Observation of a Soliton Reconstruction of Au(111) by High-Resolution Helium-Atom Diffraction

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From an analysis of diffraction data for Au(111), we deduce that the observed 23-fold periodicity in the ⟨110⟩ direction can be described by a regular superstructure of one-dimensional extended stacking faults. We propose that this surface is a realization of the Frenkel-Kontorova model of competing interactions and that the periodic changes in stacking from *ABC* to *ABA* may thus take the form of solitons. The solitons, of half-width 11.8 Å, lead to an average compression of 4% in the ⟨110⟩ direction.

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Gold has the highest ductility and malleability of any element and therefore it is not surprising that it is the only metal for which the closed-packed (111) surface of an fcc crystal has been observed to reconstruct. The Au(111) reconstruction has been studied by LEED,[1-3] reflection high-energy electron diffraction,[4] and TED[5-7] (transmission electron diffraction). For all these experiments the observed splitting of the surface layer diffraction peaks has been interpreted in terms of a $(p\times 1)$ superstructure with $p=22$–23 along the ⟨110⟩ direction corresponding to an overall contraction of 4.4%. Recent highly resolved TED experiments by Takayanagi and Yagi[7] suggest that the compression is not uniform, but localized in two narrow transition regions where the stacking changes abruptly from *ABC* to *ABA*. In contrast to these observations Marks, Heine, and Smith[8] report on electron microscopy studies with single-atom resolution which reveal an expansion of about 5% both normal to and within the surface plane in agreement with a postulated strong repulsion between the *d* shells of the atoms resulting from depletion of *sp* electrons in the surface layer. To resolve this issue we have studied Au(111) single-crystal surfaces with high-resolution helium-atom diffraction. Compared to TED experiments He-atom diffraction probes only the very first layer and is completely insensitive to the bulk.

Our diffraction results reveal up to five satellites of the specular beam along the ⟨110⟩ direction with a particularly strong second-order peak [Fig. 1(a)]. We also observe a shift and a splitting of the ⟨112⟩ diffraction spots and threefold symmetry of the full diffraction pattern in place of the sixfold symmetry seen in all previous experiments [Fig. 1(b)].

The He diffraction apparatus is the same as that used in high-resolution time-of-flight studies of surface phonons.[9] The angle between incident and detected beams was fixed at 90° and the diffraction peaks are mapped out by rotation of the cyrstal in the scattering plane and about its surface normal. The He nozzle beam source is cooled by a closed-cycle He refrigerator down to 40 K corresponding to a minimum beam energy of about 8 meV ($k_i \cong 4$ Å^{-1}, $\lambda = 1.6$ Å) with a resolution of 0.16 meV full width at half maximum (FWHM). The absolute value of k_i could be established to within better than 0.5% from a time-of-

