First-principles characterization of a heteroceramic interface: ZrO$_2$(001) deposited on an alpha-Al$_2$O$_3$(1102) substrate

Christensen, Asbjørn; Carter, Emily A.

Published in:
Physical Review B Condensed Matter

Link to article, DOI:
10.1103/PhysRevB.62.16968

Publication date:
2000

Document Version
Publisher's PDF, also known as Version of record

Citation (APA):
First-principles characterization of a heteroceramic interface: ZrO$_2$(001) deposited on an $\alpha$-Al$_2$O$_3$(1102) substrate

A. Christensen*

Department of Chemistry and Biochemistry, Box 951569, University of California, Los Angeles, California 90095-1569 and Center for Atomic-scale Materials Physics (CAMP), Department of Physics, Technical University of Denmark, Bygning 307, DK-2800 Lyngby, Denmark

Emily A. Carter†

Department of Chemistry and Biochemistry, Box 951569, University of California, Los Angeles, California 90095-1569

(Received 27 December 1999)

We have studied an alumina/zirconia interface using the all-electron projector augmented wave formalism within density functional theory. We present the electronic, structural, and energetic properties of the ZrO$_2$(001)/$\alpha$-Al$_2$O$_3$(1102) interface as well as of the free $\alpha$-Al$_2$O$_3$(1102) and ZrO$_2$(001) surfaces. We find that the generalized gradient correction significantly lowers the oxide surface energies, compared to values obtained by the local density approximation. The monoclinic-tetragonal transition in ZrO$_2$(001) thin films is discussed as well as strain effects involved in the interface formation. The stoichiometric alumina/zirconia interface is found to be weakly bonded, regardless of the film thickness, and the ZrO$_2$(001)/$\alpha$-Al$_2$O$_3$(1102) interface has a rather epitaxial character, due to a low lattice mismatch of $\sim$4%. The impact of such weak interactions on ceramic coating stability is discussed.

I. INTRODUCTION

Characterization of the properties of crystalline interfaces between metals and ceramics, as well as heterogeneous interfaces between two ceramics, is of both fundamental interest—little is understood about the atomic level interactions at such interfaces—and practical interest—these are the interfaces present in so-called thermal barrier coatings (TBC’s). These coatings are used to protect gas turbine engine components found in both aircraft and stationary power plants. The protective coatings allow fuel combustion to be carried out at the highest possible operating temperature (maximizing fuel efficiency). Current TBC’s fail after a sequence of heating and cooling cycles.

Zirconia-based materials are often chosen for TBC’s, due to their high melting temperature, low thermal conductivity, similar coefficient of thermal expansion to that of the Ni superalloy used to construct the engine parts, and excellent corrosion and thermal shock resistance. The main drawback of pure zirconia is the tetragonal-monoclinic phase transformation induced by thermal cycling. This transition is accompanied by a volume expansion of $\sim$4%, which generates cracks and eventually de-adhesion of the TBC. The tetragonal-monoclinic transition is suppressed by adding cubic oxides in small amounts ($\sim$8.5%) to zirconia. Still, TBC’s are prone to thermal cycling fatigue, due to unequal thermal expansion of the metal and the TBC, which causes the TBC to spall as a result of thermally induced stresses. Another contributing mechanism to the spallation is oxidation of the TBC/metal interface. The spallation problem is often reduced by placing a bond coat in between the TBC and the metal, but under real life operating conditions, the bond coat is oxidized. Therefore, a lot of effort has been put into refining and optimizing TBC/bond coat/metal structures to meet engineering requirements. The search for design principles has hitherto been rather phenomenological; this is a consequence of the structural and chemical complexity of the TBC/bond coat/metal structures, together with the lack of nondestructive experimental probes for in situ atomic scale characterization of buried interfaces, let alone oxide surfaces.

Atomistic modeling offers microscopic insight into otherwise inaccessible aspects of complex interface structures. Our group currently has a concerted effort to characterize, within ideal model interfaces, the interactions between different materials where they meet. In this paper, we focus on the ZrO$_2$/$\alpha$-Al$_2$O$_3$ interface, which is relevant at the TBC/bond coat interface, when the Ni-Al-Cr-Y bond coat is oxidized. Also, this interface determines mechanical and thermal properties of technologically important ZrO$_2$/Al$_2$O$_3$ composites. $\alpha$-alumina is thought to form at the TBC/bond coat junction, but other forms of Al$_2$O$_3$ may form (like $\gamma$-Al$_2$O$_3$). However, since $\alpha$-Al$_2$O$_3$ is the most stable phase and other Al$_2$O$_3$ phases have a more complex, mostly ill-characterized bulk structure, we restrict ourselves to study $\alpha$-Al$_2$O$_3$ only.

We have also examined the Al$_2$O$_3$/Ni interaction, where we learn that Al$_2$O$_3$ may be responsible for the spallation that occurs. We have also studied the ZrO$_2$/Ni(111) interface to understand on an atomistic level why the bond coat is necessary at all between the TBC and a Ni-rich superalloy. We also previously studied the bulk and surface phases of all ZrO$_2$ phases. Here, we concluded that the t-ZrO$_2$(111) and the m-ZrO$_2$(11) surfaces are most stable. This had implications for the tetragonal-monoclinic transition in ZrO$_2$ nanoparticles. Recently Stapper and co-workers modeled defects in bulk yttria-stabilized ZrO$_2$ (YSZ) using the local-density approximation (LDA) in an
96-atom unit cell and obtained insight into localized electronic states in the material.

Many experiments of ZrO$_2$ and YSZ film growth on an $\alpha$-Al$_2$O$_3$ substrate have been reported. This epitaxial system is also used as a substrate for ceramic high-$T_c$ superconductors, where the zirconia film acts as a chemical buffer layer.$^{16-18}$ On the $\alpha$-Al$_2$O$_3$($1\overline{1}02$) substrate, $m$-ZrO$_2$(001)$^{16,19}$ and YSZ(001)$^{16,19,17}$ have been observed to grow. However, at high oxygen pressure$^{16}$ or substrate temperatures$^{17}$ beyond 950 °C, YSZ($1\overline{1}02$)/

used, all with $r_\lambda=2.0\ a_0$ and $\lambda=6$. All atomic pseudopotential waves for the PAW-projector construction are generated at the atomic eigenvalue for the corresponding angular momentum channel. The auxiliary pseudowave for the $d\ channel$ is placed at the atomic vacuum level. No Zr semicore states are treated as valence in our calculation. A very accurate description of the energetics in a pure Zr metal crystal requires inclusion of the $(4s,4p)$ core states, which are rather extended and overlap slightly with $(4s,4p)$ core states at neighboring Zr ions. However, in ZrO$_2$, Zr atoms only have O ions as nearest neighbors and consequently the Zr$(4s,4p)$ states can only hybridize with O states. In ZrO$_2$, all O resonances are well separated in energy from the Zr$(4s,4p)$ resonances$^{27}$ and therefore the O-Zr$(4s,4p)$ hybridization is weak. Thus we expect the frozen-core approximation, which underlies the PAW implementation used in the present paper, to be accurate for ZrO$_2$, even if the Zr$(4s,4p)$ states are treated as core states. We will deal with this in more detail elsewhere.$^{13}$

All calculations we present in this paper, including atomic reference data for the PAW setup, were performed within a generalized gradient approximation (GGA) for exchange and correlation. More precisely, the nonspin polarized local density approximation (LDA) functional, as parametrized by Perdew and Zunger,$^{28}$ is used in conjunction with gradient corrections for exchange, as proposed by Becke,$^{29}$ and gradient corrections for correlation, as proposed by Perdew.$^{30}$ For our slab calculations (surfaces and interfaces), we use a $2\times2\times1$ grid for sampling the Brillouin-zone integrals, corresponding to a reciprocal space sampling density of $\sim0.6\ \text{Å}^{-1}$. For bulk $\alpha$-Al$_2$O$_3$ and c-ZrO$_2$ reference and test calculations, we use the same $k$-point sampling density, corresponding to a $2\times2\times2$ grid. This $k$-point sampling density is the standard choice for insulating systems as Al$_2$O$_3$, ZrO$_2$, and the surfaces and interfaces of these ceramics. Separated surface calculations (to determine interface cohesion) are performed in the same unit cells as the interface calculations to enhance error cancellation for the residual $k$-point sampling error. All slab and bulk calculations we present in this paper are performed spin restricted, which is exact for simple oxides like Al$_2$O$_3$ and ZrO$_2$, since the electrons in these systems are spin-paired completely.

The kinetic-energy cutoff for the plane-wave basis is chosen to be 30 Ry (408 eV), corresponding to a convergence of absolute total energies to within 0.2 eV/atom (but where energy differences are essentially converged). The pseudodensity is represented on a grid corresponding to twice the kinetic-energy cutoff of the electronic wave functions. In all our calculations, six empty bands are included, to improve the convergence rate of the eigenstates in the band-gap region.

