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Anisotropy of the stress on fcc(110) surfaces

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First-principles calculations for Pd(110)-1×1 and Pt(110)-1×1 slabs imply that the surface stress along the close-packed, $[1\bar{1}0]$ direction is larger than in the [001] direction, transverse to the surface channels. This agrees with the simple idea that relaxation of the outermost layer separation, at a fcc(110) surface, allows nearest-neighbor bonds with a component transverse to the channels to relax toward their desired length, while the bonds along the channel walls cannot relax their strain without a surface reconstruction. In contrast, an analysis of the surface phonons of Ni(110), based on an empirical fit to the dynamical matrix, comes to the opposite conclusion, i.e., that the stress in the $[1\bar{1}0]$ direction is only half that in the [001] direction.

I. INTRODUCTION

In this paper, I report first-principles calculations of surface stress for Pd and Pt, and particularly its anisotropy for Pd(110) and Pt(110) surfaces. The main result is that, in agreement with a simple physical picture, the stress is larger in the $[1\bar{1}0]$ direction along the surface channels than in the [001] direction, which is transverse to them. This is in qualitative disagreement with the conclusions drawn by fitting an empirical dynamical matrix to the surface phonon spectrum of Ni(110), by Lehwald *et al.*[1]

A basic aim of surface science is to discover properties of ideal, perfect surfaces that predict their own structural stability, as well as their behavior when covered with adsorbates. For example, in considering whether atomic species "*A*" will grow epitaxially on substrate "*B*," and in what orientation, one compares the lattice parameter of the various faces of crystalline "*A*" to the lattice parameter of "*B*."[2] To predict whether solute atoms "*C*" will segregate to the surface of crystalline solvent "*D*" one looks to the relative surface energies of "*C*" and "*D*."[3]

Studying surface stress has similar objectives. Stress relief has been invoked in explaining the adsorbate geometries of overlayers on semiconductors and metals,[4–6] and in understanding the (beautiful) "herringbone" reconstruction of Au(111).[7,8] In guessing what might distinguish surfaces on which adatom diffusion proceeds by substitutional exchange, rather than by ordinary hopping, surface stress has been proposed as the answer.[9]

If surface stress is to help rationalize surface behavior, it is important to investigate its systematics. Questions of interest include the following: On what surfaces is the stress large, or small, and why? How are "large" and "small" defined; i.e., what is a meaningful *dimensionless* quantity that expresses the effect of the stress at a particular surface? On anisotropic surfaces, what surface stress anisotropy should be expected? This last question is the main focus of the present work.

The specific issue is the surprising result of the analysis of Lehwald *et al.* of the surface phonon spectrum of Ni(110),[1] namely, that the stress along the channels of this surface is only half the stress transverse to them. This contradicts the simple notion, elaborated below, that on an unreconstructed surface the *intraplanar* bonds, which cannot get shorter, should be more stressed than the *interplanar* bonds, which can and do, via surface relaxation. The result of Lehwald *et al.* is of particular interest because the analysis of phonon spectra is the only means, until now, by which values of absolute surface stress have been extracted from any experiment.

There is some hope that this situation will improve. In a pioneering work, Martinez, Augustyniak, and Golovchenko showed that one can measure differential stress, i.e., change in stress associated with the addition of an adsorbate layer, by measuring the deflection of a laser beam from a thin (100 μm) Si crystal, which bends when a layer of Ga is deposited on one side.[10] Müller and Kern have recently pointed out,[11] theoretically, that if a roughly 10 μm clean film were supported at its edges and allowed to deform under the influence of gravity, a value of the absolute surface stress could be extracted from an observation of the shape it assumes. Until such a measurement is performed, however, surface phonon studies are the only experimental source of information on absolute surface stress. Assessing the reliability of the surface phonon analyses is therefore an important undertaking.

To make an educated guess concerning the anisotropy of the stress on an anisotropic surface, one must appreciate why surface stress is nonzero at all. The answer, as explained by Needs, is that because of electron spillout into the vacuum, the competition between kinetic-energy-related repulsion and electrostatic attraction is altered at a surface, relative to the interior of a crystal.[12] If the kinetic pressure is reduced at the surface, for example, then the surface atoms would "prefer" to lie closer to each other than the bulk lattice parameter allows. If the potential that determines the surface atoms' positions relative to the rest of the crystal is weakly corrugated, then a surface reconstruction can be expected, relieving the

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surface stress. On the other hand, if the surface atoms lie in a strongly corrugated potential, then reconstruction does not occur, and the intrasurface bonds remain under *tensile* stress.

