

Relaxation of hcp(0001) surfaces: A chemical view

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First-principles calculations predict 7.8% and 6.3% contractions of the outermost layer spacings of Ti(0001) and Zr(0001). Charge smoothing, slight at close-packed metal surfaces, cannot explain such large relaxations. Bond-order bond-length correlation is a more promising concept. Bonds to undercoordinated Ti or Zr should be unusually short, given the small ratio, ~ 0.7 , of dimer bond length to nearest-neighbor distance for these elements. [S0163-1829(96)00220-2]

I. INTRODUCTION

In this paper, I predict large outer-layer contractions for the close-packed surfaces of Ti and Zr, based on self-consistent linearized augmented plane-wave (LAPW) calculations.¹ The now conventional, Finnis-Heine (FH) picture implies *small* relaxations for close-packed metal surfaces.² The LAPW results, however, are a 7.8% contraction of the outermost interlayer spacing of Ti(0001), and 6.3% for Zr(0001). Coupled with the recent experimental report of a 5.8% *expansion* of the outer layer spacing of Be(0001),³ the present theoretical results for Ti and Zr are a strong argument for replacing the “physical,” FH picture of surface relaxation, based on smoothing of electronic charge density corrugation, with a “chemical” one based on promotion-hybridization ideas. They also imply the necessity of reexamining the idea that close-packed surfaces “always” manifest small relaxations.⁴

A. “Physical” and “chemical” pictures of surface relaxation

The existence of a surface relaxation information base invites one to develop a qualitative explanation for observed trends. The earliest, and perhaps most widely accepted of such explanations was provided by Finnis and Heine.² It relates relaxation at metal surfaces to Smoluchowski charge smoothing⁵ of the electron charge density. The idea is that when one cuts a crystal to form a surface, electrons reduce their total kinetic energy by rearranging in a way that weakens charge-density corrugation. Since smoothing of the electron density is equivalent to moving a charge that lies above surface atoms to the hollows between them, the Smoluchowski effect means moving electrons from the vacuum *toward* the solid. Thus, the outer layer of (positive) ion cores is pulled closer to the rest of the crystal.

Until 1992, when the remarkably large outward relaxation of the Be(0001) surface was discovered,³ the important virtues of the FH picture were that it explains why most surfaces relax inward, and why the relaxation is larger on more open surfaces.⁴ The argument is that open surfaces are more corrugated than closer packed. Thus, charge smoothing on open surfaces is a larger effect, and their inward relaxation should also be larger. The discovery that the outer-layer separation of Be(0001) is expanded, and not just a little, has

no explanation within the charge-smoothing picture. This means that the Finnis-Heine picture is not comprehensive.

Two alternatives have been offered. The first⁶ is a chemical argument⁷ based on the fact that a large energy, 2.7 eV, must be expended to promote the ground state, closed-shell Be atom to an excited configuration in which it can form chemical bonds.⁸ A large hybridization energy gain is required to overcompensate the cost of this $2s^2 \rightarrow 2s2p$ promotion. The consequence is that Be only binds strongly when it has many neighbors. The Be dimer bond length, for example, is 11% *longer* than the nearest-neighbor distance in bulk, hcp Be.⁹ For elements other than those in groups II A and II B, the dimer bond is *shorter* than the nearest-neighbor distance in the corresponding metal [see Table I (Ref. 9)].

The expansion of the Be(0001) surface, in the chemical picture, has the same source as the group II metals’ inverse bond-order bond-length correlation.¹⁰ Removing half the Be crystal to expose the surface atoms implies reducing the number of surface atom neighbors by three. This reduces the energy gained by promoting a $2s$ electron to a $2p_z$ orbital (with the z direction along the surface normal.) Shifting excess p_z electron weight in the surface layer to p_x - p_y orbitals is relatively unprofitable, because intra-first-plane bonds can only get appreciably stronger if they can also get shorter. Consequently, the p_z electrons are demoted to $2s$ states, the surface Be atoms become more noble, and the surface layer moves away from the rest of the crystal. According to this chemical argument, one should also expect Mg(0001) to have an expansive surface relaxation. Both theory and experiment agree that this is true.¹¹

Notwithstanding the apparent success of this chemical argument, Stumpf has recently set forth the following, quite different qualitative explanation of the outward relaxation of Be(0001), starting from the observation that bulk Be is “nearly” a semiconductor.¹² Be’s Fermi level lies in a deep depression in its density of states. Its c/a ratio is 1.572, the smallest among the hcp metals. (The “ideal” value, for hcp-stacked hard spheres, is 1.633.) Its phonon bands cannot be described in terms of a central force model, and its Poisson ratio is only 0.02, in contrast with values of 0.4–0.5 for most metals. These facts point to unusually anisotropic bonding in bulk Be, more like a semiconductor’s than that of a simple s - p metal.

