Structure and Vibrations of the Vicinal Copper (211) Surface

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We report a first-principles theoretical study of the surface relaxation and lattice dynamics of the Cu (211) surface using the plane-wave pseudopotential method. We find large atomic relaxations for the first several atomic layers near the step edges on this surface, and a substantial step-induced renormalization of the surface harmonic force constants. We use the results to study the harmonic fluctuations around the equilibrium structure and identify three new step-derived features in the zone-center vibrational spectrum. Comparisons of these results with previous theoretical work and with experimental studies using inelastic He atom scattering are reported.

I. INTRODUCTION

At a vicinal surface the average surface normal is tipped away from a high symmetry low-index direction, and the microscopic structure consists of an ordered array of atomic steps which separate low-index terraces. The microscopic atomic structure near a step edge is very different from that found in the bulk or at a low-index surface, and as a consequence one expects a substantial re-distribution of the valence electronic charge density near the step edges. This can play an important role in modifying the local dynamical properties and the chemical reactivity. Therefore stepped surfaces are important systems to study experimentally and theoretically. In fact the influence of steps on the surface chemistry can be so large that the macroscopic reactivity of many real surfaces is governed by dynamical phenomena at steps. Understanding these processes at the microscopic level can lead to control of surface dynamical phenomena through control and design of the surface structure.

Due to the importance of these structures, the dynamics of stepped surfaces have been the subject of several experimental investigations using modern surface-science techniques within the last several years. Witte and coworkers have studied the effects of surface steps on the surface vibrational spectra of Cu(211) and Cu(511) using inelastic He atom scattering \cite{1}. These studies were able to resolve clearly the zone-folding effects in the low frequency surface vibrational spectra due to the ordering of single atom steps on these surfaces. However, this work did not address the renormalization of the interatomic interactions which occur near the step edges, and the authors concluded that their observations could be interpreted within a model in which the parameters describing the surface atomic interactions were assigned their bulk values. More recently Niu et al. \cite{2} studied the dynamics of Ni(977) using inelastic He atom scattering. This work revealed a new step-derived branch in the surface vibrational spectrum which the authors associated with a new kind of surface sound wave, bound to the surface along the surface normal, and localized laterally to the surface step-edge. To understand the dynamics of this step-induced branch, these authors introduced a phenomenological model in which the step edge modes were interpreted as the modes of a stretched string running parallel to the surface. Using this model, the authors found that the effective elastic constants describing the harmonic fluctuations of the string were strongly renormalized from the values appropriate for bulk Ni or for a low-index Ni surface. However, subsequent theoretical work, based on a continuum model for a semi-infinite elastic medium, demonstrated that the step-derived features can be understood using continuum dynamics and enforcing the surface boundary condition appropriate to a weakly corrugated stepped surface \cite{3}. Thus the changes of the surface interatomic interactions near the step edges remains an important but unresolved issue.

In this paper we report a study of the surface structure and dynamics of the Cu(211) surface using first-principles pseudopotential theory. Previously, the equilibrium structures for various stepped vicinal surfaces have been examined theoretically using empirical interaction potentials \cite{4}, tight binding theory \cite{5}, effective medium theory \cite{6} and first-principles density functional theory \cite{7}. The former three methods are only tested in a highly coordinated bulk environment; the transferability of these approaches to the structures found on vicinal surfaces is thus open to question. First-principles total-energy calculations provide a parameter free method for studying equilibrium structures. Unfortunately the structural complexity of vicinal surfaces has made them nearly inaccessible by first-principles methods, particularly for the transition metals. Nonetheless several years ago Nelson and Feibelman \cite{8} reported the first \textit{ab initio} study of the equilibrium structure of a simple metallic vicinal surface, Al(331). These authors found that the atomic relaxations near the step edges are significantly enhanced with respect to those found at close-packed low-index surfaces, although the dynamical properties of the Al(331) surface were not investigated in their work.
Recent improvements in computational algorithms and hardware now allow the detailed exploration of realistic models for vicinal surfaces of transition metals using first-principles total-energy methods.

