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Calculations of the surface stress tensor and surface energy of the (111) surfaces of iridium, platinum and gold

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Abstract. A theoretical study of the (111) surfaces of the face-centred cubic transition and noble metals iridium, platinum and gold is reported. The surface stress tensor and surface energy of the unreconstructed (111) surfaces of each of these materials has been calculated using the pseudopotential total energy method. In each case the surface stress is tensile, with the stress for gold being the smallest. The implications of these results for surface stability are discussed.

1. Introduction

The bonding between atoms at the surface of a solid can be significantly different from that between atoms in the bulk. Recent work has indicated that a general feature of these differences is that the preferred bond-length within the plane of a metal surface is shorter than the bond-length in the bulk. This is a direct consequence of the lower coordination number of atoms at the surface. It is now becoming appreciated that this is quite a large effect; the natural bond-length within the surface plane can be up to about 10% shorter than in the bulk.

The tendency of a metal to have shorter natural bond-lengths within the surface plane has been demonstrated by a number of experiments and calculations. Experimental measurements of the lattice constants of small metal particles (Solliard and Flueli 1985, Salomons *et al* 1988) show that in general the average inter-atomic spacing is smaller than in large particles. This indicates that the surface bonds, which give a significant contribution to the equilibrium size of small particles, energetically prefer a shorter bond-length than those in the bulk. Calculations of the equilibrium lattice constant within the surface plane of thin metal slabs (Batra *et al* 1986, Dodson 1988) have shown a clear tendency for the surface region to prefer a smaller lattice constant than the bulk. In addition calculations of the surface stress tensor have shown that, in equilibrium, the surfaces of aluminium are under tensile stress (Needs 1987, Needs and Godfrey 1987, 1989), indicating a tendency for the surface to contract within the surface plane. In this work the origin of the surface stress was studied in detail and it was concluded that a tensile surface stress is to be expected at the surface of all nearly-free-electron metals.

Herring (1951) first suggested that the presence of a large surface stress might lead to surface instabilities. He suggested that surface stresses might be relieved by the

formation of defects at the surface, and that the lowest-energy structure might consist of a periodic array of such defects. Nowadays we would call this a surface reconstruction and recently there has been renewed interest in the idea that the presence of a surface stress might be a driving force for surface reconstructions.

The surfaces of gold, platinum and to a lesser extent those of iridium show a tendency to reconstruct so that the surface atoms are closely packed together (Van Hove *et al* (1981), and references therein). This behaviour could be due to the relief of large tensile surface stresses in the unreconstructed surfaces. The three elements iridium, platinum and gold lie in adjacent positions in the 5d row of the periodic table and each has the face-centred cubic structure. The (001) and (110) surfaces of each of these crystals reconstructs, but the most striking reconstruction of all is that of the (111) surface of gold. This is the only known example of a close-packed metallic surface that reconstructs. The surface forms a $23 \times \sqrt{3}$ reconstruction which appears to involve the insertion of an extra row of atoms into the surface every 23 rows (Harten *et al* 1985). This reconstruction clearly decreases the average coordination number of the atoms because to form it atoms must be taken from 12-fold-coordinated bulk sites and placed in 9-fold-coordinated surface sites. It seems likely that such a reconstruction could only be lower in energy than the unreconstructed surface if the shorter bond-lengths that are formed in the plane of the surface are energetically favourable. If this is the case then the unreconstructed gold (111) surface should exhibit a considerable tensile surface stress. It could then be argued that the driving force for the $23 \times \sqrt{3}$ reconstruction is the relief of this tensile surface stress.

However appealing such arguments may be they lack quantitative analysis. To remedy this situation we require a knowledge of the magnitude of the surface stresses and a theory of surface stability that involves these stresses. If the surface of a crystal, such as the (111) surface of gold, reconstructs, it is not possible to measure the stress at the unreconstructed surface. It can, however, be calculated and in this paper we present calculations of the surface stress tensor and surface energy of unreconstructed (111) surfaces of iridium, platinum and gold. Our calculations show that the surface stress of gold is actually smaller than that of either iridium or platinum. The essential ingredients of a theory of surface stability involving surface stress are also discussed and we conclude that although the surface stress is one factor that influences surface stability, there are other effects that must be considered as well.

