Virtual-crystal approximation that works: Locating a composition phase boundary in Pb(Zr$_{1-x}$Ti$_x$)O$_3$

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We present a new method for modeling disordered solid solutions, based on the virtual crystal approximation (VCA). The VCA is a tractable way of studying configurationally disordered systems; traditionally, the potentials which represent atoms of two or more elements are averaged into a composite atomic potential. We have overcome significant shortcomings of the standard VCA by developing a potential which yields averaged atomic properties. We perform the VCA on a ferroelectric oxide, determining the energy differences between the high-temperature rhombohedral, low-temperature rhombohedral and tetragonal phases of Pb(Zr$_{1-x}$Ti$_x$)O$_3$ at $x = 0.5$ and comparing these results to superlattice calculations and experiment. We then use our new method to determine the preferred structural phase at $x = 0.4$. We find that the low-temperature rhombohedral phase becomes the ground state at $x = 0.4$, in agreement with experimental findings.

Throughout condensed matter science, solid solutions provide unique properties which are inaccessible in pure materials. Semiconductors and ferroelectric materials are two important areas in which small changes in atomic composition dramatically change material properties. Theoretical examinations have been hampered by the difficulty of incorporating inhomogeneities into perfectly periodic systems. Several theoretical approaches have been formulated to address this specific issue, including the virtual crystal approximation (VCA) and coherent potential approximation (CPA).

The VCA has been performed for over 30 years with mixed results; a composite potential is constructed which represents the average of the component atoms comprising the inhomogeneity. Previous implementations of the VCA have studied how structural and electronic properties of semiconducting and ferromagnetic alloys depend on composition. These studies typically provide qualitative and in some cases quantitative agreement with experimental and large-scale solid-state calculations. In some cases however, these methods have given unphysical results.

The inability of these traditional versions of the VCA to represent differences in chemical bonding and ionicity accurately has been suggested as the reason for these erroneous results. In principle, the VCA affords great versatility, applicable wherever compositional inhomogeneity can be treated in an averaged way. On its own, the VCA does not describe the different local atomic environment in inhomogeneous materials. Local features can be studied by performing a VCA calculation and adding in the differences between true atomic potentials and the VCA using a linear response method.

For predictions of alloy densities of states, the CPA has achieved considerable success. In this approach, a Green’s function is constructed such that an electron encountering either element of the alloy will not scatter on average. Recently, nearest-neighbor charge correlations have been included into CPA calculations. Despite this success, it is not convenient to perform first-principles calculations within the CPA which include self-consistency, Hellmann-Feynman forces and atomic motion. Therefore, considerable effort has been exerted toward the development of a VCA appropriate to first-principles calculations.

In response to the shortcomings of traditional approaches to the VCA, we have formulated a new approach that preserves important atomic properties (atomic orbital energies, ionicity, polarizability, and average size of the virtual atom). The VCA method presented in this paper represents a considerable departure from other first-principles VCA treatments. A variety of calculations have been performed by averaging pseudopotentials of the component atoms and finding self-consistent wave functions and charge density in the presence of this average potential. As we discuss below, the nonlinearity of the self-consistent Kohn-Sham equation insure that the average potential does not yield averaged properties. Accordingly, we construct a potential which does give correctly averaged atomic eigenvalues for a wide variety of electronic configurations. We anticipate that our new VCA method, because it provides correctly averaged atomic properties, will yield more accurate virtual atoms and provide greater agreement with superlattice solid-state calculations than traditional VCAs based on averaged potentials. The VCA construction methods are described for the combination of two atoms according to $A_{1-x}B_x$. In addition, we restrict our description to homovalent atoms. These methods can be generalized to the averaging of more than two atoms and heterovalency. It is important to emphasize that since we construct a single potential at the atomic level, the use of our VCA pseudopotentials in solid-state calculations requires no additional computational effort.

We have chosen to assess the accuracy of the two methods to reproduce superlattice calculations by computing the relative energy differences between different phases of a ferroelectric solid solution ($x = 0.5$) of PbZrO$_3$ and PbTiO$_3$. This composition lies very near the tetragonal-rhombic phase boundary of this material. After establishing the accuracy of our new method, we use it to predict the energetic ordering of Pb(Zr$_{1-x}$Ti$_x$)O$_3$ (PZT) phases at another value of $x$. We have previously demonstrated the effectiveness of our new approach for phase stability and for strain-induced...
In this paper, we perform a more complete treatment of the PZT work, involving three structural phases and studying a compositional phase transition.