In this paper we apply the first-principles pseudopotential theory to study the equilibrium structure and dynamics of the Cu(211) surface. We find that atomic relaxations for Cu(211) are strongly enhanced in the first several layers near the surface step edges. This relaxation strongly changes the effective surface force constants from the values appropriate for the bulk or for a low-index surface. Nevertheless, we find that the dominant effect on the surface vibrational spectra is simply the lowering of the surface translational symmetry and the folding of the surface Brillouin zone at the stepped surface. Specifically, in our calculations we find three primary step-induced features in the vibrational spectrum at the surface Brillouin zone center. Two of these are the “backfolded” versions of the elementary surface elastic waves of the close packed (111) surface, while one is due to the renormalization of the surface interatomic force constants. One of our calculated low-energy modes is in good agreement with an excitation observed by inelastic He scattering experiments on Cu(211) [1], whereas the symmetry and energies of the other two features made them inaccessible in these measurements. In this paper we suggest other experimental probes which could be used to examine these latter excitations.

The remainder of this paper is organized as follows. In Section II we summarize the symmetry and structural features of the Cu(211) surface, and in Section III we briefly present our computational methodology. The equilibrium structure predicted in our calculations is presented in Section IV. In Section V we apply the model to determine the harmonic interlayer force constants near the surface, and use them to examine the surface vibrational excitations. In Section VI we analyze the step-induced features in the surface vibrational spectra. A discussion and summary of the results is presented in section VII.

II. STRUCTURE OF THE COPPER (211) SURFACE

The ideal lattice termination of the (211) surface of an fcc crystal is shown in the top panel of Figure 1. A more complete geometric classification of the atomic structure for stepped surfaces of fcc crystals with close-packed step terraces is given in Reference [6]. At the (211) surface the surface normal is rotated by 19.5° away from the (111) direction with the axis of rotation along the (01 ¯1) direction exposing (111) terraces containing 3 atoms separated by single atom (100) facets at the step edges. The Cu(211) surface has a primitive rectangular unit cell corresponding to a 3 x 1 reconstruction of the bulk lattice structure. The surface retains a mirror plane symmetry perpendicular to the (011) direction. Although this surface cell exhibits a microscopic faceted structure at the atomic scale, the unit cell is relatively compact and can be studied theoretically using conventional thin film supercell methods. The calculations reported below are carried out on a structural model in which a thin film containing 17 atoms in the primitive cell is terminated on its (211) and (211) planes. An illustration of this structural model, with the inequivalent lattice sites identified, is shown in the bottom panel of Figure 1.

III. COMPUTATIONAL METHODS

The calculations are carried out using density functional theory within the local density approximation (non-relativistic) [8]. The electron-ion potential for Cu is modeled using an optimized non-local soft core pseudopotential for the Cu 11+ ion. Cu, like other first row transition metals, is challenging for pseudopotential theory because it possesses an unscreened 3d valence shell. This implies that the peak in the 3d-derived valence charge density is relatively tightly bound to the core, and thus a well converged calculation requires a large energy cutoff in the plane wave basis set. This difficulty has been addressed and solved by the introduction of optimized pseudopotentials, which allow a well converged calculation of the 3d derived levels with only a modest energy cutoff in the plane wave basis set. A discussion of the construction and testing of these potentials can be found in Reference [1]. The reference state for our potential is the +1 ionic configuration for Cu with orbital occupancies 4s0.754p0.253d9. The one-electron wave functions are expanded in a plane-wave basis set, up to a kinetic energy cutoff of 50 Ry. Using this cutoff we find that the truncation error in the computed total energy is less than 1 mRy per atom. In the 17 layer thin film shown in Figure 1, the thin film structure is repeated periodically along the x direction with a 14.5 Å vacuum layer separating the neighboring films. For this structure approximately 25,000 plane waves are required in the basis set for the electronic degrees of freedom. We minimize the energy with respect to the plane-wave expansion coefficients using a pre-conditioned conjugate gradient algorithm described in detail in Reference [1].

