COMPETITION BETWEEN PAIRWISE AND MULTI-ATOM FORCES AT NOBLE METAL SURFACES

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In the bulk noble metals there is considerable tension or opposition between two sets of forces: a pairwise repulsion due to the full d shells, and a multi-atom electron gas attraction from the sp electrons. Ideal, Gibbs surfaces tend to be unstable because the two forces react differently to the surface cut, upsetting their mutual equilibrium. In particular the flow of the mobile sp electrons can lead to expansive or contractive stresses, strongly dependent upon the local geometry and also sensitive to electron donors/acceptors. These stresses may in turn result in small surface relaxations or more major changes of the surface structure. This type of analysis is applied in detail to gold surfaces, reconciling apparently inconsistent experimental data. Wider implications are also mentioned.

1. Introduction

It is well known that clean surfaces often have unusual structures. Surface relaxations or reconstructions have been studied for many years predominantly by low energy electron diffraction (LEED). Many cases are known for relatively large *contractions* near the middle of the transition series, for example 10% for W(100) [1], 11% for Ta(001) [2] and 15.4% for Fe(111) [3] whilst recent work has shown *expansions* on Pt(111) [4–7], Au(111) [8,9] and Au(110) [10–12]: but note also the contraction observed by Moritz and Wolf [13]. Considerable work has been carried out on the theoretical side to understand these phenomena based either upon cluster-type models (e.g. ref. [14]) or tight-binding approaches (e.g. ref. [15]), restricted as a rule to the particular

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element rather than investigating trends across the periodic table. One of the models is that of Finnis and Heine [16], which relates surface relaxations to modifications of the shape of the Wigner–Seitz cell at a surface, and as such is essentially an sp electron model. Refined versions of this concept have recently been successfully employed by Landman et al. [17–19] to explain multilayer relaxations [20,21].

In the bulk noble metals Cu, Ag and Au, it is well established and documented that there is a tension or opposition between two types of force. The first is a pairwise repulsion between the atoms due to the full d shells, the second is a multi-atom electron-gas attraction due to the sp electrons and the sp–d hybridization (see section 2). We believe that it is this competition which causes strange things to happen at noble metal surfaces, particularly gold. Simple truncation of the bulk leaves an unstable system which will tend to rearrange, in some cases grossly. Unfortunately no proper calculations of these forces and stresses at surfaces exist at present. However, our detailed understanding of these electrons in the bulk allows us to infer the sense of the electron redistribution at a surface. From this we can use the Hellmann–Feynman theorem (e.g. refs. [22,23]) to infer what the stresses and forces will be, and hence explain the observed surface reconstructions and relaxations.

In the bulk noble metals (discussed in detail in section 2) the main ideas are easy enough. The d shells are full, and although they do contribute to the cohesive energy, most of the binding comes from the partially filled sp electrons. Now it turns out that the sp electrons would like to have a substantially smaller atomic volume, i.e. they produce a strong attraction which is balanced by the d shells which are under compression (see fig. 1). The experimental evidence for this picture comes from a study by Nevitt [24,25] of alloy structures. These indicate that for all three noble metals (Cu, Ag and Au) the noble metal component has a substantially smaller atomic volume in those alloys where sufficient space is provided by the other element to keep the noble metal d shells out of contact. For the case of gold, the effective volume per atom in the alloys is about 20% smaller, a substantial reduction.

The theoretical reason for this is that the pseudopotential of the noble metals, particularly that for the s electrons, is unusually attractive compared to alkali atoms with the same core radius R_c [26–28] (e.g. K and Au have the same R_c but the ionization energies for the free atoms are grossly different). The pseudopotential is normally repulsive inside the core of an atom (the famous cancellation theorem [29]), but in the noble metals, because of the difference in radius between (for Au) the 5s and 5d orbitals, there remains an uncancelled anomalously attractive region on the outer edge or "mantle" of the core (see fig. 2). Electrons would like to flow into this mantle – hence the contractive effect of the sp electrons.

