SrTiO₃: An intrinsic quantum paraelectric below 4 K

K. A. Müller

IBM Zürich Research Laboratory,
8803 Rüschlikon, Switzerland

H. Burkard *

Laboratory of Solid State Physics,
ETH 8093 Zürich, Switzerland

The dielectric constants $\epsilon_{\langle 110 \rangle}$ and their change with uniaxial $\langle 1\bar{1}0 \rangle$ stress in monodomain $\langle 001 \rangle$SrTiO₃ samples have been measured as a function of temperature. Between 4 K and 0.3 K these quantities are independent of temperature. In one sample $\epsilon(T)$ was measured to 0.035 K and found to be constant. This proves the quantum-mechanical stabilization of the paraelectric phase below 4 K with a very high dielectric constant ϵ. The crossover from classical to quantum behavior on lowering the temperature is discussed, and it is shown that the coupling of the ferroelectric mode to acoustic ones is important. The $\epsilon(T)$ dependence is compared to earlier and recent theories. The former, yielding a coth $(\hbar\Omega/kT)$ term, are found to be inadequate for the crossover region. A recent biquadratic ferroelectric mode-coupling theory fits the data better.

I. INTRODUCTION

In this paper we report a dielectric investigation on two monodomain SrTiO₃ samples down to 0.3 K, and in a third sample an extension to 0.035 K. The large dielectric constant ϵ does not vary below 4 K for a given stress. This is taken as evidence for the occurrence of a quantum-mechanical regime which stabilizes large ferroelectric fluctuations in the paraelectric phase.

One can view this state as follows: consider a *dynamical* spinless Hamiltonian of the general form

$$H = \sum_i^n p_i^2/2m_i + V(u_1, u_2, \ldots, u_i, \ldots, u_n) \quad , \qquad (1)$$

where p_i, u_i, and m_i represent the ith particle momentum, its coordinate and mass, and V the total potential energy. In SrTiO₃ the interaction potential is such that a ferroelectric phase transition is about to take place at low temperatures. Our experiments prove that the presence of the dynamic momentum coordinates p_i in Eq. (1) which do not commute with the u_i, i.e., $\{p_i, u_j\} = -i\hbar\delta_{ij}$ suppress the phase transition due to the nonvanishing zero-point motion of the particles. The latter having a larger amplitude than the ferroelectric displacement, the resulting susceptibility as reported in Sec. II is high and temperature-independent below 4 K, in contrast to crystals with random paraelectric impurities.

Many years ago Barrett extended Slater's mean-field theory of BaTiO₃ to include quantum effects in cubic ferroelectrics.[1] Renewed interest in the quantum-mechanical suppression has resulted, owing to the recent rigorous calculations of Schneider, Beck, and Stoll[2] for structural short-range regimes with lattice dimensionality $d = 3$ and order-parameter dimensionality $n = 1$; 2, where an inequality was analytically derived from the Hamiltonian. These authors were able to prove rigorously the suppression therewith. Aubry[3] then proved it for general interactions including $d = 3$, $n = 3$, and long-range (ferroelectric) forces using the equivalence between a d-dimensional quantum-mechanical spinless Hamiltonian as in Eq. (1), and a $d + 1$ classical system of closed Feynman rings of length $l = \beta\hbar$ ($\beta = 1/kT$).

In Sec. III a comparison of our experiments[4] on SrTiO₃ with earlier work is made. The recent Raman-scattering data as a function of uniaxial stress obtained by Uwe and Sakudo[5] at 4.2 K are of importance in this connection because they show the existence of a paraelectric state at $T = 4.2$ K in the absence of stress. Finally, in Sec. IV, the origins of the crossing over from classical mean-field behavior $\epsilon(T) \propto (T - T_c)^{-1}$, where $kT \gg \hbar\Omega$, and $T_c = 35.5$ K — with $\hbar\Omega$ the quantum energy — to the quantum-mechanical regime $kT \ll \hbar\Omega$ are discussed. The quantum-mechanical mean-field formula[1] leads to a quantum energy of 80 K, but considerations of short-range forces of Ti-ion displacements[6] suggest the existence of mechanisms which reduce the classical T_c to a value $T_c^* < 10$ K, where quantum-mechanical suppression of the phase transition becomes operative. These are the phonon dressing[7] and the recently discovered dipolar behavior in a cubic ferroelectric.[8] A quantitative theory including both of them has recently been worked out by

SAMPLE A   SAMPLE B

GOLD ELECTRODES

SILVER-PAINTED ELECTRODES
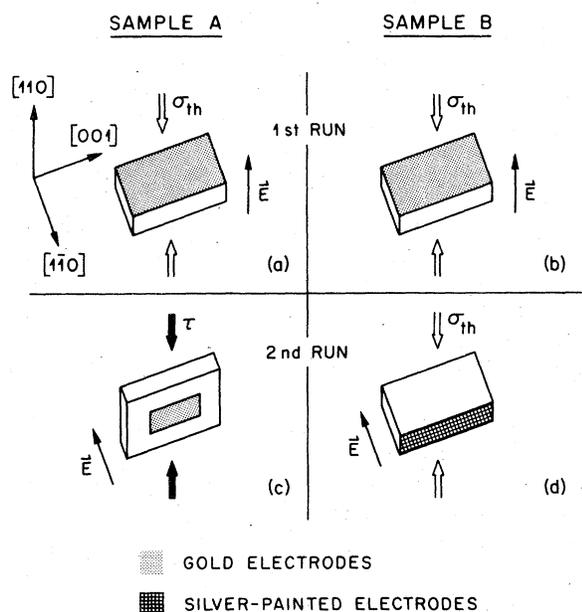
FIG. 1. Geometry of samples used for dielectric-constant measurements ($\vec{E}$ is the ac field), σ_{th} is the stress applied by thermal treatment, τ is the externally applied stress. Dimension of samples, A: $8.2 \times 3.8 \times 0.4 \, \text{mm}^3$, B: $5.0 \times 3.0 \times 0.33 \, \text{mm}^3$.

Migoni, Bilz, and Bäuerle.[9] Its clue is the anisotropic oxygen intra-ionic and biquadratic polarizability $K_{O,Ti,Ti}$. This nonlinear theory and earlier less complete ones are compared to our results. In the Appendix the mean-field result,[1] but within the self-consistent single soft-mode theory, is recalled.[10] This is helpful in understanding the physics of the suppression involved.

