Corridors-between-Adjacent-Sites Model of the Four Phases of $KNbO_3$

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Static and dynamic simulations of $KNbO_3$ with interacting polarizable ions support a model to describe the phase transitions: The niobium ions avoid their average positions in the cubic and tetragonal phases, hopping through virtual orthorhombic-phase sites between virtual rhombohedral-phase sites. This description reveals why the orthorhombic-to-rhombohedral transition fits well into the displacive model of phase transitions, while the two higher-temperature transitions exhibit both displacive and order-disorder character.

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Potassium niobate undergoes successive ferroelectric transitions upon cooling from its cubic-perovskite phase. The five-ion cubic cell has an Nb^{5+} ion at its center, K^+ at its corners, and O^{2-} in the face centers. The transitions are cubic (C) to tetragonal (T) at 708 K, then T to orthorhombic (O) at 498 K, and finally O to rhombohedral (R) at 263 K.[1] In the C phase, the lowest-frequency triply degenerate transverse-optic phonon involves motion, polarized parallel to one of the cube edges, of each Nb^{5+} against an octahedron of its six nearest O^{2-} neighbors. Upon cooling, the frequencies of these phonons "soften" to $\sim 3\times 10^{12}$ Hz when at the C-T transition one of the three modes "freezes in" leaving the Nb^{5+} displaced toward one of the six O^{2-} in directions equivalent to [100]. The frequencies of the other two phonons continue to decrease with cooling until one of them freezes in at the T-O transition, and the Nb^{5+} shifts to one of the twelve displacements from the cube center in directions equivalent to [110]. Finally, at the O-R transition, the remaining phonon freezes in leaving the Nb^{5+} displaced in one of the eight directions equivalent to [111].

The softening of these phonon frequencies followed by changes in the average positions of the ions suggests that these phase transitions might be considered the displacive type, in which each ion shifts from anharmonic motion through one site to another. However, that characterization might only apply to the O-R transition: The nonzero frequency of the soft phonon at the higher transitions and deviation of the temperature dependence of the dielectric constant from that predicted by the soft-mode frequency indicate that the C-T and the T-O transitions have some degree of disorder-to-order character.[2] The ions in a high-temperature disordered phase move not through their average positions but through more than one displaced site with some combination of spatial and temporal order and disorder. Below the transition temperature, the ions in different cells occupy the same one of these sites.

Two questions are addressed here. First, why and how is the cubic structure unstable? Second, what model of the dynamics in the high-temperature phases can explain transitions that exhibit both displacive and order-disorder character? The first question is answered by examining the statics of interacting polarizable ions. Those results lead to an answer to the second question, and the proposed model is tested in zero-stress molecular-dynamics simulations. First, the model used to describe interacting polarizable ions is explained briefly.

To begin, the lattice statics and dynamics are examined within the constraint that the crystal density be a superposition of rigid, spherical, single-ion densities. An additional constraint that the single-ion density $n_i(r)$ be a ground state of its nuclear plus an effective crystal potential energy $v_i(r)$ allows indirect variation of n_i. The crystal energy is separated into single-ion internal energies which use the kinetic-energy functional of Kohn and Sham,[3] and interaction energies which use the Thomas-Fermi functional. This energy is minimized by

$$v_i(r) = (4\pi)^{-1} \int d\Omega\, \delta W/\delta n_i \,, \qquad (1)$$

where the integration of the functional derivate of the interaction energy W is over angular variables.[4]

Given the ionic densities, it is assumed that three-body overlap in the crystal is negligible so that the interaction energy can be split into pair interactions.[5] The pair potentials are used to determine a new equilibrium structure; then the process is repeated until the structure and ionic densities are consistent. Assuming charges 1+, 5+, and 2− for the potassium, nobium, and oxide ion, respectively, the above procedure predicts stability of the cubic structure. The resulting O^{2-} $v_i(r)$ is shown as a solid line in Fig. 1. These ions are stable against charge transfer: By Eq. (1) and Janak's theorem,[6] a small transfer would change the energy by $\delta U = \sum_i \mu_i \delta o_i$, where the μ and o are the single-ion Kohn-Sham eigenvalues and occupation numbers. The O^{2-} $2p$ eigenvalues at −14.1 eV are the least bound, and since the lowest unoccupied states are the Nb^{5+} $4d$ eigenvalues at −4.8 eV, charge will not transfer.

