A first-principles scheme to phonons of high temperature phase: No imaginary modes for cubic $SrTiO_3$

Yi Wang,[a] James E. Saal, Zhigang Mei, Pingping Wu, Jianjun Wang, Shunli Shang, Zi-Kui Liu, and Long-Qing Chen
Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802, USA

(Received 30 July 2010; accepted 4 October 2010; published online 20 October 2010)

The issue of imaginary phonon modes predicted by first-principles calculations for high-temperature structures of most materials has been a longstanding problem for decades. We propose that the observed high-temperature structures are actually dynamic averages of related low-temperature structures. This theory is used to predict the phonon dispersions of cubic $SrTiO_3$. The calculated phonon dispersions for the cubic phase, using the force constants calculated from the tetragonal phases, are found to be in remarkably good agreement with existing neutron data, without exhibiting any imaginary phonon modes. © *2010 American Institute of Physics*. [doi:10.1063/1.3505338]

With advances in computer technology and software, density functional theory can now predict electron and phonon properties for many classes of materials, including simple metals, transition metals, intermetallics, semiconductors, hydrides, and Earth materials with exceptional accuracy.[1–5] However, it is mostly limited to ground state crystal structures as imaginary phonon modes are often predicted for their high-temperature structures, in disagreement with measurements where phonon frequencies are always real. For example, the well-defined Δ_2 phonon dispersion has been measured for $SrTiO_3$ along the $[(1/2)(1/2)\xi]$ (i.e., M-R) direction at temperatures across the 105 K tetragonal-cubic phase transition by Stirling.[6] However, current theoretical calculations[7–9] of cubic $SrTiO_3$ lead to imaginary phonon frequencies for this dispersion. This suggests a fundamental flaw in the current understanding of $SrTiO_3$, as well as other materials where imaginary phonon modes are predicted for the high-temperature structure, such as La_2CuO_4-based superconductors[10] and $LaMnO_3$-based colossal magnetoresistance manganites.[11]

In this work, we describe a scheme to calculate the phonon frequencies of cubic $SrTiO_3$ using the force constants obtained from tetragonal $SrTiO_3$. The present work was motivated by two observations: (i) the similarity of the measured phonon spectra[6,12–14] between the cubic and tetragonal phases and (ii) the first-principles lattice dynamics prediction[7–9] of numerous imaginary phonon modes in the cubic phase, in disagreement with the measured real phonon frequencies. We demonstrate the scheme by comparing our predictions with the experimental phonon dispersions and those conventionally calculated using the ideal cubic structure and the tetragonal structure.

We have employed the supercell method to calculate the phonon frequency. Since $SrTiO_3$ is a polar insulator, we first consider long range dipole-dipole interactions which result in the well-known LO-TO splitting (splitting between longitudinal and transverse optical phonon frequencies).[15] As described in our recent work,[5] we calculate the real-space force constants as follows:

$$\Phi_{\alpha\beta}^{jk}(M,P) = \phi_{\alpha\beta}^{jk}(M,P) + \varphi_{\alpha\beta}^{jk}, \tag{1}$$

where $\Phi_{\alpha\beta}^{jk}$ is the interaction force constants between atom j in the primitive cell M and atom k in the primitive cell P, $\phi_{\alpha\beta}^{jk}$ the cumulative contribution from short range interactions defined by Parliński *et al.*,[3] and $\varphi_{\alpha\beta}^{jk}$ the contribution from long range interactions due to dipole-dipole effects. We find that $\varphi_{\alpha\beta}^{jk}$ can be explicitly expressed as follows:

$$\varphi_{\alpha\beta}^{jk} = \frac{1}{N}\frac{4\pi e^2}{V}\frac{[\mathbf{q}\cdot\mathbf{Z}^*(j)]_\alpha[\mathbf{q}\cdot\mathbf{Z}^*(k)]_\beta}{\mathbf{q}\cdot\boldsymbol{\varepsilon}_\infty\cdot\mathbf{q}}, \tag{2}$$

where N is the number of primitive unit cells in the supercell and V is the volume of the primitive unit cell, $\mathbf{q}$ the wave vector, α and β the Cartesian axes, $\mathbf{Z}^*(j)$ the Born effective charge tensor of the j^{th} atom in the primitive unit cell, and $\boldsymbol{\varepsilon}_\infty$ the high frequency static dielectric tensor, i.e., the contribution to the dielectric permittivity tensor from the electronic polarization.[1] As a result, the dynamical matrix $\tilde{D}_{\alpha\beta}^{jk}(\mathbf{q})$ can be calculated by the following Fourier transformation:[16]

$$\tilde{D}_{\alpha\beta}^{jk}(\mathbf{q}) = \frac{1}{\sqrt{\mu_j\mu_k}}\frac{1}{N}\sum_{M,P}\Phi_{\alpha\beta}^{jk}(M,P) \times\exp\{i\mathbf{q}\cdot[\mathbf{R}(P)-\mathbf{R}(M)]\}, \tag{3}$$

where μ_j is the atomic mass of the j^{th} atom in the primitive unit cell and $\mathbf{R}(P)$ is the position of the P^{th} primitive unit cell in the supercell. Details of the physics concerning Eqs. (1) and (2) are discussed in a previous publication.[5] The present work focuses on how to extend the method to include effects of broken symmetry due to lattice distortions.