Using this method for the bulk fcc structure in copper we calculate an equilibrium nearest-neighbor separation of 2.554 Å, which agrees quite well with the experimental value of 2.553 Å. As a test of the lattice dynamical properties of Cu using this potential, we also carried out frozen-phonon calculations of the (100) zone boundary transverse and longitudinal acoustic phonons in the bulk: the calculated (experimental) energies are: TA: 32.2 (30.2) meV, and LA: 22.8 (20.7) meV [11]. The bulk modulus is 1.63 x 1011 N/m² which is larger than, although comparable to, the observed value 1.42 x 1011 N/m² [11]. All these results are in good agreement with experiment and in excellent agreement with several pre-
vious theoretical studies of the bulk elastic properties of Cu within the local density approximation. Our calculations are nonrelativistic, that is we have not included scalar relativistic corrections in our theory. These are known to introduce a slight (1% - 1.5%) additional contraction in the predicted lattice constant, and a corresponding increase in the bulk modulus.

To study the harmonic fluctuations around the equilibrium structure, we compute the distribution of forces at all of the lattice sites of the thin film produced in response to separate small displacements of each of the atoms away from their equilibrium locations. The maximum ionic displacement that we studied in these calculations is 0.05 Å. Using the Hellmann-Feynman theorem, the induced force on the \( i \)-th site in the \( \alpha \)-th polarization is

\[
F_{i,\alpha} = -\partial U/\partial x_{i,\alpha} = -\langle \partial H/\partial x_{i,\alpha} \rangle
\]

where \( H \) is the Kohn-Sham Hamiltonian for the coupled electron-ion system, and the brackets denote an expectation value in the relaxed electronic ground state in the presence of the ionic displacement. The harmonic interaction constant coupling the \( i\alpha \) and \( j\beta \) displacements is

\[
K_{\alpha,\beta}(i,j) = \partial^2 U/\partial x_{i,\alpha}\partial x_{j,\beta} = -\langle \partial^2 H/\partial x_{i,\alpha}\partial x_{j,\beta} \rangle.
\]

The displacement fields and forces calculated by this method describe the dynamics at the center of the folded Brillouin zone for the stepped surface, and in the analysis below we consider only the vibrational spectra at \( \Gamma \).

The harmonic interlayer force constants calculated from our thin film describe the physics only within the region near the surface (half the thickness of our film). This is insufficient to describe realistically the dynamics of a semi-infinite crystal terminated on the \( \{211\} \) plane. To remedy this problem, we carry out a separate calculation to obtain the analogous interlayer force constants for Cu in its bulk fcc structure. We then construct a composite model in which the surface region is recoupled to a very thick unperturbed bulk film containing \( \approx 1000 \) atomic layers. This expanded film is sufficiently large to allow us to locate critical points in the bulk phonon spectra accurately and to represent the bulk and surface modes of our system properly. Since the dynamical matrix is computed at the center of the surface Brillouin zone, mirror reflection through the \( \{011\} \) plane remains a valid symmetry, and therefore the dynamical matrix can be decoupled into two sectors describing lattice modes which are even and odd under reflection through this mirror plane.