What happens at a surface? The d shells remain full and essentially unchanged, giving an expansive pressure. The sp electrons are very mobile, and
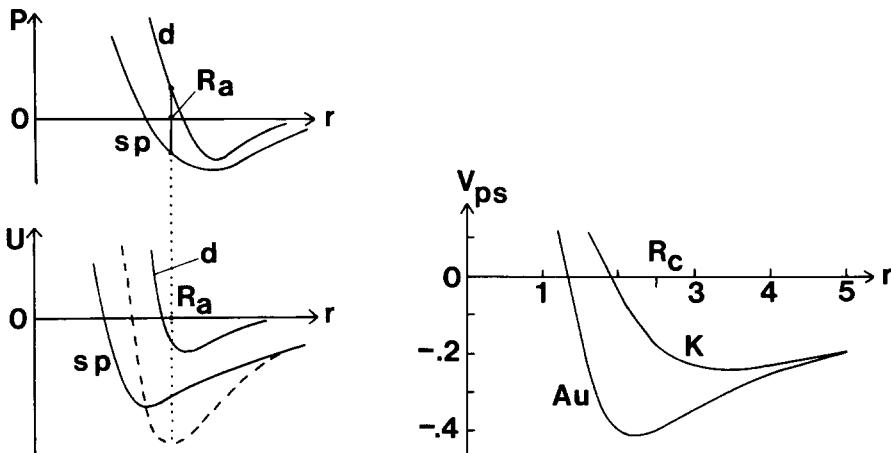
Fig. 1. The contributions of the sp electrons and d electrons to the pressure P and energy U of gold (schematic). At the equilibrium atomic radius R_a, the sp and d pressures are equal and opposite, corresponding to a minimum in the total energy. Note that at R_a the d pressure is positive (expansive) while the sp pressure is negative (attractive).

Fig. 2. Pseudopotentials $V_{ps}(r)$ of K and Au (in atomic units) (after ref. [28]). Note the strongly attractive region of V_{ps} in Au, but not in K, just inside the core radius R_c. $V_{ps}(r)$ oscillates about zero for $r < 1.5$.

can relax normal to the surface and/or (if the surface is corrugated) tangentially [30,31]. As a rule, they will lower their energy by flowing into the attractive mantle region described above. The forces that they give rise to (through the Hellmann–Feynman theorem) depend sensitively on exactly where around the mantle shell they go to. For instance, if they go into the regions between the atoms in the topmost layer, this increases the in-plane sp bonding and gives a tangential compressive stress. The question of where the electrons flow to in Au and the consequences for the surface are discussed in more detail in section 3.

In this paper we will employ this form of sp against d tension analysis to gold surfaces. Perhaps the key result is that we can reconcile apparently conflicting experimental reports of *both* expansions and contractions without any difficulty: the final result is strongly dependent upon the local geometry, and contractions for instance are not an intrinsic property of an element. The model also correlates exceedingly well with some unusual, non-crystallographic forms common to small noble metal particles. Furthermore, extensions of the model in section 4 (admittedly slightly speculative) are quite encouraging in explaining some recent experimental results such as the effect of simple electron donors/acceptors and some recent experimental data on grain

boundaries. We hope that this paper, rather than providing the final word, can help to give some physical insight into surface phenomena as well as suggesting further areas for experimental and theoretical research.

2. Competition of forces in the bulk

In the bulk noble metals (and indeed the transition metals) we believe there is sufficient experimental and computational evidence to give a clear picture of the forces due to the sp electrons and the d electrons, and the relation between them. As mentioned in section 1, it is not yet possible to do fundamental calculations of metallic forces at reconstructed surfaces of the noble metals. However, we will develop in this section a thorough understanding of the forces in the bulk, which then allows us later to infer the likely behavior at the surface.

We start with experiment. Nevitt [24,25] has shown from alloy data that Cu, Ag and Au would like to have substantially smaller atomic volumes if the d shells are kept out of contact. To be precise, he analysed the molar volumes of NM alloys with the CsCl structure where N is a noble metal and M another metal with a relative small sized core, for example the lanthanides. He finds that the molecular volumes V can be fitted quite well by the relationship

$$V = V_N^* + V_M,\tag{2.1}$$

where V_M is the atomic volume in the pure metal M and V_N^* is the *apparent* volume of the noble metal atom in the alloy, approximately constant for many alloys and smaller than the atomic volume V_N in the pure noble metal. The interpretation is that the full d shells in the pure noble metal present a hard core repulsion which prevents the sp electron gas from shrinking to a smaller volume V_N^* as they can do in the alloys where the repulsive cores are kept out of contact. This interpretation is confirmed by the exceptions, for example alloys with Pd which also has a large nearly-full d shell. The data are shown in fig. 3. The experimental points fall well below the values based upon simple addition of the atomic volumes, which are shown for comparison in the figure. The slope of the experimental data is also slightly larger, implying that the effective volume of the second element is slightly larger and that of the noble metal even smaller. This we would expect, as in a transition metal we will obtain the opposite effect to that for a noble metal, i.e. an increase in the effective volume when the atoms are separated. Using the simple expression in eq. (2.1), we find that V_N^* is about 1.8, 1.2 and 3 Å^3 less than V_N for Cu, Ag and Au (compared with $V_N = 11.8$, 17.0, and 17.0 Å^3 respectively). For Au this amounts to nearly a 20% reduction in volume, a substantial effect. Nevitt [24] also analysed the MN$_2$ alloys with MoSi$_2$ structure where each noble metal atom has only a few noble metal nearest neighbors: he found a similar effect
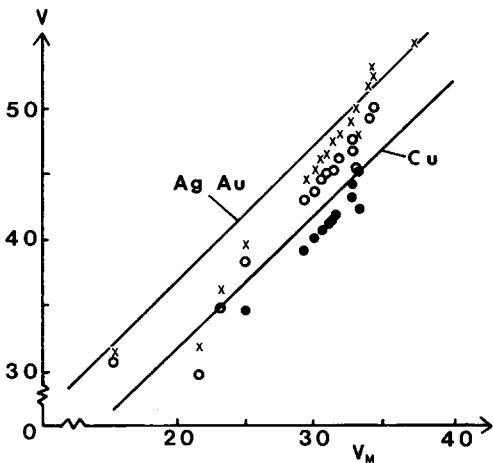
Fig. 3. Molecular volumes V for alloys of noble metals (N) with other metals (M) versus V_M. Dots, copper; crosses, silver; open circles, gold. The straight lines correspond to $V = V_N + V_M$. (After refs. [24,25].)

