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Temperature-assisted Piezoresponse Force Microscopy: Probing Local Temperature-Induced Phase Transitions in Ferroics

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Combination of local heating and biasing at the tip-surface junction in temperature-assisted piezoresponse force microscopy (tPFM) opens a pathway for probing local temperature induced phase transitions in ferroics, exploring the temperature dependence of polarization dynamics in ferroelectrics, and potentially discovering coupled phenomena driven by strong temperature- and electric field gradients. Here, we analyze the signal formation mechanism in tPFM and explore the interplay between thermal- and bias-induced switching in model ferroelectric materials. We further explore the contributions of the flexoelectric and thermopolarization effects to the local electromechanical response, and demonstrate that the latter can be significant for "soft" ferroelectrics. These results establish a framework for quantitative interpretation of tPFM observations, predict the emergence of non-trivial switching and relaxation phenomena driven by non-local thermal gradient-induced polarization switching, and open a pathway for exploring the physics of thermopolarization effects in various non-centrosymmetric and centrosymmetric materials.

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I. INTRODUCTION

For over a century, ferroelectrics (**FEs**) and relative polar materials have remained one of the central research areas in condensed matter physics and materials science [1, 2]. Many novel phenomena were discovered using piezoresponse force microscopy (**PFM**), such as chemical [3, 4] and probe-induced electro-chemical [5] polarization reversal in classical FEs, temperature-assisted and thermal-effect-induced local switching of polarization in FEs [6] and relaxors [7].

In FEs, the application of bias to the PFM probe can induce nucleation and growth of the ferroelectric domains of opposite polarity. Hence, the bias evolution of the signal, i.e., local hysteresis loops, provides insight into the domain nucleation and growth process [8, 9, 10]. For materials with more complex functionalities, such as ferroelectric relaxors or electrochemical systems, the mechanisms behind the bias- and time- dependence of electromechanical response are more complex [11, 12]. The consideration of polarization switching necessitate exploring the domain structure, interaction between topological and structural defects, and the defect dynamics [13, 14, 15].

Furthermore, understanding ferroelectric and relaxor phenomena requires probing temperature-induced and temperature-dependent processes [6, 7]. To gain insight into temperature-induced phenomena in FEs, a number of groups have explored the evolution of the PFM signal and complementary Kelvin Probe Force Microscopy signals under global heating across the phase transitions [16, 17, 18, 19]. A number of interesting phenomena including the domain branching and domain memory effects, temperature induced potential inversion [20] and potential retention, and relaxation above the Curie temperature [21] were reported and attributed to the external screening of polarization charges.

However, existing implementations and analyses of PFM are mostly limited to uniform temperature observations and, in few cases, to observation of domain structures under macroscopic thermal gradients [22]. This severely limits the range of ferroelectric phenomena that can be explored. Much like how capacitor-based PFM measurements activate all defects [23, 24, 25, 26], global heating leads to global changes in domain structures. For example, if one of the defects has a lower transition temperature, it introduces a phase transition in a macroscopic volume precluding exploration of other (weaker) defect centers. This general limitation precluded systematic studies of temperature-induced phase transitions or coupled thermal and bias-induced phenomena. Secondly, much like how strain gradients give rise to a broad range of flexoelectricity-driven

phenomena, it can be expected that sharp local temperature gradients will reveal flexo- and thermopolarization effects.

Recently, advances in the scanning probe microscopy instrumentation have allowed to combine imaging and spectroscopy modes, when both the temperature and the bias of the probe can be varied [27, 28]. In this fashion, the local biasing and local heating of the microscopic volumes of the material at the tip-surface junction can be affected simultaneously. Here we analyze the mechanisms of ferroic interaction with a heated PFM tip, explore the evolution of bias- and temperature induced polarization distributions, and derive the temperature-dependent responses. We calculate the solution of a thermo-elastic-electric probing problem fully coupled with Landau-Ginzburg-Devonshire (**LGD**) description of the ferroelectric polar properties, and analyze the temperature-induced and voltage-induced polarization redistribution, and local electromechanical response occurring under the heated PFM tip.

The manuscript is structured as following. **Section II** contains the formulation of the local thermo-elastic-electric probing problem with boundary conditions and material parameters used in calculations. **Section III** analyzes the temperature-induced polarization redistribution, elastic strains and surface displacement of a ferroelectric layer at zero voltage applied to the heated PFM tip. The changes of the ferroelectric polarization and local electromechanical response induced by the biased and heated PFM tip are considered in **Section IV**. **Section V** is a brief summary. Calculation details and auxiliary figures are listed in **Suppl. Mat**. [29].

II. THEORETICAL DESCRIPTION

A. Coupled thermo-elastic-electric problem for a ferroelectric layer

Using the laser assisted thermal band excitation PFM (**tPFM**) the local ferroelectric and mechanical properties can be measured simultaneously as a function of temperature. An ultraviolet (UV) laser is aligning normal to the PFM cantilever, and a triangular voltage wave (amplitude $\sim 0.1 - 10$ V, frequency \sim Hz) is applied to the UV laser [30]. The cantilever displacement, registered by the photodetector matrix, allows to probe the PFM response amplitude, phase, and resonant frequency in a point-by-point spectroscopy framework. Functional responses of the material are probed as a function of local heating at the tip-surface junction in a conventional way.