II. EXPERIMENTAL

The dielectric constants of two SrTiO$_3$ single-crystal samples A and B were measured in the temperature range $0.3 - 300$ K in a ^{3}He cryostat. To obtain monodomain crystals,[11] both samples were thermally treated by rapidly cycling between room temperature and liquid-nitrogen temperature five times before loading into the cryostat. A third sample C was measured between 0.035 and 4.2 K in an adiabatic demagnetization cryostat.[12] The temperature T was measured with a copper-constantan thermocouple and with carbon resistors which were calibrated for $1.25 \leqslant T \leqslant 4.2$ K against the vapor pressure of ^{4}He and for $T \leqslant 1.25$ K against the magnetic susceptibility of cerium magnesium nitrate (CMN). The capacitance measurements were performed with an au-

CURVE	SAMPLE	$\vec{E}$ ∥	τ ∥	σ_{th} ∥
1	A	[110]		[110]
2	B	[110]		[110]
3	B	[1$\bar{1}$0]		[110]
4	A	[110]	[1$\bar{1}$0]	
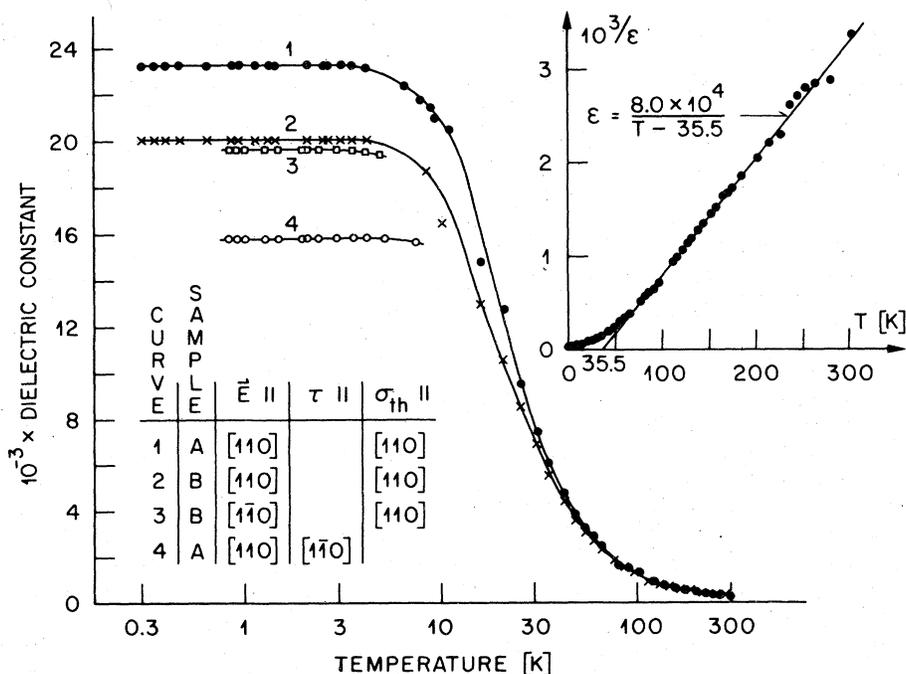
FIG. 2. Dielectric constants ϵ_{110} and $\epsilon_{1\bar{1}0}$ of the monodomain SrTiO$_3$ samples A and B (σ_{th} is the stress applied by thermal treatment). Inset: $10^3/\epsilon$ vs T.

tomatic three-terminal capacitance bridge at ac frequencies of 1, 10, and 100 kHz. The capacitance values for these frequencies agree within 0.2%.

In a first run, the dielectric constants[13] ϵ_{110} of samples A and B, with gold electrodes on the (110) faces [Figs. 1(a) and 1(b)] were obtained. Down to 4 K, the values observed increase monotonically in a well-known manner,[14,15] but for $T < 4$ K, ϵ_{110} is almost a constant (Fig. 2, curves 1 and 2) showing a very smooth maximum at 3 K (the maximum values are about 0.2% higher than the values of 1 K). For sample C, too, ϵ_{110} was found to be constant in the temperature range $0.035 \leqslant T \leqslant 4.2$ K. In a second run, the dielectric constant $\epsilon_{1\bar{1}0}$ of sample B [electrodes on the (1$\bar{1}$0) faces, Fig. 1(d)] was measured; at low temperatures, the $\epsilon_{1\bar{1}0}$ values observed (Fig. 2, curve 3) are slightly smaller than ϵ_{110}, but show exactly the same behavior. The slight difference between $\epsilon_{1\bar{1}0}$ and ϵ_{110} suggests that ϵ_a in sample B is 20 000, similar to what was obtained by Sakudo and Unoki.[13] This is half as large as measured by Uwe and Sakudo[5] and could result from plastic elongation in the thin monodomain samples along the c direction.

In the same run, the stress dependence of $\epsilon_{1\bar{1}0}$ of sample A was investigated (stress along [110]). The applied force was transferred by a stainless-steel wire from the top of the cryostat to the cell. The stress τ was calculated from the applied force by multiplication with the ratio of the lever arms, and division by the cross section of the pressed face. The error in stress resulted mainly from friction (corresponding to a stress of about 30 kPa/cm²). In sample A, electrodes were only applied to the middle part of the large faces [Fig. 1(c)].[16] To further improve the homogeneity of stress, the planes to be pressed were carefully polished and fixed to the piston with vacuum grease.

After mounting the sample into the stress cell and cooling to liquid-helium temperature without an applied force, the ϵ values were measured (Fig. 2, curve 4). A small residual stress σ_{res} might still have been present during cooling, thus a reduced ϵ resulted.

The $\epsilon_{1\bar{1}0}$, in the presence of external stress, was measured in the following way: the stress was applied at 4.2 K; and the sample then cooled down at constant stress. *The observed ϵ values taken at* 4.2, 1.3, *and* 0.8 K *agreed within 0.05%* [see Fig. 3(a)]. After warming up to 4.2 K again and removing the stress, the sample was checked for irreversible changes of the dielectric constant. This procedure was repeated for each value of applied stress. After removal of the highest applied stress (1560 kPa/cm²) the zero stress value of ϵ had decreased irreversibly by about 4%.

