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Quasiharmonic model for ferroelectric transition in ^{18}O -isotope exchanged SrTiO_3

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Abstract

By extending the quasiharmonic approximation to a quantum particle within a local potential of the double Morse type, a model describing the ferroelectric phase transition in SrTiO_3 induced by oxygen isotope replacement is developed. The theory uses the variational principle method at finite temperature with emphasis on the quantum effect manifested in zero-point vibration. The ferroelectric–paraelectric transition in $\text{SrTi}({}^{16}\text{O}_{1-x}{}^{18}\text{O}_x)_3$ is analyzed and the x – T_c phase diagram is compared with the experimental one in order to confirm the qualitative validity of the model. The quantum mechanical effect and the evolution of the ferroelectricity in $\text{SrTi}({}^{16}\text{O}_{1-x}{}^{18}\text{O}_x)_3$ are also demonstrated theoretically and the soft mode of $\text{SrTi}({}^{16}\text{O}_{1-x}{}^{18}\text{O}_x)_3$ shows a perfect softening at the ferroelectric phase transition for $x \geq x_c \approx 0.32$. Finally, the study shows the importance of the mass of component ions and that isotope introduction has several effects even if the mass effect is predominant.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The typical quantum paraelectric behavior [1] is well known for pure SrTiO_3 with ^{16}O (abbreviated as STO16) below 40 K, because it keeps paraelectricity until $T = 0$ K by the quantum fluctuation, which seems to depress the occurrence of the ferroelectric order [2–6]. Also, ferroelectricity in SrTiO_3 doped with Ca^{2+} ions or chemically equivalent (polar impurities) [7], or induced by an electric field [8] or uniaxial stress [9], has attracted unrivaled interest in the low temperature properties of this compound. Thus, the average mass of the A-site ion was found to be a determining factor for the evolution of ferroelectricity in SrTiO_3 and perovskite titanate compounds [10], suggesting the importance of mass balance between A and TiO_3 , i.e. the last mode [11] in their evolution. It is the same for the Slater mode [12] (which is the vibrational relation of Ti and O_3). Moreover, previous studies have suggested that an admixture of the two modes plays a role in the evolution of ferroelectricity in PbTiO_3 and BaTiO_3 , by increasing the nonlinear response of the vibrating system to the external field, which contributes to a softening of the modes [13].

Recently, an unexpected finding of isotope induced ferroelectricity in SrTiO_3 by the exchange of ^{16}O in STO16 by its isotope ^{18}O with the transition temperature T_c around 24 K for a maximum isotope exchange, corresponding to a broad dielectricity maximum, has renewed the interest in the quantum fluctuation dominated regime, suggesting the stabilization of the ferroelectric phase [14]. Since then, many intensive experimental and theoretical studies have been carried out in order to understand well the phase transition mechanism and to elucidate the soft mode behavior related to the quantum fluctuations of $\text{SrTi}({}^{16}\text{O}_{1-x}{}^{18}\text{O}_x)_3$ (hereafter, abbreviated as STO18- x and the fully substituted one $\text{SrTi}^{18}\text{O}_3$ for $x = 1$ as STO18), their occurrence phenomenon, the crystal structure of the ferroelectric phase and so on. Behind the giant anomalous dielectricity associated with the appearance of the peak of the static dielectric constant as the concentration of the ^{18}O ions exceeds the critical concentration $x_c = 0.33$ [14–17], the reproduction of the observed x – T phase diagram, based on the ‘multicomponent vector model’ of Schneider *et al* if the ‘critical quantum displacive limit’ is assumed to be realized at $x = x_c$, has been performed and analyzed [18, 19]. On the other hand, microscopic observations of the soft TO phonon

have recently been carried out on STO18- x by using neutron inelastic scattering technique, showing essential discrepancies with the expected characteristics of the TO phonon frequency $\omega_0(T)$ [20].

Also, some observations by inelastic neutron scattering have reported that the transverse optic E_u soft mode in STO18 softens [21], but does not condense at T_c , independently of the concentration of ^{18}O within the resolution of the neutron scattering experiment and the same as in STO16 practically [20, 22]. Thus, the softening of the polar TO soft mode [23, 24] would not be the only mechanism driving the ferroelectric transition in STO18 as assumed so far. Some other mechanism must be present too. Accordingly, a nondisplacive phase transition mechanism has been suggested in STO18 [22, 25, 26]. But recently, Takesada *et al* have reported a successful observation of the temperature dependence of the ferroelectric soft mode E_u in STO18 [27], not previously revealed by inelastic scattering [20, 22], in the extremely low frequency region, using a high resolution technique and an ultrastable optical cryostat. They have found perfect softening at the ferroelectric phase transition temperature T_c in STO18 for the first time, and the mechanism of the ferroelectric phase transition is concluded to be an ideal displacive type associated to the Slater-type polar soft mode.