Altered competition between kinetic and electrostatic contributions to the energy should affect both intrasurface-plane bonds and bonds between surface and subsurface atoms. However, geometry suggests that stress should be reduced for the latter, for two reasons: The first is that the intrasurface-plane bonds are those that lie closest to the vacuum. Their environment is therefore maximally unlike that of the bulk crystal, placing them under more stress than any other bonds. The second reason is that surface relaxation, i.e., changes in interplanar spacings, allows interplanar bond lengths to optimize without any surface reconstruction. Thus the close to 10% contractions observed for the outermost interlayer spacings of fcc(110) crystals allow the bonds between the first and second layers to contract, by more than 2%, presumably relieving some of their tensile stress.[13] The same is no true for *intrasurface*-plane bonds. They are not affected by layer relaxations except indirectly, by the changes in electronic structure that relaxation induces.

With this in mind, consider the geometry of a fcc(110) surface. In the outer layer, there are rows of nearest-neighbor atoms long the $[1\bar{1}0]$ direction, separated by relatively wide channels. The nearest neighbors of the atoms in a row are other atoms in the same row, and atoms in the second and third crystal layers. *The only nearest-neighbor bonds of the surface layer atoms that have a component transverse to the* $[1\bar{1}0]$ *rows are those that connect them to atoms in the second crystal layer.* This means that if nearest-neighbor interactions dominate the energetics of a fcc(110) surface, one should expect a larger stress component in the $[1\bar{1}0]$ direction than in the [001], exactly opposite to the conclusion that Lehwald *et al.* draw from the empirical analysis of Ni($1\bar{1}0$)'s surface phonons.

A study in the literature supports this simple geometrical argument. Chen, Krakauer, and Singh want to know if the observed reconstruction of clean W(001) can be attributed to an unusually large surface strain.[14] Their study is relevant to the present discussion, because there are no intrasurface-plane nearest neighbors on a bcc(001) surface. Each surface atom has only four nearest neighbors, and they all lie in the subsurface layer. Thus if the qualitative argument given in the last paragraphs is meaningful at all, no bcc(001) surface should be subject to much surface stress. Such stress is relieved via surface relaxation.

Chen, Krakauer, and Singh compute the W(001) surface energy and the energy of a bulk W(001) layer, both as functions of the (001)-plane lattice parameter a.[14] They find the minimum of the surface energy curve at a value of a that is only 1% smaller than the minimum for the bulk layer curve, thus concluding that the surface layer interatomic spacing on W(001) is only 1% larger than it would be, optimally. The stress at this surface can therefore be assumed to be relatively small, and Chen, Krakauer, and Singh infer that surface strain is *not* the source of the W(001) reconstruction. Be that inference as it may, the fact that the stress on W(001) is small agrees with the simple geometric argument given above. It should be small, because of the absence of nearest-neighbor bonds in the surface plane.

In what follows, I report first-principles local-density-functional (LDF) calculations[15] for Pd(110) and Pt(110) surfaces. Pd and Pt are chemically similar to Ni, but are computationally less demanding.[16] The stress anisotropies of their (110) surfaces should be similar to that of Ni, apart from magnetoelastic effects, which in any event do not alter the *geometric* fact that, barring a reconstruction, the bonds in the [001] direction can change in length while those in the $[1\bar{1}0]$ direction cannot.

In agreement with the geometrical argument, for both metals I find that the tensile stress is larger in the $[1\bar{1}0]$ than in the [001] direction. Thus it appears that the empirical central force model used by Lehwald *et al.*[1] is too crude to extract reliable values of absolute surface stress from the Ni(110) surface phonon dispersion measurements. In fact, Balden, *et al.* have already questioned the reliability of the central force fit for Ni(110) (Ref. 17); they report that the parameters of Ref. 1, designed to fit the surface phonons whose motion is along the surface normal, provide a less than satisfactory description of the shear horizontal vibrational modes.

The remainder of this paper is organized as follows: In Sec. II, I provide details of the surface stress calculations. To provide an idea of their overall reliability, in Sec. III, I present results for the Pt(111) surface; agreement with the published stress calculations of Needs and Mansfield[18] is satisfactory, if not excellent. In Sec. IV, I discuss the stress on Pd(111), which should be and is smaller than that on Pt(111). Section V is devoted to results for Pd(110) and Pt(110). Finally, in Sec. VI, I discuss the various results and outline directions for future work on the stress anisotropy of crystalline surfaces.

II. FIRST-PRINCIPLES CALCULATIONS OF SURFACE STRESS ANISOTROPY

Formally, the surface stress tensor, S_{ij}, is the strain derivative of the energy E of a surface. That is, $S_{ij} \equiv dE/d\varepsilon_{ij}$, where i and j are Cartesian indices referring to the plane of the surface, and ε_{ij} is the strain tensor. Thinking of a bounded crystal as an N-layer slab, the surface stress is nonzero because $O(N)$ bulk layers oppose the tendency to contract (or to expand) of $O(1)$ surface layers. A positive value of S_{ii} corresponds to *tensile* or contractive stress, since in that case the energy of the surface increases as the surface lattice parameter dilates. A negative S_{ii} thus implies a *compressive* stress.

