Pressure dependence of ferroelectric quantum critical fluctuations

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Phase transitions to a long-range-ordered state driven by a softened phonon mode are ubiquitious across condensed matter physics, but the evolution of such a mode as the system is tuned to or from the transition has never been explictly measured until now. We report for the first time the effect of pressure on the soft mode associated with ferroelectricity in the archetypal quantum critical paraelectric $SrTiO_3$. This is an ideal, clean, model system for exploring these effects, with pressure directly addressing the phonon modes only. We measure and report the effect of quantum critical fluctuations on the pressure and temperature dependence of the ferroelectric soft phonon mode as the system is tuned away from criticality. We show that the mean field approximation is confirmed experimentally. Furthermore, using a self-consistent model of the quantum critical excitations including coupling to the volume strain and without adjustable parameters, we determine logarithmic corrections that would be observable only very close to the quantum critical point. Thus, the mean-field character of the pressure dependence is much more robust to the fluctuations than is the temperature dependence. We predict stronger corrections for lower dimensionalities. The same calculation confirms that the Lydanne-Sachs-Teller relation is valid over the whole pressure and temperature range considered. Therefore, the measured dielectric constant can be used to extract the frequency of the soft mode down to 1.5 K and up to 20 kbar of applied pressure. The soft mode is observed to stiffen further, raising the low-temperature energy gap and returning towards the expected shallow temperature dependence of an optical mode. This behavior is consistent with the existence of a ferroelectric quantum critical point on the pressure-temperature phase diagram of $SrTiO_3$, which applied pressure tunes the system away from. This work represents the first experimental measurement of the stiffening of a soft phonon mode as a system is tuned away from criticality, a potentially universal phenomenon across a variety of phase transitions and systems in condensed matter physics.

INTRODUCTION

The incipient ferroelectric $SrTiO_3$ has been studied in great detail and is used as a dielectric or an insulating substrate in many applications [1–7] as it possess an anomalously high dielectric constant at low temperatures. $SrTiO_3$ is the clearest example of a quantum paraelectric known. The nature of the quantum paraelectric state has been an open question since Barrett [1] first attempted to describe the deviation from Curie-Weiss behavior observed in $SrTiO_3$. Recently, progress has been made [8] in describing this state but the effect of fluctuations on the pressure dependence has not been considered until this work.

$SrTiO_3$ has a cubic perovskite structure at room temperature with a well-documented antiferrodistortive transition at around 110 K [9], below which the unit cell is tetragonal. The dielectric constant, ϵ_r, of $SrTiO_3$ exhibits a classical Curie-Weiss temperature dependence at high temperatures [4], but departs from the Curie-Weiss behavior as the polarization is modified by quantum fluctuations below 50 K, and no ferroelectric ordering is observed. The system remains close to long-range order through a displacive ferroelectric transition, but the transition does not occur in pristine $SrTiO_3$. The polarisation is due to the ionic motion of a transverse optical phonon mode, which softens to approach zero energy at low temperature at the zone center Γ point. This mode, commonly described as the 'soft mode' or 'ferroelectric mode' corresponds to opposing motion of the oxygen octahedra and titanium ions along the c-axis [2, 10]. Inelastic neutron scattering experiments by Yamada et al. [11] have shown however that the soft mode is 'frozen out' at low temperatures - instead of falling to zero the phonon energy flattens out to a fixed value or gap Δ as temperature is decreased below 50 K. This means that spontaneous long-range ferroelectricity does not form, but a low-energy excitation into short range charge ordering is available to the system, leading to the very large polarizability and departures from classical predictions seen at low temperatures [5]. These phenomena have been linked to a postulated ferroelectric quantum critical point (QCP) at the equivalent of a small 'negative pressure' on $SrTiO_3$'s pressure-temperature phase diagram (Fig. 1) - quantum critical fluctuations of the polarization in the vicinity of this point lead to a modified dependence of