IV. EQUILIBRIUM STRUCTURE

Figure 2 illustrates the atomic structure of the \( \{211\} \) surface of our fcc crystal. The arrows represent magnified displacements of each of the atoms from its position in the ideal termination of the bulk Cu lattice to its position in the equilibrium structure (for clarity these displacements have been magnified by roughly a factor of 20). By symmetry the atomic displacements in the relaxed structure are confined to the plane perpendicular to the step edge (i.e. the \( \{011\} \) plane). We find that the lateral displacements, i.e. along the \( \{111\} \) direction, while allowed by symmetry, are all relatively small; the largest of these corresponds to \( \approx 1.5\% \) of the lateral spacing in the bulk. By contrast the displacements along the surface normal are quite substantial near the surface. The relaxation of the distance between the two outermost atomic layers is \(-14.4\%\) of the bulk interlayer spacing in this direction. For the fully relaxed geometry the fractional change of the nearest-neighbor distance from the step edge atoms is nearly 4% of the bulk nearest-neighbor spacing. For comparison, at the Cu(111) surface the inward relaxation of the top surface layer reduces the nearest-neighbor spacing by 0.8% and for Cu(100) the nearest-neighbor spacing is reduced by 1%. Thus for the vicinal surface the atomic relaxations along the surface normal are substantially larger than obtained for a close packed low index surface. The relaxation within the surface plane is quite small.

The displacement pattern shown in Figure 2 illustrates the Smoluchowski effect which predicts a reduction of the height of the step edge in the equilibrium structure. Qualitatively the conduction electron density leaks away from the crystal at the step edge, tending to smooth the step edge profile. It is easy to see that this generates an electric field which pulls the ion at the inside corner of the step edge away from the thin film and pushes the ion at the outside corner towards the film. A detailed tabulation of the calculated atomic displacements is given in Table I. In addition these results show that the structure obtained near the center of the slab is essentially the bulk fcc structure, and so the film thickness is sufficient to describe the relaxation of the isolated \( \{211\} \) surface accurately.

V. INTERLAYER FORCE CONSTANTS

To study the harmonic fluctuations around the equilibrium relaxed structure, we calculate the interlayer force constants in our film following the method outlined in Section III. The atomic relaxation at the surface leads to very large modifications of the harmonic interlayer force constants near the surface region. In Table II we report a set of selected interatomic interactions near the surface, and compare these with their corresponding unperturbed bulk values. We can clearly identify the following trends. The interlayer coupling constants for displacements polarized along the surface normal is much larger at the stepped surface than in the bulk. For example the harmonic interaction constant which couples the displacement of surface site \( 1 \) to the nearest-neighbor subsurface site, \( K_{xx}(1,4) \), is 4.52 eV/Å\(^2\) at the surface while the comparable interaction is 2.89 eV/Å\(^2\) in the bulk. The intra-terrace interactions are also strongly renormalized at the surface; as an example we find that \( K_{xx}(1,2) = \)

\[ \]
ample the surface (bulk) interaction constant compared with the bulk value $0.12 \, \text{eV}/\AA^2$. For displacements polarized within the surface plane, the surface force constants are again larger, although the changes of the force constants are more modest, and quite comparable to those obtained for a flat low-index surface [17]. For example, the surface (bulk) interaction constant $K_{z z}(1,2) = 3.24(2.70) \, \text{eV}/\AA^2$ and $K_{z z}(1,4) = 0.40(0.21) \, \text{eV}/\AA^2$. Note that the latter represents a very large fractional renormalization of the surface interaction; this is mainly due to the fact that the interlayer coupling between displacements parallel to the surface plane is relatively small in both environments. The renormalization of the surface interaction constants for displacements parallel to the step direction is similar, e.g., $K_{y y}(1,2) = 1.27(0.92) \, \text{eV}/\AA^2$ and $K_{y y}(1,4) = 1.47(0.92) \, \text{eV}/\AA^2$. Generally we find that all the interaction constants are strongly enhanced near the step edges at the surface and this effect tends to offset the rather large decrease in the coordination number for the surface species. This is most clearly seen by inspecting the diagonal interaction constants for atoms on a common terrace. For example, the interac-

### VI. SURFACE VIBRATIONAL SPECTRA

We combine the interlayer force constants for the Cu(211) surface region with the values calculated for bulk Cu to obtain a composite dynamical matrix for a thick Cu film which terminates on a (211) lattice plane. The dynamical matrix is decoupled into two sectors describing the modes of the combined systems which are even and odd, respectively, under reflection through the (011) mirror plane. For a slab containing $N$ atoms, the dimensions of the even and odd subspaces are $2N$ and $N$ respectively.

