Order-Disorder and Displacive Transitions in a Quantum Ising Model

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A ferrodistortive phase transition is analyzed for a quantum particles in a simple quartic potential. The interactions are taken into account by the mean-field approximation. A quantum thermodynamic treatment gives analytic expressions for the static susceptibility, the specific heat and the soft mode frequency. The Rhodes-Wohlfarth ratio is a measure whether the system is order-disorder or displacive, however, the border is fuzzy depending on the interaction strength. The quantum effect is discussed when the transition takes place at low temperature. Whether the atomic density is a single or multiple peak distributions seems to be a definite criterion for the character of the structural phase transition.

KEYWORDS: order-disorder, displacive, ferroelectric transition, anharmonic-oscillator model, quantum Ising model, susceptibility, specific heat, Debye-Waller factor

1. Introduction

In order to understand the difference between two kinds of mechanism of order-disorder (OD) and displacive (DP) type transitions in ferroelectric crystal, a unified anharmonic-oscillator model was investigated by using the mean-field approximation for interactions between classical particles.1 The single particle potential is quartic in the atomic coordinate as

\[ V(x) = ax^4 + bx^2, \quad a > 0. \] (1)

It was shown that the system behaves DP-like if \( b > 0 \) or the mean kinetic energy of the particle exceeds the potential barrier of \( b^2/4a \) (\( b < 0 \)). On the other hand, if \( b < 0 \) and the kinetic energy is below the potential barrier, then the dynamic behavior was shown to be OD-like.1

Although the treatment was rigorous in classical mechanics with the mean-field approximation, the quantum effect that a particle can tunnel the wall barrier was ignored. Another approach is to adopt a self-consistent phonon approximation to describe the feature whether the system is OD or DP. The criteria is summarized that if the Rhodes-Wohlfarth (RW) ratio \( r \) is higher than unit, the ferroelectric crystal is DP, while it is OD if RW ratio is of order of

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Here the ratio $r$ is defined as
\[ r = \frac{\text{paraelectric moment } p_c \text{ evaluated from Curie constant}}{\text{saturation moment } p_s \text{ at } T = 0}. \] (2)

The results are deduced by using quantum statistical mechanics, however, the self-consistent phonon approximation can be applicable when the phonon picture gives good description.

On the other hand, some empirical criteria have been postulated so far; OD-type crystals are characterized by i) transition entropy per atom $\Delta S$ is order of $k_B \ln 2$ where $k_B$ is Boltzmann constant, ii) Curie constant $C$ is a few times of the transition temperature $T_c$, and iii) atoms occupy equivalent positions with equal probability above $T_c$, while DP-type crystals by i') $\Delta S \ll k_B \ln 2$, ii') $C \gg T_c$, and iii') a soft mode is observable. Another statement was proposed that pressure dependence of $T_c$ is positive and negative for OD- and DP- types, respectively.

The relation between the RW ratio and the specific heat anomaly or the transition entropy $\Delta S$ was discussed with the anharmonic potential (1), but a continuous change from DP- to OD-type was recognized.

We have adopted a two-Morse potential and developed a quantum treatment instead of the classical anharmonic-oscillator model. The static susceptibility for the model is the Barrett’s relation originally introduced for perovskite crystals. The border of the OD- and DP-types was smeared because of the tunneling of quantum particles within the double well potential.

In order to elucidate the difference between OD- and DP-types of phase transitions in dielectric crystal, we investigate the unified anharmonic-oscillator model by using the quantum linear response theory. In next section, a formulation is reviewed. Numerical results for the transition temperature, susceptibility, specific heat and soft mode frequency are also shown. The potential parameter dependences are discussed in section 3. The theoretical predictions are discussed in relationship to the empirical rules as well as to previous theoretical works in final section.