Amongst other things, in spite of all these studies, the nature of the ferroelectric phase transition induced by the exchange of oxygen ^{16}O by its isotope ^{18}O and the low temperature ferroelectric state thus obtained still remains controversial. This is manifested in both theoretical and experimental works. For example, while some authors predict a displacive soft mode mechanism of the phase transition into the conventional ferroelectric state [28, 29], Zhang *et al* suggested the order-disorder nature of this phase transition [25], whereas Yamada *et al* interpreted it in terms of a transition into a three-state quantum Ising model [22]. In addition, while recently Raman scattering [30], Brillouin scattering [31], and birefringence [32] measurements etc have further confirmed the ferroelectric phase transition in STO18- x ($x \geq 0.33$), the smeared dielectric peak around T_c , the relaxation of polarization with time below T_c , the large amplitude dependence of the real part and the large bias dependence of the dielectric constant ϵ' suggest that STO18 is far from being a typical ferroelectric [16, 17, 33].

Accordingly, the origin of ferroelectricity in perovskite oxides has not been completely elucidated and, in particular, just a little is known about the quantum effect of ferroelectricity. Although different approaches have been taken to explain oxygen isotope induced ferroelectricity in SrTiO_3 , the critical temperature T_c has been usually found by dielectric constants, pyroelectricity, DE -loop measurements and so on [14, 15, 34], which depend strongly on the amplitude of the applied ac field (test signal). However, although it characterizes only the $T \leq 40$ K, indicating that the enhancement by the ac test signal is closely related to the low temperature polar state, very small shifts in peak temperature were observed as a function of frequency [16].

For the present study, in order to overcome the shortcomings and to model well the dynamic and static

properties of soft mode systems, the double Morse potential is considered [35]. Then, besides describing correctly the soft mode temperature dependence, the global lattice potential has been shown to be extremely sensitive to changes, as in the ionic masses [36]. In this work, employing the quasiharmonic approximation proposed by Salje *et al* [37], we give an analytical description of the structural phase transitions in a nonlinear simple microscopic model in which the substrate potential is a deformable double-well potential of double Morse type [36]. The interparticle potential is described by an appropriate harmonic interaction potential that reflects the change in the electronic distribution of the sites. We develop a mean-field treatment for this model to analyze structural phase transitions and examine how the disparities in the single site potential are manifested in the thermodynamics and response of the systems to external influences. The particular one developed here is a modification and extension of a theory originally introduced by Thomas [37, 38], to analyze second-order and tricritical transitions.

The organization of the paper is as follows. In section 2, we present the model formulation. The mean-field theory is used to derive the analytical expression of the free energy, and the mean-field equations are obtained and analyzed. In this connection, the origin of the thermodynamic saturation is presented, where the quantum saturation and fluctuation of order parameter have been recognized and have an important influence on the behavior of the systems. Also, the influence of the quantum effect is analyzed. In section 3, using a plausible assumption that the potential splitting d and the interaction strength ν are ^{18}O -exchange rate x dependent, the model and theory are applied to the ^{18}O -exchanged SrTiO_3 (STO18- x). The corresponding calculated x - T_c phase diagram has been investigated and analyzed, and the paraelectric phase stabilized by quantum fluctuations at low temperatures has been reinvestigated. According to this study, the oxygen isotope exchange of ^{16}O for ^{18}O affects mainly lattice vibration. The numerically calculated values of the critical fraction (exchange rate) x_c of the isotope corresponding to $T_c = 0$ K and the transition temperature for the maximum isotope exchange (STO18) are given. Calculations are also performed in order to give the temperature dependence of the susceptibility, the inverse susceptibility and the specific heat for the oxygen isotope effect. It is shown that the perfect softening phenomenon of the soft mode takes place at the ferroelectric phase transition temperature through the inverse susceptibility for $x \geq x_c$ and that the quantum fluctuations govern the low temperature regime. We devote section 4 to a discussion of results and a conclusion.

2. Formulation and theory

In a crystal consisting of N lattice sites, let Q_l be a local coordinate which describes the phase transition in the l th unit cell; then, the Hamiltonian to describe the quantum system is given by [39, 40]

$$H = \sum_l \left\{ \frac{1}{2m} p_l^2 + V(Q_l) \right\} + \frac{1}{4} \sum_{l,l'} \nu_{ll'} (Q_l - Q_{l'})^2, \quad (1)$$

where m is the effective mass associated with the local coordinates Q_l , p_l are the conjugate momenta, and $v_{ll'}$ are the interaction constants. Let us assume that the interaction $v_{ll'}$ has its maximum value $v = v_{q_0} > 0$, and $q_0 = 0$. Here, the double Morse type potential, which is formed by superposing the two Morse potentials ‘back to back’, is adopted as a local potential of the unit cell, since the Morse potential is widely accepted to be successful for a covalent-bonding atom and this characteristic is well known for various materials:

$$V(Q_l) = 2D\{\exp(-2ad) \cosh(2aQ_l) - 2 \exp(-ad) \cosh(aQ_l)\}, \quad (2)$$

where D , a , and d are the parameters proper to the initial Morse function. The splitting distance between the two potentials is given by $2d$. This local potential, which has been considered frequently, has an important property: all the characteristic points of the potential vary at the same time. Then, as d increases, the barrier height of the double-well continuously increases and the minima of the potential also vary continuously with d . Moreover, the barrier between the two wells is much lower when the two (neighboring) minima approach each other. This is an essential ingredient, which allows an easier migration of the particle [41].

