Lamellar Fluctuations Melt Ferroelectricity

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We consider a standard Ginzburg-Landau model of a ferroelectric whose electrical polarization is coupled to gradients of elastic strain. At the harmonic level, such flexoelectric interaction is known to hybridize acoustic and optic phonon modes and lead to phases with modulated lattice structures that precede the state with spontaneously broken inversion symmetry. Here, we use the self-consistent phonon approximation to calculate the effects of thermal and quantum polarization fluctuations on the bare hybridized modes to show that such long-range modulated order is unstable at all temperatures. We discuss the implications for the nearly ferroelectric $SrTiO_3$ and $KTaO_3$, and we propose that these systems are melted versions of an underlying modulated state that is dominated by nonzero momentum thermal fluctuations except at the very lowest temperatures.

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A ferroelectric (FE) material is defined by spontaneously broken inversion symmetry, usually due to a small and coherent displacement of atoms within the unit cell and hence a spontaneous electrical polarization $\boldsymbol{P}$ [1]. Because lattice displacements generate the order, the homogeneity of the polarization depends on coupling between neighboring unit cells, and over longer distances by a continuous elastic strain $\boldsymbol{\epsilon}$. In a cubic (or other high symmetry FE) the principal order parameter (OP) $\boldsymbol{P}$ belongs to a different irreducible representation from the strain fields at zero wave vector ($\boldsymbol{q} = 0$). This means that the leading order electrostrictive coupling in a uniform Landau theory for the free energy is bilinear in polarization and linear in strain [i.e., $\mathcal{O}(\epsilon P^2)$]. However, there is also a well-known *flexoelectric* coupling [2–5] [i.e., $\mathcal{O}(P\nabla\epsilon)$], which is allowed by symmetry in all insulators and gives rise to modulated incommensurate phases within a harmonic theory, provided that the coupling is big enough [6–11]. Being a harmonic interaction, flexoelectricity is in principle more relevant than the nonlinear electrostrictive coupling, and it is the focus of this Letter.

The materials $SrTiO_3$ (STO) and $KTaO_3$ (KTO) have long been cited as examples of quantum paraelectrics (QPEs). In both cases, the dielectric constant follows a Curie-Weiss (CW) law divergence with a finite-temperature intercept, yet at low temperatures saturates at extremely large values [12], and there is no FE phase transition. The idea that quantum tunneling of domains in a mean-field like (and massive) system has already grown to be very large before quantum effects take over is disconcerting and has, over the years, generated considerable interest in the general theory of a FE quantum critical point [13–21].

Recent experiments, however, have revealed phase diagrams and lattice dynamics in STO and KTO which cannot be explained by our current understanding of these materials [22]. Specifically, measurements of the dielectric response have found several crossovers (specially seen under pressure) [23–26], and very significantly, inelastic neutron scattering experiments observe softening of a transverse acoustic (TA) mode at a small but finite wave vector in STO ($\simeq$0.025 rlu) [27] and at a larger one in KTO ($\simeq$0.1 rlu) [7]. The latter results are consistent with momentum-resolved electron energy-loss spectroscopy [28] and a previous neutron scattering study [29] which show an unusual softening of the TA branch, and with a first-principle simulation [30] which found a dip in the acoustic dispersion.

Soft acoustic phonons with a minimum at a finite wave vector are characteristic of systems approaching a structural instability corresponding to the onset of a long-wavelength

modulation [32,33], and can be understood as the consequence of level-repelling hybrid modes associated with a sufficiently large coupling between a primary OP (e.g., polarization) and gradients of a secondary OP (e.g., strain) [34]. However, harmonic and mean-field solutions of such models [6–11] predict the condensation of the low energy branch at a finite wave vector $\boldsymbol{q}_{\mathrm{mod}}$, thus leading to a modulated phase that is not observed in STO and KTO. Nor can these solutions generate crossovers.