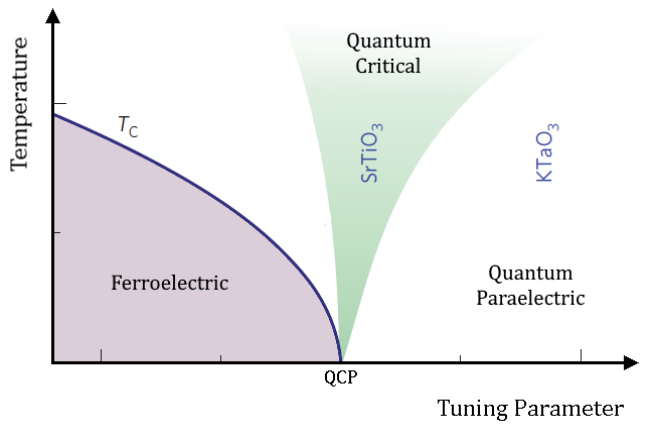

FIG. 1. Predicted phase diagram for $SrTiO_3$ and related compounds [19]. The 'tuning parameter' can be realized through either chemical doping or substitution, or by applying pressure to tune the frequencies of the phonon oscillators. $SrTiO_3$ sits naturally slightly to the right of a quantum critical point on this diagram, and pressure serves to push it further away from the quantum critical region and towards the behavior of $KTaO_3$.

the dielectric properties. The application of strain [12], or the substitution of a heavier oxygen isotope to form $SrTi^{18}O_3$ [13, 14], which both have the opposite effect on the system to applying pressure, lead to a ferroelectric phase, consistent with this QCP. Our recent work [8] has shown through detailed measurements of the dielectric constant under pressure that $SrTiO_3$ is driven away from its quantum critical regime by the application of pressure. The dielectric response was in addition seen to match that seen in $KTaO_3$ at elevated pressures, in agreement with the position on the pressure/doping phase diagram postulated for this material (Fig. 1). Additionally, the dielectric loss in $SrTiO_3$ is dominated by a series of peaks at characteristic temperatures. The largest of these peaks, at approximately 10 K, is associated with quantum fluctuations. Recent work [15] suggests that this peak reflects a localized excitation formed of quantum fluctuations of domain walls.

Critical exponents in the temperature dependence of susceptibility, resistivity and heat capacity have been used extensively to identify and characterize the various states discovered in the heavy fermion systems and incipient transition metal itinerant magnets [16]. There are good reasons for this. In particular the power of the temperature critical exponents lies in the incredible precision that temperature can be controlled and measured. This is not in general true for pressure. There are also differences in how pressure and temperature affect the energy scales - for the temperature case, the quantum critical cone is extremely narrow at low T and then widens out, with subtle exponent crossovers, and with quantum critical effects persisting to unintuitively high temperatures. In contrast, a small change in pressure at low temperature - where critical effects are strongest just above the QCP - can push the system out of the quantum critical cone. It is worth understanding why the pressure dependence is mean-field-like - widely assumed but by no means obvious from first principles. For paraelectrics such as STO, the leading effect of the electrostrictive coupling on the zone-centre fluctuations is only to renormalize its anharmonic coefficients [2], as shown later in the Theory section. Such couplings could also affect the dispersion away from $q = 0$ [17], but these are higher order effects involving fluctuations of the steric degrees of freedom which we have ignored in our model as their effect is stronger on the acoustic modes [18].

In this study the pressure dependence is measured explicitly. The relative paucity of data points compared to the temperature sweeps prohibits detailed numerical analysis. However, by considering a standard microscopic model of the ferroelectric fluctuations coupled to the volume strain and solved within the self-consistent phonon approximation (SCPA) [20, 21], we reveal that the pressure dependence is indeed mean-field-like, except very close to the QCP where weak logarithmic corrections are expected. As a consequence of this, whilst the crossovers from quantum critical to classical and quantum paraelectric are clear in the temperature exponents, this crossover does not appear in the pressure dependence. The SCPA is equivalent to the self-consistent renormalization method used for itinerant magnets [22].

The accompanying changes to the soft mode frequency have not been studied with pressure and temperature, and are reported here for the first time, extracted from the temperature and pressure dependence of the dielectric constant. The Lydanne-Sachs-Teller (LST) relation [23] allows the dielectric response of a polarizable crystal to be determined from its phonon spectrum or vice versa. The full relation including all phonon branches can be written as

$$\frac{\epsilon_r}{\epsilon_\infty} = \frac{\prod_i \omega_{iLO}^2}{\prod_i \omega_{iTO}^2}, \qquad (1)$$

where ϵ_r denotes the relative permittivity of the material, $\epsilon_\infty = n$ the refractive index or dielectric response at frequencies well above the relevant phonon frequencies and ω_{iLO}^2 and ω_{iTO}^2 are the frequencies of the longitudinal optical (LO) and transverse optical (TO) of phonon mode i at the zone center ($q = 0$). In $SrTiO_3$ a single TO mode corresponding to opposite motions of the titanium ion and surrounding oxygen octahedron is softened at the zone center [11] and dominates the dielectric properties of the system. Following Barker [24] and Yamada [11], we simplify the LST relation by assuming the pressure and temperature dependence of all modes other than the soft TO and its accompanying LO mode to be insignificant. Over the 20 kbar (2 GPa) range reported in this study, $SrTiO_3$ does not undergo any structural

