Anomalous multilayer relaxation of Pd{001}

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A low-energy electron-diffraction intensity analysis of a clean Pd{001} surface finds the first interlayer spacing expanded by about 3% and the second interlayer spacing slightly contracted by about 1% with respect to the bulk value (1.945 Å). These results contradict the trend usually observed or theoretically predicted on fcc {001} surfaces, where the first relaxation is a compression and the second is an expansion. Possible origins of this behavior are suggested.

The phenomenon of multilayer relaxation on metal surfaces is well known and well documented.[1,2] The phenomenon consists in rigid translations of one or more atomic layers in the surface region with respect to parallel atomic layers in the bulk. The translations can be perpendicular or parallel to the plane of the surface, but within each atomic layer the translational symmetry of the bulk is maintained.

A few general trends have been discovered in the results of experimental studies of multilayer relaxation. Thus surfaces with $ABAB\cdots$ stacking usually exhibit compression, expansion, and compression of the first, second, and third interlayer spacing, respectively, while surfaces with $ABCABC\cdots$ stacking may exhibit different sequences, e.g., compression, compression, expansion, compression. Surfaces with large Miller indices have larger and deeper relaxations than surfaces with small Miller indices. Relevant to the present work is the trend observed on fcc {001} surfaces, where the relaxation usually consists of small compression (1–3 %) of the first and a smaller expansion of the second interlayer spacing.[1] We report here the results of a quantitative low-energy electron diffraction (LEED) study of a clean Pd{001} surface which go against the trend and reveal an expansion of the first and a slight contraction of the second interlayer spacing.

The experiments involved cleaning a Pd{001} surface in ultrahigh-vacuum—the procedures followed for this purpose were described in an earlier publication.[3] The LEED intensity data were routinely collected from surfaces recleaned with 1-h Ar^+ bombardment followed by 1-h anneal at about 750 °C. The Auger electron spectroscopy (AES) spectra of such clean surfaces showed essentially no impurities: in particular, the ratio of the O AES line at 512 eV to the Pd AES line at 330 eV was less than 0.005, and the ratio of the two Pd AES lines at 279 and 330 eV, respectively, was about 0.25 (the C AES line at 275 eV cannot be resolved from the Pd line at 279 eV, but the absence of C from the surface region is demonstrated by the fact that the LEED pattern is a sharp 1×1).

The $I(V)$ (intensity versus energy) spectra of several beams were measured, viz., at normal incidence of the primary electron beam ($\theta=0°$): beam indices 10 (averaged from 10 and $\bar{1}0$), 11 (averaged from $1\bar{1}$ and $\bar{1}\,\bar{1}$), 20 (averaged from 20, $0\bar{2}$, and $\bar{2}0$), 21 (averaged from 21 , $2\bar{1}$, $1\bar{2}$, $\bar{1}\,\bar{2}$, and $\bar{2}\,\bar{1}$), and 22 (averaged from 22, $2\bar{2}$, and $\bar{2}\,\bar{2}$); at $\theta=11°$ and $\phi=0°$: beam indices 00, 10, and 01 (averaged from 01 and $0\bar{1}$), 11 (averaged from 11 and $1\bar{1}$), $\bar{1}\,\bar{1}$ and $\bar{2}1$ (averaged from $\bar{2}1$ and $\bar{2}\,\bar{1}$), and $\bar{2}0$. All $I(V)$ curves were normalized to constant incident electron current and smoothed; before comparison with theoretical $I(V)$ spectra the background of each curve was subspectra the background of each curve was subtracted.

The calculations of LEED intensities were done with the CHANGE computer program.[4] The Pd potential was taken from the compilation of Moruzzi, Janak, and Williams.[5] The inner potential was chosen initially to be $V_0=-(10+4i)$ eV, but the real part was varied as a fitting parameter in the course of the analysis. The final value was $V_0=-(7+4i)$ eV with an error of ±3 eV in the real part. The amplitude of the atomic vibrations was taken as $\langle u^2\rangle^{1/2}=0.125$ Å, corresponding to a Debye temperature of 280 K.

