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First-principles study of instantaneous and averaged local potential in $BaTiO_3$

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The minima of the local mode's potential energy in the unit cell of $BaTiO_3$ are studied by first-principles effective Hamiltonian numerical simulations. Instead of a constant potential with eight minima, we find a single minimum with position and depth changing in time. In agreement with the early view by Comes *et al.* [Solid State Commun. **6**, 715 (1968)] and recent nuclear magnetic resonance experiments, we find that deeper values at the paraelectric phase are mainly found when the minimum is located at eight off-centered regions at the body diagonals of the unit cell. This situation changes at the ferroelectric phase, where four of the eight noncentered regions are privileged, and deeper values are found when the minimum is located in a surface around them. This order-disorder behavior of the instantaneous potential disappears when considering the long-term time-averaged potential: The paraelectric phase single minimum of the averaged potential is located at the center of the unit cell and it becomes displaced along the local dipole axis in the ferroelectric phase.

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The mechanism leading to the ferroelectric behavior in $BaTiO_3$ has been a topic of much interest in condensed matter physics. In particular, there have been discussions concerning the order-disorder and displacive characteristics of the transition. In the first microscopic theory for $BaTiO_3$, the transition was considered to be order disorder.[1] In this theory, the potential energy of the Ti ions in the unit cell is off center. It may be considered that there are eight minima located in the eight equivalent $\langle 111\rangle$ directions of the unit cell. In the paraelectric phase, the Ti ions are disordered between the potential minima resulting in a zero-spontaneous polarization, but they order preferentially in four well-defined positions at the tetragonal ferroelectric regime. The main objection to this view came from Jaynes[2] who pointed out that the transition entropy, calculated within the framework of a purely order-disorder system, considering the change from eight minima to four minima was too large in comparison with the change observed experimentally. A different point of view came from Cochran's displacive theory for the ferroelectric transition in $BaTiO_3$.[3] In the displacive theory, the potential for the Ti motion in the paraelectric phase exhibits a minimum at the center of the cell, but it changes at the critical temperature, allowing temperature dependent off-center minima and a spontaneous polarization different from zero. This theory was later confirmed by measurements of inelastic neutron scattering[4] and Raman spectroscopy[5], which revealed the softening of a transverse optic phonon near the Brillouin zone center.

However, near the cubic-tetragonal critical temperature, the diffuse x-ray scattering was shown to be anomalous.[6] Such an anomaly was originally interpreted[6,7] as a result of the existence of off-center minima in the potential energy of Ti as corresponding to an order-disorder mechanism, but this was made compatible with a displacive model.[4,8] Of course, the possibility of a coexistence of order-disorder and displacive components in the ferroelecetric phase transition of $BaTiO_3$ cannot be discarded completely. In fact, this idea seems to be supported by first-principles-based simulations[9] and by results from recent molecular dynamics simulations.[10–12] The experimental studies to detect possible off-center potential minima of Ti in the cubic paraelectric phase of $BaTiO_3$ have been based mainly in EPR measurements[13,14] and nuclear magnetic resonance (NMR) studies.[15–17] In fact, Zalar *et al.*[18] have recently shown evidence of the coexistence of order-disorder and displacive components.

To get a clear idea about the nature of the phase transition in $BaTiO_3$ we study the behavior of the potential energy in the cubic cell of $BaTiO_3$ at the paraelectric and ferroelectric phases. In particular, it is possible to study the value of the total potential energy $V(u_i,t)$ at a particular local cell i and at a given time t as the local mode displacement $u_i = (ux_i, uy_i, uz_i)$ (or local polarization p_i) takes different values in the cell.

The most interesting feature of the potential concerning our study is the value of the local mode $u_{i,t}^{m}$ for which the local potential has a minimum at a given time t. The first question to answer is whether or not this instantaneous minimum is centered or off-centered at the different phases.