The slope of the inverse dielectric susceptibility

$\gamma_Y = 4\pi/(\epsilon_{1\bar{1}0} - 1)$ against the applied stress τ, [see Fig. 3(b)] was computed; its value ($Q_{11} + Q_{12} + Q_{66}/2$) was determined to 6.1×10^{-13} cgs, which compares well with that of 6.01×10^{-13} cgs, reported in Ref. 5. The value of $\gamma_a(T=0) = 4\pi/\epsilon_a$ could not be determined because of the plastic deformation of sample A, the absolute zero stress being unknown. Assuming the value measured by Uwe and Sakudo[5] — marked with a circle in Fig. 3(b) — is the strain-free one, then our sample had undergone a plastic deformation corresponding to application of $\delta = -0.02 \times 10 \times 10^9$ dyn/cm² on a strain-free sample.
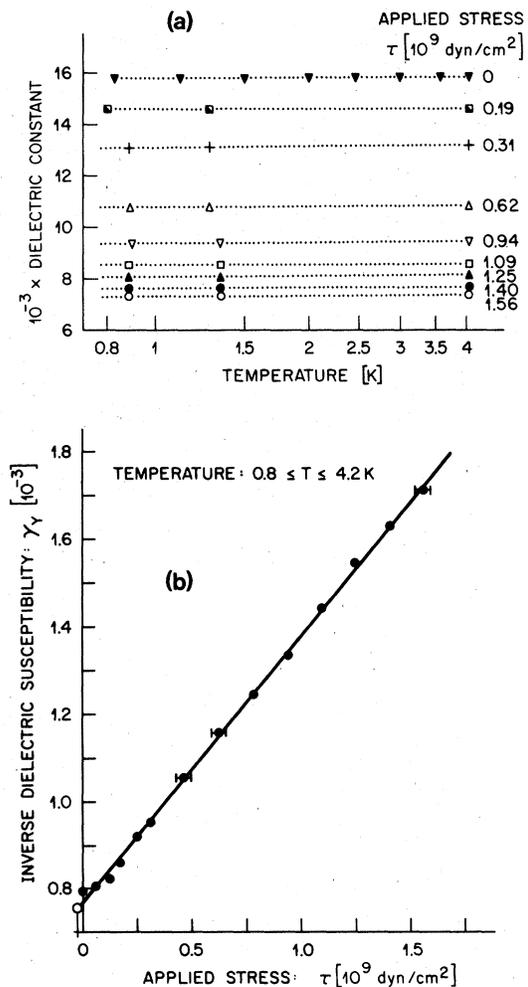
FIG. 3. (a) Dielectric constant ϵ_{110} of sample A as a function of temperature for various applied stresses τ [sample geometry see Fig. 1(c)], and (b) of inverse susceptibility as a function of stress in the quantum paraelectric regime.

III. EXISTENCE OF A QUANTUM-MECHANICAL PARAELECTRIC STATE

Earlier dielectric-constant measurements down to 4 K in multidomain $SrTiO_3$ had been fitted with the mean-field Barrett formula,[1] rederived in the Appendix within self-consistent single-mode theory [Eq. (A11)] with $T_1 = \hbar\Omega/k$, it reads,

$$\chi = \frac{M}{(T_1/2)\coth(T_1/2T) - T_c^{cl}} \cdot \quad (2)$$

They yielded[14,15] $T_1 \sim 84$ K, $T_c = 38$ K, and $M = 9 \times 10^4$ K. There are a number of reasons why the seemingly good fit was not accepted as proof of a quantum-mechanical suppression of the ferroelectric phase transition: Equation (2) was a quantum-mechanical extension of the mean-field theory of Slater, thus not a rigorous result. We shall discuss below that it could be of importance why Eq. (2) is not, in general, applicable, and T_c is too high for the suppression to occur; there can exist a crossover temperature T_r to another regime. This crossover then depresses T_c towards such a low-temperature T_c^{*cl} that quantum-mechanical suppression becomes operative at $\sim \frac{1}{10}T_r$ (see Fig. 4). That such a suppression can occur follows from recent rigorous calculations[2,3] as mentioned in Sec. I.

Experimentally the situation regarding the quantum-mechanical suppression was also far from clear. The monotonic rise of $\epsilon(T)$ down to 4.2 K is mirrored by the near proportionality to ω_{TO}^{-2} found in Raman scattering.[17] As calculated by Cowley[7] and emphasized by Worlock,[18] $\omega_{TO}(T)$ could be interpreted by the "phonon dressing." Whether such an anharmonic stabilization called "incipient ferroelec-
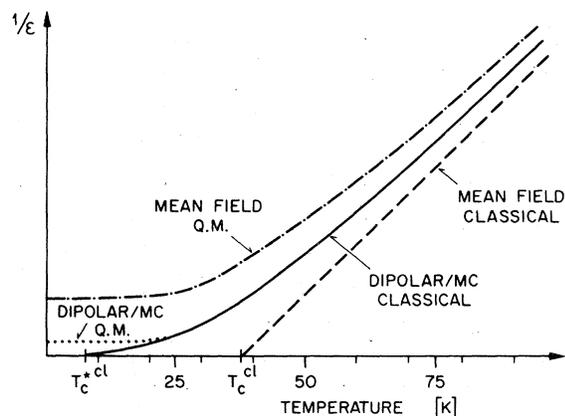
FIG. 4. Schematic representation of crossover of $1/\epsilon$ vs temperature for a mean-field quantum-mechanical regime according to Eq. (2) in the text, or via a classical dipolar mode coupling regime $\sim (T - T_c^*)^\gamma$ with $\gamma \sim 1.5$ and dipolar MC quantum-mechanical regime for $T \rightarrow 0$.

tric"[19] would lead to a quantum-mechanical dielectric behavior, and where, was not clear. In other words, experimentally there was no data indicating a flat region in either $\epsilon(T)$ or $\omega_{TO}(T)$ over a sufficiently extended temperature range. Some experimentalists expected that $\epsilon(T)$ would drop again below 2 K, in analogy to paraelectric systems.[20]

Another reason for doubt was the observation of hysteresis loops. These observations were ascribed to ferroelectricity despite the application of Eq. (2).[14] More recently, Uwe and Sakudo[5] have investigated $SrTiO_3$ at 4.2 K by means of dielectric measurements and Raman scattering as a function of uniaxial stress. At this temperature, the crystal is in its tetragonal paraelectric phase which exists below the structural transition at $T_a = 105$ K.[21,22] They showed conclusively that at 4.2 K the ferroelectric mode only freezes out under application of uniaxial [100] and [110] stress, perpendicular to the c axes at 15.6 and 56 kPa/mm^2, respectively. This finding is essential for our assertion of the existence of quantum-mechanical suppression, i.e., for stresses smaller than the critical ones that proved the crystal to be in the paraelectric state at 4.2 K. Our experiments show that for stresses below the critical stress, the paraelectric behavior is temperature independent. This is borne out in Fig. 2 for residual stresses between 4.2 and 0.3 K, and in Fig. 3 for externally applied stresses between 4.2 and 0.8 K. It is, in our opinion, conclusive proof of a quantum-mechanical regime.

