

First-principles calculations of stress induced by gas adsorption on Pt(111)

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Local-density-functional calculations show that both O and H adsorption relieve tensile stress on Pt(111) terraces. These results agree with the observation that both O and H undo the added-atom reconstruction of Pt(111) that occurs at elevated temperatures, but conflict with the idea that the direction of adsorbate-induced charge polarization determines the sign of the induced surface stress. [S0163-1829(97)08628-1]

I. INTRODUCTION

The idea behind the ongoing, substantial effort to measure and understand surface stress is that this quantity links bonding at the atomic level with the macroscopic morphology (and dynamics) of surfaces.¹ The surprising herringbone reconstruction of Au(111),² for example, and the similar reconstruction of Pt(111) that occurs at elevated temperatures³ are persuasively explained as incorporation of extra atoms into the outermost atomic layer of these nominally “close-packed” surfaces, which relieves their tensile surface stress.⁴

First-principles calculations of surface stress have as yet made little contact with experiment. The microscopic origins of stress have been explored.⁴⁻⁹ Absolute stresses have been computed for various materials and crystal faces.¹ But particularly in the case of metals, for want of corresponding data, the computed results have been compared to each other, not to experiment¹⁰—the problem is that no one has succeeded in measuring absolute surface stress reliably for single-crystal planes.¹¹

What is currently measured, by observing the bending of a thin slice of crystal when one of its surfaces is modified, is how surface stress *changes* with surface composition and atomic arrangement.^{12,13} Whether or not one understands the microscopics of stress, such observations represent a practical way to monitor surface conditions, e.g., the segregant profile near an alloy’s surface.¹⁴ At the same time, though, they provide information that should be useful in developing our understanding of stress systematics.

With this in mind, I report first-principles calculations of the effects of H and O adsorption on the surface stress of Pt(111). In a scanning tunneling microscopy (STM) experiment, Hohage *et al.*¹⁵ have discovered that H, O, and also CO adsorption on quenched, reconstructed Pt(111) undoes this surface’s high-temperature reconstruction—and as an interpretation, they offer the reasonable suggestion that these adsorbates give rise to surface compression, forcing the extra Pt atoms *in* the reconstructed outer metal layer to move to adatom sites, i.e., to sites *on* the surface.

The present theoretical results confirm the idea that both H and O relieve the tensile stress of Pt(111). I find that $\frac{1}{4}$ monolayer (ML) of O (which is saturation coverage) cuts it in half, while a full (1×1) ML of H reduces it by almost a factor of 4. Calculations for $\frac{1}{4}$ and $\frac{3}{4}$ ML H-adsorption structures also show tensile stress reduction and indeed show

that the reduction is linear with coverage to an excellent approximation.

These results are of interest not just because they confirm Hohage *et al.*’s speculation,¹⁵ but because they add to our information base regarding the systematics of surface stress. In recent reviews,¹ Ibach contends that the sign of adsorbate-induced surface stress should track the relative electronegativity of adsorbate and substrate. Supported by observations of the crystal-bending induced, for example, by Cs as against C adsorption on Ni(111),¹⁶ he argues that electron-donating adsorbates exacerbate tensile stress, because the electrons they donate to the outer metal layer strengthen in-plane bonds, while electron-withdrawing adsorbates relieve tensile stress via the opposite effect.⁵

The present results show that this simple correlation is not general. O adatoms give rise to a slight increase in work function, Φ , on Pt(111), while H adsorption produces a substantial drop. Thus O adatoms polarize charge away from the substrate, while H polarizes it toward. Nevertheless, both adsorbates relieve tensile stress.

The remainder of this paper is organized as follows: In Sec. II I specify the key details of the first-principles stress calculations. In Sec. III I discuss the calculated structure of the clean Pt(111), H- and O-covered Pt(111) surfaces. Section IV is devoted to a presentation of surface stress results. These are discussed in Sec. V in the context of various scenarios for stress-systematics that appear in the literature.

II. CALCULATIONAL DETAILS

Because O and Pt are strong pseudopotential atoms, “QUEST,” a parallel, linear combination of atomic orbitals (LCAO) implementation¹⁷ of the local density approximation (LDA),¹⁸ is a particularly useful tool for obtaining total energies and stresses. Within QUEST, I use the Ceperley-Alder potential to account for exchange and correlation,¹⁹ Hamann pseudopotentials²⁰ to represent electron interactions with Pt and H nuclei and a Troullier-Martins (TM) pseudopotential²¹ for O nuclei (the TM O pseudo wavefunctions’ relative smoothness allows for coarser coordinate-space meshes²²).