To answer this question, we calculate the potential energy using first-principles numerical simulations. It is important to stress that the calculated local mode potential energy takes into account the effect of all unit cells in the sample. The model used is the same effective Hamiltonian specified by ultrasoft pseudopotentials introduced by Zhong *et al.*[9,19] This effective Hamiltonian takes into account a local soft-mode self-energy containing intersite interactions to quartic anharmonic order, a long-range dipole-dipole coupling, a short-range correction to the intersite coupling going up to third neighbors, a harmonic elastic energy and finally, an anharmonic strain (v) -soft mode (u) coupling. Details about the model and values of the parameters may be found in Ref.19. The sequence of critical temperatures obtained by the model does not exactly match the experimental transition temperatures, mostly due to the defective description of the thermal expansions,[20] but successfully reproduces the phase transitions sequence for $BaTiO_3$ ($T_{EH} \sim 300$ K versus $T_{\exp} \sim 400$ K for the cubic-tetragonal transition,

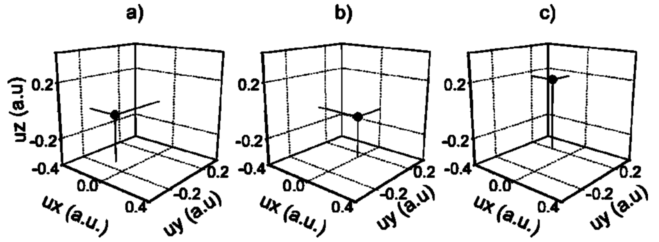

FIG. 1. Position (in atomic units) of the instantaneous local minimum $u_{i,t}^m$ at (a) $t=10\,000$ Monte Carlo Steps (MCS), (b) $t=12\,000$ MCS, and (c) $t=13\,000$ MCS. Temperature is equal to $T=400$ K corresponding to the paraelectric phase. Solid lines are just a guide for the eyes.

$T_{EH}\sim 230$ K versus $T_{\text{exp}}\sim 280$ K for the tetragonal-orthorhombic transition and $T_{EH}\sim 200$ K versus $T_{\text{exp}}\sim 180$ K for the orthorhombic rhombohedral transition). The behavior of the Hamiltonian at different temperatures may be studied using standard Monte Carlo techniques. The system is thermalized at a given temperature and then the instantaneous potential $V(u_i,t)$ for each particular equilibrium configuration of local modes and strains in the system is calculated. $V(u_i,t)$ is given by the sum of all terms in the Hamiltonian which depends on the value of u_i (i.e., the local soft mode, the dipole-dipole interaction, the short-range correction, and the strain-mode coupling). $V(u_i,t)$ is then obtained by freezing all the local modes u_j with $j\neq i$ at a given time t and retaining u_i as a variable. The value of u_i for which we get a minimum in $V(u_i,t)$ is defined as $u_{i,t}^m$. The study is focused in $BaTiO_3$ cubic systems with $9\times 9\times 9$ unit cells at a constant pressure $P=-4.8$ GPa.[9] The boundary conditions considered are periodic. In order to search for nonzero minima in the potentials and to compare among the different phases, simulations are performed at the following temperatures: $T=400$ K (cubic-paraelectric phase) and $T=250$ K (tetragonal-ferroelectric phase).

The values of $u_{i,t}^m$ for several instantaneous configurations in the paraelectric and ferroelectric phases are shown in Figs. 1 and 2. The first noticeable feature is that there is always a single minimum for any given time (the existence of a single instantaneous minimum is related to the shape of the self-energy for the model $BaTiO_3$ used, where there is just a single minimum located at the center of the cell), and the second important feature is that the position of the minimum seems to be off center for both, the paraelectric and the ferroelectric phases.

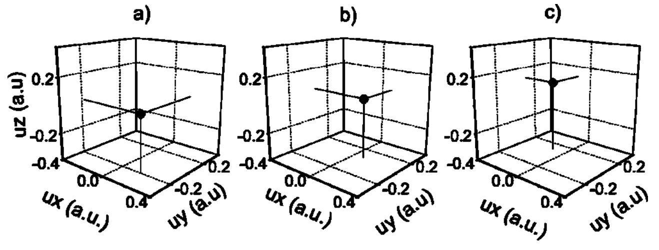

FIG. 2. Position (in atomic units) of the instantaneous local minimum $u_{i,t}^m$ at (a) $t=10\,000$ MCS, (b) $t=12\,000$ MCS and (c) $t=13\,000$ MCS. Temperature is equal to $T=250$ K corresponding to the ferroelectric phase. Solid lines are just a guide for the eyes.

