

Third-order dielectric susceptibility in a model quantum paraelectric

R. Martoňák*

International Centre for Theoretical Physics, Trieste, Italy;

International School for Advanced Studies, Trieste, Italy;

and Johannes Gutenberg-Universität, Institut für Physik, WA 331, D-55099 Mainz, Germany

E. Tosatti

International Centre for Theoretical Physics, Trieste, Italy;

International School for Advanced Studies, Trieste, Italy;

and Istituto Nazionale Fisica della Materia, Unità Trieste SISSA, Trieste, Italy

(Received 4 April 1996; revised manuscript received 29 July 1996)

In the context of quantum paraelectrics, we study the effects of a quadrupolar interaction J_q , in addition to the standard XY (“dipolar”) one, J_d . We concentrate here on the nonlinear dielectric susceptibility $\chi_p^{(3)}$, as the main response function sensitive to this interaction. We employ a three-dimensional quantum four-state lattice model and mean-field theory. The results show that inclusion of the (anti)quadrupolar coupling of moderate strength [$J_q \sim (1/4)J_d$] is clearly accompanied by a double change of sign of $\chi_p^{(3)}$ from negative to positive, near the quantum temperature T_Q where the quantum paraelectric behavior sets in. We fit our $\chi_p^{(3)}$ to recent experimental data for SrTiO_3 , where the sign change is identified close to $T_Q \sim 37$ K. [S0163-1829(96)01146-0]

I. INTRODUCTION

Classical perovskite ferroelectrics such as BaTiO_3 are very widely studied. As is well brought out by recent quantitative *ab initio* studies,¹⁻³ formation of a local dipole moment corresponds to the appearance of a shorter, partially covalent Ti-O bond, while dipole-dipole interaction is partly of Coulomb origin (long range) and partly resulting from the overlap of atomic orbitals (short range).

The situation is considerably more open and interesting in those cases, mainly SrTiO_3 (also KTaO_3) where quantum fluctuations are important to the extent that they manage to suppress ferroelectricity altogether (“quantum paraelectrics,” Müller and Burkard⁴). Experimentally, the onset of a quantum paraelectric regime in SrTiO_3 at a “quantum temperature” $T_Q \sim 30$ – 40 K has revealed a variety of intriguing features. They seem connected with a surprisingly abrupt off-center local displacement of the transition-metal ion, upon cooling down to, and across T_Q . At T_Q , there appears to be local dipole formation, without ferroelectric or structural long-range order, but still leading to phase transition-like features in EPR,^{5,6} extended x-ray-absorption fine structure,⁷ x-ray,⁸ and sound velocity.⁹⁻¹¹ A similarly abrupt phenomenon has been observed also in NMR studies of KTaO_3 .¹² In SrTiO_3 , various spectroscopic anomalies have also been found in Raman and Brillouin studies.^{13,14}

The reason why quantum fluctuations are so important in SrTiO_3 and KTaO_3 is not because the ions are particularly light. Rather, the lattice packing is so tight, as compared, e.g., to BaTiO_3 , to leave very little room for the Ti ion to move off-center and form a preferential Ti-O dipole. As the lattice is compressed, the classical ferroelectric Ti off-center equilibrium displacement gets smaller and smaller, and the system approaches the classical displacive limit, characterized by a vanishing classical Curie temperature T_C . In

SrTiO_3 , the lattice compression is close to this limit. The extrapolated classical off-center Ti displacement and Curie temperature are ~ 0.03 Å and ~ 37 K, respectively, against ~ 0.1 Å and ~ 400 K in BaTiO_3 . In such a situation, quantum fluctuations, even if involving a heavy ion such as Ti, can become dominant, removing the ferroelectric long-range order and causing a persistence of the paraelectric state down to $T \rightarrow 0$. We have previously discussed this scenario in some detail¹⁵ and also provided a quantum Monte Carlo study of a lattice model illustrating this phenomenon.¹⁶ A very recent *ab initio* quantum Monte Carlo study of SrTiO_3 and BaTiO_3 has moreover indicated that the exquisite sensitivity of the ferroelectric order parameter to this kind of quantum fluctuations is likely to be related to the very anisotropic, quasi-one-dimensional (1D) electric dipole correlations, absent for other “neutral” structural order parameters.¹⁷

The theoretical study of structural phase transitions and ferroelectricity has so far mostly been conducted on models with an anharmonic on-site potential and a bilinear intercell interaction (a standard model for structural phase transitions^{18,19}), as well as on more specific semimicroscopic shell models.^{20,21} Likewise, the studies of quantum paraelectricity have been performed within the standard model,^{22,23} or some approximate lattice version of it, like the Ising model in transverse field²⁴⁻²⁶ and the quantum four-state clock model.¹⁶ All these studies predict the existence of a critical value for the strength of quantum fluctuations, above which static ferroelectricity disappears in the ground state and the system becomes a quantum paraelectric. The crossover from the high-temperature classical paraelectric to low-temperature quantum paraelectric is predicted to be totally smooth, without any sharp features. These models are therefore unable to account for the experimentally observed abrupt phenomena at $T_Q \sim 30$ – 40 K in SrTiO_3 .

While a thorough understanding of what is going on is

still missing, it seems clear that on cooling below T_Q the individual Ti ions move off-center inside their cell with surprising abruptness, whereas their mutual ordering between different cells only progresses slowly as T is lowered and never becomes total, down to the lowest temperatures.¹⁵ An abrupt onset of the local ferroelectric lattice distortion is *not* well explained by the standard model. This appears to be true even when some microscopic details such as the local coupling of the ferroelectric (FE) polarization to the lattice strain and to the antiferrodistortive (AFD) order parameters are taken into account, as was done, based on *ab initio* calculations, by Zhong and Vanderbilt.¹⁷ In their quantum Monte Carlo study, no particular sharp features have been observed on cooling the system down to $T \sim 5$ K, contrary to observations. In principle, a possible source of discrepancy could be the fact that experimentally AFD and FE ordering tend to take place along orthogonal directions and appear to favor each other, whereas in the calculation they are parallel, and thus compete. Another possibility, which in the light of what will follow below we consider more likely, is that a satisfactory description of low-temperature regime of SrTiO₃ requires the extension of the standard model to include some physically new ingredient.

One first thing to worry about, are impurities and disorder. In the 1D quantum Ising model, disorder does indeed bring about suggestive phenomena. In the presence of disorder, the zero-temperature quantum critical point is spread out onto a critical line (Griffiths phase) (see, e.g., Ref. 27). However, these effects are believed to weaken drastically for a vector order parameter, and in $D=3$.²⁸

Restricting henceforth our analysis to the fully ordered crystal, a very natural extension is (turning for a moment to the language of the four-state lattice model^{15,16}), to drop the limitation of a simple, XY interaction $\cos(\phi_i - \phi_j)$ (which we shall conveniently call ‘‘dipolar’’ in the following) and take into account also higher angular terms (ϕ_i is the phase angle of a two-component XY order parameter in cell i , see Sec. II). The next order term with square symmetry has an angular dependence $\cos 2(\phi_i - \phi_j)$, typical of the *quadrupolar interactions*. [This is not the full form of the true Coulomb quadrupole-quadrupole interaction, much as $\cos(\phi_i - \phi_j)$ is not that of a true dipole-dipole interaction. These forms and names are adopted here for their simplicity.] In terms of the fully rotationally invariant standard model and of its local soft-mode amplitudes $\mathbf{u}(\mathbf{R}_i)$, these new terms amount to an effective interaction of the form $(\mathbf{u}(\mathbf{R}_i) \cdot \mathbf{u}(\mathbf{R}_j))^2$, in addition to the usual one $\mathbf{u}(\mathbf{R}_i) \cdot \mathbf{u}(\mathbf{R}_j)$, as will be discussed in Sec. V.

