

Dielectric susceptibility in quantum ferroelectrics

D. Rytz

*Ecole Polytechnique Fédérale de Lausanne, Laboratoire de Physique
Expérimentale, 1007 Lausanne, Switzerland*

U. T. Höchli

IBM Zurich Research Laboratory, 8803 Rüschlikon, Switzerland

H. Bilz

*Max-Planck Institut, 7000 Stuttgart 80, West Germany
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Dielectric susceptibilities are reported for $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ and $\text{K}_{1-y}\text{Na}_y\text{TaO}_3$ mixed-crystal ferroelectrics with a Curie temperature T_C close to absolute zero. According to the temperature range, the two following formulas are fitted to the experimental data: $\epsilon = A + B/[(\frac{1}{2}T_1/T) \times \coth(\frac{1}{2}T_1/T) - T_0]$ for $T > \frac{1}{2}T_1$ and $\epsilon = A + BT^{-2}$ for $T, T_C \leq \frac{1}{2}T_1$. This latter condition defines the quantum limit of a ferroelectric. Both formulas are obtained as limiting cases of a renormalized harmonic approximation of a model involving nonlinear polarizability of the oxygen shell. The constants A , B , T_1 , and T_0 are explained in terms of model parameters. The leading term of the divergence of the susceptibility at the quantum limit coincides with the one obtained by the renormalization-group approach. Although renormalized harmonic approximation in general is bound to fail close to T_C , it gives valid results for the isolated (Gaussian) fixed point $T_C = 0$.

I. INTRODUCTION

The competition between long-range ordering forces and fluctuations in dipolar systems determines the range of stability of the polar phase. In the majority of cases, the stability limit falls in a region of classical (Boltzmann) fluctuations; only two examples (KTaO_3 and SrTiO_3) are known with a stability limit in a region of predominantly quantum-statistical fluctuations. As a consequence, the temperature becomes an ineffective parameter for the phase diagram and the susceptibility. For such systems, we use the term "quantum ferroelectrics" and we intend to include the case in which polar order is marginally stable against quantum fluctuations (quantum limit) as well as the case where polar order is suppressed by quantum fluctuations (incipient ferroelectrics). For the quantum limit there are specific predictions by Schneider *et al.* and by Oppermann and Thomas¹ for the leading exponent γ of the susceptibility

$$\epsilon \sim T^{-\gamma}, \quad \gamma = 2, \quad (1)$$

which is in contrast to the Curie-Weiss exponent $\gamma = 1$.

On the other hand, there is a long-standing expression by Barrett,²

$$\epsilon = A + B/[(\frac{1}{2}T_1/T) \coth(\frac{1}{2}T_1/T) - T_0], \quad (2)$$

which has already been fitted to the dielectric suscep-

tibility of KTaO_3 ,³⁻⁵ and SrTiO_3 .⁶⁻⁸

We note, however, that Eq. (2) is in contradiction to Eq. (1) at the quantum limit, and that each of the approaches leading to the corresponding equation can, at most, have its limited nonoverlapping range of validity.

It is the purpose of the present work to determine these ranges of validity both from an experimental point of view and from an assessment of the microscopic models from which they derive. To this end, we present, in an experimental section, the first systematic data set of dielectric constants taken in the immediate neighborhood of the quantum limit, a condition which is met by mixed-crystal ferroelectrics^{9,10} and possibly by stoichiometric crystals under hydrostatic pressure.¹¹ Fits of Eqs. (1) and (2) to these data allow a visual perception of the ranges of validity.

A further section is devoted to theoretical considerations. Under certain conditions, the susceptibility can be expressed in terms of Eq. (2). At low temperatures this approach fails, and a single-exponent law is recovered.

The ranges of validity of the respective models are reviewed in a final section. Model (1) leading to Eq. (1) is based on the critical equivalence class of Hamiltonians in three dimensions at $T_C = 0$.¹ It is expected to account for the data taken on crystals transforming below a certain limiting temperature T_l and