transitions, changes in lattice parameters are well under a percent [25] and the variation of room-temperature phonon frequencies has been shown to be linear with pressure up to a much larger range [26]. The effect of these comparatively low pressures (several orders of magnitude below the bulk modulus [27]) on $SrTiO_3$ is therefore to cause a small leading-order perturbation to the lattice and phonons, with the notable exception of the soft mode. All other optical modes can be expected to tune with applied pressure in the same manner, and their terms in the LST relation cancel, leading to

$$\frac{\epsilon_r}{\epsilon_\infty} = \frac{\omega_{LO}^2}{\omega_{TO}^2}, \tag{2}$$

where ω_{TO} and ω_{LO} denote the ferroelectric soft mode and its longitudinal equivalent, which is denoted as E_g and of energy 148 cm^{-1} by Ishidate et al. [26].

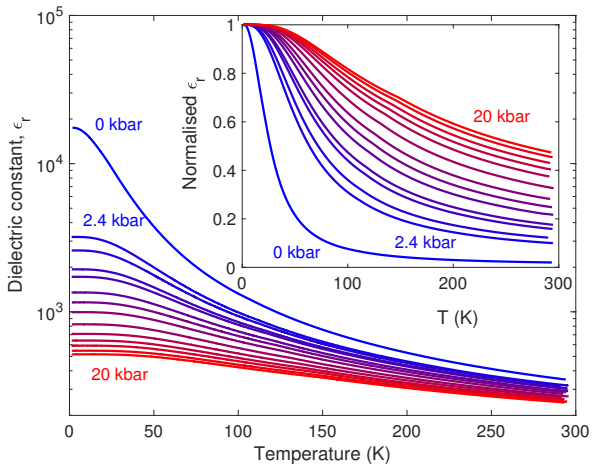

FIG. 2. Temperature dependence of the dielectric constant of $SrTiO_3$ at hydrostatic pressure values from ambient (blue) to 20 kbar (red). The inset shows the same data normalised to their 2 K values, revealing a clear evolution of the shape of the curves as pressure is increased.

EXPERIMENTS

Methods

High precision capacitance measurements were carried out on single crystal samples of $SrTiO_3$ from Crystal GmbH with gold electrodes vacuum evaporated onto the surfaces in a parallel-plate capacitor geometry. Measurements under extremely hydrostatic pressure conditions were made possible by the development, in collaboration with CamCool Research Ltd, of a piston-cylinder clamp cell with miniature shielded coaxial cables running into the sample region and electrically isolated from the cell body. This eliminates stray capacitances from the wiring and allows pF capacitance signals to be measured with stabilities of one part in a million. The shield conductors of the coaxial cables were joined together at the sample position and at the measurement instrument in the standard 2-point capacitance setup. The pressures in the measurements reported were 0/ambient, 2.4, 3.3, 4.6, 5.2, 6.9, 8.6, 9.6, 11.9, 14.1, 15.7, 17.1, 18.6 and 20.0 kbar, with a typical uncertainty of ±0.2 kbar. An Andeen-Hagerling 2550A 1 kHz capacitance bridge was used, at a voltage of 0.1 V. Sample thickness, corresponding to capacitor plate separation, was 0.5 mm. Measurements were taken on a modified 1K Dipper cryostat from ICE Oxford, allowing continuous stable temperature control down to 1.2 K, and an adiabatic demagnetization refrigerator developed in house capable of reaching 200 mK. Typical heating or cooling rates were held at 0.01 K per minute to allow the large thermal mass of the pressure cell to thermally equilibrate.

Results

Measurements were carried out of the dielectric constant of $SrTiO_3$ from room temperature down to 1.5 K at fixed hydrostatic pressures up to 20.0 kbar. The effect of pressure, as discussed in more detail in our recent paper [8], is to drastically reduce the magnitude of the low-temperature dielectric constant from ~18,000 at ambient pressure to ~500 at 20.0 kbar as the system is tuned away from a ferroelectric transition and associated quantum critical behavior - see Fig 2.