2. Formulation

Let’s consider a quantum particle in a self-potential $V(x)$ with bilinear interactions:
\[ H = \sum_j \left\{ \frac{p_j^2}{2m} + V(x_j) - h x_j \right\} - \frac{1}{2} \sum_{j,k} J_{jk} x_j x_k , \] (3)

where $h$ is an external field. The scalar amplitude $x_j$ represents the normal coordinate relevant to the structural transition. Thus $m$ is an effective mass of the coordinate. We adopt a mean-field approximation for ferrodistortive transitions, and obtain the single-particle Hamiltonian as
\[ H = \frac{p^2}{2m} + V(x) - (g\xi + h)x . \] (4)

Here $\xi = \langle x \rangle$ and $g = \sum_k J_{jk}$ are the order parameter and the interaction parameter, respectively.
Now, let us write quantum states and wave functions as following;
\[
\left\{-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)\right\} |n\rangle = \varepsilon_n |n\rangle .
\] (5)
When molecular field term \( H_1 = -(g\xi + h)x \) exists, wave functions will be represented
\[
\Psi_l = \sum_n c_{ln} |n\rangle .
\] (6)
According to the standard quantum mechanical method, the energy levels are given as
\[
E_l = \frac{\varepsilon_1 + \varepsilon_0}{2} \pm \sqrt{\left(\frac{\varepsilon_1 - \varepsilon_0}{2}\right)^2 + |\langle 0 | H_1 | 1 \rangle|^2} ,
\] (7)
if only ground and first excited states are predominant. This may be a good approximation if the system is at low temperature \( k_B T \ll \varepsilon_2 - \varepsilon_1 \).

The partition function for a \( N \)-particle system is
\[
Z = \text{Tr} e^{-H/k_B T} = (e^{-E_0/k_B T} + e^{-E_1/k_B T})^N ,
\] (8)
and the free energy per atom is
\[
F = -\frac{k_B T}{N} \ln Z + \frac{g\xi^2}{2} = -k_B T \ln \left[2 \cosh \frac{\Lambda}{k_B T}\right] + \frac{\varepsilon_0 + \varepsilon_1}{2} + \frac{g}{2} \xi^2 ,
\] (9)
where
\[
\Lambda = \sqrt{\left(\frac{\varepsilon_1 - \varepsilon_0}{2}\right)^2 + (g\xi + h)x_0^2} ,
\] (10)
and the transition matrix is defined by
\[
x_0 = \langle 0 | x | 1 \rangle .
\] (11)
Minimizing (9) with respect to \( \xi \), we obtain the self-consistent equation
\[
\xi \Lambda = (g\xi + h)x_0^2 \tanh(\Lambda/k_B T) .
\] (12)
In the paraelectric phase, the susceptibility is written from (12) as the Barrett’s equation:
\[
\chi = \lim_{h \to 0} \xi \frac{x_0^2}{k_B T} = \frac{x_0^2}{T_c} \coth \frac{T_c}{2T} - T_0 ,
\] (13)
where
\[
k_B T_1 = \varepsilon_1 - \varepsilon_0 , \quad k_B T_0 = g x_0^2 ,
\] (14)
are the energy gap and the interaction energy, respectively. The susceptibility diverges at the second order transition temperature
\[
T_c = T_1 / \ln \frac{2T_0 + T_1}{2T_0 - T_1} .
\] (15)
From (12), the spontaneous order parameter is the solution of the following equation:
\[
\frac{\Lambda_0}{k_B T_0} = \tanh \frac{\Lambda_0}{k_B T} ,
\] (16)
where $\Lambda_0^2 = (k_B T_1/2)^2 + (k_B T_0 \xi/x_0)^2$. Just below $T_c$, the order parameter is given by

$$\xi^2 \cong x_0^2 \left( 1 - \frac{T}{T_c} \right) \frac{\left[ 1 - \left( \frac{T}{2T_c} \right)^2 \right]^{\frac{T_0^2}{2T_0 T_c}}}{1 - \frac{T_0}{T_c} \left[ 1 - \left( \frac{T}{2T_c} \right)^2 \right]}.$$  \hspace{1cm} (17)