To model the experimental situation, we consider the case of a PFM tip in contact with the FE surface, common for contact mode scanning probe microscopies. The geometry of calculations

is conventional for PFM probing and is shown in **Fig. 1(a)-(c)**. The free energy *G* dependences on the polarization *P* and temperature *T* calculated for the "soft" and "hard" uniaxial FEs, $Sn_2P_2S_6$ and LiNbO₃, are shown in **Fig. 1(d)** and **1(e)**, respectively. It is evident how the temperature variation changes the potential wells of spontaneous polarization. Applied voltage makes these wells non-equivalent up to the disappearance of the shallow well at coercive voltage.



FIG. 1. (a) The temperature distribution in a FE layer of thickness *h* induced by a PFM tip heated up to the temperature $T_0 + \Delta T$. The temperature of remote bottom electrode is T_0 . Polarization distribution in the FE

layer under the PFM tip biased with either positive (**b**) or negative (**c**) voltage, respectively. The free energy dependence on the polarization P and temperature T calculated for the "soft" and "hard" uniaxial FEs, $Sn_2P_2S_6$, (**d**) and LiNbO₃ (**e**), respectively.

Here, we assume that the temperature distribution obeys a standard heat equation. The heated tip apex, the FE layer and the ambient are characterized by their own thermal conductivity equation for the temperature variation $T_m(\vec{r}, t)$ inside each region "m":

$$\frac{\partial}{\partial t}T_m = \kappa_m \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)T_m.$$
(1)

The FE layer occupies the region $0 \le z \le h$. The coefficients $\kappa_m = k_m^T/c_m$, where c_m is the heat capacity and k_m^T is the thermal conductivity of the material "*m*". The relation between the heat flux and the temperature variation is given by the conventional expression, $\vec{j}_m = -k_m^T \frac{\partial \vartheta_m}{\partial \vec{n}}\Big|_{S_m}$. Thermal boundary conditions to Eq.(1) at their physical boundaries S_m are the continuity of heat fluxes and the equality of the media temperatures (see **Appendix A** in **Suppl. Mat**. [29] for details).

Due to the very high heat conductivity of the metallic tip, moderate conductivity of a FE layer and very low ambient conductivity, one can neglect the heat flux between the FE and the ambient air or vacuum. Here we assume that the tip is heated by ΔT , and the tip is in contact with a FE layer. The temperature is equal to T_0 very far from the film surface, z = 0. In particular, $T = T_0$ at the remote part of the bottom electrode, i.e., at $z \gg h$. The tip apex is modeled as a perfectly heat-conducting disk with effective radius *R* being in a tide electric and thermal contact with the FE surface, z = 0. This model corresponds to a well-known disk-plane model of the PFM tip [31, 32], where *R* can be associated with the contact radius of the tip apex. Note that here we assume that the temperature-induced changes in polarization affect the temperature field and dynamics only weakly, i.e., adopt a decoupled approximation for the thermal field.

In order to find the spatial distribution of the acting electric field E_i and out-of-plane ferroelectric polarization component P_3 inside the uniaxial FE, one should solve a coupled problem consisting of Poisson equation for electric potential ϕ and LGD-type equation for P_3 [33]:

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\phi^{(in)} = \frac{1}{\varepsilon_0\varepsilon_b}\frac{\partial P_3}{\partial z},$$
(2a)

$$\left[\alpha_{T}(T(\vec{r}) - T_{C}) - Q_{ij33}\sigma_{ij}\right]P_{3} + \beta P_{3}^{3} + \gamma P_{3}^{5} - g_{11}\frac{\partial^{2}P_{3}}{\partial z^{2}} - g_{44}\left(\frac{\partial^{2}P_{3}}{\partial x^{2}} + \frac{\partial^{2}P_{3}}{\partial y^{2}}\right) = \mu \frac{dT}{dz} + E_{3} - F_{ijk3}\frac{\partial\sigma_{ij}}{\partial x_{k}}.$$
 (2b)

Here $\phi^{(in)}$ is the electric potential of the FE, ε_b is a background permittivity [34], $T(\vec{r})$ obeys Eq.(1), T_c is a bulk Curie temperature, Q_{ijkl} are electrostriction tensor components, σ_{ij} are elastic stresses, and μ is the coefficient of thermopolarization effect [35]; F_{ijkl} are flexoelectric tensor coefficients.

The important aspect of the Eq. (2b) is the presence of the thermopolarization coupling, μ . Here, the coefficient μ is the diagonal component of the second rank tensor μ_{ij} , whose value can be estimated as proportional to the convolution of the flexoelectric tensor F_{ijkl} and linear thermal expansion tensor β_{ij} , namely $\mu_{ij} \cong F_{ijkl}\beta_{kl}$ [36]. Note that the thermopolarization effect is omnipresent, meaning that it exists for arbitrary symmetry of the studied material [35], but its numerical values are poorly known [22]. We further restrict the analysis to the transversally isotropic thermal expansion tensor $\beta_{ij} = \delta_{ij}\beta_{ii}$ with $\beta_{11} = \beta_{22} \neq \beta_{33}$ (δ_{ij} is the Kroneker symbol).

The electric boundary conditions are: the fixed potential *V* at the tip-ferroelectric contact area, $\phi^{(in)}|_{S_t} = V$, electric potential and displacement continuity at the FE surface, $(\phi^{(out)} - \phi^{(in)})|_{z=0} = 0$ and $(-\varepsilon_0 \varepsilon_b \frac{\partial \phi^{(in)}}{\partial z} + P_3 + \varepsilon_0 \varepsilon_e \frac{\partial \phi^{(out)}}{\partial z})|_{z=0} = 0$, and potential vanishing at bottom electrode, $\phi^{(in)}|_{z=0} = 0$, (or at the infinity at $\Box \to \infty$). The electric potential outside the FE, $\phi^{(out)}$, obeys the Laplace equation. The so-called "natural conditions" are valid for the polarization at the FE surfaces, $(\frac{\partial P_3}{\partial z})|_{z=0,\Box} = 0$.

