric effect, to artificially generate large-scale stripe domains in two-dimensional ferroelectric CuInP₂S₆ with single domain lateral size at the scale of several hundred microns. With giant strain gradients ($\sim 10^6 \text{ m}^{-1}$) at nanoscale, we mechanically switch the out-of-plane polarization in ultrathin CuInP₂S₆. The

flexoelectric control of ferroelectric polarization is understood with a distorted Landau-Ginzburg-Devonshire double well model as evidenced by the shifted ferroelectric hysteresis loops and the first-principle calculations. Through substrate mechanical strain engineering, the stripe domain density is controllable. Our results not only highlight the potential of developing van der Waals ferroelectrics-based memories but also offer the opportunity to study ferroelectric domain physics in two-dimensional materials.

Keywords

two-dimensional ferroelectrics, CuInP₂S₆, flexoelectricity, polarization, artificial domains

Introduction

Atomically thin van der Waals (vdW) crystals provide the opportunity to explore ferroelectricity at two-dimensional (2D) limit which is a long-sought goal in conventional bulk ferroelectrics due to the constrain of critical size effect¹. Experimentally, a series of 2D ferroelectrics with intrinsic either in-plane or out-of-plane electric polarization have been verified, such as the SnTe family²⁻⁴, CuInP₂S₆⁵⁻¹⁰, α -In₂Se₃¹¹⁻¹⁶, Bi₂O₂Se^{17, 18}, and d1 *T*-MoTe₂¹⁹. Besides the atomic thickness, vdW material also offers the layer degree of freedom that leads to the emergence of sliding ferroelectricity induced by interlayer translation²⁰⁻²². The rich 2D ferroelectricity found in vdW crystals therefore provide the potential to revolutionize future electronic applications with exotic functions²³⁻²⁶.

For the integration of 2D ferroelectrics in electronics, how to effectively control the polarization state or ferroelectric domains is the central concern because it fundamentally determines the technical practicability. In bulk ferroelectric perovskite oxides, it can be simply realized by applying an external voltage^{27, 28}. For example, reliable domain structure can be artificially created with the aid of a conductive tip in a scanning probe microscope (SPM)²⁹⁻³¹. Nevertheless, for vdW ferroelectrics with atomic thickness, the out-of-plane switching electric field at 2D limit inevitably results in large leakage current and even material breakdown. As a result, the polarization control and especially the large-scale domain generation is relatively challenging in 2D ferroelectrics. Therefore, an alternative

method which is free of external voltage is highly in demand for domain manipulation in vdW ferroelectrics.

Here, to address the above issue, we utilize the flexoelectric effect, a voltage-free mechanical method, to switch the electric polarization and generate artificial domains at large-scale in ultrathin vdW ferroelectrics. The flexoelectric effect (or flexoelectricity) refers to the formation of net electric polarization inside a crystal when an inhomogeneous strain is applied^{32,33}. This effect is universal for all materials with arbitrary lattice symmetry and thus has been utilized to generate many extraordinary phenomena and functionalities, such as enhanced piezoelectricity³⁴⁻³⁷, the nanoscale polar vortices³⁸, and anomalous photovoltaics³⁹⁻⁴¹. To utilize flexoelectricity in polarization reorientation, the key is the generation of giant strain gradients^{42, 43}. In conventional oxides ferroelectrics, due to the bulk nature with rigid covalence/ionic bond, mechanical domain control can only be realized under the involvement of a SPM tip via nanoscale imprinting or through atomic-scale misfit lattice strain⁴⁴⁻⁴⁶. For 2D vdW ferroelectrics with genuine mechanical flexibility, the flexoelectric modulating of polarization is relatively easy^{47, 48}, offering the feasibility of further voltage-free domain engineering at large scale.