The results I report here emerge from first-principles linear combination of atomic orbitals (LCAO) electronic structure calculations for Pd and Pt slabs of 9–13 layers. More layers are needed to define the "bulk" region of a (110) slab than a (111) because, in the (110) case, the second layer of the crystal is exposed to the vacuum, and the layer spacings are relatively small. I evaluate the necessary energy derivatives analytically, via the Hellmann-Feynman-Pulay-like[19] method of Refs. 20 and

21. To fix bulk lattice parameters, I use QUEST,[22] the parallel LCAO electronic structure code of Sears and Schultz. It is a very efficient reformulation of a serial program I originally wrote. However, it does not yet incorporate the analytic stress calculational method of Refs. 20 and 21. Therefore, I used the original, slow serial code to compute surface stresses. I represent the effects of electron exchange and correlation via the exchange correlation potential of Ceperley and Alder,[23] and electron-ion-core interactions via Hamann's generalized norm-conserving pseudopotentials.[24]

A. Choice of basis sets

A basic issue in any first-principles LCAO calculation is the choice of an adequate orbital basis set. I judge basis-set quality by comparing LCAO and linear augmented plane-wave[25] (LAPW) results for thin slabs. Because LAPW calculations are systematically improvable, they provide a meaningful standard of accuracy. Unfortunately, they are slow, and therefore relatively impractical for thicker films.[26]

For Pt, I start from a basis set that includes two *s* functions, as well as a *p*- and a *d*-like radial function centered on each Pt nucleus (see Table I for details). The first of the *s* functions and the *d* function are obtained by fitting linear combinations of Gaussians to the corresponding pseudo-wave-functions[24] of the isolated Pt atom from the nucleus out to a radius of 3.5 bohrs. The second *s* function is the longest-ranged Gaussian of the first. As a low-cost alternative to using a second *d* function in the Pt basis, I reduce the coefficient of the longest-ranged Gaussian of the fit *d* function by 0.002, approximately optimizing the total energy of a five-layer Pt(111) film.[27]

Choosing Pt-centered basis functions of relatively short range reduces linear-dependence-related numerical problems, but makes it necessary to add floating orbitals to the Pt basis sets to allow for electron spillout into the vacuum and Smoluchowski smoothing, and to obtain anywhere near converged work-function values. For Pt(111), I put *p*-like floating orbitals atop each surface-layer Pt nucleus, at a height of 3 bohrs, and an *s* function in each surface hollow, 4 bohrs above the outermost Pt layer.[28] To assess this basis choice, I fix the Pt lattice parameter at 7.36 bohrs, the LAPW optimum value for bulk Pt, then compare LAPW and LCAO energy levels for an ideal five-layer Pt(111) film. Considering ten different points in the surface Brillouin zone (SBZ), the maximum discrepancy is only 0.11 eV, an improvement over the already quite good basis of Ref. 25.

TABLE I. c_α's and α's (in bohr^{-2}) for the four radial functions, $R_1(r)=r^1\sum_\alpha c_\alpha \exp(-\alpha r^2)$, centered at Pt nuclei.

α	c_α
$l=0$	
0.11	0.638 753 12
0.14	−0.114 014 61
1.08	−2.947 982 5
1.52	7.143 236 6
1.69	−4.672 959 3
0.11	0.638 753 12
0.14	−0.114 014 61
$l=1$	
0.17	1.00
0.34	−1.00
$l=2$	
0.227 134 00	0.076 328 811
0.681 611 00	0.657 544 85
1.653 540 0	1.984 931 5
4.590 109 8	−1.293 111 4

For Pd, I use a similar basis set (cf. Table II), now checking its adequacy by comparing LCAO and LAPW electron energy levels for ideal five-layer Pd(110) slabs. In this case I fix the lattice parameter at the LAPW optimum value for bulk Pd, 7.262 bohrs. Because the (110) face of an fcc crystal is relatively open, more variational freedom is required in its near-vacuum region than in the (111) case. Thus, in addition to *p*-like floating orbitals 3.2 bohrs atop the outer layer Pd nuclei, on this surface I place *s*-like Gaussians 5.9 bohrs above the nuclei of the second layer and at four different sites along and above the long bridges between first-layer Pd nuclei.[29] For five-layer Pd(110), a check of 12 *k* vectors across the SBZ reveals a maximum discrepancy between LAPW and LCAO energy levels of less than 0.09 eV, again showing that a close-to-minimal LCAO basis set can faithfully represent basis-state converged LAPW results. In calculations for thicker slabs, in which I allow the surface layers to relax, I also allow the centers of the floating orbitals to move in a way that maintains the symmetry of the surface while lowering the total energy.