Elastic stresses σ_{ij} and strains u_{ij} are calculated in a self-consistent way from elastic equations in the continuum media approach. The elastic equations of state follow from the variation of the LGD free energy with respect to elastic stresses:

$$u_{ij} = s_{ijkl}\sigma_{kl} + \beta_{ij}(T - T_0) + F_{ijkl}\frac{\partial P_l}{\partial x_k} + Q_{ijkl}P_kP_l, \quad 0 \le z \le h.$$
(3a)

The strain tensor components are related to the displacement components U_i in a conventional way, $u_{ij} = (\partial U_i / \partial x_j + \partial U_j / \partial x_i)/2$.

Note that the linearization of electrostriction terms with respect to electric field gives the piezoelectric contribution in a FE phase. Namely, using the expression for polarization, $P_k = P_k^S + \chi_{kn}E_n$, the electrostriction contribution is $Q_{ijkl}P_kP_l \cong Q_{ijkl}P_k^SP_l^S + d_{ijm}E_m + Q_{ijkl}\chi_{lm}E_m\chi_{kn}E_n$, where $d_{ijm} = 2Q_{ijkl}P_k^S\chi_{lm}$ is a piezoelectric tensor expressed via the electrostriction Q_{ijkl} , spontaneous polarization P_k^S and dielectric susceptibility χ_{lm} tensors.

Equations (3a) should be solved along with equations of mechanical equilibrium

$$\partial \sigma_{ij}(\mathbf{x}) / \partial x_i = 0,$$
 (3b)

and compatibility equations, $e_{ikl} e_{jmn} \partial^2 u_{ln}(\mathbf{x}) / \partial x_k \partial x_m = 0$, which are equivalent to the continuity of U_i [37]. The boundary conditions for elastic stresses σ_{ij} and displacement components U_i are the absence of normal stress at the free top FE surface, $\sigma_{i3}|_{z=0} = 0$, and zero elastic displacement at FE bottom surface due to complete clamping at the substrate electrode, $U_i|_{z=h} = 0$. Here we assume that the deformation of the top surface is small, otherwise we need to apply the boundary condition at the (unknown) deformed boundary.

To complement analytical derivations, finite element modeling (**FEM**) is performed in the COMSOL@MultiPhysics software, using electrostatics, solid mechanics, and general math (PDE toolbox) modules. To avoid numerical artefacts, the temperature and voltage distribution at the ferroelectric film surface is chosen as Gaussian-like with a dispersion R.

As representative model systems, here we explore different types of uniaxial FEs: a "soft" ferroelectric $Sn_2P_2S_6$ (**SPS**) with a relatively low bulk Curie temperature $T_C=337$ K and small coercive field, and a "hard" ferroelectric-pyroelectric LiNbO₃ (**LNO**) with a high $T_C = 1477$ K and ultra-high coercive field. We performed a quasi-2D simulations for a 100-nm thick SPS and LNO layers. The corresponding LGD free energy coefficients and other material parameters are listed in **Table I.** The free energy dependence on the polarization *P* and temperature *T* is shown in **Fig. 1(d)** for Sn₂P₂S₆ and in **Fig. 1(e)** for LiNbO₃, respectively.

Para-	Dimen-	Values for Sn ₂ P ₂ S ₆ collected	Values for LiNbO ₃ collected from
meter	sion	from Refs. [38, 39, 40]	Refs.[41, 42, 43, 44, 45, 46]
ε _b	1	7*	4.6 [41]
α_{T}	m/F	1.44×10^{6}	1.569×10^{6} [42]
T_C	K	337	1477 Ref. [43]
β	$C^{-4} \cdot m^5 J$	9.40×10^{8}	2.31×10 ^{9***}
γ	C ⁻⁶ ⋅m ⁹ J	5.11×10^{10}	1.76×10 ^{9***}
g_{ij}	m ³ /F	$g_{11} = 5.0 \times 10^{-10}$ **	$g_{44} = 7.96 \times 10^{-11} [44]$
-		$g_{44} = 2.0 \times 10^{-10}$	
S _{ij}	1/Pa	$s_{11} = 4.1 \times 10^{-12}, s_{12} =$	$s_{11} = 5.78 \times 10^{-12}, s_{12} = -1.01 \times 10^{-12}, s_{13} =$
		$-1.2 \times 10^{-12}, s_{44} = 5.0 \times 10^{-12}$	$-1.47 \times 10^{-12}, s_{33} = +5.02 \times 10^{-12}, s_{14} =$
			$-1.02 \times 10^{-12}, s_{44} = 17.10 \times 10^{-12} [45]$
Q_{ij}	m^4/C^2	$Q_{11}=0.22, Q_{12}=0.12$ ****	Q_{33} = +0.016, Q_{13} = -0.003
μ	V/K	6.0×10 ⁻⁵ *****	6.0×10 ⁻⁵ *****
F_{ij}	m^3/C	$F_{11}=1.0\times10^{-11}$,	$F_{11}=1.0\times10^{-11}, F_{12}=0.9\times10^{-11},$
-		$F_{12}=0.9\times10^{-11}, F_{44}=3\times10^{-11}$	$F_{44}=3\times10^{-11}$

Table I. The parameters for bulk FEs, Sn₂P₂S₆ and LiNbO₃.

