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Polarization dependence of Born effective charge and dielectric constant in $KNbO_3$

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The Born effective charge Z^* and dielectric tensor ϵ_∞ of $KNbO_3$ are found to be very sensitive to the atomic geometry, changing by as much as 27% between the paraelectric cubic and ferroelectric tetragonal and rhombohedral phases. Subtracting the bare ionic contribution reveals changes of the dynamic component of Z^* as large as 50%, for atomic displacements that are typically only a few percent of the lattice constant. Z^*, ϵ_∞, and all phonon frequencies at the Brillouin zone center were calculated using the *ab initio* linearized augmented plane-wave linear response method with respect to the reference cubic, experimental tetragonal, and theoretically determined rhombohedral ground-state structures. The ground-state rhombohedral structure of $KNbO_3$ was determined by minimizing the forces on the relaxed atoms. In contrast to the cubic structure, all zone-center phonon modes of the rhombohedral structure are stable, and their frequencies are in good agreement with experiment. In the tetragonal phase, one of the soft zone-center modes in the cubic phase is stablized. In view of the small atomic displacements involved in the ferroelectric transitions, it is evident that not only the soft-mode frequencies but also the Born effective charge and dielectric constants are very sensitive to the atomic geometry. [S0163-1829(96)01939-X]

I. INTRODUCTION

Potassium niobate ($KNbO_3$) is one of the most studied members in the important class of perovskite structure ferroelectrics. Like $BaTiO_3$, $KNbO_3$ undergoes three successive ferroelectric phase transitions as the temperature is decreased.[1] It transforms from a cubic to a tetragonal phase at 701 K, to an orthorhombic phase at 488 K, and finally to a rhombohedral phase at 210 K. Despite decades of studies on these perovskite systems, there is still controversy as to the structure of the high-temperature phases and the related character of the phase transitions, with contradictory evidence for order-disorder[2] versus soft-mode[3] behavior. The phase transitions and macroscopic polarization are strongly sensitive to chemical compositions, defects, details of domain structure, and stresses, which complicates both theoretical and experimental studies. Nevertheless, considerable insight has been gained in the past few years into the microscopic mechanism for the ferroelectric instability from first-principles calculations, based on the local-density-functional theory.[4–9] Cohen and Krakauer[4] performed a series of total-energy calculations on $BaTiO_3$ and showed that the cubic phase is unstable against zone-center distortions. They also showed that hybridization between oxygen $2p$ and transition-metal titanium $3d$ electrons is an important feature in explaining the ferroelectric instabilities in $BaTiO_3$ and $PbTiO_3$.[5] King-Smith and Vanderbilt[7] carried out systematic total-energy calculations for zone-center distortions for eight perovskite oxides. Using an effective Hamiltonian constructed from first-principles calculations, Monte Carlo simulations for $BaTiO_3$ by Zhong, Vanderbilt, and Rabe[8] obtained the phase sequence, transition temperatures, latent heats, and spontaneous polarizations, which are in good agreement with experiments. With the use of a linear-response density-functional method, Yu, Krakauer, and Wang[9] obtained a complete mapping in the Brillouin zone of the structural instability for cubic $KNbO_3$, revealing a pronounced two-dimensional character, corresponding, in real space, to chains along the [1 0 0] directions of atoms coherently displaced along the chain direction.

In this paper, we determine the zero-temperature ground-state rhombohedral structure of $KNbO_3$ by minimizing the forces acting on the relaxed atoms. Results are then presented for linear-response calculations of zone-center phonon spectra, Born effective charges, and dielectric constants for the cubic, experimental tetragonal, and theoretical ground-state rhombohedral structures, demonstrating that not only the soft-mode frequencies but also the Born effective charges and dielectric constants are very sensitive to the atomic geometry.

II. METHODS

Total-energy and force calculations were performed within the local-density approximation (LDA), using the LAPW (linearized-augmented-plane-wave) method.[10] The ground state structure was determined by minimizing the forces[11] on the relaxed atoms. Phonon spectra, Born effective charge, and dielectric tensors were obtained with the recently developed LAPW linear-response method.[9,12,13] We refer the reader to Ref. 12 for details regarding this method. The dynamical matrix at a wave vector $\mathbf{q}$ is calculated from the first-order changes in the wave functions due to a phononlike perturbation $w_{i\alpha}(\mathbf{R}) = w_{i\alpha} e^{i\mathbf{q}\cdot\mathbf{R}}$, where $w_{i\alpha}(\mathbf{R})$ indicates the Cartesian α component of the displacement of atom i in the unit cell specified by the direct lattice vector $\mathbf{R}$; the phonon

TABLE I. Ground-state structures determined by calculations and experiment for $KNbO_3$. The displacements δ are in unit of the lattice constant of the cubic structure. The energy difference (E_g-E_c) is in mRy.

k-point set	δ_K	δ_I	δ_{II}	(E_g-E_c)
(4 4 4)	0.008	0.023	0.021	-0.63
(6 6 6)	0.009	0.026	0.025	-1.86
(8 8 8)	0.010	0.026	0.025	-1.99
LMTO	~0.018[a]	~0.018[a]	~0.018[a]	~ -1.0[a]
	~0.026[b]	~0.027[b]	~0.027[b]	~ -3.0[b]
Expt.[c]	0.0130 ± 81	0.0333 ± 15	0.0301 ± 9	

[a] Estimated from Postnikov, Neumann, and Borstel's calculations at lattice constant $a=3.93$ Å (Ref. 22).