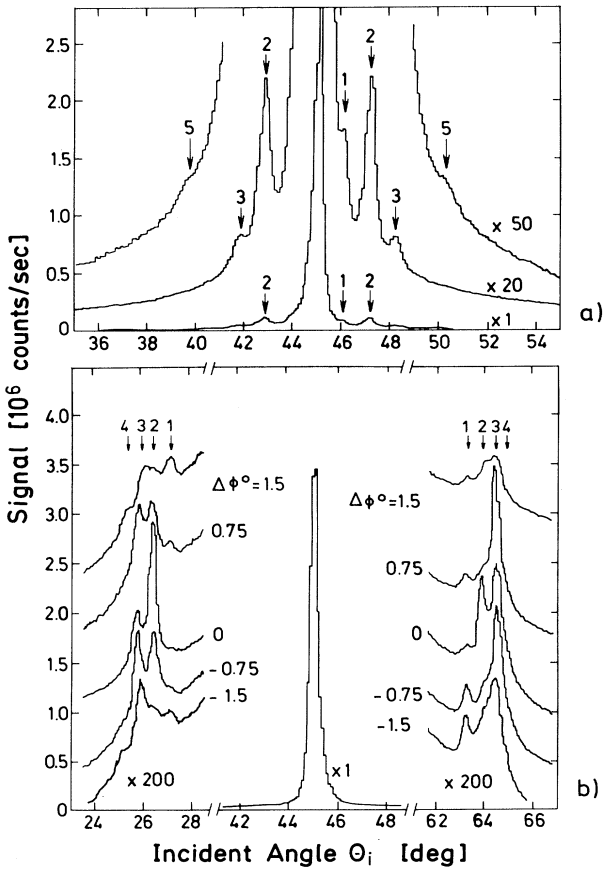

FIG. 1. He diffraction scans from the Au(111) surface. The crystal temperature was 300 K. (a) Along ⟨110⟩ at $k_i = 3.90$ Å^{-1} ($E = 7.95$ meV), (b) along ⟨112⟩ at $k_i = 5.64$ Å^{-1} ($E = 16.6$ meV).

flight measurement. At an incident momentum of $k_i = 5.64$ Å^{-1} the measured width (FWHM) of the specular peak is about 0.4° (0.05 Å^{-1}) which being greater than the apparatus resolution of 0.1° is attributed to a finite coherence length of structural order on the surface of about 140 Å. We used a crystal which was cut from a boule, mechanically polished, and cleaned in vacuum by repeated cycles of annealing at 900 K and neon-ion bombardment at 600 K. Similar results were obtained with a crystal epitaxially grown on mica.[10] The crystal was characterized by LEED with results identical to those reported by van Hove *et al.*,[3] and all impurities detected in Auger spectroscopy were below 1% of monolayer. The base pressure of the scattering chamber (He beam off) was 5×10^{-11} Torr.

Figure 1 shows angular scans along one of the ⟨110⟩ and ⟨112⟩ directions. In the ⟨110⟩ direction several satellites up to $n = 5$ were observed at the base of the specular peak separated by $\Delta K = 0.098$ Å^{-1} corresponding to a periodicity of 64 Å. The splitting of the ⟨112⟩ diffraction peaks was studied extensively in many scans taken in azimuthal steps of $\Delta\theta = 0.15°$ of which only a few representative results are shown in Fig. 1(b). These scans were also taken after rotation of the azimuth by 120° and 240°, resulting in a pattern which is schematically shown in Fig. 2. It should be noted that the measured diffraction pattern from a macroscopic surface is a superposition of diffraction from three domains of reconstructed Au(111) surface, since there are three ways in which the uniaxial reconstructed region can align with the second layer.

The implications of our major observations are the following observations: (1) From the positions of the satellites along ⟨110⟩ we conclude that there is a superlattice with a $(23 \times \sqrt{3})$ rectangular unit cell. (2) The second-order ⟨110⟩ satellite is very strong indicating that the surface corrugation has a strong second-order Fourier coefficient. Futhermore, the much weaker intensity of the third- and higher-order components implies that there are no sharp structures within the unit cell. (3) As the splitting of the ⟨112⟩ diffraction spots in the ⟨110⟩ direction cannot be due to satellites (the relative intensity between a diffraction spot and the first-order satellite should be comparable to the relative intensity of the specular spot and its first-order satellite, i.e,. less than 3%), there must be regions of shear on the surface to produce components C and E (Fig. 2) off the ⟨112⟩ direction. (4) Within the split ⟨112⟩ diffraction spots, those at large ΔK than the center ⟨112⟩ peak have higher intensity than those at lower ΔK values, indicating that *on average* the surface is compressed. (5) The threefold symmetry of the diffraction pattern, under the assumption of the existence of three domains of reconstructed surface rotated by 120° with respect to each other, indicates that a single domain possesses no rotation symmetry. (6) Finally, we observe no diffraction spot in the position expected for an unreconstructed surface. The center spot of the ⟨112⟩ diffraction group, which arises from diffraction perpendicular to the compressed ⟨110⟩ direction, is itself shifted to larger K values. This we interpret as an indication of an additional isotropic compression of about 2%. However, we observe no superlattice spots in the ⟨112⟩ direction, suggesting that the stacking here remains commensurate with the second layer. Hence, the additional contraction must extend at least to the second layer.