The values of ϵ_{110} and $\epsilon_{1\bar{1}0}$ obtained in sample B are also of importance. The two different sample lengths of 0.33 and 3.0 mm for runs 2 and 3, across which the ac dielectric constants were measured, give almost identical values ϵ_{110} and $\epsilon_{1\bar{1}0}$ eliminating possible influence of surface charges. Höchli[23] has estimated a maximum charge density of a 1 C/m^3 at zero field, which limits the maximum trapped field in our sample to 1 kV/m. This reduces the dielectric constant by as much as 0.5% with respect to its value in the virgin sample. This is compatible with the accuracy of our measurements. Below 4.2 K, motion of surface charges occurs on a slow time scale[23] and $\epsilon(T)$ was found to be independent of the ac frequency between 1 and 100 kHz.

In Fig. 5 the $\epsilon(T)$ data of curve 1 in Fig. 2 are compared to $\epsilon(T)$ as computed with Barrett's Eq. (2). The constants $M = 8.0 \times 10^4$ and $T_c = 35.5$ K, were obtained by a least-squares fit to $\epsilon^{-1} = (T - T_c)/M$ between 150 and 300 K. In this range we are certain to be in the high-temperature mean-field regime. Next, $T_1 = 80$ K was adjusted for an optimal $\epsilon(T)$ fit from 150 down to 16 K. It is seen that the quantum paraelectric temperature-independent ϵ value does not reach the experimental values. Barrett's curve B_1 bends away near 16 K and reaches too low a value, i.e., 17 800. This corresponds, in the schematic diagram of Fig. 4, to too high a value of $1/\epsilon$. The

quantum paraelectric dielectric constant of 23 000 for run 1 is significantly lower than the extrapolated strain free of about 40 000,[5] due to plastic sample elongation along the c axis. This further shows the inadequacy of Eq. (2). Of course, one can fit Eq. (2) to the observed temperature-independent dielectric constant of 23 000 by slightly changing T_1 from 80 to 77.8 K. However, as shown in Fig. 5, B_2, the fit is then poor between 4 and 70 K. Basically this is a result of the too fast bending over of Eq. (2) within a temperature interval of $\Delta T = 5$ K, instead of the observed 10 K. The other curves of Fig. 5 refer to later theoretical efforts, where coupling of the ferroelectric soft mode to acoustic modes was taken into account as discussed in the Sec. IV.

IV. CLASSICAL QUANTUM-MECHANICAL CROSSOVER

A. Static considerations and phenomenological soft-mode theories

Having established the existence of the quantum regime, we now discuss its origin. Kurtz[6] emphasized recently that the quantum suppression becomes operative when the classically calculated ferroelectric displacement Δz (of the Ti ion) for $T \ll T_c$ is smaller than the mean quantum-mechanical amplitude $\overline{\Delta}z$. In a number of ferroelectric perovskite oxides it was found that Δz is related to T_c by[24,25]

$$kT_c = \tfrac{1}{2}\kappa(\Delta z)^2 \tag{3}$$

with essentially the same force constant $\kappa \simeq 5.5 \times 10^4$ dyn/cm.

Kurtz,[6] taking into account that the short-range constant κ is compatible with elasticity data,[24] calculated the quantum-mechanical isotropic rms amplitude $\overline{\Delta}z$ from a Debye temperature of $\Theta = 400$ K. He obtained $\overline{\Delta}z = 0.03$ Å using a formula by James, $\overline{\Delta}z^2 = \hbar/2mNK(\tfrac{1}{3}\Theta)$, in which the number of atoms per volume N is included. Equation (3) yields $\Delta z(T = 0) = 0.045$Å for $T_c = 36$ K. Thus $\Delta z < \overline{\Delta}z$ is not fulfilled. Therefore, we looked for a *classical* mechanism which depresses Δz to the order of 0.02 to 0.03 Å or from Eq. (3), T_c^{*cl} below 10 K (see Fig. 4).

Before doing so, we want to make another point supporting the above conclusion: as mentioned in Sec. I it is possible to derive Eq. (2) from a single mode self-consistent mean-field phonon theory as shown in the Appendix. thus one may try to stay within this approximation to estimate whether the quantum suppression occurs. Using $T_1 = 80$ K $= \Omega\hbar/k$ to obtain $\Omega = 1.1 \times 10^{13}$ rad/sec, and identifying

m with the mass of the titanium ion, we calculate the mean QM amplitude $\overline{\Delta}z^2 = \hbar/2m\,\Omega$, $\overline{\Delta}z = 0.077$ Å, a value larger than the value $\Delta z = 0.045$ Å, obtained from Eq. (3) with $T_c = 35.5$ K, indicating that a quantum-mechanical suppression $\overline{\Delta}z > \Delta z$ takes place. However, within the same single mode approximation, Eq. (3) is also derived in the Appendix [Eq. (A14)], and yields

$$\kappa = \tfrac{2}{3}m\,\Omega^2 \quad, \tag{4}$$

with $\Omega = 1.1 \times 10^{13}(T_1 = 80$ K), one calculates $\kappa = 6.5 \times 10^3$ dyn/cm. Compared to the experimental 5.5×10^4 dyn/cm,[24] this is a factor 8.5 too small, and clearly shows that the single soft-mode approximation is inadequate and the inclusion of the coupling to other modes is necessary. These will mainly be the occupied acoustic modes.[6]