The convergence tests of Ref. 9 imply that it is appropriate to model the Pt(111) surface as a 9-layer (111) Pt slab, and to sample the irreducible $\frac{1}{12}$ of the surface Brillouin zone with 19 special k points in (1×1) geometries.²³ To determine the equilibrium surface structure of clean or adsorbate-covered Pt(111), I fix the central five Pt layers of the model

slab in bulk Pt relative positions, and allow the remaining layers to relax. In order to study the dependence of the surface stress reduction on H coverage, I optimize the structures of $\frac{1}{4}$, $\frac{3}{4}$, and 1 ML H adlayers, in each case maintaining the three-fold rotation symmetry of the clean surface, and placing the H adatoms in the fcc hollows they are known²⁴ to occupy. In the case of O adsorption, I consider only the $p(2 \times 2)$ saturation structure,²⁵ with O atoms in fcc hollows.²⁶

As a basis set for the interior seven Pt layers of the model slabs I use two s functions, as well as a p - and a d -like radial function centered on each Pt nucleus. The LCAO energy bands corresponding to this set of Pt-centered orbitals, as discussed in Ref. 9, are in excellent agreement (better than 0.11 eV) with those that emerge from linear augmented plane wave (LAPW) calculations²⁷ that are demonstrably basis converged.

In Ref. 9, I found that the added variational freedom gained by placing a second d orbital on each Pt has a $\sim 10\%$ effect on the calculated surface stress, but little effect on bulk properties. In the present calculations, I therefore center a second radial d orbital (specifically, a single Gaussian with attenuation constant $\alpha = 0.15 \text{ bohr}^{-2}$) on each surface layer Pt nucleus, but not on the interior nuclei. The result is a clean Pt surface stress in excellent agreement with that obtained in Ref. 9, where a second d orbital was assigned to all Pt nuclei.

For calculations involving O adatoms, I center two s -, two p -, and one d -like orbital at each O site, as in Ref. 28 and in the case of H absorption, I use two s - and one p -like orbital at each H nucleus.²⁹ In all cases I add floating s and p orbitals in the vacuum (cf. Ref. 9 for details) to represent electron spillout and Smoluchowski smoothing of the electron density.³⁰

Formally, the surface stress tensor S_{ij} is given by

$$S_{ij} \equiv (1/A) \frac{d}{d\varepsilon_{ij}} (AE_s), \quad (1)$$

where E_s and A are the surface energy and area of a semi-infinite crystal, i and j are Cartesian indices referring to the plane of the surface, and ε_{ij} is the surface strain tensor. Since QUEST does not yet permit Hellmann-Feynman type stress calculations,^{31,32} I compute the required derivatives by fitting cubic polynomials to surface energies for adequately thick crystal slabs at five equally spaced ‘‘standard’’ intraplanar nearest-neighbor distances (from 5.005 to 5.405 bohrs) centered on the optimal bulk value of 5.205 bohrs. To retain three-fold rotation symmetry for expanded and contracted slabs, I strain intraplanar bonds equally in the x and y directions, and then divide calculated energy derivatives by two to obtain magnitudes of the (equivalent) individual components of the surface stress tensor, S_{xx} and S_{yy} . I hold interplanar spacings fixed as I strain the intraplanar bonds.

III. NUMERICAL RESULTS FOR Pt(111), H/Pt(111), AND O/Pt(111)

To provide needed background for interpretation of the surface stress results, I now discuss the calculated structures of the clean and adsorbate-covered Pt(111) slabs. The most

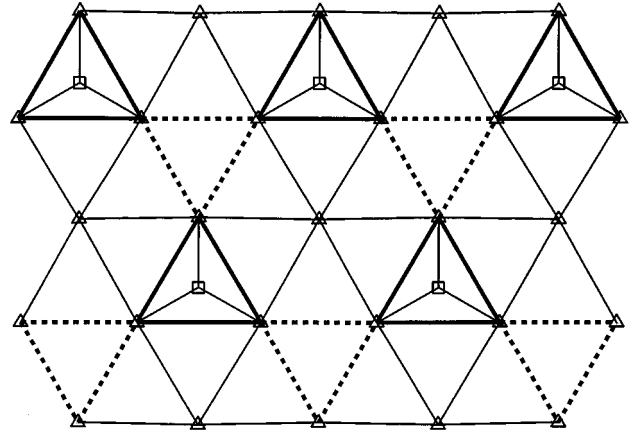


FIG. 1. Schematic top view of $p(2 \times 2)$ -O/Pt(111). Squares represent O nuclei. Triangles represent outer-layer Pt nuclei. Heavy solid (dashed) lines represent bonds that are expanded (contracted) by 2.9% relative to the bulk nearest-neighbor spacing. The remaining Pt-Pt bonds are expanded by less than 0.1%.