According to the quasiharmonic approximation, we adopt the harmonic oscillator as a trial Hamiltonian H^{tr} :

$$H^{\text{tr}} = \sum_l \left[\frac{1}{2m} p_l^2 + \frac{1}{2} m \Omega^2 (Q_l - \langle Q_l \rangle)^2 \right], \quad (3)$$

where the bracket $\langle \dots \rangle$ is the thermal average. The two variational parameters per site: an effective single site frequency Ω (same at each site), and the spontaneous displacement $Q = \langle Q_l \rangle$ equivalent to the order parameter of the ferroelectric transition, have to be determined by minimizing the free energy of the system with respect to these parameters. The density matrix is defined by using H^{tr} . The variational relation for the free energy of the model system is defined in a mean-field approximation as

$$F = \langle H \rangle - \langle H^{\text{tr}} \rangle - k_B T \ln [\text{Tr} \{ \exp(-H^{\text{tr}}/k_B T) \}]. \quad (4)$$

In this Einstein quasiharmonic approximation the mean-field description of the statistical mechanics of the system gives the variational free energy

$$F = N \left\{ k_B T \ln \left[2 \sinh \left(\frac{\hbar \Omega}{2k_B T} \right) \right] - \frac{1}{4} \hbar \Omega \coth \left(\frac{\hbar \Omega}{2k_B T} \right) \right\} + N \left\{ 2D \left[\exp(-2ad) \exp(2a^2 \sigma) \cosh(2aQ) - 2 \exp(-ad) \exp \left(\frac{a^2 \sigma}{2} \right) \cosh(aQ) \right] + \frac{1}{2} v \sigma \right\}, \quad (5)$$

and the self-consistent solutions of the following two variational mean-field equations:

$$\left\{ 2 \exp(-ad) \exp(2a^2 \sigma) \cosh(aQ) - \exp \left(\frac{a^2 \sigma}{2} \right) \right\} \sinh(aQ) = 0, \quad (6)$$

$$m \Omega^2 = v + 4Da^2 \left\{ 2 \exp(-2ad) \exp(2a^2 \sigma) \cosh(2aQ) - \exp(-ad) \exp \left(\frac{a^2 \sigma}{2} \right) \cosh(aQ) \right\}, \quad (7)$$

where $v = \sum_{ll'} v_{ll'}$. The variance σ is the mean-square vibrational amplitude of the coordinate, which is related to the temperature dependent Einstein frequency Ω by the following quantum mechanical fluctuation theorem:

$$\sigma = \langle (\delta Q_l)^2 \rangle = \frac{\hbar}{2m\Omega} \coth \left(\frac{\hbar \Omega}{2k_B T} \right). \quad (8)$$

Taking into account the variance σ_c at the stability-limit points (critical points) characterized by vanishing order parameter ($Q \rightarrow 0$ from equation (6)), the phase transition occurs at T_c when

$$\sigma_c = \frac{k_B \theta_s}{v} \coth \left(\frac{\theta_s}{T_c} \right) = \frac{2}{3a^2} (ad - \ln(2)), \quad (9)$$

if the transition is second-order one. In this expression, θ_s is the saturation temperature related to the ground state energy $E_0 = k_B \theta_s$ of the quantum oscillator associated with our quantum model lattice sites system [42], with energy level $E_n = \hbar \Omega_0 (1/2 + \langle n \rangle)$. Here, $\Omega_0 = \sqrt{v/m}$ is the bare soft mode frequency and $\langle n \rangle = 1/(e^{\hbar \Omega_0/k_B T} - 1)$, is the average number of energy quanta excited above the ground state at temperature T . Thus, $\hbar \Omega_0$ is the zero-point energy, and Ω_0 also represents the displacive limit Einstein frequency.

In equation (9), the transition is characterized by two temperatures, θ_s and T_c . The existence of a finite θ_s is a manifestation of the third law of thermodynamics, which requires that entropy changes and hence order parameter changes disappear at absolute zero temperature. However, determinations of θ_s , which presents the quantum effect dependence on the atomic mass, may also yield useful insights into the behavior of phase transitions, as it is the temperature below which the temperature dependence of the order parameter is dominated by the quantum mechanical effect [37, 43, 44]. It is the temperature of crossover between classical and quantum mechanical behavior [37, 45]. Then, if T_c and θ_s are known for the given self-potential system, the interaction parameter v can be estimated from equation (9).