In this work, for the first time, we demonstrate the mechanical formation of artificial strip domains in ultrathin CuInP₂S₆ (CIPS). The required strain gradients ($\sim 10^6 \text{ m}^{-1}$) at nanoscale in CIPS was introduced from periodic pre-strained substrate. With in-situ piezoresponse force microscopy (PFM) measurement, we observed bidirectional modulation of the polarization in rippled CIPS and large ferroelectric domains with single domain lateral size at the order of several hundred microns. The flexoelectric control of polarization in CIPS is understood with a distorted Landau-Ginzburg-Devonshire (LGD) double well model, which is evidenced by the shifted ferroelectric hysteresis loops and the first-principle calculations. Through substrate mechanical strain engineering, the stripe domain density is controllable. Our results not only highlight the potential of developing vdW ferroelectrics based high-density memories but also offer the opportunity to study ferroelectric domain physics in 2D electronic systems.

Results

Demonstration of the flexoelectric modulation in 2D CIPS. To begin with, we start from the lattice structure of CIPS. As shown in Fig. 1a, Cu, In, and P-P pair atoms are bound in a framework which is formed by S atoms through covalent bonds. In each single layer, the atomic position deviation of Cu ions breaks the lattice inversion symmetry, resulting in explicitly OOP ferroelectricity. The two thermodynamically-equivalent polarized states in ferroelectrics can be described by the LGD double well model (see Fig. 1a). When reversing the polarization, the degeneracy of the ground states should be lifted off via external stimulus such as electric field or inhomogeneous strain (i.e. strain gradients) that lowers the switching energy barrier between the two energy minima. The latter, known as the flexoelectricity effect^{32, 33}, is with the benefit of voltage-free and large-scale uniformity for 2D vdW ferroelectrics with atomic thickness and ultrahigh flexibility. Therefore, we apply this method to ultrathin CIPS as an ideal platform in this study.

We first attest the ferroelectricity of CIPS nanoflakes by employing the PFM. CIPS thin flakes were mechanically exfoliated from bulk and were transferred onto the Au/SiO₂ substrate (details can be found in Methods). The single crystal nature of the samples studied here was confirmed by Raman spectroscopy (see Fig. S1), where featured phonon modes were observed. The room-temperature ferroelectricity in CIPS can be evidenced from two aspects. As shown in Fig. 1b, typical single/butterfly-like ferroelectric hysteresis loop in the PFM phase/amplitude spectra were measured from a 20 nm thick CIPS sample. We estimate the coercive field for ultrathin CIPS to be around 3.5×10^5 V/cm. This value is consistent with the results in previous studies⁶. Furthermore, spontaneous domains with unambiguous domain wall structures are clearly visualized in Fig. 1c (PFM phase image) and Fig. S2b (PFM amplitude image). By carefully examining the domain size, we find that the domains in ultrathin CIPS are fractional with typical area of around $0.2 \mu\text{m}^2$ (see Fig. S2c). The scattered domains are due to the relatively low ferroelectric transition temperature (T_c) of CIPS at 320 K, which is close to room temperature. Therefore, under ambient condition, strong thermal fluctuation will hinder the formation of large size domains in CIPS. We also used the DC electric poling via PFM to check the quality of artificial domains. As shown in Fig. S3, a box-in-box pattern has been poled with $\pm 7 V_{DC}$ tip bias. However, consistent with others report of electric poling CIPS,^{6, 7, 10} electric field

writing does not guarantee effective switch of all the polarizations as indicated by the poor quality of artificially poled domains.

The key to flexoelectric control of the electric polarization in ferroelectrics is to apply large enough strain gradients, which scale inversely with the dimensionality and the size of materials. Benefited from the flexural out-of-plane bending mode of ultrathin 2D materials, the giant strain gradients can be introduced in regions with high curvature. Therefore, corrugating the 2D CIPS at nanoscale is a good scenario. As summarized in Fig. 2a, we developed a method to create rippled ultrathin CIPS on gold coated polydimethylsiloxane (PDMS) through the combination of substrate strain engineering and the all-dry transfer technique. For details of the corrugating process, it is described in Methods. With this method, we realized the formation of large area rippled CIPS thin flakes with lateral size at around 195 μm (see the optical image in Fig. 2b). The thicknesses of the thin flakes range from 14 to 20 nm (see Fig. S4). The polarization states of selected regions with different thicknesses are revealed by the PFM results as shown in the insets of Fig. 2b and Fig. S5. From the PFM results, we found ordered stripe domains with extremely high uniformity. The formation of uniform stripe ferroelectric domains suggests that the polarization of the entire large area CIPS thin flake can be effectively modulated by the substrate strain engineering at nanoscale. Importantly, artificial domain formation in 2D CIPS via the flexoelectric effect is valid even at scales as large as hundreds of microns.

