First-principles theory of structural phase transitions in cubic perovskites

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A review is given of recent developments in which first-principles electronic-structure calculations have been used to determine, with chemical specificity, the structural properties of cubic perovskite materials. Direct application of these methods can be used to determine the ground-state (zero-temperature) distorted structure, the lattice vibrational properties in harmonic and anharmonic order, and dielectric properties such as Born effective charges and piezoelectric constants. By the indirect construction of model effective Hamiltonians and the fitting of these to the first-principles results, one can obtain (in most cases) the correct sequence of ferroelectric and/or antiferrodistortive structural phase transitions, with predicted transition temperatures typically within 30% of the experimental ones. Prospects for the application of these approaches to solid-solution ferroelectrics, to the study of finite-temperature piezoelectric properties, and to ferroelectrics in confined geometries, are briefly discussed.

I. INTRODUCTION

It is clearly of great importance to develop a fundamental theoretical understanding of the intrinsic physical properties of the ferroelectric perovskite materials. The experimental and theoretical study of these materials, and of their structural phase transitions, has a long history; much of this is reviewed in several standard reference works [1–3]. However, virtually all of the early theoretical work was of an empirical character. Typically, a Landau model, spin model, or empirical lattice-dynamical model is fitted to reproduce certain experimental features, and then used to predict new features or systematize the experimental results. While this has been an extremely valuable approach, the development of computational methods in the electronic-structure community has made possible the application of a new class of first-principles approaches. These methods are based upon a full solution for the quantum-mechanical ground state of the electron system within the local-density approximation (LDA) to Kohn-Sham density-functional theory (DFT) [4], and in principle they take as their only inputs the atomic numbers of the atomic constituents. Such methods hold the promise for providing chemically-specific information and understanding about the structural and electronic properties of the various perovskite materials. In fact, the work of recent years has confirmed that this is the case, showing that many details of the lattice dynamics and dielectric properties, the sequence of structural phase transitions, and even the transition temperatures can be predicted using first-principles calculations directly, or using models based on such calculations.

The purpose of the present manuscript is to review the development and application of first-principles calculations for perovskite ferroelectrics and related materials. The discussion will focus first on properties that can be computed directly from the first-principles calculations, and then on indirect calculations carried out using effective Hamiltonians that have been fitted to a first-principles database. The main emphasis is on the intrinsic properties of pure bulk materials, but in the last section some discussion will be given regarding the prospects for application of the methods to some "real-world" complexities: solid solutions, ferroelectric domain boundaries, surfaces, and piezoelectric response.

II. DIRECT FIRST-PRINCIPLES CALCULATIONS

The simplest direct applications of the first-principles approach involve computing the total energies, and ideally also the forces on each atom, as a function of the atomic coordinates as the system undergoes distortions from some reference cubic perovskite structure. Such distortions include displacements of one of the ionic sublattices, linear combinations of these ("frozen phonons"), or variations of lattice constant and other lattice strains. By mapping out the energy landscape using such an approach, it is possible to check for instabilities and identify the distorted ground-state structure (although strictly only at $T = 0$ and for a classical treatment of the ionic coordinates).

LDA-DFT calculations of this type were first carried out for FE perovskites using the linear augmented plane-wave (LAPW) method [5–14] and shortly afterwards by ultrasoft pseudopotential (USPP) [15–17], linear muffin-tin orbital (LMTO) [18–21], and norm-conserving pseudopotential (NCPP) methods. The LAPW and LMTO methods use radial basis functions inside atom-centered spheres and other basis functions outside, while the pseudopotential methods use a plane-wave basis throughout; the former methods are (at least in principle) all-electron methods, while the latter approach facilitates the efficient and accurate calculation of forces. Generally the experience has been that the LAPW and USPP calculations are of high quality and are in very good agreement with each other where they have been carefully compared, and both are probably making errors that are small compared to the intrinsic errors of LDA-DFT.

These calculations quickly proved their applicability to this class of compounds by confirming the existence of FE instabilities for such prototype materials as $BaTiO_3$ [5,6,8,15,16], $KNbO_3$ [7,9,10,13,16,18–21], and $PbTiO_3$ [6,8,16,17], and successfully predicted the correct symmetry of the ground-state structure in each case. Recent work has extended these studies to a wider variety of materials, including $KTaO_3$ [12,13,18,19], $PbZrO_3$ [13,16,22], $LiNbO_3$ [14], $LiTaO_3$ [14], and others [16].

