Anomalous multilayer relaxation on a Cu{331} surface

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Three independent theoretical studies of the multilayer relaxation on a Cu{331} surface had reported a sequence of layer contractions and expansions different from that expected and found on other stepped surfaces of metals with three atom rows per terrace. A quantitative low-energy electron diffraction analysis of Cu{331} finds a 13.8% contraction of the first interlayer spacing with respect to the bulk value (0.829 Å), in fair agreement with the theoretical results, and very small relaxations of the deeper interlayer spacings. The signs of these relaxations do not reproduce exactly the theoretical predictions, but their small magnitudes allow the conclusion that the present experiment agrees with the earlier theories within the experimental error bars.

I. INTRODUCTION

Cutting a crystal at a small angle to a low-Miller-index plane produces a surface that can be described alternatively as vicinal, high-index, or stepped. The profile of such a surface features a periodic sequence of steps separated by flat terraces of the low-Miller-index surface. For suitable choices of the azimuthal direction of the cut the steps are straight, i.e., unkinked. The atoms at the top edges of the steps lie in most cases on the first plane of the corresponding high-index surface. The atoms on the terraces lie on rows that correspond to successively deeper planes of the high-index surface: the smaller the cut angle, the smaller the interplanar spacing, and the larger the distance between successive steps, i.e., the terrace width.

Owing to the important role played by steps in a number of physical and chemical phenomena (such as reactivity, corrosion, catalysis, crystal growth, etc.), the structural and vibrational properties of vicinal surfaces have been investigated intensely in the past several years. The studies have concentrated mostly on vicinals of face-centered-cubic (fcc) {001}, fcc{110}, and fcc{111} surfaces of metals, and in particular on those with unkinked monoatomic steps.

An important difference between low- and high-Miller-index surfaces is that while in the former the atoms in deeper layers are usually buried, in the latter they lie on terraces, hence they are exposed. Theory finds, and experiment confirms, that of the n atoms lying on as many rows on each terrace the first $n-1$ exhibit *inward* relaxations, thereby producing compressions of the corresponding interplanar spacings, while the final nth atom (layer) exhibits *outward* relaxation (expansion). The sequence is often periodic, with rapidly decreasing amplitude in deeper layers. This phenomenon is referred to as multilayer relaxation, and is usually described by associating a $-$ sign to a compression and a $+$ sign to an expansion of the corresponding interplanar spacing. Relaxations parallel to the surface plane are also possible on surfaces with only one mirror line.

In Table I the stepped surfaces that have been studied either theoretically[1–11] or experimentally[12–32] are grouped according to the number of atom rows exposed on the terraces and therefore exhibiting the multilayer relaxation sequences listed in the second column. We see that fcc metals, and in particular Al, Ag, Cu, and Pd, are in the majority, and that the theoretical investigations of higher-index surfaces largely outnumber the experimental ones. The reasons for this imbalance lie in the difficulties encountered in experiments on surfaces with small interlayer spacings, particularly if those spacings are significantly smaller than 1 Å, as has been explained in detail elsewhere.[31,36]

Some exceptions to the rules mentioned above are indicated in appropriate footnotes of Table I. Particularly puzzling is the case of Cu{331}, for which three independent theoretical studies[5,8,9] predict the multilayer sequence $--+-\ldots$, in contrast to the otherwise expected $--+\ldots$. The only other fcc{331} surface studied experimentally, Al{331},[22] follows the rule appropriate to surfaces with three atom rows per terrace. In fact, for almost all stepped surfaces listed in Table I the experiments have confirmed the theoretical predictions (with the possible exception of Al{410}, for which, however, the experimental result is somewhat doubtful[30]). The anomalous behavior of Cu{331} makes it desirable therefore to try and test the theoretical predictions for this surface with an experimental determination of the multilayer relaxation. We have carried out such a test by using quantitative low-energy electron diffraction (QLEED), a most successful technique in surface crystallography. The results of our study are presented herein.

We describe in Sec. II the experimental procedures, in Sec. III the structure analysis, and in Sec. IV the conclusions.

II. EXPERIMENT

A large single crystal of copper was aligned with x-ray Laue diffraction patterns in a ⟨331⟩ direction. A 2-mm-thick platelet was cut with a diamond saw, then lapped and mechanically polished to within 0.5° of a {331} plane, and finally electropolished to produce a mirrorlike surface (courtesy of Dr. David Zehner and Mr. Gary Ownby of the Oak Ridge National Laboratory). The platelet was then secured on a tantalum plate and mounted on a sample holder in an experimental chamber provided with a rear-view LEED system and a cylindrical mirror analyzer for AES (Auger electron spectroscopy) analysis.

