Polarization-Dependence of Born Effective Charge and Dielectric Constant in KNbO$_3$

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Abstract

The Born effective charge $Z^*$ and dielectric tensor $\epsilon_\infty$ 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. $Z^*$, $\epsilon_\infty$ 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. By contrast with 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 stabilized. 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.

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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. It transforms from the 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 versus soft-mode 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. Cohen and Krakauer 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 important feature in explaining the ferroelectric instabilities in BaTiO$_3$ and PbTiO$_3$. King-Smith and Vanderbilt 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 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 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 of linear response calculations of zone center phonon spectra, Born effective charges, and dielectric constants for the cubic, 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. The ground state structure was determined by minimizing the forces on the relaxed atoms. Phonon spectra, Born effective charge and dielectric tensors were obtained with the recently developed LAPW linear response method. We refer the reader to Ref. for details regarding this method. The dynamical matrix at a wavevector $\mathbf{q}$ is calculated from the first order changes in the wavefunctions due to a phonon-like perturbation, $w_{\alpha i}(\mathbf{R}) = w_{\alpha i} e^{i\mathbf{q} \cdot \mathbf{R}}$, where $w_{\alpha i}(\mathbf{R})$ indicates the Cartesian $\alpha$ component of the displacement of atom $i$ in the unit cell specified by the direct lattice vector $\mathbf{R}$; the phonon frequencies are then obtained by standard matrix diagonalization. The Born effective charge and dielectric tensors are obtained in the long wavelength limit as

$$\mathbf{q} \cdot \mathbf{\epsilon}_\infty \cdot \mathbf{q} = \lim_{\mathbf{q} \to 0} \left[ 1 - \frac{V_{\text{ind}}(\mathbf{q})}{V_{\text{total}}(\mathbf{q})} \right],$$

$$Z_{\alpha,\beta}^*(i) = Z_i + \Omega \frac{\partial P_\alpha}{\partial \omega_{i,\beta}} \bigg|_{E=0},$$

where $\mathbf{q}$ is the unit vector in the direction of wavevector, $V_{\text{ind}}$ is the induced potential when the macroscopic field is applied, $Z_i$ is the bare ionic charge of the $i$th ion, $\Omega$ is the volume of the unit cell, and $P_\alpha$ is the Cartesian $\alpha$ 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
\[ q \sim 0.01 \, 2\pi/a, \text{ where } a \text{ is the lattice constant.} \]

Kerker type pseudopotentials \cite{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 \cite{13} was used for the exchange-correlation potential. A uniform \((6 \, 6 \, 6)\) \(k\)-point set \cite{16} was used in most calculations to sample the Brillouin zone (BZ) integration, yielding 10 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 unit) 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, \(a_0=4.00\,\text{Å}\), with bulk modulus, \(B_0=194\,\text{GPa}\), and pressure derivative, \(B_0'=4.3\), by fitting the LAPW total energy calculations to the Birch-Murnaghan equation of state. \cite{17} This lattice constant is only 0.4\% smaller than the experimental value 4.016 \(\text{Å}\). \cite{1} The change in total energy due to ferroelectric distortions is very sensitive to volume \cite{1,2}, 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 \cite{7,18}. This difference is probably due to the use of different forms for exchange-correlation potential. As also seen in other systems \cite{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′ \cite{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 $\delta_K$, $\delta_I$ and $\delta_{II}$ are three independent parameters. The process of structural optimization was terminated when the maximum residual force was less than $\sim 0.3$ mRy/a.u., i.e. 8 meV/Å.

Table I presents our results of 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 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 (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 (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 mRy. Relaxing the K and O atoms sublattices
causes the energy to decrease by 1.99 mRy. 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 et al. As shown in Table I, Postnikov et al. determined the ground state structure of KNbO\textsubscript{3} at two lattice parameters, 3.93Å and 4.00Å, using the LMTO method. 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 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 \(\delta_I\) and \(\delta_{II}\)) 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 others (see discussion in V). Table I also lists experimental values, with the measured displacements \(\delta_K\), \(\delta_I\) and \(\delta_{II}\) 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 \(\epsilon_{\infty}\)**

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. Here we report on calculations of Z* and \(\epsilon_{\infty}\), the electronic component of the static dielectric constant, for the theoretical ground state rhombohedral structure and experimental tetragonal structure of KNbO\textsubscript{3}. Cubic phase Z* were previously reported. 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 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. Specifically, with the use of the \((6\ 6\ 6)\) \(k\)-point set, \(\sum_i Z^*(i)\) 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 \(\sum_i Z^*(i)\) 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 wavevector were checked and found to be negligible. For example, in the calculations of \(Z^*\) in the experimental tetragonal structure, the use of a smaller wavevector \(q=\left(0, 0, 0.002\right)2\pi/c\) yields the \(\hat{z}\)-component of \(Z^*(O_n)\) to be -5.350, very close to -5.348, the value obtained with \(q=\left(0, 0, 0.01\right)2\pi/c\).