**ADVCA (Averaged Discretized Potentials VCA):** In this approach, two independent atomic pseudopotentials ($\hat{V}_{1}^A$ and $\hat{V}_{1}^B$) are constructed. These descreened potentials are then averaged according to:

$$\hat{V}_{PS}^{ADVCA} = (1-x)\hat{V}_{PS}^A + x\hat{V}_{PS}^B. \quad (1)$$

In order to express the above semilocal VCA potential in a nonlocal form, we must also know the semilocal pseudo-wave-functions. Therefore, we solve for the reference-state pseudo-wave-functions of $\hat{V}_{PS}^{ADVCA}$ and use these to construct the nonlocal potential.

**RRVCA (New Method):** The ADVCA construction does not guarantee that the virtual atom will have atomic properties which are the correct average of the component atoms. Therefore, we impose averaged properties as a new criterion in our RRVCA construction. We define an averaged eigenvalue for the $l$-th state of the virtual atom, 

$$\varepsilon_{1}^{AVG} = (1-x)\varepsilon_{nl}^A + x\varepsilon_{nl}^B, \quad (2)$$

where $\varepsilon_{nl}^A$ and $\varepsilon_{nl}^B$ are the valence all-electron eigenvalues for the $nl$-th states of atoms A and B, and n need not equal n'. We seek a VCA potential which guarantees that $\varepsilon_{1}^{RRVCA} = \varepsilon_{1}^{AVG}$ for the reference state. As a first step, the bare nuclear Coulombic potentials of the component atoms are averaged:

$$\varepsilon_{AE}^{RRVCA} = \frac{-2((1-x)Z_{AE}^A + xZ_{AE}^B)}{r}. \quad (3)$$

In addition, we determine a core charge density that is the weighted average of the core charge densities of the all-electron component atoms ($\rho_{core}^A$ and $\rho_{core}^B$),

$$\rho_{core}^{RRVCA} = (1-x)\rho_{core}^A + x\rho_{core}^B. \quad (4)$$

By averaging the core charge densities and all-electron potentials, we insure that the resulting virtual atom will possess the proper averaged size of the two component atoms. Using this nuclear potential and frozen-core charge density, we find new all-electron wave functions for the virtual atom valence states. We accomplish this by completing a self-consistent inward solve for the valence wave functions according to

1. $\varepsilon_{1}^{RRVCA} = \varepsilon_{1}^{AVG}$,
2. $\phi_{n}^{RRVCA}(r) \rightarrow 0$ as $r \rightarrow \infty$,
3. $\int_{r_c}^{\infty} |\phi_{n}^{RRVCA}(r)|^2 r^2 dr = (1-x)\int_{r_c}^{\infty} |\phi_{n}^{A}(r)|^2 r^2 dr + x\int_{r_c}^{\infty} |\phi_{n}^{B}(r)|^2 r^2 dr$,

where $r_c$ is the pseudopotential core radius for the valence state. Operationally, we complete an inward solve well below $r_c$, insuring accurate first and second derivative determination for all values of $r$ greater than $r_c$. These derivatives are required for the optimized pseudopotential construction.

Since the form of these all-electron RRVCA wave functions will be modified within the core region when the wave functions are pseudized, the Kohn-Sham equations need not be solved between $r=0$ and $r=r_c$. We construct the remainder of the wave function as a smooth analytic form insuring norm-conservation and agreement with the inward solution. A new valence charge density is constructed, and the process is iterated to self-consistency. These wave functions are self-consistent solutions to the Kohn-Sham equation outside $r_c$, with eigenvalues and total norm outside $r_c$ which are exactly the average of the component atoms. Optimized semilocal pseudopotentials are then constructed for this set of wave functions and eigenvalues. It is important to note that any method for pseudopotential construction may be used because the averaging occurs at the all-electron level.

