Direct Observation of Elastic and Plastic Deformations at Au(111) Surfaces

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Three forms of elastic and plastic deformations at Au(111) surfaces have been observed by high-resolution electron microscopy. These are normal expansion of the first surface interplanar spacing, lateral expansions through surface dislocations, and the development of hill-and-valley structure or elastic buckling depending upon the sample morphology. These effects are interpreted as evidence for a positive, tangential surface pressure (surface stress) consistent with effects in gold alloys, and small-gold-particle internal and electronic structures.

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There has long been strong interest in expansions or contractions at metal surfaces\(^1\) but information has only been obtainable with indirect techniques. It has recently been demonstrated that high-resolution electron microscopy can directly reveal this type of information on small metal particles.\(^2\)\(^-\)\(^4\) We present here the first clear evidence on Au(111) surfaces of large, in-homogeneous elastic and plastic deformations associated with surface relaxations. These observations relate to nonuniform surfaces, not accessible to other techniques, which are of considerable relevance to real surfaces of technological importance.

Two types of specimen were employed in this study, namely, small particles on an amorphous carbon substrate,\(^5\) and continuous films with large holes which are described in detail elsewhere.\(^6\) The specimens were examined in the Cambridge University high-resolution electron microscope\(^7\) operated at 500 kV, with typical conditions being a beam convergence semiangle of 0.5 mrad, a focal spread of 16 nm, and an image magnification of 800,000\(\times\). Under these conditions, the optimum defocus could be recognized to better than \(\pm 50\) Å (see Refs. 2, 4, 6, and 8 for examples). Image interpretations were confirmed by digitally comparing the photographic negatives with theoretical image simulations: Details are described elsewhere.\(^8\) Removal of an initial amorphous carbon covering on the continuous-film samples was performed by electron-beam etching employing residual water vapor\(^9\) either from the photographic films or from a deliberate air leak. Also note that with the profile geometry of our experiments, a carbon mono-

layer on the surface would be visible if present.\(^6\)

Our results, which will be presented in full elsewhere,\(^6\) may be summarized in terms of three separate phenomena, which are shown in Figs. 1 and 2. Firstly, during removal of the carbon from the continuous films a macroscopic hill-and-valley structure developed (see Figs. 1(a) and 1(b)], typical hill heights being five or six interatomic spacings. This large surface roughening was not observed on other surfaces, such as gold (100), thus ruling out the possibility of artifacts from phenomena such as ion- or electron-beam damage. A similar type of elastic effect occurred for the discrete particles, namely, surface buckling. Secondly, following removal of the carbon, large (5\%-10\%) normal expansions occurred near free edges (see Fig. 2). (To a good approximation, the true surface expansion is roughly 5\% less than that present in the images, the difference being due to a Fresnel effect at the surface.)\(^6\) We discuss elsewhere\(^8\) the discrepancy between our observations of expansions on gold (111) and earlier brief reports of contractions. The final effect occurred later in time and can

![Image](image-url)
be described as a plastic accommodation of lateral expansions by means of surface dislocations such as that visible in Fig. 2.

These various observations can all be interpreted as manifestations of a large, positive tangential surface pressure. The hill-and-valley reconstruction on the continuous films provides a mechanism for this pressure to be accommodated, initially by surface expansions. For the discrete particles the boundary conditions are different, and the initial elastic deformation is accommodated by surface buckling. The elastic stresses involved are large, sufficient to nucleate surface dislocations as a plastic mechanism for relieving the surface pressure.

The positive tangential pressure and hence all the above effects stemming from it can be understood in terms of the forces inherent in the 5$d$ and 6$s$p electrons in Au. In the bulk at the equilibrium interatomic distance, the 5$d^{10}$ full (or nearly full) shells are under considerable compression, i.e., exerting a positive outwards pressure.\(^{7,12}\) This is balanced by the 6$s$p electrons which are under negative pressure, i.e., sucked inwards into regions of strong negative pseudo-potential. The main evidence for this picture comes from the fact that Au and Ag atoms have a 30% smaller atomic volume in alloys where the $d$ shells are not in contact,\(^{13}\) and from theoretical calculations and analysis for transition and noble metals.\(^{11,12}\) This matter will be argued more precisely elsewhere,\(^{14}\) in particular that the effect of $sd$ hybridization is predominantly a one-atom effect\(^ {15}\) to be counted therefore with the $sp$ electron attraction rather than the two-atom $d$-shell repulsion.

At a surface, we believe that this pressure balance is in a sense "short-circuited." The $sp$ electrons are free to be sucked inwards perpendicular to the surface, this one-atom atomic-volume (electron density) effect relieving their negative pressure. As a result there is a strong net repulsion left between the $d$ shells parallel to the surface, and to a lesser degree normal to the surface, i.e., a positive tangential surface pressure often referred to in the literature as a positive surface stress (see, for example, Refs. 16–18).

One immediate correlation with the existence of a tangential surface pressure arises in the structure of small gold particles, in particular the so-called multiply twinned particles\(^ {5}\) which occur profusely in gold (see, for example, Ref. 5), and less so in other fcc metals such as Pt.

The formation of these unusual noncrystallographic structures is strongly favored by exactly this form of surface pressure. Finally, given the central role of elastic distortions and plastic deformations in controlling many bulk properties, our results would imply that a similar importance should be attached to these effects in surface phenomena.

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\(^{12}\)L. D. Marks and D. J. Smith, to be published.


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FIG. 1. Large area of vicinal (111) surface [which showed the same behavior as (111) surfaces] (a) as prepared, and (b) the same area after development of hill-and-valley structure.
FIG. 2. Experimental image showing a surface dislocation (solid arrow) and relaxations, the sense of which are indicated by the hollow arrows. The latter can be best seen by viewing along the surface angle.