Quantum paraelectric behavior of SrTiO₃: Relevance of the structural phase transition temperature

Manuel I. Marqués,* Carmen Aragó, and Julio A. Gonzalo

Departamento de Física de Materiales C-IV, Universidad Autónoma de Madrid, 28049 Madrid, Spain
(Received 9 June 2005; published 27 September 2005)

It has been known for a long time that the low temperature behavior shown by the dielectric constant of quantum paraelectric SrTiO₃ cannot be fitted properly by Barrett's formula using a single zero point energy or saturation temperature (T_1). As it was originally shown [K. A. Müller and H. Burkard, Phys. Rev. B **19**, 3593 (1979)] a crossover between two different saturation temperatures ($T_{1l}=77.8$ K and $T_{1h}=80$ K) at $T \sim 10$ K is needed to explain the low and high temperature behavior of the dielectric constant. However, the physical reason for the crossover between these two particular values of the saturation temperature at $T \sim 10$ K is unknown. In this work we show that the crossover between these two values of the saturation temperature at $T \sim 10$ K can be taken as a direct consequence of (i) the quantum distribution of frequencies $g(\Omega) \propto \Omega^2$ associated with the complete set of low-lying modes and (ii) the existence of a definite maximum phonon frequency given by the structural transition critical temperature T_{tr}.

The "quantum paraelectrics" or "incipient ferroelectrics" have been a topic of considerable interest during last decades. Quantum fluctuations associated to a non-negligible zero point energy prevent the onset of ferroelectric long-range order. Actually, some nonproper ferroelectric perovskites such as strontium titanate (SrTiO₃) or potassium tantalate (KTaO₃), with very large dielectric contant values, undergo ferroelectric phase transitions when doped with small amounts of polar impurities such as calcium or lithium.[1] Recently there has been some controversy about the origin of this quantum fluctuations. It is not clear whether they come from a superposition of incoherent modes, or whether the coupling of the lowest transverse acoustic and the soft mode gives rise to a coherent quantum paraelectric state.[2] This conjecture has been stimulated by the observation of an anomaly, indicative of a possible phase transition near $T_c=35$ K measured on several experimental studies based on light,[3,4] neutron scattering,[5] sound dispersion and attenuation,[6,7] extended x-ray-absorption fine structure[8] (EXAFS) and dielectric spectroscopy.[9,10]

Almost 30 years ago Müller and Burkard[11] measured the dielectric constant (χ) of SrTiO₃ in monodomain samples down to $T=0.3$ K. The experiment showed that χ was temperature independent below $T=3$ K. This constant region was in agreement with theoretical predictions from Barrett's formula[12] which extended Slater's mean field theory of perovskites, to include quantum effects. Barrett's formula depends on the saturation or Einstein temperature T_1, which is related to the quantum mechanical zero point motion of the elementary dipoles ($T_1=\hbar\Omega/k$), with Ω being the single dipole frequency. However, Müller *et al.* noted that Barrett's formula was unable to fit $\chi(T)$ for all temperatures below $T=30$ K.[11] Actually, two saturation temperatures (T_{1h} and T_{1l}) were needed to fit the 30 K$>T>$10 K region and the $T<3$ K region respectively.[11] No single saturation temperature was able to fit the complete 30 K$>T>$0.3 K region. This breaking from the experimental data was attributed to a coupling of the single soft mode to other occupied acoustic

modes[11] considering phonon dressing[13] and dipolar behavior[14,15] in order to reduce the classical critical temperature. More recently, another approach to fit the experimental data for quantum paraelectrics in a large range of temperatures has been proposed. It is based on a generalization of Barrett's formula to a quantum Curie-Weiss-like formula by introducing a critical exponent γ.[16] The obtained value of γ for pure SrTiO₃ is $\gamma=1.7$.

Barrett's formula may be obtained rigorously[18,19] by introducing a quantum temperature scale related to the energy of the quantum oscillator

$$T_q = \frac{\hbar\Omega}{k}\left(\frac{1}{e^{\hbar\Omega/kT}-1}+\frac{1}{2}\right). \qquad (1)$$

This quantum temperature has been successfully applied to the analysis of the susceptibility in quantum paraelectrics[17] and, by means of a mean-field approach, it has been also used to explain the quantum effects found in mixed classical ferroelectric systems such as tris-sarcosine calcium chloride/bromide systems.[20,21] Using this quantum temperature instead of the classical temperature in Slater's mean-field formula for the susceptibility we obtain Barrett's formula for quantum paraelectrics,

$$\chi = \frac{C}{\frac{T_1}{2}\coth\left(\frac{T_1}{2T}\right) - T_c} + A, \qquad (2)$$

where C is the Curie-Weiss constant, T_c is the extrapolated Curie temperature of the ferroelectric transition, and A is the temperature independent part of the dielectric constant. Fitting parameters for SrTiO₃ are given by $A=0$, $C=8 \times 10^4$ K and $T_c=35.5$ K. As already mentioned, two saturation temperatures $T_1=T_{1l}$ and $T_1=T_{1h}$ are needed to fit the low ($T<3$ K) and high temperature regimes (30 K$>T >$10 K). In particular, Müller *et al.* calculated that the best fits to the experimental data were found for $T_{1l}=77.8$ K and

$T_{1h}=80$ K.[11] These two particular values are independent fitting parameters lacking a rigorous theoretical justification.