The pseudopotential construction procedure guarantees the agreement of the RRVCA eigenvalues with the averaged all-electron eigenvalues for the reference state only. To improve the transferability of the RRVCA potential to other electronic configurations, we have employed the designed nonlocal pseudopotential method. This method relies on the arbitrariness of the separation between the local and semilocal correction terms that are used in the nonlocal potential. By adjusting the separation, we can dramatically improve the transferability of the RRVCA potential. Improving the agreement with the all-electron atomic orbital energies for a range of electronic configurations insures correct ionicity and polarizability of the virtual atom. It is important to note that any method of pseudopotential construction sufficiently flexible to achieve eigenvalue agreement for many electronic configurations will also improve the quality of the virtual atom.

We have applied the ADVCA and RRVCA methods to the Zr$_{1-x}$Ti$_x$ virtual atom at $x = 0.5$. All atomic energy calculations were done within the local density approximation and the optimized and designed nonlocal pseudopotential.

**TABLE I.** Construction parameters for the Zr, Ti and Zr$_{1-x}$Ti$_x$ virtual crystal (VCA) designed nonlocal pseudopotentials. The Zr and Ti potentials were generated with the methods described in references [13] and [20]. The VCA potentials were generated using the methods described in text. Core radii ($r_c$) are in atomic units, $q_c$ parameters are in Ry$^{1/2}$, step widths are in atomic units and step heights are in Ry.

| Atom | $r_c$   | $q_c$   | Step Range  | Step Height |
|------|---------|---------|-------------|-------------|
| Zr (4s$^2$4p$^6$4d$^1$) | 1.51,1.51,1.90 | 7.07 | 0.00–1.51 | 0.77 |
| Ti (3s$^2$3p$^6$3d$^1$) | 1.32,1.20,1.40 | 7.07 | 0.00–1.15 | 5.49 |
| ADVCA ($s^2p^6d^1$) generated by averaging | |
| $x = 0.5$ | Zr and Ti potentials | |
| RRVCA ($s^2p^6d^1$) | 1.38,1.51,1.40 | 7.07 | 0.00–0.56 | 1.18 |
| $x = 0.5$ | | 0.56–0.79 | 1.34 |
| RRVCA ($s^2p^6d^1$) | 1.27,1.38,1.61 | 7.07 | 0.00–1.25 | 10.32 |

$x = 0.4$
TABLE II. Configuration testing for Zr, Ti and Zr$_{1-x}$Ti$_x$ virtual crystal (VCA) atoms generated with the ADVCA and RRVCA methods described in text. Averaged eigenvalues and total energy differences are given for the Zr and Ti all-electron (AE) and component pseudopotentials (PS). Absolute errors are computed as a difference from the averaged component pseudopotential results. All energies are in Ry.

| State | x = 0.5 | x = 0.5 | x = 0.5 | x = 0.5 |
|-------|---------|---------|---------|---------|
|       | AE      | PS      | ADCA    | RRVCA   |
|       | Energy  | Energy  | Error   | Error   |
| $s^2$ | -7.5701 | -7.5701 | 0.2108  | 0.0000  |
| $p^6$ | -5.9530 | -5.9530 | 0.1554  | 0.0000  |
| $s^0$ | -2.5554 | -2.5581 | 0.0437  | -0.0038 |
| $d^0$ | -3.4488 | -3.4488 | 0.2607  | 0.0000  |
| $\Delta E_{tot}$ | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

The experimental determined phase diagram for PZT shows two phase boundaries relevant to the present work. A nearly temperature-independent boundary at $x \approx 0.45$ separates the Ti-rich tetragonal $P4mm$ phase from the Zr-rich rhombohedral ($R3c$ and $R3m$) phases. Around 400-500K, the rhombohedral region exhibits a boundary between $R3c$ (low-temperature) and $R3m$ (high-temperature) phases, which depends weakly on composition. The $R3c$ phase shows complex oxygen octahedral tilting, which doubles the primitive unit cell to ten atoms.

Table III contains the $x = 0.5$ PZT superlattice equilibrium cell dimensions and energy differences for the tetragonal, low- and high-temperature rhombohedral phases for both cation orderings. For all rhombohedral calculations, we have neglected the small shear relaxations. Energy differences have been computed relative to the tetragonal phase. For the $(111)$ ordering, we find that the low- and high-temperature rhombohedral phases are 0.035 eV and 0.05 eV higher in energy than the tetragonal phase. For the $(011)$ ordering, we find the low- and high-temperature rhombohedral phases are 0.093 eV and 0.115 eV above the tetragonal ground state. For both orderings, the low-temperature rhombohedral phase is lower than the high-temperature phase.