[b] Estimated from Postnikov, Neumann, and Borstel's calculations at lattice constant $a=4.00$ Å (Ref. 22).

[c] Measurement for the rhombohedral phase at $T=230$ K by Hewat (Ref. 21).

frequencies are then obtained by standard matrix diagonalization. The Born effective charge and dielectric tensors are obtained in the long-wavelength limit as

$$\hat{\mathbf{q}}\cdot\epsilon_\infty\cdot\hat{\mathbf{q}}=\lim_{\mathbf{q}\to\mathbf{0}}\left[1-\frac{V_{\mathrm{ind}}(\mathbf{q})}{V_{\mathrm{total}}(\mathbf{q})}\right], \tag{1}$$

$$Z^*_{\alpha,\beta}(i)=Z_i+\Omega\left.\frac{\partial P_\alpha}{\partial\omega_{i\beta}}\right|_{\mathbf{E}=\mathbf{0}}, \tag{2}$$

where $\hat{\mathbf{q}}$ is the unit vector in the direction of the wave vector, V_{ind} is the induced potential when the macroscopic field is applied, Z_i is the bare ionic charge of the ith ion, Ω is the volume of the unit cell, and P_α is the Cartesian α component of the macroscopic electronic polarization under the phonon-like perturbation while constraining the macroscopic electric field to be zero. We calculated the Born effective charge and dielectric tensors at very small values of $q\sim 0.01\ 2\pi/a$, where a is the lattice constant. Kerker-type pseudopotentials[14] were used to bypass the need to treat the chemically inert localized inner core states. The shallow semicore states K(3s) and Nb(4s,4p) were pseudized and included in a lower-energy window of a two-window variational calculation. The Wigner interpolation formula[15] was used for the exchange-correlation potential. A uniform (6 6 6) k-point set[16] was used in most calculations to sample the Brillouin zone (BZ) integration, yielding ten special-k points in the irreducible BZ wedge for the cubic structure, 18 special-k points for the tetragonal structure, and 28 special-k points for the rhombohedral structure. The muffin-tin radii were chosen as 2.50 a.u. (atomic units) for K, 1.92 a.u. for Nb, and 1.58 a.u. for O. The kinetic-energy cutoff was 22.5 Ry, yielding approximately 810 LAPW basis functions at each k point.

For cubic $KNbO_3$, we obtained the theoretical equilibrium lattice constant $a_0=4.00$ Å, with bulk modulus $B_0=194$ GPa, and pressure derivative, $B_0'=4.3$, by fitting the LAPW total-energy calculations to the Birch-Murnaghan equation of state.[17] This lattice constant is only 0.4% smaller than the experimental value 4.016 Å.[1] The change in total energy due to ferroelectric distortions is very sensitive to volume,[4,6] so despite this small difference the experimental lattice constant was used in all the calculations described below. Our lattice constant is slightly larger than previous LDA calculations.[7,18] This difference is probably due to the use of different forms for exchange-correlation potential. As also seen in other systems,[19,20] the Wigner form tends to yield slightly larger equilibrium lattice constants than other forms, and as expected the bulk modulus is accordingly slightly smaller.

III. GROUND-STATE STRUCTURE

To determine the lowest-energy geometry, the atomic positions were relaxed, minimizing the forces on all atoms while constraining the system to have at least rhombohedral symmetry. This was done using a cubic unit cell, based on the experimental observation that the rhombohedral strains are extremely small [the sheer strain angle is merely 11′ (Ref. 21)]. We checked that distorting the cubic cell with the experimentally observed rhombohedral strain results in only slightly larger residual forces on the atoms, indicating that the strain has little effect on the relative atomic displacements.

In units of the lattice constant (4.016 Å), the atomic positions in the reference cubic perovskite structure were taken as (0.5, 0.5, 0.5) for K, (0, 0, 0) for Nb, and (0.5, 0, 0), (0, 0.5, 0), and (0, 0, 0.5) for the three O atoms O_1, O_2, and O_3, respectively. Without any loss of generality, the Nb atom was chosen as a fixed reference point, with respect to which the K atom was displaced to $(0.5+\delta_K,\ 0.5+\delta_K,\ 0.5+\delta_K)$ and the oxygen atoms to $(0.5+\delta_I,\ \delta_{II},\ \delta_{II})$ and symmetric permutations, where δ_K, δ_I, and δ_{II} are three independent parameters. The process of structural optimization was terminated when the maximum residual force was less than ~0.3 m Ry/a.u., i.e., 8 meV/Å.