LST Analysis : Such a drastic change in the dielectric properties must reflect a change in the phonon spectrum of the system as the two are linked by the LST - the phonon frequencies directly determine the dielectric response. Eq. 2 was used to extract the temperature and pressure dependence of the frequency ω_{TO} of the ferroelectric soft mode $\omega_{TO}^2 = \frac{\epsilon_\infty \omega_{LO}^2}{\epsilon_r}$ at the zone centre. ϵ_∞ and ω_{LO} only change by ~1% over the pressure and temperature ranges studied, as will be shown in the rest of this section, so a good approximation of ω_{TO} can be found by simply setting these to be constant. Including the known pressure and temperature dependencies of these parameters will give a more accurate estimate of the phonon frequency however, and this was done to find the data presented in Fig. 3(a).

The refractive index at high frequencies ϵ_∞ was assumed to be temperature independent, in line with the conclusions of Kamarás et al. [29], but the pressure, p, dependence was considered. The linear pressure dependence with a value of $\left.\frac{d\epsilon_\infty}{dp}\right|_{300\,K} = -1.43 \times 10^{-4}\,\text{kbar}^{-1}$ found by Giardini [30] for optical frequencies at room

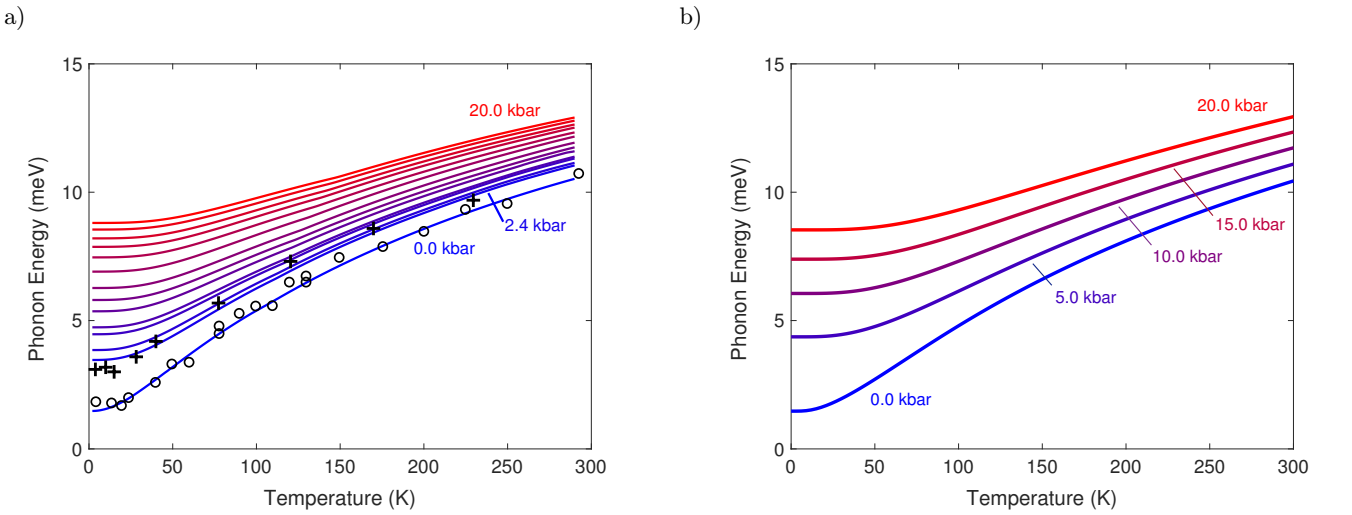

FIG. 3. a) Zone-center soft mode phonon energy of $SrTiO_3$ extracted from the dielectric constant via the Lydanne-Sachs-Teller relation, plotted against temperature for applied pressures from ambient (blue, lowest) to 20 kbar (red, topmost). The variation of the frequencies of other phonon branches and the refractive index with temperature and pressure were modeled as described in the text. Neutron scattering data from Yamada et al. [11] are shown as open circles and the corresponding data for $KTaO_3$ from Shirane et. al. [28] as crosses. b) Calculated temperature dependence of the TO phonon energy for several pressures.

temperature was used to model the changes in ϵ_∞. An exact numerical value for ϵ_∞ is hard to define, as n exhibits frequency dependence out to the highest frequencies measured [31, 32], but can be estimated as between 2.7 - 3.0 under ambient conditions. The numerical value for $\epsilon_\infty(p = 0)$ was therefore set to 2.87 by fitting the extracted phonon frequencies at ambient pressure to the experimental values found by Yamada et al. [11] from inelastic neutron scattering.