Quantification of the flexoelectric effect in 2D CIPS. We next investigate the relationship between the polarization state and the strain gradients ($\frac{\partial u}{\partial z}$). Fig. 3a shows the topography of a periodic rippled CIPS with PFM contact mode under low loading force (60 nN). We found two regions with the thicknesses identified to be 4 nm (marked by green line) and 22 nm (marked by red line), respectively. By examining the piezoresponse from a single periodic area including both the upward and downward bending, the flexoelectric control on polarization is elusively confirmed by the observation of domain wall with vanished PFM amplitude and the clear 180° phase contrast between domains as presented in Fig. 3b and Fig. 3c, respectively. It must be emphasized here, relative to the continuously changing topography, the two plateaus of the phase profile and the rapid switching behavior

implies that the phase is not disturbed by crosstalk of surface topography. Since the flexoelectric modulation relies on substrate strain transfer, it is necessary to check the adhesion between the CIPS and the PDMS substrate. Therefore, we extracted the line profiles of height along (marked by red line in Fig. 3a) and perpendicular to (marked by black line in Fig. 3a) the rippled structure. As shown in Fig. 3d, the rippled structure has a near-symmetric double-arc geometry of upward and downward bending. In the region with CIPS samples, there is an offset change in height. By comparing the offset with the CIPS sample thickness, we found that they are in high consistence. This result demonstrates that the CIPS samples have good adhesion to the PDMS substrate, which guarantees the transfer of the strain.

From the observed tomography, the corrugated periodic structure in CIPS can be simplified into an arch model (see the schematic in Fig. 3e) by considering the sample bending nature of the flexoelectric control. The geometry parameters of this model are obtained from the in-situ morphology measurements. For CIPS thin flakes with a certain thickness d , upon bending, the upper part experiences tensile strain, while the lower part undergoes compressive strain. Thus, the strain gradients $\frac{\partial u}{\partial z}$ is perpendicular to the surface and can be written as⁴³

$$\frac{\partial u}{\partial z} \sim \frac{u_1 - u_2}{d} = \frac{\frac{(R+\frac{d}{2})\frac{l_0}{R} - l_0}{l_0} - \frac{(R-\frac{d}{2})\frac{l_0}{R} - l_0}{l_0}}{d} = \frac{1}{R}, \quad (1)$$

where u_1 and u_2 are the in-plane strain of the upper surface and the lower surface respectively, l_0 is the original length of the sample, and R is the ideal radius of curvature of the bended sample. From equation (1), the strain gradients $\frac{\partial u}{\partial z}$ is inversely proportional to R , which can be calculated by the Pythagorean theorem as

$$R = \frac{h^2 + (\frac{t}{2})^2}{2h}, \quad (2)$$

where h and t are the half of the wrinkle depth and the half of the periodicity. From the height profile in Fig. 3d, the h and t are found to be 50 nm and 600 nm, respectively. In this case, R is calculated to be 925 nm, and $\frac{\partial u}{\partial z}$ is as large as $1.08 \times 10^6 \text{ m}^{-1}$. Comparing to previously studies of mechanical bending in bulk materials at macroscopic scale, where the

strain gradients is usually less than $0.1 \text{ m}^{-141, 49, 50}$, our result achieves 7 orders of improvement in magnitude. Although the applied strain gradients is giant in this study, the ultrathin CIPS samples remain intact other than collapse. This is benefited from the unique near-zero Poisson ratio found in CIPS⁵¹, there is almost no out-of-plane strain in our bending geometry. Meanwhile, the in-plane strain in CIPS thin layers (the top and the bottom) is only around $\pm 1\%$.