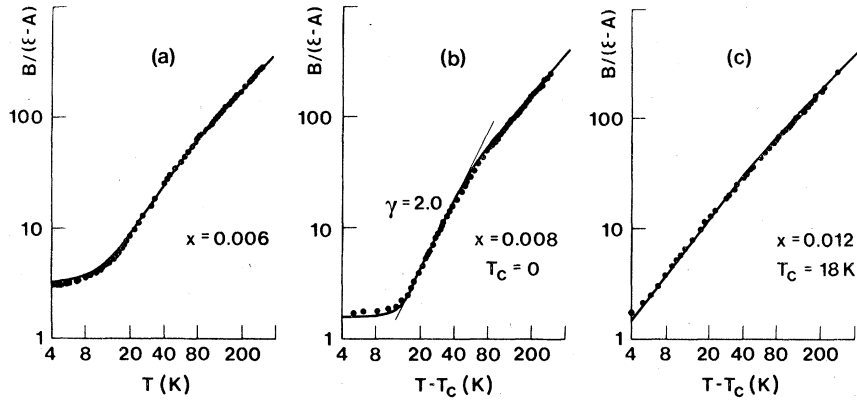


FIG. 1. Log-log diagrams of the temperature dependence in the paraelectric phase of the dielectric susceptibility for $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ crystals with x near the quantum-limit value x_c : (a) $x < x_c$, (b) $x = x_c$, and (c) $x > x_c$. The solid lines represent the fits of $B/(\epsilon - A) = (\frac{1}{2}T_1) \coth(T_1/2T) - T_0$ to our experimental data. In case (b), a fitted power law $B/(\epsilon - A) = T^\gamma$ with $\gamma \approx 2$ is also shown.

in a temperature range extending from T_C into the paraelectric phase. Model (2) leading to Eq. (2) takes into account specific harmonic and anharmonic interactions between nearest- and next-nearest-neighbor constituents of perovskite oxides.^{12,13} It will be pointed out that under the specific condition $T_C = 0$, and only then, is the Hamiltonian of model (2) of the same critical equivalence class as that of model (1).

II. EXPERIMENT

$\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ (potassium-tantalate niobate) and $\text{K}_{1-y}\text{Na}_y\text{TaO}_3$ (potassium-sodium tantalate) mixed crystals were grown by slow cooling of the melt. Crystal growth, composition inhomogeneities, and ferroelectric phase diagrams were described earlier.^{9,10}

The transition temperatures were determined by measuring the elastic properties. In pure KTaO_3 , no ferroelectric phase transition is observed, but in mixed crystals, ferroelectricity occurs for concentrations larger than critical values x_c or y_c , respectively. These critical values defining the quantum limit were found to be $x_c = 0.008$ and $y_c = 0.12$, respectively. In addition, crystals were grown with x or y differing from x_c or y_c by about 20% to obtain information immediately below and immediately above the quantum limit.

The dielectric constant of these crystals was measured at 1 kHz on a GE 1616 capacitance bridge. The frequency independence of the data was checked at room temperature. The resulting susceptibilities are plotted as a function of temperature in Figs. 1 and 2 for $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ and $\text{K}_{1-y}\text{Na}_y\text{TaO}_3$, respectively, all on log-log scale. The different plots are denot-

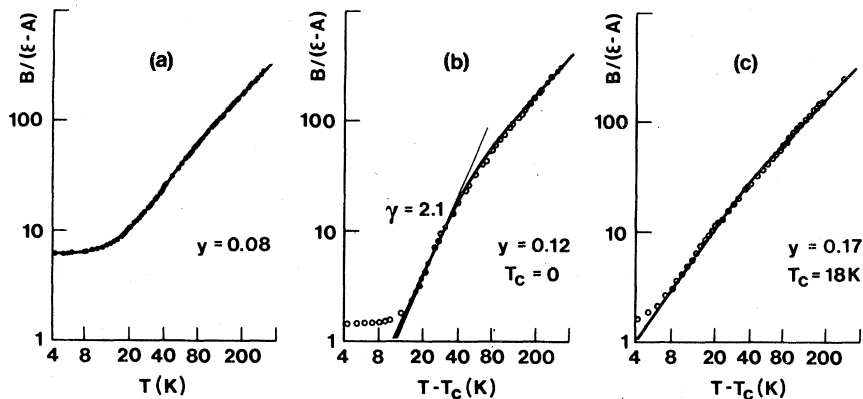


FIG. 2. Log-log diagrams of the temperature dependence in the paraelectric phase of the dielectric susceptibility for $\text{K}_{1-y}\text{Na}_y\text{TaO}_3$ crystals with y near the quantum-limit value y_c : (a) $y < y_c$, (b) $y = y_c$, and (c) $y > y_c$. The solid lines represent the fits of $B/(\epsilon - A) = (\frac{1}{2}T_1) \coth(T_1/2T) - T_0$ to our experimental data. In case (b), a fitted power law $B/(\epsilon - A) = T^\gamma$ with $\gamma \approx 2$ is also shown.