To interpret the electronic spectra, the atom-projected density-of-states (DOS) is generated by projecting the Kohn-Sham wave functions onto spherical harmonics inside spheres centered on ions. These spheres have the same radii for each species in all our calculations: $r$(Zr)$=1.60\ \text{Å}$, $r$(Al)$=1.30\ \text{Å}$, and $r$(O)$=0.81\ \text{Å}$. This corresponds to weakly overlapping (but not space-filling) spheres for both oxides. These radii correspond to the covalent radius multiplied by a factor of 1.1053, which is the ratio between the radii of space filling to touching spheres in an fcc crystal;
this is a standardized choice in the PAW code. For charge distribution analysis, ionic charges are calculated by integration inside spheres of the atom-projected DOS. This approach for projecting/partitioning collective quantities as charge and energy in a solid is not absolute and only differences are indicative for changes in the local chemistry. For visual convenience, a Gaussian broadening of $\Delta E = 0.5$ eV is performed for all DOS spectra displayed in this paper.

B. Ionic and electronic relaxation

1. Structural quenching

Ions are relaxed to the equilibrium configuration in the slab unit cells using 2nd order damped molecular dynamics in the Car-Parrinello (CP) framework, i.e., ionic and electronic degrees of freedom are relaxed simultaneously using a fictitious Lagrangian (with a viscosity term added to the equation of motion for quenching). The friction term is adaptive, i.e., the viscosity coefficient is decreased as the ground state is approached, so that the system does not get stuck close to the minimum; variable friction also ensures that the entire frequency spectrum is being damped efficiently. The Car-Parrinello equations of motion are integrated by the Verlet algorithm with a time step of 7 a.u. = 0.17 fs. The quench time for our slab systems is in the range 0.1–1.2 ps, including the initial descent of the electronic wave functions to the Born-Oppenheimer surface. Ions are relaxed to a precision of 10 meV per unit cell.

Apart from periodic boundary conditions on the unit cell, no symmetry or constraints are imposed on the electronic density and ionic motion. The unit cells (lattice constants and cell angles) for interface structures considered are not relaxed, but fixed to the values derived from the fully relaxed bulk unit cell of our substrate $\alpha$-Al$_2$O$_3$, described in Sec. III. Including relaxation of slab unit cells parallel to the surface/interface is undesirable when the structures are intended to represent bulk terminations. Further, unit-cell relaxation based on the quantum-mechanical stress theorem$^{33}$ is associated with calculational problems, like artificial Pulay stresses.$^{34}$ (For our bulk calculations, we circumvent these problems by fitting a smooth envelope to the total energies corresponding to a series of lattice constants.) Therefore, in Sec. IV B, relaxed energies and structures refer to structures where only intracell ionic coordinates are relaxed to their equilibrium values.

2. Finite temperature molecular dynamics

We have performed finite temperature molecular dynamics to investigate the thermal stability of some of the quenched interface structures. The initial ionic temperatures are chosen to be $T = 1600$ K within a canonical distribution. The system is kept at this temperature using a Nose thermostat$^{35}$ with a frequency of 10.0 THz. A low electronic friction is used to maintain the electronic system close to the Born-Oppenheimer potential-energy surface. We use the simulation temperature $T = 1600$ K because it is well above the temperature for the bulk ($m \rightarrow t$)-ZrO$_2$ transition temperature ($1450$ K) and further this temperature is relevant to the environment inside a combustion engine.

The trajectory lengths are 1.4 ps, with a time step of 0.4 fs (after the electronic wave functions are relaxed to their electronic ground state corresponding to the initial ion positions). Mass renormalization of the ions is applied, to compensate for the artificial electronic drag$^{23}$ on the ions within the Car-Parrinello formalism. The PAW CP code$^{23}$ was run in parallel on 2, 4, 8, and 16 nodes on IBM SP2 platforms.

III. BULK PHASES OF $\alpha$-Al$_2$O$_3$ AND ZrO$_2$

The purpose of this section is to introduce the bulk phases of $\alpha$-Al$_2$O$_3$ and ZrO$_2$ as well as testing our PAW method setup. Readers not interested in this may skip directly to Sec. IV. In Figs. 1(a)–1(b), we show the two low-pressure and low-temperature polymorphs of ZrO$_2$. The most stable low-temperature structure, shown in Fig. 1 (a), has monoclinic symmetry ($P2_1/c$) with sevenfold cation coordination, and alternating threefold and fourfold anion coordination. At intermediate temperatures ($1180–2370$ °C), the stable phase has tetragonal symmetry ($P4_2/nmc$) with eightfold cation coordination and (distorted) tetrahedral anion coordination [Fig. 1(b)]. This polymorph can be made stable at room temperature in the presence of certain dopants, e.g., up to a few percent cubic oxides such as Y$_2$O$_3$. From 2370 °C to the melting temperature (2600 °C), the stable phase is fluorite, which has full cubic symmetry ($Fm\overline{3}m$) and also eightfold cation coordination and tetrahedral anion coordination. The difference between the cubic and tetragonal structure is the small alternating distortion of the O-atom columns along the 4$_2$ axes [directed along [001] in Fig. 1(b)], together with a small elongation of the unit cell along

![FIG. 1. Unit cells for bulk ZrO$_2$ and $\alpha$-Al$_2$O$_3$. Oxygen ions are small and dark. Cations are larger and bright. (a) $m$-ZrO$_2$ with conventional axis assignments (i.e., $\beta > 90^\circ$), (b) $t$-ZrO$_2$ with the tetragonal distortion along [001]. (c) and (d) The conventional hexagonal $\alpha$-Al$_2$O$_3$ unit cell viewed from two angles along the (102) Miller planes (seen as horizontal lines in the figure from these view angles). Since only one unit cell is displayed, (d) might give the false impression of large interstitials in the crystal—this disappears, when the unit cell is repeated in all periodic directions.

The trajectory lengths are 1.4 ps, with a time step of 0.4 fs (after the electronic wave functions are relaxed to their electronic ground state corresponding to the initial ion positions). Mass renormalization of the ions is applied, to compensate for the artificial electronic drag on the ions within the Car-Parrinello formalism. The PAW CP code was run in parallel on 2, 4, 8, and 16 nodes on IBM SP2 platforms.
the [001] direction. We will not focus on the cubic modification in this paper because it is metastable at low temperatures. For many purposes, the tetragonal phase may be considered a perturbation of the cubic phase, due to the smallness of the tetragonal distortion distinguishing it from the cubic phase. Throughout this paper, the letters c, t, and m refer to zirconia’s cubic, tetragonal, and monoclinic phases, respectively. The bulk phases of ZrO$_2$ have been studied quite extensively theoretically, using DFT techniques,$^{37,27,38,39,14,40,15}$ the Hartree-Fock ($\text{HF}$) method,$^{41}$ tight-binding techniques,$^{42,43}$ as well as semiempirical atomistic models.$^{42,44}$

In Fig. 1(c)–1(d), we show two views of the stable low-pressure and low-temperature polymorph of Al$_2$O$_3$, which has the corundum structure. This phase has rhombohedral symmetry ($\mathbf{R}\bar{3}c$) and is conventionally referred to as $\alpha$-Al$_2$O$_3$. In this structure, Al has sixfold coordination, whereas the O ions are tetrahedrally coordinated. Figures 1(c)–1(d) shows one single conventional hexagonal unit cell, rotated so that the view is along certain characteristic crystallographic directions, parallel to the (1 T02) Miller planes. The complete view of $\alpha$-Al$_2$O$_3$ along the directions in Figs. 1(c)–1(d) is obtained by repeating the unit cell along periodic directions [making the crystal look denser than in Fig. 1(d)]. $\alpha$-Al$_2$O$_3$ will act as the substrate in our paper, therefore we consider only this polymorph.

With the calculational setup described in Sec. II, the bulk structures of ZrO$_2$ and $\alpha$-Al$_2$O$_3$ are well reproduced. We obtain the lattice constant $a_0=5.071$ Å for $c$-ZrO$_2$, in excellent agreement with the experimental value $a_0=5.07$ Å.$^{36}$ The tetragonal distortion of the oxygen ions is found to be $|d_{\text{z}^2}/z|=0.044$, in slightly better agreement with the experimental value ($|d_{\text{z}^2}/z|=0.065$ at $T=1523$ K$^{49}$) than the corresponding value $|d_{\text{z}^2}/z|=0.03$ (Refs. 14,27) obtained using the LDA for exchange-correlation effects. The discrepancy between theory at $T=0$ and experiment at $T=1523$ K here is primarily due to thermal volume expansion, whereby the tetragonal distortion of the oxygen ions $|d_{\text{z}^2}/z|$ increases with temperature. For the monoclinic phase, we obtain $a_0=5.14$ Å, $b_0=5.25$ Å, $c_0=5.27$ Å, and $\beta=99.43^\circ$, with ion positions generated by Zr(0.278, 0.044, 0.208), O1(0.073, 0.342, 0.338), and O2(0.449, 0.759, 0.481) from symmetry group $P2_1/c$. This compares well with the experimental structure$^{45}$ obtained by neutron powder diffraction at 295 K $a_0=5.1505$ Å, $b_0=5.2116$ Å, $c_0=5.3137$ Å, and $\beta=99.230^\circ$, with ion positions generated by Zr(0.2754,0.0395,0.2083), O1(0.0700, 0.3317, 0.3447), and O2(0.4496, 0.7569, 0.4792) from symmetry group $P2_1/c$. Likewise, the calculated lattice constants for $\alpha$-Al$_2$O$_3$ ($a_0=4.813$ Å and $c_0=13.131$ Å) agree well with the experimentally determined $a_0=4.76$ Å and $c_0=13.00$ Å.$^{36}$ In this case all ionic degrees of freedom (including the lattice constants) are relaxed (consistent with space group $R\bar{3}c$). For the internal cell coordinates (referenced to the hexagonal cell for space group $R\bar{3}c$) we obtain $z=0.3531$ for Al in Wyckoff position 12c and $x=0.3079$ for O in Wyckoff position 18e. The corresponding experimental values$^{36}$ are $z=0.352$ and $x=0.306$. The good agreement with experiment for the bulk structures lends confidence to the predictions we make below for thin films of ZrO$_2$ and $\alpha$-Al$_2$O$_3$, albeit within the constraint that large length scale changes in structure will be excluded due to the necessary imposition of periodic boundary conditions within a tractably sized unit cell.