2. The surface stress tensor

When a solid surface is formed the equilibrium structure is in general one in which a stress exists within the surface region. The equilibrium condition is that the surface free energy be minimised, not that the surface stress be zero. A two-dimensional surface stress tensor $g_{\alpha\beta}$ can be defined by analogy with the usual three-dimensional stress tensor of elasticity theory. The surface stress is the strain derivative per unit area of the energy required to form the surface. This is given by

$$g_{\alpha\beta} = (1/A)d(A\gamma)/d\varepsilon_{\alpha\beta} = \gamma\delta_{\alpha\beta} + d\gamma/d\varepsilon_{\alpha\beta} \quad (1)$$

where $g_{\alpha\beta}$ is the surface stress tensor, $\varepsilon_{\alpha\beta}$ is the strain tensor, $\delta_{\alpha\beta}$ is the Kronecker delta function, γ is the surface free energy per unit area and A is the total surface area. Equation (1) was first derived by Shuttleworth (1950) (in scalar form) and also by Herring (1951). A positive value for the surface stress, known as a tensile stress, favours

contraction within the surface plane whereas a negative or compressive surface stress favours expansion.

3. The pseudopotential total energy method

The pseudopotential total energy method is a highly successful technique for performing quantum mechanical calculations of total energies. This method has been applied to a wide range of systems, including both surface and bulk structures, giving generally excellent agreement with experimental results where available. A review of this method and applications of it are given in a recent paper by Ihm (1988).

For our calculations we used a local density functional scheme and the Ceperley–Alder form (Ceperley and Alder 1980, Perdew and Zunger 1981) of the local density approximation to the exchange–correlation energy. The calculations were performed using the super-cell technique where a unit cell, containing a slab of metal and a vacuum region, is repeated periodically throughout space. The valence wavefunctions and potentials were expanded in a plane-wave basis set and the resulting local density equations were solved self-consistently in reciprocal space using an iterative diagonalisation technique (Nex 1987, Hodgson and Nex 1988). Integrations over the Brillouin zone were performed by sampling on a regular mesh of points in reciprocal space using the scheme due to Monkhorst and Pack (1976). For each of the surface calculations a total of 37 points in the irreducible wedge of the Brillouin zone were sampled. The total energy, the forces on the atoms and the stress tensor were evaluated using the reciprocal-space expressions (Ihm 1988, Nielsen and Martin 1985).

It is unusual to apply plane-wave pseudopotential techniques to transition and noble metals such as iridium, platinum and gold. Two problems arise in such calculations. The first problem is that the energy-independent pseudopotentials used in our calculations work less well in these cases because of so-called ‘resonance effects’ which result in a strong energy dependence of the scattering properties of the atomic cores. The norm-conserving pseudopotentials (Hamann *et al* 1979, Kerker 1980, Bachelet *et al* 1982) used in this work were evaluated at the atomic energies and do not correctly reproduce the scattering properties at energies that are greatly different from these. The second problem is that the strength of a transition-metal *d* pseudopotential means that a large plane-wave basis set is required for the Fourier expansions of the potential and wavefunctions. In fact this problem is not particularly serious for the 5*d* elements because of the repulsive pseudopotential due to the presence of 3*d* and 4*d* core electrons. The iridium, platinum and gold pseudopotentials used in this work were generated using the norm-conserving scheme due to Kerker (1980). Because of the presence of 3*d* and 4*d* core electrons these pseudopotentials are actually weaker than, for instance, the norm-conserving pseudopotentials that have been used for carbon in a number of pseudopotential total energy calculations (e.g. Biswas *et al* 1987). Nevertheless we found that a basis set including all plane waves with kinetic energy less than 40 Ryd was required to give a good description of the bulk properties of these elements. This size of basis set energy was retained for the surface calculations, giving a basis set containing about 3000 plane waves in the case of gold, and a slightly smaller number for platinum and iridium which have smaller lattice constants. A further complication arises because of the importance of relativistic effects in heavy atoms such as the 5*d* elements. The calculations reported here included scalar relativistic effects in the same manner as the pseudopotentials of Bachelet *et al* (1982) but did not include the spin–orbit splitting.

Table 1. The calculated and experimental values of the lattice constants of iridium, platinum and gold (in units of Å). The experimental values were obtained from Wyckoff (1965).

	a_0 (calculated) (Å)	a_0 (experimental) (Å)
Ir	3.760	3.8394
Pt	3.867	3.9231
Au	4.025	4.07825

Table 2. The calculated and experimental values of the bulk moduli of iridium, platinum and gold (in units of Mbar). The experimental values were obtained from the compilation given by Kittel (1976).

	B (calculated) (Mbar)	B (experimental) (Mbar)
Ir	4.22	3.55
Pt	3.09	2.783
Au	1.93	1.732

Table 3. The calculated and experimental values of the $T(X)$ and $L(X)$ phonon frequencies of iridium, platinum and gold (in units of THz). The experimental values for gold were obtained from Lynn *et al* (1973) and those for platinum from Dutton *et al* (1972). Experimental data for iridium could not be located in the literature.