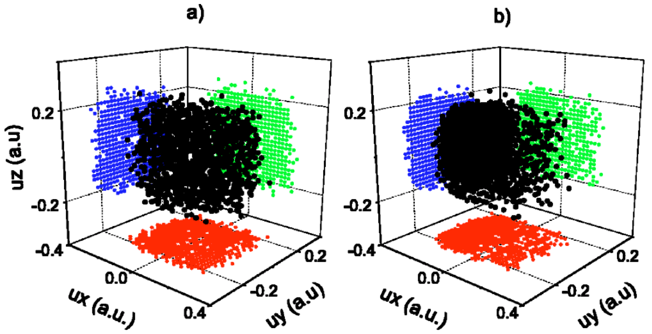

FIG. 3. (Color online) Position (in atomic units) of all the instantaneous local minima $u_{i,t}^m$ found after thermalization from $t=1$ MCS to $t=20\,000$ MCS. Temperature is equal to (a) $T=400$ K corresponding to the paraelectric phase and (b) $T=250$ K corresponding to the ferroelectric phase. Projections over the planes are represented with green (light gray), red (gray) and blue (dark gray) points.

With this result, we answer the question of the existence of off-centered minima but, in order to have an idea of the behavior of the system, we should collect the position of all these instantaneous minima for a given period of time to get an idea of where they are localized. Results for $N_{\text{conf}}=20\,000$ different instantaneous configurations [i.e., after $t=20\,000$ Monte Carlo steps (MCS)] in the paraelectric and the ferroelectric phase are shown in Fig. 3

Figure 3 shows how instantaneous minima are homogeneously distributed inside the studied region in the paraelectric phase and how they seem to be more concentrated in one-half of the studied box (displaced in the $-x$ direction) at the ferroelectric phase. Note how no instantaneous minimum is located outside the studied region (i.e., the studied region considered is large enough). In principle, a structure of the minima as the one given by the eight-site model proposed a long time ago by Comes *et al.*[6] does not seem to hold from Fig. 3. However, in order to analyze this result in more detail, we need to consider not just the position $u_{i,t}^m$ of the different minima but also the value of the potential minima $V(u_{i,t}^m,t)$ at each particular instantaneous configuration t. Clearly, the most important minima are the deeper minima. To show them up, we plot in Fig. 4 the deepest minimum found V^m together with all minima $V(u_{i,t}^m,t)$ fulfilling,

$$V(u_{i,t}^m,t) < (V^m + fV^m) \tag{1}$$

for a given factor f. We consider $f=0.5$.

Figure 4(a) shows how the early view by Comes *et al.*,[6] later investigated in detail by Chaves *et al.*,[7] of a Ti ion—located at eight positions shifted from the center along the body diagonals of the unit cell—turns out to be not far from the truth, at least from the point of view of the results obtained by first principles numerical simulations. Note how the eight off-centered regions are clearly shown in the three projections. However, Fig. 4(b) seems to indicate that in the ferroelectric phase, deeper minima are located in an extended surface formed mostly by only four of the eight previously reported regions. The surface is slightly displaced toward the direction given by the axis of the local dipole. These results

