Calculations of the Surface Stress Tensor at Aluminum (111) and (110) Surfaces

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(Received 2 September 1986)

Quantum mechanical calculations of the surface stress tensor at the aluminum (111) and (110) surfaces are presented. In each case the stress is tensile, favoring contraction in the plane of the surface. This tensile stress is caused by smoothing of the electronic wave functions at the crystal surface.

We have performed a first-principles calculation of the surface stress tensor at the aluminum (111) and (110) surfaces. Surface stress arises when the surface layer of a material energetically favors a lattice constant different from the bulk value in directions *parallel* to the surface.

The surface layer of a crystal may reduce its energy by relaxation of the atomic layers in the direction perpendicular to the surface or by a surface reconstruction in which the periodicity of the reconstructed layer is different from that of the bulk. The lowest-energy configuration of the crystal will have the surface layer stressed in its own plane, while the bulk of the material exerts an opposing stress such that equilibrium is maintained, i.e., the *total* stress due to both surface and bulk material is zero.[1] The surface stress may be so large that it is energetically favorable to relieve it partially by surface reconstruction or the creation of surface defects. For example, the $23 \times \sqrt{3}$ reconstruction of the Au(111) surface[2] appears to involve the insertion of an extra row of atoms every 23 rows and may be explained by the relief of a tensile surface stress.

Clearly it is important to clarify the role of surface stresses in the determination of surface structure. As a step in this direction I present the first accurate calculations of stress at a metal surface.

When a liquid film is stretched atoms or molecules move out from the bulk to form new surface which is structurally identical to the existing surface. Thus the processes of the creation and deformation of a liquid surface are identical and described in γ, the energy required to create unit area of surface. However, when a crystal is stretched the distance between the atoms increases and the nature of the surface itself changes. This process is quite different from the creation of new surface by the cutting of bonds. The energy to create unit area of surface of some crystallographic orientation is again denoted by γ, but deformation of the crystalline surface is described by the surface-stress tensor $g_{\alpha\beta}$.[3] The surface-stress tensor is the strain derivative per unit area of the energy to create the surface[1,4]:

$$g_{\alpha\beta} = A^{-1}\partial(\gamma A)/\partial\varepsilon_{\alpha\beta} = \gamma\delta_{\alpha\beta} + \partial\gamma/\partial\varepsilon_{\alpha\beta}, \qquad (1)$$

where A is the surface area per atom, $\varepsilon_{\alpha\beta}$ denotes the

strain tensor, and $\delta_{\alpha\beta}$ is the Kronecker delta function. The indices α and β label directions in the plane of the surface. In a discussion involving stress it is important to make clear the sign convention that is being used. Throughout this paper I employ the convention consistent with the standard form of Eq. (1) given above. For example, in the convention used here, the kinetic energy of an electron gas which always pushes outwards gives rise to a negative diagonal stress.

For a liquid $\partial\gamma/\partial\varepsilon_{\alpha\beta}$ is zero and hence the diagonal components of $g_{\alpha\beta}$ are numerically equal to γ. However, for a crystal $\partial\gamma/\partial\varepsilon_{\alpha\beta}$ is of the same order as γ and the resulting surface stress may be positive (tensile) or negative (compressive). Crudely speaking a tensile surface stress is associated with a surface which energetically favors contraction in the plane of the surface while a compressive surface stress favors expansion. This situation is pictured in Fig. 1.

I have performed self-consistent local-density-functional calculations using norm-conserving pseudopotentials on the Al (111) and (110) surfaces. For the Al(111) calculations I used a supercell containing a nine-layer-thick slab of aluminum with six layers of vacuum.[5] The forces acting on each atomic layer perpendicular to the surface were calculated and the structure relaxed until these forces were less than 5×10^{-4} Ry
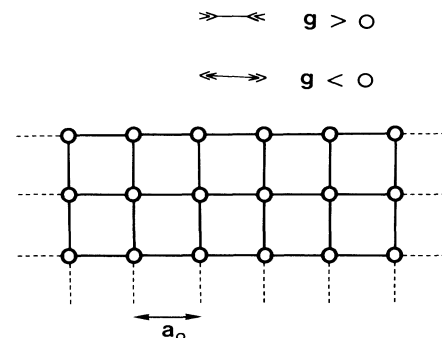

FIG. 1. A surface with a tensile stress ($g > 0$) favors a smaller lattice constant than the bulk value a_0 in directions parallel to the surface, while a surface with a compressive surface stress ($g < 0$) favors a larger one.