The longitudinal optical mode frequency ω_{LO} has been found to be $150\,\mathrm{cm}^{-1} = 18.6\,\mathrm{meV}$ under ambient conditions by Ishidate et al. [26] and Lebedev [33]. Ishidate measured room temperature phonon frequencies in $SrTiO_3$ up to a pressure range an order of magnitude higher than that reported in this work, and found a linear pressure dependence throughout, with $\frac{\mathrm{d}\omega_{LO}}{\mathrm{d}p}\Big|_{300\,K} = 1.8\,\mathrm{cm}^{-1}\mathrm{GPa}^{-1} = 0.0223\,\mathrm{meV\,kbar}^{-1}$. The temperature variation of ω_{LO} at ambient pressure was reported by Servoin et al. [34], and this was fitted with a linear relationship to extract a gradient $\frac{\mathrm{d}\omega_{LO}}{\mathrm{d}T}\Big|_{p=0} = 0.0066\,\mathrm{cm}^{-1}\mathrm{K}^{-1} = 0.00082\,\mathrm{meV\,K}^{-1}$. Both pressure and temperature effects are therefore on order a percent over the ranges studied, just as with the refractive index changes, so all three must be considered for a rigorous analysis.

Holding ω_{LO} and ϵ_∞ constant as in Yamada et al. and fitting the resulting constant of proportionality to match the Yamada data gives $\omega_{TO}^2 = \frac{39204}{\epsilon_r}$, with frequencies ω in meV and $\epsilon_r = \epsilon/\epsilon_0$ dimensionless. Yamada had a similar conversion factor of 37790, suggesting comparable sample quality - the dielectric constant is very sensitive to sample purity and surface finish, easily explaining the slight difference. Including the variation in ω_{LO} and ϵ_∞ leads to:

$$\omega_{TO}^2 = \frac{(2\pi)^2}{\epsilon_r}\left[2.87 - \frac{p}{6993}\right]\left[18.6 + \frac{p}{44.8} + \frac{(T-300)}{1220}\right]$$

(pressures in kbar, temperature in K).

Phonon Frequency Results : This last equation was used to extract the values for ω_{TO} shown in Fig. 3(a). As pressure is increased the phonon frequency markedly flattens off and returns towards the flat temperature dependence of an archetypal optical mode. The low-temperature gap, Δ, is doubled from 2 meV by even 2.4 kbar, the smallest pressure applicable with this setup. The small phonon energy or gap is directly linked to the ferroelectric quantum critical fluctuations observed in this material, so the gap widening as seen and becoming energetically inaccessible as the system is tuned away from criticality is an expected result. The prediction that pressure will tune the system towards the behavior seen in $KTaO_3$ is supported by the data as well - the soft mode energy for $KTaO_3$ overlayed on Fig. 3(a) lie by inspection at where $SrTiO_3$ values at around 2 kbar would be found.

Fig. 4(a) shows the pressure dependence of ω_{TO} at fixed temperatures, taken directly from the data of Fig. 3(a). The data at 1.5 K, 2 K, 5 K and those extrapolated to 0 K all overlap as the dielectric response flattens off as temperature approaches zero, so any data in this range can be taken as the zero-temperature value. The inset of Fig. 4(a) shows the square of the phonon energy at

