First Order Phase Transition in Quantum Paraelectrics

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We discuss the nature of pressure induced phase transitions in standard Quantum Paraelectrics near quantum critical point. From a microscopic theory we first show that near the critical point the transition temperature $T_c(p)$ varies as $(1 - p/p_c)^{\xi}$ with $\xi = \frac{1}{2}$. Within the Landau scheme, it is shown that for $\xi \leq 1$, a condition satisfied by most quantum paraelectrics the transition is inevitably first order in nature. The present analysis is valid for non-polar impurity induced transitions in these materials and is supported by some recent experiment.

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I. INTRODUCTION AND SUMMARY

The static dielectric susceptibility in the materials like SrTiO3 and KTaO3 does not show any divergence down to zero Kelvin, it rather saturates at a very high value ($O(10^4)$). Ferroelectric transitions in materials which are similar in structure, for example in BaTiO3, are of displacive type and are well described by softening of a zone center transverse optical mode. This scenario, that is, absence of transition and high dielectric susceptibility, has been attributed to smallness of the gap in the corresponding optical branch, smallness of the optical gap makes quantum fluctuations relevant in these materials. These materials are, therefore, called quantum paraelectrics. There is a revival of interest, particularly regarding the nature of phase transition at quantum critical point in these materials. The effects of pressure and impurities on the dielectric susceptibilities have been well studied experimentally. One recent experimental report indicates that these materials show phase separation near QCP. A general consensus arising form these experiments is that application of hydrostatic pressure moves them away from criticality and the possibility of transition is suppressed. One needs to apply some kind of negative pressure to induce phase transitions in these materials. One way to apply negative pressure is to put non-polar impurities which creates local pressure deficiencies and thus induce phase transitions. Remarkably when experimentally one finds $T_c \sim (n - n_c)^{\frac{1}{2}}$ (where $n$ is the average impurity concentration and $n_c$ is the critical value), the theoretically estimated transition temperature for pressure induced transition goes as $T_c \sim (p + p_c)^{\frac{1}{2}}$ (where $p$ is hydrostatic pressure and $p_c$ is the critical value). This motivates us to develop a description, suitable for properties of pressure induced phase transition, which can be used to understand the newly found phase separation in ferroelectric transition near ferroelectric quantum critical point. In the following, using a microscopic theory in the paraelectric phase, we first show that $T_c \sim (p + p_c)^{\frac{1}{2}}$ within some reasonable approximation. Then we use this scaling behavior of $T_c$ in a Landau functional to discuss ferroelectric transition in such systems.

II. MEAN FIELD ANALYSIS

Application of hydrostatic pressure (also the effect of non-polar impurity) will couple to optical mode via strain. In this case our starting Hamiltonian takes the form

$$
H = \int dq \left[ \frac{1}{2} p_q^2 + \frac{1}{2} (\omega_0^2 - vq^2) u_q u_{-q} + \frac{1}{4} \lambda \int \Pi_i dq_i u_{q_1} u_{q_2} u_{q_3} u_{-q_1-q_2-q_3} + \frac{1}{2} K \int dq^2(q) + g \int dk dq e(k) u_{q_k} - p \int dq \delta(q) e(q) \right]
$$

(1)

Here terms in the parentheses describe optical phonons in harmonic approximation, the quartic term describes the anharmonic coupling between these phonons. Last three terms describe the result of application of pressure to lowest possible order. The strain field $e(q)$ couples to unit cell displacement related to optic mode with amplitude $g$, the harmonic acoustic phonons have force constant $K$ and in the last term the coupling of the hydrostatic pressure $p$ to the static strain has unit strength. The details of this hamiltonian are described in our earlier work. On Integrating out the strain field, we get an effective Hamiltonian of the form

$$
H = \int dq \left[ \frac{1}{2} p_q^2 + \frac{1}{2} (\omega_0^2 - vq^2 + vq^2 \delta q^2) u_q u_{-q} + \frac{1}{4} \lambda_R \int \Pi_i dq_i u_{q_1} u_{q_2} u_{q_3} u_{-q_1-q_2-q_3} \right]
$$

(2)

where the normalized quartic coupling

$$
\lambda_R = (\lambda - 2g^2/K).
$$

(3)

Now with $p_q = \dot{u}_q = -i\omega u_q$ in the kinetic energy term, and within the quasi harmonic approximation, for the quartic term, i.e.

$$
\sum_i u_i^4 \approx 6N (\sigma + \frac{1}{2} (u)^2) \sum_{q_1} u_{q_1} u_{-q_1}
$$

(4)
the Hamiltonian is given by,
\[ H = \frac{1}{2} \sum_q (\omega_q^2 - \omega^2) u_q u_{-q}. \]  \hspace{1cm} (5)