If we apply an external field E to our model, which has the effect of adding a term $-EQ$ to the free-energy expression (5), the minimization of equation (5) yields the equation

$$E = 4Da \exp(-ad) \sinh(aQ) \times \left\{ 2 \exp(-ad) \exp(2a^2 \sigma) \cosh(aQ) - \exp \left(\frac{a^2 \sigma}{2} \right) \right\}, \quad (10)$$

instead of (6). Differentiating both sides of equation (10) with respect to E and setting $Q = 0$ ($T > T_c$), we can estimate the static susceptibility of the system as follows:

$$\chi^{-1} = 4Da^2 \exp(-ad) \times \left\{ 2 \exp(-ad) \exp(2a^2 \sigma) - \exp \left(\frac{a^2 \sigma}{2} \right) \right\}, \quad (11)$$

which can be reduced to

$$\chi = \frac{\lambda^2}{\hbar^2\Omega^2 - \lambda^2\nu} \quad (12)$$

where $\lambda = \hbar/\sqrt{m}$ represents a measure of the zero-point fluctuations. Thus, we can properly identify the quantity $\hbar^2\Omega^2 - \lambda^2\nu \equiv \omega_0^2$ with the soft mode if the divergence of the static susceptibility is to be associated with the long-range wavelength phonon becoming soft [46]. From equation (9), the corresponding transition temperature is the temperature of continuously vanishing order parameter. Then, the system changes continuously from the paraelectric phase ($Q = 0$) to the ferroelectric phase ($Q \neq 0$) when its temperature decreases from above T_c to below. Therefore, the second-order transition temperature, which corresponds to the divergence of the static susceptibility, is

$$T_c = \theta_s / \coth^{-1} \left(\frac{T_c^{(\theta_s=0)}}{\theta_s} \right), \quad (13)$$

where $T_c^{(\theta_s=0)}$ is the classical transition temperature defined by $T_c^{(\theta_s=0)} = \nu\sigma_c/k_B = T_0$.

This transition temperature is valid for all self-consistent solutions. An important point is that, unlike T_c , it seems that θ_s is not greatly altered by chemical doping, or the application of external fields [47]. In order to improve well our theoretical understanding of the mechanism of phase transitions, and investigate the quantum effects, the following parameters are introduced for convenience:

$$\begin{aligned} \eta &= \hbar/(2m\Omega_0\sigma_c), \\ T_1 &= 2\eta T_0 = 2\theta_s. \end{aligned} \quad (14)$$

Here, dimensionless parameter η is a measure of the quantum influence (quantum effect magnitude) and T_1 is another characteristic temperature. It is important to remark here that η originates not in the tunneling motion, but in the quantum vibration (such as zero-point energy) and $\eta = 0$ yields the classical result [36, 41]. In the fully dispersive limit, Ω_0 may be visualized as a characteristic frequency which is the Einstein mode frequency for oscillations with the intersite interactions, in the coupling to Einstein oscillators as dynamical dominant excitations. Then, a reduction of the transition temperature due to quantum influences leads to the following result:

$$T_c = \frac{2\nu\sigma_c}{k_B}\eta / \ln \frac{1+\eta}{1-\eta} = 2T_0\eta / \ln \frac{1+\eta}{1-\eta}. \quad (15)$$

Thus, equation (15) shows the influence of the quantum mechanical effects on the behavior of the system, and the effect of increasing the involved mass (mass dependence) on transition temperature through the quantum effect magnitude η .

3. Isotope-effect-induced transition in strontium titanate perovskite

In this section, by extending the quasi-harmonic approximation using a mean-field treatment for the above model, we apply

it to the study of the induced ferroelectric phase transition in STO18- x in order to explain the experimental result that the incipient quantum paraelectric STO16 can be driven to a ferroelectric state by replacing ^{16}O by its isotope ^{18}O [14]. We will assume here that the potential splitting d and the interaction strength ν increase with x . This plausible assumption takes into account the fact that from the viewpoint of the crystal stability the induced ferroelectricity of SrTiO₃ originates from the crystal status of this material [14], which may increase the nonlinear response of the vibrating system to the external field, contributing to a softening of the modes [21–24, 48–50]. Also, the introduction of isotopes has several effects (mass effect, volume effect and so on), with usually the mass effect predominating as in the case of STO18- x [10, 11, 14, 17, 34], and the properties of these crystals can be expected to be strongly x dependent. Thus, in order to explain the evolution of the ferroelectricity in ^{18}O -isotope exchanged SrTiO₃, it is necessary to consider how the parameters will be affected by the oxygen isotope replacement. According to all this and to the probable exchange rate x dependence of some model parameters of STO18- x , and in order to reproduce experimental results, we adopt the following x dependence for d and ν :

$$d = 0.24 + 0.046x \quad \text{and} \quad \nu = 0.13 + 0.003x, \quad (16)$$

where d and ν are in unit of Å and eV Å⁻².

However, the mass change of constituent ions causes a change in the vibrational frequencies of relevant ion pairs, and for the SrTiO₃ model with the O-atom displacements the potential energy must be expressed in terms of normal coordinates with the effective mass equivalent to the reduced mass of the relevant vibrating system, including ^{16}O and ^{18}O , respectively. Thus, the effective mass of the SrTiO₃ system is estimated as about 45.78 amu for STO16 and 47.11 amu for STO18. This represents the reduced mass of the corresponding vibrating system constituted of the Sr ion of mass $M_{\text{Sr}} = 87.62$ amu and the TiO₃ cluster of mass $M_{\text{TiO}_3} = 95.9$ amu for the STO16 and 101.9 amu for the STO18, respectively. Then, according to quantum mechanics, if the force constant is not changed via the isotope replacement of ^{16}O with ^{18}O , the zero-point energy (quantum fluctuation) is proportional to the inverse square root $1/m^{1/2}$. Accordingly, on the replacement of ^{16}O with ^{18}O , the reduced mass increases and $(m_{18}/m_{16})^{1/2}$ is calculated to be ~ 1.029 , which corresponds to the frequency change in the Slater mode [11, 15], due to oxygen isotope exchange. In addition, the exchange rate x dependence of the saturation temperature is given by

$$\theta_s = \theta_{s_0} \left(1 + \frac{0.003x}{0.13} \right)^{1/2} \left(1 + \frac{1.33x}{45.78} \right)^{-1/2} \quad (17)$$

where θ_{s_0} is the saturation temperature of the STO16 crystal.