For the calculations described below that involve *bulk* Pt and Pd, I use the nucleus-centered orbitals of Tables I and II, respectively, with no floating functions. For the Pd(111) and Pt(110) surfaces, I add floating orbitals to the nucleus-centered orbital set analogously to the cases of Pt(111) and Pd(110). I directly verify that this procedure yields an excellent description of Pd(111) with virtually no "tweaking." Using the same orbitals to describe the Pd atoms as for Pd(110), placing floating *p* orbitals atop

TABLE II. c_α's and α's (in bohr^{-2}) for the four radial functions, $R_l(r)=r^1\sum_\alpha c_\alpha \exp(-\alpha r^2)$, centered at Pd nuclei.

α	c_α
$l=0$	
0.0974	0.508 167
0.6439	−0.722 407
1.288	0.296 326
0.0974	1.000 000
$l=1$	
0.16	0.422 945
0.32	−0.383 563
$l=2$	
0.2124	0.052 461
0.6146	0.465 647
1.4522	1.889 024
3.2802	3.427 922
6.5610	−2.711 885

the outer Pd's at a height of 1.5 bohrs and *s* orbitals in the hollows at a height of 4 bohrs, I find that the worst discrepancy between LAPW and LCAO energy levels, for a five-layer film, is only 60 meV, throughout the SBZ. The LCAO work function, 5.64 eV, is also in good agreement with the LAPW result, 5.67 eV. The experimental value is 5.95 eV.[30] Unfortunately disagreements of 0.3 eV between LDF and measured work functions are common.

B. Brillouin-zone sample

Because the *d* bands of Pd and Pt are rather flat, the *k*-vector sample need not be especially fine. I use 35 equally spaced points in the irreducible $\frac{1}{4}$ of the SBZ for (110) slabs, and 19 equally spaced *k* vectors in the irreducible $\frac{1}{12}$ of the zone in the (111) cases. As described below, I find the effect of using a 40-*k*-vector honeycomb sample[31] for the (111) case to be quite small on the scale of the other systematic errors in the calculations. I also find that the difference between a 24- and a 35-*k*-vector sample for the Pt(110) case is small relative on the scale of the calculated stress anisotropy.

C. Lattice parameters

I fix the lattice parameters of Pd and Pt, via LCAO-LDA total-energy calculations for the bulk fcc crystals. For these calculations, I represent the crystals as repeated supercells comprised of six (111) layers of whichever metal. I use an SBZ sample of 19 *k* vectors in the (111) plane for each of two special points along the (111) direction. Fitting cubic polynomials to the energies calculated at five lattice parameters for each metal, I find that the minimum energy for Pt corresponds to a unit cube side of 7.36 bohrs, while for Pd the optimal lattice parameter is 7.27 bohrs. These values are 0.6% and 1.1% smaller than the experimental results for Pt and Pd, as is typical of LDA calculations. They also agree very well with LAPW results, namely, 7.36 bohrs for Pt and 7.26 bohrs for Pd.

D. Analytic evaluation of surface stress components

In order to calculate components of the surface stress tensor, one needs to evaluate the surface contribution to the derivative of a sufficiently thick slab's total energy E^{slab} with respect to a strain ε_{ij}. Because I choose values for the Pd and Pt lattice parameters by minimizing the LDF energy of the corresponding bulk crystals, the contribution to $dE^{\text{slab}}/d\varepsilon_{ij}$ from the slab interior (the "bulk contribution") should approach zero with increasing number of layers. But because the slabs I use are limited to a few layers' thickness, and because of different numerical approximations in bulk and slab calculations, e.g., the different *k*-vector sampling, there always is a residual bulk contribution to $dE^{\text{slab}}/d\varepsilon_{ij}$.

Although I can choose parameters of the calculation such that this contribution is small, I still wish to subtract the residual bulk stress from the total to obtain accurate surface stress components. This raises the question of how to compute the residual bulk stress tensor. An answer is provided in Ref. 21. $dE/d\varepsilon_{ij}$ can be decomposed into "bulk" and "surface" parts, by setting up "bins" corresponding to the various slab layers, and assigning fractions of each contribution to $dE/d\varepsilon_{ij}$ to appropriate bins. Making this assignment in a consistent manner, and assuming that the contributions to $dE/d\varepsilon_{ij}$ are sufficiently "local," then the bins corresponding to the layers near the middle of a thick enough film will contain almost equal contributions. The average of these central bin contributions is a good approximation to any "bulk" contribution to $dE/d\varepsilon_{ij}$. Knowing the "bulk," per layer contribution to $dE/d\varepsilon_{ij}$, and the total $dE/d\varepsilon_{ij}$ for the slab, it is straightforward to determine the surface stress via the equation,

$$S_{ij}^{\text{surf}} = (S_{ij}^{\text{total}} - NS_{ij}^{\text{bulk}})/2 \ , \tag{1}$$

where *i* and *j* = *x* or *y* and *N* is the number of slab layers. The factor $\frac{1}{2}$ corresponds to the fact that the slab has two surfaces.