A. The bulk $\alpha$-Al$_2$O$_3$ and ZrO$_2$ electronic structure

To facilitate the discussion of the electronic structure of the surfaces and interfaces of $\alpha$-Al$_2$O$_3$ and ZrO$_2$, we briefly review the main characteristics of the bulk electronic structure of $\alpha$-Al$_2$O$_3$ and $t$-ZrO$_2$ (as representative of the ZrO$_2$ phases). In Fig. 2, we show the one-electron energy-resolved valence DOS projected onto anions/cations and resolved into angular momenta for both $\alpha$-Al$_2$O$_3$ and $t$-ZrO$_2$. For both oxides in this figure, the energy zero is chosen to be the middle of the band gap.

The classical picture of these two oxides assumes a complete charge transfer of valence electrons from metal to oxygen, thereby obtaining a closed O(2p) shell. The O$^{2-}$ anion charge state is stabilized by the Madelung potential created by the charge transfer. From this point of view, the electronic structure of these oxides is similar to that of compressed
noble gases.\textsuperscript{48} As expected from the classical picture, the occupied anion valence DOS is larger than the cation valence DOS, but the cation DOS is significantly larger than zero, reflecting the fact that the charge transfer is incomplete. The band structures of \( \text{Al}_2\text{O}_3 \) and \( \text{ZrO}_2 \) share some characteristics: the lowest band in the valence region is derived from the \( \text{O}(2s) \) state and is centered around 20 eV below the valence-band maximum. This band has a weak dispersion, with a bandwidth around 1–2 eV, indicating the \( \text{O}(2s) \) electrons are very localized. The valence band is derived from with a bandwidth around 1–2 eV, indicating the \( \text{O}(2s) \) trons are very localized. The valence band is derived from the \( \text{O}(2s) \) state and shows a larger dispersion than the \( \text{O}(2s) \) band, indicating significant delocalization. Both the \( \text{O}(2s) \) and \( \text{O}(2p) \) bands are broader for \( \text{Al}_2\text{O}_3 \) than for \( \text{ZrO}_2 \). The conduction bands are derived from the empty cation valence states, with the bottom of the conduction bands being mainly \( s \)-like for \( \text{Al}_2\text{O}_3 \) and mainly \( d \)-like for \( \text{ZrO}_2 \).

Generally, covalent interactions are visible in the DOS spectrum as a simultaneous down and up shift of occupied and unoccupied states, respectively, and mixing of electronic states of the interacting elements. Conduction-band valence-band interactions give rise to stabilizing covalent effects for these oxides, the nature of which is revealed in the cation projections of the \( \text{O}(2p) \) derived band. These covalent interactions, considered alone, increase the intrinsic single-particle band gap in these oxides. Valence-valence interactions between the oxygens are mainly nonbonding and dispersive, because the valence states are completely filled; these tend to decrease the band gap by pushing up the valence-band maximum. \( \text{Al}_2\text{O}_3 \) has a larger intrinsic ionity and band gap, due to a larger intrinsic separation of the \( \text{Al}(3s) \) and \( \text{O}(2p) \) resonances in the ionic crystal leading to a more complete charge transfer for \( \text{Al}_2\text{O}_3 \).

Comparing Figs. 2(a) and 2(b) suggests that \( \text{ZrO}_2 \) is more covalent than \( \text{Al}_2\text{O}_3 \), due to the relatively larger weight of the valence bands on \( \text{Zr} \) ions compared to \( \text{Al} \) ions. Thus \( \text{Zr} \) is likely to be more \( \text{Zr} \)(II)-like, which is consistent with the fact that it is typically easy to strip \( \text{Zr}(5s) \) electrons off the \( \text{Zr} \) atoms, while the ionization potential for the \( \text{Zr}(4d) \) electrons is considerably higher.\textsuperscript{49}

Although it is not formally correct to associate the eigenvalue band gap in DFT with the experimental optical band,\textsuperscript{50} comparison is frequently made. Generally, the calculated eigenvalue band gaps are smaller than the corresponding experimental optical band gaps for the LDA and GGA. For \( m\text{-ZrO}_2 \), the calculated (direct) band gap is 3.6 eV, to be compared with the experimental optical band gap around 5 eV.\textsuperscript{51} For \( \alpha\text{-Al}_2\text{O}_3 \), the calculated band gap (direct) is 5.8 eV, considerably lower than the accepted experimental value of 8.7 eV.\textsuperscript{52}

B. Origin of phase stability in \( \text{ZrO}_2 \)

Since the energy differences between competing \( \text{ZrO}_2 \) bulk phases are relatively small, and the corresponding unit cells have different shapes, we increased the kinetic-energy cutoff to 55 Ry (749 eV) for the plane-wave basis, to achieve absolute convergence of total energies reported in this section. This is feasible, because the bulk unit cells are much smaller than the interface unit cells in Sec. IV B.

Our PAW calculations suggest that the structural energy difference \( E^{t-c} = E^t - E^c \) between \( t\text{-ZrO}_2 \) and \( c\text{-ZrO}_2 \) is \(-0.038\) eV/ion, in favor of \( t\text{-ZrO}_2 \), in agreement with the experimental phase ordering. The fact that the PAW method is an all-electron formalism allows direct decomposition of the structural energies into native DFT components:

\[
E^{t-c} = E_{\text{kinetic}}^{t-c} + E_{\text{electrostatic}}^{t-c} + E_{\text{exchange-coulomb}}^{t-c}.
\]

This yields \( E_{\text{kinetic}}^{t-c} = 0.912 \text{ eV/ion}, \ E_{\text{electrostatic}}^{t-c} = -0.924 \text{ eV/ion}, \text{ and } E_{\text{exchange-coulomb}}^{t-c} = -0.025 \text{ eV/ion}, \) so that the \( c \rightarrow t \) transition is driven by electrostatics. Given that the one-electron kinetic-energy and classical electrostatic terms cancel each other nearly exactly, a major part of the net stabilization of \( t\text{-ZrO}_2 \) is derived from the nonclassical exchange-correlation term. This is not surprising, since the \( c \rightarrow t \) transition has character of an anion-cation bond stretching, where correlation is expected to play an important role. For the \( t\text{-ZrO}_2 \) and \( m\text{-ZrO}_2 \), our PAW calculations suggest that the structural energy difference \( E^{m-t} \) is \(-0.063 \text{ eV/ion}, \) in favor of \( m\text{-ZrO}_2 \), also in agreement with the experimental observed phase ordering. Decomposing this structural energy into native DFT components gives \( E_{\text{kinetic}}^{m-t} = -0.733 \text{ eV/ion}, \ E_{\text{electrostatic}}^{m-t} = 0.370 \text{ eV/ion}, \text{ and } E_{\text{exchange-coulomb}}^{m-t} = 0.300 \text{ eV/ion}, \) so that the \( t \rightarrow m \) transition is driven by kinetic-energy lowering. This is understandable because the \( t \rightarrow m \) transition is accompanied by a significant volume expansion of 4%, and the kinetic-energy term is stabilizing when expanding a solid (further electron delocalization). The experimental value\textsuperscript{53} for \( E^{m-t} \) is \(-0.02 \text{ eV/ion}, \) so that the structural energy difference between \( m\text{-ZrO}_2 \) and \( t\text{-ZrO}_2 \) is overestimated somewhat. This is a consequence of the GGA for exchange-correlation effects, and this effect has also been noted previously for \( \text{ZrO}_2 \) by Jomard et al.\textsuperscript{50} For this physical quantity, the LDA seems to give a result\textsuperscript{14} in better agreement with experiments: \( E^{m-t} = -0.026 \text{ eV/ion}. \) The apparent overestimation of \( E^{m-t} \) is a consequence of using a GGA, not the omission of \( \text{Zr} \) semicore states from the valence; we tested this issue, using the pseudopotential code VASP (Vienna \textit{ab initio} simulation program).\textsuperscript{54} Here we find that the structural energy \( E^{m-t} \) obtained with a GGA (Ref. 55) is decreased by 2% when including the \( \text{Zr}(4p) \) semicore states. Generally for \( \text{ZrO}_2 \), we expect the effect of \( \text{Zr} \) semicore states to be less than the sensitivity of which particular GGA parametrization is applied.\textsuperscript{13}

IV. SURFACES AND INTERFACES OF \( \alpha\text{-Al}_2\text{O}_3 \) AND \( \text{ZrO}_2 \)

In Sec. IV A we start by investigating the geometrical aspects of forming an interface between \( \alpha\text{-Al}_2\text{O}_3 \) and \( \text{ZrO}_2 \) crystals from a very general point of view. This investigation attracts our attention to two particular surfaces of \( \alpha\text{-Al}_2\text{O}_3 \) and \( \text{ZrO}_2 \), which should form a stable interface from an elasticity point of view. This particular choice of surfaces is also supported by experiments. Then in Sec. IV B we investigate the properties of these particular ceramic surfaces, we discuss \( m\text{-t} \) phase stability in \( \text{ZrO}_2 \) films in Sec. IV C and finally in Secs. IV D–IV H, we analyze the interface formed by these ceramic surfaces.
A. Interface geometry