though not quite as pronounced, presumably because the noble metal atoms are not kept wholly out of contact. All this contrasts with the situation in many alloys where Vegard's rule is fairly well satisfied. The alloys of Au with the alkali metals also show a large volume contraction [32,33]. This clearly indicates the existence of an effect solely due to Au, since the alkali metals have no d electrons. Here the case of AuLi is particularly interesting because Au and Li have roughly similar atomic volumes in the pure metals so that the effect cannot be due to a difference in Fermi pressure from the two constituents.

The origin of the effect is demonstrated by the computed charge density in AuCs [32,33]. Fig. 4 shows the extra charge density $\Delta\rho(r)$ around the Au atom [33] and comparison with ref. [32] shows that $\Delta\rho$ comes almost entirely from the $l = 0$ components of the wavefunctions. There is a positive additional electron density around the Au atom, attracted from the Cs atom as expected from the electronegativity difference. What is particularly significant is the
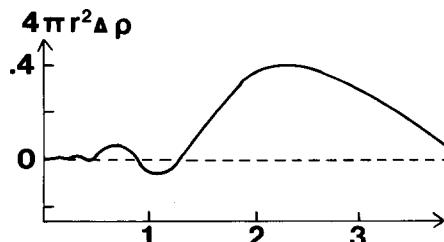

Fig. 4. Additional charge density $\Delta\rho(r)$ around a gold atom in AuCs (after ref. [33]).

heaping up of this charge in the radius range 1.9 to 2.5 au (atomic units: Bohr radii) with a maximum around 2.3 au. This is considerable smaller than the atomic radius of 3.0 au and correlates with an anomalously attractive $l = 0$ pseudopotential in this range. Fig. 2 compares the $l = 0$ pseudopotentials of Au^+ and K^+ which have equal charge and equal core radius R_c so that by a naive application of the cancellation theorem one might expect closely comparable pseudopotentials. In fact the figure shows that the pseudopotential of Au has an *anomalously attractive region around the outer mantle of the core* which is due to the softness of the d shell as discussed in detail by Austin and Heine [27] and which is not found in normal sp atoms such as K. In this context it is significant that the $l = 1$ pseudopotential of Au is practically "normal" like that of K for the reasons discussed in ref. [27]: this corresponds to the fact that the $\Delta\rho(r)$ arises mostly from the $l = 0$ components [32,33]. Note also that $\Delta\rho(r)$ refers to the charge density in AuCs not relative to pure Au but to a fictitious Au where the Au has been expanded and the Cs compressed to half the molecular volume of AuCs to equalise the two Fermi pressures. Incidentally the pseudopotentials of fig. 2 were calculated from eq. (VI.10) of ref. [26] so that they correspond very nearly to the smoothest pseudo wavefunctions in the manner of ref. [29]. In that sense their forms arise "naturally", reflecting the physics of the situation, not imposed extraneously. These details amount to a convincing case that the charge flow and volume contraction in gold alloys is indeed related to the anomalously attractive $l = 0$ pseudopotential at the edge of the core. The pseudopotential arguments apply equally to all the noble metals [27]; taken together with the results of Nevitt above, this implies that our picture for gold is also applicable to copper and silver, the effect being strongest in gold and least in silver.

We conclude that in pure bulk gold as well as in copper and silver, the sp electrons are under a negative pressure due to their wanting to retreat into this anomalously attractive mantle region from the outer parts of the atomic cell in order to lower their energy. As a result, the full d shells are under compression, exerting an expansive pressure to balance the contractive stress due to the sp electrons, the balance of forces being represented by fig. 1. Incidentally the d shells still contribute significantly to the total cohesive energy [30,34] but they are compressed to a point inside their equilibrium separation (fig. 1).