III. SURFACE GEOMETRY, ENERGY, AND STRESS, FOR Pt(111)

This section is devoted to Pt(111) surface calculations, and comparison to Needs and Mansfield's[18] (NM's) corresponding results. Because NM studied only an ideal four-layer film, and used a relatively poorly converged plane-wave basis, perfect agreement should not be anticipated, nor is it achieved. The best converged of the present results for Pt(111) and the stress obtained in Ref. 18 agree to about 11%.

The present LCAO stress calculations are based on the bin-decomposition method developed in Ref. 21 and outlined in the previous section. The first step is to relax the Pt(111) surface to equilibrium. I represent the (111) surface via a nine-layer Pt(111) slab, fixing the in-plane nearest-neighbor distance at 5.21 bohrs, in accord with the bulk optimization described above. Then the forces on all the film atoms are less than 35 meV/bohr if the outer layer separation is 1% expanded, while all the subsurface layers remain in their ideal positions. This expansion, incidentally, agrees with the most recent results of low-energy electron diffraction (LEED) analysis,[32] while the computed work function, $\Phi = 6.16$ eV, is very close to the value 6.10 eV measured by Derry and Zhong.[33]

The total valence electron energy of the optimized nine-layer film, per unit cell, is 476.1039 Ry. Optimization of the bulk Pt lattice parameter yields a per (111) layer valence energy of 52.9151 Ry. Together, these results imply that the Pt(111) surface energy is 0.137 eV/Å^2. NM also quote 0.137 eV/Å^2 as the surface energy they obtain for an ideal four-layer film. The three-place agreement of these values is certainly[34] accidental.

I compute the stress on the Pt(111) surface using Eq. (1), using the layerwise contributions to the stress given in Table III. Notice that in agreement with the fact that the bulk Pt total energy is minimized at the chosen nearest-neighbor separation, the stress contributions in the central film layers, which must approach zero as the film becomes thicker, are already close to zero.[35]

Substituting from Table III into Eq. (1), I find that the

TABLE III. For the nine-layer Pt(111) slab, with a 19-k-vector SBZ sample and four radial functions centered at each Pt nucleus, layer heights relative to the slab center, residual forces after relaxing the layer spacings, and bin decomposition of the stress.

Pt(111) layer	z (bohr)	Residual F_z (eV/bohr)	Contribution to S_{xx} (eV/atom)
1,9 (surface)	17.04	0.03	2.566
2,8 (subsurface)	12.75	0.02	0.044
3,7	8.50	0.01	0.044
4,6	4.25	0.02	−0.060
5 (central)	0.00	0.00	−0.026

Pt(111) surface stress is 0.426 eV/Å^2, roughly 20% larger than what NM report.[18] Some of this discrepancy is surely the result of the relatively low level of convergence, both with respect to basis size and film thickness in the plane-wave calculations of Ref. 18. To see how much of it can be attributed to the present calculations, however, I have conducted several convergence tests.

To assess convergence with respect to the k sample, I hold the geometry of the nine-layer slab fixed and recompute both forces and the stress, replacing the original sample of 19 equally spaced k points in the irreducible SBZ with 40 k points on a honeycomb mesh.[31] The result is that the Pt's now experience force components along the surface normal smaller than 0.031 eV/bohr. The largest force is on the layer adjacent to the central film layer. At the same time the average stress in the three central film layers is -0.028 eV/Å^2. Thus with the finer k-point sample, the bulk lattice parameter should be slightly larger. Nevertheless, I find that the surface stress is 0.424 eV/Å^2, only about 0.5% smaller than with the 19-k-point sample.

To check convergence with respect to slab thickness, I repeat the 40-k-vector calculations for an *11-layer* Pt(111) slab, again holding the bulk lattice parameter and the surface geometry fixed. Now the stress turns out to equal 0.422 eV/Å^2. These tests indicate that the smaller k sample and film thickness do not have a serious effect on the calculated stress, at most 1%. This conclusion is reasonable: The bands of Pt are rather flat and also, because of Pt's high electron density, screening of the surface-related potential is rapid as one moves into the interior of the crystal.

The most serious convergence issue in the stress calculation concerns the use of a very small set of basis functions. To test basis convergence, I add a second d function to the set of orbitals centered at each Pt nucleus. The radial function for this added orbital corresponds to a single Gaussian of attenuation constant $\alpha=0.15$ bohr^{-2}. Reoptimizing the bulk lattice parameter in the new basis implies only a very small new contraction, by about 0.1%. Leaving the lattice parameter unchanged and reoptimizing the nine-layer film geometry also leads to only a small change in the surface relaxation: the outer layer separation contracts by -0.52% while the spacing between the subsurface and third crystal layers expands by 0.26%. With the extra d function, and the reoptimized surface geometry I now compute a surface stress of 0.390 eV/Å^2, i.e, a value that is reduced by 8.5% relative to the single d-function basis. The extra d orbital allows the system an improved description of both s-d mixing and the radius of the valence d function, as the lattice contracts, and the result is improved agreement with Needs and Mansfield's value of 0.350 eV/Å^2.