Table I presents our results for ground state structures with three different k-point sets. The energy difference between the ground and cubic states are also shown. Previous LDA calculations with the LMTO (linearized-muffin-tin-orbitals) method[22] and experimental measurements are also included for comparison. Table I reveals that the structural parameters are essentially converged using a (6 6 6) k-point set. Use of the (6 6 6) set increases the difference between the rhombohedral ground state and the ideal cubic structure energy, (E_g-E_c), by 200% compared with (4 4 4) set. Increasing the BZ sampling to an (8 8 8) set changes the energy difference by just 7% compared with the (6 6 6) set, suggesting that the (6 6 6) set would be adequate in many calculations. This is confirmed by the fact that the ground-state structural parameters determined with (6 6 6) and (8 8 8) sets exhibit little difference. Negative values of $(E_g - E_c)$ mean that the cubic structure is unstable against zone-center distortions.

It should be emphasized that the ground-state structure is not simply a displacement of the Nb atoms against the rigid sublattices of K and O. The relaxation of these sublattices significantly affects the stability of the rhombohedral structure. For example, with the use of the (8 8 8) k-point set, moving the Nb atom from the origin to (0.025, 0.025, 0.025) (in units of the lattice constant), while keeping other atoms fixed, causes the total energy of the system to decrease, but only by 0.45 m Ry. Relaxing the K- and O-atom sublattices causes the energy to decrease by 1.99 m Ry. Thus the displacement of the Nb sublattice against the rigid lattice of all the other atoms is not the lowest energy configuration. This conclusion contradicts the results of Postnikov, Neumann, and Porstal.[22] As shown in Table I, Postnikov, Neumann, and Porstel determined the ground-state structure of $KNbO_3$ at two lattice parameters, 3.93 and 4.00 Å, using the LMTO method.[22] In both cases, they find K-atom displacements that are essentially the same as rigid oxygen octahedron displacements ($\delta_K \approx \delta_I = \delta_{II}$), which means that the ground-state structure corresponds to an essentially pure distortion of the Nb sublattice against the rigid lattice of all the other atoms. This result is strikingly different from our calculations. This discrepancy cannot be fully ascribed to the approximation of rigid oxygen octahedra used in their calculations, since we find that the distortion of the oxygen octahedra (i.e., the difference between δ_I and δ_{II}) is small. Furthermore, their calculated zone-center phonon eigenvectors for the cubic structure with the same method are quite different from the results of our calculations and other's (see discussion in V). Table I also lists experimental values, with the measured displacements δ_K, δ_I, and δ_{II},[21] all about 20% larger than our calculations. This level of agreement is satisfactory, given the sensitive dependence of atomic positions on the volume.

IV. CALCULATIONS FOR Z^* AND ϵ_∞

The Born effective charge tensor Z^* characterizes the influence of long-range Coulomb interactions on the vibrational and optical properties of ionic insulators. First-principles calculations of these charges in perovskite ferroelectrics have become available only very recently.[9,23–25] Here we report on calculations of Z^* and ϵ_∞, the electronic component of the static dielectric constant, for the theoretical ground-state rhombohedral structure and experimental tetragonal structure[26] of $KNbO_3$. Cubic phases Z^* were previously reported.[9] We find that the eigenvalues of these tensors are quite different from their counterparts in the cubic structure. To ensure the reliability of the comparison, we recalculated these quantities for the cubic structure with the denser k-point sampling in the BZ, i.e., the (6 6 6) set that is used for rhombohedral and tetragonal structures. We have examined the convergence of the Born effective charges with respect to k-point sampling. The (6 6 6) set reduces the violation of the acoustic sum rule by an order of magnitude compared with the (4 4 4) set.[9] Specifically, with the use of the (6 6 6) k-point set, $\Sigma_i Z^*(i)$ is reduced from 0.35 using the (4 4 4) set to 0.03 for the cubic structure; for the rhombohedral structure, the diagonal and off-diagonal terms are reduced from 0.11 and 0.56 to -0.07 and 0.02, respectively. For the tetragonal structure, the three diagonal terms of $\Sigma_i Z^*(i)$ are -0.02, -0.02, and 0.07 with the use of the (6 6 6) k-point set. This level of convergence is comparable to that obtained in simple semiconductors.[19] The errors due to the use of a small but finite wave vector were checked and found to be negligible. For example, in the calculations of Z^* in the experimental tetragonal structure, the use of a smaller wave vector $\mathbf{q}=(0,\,0,\,0.002)2\pi/c$ yields the $\hat{z}$ component of $Z^*(O_3)$ to be -5.350, very close to -5.348, the value obtained with $\mathbf{q}=(0,\,0,\,0.01)2\pi/c$.