telling result is the lengthening of intra-first-layer bonds between Pt atoms that are first neighbors to the same adatom, when symmetry allows, and the shortening of those between Pt’s that are first neighbors to different adatoms (see Fig. 1). Thus by weakening the bonds between its first neighbors, the adatoms allow the remaining bonds to contract, relieving their tensile stress.^{5(c)} This is true for both H and O, even though H gives rise to a work function decrease and O to an increase.

The atomic geometries and work functions I calculate for the clean surface and $p(2 \times 2)$ -O/Pt(111) are in good agreement with experiment. The H/Pt(111) results agree qualitatively [i.e., a (1×1) H adlayer causes Pt surface expansion and a decrease in the work function) but quantitative correspondence between theory and measurements is less persuasive in this case. A summary of the structural results discussed in this section can be found in Tables I–III.

A. Structure of clean Pt(111)

Allowing the outer two Pt layers on either side of a clean, 9-layer, Pt(111) slab to relax, I find in agreement with experiment that the outermost layer separation expands relative to the bulk. The calculated expansion, 0.44% is somewhat smaller than the most recent experimental value,²⁶ while the second spacing’s contraction, -0.31% , may be somewhat larger. The elaborate, most recent low-energy electron diffraction (LEED) analysis²⁶ implies an outer layer expansion of $1.1 \pm 0.4\%$, and a second interlayer relaxation consistent with 0%, but with a quoted error of $\pm 1.3\%$. The LDA work function for Pt(111) is 6.12 eV in excellent agreement with the measured value, $6.10 \pm 0.06 \text{ eV}$.³³

TABLE I. Calculated percentage outer layer relaxations for 1×1 surfaces.

System	$\delta d_{12}/d_{\text{bulk}}$	$\delta d_{23}/d_{\text{bulk}}$
Pt(111)	+0.44%	-0.31%
H(1×1)/Pt(111)	+2.3%	+0.075%

TABLE II. For $p(2 \times 2)$ -O/Pt(111), the optimal atomic coordinates for the O adatom and the Pt atoms of the first two crystal layers, in units of the nearest-neighbor spacing in bulk Pt. The LDA results are normalized to the LDA nearest-neighbor spacing. The LEED results, from Ref. 26, are normalized to the experimental nearest-neighbor spacing.

Atom	X (LDA)	Y (LDA)	Z (LDA)	X (LDA)	Y (LEED)	Z (LEED)
O	0.000	0.000	0.000	0.000	0.000	0.000±0.007
Pt	0.00	0.594	-0.416	0.000	0.588±0.007	-0.429±0.007
Pt	-0.515	-0.297	-0.416	-0.509	-0.294	-0.429
Pt	0.515	-0.297	-0.416	0.509	-0.294	-0.429
Pt	1.000	0.577	-0.454	1.000	0.577	-0.454±0.011
Pt	-1.000	-0.577	-1.221	-1.000	-0.577	-1.229±0.014
Pt	-0.499	0.288	-1.256	-0.497	0.288	-1.265±0.007
Pt	0.000	-0.576	-1.256	0.000	-0.576±0.014	-1.265
Pt	0.499	0.288	-1.256	0.497	0.288	-1.265

B. Structure of the $p(2 \times 2)$ -O/Pt(111) surface

The excellent quality of the LDA atomic geometry I obtain for $p(2 \times 2)$ -O/Pt(111) is evident in Table II in which I compare the LDA results with those of Materer *et al.*'s LEED analysis.²⁶ Because the bulk lattice parameter of Pt is 0.71% smaller in LDA than experiment, I normalize the theoretical and LEED atomic positions in the table to the corresponding bulk Pt-Pt spacing (5.205 bohrs for the LDA and 5.242 bohrs for LEED results). With this normalization, the LDA and LEED in-plane relaxations of the Pt atoms agree to within experimental uncertainty. The relaxations normal to the (111) planes are close.