We are considering the situation where ZrO$_2$ is deposited on top of a crystalline $\alpha$-Al$_2$O$_3$ surface. The structural possibilities for constructing a ZrO$_2$/\textit{$\alpha$}-Al$_2$O$_3$ interface are immense. First, there is the choice of which stable crystal surface of each ceramic to match against each other and how each should be oriented relative to each other. Then there is the question about termination and stoichiometry of both the ZrO$_2$ and Al$_2$O$_3$ sides of the interface. Finally, there is the issue of how the ZrO$_2$ and Al$_2$O$_3$ crystals will lock-in to each other. The latter generally requires atomistic simulations. Nature allows for aperiodicity at the interface, but our computational method relies on periodic boundary conditions, so it is necessary to enforce some degree of interface coherency, which translates into a choice of a unit cell for the interface. Of course, if the unit cell is sufficiently large, an aperiodic interface can be modeled, but this is currently far out of reach of \textit{ab initio} methods. Educated guesses are necessary here. The key objective is the matching of lattice vectors in the interface plane of each ceramic, so that the overall strain is small, when the interface is formed. Many related approaches may be used to achieve this, but we will apply a rather simple geometrical principle, which is illustrated in Fig. 3. Some surface unit cell of ZrO$_2$ with area $A_2$ is forced into coherency with a substrate ($\alpha$-Al$_2$O$_3$) surface unit cell with area $A_1$. By overlaying these unit cells, as indicated on the right-hand side of Fig. 3, we calculate the overlap area $\Omega$. We then define a misfit $\mu$ as

$$\mu = 1 - \frac{2\Omega}{A_1 + A_2}. \quad (2)$$

The measure $\mu$ is positive definite and quantifies the relative average length scale misfit (and not area mismatch) between two unit cells, which is seen by first-order expansion in the shape difference between two unit cells. In Table I we show the best matching unit-cell pairs, according to their $\mu$ value, for cells with area less than 50 Å$^2$. For simplicity and to compare with experiments, we use the c-ZrO$_2$ lattice in this scanning process. Because the lattice constants of the ZrO$_2$ polymorphs differ by only a few percent, the matches in Table I also apply to the other ZrO$_2$ polymorphs as well. However, one has to take into account all inequivalent lattice directions that correspond to each high-symmetry direction in c-ZrO$_2$. We exclude some very elongated unit cells, which are rather unrealistic as interface unit cells. As seen from this table, the c-ZrO$_2$(001)|$\alpha$-Al$_2$O$_3$(11$\bar{2}$0) combination has an acceptably low misfit $\mu$ of 4%. Moreover, this unit cell is orthogonal, and manageably small, 4.76 Å × 5.13 Å. The corresponding directions of the interface basis vectors are [11$\bar{2}$0] and [10$\bar{1}$0]. Experimentally, the growth direction of deposited YSZ has been observed as $\alpha$-Al$_2$O$_3$(11$\bar{2}$0)||YSZ(001). The ZrO$_2$/(11$\bar{2}$0) interface using a slab geometry and the unit-cell match corresponding to the first entry in Table I. We choose the $\alpha$-Al$_2$O$_3$ substrate to be 10.5 Å thick, corresponding to three $\alpha$-Al$_2$O$_3$(11$\bar{2}$0) layers. This substrate thickness is usually enough to emulate a bulk ceramic surface, both with regard to electronic structure and ionic relaxation effects. We will validate this assertion in Secs. IV D, IV E, and IV G.

A side view of the interface structures studied in our paper is shown in Figs. 4(a)–4(c). Each ZrO$_2$(001) overlayer is approximately 3 Å thick. Our geometry corresponds physically to an infinite array of ZrO$_2$/\textit{$\alpha$}-Al$_2$O$_3$ thin-film couples, with vacuum between them. We use 10 Å vacuum in between the thin-film couples, which is usually enough to ensure negligible coupling between the thin-film couples, unless a large dipole is present at the interface.

Table I. Best matching unit cells, according to the misfit measure $\mu$ defined in Eq. (2), of different $\alpha$-Al$_2$O$_3$ and c-ZrO$_2$ surfaces (restricted to surface areas less than 50 Å$^2$).

<table>
<thead>
<tr>
<th>Faces</th>
<th>Unit-cell</th>
<th>Misfit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-Al$_2$O$_3$</td>
<td>c-ZrO$_2$</td>
<td>(Å$^2$)</td>
</tr>
<tr>
<td>1102</td>
<td>001</td>
<td>24.4</td>
</tr>
<tr>
<td>0001</td>
<td>001</td>
<td>39.2</td>
</tr>
<tr>
<td>0010</td>
<td>110</td>
<td>39.2</td>
</tr>
<tr>
<td>1120</td>
<td>110</td>
<td>35.7</td>
</tr>
<tr>
<td>1120</td>
<td>110</td>
<td>35.7</td>
</tr>
</tbody>
</table>
FIG. 4. Lowest-energy structures ZrO$_2$(001)/α-Al$_2$O$_3$(1102) interface structures (a)–(c). Oxygen ions are drawn small and dark, Al ions medium sized and light gray, Zr ions largest and brightest. In (a)–(c), the Al$_2$O$_3$ subrate has three layers, corresponding to a thickness of 10.5 Å. The directional arrows in (a)–(c) refer to the α-Al$_2$O$_3$ substrate lattice. One ZrO$_2$ overlayer corresponds to approximately 2.9 Å. (a) One layer ZrO$_2$ deposited, (b) two layers ZrO$_2$ deposited, (c) three layers ZrO$_2$ deposited. (d)–(f) ZrO$_2$(001) surface slabs for the c, t, and m phase of ZrO$_2$, each with three layers. (d) c-ZrO$_2$: if ions are relaxed, c-ZrO$_2$(001) transforms into t-ZrO$_2$(001). (e) t-ZrO$_2$, ions relaxed. (f) m-ZrO$_2$, ions relaxed.

Table II, DFT-GGA surface energies for α-Al$_2$O$_3$(1102) and t-ZrO$_2$(001) (ions relaxed; equilibrium bulk lattice constants).

<table>
<thead>
<tr>
<th>Layers</th>
<th>α-Al$_2$O$_3$(1102)</th>
<th>t-ZrO$_2$(001)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>675</td>
<td>757</td>
</tr>
<tr>
<td>2</td>
<td>1055</td>
<td>803</td>
</tr>
<tr>
<td>3</td>
<td>1014</td>
<td>785</td>
</tr>
</tbody>
</table>

B. The clean α-Al$_2$O$_3$(1102) and ZrO$_2$(001) surfaces

In Table II we show the surface energies of α-Al$_2$O$_3$(1102) and t-ZrO$_2$(001) after an ionic relaxation is performed. Allowing for ionic relaxation, a c-ZrO$_2$ slab transforms into a t-ZrO$_2$ slab by a barrierless transition, even when the unit-cell dimensions are frozen. For the t-ZrO$_2$(001) surface, the tetragonal distortion is oriented along the surface normal, as seen in Fig. 4(e), which reduces the surface energy significantly.14 The results in Table II refer to the case where the surface unit-cell lattice vectors are fixed to their respective bulk value. The surface energy converges fast with slab thickness, as is also the case for transition-metal surfaces. A nearsightedness principle is also valid for these ceramic surfaces, as discussed by Christensen and Carter,14 due to the localized and inert nature of the electronic structure. In Table II we observe an oscillation in the surface energy for t-ZrO$_2$, apparently depending on the t-ZrO$_2$ slabs being odd layered/even layered. This may be related to the fact that odd-layered crystalline t-ZrO$_2$(001) slabs have symmetry P4$\bar{m}$2, whereas even-layered crystalline t-ZrO$_2$(001) slabs have symmetry Pmn$. When forming the ZrO$_2$/Al$_2$O$_3$ onto Al$_2$O$_3$, ZrO$_2$ becomes slightly strained to accommodate the 4% mismatch. In Sec. IV F we return to this issue.