In the cubic structure, the Born effective charge tensors Z^*(K) and Z^*(Nb) are both isotropic due to the high site symmetry. At the O sites, however, there exist two inequivalent directions: one along the Nb-O bond and the other perpendicular to this bond, denoted by $\parallel$ and $\perp$, respectively. Thus Z^*(O) is diagonal but with two distinct values, $Z^*(\mathrm{O})_\parallel$ and $Z^*(\mathrm{O})_\perp$. In the tetragonal structure, all Born effective charge tensors are diagonal, and Z^* of K, Nb, and O_3 each have two distinct values, whereas Z^* of the equivalent O_1 and O_2 atoms have three distinct values. In the rhombohedral phase, the Born effective charge tensors no longer have a simple diagonal form due to the lower symmetry, and we have found

$$Z^*(\mathrm{K}) = \begin{pmatrix} 1.14 & -0.01 & -0.01 \\ -0.01 & 1.14 & -0.01 \\ -0.01 & -0.01 & 1.14 \end{pmatrix}, \tag{3}$$

$$Z^*(\mathrm{Nb}) = \begin{pmatrix} 8.16 & -0.35 & -0.35 \\ -0.35 & 8.16 & -0.35 \\ -0.35 & -0.35 & 8.16 \end{pmatrix}, \tag{4}$$

and

$$Z^*(\mathrm{O}_1) = \begin{pmatrix} -6.27 & 0.14 & 0.14 \\ 0.24 & -1.55 & 0.00 \\ 0.24 & 0.00 & -1.55 \end{pmatrix}. \tag{5}$$

For purpose of comparison, it is convenient to focus on the eigenvalues of these tensors, presented in Table II. The Berry phase calculations for the cubic structure[24] and the tetragonal structure[23,24] are also included for comparison.

There is no requirement that the Born effective charge tensor be symmetric, because it is a mixed second derivative of the total energy, $\mathcal{E}_{\mathrm{total}}$, with respect to macroscopic electric-field component E_α and atomic displacement component $\tau_{i,\beta}$: $Z^*(i) = \partial^2 \mathcal{E}_{\mathrm{total}} / \partial E_\alpha \partial \tau_{i,\beta}$. Thus the Born effective charge can either be regarded as the derivative of the polarization with respect to atomic displacement at zero macroscopic field, or as the derivative of the force on an atom with respect to the macroscopic field at zero atomic

TABLE II. Eigenvalues of Born effective charge tensors for $KNbO_3$ in the cubic, experimental tetragonal, and theoretical ground-state rhombohedral structures. $Z^*(O_1)$ is presented as representative of the three equivalent oxygen atoms in the rhombohedral structure. In the experimental tetragonal structure, we show only the eigenvalues of $Z^*(O_1)$ and $Z^*(O_3)$, since O_2 is equivalent to O_1 by symmetry. The eigenvectors for $Z^*(K)$ and $Z^*(Nb)$ of tetragonal and rhombohedral structures are shown as subscripts (see text).

	Present Cubic	Present Tetragonal	Present Rhombohedral	PW-BP[a] Cubic	PW-BP[a] Tetragonal[b]	LAPW-BP[c] Tetragonal
$Z^*(K)$	1.12	$1.12_{[100]}$	$1.16_{[1\bar{1}0]}$	1.14		
	1.12	$1.12_{[010]}$	$1.16_{[11\bar{2}]}$	1.14		
	1.12	$1.17_{[001]}$	$1.13_{[111]}$	1.14	$1.14_{[001]}$	$0.82_{[001]}$
$Z^*(Nb)$	9.67	$9.17_{[100]}$	$8.51_{[1\bar{1}0]}$	9.23		
	9.67	$9.17_{[010]}$	$8.51_{[11\bar{2}]}$	9.23		
	9.67	$7.05_{[001]}$	$7.47_{[111]}$	9.23	$9.36_{[001]}$	$9.13_{[001]}$
$Z^*(O)_{\parallel}$	-7.28	-6.99(O_1) -5.35(O_3)	-6.28(O_1)	-7.01	-7.10(O_3)	-6.58(O_3)
$Z^*(O)_{\perp}$	-1.74	-1.77(O_1) -1.55(O_3)	-1.54(O_1)	-1.68	-1.70(O_1)	-1.68(O_1)
	-1.74	-1.40(O_1) -1.55(O_3)	-1.55(O_1)	-1.68	-1.70(O_1)	-1.68(O_1)

[a] Plane wave-Berry phase calculation by Zhong, King-Smith, and Vanderbilt (Ref. 24).

[b] Note an ideal tetragonal structure (without observed internal strains) was used (private communication with Zhong and Vanderbilt).

[c] LAPW Berry phase calculation by Resta *et al.* (Ref. 23).

displacement. The Born effective charge tensors for K and Nb in the rhombohedral structure are symmetric, and the macroscopic polarization direction [1 1 1] is an obvious principal axis, with corresponding eigenvalues of $Z^*(K)=1.13$ and $Z^*(Nb)=7.47$, respectively. The other two perpendicular eigenvectors with degenerate eigenvalues may be chosen as [1 1 0] and [1 1 2]. For the three equivalent oxygen atoms, the three eigenvectors of the Born effective charge tensors are no longer perpendicular to each other since the tensors are no longer symmetric. For example, for the O_1 atom at $(0.5+\delta_I, \delta_{II}, \delta_{II})$ in the rhombohedral structure, [0 1 1] is an eigenvector direction and the corresponding eigenvalue is $Z^*(O_1)=$ -1.55, as shown in Table II, but the other two eigenvectors cannot be determined by symmetry alone and depend on the details of interactions in the material. Nevertheless, we still use $Z^*(O)_{\parallel}$ and $Z^*(O)_{\perp}$ to denote the eigenvalues for convenience, although the corresponding eigenvectors deviate slightly from their counterparts in the cubic structure.