Both theory and experiment agree that the sides of the triangle of Pt atoms directly beneath each adsorbed oxygen atom lengthen by 2% to 3% resulting in an equal contraction of the bonds between Pt atoms of neighboring triangles (see Fig. 1). Similar results have been correlated with reduction of tensile stress for a number of adsorption systems.⁵

I compute a work function change of +0.08 eV, from 6.12 to 6.20 eV, when the $p(2 \times 2)$ -O overlayer is adsorbed on Pt(111). Considering the inherent systematic error of the LDA and the difficulty of measuring work functions accurately, measured work function changes are in reasonable agreement. Parker, Bartram, and Koel³⁴ find an O-induced shift of +0.18 eV, while Derry and Ross³⁵ report a value of +0.15 eV.

TABLE III. Optimal atomic coordinates for 1/4 ML, $p(2 \times 2)$ -H/Pt(111), in units of the nearest-neighbor spacing in bulk Pt.

Atom	X	Y	Z
H	0.000	0.000	0.000
Pt	0.00	0.587	-0.333
Pt	-0.509	-0.294	-0.333
Pt	0.509	-0.294	-0.333
Pt	1.000	0.577	-0.348
Pt	-1.000	-0.577	-1.158
Pt	-0.501	0.288	-1.162
Pt	0.000	-0.576	-1.162
Pt	0.501	0.288	-1.162

The molecular dissociation energy of O₂ is 5.115 eV. Thus, using Derry and Ross' experimental enthalpy of O absorption,³⁵ 240±0.37 eV, the experimental heat of adsorption, per O atom, amounts to 3.76±0.19 eV. Parker *et al.*'s analysis of the O/Pt thermodynamics³⁴ suggests the somewhat smaller value of 3.32 eV. Characteristically, the LDA overestimates the O binding energy considerably, yielding a value of roughly 5.5 eV per O atom in the $p(2 \times 2)$, 1/4 ML structure.³⁶

C. Structure of H/Pt(111) surfaces

Quantitative agreement between theory and experiment for H/Pt(111) is less satisfying than for O adsorption, but there are no qualitative problems. In both LDA theory and experiment, rather than "healing" the expansion of clean Pt(111), a monolayer of H on either side of the slab, in fcc threefold hollows, causes the outer Pt layer separation to expand. In the QUEST calculation the expansion is 0.1 bohr, to a value 2.3% greater than in the bulk. Experimentally, the spacing between the outermost Pt layers of the H-saturated Pt(111) surface is thought to expand by (1.3±0.4)%.³⁷

According to the calculations, an H (or preferably a D, since zero-point motion is neglected) monolayer optimally resides at a height of 1.77 bohrs above the outermost plane of Pt nuclei, corresponding to a H-Pt bond length of 3.49 bohrs and a H radius of 0.89 bohr.³⁸ Mortenson *et al.*'s transmission channeling experiment for D/Pt(111) (Ref. 24) yields a considerably smaller height above the surface Pt layer, 1.10±0.08 bohrs, corresponding to a bond length of 3.22 bohrs and a D radius equal to 0.60 bohr.³⁸

Beyond this, the LDA calculations predict a large work function decrease, from 6.12 to 5.40 eV at monolayer H coverage. Christmann, Ertl, and Pignet's early measurement³⁹ does yield a work function decrease, but a much smaller one, in the neighborhood of -0.2 eV at saturation (which Mortensen *et al.* identify as 1 ML).

These discrepancies might be related, since the theoretical work function shift would be very close to experiment if the H layer were shifted to the experimental distance above the surface.⁴⁰ However, the reason for the discrepancies is not clear. Choice of basis set is always a concern in LCAO calculations. However, the present results are in quite good