After pumping, baking, and outgassing, the base pressure in the experimental chamber was routinely 1×10^{-10} Torr or

TABLE I. Stepped surfaces of fcc and bcc metals studied either theoretically or experimentally, grouped according to the number of atom rows on each terrace. The relaxation sequences of compressions (−) and expansions (+) are often periodic. The last two columns list the references to theoretical and experimental studies, respectively.

Atom rows on terraces	Relaxation sequence	Surface	Terrace/step	Theory [Ref.]	Experiment [Ref.]
		fcc{110}	{111}/{111}	Al [1, 4, 9], Ag [9], Cu [9], Pd [2, 9]	Al [12], Ag [14, 15, 23], Cu [13, 14], Pd [21]
2	−+⋯	fcc{311}	{111}/{100}	[3], Al [7, 9], Ag [9], Cu [5, 9], Pd [9]	Al [19], Cu [24, 26] Ni [20]
		bcc{211}	{110}/{110}		Fe [16]
		bcc{310}	{110}/{100}	[3]	Fe [17], W [27][a]
		fcc{211}	{111}/{100}	[3], Al [9], Ag [9], Cu [8, 9, 11] Pd [9]	Cu [28]
		fcc{511}	{100}/{111}	Al [7, 9], Ag [9],	Cu [29]
3	−−+⋯			Cu [5, 8, 9], Pd [9]	
		fcc{210}	{110}/{100}		Al [24]
		fcc{320}	{110}/{100}		Cu [31]
		fcc{331}	{111}/{111}	Al [6, 9], Ag [9]	Al [22]
				Cu [5, 8, 9],[b] Pd [9]	Cu [this work]
		bcc{210}	{110}/{100}	3	Fe [18]
		fcc{221}	{111}/{111}	Al [9], Ag [9],[c]	
4	−−−+⋯			Cu [9],[d] Pd [9]	
		fcc{410}	{100}/{110}	[3], Cu [10]	Cu [32], Ag [30][e]
		fcc{711}	{100}/{111}	Al [7]	

[a]Experiment finds −−−−, but the relaxations of the spacings beyond the first are all very small.
[b]Theory predicts −+−−−.
[c]Theory predicts −−++.
[d]Theory predicts −−+−.
[e]Experiment finds 0−++.

lower. The sample surface was then cleaned with several cycles of argon-ion bombardments (5×10^{-5} Torr of Ar, 500 V, 2 μA) and anneals (800–900 °C for 0.5 h) until the AES signals of *C*, *S* and *O* (the only impurities present) were indistinguishable in the background noise of the analyzer.

The LEED pattern was the 1×1 pattern expected from an fcc{331} surface (depicted schematically in Fig. 1, bottom), featuring only one mirror line, which results from a bulk mirror plane perpendicular to the {331} surface. With the choice of unit mesh depicted in Fig. 1 (top) the mirror plane is perpendicular to the *x* axis, i.e., in reciprocal space, along the k_y axis, as drawn in Fig. 1 (bottom). The mirror line produces normal-incidence degeneracies such as, e.g., $10=\bar{1}\bar{1}$, $20=\bar{2}\bar{2}$, $1\bar{1}=\bar{1}0$, etc.

The orientation of the sample for normal incidence of the primary electron beam, the orientation desired for collection of diffracted intensity data, presented some difficulties, which were resolved as described in our study of the Cu{320} surface.[31] The intensities of several diffracted beams were collected as functions of the incident electron energy [the so-called $I(V)$ curves or spectra] with a video-LEED system involving a television camera and a computer as described elsewhere.[33] Many $I(V)$ spectra were collected, some of which were pairwise degenerate and accordingly averaged, providing 15 nondegenerate curves for the structure analysis. The total energy range amounts to $\Delta E=2880$ eV.

III. ANALYSIS

The calculations of diffracted intensities were done with the CHANGE computer program[34] on a desk-top personal computer. The Cu potential was taken from the collection of Moruzzi, Janak, and Williams:[35] eight phase shifts were used, and the number of beams was increased with the electron energy (the maximum being 113 beams at 380 eV). The inner potential was put equal to $-(10+4i)$ eV, with the real part adjustable in the course of the analysis, and the root-mean-square amplitude of thermal vibrations was $(\langle u^2\rangle)^{1/2}=0.15$ Å, corresponding to a Debye temperature $\Theta_D=304$ K.

Since the CHANGE program allows the bunching of several atomic layers into slabs,[34,36] with the present bulk interlayer spacing of 0.829 Å we decided to treat the bulk of the crystal as composed of slabs including three atomic layers each (calculations bunching four layers in each slab did not produce significant differences in the spectra), and initially two, then three, finally four atomic layers in the surface slab, thereby testing the first (12), the second (23), the third (34), and the fourth (45) interlayer spacing.