Generally, the agreement between the first-principles theory and experiment has been good, but two limitations should be noted. First, DFT being a theory of the electronic ground state only, one finds that band gaps of virtually all insulators are seriously underestimated, by up to $\sim$50%. (This is an intrinsic limitation even in exact DFT theory, and is not arising from the LDA.) Thus, band gaps and optical properties cannot be taken directly from the DFT-LDA theory. Second, it is well known that, as a result of the LDA, the theory tends to underestimate the equilibrium lattice constants by roughly 1% (see, e.g., Ref. [16]). As a result, quantities that depend sensitively on lattice constant, such as the ground-state distortion amplitude or the spontaneous polarization, can be seriously in error if one works at the theoretical equilibrium lattice constant. Generally, the experience of the above works is that the results are more accurate if one works instead at the experimental lattice constant. This will be discussed further at the end of the next section.

The long-range Coulomb interaction obviously plays a crucial role in ferroelectric materials. It is therefore critical to be able to calculate the spontaneous (i.e., zero-field) electric polarization P as a function of structural degrees of freedom. Recently it has been understood how to calculate P directly as a Berry phase of the Bloch states [23,24], and when this calculation is carried out for the experimentally determined ground-state structure, one obtains satisfactory agreement with the experimental spontaneous polarization [25]. As for the dependence of P upon structure, the first-order variation of P with atomic displacements is given by the dynamical effective charge Z^*, which can be computed either directly using linear-response methods [26], or numerically by finite differences. The latter method was applied to $KNbO_3$ by the authors of Ref. [9], with the remarkable result that the $Z^* = 9.13$ for Nb is significantly larger than its nominal ionic value $Z = 5$ (with a corresponding anomalous Z^* for oxygen motion along the Nb–O bond). This pattern of anomalous Z^* values was found to be a universal feature of virtually all of the ferroelectric perovskites [25], and its origin was traced to the borderline ionic-covalent character and specifically to the hybridization between O $2p$ and B-atom $3d$ or $4d$ orbitals in the ABO_3 material [9,10,25]. Subsequent work has more carefully characterized these anomalous Z^* values, especially their dependence upon structural parameters and their band-by-band decomposition [27–31]. Such investigations have also provided insight into the origin of the FE instability and its relation to the long-range Coulomb interactions [32] and to many-body electron correlation effects [33].

Having characterized the strength of the long-range Coulomb interactions through the Z^*'s, one can move on to a study of the lattice dynamics. Actually, the transverse optic (TO) modes at Γ can be computed without Z^*; some early frozen-phonon studies [5,7,8,12,13,16,19–21] were able to identify the eigenvectors and frequencies of the TO modes, and especially to provide detailed knowledge of the FE soft mode. With the additional knowledge of the Z^* values, it is then fairly straightforward to obtain also the corresponding longitudinal optic (LO) modes at Γ [25].

While zone-boundary phonons and phonons at other rational wavevectors are accessible in principle by applying the frozen-phonon approach to supercells, linear-response methods [26] are the methods of choice for computing phonon properties on a mesh of wavevectors. Developed in the NCPP context [26], this approach was then extended to LAPW methods by Krakauer and coworkers [34]. In most cases, the analysis of the phonon spectrum in perovskites has been carried out in the reference ideal cubic structure, so that the FE or other instabilities show up as imaginary phonon frequencies. For example, applying such an approach to $KNbO_3$ [31,35] one finds that the portion of the Brillouin zone at which imaginary frequencies (potential FE instabilities) occur comprises a set of three "sheets" surrounding the $x - y$, $x - z$, and $y - z$ planes, consistent with a picture in which the FE dipoles associated with each unit cell are strongly correlated in longitudinal chains along the Cartesian axes. Similar results have been reported for the similar material $BaTiO_3$ [36]. On the other hand, for $PbZrO_3$ [37] and $SrTiO_3$ [38], the same approach demonstrates that both FE and antiferrodistortive instabilities are simultaneously present in the cubic reference structure, and nicely characterizes the portions of the Brillouin zone where each kind of instability is strongest.

Of course it is also of interest to first identify the $T = 0$ ground state structure by a careful total-energy minimization, and then apply the linear-response calculation to study the phonons in the ground state. A good example of this kind is a recent study of the rhombohedral ground-state structure of $KNbO_3$ [30].

III. INDIRECT MODELING VIA EFFECTIVE HAMILTONIANS

The methods discussed so far are essentially restricted to study the zero-temperature properties of the materials. Clearly it is of the first importance to see whether one can understand such features as the phase transition sequence and transition temperatures on a material-specific basis. A very successful approach to this problem has been the effective Hamiltonian approach [39–41]. Here, one defines a reduced number of degrees of freedom per unit cell (typically, a FE mode vector and a displacement vector in each unit cell), and constructs a model Hamiltonian, written as a function of these reduced degrees of freedom, that reproduces the spectrum of low-energy excitations (FE soft modes and strains) for the given material as obtained from the ab-initio DFT-LDA calculations. One then arrives at a model, typically containing 10-20 parameters, that can be subjected to Monte Carlo (MC) [41–43,22,44] or molecular dynamics (MD) [45] simulations in order to determine the finite-temperature properties of the material.