The same cannot be said of bonding at the Be(0001) surface, because of surface states that are occupied in the near

TABLE I. Comparison of dimer bond lengths and elemental crystal nearest-neighbor distances. Experimental dimer bond lengths, the nearest-neighbor distance in the corresponding bulk metal, and the ratio of these two lengths, for various elements. Ratios larger than 1 are italicized and those less than 0.75 are in boldface, for emphasis. See Ref. 9 for sources of dimer bond lengths.

Element	Group	R_{dimer}	R_{nn}	$\rho_{d;nn} \equiv R_{\text{dimer}}/R_{nn}$
Li	I A	5.05	5.71	0.88
Na	I A	5.82	6.91	0.84
K	I A	7.38	8.55	0.86
Be	II A	4.66	4.20	<i>1.11</i>
Mg	II A	7.35	6.05	<i>1.22</i>
Al	III A	5.10	5.40	0.95
Bi	V A	5.03	5.80	0.88
Cu	I B	4.20	4.84	0.87
Ag	I B	4.78	5.46	0.88
Au	I B	4.67	5.44	0.86
Zn	II B	7.56	5.03	<i>1.50</i>
Cd	II B	9.10	5.63	<i>1.62</i>
Hg	II B	6.86	5.69	<i>1.21</i>
Ti	IV B	3.67	5.46	0.67
Zr	IV B	4.25	5.99	0.71
V	V B	2.99	4.95	0.60
Mo	VI B	3.66	5.14	0.71
Fe	V III	3.82	4.69	0.81
Ru	V III	4.57	5.01	0.91
Ni	V III	4.07	4.71	0.86

gap around E_f .^{6,12–14} The local density of states near E_f , in the outer Be(0001) layer, is roughly four times higher than in the bulk metal, and the bonding there is also more isotropic. Evidence for surface isotropy is that the Be(0001) surface phonons are well described by a few neighbor central force model, while noncentral forces are indispensable in fitting to the vibration spectrum of bulk Be.^{12,15}

Stumpf argues that if the Be(0001) surface region can be thought of as an isotropic metallic layer, then the local c/a ratio should be close to ideal, i.e., 1.633 rather than the bulk value of 1.572. Since a is fixed by the bulk lattice, this means that the “local c ,” represented by the outer-layer spacing, must increase by $(1.633/1.572 - 1) = 3.9\%$, in good agreement with first-principles electronic structure calculations that yield a 2.5–3.0% expansion, depending on details.^{6,16,17} Experimentally, Be(0001)’s outer-layer separation is reported to expand by more than that, namely, 5.8%.³ But there is evidence that the low-energy electron-diffraction (LEED) analysis needs to be reconsidered.¹⁸

B. Which explanation is valid for other surfaces?

A qualitative explanation of a physical phenomenon is only meaningful if predictive. Thus, the fact that Mg(0001)’s 1.9% outer-layer expansion¹¹ overshoots the ideal c/a by 1.3% argues against the c/a model. Since the bulk Mg density of states, unlike that of Be, is close to that of a free-electron metal, one might counter that there is no basis for applying Stumpf’s argument to Mg(0001). On the other hand, if Be(0001)’s ideal surface c/a is a consequence of its

isotropic surface electronic structure, it is hard to escape the thought that since Mg is an isotropic metal, with a bulk $c/a = 1.624$, the Mg(0001) surface should hardly relax at all. Instead it expands to a “surface c/a value” of 1.654.