We can now characterize the two types of force with a view to the discussion in section 3 about their behavior at a free surface. The closed-shell repulsion of the d shells is clearly a simple *pairwise* interatomic force. The description of the sp bonding is a more complicated matter. They form a gas of nearly free electrons in the usual sense of pseudopotential theory. Such an electron gas cannot have abrupt density changes and the drawing out of the sp electrons into a roughly uniform electron gas is a multi-atom effect. The lowering of the kinetic energy by forming the atomic states into an electron gas depends to a good approximation only on the volume available to them. The volume

available in the bulk metal is determined by the cage of nearest neighbors which therefore gives to the sp binding somewhat the nature of a many-atom force. But the driving force for the contractive sp electron stress is the anomalously attractive mantle in the atomic pseudopotential which is a one-atom effect. We may therefore describe the sp electrons as a ubiquitous glue: they want to collapse into the attractive pseudopotential, which is strictly a *one-atom* effect independent of the positions of the neighbors, but their distribution in the system is controlled by the distribution of the atoms as a whole and by such effects as the electron gas surface tension.

Finally, we want to refer to the computational results for the sp and d electron pressures which we believe support the above picture. Pettifor [30,31] considered Ag and the 4d transition series. The situation for the transition metals in the middle of the series is quite clear: the d electrons want to have shorter bonds and thus they compress the sp electrons, giving the opposite picture to that in fig. 1. Other authors [35–38] reach the same conclusion, and there is experimental support from reduced bond lengths in molecules where the sp pressure is partially removed, for example by electronegativity effects [39]. In the noble metals the d shell is at least nominally full, all the electron pressures are an order of magnitude smaller than in the transition metals proper (see e.g. ref. [31]), and we have argued that the relationship between sp and d electron pressure has reversed in sign. Because the d bonding pressure is so strong in the transition metals proper, the reversal of sign as we move towards the noble metals only occurs when the d shell is very nearly full. Pettifor [31] puts the crossover at Pd in the 4d series: remembering that the effect is considerably stronger in Au, it is entirely plausible that Pt should be classified with the noble metals.

At this point we need to address a technical point which we have so far glossed over, namely how to classify the sd hybridisation contribution to the pressure equilibrium. The simple view is to say that for electron states k above the d band the effect of hybridisation is equivalent to a pseudopotential

$$\sum_m \frac{\gamma_{km}^* \gamma_{km}}{E_k - E_{dm}},\tag{2.2}$$

where $m = 1$ to 5 enumerates the d bands and γ_{km} is the *intra*-atomic hybridisation matrix element. To lowest order we may approximate $E_{dm}(k)$ by some mean energy E of the d band and to that order (2.2) is purely a one-atom pseudopotential. The same is true when we sum over all states up to the Fermi level E_F: formula (2.2) is not valid inside the d band but by the usual trace property the hybridisation summed from $E = -\infty$ to $+\infty$ has to be zero so that the sum up to E_F equals minus the sum from E_F to infinity where the form (2.2) is valid. Thus we count the hybridisation in with the sp electron pressure as (to lowest order) a one-atom effect and have done so in interpreting Pettifor's [31] results. Its one-atom nature is also true in Pettifor's analysis [31]

of the hybridisation. The same approach has been adopted by Christensen [40] who has carefully decomposed the expression for the total pressure into a number of terms. He has also done calculations for the noble metals and finds contractive "one-atom" pressures from the sp electrons (including hydridisation) for Cu, Ag and Au respectively, balanced by expansive "two-atom" closed d shell repulsions of equal magnitude. It must be recognised that the sp electrons interact with the d electrons both through hybridisation and electrostatics which makes a unique classification impossible as has been noted by several authors (see e.g. refs. [30,36,40]). When A interacts with B, their interaction energy is mutual and cannot be assigned either to A or B. However, we are not interested in a semantic classification for its own sake: we want a physically valid description of the bulk in terms of one-atom, two-atom, etc. effects which allows us to infer the behavior under the more general circumstances holding at a free metal surface. For example Moriarty [37] has shown that the d bands are only nominally full in the noble metals and that from the point of view of the electron density one must have about 0.6 holes per atom in the d band of copper. Such d band holes are of course "virtual" holes, not "real" holes, in the standard distinction between "virtual" and "real" transitions in quantum mechanics. We regard this as a manifestation of the hybridisation (2.2) which mixes d states into the sp states including the unoccupied part of the band above E_F. We therefore see no contradiction with our point of view. For our purposes the point is that to lowest order hybridisation is a one-atom effect, not to be confused with the pairwise bonding or repulsion between d shells on neighboring atoms. Incidentally Moriarty [36,37] has developed a more accurate and sophisticated expression than (2.2) for the hybridisation interaction but the one-atom nature to lowest approximation remains. Other authors, for example in refs. [35,38], have not been interested in one-atom, two-atom, multi-atom effects and have used a different classification, namely according to angular momentum l which includes the hybridisation (2.2) with the d band effects all as $l = 2$. This is correct because the interaction in (2.2) is with the $l = 2$ component of the plane waves which in turn is due to the variation of the degree of sp bonding/antibonding through the band. However, such an angular momentum decomposition is not the appropriate classification for our purposes here.