ed by (a), (b), and (c) according to whether the variables x and y are subcritical, critical, or above critical. The following are identified: a high-temperature regime ($T > 80$ K) where the Curie-Weiss law with $\gamma = 1$ is valid,¹⁴ a temperature range ($80 > T > 35$ K) for which a fit with Eq. (2) appears appropriate, and, when $x = x_c$ or $y = y_c$ [case (b)] another range ($35 > T > 15$ K) with $\gamma \sim 2$. In the lowest temperature range ($T < 15$ K in the quantum-limit case and $T < 35$ K otherwise), there is a flattening of the dielectric susceptibility near values 10^{-4} . Such susceptibility limits are commonly encountered in ferroelectrics⁸ and reduce the accessible range of critical behavior. In cases (a) and (c), flattening is directly adjacent to the medium temperature range. We have not attempted to fit Eq. (2) to the flat part of ϵ^{-1} because we found the limiting value to be sample dependent.

The parameters used to fit the high- and medium-temperature behaviors of ϵ^{-1} are summarized in Table I. The low-temperature regime of the data set for the quantum limit [case (b)] could be fitted with a pure "power law" [Eq. (1)]. This fit is definitely better than an extension of Eq. (2) to low temperatures as indicated by the standard deviations also entered in Table I, although the difference is sufficiently small to escape a superficial inspection on a log-log plot. The exponent determined by the least-squares

fit (also in Table I) is close to $\gamma = 2$, the value predicted¹ on the basis of renormalization-group arguments.

Thus, we present the first experimental evidence for this peculiar temperature dependence of the dielectric susceptibility. Such a high value of the critical exponent γ had not been observed in previous work, as all the crystals studied were out of the quantum-limit extension. This extension may be expressed as $x_c \pm \Delta x$ for $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ and $y_c \pm \Delta y$ for $\text{K}_{1-y}\text{Na}_y\text{TaO}_3$, where Δx and Δy are the deviations in concentration above which the quantum-limit regime with $\gamma = 2$ disappears. With the present homogeneity of the samples, only the following upper bounds could be determined, i.e., $\Delta x \leq 0.002$ and $\Delta y \leq 0.04$, as obtained from Figs. 1 and 2. In terms of the ferroelectric phase diagram, an increase of the transition temperature from 0 to 18 K has dramatic implications on the observation of the quantum-limit regime. No fit is possible with Eq. (1) for samples with $T_C \geq 18$ K.

The one-to-one correspondence between $\gamma = 2$ and a vanishing T_C allows attribution of this observation to the crossover from classical ($\gamma = 1$) to quantum behavior ($\gamma = 2$). The crossover region from pure-quantum to classical regime is thus rather large. Figure 3 shows the phase diagram of quantum ferroelectrics and the pertinent regions of classical, quantum,

TABLE I. Parameters of the fits of Barrett's formula $\epsilon = A + B[\frac{1}{2}T_1 \coth(\frac{1}{2}T_1/T) - T_0]$ [Eq. (2)] and of $\epsilon \sim T^{-\gamma}$ [Eq. (1)] for crystals near the quantum limit.

	Fit to Eq. (2)				Fit to Eq. (1)				
	A	B (K)	T_1 (K)	T_0 (K)	Standard deviation (percent)	Temperature range (K)	Quantum regime	Standard deviation (percent)	
SrTiO ₃ Ref. 6	0	86400	100	45		1-300	No	...	
	0	90000	84	38		4-300	No	...	
	0	80000	80	35.5		16-150	No	...	
KTaO ₃ Ref. 3	48.3	55200	53.3	11.8		4-300	No	...	
	47.5	54500	56.9	13.1		4-300	No	...	
	48.5	50100	52.8	12.3	2	10-300	No	...	
KTa _{1-y} Nb _x O ₃									
	$x = 0.006$	59	50000	47	20	8-300	No	...	
	$x = 0.008$	72	45000	64	30	14-35	$\gamma = 2.0 \pm 0.1$	0.3	
					5.5	14-300			
$x = 0.012$	60	46000	57	32	4.2	24-300	No	...	
K _{1-y} Na _y TaO ₃									
	$y = 0.08$	57	52000	52	19	10-300	No	...	
	$y = 0.12$	58	49000	57	28	9.7	14-35	$\gamma = 2.1 \pm 0.1$	0.7
						6.5	15-300		
$y = 0.17$	49	52000	59	33	3.3	26-300	No	...	