Very recently, Yuan et al.[22] have modeled this crossover beteween $T_{1l}=77.8$ K and $T_{1h}=80$ K by introducing a continuous, temperature dependent T_1, given by a hyperbolic tangent that fits very well dielectric experimental results for SrTiO$_3$ in the whole range of temperatures. The proposed temperature dependence is given by

$$T_1 = T_{1l} + \frac{T_{1h}-T_{1l}}{2}\left[1 + \tanh\left(\frac{T-\theta}{\alpha}\right)\right], \qquad (3)$$

where θ and α are two new free parameters introduced to describe the crossover temperature (close to 10 K) and the crossover rate respectively. Note that four fitting parameters are needed to describe the crossover.

However, the reason for the existence of this crossover dependence on the saturation temperature is unknown. Why are the characteristic saturation temperatures associated with the quantum mechanical zero point energy of the elementary dipoles given by $T_{1l}=77.8$ K and $T_{1h}=80$ K? Why is there a change on the dielectric behavior of the quantum paraelectric between these two particular values precisely at $T\sim 10$ K?

In the following, we will show how this crossover between these two particular saturation temperatures can be taken as due to the existence of the quantum distribution of frequencies $g(\Omega)\propto\Omega^2$ associated with the complete set of low-lying oscillations[23,24] and to a specific maximum value for the phonon frequencies given by the structural transition critical temperature.

Let us consider the general case where, instead of $\Omega = cte$, the system presents a distribution of frequencies given by $g(\Omega)$. Due to the existence of this distribution, it is not appropriate to relate the quantum temperature T_q to a single frequency Ω but to an average value ($\langle\Omega\rangle$) which is temperature dependent. The temperature dependence of the average frequency value is given by

$$\langle\Omega\rangle\left(\frac{1}{e^{\hbar\langle\Omega\rangle/kT}-1}+\frac{1}{2}\right) = \frac{\displaystyle\int_0^{\Omega_{max}}\Omega\left(\frac{1}{e^{\hbar\Omega/kT}-1}+\frac{1}{2}\right)g(\Omega)d\Omega}{\displaystyle\int_0^{\Omega_{max}}g(\Omega)d\Omega},$$

$$(4)$$

with Ω_{max} being the maximum possible value for the frequency of the phonon oscillations at low temperatures.

Once the frequency distribution of the system is fixed as $g(\Omega)\propto\Omega^2$, corresponding to the low-lying modes, it is possible to solve this equation numerically to obtain the temperature dependence of $\langle\Omega\rangle$ and the behavior of $T_1 = \hbar\langle\Omega\rangle/k$. In order to know the value of Ω_{max} we consider the following. The structural cubic-tetragonal phase transition in SrTiO$_3$ at $T_{tr}\sim 104$ K, associated with an acoustic soft mode behavior,[25] should mark an upper boundary for the frequency of the oscillations at low temperatures. Higher values of Ω should be unstable at these low temperatures. The maximum possible value for the frequency of the phonon oscillations is then given by $\Omega_{max}=T_{tr}k/\hbar$.
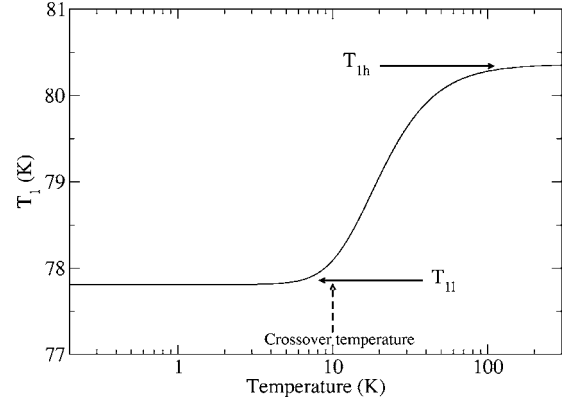

FIG. 1. Behavior of the saturation temperature of the system vs temperature.

