Softening behavior of the ferroelectric A_1(TO) phonon near the Curie temperature

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(Received 7 August 2009; published 22 October 2009)

It is well known that the A_1(TO) phonon with its eigenvector parallel to the unique c axis of the 4mm symmetry is primarily responsible for the manifestation of displacive ferroelectricity in ABO_3-type perovskites. We have theoretically examined the softening behavior of this A_1(TO) phonon, particularly paying attention to its mode frequency around the Curie temperature (T_o). Our unusual approach is that we examine the microscopic Landau potential in terms of the displacement from the double-well minimum, rather than the displacement from the symmetry point. Adopting $PbTiO_3$ as an ideal underdamped phonon system to test our formalisms, we have shown that the mode frequency of the "soft" A_1(TO) phonon does not converge to zero even at the phase transition temperature, T_c, and that the computed mode frequency accurately reproduces the experimentally observed frequency over a wide range of temperature below T_c (763 K).

DOI: 10.1103/PhysRevB.80.132105 PACS number(s): 77.84.−s, 77.80.Bh, 63.70.+h, 63.20.Ry

It is now well established that a displacive first-order phase transition involving polar ions is driven by a softening of relevant phonons.[1–3] Phonon softening and associated lattice dynamics in ABO_3-type ferroelectric perovskites have been investigated extensively[1–15] and are still important subjects in displacive phase transitions.[14–20] The softening of transverse optic (TO) phonons was predicted for the first time by Fröhlich who combined the Lyddane-Sachs-Teller (LST) relation with the Curie-Weiss law.[21] According to this prediction, the mode frequency of the TO phonon related to a certain displacive transition becomes zero at the Curie temperature (T_o) where the static dielectric permittivity diverges to an infinite value. Followed by the Fröhlich's suggestion, several different theoretical models were proposed to account for the softening of the TO phonon near the Curie temperature. These include: (i) a simple statistical mechanical theory of Lines,[3] which is based on the effective model Hamiltonian, (ii) a simplified conceptual lattice dynamic theory of Barker,[22] and (iii) a lattice dynamical approach based on a polarizable-anion core shell.[23,24]

The most comprehensive and quantitative theoretical treatment of the phonon softening is based on the core-shell model proposed by Cochran. According to the Cochran's theory,[23] the frequency of the "soft" TO phonon converges to zero ($\omega_o(\mathrm{TO}) \rightarrow 0$) at T_o if the short-range interaction force is compensated by the long-range Coulomb force, leading to an instability of the crystal lattice with respect to the soft TO phonon. The compensation of these two distinct types of forces occurs only if the electronic polarizability is sufficiently high to enhance the dipolar force.[23] However, such an instability is not expected in alkali halides as, in these materials, the short-range force is always almost two times stronger than the Coulomb interaction.

Now, our question is: in the case of a typical displacive ferroelectric such as $PbTiO_3$, is the cancellation perfect? In other words, is the long-range Coulomb interaction strong enough to compensate the short-range force? To obtain a clue to this question, we have considered the microscopic Landau potential, $\Phi(q)$, for a first-order displacive ferroelectric phase transition, namely,[7,25]

$$\Phi(q) = \frac{1}{2}\chi q^2 + \frac{1}{4}\xi q^4 + \frac{1}{6}\varsigma q^6, \tag{1}$$

where χ is the dielectric stiffness (inverse static susceptibility) in q representations, and ξ and ς are high-order dielectric stiffness coefficients. $\chi \equiv (T-T_o)/C_E < 0$ below T_o, where C_E is the microscopic Curie constant,[7] and $\xi < 0$ and $\varsigma > 0$ for a first-order displacive phase transition.[25] Equation (1) is schematically plotted in Fig. 1 at various temperatures. It can be realized from Fig. 1 that because of a finite curvature at the minimum of the double-well potential, the vibration frequency, $\omega_o(T)$, does not strictly converge to zero at T_o or even at T_c.