Here \( \omega_q \) is renormalized optical frequency in the paraelectric phase where \( < u > \) is identically zero and is given by,
\[ \omega_q^2 = \omega_0^2 + gp + v \delta \cos q \delta a^2 q^2 + 3 \lambda_R \sigma \]
\[ \simeq \omega_0^2 - v + gp + v \delta a^2 q^2 + 3 \lambda_R \sigma. \]  \hspace{1cm} (6)

and
\[ \sigma = \sum_q (T u_q(0) u_{-q}(0^+)) \]  \hspace{1cm} (7)

is the mean square fluctuations of displacement in optical mode. The susceptibility, which is related to \( < u^2 > \), is essentially the phonon propagator,
\[ \chi(q, n) = -\frac{1}{(i\omega_n)^2 - \omega_q^2} \omega_n = 2n\pi T. \]  \hspace{1cm} (8)

With \( \omega_q \), already defined we have a self consistent equation for the fluctuation in the optical mode,
\[ \sigma = \sum_q \frac{1}{2\omega_q} \coth \left( \frac{\omega_q}{2T} \right) \]  \hspace{1cm} (9)

Which in its asymptotic forms reduces to,
\[ \sigma \sim \int \frac{Td^3q}{\omega_0^2 - v + gp + v \delta q^2 + 3\lambda_R \sigma} \]  \hspace{1cm} (10)
in the high temperature limit and to
\[ \sigma \sim \int \frac{d^3q}{\sqrt{\omega_0^2 - v + gp + v \delta q^2 + 3\lambda_R \sigma}} \]  \hspace{1cm} (11)
in the low temperature limit. Defining the parameters
\[ \Delta = \frac{(\omega_0^2 - v)}{3\lambda} \text{ and } p_c = \frac{3K\Delta\lambda}{g}, \]  \hspace{1cm} (12)

which give vicinity to the quantum critical point and the critical pressure respectively, we can write
\[ \omega^2(q) = 3\Delta \lambda(1 + p/p_c) - v \delta q^2 a^2/2 + 3\lambda_R \sigma. \]  \hspace{1cm} (13)

In absence of coupling to strain, \( \Delta \) completely determines the quantum phase diagram, with \( \Delta = 0 \) giving the quantum critical point. Up to this point the result is just the renormalization of the factor \( \Delta \) to \( \Delta(1 + p/p_c) \) and it becomes an experimentally controllable parameter. To find out the dependence of \( T_c \) on pressure, one needs to find out temperature dependence of \( \sigma \) at certain value of \( p \) and then \( T_c \) can be found out from the equation \( \omega^2(q, T_c) = 0 \). Near quantum critical point a non-self consistent calculation, with a temperature dependent momentum cut off \( (q_{\text{max}} \sim T) \) gives \( \sigma \sim T^2 \) which thereby imply \( T_c \sim (1 + p/p_c)^{\frac{1}{2}} \).

III. LANDAU EXPANSION

Now using this scaling behavior for \( T_c \), we switch over to a Landau description for the ordered phase, that is, we write the variational Gibbs free energy functional as,
\[ F(P, \epsilon : p, T) = \frac{\alpha}{2}(T - T_c(\epsilon))P^2 + \frac{\lambda}{4}P^4 + \frac{1}{2}K\epsilon^2 - pc. \]  \hspace{1cm} (14)

Here \( \alpha, \lambda \geq 0 \), and \( K \) is the stiffness constant for strain and \( p \) is external hydrostatic pressure. \( P \) and \( \epsilon \) are the average values of polarization and strain respectively. In this scheme we can proceed up to the tricritical point along a second order line, i.e. the coefficient of quartic term is positive and truncation of free energy functional at quartic term is sufficient. A similar function was used recently by Gehring to describe various aspects of pressure induced quantum phase transition in itinerant magnets. Starting from equation \( \textbf{11} \), if we consider only mean field behavior of both the order parameter and strain, we get \( < \epsilon(\epsilon) > = \frac{\lambda}{4}\delta(q) \) and \( T_c \sim (1 + p/p_c) \). It is to be noted that the behavior near QCP can be understood only beyond the Landau scheme and a proper account of local quantum fluctuations as well as the spatial variations of order parameter in the free energy functional is needed. With introduction of one more variational parameter (\( \sigma \)), the mean square fluctuations defined in the equation \( \textbf{7} \) and elimination of it through minimization of free energy, will lead to the self consistent equation in the disordered phase. To a good approximation we neglect fluctuations in strain (when \( K \gg 0 \)) and considering its mean field value \( \frac{\lambda}{4}\delta(q) \), it leads to \( T_c \sim (1 + p/p_c)^{\frac{1}{2}} \). The reason for such behavior in the ordered phase is that in the self consistent calculation there \( \sigma \) will be replaced by \( \sigma + < u >^2 \) in the expression for renormalized frequency \( \textbf{10} \). Here \( < u > \) is the mean average displacement and the polarization \( (P) \) is proportional to it. Classically \( < u > \sim (T_c(p))^\frac{1}{2} \), hence its contribution retains the form of equation \( \textbf{13} \) same except modifying the numerical factor in the right hand side. In quantum domain there is possibility that \( < u > \sim T_c^{\nu} \). As long as \( \nu \geq \frac{1}{2} \), this assumption is valid. One can also question the validity of the linear expansion in temperature around \( T_c \) when \( T_c \rightarrow 0 \). In a suitable description for the phase transition at finite temperature near QCP, a higher power of \( T \) should appear. Here we focus only on QCP at zero temperature. Now we solve the coupled equation obtained from the minimization of free energy with respective to these parameters which gives their physical values. Minimization of free energy with respective to polarization gives
\[ \frac{\partial F(P, \epsilon : p, T)}{\partial P} = 0 = P \left[ \alpha(T - T_c(\epsilon)) + \lambda P^2 \right]. \]  \hspace{1cm} (15)