The analysis was done first with the normal-incidence data and concentrated on varying the first (d_{12}) and the second (d_{23}) interlayer spacing. The changes of these quantities (called Δd_{12} and Δd_{23}, respectively) from the bulk value 1.945 Å ranged from -0.1 to $+0.1$ Å in steps of 0.025 Å in the first stage and of 0.005 Å in the last stage. The fit to experiment was checked both visually and by means of R factor analysis, using the Van Hove–Tong[6] $R_{\rm VHT}$, the Pendry[7] R_P, and the Zanazzi-Jona[8] $r_{\rm ZJ}$ reliability factors. Contour plots of these reliability factors versus first and second interlayer spacing are depicted in Fig. 1. The best overall fit to experiment was found for $\Delta d_{12}=0.056\pm0.03$ Å and $\Delta d_{23}=-0.015\pm0.03$ Å, with $R_{\rm VHT}=0.32$, $R_P=0.35$, and $r_{\rm ZJ}=0.14$. Curves calculated with these parameters can be compared with experiment in Fig. 2.

The analysis was then extended to the off-normal incidence data (and included fitting of the θ angle around the experimental value) with the results $\Delta d_{12}=0.056\pm0.03$ Å and $\Delta d_{23}=-0.035\pm0.03$ Å,

$R_{VHT}=0.28$, $R_P=0.46$, and $r_{ZJ}=0.16$. The theoretical and experimental $I(V)$ curves for off-normal incidence are depicted in Fig. 3. We summarize the overall results as follows:

$$\Delta d_{12}=+0.06\pm0.03 \text{ Å},$$

$$\Delta d_{23}=-0.02\pm0.03 \text{ Å},$$

$$d_{\text{bulk}}=1.945 \text{ Å}.$$

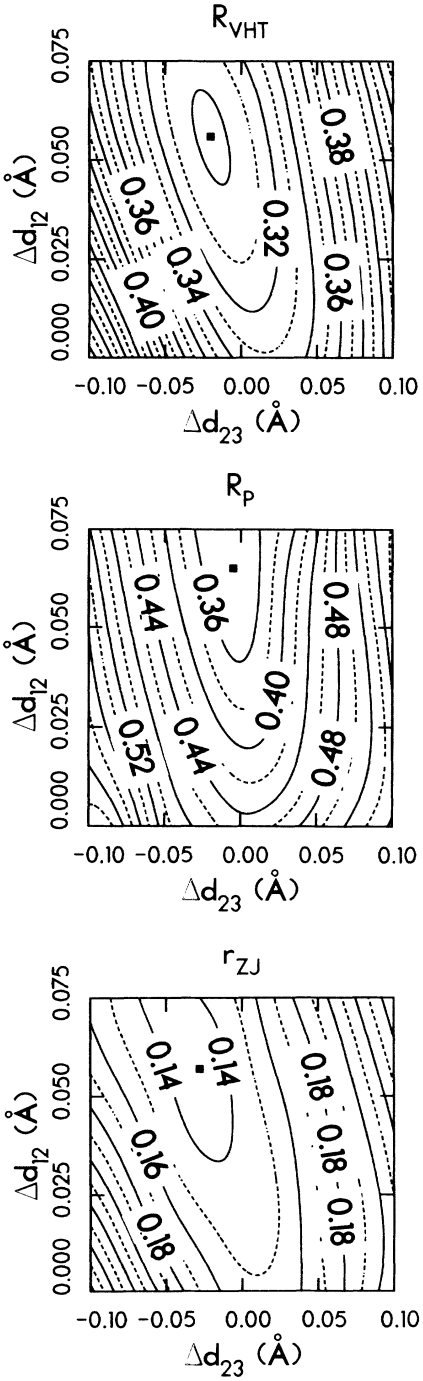

FIG. 1. Contour plots of Van Hove–Tong's R_{VHT}, Pendry's R_P, and Zanazzi-Jona's r_{ZJ} reliability factors vs changes of first (Δd_{12}) and second (Δd_{23}) interlayer spacing on Pd{001}. The minimum in each panel is indicated by the solid square.

These results are consistent with the only other study of surface relaxation on Pd{001} known to us, by Behm *et al.*[9] These authors report "possibly a slight expansion by 0.05±0.05 Å or (2.5±2.5)% of the top layer spacing relative to the bulk value."

The 3% expansion of d_{12} and 1% contraction of d_{23} found here differs in sign from the relaxation of most fcc {001} surfaces studied.[1] However, we note that a similar relaxation occurs in fcc Fe{001}, grown epitaxially[10] on Cu{001} (hence under strain), where d_{12} is expanded by (4±2)% and d_{23} is compressed by (0.5±2)% with respect to the strained bulk spacing. Also, fcc Rh{001} is reported[11] to show a similar relaxation: $\Delta d_{12}=(1.0\pm0.9)\%$ or (0.5±1.2)%, depending on a choice of scattering potential; only d_{12} was varied in that analysis.