At $T = 0$, the order parameter saturates to the value of

$$\xi(0)^2 = x_0^2 \left\{ 1 - \left( \frac{T_1}{2T_0} \right)^2 \right\}.$$ \hspace{1cm} (18)

The ferroelectric susceptibility is given by the following analytic form

$$\chi = \frac{x_0^2}{\xi} - k_B T_0,$$ \hspace{1cm} (19)

where

$$\Xi = \frac{\Lambda_0}{k_B T_0} \left\{ 1 + \left( \frac{k_B T_0}{\Lambda_0} \right)^2 \left[ -1 + \frac{T_0}{T \cosh^2 \left( \frac{\Lambda_0}{k_B T} \right)} \right] \right\}.$$ \hspace{1cm} (20)

The entropy per atom is

$$S = -\frac{\partial F}{\partial T} = k_B \ln \left( 2 \cosh \frac{\Lambda}{k_B T} \right) - \frac{\Lambda}{T} \tanh \frac{\Lambda}{k_B T},$$ \hspace{1cm} (21)

and the specific heat is given by

$$c = T \frac{\partial S}{\partial T} = k_B \left( \frac{T_1}{2T} \right)^2 \sech^2 \frac{T_1}{2T} \quad (T > T_c),$$ \hspace{1cm} (22)

and

$$c = \frac{\Lambda^2}{T \cosh^2 \frac{\Lambda}{k_B T} - T_0} \quad (T < T_c).$$ \hspace{1cm} (23)

Finally the frequency of the elementary excitation (soft phonon) $\omega_p$ is given by the pole of the dynamic susceptibility.\hspace{1cm} (10) If we neglect the coupling of the relevant mode with other degree of freedom and a damping mechanism of the mode, the $\Gamma$-point frequency is calculated straightforwardly:

$$\hbar \omega_p = k_B T_1 \sqrt{1 - \frac{2T_0}{T_1} \tanh \frac{T_1}{2T}} \quad (T > T_c),$$ \hspace{1cm} (24)

$$\hbar \omega_p = 2k_B T_0 \frac{\xi}{x_0} \quad (T < T_c).$$ \hspace{1cm} (25)

Some of the relations from (8) to (25) have already been derived for the quantum Ising model previously.\hspace{1cm} (12–15) In this report, all analytic equations are expressed compactly by using three parameters $x_0$, $T_1$ and $T_0$. Thermodynamic properties depend on the ratio of two characteristic temperatures $T_0$ and $T_1$. The normalized order parameter $\xi/x_0$, the normalized susceptibility $k_B \chi/x_0^2$ and normalized specific heat $c/k_B$ are given as functions of $T/T_0$ and $T_1/T_0$. In other words, they do not depend on the detail of the self-potential $V(x)$, but through
Fig. 1. (Color online) The temperature dependence of the susceptibility and the inverse susceptibility for five parameter cases $T_1/T_0 = 0.5, 1.4, 1.9, 1.999$ and 2.01. The temperature and the susceptibility are normalized by $T_0$ and $x_0^2/k_B T_0$, respectively.

Fig. 2. (Color online) The temperature dependence of the order parameter and the specific heat for three parameter cases $T_1/T_0 = 0.5, 1.4, 1.9$. The order parameter and the specific heat are normalized by $x_0$ and $k_B$, respectively.