We need one more equation to eliminate \( \epsilon \) from the above equation and this equation is obtained from the minimization of free energy with respective to strain as fol-
lows,
\[
\frac{\partial F(P, \epsilon : p, T)}{\partial \epsilon} = 0 = \frac{\alpha}{2} \frac{\partial T_c(\epsilon)}{\partial \epsilon} P^2 + K \epsilon - p \tag{16}
\]
One needs to solve coupled equation (6) and (9) to get physically observable quantities.

**Paraelectric Phase:** This phase is characterized by zero average value of polarization and leads to the solutions
\[
P = 0, \quad \epsilon = p/K \quad \text{and} \quad F_0(p, T) = -\frac{p^2}{2K} \tag{17}
\]

**Ferroelectric Phase:** In this phase average polarization takes non zero value and interplay between strain and polarization becomes interesting. Here,
\[
P = \pm \sqrt{\frac{\alpha(T_c(\epsilon) - T)}{\lambda}},
\epsilon - \frac{p}{K} = \frac{\alpha^2}{2\lambda K}(T_c(\epsilon) - T) \frac{\partial T_c(\epsilon)}{\partial \epsilon}
\equiv g(\epsilon) \quad \text{(say)} \tag{18}
\]
and on substituting this expression the free energy in the polar phase becomes
\[
F_{pol}(p, T) = F_0(p, T) - \frac{\alpha^2}{4\lambda}(T_c(\epsilon_0) - T)^2 + \frac{Kg^2(\epsilon_0)}{2}
= F_0(p, T) - \frac{\alpha^2}{4\lambda}(T_c(\epsilon_0) - T)^2
\times \left[1 - \frac{\alpha^2}{2\lambda K}(\frac{\partial T_c(\epsilon)}{\partial \epsilon})_{\epsilon_0}^2\right] \tag{19}
\]
Where \(\epsilon_0\) is a solution of equation (13). The second term in the right hand side of the equation (19) vanishes at \(T_c\) and also below \(T_c\) if
\[
1 - \frac{\alpha^2}{2\lambda K}(\frac{\partial T_c(\epsilon)}{\partial \epsilon})_{\epsilon_0}^2 = 0 \tag{20}
\]
Clearly the above equation is the condition for tricriticality. Thus the condition to achieve first order transition is given by
\[
F_{pol}(p, T) \geq F_0(p, T) \Rightarrow \frac{\alpha^2}{2\lambda K}(\frac{\partial T_c}{\partial \epsilon})^2 \geq 1 \tag{21}
\]
In terms of pressure this relation becomes
\[
\frac{\alpha^2}{2K\lambda} \left(\frac{\partial T_c}{\partial p}\right)^2 \geq 1 \Rightarrow \frac{\alpha^2K}{2\lambda} \left(\frac{\partial T_c}{\partial p}\right)^2 \geq 1 \tag{22}
\]
The point in p-T phase diagram satisfying the equality marks the transition between second and first order is called “tricritical point”. In our estimation of \(T_c(\epsilon)\) or \(T_c(p)\) (estimated microscopically and supported experimentally) is taken as
\[
T_c(p) = (1 - p/p_0)^\xi \tag{23}
\]
where \(\xi = \frac{1}{12} \leq 1\), which tells that at quantum critical point the transition is inevitably first order.

**IV. DISCUSSIONS**

The above mentioned analysis is a qualitative answer to the recently found phase separation behavior near ferroelectric quantum critical point and its absence when one is away from the quantum critical point. Our analysis shows that the exponent \(\xi\) which determines the scaling behavior of \(T_c\) with pressure near quantum critical point, determines whether phase separation is there or not. The fact that \(\xi \leq 1\) is clearly a consequence of the large quantum fluctuations near QCP. Near QCP system becomes very much sensitive to any perturbation and is manifested by the divergence of \(\frac{\partial T_c}{\partial p}\). These tells that in the proposed form of free energy in equation (14) some amount of fluctuation effects are included and the first orderliness and the occurrence of phase separation is essentially fluctuation induced. Here we have estimated exponent \(\xi\) in a qualitative manner. Correct estimation needs to take higher order correlations into account and needs more involved calculations. For the present purpose only relevant aspect about \(\xi\) is, whether it is \(\leq 1\) or not. As long as one have \(\xi \leq 1\) (from theory or experiments) the whole discussion is true.

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