In the cubic structure, the Born effective charge tensors \(Z^*(K)\) and \(Z^*(\text{Nb})\) 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, \(Z^*(O)\parallel\) and \(Z^*(O)\perp\). 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

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

\[
Z^*(\text{Nb}) = \begin{pmatrix}
8.16 & -0.35 & -0.35 \\
-0.35 & 8.16 & -0.35 \\
-0.35 & -0.35 & 8.16
\end{pmatrix}, \tag{4}
\]
\[
\begin{bmatrix}
-6.27 & 0.14 & 0.14 \\
0.24 & -1.55 & 0.00 \\
0.24 & 0.00 & -1.55 \\
\end{bmatrix}
\] \quad (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 \cite{24} and the experimental tetragonal structure \cite{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, \( E_{\text{total}} \), with respect to macroscopic electric field component, \( E_\alpha \), and atomic displacement component, \( \tau_{i,\beta} \): \( Z^*(i) = \partial^2 E_{\text{total}} / \partial E_\alpha \partial \tau_{i,\beta} \). 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 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 \( \bar{1} \) 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 \( \bar{1} \)] 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 of the 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 transition metal and the oxygen atoms in these materials. This has been demonstrated recently by Posternak, Resta, and Baldereschi, who observed that the unusually large Born effective charges are reduced to their nominal values when the covalence between Nb 4d and O 2p orbitals is artificially suppressed. These large Born effective charges give rise to strong long-range ionic interactions, which favor the ferroelectric instability. 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 $Z^\ast(O)_{\parallel}$ and the component of $Z^\ast(Nb)$ along 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 $Z^\ast(Nb)$ and $Z^\ast(O)_{\parallel}$ 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 $Z^\ast$ can be as large as 50%. This sensitivity originates from the strong dependence of the Nb 4d and O 2p 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, they used an ideal tetragonal structure with experimental lattice constants but without observed internal strains. Resta et al. 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 strongly depend on the structural details. Recently Ghosez et al. calculated the Born effective charge tensors for different phases of BaTiO3, 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 Å to 3.997 Å), $Z^\ast$(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 $Z^\ast$(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

$$\Delta P = P(\tau) - P(0) = \sum_{i} \int_{0}^{\tau} \frac{e}{\Omega} Z^\ast(i, u) du,$$

(6)

where $u$ is a symbolic parameter characterizing the structure and 0 and $\tau$ correspond to the starting and ending structures; $i$ is the atomic index and $\Omega$ 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 $Z^\ast$ for (i) the cubic structure, and (ii) the tetragonal structure, yielding two different values of $\Delta P$, 0.44 C/m$^2$ 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 $\epsilon_{\infty}$ for the cubic, experimental tetragonal, and theoretical ground state rhombohedral structures and presented the eigenvalues in Table II.
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 $[0 0 1]$ 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 wavevector $\mathbf{q}$, the first order change in the wavefunctions 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, $\mathbf{q}=0$. Table IV compares our zone center phonon frequencies of the cubic structure with the frozen phonon LAPW calculations of Singh and Boyer [3], planewave pseudopotential calculations of Zhong, King-Smith, and Vanderbilt [24], and LMTO calculations of Postnikov et al. [29].

In the cubic phase the twelve 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 labelled 4 whereas the other three $F_{1u}$ modes are labelled as 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:

\[
D_{ia,j\beta}^{LO} = D_{ia,j\beta}^{TO} + \frac{4\pi e^2}{\Omega \sqrt{M_i M_j}} (q \cdot Z^*(i))_\alpha (q \cdot Z^*(j))_\beta, \tag{7}
\]

where \(M_i\) and \(Z^*(i)\) are the mass and Born effective charge tensor of atom \(i\), \(\epsilon_\infty\) is the dielectric tensor, \(\Omega\) is the volume of unit cell, \(\alpha, \beta\) are Cartesian indices. This partitioning of the dynamical matrix is necessary precisely at the zone center, \(q=0\), because the distinction between transverse and longitudinal modes becomes delicate. At finite wavevectors, we can directly calculate the full dynamical matrix from the first order forces on the atoms. Frequencies calculated this way for very small wavevectors \(q \sim 0.01 \, 2\pi/a\) 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 \(\text{TO}_4\) mode with frequency \(243 \, \text{cm}^{-1}\) 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 \(\text{LO}_3\) frequency increases by \(131 \, \text{cm}^{-1}\) when the smaller dielectric constant \(\epsilon_\infty=4.69\) is used. Compared to our previous results with \((4\,4\,4)\) \(k\)-point set \([9]\), the soft mode frequencies is found to be more unstable by about \(50 \, \text{cm}^{-1}\), consistent with the observation in Table I that \((6\,6\,6)\) \(k\)-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 atomic mass. The basic features of the \(\text{TO}\) phonon eigenvectors are as follows. In the soft \(\text{TO}_1\) mode, Nb vibrates against three oxygen atoms with K essentially unmoved. In the \(\text{TO}_2\) mode, K vibrates against all of the other atoms. The \(\text{TO}_3\) 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 \(\text{TO}_4\) mode, K and Nb are exactly at rest, and the oscillations involve only O atoms. When the \(\text{TO}_4\) 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, 0.5$a$) 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 et al [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

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

The 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 et al. [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 et al. [29] observed that 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. Both frozen phonon calculations of the soft TO$_1$ mode with LAPW method [6] and plane wave method [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 tetragonal structure cannot strictly correspond to the soft phonon TO$_1$ mode in cubic phase. This accounts in part for the difference between the LDA eigenvectors and the experimental values extracted from the observed tetragonal structure.