We observe a dramatic lowering (by more than a factor of 2) of the surface energy of t-ZrO$_2$(001) when applying the GGA instead of the LDA. The latter yields a surface energy of 1577 mJ/m$^2$, (Ref. 14) similar to predictions from periodic Hartree-Fock calculations of a surface energy of 1630 mJ/m$^2$ for a three layer slab.58 A similar effect has been found by applying the GGA to the TiO$_2$(110) and SnO$_2$(110) surfaces.59,60 In contrast, Guo et al.56 using the SCF-DV embedded cluster method for α-Al$_2$O$_3$ surfaces, found only very small changes by applying a GGA; for the α-Al$_2$O$_3$(1102) surface they found a surface energy of 2950 mJ/m$^2$ (ions unrelaxed), which is in quantitative disagreement with our all-electron calculations, which yield 1702 mJ/m$^2$ for a three layer slab with unrelaxed ions. One might speculate that the source of the discrepancies are the boundary conditions introduced by the embedding method used by these authors. Manassidis and Gillan51 studied five low index α-Al$_2$O$_3$ surfaces with the LDA and the pseudo-potential formalism and found relaxed surface energies in the range 1400–2550 mJ/m$^2$, further supporting the trend of the GGA dramatically lowering the surface energies of oxides. Hartree-Fock calculations also yield very large values of surface energies for relaxed low index α-Al$_2$O$_3$ surfaces, of order 5000 mJ/m$^2$.52
In conclusion, a tendency for smaller surface energies when using the GGA instead of the LDA is clear. Comparison with experiments suggest that the GGA results are closer to reality than LDA or Hartree-Fock results for surface energies; the surface free energies of typical metal oxides fall in range 300–900 mJ/m².63 Virtually all ab initio calculations refer to T=0 K, so an entropy correction of order 0.4 mJ/m² must be included for a proper comparison,64 but still the GGA results are closer to reality than LDA results for surface energies. This is not particularly surprising, since it is well known that both the LDA and the HF methods will overestimate the energy to break bonds. Since the energy to form a surface involves exactly this process (bulk bond breaking), it is to be expected that the GGA would improve greatly upon the overestimates from the other two theories.

In Figs. 5(a) and 5(b) we show the DOS of surface anions (solid lines) for α-Al₂O₃(1 0 0 2) and t-ZrO₂(001), respectively, compared to a corresponding bulk anion in each oxide (dashed lines). The DOS for t-ZrO₂(001) corresponds to the unstrained unit cell. The surface ions are relaxed in both cases. For both oxides, a surface band narrowing is visible, due to decreased coordination, and localization of electronic charge as for covalent surfaces. A corresponding upshift of all electronic states at the surface due to the decreased surface Madelung potential is also clear. Further, the characteristic Zr(d) features in the t-ZrO₂ valence band is smoothed at the surface, indicating again the decreased coordination at the surface, which decreases the crystal-field splittings of the bands [compare to Fig. 2(b) which shows that the t-ZrO₂ valence-band character has strong Zr(d) character].

C. The monoclinic-tetragonal phase transition in thin ZrO₂(001) films

Since the stable low-temperature phase of zirconia is m-ZrO₂, t-ZrO₂ slabs will eventually transform into m-ZrO₂ at low temperatures, if the slabs are sufficiently thick. An interesting question is if there exists an ultrathin-film regime, where t-ZrO₂ is actually more stable than the corresponding m-ZrO₂ thin film at low temperatures. Experimentally, thin t-ZrO₂ films have been stabilized in dense sandwich structures with amorphous alumina.22 For the bulk (t→m) transition an orientational relationship exists65 between crystalline directions in the (t,m) phases. This relationship implies that the t-ZrO₂(001) transforms into the m-ZrO₂(001) surface. Our previous work14 suggests that the surface energy for the m-ZrO₂(001) surface is ~200 mJ/m² higher than for t-ZrO₂(001). Since the bulk (t→m) transformation energy obtained in our calculations is ~0.06 eV/ion, a back-of-the-envelope estimate suggests that only a few layers of t-ZrO₂(001) may be stable at low temperatures. However, the m phase is not rigorously distinguishable from the t phase for very thin films; establishing the characteristic sevenfold Zr-cation coordination requires at least three ZrO₂(001) layers. On the other hand, the pinning provided by the substrate might increase the absolute stability regime of t-ZrO₂(001) at low temperatures, due to the significant volume increase of 4% for the bulk t→m-ZrO₂ transition.

Table III shows the transformation energy, normalized per unit area, between isolated t-ZrO₂(001) and m-ZrO₂(001) slabs for different numbers of ZrO₂ layers. The unit cell is fixed to the dimensions given by the lock-in to the α-Al₂O₃(1 0 0 2) substrate, which corresponds to a ~4% lattice mismatch, as discussed in Sec. IV A. In all three cases, the slab structure relaxes to a structure appearing like the m-ZrO₂(001); see Fig. 6 (upper row) and compare to the bulk unit cell in Fig. 1(a). Thus the t-ZrO₂(001) slabs, see Fig. 6 (lower row), are only locally stable. Strictly speaking, as mentioned above, it only makes sense to talk about the

<table>
<thead>
<tr>
<th>ZrO₂ layers</th>
<th>t→m energy (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>21</td>
</tr>
<tr>
<td>2</td>
<td>55</td>
</tr>
<tr>
<td>3</td>
<td>96</td>
</tr>
</tbody>
</table>
monoclinic structure for 3 or more layers of ZrO₂, but from Fig. 6 it seems that the one- and two-layer ZrO₂(001) slabs transform into a precursor of m-ZrO₂(001). The transition is incomplete, though, as revealed by the coordination around the middle layer cations in Fig. 6(c), which have anion-cation bond lengths of (1.98, 2.04, 2.04, 2.08, 2.20, 2.38, 2.38) Å and (1.98, 2.02, 2.04, 2.06, 2.20, 2.38, 2.42) Å, respectively. There are two sets of bond lengths, because the symmetry is broken and the two middle cations are inequivalent. The corresponding m-ZrO₂ bulk anion-cation bond lengths are (2.06, 2.06, 2.14, 2.16, 2.16, 2.22, 2.26) Å. This incomplete transition is mainly related to the fact that we froze the surface lattice vectors to those in registry with the α-Al₂O₃(1102) substrate. Despite this confinement, the t-ZrO₂ slabs transform into a structure close to m-ZrO₂. Furthermore, this transition is in accord with the direction relation established by Bansil and Heuer, 65 i.e., t-ZrO₂(001)||m-ZrO₂(001), as is apparent when comparing Fig. 6 and Figs. 1(a) and 1(b).

It is unlikely that the t→m-ZrO₂ transition we find in ultrathin ZrO₂ films is strain induced, because the straining necessary to obtain lock-in with the α-Al₂O₃(1102) substrate actually corresponds to a 3% volume decrease of the t-ZrO₂ crystal, whereas the t→m-ZrO₂ transition is accompanied by a 4% volume increase. Thus, if anything, the α-Al₂O₃(1102) substrate should inhibit the t→m transition, and yet we observe it to occur.

D. Interface structure

In this section we address the structural properties in the interface region of ZrO₂(001)/α-Al₂O₃(1102). ZrO₂ in the c phase is deposited onto Al₂O₃ as thin films and the structure is subsequently relaxed. This procedure is meant to mimic plasma spraying or another process leading to granular microstructure, but is not meant to represent an atomic growth mechanism, like vapor deposition. Such processes are next to impossible to simulate on the ab initio level, due to the long-time scales involved in diffusion, but also the additional complexity introduced by needing to consider chemical potentials, which may give rise to nonstoichiometry in the interface region.

In Fig. 4 we show the lowest-energy quenched interface structures we find for one, two, and three deposited ZrO₂ overlayers, juxtaposed with a three-layer (001) slab of each ZrO₂ phase, c, t, and m. These ZrO₂ overlayers are deposited onto a three-layer α-Al₂O₃(1102) substrate, corresponding to a thickness of 10.5 Å, which emulates the macroscopic α-Al₂O₃(1102) substrate. We will return to the issue of finite substrate thickness later.

The interface structure with two ZrO₂ overlayers [Fig. 4(b)] seems to have the ZrO₂ overlayers translated with respect to the Al₂O₃ substrate. However, the two Al₂O₃(1102) surface anions in the unit cell are symmetry equivalent, so that the ZrO₂ film has simply been locked into the substrate at a different, but equivalent point.

The general impression is that the α-Al₂O₃(1102) substrate maintains its crystallinity more than the ZrO₂ adlayers, which appears more glassy. This is especially the case for the anion lattice on the ZrO₂ side of the interface. Also, the Zr layers close to the interface buckle more than Zr layers farther from the interface as seen in Figs. 4(b) and 4(c). The fact that the ZrO₂ adlayers seem to become most perturbed from crystallinity is understandable considering the fact that ZrO₂ is forced into registry with the substrate and further that bulk α-Al₂O₃ has a stiffness twice that of bulk ZrO₂.

We performed molecular-dynamics sequences at T = 1600 K for the interface structures with one- and two-layered ZrO₂ films to explore the stability of the quenched structures. In both cases, at high temperatures, there are cation-cation interactions at the interface, between cations closest to the interface. When we quench the structures, the cation-cation interaction disappears for the monolayer ZrO₂ film, because the Zr dives back into the ZrO₂ film and we reobtain the original low-temperature structure. However, for the bilayered ZrO₂ film, the cation-cation interaction remains stable after quench. We show this structure in Fig. 7(b), along with the structure we obtain by just depositing a two-layered ZrO₂ film and quenching the structure in Fig. 7(a)—this structure corresponds to a local minimum in the total energy. Figure 7(b) is 0.09 eV/unit cell lower in energy than Fig. 7(a). The shortest Al/Zr distances across the interface for the structures in Fig. 7 are 3.03 Å and 2.85 Å for Figs. 7(a) and 7(b), respectively. For comparison, the smallest bulk cation-cation bond lengths are d(Zr-Zr) = 3.34 Å in m-ZrO₂ and d(Al- Al) = 2.68 Å in α-Al₂O₃. The simple average of these bulk values is d(Al-Zr) = 3.01, relatively close to most values in Table IV, but 0.16 Å longer than for the interface structure displayed in Fig. 7(b. [In Table IV, 2a and 2b refers to Figs. 7(a) and 7(b), respectively.] We also see that this recoordination of the Zr ion closest to the interface generally induces some distortion in the anion lattice in the three-layer ZrO₂ film. We will discuss how this affects the electronic density of states in Sec. IV H.
FIG. 7. Two minima for $\alpha$-$\text{Al}_2\text{O}_3$(1102) + two layers $\text{ZrO}_2$(001). Oxygen ions are drawn small and dark, Al ions medium-sized and light gray, Zr ions largest and brightest. (a) is obtained by deposition of $c$-$\text{ZrO}_2$ and just quenching the structure. (b) is obtained by heating (a) to $T = 1600$ K and requenching the structure. (b) is identical to Fig. 4(b). (b) is 0.09 eV/unit cell more stable than (a). The shortest Al-Zr distances across the interface for the structures in (a) are 3.03 Å and 2.85 Å in (b). For comparison, the smallest bulk cation/cation bond lengths are $d(\text{Zr-Zr}) = 3.34$ Å in $m$-$\text{ZrO}_2$ and $d(\text{Al-Al}) = 2.68$ Å in $\alpha$-$\text{Al}_2\text{O}_3$.