Å^{-1}. The only significant relaxation was of the first layer which moved outwards by 1.0%, in good agreement with the LEED data of Nielsen and Adams[6] who found $\Delta d_{12}^{(111)} = 0.9\%$. For the (110) surface I used a supercell with a nine-layer slab of aluminum and seven layers of vacuum. I did not perform a relaxation of the surface layers but instead used the coordinates of Ho and Bohnen.[7] They performed highly accurate self-consistent pseudopotential calculations on the Al(110) surface and obtained $\Delta d_{12}^{(110)} = -6.8\%$, $\Delta d_{23}^{(110)} = +3.5\%$, $\Delta d_{34}^{(110)} = -2.4\%$, and $\Delta d_{45}^{(110)} = +1.6\%$. My calculations with these relaxed atomic positions gave forces on the atoms of less than 2×10^{-3} Ry Å^{-1}, confirming that this structure is indeed close to an energy minimum.

The volume-averaged stress tensor and total energy were evaluated for each of the two crystallographic orientations. The calculation of the stress tensor was performed by use of the stress theorem of Nielson and Martin.[8] The following three types of structure were investigated: (1) A supercell full of bulk aluminum (i.e., with no surfaces). The number of atoms in the supercell, N_b, is thus fifteen for the (111) surface and sixteen for the (110) surface. The energy per supercell is denoted by E_b and the volume-averaged stress is $\sigma_{\alpha\beta}^b$. (2) The same supercell as above but containing a slab of N_s ($=9$) layers of atoms and $N_b - N_s$ layers of vacuum with unrelaxed atomic positions. The energy per supercell and volume-averaged stress are E_{su} and $\sigma_{\alpha\beta}^{su}$, respectively. (3) Again the same supercell with N_s ($=9$) atoms and $N_b - N_s$ layers of vacuum but with relaxed atomic positions. Only relaxations in the direction perpendicular to the surface were allowed. The energy per supercell and volume-averaged stress are E_{sr} and $\sigma_{\alpha\beta}^{sr}$, respectively.

From these calculations I obtained the surface energy per unit area, γ, since this may be written as

$$\gamma = \tfrac{1}{2}(1/A)[E_s - (N_s/N_b)E_b], \qquad (2)$$

where A is the surface area per atom and E_s refers to the energy per supercell with relaxed or unrelaxed atomic positions as appropriate. The surface stress tensor $g_{\alpha\beta}$ was also obtained as it follows directly from Eqs. (1) and (2):

$$g_{\alpha\beta} = \tfrac{1}{2}(V/A)[\sigma_{\alpha\beta}^s - (N_s/N_b)\sigma_{\alpha\beta}^b], \qquad (3)$$

where V is the volume of the supercell and $\sigma_{\alpha\beta}^s$ refers to the stress with relaxed or unrelaxed atomic positions.

I used a lattice constant of $a_0 = 4.02$ Å obtained from an extrapolation to zero temperature of the value of $a_0 = 4.05$ Å at 298 K given by Wyckoff.[9] However, this choice does not give zero bulk stress ($\sigma_{\alpha\beta}^b \neq 0$) because of the various approxiations involved in the calculations. The most important of these are the use of the local-density approximation (LDA), the neglect of zero-point motion, and the use of an incomplete basis set. The results presented in this paper were obtained with the

Wigner form[10] of the LDA. Repeating the calculations for the (111) surface by use of the Ceperley-Alder[11] form increased $\sigma_{\alpha\beta}^b$ by 29 kbar, favoring a smaller lattice constant than the Wigner formula. This fortuitously gives a value of $\sigma_{\alpha\beta}^b$ close to zero, but the values of γ and $g_{\alpha\beta}$ obtained from Eqs. (2) and (3) are not significantly altered.