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 stabilized 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 VII. 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 \cite{33}. 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 VII are from quasi-mode Raman scattering in the rhombohedral phase \cite{32}. Nevertheless, they are in reasonable agreement with our calculations. The eigenvectors of the $TO_1$ modes with frequencies 208 cm$^{-1}$ and 237 cm$^{-1}$ in Table VIII correspond most closely to the unstable phonon modes in the cubic structure.

**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 their frequencies are in good agreement with experiment. In the tetragonal phase, one of the soft zone center modes in the cubic phase is stabilized. 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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TABLES

TABLE I. Ground state structures determined by calculations and experiment for KNbO$_3$. The displacements $\delta$ are in unit of the lattice constant of the cubic structure. The energy difference $(E_g - E_c)$ is in mRy.

| $k$-point set | $\delta_K$ | $\delta_I$ | $\delta_{II}$ | $(E_g - E_c)$ |
|---------------|-----------|-----------|-------------|-------------|
| (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          | $\sim 0.018^a$ | $\sim 0.018^a$ | $\sim 0.018^a$ | $\sim -1.0^a$ |
|               | $\sim 0.026^b$ | $\sim 0.027^b$ | $\sim 0.027^b$ | $\sim -3.0^b$ |
| Expt.$^c$     | 0.0130 ± 81 | 0.0333 ± 15 | 0.0301 ± 9  |              |

$^a$ Estimated from Postnikov et al.’s calculations at lattice constant $a=3.93$ Å $^{22}$.

$^b$ Estimated from Postnikov et al.’s calculations at lattice constant $a=4.00$ Å $^{22}$.

$^c$ Measurement for the rhombohedral phase at $T= 230$ K by Hewat. $^{21}$
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 | Present | Present | PW-BP$^a$ | PW-BP$^a$ | LAPW-BP$^c$ |
|---------------|---------|---------|---------|-----------|-----------|-------------|
|               | Cubic   | Tetragonal | Rhombohedral | Cubic   | Tetragonal$^b$ | Tetragonal |
| $Z^*(K)$      | 1.12    | 1.12$_{[100]}$ | 1.16$_{[110]}$ | 1.14    | —          | —           |
|               | 1.12    | 1.12$_{[010]}$ | 1.16$_{[112]}$ | 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$_{[110]}$ | 9.23    | —          | —           |
|               | 9.67    | 9.17$_{[010]}$ | 8.51$_{[112]}$ | 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 et al. [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. [23].
TABLE III. Eigenvalues of calculated dielectric tensors $\epsilon_\infty$ of KNbO$_3$ in the cubic, experimental tetragonal, and theoretical ground state rhombohedral structures.

| Structure       | $\epsilon_\infty$ [001] | $\epsilon_\infty$ [100] | $\epsilon_\infty$ [010] |
|-----------------|--------------------------|--------------------------|--------------------------|
| cubic           | 6.63                     | 6.63                     | 6.63                     |
| tetragonal      | 6.28                      | 6.28                      | 5.07                      |
| rhombohedral    | 5.93                      | 5.93                      | 5.49                      |

TABLE IV. Calculated zone center optic phonon frequencies (cm$^{-1}$) in cubic KNbO$_3$.

| Mode  | Present | LAPW$^a$ | LMTO$^b$ | PW$^c$ | Experiment$^d$ |
|-------|---------|----------|----------|--------|----------------|
| 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      |        |                |
| 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 [24] from experiment.

$^a$ LAPW frozen phonon calculations by Singh et al. [6].

$^b$ LMTO frozen phonon calculations by Postnikov et al. [29].

$^c$ Planewave frozen phonon calculations by Zhong et al. [24].

$^d$ Infrared reflectivity spectroscopy at 710 K by Fontana et al. [1].

$^e$ Measured in the tetragonal phase, $T = 585$ K.
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$_1$ | 197$i$              | 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$^d$ | 0  | -1 | 1.1   | 1.1   | 1.3   |

$^a$ LAPW frozen phonon calculation by Singh and Boyer [6].

$^b$ Plane wave frozen phonon calculation [30].

$^c$ LMTO frozen phonon calculation [28].
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. [1]

$^b$ Roman scattering measurement at 543 K by Fontana et al. [31]

$^c$ Measured in [110] direction.
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 quasi-mode 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                |
| [110]   | 389     |                     |
| LO$_2$ [111] | 177     | 198                |
| [110]   | 172     |                     |
| LO$_3$ [111] | 794     | 837                |
| [110]   | 803     |                     |
| LO$_4$ [111] | 265     | 301                |
| [110]   | 265     |                     |

$^a$ Fontana et al., Reference [1].

$^b$ Kugel et al., Reference [32].