Polarizability is the next freedom to allow the ions.

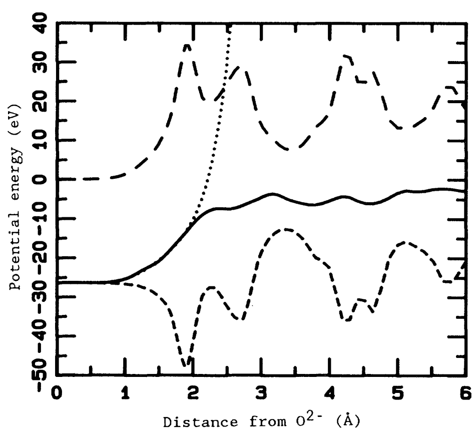

FIG. 1. Contributions of the kinetic, exchange, and correlation functionals (long-dashed line), and of the nuclear and Hartree interactions (short-dashed line) to the total (solid line) effective crystal potential v_i, which stabilizes the O^{2-}. An eighth-order polynomial fitted to v_i between the origin and the nearest-neighbor distance (dotted line) was used as a polarizing well.

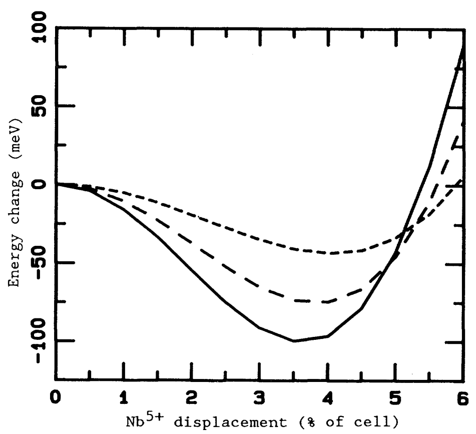

FIG. 2. Crystal-energy change vs zone-center displacement of Nb^{5+} in the [100] (short-dashed line), [110] (long-dashed line), and [111] (solid line) directions from the cubic-cell center.

Here a simple model described previously is used for the interactions between polarizable ions.[7] A description of the changes in the ionic internal energies caused by induction of dipole moments is also required. There is not a unique relationship between moment and internal energy, but one approach is to try to simulate the way in which an O^{2-} is polarized in a crystal by displacing its nucleus from the center of the energy well v_i in Fig. 1. However, that produces a very polarizable O^{2-} because the electronic structure can evolve into an oxygen atom separated from two electrons which occupy the well v_i (the proper thing for an unstable ion to do). This leads to "polarization catastrophe," an explosion that can occur in the present approach unless the internal energies are described beyond their lowest-order dependence on dipole moments.

If, however, the O^{2-} is displaced in the potential well shown as a dotted line in Fig. 1, then a rhombohedral equilibrium structure is found by simulated annealing. The dotted line in Fig. 1 is an eighth-order polynomial fitted to v_i out to the nearest-neighbor distance, but allowed to diverge beyond that. The field polarizability of the O^{2-} displaced in this well is 0.483 Å^3. The equilibrium structure is only slightly sensitive to the polarizabilities of the K^+ and Nb^{5+}, so the empirical value 1.133 Å^3 was used for K^+, and an extrapolation of the isoelectronic series to 0.259 Å^3 was used for Nb^{5+}.[8] The static-cell parameters are $a=b=c=3.822$ Å and $\alpha=\beta=\gamma=89.71°$. Corresponding experimental values at $T=230$ K are $a=4.016$ Å and $\alpha=89.83°$.[1] The respective dipole moments of the K^+, Nb^{5+}, and O^{2-} are 0.135, 0.177, and 0.376 a.u. The cation moments are directed along the polar axis, and the anion moments are approximately parallel to the cell vectors. The anion moments contribute 10.8% and the cation moments 8.3% to the 56.9-μC/cm^2 polarization.