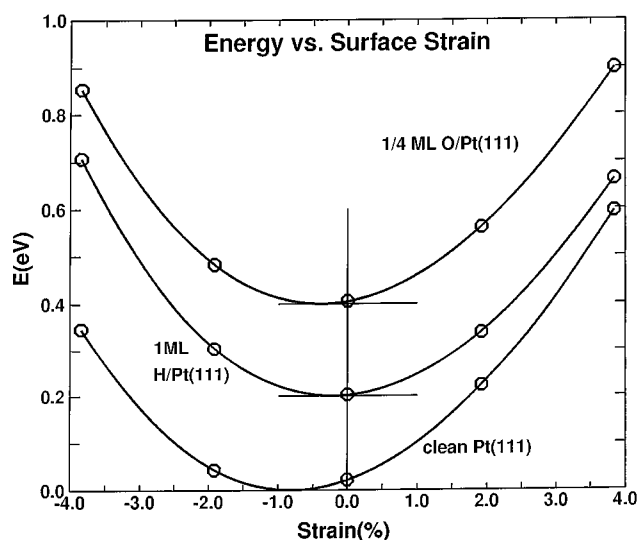


FIG. 2. Energy change per outer-layer Pt atom vs surface strain for Pt(111), (1×1) -H/Pt(111), and $p(2 \times 2)$ -O/Pt(111) slabs. The solid curves are cubic polynomial fits to the computed results, which are shown as open triangles. The H/Pt and O/Pt curves are displaced along the y axis for clarity. For each system, the stress is proportional to the zero strain slope of the energy vs strain curve. Notice how much smaller this slope is in the curves corresponding to H and to O adsorption than for clean Pt(111).

agreement with those of an earlier LAPW study of the same system, in which the H atoms were found to reside 1.80 bohrs above the Pt outer layer and the computed work function for the H monolayer was 5.32 eV.⁴⁰

The work function measurement of Christmann, Ertl, and Pignet predates the discovery that Pt surfaces often contain Si, S, and P impurities, which are hard to see because of Auger line overlaps, and which must be removed before trustworthy results can be obtained.⁴¹ A more recent, though unpublished, study yields a -0.49 -eV work function shift for saturation H coverage, in considerably better agreement with the LDA value.⁴²

In order to study the coverage dependence of the stress induced by H on Pt(111), I compute LDA optimal structures for 1/4 and 3/4 ML arrangements of H adatoms in $p(2 \times 2)$ supercells (though there is no evidence that such structures ever form). The 1/4 ML structure provides a worthwhile comparison to the O-saturated surface. Note in Table III that the nature of the H-induced displacements of the outer Pt atoms is the same for both the H and O quarter monolayers.

Not surprisingly, the H effect is smaller in magnitude, corresponding to weaker binding to Pt.

IV. RESULTS FOR ADSORBATE-INDUCED SURFACE STRESS

Consider now the H- and the O-induced stresses, computed for the LDA equilibrium structures of clean, H-, and O-covered Pt(111) presented in the preceding section. I evaluate stresses via cubic fits to the calculated slab energy versus surface strain as in Fig. 2—but no numerical analysis is needed to appreciate the main result: when either H or O is adsorbed, the surface-strain derivative of the slab energy at zero surface strain is reduced. Thus, as Hohage *et al.* infer from their STM observations,¹⁵ both O and H adsorption relieve the tensile stress of clean, unreconstructed Pt(111).

Several aspects of the results (which are summarized in Table IV) are worthy of note: As mentioned in Sec. III above, the value of $392 \text{ meV}/\text{\AA}^2$ for clean (1×1) Pt(111) (Ref. 43) is in excellent agreement with that obtained earlier with a more elaborate basis set, and is in rough (11%) agreement with the value obtained by Needs and Mansfield in a less well converged, plane-wave calculation.⁴⁴

As suggested by the expansion of the triangle of Pt nuclei beneath either H or O adatoms in 1/4 ML $p(2 \times 2)$ structures (cf. Tables II and III), both H and O weaken the bonds between the Pt atoms that are their immediate neighbors. Thus the effect of either of these adatoms is to relieve Pt(111)'s tensile stress. For H adsorption, where saturation occurs at a full monolayer, the stress relief is linear with coverage (cf. Fig. 3), consistent with a negligible H-H interaction. This is an interesting result because at monolayer coverage, (1×1) symmetry prevents any in-plane relaxation of Pt atomic positions. The stress relief that the H adatoms induce must therefore be interpreted as an electronic effect, not one that depends to any appreciable extent on an actual H-induced displacement of substrate nuclei. This result is consistent with Needs' observation that the stress of Al is not very different from that of semi-infinite jellium at the electron density of Al, and depends weakly on relaxation of interlayer spacings.⁶

The stress reduction that O adsorption induces is roughly 3 times that induced by H, on a per atom basis. This is consistent with stronger binding to the Pt surface, and correspondingly more disruption of the bonds in the outer Pt layer. The relative expansions of the nearest neighbor Pt nuclear triangle for the 1/4 ML H and O structures (cf.

