Self-consistent Phonon Theory of Quantum Paraelectrics

Katsuhiko FUJII, Juntaro YAMADA and Takeo MATSUBARA

Department of Applied Physics, Okayama University of Science

1−1 Ridaicho, Okayama 700 Japan

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A theory of quantum paraelectricity is presented to explain the nearly ferroelectric properties of some perovskite structure substances such as $SrTiO_3$ and $KTaO_3$ on the basis of the self-consistent phonon approximation. Particular emphasis is laid upon the effect of the mode-mode couplings on the phase boundary between ferro and paraelectric regions and it is shown that the trend toward the quantum paraelectricity is suppressed by short range interaction and enhanced by long range dipole interactions.

§1. Introduction

It is now well known that some of the perovskite structure oxides such as $SrTiO_3$ and $KTaO_3$ exhibit large dielectric constant at low temperatures and yet do not make any transition to the ferroelectric phase. This is believed to be due to large zero point vibrations, and such a dielectric substance is sometime called quantum paraelectrics, bearing close similarity with the "quantum liquid" in which the long range crystalline order is prevented by large zero point motions. The possibility for the existence of quantum paraelectrics was suggested as early as in 1952 by Barrett[1], who worked out a simple theory to give an expression for the dielectric constant of the form

$$\varepsilon = \frac{M}{(T_1/2)\coth(T_1/2T) - T_0} \tag{1}$$

It is obvious that ε given by (1) tends to a constant value $2M/(T_1-2T_0)$ near absolute zero temperature ($T \to 0$) and follows the Curie-Weiss law $\varepsilon \sim M/(T-T_0)$ at high temperatures. The parameter T_1 is related to a frequecy Ω of the relevant harmonic oscillator as $T_1 = h\Omega/k_B$, k_B being Boltzmann constant. As to the cross over from clssical to quantum regimes, Kurtz made an argument that when the ionic displacement Δx, estimated from extrapolated Curie temperature T_0 by a formula

$$k_B T_0 = \frac{1}{2} K (\Delta x)^2, \tag{2}$$

becomes smaller than the ionic displacement Δx of zero point vibration, the quantum

effect should suppress the ferroelectricity[2]. The force constant K in (2) turns out experimentally to be nearly the same value 5.5×10^4 dyne/cm for most ferroelectric perovskite oxides.

Detailed experimental measurement of dielectic constant at very low temperatures for $SrTiO_3$ was performed by Müller and Burkard[3], who compared their observed data with Barrett formula (1) taking the following parameters:

$$T_1=84\,K,\quad T_0=38\,K,\quad M=9\times10^4\,K \tag{3}$$

Although the expression (1) can realize qualitative feature of their observation, it fails to give a quantitatively good fit to the experimental data for some range of the measured temperatures. This discrepancy would be caused by the simplified single mode mean field theory of Barrett, and in order to have a more quantitative explanation it is pointed out that mode-mode couplings and multi-mode argument must be introduced. One aim of the present paper is to undertake such a task for understanding of quantum paraelectricity on a more quantitative basis.

More recently, Rytz, Höchli and Biltz[4] have determined the temperature dependence of dielectric constants of quantum paraelectrics $KTaO_3$, $KTa_{1-x}Nb_xO_3$ and $K_{1-y}Na_yTaO_3$. In particular they report that the mixed crystals with $x_c = 0.008$ for $KTa_{1-x}Nb_xO_3$ and $y_c = 0.12$ for $K_{1-y}Na_yTaO_3$ show the existence of temperature ranges in which a characteristic temperature variation of dielectric constant appears such that

$$\varepsilon\sim T^{-\gamma},\quad \gamma=\begin{cases}2.0 & \text{for } x_c\\ 2.1 & \text{for } y_c\end{cases}. \tag{4}$$

This behaviour would closely related to a cross over phenomenon between quantum para and ferroelectricity, and may be explained within the framework of renormalization group approach as have been tried by Schneider, Beck and Stroll[5]. Another important point to be asked is to explore the phase boundary which separates the quantum para phase and ordinary ferroelectric phase.[6] By introducing a suitable variable S and ferroelectric phase transition temperature T_c, the boundary may be described in T_c-S plane as

$$T_c\sim(S-S_c)^n \tag{5}$$

where $S<S_c$ corresponds to the quantum para region. The meaning of S is however not quite clear and hence the second aim of this paper will be to present a simple and systematic description of the cross over and phase boundary problems based on a simple model.