The other model parameters are selected to be $a = 3.9 \text{ \AA}^{-1}$ and $D = 0.01 \text{ eV}$. Using the model, we estimate the saturation temperature and the Curie (classical transition) temperature of STO16 as $\theta_{s_0} \approx 20 \text{ K}$ and $T_0 \approx 16 \text{ K}$. These values are in good agreement with those obtained by Hayward *et al* [45], using the quantum Landau model and

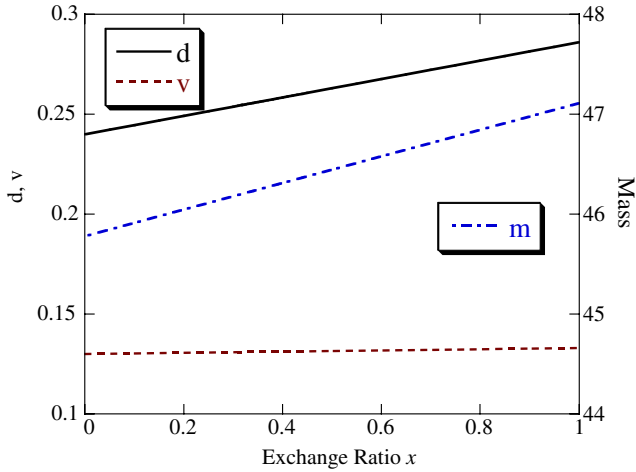


Figure 1. Adopted parameters d , v and m . The exchange ratio dependences are displayed. The interaction v is almost constant; however, the splitting distance d increases a little with increasing x .

Barret equation for the dielectric susceptibility to determine the best fit parameters to the paraelectric–ferroelectric phase transition in SrTiO₃ as a function of temperature and [100] stress, determined experimentally by Fujii *et al* [51], to fit the temperature dependence of the reciprocal of the dielectric susceptibility of SrTiO₃ according to measurements of Müller and Burkard [2], or to fit the phase diagram for the ferroelectric phase in SrTiO₃ as a function of isotope exchange using the peak in the dielectric susceptibility to measure transition temperature, experimentally obtained for different oxygen-exchanged samples by Itoh and Wang [15, 34]. Moreover, θ_{s0} is also similar to that obtained by Dec and Kleemann [52], and agrees with the direct inspection of the temperature dependence of the inverse dielectric constant ϵ^{-1} data of SrTiO₃ due to the fact that the quantum mechanical zero point is reached at $10\text{ K} \approx \theta_s/2$, with essentially temperature independent dielectric susceptibility below it [53].

From the assumption, the exchange ratio dependences of potential splitting distance d , interaction parameter v , and effective mass m are presented in figure 1. It is obvious that interaction parameter v is almost constant with x , while the splitting parameter d monotonically increases a little with increasing x . From the calculation, we can determine the x dependence of transition temperature T_c , characteristic temperature T_0 , and saturation temperature θ_s . The results are presented in figure 2. According to this, it is possible to recognize that the effect of quantum fluctuations characterizes low- T_c systems. Here also, it is obvious that the saturation temperature θ_s is almost constant with x , while the characteristic temperature T_0 monotonically increases with increasing x . This clarifies the mechanism of the quantum phase transition of STO18- x as the ¹⁸O exchange suppresses the quantum fluctuation through the decrease of the quantum effect magnitude η to induce the ferroelectric interaction (ferroelectricity).

The calculated composition dependence of transition temperature T_c due to the oxygen isotope exchange, as shown in figure 2, confirms the existence of the critical

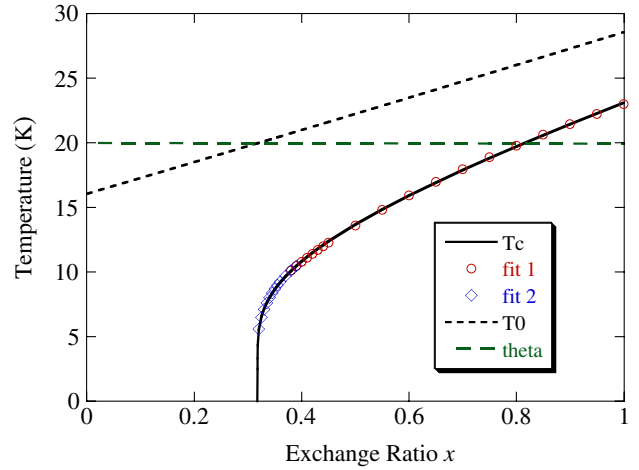


Figure 2. The x dependences of transition temperature T_c , classical transition temperature T_0 and saturation temperature θ_s . The transition temperature can be approximated by a power law: fit-1 shows $T_c \sim (x - x_c)^{0.5}$ in a range of $0.4 < x < 1$, while fit-2 shows $T_c \sim (x - x_c)^{0.25}$ in a range of $x_c < x < 0.4$.