Equation (3) was originally derived to consider surface effects.[16] Otherwise, for a crystal possessing periodic translational symmetry, the summation over M can only result in a prefactor N since the translational invariance makes $\Phi_{\alpha\beta}^{jk}$ depend on M and P only through the difference $\mathbf{R}=\mathbf{R}(P)-\mathbf{R}(M)$.[1] For the present purpose of calculating the phonon frequencies of the high-temperature cubic phase from the force constants of the low-temperature tetragonal phase, we propose to use the summation over M as an average in the reciprocal space over the lattice distortion.

[a]Electronic mail: yuw3@psu.edu.

For first-principles static calculations at 0 K, we employed the projector-augmented wave (PAW) method[17,18] implemented in the Vienna *ab initio* simulation package (VASP, version 5.2). The exchange-correlation functional according to Ceperley and Alder as parameterized by Perdew and Zunger[19] was employed in all calculations. For the calculation of the static energies, we used the Γ-centered k mesh with over 8000 k points per atom and energy cutoff of 500 eV. For the calculation of Born effective charge tensor and the high frequency static dielectric tensor, we employed the linear-response theory implemented in VASP 5.2 by Gajdos *et al.*[20] and the same parameter settings as the static calculations. For the calculation of the phonon frequencies, the force constants were calculated adopting the supercell approach implemented in VASP 5.2 using the energy cutoff of 400 eV, together with $3\times3\times3$ k-mesh and $4a\times4a\times2c$ 160-atom supercells for both cubic $SrTiO_3$ and tetragonal $SrTiO_3$.

A good summary of experimental phonon frequencies of $SrTiO_3$ (Refs. 6, 12, and 13) was given by Stirling[6] for both the high-temperature cubic phase (at 297 K) and the low-temperature tetragonal phase (at 97 K). In particular, Stirling[6] reported the temperature dependence of the lowest branch along the M-R direction at 78, 118, 201, and 297 K.

In Fig. 1, we show the calculated and measured phonon frequencies for $SrTiO_3$. Three types of phonon calculations are plotted: (i) a cubic calculation using the ideal cubic structure (i.e., restricting the strontium atom to the body center and the oxygen atoms to the face centers), (ii) a pseudocubic calculation using the tetragonal shape of $SrTiO_3$ but limiting c/a to be ideal $1/\sqrt{2}$ while the internal positions of oxygen atoms are allowed to fully relax, and (iii) a tetragonal calculation using the tetragonal structure in which the internal positions of the strontium atom, the internal positions of the oxygen atoms, and the lattice shape are all allowed to relax. The results are compared with experiments in three ways: (i) phonon frequencies from the cubic calculation vs. the measured phonon frequencies for the cubic phase at 297 K,[6,12,14] (ii) phonon frequencies from the pseudocubic calculation versus the measured phonon frequencies for the cubic phase at 297 K,[6,12,14] and (iii) phonon frequencies from the tetragonal calculation vs. the measured phonon frequencies at 78 K,[6] 90 K,[6] and 110 K (Ref. 13) which are around the tetragonal-cubic phase transition temperature of 105 K.[6]

From Fig. 1(a), the cubic calculation predicts many imaginary phonon modes for $SrTiO_3$ along the M-R direction. In comparison, we see no imaginary phonon frequencies for the M-R dispersions from the pseudocubic calculation, as shown in Fig. 1(b). In particular, the measured low frequency branch along M-R direction [solid circles (red) in Fig. 1] by Stirling[6] is predicted rather well. Furthermore, comparing Fig. 1(b) with Fig. 1(c), the only difference between the cubic and tetragonal phases is that this low frequency branch for the tetragonal phase along the M-R direction is slightly lower than that for the cubic phase.

In summary, we have addressed the longstanding imaginary-phonon-mode issue in calculating phonon frequencies for the high-temperature phase of a solid by introducing a scheme in which the phonon frequencies of a high-temperature structure are computed using the force constants calculated for related low-temperature structures. The application of this scheme to $SrTiO_3$ shows no imaginary phonon