It is clear from Figs. 4(a)–4(c), compared to Fig. 4(d)–4(f) that the $m$ phase of the $\text{ZrO}_2$ overlayers are also energetically preferred, when the interface to $\alpha$-$\text{Al}_2\text{O}_3$(1102) is formed. Table IV shows the ionic bond lengths in the interface region, divided according to whether the bonds are across or mostly parallel to the interface, i.e., within the surfaces of each oxide forming the interface. No systematic trend is apparent with the variation in number of $\text{ZrO}_2$ layers. Bonds across the interface are typically close to the shortest value in the bulk crystal [1.88 Å for $\alpha$-$\text{Al}_2\text{O}_3$, 2.06 and 2.09 for ($m$,t)-$\text{ZrO}_2$, respectively]. Parallel to the interface, a range of bond lengths is observed. On the $\text{Al}_2\text{O}_3$ side, these ranges are mostly delimited by the bulk values (1.88 and 1.99 Å), whereas on the $\text{ZrO}_2$ side, bond lengths are shorter than the smallest bulk values. Comparing results for a $\text{ZrO}_2$ monolayer deposited onto three and four layers of $\alpha$-$\text{Al}_2\text{O}_3$(1102), respectively, suggests that also interface structural properties are well converged with respect to substrate thickness at three layers of alumina.

Figure 4(b)–4(c) shows that both $\alpha$-$\text{Al}_2\text{O}_3$(1102) and $\text{ZrO}_2$(001) have four anion-cation bonds between each layer per unit cell in the bulk part. However, there are only three anion-cation bonds across interface [except for the bilayer $\text{ZrO}_2$ film, where some (screened) cation-cation interaction is found, adding stability to this structure]. One $\text{Al}_2\text{O}_3$-side oxygen ion is unsaturated (does not coordinate with a Zr ion), partly due to a Zr-layer buckling normal to the interface, but also an intrinsic symmetry mismatch for the interface combination $\text{ZrO}_2$(001)$\mid \alpha$-$\text{Al}_2\text{O}_3$(1102); although the crystalline length scales fit very well, the anion-cation alignment across the interface is not ideal. Such a situation of interface structural frustration is also expected for other heterogeneous interfaces. This nonideal alignment of anion-cation pairs across the interface partly explains the weak $\text{ZrO}_2$(001)$\mid \alpha$-$\text{Al}_2\text{O}_3$(1102) cohesion, discussed in the next section.

### E. Interface cohesion

In this section we focus on the energetic aspects of the $\text{ZrO}_2$/$\text{Al}_2\text{O}_3$ interface. The main quantity is the adiabatic work of adhesion $W > 0$:

$$ W = E_{\text{Al}_2\text{O}_3} + E_{\text{ZrO}_2} - E_{\text{ZrO}_2\mid \text{Al}_2\text{O}_3}, $$. (3)

where $E_{\text{Al}_2\text{O}_3}$, $E_{\text{ZrO}_2}$, and $E_{\text{ZrO}_2\mid \text{Al}_2\text{O}_3}$ refer to the total energies of the relaxed, isolated $\text{Al}_2\text{O}_3$ and $\text{ZrO}_2$ films and $E_{\text{ZrO}_2\mid \text{Al}_2\text{O}_3}$ refers to the total energy of the relaxed interface structure. Generally, the mechanical work needed to separate an interface is larger than the adiabatic work of adhesion $W$ due to dissipative processes, as discussed by Finnis. Thus our predictions may be considered as rough lower bounds for the work of adhesion obtained by any cleavage experiment.

In Table V we show the calculated adiabatic work of adhesion $W$ for $\alpha$-$\text{Al}_2\text{O}_3$(1102) with various numbers of $\text{ZrO}_2$(001) layers deposited and the interface subsequently relaxed. In Eq. (3), $E_{\text{ZrO}_2\mid \text{Al}_2\text{O}_3}$ refers to the energy of the isolated, relaxed $\text{ZrO}_2$(001) slabs subject to the same periodic boundary conditions as in the interface calculation that produces $E_{\text{ZrO}_2\mid \text{Al}_2\text{O}_3}$, i.e., in the incomplete monoclinic phase, as discussed in Sec. IV C. It is important to subtract this quantity from $E_{\text{ZrO}_2\mid \text{Al}_2\text{O}_3}$ and not the energy of an $m$-$\text{ZrO}_2$(001) slab with bulk $m$-$\text{ZrO}_2$ lattice constants, because then the value obtained for $W$ contains a bulk plastic component, which diverges with increasing numbers of $\text{ZrO}_2$ layers deposited. Moreover, this bulk strain component is unrelated to the local cohesive properties of the interface per se, which we

### Table IV. Bond lengths (Å) in the $\text{ZrO}_2$/Al$_2$O$_3$(1102) interface region. [ ] = indicates a range of bond lengths present.

<table>
<thead>
<tr>
<th>Ceramic layers in slab</th>
<th>Direction of bonds with respect to interface</th>
<th>Parallel</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Across</td>
<td></td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>$\text{Al-O}$</td>
<td>$\text{Zr-O}$</td>
</tr>
<tr>
<td></td>
<td>$\text{ZrO}_2$</td>
<td>$[1.88\text{,}1.94]$</td>
</tr>
<tr>
<td>3</td>
<td>$2\text{a}$</td>
<td>$1.86\text{,}1.87$</td>
</tr>
<tr>
<td>3</td>
<td>$2\text{b}$</td>
<td>$1.85\text{,}1.87$</td>
</tr>
<tr>
<td>4</td>
<td>$1$</td>
<td>$1.90\text{,}1.91$</td>
</tr>
</tbody>
</table>

$^a$Two layers of $\text{ZrO}_2$, with structure corresponding to Fig. 7(a). See Sec. IV D for more details.

$^b$Two layers of $\text{ZrO}_2$, with structure corresponding to Fig. 7(b). See Sec. IV D for more details.
TABLE V. DFT-GGA adiabatic adhesion energies $W$ for the ZrO$_2$(001)/α-Al$_2$O$_3$(1 1 0 2) interface.

<table>
<thead>
<tr>
<th>Number of oxide layers</th>
<th>$W$ (mJ/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$</td>
<td>ZrO$_2$</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>2$^a$</td>
</tr>
<tr>
<td>3</td>
<td>2$^b$</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
</tr>
</tbody>
</table>

$^a$Two layers of ZrO$_2$, with structure corresponding to Fig. 7(a). See Sec. IV D for more details.
$^b$Two layers of ZrO$_2$, with structure corresponding to Fig. 7(b). See Sec. IV D for more details.

want to characterize. Of course, this means in principle that one has to subtract an accommodation energy for the ZrO$_2$ adlayers from our value of $W$ to obtain an “experimental” value. This accommodation energy will represent dislocations and other defects possibly created on the ZrO$_2$ side on intermediate length scales.

It is seen that $W$ has values ~1200 mJ/m$^2$ and that there is no systematic variation with the number of layers—in other words, the chemistry of the ZrO$_2$/Al$_2$O$_3$ is rather local. Of course, this definition is only unique for stoichiometric and crystalline structures. The sign and magnitude of $\sigma_{\text{ZrO}_2||\text{Al}_2\text{O}_3}$ tells whether the interface bonds are stronger than the constituent bulk oxide bonds. This fact is also expressed quantitatively, normalized by interface area, in the interface tension $\sigma_{\text{ZrO}_2||\text{Al}_2\text{O}_3}$:

$$\sigma_{\text{ZrO}_2||\text{Al}_2\text{O}_3} = \sigma_{\text{Al}_2\text{O}_3} + \sigma_{\text{ZrO}_2} - W,$$

which follows from Eq. (3) by using the definition of the surface-interface tension for a given structure $i$ from its total energy $E_i$:

$$E_i = \sigma_i + E_{i\text{Bulk reference}}.$$

In this equation $E_{i\text{Bulk reference}}$ is total energy of the structure $i$ embedded in its appropriate reference bulk environment. Of course, this definition is only unique for stoichiometric and crystalline structures. The sign and magnitude of $\sigma_{\text{ZrO}_2||\text{Al}_2\text{O}_3}$ may reflect a propensity to form an intermediate phase (chemically mixed) at the interface.