With the quantification of the strain gradients, we can estimate the value of effective flexoelectric field E_{flexo} . The flexoelectric field can be expressed as^{32, 42, 43}

$$E_{flexo} = \frac{P_{flexo}}{\epsilon_r \epsilon_0} = \frac{1}{\epsilon_r \epsilon_0} \left(\mu \frac{\partial u}{\partial z} \right), \quad (3)$$

where ϵ_0 is the permittivity of free space and ϵ_r is relative dielectric permittivity, respectively, P_{flexo} is the polarization induced by flexoelectricity, and μ is the flexoelectric coefficient. According to Tagantsev's phenomenological studies of the flexoelectric effect in crystalline materials, μ can be approximately expressed as^{32, 33}

$$\mu \sim \chi \frac{e}{a}, \quad (4)$$

where χ is the dielectric susceptibility ($\chi = \epsilon_r - 1 \approx \epsilon_r$), and a is the lattice constant. For CIPS, the ϵ_r is 40 and a is $6 \times 10^{-10} \text{ m}$. We have the flexoelectric coefficient μ to be 10.8 nC/m . Therefore, the flexoelectric field E_{flexo} in the rippled structure is around $3 \times 10^5 \text{ V/cm}$. The strength of the flexoelectric field is comparable to the coercive field of CIPS nanoflakes extracted from the hysteresis loops measurement ($\sim 3.5 \times 10^5 \text{ V/cm}$) and in previous report.⁶ It further proves the validity of flexoelectric modulation on the electric polarizations of CIPS in this study. Furthermore, it should be pointed out that the flexoelectric coefficients μ of ferroelectric materials is much larger near the Curie temperature T_c .⁵² The T_c of CIPS is 320 K which is relatively low and close to the room temperature.⁸ Thus, the flexoelectric coefficients μ and the flexoelectric field E_{flexo} in our bending geometry under ambient conditions may be much larger than we estimated.

Modeling of the flexoelectric effect in 2D CIPS. The demonstrated geometry-induced flexoelectric effect in 2D CIPS can be understood through the distorted LGD double-well

potential model. As a phenomenological theory, it is often employed to qualitatively explain the flexoelectric effect in ferroelectrics. Here, in this work, the potential energy profiles (PEP) are quantificationally obtained for CIPS system based on first-principle calculations as shown in Fig. 4a. The details of calculation methods and models are given in Supplementary note1. From the calculations, for both the flat and bended CIPSs, the migration barriers of Cu from one surface to the other surface are calculated (see Fig. 4e and Fig. S10). It is found that, the PEP of the flat CIPS has a symmetric double well for the migration of Cu (see Fig. S8); and the PEP of the bended CIPS also has a double-well structure, but is asymmetric (see Fig. 4a). Obviously, it is the strain gradients that break the symmetry of potential energy surface. These calculated results are consistent with the phenomenological theory. It is worth noting that, in bended CIPS the migration barrier of Cu from the contraction surface to stretched surface is much smaller than that between upper and lower surfaces in flat CIPS. The former has only a value of 10 meV, which means that the substrate geometry-induced flexoelectric effect can be observed even at very low temperature.

To verify the distorted LGD double-well potential model, we further investigate the ferroelectric switching behavior of rippled CIPS nanoflakes via single electric poling. Fig. 4b shows the hysteresis loops from the downward and upward bending area of a 14 nm thick CIPS, respectively. Due to the symmetrical geometry, downward and upward bending regions should have the same coercivity. The coercive field which equals to half-width of the hysteresis loop was found to be around 3.7×10^5 V/cm at both of downward and upward bending regions, which is close to the value we estimated above. Importantly, the hysteresis loops of downward/upward bending regions are entirely shifted to the negative/positive voltage range accordingly. This result suggests that the degenerate electric polarizations in CIPS are not stable in bending state. Only either up or down electric polarization can be stabilized subject to the bending direction, which is the manifestation of flexoelectric effect. When the flexoelectric field induced by strain gradients is parallel to the ferroelectric polarization, it could increase the required external coercive voltage. On the contrary, the flexoelectric field would decrease the required external coercive voltage.