It is clear from the definition of surface stress in Eq. (1) that to calculate $g_{\alpha\beta}$ accurately we must use a slab thick enough to give good values of the surface energy γ at the particular bulk lattice constant chosen and at values close to it. My value of γ for the (110) surface of 0.65 eV per surface atom is reasonably close to the 0.77 eV per surface atom obtained by Ho and Bohnen.[7] Furthermore, Ho and Bohnen[7] performed calculations on slabs of between nine and fifteen layers showing that the surface energy had already well converged for a nine-layer slab.

The values of γ and the nonzero components of $g_{\alpha\beta}$ for the relaxed surfaces calculated from Eqs. (2) and (3) for the (111) and (110) surfaces are shown in Table I. The values of $\partial\gamma/\partial\varepsilon_{\alpha\beta}$ as deduced from Eq. (1) are also given. In order to clarify the mechanisms leading to surface stress the various quantities are broken down into kinetic, exchange-correlation, and electrostatic contributions. Although these are pseudopotential calculations where smooth pseudo wave functions replace the real wave functions in a process which can be thought of as swapping kinetic for potential energy, this decomposition is meaningful because the quantities γ and $g_{\alpha\beta}$ are defined in terms of differences in energies and stresses between two structures.

As is clear from Table I, $\partial\gamma/\partial\varepsilon$ is of the same order as γ itself. The surface stresses on the (111) and (110) surfaces are of approximately the same magnitude and are tensile, corresponding to a preference for a contracted surface layer. The (110) surface contains inequivalent perpendicular directions which can be taken to be along [001] and [$\bar{1}$10] vectors of the cubic cell. The calculated surface stresses in these two directions are 0.115 and 0.124 eV/Å^2, respectively, while on the isotropic (111) surface the surface stress is 0.145 eV/Å^2. It is well known that the relaxation energy of the atomic planes perpendicular to the surface from the bulk separation to the minimum-energy positions is at most a few percent of the surface energy.[7] Indeed, I found relaxation energies of 10^{-3} eV/Å^2 on the (110) surface and 10^{-4} eV/Å^2 on the (111) surface which are respectively 1.7% and 0.2% of the surface energy. Similarly the surface stress is insensitive to these relaxations which give rise to increases of only 8.1% and 1.4% in the surface stress along the [001] and [$\bar{1}$10] directions in the (110) surface and 2.6% on the (111) surface.

Because the surface stress appears to be insensitive to the precise atomic positions at the surface, it seems clear that it originates from quite general features of the sur-

TABLE I. Energetics of the Al (111) and (110) surfaces and of a jellium surface with the same average electron density in the bulk of $r_s = 2.06$. The jellium results were deduced from the data of Lang and Kohn (Ref. 12). The surface energy γ, strain derivative $\partial\gamma/\partial\varepsilon$, and surface stress g are given, broken down into kinetic, exchange-correlation, and electrostatic parts. All entries are in units of electronvolts per square angstrom.

	Kinetic	Exchange correlation	Electrostatic	Total
		Al(111)		
γ	−0.346	+0.173	+0.217	+0.044
$\partial\gamma/\partial\varepsilon$	+0.635	−0.226	−0.308	+0.101
g	+0.289	−0.053	−0.091	+0.145
		Al(110)		
γ	−0.330	+0.184	+0.202	+0.057
$\partial\gamma/\partial\varepsilon_{(001)}$	+0.558	−0.240	−0.261	+0.058
$\partial\gamma/\partial\varepsilon_{(\bar{1}10)}$	+0.615	−0.240	−0.308	+0.067
$g_{(001)}$	+0.228	−0.055	−0.058	+0.115
$g_{(\bar{1}10)}$	+0.285	−0.055	−0.106	+0.124
		Jellium $r_s = 2.06$		
γ	−0.303	+0.183	+0.072	−0.048
$\partial\gamma/\partial\varepsilon$	+0.489	−0.215	−0.118	+0.156
g	+0.186	−0.032	−0.046	+0.108

faces. It is informative to compare the calculated surface stresses and energies for aluminum with those of jellium. To determine these quantities for jellium it is necessary to define the energy required to cut and deform the positive background charge. Here I make the choice that the positive background has rigidity but no mechanical strength so that the required energies are purely electrostatic. This leads to the normal definition of the surface energy as used, for instance, in Ref. 12. The surface stress is then