Using $\sigma_{t-\text{ZrO}_2} = 800 \text{ mJ/m}^2$ and $\sigma_{\text{Al}_2\text{O}_3} = 1000 \text{ mJ/m}^2$ (approximate asymptotic values in Table II) gives $\sigma_{\text{ZrO}_2||\text{Al}_2\text{O}_3} \sim +600 \text{ mJ/m}^2$. It would be slightly more correct to use $\sigma_{m-\text{ZrO}_2}$ in Eq. (4), since even very thin ZrO$_2$(001) films transform to a monoclinic structure, as is discussed in Sec. IV C. This quantity is not readily available from our calculations, due to the strained state of these films when constrained to the substrate lattice vectors as in our calculation, but a previous study of ZrO$_2$ surfaces$^{14}$ within the LDA for exchange-correlation effects suggests that the surface energy for $m$-ZrO$_2$(001) is ~200 mJ/m$^2$ higher than $t$-ZrO$_2$(001). Whatever specific value is used for $\sigma_{\text{ZrO}_2}$, the sign and magnitude of $\sigma_{\text{ZrO}_2||\text{Al}_2\text{O}_3}$ does not change. This is also in accordance with the two-component phase diagram$^{66}$ of ZrO$_2$/Al$_2$O$_3$, which shows that this system only displays entropy-driven mixing.

F. Interface strain

In this section we address the issue of strain in the deposited ZrO$_2$ film and the influence of strain on cohesion and structure. In Table VI we show the energy required to strain thin $t$-ZrO$_2$ films from the natural square lattice with the bulk lattice constant $a_0=5.07$ Å to the $\alpha$-Al$_2$O$_3$(1 1 0 2) coherent substrate cell with dimensions 4.76 Å×5.13 Å, see Sec. IV A. Ions are allowed to relax in both cases with the lattice constants fixed. The dilations perpendicular to the surface, measured from outermost anion to outermost anion on each side of the slab, are given in Table VI. Some even-odd oscillation with number of layers is present, which can be related to the fact that even- and odd-layered $t$-ZrO$_2$(001) slabs have different symmetry, $P4m2$ and $Pmn2$ for even- and odd-layered slabs, respectively (subsequent layers are not translational copies of each other, but related by a 90° screw or inversion operation). The strain energy for $m$-ZrO$_2$(001) slabs forced into registry with the substrate is expected to be significantly larger, due to the large volume expansion accompanying the ($t$→$m$) transition. Despite the compressive strain providing a driving force against the ($t$→$m$) transition, the (incomplete) $m$ phase is energetically preferred over the $t$ phase, as discussed in Sec. IV C. The magnitude of the strain energy in ZrO$_2$ films forced into registry with the $\alpha$-Al$_2$O$_3$(1 1 0 2) substrate, compared to

```
<table>
<thead>
<tr>
<th>Layers</th>
<th>Strain energy (mJ/m$^2$)</th>
<th>Absolute slab dilation along [001] direction (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11</td>
<td>0.03</td>
</tr>
<tr>
<td>2</td>
<td>124</td>
<td>0.12</td>
</tr>
<tr>
<td>3</td>
<td>323</td>
<td>0.08</td>
</tr>
<tr>
<td>4</td>
<td>488</td>
<td>0.11</td>
</tr>
</tbody>
</table>
```
the interface adhesion energy, suggests that only partial registry at the ZrO$_2$ (001)/\(\alpha\)-Al$_2$O$_3$ (11\(\overline{2}\)) interface is likely to be present at the real interface. This further suggests that dislocations may play a role in interface de-adhesion.

G. Charge distribution

In Table VII we display for each ion the approximate charge transfer upon interface formation, as function of the number of deposited ZrO$_2$ layers. In other words, from the charge on each ion in the interface region, we subtract the charge on the corresponding surface ion in the respective isolated oxide surface. These charges are obtained by spatial integration inside spheres around each ion, as discussed in Sec. II A. These spheres are not strictly space dividing, therefore charge conservation is not ensured, however some error cancellation is obtained when taking differences. Therefore we take these charge differences as a qualitative indicator of the charge transfer on forming the interface.

Generally, this interface formation is accompanied by almost no charge transfer. This is not surprising, because each oxide in our calculation is stoichiometric so that each ion remains mostly in its conventional charge state, due to oxygens large electron affinity. However, a minor trend is apparent: the cations closest to the interface on each side loses a small amount of charge, which is partly donated to the first oxygen atoms on the ZrO$_2$ side of the interface. The magnitude of charge redistribution within ions seems rather sensitive to the number of deposited ZrO$_2$ layers but is confined to the ions with direct interface contact.

H. Density-of-states at the interface

Figure 8 displays the total valence DOS for the interface structure with three layers \(\alpha\)-Al$_2$O$_3$ (1\(\overline{1}\)02) + three layers ZrO$_2$(001). Juxtaposed are the DOS for the corresponding isolated \(\alpha\)-Al$_2$O$_3$ (1\(\overline{1}\)02) and ZrO$_2$(001) surface slabs for comparison. The spectra for the interface structure and the respective surface slabs are shifted, so that the DOS, projected onto ions on the vacuum sides of the interface slab, is coincident with the DOS projected onto ions on the vacuum sides of the corresponding surface slabs—in other words, the spectra are aligned according to ions far from the physical interface, so that shifts in the DOS can be read off Fig. 8.

Figure 8 shows that \(\alpha\)-Al$_2$O$_3$ fixes the valence-band maximum whereas ZrO$_2$ defines the conduction-band mini-

---

**Table VII. Charge transfer (electrons/atom) projected onto atoms in the ZrO$_2$ and Al$_2$O$_3$ layers at the interface.**

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2a</th>
<th>2b</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Interface ZrO$_2$ layer</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>0.03</td>
<td>0.00</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>O</td>
<td>0.05</td>
<td>0.04</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td><strong>Interface Al$_2$O$_3$ layer</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>−0.06</td>
<td>−0.07</td>
<td>−0.07</td>
<td>−0.03</td>
</tr>
<tr>
<td>O</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td><strong>Interface plane</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>0.00</td>
<td>0.00</td>
<td>−0.01</td>
<td>−0.02</td>
</tr>
<tr>
<td>Al</td>
<td>−0.05</td>
<td>−0.04</td>
<td>−0.02</td>
<td>−0.02</td>
</tr>
<tr>
<td>O</td>
<td>0.00</td>
<td>0.00</td>
<td>0.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>

---

\textsuperscript{a}Two layers of ZrO$_2$, with structure corresponding to Fig. 7(a). See Sec. IV D for more details.

\textsuperscript{b}Two layers of ZrO$_2$, with structure corresponding to Fig. 7(b). See Sec. IV D for more details.
formed. A weakly covalent conduction-band-valence-band interface anion is broadened more than the valence-band width on the Al$_2$O$_3$ side, whereas the anions on the ZrO$_2$ side go from threefold to fourfold coordination on forming the interface, whereas the anions on the ZrO$_2$ side experience significant stabilizing Madelung potential shifts, when the interface is formed. These Madelung shifts make a significant contribution to the cohesion, due to the relatively epitaxial character of the interface, see Fig. 4(right) that the Al$_2$O$_3$-derived conduction band has disappeared for the interface—this is due to the fact that only 6 empty bands are included in all our calculations, and for the interface structure these 6 empty bands will only represent the ZrO$_2$-derived conduction band on the ZrO$_2$ side. More unoccupied bands must be included for the Al$_2$O$_3$-derived conduction band to appear. This, however, has no effect on the occupied valence bands on either side of the interface.

Figure 9 displays the DOS projected onto representative interface ions on each side of the interface, compared to the DOS for the corresponding isolated surface ions. The interface DOS is derived from the three layers $\alpha$-Al$_2$O$_3$($1\bar{1}02$) + three layers ZrO$_2$(001) structure, while the surface DOS is from the corresponding isolated surface slabs. We apply same spectrum alignment procedure as in Fig. 8. Both isolated surface slabs are oxygen terminated, therefore the surface anions of both oxides experience significant stabilizing Madelung potential shifts, when the interface is formed. These Madelung shifts make a significant contribution to the cohesion, due to the relatively epitaxial character of the interface, see Fig. 4(a)–4(c) (in the same way as the Madelung potential is the main stabilizing component in ionic bonding). The Madelung shift is slightly larger for anions on the ZrO$_2$ side, monitoring the O(2$s$)-derived states. This follows from simple steric considerations, because the anions on the Al$_2$O$_3$ side go from threefold to fourfold coordination on forming the interface, whereas the anions on the ZrO$_2$ side goes from twofold to threefold coordination by the interface formation, which is a larger relative change. In other words, trends in Madelung potential shifts are related to the relative compactness of $\alpha$-Al$_2$O$_3$(1$\bar{1}02$) versus ZrO$_2$(001). This is also supported by the fact that valence-band width on the ZrO$_2$ interface anion is broadened more than the valence-band width on the Al$_2$O$_3$ anion, when the interface is formed. A weakly covalent conduction-band-valence-band interaction is visible, mediated through Zr to interface oxygen ions on the Al$_2$O$_3$ side—this is because the Al$_2$O$_3$ valence band lies higher than the ZrO$_2$ valence band and the ZrO$_2$ conduction band lies lower than the Al$_2$O$_3$ conduction band.