This paper is devoted to a study of the effects of this quadrupolar-type interaction, $\cos 2(\phi_i - \phi_j)$, on the onset of quantum paraelectricity in SrTiO₃. Deferring to Sec. II a more detailed presentation of a simplified lattice Hamiltonian which takes both dipolar and quadrupolar coupling into account, we have strong reason to suspect that the new coupling might be of qualitative importance. In fact, as we pointed out in Ref. 15, quantum effects in a quadrupolar system are very different from those in a dipolar system. A purely quadrupolar quantum system can exhibit *reentrance* in its phase diagram, while a dipolar one does not. Reentrance in quantum quadrupolar systems is beautifully exemplified by the data of Moshary, Chen, and Silvera on order-

ing of solid HD under pressure.²⁹ There is a pressure range there, where cooling solid HD from the high-temperature orientationally disordered phase produces first an ordered phase but eventually reverts back to disorder at very low temperatures. The same behavior also appears very straightforwardly in simple models, at least in mean-field theory.^{15,30}

The ferroelectric perovskites, unlike HD, are unlikely to be completely dominated by the quadrupolar interaction. Our point, however, will be that they exhibit features which cannot be explained by purely dipolar couplings. Experimentally, direct detection of quadrupolar couplings in a ferroelectric system is not completely straightforward, since the main quantity, the linear dielectric susceptibility $\chi_P^{(1)}$, is unaffected by them, at least at the mean-field level.³¹ However, the third-order nonlinear dielectric susceptibility $\chi_P^{(3)}$, defined by $P = \chi_P^{(1)}E + \chi_P^{(3)}E^3 + \dots$, turns out to be very sensitive to quadrupolar couplings. In particular, Morin and Schmitt³¹ (in a completely parallel magnetic context) showed that $\chi_P^{(3)}$ will change sign from negative to positive, as a system reaches a temperature region where quadrupolar effects become important, while it will stay negative so long as they are unimportant.

Very recently, detailed data have been obtained by Hemberger *et al.*,³² who measured $\chi_P^{(3)}$ in SrTiO₃. They find strong structures in $\chi_P^{(3)}$ between 30 and 60 K, precisely in the region near T_Q , where the Ti ions suddenly move off-center on cooling, giving rise to quantum fluctuating local dipoles, and where quantum paraelectricity sets in.

In this paper we study this problem, and show that the behavior of $\chi_P^{(3)}$ can be understood if we assume the existence of quadrupolar interactions of appropriate strength in SrTiO₃, besides the standard dipolar ones. In Sec. II, we first introduce a simple quantum lattice model including dipolar as well as quadrupolar couplings. In Sec. III we calculate $\chi_P^{(3)}$ within mean-field theory, and find that depending on the relative strength of the quadrupolar and dipolar interactions, $\chi_P^{(3)}$ exhibits a rich behavior as a function of temperature. In Sec. IV we consider the application of this calculation to the case of SrTiO₃. By comparing the calculated temperature dependence of the third-order dielectric susceptibility to the observed data,³² we estimate the strength of effective quadrupolar interactions in SrTiO₃, where a double change of sign of $\chi_P^{(3)}$ is shown to take place, respectively, above and below $T \sim T_Q$, with decreasing temperature. The upper one from negative to positive $\chi_P^{(3)}$ is related to the onset of quadrupolar effects; the lower one from positive back to negative $\chi_P^{(3)}$, to the onset of quantum paraelectricity. Before concluding the paper, we shall briefly discuss in Sec. V the possible origin of the quadrupolar interactions in connection with the known physics of SrTiO₃.

II. SIMPLIFIED LATTICE MODEL OF SrTiO₃

The structural Hamiltonian for a perovskite is quite generally a function of $3 \times 5 = 15$ continuous coordinates per cell in the cubic phase (five atoms per unit cell). Even simplifying to include only polarization, strain, and antiferrodistortive degrees of freedom, we are still forced to include at least $3+3+3=9$ degrees of freedom per cubic cell. A proper quantum Monte Carlo treatment¹⁷ of so many continuous degrees of freedom is at present very demanding. A useful

and simpler counterpart is a quantum *lattice* model. The latter, although much less realistic, and incapable of describing the displacive behavior of a perovskite in its classical regime ($T \gg T_Q$), still contains the physics of quantum paraelectricity (QPE), and is more directly amenable to study either via quantum Monte Carlo,¹⁶ or, much more simply, via mean-field theory. A discussion of such simple models in the context of quantum paraelectricity of SrTiO₃ has already been presented in Refs. 15 and 16, where a variety of lattice models has been introduced and considered. For convenience we briefly repeat here the main ideas.

The simplest lattice model for quantum paraelectricity is the Ising model in transverse field, proposed in Ref. 24. Its mean-field treatment²⁵ yields for $\chi_P^{(1)}$ the well-known Barrett formula, derived in many different contexts^{33,4} and commonly used to fit the experimental data of QPE materials.^{4,32,34} It accounts, at least qualitatively, for the basic features of behavior of $\chi_P^{(1)}$ as a function of temperature, in particular saturation at a high value as $T \rightarrow 0$.

As it turns out, however, the experimental data for $\chi_P^{(3)}$ (Ref. 32) *cannot* be accounted for within the Ising model in transverse field. Our goal in this section thus is to generalize the simplest lattice model and make it more appropriate to understand the QPE state of SrTiO₃, while still preserving the possibility of a simple mean-field treatment. The inadequacy of the Ising model in transverse field to SrTiO₃ arises from the fact that the experimentally observed character of the incipient ferroelectricity in tetragonal SrTiO₃ is not Ising-like, but rather *XY*-like. The physical reason why at zero stress and field the polarization is confined to the (x,y) plane is given by the presence (below 105 K) of the antiferrodistortive order parameter. This consists of a staggered cage rotation along the z axis, coincident with the (001) direction, which as a side effect expands the Ti-O bond lengths in the (x,y) plane more than along z . The onset of ferroelectric polarization is thus favored in the (x,y) plane, and disfavored along z .³⁵ In the (x,y) plane, the polarization has four easy directions, namely (± 100) , (0 ± 10) .

The quantum four-state clock model introduced in Ref. 16 and considered in various versions in Ref. 15 appears thus to be a minimal model for the description of SrTiO₃ at sufficiently low temperatures. The model neglects the radial degrees of freedom associated with the continuous displacement of the Ti ion from the center of the oxygen cage in the crystal. It assumes that the displacement in the cell i is of fixed magnitude and can be completely characterized by a discrete plane rotor angular variable ϕ_i . This variable is allowed four possible values $\phi_i = \pi/2, \pi, -\pi/2, 0$, and the corresponding four quantum states labeled as $|1\rangle, |2\rangle, |3\rangle, |4\rangle$ constitute the basis of the on-site Hilbert space. The quantum effects are strictly on-site, and are introduced by allowing the clock variable ϕ_i to hop onto its two nearest orientations, i.e., from ϕ_i into $\phi_i \pm \pi/2$ with amplitude $-t$. This is expressed by a Hamiltonian term H_i^{hop} , represented in the site i basis by the matrix

$$H_i^{\text{hop}} = t \begin{vmatrix} 0 & -1 & 0 & -1 \\ -1 & 0 & -1 & 0 \\ 0 & -1 & 0 & -1 \\ -1 & 0 & -1 & 0 \end{vmatrix}. \quad (1)$$

The interaction between different cells $i \neq j$ can be of arbitrary range, and consists of two different terms, the usual ‘‘dipole’’ interaction

$$H^d = -\frac{1}{2} \sum_{i,j} J_d^{ij} \cos(\phi_i - \phi_j), \quad (2)$$

and a ‘‘quadrupole’’ interaction

$$H^q = -\frac{1}{2} \sum_{i,j} J_q^{ij} \cos 2(\phi_i - \phi_j). \quad (3)$$

While the origin of H^d is widely discussed, that of H^q is not, and there is no previous place, apart from our earlier paper,¹⁵ where this kind of higher-order interaction is invoked for a displacive ferroelectric crystal. It is just this term which makes the model nontrivial. In fact, the quantum four-state clock model with $J_q^{ij} = 0$, and strictly dipole interaction $J_d^{ij} \neq 0$, can be exactly mapped onto two decoupled Ising models in transverse field.¹⁶ The strength of the H^q term in SrTiO₃ will be estimated in Sec. IV and its possible origin will be discussed in Sec. V. We note here that the *classical* four-state model $H = H^d + H^q$ is the well-known Ashkin-Teller model.³⁶ The 2D classical AT model is itself considerably richer than the purely dipolar model Eq. (2).