TABLE IV. LDA energetics for clean and adsorbate-covered Pt(111), including the work function Φ , the adatom binding energy (B.E.) (Ref. 36), the calculated surface stress, and the kinetic energy (K.E.) contribution to the surface stress.

System	Coverage	Φ (eV)	Per adatom B.E. (eV)	Surface stress ($\text{meV}/\text{\AA}^2$)	Surface K.E. stress ($\text{eV}/\text{\AA}^2$)
Pt(111)	Clean	6.12		392	4.67
H (2×2) /Pt(111)	1/4 ML	5.98	2.70	324	4.17
H (2×2) /Pt(111)	3/4 ML	5.61	2.64	174	2.80
H (1×1) /Pt(111)	1 ML	5.40	2.62	106	2.41
fcc-O (2×2) /Pt(111)	1/4 ML	6.20	5.51	192	2.58

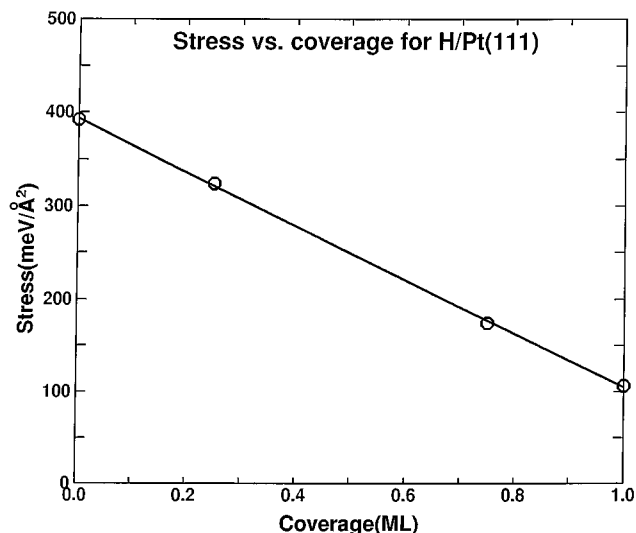


FIG. 3. Calculated surface stress vs H coverage for H/Pt(111).

Tables II and III) are consistent with this idea.

According to measurements of Grossmann, Erley, and Ibach⁴⁵ the stress reduction produced by 1/4 ML O is -4.0 N/m or equivalently -250 eV/Å². The calculated result (cf. Table IV) is -200 eV/Å². It is not hard to imagine sources of the 20% discrepancy between these values. The theoretical number can certainly be refined by adding variational freedom to the basis set,⁹ and by improving on the LDA. The experimental O-induced stress change is extracted from data on the basis of a number of assumptions: crystal uniformity, freedom from impurities, and, importantly, the effect of sample clamping on the nature of the stress-induced sample bending.⁴⁵ Ibach estimates that experimental error alone might account for the 20% discrepancy.⁴⁶

V. DISCUSSION: THE SYSTEMATICS OF SURFACE STRESS

First-principles efforts notwithstanding, there are no rigorous theorems concerning the systematics of surface stress. Calculations thus far imply that all clean metal surfaces are subject to tensile surface stress. But we cannot show that this *must* be so. This is a key issue, because knowing the source of tensile stress would allow us to draw conclusions regarding adsorbate effects. Consider the results of the preceding section in relation to some possible scenarios:

A. Bond order model

The reason that Pt crystallizes as a fcc metal is that it is energetically advantageous to Pt atoms to maximize their coordination, and to distribute their bonds as uniformly as possible over 4π steradians. More, weaker bonds, according to Pauling's bond-order bond-length correlation,⁴⁷ is energetically favorable relative to fewer strong ones. Each Pt atom in the outer layer of a Pt(111) surface is missing three neighbors, and its bonding electrons are confined to $\sim 2\pi$ steradians. In a covalent picture of bonding, adding a layer of impurity atoms means providing the outer layer of metal atoms with new neighbors, such that their valence electrons can redistribute more isotropically in space, as in the bulk crystal. Adsorption thereby weakens individual inter-metal-

atom bonds and (assuming negligible adatom-adatom attraction) relieves tensile surface stress.

Thus, viewing O and H as covalent adsorbates on Pt(111), despite the fact that both induce work function shifts (in opposite directions), both should relieve tensile stress, as indeed the present calculations imply they do. Moreover, both H and O should cause their nearest-neighbor Pt atoms to relax away from the underlying substrate. This is confirmed by the results in Tables II and III.