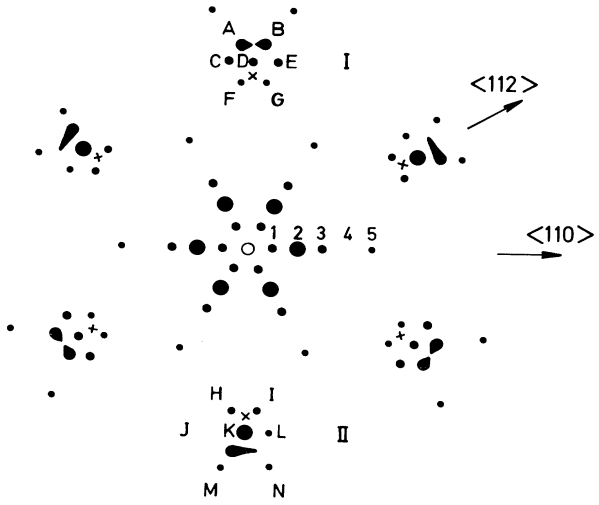

FIG. 2. Schematic representation of full diffraction pattern. The patterns in the ⟨112⟩ direction have been shifted towards the center, but otherwise the relative positions are to scale. (The spot size is proportional to intensity and magnified by a factor of 10 in the case of the ⟨112⟩ diffraction spots.) The crosses indicate the diffraction peak locations expected for the unreconstructed surface. The central diffraction peaks D and K are shifted outward by $\Delta G = 0.054$ Å from the expected location $G = 2.515$ Å.

Observations (1) and (4) are compatible with the first model for the reconstructed Au(111) surface,[3,4] involving a uniform compression of the surface layer in the ⟨110⟩ direction and also giving three possible domains. Observation (3) provides support for a new model recently proposed by Takayanagi and Yagi[7] in which the contraction along ⟨110⟩ is localized into two narrow sheared transition regions from a C position (*ABC* stacking, expected for fcc lattice) to an A position (*ABA* stacking) per unit superlattice cell, the transition regions containing 0.5 excess atom each. But this model fails to explain the detailed intensity behavior of the superlattice spots [see (2)], or the exact positions of the components of the ⟨112⟩ peaks.

Therefore, we propose (Fig. 3) the following im-

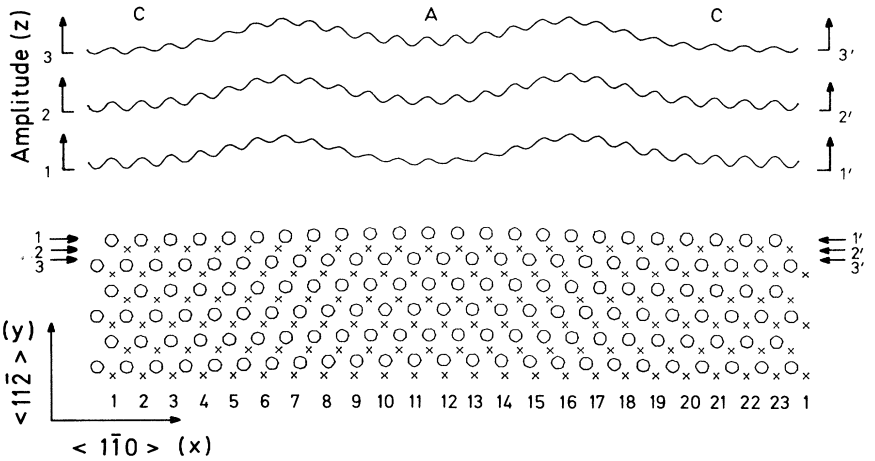

FIG. 3. Top: hard-wall corrugation functions at three points in the unit cell. Vertical scale exaggerated for clarity. Bottom: proposed structure. Crosses represent the second-layer and circles the surface-layer atoms.

proved model: (a) Within C and A regions atoms are at positions defined by bulk lattice spacing, i.e., in registry with the second layer. (b) The transition between C and A regions is described by a gradual x-dependent shift (x along $\langle 110\rangle$) given by the soliton expression[11]

$$f(x) = (2/\pi)\arctan[\exp(X/\Delta S)], \quad (1)$$

where $2\Delta S$ is the half-width (FWHM) of a soliton centered at the boundary between A and C regions. The introduction of this finite half-width of the transition region "relaxes" the physically quite implausible very narrow transition regions (containing 0.5 excess atom) proposed in the Takayanagi model. (c) The atoms in the transition region are raised up in the z direction by an x-dependent amount $H(x)$, modeled by a Gaussian with height H and half-width ΔS centered at the solitons. (d) To take account of (5) we allow the C and A regions to have different relative size R which removes the otherwise twofold rotation symmetry of the surface layer.