In the case of ABO_3-type ferroelectric perovskites such as $PbTiO_3$ (PTO) and $BaTiO_3$ (BTO), two distinct transverse optic modes, A_1(TO) and E(TO), are known to exhibit phonon softening near the Curie temperature, T_o.[5,6,10–13] Based on rigid-ion lattice dynamic calculations,[14,26] we have qualitatively sketched the eigenvectors of the lowest-frequency A_1(TO) and E(TO) modes in Fig. 2 [termed A_1(1TO) and E(1TO), respectively]. Among these two 'soft' mode phonons, the A_1(1TO) phonon with its eigenvector parallel to the unique c axis of the tetragonal 4mm symmetry is primarily responsible for the manifestation of ferroelectricity below the m3m-4mm paraelectric-ferroelectric transition point (T_c).[11,13]

In the present study, we will quantitatively examine the softening behavior of this ferroelectric A_1(1TO) phonon, particularly paying attention to its mode frequency in the vicinity of T_o. We will show that the mode frequency of the A_1(1TO) phonon does not converge to zero at T_o (or even at T_c) provided that the Landau expansion based on the symmetry argument remains valid for a ABO_3-type perovskite. In the present study, we adopt PTO as an ideal system to test our theoretical formalisms because unlike BTO, it is known to be the best example of displacive ferroelectrics without exhibiting any overdamping (line broadening) of the resonance-type soft phonon.[4,5,7,13]

Our approach in the present study is that we have recon-

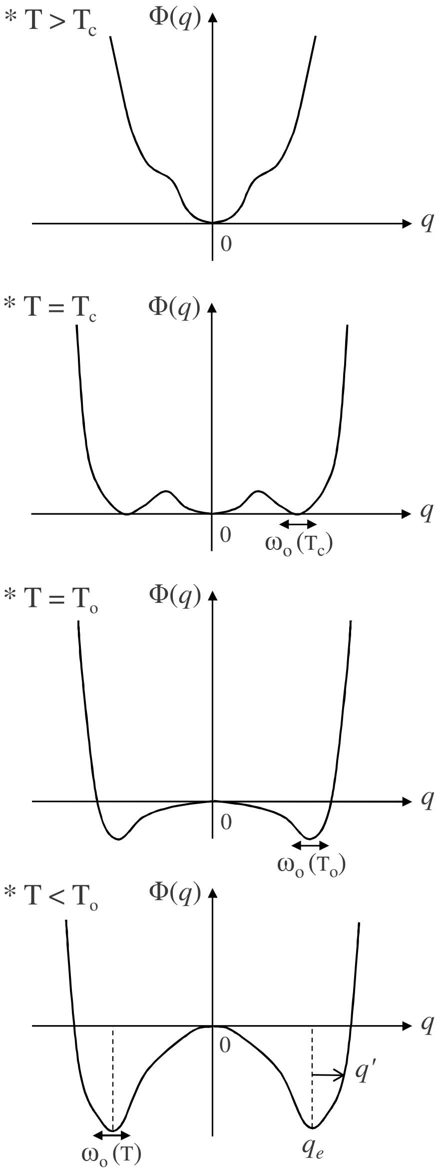

FIG. 1. Temperature dependence of the microscopic Landau potential for a system undergoing a displacive ferroelectric phase transition. The Landau potential for the ferroelectric A_1(TO) phonon is schematically plotted at four different temperatures around the Curie point (T_o), where the inverse dielectric susceptibility (χ) becomes zero.

sidered the Landau potential in terms of the displacement (q') from the double-well minimum, rather than the displacement from the paraelectric symmetry point, where $q=0$ (Fig. 1). To quantitatively correlate the soft mode frequency with the variation of temperature, we have first transformed $\Phi(q)$ into $\Phi(q')$. The q-value corresponding to the minimum of the double-well (q_e) can be obtained directly from Eq. (1), namely,

$$q_e^2 = \frac{|\xi| + \sqrt{\xi^2 - 4\chi\varsigma}}{2\varsigma}. \tag{2}$$

Since $q=q_e+q'$, it can be shown that using Eq. (2), $\Phi(q)$ is transformed to $\Phi(q')$ in the following form:

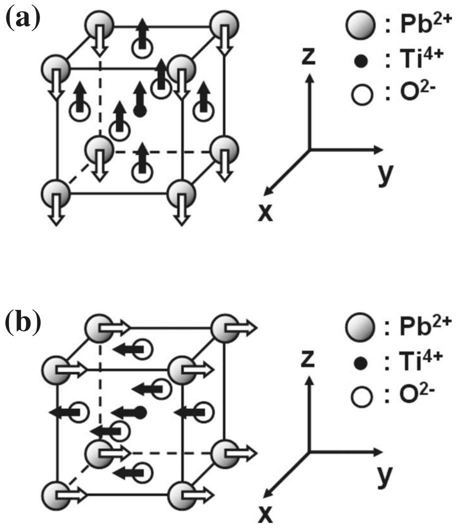

FIG. 2. A graphical representation of the eigenvectors of (a) the nondegenerated A_1(1TO) mode and (b) the doubly degenerated E(1TO) mode of a ABO$_3$-type perovskite (e.g., PbTiO$_3$) having tetragonal 4mm symmetry.

$$\Phi(q') = \Phi(q'=0) + aq' + bq'^2 + cq'^3 + dq'^4 + \cdots, \tag{3}$$

where the expansion coefficients, a, b, c, and d can be expressed in terms of the dielectric stiffness coefficients (χ,ξ,ς) and q_e as

$$a = -(q_e)^{1/2}\left\{\frac{\xi^2 - \xi\sqrt{\xi^2-4\chi\varsigma} + 2\xi\varsigma}{2\varsigma}\right\} < 0,$$

$$b = \frac{1}{2\varsigma}\{-4\chi\varsigma + \xi^2 - \xi\sqrt{\xi^2-4\chi\varsigma}\} > 0,$$

$$c = -\frac{1}{3}(q_e)^{1/2}\{-2\xi + 5\sqrt{\xi^2-4\chi\varsigma}\} < 0,$$

$$d = \frac{1}{4}\{-6\xi + 5\sqrt{\xi^2-4\chi\varsigma}\} > 0 \tag{4}$$

For simplicity, let us take thermal ensemble average for $(q')^3$. $\Phi(q')$ now reads

$$\Phi(q') = \Phi(0) + a'q' + b'q'^2 + \cdots, \tag{5}$$

where $a' \equiv a + c\langle q'^2\rangle$ *and* $b' \equiv b + d\langle q'^2\rangle$, and the bracket denotes the ensemble average. Then, the Hamilton function can be written as $H(q') = (p^2/2m) + a'q' + b'q'^2$. Applying the Hamilton equation of motion $(\partial H/\partial q = -\dot{p})$, one obtains

$$\frac{d^2q'}{dt^2} + \frac{k}{m}q' + \frac{a'}{m} = 0, \tag{6}$$

where $k=2b'$. Then, the solution of Eq. (6) can be written as

$$q' = q_0' \sin \omega_o t - (a'/2b'), \tag{7}$$

where $m\omega_o^2$ is given by the following relation:

$$m\omega_o^2 = k = 2b' = 2\{b + d\langle q'^2\rangle\}. \tag{8}$$

Therefore, $a'q'$-term in Eq. (5) does not contribute to the modulation of the mode frequency. The vibrating dipole described by Eq. (7) is apparently harmonic. However, the effective force constant $k(=2b')$ is now modulated by the anharmonicity term, $d\langle q'^2\rangle$. Therefore, the present theoretical approach summarized in Eqs. (7) and (8) can be regarded as a quasiharmonic approximation.

Let us now estimate $\langle q'^2\rangle$-term appeared in Eq. (8) in terms of k and thermal energy. To do this, we have reconsidered the Landau potential. $\Phi(q')$ in the vicinity of q_e can be approximated by a harmonic potential, namely, $\Phi(q') = (1/2)kq'^2 = bq'^2$. According to the classical equipartition law of energy, we establish the following equality: $(1/2)\langle E(\omega_o)\rangle = (1/2)k\langle q'^2\rangle$. For a quantum harmonic oscillator, we further have: $\langle E(\omega_o)\rangle = (\hbar\omega_o/2)\cdot\cot h(\hbar\omega_o/2k_BT)$. Therefore, the following equality can be obtained from these two relations,

$$\langle q'^2\rangle = \frac{\hbar\omega_o}{2k}\cot h\left(\frac{\hbar\omega_o}{2k_BT}\right) \approx \frac{k_BT}{k} = \frac{k_BT}{2b'} \tag{9}$$

where the right-hand-side expression comes from the high-temperature approximation ($\hbar\omega_o < k_BT$). Substituting Eq. (9) into Eq. (8) and solving the resulting equation with respect to $m\omega_o^2$ yields the following equation:

$$m\omega_o^2 = b\left\{1 + \sqrt{1 + \frac{2dk_BT}{b^2}}\right\} = 2b + \left(\frac{d}{b}\right)k_BT > 0, \tag{10}$$

where the last expression of Eq. (10) was obtained by applying the binomial expansion theorem to the second term. One can eventually obtain the following expression of $m\omega_o^2$ using Eqs. (4) and (10):[27]

$$m\omega_o^2(T) = \frac{2\xi^2}{\varsigma} - 6\chi - \frac{2\varsigma\chi^2}{\xi^2} + \frac{\varsigma}{12|\xi|}\left\{10 + \frac{23\xi^2}{(\xi^2 - 3\varsigma\chi)}\right\}. \tag{11}$$

The first three terms of the right-hand side of Eq. (11) originate from the harmonicity (i.e., the $2b$ term) in $\Phi(q')$ near the double-well minimum where $q'=0$. On the other hand, the last term comes from the d term, thus, from the anharmonicity term in $\Phi(q')$ near $q'=0$ and always contributes to the phonon hardening.

The mode frequency at the Curie temperature (T_o) can be obtained in terms of T_o using the Curie-Weiss relation $\{\chi = (T-T_o)/C_E\}$, namely,[27]

$$m\omega_o^2(T_o) = \frac{2\xi^2}{\varsigma} + \frac{11\varsigma k_BT_o}{4|\xi|} > 0 \tag{12}$$

This relation tells us that the mode frequency does not go to zero at T_o. One can further derive the following equation for the inverse static dielectric susceptibility (χ_c) at the phase transition temperature (T_c):[25]

$$\chi_c = \frac{3\xi^2}{16\varsigma} = \frac{1}{C_E}(T_c - T_o) > 0, \tag{13}$$

where $T_c > T_o$ for a first-order displacive transition. Using Eq. (13), one can obtain the following expression of $m\omega_o^2$ at T_c after doing a tedious rearrangement procedure.[27]

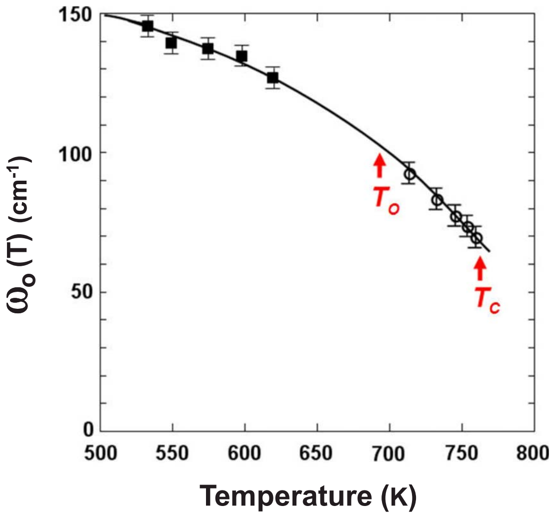

FIG. 3. (Color online) The computed mode frequency of the A_1(1TO) phonon plotted as a function of temperature (a solid line). The calculation was performed using Eq. (11) with optimized values of the Landau expansion coefficients: $\xi = -2.57\times10^{22}$ J/m^4, and $\varsigma = +6.87\times10^{42}$ J/m^6 per unit cell. Following Hidaka (Ref. 7), we adopted T_o of 693 K in our calculations. Both the open circles and the filled squares denote the mode frequency obtained from our temperature-dependent Raman scattering data.

$$m\omega_o^2(T_c) = \frac{103\xi^2}{128\varsigma} + \frac{73\varsigma}{14|\xi|}\left\{\frac{3C_Ek_B\xi^2}{16\varsigma} + k_BT_o\right\} < m\omega_o^2(T_o). \tag{14}$$

Since both ς and C_E are positive, $m\omega_o^2(T_c)$ is also greater than zero. Thus, the mode frequency of the ferroelectric A_1(1TO) phonon does not converge to zero even at T_c. The equilibrium off-center displacement (i.e., the position of the double-well minimum) at T_c can further be derived in terms of high-order dielectric stiffness coefficients, namely, $\{q_e(T_c)\}^2 = 3|\xi|/4\varsigma$.[25]