In Figures 3 and 4 we present results for the symmetry-projected densities of vibrational states as a function of frequency at the $\bar{\Gamma}$-point in the surface Brillouin zone. Figure 3 gives the density of modes which are even under reflection through the surface mirror plane. The thin solid curve is obtained from a sum over all the modes of the composite slab, while the bold solid curve gives the local density of states $n_s(\omega) = \sum_n \sum_{\alpha,\alpha'} |\phi_{\alpha,n}|^2 \delta(\omega - \omega_n)$ where $\phi_{\alpha,n}$ is the amplitude of the $n$-th normal mode on site $i$ with polarization $\alpha$, and where the sum over $\alpha$ runs over the symmetry allowed displacements of the three atoms on the outermost surface terrace, and the sum over $n$ runs over all the modes of the slab.

The surface projected density of even states clearly reveals two step-induced features in the surface vibrational spectrum at $\bar{\Gamma}$. The lower of these, at an energy of 11.5 meV, is a backfolded image of the Rayleigh wave of the “flat” (211) surface which would appear at a momentum $q = 1.005 \, \text{Å}^{-1}$ along the (111) direction in a continuum theory. We find that the $q = \pm 1.005 \, \text{Å}^{-1}$ backfolded branches are strongly mixed by the cell periodic variations in the surface dynamical matrix so that only the lower branch remains localized below the nearby bulk transverse threshold at 12.4 meV. This excitation is a surface “standing wave” trapped on the surface terrace. This can be seen more clearly in the map of the displacement pattern for this feature plotted in Figure 5. It shows that the largest atomic displacements occur at the center of the surface terraces and are reduced at the step edges, an effect which can be seen clearly in the subsurface displacement field. Nevertheless this mode possesses a large amplitude at the surface, polarized along the surface normal, and so this branch is expected to be strongly allowed in inelastic atom scattering from the surface. Indeed, the calculated frequency agrees closely with the 10.9 meV feature observed in inelastic He scattering experiments from Cu(211) [1].

The backfolded Rayleigh branch overlaps the projected bulk continuum at $\bar{\Gamma}$, yet the mode remains quite sharp in the surface-projected vibrational spectrum. Within a continuum elastic theory, mixing between the backfolded Rayleigh mode and the projected bulk modes is dynamically forbidden at $\bar{\Gamma}$, since in the continuum theory the coupling between the two is mediated by the surface strain which vanishes for the lowest branch of bulk acoustic waves at $\bar{\Gamma}$ [3]. This dynamical symmetry can be weakly violated in a lattice model. However, the sharpness of this surface-derived feature in the vibrational spectrum shows that the mixing remains very weak, even for the relatively narrow terraces found on Cu (211).

At higher energy we find a second strong step induced surface feature at 24.7 meV which corresponds to a backfolded image of the surface longitudinal resonance of a flat surface. The displacement field associated with this mode is illustrated in Figure 6. Note that the surface displacements have their largest amplitudes polarized mainly parallel to the plane containing the surface terraces. This mode can also be understood as a surface standing wave which is trapped laterally by repeated scattering from the step edges. However, it is apparent from the plot of the displacement field, that the effect of scattering from the step edges is much weaker than one finds for the lower energy backfolded Rayleigh mode. This is because this higher energy feature is not a true surface-localized mode, but is resonantly mixed with propagating bulk acoustic waves which penetrate infinitely deeply into the bulk. Since the displacement field for this mode is polarized mainly within the surface plane we expect it to be a poor candidate for study by inelastic atom scattering, which is most sensitive to atomic displacements along the surface normal. Nevertheless, it is very interesting that, unlike the situation
for a flat low index surface, a linear coupling between the backfolded longitudinal resonance and charge fluctuations along the surface normal is allowed by symmetry in this system since both excitations are even with respect to the (011) mirror plane. This opens the possibility of probing this excitation by inelastic scattering of a charged probe (e.g., high resolution inelastic electron scattering) from the surface. Further theoretical work is needed to quantify the magnitude of the charge fluctuations coupled to this mode. We expect that the important charge fluctuations coupled to the zone folded longitudinal resonance will be found at the step edges, and that this coupling can be used to probe the dynamics of the conduction electrons near the steps.