Theoretical treatments of multilayer relaxation at metal surfaces do not usually predict expansions of the first fcc {001} layer.[12–17] However, a first-principles total-energy treatment[18] of Al{001} found a small expansion of d_{12} by (1.2±0.4)%. A simple, moderately successful, electrostatic model of relaxation[14] predicts universal curves for relaxation at surfaces of bcc and fcc lattices against openness.[19] These curves show a 1% *compression* of the first layer spacing of fcc {001} with respect to bulk, and a 4% compression of the more open bcc {001} first spacing. Hence the 3% expansion of the Pd{001} first spacing suggests that some new physical mechanism is present which is not contained in the assumptions of the theoretical models.

We note two possible mechanisms for expansion of d_{12}

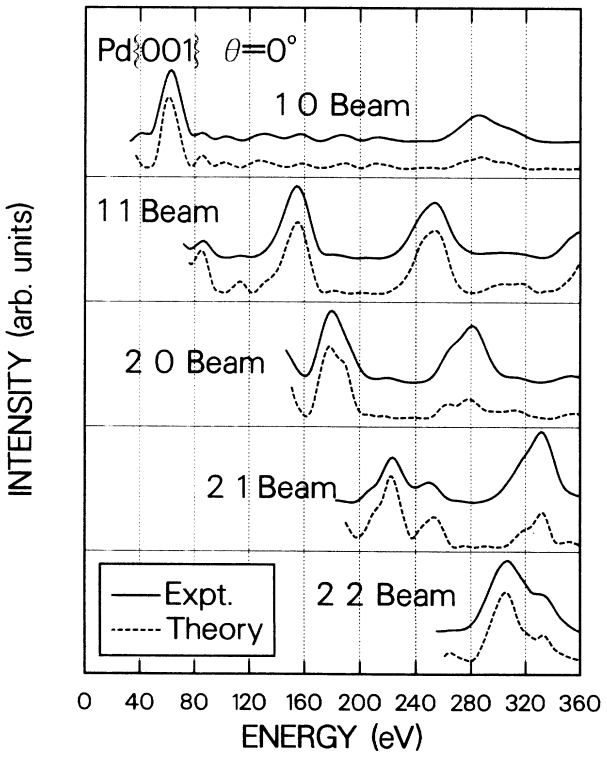

FIG. 2. Experimental (solid) and theoretical (dotted) LEED $I(V)$ curves from clean Pd{001} for normal incidence of the primary electron beam.

over bulk. The first involves the presence of interstitial hydrogen in the surface layers of Pd—the hydrogen atoms would expand the lattice owing to the pressure of their zero-point and vibrational motion. The second involves the presence of a magnetic moment in the surface layers of Pd, which could be ferromagnetic or antiferromagnetic.

The interstitial-hydrogen mechanism, which is suggested by the well-known affinity of Pd for hydrogen, is made plausible by the fact that at pressures in the low 10^{-10} Torr range the residual atmosphere in the experimental chamber is predominantly hydrogen gas. A recent study of electrochemical loading of deuterium in palladium[20] found that the deuterium atoms occupy the octahedral sites of the Pd structure and cause, at high concentrations, an increase in lattice constant from 3.89 Å (for the pure metal) to 4.02 Å, i.e., an increase of 3.3%. Furthermore, a multilayer LEED analysis of a monolayer of Cu on Pd{001} (Ref. 21) found the expansion of the first Pd interlayer spacing to be reduced to 1%. This result is consistent with the larger expansion of clean Pd{001} if the presence of H in the Pd is due to a dynamic process, hence the concentration of H in the first Pd spacing would be reduced by a reduced sticking coefficient of H on the Cu monolayer.[22]