Nevertheless, it is worth asking how the c/a argument fares for a surface that is more comparable to Be(0001). An obvious thought is to consider other Be faces, e.g., Be(11 $\bar{2}$ 0) and Be(10 $\bar{1}$ 0), for which LEED results are available.¹⁹ But the c axis does not lie along the normal to either of these crystal faces. Therefore the c/a argument cannot apply to their relaxation. [The contraction of Be(10 $\bar{1}$ 0), found in LEED,^{19b} is a relevant issue for the chemical argument. I discuss it below, in Sec. III. Relaxation is a moot point for Be(11 $\bar{2}$ 0); this face is reconstructed.^{19a}]

One is forced to consider (0001) faces of other hexagonal metals. Here I report theoretical results for the close-packed faces of Ti and Zr. Like Be, the Fermi levels of these hcp metals lie in deep density-of-states depressions.^{20,21} The c/a ratios of bulk Ti and Zr are 1.588 and 1.592 at room temperature, i.e., they are less than ideal by about 3%. Also, at the Ti(0001) and Zr(0001) surfaces, surface states give rise to prominent local density-of-states peaks about the Fermi energy.^{20,21} Thus, from the perspective of the c/a argument, one has reason to expect the Ti(0001) and Zr(0001) surfaces to expand.

On the other hand, the chemical argument implies that they should contract. Promoting a Ti atom from its ground-state $3d^24s^2$ configuration to $3d^34s^1$, such that all four valence electrons can participate in bond formation, requires only 0.8 eV.⁸ The analogous $4d^25s^2 \rightarrow 4d^35s^1$ promotion in Zr costs only 0.5 eV.⁸ (Remember that the minimum promotion energy for Be is 2.7 eV.) Thus, Ti and Zr’s bond-order bond-length correlation is not only in the usual direction, but it is unusually strong (cf. Table I). A d shell also offers more spatial flexibility than a p shell does, because there are three d orbitals with significant interplanar weight rather than only one. This means that removing half a Ti or Zr crystal to expose the (0001) surface should not cause d - to s -electron demotion. The energy recaptured by such a demotion is rather small compared to what can be gained by strengthening and shortening the first-layer atoms’ bonds to their second-layer neighbors.

Thus, whereas chemical and physical qualitative arguments both “explain” the expansion of the Be(0001) surface, their predictions are contradictory for the close-packed surface of Ti, and equally for Zr. The c/a argument suggests that the Ti and Zr(0001) surfaces should expand. Chemical reasoning implies that they must contract.

Experiment resolves the issue if one accepts Shih *et al.*’s early LEED study of Ti (Ref. 22) as definitive. Reference 22 concludes that clean Ti(0001) contracts by $\sim 2\%$. The 1979 study of Zr(0001), by Moore *et al.*, is less clear, yielding a relaxation of $(-1 \pm 2)\%$.^{23(a)} In Ref. 22, the authors make clear their precautions aimed at producing a clean surface, not easy to do for such a reactive material. On the other hand, Ref. 22 predates R -factor analysis—so the geometry that provides the best comparison of data and theory was chosen “by eyeball.” Multilayer relaxations were not considered. Finally, the level of H contamination was not monitored as the data were accumulated—something to worry about for a material that getters H efficiently enough to be

TABLE II. Comparison of theoretical and experimental lattice constants for bulk Ti and Zr crystals.

Element	Structure	Method	a (a.u.)	c (a.u.)	c/a	Volume (a.u.) ³ / atom
Ti	hcp	LAPW ^a	5.443	8.610	1.581	110.454
Ti	hcp	experiment	5.575	8.855	1.588	118.758
Ti	fcc	LAPW ^a	7.613			110.289
Zr	hcp	LAPW ^a	6.017	9.585	1.593	150.263
Zr	hcp	mixed basis ^b	6.017	9.688	1.610	151.878
Zr	hcp	experiment	6.108	9.726	1.592	157.121
Zr	fcc	LAPW ^a	8.414			148.918
Zr	fcc	mixed basis ^b	8.448			150.731
Zr	fcc	LMTO ^c	8.29			142.431
Be	hcp	experimental	4.319	6.791	1.572	54.853

^aPresent work.^bReference 21.^cReference 24.

used as a H-pump element. H contamination is equally a concern for studies of Zr(0001),²³ including the recent LEED study by Wang, Li, and Mitchell, which yields an outer-layer contraction of 1.6%.^{23(b)}

Given the difficulty of making structural measurements on demonstrably clean Ti and Zr surfaces, I have calculated first-principles theoretical atomic geometries for Ti(0001) and Zr(0001). The results are outer-layer surface relaxations of -7.7% and -6.3% . These do not agree very well with the LEED analyses, but leave little doubt that the close-packed Ti and Zr surfaces are contracted. Thus, I conclude that a promotion-hybridization argument contains the seeds of a qualitative picture of surface relaxation trends across the Periodic Table.