We shall treat our model on a 3D cubic lattice and for the sake of simplicity use a mean-field theory. This approximation, while probably far from accurate, is at least not totally unacceptable in (3+1)D and is attractive due to its great simplicity. We will comment more on the validity of the mean-field theory in the next section.

The complete Hamiltonian that will be considered in the following is then given by

$$H = \sum_i H_i^{\text{hop}} + H^d + H^q. \quad (4)$$

III. MEAN-FIELD THEORY OF THIRD-ORDER DIELECTRIC SUSCEPTIBILITY

In this section we start from our microscopic Hamiltonian Eq. (4) and derive a free-energy expansion, using a mean-field approximation. From the free-energy expansion we then calculate the third-order dielectric susceptibility $\chi_P^{(3)}$ as a function of temperature. Our treatment will parallel very closely that of Morin and Schmitt³¹ for the magnetic case. We will show that the behavior of $\chi_P^{(3)}$ at low and intermediate temperatures relative to the quantum temperature T_Q is profoundly modified by the presence of the quadrupolar interactions.

We take as our mean-field Hamiltonian a sum of on-site mean-field Hamiltonians,

$$H^0 = \sum_i H_i^0 = \sum_i (H_i^{\text{hop}} - eP_{xi} - qR_i), \quad (5)$$

corresponding to a single quantum rotor in external fields e and q , coupling to the on-site polarization $P_{xi} = \cos \phi_i$ and quadrupole moment $R_i = \cos 2\phi_i$, respectively. For simplicity, we shall assume from now on that the polarization component P_y is always zero and omit the subscript x on P_x ; we

also set $|t|=1$ as the energy and temperature scale. The matrix of the on-site Hamiltonian Eq. (5) in the basis of the four states $|1\rangle, |2\rangle, |3\rangle, |4\rangle$ reads

$$H_i^0 = \begin{pmatrix} q & -1 & 0 & -1 \\ -1 & e-q & -1 & 0 \\ 0 & -1 & q & -1 \\ -1 & 0 & -1 & -e-q \end{pmatrix}. \quad (6)$$

The trial free energy $F_t(e, q)$ per site as a function of the mean-field variational parameters e, q is given by

$$\begin{aligned} F_t(e, q) &= F_0 + \langle H - H^0 \rangle_0 \\ &= F_0 - 6J_{d/2} P^2 - 6J_{q/2} R^2 + eP + qR, \end{aligned} \quad (7)$$

where

$$F_0 = -\frac{1}{\beta} \ln \text{Tr} e^{-\beta H^0}, \quad (8)$$

and $\beta = t/(k_B T)$. Here, we defined $P = \langle \cos \phi \rangle$ and $R = \langle \cos 2\phi \rangle$ as ferroelectric and a quadrupolar order parameters, respectively. In the mean-field theory, the couplings J_d^{ij}, J_q^{ij} have been lumped into just two interaction parameters $J_d = \frac{1}{6} \sum_j J_d^{ij}$, $J_q = \frac{1}{6} \sum_j J_q^{ij}$, and we shall assume $J_d > 0$ (dipolar), $J_q > 0$ (antiquadrupolar). Even without diagonalizing explicitly the matrix Eq. (6), the expansions of the energy levels in powers of the fields e, q around their zero values (we assume our system, like SrTiO₃ in the absence of fields, to be paraelectric) can be found by perturbation theory. For our purpose it is sufficient to find the expansion to fourth order in e and to second order in q . The following expressions are found for the eigenvalues of H_i^0 :

$$E_0 = -2 - \frac{1}{4}e^2 + \frac{1}{64}e^4 - \left(\frac{1}{4} + \frac{3}{2}e^2\right)q^2 + \frac{1}{4}e^2q + \dots, \quad (9)$$

$$E_1 = -q, \quad (10)$$

$$E_2 = \left(1 - \frac{1}{2}e^2\right)q + \dots, \quad (11)$$

$$E_3 = 2 + \frac{1}{4}e^2 - \frac{1}{64}e^4 + \left(\frac{1}{4} + \frac{3}{4}e^2\right)q^2 + \frac{1}{4}e^2q + \dots, \quad (12)$$

whence the power expansion of free energy Eq. (8) can be calculated,

$$F_0 = -\frac{1}{2}\chi_0^{(1)}e^2 - \frac{1}{2}\chi_2q^2 - \chi_2^{(2)}e^2q - \frac{1}{4}\chi_0^{(3)}e^4 + \dots, \quad (13)$$

where

$$\begin{aligned} \chi_0^{(1)} &= \frac{1}{2} \tanh \beta, \\ \chi_0^{(3)} &= \frac{1 + 4\beta e^{2\beta} - e^{4\beta}}{16(1 + e^{2\beta})^2}, \\ \chi_2 &= -\frac{1 - 4\beta e^{2\beta} - e^{4\beta}}{2(1 + e^{2\beta})^2}, \\ \chi_2^{(2)} &= -\frac{1}{4} \tanh^2 \beta. \end{aligned} \quad (14)$$

The polarization and quadrupolar order parameters P and R can now be calculated as derivatives of Eq. (13) with respect to the fields e and q

$$P = -\frac{\partial F_0}{\partial e} = \chi_0^{(1)}e + 2\chi_2^{(2)}eq + \chi_0^{(3)}e^3 + \dots, \quad (15)$$

$$R = -\frac{\partial F_0}{\partial q} = \chi_2q + \chi_2^{(2)}e^2 + \dots. \quad (16)$$

In order to obtain an expansion of the free-energy term F_0 in terms of the order parameters P, R , we must invert the expansions (15) and (16) and express the fields e, q in terms of powers of P and R . We find the expressions

$$\begin{aligned} e &= \frac{1}{\chi_0^{(1)}}P - \frac{2\chi_2^{(2)}}{(\chi_0^{(1)})^2\chi_2}PR \\ &\quad - \frac{1}{(\chi_0^{(1)})^4} \left(\chi_0^{(3)} - \frac{2(\chi_2^{(2)})^2}{\chi_2} \right) P^3 + \dots, \end{aligned} \quad (17)$$

$$q = \frac{1}{\chi_2}R - \frac{\chi_2^{(2)}}{(\chi_0^{(1)})^2\chi_2}P^2 + \dots, \quad (18)$$

which after substituting into Eq. (13) yield the desired form

$$\begin{aligned} F_0 &= -\frac{1}{2}(\chi_0^{(1)})^{-1}P^2 - \frac{1}{2}(\chi_2)^{-1}R^2 + \frac{2\chi_2^{(2)}}{(\chi_0^{(1)})^2\chi_2}P^2R \\ &\quad + \left(\frac{3}{4} \frac{\chi_0^{(3)}}{(\chi_0^{(1)})^4} - \frac{3}{2} \frac{(\chi_2^{(2)})^2}{\chi_2(\chi_0^{(1)})^4} \right) P^4 + \dots. \end{aligned} \quad (19)$$