Here, we invoke a well-known model of flexoelectricity [2–5] and, crucially, solve it within the self-consistent phonon approximation (SCPA) in order to account for thermal and quantum fluctuations of polarization of the disordered phase. We show that in the presence of purely thermal fluctuations, the phase space for orientational fluctuations is large enough that the modulated transition is suppressed to zero temperature, and that by including zero-point quantum fluctuations, the correlation length will remain finite even at absolute zero. We estimate the parameters in comparison to KTO and STO, and we find reasonable agreement with a model where the flexoelectric coupling is close to the classical critical value for the onset of a modulated phase. Our analysis suggests that the putative QPE phase of STO and KTO is largely explained by classical thermal-modulated fluctuations, and there is a second crossover to a regime dominated by quantum fluctuations at much lower temperature. However, the quantum regime in our theory does not require macroscopic quantum tunneling, and instead arises more trivially due to zero-point occupation of orientational zero modes. In the light of these results, we propose that STO and KTO are incipient modulated dielectrics with incommensurate order caused by the coupling of polarization and strain inhomogeneity. In the underlying ordered phase, the rotational symmetry of the crystal is broken as well as its translational symmetry, but only in one direction ($\boldsymbol{q}_{\mathrm{mod}}$). This would lead to intertwined stripe order parameters where the polarization and elastic strain are periodic with a wave vector $\boldsymbol{q}_{\mathrm{mod}}$ [32]. Such stratified ordering resembles the structural organization of the "lamellar" or "smectic" phases in liquid crystals: a nearly periodic array of parallel layers of polarizable molecules that do not possess long-range positional order within a layer [35]. In a smectic, the director vector $\boldsymbol{n}$ points orthogonal to the planar lamellae, as does here the wave vector $\boldsymbol{q}_{\mathrm{mod}}$. Lastly, we comment on lacunae in the model, the most important of which is the neglect of crystal anisotropy and compositional disorder. We expect anisotropy to lead to an ordered (striped) phase at low enough temperatures, and disorder to a glassy frozen version of the same. Both of these effects can suppress the quantum regime. We also suggest experiments to further test our proposed picture.

We consider an isotropic polarizable, elastic medium with a polarization OP $P_\alpha(\boldsymbol{x})$ and a linear strain $\epsilon_{\alpha\beta}(\boldsymbol{x}) = (1/2)(\partial u_\alpha/\partial x_\beta + \partial u_\beta/\partial x_\alpha)$ as a secondary OP in which $u_\alpha(\boldsymbol{x})$ is the displacement field due to long-wavelength acoustic phonons ($\alpha, \beta = 1, 2, 3$). $P_\alpha(\boldsymbol{x})$ is associated with a soft transverse optic (TO) mode, the condensation of which leads to the FE transition. We propose a Ginzburg-Landau Hamiltonian that is a sum of three terms: for the polarization H_{pol}, the elastic modes H_{elastic}, and the flexoelectric coupling H_{flexo} [3],

$$H = H_{\mathrm{pol}} + H_{\mathrm{elastic}} + H_{\mathrm{flexo}},$$

where

$$H_{\mathrm{pol}} = \frac{1}{2}\int d^3x d^3x' \sum_{\alpha,\beta} U_{\alpha\beta}(\boldsymbol{x},\boldsymbol{x}') P_\alpha(\boldsymbol{x}) P_\beta(\boldsymbol{x}') + u\int d^3x \sum_{\alpha,\beta} P_\alpha^2(\boldsymbol{x}) P_\beta^2(\boldsymbol{x}),$$

$$H_{\mathrm{elastic}} = \frac{1}{2}\int d^3x \sum_{\alpha,\beta,\gamma,\lambda} C_{\alpha\beta\gamma\lambda}\epsilon_{\alpha\beta}(\boldsymbol{x})\epsilon_{\gamma\lambda}(\boldsymbol{x}),$$

and

$$H_{\mathrm{flexo}} = \frac{1}{2}\int d^3x \sum_{\alpha\beta\gamma\lambda} f_{\alpha\beta\gamma\lambda}\left[\epsilon_{\beta\gamma}(\boldsymbol{x})\frac{\partial P_\alpha(\boldsymbol{x})}{\partial x_\lambda} - P_\alpha(\boldsymbol{x})\frac{\partial \epsilon_{\beta\gamma}(\boldsymbol{x})}{\partial x_\lambda}\right].$$

Here, $U_{\alpha\beta}(\boldsymbol{x},\boldsymbol{x}') = r\delta_{\alpha\beta}\delta(\boldsymbol{x}-\boldsymbol{x}') + F_{\alpha\beta}(\boldsymbol{x},\boldsymbol{x}')$ is the bare propagator of the optic phonons, and $F_{\alpha\beta}(\boldsymbol{x},\boldsymbol{x}')$ is the dipole tensor with Fourier transform $F_{\alpha\beta}(\boldsymbol{q}) = cq^2\delta_{\alpha\beta} + g_0(q_\alpha q_\beta/q^2) - h_0 q_\alpha q_\beta$ [36]. $C_{\alpha\beta\gamma\delta}$ is the elastic constant tensor, $f_{\alpha\beta\gamma\lambda}$ is the flexocoupling tensor, and $r = r_0(T - T_0)$ where T_0 is the mean-field transition temperature to a homogeneous FE state at $f_{\alpha\beta\gamma\lambda} = 0$.