The small outer-layer expansion of Pt(111) is a problem for the bond-order bond length model. Within the model, it is hard to see why the outer Pt layer of the clean surface should not relax inward. Whether this is just a "detail" that one should not hope to understand in so simple a picture, or represents a fatal contradiction, is not easy to decide.⁴⁸

B. Effective medium model

Needs, Godfrey, and Mansfield (NGM) explain the tensile surface stress they find for Ir(111), Pt(111), and unreconstructed Au(111) via an effective medium picture of bonding.⁴ The basic argument, designed to embody bond-order bond-length correlation in metals with full or nearly full d shells, is that every metal atom prefers to reside at a site where the electron density contributed by its neighbors has a particular, species-dependent optimal value. At a surface, because half the crystal is missing, the outer-layer atoms would ideally displace toward their remaining neighbors to compensate for the absent electron density of the missing half crystal. Coulombic repulsive forces, however, prevent them from making up for the electron density deficit by simply reducing the first interlayer spacing of the crystal—though such relaxation does abate the problem. The upshot is that the intra-first-layer bonds would optimally be shorter than the underlying lattice allows, and the surface is under tensile stress.

In this scenario, a layer of adatoms too small to interact with each other appreciably should reduce tensile stress by restoring the missing charge. Thus again one anticipates that an adlayer will relieve tensile stress, just as the present LDA calculations predict, both for H and for O adsorption.

Despite this apparent agreement, one must remember that the effective medium picture does not account for the expansion of the clean Pt(111) surface.²⁶ Nor, without a serious elaboration, does it allow a discussion of any correlation between adsorbate effects on stress and work function.

C. Relief of kinetic pressure

Needs, in the context of what were the first *first-principles* surface-stress calculations for a metal,⁶ explains that at a surface, the balance that determines a metal's lattice parameter, between electrostatic cohesion and Pauli repulsion, is altered by electron spillout into the vacuum. From a decomposition of contributions to the surface stresses of clean Al(110) and Al(111), he infers that the decisive effect is that spillout weakens the Pauli repulsive pressure more than it weakens intra-first-layer cohesion. This, Needs maintains, is why the optimal length of the intra-first-layer bonds is shorter than the bulk nearest-neighbor distance of Al, or in other words, why the Al(111) and (110) surfaces are subject to tensile stress.

Needs' argument is worthy of a test. An obvious reason is that if depletion of electrons in the outermost atomic layer is the source of tensile stress, then atoms that restore charge to the surface should relieve tension, while electron withdrawing adsorbates should increase it. Another concern is a technical one. Needs and collaborators' stress calculations for Al surfaces are based on a Hellmann-Feynmann theorem approach,³¹ which makes it impossible to separate the actual "kinetic" and "potential" contributions to the surface stress.^{6,8} Thus, until now, Needs' qualitative picture of stress has only been loosely supported by numerical evidence.

The results in the last column of Table IV do, however, provide direct support for the kinetic-pressure argument. Since the present stress calculations are based on direct evaluation of the total energies of slabs versus surface strain, it is straightforward to extract the surface contribution to the strain derivative of the slabs' kinetic energy, for interpretive purposes. The interesting result for all the cases considered is that although the kinetic energy of a finite thickness slab increases as its intra-planar bonds shrink, it increases less per layer than in a bulk crystal. Thus, as Needs contends in the case of Al, the kinetic energy contribution to the surface stress is tensile for Pt(111). On the other hand, the calculated total stress is much less than its kinetic energy contribution. Thus the ratio of kinetic and potential energy contributions is much closer to 1 in the Pt calculations than Needs' results for Al suggest.

Accepting the idea that electron spillout is the source of tensile surface stress, via its tensile effect on the kinetic energy, what should we expect when H or O is adsorbed on Pt(111)? In an ionic picture, H, which causes a work function decrease, donates electrons to the surface while O withdraws them. Thus O exacerbates the effect that gives rise to tensile stress, while H abates it. In fact, however, Table IV shows that both adsorbates relieve surface tensile stress, and indeed that the kinetic energy contribution to the stress becomes less tensile when either species is adsorbed. This result suggests that a covalent picture of the effects of H and O is more appropriate than an ionic one.