The remainder of this paper is organized as follows: In Sec. II, I provide details of the LAPW calculations, first (Sec. II A) for bulk Ti and Zr, then (Sec. II B) for the (0001) surfaces of these metals. I compare present results to earlier work, with particular emphasis on understanding the rather small relaxation found for Zr(111) by Methfessel, Hennig, and Scheffler.²⁴ To show that surface relaxation is dominated by nearest-neighbor interactions, in Sec. II C, I compare the structures of the (0001) surfaces to what one finds for the (111) faces of hypothetical fcc Ti and Zr crystals; I relate the results of this comparison to these surfaces' local state densities. Finally, Sec. III, I discuss the prospects for developing a widely valid chemical picture of surface structure. Several examples make it clear that refinements are necessary, beyond the comparison of dimer bond length and nearest-neighbor distance in the corresponding metal.

II. LAPW CALCULATIONS FOR Ti AND Zr

The results reported in this paper are derived from first-principles total-energy calculations, using the LAPW computational scheme and computer code of Hamann.¹ In this version of the LAPW method, the one-electron potential is not subject to any shape approximation. Exchange and correlation xc effects are represented via the local-density approximation²⁵ based on the Ceperley-Alder xc potential.²⁶ Semirelativistic corrections are included. Core electrons enter via a rigid core approximation.

A. Bulk lattice parameters

Generally, the relation between an assumed in-plane lattice parameter and the resulting surface relaxation conserves surface-atom volume,²⁷ and the atomic separations that optimize the local-density functional (LDF) are smaller than the experimental values. Thus, LDF calculations can be expected to predict substantially larger inward surface relaxations if based on the experimental bulk lattice constants than if based on those that optimize the LDF. The more consistent approach is to assume that both bulk and surface of a crystal are described in the same way, i.e., by the LDF, for the purpose of first-principles calculations. I therefore begin each surface relaxation study by optimizing the lattice parameter of the underlying crystal. The calculated lattice constants for Ti and Zr are given in Table II.

In order to see if nearest-neighbor interactions dominate surface relaxation, it is useful to compare results for Ti(0001) and Zr(0001) to what one obtains for the (111) surfaces of hypothetical fcc Ti and Zr crystals. If nearest-neighbor effects dominate, then the difference between $abcabc\dots$ and $ababab\dots$ stacking should have little effect on the computed relaxation. In Table II, therefore, I include calculated lattice parameters for both hcp and fcc Ti and Zr crystals.

For the hcp crystals, the present LAPW results in Table II correspond to sampling the irreducible $\frac{1}{24}$ of the Brillouin zone with three equally spaced points in the c direction times 19 equally spaced k points in the k_x - k_y plane. In the fcc cases, I sample the irreducible $\frac{1}{48}$ of the Brillouin zone with 60 special k points. For the Ti calculations, I use a basis set cutoff of 12.5 Ry and a muffin-tin radius of 2.43 bohr. Generally, LAPW calculations for d -band materials are converged with respect to basis set when the maximum APW wave vector times the muffin radius is at least 7.²⁸ For Ti, this product is 8.6, which should be ample. For Zr, a larger atom, I use a muffin-tin radius of 2.77 bohr and an APW cutoff of 10.0 Ry. This implies a convergence product of 8.8. I determine optimal lattice parameters by fitting the energies of 12 or more geometries to a cubic polynomial in a and c , for the hcp cases, and the energies of five geometries to a cubic in a , for the fcc crystals.

TABLE III. Calculated results for close-packed Ti and Zr surfaces. Comparison of calculated percent surface relaxations, $\Delta d_{12}/d_{\text{bulk}}$ and $\Delta d_{23}/d_{\text{bulk}}$, surface energies, E_s , and work functions, Φ , for close-packed, several-layer Ti and Zr slabs. The indication “(nr)” means “calculated nonrelativistically,” as opposed to semirelativistically. n.c. denotes not calculated.