As mentioned above, the unit mesh in real space was chosen as the rhombus depicted in Fig. 1 (top), with one edge of 2.556 Å along the *x* axis (pointing to the left) and the other of 5.715 Å along the *y* axis (pointing up). The angle between *x* and *y* is 102.9°, and the *z* axis points *into* the bulk

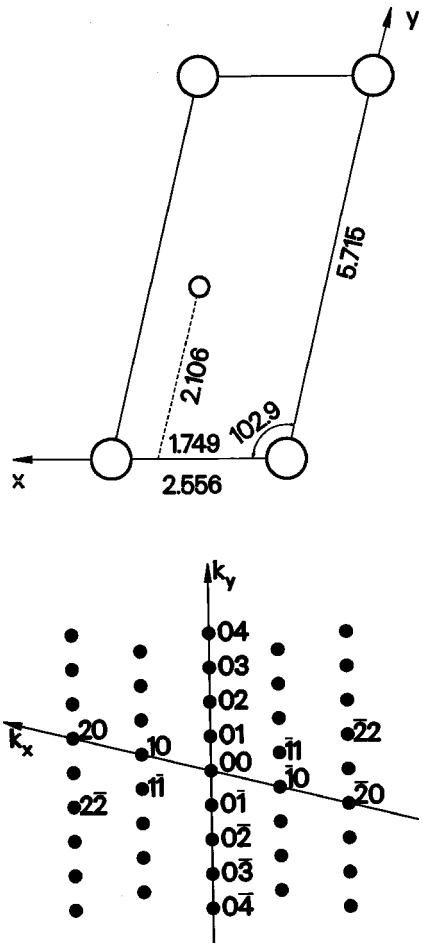

FIG. 1. Top: unit mesh of Cu{331}: distances in Å, angle in degrees. The *z* axis points *into* the bulk: the interlayer spacing is $d_{\text{bulk}}=0.829$ Å. Bottom: schematic LEED pattern with representative indexing. The k_y axis is a mirror line.

of the crystal, with interlayer spacing $d_{\text{bulk}}=0.829$ Å.

The search for the best structure parameters started with the determination of the azimuthal orientation of the sample in the experimental setup, as described, e.g., in Ref. 31. This determination is necessary in order to obtain correspondence between theoretical and experimental beam indices. The quality of fit between theory and experiment was judged both visually and by three *R* factors: R_{VHT},[37] r_{ZJ},[38] and R_P.[39]

With known orientation of the sample the first three interlayer spacings 12, 23, and 34 were varied systematically, each time keeping two of them constant and varying the third one. We use the notation, e.g., $\Delta d_{12}=-0.20(0.02)+0.10$ to indicate that the change Δd_{12} of the first interlayer spacing 12 was varied from -0.20 to $+0.10$ Å in steps of 0.02 Å. After several tests with different parameter values, the refinement was done on a ''grid search'' including $\Delta d_{12}=-0.14(0.01)-0.09$, $\Delta d_{23}=-0.050(0.025)+0.075$, $\Delta d_{34}=-0.02(0.01)+0.04$, and $\Delta d_{45}=-0.05(0.01)+0.05$.

With the best parameters thus found an attempt was made at testing the existence of possible parallel relaxations, since a shift of atoms along the mirror plane is possible. Normal-incidence LEED is not very sensitive to in-plane atom shifts, but we nevertheless tried to displace the atoms in the first four layers by the amounts found in the theoretical studies[8,9] involving registry shifts up to ± 0.02 Å in the direction perpendicular to the *x* axis. No improvement of the *R* factors was obtained.

Two of the *R* factors (R_{VHT} and R_P) have practically equal minima for slightly different values of the structural parameters. We find: $R_{VHT}=0.208/0.209$ for $\Delta d_{12}=-0.11/-0.12$ Å, $\Delta d_{23}=-0.005/+0.01$ Å, $\Delta d_{34}=+0.02/+0.03$ Å, and $\Delta d_{45}=-0.04/-0.04$ Å; $r_{ZJ}=0.079$ for $\Delta d_{12}=-0.11$ Å, $\Delta d_{23}=-0.005$ Å, $\Delta d_{34}=+0.004$ Å, and $\Delta d_{45}=-0.04$ Å; $R_P=0.344/0.348$ for $\Delta d_{12}=-0.11/-0.12$ Å, $\Delta d_{23}=+0.005/+0.01$ Å, $\Delta d_{34}=+0.03/+0.03$ Å, and $\Delta d_{45}=-0.03/-0.03$ Å. The experimental error is estimated to be ± 0.03 Å.