§2. Fomulation

Focussing on the sublattice of ions which play primary role in ferroelectricity, we

start with a model Hamiltonian of the following form:

$$H=\frac{1}{2}m\sum_i \dot{Q}_i+\frac{1}{2}m\omega_s^2\sum_i Q^2{}_i+\frac{1}{4}\sum_i Q^4{}_i$$

$$-\sum_{ij} S_{ij}Q_iQ_j-\sum_{ij} D_{ij}Q_iQ_j \qquad (6)$$

where Q_i is the displacement of the i-th atom with mass m, S_{ij} the short range interaction parameter, and D_{ij} denotes the coefficient of long range (dipole-dipole) interaction. Assuming certain crystalline symmetry, we introduce Fourier transformed quantities : For instance the Fourier components of atomic displacement are defined as

$$Q(q)=(N)^{-\frac{1}{2}}\sum_i Q_i\exp(-iq\cdot r_i) \qquad (7)$$

and for short range interaction

$$S(q)=\sum_{ij} S_{ij}\exp(-iq\cdot r_{ij}) \qquad (8)$$

which may be put in the form when only nearest neighbour interactions are considered

$$S(q) = S(0)C(q) \qquad (9)$$

with

$$C(q)=(1/z)\sum_{\Delta}\exp(-iq\cdot\Delta)\ , \qquad (10)$$

z being the number of nearest neighbours. Δ are the vectors connecting a center and its nearest neighbour atoms. For the long range interaction we have

$$D(q)=e^2\sum_{ij}[\,3z^2{}_{ij}-r^2{}_{ij})/r^5{}_{ij}\,]\exp(iq\cdot r_{ij}) \qquad (11)$$

which is approximated by the continuum model in later simplifying argument,taking

$$D(q)=D(0)(1-3\cos^2\theta)(3/q^3a^3)(\sin qa-qa\cos qa)$$

$$\equiv D(0)\,\delta(q,\cos\theta) \qquad (12)$$

with

$$\cos\theta=q_z/q,\quad q=(q_x^2+q_y^2+q_z^2)^{\frac{1}{2}} \qquad (13)$$

D(0) is the limiting value of D(q) for q = 0 and $\cos\theta = 0$. By making use of the Fourier tranform, the potential energy part of (6) can be written as

$$V=\sum_q \frac{1}{2}[\,m\omega_s^2-S(q)-D(q)\,]\,|\,Q(q)\,|^2$$

$$+(B/4N)\sum_{q_1}\sum_{q_2}\sum_{q_3} Q(q_1)Q(q_2)Q(q_3)Q(-q_1-q_2-q_3) \qquad (14)$$

The self-consistent phonon approximation amounts to replace the quartic term V_4 in the potential energy V by a quadratic form such as

$$V_4=(3B/2N)\sum_q\sum_k <|\,Q(k)\,|^2>\,|\,Q(q)\,|^2 \qquad (15)$$

and hence the potential energy is assumed to take on

$$V=\sum_q \frac{1}{2} m\omega^2(q)\,|\,Q(q)\,|^2 \qquad (16)$$

where

$$m\omega^2(q)=m\omega_s^2-S(q)-D(q)+(3B/N)\sum_{q'} <|\,Q(q')\,|^2>. \qquad (17)$$

The mean square average of q-mode amplitude $<|\,Q(q)\,|^2>$ in (17) may be evaluated as

$$<|\,Q(q)\,|^2>=(\hbar/2m\omega(q))\coth[\,\hbar\omega(q)/2k_BT\,] \qquad (18)$$

and equations (17) and (18) give a set of basic formulae in the present self-consistent phonon approximation. Writing as

$$A=J(0)-m\omega_s^2 \qquad (19a)$$

$$J(0)=S(0)+D(0) \qquad (19b)$$

the ferroelectric soft mode frequency ω (0) is determined from

$$m\omega^2(0)/A=(3\hbar B/2mAN)\sum_q \omega(q)^{-1}\coth[\,\hbar\omega(q)/2k_BT\,]-1 \qquad (20)$$

For later numerical computation, we make the equation (20) dimensionless form by introducing the following quantities

$$y=m\omega(0)^2/J(0),\quad t_o=J(0)/A,\quad D=D(0)/J(0), \qquad (21a)$$

and two characteristic temperatures

$$T_0 = AJ(0)/3k_B B, \quad T_1 = \hbar J(0)^{\frac{1}{2}}/2k_B m^{\frac{1}{2}} \tag{21b}$$

T_0 is served as a temperture scale and T_1/T_0 is a (quantum) parameter such that the larger T_1/T_0 is, the more favaourable is the quantum para state. The dimensionless equation determining y is

$$t_0 y = \frac{T_1}{T_0}\frac{1}{N}\sum_q \frac{\coth[\,(T_1/T)\{y+1-C(q)+D(C(q)-\delta(q,\cos\theta))\}^{\frac{1}{2}}\,]}{[\,y+1-C(q)+D(C(q)-\delta(q,\cos\theta))\,]^{\frac{1}{2}}} - 1 \tag{22}$$

In §3 will perform numerical analysis on the basis of this equation, by calculating y as a function of T/T_0 for various values of the parameters t_0 , T_1/T_0 and D.