Surface	Method	Layers	$\Delta d_{12}/d_{\text{bulk}}$	$\Delta d_{23}/d_{\text{bulk}}$	E_s (eV/Å ²)	Φ (eV)
Ti(0001)	LAPW ^a	7	-7.7%	2.8%	0.137	4.64
Ti(111)	LAPW ^a	7	-7.1%	1.4%	0.134	4.71
Zr(0001)	LAPW ^a	7	-6.3%	n.c.	0.108	4.43
Zr(0001)	mixed basis ^b	10	-4.7%	1.2%	0.128	4.26
Zr(0001)	mixed basis ^b	8	-4.4%	1.0%	0.128	4.37
Zr(111)	LAPW ^a	7	-5.9%	n.c.	0.108	4.47
Zr(111)	LAPW (nr) ^a	7	-5.2%	n.c.	0.108	4.45
Zr(111)	LMTO (nr) ^c	7	-2.5%	n.c.	0.109	4.38

^aPresent work.

^bReference 21.

^cReference 24.

Several results in Table II are worthy of note. For both hcp Ti and Zr, the computed c/a ratio is very close to experiment. Thus, the usual overbinding of the local-density approximation yields the same contraction of both a and c relative to experiment, about 2.4% for Ti, and 1.5% for Zr. Notice that the ratio of the computed volumes per atom for Ti in the hcp and fcc structures is 1.0015. For Zr it is 1.0090, somewhat larger, but still close to the value 1, which represents atomic volume conservation.

There is one significant disagreement in Table II, between the fcc Zr lattice constant reported by Methfessel, Hennig, and Scheffler (MHS) (Ref. 24) and those obtained by Yamamoto, Chan, and Ho,²¹ and in the present LAPW calculation. The latter two values of a_{fcc} agree to 0.4%. MHS find a value 1.5% smaller than the LAPW prediction. One cannot compare these calculated lattice parameters directly to experiment, since Zr is an hcp, not a fcc crystal. However, one can estimate an experimental a_{fcc} via the argument that the volume per Zr atom should, to a reasonable approximation, be independent of hcp vs fcc stacking. Thus, defining a_{fcc} by the equation,

$$a_{\text{fcc}}^3 \equiv a_{\text{hcp}}^2 c_{\text{hcp}} \sqrt{3}, \quad (1)$$

its “experimental” value is 8.566 bohr. The LAPW value of a_{fcc} (cf. Table II) is 1.8% smaller than this, while MHS’s full potential linear muffin-tin orbital (FP-LMTO) value is 3.3% smaller. The MHS calculation is nonrelativistic. However for fcc Zr, I find that the inclusion of semirelativistic corrections has only a small effect on a_{fcc} , decreasing it by 0.1%. The LDA generally predicts interatomic spacings to better than 3%, among the $4d$ metals.⁴ This casts doubt on the MHS result.²⁴

It should be noted that in their treatment of $4d$ metal surface relaxations, MHS allow the “semicore” $4p$ orbital to relax, rather using a “frozen-core” approach, as in the present calculation. For Rh(001), they find that relaxing the $4p$ orbital reduces the computed surface contraction by about 1%. The effect on the bulk lattice constant is not stated. Reference 24 provides only a sketch of the calculational methods used. It is not made clear, for example, how wave-function orthogonality is maintained in the “two-

panel” treatment of the $4p$ orbital. Evidence for the accuracy, not just the stability of the method used to solve Poisson’s equation would also be welcome.²⁹

B. Relaxation of close-packed Ti and Zr surfaces

In Table III, I present calculated relaxations for the close-packed surfaces of both Ti and Zr crystals, and compare them to earlier published work. All the LAPW calculations are for seven-layer slabs. For hcp Ti(0001) and fcc Ti(111) I allow (symmetric) relaxation of the outer two atomic layers on either side of the slab. For Ti, relaxation of the second interlayer spacing has little effect on the calculated magnitude of the first. Accordingly, for the Zr surfaces, I only optimize the position of the outermost atomic layer on either side of the hcp or fcc slab, fixing the remaining ones at their LDF bulk separations. The optimizations are performed by fitting calculated energies for various outer-layer geometries to general cubic polynomials.