Artificially stripe domain control in 2D CIPS. Finally, we show that the stripe domains in 2D CIPS can be effectively tuned in density with the developed substrate strain engineering technique. Controlled arrays of domains in ferroelectrics is important for the practical applications such as nonlinear optics, anomalous photovoltaic effect, etc. In this study, the stripe domains in CIPS is controlled by the periodicity of the rippled substrate. By adjusting the periodicity of the rippled substrate (details can be found in Methods), we generated different stripe domains with periodicities of 530, 750, and 1200 nm, respectively as shown in Figure 5a-c. It should be noted that although the depth of the ripples changed along with the periodicity, the corresponding strain gradients does not change drastically and remains at the order of $1 \times 10^6 \text{ m}^{-1}$ which ensures the reversal of the polarization (see Fig. S10).

The formation and control of stripe domains in CIPS can be numerically interpreted by studying the bending strain on the direction of polar displacement of Cu. We compared the energies with and without stripe domain for the same corrugated structures of CIPS, denoted by E_{Stripe} and $E_{\text{Non-stripe}}$, respectively. The calculated energy differences ($\Delta E = E_{\text{Stripe}} - E_{\text{Non-stripe}}$) are given in Fig. 5e. The structures with and without stripe domain are shown by the sketch in Fig. 5d. The degree of bending strain can be depicted by a scale factor $\lambda = 1 - t/l_0$, where l_0 and t are the length of flat and corrugated supercell including the same number of unit cells, respectively (see the inset in the bottom left corner of Fig. 5e). This scale factor determines the density of stripe domains. In our experiments for stripe domains with periodicity of 1200 nm, the corresponding scale factor (λ) is 6.1%, being in the range of our simulated λ values (5.5%~6.3%, see the abscissa axis of Fig. 5e). According to the definition of ΔE , the negative values of ΔE indicate that the formation of stripe domain is more preferred in energy. Furthermore, in the structure with stripe domains the Cu ions always prefer to locate at the stretched surface (see Fig. 5d), instead of the contraction surface. The latter case corresponds to a metastable state with a higher energy compared to the former, according to calculations. These polarization behaviors are attributed to the flexoelectric effect of ferroelectric CIPS. The evolution trend of ΔE along the λ (or density) indicates that the relative stability of stripe structures increases with the curvature degree of corrugated CIPS.

Discussion

In summary, we report the flexoelectric method to artificially generate large-scale stripe domains in 2D ferroelectric CuInP_2S_6 . Giant strain gradients ($\sim 10^6 \text{ m}^{-1}$) at nanoscale is achieved via substrate engineering. The electric polarizations in ultrathin CuInP_2S_6 are mechanically switched via nanoscale bending. Together with first-principle calculations, the flexoelectric control of ferroelectric polarization in 2D CIPS is verified via distorted LGD double well model. Our work highlights the potential of ultrathin 2D ferroelectrics for developing vdWs ferroelectrics-based memories with ultrahigh density.

Methods

Substrate formation and sample preparations. The home-made PDMS substrate was fabricated by using a two-part silicone elastomer kit (Dow Corning, Sylgard 184). The two-part silicone was mixed at a 10:1 mass ratio and was then cast onto a mold with volume at $60 \times 20 \times 2 \text{ mm}^3$ to produce desired PDMS. The shaped PDMS was placed in a vacuum desiccator for degassing for 1 hour. The degassed PDMS was heated in an oven at 130°C for 3 hours to expedite the polymer cross-linking. To produce strain gradients, the PDMS was pre-stretched via a linear stage with 10% extension. The pre-stretched PDMS was treated with oxygen plasma by using a vacuum plasma system (Tonson Tech, TS-PL02) to form highly stiff film on the surface⁵³. By suddenly releasing the strain, the stiff film spontaneously buckled to ripples with certain periodicity. The periodicity of the rippled structure can be well controlled by setting the time of the plasma treatment. For example, rippled PDMS substrates with periodicities of 530, 750, and 1200 nm were obtained under 3, 4, and 5 minutes of oxygen plasma treatment, respectively. Finally, 5 nm nickel (Ni) and 30 nm gold (Au) were evaporated onto the rippled PDMS substrate to facilitate peeling large-scale CIPS thin layer from the bulk crystal⁵⁴ and to serve as a bottom electrode to ensure the operation of PFM.