§3 Numerical Analysis

Let us first examine the case of D = 0. Fig. 1 shows the calculated y - T/T_0 relation for three different values of the quantum parameter T_1/T_0 = 2.0, 0.9, 0.5 and for three values of the short range interaction parameter t_0 = 0.1, 1, 10. For large T_1/T_0 there appears no softening and y, which is proportional to the inverse of dielectric constant due to LST relationship, tends to a constant value at low temperatures, while for small T_1/T_0 = 0.5 softening in y eventually gives rise to a phase transition at a critical temperature T_c which is independent of t_0 . At sufficiently high temperatures, however, for all cases the Curie-Weiss law becomes to hold. From these figures it is seen that the temperature dependence of y is governed by T_1/T_0 at low temperatures and by t_0 at high temperatures. In Fig. 2 a comparison between the present theory and experimental data due to Müller and Burkard is made for dielectric constant normalized with the saturated value ε_0 ($\sim 1/y_0$) at very low temperature. We note that theoretical fit is improved much better than Barrett theory. Fig. 3 indicates an example of y-T/T_0 relation for a model quantum paraelectrics having quantum parameter near a critical value $(T_1/T_0)_c$ = 0.8965 (see Fig.4). If we assume $y(\sim 1/\varepsilon) \sim T^{\gamma}$, it turns out that γ is about 2.1 in certain temperature region as experimentally observed.

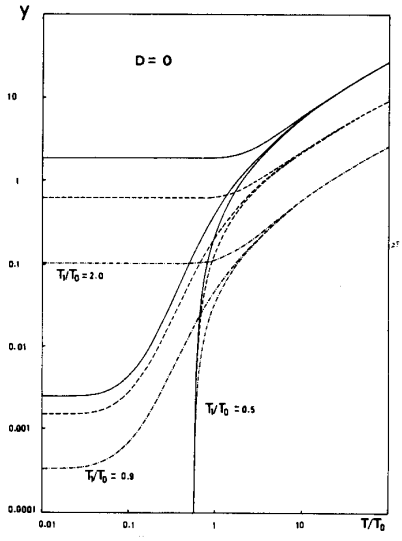

Fig. 1 Square of reduced ferroelectric soft phonon frequency vs reduced temperature T/T_o. The used values of t_o are: $t_o = 0.1$: (——), $t_o = 1$: (……), $t_o = 10$: (– – –)

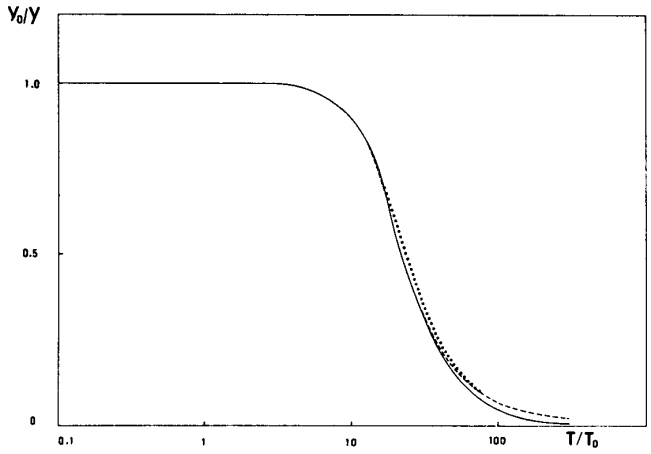

Fig. 2 Comparison of experimental and calculated values of (y_o/y) as a function of T/T_o. • :experiment, ——— : present theory

In order to determine the phase boundary between quantum para and ferroelectric states, we put in (22) $y = 0$ and $T = T_c$, obtaining an equation to fix T_c :

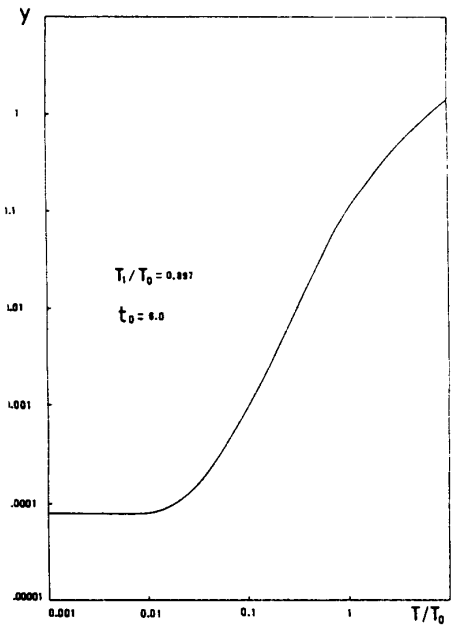

Fig. 3 A typical y-T/T_o curve for a model quantum paraelectrics with (T_1/T_o) value near $(T_1/T_o)_c$. It is seen that there is a certain temperature range where $y \approx T^2$ holds.