Figure 4 shows the zone center vibrational spectra for modes that are odd with respect to the (011) mirror plane. The thin solid curve represents the spectrum summed over all the modes of the film, while the bold curve gives the modes weighted by the squares of the displacement fields in the surface terrace. Here the step induced features, though present, are much more subtle. A broad transverse resonance, labeled TA2, is found centered at 11.3 meV just below the bulk projected critical point. The displacement field for this excitation is plotted in Figure 7. We see that the mode corresponds to a transverse shear wave which is strongly laterally confined at the step edges. This mode is completely absent within a simple continuum elastic theory, and its appearance in the spectrum directly reflects the rather substantial renormalization of the interatomic force constants within the surface region. This mode is a poor candidate for study using neutral-atom scattering since, as shown in Figure 7, it is polarized in the surface plane, along the (011) direction and is odd under the surface mirror plane. Likewise linear coupling between this mode and z-polarized charge fluctuations is symmetry forbidden, and therefore this mode will be silent in charged-particle scattering as well.

VII. DISCUSSION

In this section we compare our results to experimental measurements of the surface phonon spectra on the Cu(211) surface and to related previous theoretical work. Witte et al. used inelastic He scattering to study the phonons of the Cu(211) surface. These authors experimentally studied the surface vibrational excitations below 15 meV as a function of momentum transfer in the surface plane, both parallel and perpendicular to the surface steps. At the surface Brillouin zone center, $\Gamma$, an excitation polarized along the surface normal at an energy of 10.9 meV was observed and assigned to the backfolded image of the Rayleigh wave of a flat surface. This agrees quite well with the Rayleigh mode we calculate at 11.5 meV. The experiments do not extend to sufficiently high energy to detect the backfolded LA resonance, which we find at 24.7 meV. Furthermore, as we commented in the previous section, the 11.3 meV TA2 resonance has atomic displacements parallel to the surface plane, and would normally be undetectable by neutral-atom scattering.

These authors also report a study of the surface dynamics using a central nearest-neighbor harmonic force constant model. Qualitatively, this simple model correctly reproduces the zone-center surface excitations which we have calculated. The agreement between the two theories is at first surprising in view of the rather large changes of the surface harmonic interactions which we presented in Tables 2 and 3. However, in the long wavelength limit these surface features are “leaky” excitations which penetrate well below the first atomic layer of the surface. The calculated frequency of such an excitation is relatively insensitive to the precise value of the surface interatomic interactions, and instead depends on the fact that propagating elastic waves will be perfectly reflected from the surface. Close to the surface Brillouin zone boundaries the effective penetration depth of these modes is substantially smaller, and the frequencies are much more sensitive to the surface interatomic potentials.

More recently Durukanoglu, Kara and Rahman (DKR) reported a theoretical study of the equilibrium structure and dynamics of Cu vicinals using the embedded atom method (EAM). For Cu(211), these authors also observed enhanced structural relaxations near the step edges as we do, and the magnitudes of their predicted relaxations are consistent with the trends we display in Table I. They also compute interatomic force constants near the step edges, and find that the interatomic force constants are enhanced near the step edges. DKR also note that the diagonal elements of the dynamical matrix are decreased relative to their bulk values; this follows directly from the lower coordination of the surface atoms. Thus the off-diagonal terms provide a useful quantitative measure of the enhancement of the “back bonding” of under-coordinated atoms near the step edges. Although the EAM and LDA results both indicate an enhancement of these interactions, the enhancement is approximately twice as large within the LDA than that obtained with the EAM model. The local density approximation provides a more complete description of the relaxation of the conduction charge density, particularly near the step edges. In our view this quantitative discrepancy between the calculated force constants reflects the fact that these depend rather sensitively on the relaxation of the charge density near the step sites.