In the absence of flexoelectric coupling and nonlinearities ($u = 0$), the phonon excitations of H are well known: there are two doubly-fold degenerate TO and TA modes with (squared) frequencies $\omega_{\mathrm{TO}}^2(\boldsymbol{q}) = r + cq^2$ and $\omega_{\mathrm{TA}}^2(\boldsymbol{q}) = (\hbar^2 C_s/\rho)q^2$, respectively, and two singly degenerate longitudinal optic (LO) and acoustic modes with (squared) frequencies $\omega_{\mathrm{LO}}^2(\boldsymbol{q}) = r + g_0 + (c + h_0)q^2$ and $\omega_{\mathrm{LA}}^2(\boldsymbol{q}) = \{\hbar^2[C_v + (4/3)C_s]/\rho\}q^2$, respectively. C_v and C_s are the bulk and shear elastic moduli, respectively, and ρ is the density of the solid.

We focus on the hybrid transverse modes only, as the level repulsion is significantly weaker in the longitudinal branches due to the large depolarizing fields of FEs, which gap the LO excitations. Moreover, flexoelectricity does not mix the transverse and longitudinal excitations in isotropic media, as shown in the Supplemental Material, Sec. 1 [37].

We now discuss our results. Figure 1(a) shows schematics of the phase boundary (PB) computed from the condensation of the bare modes ($u = 0$) in the parent phase (see the Supplemental Material, Sec. 1) [37]. For small

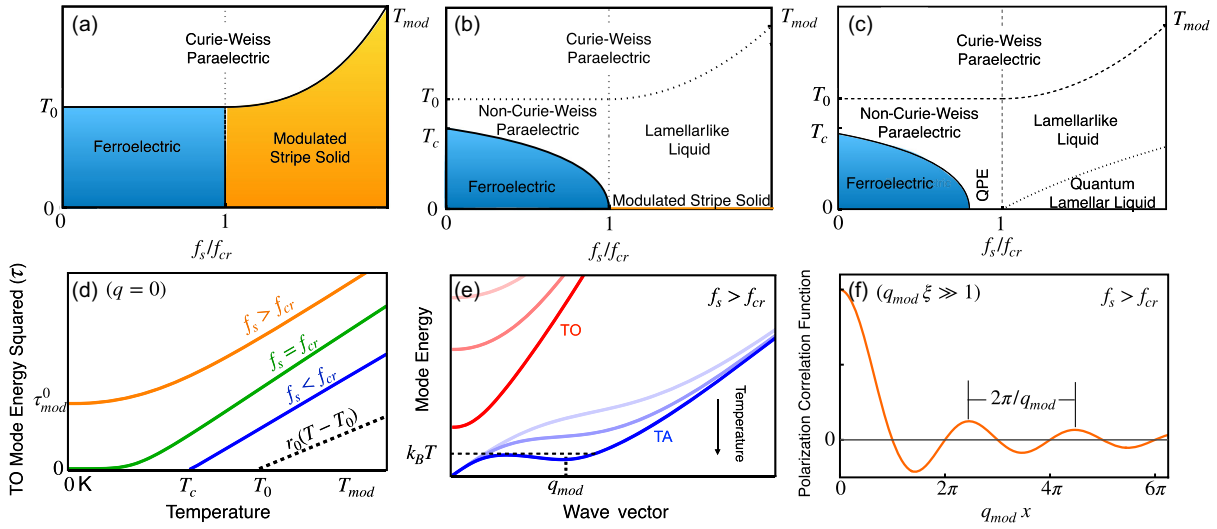

FIG. 1. Phase boundaries in the (a) harmonic approximation and in the self-consistent phonon approximation (SCPA) (b) ignoring and (c) including quantum fluctuations of polarization. (d) SCPA schematics of the temperature dependence of the zone-center hybrid TO mode and the (e) hybrid TA and TO phonon dispersions in the disordered phase. (f) Schematic correlation function of polarization in the lamellarlike liquid with correlation length ξ [see Eq. (1)]. QPE = quantum paraelectric.