To test this improved model we performed hard-wall eikonal[12] calculations. The hard corrugated wall is defined by our placing Gaussians at the surface layer atom positions, giving an effective peak-to-peak corrugation amplitude h. The four parameters which provided a best fit of the intensities were $h = 0.07$ Å, $R = 0.7$, $\Delta S = 5.9$ Å, and $H = 0.15$ Å. Table I shows a comparison between experiment and results of calculation. Figure 3 compares the surface layer (circles) with the substrate (crosses) positions. Also shown are the hard-wall corrugation amplitudes for three cuts along the $\langle 110\rangle$ direction. Note that the soliton causes a very gradual shift from the A to the C stacking. The fitted height H agrees with a hard-sphere model for placing atoms in the intermediate bridge site position. The very satisfactory agreement between experiment and theory indicates that the model is able to reproduce all features of our data, if we assume an additional uniform contraction of 2% extending to subsurface layers.

If the soliton superlattice proposed in this model is

TABLE I. Comparison of experimental and calculated beam intensities for $k_i = 5.65$ Å^{-1}. All values are expressed as per mil of specular intensity.

Superlattice peaks			Diffraction peaks in $\langle 112\rangle$ direction					
Peak	Expt.	Theory	Peak	Expt.	Theory	Peak	Expt.	Theory
1	4	7.4	A	1.3	1.0	H	0.1	0.1
2	26	24.7	B	1.0	1.0	I	0.1	0.1
3	5.5	5.3	C	0.5	0.5	J	· · ·	0.2
4	· · ·	0.5	D	0.7	1.2	K	2.0	2.0
5	0.5	0.7	E	0.5	0.5	L	0.05	0.2
			F	0.2	0.2	M	0.9	0.8
			G	0.2	0.1	N	0.6	0.8

correct, it may well be indicative of the existence of two competing potential contributions at the surface of different periodicities.[11] The top layer, due to a change in electronic structure relative to the bulk, favors a uniform contraction to a smaller lattice constant, whereas the competing interaction with the bulk wants to pin the surface atoms in their normal (bulk) positions. This situation may well be a physical realization of the Frenkel-Kontorova model of competing interactions.[13] The ground states of this model have been calculated by Frank and van der Merwe[14] and indeed one of the solutions is a lattice of regularly spaced soliton-type walls which separate commensurate regions. The soliton superlattice can be regarded as a compromise between a fully incommensurate, and in this case compressed, structure in which the surface layer forces dominate, and an unreconstructed surface with bulk forces dominating, as in the case for all other close-packed metal surfaces yet studied. As we see no dependence of the diffraction pattern on crystal temperature between 120 and 700 K, the interaction between the solitons is probably so strong that it overrides the entropy contribution to the free energy which might otherwise cause temperature-driven transitions between phases of different soliton density or disordering (bending) of the walls. For Au(111) Heine and Smith[15] have recently proposed that the redistribution of *sp* electrons at the surface can lead to a reduction in the repulsion between the full *d* shells, whereby the surface layer is expected to favor a smaller lattice constant. This reduction in *d*-shell repulsion is consistent with the measured acoustic-phonon dispersion relations which indicate a significant decrease of the surface force constants with respect to bulk values. The phonon spectra show the usual transverse Rayleigh mode, but also an additional longitudinal mode. The latter is also present[16] on Ag(111)[16] and has been attributed to a 50% reduction in the lateral force constants of the surface layer. For the reconstructed Au(111) surface the phonon dispersion relations indicate an even greater softening corresponding to a 70% reduction. Bortolani[17] has attributed these effects to a similar electronic mechanism, namely, a decrease in the *sd* hybridization at the surface.

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