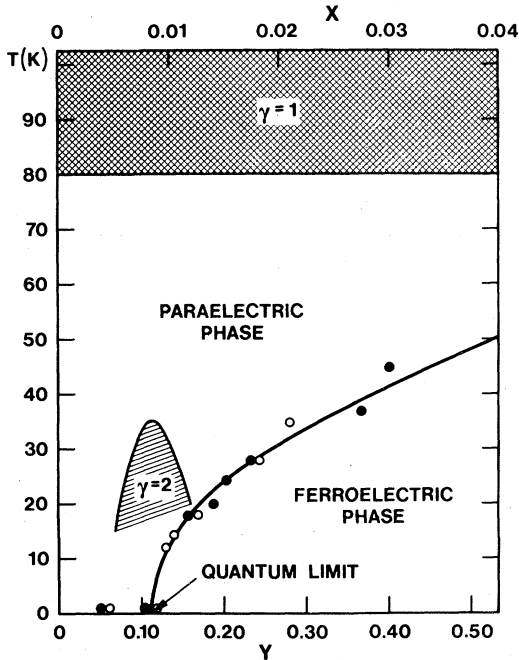


FIG. 3. Ferroelectric phase diagram for (●) $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ (upper scale) and (○) $\text{K}_{1-y}\text{Na}_y\text{TaO}_3$ (lower scale). The solid line is the transition line between paraelectric and ferroelectric states. The crosshatched and the hatched areas indicate the temperature and concentration ranges where $\gamma = 1$ and $\gamma = 2$ hold, respectively.

and intermediate behavior.

To complete the picture, we should like to mention preliminary measurements on Verneuil-grown $\text{Sr}_{1-z}\text{Ca}_z\text{TiO}_3$ crystals,¹⁵ where a quantum regime with $\gamma = 2$ was also obtained for $z = 0.003$. Furthermore, in Fig. 4 we reinterpret data from Samara¹¹ for a quan-

tum ferroelectric with hydrostatic pressure being the interaction parameter, KH_2PO_4 . Neither the interchange of composition by pressure nor the fact that the symmetry of KH_2PO_4 is lower than that of KTaO_3 seems to affect the results: the data show a fit of ϵ^{-1} with $\gamma \sim 2$ at $T_C \sim 0$ [Fig. 4(b)] and the impossibility of such a fit at $T_C \neq 0$ [Figs. 4(a) and 4(c)]. High-temperature data appear to be unavailable for those pressures. Therefore, no fits of Eq. (2) can be shown. Nevertheless, the behavior of potassium dihydrogen phosphate (KDP) at $T_C = 0$ agrees well with our findings described in the next section.

III. REVIEW OF THEORY

The Hamiltonian used¹ to predict critical behavior at the quantum limit is given by

$$H = \sum_{l,\alpha} \frac{1}{2} m \dot{u}_{l\alpha}^2 + \frac{1}{2} D \sum_{l,\alpha} u_{l\alpha}^2 + \frac{E}{4n} \sum_l \left(\sum_{\alpha} u_{l\alpha}^2 \right)^2 - F \sum_{l,l',\alpha} u_{l\alpha} u_{l'\alpha} \quad (3)$$

l denotes the lattice sites, and $u_{l\alpha}$ is the α th component ($\alpha = 1, \dots, n$) of the displacement of particles with mass m . The model parameters are D , E , and F .

H involves nearest-neighbor interaction of a simple d -dimensional cubic lattice. Upon setting $T = 0$ and introducing an interaction parameter $S = 4dF - D$, it was shown that this Hamiltonian is in the same critical equivalence class¹⁶ as a four-dimensional Hamiltonian in interaction-parameter (rather than temperature) space. The fixed point of this Hamiltonian is thus Gaussian and at $T = \text{const} = 0$, $\epsilon(S) \sim (S - S_c)^{-1}$.