From these convergence tests (see Table IV for a summary compilation) I conclude that using the basis that incorporates only ten orbitals about each Pt nucleus, together with the 19-k-vector sample and a nine-layer Pt(111) slab, provides stress tensor components to about 10% accuracy. The results presented below show that the anisotropy of the stress on Pt(110) and Pd(110) is considerably larger than 10%. Thus to obtain a reasonable idea of the stress anisotropies, while containing computational expense, I use the small basis tests.

IV. STRESS OF Pd(111)

Surfaces of the 5d metals are less stable than those of the 4d's. The (110) faces of Ir, Pt, and Au adopt 2×1, missing-row configurations, while Rh, Rd, and Ag(110) do not; their (100) surface layers reconstruct into hexagonal arrangements while Rh, Pd, and Ag(100) remain 1×1.[36] Finally, Au(111) is reconstructed at room temperature[37] and Pt(111) above 1329 K,[38] while Ag and Pd(111) remain 1×1.[36] These 5d surface reconstructions are attributed to high stress.[7,18,39] It is therefore of some interest to compare the stress of the Pd(111) surface to that of Pt(111). Bin-decomposition results for a nine-layer Pd(111) film are given in Table V. Averaging the contributions in the central three bins to obtain a residual bulk stress, I find that Pd(111)'s surface stress is 0.230 eV/Å^2. Thus Pt(111)'s tensile stress is close to double that of Pd(111). At the same time, its cohesive energy is only 50% lager and its (111) shear modulus is bigger by only 34%.[40] The question of how to normalize surface stress, in distinguishing more from less stable surfaces, is one that has not been settled.[39] Nevertheless, these results certainly do not contradict the idea that Pt(111)-1×1 is less stable than Pd(111)-1×1 by virtue of being under higher surface tensile stress.

V. STRESS ANISOTROPY ON Pd(110) AND Pt(110)

This section is devoted to the structure of the (110) faces of Pd and Pt, their surface stress, and its anisotropy. As discussed in Sec. I, geometry suggests that the stress should be higher along the $[1\bar{1}0]$ than the [001] direction on these surfaces. The LDA results agree with this idea. For Pd(110), the $[1\bar{1}0]$ stress is 50% higher than the [001]; for Pt(110) the ratio is much bigger, almost a factor of 3. On a per surface atom basis, the stress along the close-packed direction on the (110) surface is roughly 20% higher than the surface stress on the (111) face of the same metal.

To determine the geometry of the Pt and Pd (110)-1×1 surfaces, I use the same bulk lattice parameters as for the (111) calculations. But because (110) planes in a bulk fcc metal are separated by only $a/2^{3/2}$, where a is the lattice parameter, it is necessary to represent the Pd and Pt (110) surfaces by slabs with more layers. [The (111) planes are

TABLE IV. Summary of convergence tests of stress results. All results refer to relaxed surfaces except the rows marked "Ideal Pt(110)" and "Ideal Pt(110)." In those cases all layer spacings are fixed at the values corresponding to the bulk, fcc crystals.

System	No. of k's	No. of d orbitals	No. of layers	$S_{1\bar{1}0}$ (eV/Å^2)	S_{001} (eV/Å^2)	$S_{1\bar{1}0}$ (eV/atom)	S_{001} (eV/atom)
Pt(111)	19	1	9	0.426		2.79	
Pt(111)	40	1	9	0.424		2.79	
Pt(111)	40	1	11	0.422		2.77	
Pt(111)	19	2	9	0.413		2.72	
Pt(110)	24	1	13	0.285	0.118	3.06	1.27
Pt(110)	35	1	13	0.317	0.113	3.40	1.21
Ideal Pt(110)	35	1	13	0.453	0.309	4.86	3.32
Pd(111)	19	1	9	0.230		1.48	
Pd(110)	35	1	13	0.171	0.116	1.79	1.22
Ideal Pd(110)	35	1	13	0.236	0.224	2.46	2.34

separated by $a/3^{1/2}$.] I use 13-layer slabs, fixing the central 7 layers at their ideal bulk separations. Tables VI and VII show that in this case the stress contributions from the central three film layers are close to equal.