β_{ij}	1/K	$\beta_{11}=\beta_{22}=4\times10^{-5}, \beta_{33}=9\times10^{-6}$	$\beta_{11}=14.4\times10^{-6}, \beta_{22}=15.9\times10^{-6},$
			β ₃₃ =7.5×10 ⁻⁶ [46]

^{*} The value is estimated from a refraction index value

** The order of magnitude is estimated from the uncharged domain wall width [38, 39].

*** The estimation is based on the values of the spontaneous polarization and permittivity at room temperature

**** The estimation of electrostriction is based on thermal expansion data from Say et al.[40]

***** The value is estimated as a convolution of the flexoelectric and thermal expansion tensors, and the numbers order is the same as in Ref.[22]

From Eqs.(3a), the local elastic strain (and hence PFM response) has several contributions coming from the thermal expansion [47], flexoelectric effect [48], and from the electrostriction coupling, which includes the piezoelectric [49] and thermopolarization [35] contributions. The flexoelectric and thermopolarization contributions are universal, while the piezoelectric contribution is symmetry-sensitive being dominant in the ferroelectric phase without inversion symmetry. In the analysis below, we also neglect the chemical pressure (Vegard contributions) that underpins signal formation mechanisms in electrochemical strain microscopy [48, 50, 51], and temperature-induced shifts of electrochemical equilibrium at the free surfaces [3, 52, 53], and defer these mechanisms to future studies.

III. POLARIZATION AND STRAINS CHANGES INDUCED BY LOCAL HEATING AT ZERO TIP VOLTAGE

In this section, we analyze the phenomena emerging under the local heating. Note that the basic insight into the relevant phenomena can be derived from joint consideration of the temperature dependence of polarization and long-range nature of depolarization fields in FEs. Namely, local heating of the ferroelectric surface necessarily reduces the polarization below the tip, resulting in the polarization gradient within the material. The polarization gradient is associated with the polarization bound charge, that can be minimized via the penetration of the region with reduced polarization inside the FE material, or clamping of polarization below the tip to higher (relative to equilibrium) values.

To gain insight in these phenomena, we consider a thick FE layer placed under the heated tip when the voltage applied between the tip and the bottom electrode is zero, V = 0. The layer was homogeneously polarized before the heating. Spatial distributions of the temperature excess T, polarization P_3 and vertical displacement U_3 of the FE layer are shown in **Fig. 2**. XZ cross-sections are calculated by FEM for the tip "overheating" on $\Delta T = 50$ K at $T_0 = 293$ K for SPS (left column) and $\Delta T = 100$ K at $T_0 = 700$ K for LNO (right column), tip-surface contact radius R = 10 nm and zero applied voltage, V = 0. The heated region has a semi-spherical profile [compare **Fig. 2(a)** with **2(d)**].

At zero voltage, the heating-induced changes of P_3 is primarily caused by the temperature changes of the coefficient $\alpha_T(T(\vec{r}) - T_C)$, and also by the thermopolarization and flexoelectric effects [see the right-hand side of Eq.(2b)]. Based on numerical estimates for materials explored here, the flexoelectric contribution is small in comparison with the thermopolarization contribution for initially homogeneously polarized FE (see **Appendix B, Suppl. Mat**. [29]).

A small overheating on $\Delta T = 50$ K significantly decreases the ferroelectric polarization P_3 in the overheated region of SPS [see **Fig.2(b)**]. The region of reduced polarization growth through the SPS layer depth in order to minimize the strong depolarization field produced by a charged domain wall [54, 55]. The polarization behavior is relatively easy to rationalize – the thermal field is localized below the probe, but the ferroelectric polarization cannot form z-gradients due to the strong depolarization filed. As a result, the area with reduced polarization extends far beyond the heated region and induced corresponding changes of the elastic fields in the same region. Note that this effect is dual, and polarization below the tip is also clamped by the surrounding material.

In comparison, for LNO a higher overheating on $\Delta T = 100$ K neither induces the polarization decrease nor the nanodomain formation in the overheated region of LNO [see **Fig.2(c)**]. Only the bulb-like region of slightly suppressed polarization appears in the case. The polarization behavior is explained by the fact that the tip temperature, $T_0 + \Delta T = 800$ K, is still very far from high $T_c \approx 1477$ K of LNO, and so the FE remains insensitive to the overheating.

Further shown are the corresponding changes of the vertical displacement U_3 originated from the thermal expansion (i.e., from the thermoelastic effect), electrostriction and flexoelectric effects [see the right-hand side of Eq.(3a)]. Since the flexoelectric contribution appeared negligibly small, U_3 profiles are controlled by the thermoelastic and electrostriction contributions. The region of the heating-induced U_3 is much wider and much more diffuse than the region of temperature excess for both SPS and LNO layers [compare **Fig. 2(a)** with **2(c)**, and **Fig. 2(d)** with **2(f)**, respectively]. Both x- and z-profiles of U_3 "falls down" as a whole in the region with radius $r \gg$ R; and reveal a diffuse maximum in the region with radius $r \cong 2R$. The diffuseness means that the region with enhanced U_3 is extended. In theoretical calculations for LNO we ignore any sort of tip damage due to its overheating on $\Delta T = 100$ K in comparison with the high temperature of surrounding, $T_0 = 700$ K. Indeed, the tip temperature is 800 K in the case. This temperature cannot cause any damage for the tip made of refractory metal, e.g., tungsten with the melting temperature above 3400 K, or platinum-iridium alloy with the melting temperature between 1700 K and 2400 K.



FIG. 2. Spatial distributions of the temperature *T* (**a**, **d**), polarization P_3 (**b**, **e**) and vertical displacement U_3 (**c**, **f**) of the FE layer calculated by FEM for two values of the tip overheating ΔT and T_0 , $\Delta T = 50$ K and $T_0 = 293$ K for SPS parameters (**a-c**), $\Delta T = 100$ K and $T_0 = 700$ K for LNO parameters (**d-f**); tip-surface

contact radius R = 10 nm. X-Z cross-sections are shown. Applied voltage is absent, V = 0. The FE was homogeneously polarized before the heating.