In conclusion, therefore, the experimental evidence and theoretical analysis combine consistently to give a picture of the electronic forces in noble metals. Moreover this picture is in a form which should allow an analysis of relaxation effects at surfaces, as sketched in section 1.

3. sp and d electron pressures at gold surfaces

We have previously seen the basic nature of the bulk competition between the pairwise (d shell) repulsion and the multi-atom sp electron attraction. The
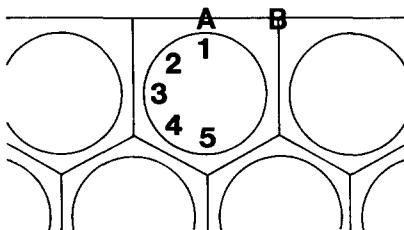
Fig. 5. Illustrative Wigner–Seitz cell for an atom at a surface. The nearly free sp electrons at the surface (locations A and B as marked) are drawn into the anomalously attractive regions 1–5 around the core as marked in the figure. The resulting forces depend upon where around the core the electrons reside among these locations as discussed in the text.

latter acts as a ubiquitous glue, not truly a volume effect but in a sense a one-atom phenomenon as the electron density wants to sit in the attractive mantle region as far as it is allowed, consistent with being an electron gas and the cost in kinetic energy of being heaped up.

We now consider what happens at a gold surface, initially the open (100) and (110) 1 × 1 surfaces. In three dimensions, a set of hard spheres compressed uniformly together in a box will result in a close packed structure, either fcc or hcp. Similarly in two dimensions at a surface the sp electron tension wants to produce the close packed (111) surface with the least amount of surface corrugation. Hence it is not surprising that for gold the (100) surface has a (111) monolayer overgrowth [41], whilst the (110) surface tends to decompose into (111) type microfacets [9,42,43].

We turn therefore to the more basic (111) type surface, considering an ideal Gibbs surface with the electron density simply chopped off. Where will the sp electrons go? Of course the electron density corrugations along the surface will smooth off due to the surface tension of the electron gas, as described by Finnis and Heine [16]. In addition the sp electrons will be pulled into the attractive mantle in order to lower their energy. Electrons will leave the regions A and B as marked in fig. 5, both A and B since the electron gas surface is flat [16]. Electrons leaving from B yield by their absence an expansive tangential pressure thus ← → . We will use a horizontal pair of arrows to indicate the surface pressure or stresses, and a vertical arrow for the normal relaxation, the sense of the changes coming from the Hellmann–Feynman theorem. This theorem states that the forces and stresses on the atom cores are determined by the electrostatic forces on the positively charged cores due to the surrounding valence electrons. Therefore putting electrons between the atoms gives stresses of the form → ← , while putting them on top at the surface gives a normal force ↑. The question of ← → or → ← depends upon the *net* flow, and we need to consider into which of positions 1 to 5 (as marked in fig. 5) the electrons flow. For instance, if the transfer is to 1, then clearly ← ↑ → ; ← →

due to the electrons leaving from B, and ↑ because the electron density is now closer to the nucleus. Similarly if the flow is to position 3, the stresses/forces on the cores are of type → ↓ ← . For an intermediary position such as 2, there will probably be a small, in-plane contractive stress → ← together with an outward force ↑. Similar arguments hold for locations 4 and 5. However, locations 4 and 5 are almost certainly less important since they are probably in the region of the first dip in the Friedel oscillations of the electron gas [44,45]. Friedel oscillations would imply some transfer of charge from 4 and 5 into 2 and 3, which may well be an important effect in its own right, worthy of further study. Clearly there is a good case for detailed self-consistent-field calculations comparing the surface electron density with the bulk and indicating the sense of the electron transfer and the resulting tangential surface pressures and normal forces: unfortunately such results are not available at present. We believe that the Friedel oscillations give either → ← or ← → pressures, but that they certainly contribute an outward vertical force ↑. We conclude the overall picture with both the sp transfer and the Friedel oscillations a little unclear as to tangential stresses → ← or ← → , but clearly giving a normal relaxation ↑.