To converge results for the (110) surfaces one not only needs to use more layers than for the (111) cases, but also a larger set of k vectors in the surface Brillouin zone sample. The reason is the lower symmetry of the (110) surface. In the (111) case, one only needs to sample one-electron wave functions in the irreducible $\frac{1}{12}$ of the SBZ, whose area is $2/3^{3/2}(\pi/s)^2$, where s is the nearest-neighbor spacing. For the (110) surface, whose point group operations include only a twofold rotation and two mirror planes, one needs k's in the irreducible $\frac{1}{4}$ of the SBZ. Its area equals $2^{-1/2}(\pi/s)^2$, about 1.84 times as large as the (111) face's irreducible zone. This permits the rough inference that if 19 k vectors was a large enough sample for a (111) surface, 35 are required for the (110)'s. The final results quoted in Tables VI and VII were calculated using 35-k-vector samples. For reference, in Table IV, I compare stresses and surface energies computed for Pt(110) using 24- and 35-k-vector samples. The result agree to about 10%.

The outermost layer separations of fcc(110) surfaces generally are considerably contracted, while successively deeper layer relaxations alternate and get smaller.[41] For Pt(110)-1×1, I calculate optimal outer layer relaxations of −11.6%, +5.4%, and −1.6% for the first three interlayer spacings. For Pd(110)-1×1 the corresponding relaxations are somewhat smaller, viz., −9.0%, +3.3%, and −0.5%.

For Pd one can compare to experiment—Pd(110)-1×1 is a stable surface, while Pt(110)-1×1 is not. The LEED analysis of Barnes *et al.*,[42] yields percent relaxations of −6±2% and 1±2% for the first two interlayer spacings. A second paper by the same group refines these values to −5.7±2% and 0.5±2%.[43] Skottke *et al.* obtain relaxations of −5.1±1.5% and 2.9±2%.[44] Finally, the most recent LEED study, by Warren and Thiel, yields a somewhat smaller contraction of the first interlayer spacing, 4.4±1.5%, and 1.5±1.5% for the second.[45] Thus theory and experiment agree qualitatively—both imply a large contraction of the first interlayer spacing and a smaller expansion of the second. The LCAO calculation appears to overestimate the contraction of the first spacing, however, while theory and experiment agree on the second-layer expansion, within the experimental error bars. Whether this quantitative disagreement is the result of systematic error in the LDF-LCAO calculation, or is a product of the LEED analysis, remains to be determined.

For reference, the calculated work functions for the 13-layer 1×1 Pd(110) and Pt(110) slabs are, respectively, 5.16 and 5.54 eV, while the measured work function for Pd(110)-1×1 is 5.25 eV. The LCAO surface energies are 0.147 eV/Å^2 for Pd(110) and 0.172 eV/Å^2 for Pt(110). As expected for these more open surfaces, their surface energies are larger than the corresponding values for Pd(111) and Pt(111), respectively, 0.124 and 0.137 eV/Å^2. Since the cohesive energy of Pt is 50% higher than that of Pd, it is not surprising that the Pt surface energies are higher than for the corresponding Pd faces. The reason that they are only between 10% and 20% higher is not clear to me.

Results of the bin-decomposed surface stress calculations for Pt(110) and Pd(110) are given in Tables VI and VII. In both cases the stress contributions from the central three slab layers are roughly constant, suggesting that 13-layer slabs are thick enough to provide meaningful values of surface stress. Thus, I compute the average of the stress contributions from the central three layers for each metal, and use it as a "bulk" value to be substituted into Eq. (1). This procedure leads to tensile surface

TABLE V. For the nine-layer Pd(111) slab, with a 19-k-vector SBZ sample and four radial functions centered at each nucleus, layer heights relative to the slab center, residual forces after relaxing the layer spacings, and bin decomposition of the stress.

Pd(111) layer	z (bohr)	Residual F_z (eV/bohr)	Contribution to S_{xx} (eV/atom)
1,9 (surface)	16.80	0.00	1.303
2,8 (subsurface)	12.59	0.01	0.069
3,7	8.40	0.02	−0.011
4,6	4.20	0.02	−0.034
5	0.00	0.00	−0.045

TABLE VI. For the 13-layer Pt(110) slab, with a 35-k-vector SBZ sample and four radial functions centered at each Pt nucleus, layer heights relative to the slab center, residual forces after relaxing the layer spacings, and bin decomposition of the stress. The "x direction" refers to [001] and the "y direction" to $[1\bar{1}0]$.

Pt(110) layer	z (bohr)	Residual F_z (eV/bohr)	Contribution to S_{xx} (eV/atom)	Contribution to S_{yy} (eV/atom)
1,13 (surface)	15.41	0.02	1.523	2.459
2,12 (subsurface)	13.11	0.01	−0.929	0.023
3,11	10.37	0.04	+0.208	0.052
4,10	7.81	0.03	−0.458	−0.279
5,9	5.21	0.01	−0.228	−0.241
6,8	2.60	0.07	−0.224	−0.232
7 (central)	0.0	0.00	−0.208	−0.261

stresses of 0.317 and 0.113 eV/Å^2 for the $[1\bar{1}0]$ and [001] directions on Pt(110), and 0.171 and 0.116 eV/Å^2 for the $[1\bar{1}0]$ and [001] directions on Pd(110). In both cases the stress along the close-packed $[1\bar{1}0]$ direction is considerably larger, as expected.