shears of the flexocoupling tensor ($f_s < f_{cr} = \sqrt{cC_s}$), the soft zone-center TO mode condenses at a transition temperature which is independent of f_s and equal to T_0, thus leading to a FE transition. For large flexoelectric shears ($f_s > f_{cr}$), a soft minimum develops at a nonzero wave vector $\boldsymbol{q}_{\rm mod}$ of the TA branch, which upon condensation at a temperature $T_{\rm mod} > T_0$, would lead to the modulated phase with coupled strain and polarization OPs that are periodic with a wave vector $\boldsymbol{q}_{\rm mod}$ [32]. The zone-center TO mode remains gapped with energy squared $\tau^0_{\rm mod} \equiv r_0(T_{\rm mod} - T_0)$. At $f_s = f_{cr}$, $\boldsymbol{q}_{\rm mod} = 0$ and both the TO and TA modes condense $T_{\rm mod} = T_0$.

We now assess the stability of the bare PB. Near above T_0 and $T_{\rm mod}$ and in the classical limit, the local correlation functions of polarization are approximately given as follows, $\langle \boldsymbol{P}^2 \rangle_0 \propto 1 - b(T - T_0)^{1/2}$ for $f_s < f_{cr}$, $\langle \boldsymbol{P}^2 \rangle_0 \propto (T - T_0)^{-1/4}$ for $f_s = f_{cr}$ $\langle \boldsymbol{P}^2 \rangle_0 \propto (T - T_{\rm mod})^{-1/2}$ for $f_s > f_{cr}$, where $\langle \ldots \rangle_0$ denotes thermal average at the Gaussian level and b is a constant (see the Supplemental Material, Sec. 2) [37]. The PB is thus strongly modified by the inclusion of fluctuations: while the FE transition prevails at T_0, the long-range modulated phase change is unstable, except at absolute zero where $\langle \boldsymbol{P}^2 \rangle_0 = 0$.

We now consider nonlinearities ($u > 0$) in the SCPA (see the Supplemental Material, Sec. 3) [37]. We first discuss the impact of thermal fluctuations alone and then introduce quantum effects. Figure 1(b) shows the purely classical PB. For $f_s < f_{cr}$, the coupling to finite-momentum elastic fluctuations suppresses the FE transition temperature and leads to a thermal regime where the square of the soft zone-center TO frequency τ (or equivalently the inverse dielectric constant) separates from the CW law behavior, as shown in Fig. 1(d). For $f_s > f_{cr}$, the bare PB turns into a crossover. This is illustrated best by the SCPA dispersions shown in Fig. 1(d). As mentioned above, the bare coupled acoustic mode softens to zero at a nonzero momentum $\boldsymbol{q}_{\rm mod}$. However, in an isotropic theory such as ours, only the modulus of $\boldsymbol{q}_{\rm mod}$ is determined but not the direction. The phase space for fluctuations in the direction of $\boldsymbol{q}_{\rm mod}$ lies on the surface of a sphere of one dimension less than the physical dimension. This all but guarantees that thermal fluctuations at any finite temperature will disorder the direction, so there will be no long-range stripe order. This is very analogous to fluctuating laminar or nematic soft matter systems [35]. Consequently, the harmonic transition in Fig. 1(a) becomes a crossover in Fig. 1(b), and the acoustic excitations in the vicinity of $\boldsymbol{q}_{\rm mod}$ acquire a gap, as seen in Fig. 1(e). The polarization correlations of the melted phase are quasisinusoidal functions attenuated by an exponentially decaying envelope with a correlation length $\xi \propto (\tau - \tau^0_{\rm mod})^{-1/4}$ much longer than the period of the modulation, i.e.,

$$\langle \boldsymbol{P}(\boldsymbol{x}) \cdot \boldsymbol{P}(\boldsymbol{0}) \rangle \sim e^{-x/(2q_{\rm mod}\xi^2)} \sin(q_{\rm mod}x)/(q_{\rm mod}x) \qquad (1)$$

where $q_{\rm mod}\xi \gg 1$, $x = |\boldsymbol{x}|$ and $q_{\rm mod} = |\boldsymbol{q}_{\rm mod}|$ (see the Supplemental Material, Sec. 3) [37]. This is schematically shown in Fig. 1(f). Upon cooling, ξ would grow as τ approaches $\tau^0_{\rm mod}$ [Fig. 1(d)] and diverge at absolute zero, thus restoring the long-range stripe order, as shown in Fig. 1(b).