This approach has been applied with considerable success to the FE materials $BaTiO_3$ [41], $PbTiO_3$ [44], and $KNbO_3$ [45], with the theory correctly reproducing the experimental phase transition sequence in each case, as summarized in Table I. It can be seen that the theoretical values tend to be too low, typically by 20% or so, but in the worst case by almost 50%. Given that the calculations are based almost entirely on first principles, taking no input from experiment (except for the experimental lattice constant), this is overall a satisfying level of agreement. Moreover, the calculations give other useful information about the nature (soft-mode vs. order-disorder) of the transitions and their latent heats, and the correlations, fluctuations, and dynamics [45] in the various phases. They can also be helpful in identifying the role of strain coupling in the FE transitions [46].

For more complex materials such as $SrTiO_3$ [42,43], $PbZrO_3$ [22], $CaTiO_3$ [43], and $NaNbO_3$ [43], one has antiferrodistortive instabilities competing with the FE ones. In $SrTiO_3$ one has reasonable agreement (130K theory vs. 105K experiment) for the cubic-to-tetragonal antiferrodistortive transition, but the simulation also shows FE phases below 70K [42,43]; however, when quantum fluctuations are taken into account, the former transition changes to 110K, and the FE phases disappear [47], in excellent agreement with experiment. In the more complex materials $PbZrO_3$, $CaTiO_3$, and $NaNbO_3$, the behavior is more complicated, and the predicted sequence of phase transitions does not always exactly follow the experimental one [22,43]. Further work is needed to understand where the limitations of the theory lie, e.g., whether it is the LDA approximation to DFT itself that is inadequate, or whether the formulation of the effective Hamiltonian was oversimplified.

As mentioned earlier, the theories tend to underestimate the lattice constants with respect to experiment by approximately 1%. In the above works, this was corrected by working at a negative fictitious pressure [41], by artificially dropping the term linear in strain in the effective Hamiltonian [44], or by a fortuitous choice of exchange-correlation potential [45]. These effects are not small; in $BaTiO_3$, e.g., the C–T transition temperature falls to ~160K if the negative fictitious pressure is removed [41]. The necessity of fixing the lattice constant with reference to experiment clearly constitutes an unsatisfying retreat from the goal of a completely first-principles approach. In a very encouraging development, Singh has recently shown that use of the the weighted-density approximation (WDA) in place of the LDA appears to give good systematic improvement at the expense of only modest computational cost [13].

TABLE I. Comparison of theoretical and experimental ferroelectric transition temperatures (Kelvin). Symbols C, T, O and R refer to cubic, tetragonal, orthorhombic, and rhombohedral phases, respectively.

Material	Transition	T_c (theo.)	T_c (expt.)
$BaTiO_3$ (Ref. [41])	C–T	290	403
	T–O	230	278
	O–R	197	183
$KNbO_3$ (Ref. [45])	C–T	370	710
	T–O	260	488
	O–R	210	210
$PbTiO_3$ (Ref. [44])	C–T	660	763

IV. PROSPECTS

In the coming years, the first-principles theories will increasingly need to address some of the complexities associated with applications of FE materials. For example, the behavior of the material under conditions of applied electric fields and strains is often of primary importance. Thus, the study of the piezoelectric properties of these materials is now beginning, with a recent calculation on $PbTiO_3$ illustrating one way to proceed [48]. Many of the materials of interest for applications are solid solutions, e.g., PZT ($PbZr_{1-x}Ti_xO_3$), BST ($Ba_{1-x}Sr_xTiO_3$), and PMN ($PbMn_{1/3}Nb_{2/3}O_3$). Studies of the cation ordering and its consequences in such compounds are just beginning [49,50], and eventually the program of construction of an effective Hamiltonian and its use in MC or MD simulations will have to be carried through for such materials. Finally, the real materials are frequently ceramics or films, and a critical role is often played by boundaries and defects of various kinds, including grain boundaries, surfaces, interfaces, contacts, and FE domain walls. The 180° domain wall in $BaTiO_3$ has recently been studied using the effective-Hamiltonian approach [51], and some first studies of $BaTiO_3$ free surfaces have also appeared [52,53].

Clearly there is a great deal that remains to be done. In the real world, the material properties are frequently dominated by effects that have not yet even been mentioned above. For example, in order to understand hysteresis and fatigue effects, much more knowledge is needed regarding the role of grain boundaries, dislocations, impurities, oxygen vacancies, stoichiometric variations, electronic carriers, pinning of domain walls, etc. While these are certainly hard problems, it can be expected that clever and judicious applications of first-principles methods will contribute to solving many of these problems over the coming years.

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