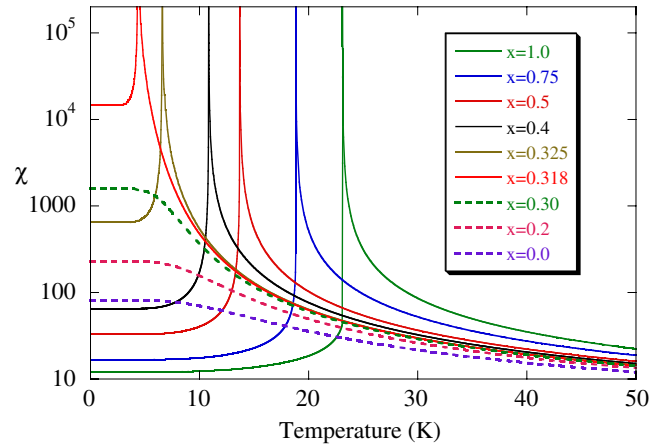


Figure 3. Temperature dependence of static susceptibility χ for STO18- x for several substituted fractions x of the isotope ¹⁸O. The exchange ratio x is selected as 0, 0.2, 0.3, 0.318, 0.325, 0.4, 0.5, 0.75, and 1.

concentration x_c (critical point), above which ferroelectricity evolves [15]. This quantum critical point marks the beginning of the novel quantum phase transition nature [17], and might characterize the domination of the ferroelectric phase behavior and the occurrence of ferroelectric order. From figure 2, the ferroelectricity is induced at the transition temperature $T_c \approx 23.1\text{ K}$ for a maximum isotope exchange. Hence, we estimate the critical value $x_c \approx 0.32$. The phase transition temperature T_c shifts to a high temperature with x in a nonlinear manner as seen in figure 2, and a relation $T_c \sim (x - x_c)^{1/2}$ holds in a wide range of x , which agrees with the value obtained by fitting the experimental data to the quantum ferroelectric relation [15, 17, 32].

In addition, calculations are performed to give the temperature dependence of the static susceptibility and the inverse static susceptibility. Figure 3 presents the temperature dependence of the static susceptibility χ for different values

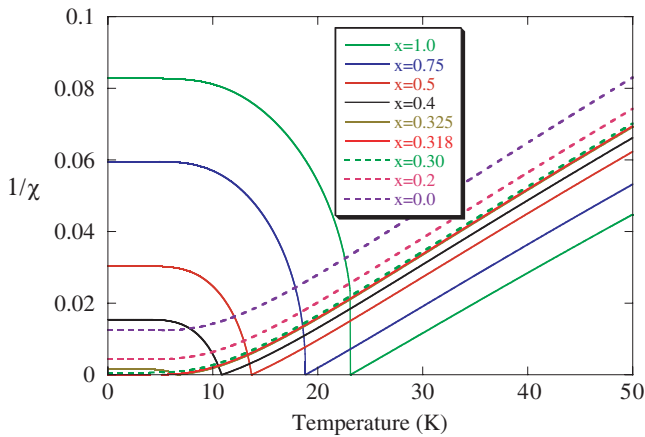


Figure 4. Temperature dependence of the inverse of static susceptibility χ^{-1} for STO18- x for several ^{18}O -isotope exchange rates x selected as 0, 0.2, 0.3, 0.318, 0.325, 0.4, 0.5, 0.75, and 1.

of the ^{18}O -exchange rate. The susceptibility χ for STO16 increases with decreasing T monotonically, and becomes almost temperature independent at low temperatures ($T < 5 \text{ K} < \theta_s/2$), showing the typical quantum paraelectricity. For $x < x_c$, the transition does not take place and the susceptibility has a rounded and finite maximum at low temperature even near 0 K, which increases with x . The phase transition characterized by the divergence of the static susceptibility [1, 2, 54], takes place for the composite rate $x \geq 0.32$, confirming their probable ferroelectricity, and as x increases the divergent behavior shifts to higher temperature, increasing the transition temperature T_c , which is always finite.

From the inverse susceptibility χ^{-1} curves, figure 4, the ferroelectric phase also shows stabilization in the low temperature region against the quantum fluctuations, and the larger is T_c , the higher is the value at $T = 0 \text{ K}$. The vanishing of χ^{-1} at T_c , and the precursor decrease of its value on approaching T_c from above, justify the term ‘soft mode’ used to qualify the normal mode associated with the order parameter of the transition [14, 21, 22, 27, 45]. The temperature dependence of the inverse static susceptibility confirms that of the soft mode (frequency), indicating clearly the perfect soft mode type ferroelectric phase transition (continuously complete vanishing at T_c of the soft mode frequency of the ferroelectric soft mode) for $x \geq x_c$.