Note that **Figs. 2(a)** and **2(d)** show high temperature gradients near the ferroelectric surface, which can reach (0.5 - 1) K/nm, respectively. Thermodynamically, it is not clear if the temperature is still a meaningful concept in this case, as well as the validity the thermodynamic LGD approach becomes questionable. More important question is the realizability of high temperature gradients in FEs.

The gradients ~K/nm are can be created in thin ferroelectric layers. Let us give several examples. Paruch et al. [6] measured the evolution of domain wall roughening as a result of heatquench cycles up to 735 °C. They used PFM in epitaxial rough PZT films with thickness 50-100 nm. The effective roughness exponent changed from 0.25 to 0.5 in the experiments. In such conditions, the temperature gradients can be high and comparable with the ones considered in our work. Recently, Kelley et al. [30] perform tPFM experiments for SPS. The PFM tip was heated up to 80°C, so the overheating $\Delta T = 60$ K for $T_0 = 20^{\circ}$ C. The curvature of the PFM tip apex was not more than 25 nm, and so the temperature gradient was not less than 2 K/nm. The estimate is corroborated by the FEM modeling [30]. The experimental works [6, 30] speak in favor that the strong temperature gradients, appeared in our theoretical calculations, can be realistic. Moreover, FEM results obtained for SPS in Ref.[30] appeared in a good semi-quantitative agreement with tPFM experiments, disregarding that we use temperature-independent elastic constants and thermal conductivity in the FEM.

However, since the experimental works [6, 30] do not study LNO, we also performed FEM for LNO at the different tip overheating, $\Delta T = (25 - 150)$ K, and lead to the conclusion that ΔT smaller than 100 K does not affect the polarization distribution if the surrounding temperature T_0 is far from the LNO Curie temperature $T_c > 1000$ K (the case $\Delta T = 100$ K at $T_0 = 700$ K is discussed in details below). In other words, to provide an effective tPFM study and/or manipulation of polarization distribution in a ferroelectric material using a small overheating ΔT , the surrounding temperature must be close enough to T_c . This simple qualitative result is independent on the possible problems with the thermodynamics and mean field theory applicability for high temperature gradients.

IV. POLARIZATION CHANGES, STRAINS, AND ELECTROMECHANICAL RESPONSE INDUCED BY LOCAL HEATING AT NONZERO TIP VOLTAGES

In this section we consider a thick FE layer placed under the heated tip when the voltage is applied between the tip and the bottom electrode. The layer was homogeneously polarized before probing.

Note that in the case of PFM geometry the temperature gradient is mainly depends on tip radius of curvature R in the films with thickness $h \gg R$ [see semi-spherical colored regions in **Figs.2(a)** and **2(d)**]. The gradient depends on both, the radius R and film thickness h, for thin films with $h \leq R$. Thus a 100-nm film, considered in FEM, can be regarded "thick" in comparison with a 10-nm tip radius. The increase of the film thickness very weakly influences on FEM results, but significantly increases the calculation time.

A. FEM results for polarization and elastic displacement

We further explore the joint effect of probe heating and bias in the tPFM experiments. Typical spatial distributions of the polarization P_3 and vertical displacement U_3 of the FE calculated by FEM for small and high values of applied voltage, $V = \pm 0.1$ V, ± 1 V and ± 10 V, and tip overheating $\Delta T = 50$ K for SPS and $\Delta T = 100$ K for LNO are shown in **Fig. 3** and **4**, respectively.

For a chosen "up" direction of the spontaneous polarization [shown in **Figs. 1(b)-(c)**], the negative voltage increases the polarization under the heated tip, but quantitatively the polarization enhancement is different for SPS [**Fig. 3(a)**] and LNO [**Fig. 4(a)**]. Specifically, for SPS the polarization enhancement occurs in the stripe region that penetrates through the layer depth; and the stripe is surrounded by the region of suppressed polarization [**Fig. 3(a)**]. For LNO the polarization enhancement occurs in a small semi-ellipsoidal region that does not penetrates into the layer [**Fig. 4(a)**]. Also, note the unusual structure of the tip-induced polarization suppression for both small and higher negative voltages, shown by dark-blue satellites in **Fig. 3(a)** and **4(e)**.

Positive voltages decrease the polarization. For sufficiently high magnitude $V > V_{th}$, the bias applied to the tip can reverse local polarization and induce the nanodomain [13, 14]. The threshold voltage V_{th} is estimated to be very low for an SPS film (less than 10 mV), and rather high for LNO – more than 5 V [compare **Fig. 3(b)** and **4(f)**]. Note that these estimates strongly depend on tip radius of curvature and potential drop at the tip-surface junction (i.e., on the dead layer effect, [13, 14]). The nanodomain breakdown through the layer immediately occurs in SPS

at $V > V_{th}$ [Fig. 3(b)]. In LNO the spike-like nanodomain nucleus occurs at high voltage $V_{th} \cong 5$ V, and its breakdown happens at significantly higher voltages [Fig. 4(f)]. The structure is conditioned by the system tendency to minimize the depolarization field energy that appear near any sort of polarization gradient with nonzero divergency.