the energy gap between the ground and excited states, and the interaction strength $gx_0^2$, where the transition matrix $x_0$ depends on wave functions slightly. The temperature dependence of the susceptibility (13) and (19) is shown in Fig. 1. If the interaction energy is stronger than the energy gap ($T_0 > T_1$), the system is classical so that $T_c \sim T_0$, and the Curie-Weiss relation gives a classical exponent 1. On the other hand, if $T_0 < T_1$ then the transition temperature lowers and the deviation from the classical Curie-Weiss relation takes place; the exponent approaches 2. The susceptibility takes a large value within the ferroelectric phase because of quantum fluctuations. At last, the transition disappears if $2T_0 < T_1$; it is quantum paraelectric at low temperature.
Figure 2 displays the temperature dependence of the order parameter $\xi$. The specific heat contributed from the relevant mode is drawn also in Fig. 2. The anomalous part rides on the Schottky type specific heat. The heat anomaly becomes small with increasing the ratio $T_1/T_0$. The magnitude of the specific heat jump at $T_c$ is plotted in Fig. 3; the jump $\Delta c$ approaches to the classical Ising value of $1.5k_B$ as the ratio $T_1/T_0$ vanishes.

The temperature dependence of the soft mode frequency (24) and (25) is plotted in Fig. 4. At high temperature, the frequency approaches the gap energy, and it vanishes in the classical Ising limit. At zero temperature, the frequency is finite even in the OD-type system. Just around the transition temperature $T_c$, $\omega_p \propto \sqrt{|T-T_c|}$ as expected from the mean-field approximation. In the DP-type system, the ratio

$$\left| \frac{d\omega_p^2}{dT} \right|_{T>T_c} / \left| \frac{d\omega_p^2}{dT} \right|_{T<T_c}$$

at $T_c$ is one half; however, it becomes smaller in the OD-type system. The overall temperature dependence deviates from the simple relation because of the quantum effect.

Now we introduce the Rhodes-Wohlfarth (RW) ratio $r$ as\(^2,3\)

$$r = \frac{x_0}{\xi(0)} = 1/\sqrt{1 - \left( \frac{T_1}{2T_0} \right)^2},$$

which is also plotted in Fig. 3. In the classical Ising limit of $T_1 \ll T_0$, $r \to 1$ and $T_c \to T_0$. The order parameter grows up to the local minimum of the self potential at $T = 0$. The susceptibility obeys the Curie-Weiss relation, and the specific heat takes a large discontinuity at $T_c$; the transition entropy is as large as $k_B \ln 2$.

On the other hand, $T_1 \approx 2T_0$, $r \gg 1$ is the displacive limit, and $T_c$ is small as compared to $T_0$. Since the quantum fluctuation disturbs the development of the order parameter even
Fig. 4. (Color online) Temperature dependence of soft mode frequencies for five parameter cases $T_1/T_0 = 0.5, 1.4, 1.9, 1.999$ and $2.01$. The temperature and the frequency are normalized by $T_0$ and $k_B T_0$, respectively.

$T = 0$, the saturated value $\xi(0) \ll x_0$. The susceptibility deviates from the Curie-Weiss relation near $T_c$ if $T_c$ is low enough. The discontinuity of the specific heat at $T_c$ is small. The transition entropy is small, however, the entropy increases gradually within the paraelectric phase and becomes $k_B \ln 2$ as $T \to \infty$.

In the middle range of $r$, the macroscopic character changes only continuously. Since $T_c$, $\Delta c$ and the entropy $S(T_c)$ in the paraelectric phase are also given by $T_1/T_0$, we can give other RW plot as given in Fig. 5. Our results are essentially in agreement with the classical prediction by Onodera and his coworkers.\textsuperscript{6,7} The quantum treatment can give the really unified picture between OD- and DP-type transitions.

Here let’s show another RW plot shown in Fig. 6. The ratio (26) at $T_c$ is indicated as temperature derivative by ordinate. The ratio $\omega_p(T = \infty)/\omega_p(T = 0)$ is indicated as saturated frequency. Both quantities decrease monotonically with decreasing the RW ratio, and vanish at the classical Ising limit ($r = 1$).