We now assess the effects of quantum polarization fluctuations. In our model, the nonlinearity of the theory is controlled by the quartic coefficient u, as shown in Fig. 2. For $f_s = 0$, the FE transition temperature drops approximately linearly in u, vanishing at a quantum critical

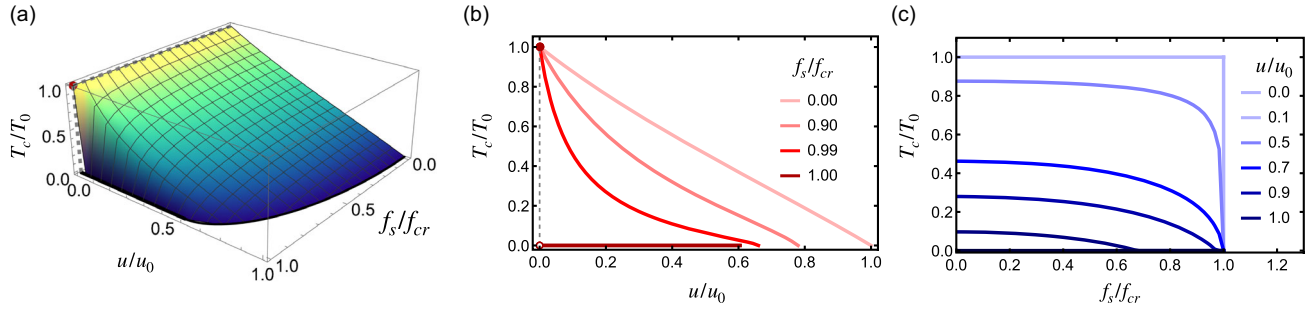

FIG. 2. (a) Dependence of the ferroelectric transition temperature T_c on the flexoelectric shear coupling constant f_s and the quartic anharmonic coefficient u of the polarization. (b)–(c) Cross-sections of (a) in the $T_c - u$ and $T_c - f_s$ planes, respectively. u_0 is the value of u at $T_c = 0$ K and $f_s = 0$.

point. For $0 < f_s < f_{cr}$, the critical nonlinearity is reduced, and there is a more substantial parameter regime where quantum fluctuations alone destroy the transition and lead to the standard QPE phase, as it is shown in Fig. 1(c). This is consistent with the much larger phase space for orientational fluctuations when the long-range modulated order would be at finite $\boldsymbol{q}$.

For $f_s > f_{cr}$, the zero-point fluctuations keep the energy gap at $\boldsymbol{q}_{\mathrm{mod}}$ open even at absolute zero, thus destabilizing the classical $T = 0$ K transition shown in Fig. 1(b). In addition, the temperature at which the quantum fluctuations become relevant marks another crossover in the spectrum, where the correlation length will saturate. This occurs when $k_B T$ is comparable to the energy of the excitations around $\boldsymbol{q}_{\mathrm{mod}}$, as shown in Fig. 1(e). So, for $f_s > f_{cr}$ we predict that there will be two crossovers as T is lowered, and no long-range stripe order, as shown in Fig. 1(c). When zero-point quantum fluctuations are included, the only ordered phase that we find is ferroelectricity. But outside the envelope shown in Fig. 2(a) and for $f_s > f_{cr}$, we expect the lamellarlike fluctuations to have very long-range correlation.