$$T_o/T_1 = 1/N \sum_q \frac{\coth[\, T_1/T_c(1-C(q))^{\frac{1}{2}}\,]}{(1-C(q))^{\frac{1}{2}}} \qquad (23)$$

If we use a simple mean field approximation by discarding the phonon dispersion, the equation (23) reduces to the Barrett theory

$$T_o/T_1 = \coth\,(\,T_1/T_c\,) \qquad (24)$$

In Fig. 4 we depict T_c calculated from (23) and (24) as functions of the quantum parameter T_1/T_o . We can see from this that self consistent phonon theory which takes account of multi-phonon modes yields narrower quantum para region in (T_c/T_o) -(T_1/T_o) diagram compared with Barrett (single mode mean field) theory.

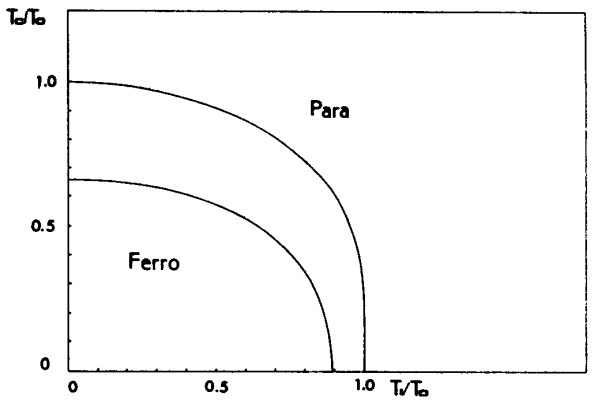

Fig. 4 Phase diagram in (T_c/T_o) - (T_1/T_o) plane. The outer boundary corresponds to the Barrett theory and inner boundary to the present theory.

Now turning to the case $D \neq 0$, we examine the effect of long range dipole interaction on quantum paraelctricity. Fig. 5 shows calculated y-T/T_0 relation for various D values when $t_0 = 0.01$ and $T_1/T_0 = 0.94$ are fixed. Since the chosen $T_1/T_0 = 0.94$ exceeds $(T_1/T_0)_c$ obtained in Fig. 4, the uppermost curve ($D = 0$) belongs to the quantum para state with no softening. However with increasing D value, the temperature variation of y becomes more enhanced and at last around $0.22 < D < 0.23$ a softening takes place and ferroelectric phase is realized. Thus we find that long range dipole-dipole interactions act to strengthen the trend toward ferroelectricity. But more careful calculation suggests that for large D value different softening in zone boundary mode may be possible, indicating the existence of some kind of antiferroelectric phase. In order to discuss such a new possibility, however, our model is too simple and it is out of scope of the present theory.

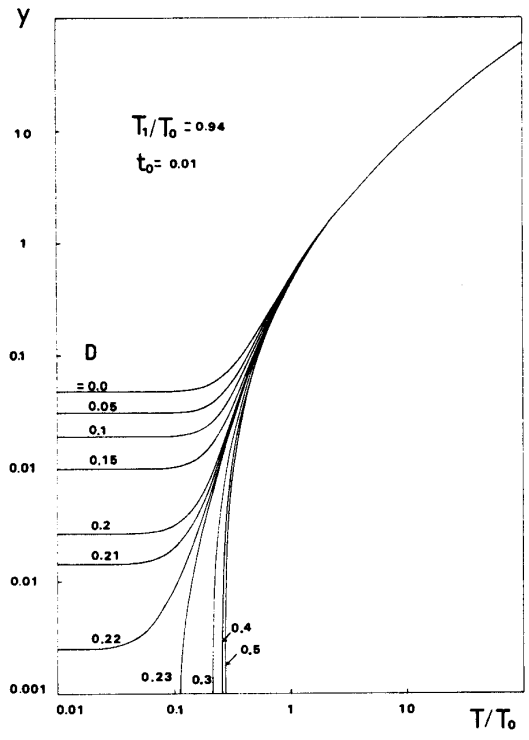

Fig. 5 The effect of long range interaction D on y - T/T_0 relation.

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