$$g = \gamma + \tfrac{1}{3} r_s \, \partial\gamma/\partial r_s, \qquad (4)$$

where r_s is the radius of the sphere occupied by one electron. Lang and Kohn[12] have calculated the surface energy of jellium at a number of values of r_s. By fitting their results to a Chebyshev polynomial and differentiating the resulting series[13] I have calculated g from Eq. (4). The values of g, γ, and $\partial\gamma/\partial\varepsilon$ broken down into their component parts are given in Table I. With reference to Table I it is clear that the kinetic and exchange-correlation contributions to the surface energy and stress are reasonably described by those of jellium. The most significant differences between the results for the aluminum surfaces and those for jellium are between the electrostatic terms. In particular, the positive electrostatic contribution to the surface energy of jellium is very small and as a result the surface energy at this density is negative. The electrostatic contribution to the surface stress is also much smaller than in the calculations for aluminum itself.

Because of the qualitative agreement between the results for aluminum and jellium it seems likely that the

surface energetics of aluminum can be reasonably well described in terms of a simple model of the charge density at the surface. In the following section I give arguments which lead to a tensile surface stress. These depend only on the electronic wave functions being smoothed at the surface.

The kinetic contribution to the surface energy is negative because the electrons spill out in the direction perpendicular to the surface and smooth off their wave functions parallel to the surface. The resulting lower electron density at the surface reduces the magnitude of the exchange-correlation term and hence gives a positive contribution to the surface energy. The separation of positive and negative charge caused by the spillout leads to a positive electrostatic term in γ. The exchange-correlation and electrostatic terms dominate to give a positive surface energy.

The balance of terms comprising the surface stress is quite different. In the bulk the kinetic energy of the electrons contributes a negative diagonal stress favoring expansion. The reduced kinetic energy at the surface leads to a reduction in the magnitude of this kinetic term and hence a positive or tensile contribution to the surface stress which favors contraction in the plane of the surface. The electrostatic and exchange-correlation terms oppose the kinetic term and give negative contributions to the surface stress. In the bulk the exchange-correlation term gives a positive diagonal stress favoring smaller volumes. Because of the lower charge density at the surface the magnitude of this term is reduced and a negative or compressive surface stress results. A negative electrostatic contribution to the surface stress is ob-

tained if the charge separation resulting from the electronic spillout is modeled by a charged parallel-plate capacitor giving an electric field between the plates in the direction perpendicular to the surface. The electric field $E(r)$ produces a Maxwell stress[14] $\sigma_{\alpha\beta}$ given by

$$\sigma_{\alpha\beta}V = \frac{1}{4\pi}\int [E(\mathbf{r})_\alpha E(\mathbf{r})_\beta - \tfrac{1}{2}E(\mathbf{r})^2\delta_{\alpha\beta}]d^3r, \qquad (5)$$

which is negative in the plane of the capacitor plates. In jellium the components of $\mathbf{E}$ in the plane of the surface are strictly zero and hence the electrostatic surface stress is always negative. At a real solid surface the situation is qualitatively different; the components of $\mathbf{E}$ in the plane of the surface are nonzero and contribute to the Maxwell stress.

In conclusion, I note that while the exchange-correlation and electrostatic energies determine the positive sign of the surface energy, it is the kinetic term that dominates $g_{\alpha\beta}$ to give a positive surface stress. The gross features of the surface energy and stress are similar to those of a jellium surface but a more detailed comparison reveals significant differences. If the surface stress arises principally from the charge spillout at the surface then it will be largely confined to the outermost layer of atoms. If this is the case then the stress averaged over the thickness of the top layer of an aluminum surface will be of the order of 90 kbar. To estimate the reduction in lattice constant in the outermost atomic layer necessary were this surface stress to be relieved we might treat the surface layer as a sheet, of modulus equal to the bulk modulus of aluminum. This would give a reduction in lattice constant of roughly 4%. But as the Al (110) and (111) surfaces are not generally thought to reconstruct they must be stable with this magnitude of surface stress present. Larger surface stresses on the surfaces of materials other than nearly-free-electron-like metals may cause reconstructions or defect formation. It would be of great interest to calculate the surface stress tensor on surfaces such as those of gold to test this conjecture.

I would like to thank M. Godfrey, Professor V. Heine, Dr. C. Herring, and Dr. R. M. Martin for enlightening discussions and Dr. O. H. Nielsen for development of the

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