For the hcp crystals, I sample the irreducible 1/12 of the surface Brillouin zone with the same 19 equally spaced points as in the corresponding bulk crystal. For the fcc(111) surfaces, I also use a 19-point sample. To test convergence of Brillouin-zone sampling, for Zr(0001) I reoptimized the outer-layer position using a honeycomb arrangement of 30 k vectors (without reoptimizing the bulk lattice constants). The effect on the calculated relative change of outermost interlayer spacing is to reduce the contraction from 6.5% to 6.3%. I also tested the convergence of the LAPW basis set, by increasing the cutoff from 10 to 12 Ry. This has no effect on the outer layer relaxation at the level of 0.1%.

The LAPW relaxations for all four close-packed surfaces are unusually large compared to experimental relaxations for a wide range of metals,³⁰ unfortunately including Ti and Zr. The computed outer-layer contractions are between 7 and 8% for the Ti surfaces and about 6% for Zr. The LEED measurement of Shih *et al.* for Ti(0001) (Ref. 22) yields an outer-layer contraction of roughly 2% compared to the present calculated value of 7.7%. The LEED studies of Moore *et al.* and of Wang, Li, and Mitchell,^{23(b)} yield contractions of $1 \pm 2\%$ and of 1.6% compared to the present calculated value of 6.3%.

Where comparison with published theoretical work is possible, the present relaxations are also larger. Specifically, Yamamoto, Chan, and Ho (YCH) (Ref. 21) find, via a mixed-basis pseudopotential calculation, that the outer-layer spacing of Zr(0001) contracts by 4.3%. The nonrelativistic, full-potential LMTO method, of Methfessel, Hennig, and Scheffler, yields a contraction of only 2.5% for the outer-layer spacing of Zr(111),²⁴ compared to the present nonrelativistic value of 5.2%.

It is not clear which of several methodological differences accounts for the disagreement between YCH's and the present results for the Zr(0001) outer-layer relaxation. YCH sample the surface Brillouin zone with only six k vectors, commenting that with 18 or 20 k -point samples "the top layer relaxations differ by less than 1.5% of the interlayer spacing." Since the present contraction is 6.3%, for a seven-layer film, and YCH find 4.4% for an eight-layer slab, poor k -vector convergence is likely to make a significant contribution to the discrepancy. YCH did not include nonlinear core-valence overlap corrections to the exchange-correlation energy,³¹ such corrections are not needed in the LAPW method. On the other hand, they treated the $4p$ as a valence orbital. They state that "the bulk structure and relaxation of surface structure... (are not significantly different if the $4p$'s are treated) as core states." It seems unlikely that any substantial disagreement could result from YCH's using the Hedin-Lundqvist,³² rather than the Ceperley-Alder²⁶ xc potential. Basis set convergence also does not appear to be an issue. Reference 21 does not state whether semirelativistic corrections were or were not included.

Given the surprisingly small lattice parameter that Methfessel, Hennig, and Scheffler find for bulk, fcc Zr, conservation of atom volume in itself might account for the small contraction they find for Zr(111). A 1.5% reduction in lattice parameter should reduce the expansion of the surface layer by 3.0%. This is close to the difference of 2.7% between MHS's 2.5% contraction of the outer-layer spacing of Zr(111) and the value of 5.2% that I find in a nonrelativistic LAPW calculation.

C. What causes the relaxations of the Ti and Zr surfaces?

Examining local state densities is a useful way to interpret calculated surface atomic geometries. Thus, in Figs. 1(a) and 1(b), I compare the densities of states associated with the central and outer Ti muffin tins of a seven-layer Ti(0001) slab. The dashed curves in the figures correspond to an "ideal" slab in which all layers are fixed in their bulk relative positions. The solid curves correspond to the relaxed slab, in which the outer two layers on either side have been displaced to optimize the surface energy.

In the inner muffin-tin curves [Fig. 1(a)], the key feature is the deep valley, on the high-energy edge of which the Fermi level resides. Reassuringly, relaxation of the surface causes little change in the central layer's state density. Figure 1(b) shows that in the outer-layer muffin tin, near the Fermi energy, the deep valley is replaced by a prominent surface-state peak. Comparison of the solid and dashed curves in those figures yields the straightforward interpretation that the relaxation is associated with a strengthening of covalent