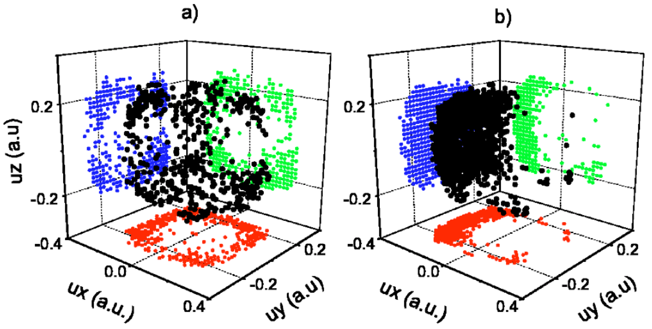

FIG. 4. (Color online) Position (in atomic units) of all the instantaneous local minima $u^m_{i,t}$ found after thermalization from $t=1$ MCS to $t=20\,000$ MCS with $V(u^m_{i,t},t) < (V^m + fV^m)$. Temperature is equal to (a) $T=400$ K corresponding to the paraelectric phase with $f=0.5$ and (b) $T=250$ K corresponding to the ferroelectric phase with $f=0.5$. Projections over the planes are represented with green (light gray), red (gray), and blue (dark gray) points.

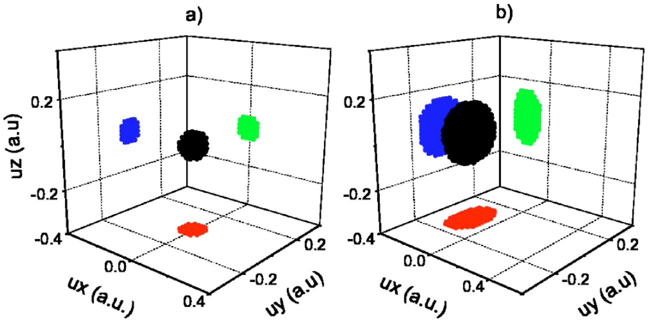

FIG. 5. (Color online) Position (in atomic units) of all local modes u_i with $\overline{V}(u_i) < [\overline{V}(u_i^m) + f\overline{V}(u_i^m)]$ for (a) $T=400$ K with $f=50$ and (b) $T=250$ K with $f=0.5$, after performing a time average with $t=20\,000$ MCS. Projections over the planes are represented with green (light gray), red (gray), and blue (dark gray) points.

are compatible with previous ones obtained for $BaTiO_3$ using the shell model.[21] In order to study in more detail around which ⟨111⟩ direction the minima are located in both the ferroelectric and the paraelectric phase, the cell shown in Fig. 4 has been divided in eight cubic regions, corresponding to the eight ⟨111⟩ directions and the percentage of minima located at each region has been calculated. Results are summarized in Table I. Note how all percentages are very similar at the paraelectric phase, indicating that the eight regions are almost equally populated. On the other hand, only the directions with $ux_i < 0$ are populated in the ferroelectric phase.

TABLE I. Percentage of instantaneous local minima $u^m_{i,t}$ found around the eight possible ⟨111⟩ directions. Minima were found after thermalization from $t=1$ MCS to $t=20\,000$ MCS using $f=0.5$ at the paraelectric $T=400$ K and ferroelectric $T=250$ K phases.

	$T=400$ K	$T=250$ K
1 1 1	6.65	0.05
1 −1 1	8.45	0.19
1 1 −1	14.74	0.7
1 −1 −1	13.31	1.12
−1 1 1	12.05	20.75
−1 −1 1	17.80	32.80
−1 1 −1	15.48	17.21
−1 −1 −1	11.33	26.63

However, there is still the question of why experimental results have mainly extended an opinion of a Ti ion sitting at the center of the unit cell in the paraelectric phase and displaced at the ferroelectric phase. From extended x-ray-absorption fine structure, pair-distribution function, and NMR, it is concluded that the local structure of high-T_c superconductors[22–26], and oxide ferroelectrics[27] deviates from the average structure obtained from x-ray or neutron crystallography. As former experiments are based on a much faster time scale than the conventional scattering methods, the results are in fact not in conflict but show that the various collective particle dynamics are governed by different time scales[28,29]. A molecular dynamics simulation of a model ferroelectric[10] has shown that the coexistence of these various times scale gives rise to a central peak in addition to mode softening, and a coexistence regime of order-disorder and displacive behavior. So, to address the question we need to take into account that the response of the system when considering the instantaneous value of the potential is going to be different from the one obtained when considering the long-term time-averaged value. In this study, the temporal average means the average over MCS. Next we study the temporal averaged value of the potential at any point of the studied region for $N_{\text{conf}}=20\,000$ different instantaneous configurations ($t=20\,000$ MCS):

$$\overline{V}(u_i) = \frac{1}{N_{\text{conf}}}\sum_{t=1}^{N_{\text{conf}}} V(u_i,t). \tag{2}$$