An apparent step in this direction was the recent approach by Chaves *et al.*,[26] who considered the anharmonic phonon coupling

$$\sum_{\substack{qq' \\ q''q'''}} C(q,q',q'',q''')Q(q)Q(q')X(q'')X(q''') \tag{5}$$

between the TO $\omega_{TO}(T,q)$ and the acoustic $\Omega(T,q)$ branch with normal coordinates Q and X, respectively. Substituting the summation over acoustic modes in the Hamiltonian by an effective term C they arrived at a formula for the center of the Brillouin zone $q = 0$,

$$\overline{\omega}_{TO}^2(T) = \omega_{TO}^2(0) + (C^3/\Omega)[\tfrac{1}{2} + n(\Omega)] \quad. \tag{6}$$

For SrTiO₃ they used the following empirical parameters to fit the temperature variation of the TO mode $\omega_{TO}(0) = i\,35.1$ cm⁻¹, $\Omega = 62.3$ cm⁻¹, $C = 55.5$ cm⁻¹. Using these values, they claimed to get an excellent fit down to 4 K. We have computed $\epsilon(T) \propto 1/\omega_{TO}^2(T)$ with their Eq. (6) and show this in Fig. 5. As can be seen, their curve does not give a better fit than Barrett's formula. Thus this theory does not provide an improvement. Furthermore, the value of the constant C is unrealistically high. Clearly a better and microscopic theory including the soft-phonon acoustic mode coupling is needed.

Earlier than the above authors, Pytte[27] theoretically investigated a triply degenerate ferroelectric soft mode including piezoelectric coupling. Within his approximations the temperature dependence of the soft mode is as given by the single frequency formulas (A8) and (A10), but with the fourth-order constant γ replaced by $3\Gamma_1 + 2\Gamma_2 - 2C_2$, where Γ_1 and Γ_2 are the two local fourth-order constants allowed in cubic systems and

$$C_2 = (G_{11} + 2G_{12})^2/(C_{11} + 2C_{12}) \quad,$$

G_{ij} and C_{ij} are the electrostrictive coupling and strain constants, respectively. The latter are known,[5] but Γ_1

and Γ_2 are not. Thus the temperature dependence has to be fitted by choosing $3\Gamma_1 + 2\Gamma_2$ to the same analytic form as Eq. (2), and the same comments are valid.

The difficulties with these phonon theories indicates the lack of an additional clue to the understanding of why the classically extrapolated T_c^{cl} of 35.5 K is depressed to < 10 K. Now, Kind and Müller[8] in $KTa_{0.9}Nb_{0.1}O_3$ recently showed that a crossover from the mean-field region to another regime occurs below $T_r \approx 120$ K. The exponent of the susceptibility found in this regime was $\gamma \sim 1.7 \pm 0.2$, therefore T_c^{*cl} is lower than T_c^{cl}, because $\epsilon^{-1} \propto (T - T_c^{*cl})^\gamma$ is flatter for higher γ (Fig. 4). Note also that in $KTa_{0.9}Nb_{0.1}O_3$ a real ferroelectric phase transition occurs at $T_c^{*cl} \cong 92$ K, and no quantum paraelectric behavior exists. This supports the existence of another regime in this mixed crystal.

Two causes for the occurrence of a regime different from that of Landau with a value of $\gamma = 1$ were discussed in Ref. 8: (a) the randomness of the $KTa_{0.9}Nb_{0.1}O_3$ mixed crystal, and (b) dipolar behavior as originally proposed by Bruce.[28] Cause (a) can obviously be ruled out for $SrTiO_3$. In Ref. 8 it was found that the transition T_r in $KTa_{0.9}Nb_{0.1}O_3$ occurs when the thermal energy kT becomes lower than about half the dipolar energy W_D. The latter is measured by the splitting between the longitudinal[29] ω_{LO} and transverse[15] ω_{TO} modes. Thus we have $kT_r \sim \frac{1}{2}(\omega_{LO} - \omega_{TO})\hbar$. Using the measured $\omega_{LO} = 188$ cm^{-1} and $\omega_{TO} = 45$ cm^{-1} energies in $SrTiO_3$, we find that this rough empirical formula holds for $SrTiO_3$ $T_r \sim 100$ K (see Fig. 2 and Ref. 13−15), and $(\omega_{LO} - \omega_{TO})\hbar k = 210$ K, respectively. Therefore, crossover to dipolar-cubic behavior appears as a possibility. However, one may have to use for ω_{LO} a higher and not the lowest mode. This reduces kT_r to a fraction of W_D. More important is that the observed regime is sufficiently far from T_c that one may claim it to be critical dipolar in a true sense. The dipolar ferroelectric interaction is, on the other hand, certainly involved.

An additional mechanism was proposed by Bilz.[30] The coupling of the ferroelectric mode ω_{TO} to the acoustic modes ω_A occurs over the whole Brillouin zone. Thus its interaction with the acoustic modes becomes stronger than just perturbative once $\omega_{TO}(T)$ at $q = 0$ has lowered so much on cooling the crystal that it is lower than one or several acoustic modes at the Brillouin-zone edge. The acoustic modes at the zone edge have energies of the order of 150 K.[29] This means the ferroelectric mode "plunges" into the "sea" of acoustic modes spanned over the Brillouin zone, coupling to them with strong momentum transfer. Naively, one would also expect from this plunging mechanism to observe this new regime in ferroelectrics with high T_c as the plunging of ω_{TO} is present there too. This is, however, not the case, as

it has up to now only been seen in systems with low T_c as KTN [K(Ta:Nb)O$_3$] or in quantum paraelectrics. Apparently, the regime is only observed as long as $kT < \hbar\omega_A$ $(q = \pi/a)$, but not if kT_c and thus $kT > \hbar\omega_A$ $(q = \pi/a)$. In this latter case the whole acoustic branch is occupied. Thus the new regime is only seen when this is not the case, i.e., when the Brillouin edge ω_A is not yet occupied. Then renormalization via phonon occupation due to $\omega_{LO} - \omega_A$ coupling is possible. The self-consistent theory to be described in Sec. IV B appears to implicitly include both mechanisms.

