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Virtual-crystal approximation that works: Locating a compositional phase boundary in $Pb(Zr_{1-x}Ti_x)O_3$

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We present a 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 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) (Refs. 1 and 2) and coherent potential approximation (CPA).[3–5]

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.[6,7] In some cases however, these methods have given unphysical results.[8,9] 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.[8] 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.[10,11]

For predictions of alloy densities of states, the CPA has achieved considerable success.[12–14] 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.[15] 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 an 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 insures 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 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 VCA's 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-rhombohedral morphotropic phase boundary of this material. After establishing the accuracy of our 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 approach for phase stability and for strain-induced phase transitions.[16] 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 Descreened Potentials VCA): In this approach, two independent atomic pseudopotentials ($\hat{V}_{\rm PS}^{\rm A}$ and $\hat{V}_{\rm PS}^{\rm B}$) are constructed. These descreened potentials are then averaged according to

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

In order to express the above semilocal VCA potential in a nonlocal form,[17] we must also know the semilocal pseudo-wave-functions. Therefore, we solve for the reference-state pseudo-wave-functions of $\hat{V}_{\rm PS}^{\rm ADVCA}$ and use these to construct the nonlocal potential.

RRVCA (Present 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 lth state of the virtual atom,

$$\varepsilon_l^{\rm AVG}=(1-x)\varepsilon_{nl}^{\rm A}+x\varepsilon_{n'l}^{\rm B}, \tag{2}$$

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

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

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

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

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[18] for the valence wave functions according to

$$\varepsilon_l^{\rm RRVCA}=\varepsilon_l^{\rm AVG}, \quad \phi_l^{\rm RRVCA}(r)\rightarrow 0 \ \text{ as } \ r\rightarrow\infty,$$

$$\int_{r_c}^{\infty}|\phi_l^{\rm RRVCA}(r)|^2r^2dr$$

$$=(1-x)\int_{r_c}^{\infty}|\phi_{nl}^{\rm A}(r)|^2r^2dr+x\int_{r_c}^{\infty}|\phi_{n'l}^{\rm B}(r)|^2r^2dr,$$

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.[19]

Since the form of these all-electron RRVCA wave functions will be modified within the core region when the wave functions are pseudized,[19] 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.[20] 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 $\mathrm{Zr}_{1-x}\mathrm{Ti}_x$ virtual atom at $x=0.5$. All atomic energy calculations were done within the local-density approximation, and the optimized[19] and designed nonlocal pseudopotential[20] methods were used. The generation parameters for the component potentials and the VCA potentials are included in Table I. For all atoms, semicore states were included as valence. It is important to note that although we have included multiple s-channel states, only one s nonlocal projector is included. For all atoms we have used the s potential as the local potential onto which we add one or two square-step augmentation operators. The transferability data for the ADVCA and RRVCA atoms are presented in Table II. For comparison we have also included the all-electron averaged eigenvalues and the averaged component pseudopotential eigenvalues. All errors in the VCA methods are computed as the difference from the averaged component pseudopotential eigenvalues. From the table it is clear that the RRVCA provides the more transferable potentials; the RRVCA gives atomic properties which are orders of magnitude closer to the weighted average of the component atoms than the ADVCA. We now test both VCA potentials, using them in solid-state calculations and comparing to superlattice results. We have completed first-principles calculations using density-functional theory and the local-density approximation on a $\mathrm{Pb(Zr_{0.5}Ti_{0.5})O_3}$ superlattice with stacking in the (111) direction[21] and (011) direction. The electronic wave functions are expanded in a plane-wave basis using a cutoff energy of 50 Ry. In addition to the semicore states mentioned above, the $5d$ shell is included in the Pb potential. Scalar relativistic effects are included in the generation of the Pb

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 Refs. 19 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 $\mathrm{Ry}^{1/2}$, step widths are in atomic units, and step heights are in Ry.

Atom	r_c	q_c	Step Range	Step Height
Zr ($4s^2 4p^6 4d^0$)	1.51,1.51,1.90	7.07	0.00–1.51	0.77
Ti ($3s^2 3p^6 3d^0$)	1.32,1.20,1.40	7.07	0.00–1.15	5.49
ADVCA ($s^2p^6d^0$) $x=0.5$	generated by averaging Zr and Ti potentials			
RRVCA ($s^2p^6d^0$) $x=0.5$	1.38,1.51,1.40	7.07	0.00–0.56	1.18
			0.56–0.79	1.34
RRVCA ($s^2p^6d^0$) $x=0.4$	1.27,1.38,1.61	7.07	0.00–1.25	10.32

pseudopotential. Brillouin zone integrations are approximated accurately as sums on a $4\times4\times4$ Monkhorst-Pack k-point mesh.[22]