All LDA calculations in Table II show unusually large Born effective charges $Z^*(Nb)$ and $Z^*(O)_{\parallel}$. These values are by far larger than their corresponding nominal ionic charges $+5$ and -2, revealing large dynamic charge transfers along the Nb-O bond as the length of the bond is varied. These large Born effective charges result from the strong covalent interactions between the transition metal and the oxygen atoms in these materials.[4] This has been demonstrated recently by Posternak, Resta, and Baldereschi,[27] who observed that the unusually large Born effective charges are reduced to their nominal values when the covalence between Nb 4*d* and O 2*p* orbitals is artificially suppressed. These large Born effective charges give rise to strong long-range ionic interactions, which favor the ferroelectric instability.[4] It is not surprising, therefore, that ferroelectricity is sensitive to the size and formation of domains as well as electric boundary conditions.

Our calculations show that the eigenvalues of the Born effective charge tensors, especially $Z^*(O)_{\parallel}$ and the component of $Z^*(Nb)$ along the macroscopic polarization direction, are quite sensitive to the changes in atomic geometry. The atomic displacements involved in the transformation from the cubic to the tetragonal and ground-state rhombohedral structures are rather small, typically only a few percent of the lattice constant. Nevertheless, the values of $Z^*(Nb)$ and $Z^*(O)_{\parallel}$ are reduced by up to 23% in the rhombohedral structure and by about 27% in the tetragonal structure. Subtracting the bare ionic charges associated with the atoms ($+5$ for Nb and -2 for O) shows that the change of the dynamic charge component of Z^* can be as large as 50%. This sensitivity originates from the strong dependence[27] of the Nb 4*d* and O 2*p* hybridization on the ferroelectric distortion, which changes the Nb-O bond length and site symmetry of atoms in crystal. As shown in Table II, Zhong *et al.*'s Berry phase calculations agree with our results within a few percent for the cubic structure. It should be noted that in their calculation for the tetragonal phase,[24] they used an ideal tetragonal structure with experimental lattice constants but without observed internal strains. Resta *et al.*[23] extracted Born effective charges for the tetragonal phase from the finite differences of polarization and argued that the Born effective charges are approximately independent of the atomic displacements and that the macroscopic polarization is therefore linear with the internal strain. Our results differ from this. We find that the Born effective charges depend strongly on the structural details. Recently Ghosez *et al.*[25] calculated the Born effective charge tensors for different phases of

TABLE III. Eigenvalues of calculated dielectric tensors ϵ_∞ of $KNbO_3$ in the cubic, experimental tetragonal, and theoretical ground-state rhombohedral structures.

cubic	6.63	6.63	6.63
tetragonal	$6.28_{[100]}$	$6.28_{[010]}$	$5.07_{[001]}$
rhombohedral	$5.93_{[1\bar{1}0]}$	$5.93_{[11\bar{2}]}$	$5.49_{[111]}$

TABLE IV. Calculated zone-center optic-phonon frequencies (cm^{-1}) in cubic $KNbO_3$.

Mode	Present	LAPW[c]	LMTO[d]	PW[e]	Experiment[f]
TO_1	197*i*	115*i*	203*i*	143*i*	soft
TO_2	170	168	193	188	198
TO_3	473	483	483	506	521
TO_4	243	266	234		280[g]
LO_1	393[a] 403[b]			407[b]	418
LO_2	167[a] 167[b]			183[b]	190
LO_3	757[a] 888[b]			899[b]	826

[a] Obtained with calculated $\epsilon_\infty = 6.63$.

[b] Obtained with $\epsilon_\infty = 4.69$, extracted (Ref. 24) from experiment.

[c] LAPW frozen-phonon calculations by Singh and Boyer (Ref. 6).

[d] LMTO frozen-phonon calculations by Postnikov, Neumann, and Borstel (Ref. 29).

[e] Plane-wave frozen-phonon calculations by Zhong, King-Smith, and Vanderbilt (Ref. 24).

[f] Infrared reflectivity spectroscopy at 710 K by Fontana *et al.* (Ref. 1).

[g] Measured in the tetragonal phase, $T = 585$ K.

$BaTiO_3$, and found that they are also strongly dependent on the atomic positions, in agreement with the present calculations for $KNbO_3$.

In the absence of macroscopic strain, symmetry requires that the changes in the Born effective charge are even functions of the amplitude of the internal displacements, when expanded about the cubic structure. In the absence of internal displacements, the volume dependence and macroscopic strain, which are important in minimizing the total energy, are found to have little influence on the Born effective charges. Reducing the lattice constant by 0.47% in the cubic structure (from 4.016 to 3.997 Å), Z^*(Nb) decreases by only 0.85%. The effect of a pure tetragonal strain is examined in a calculation in which $a = b =$ 3.997 Å, and all atoms are kept at their ideal positions, i.e., there are no internal strains. For c/a ratios of 0.9835, 1.0, and 1.0165 (the last being the strain in the observed tetragonal structure), the values of the z component of Z^*(Nb) are 9.626, 9.586, and 9.556, respectively, with the overall change being only 0.7%. Thus the variation of the Born effective charges between different atomic geometries reported above are almost entirely due to the internal strains.