B. Comparison to recent dynamic microscopic theory

Application of the most recent anharmonic theory of Migoni, Bilz, and Bäuerle[9] to three different oxide perovskites has indeed borne out the existence of the above-mentioned dipolar mode coupling regime.[31] This self-consistent microscopic theory[9] includes the aforementioned phonon dressing,[7,17,18] and automatically yields a coupling to mainly acoustic modes at temperatures below T_r, in agreement with the considerations at the beginning of Sec. IV A. In this theory,[9] a nonlinear and anisotropic polarizability $\alpha_{Oi}(O^{2-})$, i: A or B ion, of the oxygen is assumed due to the volume dependence. Along the $O - B$-ion axis the polarizability is an order of magnitude larger than along an $O - A$ direction and takes the approximate form

$$\alpha_{OB} = Y_O^2/K_{OB} \ , \tag{7}$$

where Y_O^2 is the oxygen-shell effective charge and

$$K_{OB}(T) = K_{OB} + \frac{1}{2}K_{OB,B} \langle r(O)_B^2 \rangle_T \ , \tag{8}$$

the force constant between the oxygen shell and core center, $K_{OB,B}$ is the crucial anharmonic fourth-order coupling parameter of the local potential $\phi^{(4)}$,

$$\phi^{(4)} = (1/4!)K_{OB,B} \sum_{l\alpha} r_\alpha^4 (O_\alpha^l) \ , \tag{9}$$

$\langle r(O)_B^2 \rangle_T$ is the mean fluctuation amplitude of the oxygen-shell displacement in direction of B given by

$$\langle r(O)_B^2 \rangle_T = (\hbar/2Nm_O) \sum_\lambda |f_\alpha^2 (O_\alpha|\lambda)/\omega_\lambda|$$

$$\times \coth(\hbar\omega_\lambda/2kT) \ . \tag{10}$$

The f_α's are shell eigenvectors, $\lambda \equiv (\vec{q},j)$, and the other quantities are given in a standard notation. O_α denotes the oxygen whose neighboring B ions lie in α direction (x,y or z). The temperature dependence of ω_F is given by

$$\omega_F^2(T) = \omega_0^2 + \frac{1}{2}(K_{OB,B}f_O^2/M_O) \langle r(O)_B^2 \rangle_T + \cdots \ , \tag{11}$$

where the dots indicate higher-order terms, ω_0 is the harmonic frequency which is imaginary, and f_O is the shell eigenvector of the oxygen whose B neighbors lie in the direction of polarization of the ferroelectric mode. ω_0 and f_O are complicated functions of the harmonic parameters, the latter being known from inelastic neutron scattering. Using $\omega_F^2(T)$ at high temperatures, where $\coth X \approx 1/X$ [Eqs. (9) − (11)] were solved iteratively to obtain parameter $K_{OB,B}$. With this constant known, the low-temperature behavior of $\omega_F^2(T)$ was calculated. The results yield in a natural way the coupling of the ferroelectric mode ω_F to the acoustic modes via $\langle r(O)_B^2 \rangle_T$ from Eq. (11) in the region where the acoustic $\omega_A \hbar < kT$, as well as the quantum paraelectric dominated low-temperature regime.

For SrTiO₃ the following constants were obtained, $\omega_0^2 = -9000$ cm⁻², $K_{OB,B} = 749e^2/va^2$ with v the volume of the elementary cell and a the lattice constant. In Fig. 5 the calculated dielectric constant $\epsilon(T)$ is displayed and marked MC (mode coupling). In the crossover region it is somewhat lower than the measured one, i.e., its crossover curvature to $\epsilon(0) = 23\,000$ is *less* than the experimental one. This is not unreasonable, because the negative ω_0^2 was slightly adjusted to yield $\epsilon(0) = 23\,000$. If the strain-free value is indeed $\epsilon(0) = 40\,000$,[5] the fit with adjustment of ω_0^2 will be better, whereas the mean-field B curve with its too small radius of curvature worsens.

A most recent comparison of dielectric constants and soft-mode behavior in SrTiO₃, KTaO₃ and KTa₀.₉Nb₀.₁O₃ showed[31] that immediately below the mean-field (MF) regime the MC regime existed with an exponent $\gamma = 1.4 \pm 0.2$. the T_c for mode-coupling regime $T_{MC} = 8.9$ K is indeed depressed from the mean-field value $T_{MF} = 25$; in the present study we obtained $T_{MF} = 35.5$ K from $1/\epsilon(T)$ above 150 K by linear regression. The discrepancy arises because in Ref. 31 the fitting was done on the Raman data[17] taken on different samples. Now, T_{MF} has been found to be strongly sample dependent in KTaO₃, as well. Furthermore, the fitting in Ref. 31 was carried out on a logrithmic scale which gives accurate values for γ and $T_r = 149$ K but is sluggish in T_{MF}. On the other hand, $T_r \approx 100$ K is inaccurate from the ϵ^{-1} vs T fit.

In SrTiO₃ at $T_a = 105$ K, the structural phase transition (SPT) from the cubic to the tetragonal paraelectric phase occurs.[21] Thus, one may argue that this transition to tetragonal symmetry, which reduces the ferroelectric order-parameter dimensionality from $n = 3$ to $n = 2$, may influence $\omega_{TO}(T)$ near T_a. We can rule out this possibility by comparing the behavior of SrTiO₃ with that of KTaO₃. The dielectric constant[32] and soft phonons[17,33] of KTaO₃ down to 4 K also show quantum paraelectric behavior, and the crossover to dipolar mode-coupling regime exists there too.[31] Now KTaO₃ remains cubic

down to at least 10 K. Thus, the SPT cannot be the primary cause. Actually, the anisotropy in ϵ measured is very small near $T_a = 105$,[13] i.e., essentially cubic behavior is still seen on the average, $\epsilon = \frac{1}{3}(\epsilon_\parallel + 2\epsilon_\perp)$. Perhaps at lower temperatures the $d = 3$, $n = 2$ regime further depresses T_c^{*cl} of $\epsilon_\perp$ due to the lowered order-parameter dimensionality n. An accurate ϵ measurement in KTaO₃ below the liquid-helium range may be of interest for comparison, as there the dimensionality $n = 3$ remains till $T = 0$. A recent dielectric and ultrasound investigation in mixed crystal of KTa₁₋ₓNbₓO₃ has shown that the ferroelectric transition remains quantum-mechanically suppressed up to $x = 0.8\%$.[34]

SbSI, under a hydrostatic pressure of $p_c = 9.1$ kbar, displays[35] a dielectric constant parallel to the c axis ϵ_c, which varies in a similar way as found in SrTiO₃ down to 4 K. Thus, ϵ_c measurements for $T < 4$ K may reveal that under hydrostatic pressure $p > p_c$, SbSI is also a quantum paraelectric.