3. Potential Parameter Dependence

So far, we have shown how the OD-type transition changes to DP-type one continuously by using quantum Ising model. Now in order to elucidate the opaque change from OD-type to DP-type, let us consider the Onodera potential (1), concretely. Here atomic mass unit, Angstrom, and electron Volt are the units of mass, length and energy, respectively. Then the Schrödinger equation (5) is rewritten as

$$\frac{d^2}{dx^2}\Psi_n = 478.46M \left\{ A x^2 (x^2 - B) - E_n \right\} \Psi_n .$$

(28)

This equation is solved numerically. Because mass number $M$ is considered as energy scale, we put $M = 16$, hereafter.
Fig. 5. (Color online) Rhodes-Wohlfarth plot for the quantum Ising model. (a) Rhodes-Wohlfarth ratio is plotted against $T_c/T_0$, and (b) the ratio is plotted against the transition entropy normalized by $k_B \ln 2$ or the specific heat jump normalized by $1.5k_B$, the classical Ising value.

The quantum states can be characterized by the energy gap $T_1$ (in unit of Kelvin) and the variance of the ground-state wave-function:

$$\sigma = \int x^2 |\Psi_0|^2 dx = x_0^2 + \sum_{n=3}^{\infty} |\langle 0 | x | n \rangle|^2.$$  (29)

With neglecting the upper energy states, $\sigma$ can be approximated to $x_0^2$. At low temperature, $\sigma$ is related to the Debye-Waller factor of the atom. By solving (28) numerically for given potential parameters $A$ and $B$, the variance $\sigma$ and the energy gap $T_1$ are calculated as given in Table I. The relation between them is represented in Fig. 7.

Both for $B < 0$ (a single minimum potential) and for $B > 0$ but the double minimum potential is so shallow that the ground state energy $\varepsilon_0$ is above the potential barrier $\varepsilon_b$ (equal to zero in the present model), the ground state wave-function takes a single peak. In such case, with increasing the potential parameter $A$, the variance $\sigma$ decreases inversely proportional to $T_1$. The $\sigma - T_1$ curve rides on almost a universal relation ($\sigma \approx 1.49/T_1$) irrespective to the potential parameter $B$.

Further increasing $A$, the double well potential becomes deeper enough so that the ground state energy is below the potential barrier, i.e. $\varepsilon_0 < 0$, the ground state wave function becomes
Fig. 6. (Color online) Soft mode frequency derivative and the saturated frequency against the Rhodes-Wohlfarth ratio.

Fig. 7. (Color online) The relation between the inverse variance $\sigma$ and the characteristic temperature $T_1$. The effective mass is fixed to $M = 16$. The inverse variance is almost proportional to $T_1$, if the ground state is represented by a single peak wave-function (broken lines).

double peaks. Then the energy gap $T_1$ decreases with increasing $A$, and the variance $\sigma$ turns to increase a little. In Fig. 7, single- and double-peak cases are indicated by broken and solid lines, respectively. For a given $B$, the $\sigma - T_1$ relation gets a turning point when $\varepsilon_0$ crosses $\varepsilon_b$ as $A$ changes.

From the structural point of view, single and double peak wave-functions correspond to DP- and OD-type situations. Therefore, whether $\varepsilon_0$ is higher or lower than $\varepsilon_b$ is the criterion of DP- or OD-type transition, which was first demonstrated by Onodera in classical model. However, the DP-type transition changes continuously to the OD-type one in quantum model as described in the previous section.

It should be noted again that Fig. 7 is displayed for the effective mass $M = 16$. The
Table I. The energy gap $T_1$ and the variance $\sigma$ of the ground state wave-function. The values are obtained for $M = 16$ and $B = 0$ or 0.1, by solving Schrödinger equation (27) numerically. If $B$ is magnified by $\nu$, then $A$, $T_1$ and $\sigma$ should be multiplied by $\nu^{-3}$, $\nu^{-1}$ and $\nu$, respectively.