At small voltages, the displacement maps are almost insensitive to the direction of SPS polarization under the tip [see **Fig. 3(c)** and **Fig. 3(d)**], and the difference becomes even smaller for LNO with voltage increase [see **Fig. 4(c)**, 4(d), 4(g) and 4(h)]. This insensibility is caused by the quadratic electrostriction effect. Only the voltage derivative (i.e., piezoelectric contribution) can be sensitive. Spatial distributions of the temperature *T* are voltage-independent, so they are the same as shown in **Fig. 2(a)** and **2(d)**.



FIG. 3. Spatial distributions (*xz* cross-sections) of the polarization P_3 (**a**, **b**) and vertical displacement U_3 (**c**, **d**) of a thick SPS layer calculated for applied voltage V = -0.1 V (**a**, **c**), V = +0.1 V (**b**, **d**), tip-surface contact radius R = 10 nm, tip overheating $\Delta T = 50$ K, and $T_0 = 293$ K. Before heating the SPS layer was homogeneously polarized. Material parameters are listed in Table I.



FIG. 4. Spatial distributions (*xz* cross-sections) of the polarization P_3 (**a**, **b**, **e**, **f**) and vertical displacement U_3 (**c**, **d**, **g**, **h**) of a thick LNO layer calculated for applied voltage V = -1 V (**a**, **c**), V = +1 V (**b**, **d**), V =

-10 V (e, g), and V = +10 V (f, h) for the tip-surface contact radius R = 10 nm, tip overheating $\Delta T = 100$ K, and $T_0 = 700$ K. Before heating the LNO layer was homogeneously polarized. Material parameters are listed in **Table I.**

Figures 3-4 are calculated for nonzero flexoelectric coefficients, $F_{ij} \neq 0$, which are listed in Table I, and whose order of magnitude are the same as for other FEs [56]. It is seen from the Fig. A1, that the flexoelectric coupling does not affect the displacement distribution significantly. In fact, the flexoelectric effect contribution is negligibly small even at the diffuse domain walls shown in Fig. 3-4 and Fig. A1. However, this observation can be readily rationalized since for heating of $\Delta T > 5$ K and nonzero voltages |V| > 0.05 V the piezoelectric and electrostriction contributions strongly dominate over the flexoelectric contribution, and as well as over the thermopolarization contribution.

The profiles of polarization P_3 and vertical displacement U_3 at the FE surface calculated for tip overheated at $\Delta T = 50$ K and $\Delta T = 100$ K, positive, zero and negative voltages V are shown in **Figs. 5(a)**-**5(b)** for SPS layer and in **Figs. 5(c)**-**5(d)** for LNO layer, respectively. Black solid curves in **Figs. 5(a)** and **5(c)**, calculated for zero voltage V = 0, show the changes of the P_3 surface profiles induced by the thermopolarization effect, whose role is little more pronounced for SPS in comparison with LNO. The P_3 profiles calculated for nonzero voltages [colored curves in **Figs. 5(a)** and **5(c)**] are smoother for SPS, where the ferroelectric polarization is enhanced or reversed by the biased heated tip at much lower voltages (~0.1 V) than for LNO (~ 10 V). Note that SPS is very a "soft" ferroelectric for tPFM in comparison with a "hard" LNO. Interestingly, that the field-induced polarization conserves regardless the heating in LNO up to very high temperatures (more than 1000 K). For a hard ferroelectric, the tip overheating well above T_C (on more than 100-150 K) is required to induce a local transition to the paraelectric phase, but such strong overheating can rather melt the ferroelectric.

The temperature- and voltage-induced surface profiles of U_3 , which are caused by the thermoelastic and electrostriction effects, look very different for SPS and LNO [compare **Figs. 5(b)** and **5(d)**]. For SPS the U_3 profiles have a maximum at the center for both negative and positive voltages. The maxima height depends on the tip voltage in a very specific way: it is the smallest for 0.1 V, becomes biggest for 0, -0.1V, +0.5V, -0.5V, +1V and highest for -1V. The "alternating" sequence is related with the interplay of elastic responses from the overheated nanoregion (or reversed nanodomain) and colder FE surrounding. For LNO the U_3 profiles have a

single central maximum for negative and relatively small positive voltages, which splits in 2 or 3 maxima for higher voltages. The maxima height depends on the tip voltage in a monotonic way: it is the smallest for 10 V, becomes biggest for 5 V, 1 V, 0, -1 V, -5 V and highest for -10 V.



FIG. 5. Polarization (**a**, **c**) and vertical displacement U_3 (**b**, **d**) profiles at the FE surface calculated for the tip overheating $\Delta T = 50$ K, $T_0 = 293$ K and SPS parameters (**a**, **b**); $\Delta T = 100$ K, $T_0 = 700$ K and LNO parameters (**c**, **d**). Tip voltage V varies from -1V to +1V for SPS, and from -10V to +10V for LNO (see legends). Before heating the FE was homogeneously polarized. Other parameters are the same as in Fig. 4.

B. Temperature dependences of polarization, elastic displacement and local electromechanical response

The temperature dependences of the polarization P_3 and vertical displacement U_3 (in pm) calculated under the heated tip (centered at x=0) are shown in **Figs. 6(a)-6(b)** for SPS layer and in **Fig. 6(c)-6(d)** for LNO layer, respectively. Note that the temperature dependences look very different for SPS and LNO; and they have very different sensitivity to the temperature and applied voltage.