At this point, we can express the full free energy F_t [Eq. (7)] as an expansion in powers of the order parameters, namely the polarization P and the quadrupole moment R . It reads

$$\begin{aligned} F_t(P, R) &= \frac{1}{2} [(\chi_0^{(1)})^{-1} - 6J_d]P^2 + \frac{1}{2} [(\chi_2)^{-1} - 6J_q]R^2 \\ &\quad - \frac{\chi_2^{(2)}}{(\chi_0^{(1)})^2\chi_2}P^2R - \frac{1}{4} \frac{1}{(\chi_0^{(1)})^4} \\ &\quad \times \left(\chi_0^{(3)} - 2 \frac{(\chi_2^{(2)})^2}{\chi_2} \right) P^4 + \dots. \end{aligned} \quad (20)$$

As in SrTiO₃ at zero stress and field, we assume $P=R=0$. In the neighborhood of this minimum of F_t , we now wish to eliminate R , yielding an effective free-energy expansion in powers of the polarization P alone. Minimizing Eq. (20) with respect to R , we obtain

$$R = \frac{\chi_2^{(2)}}{(\chi_0^{(1)})^2(1 - 6J_q\chi_2)}P^2, \quad (21)$$

and after substituting this expression back into Eq. (20) we obtain the expansion of F_t in terms of P only

$$F_t(P) = \frac{1}{2} [(\chi_0^{(1)})^{-1} - 6J_d]P^2 - \frac{1}{4} \frac{1}{(\chi_0^{(1)})^4} \times \left(\chi_0^{(3)} + \frac{12J_q(\chi_2^{(2)})^2}{1-6J_q\chi_2} \right) P^4 + \dots \quad (22)$$

It is worth noticing that the coefficient of P^4 has been renormalized downwards (i.e., towards negative values) by the quadrupolar coupling J_q . This follows because $\chi_0^{(3)}$ is negative definite, while the other term dependent on J_q is positive as long as $J_q < (6\chi_2)^{-1}$.

By adding an interaction term $-EP$, corresponding to an external electric field E , to the free energy Eq. (22) and minimizing with respect to the polarization P , we can calculate the first-order (linear) and third-order (nonlinear) dielectric susceptibilities $\chi_P^{(1)}$ and $\chi_P^{(3)}$, defined as usual by the expansion

$$P = \chi_P^{(1)}E + \chi_P^{(3)}E^3 + \dots \quad (23)$$

In our model we find

$$\chi_P^{(1)} = \frac{\chi_0^{(1)}}{1-6J_d\chi_0^{(1)}}, \quad (24)$$

$$\chi_P^{(3)} = \frac{1}{(1-6J_d\chi_0^{(1)})^4} \left(\chi_0^{(3)} + \frac{12J_q(\chi_2^{(2)})^2}{1-6J_q\chi_2} \right). \quad (25)$$

The nonlinear susceptibility Eq. (25) can also be written in a slightly more transparent form

$$\chi_P^{(3)} = \chi_P^{(3)}(J_q=0) + \frac{12J_q(\chi_P^{(1)})^4}{1-6J_q\chi_2}, \quad (26)$$

where we made use of the relation $(\chi_2^{(2)})^2 = (\chi_0^{(1)})^4$, verified by Eq. (14). While the first-order dielectric susceptibility $\chi_P^{(1)}$, in the mean-field approximation, is independent of J_q , we see that the third-order susceptibility $\chi_P^{(3)}$ is a sum of its original value in the absence of quadrupolar coupling which is always *negative*, and of an additional *positive* term. The latter can eventually overbalance the negative term and reverse the sign of $\chi_P^{(3)}$, if J_q is large enough. The temperature dependences of $\chi_P^{(3)}$ for $J_d=0.273$ and a series of values of quadrupolar coupling J_q are plotted in Fig. 1. We see that (a) the renormalization effect of $\chi_P^{(3)}$ by J_q is most pronounced at intermediate temperatures, and (b) there is a region of values of J_q where $\chi_P^{(3)}$ now turns positive at intermediate temperatures, while staying negative at sufficiently high and low temperatures. Finally, if J_q is stronger, there is a temperature where $\chi_P^{(3)} \rightarrow \infty$ and an independent (anti)quadrupolar ordering takes place.

For quantitative use, we wish to convert the formulas (24) and (25) from dimensionless units back to normal ones. If the displacement of the Ti ion from the center of the cage is associated with a dipole moment μ , the dipole density per unit volume being n , then $\chi_P^{(1)}$ can be conventionally written in form of the familiar Barrett formula^{33,25,4,34}

$$\chi_P^{(1)} = \frac{n\mu^2/2k_B\epsilon_0}{(T_1/2)\coth(T_1/2T) - T_0}. \quad (27)$$

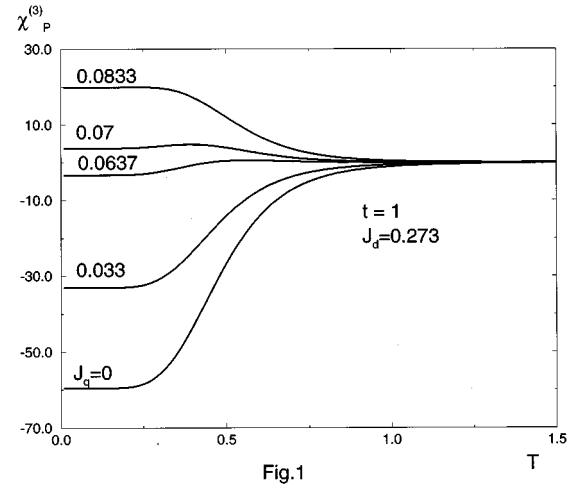


FIG. 1. Third-order nonlinear dielectric susceptibility $\chi_P^{(3)}$ as a function of temperature for a fixed value of dipolar coupling J_d and various values of quadrupolar coupling J_q .

The temperatures T_0 and T_1 are given by $T_0 = 3J_d/k_B$, $T_1 = 2t/k_B$, and have the meaning of classical Curie temperature and of quantum temperature, respectively.

The complete expression obtained for $\chi_P^{(3)}$ reads

$$\chi_P^{(3)} = \frac{n\mu^4 t / \epsilon_0}{(t-6J_d\chi_0^{(1)})^4} \left(\chi_0^{(3)} + \frac{12J_q(\chi_2^{(2)})^2}{t-6J_q\chi_2} \right), \quad (28)$$

which is our main result.

Before closing this section, we would like to discuss the validity of the mean-field approximation used, particularly concerning the change of sign of $\chi_P^{(3)}$ induced by the quadrupolar interaction. We note, first of all, that precisely the same mean-field treatment agrees well with the experimental data in the case of 3D magnetic systems.³¹ For additional safety, we decided to check our results by comparison to an exact result for the simplest particular case of our model such where an exact solution can be found. We therefore considered a 1D chain of classical four-state rotors interacting via nearest-neighbor quadrupolar interaction and solved it by means of the transfer-matrix technique. The corresponding calculation is included in the Appendix. To our satisfaction, it predicts $\chi_P^{(3)}$ to change sign from negative at high temperatures to positive at low temperatures. In order to compare the exact result to the mean-field one we search the classical limit of the expression (28) for $J_d=0$ and $J_q = J_q^{\text{NN}}/3$ (1D chain). This corresponds to zero hopping amplitude $t \rightarrow 0$ and reads (assuming $k_B=1$)

$$\lim_{t \rightarrow 0} \chi_P^{(3)} = -\frac{n\mu^4}{\epsilon_0} \frac{1}{24T^3} \frac{T-8J_q^{\text{NN}}}{T-2J_q^{\text{NN}}}. \quad (29)$$

This expression is negative for $T > T^* = 8J_q^{\text{NN}}$ and changes sign to positive for temperatures $2J_q^{\text{NN}} < T < T^*$. The mean-field prediction for the temperature of the sign change $T^* = 8J_q^{\text{NN}}$ compares well with the exact result $T^* = 6.95J_q^{\text{NN}}$ (see the Appendix). Below $T < 2J_q^{\text{NN}}$ our expression obviously ceases to be valid, since it was derived for the disordered phase and the mean-field approximation in 1D incorrecly predicts an ordered phase at nonzero temperature.