V. CONCLUSIONS

We have shown that SrTiO₃ is an intrinsic quantum paraelectric,[4,36] i.e., its high dielectric constant implies by the fluctuation dissipation theorem, large ferroelectric fluctuations of wave vector $q = 0$, which are quantum-mechanically stabilized below 4 K in the paraelectric phase. The crossing over from high temperature to this state cannot be fitted appropriately by the analytical expression deduced from quantum mean-field theory[1] (see Fig. 5). This also pertains to other analytical expressions containing a $\coth(\hbar\Omega/kT)$ term.[26,27] Furthermore, it is shown that the single-mode quantum mean-field theory[10] yields a constant κ in the dependence of the classical $T_c = \frac{1}{2}\kappa\Delta z^2$ on ferroelectric ion displacement $\Delta z(T = 0)$, which is a factor 8.5 smaller than the measured one.[24] It is important to take into account the coupling of the ferroelectric soft mode with the acoustic modes as pointed out by Kurtz.[6] This mode coupling and the recently discovered new regime[8] in KTa₀.₉Nb₀.₁O₃ different from Landau behavior for thermal energies inferior to $T_r \approx 120$ K are accounted for in the nonlinear shell model by Migoni, Bilz, and Bäuerle.[9] In this very recent theory the dependence of the soft-ferroelectric mode and measured $\epsilon(T)$ in SrTiO₃ is quantitatively computed using the anharmonic biquadratic force of the oxygen shell towards the B(Ti) ion. This dipolar-MC regime yields an $\epsilon \propto (T - T_c)^{-\gamma}$, $\gamma = 1.4 \pm 0.2$ dependence which is universally observed in other oxide perovskites as well, with $\omega_{TO}(T) > 0$ below $T_r \approx 120$ K,[31] as KTaO₃ and KTN. It depresses the classical $T_c = 35.5$ K observed in the Landau $\gamma = 1$ regime in SrTiO₃ to such a low value $T_{MC} = T_c^{cl} < 10$ K that the quantum-mechanical suppression becomes operative (Fig. 4).
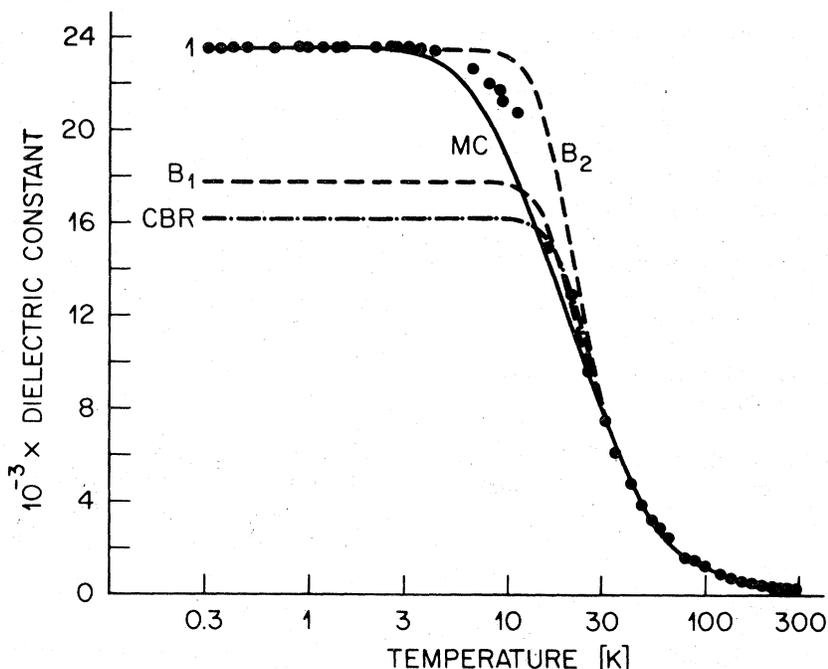
FIG. 5. Comparison of experimental data in the quantum-fluctuation dominated temperature region with the mean-field theory of Barrett (Ref. 1). (a) adjusted to fit crossover below 150 K: B_1; (b) adjusted to fit ϵ at $T \rightarrow 0$: B_2; (c) of the effective acoustic mode coupling by Chaves, Baretto and Ribeiro (CBR) and (d) dipolar mode coupling (MC) with biquadratic electron-phonon interaction (Refs. 9 and 31).

There is an essential difference between the present intrinsic quantum-paraelectric system and those resulting from paraelectric impurities in orthoelectric[36] lattices such as OH⁻ in KCl.[17] *In our intrinsic one, the dielectric constant remains very high and constant till T → 0* [see Fig. 6(a)]. In the impurity case, the dielectric constant first rises according to

a single-particle Curie law $\sim 1/T$ on lowering T. When, for the *single* center, the thermal energy becomes lower, than the local tunneling energy Δ, i.e., $kT < \Delta$, $\epsilon(T)$ flattens. However, because of the dipolar *interaction between the randomly distributed centers*, for $T \rightarrow 0$ $\epsilon(T)$ drops again to a small value [see Fig. 6(b)][20,37] due to possible *polar-glass* behavior.[38]
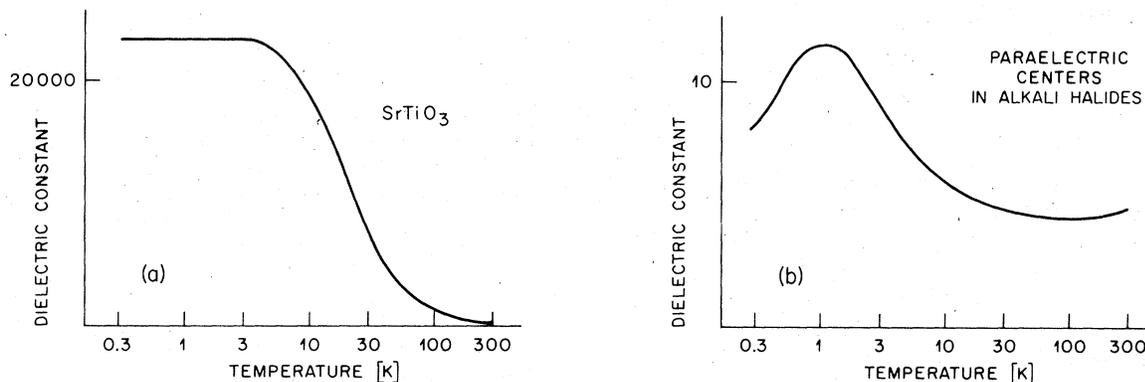
FIG. 6. Comparison between (a) intrinsic and (b) impurity-quantum behavior (Ref. 37) of the dielectric constant as a function of temperature.