D. Backbond model

If tensile surface stress is the result of charge deficiency in a metal's outermost atomic plane, as the preceding views all agree, then only adatoms that abstract surface charge, or that attract each other strongly, can exacerbate tension. Results for both Cs adsorption on Ni(111) and (low-temperature) K adsorption on Pt(111), however, appear to conflict with this conclusion. According to Grossmann and Ibach's (GI's) crystal-bending measurements,¹⁶ adsorbing these alkalis induces additional tensile stress, even though they are electron donors, whose mutual interaction on the surface is repulsive.

To explain the Cs/Ni and K/Pt data, Ibach invokes a picture of surface stress diametrically opposed to the preceding three.^{1,5(a),(b)} He starts from the notion that "dangling" electrons at a clean metal surface redistribute into bonds between first-layer atoms and their neighbors in both the first and second layers. The resulting strengthening of first-to-second layer bonds causes the usual contraction of the outermost interlayer spacing. The strengthening of intra-first-layer bonds implies that those bonds "ought to be shorter," and are therefore under tensile stress. From this perspective,

electron-donating adsorbates should make bonds in the outer layer still stronger, increasing tensile stress, while electron-withdrawing adatoms should produce the opposite effect.

Though it accounts for the Cs/Ni and K/Pt stress-change data, this backbonding picture suffers from serious problems. The first is a consistency issue: the unfilled bands of Ni and Pt are *antibonding*, not bonding; adding electrons into the unfilled states of Ni or Pt should weaken rather than strengthen inter-Pt or inter-Ni bonds.⁴⁹ This may account for the second problem, namely, meager evidence for correlation between outer-layer relaxation and the sign or magnitude of a metal's surface stress. Pt(111) is a case in point. In spite of its tensile surface stress, Pt(111)'s outermost interlayer spacing is slightly expanded²⁶ rather than manifesting "the usual contraction."⁵⁰ Finally, it is not entirely clear where the charge that alkalis donate actually goes. In the case of Cs/W(110), for example, Wertheim *et al.* argue that the adatoms do not add charge into the substrate bands, even as they cause a work function decrease.⁵¹

Direct theoretical investigations of stress for alkali-covered metals promise to clarify the meaning of GI's alkali-adsorption results. Preliminary calculations for 1/3 ML K/Pt(111) imply that K exacerbates the tensile stress, and thus behaves quite differently from H.⁵² According to Needs and Rajagopal⁵³ (NR) the stress induced by 1/3 ML of K on Al(111) depends on binding geometry, both in sign and in magnitude. In the favored substitutional adsorption site, they find K enhances surface tensile stress by 11%. Given the repulsion between adsorbed K atoms, the weakness of K-Al relative to Al-Al bonding,⁵⁴ and the large size of the K atom, this result is more than a little surprising, but NR do not discuss its origin.

VI. THE FUTURE

The successful application of stress-based models of surface reconstruction, and the use of crystal-bending measurements as a surface structural diagnostic, underline the importance of understanding surface stress and its systematics. In agreement with STM observations of the dereconstruction of Pt(111) by H and O adatoms,¹⁵ the present results demonstrate that both work-function-raising and work-function-lowering adsorbates can give rise to compressive surface stress on a group VIII metal's close-packed surface. But experimental results for alkali adsorption stand in the way of any general statement. Further theoretical efforts should evidently be directed at interpreting the alkali-adsorption results of Grossmann and Ibach.¹⁶

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Nevertheless it is likely to be smaller the 2.47 Å measured for Au₂, whose binding energy is 0.84 eV less, and is probably between 2.25 and 2.40 Å in the vapor phase [M. D. Morse (private communication)]. On graphite, average bond lengths for Pt₂ and Pt₃ are 2.45 and 2.66 Å, according to the in-air, STM study of U. Muller, K. Sattler, J. Xhie, N. Venkateswaran, and G. Raina, *J. Vac. Sci. Technol. B* **9**, 829 (1991). These values are appreciably smaller than the nearest-neighbor distance, 2.77 Å, in fcc Pt, and increase with the number of nearest neighbors. For Ni, which occupies the same column in the Periodic Table, the dimer bond length is 2.155 Å, according to J. C. Pinegar, J. D. Langenberg, C. A. Arrington, E. M. Spain, and M. D. Morse, *J. Chem. Phys.* **102**, 666 (1995), compared to a nearest-neighbor distance of 2.49 Å in the fcc crystal.

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