We now compare to STO and KTO. Table S1 in the Supplemental Material, Sec. 4, gives the values for the model parameters, which for the most part were taken from the literature while others were obtained from experimental data, e.g., f_s was fitted to the reported TA anomalies (0.025 rlu for STO [27], and 0.1 rlu for KTO [7]). For both materials, we find agreement between the calculated and measured temperature dependence of the TO frequency, as shown in Figs. 3(a) and 3(b). We note the apparent kink in the calculated frequencies is a consequence of the small values of u in our parametrization. As shown in the Supplemental Material, Sec. 3 [37], τ is a smooth function of T at all temperatures. Figures 3(c) and 3(d) show the calculated and observed phonon dispersion curves. While our model and parametrization overestimate the repulsion between the TA and TO branches, it generates a minimum at a finite q in the hybrid acoustic dispersion while preventing symmetry breaking down to the lowest temperatures, as observed in experiments [7,27]. We stress that no such behavior occurs for $f_s \leq f_{cr}$, nor could we obtain a physically reasonable parametrization in this regime (see the Supplemental Material, Sec. 4) [37]. We attribute the quantitative discrepancies to ignoring crystal anisotropy (e.g., low temperature STO is tetragonal while KTO is cubic), broadening, nonzero lifetimes, electrostriction, and coupling to other lattice modes (e.g., rotations of the TiO_6 octahedra). Our fits place both materials in the liquid phase of Fig. 1(c) ($f_s/f_{cr} = 1.17$ for STO and $f_s/f_{cr} = 1.12$ for KTO). Of course, these values should be taken as rough estimates, as our simplified model, approximate solution, and currently available experimental data prevent us from determining f_s precisely. Nonetheless, they show that both materials are near a modulated instability.

This point connects to a long debate about the nature of the FE phase transition as "displacive" or "order-disorder" [50,51]. Polar nanodomains are clearly seen at room temperature in strained films of STO, though their presence has been attributed to long-range Coulomb forces rather than strain [52]. Nuclear magnetic resonance (NMR) is a technique that is sensitive to local charge disproportionation and electric field gradients, and was useful in identifying charge-density waves in transition metal dichalchogenides, even when not fully ordered [53,54]. NMR measurements on STO [55] have been interpreted in terms of dynamic fluctuations of the Ti ion into off-center sites coupled in a biased way to elongations of the unit cell; however the length scale of this correlation could not be determined, and the measurements did not go below 25 K. *Ab initio* calculations of STO [56] concluded that quantum lattice fluctuations are necessary to stabilize the PE phase—but spatially modulated phases were not considered in that work. Modulated phases could also be in principle seen in *ab initio* calculations, albeit using very large supercells. In that context, recent calculations [57,58] predict that STO and cubic $BaTiO_3$ should be polymorphic at $T = 0$ K, with a disordered arrangement of off-site Ti distortions. A disordered ground state at absolute zero violates the third law, and perhaps is associated instead with not matching the supercell to the natural incommensurate period.