The value of u_i in this equation is not averaged over the MCS. Now there is a total minimum of the averaged potential for a particular value of the local mode that we will denote as u_i^m. We find that $u_i^m \sim 0$ in the paraelectric phase and $u_i^m \neq 0$ at the ferroelectric phase. So, the question about why $BaTiO_3$ behaves as if the Ti atom is centered at paraelectric phase and displaced at the ferroelectric phase is now answered considering the long-term averaged behavior of the potential. In Fig. 5, we plot the position of the minimum for both phases together with all values of local modes fulfilling

$$\overline{V}(u_i) < \left[\overline{V}(u_i^m) + f\overline{V}(u_i^m)\right] \tag{3}$$

for a given factor f.

In order to get an idea about the behavior of the averaged potential energy inside the cell, it is useful to plot $\overline{V}(u_i)$ versus u_i for $u_i=(ux_i,0,0)$. Results are presented in Fig. 6 for both, the paraelectric and the ferroelectric phases. Note how in the paraelectric phase the minimum of $\overline{V}(u_i)$ is almost zero and it is located at the center of the unit cell. However, in the ferroelectric phase, the minimum is negative and different from zero, and it is displaced from the center of the unit cell as corresponding to a typical displacive transition.

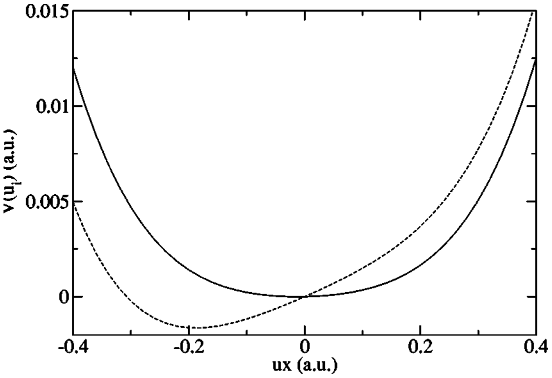

FIG. 6. $\overline{V}(u_i)$ versus u_i with $u_i=(ux_i,0,0)$ for $T=400$ K (continuous line) corresponding to the paraelectric phase and $T=250$ K (dashed line) corresponding to the ferroelectric phase. The time- average performed is $t=20\,000$ MCS.

To conclude, a first-principles numerical simulation of the instantaneous local potentials in $BaTiO_3$ shows how the energy felt by the Ti ion is not due to a constant potential with eight minima but to a single minimum with position and depth changing in time. This single minimum is noncentered in both the paraelectric and the ferroelectric phases. In the paraelectric phase, the deeper values are found when the minimum is localized in eight regions along the body diagonals. In contrast, in the ferroelectric phase, deeper values are found when the minimum is localized in a surface formed mostly by four of the eight previously reported regions. The long-term time-averaged behavior of the potential energy behaves completely different and presents a single minimum at the center of the local cell in the paraelectric phase at $T=400$ K and a noncentered minimum in the ferroelectric phase at $T=250$ K, as corresponding to a displacive transition.

The results obtained show how the soft-mode long-term behavior is compatible with the order-disorder component when considering the existence of a single dynamic minimum instead of a constant potential with eight minima. Basically, the behavior of the system depends on how fast the response of the local mode is to the dynamic changes of the instantaneous minimum. A fast response is responsible for the order-disorder component and a slow response is responsible for the displacive component. Since the position of the single minimum is due to the overall status of the sample, it is possible to state that the degree of order-disorder and displacive components in $BaTiO_3$ is a measurement of the response of a single Ti ion compared to the cooperative evolution of the whole sample.