Figure 10 shows the DOS projected onto anions and cations at the interface and farther from the interface. Thus, Fig. 10 represents a primitive DOS profile across the interface region. The reference ‘‘bulk’’ ions are situated in approximately in the middle of each oxide in the interface structure. More specifically, they have the following distances from the interface (distance from the nearest surface given in parentheses): Al: 4.6 Å (5.2 Å), O (Al$_2$O$_3$ side): 4.2 Å (5.6 Å); Zr: 4.2 Å (4.0 Å), O (ZrO$_2$ side): 3.3 Å (4.8 Å). The DOS is extracted from the largest calculation, three layers $\alpha$-Al$_2$O$_3$(1$\bar{1}02$) + three layers ZrO$_2$(001).
On the ZrO$_2$ side, the characteristic $d$ features of the valence band are smoothened for the ions with direct interface contact. On the Al$_2$O$_3$ side, the DOS features for the interface ions are more similar to bulk Al$_2$O$_3$. The ZrO$_2$ conduction band around +2 eV has a visible tail on the Al$_2$O$_3$ side, which decays away as one moves further into the Al$_2$O$_3$ side. The average penetration depth for this tail is 2.0 Å, as determined from the integrated weight in the ion-projected DOS spectrum. No band bending effects are visible. These would mainly appear as uniform shifts in the ion-projected DOS spectra.

Figure 11 depicts the DOS projected onto interface Al-Zr ions for the two interface structures displayed in Fig. 7 with two layers ZrO$_2$(001) deposited. The structure in Fig. 7(b) has some Al-Zr coordination at the interface, as is apparent in Table IV and Fig. 7(b), whereas Al-Zr coordination is less prominent in the structure in Fig. 7(a). Figure 11 suggests some covalent Al-Zr interaction between the Al$_2$O$_3$ valence-band projection on Al and the ZrO$_2$ conduction band projection on Zr for the interface [Fig. 7(b)]. This interaction seems to increase the local band gap. Conversely, an Al$_2$O$_3$ conduction-band ZrO$_2$ valence-band interaction is not apparent for the coordinating Al-Zr pair in Fig. 7(b).

V. DISCUSSION

Our calculations show that $m$-ZrO$_2$(001) is energetically favored over $t$-ZrO$_2$(001) on the $\alpha$-Al$_2$O$_3$(1$\bar{1}$02) substrate. This is consistent with experiments. On the $\alpha$-Al$_2$O$_3$(10$\bar{1}$2) substrate, Moulzolf et al. observed $m$-ZrO$_2$(001) growth. However, for slow deposition rates on $\alpha$-Al$_2$O$_3$(10$\bar{1}$2), they observed $c$-ZrO$_2$(001) to grow in films up to 400 Å thick. This is an intriguing observation, because our electronic structure calculations show that bulk $c$-ZrO$_2$ can undergo a barrierless transformation to quasi-$t$-ZrO$_2$ at low temperatures even if the unit cell is frozen to the dimensions of bulk $c$-ZrO$_2$; this leaves open the possibility that $c$-ZrO$_2$(001)/$\alpha$-Al$_2$O$_3$(1$\bar{1}$02) is entropy stabilized. An energetic order-of-magnitude argument suggests that it is unlikely the $c$-ZrO$_2$(001)/$\alpha$-Al$_2$O$_3$(1$\bar{1}$02) should be absolutely stable over $m$-ZrO$_2$(001)/$\alpha$-Al$_2$O$_3$(1$\bar{1}$02). Taking the ($c\rightarrow m$)-ZrO$_2$ potential transformation energy release to be $\sim$0.06 eV/ion translates to 90 mJ/m$^2$ per Å thickness in a ZrO$_2$ film. Comparing this to the order of magnitude of differences in surface and interface energies leaves it unlikely that $c$-ZrO$_2$-films up to 400 Å thick on $\alpha$-Al$_2$O$_3$ should be globally stable at low temperatures. This corresponds to $\sim$36 000 mJ/m$^2$ releasable bulk energy, of which a small amount can be used to compensate for an unfavorable interface coordination. Thus, we believe the deposited $c$-ZrO$_2$(001) films ultimately transform into $m$-ZrO$_2$(001) upon thermal cycling. Likewise, the nanolaminates $t$-ZrO$_2$ amorphous Al$_2$O$_3$ structures studied by Scanlan et al. are likely to be kinetically stabilized. The polycrystalline nature of the nanolaminates may serve to stabilize small crystallites of $t$-ZrO$_2$, as we have suggested previously.

VI. CONCLUSIONS

We have studied the ZrO$_2$(001)/$\alpha$-Al$_2$O$_3$(1$\bar{1}$02) interface using the all-electron PAW formalism and a GGA functional for exchange-correlation effects. We characterize this interface as weakly coupled, but relatively epitaxial, due to the small lattice-constant mismatch between ZrO$_2$(001)/$\alpha$-Al$_2$O$_3$(1$\bar{1}$02). Three out of four anion-cation bonds, which are broken when forming each of the $\alpha$-Al$_2$O$_3$(1$\bar{1}$02) and ZrO$_2$(001) surfaces, are reestablished when the ZrO$_2$(001)/$\alpha$-Al$_2$O$_3$(1$\bar{1}$02) interface is formed. Rather interestingly, we find that a stabilizing (screened) cation-cation interaction across the interface is possible, where the Al-Zr distance across the interface is 0.15 Å shorter than the average cation-cation distances for these oxides. This could be due to interactions of the remaining Zr $d$ electrons with empty sp states on the Al cations. It is questionable whether this slightly counterintuitive feature will be
reproduced by semipirical model potentials currently available for modeling ionic materials. The covalent effects at this interface are found to be relatively weak, though. The calculated adiabatic work of adhesion is \( \sim 1200 \text{ mJ/m}^2 \), and this value is roughly independent of the number of deposited \( \text{ZrO}_2 \) layers. In other words, the interface chemistry is this value is roughly independent of the number of deposited \( \text{ZrO}_2 \), although the phase stability ordering is correct.

The study of complex structures like the \( \text{ZrO}_2 \) films, but characteristic monoclinic precursor structures are found in these cases. We find it unlikely that the incomplete tetragonal \( \rightarrow \) monoclinic transition is strain induced, due to the fact that the strain is compressive and that the tetragonal \( \rightarrow \) monoclinic transition accompanied by a 4\% volume increase. We find that \( \text{ZrO}_2 \) adhesion onto the \( \alpha\text{-Al}_2\text{O}_3(1\overline{1}02) \) surface is not sufficient to suppress the tetragonal \( \rightarrow \) monoclinic transition, even as it induces significant compressive strain in the \( \text{ZrO}_2 \) overlayer, due to the larger specific volume of the monoclinic \( \text{ZrO}_2 \) phase.

We investigate the effect of finite \( \text{Al}_2\text{O}_3 \)-substrate thickness and find that in most respects, for electronic structure as well as for structural aspects, a film thickness of \( \sim 10 \) Å is sufficient to emulate the infinite \( \text{Al}_2\text{O}_3 \) substrate, as long as the surface lattice vectors of \( \text{Al}_2\text{O}_3 \) are kept fixed to prevent artificial substrate creep parallel to the surface.

We find that GGA, compared to LDA, for exchange-correlation effects within density-functional theory significantly lower the surface energies for both \( \text{Al}_2\text{O}_3 \) and \( \text{ZrO}_2 \), which bring their values closer to those implied by experiments. Conversely, we find that GGA functionals overestimate structural energy differences between bulk phases of \( \text{ZrO}_2 \), although the phase stability ordering is correct.

The study of complex structures like the \( \text{ZrO}_2 \)[\( \alpha\text{-Al}_2\text{O}_3(1\overline{1}02) \)] interface illustrates the importance of annealing via molecular-dynamics simulations. Many competing, locally stable, interface structures exist, and it is important to heat up and reequilibrate the relaxed interface to make sure that the system has not been caught in an energetically unfavorable local minimum.

The low adhesion energy is probably due to the fact that these surfaces of \( \text{ZrO}_2 \) and \( \text{Al}_2\text{O}_3 \) relax to obtain approximate coordinative saturation and therefore the lack of dangling bonds on these surfaces minimizes the interaction they have between them. This suggests that the role of the \( \text{Al}_2\text{O}_3 \) in the nanolaminate coatings is simply to act as a physical barrier to growth of the \( \text{ZrO}_2 \) layer and that there is no true chemical bonding between these layers. Further, this weak interaction has important implications for thermal barrier coatings. When the bond coat oxidizes, it is known that \( \text{Al}_2\text{O}_3 \) forms and that the lifetime of the TBC is tied to the oxidation kinetics of the bond coat.\(^{2,6,67,70}\)

ACKNOWLEDGMENTS

We are very grateful to Peter E. Blochl for use of his CP-PAW code and many useful and inspiring discussions, as well as advice on the PAW-Car-Parrinello method. Further we wish to thank Niranj C. Govind, Stuart C. Watson, and Emily A. A. Jarvis for useful comments. We acknowledge also computing time granted on the parallel IBM SP2 platforms at the Maui High-Performance Computing Center (MHPCC) and the Office of Academic Computing, UCLA. This work was supported by the Air Force Office of Scientific Research (Grant No. F49620-96-1-0064).

\(^{*}\)Email address: asbjorn@chem.ucla.edu

\(^{1}\)Email address: eac@chem.ucla.edu


32 L. Verlet, Phys. Rev. 159, 98 (1967).