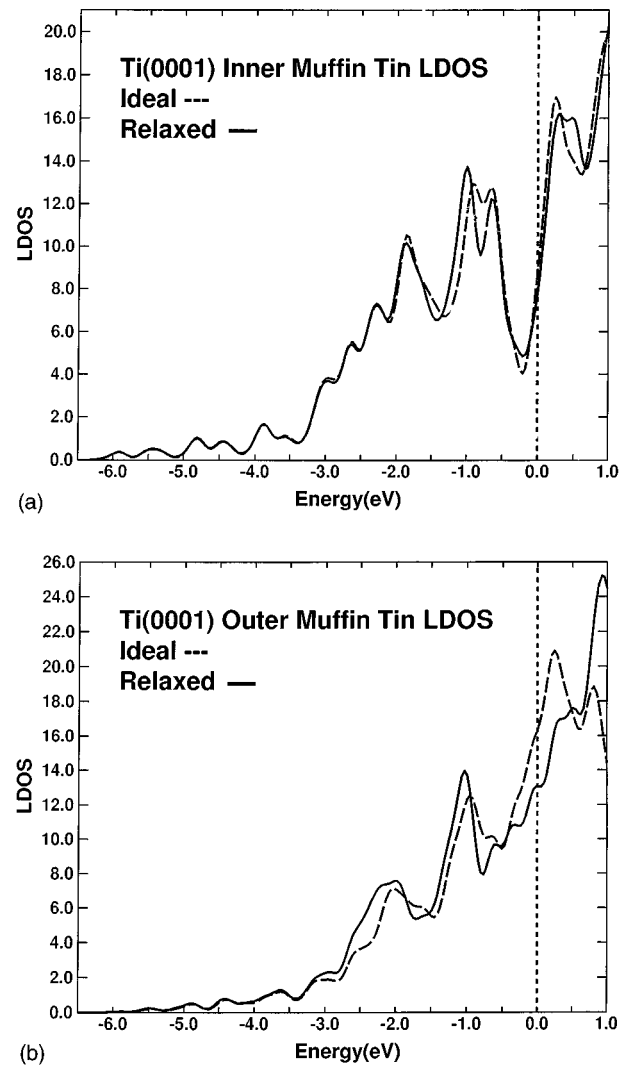


FIG. 1. Muffin-tin-integrated local densities of states for a seven-layer Ti(0001) film: (a) central-layer muffin tin, (b) outer-layer muffin tin. Dashed lines correspond to an "ideal" film, the layer separations of which are fixed at the bulk value. Solid lines correspond to a film, the outer two layers on either side of which are positionally relaxed.

bonding. Improved hybridization removes state density from the region near the Fermi energy and adds it back at considerably lower energies.

Figures 2(a) and 2(b), corresponding to the central and outer muffin-tin densities of states of a fcc Ti(111) seven-layer slab, are intended to address the importance of the surface state—more generally, of localized vs delocalized electron states—in determining the degree of surface relaxation. Notice in Fig. 2(a) that a consequence of the fcc stacking of the Ti(111) film, its central muffin-tin density of states has no deep valley. Surface states can only exist where bulk states are forbidden. Accordingly, in Fig. 2(b), one sees a density of states that is narrower than that of Fig. 2(a), reflecting the reduced coordination of the surface atoms, but with no new peak near the Fermi energy. Nevertheless (cf. Table III), the outer-layer relaxation calculated for Ti(111) is only slightly smaller than what is found for hcp Ti(0001), and the same can be said for Zr(0001) and Zr(111). The