One feature of the above analysis that may initially come as a surprise is that we obtain vertical expansions at a metal surface. A widely used argument for surface contractions is that at a surface the atomic coordination drops so that there is more bonding to the remaining atoms and hence shorter interatomic distances. This is based on the well-known example of organic molecules where we have for the carbon bond lengths $C\equiv C < C=C < C-C$. However, carbon has a half-full shell (assuming sp hybridisation), and therefore should *only* be used as an analogue of other systems with half-filled shells, i.e., metals in the middle of the transition series. Many examples can be found of the opposite effect when shells are nearly or completely full, for instance magnesium; "single bonded" magnesium metal is stable, as are single Mg–Mg bonds in molecules derived from Grignard reagents [46]. The "double bonded" Mg_2 molecule has a substantially larger bond length – it is in fact unstable. With Mg we have a full (repulsive) 3s shell and an empty (attractive) 3p shell, analogues of respectively the d band sp electrons in Au. In the Mg_2 molecule the 3s repulsion dominates, making the molecule unstable. Removing some of these electrons stabilises the Mg–Mg bond, the bond length depending on how efficient is the electron removal, i.e. the electronegativity of the attached atoms or groups of atoms [46]. Bond lengths decrease when increasing the number of electrons involved in the bond only if these electrons go into attractive, bonding levels, whilst they increase if the electrons go into repulsive, antibonding levels. A simple example of this is the following: whereas O_2^+ has a shorter bond length than O_2, N_2^+ has a longer one than N_2 (see, for example, ref. [47]).

Returning to surfaces, how can we relate the tension model to the experimental data? For Au(111) there is contradictory evidence. For large, flat
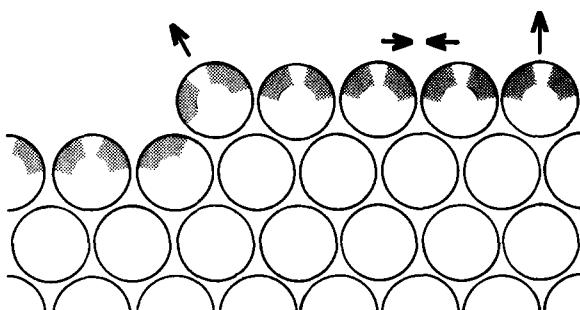
Fig. 6. Area of surface with a step. If the sp electrons are attracted into the shaded region, this gives → ↑ ← on a flat surface. The *same* process produces a large sideways (expansive) and outwards ↑ at a step as indicated. An edge would be similar.

surfaces the data indicate → ? ← , the vertical component currently being unresolved. The most definite evidence for the in-plane contraction is from the high-voltage diffraction and imaging experiments [48–50]. (X-ray evidence [51] indicates ↑, although there are ambiguities as to the cleanliness of the surfaces in these experiments.) Apparently contradicting this are recent high-resolution electron microscopy results [8–10] which clearly indicate an expansion. However, the geometry in these latter experiments was not that of a large, flat surface, but instead, somewhat rough surfaces with many short surface rafts.

Thus gold (111) both expands and contracts, which sounds contradictory. When we include the differences in the surface geometry, however, this apparent contradiction vanishes. On the large, flat surfaces, stresses → ↑ ← correspond to sp electron transfer to location 2, as shown in figs. 5 and 6. Even though much of the redistribution is towards the top of the attractive mantle, the geometry of a flat surface forces much of the additional electron density to lie in between the atoms, thus giving a contractive surface stress → ← . What happens if we change the surface geometry, for instance, by introducing a surface step? *Exactly* the same electron redistribution (to position 2) no longer produces so much additional charge density between the atoms at the step, leaving primarily the expansive component, as illustrated in fig. 6. Indeed, to prevent expansion at a step we would need the sp electrons to flow into position 4 or 5 rather than position 2. Since we cannot just move one atom without also affecting its neighbours, this gives us a definite tangential expansive stress for a short surface raft or a rough surface with steps.

Clear experimental evidence for the ambiguity of expansive ← → or contractive → ← stresses on (111) surfaces is provided by the work of Toennies and co-workers [52–54]. They found that on Cu, Ag and Au(111) there are anomalously low longitudinal phonon frequencies parallel to the surface, this corresponding for Au to about a 25% drop in the strength of the

surface bonding. The softening of the photon indicates that the electrons can readily redistribute themselves among positions 1, 2 and 3, and are not firmly fixed in place. This indicates that different possible arrangements have similar energies – there is no deep potential energy minimum and the energy to distort the surface tangentially is small.

These same ideas can be invoked to explain the large expansions observed experimentally on (311) microfacets by Smith and Marks [43]. This surface can be viewed as very short (111) facets with steps, which can expand in the manner described for steps above. The situation on the reconstructed (110) surface is less clear. It can also be regarded as consisting of extremely short (111)-type facets, suggesting an expansion as observed by Marks [10]. However Moritz and Wolf [13] report a more complex pattern of normal and sideways displacements amounting to a rotation of the (111)-type facets.

Leaving (111)-type surfaces, we can extend these ideas to some extent to Au(100). For the unreconstructed 1×1 surface, there are unfavorably large holes forcing large corrugations in the electron gas. These holes can be partially filled by one column of atoms sliding across to one side. This would lead to surface Shockley partial dislocations, as observed by Marks and Smith [55]. The (100)1×1 surface is metastable, and with a little thermal activation energy transforms to a 5×20 structure with an fcc (111) monolayer over the (100) bulk [41]. There must be some gaps between this top layer and the (100) substructure, which will result in the electron density in the top layer being pulled down towards position 3 rather than perhaps position 2, and hence lead to a tangential contraction, in agreement with the experimental data [41]. However, there is a very large elastic energy in fitting a (111)-type layer onto a (100) substructure. This could easily override any natural tendency for a contraction, or an expansion, and be the dominant effect in determining the tangential spacing (as opposed to an electronic source of the tangential relaxations).