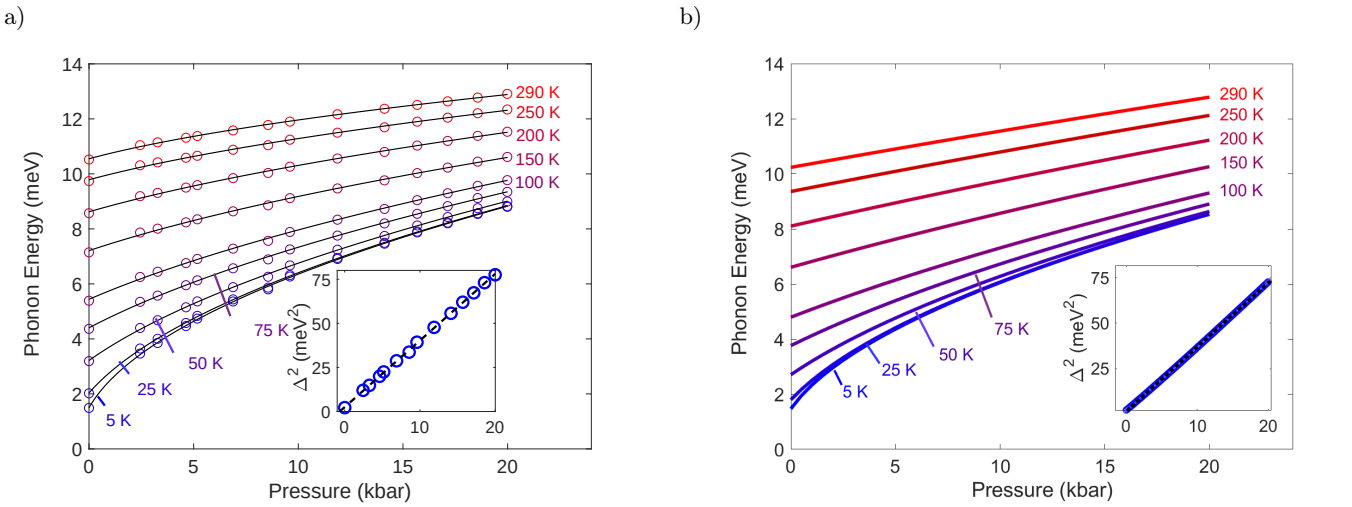

FIG. 4. a) Zone-center soft mode phonon energy of $SrTiO_3$, plotted against pressure at fixed temperatures. The solid lines show fits to $\omega_0(p-p_c)^{0.5}$ with ω_o and p_c free fitting parameters to guide the eye. The inset gives the square of the zero-temperature extrapolated phonon gap, Δ, against pressure, with a linear fit shown as a solid line. b) Calculated pressure dependence of the TO phonon energy for several temperatures. Inset. Calculated pressure dependence of the TO phonon gap.

2 K, equivalent to the zero-temperature gap, Δ, plotted against pressure. This shows very good agreement to a linear fit, giving the behavior expected from Landau theory $\omega = \omega_0(p-p_c)^{0.5}$ with the critical pressure p_c at which the ferroelectric quantum critical point occurs equal to -0.7(1) kbar. This is in agreement with the analysis in our earlier paper [8] and with observations that strain or oxygen-18 substitution (both equivalent to 'negative pressure' in $SrTiO_3$) drive the system to a ferroelectric state [12–14].

THEORY

Model

We consider a standard model Hamiltonian for displacive ferroelectrics with normal mode coordinates that describe local displacements $\phi_{i\alpha}$, with $\alpha = 1, 2, ..., n = d$ in the unit cell $i = 1, 2, ...N$ that are associated with the soft TO mode, the condensation of which is driven by the dipolar force and leads to the ferroelectric transition. We also consider the coupling to volume strain η_i. The Hamiltonian is as follows, [21]

$$H = H_\phi + H_\eta + H_{\phi\eta}, \tag{3}$$

where H_ϕ is the Hamiltonian of the polar degrees of freedom alone,

$$H_\phi = \frac{1}{2}\sum_{i,\alpha}\Pi_{i\alpha}^2 + \frac{\omega_0^2}{2}\sum_{i,\alpha}\phi_{i\alpha}^2 + \sum_{i,\alpha\beta}\left[u + v\delta_{\alpha\beta}\right]\phi_{i\alpha}^2\phi_{i\beta}^2 + \frac{1}{2}\sum_{ij,\alpha\beta}F_{\alpha\beta}\left(i-j\right)\phi_{i\alpha}\phi_{j\beta},$$

H_η is the elastic energy,

$$H_\eta = \frac{K}{2}\sum_i \eta_i^2 + P\sum_i \eta_i,$$

and $H_{\phi\eta}$ is a linear-quadratic coupling between $\phi_{i\alpha}$ and η_i,

$$H_{\phi\eta} = -\lambda\sum_{i,\alpha}\eta_i\phi_{i\alpha}^2.$$

Here, $\Pi_{i\alpha}$ is the conjugate momentum of $\phi_{i\alpha}$; and $F_{\alpha\beta}\left(i-j\right)$ is the dipolar interaction with Fourier transform $F_{\alpha\beta}\left(\boldsymbol{q}\right) = q^2\delta_{\alpha\beta} + g_0 q_\alpha q_\beta/q^2$, where g_0 is a constant that depends on the lattice structure. ω_0 is the frequency of the purely harmonic model; u and v are coefficients of the isotropic and anisotropic cubic anharmonicities, respectively; λ is the coupling constant between the polarization and volume strain; and K and P are, respectively, the bulk modulus and applied hydrostatic stress (e.g. biaxial stress for $d = 2$ and pressure for $d = 3$).