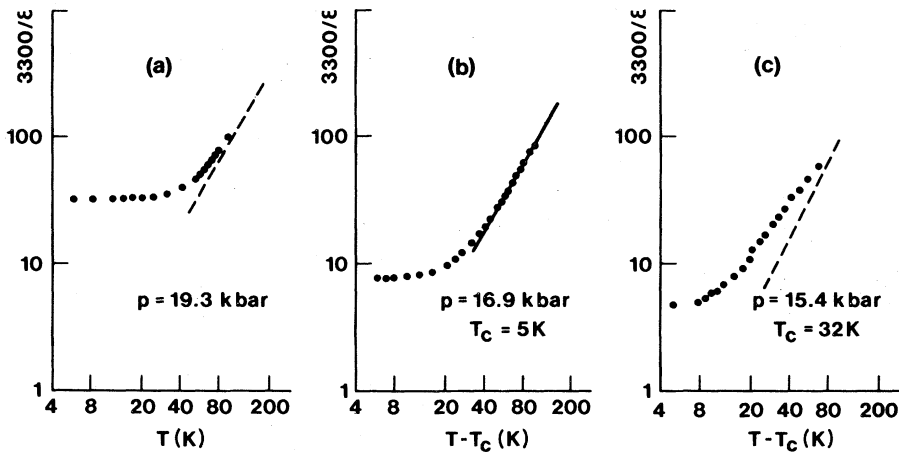


FIG. 4. Log-log diagrams of the temperature dependence in the paraelectric phase of the dielectric susceptibility for KH_2PO_4 crystals under hydrostatic pressure. The data sets and the quantum-limit value p_c are taken from Ref. 11: (a) $p > p_c$, (b) $p \approx p_c$, and (c) $p < p_c$. The broken straight lines correspond to $\epsilon = T^{-2}$. The attempted fit is reasonable only at the quantum limit [case (b)].

In view of the criticality of the phase diagram $T_c \sim (S - S_c)^{1/2}$, this leads to $\epsilon(T) \sim T^{-2}$ neglecting logarithmic corrections. Since this Hamiltonian is stripped of all but the essential qualitative features,¹⁶ it cannot account for any observation outside the critical region. This region is in turn covered by the renormalized harmonic phonon approximation.¹⁷ A shell model was constructed¹² in such a way as to account for the Raman spectra observed in quantum ferroelectrics and to point to the probable origin of ferroelectricity in terms of anisotropic oxygen polarizability. The 15-parameter version of Migoni *et al.* has recently been simplified to a three-parameter (pseudolinear) model¹³ which represents the temperature dependence of the soft modes in perovskites quite well. The Hamiltonian considers nearest- and next-nearest-neighbor interaction within a linear chain and, in particular, the anharmonic force between the oxygen core and its ligand (Fig. 5):

$$H = \sum_l \left[\frac{1}{2} m_1 \dot{u}_{1l}^2 + \frac{1}{2} m_2 \dot{u}_{2l}^2 + \frac{1}{2} m_e \dot{v}_l^2 \right] + \sum_l \left[\frac{1}{2} f' (u_{1l+1} - u_{1l})^2 + \frac{1}{2} g_2 (v_l - u_{1l})^2 + \frac{1}{4} g_4 (v_l - u_{1l})^4 + \frac{1}{2} f (u_{2l} - v_l)^2 + \frac{1}{2} f (u_{2l} - v_{l+1})^2 \right]. \quad (4)$$

Introducing the relative displacement between shell and core,

$$w_l = v_l - u_{1l},$$

the following equations of motion are derived:

$$m_1 \ddot{u}_{1l} = g_2 w_l + g_4 w_l^3 + f' (u_{1l+1} + u_{1l-1} - 2u_{1l}), \quad (5)$$

$$m_2 \ddot{u}_{2l} = f (w_{l+1} + w_l) + f (u_{1l+1} + u_{1l} - 2u_{2l}),$$

with the condition for adiabaticity of the oxygen electronic shell

$$m_e \ddot{w}_l = (2f + g_2) w_l + g_4 w_l^3 - f (u_{2l} + u_{2l-1} - 2u_{1l}) = 0.$$

In the spirit of the renormalized harmonic

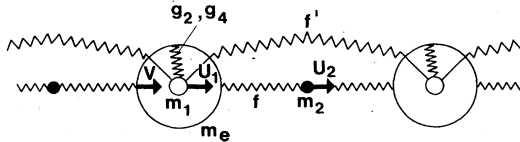


FIG. 5. Linear chain model (after Ref. 13). Notation: m_1, m_2 are the masses of anions and cations; f, f' : nearest- and next-nearest-neighbor coupling constants; g_2, g_4 : harmonic and quartic shell-core coupling constants. u_1, u_2 denote displacements of particles 1 and 2, respectively, v being the shell displacement.

approximation,

$$g_4 w_l^3 \approx 3g_4 w_l \langle w^2 \rangle_T \equiv g_T w_l, \quad (6)$$

where $\langle w^2 \rangle_T$ is the thermal average of the mean-square shell displacements of w arriving from all modes.