The polarization change is defined as

$$\Delta\mathbf{P} = \mathbf{P}(\tau) - \mathbf{P}(0) = \sum_i \int_0^\tau \frac{e}{\Omega} Z^*(i,u)\,du, \tag{6}$$

where u is a symbolic parameter characterizing the structure, and 0 and τ correspond to the starting and ending structures; i is the atomic index and Ω is the volume of unit cell. In order to estimate the integral in Eq. (6), we consider two approximations to estimate the range of macroscopic polarization for the experimental tetragonal structure. This is done by ignoring the u dependence of Born effective charge tensors and instead using our calculated values of Z^* for (i) the cubic structure, and (ii) the tetragonal structure, yielding two different values of $\Delta\mathbf{P}$, 0.44 and 0.33 C/m^2, respectively. The measured value is 0.37 C/m^2,[28] close to the average of the two estimates above. The large difference between the two estimated values demonstrates that the ferroelectricity is essentially a nonlinear phenomenon.

We have calculated the dielectric tensors ϵ_∞ for the cubic, experimental tetragonal, and theoretical ground-state rhombohedral structures and presented the eigenvalues in Table III. The cubic structure has an isotropic dielectric tensor, $\epsilon_\infty = 6.63$. The tetragonal structure has a diagonal dielectric tensor, and the eigenvalue in the direction of polarization [001] is 5.07, about a 24% reduction from the cubic phase. For the rhombohedral structure, the dielectric tensor has a symmetric form and $\epsilon_{\infty,11} = \epsilon_{\infty,22} = \epsilon_{\infty,33} = 5.79$ and $\epsilon_{\infty,12} = \epsilon_{\infty,13} = \epsilon_{\infty,23} = -0.15$. The three eigenvalues are 5.93, 5.93, and 5.49, with eigenvectors along $[1\,\bar{1}\,0]$, $[1\,1\,\bar{2}]$, and [1 1 1], respectively. Compared to the cubic phase, the largest reduction of eigenvalues is 17%, also along the direction of polarization. Both the tetragonal and rhombohedral cases show that the dielectric tensors also strongly depend on atomic geometry.

V. ZONE-CENTER PHONON CALCULATIONS

Due to the lower symmetry of the reference rhombohedral and tetragonal structures, the linear-response calculations take significantly longer compared to similar calculations using the cubic phase as the reference structure. For each phonon wave vector $\mathbf{q}$, the first-order change in the wave functions must be calculated at many more k points in the Brillouin zone due to the lower symmetry. For this reason, we have limited our calculations of the dynamical matrix in the rhombohedral and tetragonal phases to the zone center, $\mathbf{q} = \mathbf{0}$. Table IV compares our zone-center phonon frequencies of the cubic structure with the frozen phonon LAPW calculations of Singh and Boyer,[6] plane-wave pseudopotential calculations of Zhong, King-Smith, and Vanderbilt,[24] and LMTO calculations of Postnikov, Neumann, and Borstel.[29] In the cubic phase the 12 optical phonons at $\mathbf{q} = \mathbf{0}$ are classified as three F_{1u} and one F_{2u} modes, each of which is triply degenerate. The F_{2u} mode is labeled 4, whereas the other three F_{1u} modes are labeled 1, 2, and 3 in order of increasing frequency. All the calculations find unstable TO modes at the zone center with similar imaginary frequencies corresponding to the observed soft mode. The longitudinal-optic (LO)-phonon frequencies were obtained from a dynamical matrix which is a combination of a zone-center dynamical matrix without macroscopic field, D^{TO}, and a term arising from the long-range Coulomb interaction

TABLE V. Calculated eigenvectors of the zone-center optic-phonon modes in cubic $KNbO_3$. O_1, O_2, and O_3 refer to oxygen atoms at $(0.5, 0, 0)a$, $(0, 0.5, 0)a$, and $(0, 0, 0.5)a$, respectively. Note that we have chosen the representative modes in which the atoms move in the $\hat{z}$ direction.

Modes	Frequency (cm^{-1})	K	Nb	O_1	O_2	O_3
TO_1	$197i$	0.01	-0.59	0.42	0.42	0.55
TO_2	170	0.88	-0.37	-0.18	-0.18	-0.15
TO_3	473	0.02	-0.08	0.46	0.46	-0.76
TO_4	243	0	0	1	-1	0
LO_1	393	-0.06	-0.38	0.63	0.63	-0.23
LO_2	167	0.88	-0.45	-0.11	-0.11	-0.09
LO_3	757	0.09	0.37	-0.06	-0.06	-0.92

TABLE VI. Relative atomic displacements in the soft TO_1 mode of cubic $KNbO_3$. Note that the K atom is taken as the reference point and the magnitude of the displacement of the Nb atom is taken as the displacement unit. The experimental values are extracted from the observed tetragonal structure. See text.