The value of T_{tr} for SrTiO$_3$ depends somewhat on the sample;[26] however, most of the values found in the literature are close to $T\sim 104$ K. So, for the particular case studied in this work (sample A from Ref. 11) we take the value $T_{tr}=104$ K (corresponding to $\Omega_{max}=13.6$ T Hz). Once this value for Ω_{max} is introduced in Eq. (4), the existence of a crossover for $T_1(\langle\Omega\rangle)$ between the two saturation temperatures ($T_{1l}=77.8$ K and $T_{1h}=80$ K) appears as a natural consequence of the existence of the frequency distribution $g(\Omega)$ of low-lying modes with $\Omega_{max}=T_{tr}k/\hbar$ (see Fig. 1). Note how the crossover starting point at approximately $\theta=10$ K appears also straightforwardly.

Of course, once we know the temperature dependence of T_1 it is possible to obtain the behavior of the dielectric constant using Barrett's formula [Eq. (2)]. The final result is shown in Fig. 2 together with the two fittings given by Müller et al.[11] for the low and high temperature regimes. Note how the data between both regimes (30 K $> T > 10$ K and $T < 3$ K) is now explained by means of a single distribution of frequencies in SrTiO$_3$ given by $g(\Omega)\propto\Omega^2$ with $\Omega_{max}=T_{tr}k/\hbar$.
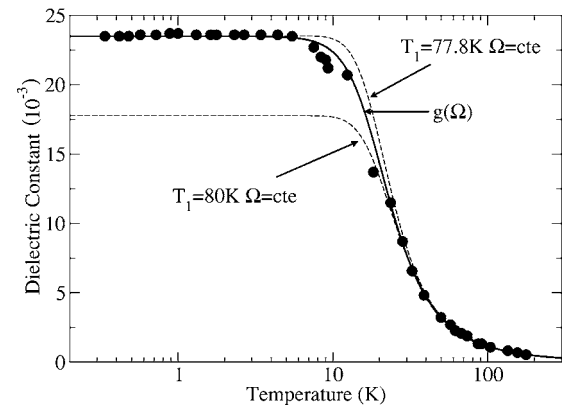
This relation found between the structural critical tem-

FIG. 2. Dielectric contant vs temperature for SrTiO$_3$. Dotted lines are results from Barrett's formula with $T_1=77.8$ K and $T_1=80$ K and using a constant value for the frequency associated with the quantum mechanical zero point motion. Full line is the result obtained using a distribution $g(\Omega)\propto\Omega^2$ and a structural critical temperature for the system equal to 104 K.

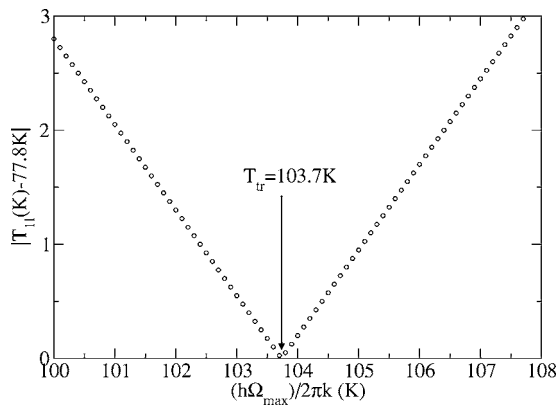FIG. 3. Absolute value of the difference between the $T=0$ K saturation temperature (T_{1l}) and the saturation temperature that fits the dielectric behavior at $T \sim 0$ K (Ref. 11) vs $\hbar\Omega_{max}/k$. We find that the value corresponding to this particular SrTiO$_3$ system is $T_{tr} = 103.7$ K, which may be associated with the structural critical temperature of the sample.

perature and the low temperature value of the dielectric constant, allows determining the critical temperature with very high precision. In order to get T_{tr} we scan Ω_{max} to obtain successive T_{1l} values until we match the particular value $T_{1l} = 77.8$ K given by Müller *et al.*[11] to fit the dielectric constant in the low temperature region (sample A). In Fig. 3 we present $|T_{1l} - 77.8 \text{ K}|$ vs $\hbar\Omega_{max}/k$. Note how the difference is zero at $\hbar\Omega_{max}/k = 103.7$ K, which is very close to the average critical value $T_{tr} \sim 104$ K for SrTiO$_3$.

Note that, in this way, we have obtained the structural transition critical temperature $T_{tr} = 103.7$ K by means of an indirect method, using only data from low temperature dielectric constant measurements. Since the value for T_{1l} or, equivalently, the dielectric constant at $T \sim 0$ K, is very sensitive to the value of $\hbar\Omega_{max}/k$ this method turns out to be a very precise way to determine the structural critical temperature of a particular sample (for example, knowing that the value of the dielectric constant at zero temperature of sample B in Ref. 11 is 20^{-3} we get a critical temperature $T_{tr} = 105.3$ K, slightly higher than the one corresponding to sample A).