Apart from this obvious shortcoming, which is particular to the 1D case, the qualitative features of behavior of $\chi_P^{(3)}$, in particular the change of sign, are correctly predicted on the mean-field level. We can therefore expect an even better agreement for our real 3D system, which stays disordered down to zero temperature.

It would be, of course, interesting to have a possibility to calculate $\chi_P^{(3)}$ for our quantum 3D model by some essentially exact technique, like, e.g., path integral Monte Carlo. So far, we tried such a calculation in 2D,³⁷ but it turned out that obtaining the *nonlinear* response function $\chi_P^{(3)}$ with reasonable accuracy is prohibitively CPU time expensive. The preliminary results were compatible with the mean-field prediction but the large statistical error has precluded a detailed comparison. This notwithstanding, we have no doubt that our mean-field theory of $\chi_P^{(3)}$ is qualitatively correct for the 3D case. Provided an improved and more efficient algorithm were available, it would be worthwhile to undertake such a numerical simulation aimed apart from calculation of the response functions also at determining the phase diagram of the 2D or 3D quantum Ashkin-Teller model.

IV. APPLICATION TO THE CASE OF SrTiO₃

We now wish to apply the above scheme to the case of SrTiO₃ and attempt a comparison between experimental data³² and our results Eqs. (27) and (28). As mentioned in the Introduction, SrTiO₃ belongs rather to the class of displacive than to the order-disorder ferroelectrics. The use of a continuous model should, in principle, be preferred to a discrete one, if a realistic comparison to experiment is to be attempted. However, the main purpose of this paper is to pursue the qualitative differences induced in the behavior of $\chi_P^{(3)}$ by a presence of a quadrupolar interaction with its different angular dependence, and these features should be correctly reproduced also by a discrete model. It is clearly beyond the possibilities of such a discrete model to describe the sharp dipole onset observed at $T_Q \sim 37$ K, since the local off-center displacement is described just by the radial part of the local mode which is left out completely in the present discrete model.

We consider first the linear dielectric susceptibility. The Barrett formula Eq. (27) has been used to fit the $\chi_P^{(1)}$ data on SrTiO₃,^{4,34} and yields a reasonable fit over a temperature range from 0 to 100 K with $T_1 \sim 88$ K, $T_0 \sim 36$ K, and $n\mu^2/2k_B\epsilon_0 \sim 10^5$ K. The microscopic Hamiltonian parameters corresponding to these values of T_0 and T_1 are $J_d = 12$ K, $t = 44$ K. We note in particular that the ratio $J_d/t = 0.273$ is not far from the critical mean-field value of $(J_d/t)_c = 1/3$, where, in three dimensions, our four-state quantum clock model undergoes at $T=0$ a transition from para ($J < J_c$) to ferro ($J > J_c$).

A problem arises, however, with the prefactor $n\mu^2/2k_B\epsilon_0$, since with one dipole per cell we obtain $n = 1/a^3 = 1.68 \times 10^{28} \text{ m}^{-3}$, where $a = 3.9 \text{ \AA}$ is the lattice constant of SrTiO₃, and the required value of the dipole moment per cell is $\mu = 3.4 \times 10^{-29} \text{ cm}$. If we take the effective charge to be $Z^* \sim 8$,³⁸ the corresponding displacement should be $d \sim 0.26 \text{ \AA}$, which is an order of magnitude larger than the value of $\sim 0.03 \text{ \AA}$ realistically estimated in Ref. 4, as well as in *ab initio* calculations.³⁹ The discrepancy is, in our opinion,

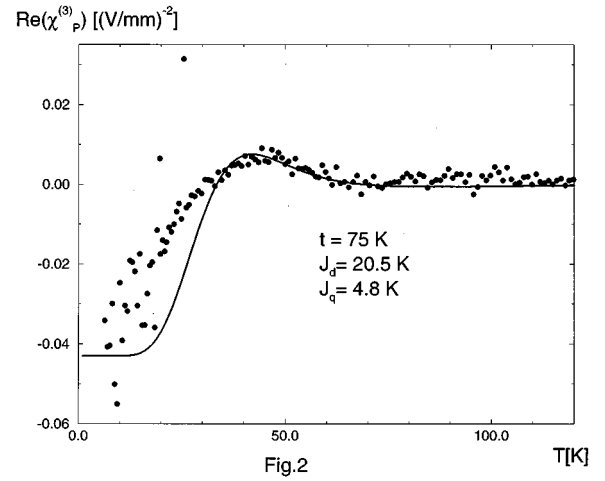


FIG. 2. Fitting of the experimentally measured $\text{Re}(\chi_P^{(3)})$ (Refs. 32, 40, and 34) of SrTiO₃ with formula (28). Full points correspond to experimental data, solid line to the theoretical curve.

related to the quantitative inadequacy of the discrete model for SrTiO₃, as well as to the mean-field treatment. Once again, Barrett's formula reproduces the essential features of the temperature behavior of the linear susceptibility well enough, but fails at the quantitative level.

Let us now come to the nonlinear susceptibility, and the related quadrupolar effects. We would like to try to fit the formula (28) to the $\chi_P^{(3)}$ data measured on SrTiO₃.³² For this purpose, however, the form in which the data were presented in Ref. 32, namely $\log|\chi_P^{(3)}|$ vs temperature is not so well suited, since a mere knowledge of the magnitude of the complex quantity $\chi_P^{(3)}$ (measurements were done at small, but finite frequency) without its phase angle, mixes together the real and imaginary part and conceals the desired information about the sign of the real part. Our static mean-field theory produces, of course, a *real* static $\chi_P^{(3)}$. We have therefore attempted to extract $\text{Re} \chi_P^{(3)}$ from the data,³² making use of the corresponding phase angles kindly provided by Hemberger.⁴⁰ The resulting experimentally derived $\text{Re} \chi_P^{(3)}$ (corresponding to the lowest electric-field intensity $E_0 = 50$ V/mm) is shown in Fig. 2 as a function of temperature. While at low temperatures this quantity is negative, it crosses zero on heating at $T = 33$ K where it becomes positive, passes through a maximum at $T = 45$ K and then approaches zero again, from the positive values. Above $T \sim 60$ K, it probably turns small and negative again, although experimental uncertainty appears larger in this regime. With hindsight, we re-examined also some old data of Fleury and Worlock⁴¹ for SrTiO₃ and found that evidence for a positive $\chi_P^{(3)}$ at $T = 40$ K can be evinced there, too [Fig. 5(b), Ref. 41].