In Table IV, to give an idea of the source of the greater stress in the $[1\bar{1}0]$ direction, I compare stress components for ideal (i.e., unrelaxed) and relaxed Pt(110) and Pd(110) 13-layer films. Notice that for both metals the surface relaxation results in a decrease of both the [001] and the $[1\bar{1}0]$ stress components, but that the [001] component of the stress decreases about twice as much. I attribute the decrease in the $[1\bar{1}0]$ stress with surface relaxation to the fact that the first-layer atoms relax toward the rest of the crystal. Thus the intrasurface-plane bonds relax into a region where the electron gas of the rest of the crystal is less tenuous, and the $[1\bar{1}0]$ stress is reduced accordingly.

The larger relaxation effect on the [001] stress component is the result of the fact that surface relaxation means optimizing the bond lengths between the first-, second-, and third-layer atoms. If it were not for the resistance of the first-to-third layer bonds being compressed too much, the first-to-second layer bond lengths could be strain free. As it is, their strain is much reduced relative to that of the intrasurface-plane bonds.

Because the theoretical surface relaxation is greater in the Pt(110) case, greater relief of tension in the [001] direction should occur on this surface than on Pd(110). Assuming that the nearest-neighbor bonds on the (110) surfaces are not much different from those on the corresponding (111) faces, one might also expect the $[1\bar{1}0]$ direction stresses to be comparable in magnitude in the two crystal planes. Table IV shows that both these qualitative expectations are also realized.

Finally, since Ni(110), from the geometric point of view, is just another fcc (110) crystal surface, it is reasonable to expect that the stress anisotropy would have the same sign on that face as I have found for Pt(110) and Pd(110).

VI. DISCUSSION AND FUTURE DIRECTIONS

The present results suggest that it is worth attempting a more rigorous interpretation of the phonon dispersion data for Ni(110). As noted in the Introduction, the measurement of shear horizontal phonons on this surface has already cast doubt on the stress values derived from the study of phonons polarized perpendicular to the (110) plane.[17] What would be most desirable would be a direct, first-principles evaluation of the Ni(110) dynamical matrix and thus a first-principles calculation of the corresponding phonon spectrum. Such a calculation is now or should soon be possible.[46]

A second area that demands attention is development of a better understanding of the predictive value of the stress tensor. Granted that the $[1\bar{1}0]$ component of the surface stress tensor on Pd(110) and Pt(110) is larger than

TABLE VII. For the 13-layer Pd(110) slab, with a 35-k-vector SBZ sample and four radial functions centered at each nucleus, layer heights relative to the slab center, residual forces after relaxing the layer spacings, and bin decomposition of the stress. The "x direction" refers to [001] and the "y direction" to $[1\bar{1}0]$.

Pd(110) layer	z (bohr)	Residual F_z (eV/bohr)	Contribution to S_{xx} (eV/atom)	Contribution to S_{yy} (eV/atom)
1,13 (surface)	15.27	0.01	+1.406	+1.565
2,12 (subsurface)	12.93	0.01	−0.401	+0.015
3,11	10.27	0.02	+0.031	−0.058
4,10	7.71	0.02	−0.104	−0.075
5,9	5.14	0.01	−0.013	−0.019
6,8	2.57	0.01	−0.061	−0.071
7	0.00	0.00	−0.058	−0.074

the [001] component, what does this result tell us about the nature or likelihood of the reconstructions of these surfaces? The missing-row structure of Pt(110)-2$\times$1 would appear to relieve stress in the [001] direction, i.e, the crystal direction for which the stress is lower. Why is this so?[47]

Finally, it is interesting to compare the present results for transition metal (110) surfaces to Needs's calculation of the stress anisotropy on Al(110). He finds that it is quite weak, quoting the values 0.124 and 0.115 eV/Å^2 for the $(1\bar{1}0)$ and (001) directions.[48] The $[1\bar{1}0]$ component of the strain is the larger, once again, but now only by 8%. This is a consequence of the weakness of the crystal potential in Al; i.e., as Needs points out, much of the stress at Al surfaces is a jellium effect.

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[29] Specifically, I place *s*-like Gaussians with attenuation constants 0.3 and 0.5 bohr^{-2} both at the midpoint of the long bridge and also directly above second-layer Pd's, at a height of 3.37 bohrs above the first layer. I also place *s* Gaussians with attenuation constant 0.19 bohr^{-2}, 2.1 bohrs along the long bridge on either side of each outer layer nucleus and also above the midpoint of the long bridge, 0.37 bohrs above the outermost layer of Pd's.

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