	$T(X)_{\text{calc}}$ (THz)	$T(X)_{\text{exp}}$ (THz)	$L(X)_{\text{calc}}$ (THz)	$L(X)_{\text{exp}}$ (THz)
Ir	4.20	—	4.83	—
Pt	3.60	3.84	5.30	5.80
Au	2.33	2.75	4.06	4.61

Because of the approximations discussed above it is necessary, before proceeding to the surface study, to demonstrate that these pseudopotential calculations provide a good description of the properties of the corresponding bulk materials. We have performed a number of calculations of various properties of bulk face-centred cubic iridium, platinum and gold. Each of these calculations was performed with a basis set including all planes waves with kinetic energy less than 40 Ryd; exactly the same basis set energy as was used for the surface calculations. Table 1 gives the values of the calculated and experimental lattice constants for each of the elements, table 2 gives the calculated and experimental bulk moduli and table 3 gives the values of the calculated and experimental $T(X)$ and $L(X)$ phonon frequencies. From these tables one can see that in each case there is good agreement between the calculated and experimental values. The calculated band structures for each of the elements are shown in figures 1, 2 and 3. These may be compared with band structures for these elements that can be found elsewhere in the literature, for example those of Papaconstantopoulos (1986). Such a comparison confirms that the band structures presented in this paper are in excellent agreement with previously published ones.

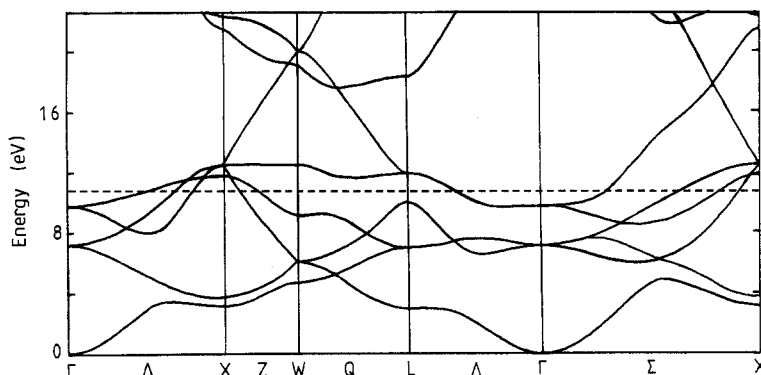


Figure 1. The calculated band structure of iridium.

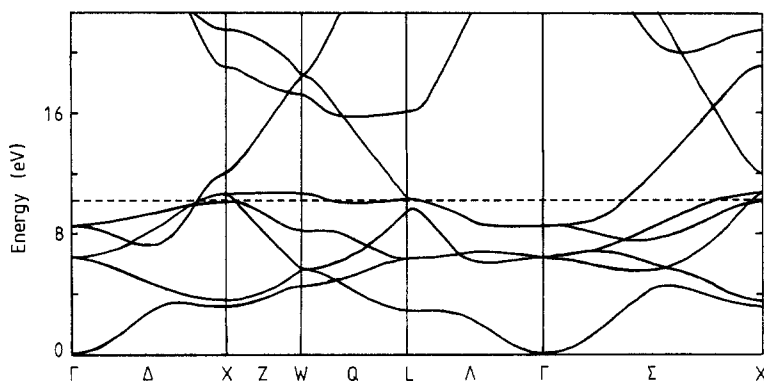


Figure 2. The calculated band structure of platinum.

4. Calculations of the surface stress tensor and surface energy

The pseudopotential total energy calculations were performed within a super-cell geometry where a unit cell is repeated periodically throughout space. For each calculation the experimental lattice constants of the bulk crystals, which are listed in table 1, were used. For each of the surface calculations the unit cell consisted of a slab of four layers of close-packed atoms and a vacuum region of thickness equivalent to two atomic layers. This is a very restricted geometry but because of the computational expense it was not possible to test whether it was sufficient by increasing the thickness of the metal or vacuum regions. However, calculations have been performed for aluminium surfaces with from three to nine layers of close-packed aluminium atoms separated by from two to six layers of vacuum (Needs and Godfrey 1989). In these calculations four layers of aluminium atoms and two layers of vacuum was perfectly adequate for determining the surface stress and the surface energy. There is no obvious reason why this should not also be true for iridium, platinum and gold.