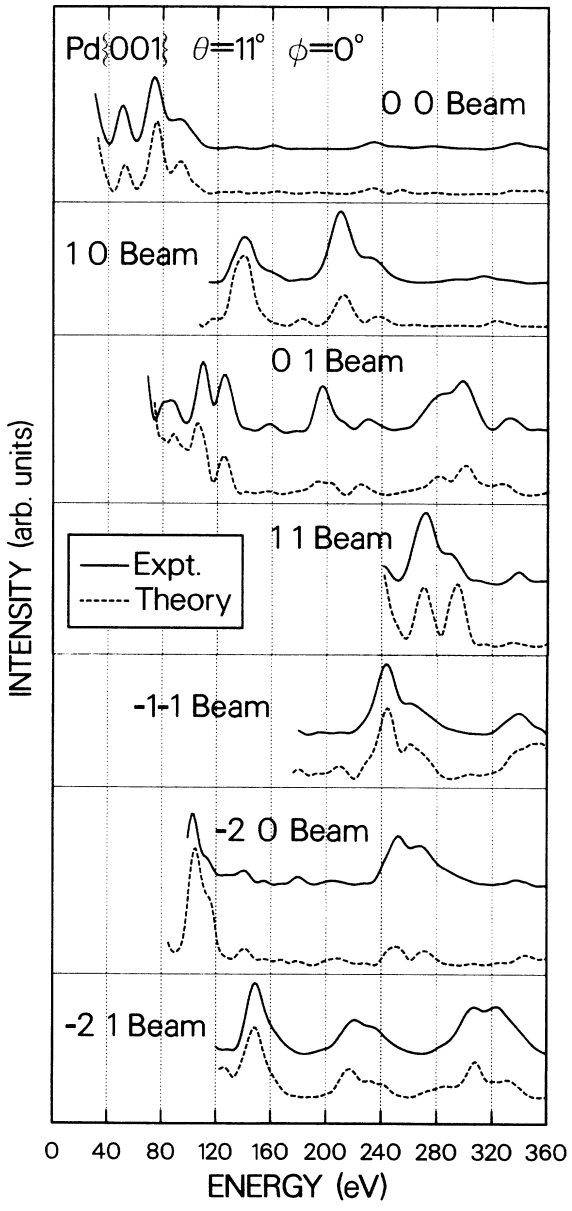

FIG. 3. Experimental (solid) and theoretical (dotted) LEED $I(V)$ curves from clean Pd{001} for incidence of the primary electron beam at $\theta=11°$ and $\phi=0°$.

The magnetic-moment mechanism depends on the increase in volume associated with the increase in spin magnetic moment found in first-principles calculations of magnetic phases of transition elements.[23] The volume increase is a consequence of the magnetic pressure produced by an unbalanced spin distribution.[24] The surface layer will have larger moments than the bulk because of the smaller number of neighbors, hence the corresponding increase in magnetic pressure will expand the volume per surface atom. Bulk Pd is nonmagnetic in (zero-pressure) equilibrium[25] while a monolayer with the bulk spacing is ferromagnetic[26] with a moment of $0.4\mu_B$/atom. Thus it is possible that the surface layer is ferromagnetic, although a surface calculation has not been made. The bulk calculation[25] shows that 2% expansion of the Pd lattice is required to reach the ferromagnetic phase with moment $0.12\mu_B$/atom, and an additional 4% expansion raises the moment to $0.34\mu_B$/atom. Hence a surface moment of about $0.2\mu_B$/atom would correspond to the observed 3% expansion.

Stronger evidence for the magnetization mechanism in the first interlayer expansion exists for fcc Fe, where both a relaxation measurement[10] and a surface calculation[27] have been made. A self-consistent band calculation of a five-layer slab of fcc Fe has shown the first layer to have a magnetic moment 20% greater than the second layer and even more with respect to bulk layers.[27] Bulk calculations of fcc Fe show[28] that a 20% increase in moment from the value at the Cu spacing will expand the lattice constant about 3.6%, hence the calculated increased surface moment is consistent with the observed relaxation. A spin-polarized total-energy calculation of a slab with relaxed surface interlayer spacing is needed to make a quantitative check.

Another example of a similar anomalous relaxation is bct (body-centered-tetragonal) Mn. The structure of a ten-layer pseudomorphic film grown on Pd{001} shows a 5% expansion of the first interlayer spacing over bulk.[3] Mn bulk calculations[28] and measurements of Mn dilute alloys[29] show that the film is antiferromagnetic when stretched to the Pd lattice constant and that the sublattice moment rises with lattice constant. If the increase in the surface moment is similar to that of fcc Fe, a 5% increase in first interlayer spacing is readily explained.

However, there are some difficulties with the magnetization mechanism. Experiments of Liu and Bader[30] with the surface Kerr effect have not found ferromagnetism in the surface layer of clean Pd{001}, but do not exclude antiferromagnetism. LEED structure analyses of bcc Fe{001} and bcc Ni{001} surfaces show 5% *contraction*

in each case.[31] These surfaces are certainly ferromagnetic, and the enhancement of the surface-layer moment of bcc Fe{001} has been found to be about 33% over bulk.[32] However, it should be noted that the more open bcc {001} surfaces are expected to show a larger contraction than fcc {001}, hence the 5% values could represent a compression of reduced magnitude—e.g., bcc {001} Mo, Ta, V, and W show larger compressions of d_{12} (up to 11%).[1]

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