To conclude, as it is well known, Barrett's formula is insufficient to explain the dielectric behavior in SrTiO$_3$ for $T < 30$ K when using a single, contant value, for the frequency associated with the quantum mechanical zero point motion of the elementary dipoles. This problem is solved when considering a quantum distribution of frequencies $g(\Omega) \propto \Omega^2$ associated with the complete set of low-lying oscillations which are dominant at low temperatures and a upper frequency given by $\Omega_{max} = T_{tr}k/\hbar$. This distribution gives rise to the existence of a crossover between two saturation temperatures capable of explaining satisfactorily the behavior of the dielectric constant at any temperature. Since, the maximum value for the frequency in the $g(\Omega)$ distribution is given by the structural transition critical temperature, it is also possible to obtain very precise values for the structural critical temperatures by using the measured $T=0$ K dielectric constant of the quantum paraelectric.

*Electronic address: manuel.marques@uam.es

[1] See U. Bianchi, J. Dec, W. Kleeman, and J. G. Bednorz, Phys. Rev. B **51**, 8737 (1995), and references therein.

[2] K. A. Müller, W. Berlinger, and E. Tosatti, Z. Phys. B: Condens. Matter **48**, 277 (1991).

[3] R. Vacher, J. Pelous, B. Hennion, G. Coddens, E. Courtens, and K. A. Müller, Europhys. Lett. **17**, 45 (1992).

[4] B. Hehlen, A.-L. Pérou, E. Courtens, and R. Vacher, Phys. Rev. Lett. **75**, 2416 (1995).

[5] E. Courtens, G. Coddens, B. Hennion, B. Hehlen, J. Pelous, and R. Vacher, Phys. Scr., T **49A**, 430 (1993).

[6] E. V. Balashova, V. V. Lemanov, K. Kunze, G. Martín, and M. Weihnacht, Solid State Commun. **94**, 17 (1995).

[7] O. M. Nes, K. A. Müller, T. Suzuki, and F. Fossheim, Europhys. Lett. **19**, 397 (1992).

[8] M. Fischer, A. Lahmar, M. Maglione, A. San Miguel, J. P. Itié, A. Polian, and F. Baudelet, Phys. Rev. B **49**, 12451 (1994).

[9] R. Viana, P. Lunkenheimer, J. Hemberger, R. Böhmer, and A. Loidl, Phys. Rev. B **50**, 601 (1994).

[10] J. Hemberger, M. Nicklas, R. Viana, P. Lunkenheimer, A. Loidl, and R. Böhmer, J. Phys.: Condens. Matter **8**, 4673 (1996).

[11] K. A. Müller and H. Burkard, Phys. Rev. B **19**, 3593 (1979).

[12] J. H. Barrett, Phys. Rev. **86**, 118 (1952).

[13] R. A. Cowley, Philos. Mag. **11**, 673 (1965).

[14] R. Kind and K. A. Müller, Commun. Phys. (London) **1**, 223 (1976).

[15] R. Migoni, H. Bilz, and D. Bäuerle, Phys. Rev. Lett. **37**, 1155 (1976).

[16] J. Dec and W. Kleemann, Solid State Commun. **106**, 695 (1998).

[17] W. Kleemann, J. Dec, and B. Westwanski, Phys. Rev. B **58**, 8985 (1998).

[18] E. K. H. Salje, B. Wruck, and H. Thomas, Z. Phys. B: Condens. Matter **82**, 399 (1991).

[19] E. K. H. Salje, B. Wruck, and S. Marais, Ferroelectrics **124**, 185 (1991).

[20] J. A. Gonzalo, Ferroelectrics **168**, 1 (1995).

[21] C. Aragó, J. García, J. A. Gonzalo, C. Wang, W. Zhong, and X. Xue, Ferroelectrics **301**, 113 (2004).

[22] M. Yuan, C. L. Wang, Y. X. Wang, R. Ali, and J. L. Zhang, Solid State Commun. **127**, 419 (2003).

[23] A. B. Rechester, Zh. Eksp. Teor. Fiz. **60**, 782 (1971) [Sov. Phys. JETP **33**, 423 (1971).].

[24] D. E. Khmel'nitskii and V. L. Shneerson, Fiz. Tverd. Tela (Leningrad) **13**, 832 (1971) [Sov. Phys. Solid State **13**, 687 (1971)].

[25] G. Shirane, Rev. Mod. Phys. **46**, 437 (1974).

[26] H. Hünnefeld, T. Niemöller, J. R. Schneider, U. Rütt, S. Rodewald, J. Fleig, and G. Shirane, Phys. Rev. B **66**, 014113 (2002).