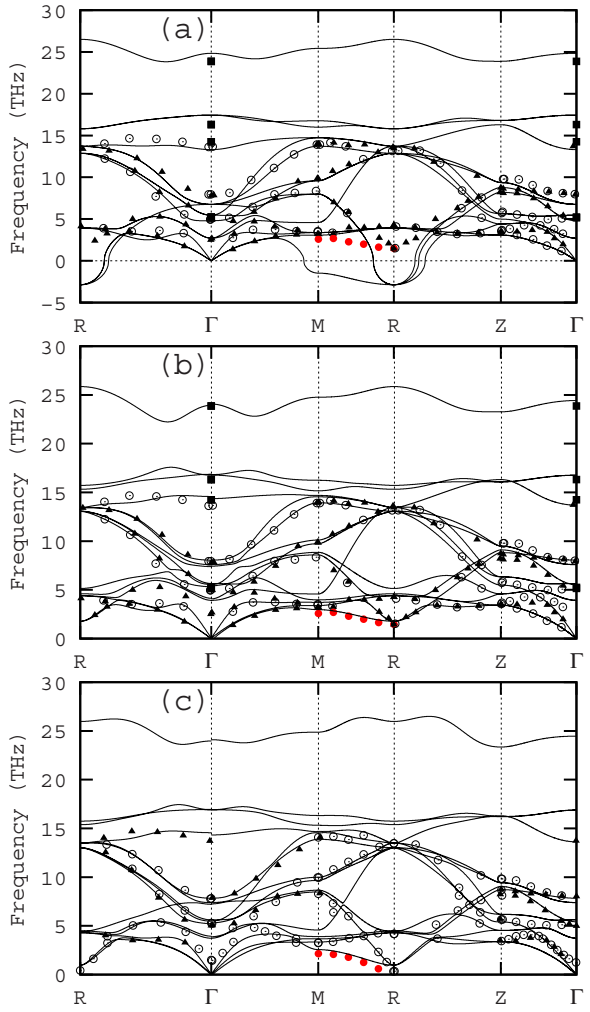

FIG. 1. (Color online) Phonon dispersions of $SrTiO_3$. (a) cubic calculation (solid lines, see the text) together with the measured phonon frequencies (symbols) for the cubic phase (Refs. 6, 12, and 14) (297 K); (b) pseudocubic calculation (solid lines, see the text) together with the measured phonon frequencies (symbols) at 297 K (Refs. 6, 12, and 14); and (c) tetragonal calculation (solid lines, see the text) together with the measured phonon frequencies (symbols) at 78 K [solid circles (red)] (Ref. 6), 90 K [open circles] (Ref. 6), and 110 K (solid triangles) (Ref. 13).

modes and good agreement with experiments is obtained for both the cubic high-temperature phase and the tetragonal low-temperature phase. The present procedure is not limited to tetragonal-cubic perovskite systems and can be used for calculating other materials where imaginary phonon modes are predicted for the high-temperature structure, such as La_2CuO_4-based superconductors[10] and $LaMnO_3$-based colossal magnetoresistance manganites.[11]

This work was funded by the Office of Naval Research (ONR) under Contract No. N0014-07-1-0638, the National Science Foundation (NSF) through Grant No. DMR-1006557, and DOE Basic Sciences under Grant No. DOE DE-FG02-07ER46417 (Yi Wang and Chen), and in part supported by instrumentation funded by the National Science Foundation through Grant No. OCI-0821527. Calculations were also conducted at the LION clusters at the Pennsylvania State University and at the National Energy Research Scientific Computing Center, which is supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. This work was also supported in

part by a grant of HPC resources from the Arctic Region Supercomputing Center at the University of Alaska Fairbanks as part of the Department of Defense High Performance Computing Modernization Program.

[1]S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, Rev. Mod. Phys. **73**, 515 (2001).
[2]S. Baroni, P. Giannozzi, and E. Isaev, Rev. Mineral. Geochem. **71**, 39 (2010).
[3]K. Parliński, Z. Q. Li, and Y. Kawazoe, Phys. Rev. Lett. **78**, 4063 (1997).
[4]A. van de Walle and G. Ceder, Rev. Mod. Phys. **74**, 11 (2002).
[5]Y. Wang, J. J. Wang, W. Y. Wang, Z. G. Mei, S. L. Shang, L. Q. Chen, and Z. K. Liu, J. Phys.: Condens. Matter **22**, 202201 (2010).
[6]W. G. Stirling, J. Phys. C **5**, 2711 (1972).
[7]N. Choudhury, E. J. Walter, A. I. Kolesnikov, and C. K. Loong, Phys. Rev. B **77**, 134111 (2008).
[8]Y. Xie, H. T. Yu, G. X. Zhang, and H. G. Fu, J. Phys.: Condens. Matter **20**, 215215 (2008).
[9]A. I. Lebedev, Phys. Solid State **51**, 362 (2009).
[10]J. G. Bednorz and K. A. Muller, Z. Phys. B Condens. Matter **64**, 189 (1986).
[11]J. Fontcuberta, B. Martinez, A. Seffar, S. Pinol J. L. GarciaMunoz, and X. Obradors, Phys. Rev. Lett. **76**, 1122 (1996).
[12]R. A. Cowley, Phys. Rev. **134**, A981 (1964).
[13]G. Shirane and Y. Yamada, Phys. Rev. **177**, 858 (1969).
[14]J. L. Servoin, Y. Luspin, and F. Gervais, Phys. Rev. B **22**, 5501 (1980).
[15]W. Cochran and R. A. Cowley, J. Phys. Chem. Solids **23**, 447 (1962).
[16]D. C. Wallace, *Thermodynamics of Crystals* (Wiley, New York, 1972).
[17]P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).
[18]G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[19]J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[20]M. Gajdoš, K. Hummer, G. Kresse, J. Furthmuller, and F. Bechstedt, Phys. Rev. B **73**, 045112 (2006).