On the other hand, for $x \geq x_c$, above T_c the soft mode through χ^{-1} follows the Curie–Weiss law except around the transition temperature if it is finite, while below the transition the soft mode is finite but does not follow a Curie–Weiss law. In contrast, for $x < x_c$, the soft mode stops softening and becomes also temperature independent in the low temperature region near 0 K. But as x approaches a critical value x_c from below, the soft mode shows a strongly rounded softening and a weakened freezing tendency, suggesting the occurrence of a ferroelectric state in the low temperature region. Also from figure 4, as the rate x increases, the influence of quantum effect on inverse susceptibility decreases.

Figure 5 shows the inverse susceptibility at $T = 0 \text{ K}$, $\chi^{-1}(T = 0)$, plotted as a function of the ^{18}O -exchange rate x .

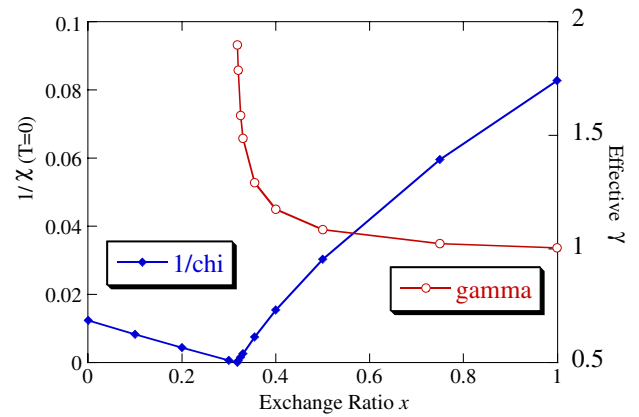


Figure 5. The inverse zero temperature static susceptibility $\chi^{-1}(T = 0)$ and the effective exponent for χ above the transition temperature of STO18- x .

As clearly shown, when $x < x_c$, $\chi^{-1}(T = 0)$ linearly decreases to zero as x increases, while for $x \geq x_c$, $\chi^{-1}(T = 0)$ increases strongly and monotonically, but not in a perfect linear manner, with x . This result clarifies the typical quantum paraelectric behavior for $x < x_c$, and quantum behavior of the ferroelectric phase transition mechanism for $x \geq x_c$, with evidence of suppression of the quantum effect as x increases.

Also presented in figure 5 is the x dependence of the effective exponent γ for static susceptibility χ for $x \geq x_c$, obtained by fitting the inverse susceptibility χ^{-1} to the relation of $(T - T_c)^\gamma/C$ by least-squared calculations in a range of $T_c < T < T_m$, where $T_c + 2 \text{ K} \leq T_m \leq T_c + 10 \text{ K}$. At the full ^{18}O -exchange rate limit $x = 1$, $\gamma = 1$ in good agreement with the classical Landau-type behavior, confirming however the important weakening of the quantum effect in the fully exchanged limit. As x decreases from the maximum value of unity, the effective exponent γ increases slowly. But, while quantum critical point x_c is approached from the high x value, γ increases strongly and shows a maximum around 1.90 at x_c . This effective exponent can be compared to the critical exponent, characterizing a critical behavior of the susceptibility, obtained from quantum ferroelectric relation whose theoretical value for quantum ferroelectric phase transition at x_c is 2 (ideal value for quantum ferroelectrics) [18, 19], and from experimental results by fitting dielectric constant data with a theoretical generalized quantum law [15, 17].

In order to understand well the origin and conditions of appearance of the phase transition, and thus of the ferroelectricity, we present in figure 6 the temperature dependence of specific heat for different ^{18}O -isotope exchange rates x obtained by numerical calculation. We can see that for $x < x_c$ no discrepancy has been observed on the specific heat, confirming the overall quantum paraelectric behavior, while for $x \geq x_c$, upon further increasing x , the specific heat shows a peak at low temperatures (low- T_c ferroelectric phase transition). These peaks of the specific heat curves shift to higher temperature as x increases. According to all this, the specific heat values are strongly suppressed in STO18- x due to the quantum effect.

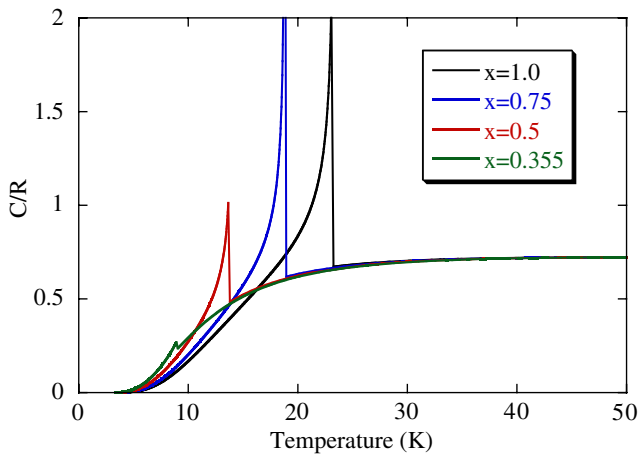


Figure 6. Specific heat as a function of temperature for STO18- x and for four different exchange rate values between x_c and 1.