First, we discuss the temperature dependence of polarization, displacement, and electromechanical response for a soft FE – SPS. Black solid curves in **Figs. 6(a)**, calculated for zero voltage, show the temperature dependence of the P_3 induced by the thermopolarization effect. Black solid curves in **Figs. 6(b)**, also calculated for V = 0, show the temperature dependences of U_3 induced by the thermoelastic effect and electrostriction. Both these dependences have a feature at about $\Delta T_{cr} = 80$ K, where the ferroelectric polarization is destroyed under the heated tip, indicating on the local temperature-induced transition to a paraelectric phase. Dashed black curves, calculated for very small voltages, $V = \pm 10$ mV, are relatively close to the solid black curves for polarization and displacement. Dark red, red and orange curves calculated for positive voltages V = (0.1 - 1) V are mostly linear, except for the very thin temperature region of polarization reversal at V = 0.1 V. For higher voltages the field-induced polarization conserves during the heating. Dark blue, blue and teal curves calculated for negative voltages V = -(0.1 - 1)V are quasi-linear for the same reasons. The displacements for positive and negative voltages become closer with temperature increase [see **Fig. 6(b)**].

The situation for a hard FE – LNO differs strongly from SPS. A black solid curve in **Figs. 6(c)**, calculated for V = 0, shows the linear temperature dependence of the P_3 mostly induced by the linear thermal expansion and also by the thermopolarization effect. The tip overheating well above T_C (on more than 100 K) is required to induce a local phase transition at V = 0, but such strong overheating can rather destroy the ferroelectric. For high voltages (both positive or negative) the field-induced polarization conserves during the heating. At the same time, the nucleation of a spike-like nanodomain occurs at high voltages (~5 – 10 V). Displacement curves, calculated for both negative, zero and positive voltages, are linear due to the dominant contribution of the linear thermal expansion [see all curves in **Figs. 6(d)**], and the polarization reversal occurs at voltages about 5 V [see the red curve in **Figs. 6(c)**]. The displacement curves for positive and

negative voltages remain almost parallel with temperature increase as anticipated for the linear thermal expansion mechanism.



FIG. 6. Surface polarization P_3 (**a**, **c**) and vertical displacement U_3 (**b**, **d**) versus ΔT calculated under the heated tip (centered at x=0). Solid curves are calculated for different voltages *V* varying from -1V to +1V for SPS, and from -10V to +10V for LNO (see legends). Dashed black curves in plots (a)-(b) correspond to $V = \pm 10$ mV. Before heating the FE was homogeneously polarized. Other parameters are the same as in Fig. 5.

The temperature dependence of the effective local electromechanical response d_{33}^{eff} , which determines the PFM response, can be calculated from the expression

$$d_{33}^{eff}(x,V) = \frac{dU_3(x,V)}{dV} \approx \frac{U_3(x,V+\delta V) - U_3(x,V-\delta V)}{2\delta V},$$
(4)

where δV must be very small (e.g., not more than several mV). FEM results are shown in **Fig. 7**.

Note that the temperature dependences look very different for SPS [Fig. 7(a)] and LNO [Fig. 7(b)]; and for SPS we can expect more strong dependence on the temperature and applied voltage.

In particular, the temperature dependence of d_{33}^{eff} for SPS has a diffuse maximum (or break) at about $\Delta T_{cr} = 85$ K indicating on the temperature-induced local paraelectric transition under the heated tip. Since SPS surface displacement for positive and negative voltages becomes rather close with temperature increase [**Fig. 6(a)**], their voltage derivatives are also close, but have different signs and demonstrate a noticeable break at ΔT_{cr} for $V = \pm 0.1$ V and 0.1 V [see dashed curves in **Fig. 7(a)**].

The temperature-induced local paraelectric transition is absent for LNO for all voltages (see black, blue and brown curves in **Fig. 7(b**)), except for 5 and 10 V (see pink and red curves in **Fig. 7(b**)). A sufficiently high positive voltage, $V \ge 5$ V, leads to the local polarization reversal under the tip, and the further increase of nanodomain length leads to its breakdown through the sample depth. In this case, the contributions of reversed polarization and thermal expansion to the local surface displacement have different signs. The sign of the d_{33}^{eff} does not change in comparison with a uniformly polarized medium for a small nanodomain, but the slope of its temperature dependence changes due to the influence of the nanodomain walls [see the red curve in **Fig. 7(b**)]. For $V \ge 10$ V effective piezoelectric response change its sign with voltage increase due to the nanodomain lateral and vertical growth [see the pink curve in **Fig. 7(b**)].



FIG. 7. Effective response d_{33}^{eff} versus ΔT calculated under the heated tip (centered at x=0). Different curves are calculated for different voltages *V* varying from -1V to +1V for SPS, and from -10V to +10V for LNO (see legends). Before heating the FE was homogeneously polarized. Other parameters are the same as in **Fig. 5.**

C. Approximate analytical description of the local electromechanical response

Finally, we analyze the image formation mechanism in the thermal PFM can be considered within a continuous medium approach, which offers possibilities for analytical calculations in various ferroics within e.g., decoupling approximation [57, 58] well-elaborated for classical FEs [49]. Here, PFM response has several contributions coming from the thermal expansion, flexoelectric, and electrostriction including thermopolarization and piezoelectric effects [see Eq.(3a)]. At that the piezoelectric effect is a derivative of the electrostriction term [see comments to Eq.(3a)]. Below we analyze and list approximate expressions for all these contributions.