Bearing in mind the difficulties related to the prefactor, encountered in the case of $\chi_P^{(1)}$, we decided to allow this to be a free parameter. Anticipating that the best fit of $\chi_P^{(3)}$ does not necessarily have to lead to the same values of J_d and t as the fit of $\chi_P^{(1)}$, we decided to preserve the value of $J_d/t = 0.273$ and allow for J_q and t to be free parameters. The result of this fit is the curve in Fig. 2, which corresponds to $t = 75$ K, $J_d = 0.273t = 20.5$ K, and $J_q = 4.8$ K. With these values, the positive maximum of $\chi_P^{(3)}$ is well reproduced, although at lower temperatures the fit is less perfect within

the present theory. At higher temperatures, on the other hand, it is hard to assess the agreement between the theory and data; in any case the theory predicts $\chi_p^{(3)}$ to become negative again at high temperatures and approach zero from below. From Fig. 2 it is clear that by assuming a quadrupolar interaction of strength about 5 K, the theory can qualitatively account for the temperature dependent double change of sign of $\chi_p^{(3)}$. Quantitatively, the agreement is worse than in the case of $\chi_p^{(1)}$, which is perhaps not surprising for a thermodynamic quantity which is a higher-order derivative of the free energy. The required value of t is now larger by $\sim 70\%$ and the value of the displacement required in order to obtain the necessary value of the prefactor is even an order of magnitude larger than in case of $\chi_p^{(1)}$, namely 2.3 \AA , which is clearly unphysical. As in the case of $\chi_p^{(1)}$, we attribute these discrepancies to the crudeness of the discrete model. On the other hand, a firm result of this calculation and fit is that the presence of J_q provides a simple and plausible scenario in order to account for a positive $\chi_p^{(3)}$ at intermediate temperatures, $T \sim T_Q$. Of course, it does not exclude other possibilities but rather points to the definite effect of including an interaction with a different angular dependence and symmetry.

To end this section, we point out here that a positive $\chi_p^{(3)}$, which means a negative overall coefficient in front of the P^4 term in Eq. (22), would imply the ferroelectric transition at the classical level to be of *first order*. The QPE state for positive $\chi_p^{(3)}$ can therefore be seen as the outcome of a frustrated *first-order* transition.

V. POSSIBLE ORIGIN OF THE QUADRUPOLEAR INTERACTION IN PEROVSKITES

Before closing, we very tentatively discuss the possible microscopic origin of an effective (anti)-quadrupolar interaction J_q in perovskites. First we show that the results of previous sections which indicate a nonzero and positive J_q in SrTiO₃, point directly to the importance of *anharmonic* interactions in the system.

Introducing our model in Sec. II, we have actually assumed a particularly simple, rotationally invariant form for both dipolar and quadrupolar intersite interactions Eqs. (2) and (3), depending only on the angle difference $\phi_i - \phi_j$. In a real material, the interactions will not be of that simple form. However, for our mean-field approximation, the only important ingredient is the energy of a single rotor ϕ_i interacting with all the other rotors of the system when aligned along a common direction ϕ . Clearly, upon summation over the whole lattice, the rotational symmetry is restored and this interaction energy can always be written in the form $-6J_d \cos(\phi_i - \phi) - 6J_q \cos 2(\phi_i - \phi)$. As $(\phi_i - \phi)$ takes the values $0, \pi, \pm \pi/2$, it will acquire the values E_p, E_a, E_o corresponding to the given four-state rotor being parallel, antiparallel, and orthogonal to the rest of the system, respectively. The two parameters J_d, J_q which lump together all the intersite interactions in the system are obviously related to the three energies E_p, E_a, E_o via relations $6J_d = (E_a - E_p)/2$, $6J_q = [E_o - 1/2(E_p + E_a)]/2$.

Now assume for a moment that the interactions between the displacement vectors $\mathbf{u}(\mathbf{R}_i)$ (fixed length vectors with polar angle ϕ_i on site i) on different sites have arbitrary (rota-

tionally noninvariant) directional dependence, but are harmonic, i.e., bilinear. The bilinearity implies a change of sign of each interaction term under reversal of the direction of the displacement vector of our single rotor, and therefore $E_p = -E_a$. Since there are two possible orthogonal orientations of a given rotor with respect to the rest of the system, which differ just by reversal of the direction of the single rotor, and which have to be degenerate in energy, it follows $E_o = -E_o$ and therefore $E_o = 0$. The former and the latter conditions together, however, imply that $E_o = (E_p + E_a)/2$, which just means $J_q = 0$. In conclusion, harmonic interactions alone cannot give rise to nonzero J_q and its origin *must* be in the higher-order, anharmonic interactions.

A possible mechanism may originate from coupling to the elastic degrees of freedom. Recently, we did in fact invoke for SrTiO₃ (Ref. 15) the possible importance of an effective quadrupolar coupling J_q between the dipoles in different cells, in addition to the dipolar one J_d . The sign of this interaction is negative, $-J_q < 0$ (antiquadrupolar), such that dipoles prefer to be either parallel or antiparallel, than to be orthogonal. One physical source anticipated in Ref. 15 was related to a lattice strain effect, as follows. When a dipole bond appears in one cell, it will cause an elongation of that cell along the dipole direction, and a shrinking in the orthogonal direction via electrostriction. This deformation, to avoid strain gradients, will extend to the neighboring cells where it will favor equally well a parallel or an antiparallel dipole orientation, but will disfavor the orthogonal one. The coupling then arises so as to reduce strain *gradients* associated with orthogonal dipoles, which are instead absent for parallel or antiparallel dipoles. In order to estimate the strength of the resulting interaction, these intuitive considerations have to be formalized.

The term representing the coupling between the local polarization and strain is, for a perovskite structure, linear in strains and quadratic in polarizations, and according to Ref. 3 it reads

$$H^{\text{int}} = \frac{1}{2} \sum_i \sum_{l\alpha\beta} B_{l\alpha\beta} \eta_l(\mathbf{R}_i) u_\alpha(\mathbf{R}_i) u_\beta(\mathbf{R}_i), \quad (30)$$

while the elastic energy is given by

$$H^{\text{el}} = \frac{1}{2} \sum_i \sum_{lk} C_{lk} \eta_l(\mathbf{R}_i) \eta_k(\mathbf{R}_i). \quad (31)$$

Here, $\eta_l(\mathbf{R}_i)$ and $u_\alpha(\mathbf{R}_i)$ are the strain and local FE soft-mode amplitude components at site i , respectively, $B_{l\alpha\beta}$ are the strain-ferroelectric mode coupling constants, and C_{lk} are the elastic constants. The total strain at site i consists of the homogeneous component arising from the uniform deformation of the whole system as well as of the inhomogeneous local strain. The six local strain components per cell are not in fact independent quantities, but rather suitable linear combinations of the three independent acoustic displacement components per cell. To proceed, one has to express the local strains in both Eqs. (30) and (31) in terms of the acoustic displacements. Integrating out the acoustic displacements from the total Hamiltonian, one finds the effective interaction between the polarizations in different cells, which turns out to be of fourth order in polarizations and contains also the quadrupolar interaction which we are interested in. In our

case, however, such a procedure would not be as straightforward as in the corresponding classical case, because the complete Hamiltonian contains the quantum kinetic energy term which does not commute with the coupling term containing the polarization. The simpler classical calculation should, however, provide at least a rough estimate of the strength of the effective J_q induced in this way.