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[1] W. P. Mason and B. T. Matthias, Phys. Rev. **74**, 1622 (1948); J. C. Slater, *ibid.* **78**, 748 (1950).
[2] E. T. Jaynes, Phys. Rev. **79**, 1008 (1950).
[3] W. Cochran, Adv. Phys. **9**, 387 (1960).
[4] J. Harada, J. D. Axe, and G. Shirane, Phys. Rev. B **4**, 155 (1971).
[5] P. A. Fleury and J. M. Worlock, Phys. Rev. **174**, 613 (1968).
[6] R. Comes, M. Lambert, and A. Guinier, Solid State Commun. **6**, 715 (1968).
[7] A. S Chaves, F. C. S. Barreto, R. A. Nogueira, and B. Zeks, Phys. Rev. B **13**, 207 (1976).
[8] W. Cochran, Phys. Status Solidi **30**, K157 (1968).
[9] W. Zhong, D. Vanderbilt, and K. M. Rabe, Phys. Rev. Lett. **73**, 1861 (1994).
[10] M. Stachiotti, A. Dobry, R. Migoni, and A. Bussmann-Holder, Phys. Rev. B **47**, 2473 (1993).
[11] A. Bussmann-Holder and A. R. Bishop, Phys. Rev. B **56**, 5297 (1997).
[12] A. Bussmann-Holder, Physica B **263**, 408 (1999).
[13] K. A. Müller and W. Berlinger, Phys. Rev. B **34**, 6130 (1986).
[14] K. A. Müller, W. Berlinger, K. W. Blazey, and J. Albers, Solid State Commun. **61**, 21 (1987).
[15] O. Kanert, H. Schulz, and J. Albers, Solid State Commun. **91**, 465 (1994).
[16] T. J. Bastow, J. Phys.: Condens. Matter **1**, 4985 (1989).
[17] T. J. Bastow and H. J. Whitfield, Solid State Commun. **117**, 483 (2001).
[18] B. Zalar, V. V. Laguta, and R. Blinc, Phys. Rev. Lett. **90**, 037601 (2003).
[19] W. Zhong, D. Vanderbilt, and K. M. Rabe, Phys. Rev. B **52**, 6301 (1995).
[20] S. Tinte, J. Íñiguez, K. M. Rabe, and D. Vanderbilt, Phys. Rev. B **67**, 064106 (2003).
[21] S. Tinte, M. G. Stachiotti, M. Sepliarsky, R. L. Migoni, and C. O. Rodriguez, J. Phys.: Condens. Matter **11**, 9670 (1999).
[22] T. Egami, W. Dmowski, T. R. Sendyka, R. S. McQueeney, N. Seigl, H. Yamanchi, Y. Hinatsu, S. Uchida, and M. Arai, in *Proc., International Workshop on Anharmonic Properties of High-T_c Cuprates, Bled, 1994*, edited by D. Mihailovic, G. Ruani, E. Kaldis, and K. A. Müller (World Scientific, Singapore, 1995), p. 118.
[23] H. L. Edwards, A. L. Bari, J. T. Markert, and A. L. de Lozanne, Phys. Rev. Lett. **73**, 1154 (1994).
[24] S. D. Corradson, J. D. Raistrick, and A. R. Bishop, Science **248**, 1394 (1990).
[25] J. M. Tranquada, B. J. Sternlieb, J. D. Axe, Y. Nakamura, and S. Uchida, Nature (London) **375**, 561 (1995).
[26] A. Bianconi, N. L. Saini, A. Lanzara, M. Missori, T. Rossetti, H. Oyanagi, H. Yamaguchi, K. Ota, and T. Ito, Phys. Rev. Lett. **76**, 3412 (1996).
[27] N. Sircon, B. Ravel, Y. Yacoby, E. A. Stern, F. Dogan, and J. J. Rehr, Phys. Rev. B **50**, 13 168 (1994).
[28] A. Bussmann-Holder and A. R. Bishop, Philos. Mag. B **73**, 657 (1996).
[29] A. Bussmann-Holder, A. R. Bishop, and G. Benedek, Phys. Rev. B **53**, 11 521 (1996).