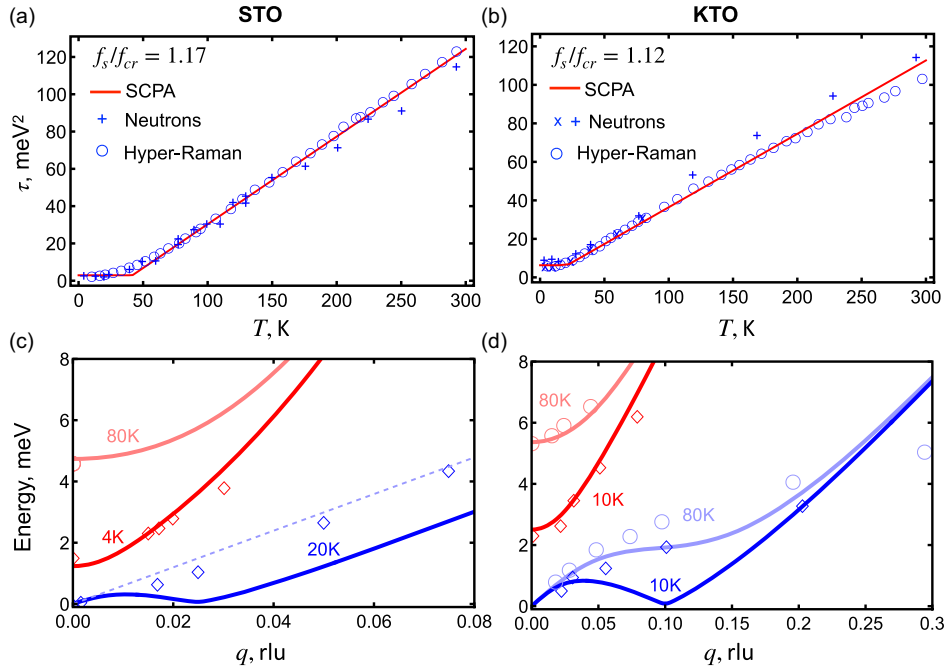

FIG. 3. (a),(b) Calculated temperature dependence of the zone center hybrid TO mode compared to neutron [46–48] and hyper-Raman [49] scattering experiments. (c),(d) Calculated dispersion of the hybrid TA and TO phonons (solid lines) compared to neutron scattering experiments (circles and diamonds) [27,48]. Dashed line in (c) is the bare linear TA dispersion for $f_s = 0$ with a sound velocity of 4800 m/s (as shown in Ref. [27] for comparison). Model parameters are given in Table S1 of the Supplemental Material, Sec. 4 [37].

We now discuss our simplifying approximations. We have ignored crystal anisotropy, in which case the orientational modes will have a preferred direction. Once the temperature becomes considerably smaller than the anisotropy in the spectrum, the phase space volume of critical fluctuations will be reduced, which may lead to the stabilization of the incommensurate phase, as with quartz [59] (though nonlinearities could also lock in the modulation to a commensurate wave vector, as with $PbZrO_3$ [60]). Compositional disorder will also break the $\mathcal{O}(3)$ symmetry and should be expected to lead to a glassy phase where orientational fluctuations are frozen. This is a familiar situation in charge-density-wave systems, where impurities and disorder pin its OP and generate a strongly nonlinear response to applied electric fields [61,62]. Our finding that STO should be near a modulated instability is in stark contrast with *ab initio* calculations [63], which suggest that $f_s/f_{cr} \simeq 0.7$ at most. However, we are using a phenomenological continuum theory where the parameters are determined from experiment (but nonetheless can make explicit predictions because the number of parameters is small). We cannot assert that the parameters can be directly calculated from harmonic microscopic theory because we have already coarse grained to a scale of many unit cells, so that, for example, twin boundaries and defect structures have been integrated over [64]. The difference between parameters obtained from macroscopic fits and those determined by microscopic calculations hints at some mesoscale physics to be unearthed.

Our self-consistent solution of the model implicitly assumes that in the melted phases, the amplitudes of fluctuations are small. Beyond this regime, electrostrictive couplings which are effectively quartic in the primary OP will be important. These would not only enhance the anisotropy at least at very long length scales, but also effectively soften the sound velocity and hence enhance the flexoelectric effect. In a strong coupling theory, the model would become one of quasiperiodic FE domains separated by fluctuating, sharp domain walls. In a better theory, the modes would acquire a linewidth, as seen in experiment. This is an interesting matter for future exploration, but we expect that the qualitative features of our theory should survive.

We conclude that a strong enough flexoelectric coupling and purely thermal fluctuations of polarization can mimic quantum paraelectricity by saturating the low-temperature dielectric constant. In an isotropic system, the divergent orientational fluctuations suppress ordering even at low temperatures, so that one should expect a series of crossovers upon cooling: from a high-temperature CW law to a classical fluctuating lamellar phase to a quantum lamellar phase, and finally to a striped phase when crystal anisotropy becomes important. Such a sequence of crossovers is consistent with those identified from dielectric measurements in STO [23,24], and labeled as classic CW paraelectric, "quantum critical," "quantum paraelectric," and "quantum polar-acoustic." The standard theory of quantum ferroelectric criticality [22] does not predict the

existence of the lowest crossover. Our model is consistent with the experiments of Fauqué *et al.* [27] showing a 40% softening of the TA mode at the longest wavelength measured, down to 20 K, with no resolvable signal below that temperature. Coak *et al.* [23] ventured that a loss peak seen in their data might be ascribed to quantum fluctuations of domain walls. The quantum regime of our theory does not require tunneling of heavy atoms through potential barriers, but is simply zero-point physics in a quasiharmonic well. As a further test, measurements of the dynamical structure factor $S(\boldsymbol{q},\omega)$ would detect fluctuations associated with the melting of the modulated phase. $S(\boldsymbol{q},\omega)$ has been measured by neutrons and x rays in STO [29,31,47] and KTO [7,48], but more data are needed to clearly resolve any dips along their acoustic branches. Finally, we note our model could be adapted to study oxide membranes [65] and could be relevant to superconductivity in doped STO [66].

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