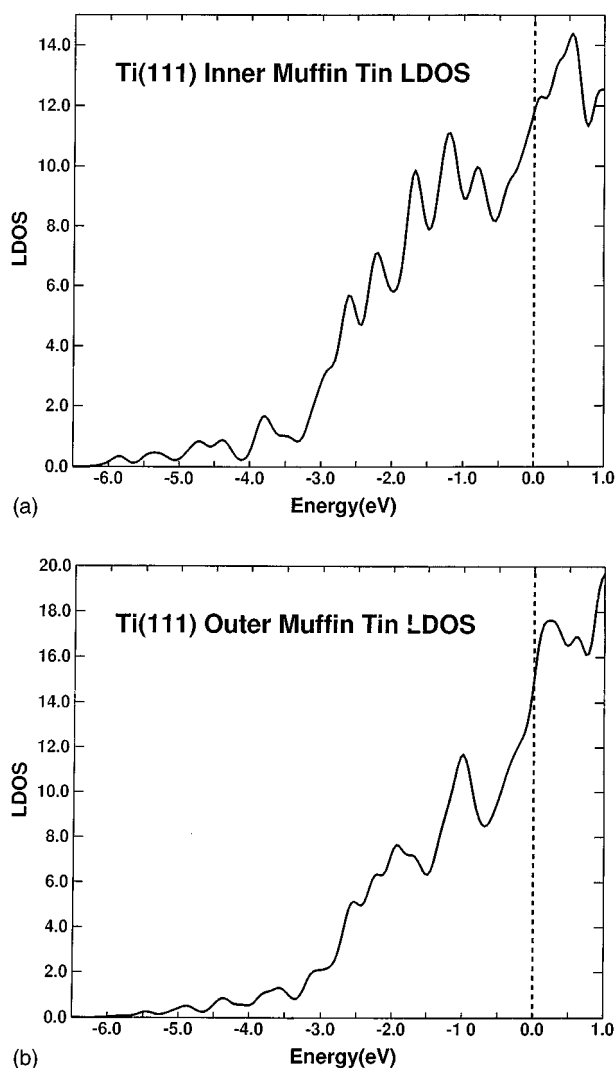


FIG. 2. Muffin-tin-integrated local densities of states for a seven-layer Ti(111) film, the outer two layers on either side of which are positionally relaxed: (a) central-layer muffin tin, (b) outer-layer muffin tin.

conclusion is that neither the gap in the bulk density of states, nor the surface states it allows are the source of the large Ti(0001) and Zr(0001) surface relaxations. These relaxations are a local effect. “Bonds” between outer-layer atoms and their neighbors are cut when one exposes a surface. The consequence is that bonding between the outer and second crystal layer is strengthened.

III. TOWARDS A COMPREHENSIVE CHEMICAL PICTURE OF SURFACE STRUCTURE

The fact that outer-layer contractions substantially larger than 2% have not been observed for the closest-packed sur-

face of any transition metal,³³ including Ti(0001) and Zr(0001),³⁰ is widely accepted as evidence supporting Finnis and Heine’s identification of charge smoothing as the source of surface relaxation.² However, the present LAPW results disagree with published LEED analyses for Ti(0001) and Zr(0001). They say that clean, perfect Ti(0001) and Zr(0001) surfaces should show *large* outermost layer relaxations, -7.7% and -6.3% , contradicting the FH picture, but in agreement with chemical ideas.

This does not mean, however, that the interpretation of surface relaxation via promotion-hybridization arguments is without its own potential difficulties. Specifically, although large outer-layer contractions for Ti(0001) and Zr(0001) can be rationalized as the consequence of Ti and Zr’s very strong bond-order bond-length correlation, observation does not support the idea surface relaxation is just a function of the ratio of dimer bond length to nearest-neighbor distance, $\rho_{d;nn}$. Other variables certainly play a role. Consider the following examples.

(1) The Al(111) surface is found theoretically (and experimentally) to expand slightly, even though it “ought to” contract somewhat, since $\rho_{d;nn}(\text{Al}) < 1$ (see Table I). This may be an electron spillout effect,³⁴ in a situation where because $|\rho_{d;nn}(\text{Al}) - 1|$ is small, rehybridization of first- to second-layer bonds is expected to be weak.

(2) The Mo(110) surface is predicted to relax inward by 4.5%,³⁵ i.e., considerably less than the close-packed surfaces of Ti or Zr, even though $\rho_{d;nn}$ is about the same for Mo, Ti, and Zr. This may have to do with bond-angle forces, which are stronger for bcc metals than for close-packed ones.

(3) Recent LEED analysis and theory agree that the outer-layer spacing of Be(10 $\bar{1}0$) contracts,^{19b} even though its surface-layer atoms have fewer neighbors than the Be’s do in Be(0001), which expands. A plausible explanation is that as the outer Be(10 $\bar{1}0$) layer moves in, its bonds to second-layer atoms not only become shorter, but significantly closer to the surface plane. This makes it advantageous to move p_z electrons into p_x and p_y orbitals, instead of demoting them into s states. Geometry dictates that this must be a much weaker effect at a (0001) face. LAPW calculations show that the p_x - p_y populations on this surface change negligibly as relaxation occurs.^{6,36}

Needless to say, it would be desirable to substantiate the plausible interpretations I have offered for these examples, using first-principles calculations—then to incorporate them into a more detailed chemical picture of surface structure.

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