We are now in a position to examine temperature-dependent ω_o of the lowest-frequency A_1(1TO) phonon of PTO. Computational details are given in the EPAPS document.[27] In Fig. 3, we compare the computed mode frequency of the A_1(1TO) phonon with the experimental values. This shows that the present theoretical prediction [Eq. (11)] based on the symmetry argument of the Landau potential accurately reproduces the mode frequency of the A_1(1TO) phonon over a wide range of temperature below T_c. The experimental frequency values marked with circles denote our estimated A_1(1TO) frequencies indirectly obtained by applying the Merten's equation to the oblique phonon data (45° inclined to the unique c axis of 4mm symmetry). These values agree well with the previously reported values obtained by the same oblique phonon method.[5] On the other hand, the data points marked with filled squares denote our directly measured values of the A_1(1TO) mode frequency in $x(zz)x$ polarized backscattering geometry.[12] As indicated in Fig. 3, the mode frequency at T_c (763 K) does not converge to zero but remain at $\sim$65 cm^{-1}, supporting our theoretical prediction presented in Eq. (14).

Finally, we have considered a possibility of crossover between a displacive to an order-disorder transition near the critical point. According to the Eyring's transition-state theory of rate process,[28] the hopping frequency of relaxational dipoles across the barrier of the double-well potential increases rapidly with temperature and can be described by the following equation at high temperatures near T_c:

$$\omega_{hop} = \frac{k_B T}{h}\exp\left(\frac{-\Phi_b}{k_B T}\right), \tag{15}$$

where Φ_b is the height of a double-well $[=(\Phi_{q=0}-\Phi_{q=q_e})]$ and can be expressed in terms of the Landau coefficients. For examples, $\Phi_b=|\xi^3|/12\varsigma^2$ at $T=T_o$ and $\Phi_b=|\xi^3|/96\varsigma^2$ at $T=T_c$.[7] Thus, the barrier height decreases rapidly as temperature approaches T_c (Fig. 1), which catastrophically enhances the hopping rate across the double-well barrier [Eq. (15)]. On the other hand, the mode frequency of the soft phonon decreases with increasing temperature (Fig. 3). Under suitable conditions (e.g., $|\xi|/\varsigma \gg 1$ and high T_c),[7] thus, one would expect a crossover from the displacive soft mode phonon (a vibrating dipole confined to one of the double wells) to the relaxation-type dipole hopping (Debye-type order-disorder).[8] We have computed the hopping frequency at T_o and T_c using Eq. (15): $\omega_{hop}=6.24\times 10^{11}$ $\text{s}^{-1}=3.32$ cm^{-1} at $T=T_o$ (693 K), and $\omega_{hop}=8.89\times 10^{12}$ $\text{s}^{-1}=47.2$ cm^{-1} at $T=T_c$ (763 K). Thus, the hopping frequency at the phase transition temperature (T_c) is comparable to the soft mode vibration frequency even in PTO which unlike BTO, has long been regarded as a typical displacive ferroelectric characterized by the resonance-type soft phonon up to the critical point.

When these two mode frequencies are comparable to each other near the critical point, a dynamic coupling between two distinct modes is expected.[29] In this case, one would observe the "so-called" central peak in the dynamic structure factor, $S(\omega)$, at $\omega=0$, in addition to the Stokes and anti-Stokes lines at $\pm\omega_o$.[8] This central peak was indeed observed in the E-symmetry phonon (Raman) spectrum of a PTO single crystal between T_o and T_c.[6] Since the central peak is known to be a direct consequence of the mode-mode coupling, this observation suggests an existence of the relaxation mode even in PTO which has been known to have little tendency of the order-disorder-type relaxation.[7] Our estimate of the hopping frequency also does not exclude a possibility of the relaxational hopping near T_c.

In conclusion, our theoretical formalisms based on the microscopic Landau potential in the vicinity of the double-well minimum predict that the mode frequency of the A_1(1TO) phonon does not converge to zero even at the phase transition temperature, T_c. The computed mode frequency of the A_1(1TO) phonon accurately reproduces the observed frequency of PbTiO_3 over a wide range of temperature below T_c (763 K).

This work was supported by the Korea Research Foundation (KRF) under Contract No. KRF-2008-313-C00252 and by the Basic Science Research Institute (BSRI) at POSTECH through the 2008 Basic Science Research Grant.

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