What we really have for all the gold surfaces is an instability in the system which can be relieved in more than one way, the precise mechanism being strongly sensitive to additional factors such as the local geometry. In many respects we have a bifurcation – a physical situation where there is more than one possible minimum available. These are not uncommon; see, for instance, the article by Haydock [56]. We can represent the (111)-type surfaces schematically by a potential energy surface for the normal and tangential surface spacings as shown in fig. 7. Starting from the bulk (Gibbs) location G as shown in the figure, two possible local minima M_1 and M_2 are available to the system. For a large surface the epitaxial constraint strongly prefers M_1. Here we are including the long-range misfit strains stretching far beneath the surface and the associated strain energy due to the change in the tangential spacing. With a change in geometry much of this long-range strain field is short circuited – hence the expansions at small surface rafts, the system now being
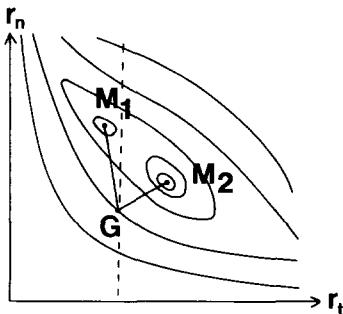
Fig. 7. Schematic potential energy surface for the normal, r_n, and tangential, r_t, surface spacings, with the epitaxial constraint r_t = constant indicated. For a long, flat surface the system is forced into the region near the M_1 minimum, because of the large epitaxial energy involved in changing r_t. For a short or stepped surface this epitaxial energy is far smaller, so that the deeper minimum M_2 becomes available with an increase in both r_t and r_n.

able to find the other minimum, M_2. Because of the separate and different d and sp forces, it is *not* like an elastic medium under *one* simple strain. It is like a structure with *two* strong springs in different places and a change in the external constraints can allow the structure to slip into two possible states – a bifurcation.

To summarise this section, at a noble metal surface the sp electrons redistribute into the attractive mantle core region, the precise redistribution being strongly dependent upon the local surface geometry. Detailed self-consistent calculations are needed to give the full picture, including the precise stresses and forces, but some simple points are apparent. Whilst long, flat (111) surfaces are probably tangentially contractive with a normal expansion, steps and short surface rafts are clearly expansive, consistent with the experimental results. The qualitative sense of the surface relaxations for (111), (110), (311) and (110) Au surfaces all fit the same electronic model of sp transfer, the different end results being due to the different geometries.

4. Discussion

Having discussed the theoretical and experimental data for gold surfaces, we now turn to some closely related effects.

Multiply-twinned particles or MTPs are non-crystallographic structures commonly found among small particles, particularly so for Au and Ag (e.g. refs. [57–60]). These can be thought of as being constructed from 5 or 20 inhomogeneously strained fcc tetrahedra, the simpler five-fold structure being illustrated in fig. 8. The energy cost of the inhomogeneous strains [60] is primarily offset by a favorable permutation of low energy surface facets
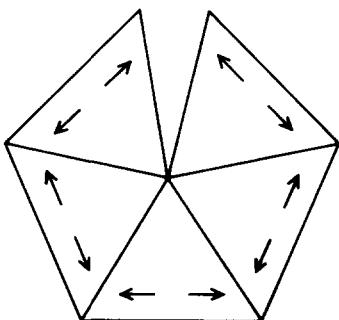
Fig. 8. Schematic diagram of a decahedral multiply-twinned particle. These particles consist of five fcc tetrahedra inhomogeneously strained to close the angular gaps as indicated by the arrows. The angular deficit is 7.5°, and has been exaggerated in the figure. For further details see refs. [56–59] and the references therein. Note that closing the gaps allows a relaxation of the surface expansive stress.

[59,60]. However, this simple model (of a surface energy gain versus a strain energy cost) fails to explain these particles completely; it is necessary to include the energy cost of a surface strain, i.e. the work done against the surface stresses or pressures by a tangential expansion of roughly 2%. Here the direct experimental evidence is unclear; apparent measurements of the surface stresses have appeared in the literature (e.g. refs. [61,62]), but these are by no means unique or free from artifacts arising from surface contaminants [63]. One experimental fact is however uncontroversial – MTPs occur far more frequently for Au and Ag (almost all the time in fact) and are comparatively rare for other metals such as Pt. We believe that the cost of the surface strains is substantially smaller for Au and Ag than, for instance, for Pt, hence strongly favoring MTP formation. We note that the results of Toennies [52–54] as discussed earlier directly support this view.