The average values of the relaxations given by the three *R*-factor minima are given in Table II together with the theoretical values published in Refs. 5, 8 and 9. We note that the *R* factors for the *unrelaxed* surface are: $R_{VHT}=0.356$, $r_{ZJ}=0.164$, and $R_P=0.579$, showing that the relaxed structure is a 58, 48, and 59% improvement, respectively, over the unrelaxed, bulk-terminated structure. In Figs. 2 and 3 we show experimental and calculated curves for all beams used in this analysis. The calculated curves correspond to the structure chosen by r_{ZJ}—they are visually almost indistinguishable from those chosen by the other two *R* factors.

IV. CONCLUSION

The structure of a clean Cu{331} surface was found by quantitative low-energy electron diffraction (QLEED) to have 13.8% contraction of the first interlayer spacing and

TABLE II. Multilayer relaxation of Cu{331}. Δd_{ij} is the change in the distance between layer *i* and layer *j*. The % column gives the value of $\Delta d_{ij}/d_{\text{bulk}}$, where d_{bulk} is the value of the interlayer spacing deep in the bulk: $d_{\text{bulk}}=0.829$ Å. The experimental error is estimated to be ± 0.03 Å, i.e., about $\pm 4\%$.

	Δd_{12}		Δd_{23}		Δd_{34}		Δd_{45}	
	Å	%	Å	%	Å	%	Å	%
Theory LGPL[a]	−0.073	−8.8	+0.022	+2.7	−0.015	−1.8	−0.001	−0.1
Theory DKR[b]	−0.086	−10.42	+0.014	+1.72	−0.014	−1.66	−0.002	−0.27
Theory SRC[c]	−0.087	−10.5	+0.017	+2.0	−0.012	−1.5	−0.003	−0.4
This work	−0.114	−13.8	+0.003	+0.4	+0.03	+4	−0.036	−4

[a]Reference 5.
[b]Reference 8.
[c]Reference 9.

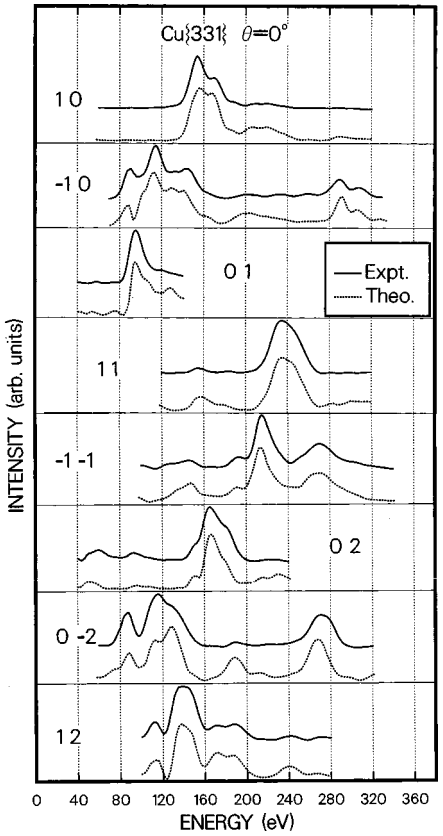

FIG. 2. Eight experimental (solid) and theoretical LEED $I(V)$ spectra for Cu{331}.

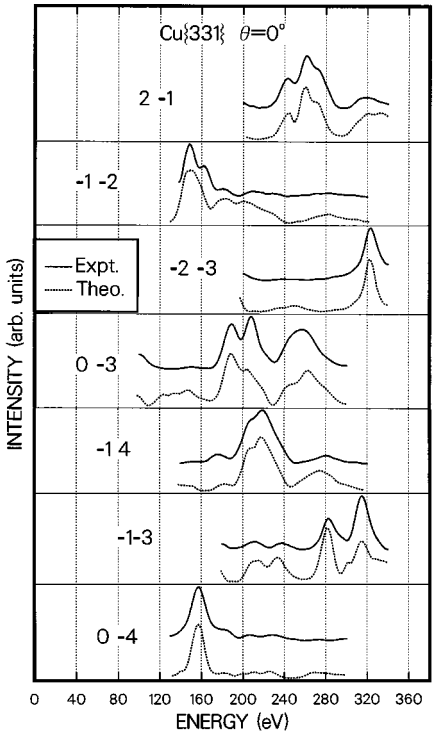

FIG. 3. Seven more experimental (solid) and theoretical (dotted) LEED $I(V)$ spectra for Cu{331}.

very small relaxations of the second, third, and fourth interlayer distance. The multilayer sequence found in the present work (see Table II) is $-++-$, apparently in contrast with the predicted $-+--$. But the relaxations of the layers beyond the first are so small, both in the theories and in the experiment (where in fact they are equal to, or smaller than, the experimental error) that one can claim agreement between theoretical predictions and experimental results. Just why the multilayer relaxation of Cu{331} is anomalous in the family of surfaces with three atom rows on each terrace is not clear at this time. A first-principle electronic structure study is necessary in order to advance our understanding of this phenomenon.

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