	K	Nb	O_1	O_2	O_3
Present	0	-1	1.6	1.6	2.2
LAPW[a]	0	-1	1.4	1.4	1.9
PW[b]	0	-1	1.5	1.5	2.0
LMTO[c]	0	-1	0.18	0.18	0.67
Experiment	0	-1	1.1	1.1	1.3

[a] LAPW frozen-phonon calculation by Singh and Boyer (Ref. 6).
[b] Plane-wave frozen-phonon calculation (Ref. 30).
[c] LMTO frozen-phonon calculation (Ref. 29).

$$D^{LO}_{i\alpha,j\beta}=D^{TO}_{i\alpha,j\beta}+\frac{4\pi e^2}{\Omega\sqrt{M_iM_j}}\frac{(\mathbf{q}\cdot\mathbf{Z}^*(i))_\alpha(\mathbf{q}\cdot\mathbf{Z}^*(j))_\beta}{\mathbf{q}\cdot\epsilon_\infty\cdot\mathbf{q}}, \quad (7)$$

where M_i and $\mathbf{Z}^*(i)$ are the mass and Born effective charge tensor of atom i, ϵ_∞ is the dielectric tensor, Ω is the volume of unit cell, and α and β are Cartesian indices. This partitioning of the dynamical matrix is necessary precisely at the zone center, $\mathbf{q}=\mathbf{0}$, because the distinction between transverse and longitudinal modes becomes delicate. At finite wave vectors, we can directly calculate the full dynamical matrix from the first-order forces on the atoms. Frequencies calculated this way for very small wave vectors $q \sim 0.01\ 2\pi/a$ agree with Eq. (7), showing the internal consistency of our linear response calculations. All LO modes are stable due to the contribution of the macroscopic field. The TO_4 mode with frequency 243 cm^{-1} is both Raman and infrared inactive, and thus does not exhibit LO-TO splitting. Zhong, King-Smith, and Vanderbilt obtained their LO frequencies by using $\epsilon_\infty=4.69$, extracted from experiment, whereas we used both $\epsilon_\infty=4.69$ and our larger calculated dielectric constant $\epsilon_\infty=6.63$. The highest LO_3 frequency increases by 131 cm^{-1} when the smaller dielectric constant $\epsilon_\infty=4.69$ is used. Compared to our previous results with the (4 4 4) k-point set,[9] the soft-mode frequencies are found to be more unstable by about $50i$ cm^{-1}, consistent with the observation in Table I that the (6 6 6) k-point set yields a deeper well depth. The other modes are relatively unaffected.

We present the eigenvectors of zone center optic phonon modes in the cubic structure in Table V. Note that the eigenvectors are the actual displacements weighted by the square root of the atomic mass. The basic features of the TO-phonon eigenvectors are as follows. In the soft TO_1 mode, Nb vibrates against three oxygen atoms with K essentially unmoved. In the TO_2 mode, K vibrates against all of the other atoms. The TO_3 mode is dominated by the vibration of one O atom against the other two O atoms, whereas Nb and K atoms oscillate with only slight amplitudes. In the TO_4 mode, K and Nb are exactly at rest, and the oscillations involve only O atoms. When the TO_4 mode is viewed along the $\hat{z}$ direction as shown in Table V, the O_1 at $(0.5a, 0, 0)$ and O_2 at $(0, 0.5a, 0)$ move with the same amplitudes but in opposite directions, and O_3 at $(0, 0, 0.5a)$ is undisplaced. This mode has no instantaneous dipole moment, so the TO_4 phonon is infrared inactive. LO and TO modes have quite different eigenvectors, as previously noted by Zhong, King-Smith, and Vanderbilt.[24] The correlation between the infrared active modes may be characterized by the eigenvector overlap matrix $A_{ij} = \langle u_i^{TO}|u_j^{LO}\rangle$, and we have

$$A=\begin{pmatrix} 0.63 & 0.13 & 0.77 \\ 0.10 & 0.99 & 0.10 \\ 0.78 & 0.02 & 0.62 \end{pmatrix}. \quad (8)$$

Matrix A indicates that there exists no one-to-one correspondence between the TO and LO modes in the perovskite ferroelectrics, and that the soft TO_1 mode is most closely coupled with the highest-frequency mode LO_3.[24]

Our zone-center optical-phonon modes agree well with the LAPW frozen-phonon calculations by Singh and Boyer,[6] but differ significantly from those by Postnikov, Neumann, and Borstel[29] using the LMTO method. One of the striking differences lies in the eigenvectors of the soft TO_1 modes. We observed that K is essentially unmoved in the soft modes, while Postnikov, Neumann, and Borstel[29] observed that the K atom tends to move with the oxygen octahedron. Table VI displays the relative atomic displacements in the soft mode from LDA calculations, as well as the experimental values from the observed tetragonal structure. Frozen-phonon calculations of the soft TO_1 mode with both LAPW (Ref. 6) and plane-wave methods[30] yield results similar to the present linear-response results; the minor differences may be due in part to the the use of small but finite distortions in the frozen-phonon calculations to extract the dynamical matrix. Due to the anharmonic interactions, the observed atomic displacements in the tetragonal structure cannot strictly correspond to the soft-phonon TO_1 mode in the cubic phase. This accounts in part for the difference between the LDA eigenvectors and the experimental values extracted from the observed tetragonal structure.