Before doing this calculation in detail, however, it is actually possible to estimate an upper limit to the strength of the effective J_q by means of a simple argument. The induced *intersite* interaction term of the form $(\mathbf{u}(\mathbf{R}_i) \cdot \mathbf{u}(\mathbf{R}_j))^2 = \frac{1}{2}u(\mathbf{R}_i)^2u(\mathbf{R}_j)^2[1 + \cos 2(\phi_i - \phi_j)]$, $i \neq j$ must be weaker than a similar on-site term for $i = j$, $(\mathbf{u}(\mathbf{R}_i) \cdot \mathbf{u}(\mathbf{R}_i))^2 = u^4(\mathbf{R}_i)$, which represents a renormalization of the on-site quartic term $u^4(\mathbf{R}_i)$. This renormalization is clearly of the order of $B_{1\alpha\beta}^2/C_{lk}$. In order to get an upper estimate for the interaction strength J_q for our discrete model Eq. (3), we must also multiply by $(1/2)d^4$, where d is the typical value of the local displacement. Taking the typical values of $B_{1\alpha\beta} \sim 1.4$ hartree/bohr² and $C_{lk} \sim 5$ hartree (from Ref. 39), together with the displacement $d \sim 0.03$ Å, we arrive at a value about 0.5 K, which is an order of magnitude lower than the value of 5 K estimated in the previous section as necessary to explain $\chi_p^{(3)}$ in SrTiO₃.

A more accurate classical calculation of J_q^{strain} is most conveniently performed in the Fourier representation, due to the translational invariance of the Hamiltonian. The long-wavelength limit of the problem has been studied long ago,^{42,18} when it was shown that the resulting interaction is nonanalytical in k space and has a long-range tail in real space. A similar 2D calculation of indirect strain-induced coupling can be done for the case of SrTiO₃,⁴³ taking into account all the Fourier components from the Brillouin zone, which allows extraction of the induced interaction for each pair of lattice sites $i \neq j$. Here we will not go into full detail of that calculation and merely quote the main result, which is that the strength of the induced interaction is of the order of 0.1 K, a factor of 5 lower than the previous upper limit estimate. We conclude that the origin of the effective quadrupolar interactions of the required strength is not likely to be elastic, and should be sought elsewhere.

The strongest possibility is that such interactions could arise from short-range anharmonic terms like $(\mathbf{u}(\mathbf{R}_i) \cdot \mathbf{u}(\mathbf{R}_j))^2$ of nonstrain origin, due to effects related to the overlap of the atomic orbitals. At this stage, however, we are simply not in a position to decide. It would therefore be highly desirable to extend *ab initio* studies similar to those in Ref. 3 beyond the lowest order considered there (“local anharmonicity approximation”), and try to determine also the required higher-order terms of the energy expansion.

VI. CONCLUSIONS

In this paper, we have considered the nonlinear dielectric susceptibility $\chi_p^{(3)}$, and its behavior with temperature for a model system exhibiting quantum paraelectricity below a “quantum temperature” T_Q . The model is chosen so as to include a quadrupolar coupling in addition to the normal dipolar one. It is found that the effect of a moderate quadrupolar coupling can be to cause a temporary switch of sign of $\chi_p^{(3)}$ from negative, well above and well below T_Q , to posi-

tive at $T \sim T_Q$. Recent data for $\chi_p^{(3)}$ of SrTiO₃ appear to agree well with this predicted behavior implying an effective quadrupolar coupling $J_q \sim (1/4)J_d$. Work which remains to be done includes:

(a) better understanding of the true microscopic origin of J_q , presently still unclear;

(b) a proper formulation of the quadrupolar couplings in terms of the continuous displacement variables;

(c) understanding the possible relationship of this coupling to the exciting and largely unexplained phenomenology observed near T_Q , in Müller’s original experiments,⁵ and those which followed it.^{6,14} For the time being, we have noted that a positive $\chi_p^{(3)}$ at T_Q implies that the QPE state can be seen as arising due to quantum frustration of an otherwise first-order ferroelectric transition. If confirmed, the role of the quadrupolar couplings discussed here could be relevant to other perovskite systems, including quantum paraelectrics such as KTaO₃ as well as the regular classical cases. However, the net effect of these couplings on classical ferroelectric transition temperature must be relatively weak, since, as mentioned in Sec. III, their effect on the linear dielectric susceptibility $\chi_p^{(1)}$ vanishes within the mean-field theory.

ACKNOWLEDGMENTS

We are grateful to A. Loidl, P. Lunkenheimer, R. Böhmer, and J. Hemberger for sharing with us their results prior to publication and especially to J. Hemberger, for providing a copy of his Diploma thesis (Ref. 34) and numerical values for the phase angle of $\chi_p^{(3)}$ (Ref. 40). R. M. would also like to thank K. Binder, R. Böhmer, E. Courtens, J. Hemberger, R. Hlubina, A. Loidl, P. Lunkenheimer, M. Maglione, and A. Milchev for interesting and stimulating discussions and correspondence. E.T. acknowledges correspondence with K. A. Müller and E. Courtens. We are especially grateful to R. Migoni for offering his insight in the ferroelectric perovskites. R.M. would also like to acknowledge financial support from the Max Planck Institut für Polymerforschung, Mainz, Germany, as well as the hospitality provided by SISSA and ICTP, Trieste, Italy. Work at SISSA/ICTP was partly sponsored under EU Contracts No. ERB-CHRXCT 920062 and ERBCHRXCT 940438.

APPENDIX: 1D CLASSICAL ASHKIN-TELLER MODEL

In this appendix we consider a special case of the classical 1D Ashkin-Teller model with nearest-neighbor interactions in the presence of an external electric field, which can be exactly solved by the transfer-matrix method. We are interested in the change of behavior of the linear and nonlinear dielectric susceptibilities as a function of temperature induced by the presence of the quadrupolar coupling J_q . For simplicity, we set the dipolar couplings $J_d^{ij} = 0$ and consider only nearest-neighbor coupling $J_q^{\text{NN}} > 0$. We also assume periodic boundary conditions. The Hamiltonian of the model in an external field E reads

$$H = \sum_{\langle ij \rangle} H_{ij} - \sum_i P_{xi} E, \quad (\text{A1})$$

where

$$H_{ij} = -J_q^{\text{NN}} \cos 2(\phi_i - \phi_j). \quad (\text{A2})$$

The partition function reads

$$Z = \text{Tr} e^{-\beta H} = \sum_{\phi_1} \dots \sum_{\phi_N} e^{-\beta[H_{12} + 1/2(P_{x1} + P_{x2})E]} \dots e^{-\beta[H_{N1} + 1/2(P_{xN} + P_{x1})E]}, \quad (\text{A3})$$

where N is the number of sites in the chain. Since the allowed discrete values of the angular variables ϕ_i are $\phi_i = k_i(\pi/2)$, $k_i = 1, 2, 3, 4$, we can define a 4×4 transfer matrix T by $T_{\phi_i, \phi_{i+1}} = e^{-\beta[H_{i,i+1} + 1/2(P_{x,i} + P_{x,i+1})E]}$. The partition function can now be rewritten in the standard way as

$$Z = \sum_{\phi_1} \dots \sum_{\phi_N} T_{\phi_1, \phi_2} T_{\phi_2, \phi_3} \dots T_{\phi_N, \phi_1} = \text{Tr} T^N. \quad (\text{A4})$$

In the thermodynamic limit the free energy f per site is given by

$$f = -\frac{1}{\beta} \lim_{N \rightarrow \infty} \frac{1}{N} \ln \text{Tr} T^N = -\frac{1}{\beta} \ln \lambda_0, \quad (\text{A5})$$

where λ_0 is the largest eigenvalue of the transfer matrix T .