The total energies and stresses were calculated for the unrelaxed surface and for the perfect bulk structures. In order to make an accurate comparison between bulk and surface properties the bulk quantities were calculated in the same super-cells as the surface ones. The surface energy per unit area, γ , is given by

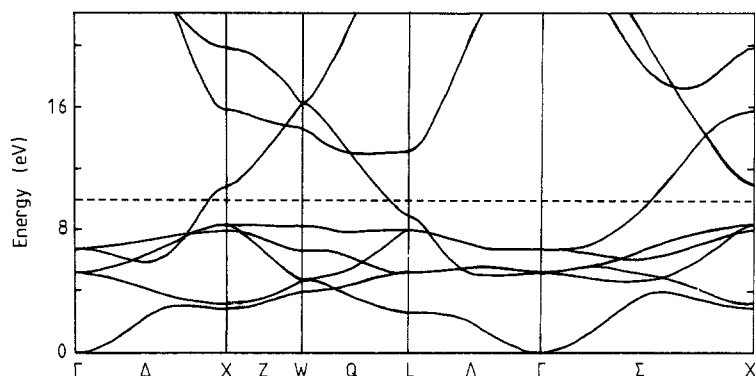


Figure 3. The calculated band structure of gold.

Table 4. The surface stress g , the surface energy γ and its strain derivative $d\gamma/d\varepsilon$ for the (111) surfaces of iridium, platinum and gold. (All entries are in units of eV \AA^{-2} .)

	g (eV \AA^{-2})	γ (eV \AA^{-2})	$d\gamma/d\varepsilon$ (eV \AA^{-2})
Ir	0.331	0.204	0.128
Pt	0.350	0.137	0.213
Au	0.173	0.078	0.096

$$\gamma = (E^s - E^b)/2A \quad (2)$$

where A is the area of the surface, E^s is the total energy per unit cell for the surface calculation and E^b is the bulk energy for the same number of atoms as the surface calculation. The surface stress tensor $g_{\alpha\beta}$ follows directly from equations (1) and (2)

$$g_{\alpha\beta} = (\sigma_{\alpha\beta}^s - \sigma_{\alpha\beta}^b)/2A \quad (3)$$

where $\sigma_{\alpha\beta}^s = dE^s/d\varepsilon_{\alpha\beta}$ and $\sigma_{\alpha\beta}^b = dE^b/d\varepsilon_{\alpha\beta}$. The energies and stresses appearing in equations (2) and (3) were evaluated for each of the surface and bulk structures using the total energy pseudopotential method.

The results of the surface stress and surface energy calculations are given in table 4. The values of the surface energy γ may be compared with experiment. For gold Tyson and Miller (1977) give $\gamma = 0.096 \text{ eV \AA}^{-2}$ and for platinum Miedema (1978) gives $\gamma = 0.159 \text{ eV \AA}^{-2}$ and so the agreement with the calculated values is quite good. Note also that the strain derivative contribution $d\gamma/d\varepsilon$ to the surface stress is quite large in the case of the 5d metals.

Before discussing these results in detail we should mention the effect of relaxation of the atomic positions in the direction perpendicular to the surface plane. All the results given in table 4 are for ideal unrelaxed surfaces. We have calculated the forces of the atoms in these ideal surface structures and find that in each case the force on the surface layer is directed towards the centre of the metal slab. These forces are, in unit of millidynes, 0.45 for iridium, 0.11 for platinum and 0.04 for gold. Calculations for the aluminium (110) surface (Ho and Bohnen 1985, Needs 1987), the aluminium (111) surface (Needs 1987) and the tungsten (100) surface (Fu *et al* 1984) have shown that the reduction in the surface energy due to relaxations of the atomic layers in the direction

perpendicular to the surface is a very small fraction of the total surface energy. We therefore suppose that this is also the case for the iridium, platinum and gold (111) surfaces. This is supported by the fact that the calculations reported here give values for the surface energies that are in good agreement with experiment. We have also tested this assumption by relaxing the platinum (111) surface and find a reduction in the surface energy of less than 5% and a reduction in the surface stress of less than 15%. Note that although calculations for thin metal slabs can give good values for gross surface properties such as the surface energy and surface stress the size of the atomic relaxations perpendicular to the surface is not given reliably.

5. Discussion

Our calculations of the bulk properties of iridium, platinum and gold are in good agreement with experiment. These results show that the total energy pseudopotential method, using norm-conserving pseudopotentials, can be used to perform calculations of the properties of 5d transition and noble metals. Calculations on aluminium have shown that the geometry used in the work reported in this paper, consisting of slabs of four layers of atoms separated by two layers of vacuum, is perfectly adequate for calculating gross surface properties such as the surface stress and surface energy. These results give considerable confidence in the application of the total energy pseudopotential method to the calculation of surface properties of 5d elements.