The <u>thermoelastic contribution</u> to the surface displacement comes from the inhomogeneous thermal expansion of the FE caused by the contact with a heated tip. The contribution is

proportional to the specific integral convolution of the material thermal expansion tensor β_{ij} with the temperature variation. For the temperature excess given by a uniformly heated disk, the vertical displacement of the FE surface caused by the thermoelastic effect is given by expression:

$$U_{3}^{TE}(r) = \Delta T \frac{\beta_{11}(1+4\nu)+3\beta_{33}}{2\pi} \arcsin\left(\frac{2R}{|r-R|+|r+R|}\right),$$
(5)

where the factor ν is the Poisson ratio. Expression (5) is derived in **Appendix A** in [29]. As it was expected, the magnitude of the thermoelastic contribution to PFM response is proportional to the tip temperature variation ΔT and thermal expansion coefficients combination $\beta_{11}(1 + 4\nu) + 3\beta_{33}$. The thermoelastic effect is voltage-independent, and the spatial region of its maximal values is $r \leq R$, so the contribution is not responsible for the wide region $r \gg R$ of U_3 changes. Since the thermoelastic effect is voltage-independent, it does not contribute to the PFM signal detected via the lock-in or band-excitation [59] detection.

In decoupling approximation, the <u>electrostriction contribution</u> to the surface displacement is proportional to the integral convolution of the local term $Q_{ijkl}P_k(\mathbf{r})P_l(\mathbf{r})$ with elastic Green function (see **Appendix A** in **Suppl. Mat**. [29] and Refs. [49], [60], and [61]). The displacement profile complexly depends on the temperature profile due to the integration. The following Padeapproximation can be used for semi-quantitative analysis of the FEM data:

$$U_{3}^{EL}(r) \sim Q \, \frac{2\pi R^2 h}{\sqrt{R^2 + \varepsilon r^2}} P_3^2(r). \tag{6a}$$

Here *Q* is the combination of electrostriction coefficients and elastic constants, ε is the fitting parameter varying in the range $0 \le \varepsilon \ll 1$. Hence, the denominator $\sqrt{R^2 + \varepsilon r^2}$ has a diffuse maximum in the region $r \gg R$. In order to obtain a simple expression for $P_3^2(r)$, let us regard $\beta > 0$ and neglect γ in Eq.(2b). The amplitude of the FE polarization is proportional to,

$$P_{3}(r) \sim \mu \frac{dT}{dZ} + \chi V + \sqrt{\frac{\alpha_{T}}{\beta}} \begin{cases} \sqrt{T_{C} - T_{0} - \epsilon \Delta T}, & T_{C} - T_{0} \ge \epsilon \Delta T, \\ 0, & T_{C} - T_{0} < \epsilon \Delta T, \end{cases}$$
(6b)

where the fitting parameters are μ , χ and ϵ ; and $0 \le \epsilon < 1$. The first term originates from the thermopolarization effect, the second term is proportional to the tip voltage and dielectric susceptibility χ , and the third term is the spontaneous polarization.

Using a disk-plane model of the tip-surface contact, the <u>piezoelectric contribution</u> to the vertical PFM response from a <u>homogeneously polarized</u> FE region is [31]:

$$d_{33}^{eff} = \frac{dU_3}{dV} \approx \left(\frac{1}{4} + \nu\right) d_{31} + \frac{3}{4} d_{33} + \frac{d_{15}}{4}.$$
 (7a)

The expression (7a) is valid for a "cold" PFM response. For the heated tip the effective piezoelectric coefficients d_{ij} are dependent on the distance from the tip apex r. They can be estimated in the local approximation:

$$d_{ij}(r) \cong d_{ij3}^0 \chi P_3(r), \tag{7b}$$

Expressions (7) are valid is the case of very smooth polarization changes under the tip and for small heating, e.g., at $\epsilon \Delta T \ll T_C - T_0$.

V. CONCLUSION

Here we explored the solution of a thermo-elastic-electric problem fully coupled with the Landau-Ginzburg-Devonshire description of ferroic properties on examples of two different types of uniaxial FEs: a "soft" ferroelectric SPS with a relatively low bulk Curie temperature T_C <350 K and relatively small coercive field, and a "hard" ferroelectric-pyroelectric LNO with a high T_C >1000 K and ultra-high coercive field. The solution is used to analyze the signal formation mechanisms of tPFM.

The temperature-induced polarization redistribution and local electromechanical response occurring in uniaxial FEs under the heated PFM tip strongly depend on the material parameters and, surprisingly, reveal very different sensitivity to the temperature T and tip voltage V. Specifically, for a soft ferroelectric the tip overheating of 30°C above T_C leads to the local paraelectric transition in the nanoscale region at V = 0. The tip-induced nucleation of a nanodomain and its subsequent breakdown through the film depth occurs at very low voltages V~ (10 - 100) mV. The contribution of the thermopolarization effect to the local electromechanical response of the soft ferroelectric appears very important.

For a hard ferroelectric the tip overheating well above T_C of more than 100 K is required to induce the local paraelectric transition at V = 0, but such strong overheating can rather melt the ferroelectric. The nucleation of a spike-like nanodomain occurs at high tip voltages V~(5 – 10) V. The contribution of the thermopolarization effect to the local electromechanical response of the hard ferroelectric is less significant than that for a soft ferroelectric. As anticipated, tPFM response is not very sensitive to the flexoelectric effect in both types of FEs, and the response is determined by the piezoelectric and electrostriction contributions.

Overall, tPFM opens a pathway for probing local temperature-induced phase transitions in ferroics, exploring the temperature dependence of polarization dynamics in FEs, and can potentially discover phenomena driven by strongly coupled temperature and electric field

gradients. Also, tPFM is a promising tool for the exploration of the temperature-induced nanoscale phase transitions in ferroics, such as ferroelectrics, antiferroelectrics, quantum paraelectrics and related materials.

Authors' contribution. A.N.M. and S.V.K. stated the problem, interpreted theoretical results and wrote the manuscript draft. A.N.M. propose the mathematical model and performed analytical calculations, E.A.E. performed FEM. K.K. worked on the manuscript improvement and results interpretation.

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