A second, related area, admittedly a bit speculatively, is an extension of the model to include the effects of adsorbed chemicals. For instance, a simple alkali metal additive will donate an electron to the noble metal, increasing the electron density in the surface. This would increase the instability in the noble metals by providing more electrons to flow into the low energy mantle regions 1–5 as discussed in section 3. It is quite encouraging that this simple idea is quite consistent with the experimental facts: less than 10% of a monolayer of alkali metals induces the stable Cu and Ag(110) 1 × 1 surfaces to convert to 2 × 1 reconstructed surfaces [64–66]. We would suggest that alkali metals will probably also induce Ag(100) to reconstruct. (There are some indications in the experimental literature for the opposite effect due to electron acceptors, although here the evidence is not as yet so clearcut.) These ideas concerning the effects of chemical modifiers have some interesting catalytic consequences, as discussed elsewhere [67].

Somewhat more speculative, some very interesting results have recently been obtained by Lamarre et al. [68] on relaxations at grain boundaries. These authors found that electron diffraction patterns from grain boundaries showed streaks outside the bulk diffraction spots for silicon, but inside for gold, the same type of boundary being analysed in both cases. These results imply a contraction associated with the grain boundary for silicon but an expansion for gold. Remembering that silicon has a half-filled sp shell so increasing the bond order will lead to a contraction, these results also fit with the general sense of our analysis herein.

What do we expect the tension between the sp and d electrons to yield across the transition metal series? The competition between the d electrons and the sp electron forces is well understood in the *bulk* transition metals (e.g. refs. [31,32]). The d electrons would like to have much smaller interatomic distances, while the sp electrons resist being squeezed into the repulsive regions of the pseudopotential near the atomic cores. This is of course the reverse of the situation in the noble metals. Again there are instabilities due to the opposition of the two forces, in addition to instabilities due to partial occupancy of the d band as discussed for instance by Heine and Samson [69]. For example, the sp electrons being squeezed out clearly leads to contractions normal to the surface, as are known to occur (e.g. refs. [1–3]). Here we may legitimately consider the bond order at the surface as increasing (leading to shorter separations) since we are dealing with bonding levels. However, which of the locations 1–5 as described in section 2 the sp electrons leave may also be important, and there will almost certainly be geometry dependent effects. One feature that is clear is that there will be a trend across the series from contractive in the middle to repulsive on the right when the d shell is full, and also a similar trend for sp bonded elements as those shells fill up as sketched in fig. 9. From considerations of the bulk, the cross-over from the typical transition metal behavior to the noble metal situation probably occurs very close to the noble metal end. We note that there is evidence [4–7] of a small normal expansion for Pt(111), which might place the border slightly to the left of Pt. It would clearly be of interest to investigate in detail the (111) surfaces of the other fcc and hcp metals.

Finally, it is worthwhile to repeat the standard point that electronic analyses of the type described herein are strictly speaking 0 K analyses. It does not follow that the entropy contributions are minimal. For instance, we suspect that the (111) type overlayer on the (100) surfaces may well have a large entropic component, particularly for metals such as Ir where high temperatures are required to nucleate the phase transition. Furthermore we may in many cases be observing kinetic minima, i.e. the nearest local minimum which the kinetics of the surface makes available, rather than a true thermodynamic minimum, and the surfaces may not be well ordered. One of the more striking results from high-resolution electron microscopy of surfaces has been the
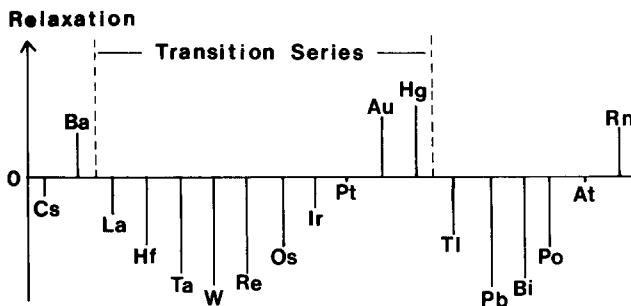
Relaxation

Fig. 9. Schematic sketch of the gross trends in surface relaxations that we would expect across the periodic table, labelled for the sixth period and excluding the lanthanide series. The sign of the relaxations for the group IIb (Zn, Cd and Hg) and the magnitude of the contractions for the group IVb (C, Si, Ge, Sn and Pb) and group Vb (N, P, As, Sb, Bi) will depend upon the strength of sp hybridisation and any lone-pair effect.

failure to find, in practice, nice, well-ordered surfaces – entropic disorder is present. We have already seen in section 3 how the local geometry can influence the type of surface relaxation arising. This is not simply an academic point as most surfaces of technological importance (such as small catalyst particles) are not idealized flat surfaces. Here the ability of electron microscopy and scanning tunnelling microscopy to image non-average behavior may lead to some interesting developments in the future.

Acknowledgements

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