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characteristic temperature $T_1$ is 73 K for $\sigma = 0.02 \text{ Å}^2$. If the mass changes to 18, for example, the parameter $T_1$ becomes 65 K even if all other parameters are kept the same. Assuming that $T_0 = 36$ K, we can estimate the transition temperature as $T_c = 22$ K for $M = 18$, but the transition does not take place for $M = 16$ system. This shows that the mass isotope effect is critically important for the low temperature phase transition in some oxide crystals.

4. Summary and Discussion

In order to discuss the successive change between order-disorder(OD) and displacive(DP) type transitions, we have considered the quantum Ising model(QIM). Both typical cases correspond to unit and a large value of the Rhodes-Wohlfarth (RW) ratio. The thermodynamic quantities depend on two energy $T_1$ and $T_0$, irrespective to the potential parameters $A$ and $B$. As it was demonstrated previously, even in the OD case, the dynamic susceptibility may take a resonance character, if the damping of the soft mode is weak enough, because the quantum tunneling motion gives the resonance frequency. The OD or DP character is reflected definitely in the shape of the wave function, whether it has double peaks or a single peak. In the former case the ground state of the relevant mode is below the potential barrier and it is above in the latter case. This criterion is consistent with the classical picture predicted previously.

In this report, we considered the quartic potential (1), concretely. Since the quantum states are not sensitive to the detail of the potential function, the theoretical results are characterized by $T_1$, $T_0$ and $x_0$ as shown in section 2, irrespective to the details of the self-potential $V$. For instance, the similar results can be calculated for double-Morse potential(DMP). The similar $\sigma - T_1$ relation of Fig. 7 is also obtainable for DMP.

Once quantum states in the self-potential are solved, the free energy, entropy, specific heat
and susceptibility are obtained by quantum thermodynamics. If the phase transition takes at low enough temperature, only two quantum states are decisive for the thermodynamic quantities; this is a QIM limit. Another tractable method is to replace $V(x)$ by an effective harmonic potential; this is called here as quasi-harmonic model (QHM), where the effective frequency is determined by a self-consistent relation.\textsuperscript{17,18} Both QIM and QHM give the Barrett’s relation for the susceptibility. Therefore the quantum behaviors at low temperature are able to take into account in the simple QIM. The anomalous part of the specific heat of QHM is similar to that of QIM.\textsuperscript{19} If the phase transition takes place at low temperature, the anomalous part $\Delta c$ will be negligible compared to Debye’s specific heat stemmed from acoustic phonon contribution, and may be too small to detect experimentally. At high temperature the QHM satisfies the Dulong-Petit low as a matter of course; however, the QIM does not, because it ignores the contribution form the higher quantum states.

The proposed QIM has four adjustable parameters; the effective mass $m$, the potential parameters $A$ and $B$, and the interaction strength $g$. If the dielectric permittivity obeys the Barrett’s relation, then $T_1$ and $T_0$ will be determined by experimental fitting. From the structural data, the variance $\sigma$ will be specified by the Debye-Waller factor. Finally the effective mass should be consistent with the physical picture of the relevant soft mode. Thus four parameters will be given almost without ambiguity. Actually the parameters can be fitted by iterative processes. In this way, one of the authors (HM) described the isotope and pressure effects on the transition temperature in KH$_2$PO$_4$ by the use of QIM.\textsuperscript{8,20} In similar fashion, the isotope effect of the ferroelectric phase of SrTiO$_3$ will be discussed elsewhere.

Finally we comment on Samara’s criterion: the pressure coefficient $dT_c/dp$ is positive for the OD-type ferrodistortive transition.\textsuperscript{5} The rule holds if the double minima of the potential are well separated. The interactions may increase with applying the pressure, and the transition temperature will increase. But if the potential minimum separation is small, the decrease of atomic distance by pressure will decrease the potential barrier; therefore the tunneling energy $T_1$ will decrease. In such quantum case, $T_c$ will decrease with applying pressure ($dT_c/dp < 0$). This is considered to be realized in KDP and the related crystals under pressure.\textsuperscript{20}

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References