It is convenient to introduce new variables $Q = e^{-\beta J_q^{\text{NN}}}$, $K = e^{-\beta E}$, in terms of which the matrix T reads

$$T = \begin{pmatrix} Q^{-1} & QK & Q^{-1} & QK^{-1} \\ QK & Q^{-1}K^2 & QK & Q^{-1} \\ Q^{-1} & QK & Q^{-1} & QK^{-1} \\ QK^{-1} & Q^{-1} & QK^{-1} & Q^{-1}K^{-2} \end{pmatrix}. \quad (\text{A6})$$

Its eigenvalues are $0, 0, [1 + 2K^2 + K^4 \pm (1 - 4K^2 + 6K^4 - 4K^6 + K^8 + 8K^2Q^4 + 8K^6Q^4)^{1/2}]/(2K^2Q)$. The largest eigenvalue is clearly $\lambda_0 = [1 + 2K^2 + K^4 + (1 - 4K^2 + 6K^4 - 4K^6 + K^8 + 8K^2Q^4 + 8K^6Q^4)^{1/2}]/(2K^2Q)$ and the free energy per site in the thermodynamic limit is given by Eq. (A5).

In order to calculate the linear and nonlinear susceptibilities, we expand the free energy in powers of the external field E up to fourth order and find

$$f = -\frac{1}{\beta} \ln \frac{2(1+Q^2)}{Q} - \frac{\beta}{4} E^2 - \beta^3 \frac{3-4Q^2}{96Q^2} E^4 + \dots. \quad (\text{A7})$$

The polarization order parameter is given by

$$P = -\frac{\partial f}{\partial E} = \frac{\beta}{2} E + \beta^3 \frac{3-4Q^2}{24Q^2} E^3 + \dots, \quad (\text{A8})$$

which yields the expressions for the linear and nonlinear susceptibilities

$$\chi_P^{(1)} = \frac{\beta}{2}, \quad (\text{A9})$$

$$\chi_P^{(3)} = \beta^3 \frac{3-4Q^2}{24Q^2} = \frac{\beta^3}{24} (3e^{2\beta J_q^{\text{NN}}} - 4). \quad (\text{A10})$$

The linear susceptibility represents just the Curie law and is independent of the quadrupolar coupling J_q^{NN} . The third-order susceptibility at high temperatures, where the exponential term is close to 1, is negative and proportional to β^3 . At low temperatures, comparable to the coupling J_q^{NN} , the exponential term dominates and changes the sign of $\chi_P^{(3)}$ to positive. The change of sign occurs at temperature $T^* = 2J_q^{\text{NN}}/\ln(4/3) = 6.95J_q^{\text{NN}}$. The exponential divergence of $\chi_P^{(3)} \rightarrow +\infty$ as temperature goes to zero is a consequence of the 1D model undergoing a phase transition into the ground-state phase with quadrupolar long-range order.

*Permanent address: Department of Physics, Faculty of Electrical Engineering, Slovak Technical University, Ilkovičova 3, 812 19 Bratislava, Slovakia.

¹R. E. Cohen, *Nature (London)* **358**, 136 (1992).

²M. Posternak, R. Resta, and A. Baldereschi, *Phys. Rev. B* **50**, 8911 (1994).

³W. Zhong, D. Vanderbilt, and K. M. Rabe, *Phys. Rev. B* **52**, 6301 (1995).

⁴K. A. Müller and H. Burkard, *Phys. Rev. B* **19**, 3593 (1979).

⁵K. A. Müller, W. Berlinger, and E. Tosatti, *Z. Phys. B* **84**, 277 (1991).

⁶K. A. Müller, *Ferroelectrics* **183**, 15 (1996).

⁷M. Fischer, A. Lahmar, M. Maglione, A. San Miguel, J. P. Itié, A. Polian, and F. Baudalet, *Phys. Rev. B* **49**, 12 451 (1994).

⁸H.-B. Neumann, H. F. Poulsen, U. Rütt, J. R. Schneider, and M. v. Zimmermann, *Phase Transitions* **55**, 17 (1995).

⁹O.-M. Nes, K. A. Müller, T. Suzuki, and K. Fossheim, *Europhys. Lett.* **19**, 397 (1992).

¹⁰E. V. Balashova, V. V. Lemanov, R. Kunze, G. Martin, and M. Weihnacht, *Solid State Commun.* **94**, 17 (1995).

¹¹B. Hehlen, Z. Kallassy, and E. Courtens, *Ferroelectrics* **183**, 265 (1996).

¹²S. Rod, F. Borsa, and J. J. van der Klink, *Phys. Rev. B* **38**, 2267 (1988).

¹³E. Courtens, G. Coddens, B. Hennion, B. Hehlen, J. Pelous, and R. Vacher, *Phys. Scr.* **T49B**, 430 (1993).

¹⁴E. Courtens, *Ferroelectrics* **183**, 25 (1996).

¹⁵E. Tosatti and R. Martoňák, *Solid State Commun.* **92**, 167 (1994).

¹⁶R. Martoňák and E. Tosatti, *Phys. Rev. B* **49**, 12 596 (1994).

¹⁷W. Zhong and D. Vanderbilt, *Phys. Rev. B* **53**, 5047 (1996).

¹⁸A. D. Bruce and R. A. Cowley, *Structural Phase Transitions* (Taylor & Francis, London, 1981).

¹⁹M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Clarendon, Oxford, 1977).

- ²⁰H. Bilz, G. Benedek, and A. Bussmann-Holder, *Phys. Rev. B* **35**, 4840 (1987); A. Bussmann-Holder, H. Bilz, and G. Benedek, *ibid.* **39**, 9214 (1989).
- ²¹R. Migoni, H. Bilz, and D. Bäuerle, *Phys. Rev. Lett.* **37**, 1155 (1976).
- ²²R. Oppermann and H. Thomas, *Z. Phys. B* **22**, 387 (1975).
- ²³R. Morf, T. Schneider, and E. Stoll, *Phys. Rev. B* **16**, 462 (1977).
- ²⁴P. G. de Gennes, *Solid State Commun.* **1**, 132 (1963).
- ²⁵R. Blinc and B. Žekš, *Soft Modes in Ferroelectrics and Antiferroelectrics* (Elsevier, New York, 1974).
- ²⁶M. Kolb, *Phys. Rev. Lett.* **51**, 1696 (1983).
- ²⁷D. S. Fisher, *Phys. Rev. B* **51**, 6411 (1995).
- ²⁸A. P. Young (private communication).
- ²⁹F. Moshary, N. H. Chen, and I. F. Silvera, *Phys. Rev. Lett.* **71**, 3814 (1993).
- ³⁰Yu. A. Freiman, V. V. Sumarokov, A. P. Brodyanskii, and A. Jezowski, *J. Phys. Condens. Matter* **3**, 3855 (1991).
- ³¹P. Morin and D. Schmitt, *Phys. Rev. B* **23**, 5936 (1981).
- ³²J. Hemberger, P. Lunkenheimer, R. Viana, R. Böhmer, and A. Loidl, *Phys. Rev. B* **52**, 13 159 (1995).
- ³³J. H. Barrett, *Phys. Rev.* **86**, 118 (1952).
- ³⁴J. Hemberger, Ph.D. thesis, Technische Hochschule Darmstadt, 1994.
- ³⁵H. Uwe and T. Sakudo, *Phys. Rev. B* **13**, 271 (1976).
- ³⁶R. J. Baxter, *Exactly Solved Models in Statistical Mechanics* (Academic, London, 1982).
- ³⁷R. Martoňák (unpublished).
- ³⁸W. Zhong, R. D. King-Smith, and D. Vanderbilt, *Phys. Rev. Lett.* **72**, 3618 (1994).
- ³⁹R. D. King-Smith and D. Vanderbilt, *Phys. Rev. B* **49**, 5828 (1994).
- ⁴⁰J. Hemberger (private communication).
- ⁴¹P. A. Fleury and J. M. Worlock, *Phys. Rev.* **174**, 613 (1968).
- ⁴²G. Bender, *Z. Phys. B* **23**, 285 (1976).
- ⁴³R. Martoňák (unpublished).