The largest value for the calculated surface stress is that for platinum, which is a little greater than the value obtained for iridium. The surface stress for gold was found to be significantly smaller than those for platinum and iridium. At first sight this appears to invalidate the suggestion that the observed reconstruction of the gold (111) surface is driven by the relief of a large tensile surface stress in the unreconstructed surface. However, it will now be argued that the magnitudes of the surface stresses are not the correct quantities to compare in order to study the stability of the surface against reconstructions involving a change in the density of surface atoms.

In fact the stability of a real surface against such reconstructions is controlled by a number of factors. Firstly, if the natural bond-length within the surface layer is different from that in the bulk then the surface bonds will be strained and this leads to a tendency for the surface density of atoms to be different from the bulk density. However, if a particular reconstruction involves a change in the density of atoms at the surface then extra atoms must be transferred into or out of the surface layer. Steps on the surface can act as sources or sinks of atoms but removing atoms from step sites and incorporating them within the surface layer or vice versa will, in general, involve a change in energy. We believe that it is vital that this energy change be included in a theory of such surface reconstructions. If the resulting structure was determined solely by the competition or collaboration between the tendency to have a different bond-length within the surface and the energy change involved in adding or removing atoms from the surface then the unreconstructed surface would not be stable; it would always undergo a reconstruction in which the density of surface atoms was either increased or decreased. This problem is resolved by including the interaction of the surface atoms with the substrate. If the density of surface atoms is altered then the surface-substrate bonding will be disrupted and this will, in general, cost energy. This effect will tend to stabilise the unreconstructed surface.

In summary we believe that there are three effects that must be included in a theory of surface reconstructions involving a change in the density of surface atoms:

(i) The theory must include an inter-atomic interaction which leads to natural bond-lengths within the surface region that are different from the bulk bond-length.

(ii) If the reconstruction changes the density of atoms within the surface layer then atoms must be added to or subtracted from the surface layer. The energy changes associated with these processes must be included in the theory.

(iii) The theory must include an interaction between the surface and substrate atoms that accounts for the possible disruption of the surface–substrate bonding caused by surface reconstruction.

We believe that it is vital that *all* of these effects be included in any proper theory of such surface reconstructions. Effect (ii) in this list is extremely important and does not seem to have been included in any theories published to date. A simple theory that includes all of these effects, based on the Frenkel–Kontorova model (Frenkel and Kontorova 1938), will be published elsewhere (Mansfield and Needs 1989). One inter-atomic interaction scheme that includes all of the effects discussed here is the highly successful empirical ‘glue’ model. ‘Glue’ model calculations on the (001), (110) and (111) surfaces of gold (Ercolessi *et al* 1987) have yielded good agreement with experimental observations of the surface structures and clearly reproduce the tendency to close packing at the surface. It would be interesting to calculate the surface stress from the ‘glue’ model and compare it with the results presented here.

It is quite clear that the surface stress does not give information about all of the three effects listed above. The surface stress tells us about the change in the surface energy when the surface and substrate are strained *together* in a *uniform* manner. Therefore the surface stress contains no information whatsoever about effect (iii) in our list and a knowledge of the surface stress alone cannot suffice to determine the stability of the surface. Note that our discussion concerns a particular type of instability where the density of surface atoms is increased or decreased; of course many other types of reconstruction can occur and the concept of surface stress may or may not be relevant to them. For instance it is known that the surface of an elastic continuum is unstable to crumpling if the surface stress or its strain derivative is negative (Andreussi and Gurtin 1977, Needs and Godfrey 1987).

Of course the work presented in this paper has not explained why the (111) surface of gold reconstructs while those of iridium and platinum do not. Presumably the energy change associated with adding atoms to or subtracting from the surface layer and the surface–substrate interaction must be considered before this point is understood. It is possible that a significant difference between the three metals studied here is that the energy cost due to disruption of the surface–substrate bonding for gold may be much smaller than for platinum or iridium. This could arise because the 5d shell of gold is full, so directional bonding forces are less important than in the transition metals iridium and platinum.

6. Summary

We have shown that the total energy pseudopotential method can be used to perform accurate calculations of the properties of 5d transition and noble metals. We have calculated the surface stress and surface energy of the unreconstructed (111) surfaces of

iridium, platinum and gold. The calculated surface stress for gold was smaller than that for either iridium or platinum. We have argued that the surface stress alone does not contain sufficient information to determine whether a surface is stable to a change in the density of surface atoms and have discussed the necessary ingredients for a proper theory of such reconstructions.

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