Though the low temperature paraelectric lattice structure of $SrTiO_3$ is tetragonal, we will follow previous work [19] and assume cubic symmetry for simplicity. The TO excitations of (3) are thus doubly degenerate,

$$\Omega_{\boldsymbol{q}}^2 = r(T,P) + q^2, \tag{4}$$

where $r(T,P) \equiv \Delta^2(T,P)$ is the square of the phonon gap at the zone-center. In addition to (4), there is a singlet LO mode which we will neglect as it is gapped out by the large depolarizing field of order $\mathcal{O}\left(g\right)$. Within the SCPA, [20, 21] $r(T,P)$ is given as follows,

$$r(T,P) = \omega_0^2 + \left[4\left(d+2\right)u + 12v\right]\left\langle|\boldsymbol{\phi}|^2\right\rangle - 2\lambda\left\langle\eta\right\rangle, \tag{5}$$

where $\left\langle |\boldsymbol{\phi}|^2 \right\rangle$ are the fluctuations of polarization,

$$\left\langle |\boldsymbol{\phi}|^2 \right\rangle = \frac{1}{N}\sum_{\boldsymbol{q}} \frac{1}{\Omega_{\boldsymbol{q}}}\left[n\left(\Omega_{\boldsymbol{q}}/k_BT\right)+\frac{1}{2}\right], \tag{6}$$

with $n(\xi) = \left(e^{\xi}-1\right)^{-1}$ a Bose factor and $\langle\eta\rangle$ is the average volume strain,

$$\langle\eta\rangle = \frac{\lambda}{K}\left\langle |\boldsymbol{\phi}|^2 \right\rangle - \frac{P}{K}. \tag{7}$$

By substituting Eqs. (6) and (7) into Eq. (5), we separate the contributions from thermal and quantum fluctuations as follows [35],

$$\begin{aligned} r(T,P) = {} & \frac{2\lambda}{K}\left(P-P_c\right) \\ & + \Gamma\left\{\left(T/T_D\right)^{d-1}\Phi\left[r\left(T,P\right)/\left(k_BT\right)^2\right]\right. \\ & \left. + Z_0\left[r\left(0,P\right)\right] - Z_0\left[0\right]\right\}, \end{aligned} \tag{8}$$

where P_c is the critical pressure at $T = 0\,\mathrm{K}$,

$$\frac{2\lambda}{K}P_c = -\left[r(0,0) + \Gamma\left\{Z_0\left[0\right] - Z_0\left[r\left(0,0\right)\right]\right\}\right], \tag{9}$$

and,

$$\begin{aligned} \Phi\left[R\right] = {} & \frac{\left(k_BT_D\right)^{d-1}}{\left(2\pi\right)^d} \\ & \times \int_0^{T_D/T} dx x^{d-1}\frac{1}{\sqrt{R+x^2}}n\left(\sqrt{R+x^2}\right), \end{aligned} \tag{10a}$$

$$Z_0(r) = \frac{\left(k_BT_D\right)^{d-1}}{2\left(2\pi\right)^d}\int_0^1 dx x^{d-1}\frac{1}{\sqrt{r/\left(k_BT_D\right)^2+x^2}}, \tag{10b}$$

where $r(0,0) = \omega_0^2 + \Gamma Z_0\left[r\left(0,0\right)\right]$, $\Gamma = 4\left(d+2\right)u + 12v - 2\lambda^2/K$, and $T_D = \Lambda/k_B$ is the Debye temperature. Eqs. (8), (9), and (10) self-consistently determine the temperature and pressure dependence of $r\left(T,P\right)$.

Results

The non-adjustable model parameters are $\omega_0, \Gamma, \lambda, K$, and Λ which we fit experimental data reported for $SrTiO_3$ as follows: ω_0 and Γ are determined from the temperature dependence of the transverse optic phonon gap measured by neutron scattering, [11]; λ/K is obtained from the slope of Δ^2 versus P measured here (see inset of Fig. 4(b)); and Λ from specific heat data ($T_D = \Lambda/k_B = 400\,\mathrm{K}$) [36]. The resulting parameters are $\omega_0 = 10.2i\,\mathrm{meV}$, $\Gamma = 90.0\,\mathrm{meV}^3$, $\lambda/K = 0.054\,\mathrm{meV}^2$, and $\Lambda = 34.5\,\mathrm{meV}$. The calculated temperature and pressure dependence of $r(T,P)$ is in good qualitative and quantitative agreement with experiments, as shown in Figs. 3 and 4.