4. Discussion and conclusion

In this study we have shown the important influences of the quantum fluctuations on the phase transition, especially at low temperatures. A quantum particle within a local potential of the double Morse type is considered by a mean-field interaction under the quasiharmonic approximation. Obviously, the model analytically takes into account the possibility to shift the potential minima and hump, in order to reproduce the richness of the physics of molecular solids whose backbones are often so flexible that chemical bonds must continuously relax or contract to avoid bond breaking. Furthermore, our simple model is successful qualitatively to describe a structural ferroelectric phase transition and phase diagram induced by or due to appropriate applying external fields. Also the quantum effects are important if the transition takes place at low temperature. Moreover, depending on the model parameters, the ferroelectric localized distortions involving also heavy atoms do exhibit double wells, whose ground state lies below the barrier, thus allowing tunneling. Through our renormalization process (quasiharmonic approximation), due to the zero-point vibration of the particle, the effective single-site frequency Ω is nothing but the so-called ‘soft mode’ frequency characterizing the displacive ferroelectricity. The quantum mechanical temperature θ_s is also related directly to the energy scale of the transition mechanism [37, 54]. Accordingly, the softening phenomenon of the soft mode is one important mechanism for driving the ferroelectric transition in the perovskite oxides.

The pseudo-Barrett equation obtained confirms the important role of the Barrett equation in the investigation of theory of the ferroelectric phase transition, which fitted well some experimental data. The mechanism of phase transition here is attributed to the dominance of the softening of optic phonon branches so that the Einstein mode approximation appears to be appropriate for ferroelectric and most improper ferroelastic phase transitions [40, 47].

A number of quantum paraelectric systems have been identified, including KTaO_3 [55]. However, SrTiO_3 is

the first system in which quantum paraelectricity was identified and one of the best-studied materials in the current literature, which induces ferroelectricity by applying external fields [15, 32–34, 49, 51]. In order to explain the evolution of the ferroelectricity in STO18- x , it is necessary to consider how the parameters will be affected by the oxygen isotope replacement. With an appropriate choice of oxygen-exchange rate x dependence of model parameters in STO18- x , we try to explain the quantum paraelectric–ferroelectric transition induced by the change of the oxygen effective mass. For quantum paraelectric–ferroelectric transition through the chemical substitution, we have paid attention to the inclusion of zero-point energy and a critical concentration was found to exist in the vicinity of $x = 0.32$ for STO18- x , which is in good agreement with the experimental value of 0.33 obtained by Itoh and Wang [15] and other experimental measurements [30–32]. At the ‘quantum displacive limit’ defined by the set of coupling parameters for which the critical temperature T_c of the phase transition is equal to zero, the quantum mechanical effect becomes extremely important. All these results support the quantum mechanical ‘vector model’ proposed by Schneider *et al* [18, 19]. The change in the vibrational system due to the oxygen isotope is then comparable to the zero-point vibration in quantum paraelectrics.

From our assumption, the interaction strength ν for STO18- x increases from 0.13 to 0.133 eV \AA^{-2} for STO16 and STO18 respectively, which might support the absence of change in their lattice parameters [14, 34]. However, the potential splitting parameter d increases from 0.24 for STO16 to 0.286 \AA for STO18, which might characterize the volume effect. Taking into account the mass effect through the oxygen isotope substitution, we can conclude that the oxygen isotope exchange effect on the evolution of ferroelectricity in SrTiO_3 depends on both volume and mass even if it is predominated by the mass effect [17, 34].

Amongst other things, although the crystal structure of the SrTiO_3 ferroelectric phase has not been determined and the symmetry is clearly not the same as that of the ferroelastic phase $I4/mcm$ corresponding to paraelectric one, this study bears theoretical discussion to clarify the phase transition mechanism and reports that the paraelectric–ferroelectric phase transition in STO18- x is second order, as already concluded by Dec *et al* from an absence of thermal hysteresis [56]. This result also agrees with experimental results of Itoh *et al*, who have reported that the ferroelectric transition is expected to be of first or second order [49, 57].

The calculated phase diagram as a function of ^{18}O -exchange rate shows that the STO18- x with $x \geq 0.32$ are quantum ferroelectrics, in good agreement with the experimental data [14, 15, 23, 30–32]. On the other hand, knowing that STO16 is a quantum paraelectric, by increasing x (‘effective mass’) through ^{18}O -isotope exchange, the soft mode shifts to smaller frequencies and the system is closer to a lattice instability. The soft mode shifts have a parallel behavior here, as shown by inverse susceptibility in figure 4. The displacive type phase transition was recognized in SrTiO_3 and the crucial role played by the oxygen atoms in the softening mechanism of the ferroelectric mode in STO18- x , through exchange rate

concentration x , was confirmed theoretically [14, 15, 27]. Thus, the inclusion of the zero-point energy in the framework of the quasiharmonic approximation describes well the detailed evolution of the ferroelectricity and the phase transition in STO18- x systems.

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