VI. ACKNOWLEDGMENTS

APPENDIX: THE DYNAMIC MEAN-FIELD APPROACH

The mean-field theory, where the single soft mode $\omega_q(T)$ is coupled to itself,[10] yields, for the dynamic susceptibility,

$$\chi_q(\omega; T) = 1/m(\omega_q^2 - \omega^2) , \qquad (A1)$$

with the soft mode given by

$$m\omega_q^2 = m\Omega_0^2 + 3\gamma\delta(T) - V_q = m\Omega^2(T) - V_q . \qquad (A2)$$

Here, $m\Omega^2(T) = m\Omega_0^2 + 3\gamma\delta(T)$ is the single-particle frequency at temperature T, resulting from the short-range repulsion $m\Omega_0^2$ its harmonic part, V_q is the interaction potential at wave vector q, owing to short- and long-range forces, and γ the anharmonic force constant in the single-ion potential

$$V(Q) = \tfrac{1}{2}m\Omega_0^2 Q^2 + \tfrac{1}{4}\gamma Q^4 , \qquad (A3)$$

and δ is the variance in amplitude $\delta(T) = \langle\delta Q(T)^2\rangle$.

From Eq. (A2) it is clear that the high symmetry phase with real $\omega_q(T)$ is stabilized by the anharmonicity felt by the fluctuations $\delta(T)$. The stability limit, $\omega_q(T_c) = 0$, gives from Eq. (A2)

$$3\gamma\langle\delta Q(T)^2\rangle = m\Omega_0^2 - V_q . \qquad (A4)$$

In a classical crystal,

$$\langle\delta Q^2\rangle_{cl} = kT/m\Omega^2(T) , \qquad (A5)$$

by equipartition. From this Eq. (A4) gives,

$$3\gamma\frac{kT_c^{cl}}{m\Omega^2(T)} = V_q - m\Omega_0^2 . \qquad (A6)$$

For a ferroelectric with soft mode at $q = 0$, ω_q near T_c^{cl} one finds that

$$m\omega_{q=0}^2 = 3\gamma(\delta - \delta_c) = 3\gamma\frac{T - T_c}{m\Omega(T)} . \qquad (A7)$$

At frequency $\omega = 0$, Eqs. (A1) and (A7) give the Curie-Weiss law

$$\chi(q = 0, \omega = 0) = \frac{m\Omega^2}{3\gamma k(T - T_c^{cl})} = \frac{M}{T - T_c^{cl}} , \qquad (A8)$$

with $M = m\Omega^2/3\gamma k$.

In a quantum crystal the variance is

$$\delta(T) = \langle\delta Q^2\rangle_{qu} = (\hbar/2m\Omega)\coth\tfrac{1}{2}(\hbar\Omega/kT) . \qquad (A9)$$

At low temperature this quantity is always larger than the classical analog of Eq. (A5), which tends to zero for $T \to 0$, whereas Eq. (A9) tends toward $\hbar/2m\Omega$. Therefore, if in Eqs. (A1) and (A2) $m\Omega_0^2 - V_q \lesssim 0$ is negative but small, classically a transition T_c^{cl} will occur, whereas quantum-mechanically one may have at $T = 0$ from Eq. (A9)

$$3\gamma\delta(T) = 3\gamma\hbar/2m\Omega > V_q - m\Omega_0^2 ,$$

and ω_q in Eq. (A2) for $q = 0$ remains finite. This is then the quantum-mechanical suppression.

Using Eq. (A9) we get for the ferroelectric susceptibility from Eqs. (A1), (A2), and (A6), at $q = 0$ and $\omega = 0$,

$$\chi = \frac{m\Omega^2}{3\gamma[\tfrac{1}{2}\hbar\Omega\coth(\tfrac{1}{2}\hbar\Omega/kT) - kT_c^{cl}]} , \qquad (A10)$$

or by setting $\hbar\Omega/k = T_1$, with M from Eq. (A8),

$$\chi = \frac{M}{(T_1/2)\coth(T_1/2T) - T_c^{cl}} . \qquad (A11)$$

Equation (A11) is the formula derived by Barrett[1] for the cubic case without using soft modes.

Within the classical formalism, we can derive a useful relation between T_c^{cl} and the expected displacement $\langle Q\rangle = \Delta z$ at $T = 0$, which we use in Sec. IV. For $T < T_c^{cl}$, the square of the total translational displacement is, from Ref. 10,

$$\langle\Delta Q^2(T)\rangle = 3[\delta_c - \delta(T)] . \qquad (A12)$$

For classical mean field at $T = 0$, the fluctuations are $\delta(T = 0) = 0$, thus with Eq. (A4),

$$\Delta z^2(T = 0) = 3\delta_c = \frac{V_q - m\Omega_0^2}{\gamma} . \qquad (A13)$$

The difference between the particle interaction potential V_q and the single-particle frequency term at $T = 0$, $m\Omega_0^2$ in Eq. (A6) allows the elimination of the anharmonic force constant γ, and we arrive at

$$kT_c^{cl} = \tfrac{1}{3}m\Omega^2\Delta z^2(T = 0) , \qquad (A14)$$

i.e., T_c^{cl} is proportional to Δz^2 if $\Omega \simeq \Omega_0$ given by the local potential is constant, and V_q varies. Or in Kurtz's words,[6] T_c^{cl} is proportional to Δz^2 if the short-range force constant $\tfrac{1}{2}\kappa = (m\Omega^2)/3$ does not vary, whereas the longer range ones contained in V_q do, as a result of different lattice geometries.

*Present address: Brown Boveri & Cie., 5401 Baden, Switzerland.

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