Figure 2 shows the crystal-energy change vs Nb^{5+} displacements in the [100], [110], and [111] directions, with the K^+ and O^{2-} ions fixed at their sites in a rigid cubic lattice ($a=3.83$ Å). Similar curves are obtained with slightly different lattice constants or if the K^+ is moved with the Nb^{5+}. The electrostatic parts of the interactions between Nb^{5+} monopoles and O^{2-} dipoles are the primary negative contributions to the energy change. The internal and overlap energies oppose the displacements.

The cubic structure is unstable because the Nb^{5+} is drawn toward the midpoint between three O^{2-} (the center of an octahedral face) in order to polarize those ions. The moments of the three O^{2-} point generally away from this Nb^{5+}, meaning their electron clouds are drawn closer to the latter. The Nb^{5+} moment allows its nucleus to move closer to the O^{2-} electrons than its own electrons. Equivalent displacements of the Nb^{5+} in neighboring cells, combined with the rhombohedral strains, allow the O^{2-} moments to point away from the Nb^{5+} but not directly toward another. The [100] and [110] displacements lead to saddle points between the eight minima of the potential-energy surface. The [110]-displaced Nb^{5+} polarizes an O^{2-} pair, also without causing the moments to point at neighboring cations. In contrast, the [100]-displaced Nb^{5+} induces a small moment on only one O^{2-}. A final note about Fig. 2 is that the [110] and [100] saddle points and the origin are $\Delta U/k_B=315$, 789, and 1183 K above the depth of the [111] well, respectively.

Figure 2 and the experimental facts[9] support the eight-site model of the phase transitions: As the C phase is cooled, an Nb^{5+} visits its average position less frequently as it becomes confined to the six planes which

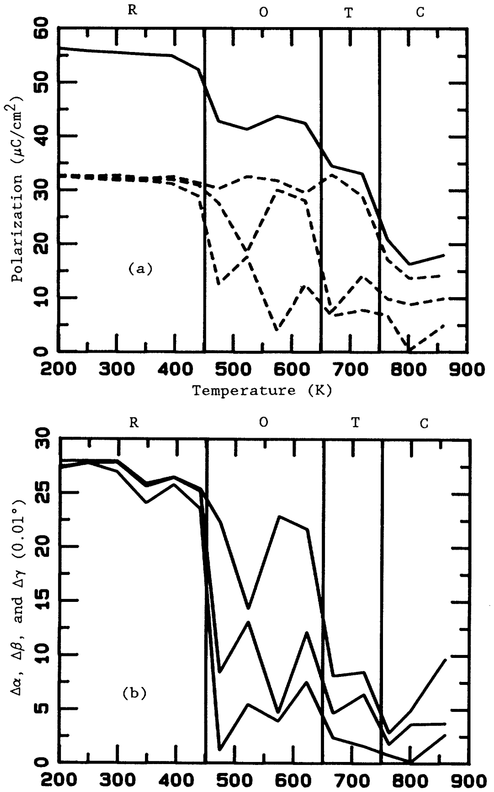

FIG. 3. Temperature dependence of (a) polarization (solid line) and its projections on lattice vectors (dashed lines), and (b) deviation of average angles α, β, and γ from 90°, during heating of 135 ions/cell at a rate of 1 psec/point. The points are connected without crisscrossing. The rhombohedral (*R*), orthorhombic (*O*), tetragonal (*T*), and cubic (*C*) phases are separated by vertical lines.