The experimentally determined phase diagram for PZT shows two phase boundaries relevant to the present work. A nearly temperature-independent boundary at $x\approx0.45$ separates the Ti-rich tetragonal $P4mm$ phase from the Zr-rich rhombohedral ($R3c$ and $R3m$) phases.[23,24] Around 400–500 K, the rhombohedral region exhibits a boundary between $R3c$ (low-temperature) and $R3m$ (high-temperature) phases, which depends weakly on composition.[25,26] The $R3c$ phase shows complex oxygen octahedral tilting, which doubles the primitive unit cell to ten atoms.[27]

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

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	$x=0.5$ AE Energy	$x=0.5$ PS Energy	$x=0.5$ ADVCA Error	$x=0.5$ RRVCA 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
ΔE_{tot}	0.0000	0.0000	0.0000	0.0000
s^2	-6.7832	-6.7808	0.1942	0.0016
p^6	-5.1737	-5.1720	0.1398	0.0015
s^1	-2.0292	-2.0304	0.0335	-0.0009
d^0	-2.7037	-2.7034	0.2362	0.0041
ΔE_{tot}	-2.3049	-2.3067	0.0387	-0.0019
s^2	-5.6569	-5.6586	0.1266	-0.0029
p^6	-4.0711	-4.0734	0.0764	-0.0047
s^1	-1.3449	-1.3453	0.0119	0.0011
d^1	-1.6814	-1.6889	0.1549	-0.0018
ΔE_{tot}	-4.4856	-4.4923	0.2348	-0.0004
s^2	-4.1762	-4.1730	0.0398	-0.0077
p^6	-2.6089	-2.6064	-0.0059	-0.0106
s^2	-0.3301	-0.3293	-0.0097	0.0018
d^2	-0.3205	-0.3239	0.0586	-0.0072
ΔE_{tot}	-6.2574	-6.2696	0.3397	-0.0037

TABLE III. Solid-state calculation results for superlattice and virtual crystals of $x=0.5$ and $x=0.4$ compositions of $Pb(Zr_{1-x}Ti_x)O_3$ with (111) and (011) orderings. The energy differences are relative to the tetragonal phase in all cases. Energies and structural parameters are given for a 40-atom unit cell.

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

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 RRVCA 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 results for $x=0.5$, we use the RRVCA to examine further the compositional phase transition in PZT. We have chosen to study the $x=0.4$ composition of PZT, since the ground-state structure for this composition lies in the low-temperature rhombohedral phase region of the phase diagram. We have constructed a $x=0.4$ $\mathrm{Zr}_{1-x}\mathrm{Ti}_x$ potential using the RRVCA according to the parameters in Table I. The transferability of this potential is equal to that of the $x=0.5$ RRVCA potential. We have completed structural relaxations of the two five-atom unit-cell structures described above as well as the ten-atom low-temperature rhombohedral phase. The last column of Table III contains the structural parameters for the three phases and energy differences relative to the tetragonal phase. We find that moving from $x=0.5$ to $x=0.4$ composition shifts both rhombohedral phases lower in energy relative to the tetragonal phase. The high-temperature rhombohedral phase energy drops by approximately 0.012 eV and the low-temperature phase decreases by 0.094 eV, becoming the ground-state structure for the $x=0.4$ composition. This result is in direct agreement with the experimental findings and demonstrates the ability of the RRVCA to predict compositional phase transitions.

In this paper we have presented a method for constructing virtual crystal pseudopotentials and have applied this method to the Ti and Zr atoms. Our method is based on the self-consistent determination of averaged all-electron properties which insures exact agreement of the proper averaged all-electron eigenvalues for the reference configuration of the virtual atom. This procedure also yields the proper averaged atomic size. To improve the electronic properties of the virtual atom at all other electronic configurations, we employed the designed nonlocal pseudopotential approach. We have compared our method to a more traditional one in which the descreened pseudopotentials are averaged, computing the relative energy differences for the high-temperature rhombohedral, low-temperature rhombohedral, and tetragonal phases of $\mathrm{Pb}(\mathrm{Zr}_{1-x}\mathrm{Ti}_x)\mathrm{O}_3$ and comparing those results to superlattice calculations with two different cationic orderings. For this more traditional method, we find neither quantitative nor qualitative agreement with superlattice results. However, for our method, we find excellent agreement not only in the energetics of the three phases but also the structural parameters. Finally we use our method to predict the compositional phase transition between $x=0.5$ and $x=0.4$ $\mathrm{Pb}(\mathrm{Zr}_{1-x}\mathrm{Ti}_x)\mathrm{O}_3$. Our 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, to our knowledge, 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 Vanderbilt[28] apply the nonlocal projectors of all the component atoms at the site of the virtual atom. Using ultrasoft pseudopotentials,[29] they find accurate piezoelectric and ferroelectric properties for $\mathrm{Pb}(\mathrm{Zr}_{0.5}\mathrm{Ti}_{0.5})\mathrm{O}_3$ using their approach.

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