For both VCA methods, we have completed full electronic and structural relaxations for five-atom unit cells which possess tetragonal and $R3m$ symmetries. For the low-temperature rhombohedral phase, we have studied a 10-atom unit cell which possesses $R3c$ symmetry. In Table III, we report the results of the ADVCA. ADVCA predicts that the ground-state phase for this composition of PZT is the high-temperature rhombohedral phase, in direct opposition to the superlattice calculations and experimental observations. In addition we find that ADVCA significantly underestimates the $c/a$ ratio for the tetragonal phase. We attribute the lack of agreement to the poor quality of the ADVCA virtual atom. The second to last column of Table III contains the results from the RRVCA. We find the same energy ordering as the superlattice calculations and experiment, with the low- and high-temperature phases 0.05 eV and 0.072 eV higher than the tetragonal phase. Finally, we find excellent agreement in the structural parameters between the RVCA and superlattice calculations. We attribute the quantitative agreement in the energetic and structural results to the improved quality of the RRVCA virtual atom.

Having demonstrated the effectiveness of the RRVCA and the inability of the ADVCA to reproduce the superlattice re-
TABLE III. Solid-state calculation results for superlattice and
tetragonal phases of $x = 0.5$ and $x = 0.4$ compositions of
Pb(Zr$_{1-x}$Ti$_x$)O$_3$ with (111) and (011) orderings. Energy differences
are relative to the tetragonal phase in all cases. Energies and struc-
tural parameters are given for a 40-atom unit cell.

| Structure      | Superlattice | Tetragonal | Rhombohedral |
|---------------|-------------|------------|--------------|
|               | $x = 0.5$ | $x = 0.5$ | $x = 0.5$ | $x = 0.5$ | $x = 0.4$ | $x = 0.4$ | $x = 0.5$ | $x = 0.5$ |
|               | (111)   | (011)     | ADVCA       | RVCA       | RVCA       | RVCA       |
| Rhombohedral  | $a$      | $8.052$   | $8.029$     | $8.077$    | $8.043$    | $8.033$    |
| (R3m)         | $\Delta E$ | $0.050$   | $0.115$     | $-0.041$   | $0.072$    | $0.048$    |
| Tetragonal    | $c$      | $8.199$   | $8.219$     | $8.131$    | $8.210$    | $8.199$    |
| (P4mm)        | $a$      | $7.869$   | $7.989$     | $8.054$    | $7.952$    | $7.957$    |
|               | $c/a$    | $1.041$   | $1.029$     | $1.010$    | $1.033$    | $1.030$    |
|               | $\Delta E$ | $0.000$   | $0.000$     | $0.000$    | $0.000$    | $0.000$    |
| Rhombohedral  | $a$      | $8.026$   | $8.004$     | $8.046$    | $8.007$    | $8.019$    |
| (R3c)         | $\Delta E$ | $0.035$   | $0.093$     | $-0.067$   | $0.050$    | $0.044$    |

For this more traditional method, we find neither quantitative
nor qualitative agreement with superlattice results. However,
for our new method, we find excellent agreement not only in
the energetics of the three phases but also the structural pa-
rameters. Finally we use our new method to predict the composi-
tional phase transition between $x = 0.5$ and $x = 0.4
Pb(Zr$_{1-x}$Ti$_x$)O$_3$. Our new method predicts that the low-
temperature rhombohedral phase is the ground-state structure
for the $x = 0.4$ composition in agreement with experiment.
This calculation represents the first ab initio determination of
a compositional phase boundary in a ferroelectric oxide.

We have recently become aware of an alternative approach
to improving the first-principles VCA. Bellaiche and Van-
derbilt apply the nonlocal projectors of all the component
atoms at the site of the virtual atom. Using ultrasoft pseudo-
 potentials, they find accurate piezoelectric and ferroelec-
tric properties for Pb(Zr$_{0.5}$Ti$_{0.5}$)O$_3$ using their approach.

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