To further explore the behavior of the excitations, we study the pressure dependence of the fluctuations near the QCP. At $T = 0\,\mathrm{K}$, Eq. (8) gives,

$$r(0,P) = \frac{2\lambda}{K}\left(P-P_c\right) + \Gamma\left\{Z_0\left[r\left(0,P\right)\right] - Z_0\left[0\right]\right\}. \tag{11}$$

For $r \to 0$,

$$Z_0\left[r\right] - Z_0\left[0\right] \simeq \begin{cases} -b\ln r + cr, & d=1, \\ -br^{1/2} + cr, & d=2, \\ -br + cr\ln r, & d=3, \\ -br + cr^{3/2}, & d=4, \end{cases} \tag{12}$$

with b, c positive constants. Thus the lower (upper) critical dimension is $d_{lc} = 1$ ($d_{uc} = 4$). While there are strong deviations from mean field behavior for $d = 2$, the corrections are only logarithmic for $d = 3$. Equation. (11) then gives,

$$r(0,P) \propto \begin{cases} \left(P-P_c\right)^2, & d=2, \\ \left(P-P_c\right), & d\geq 3, \end{cases} \tag{13}$$

with weak logarithmic corrections for $d = 3$. Such corrections should be observable only when extremely close to the QCP ($\left|\left(P-P_c\right)/P_c\right| \ll 1$) and a renormalization group analysis would be required for a quantitative description. For the present experiments, $\left|\left(P-P_c\right)/P_c\right| \gtrsim 1$, and thus are not observable.

Quantum critical excitations in uniaxial and XY ferroelectrics are generally expected to differ from those of cubic systems. We briefly consider such cases in Appendix A.

CONCLUSIONS

The Lydanne-Sachs-Teller relation was used to extract the pressure and temperature dependence of the transverse optical soft mode frequency in $SrTiO_3$ from precision measurements of the dielectric constant under pressure. The mode was seen to stiffen as pressure was applied, moving towards a more typical flat optical mode. The low-temperature phonon gap Δ widened with increasing pressure, showing excellent agreement to the $\Delta \propto (p-p_c)^{0.5}$ predicted by Landau theory and with an extrapolated critical pressure p_c of -0.7(1) kbar.

By treating the pressure within a self-consistent model for the quantum ferroelectric excitations, we have shown that the pressure dependence is robustly mean-field like. There are logarithmic corrections very close to absolute zero but these extend only to very low pressures (much less than 1 kbar). At the same time we verify the applicability of the LST over the whole of the phase space considered.

$SrTiO_3$ forms an ideal model system for the study of the physics of soft phonon modes and of quantum criticality, and pressure allows direct and clean tuning of the phonons - the driving mechanism of the whole system. Our results provide the first measurement of the stiffening of a soft phonon mode as a system is tuned away from criticality in a clean and direct manner by the application of hydrostatic pressure - a potentially universal phenomenon across a variety of phase transitions and systems in condensed matter physics.

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Uniaxial and XY ferroelectrics

For uniaxial ferroelectrics, there is an preferred polarization direction which we choose to be the x_3-axis. The Hamiltonian is similar to that of Eq. (3) except that $\alpha = \beta = 3, v = 0$, and $F(\boldsymbol{q}) = q^2 + g\left(q_3/q\right)^2$. The phonon excitations are $\Omega_{\boldsymbol{q}} = \sqrt{r + q^2 + g\left(q_3/q\right)^2}$, [37] which give

$$Z_0\left[r\right] - Z_0\left[0\right] = \begin{cases} br + cr\ln r + \mathcal{O}\left(r^2\right), & d = 2, \\ br + \mathcal{O}\left(r^{3/2}\right), & d = 3. \end{cases} \quad (14)$$

The upper critical dimension is thus $d_{uc} = 3$ and there are weak logarithmic corrections in $d = 2$.

For XY ferroelectrics, there is an easy plane of polarization and the Hamiltonian is again similar to that of Eq. (3) except that $\alpha = \beta = 1, 2$. The excitations are $\Omega_{\boldsymbol{q}} = \sqrt{r + q^2}$ and $\Omega_{\boldsymbol{q}} = \sqrt{r + q^2 + g\left(q_1^2 + q_2^2\right)/q^2}$. The former isotropic dispersion dominates the critical behavior and the corrections to mean-field behavior are thus the same as those given in Eq. (12).

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