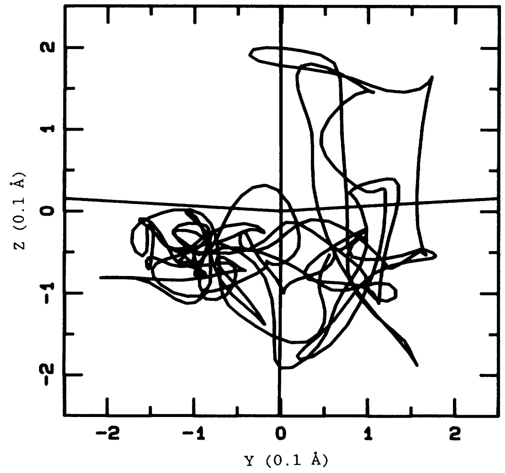

FIG. 4. An Nb^{5+} trajectory at 606 K in the orthorhombic phase of a forty-ion cell. The straight lines indicate directions from the average position to those of four O^{2-}.

pass through all of the saddle points and minima. At the *C-T* transition, the Nb^{5+} ions become ordered from all six into only one of these planes. During cooling in the *T* phase, visits by an Nb^{5+} to its average site become less frequent as it is channeled into the four corridors at the edges of its plane of motion. These corridors are parallel to the cube edges, pass through [110] saddle points, and connect four adjacent [111] minima. At the *T-O* transition, the Nb^{5+} ions become ordered into one corridor, each moving between the [111] and $[11\bar{1}]$ minima, through its average position at the [110] saddle point. Finally, below the *O-R*-transition temperature the Nb^{5+} ions stay in the [111] minimum.

This model reveals why the stabilization of a softening [100]-polarized phonon occurs at each transition: The major component of the motion associated with this phonon is the Nb^{5+} moving between [111] minima through corridors parallel to the cube axes. Some of these corridors are closed at both the *C-T* and *T-O* transitions, but the basic curvature of the energy surface along the ones remaining is unchanged. Thus, the temperature dependence of the frequency appears to be that of coupled anharmonic oscillators until the last corridor is closed by the displacive *O-R* transition.

In order to determine if the present energy model can produce the observed transitions and the dynamics just described, zero-stress simulations,[10] in which the shape of the cell can evolve with temperature, have been performed for cells doubled (40 ions) or tripled (135 ions) in each direction. Figure 3 shows the dependence upon temperature of the polarization and lattice angles. The lattice mass during these simulations was 200 amu, and the motion was restarted at each temperature with a Maxwell distribution of ion velocities. The *O* structure is obtained from the *C* cell by changing the length of one axis and making the angle opposite that axis obtuse. That phase appears in Fig. 3 as two polarization projections and one angle that are the same size as in the *R* phase, except for the point at 522 K at which the *O* axes interchanged roles during averaging. Notice that the polarization magnitude is essentially constant through that point. In the *T* phase, only one polarization projection remains and the average angles are near 90°, and in the *C* phase that last component of polarization vanishes.

These transitions can be identified also in lattice-vector lengths, volume, and specific heat, and are reproducible during either heating or cooling. However, averaging (particularly the forty-ion cell) for times longer than a few picoseconds can lead to noisy quasicubic results for the direction-dependent quantities in the *O* and *T* phases, caused by those spontaneous interchanges in cell-axes roles.

Figure 4 shows 2.5 psec of an Nb^{5+} trajectory at 606 K. During this time, the average forty-ion cell parameters were orthorhombic and most of the eight Nb^{5+} visited only two sites. This one and two others visited a third site near the end of this time, indicating that the *O* axes might switch in a longer simulation. Initially at the $[1\bar{1}\bar{1}]$ site, this Nb^{5+} hopped between there and the $[11\bar{1}]$ site twice; then during the third excursion to the latter site, it completed two oscillations with frequency $\sim 3.9\times 10^{12}$ Hz between that and the [111] site. In contrast with the Nb^{5+} trajectories, each K^+ and O^{2-} trajectory is monocentered and isotropic.

Thus, my conclusions are that the phase transformations in $KNbO_3$ can be explained in terms of isotropically polarizable ions. The Nb^{5+} motion might be described as evolving upon cooling from occupying first the volume of a small cube around its average *C*-phase position, then the surfaces of that cube, then one surface only, then the edges of that surface, then one edge, and, finally, one end of that edge. This model accounts for the character of each transformation and the behavior of the soft transverse-optic phonon.

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