This leads to a renormalization of the rigid-ion frequency of the linear chain, ω_0 , as

$$\omega_F^2(T) = \omega_0^2 \frac{g}{2f+g}, \quad (7)$$

where

$$g = g_T + g_2. \quad (8)$$

Note that $g_2 < 0$. In virtue of Eq. (6),

$$g_T = 3g_4 \langle w^2 \rangle_T = 3g_4 \int d^3q C_\omega(q) w_F^{-2} \omega_0^{-3} \coth \hbar \omega_F(q) / 2kT. \quad (9)$$

For temperatures near T_1 , given by the self-consistency equation $T_1 = \hbar \omega_F(T_1) / k$, the integral in Eq. (9) may be approximated by its integrand

$$g_T = \frac{1}{2} G \coth \hbar \omega_F(T_1) / 2kT, \quad (10)$$

where G contains all multiplicative constants.

Inserting Eqs. (8) and (10) into Eq. (7), Eq. (2) is recovered,¹⁸ in which the constants are identified as

$$A = \epsilon(T \rightarrow \infty) = \omega_0^{-2}; \quad B = \frac{2\hbar f \omega_0^{-2} \omega_F(T_1)}{kG}; \quad (11)$$

$$T_1 = \frac{\hbar \omega_F(T_1)}{k}; \quad T_0 = \frac{\hbar |g_2| \omega_F(T_1)}{kG}.$$

Note that, at the quantum limit, Eq. (6) is replaced¹³ by a self-consistent equation from which a leading exponent $\gamma = 2$ is derived. This exponent is the same as the one obtained by the renormalization-group (RG) theory.

This compatibility between a renormalized harmonic approximation and the strict result from RG theory can only be expected at the actual quantum limit.

There, the Hamiltonian has a Gaussian fixed point; a condition necessary for the validity of the renormalized harmonic approximation.

IV. SUMMARY

The shell model involving a large oxygen polarizability has been shown to account for the susceptibility of several cubic quantum ferroelectrics. It produces two analytical formulas [Eqs. (1) and (2)] valid for the high- and low-temperature regimes, respectively. The high-temperature regime extends to ~ 60 K in KTaO_3 and ~ 80 K in SrTiO_3 . These temperatures

were considered as a lower bound for the validity of the approach leading to Eq. (2). The low-temperature regime extending to ~ 35 K is described by Eq. (1) which, for $T_C = 0$, can alternately be gained by the shell model or the RG approach. The intermediate range is reasonably closely covered by either approach. In the low-temperature regime, and in samples with $T_C = 0$, the standard deviation of the fitted RG results is lower by an order of magnitude than that of the shell-model results. For samples which are stable and cubic down to the absolute zero ($x < x_c$, no T_C), the quality of the fit is good for the shell model (the deviations are 0.6% for $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ and 1.8% for $\text{K}_{1-y}\text{Na}_y\text{TaO}_3$) while, for samples having $T_C \sim 30$ K, a fit of the shell model yields a deviation of about 4%. We attribute the lower quality of the shell model in the latter case to the failure of the renormalized harmonic phonon approximation near T_C in three dimensions.¹⁷ For those samples, alternate fits to power laws with an intermediate exponent can

be attempted within relatively small temperature range above T_C . At the very quantum limit, the susceptibility exponent coincides for cubic and axial symmetry: $\gamma = 2$ has been obtained for $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ ($x = 0.008$), $\text{K}_{1-y}\text{Na}_y\text{TaO}_3$ ($y = 0.12$), and KH_2PO_4 under hydrostatic pressure ($p = 17$ kbar). This is a clear indication for the presence of a Gaussian fix point which has in common all equivalence classes for $d = 4$ including arbitrary degeneracy of the order parameter $n = 1, 2, 3$ and anisotropy of the dipolar interaction.

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¹⁸Equation (2) has previously been derived by a mean-field approach. See Ref. 8.