The bulk CIPS crystals used in this study were synthesized by using chemical vapor transport method⁵⁵. The large-scale thin CIPS flakes was prepared by gold-assisted peeling

method⁵⁶ and was post transferred to the rippled PDMS substrate by using thermal release tape⁵⁷.

Raman spectroscopy characterization. Raman spectrum was conducted on a Horiba micro-Raman system (LabRAM HR Evolution) with a 100x objective lens (NA = 0.9) to verify the lattice structure of CIPS. The excitation wavelength was 532 nm with on-sample power at 150 μ W. As shown in Fig. S1, the characteristic Raman modes of single crystal CIPS were observed to be at 275, 325, and 384 cm^{-1} , respectively, which confirm the ferroelectric phase and are consistent with previous studies⁶.

PFM characterization. PFM measurements were performed with a commercial atomic force microscope (AIST-Smart SPM system) in near-resonance enhanced mode under ambient condition. A Pt/Ir coated soft tip (Bruker Scm-pit v2) with a spring constant 3 N/m was driven with an AC voltage ($V_{AC} = 1$ V) under the tip-sample contact resonant frequency (~ 270 kHz). To screen the local electrostatic field that has huge effect on the PFM hysteresis loop measurement and the electric poling, we used grounded metallic contact which is connected to the bottom electrode of the rippled CIPS.

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Author Contributions

H. Z. conceived the idea and supervised the research. C. C., H. L. and Q. L. prepared the

samples, fabricated the devices and carried out the PFM measurements. C. C., Z. F. and H. Z. analyzed the data and wrote the paper. All authors commented on the manuscript.

Competing Interests

The authors declare no competing interests.

Author Information

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Data Availability

The data that support the findings of this study are available from the corresponding author on reasonable request.

Figures and Captions

Figure 1. Methods of polarization switching in 2D ferroelectrics. (a) (Left panel) Crystal structure of CIPS and the approaches to switch the polarization. The polarization direction is indicated in by the blue arrows. (Right panel) The corresponding Landau-Ginzburg-Devonshire double well models for ferroelectric phase and polarization switching process. (b) The PFM hysteresis loops and (c) the spontaneous ferroelectric domains from a 14 nm thick CIPS flake.

Figure 2. Artificial domain engineering in 2D CIPS via flexoelectricity. (a) Schematic illustration of the fabrication process of the corrugated periodic structure in 2D CIPS. (b) Optical image of the rippled CIPS thin flakes (14-20 nm thickness). The maximum length of the sample along the stripe direction is $195\ \mu m$. The insets show the PFM phase images of uniform stripe domains at selected regions.

Figure 3. Quantification of the flexoelectric effect in 2D CIPS. (a) Topography image of the rippled CIPS thin flake. Zoomed PFM amplitude (b) and phase (c) images of one period including both upward and downward bending thin CIPS as indicated in the white square region in (a). The insets show the corresponding lateral profiles of amplitude and phase. (d) Selected line profiles of height derived from (a). (e) Simplified arch model for the flexoelectric control of polarization in 2D CIPS. The parameters such as ideal radius of curvature (R), sample thickness (d), wrinkle depth ($2h$), periodicity ($2t$), and original sample length (l_0) can be directly obtained from (d).

Figure 4. The distorted LGD model for the flexoelectric switch of polarization. (a) Calculated potential energy profiles with asymmetric double-well potential for bended CIPS. The inset shows the side view of the corrugated crystal structures of 2D CIPS with the out-of-plane strain gradients displayed by red arrows. (b) Shifted PFM hysteresis loops measured from the upward bending region and down bending region.

Figure 5. Controlled stripe domain generation in 2D CIPS. (a)-(c) The stripe domains with varied periodicities. The periodicity is 530, 705, and 1200 nm, respectively. (d) Side view of the corrugated crystal structures of CIPS flakes with and without stripe domains. The positions of Cu ions are highlighted to distinguish the strip domain and single domain. (e) Comparison between the lattice stabilities of corrugated CIPS strip domain and single domain. The inset shows the degree of bending, which is depicted by a scale factor $\lambda = 1 - t/l_0$, where l_0 and t are the length of flat and corrugated supercell including the same number of unit cells, respectively.

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