TABLE VII. Calculated zone-center phonon frequencies of tetragonal KNbO$_3$. Note that in all A and B modes, atoms move in the $\hat{z}$ direction, i.e., [0 0 1].

Mode	Frequency (cm^{-1})		
	Present	Expt.[a]	Expt.[b]
TO$_1$ E	134i	soft	soft
A	306	295	280
TO$_2$ E	174	199	190
A	171	190	200
TO$_3$ E	479	518	590
A	613	600	600
TO$_4$ E	253	280	285
B	262		290
LO$_1$ [100]	391	418	
[001]	401	423	430
LO$_2$ [100]	171	191	185[c]
[001]	178	192	
LO$_3$ [100]	764	822	835
[001]	834	835	840
LO$_4$ [100]	253	279	285[c]
[001]	262		290

[a] Infrared reflectivity spectroscopy at 585 K by Fontana *et al.* (Ref. 1).

[b] Roman scattering measurement at 543 K by Fontana *et al.* (Ref. 31).

[c] Measured in the [110] direction.

We also performed zone-center phonon calculations for the experimental tetragonal structure. The phonon frequencies are presented in Table VII. In the tetragonal phase, each triply degenerate F_{1u} phonon in the cubic phase splits into A_1+E modes, and the F_{2u} mode splits into B_1+E modes, where the doubly degenerate E modes are polarized in [1 0 0] and [0 1 0] axes, and the A_1 and B_1 modes are polarized along the [0 0 1] direction. Compared to the cubic phase, one of the TO$_1$ modes (TO$_1$-A_1) is stablized due to the tetragonal distortions, resulting in large spatial anisotropy among the three TO$_1$ components. Again we used Eq. (7) and the calculated Born effective charge and dielectric tensors to obtain the frequencies of LO modes. Since the LO frequencies are no longer isotropic, we display the calculated values in two different directions, [0 0 1] and [1 0 0], to present the magnitude of this effect. Except for the soft mode, the calculated frequencies are in good agreement with the measurements.

The linear-response calculations for the zone center phonon modes of the theoretical ground state rhombohedral structure are presented in Table VIII. The most notable feature is that there are no unstable modes in the rhombohedral phase. In fact none of the modes is especially soft either. This is consistent with the observed ground-state structure of KNbO$_3$. It is also consistent with the disappearance of two-dimensional x-ray diffuse intensities in the rhombohedral phase.[32] As in the tetragonal phase, the LO frequencies depend on the direction along which they are measured, and LO frequencies along two directions, [1 1 1] and [1 $\bar{1}$ 0], are displayed. The experimental frequencies shown in Table VIII are from quasi-mode Raman scattering in the rhombohedral phase.[33] Nevertheless, they are in reasonable agreement with our calculations. The eigenvectors of the TO$_1$ modes with frequencies 208 and 237 cm^{-1} in Table VIII correspond most closely to the unstable phonon modes in the cubic structure.

TABLE VIII. Calculated zone-center optic-phonon frequencies (cm^{-1}) for the theoretical ground-state rhombohedral KNbO$_3$ structure. Note that the listed experimental frequencies are from quasimode Raman scattering in the rhombohedral phase.

Mode	Present	Experiment[a b]
TO$_1$$E$	208	220
A$_1$	237	265
TO$_2$ E	170	198
A$_1$	176	198
TO$_3$ E	519	536
A$_1$	570	602
TO$_4$ E	265	301
A$_2$	238	301
LO$_1$ [111]	404	423
[1$\bar{1}$0]	389	
LO$_2$ [111]	177	198
[1$\bar{1}$0]	172	
LO$_3$ [111]	794	837
[1$\bar{1}$0]	803	
LO$_4$ [111]	265	301
[1$\bar{1}$0]	265	

[a] Fontana *et al.*, Ref. 1.

[b] Kugel *et al.*, Ref. 33.

VI. SUMMARY

By minimizing the forces acting on the relaxed atoms, we have determined the ground-state rhombohedral structure of KNbO$_3$, and the calculated atomic positions compare well with measurement. We find that all zone-center phonon modes in the rhombohedral structure are stable, and that their frequencies are in good agreement with experiment. In the tetragonal phase, one of the soft zone-center modes in the cubic phase is stablized. We have calculated the Born effective charge tensors for KNbO$_3$ in the cubic, experimental tetragonal, and theoretical ground-state rhombohedral structures. The Born effective charges are found to exhibit great sensitivity to the small atomic displacements in the ferroelectric phase transitions. The dielectric tensors are also calculated, revealing about a 20% reduction compared the cubic phase of the component in the direction of macroscopic polarization.

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