Our calculations point to an important piece of new physics at the stepped surface. As we emphasized in Section VI, the surface lattice dynamics is dominated by a simple zone folding effect by which the finite momentum Rayleigh wave, and longitudinal resonance are folded back through the surface Brillouin zone center $\Gamma$. Normally these excitations are observed as modes with finite momentum transfer in the surface plane and are accessible only by neutral atom scattering or by inelastic...
electron scattering in the impact regime. On the vicinal surface, these backfolded modes can be coupled to charge fluctuations near the surface, an effect which we expect to be particularly strong near the step edges. Thus these excitations can be coupled to a macroscopic charge fluctuation of the surface dipole layer, and are accessible by inelastic electron scattering. This is particularly significant because inelastic electron scattering can be used to study the dynamics of the conduction charge near step edges, and to examine the effects of adsorbates, step wandering, etc. on this coupling. These are central issues in the surface chemistry associated with the step edges, and we are therefore currently investigating this effect theoretically by calculating the strength of this coupling.

In summary, we have reported the first ab-initio study of the structure and dynamics of a stepped surface for a transition metal. We find that atomic relaxations near the step edges for the Cu(211) surface are substantially enhanced with respect to their counterparts at a low index surface. This produces very large changes of the surface harmonic force constants, much larger than inferred from previous experiment and theory. For the Cu(211) surface we find that there are three important step-derived excitations in the Brillouin zone center vibrational spectrum. Our result for the frequency of one mode, corresponding to a backfolded Rayleigh wave agrees well with experimental measurements using inelastic He scattering. The two other features were inaccessible to these measurements, and we have suggested a method for observing these other excitations.

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**TABLE I.** Summary of data for the calculated equilibrium structure of Cu(211). The data give the percentage changes in interatomic spacings with respect to the ideal termination of the bulk fcc lattice along a (211) plane. $d_{ij}$ label interlayer distances along the surface normal, and $l_{ij}$ label distances parallel to the surface plane, along the (111) direction.

| Relaxation (%) | Registry (%) |
|----------------|--------------|
| $d_{12}$       | $l_{12}$     |
| $d_{23}$       | $l_{23}$     |
| $d_{34}$       | $l_{34}$     |
| $d_{45}$       | $l_{45}$     |
| $d_{56}$       | $l_{56}$     |
| $d_{67}$       | $l_{67}$     |
| $d_{78}$       | $l_{78}$     |
| $d_{89}$       | $l_{89}$     |

| Polarization | $K_{\alpha}(1,4)$ | $K_{\alpha}(1,2)$ |
|--------------|------------------|------------------|
| surface      | $\alpha = x$     | 4.52             | 0.41             |
| bulk         | $\alpha = x$     | 2.89             | 0.12             |
| surface      | $\alpha = y$     | 1.47             | 1.27             |
| bulk         | $\alpha = y$     | 0.92             | 0.92             |
| surface      | $\alpha = z$     | -0.49            | 3.24             |
| bulk         | $\alpha = z$     | -0.21            | 2.70             |

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TABLE III. Diagonal components of the harmonic force constants for the surface terrace atoms on Cu(211). The values of $K_{xx}(i, i)$ are given in eV/Å$^2$ for the three atoms along the surface terrace, using the labeling convention of Figure 1.

| $K_{xx}(1,1)$ | $K_{xx}(2,2)$ | $K_{xx}(3,3)$ |
|---------------|---------------|---------------|
| -5.77        | -4.61         | -4.37         |

FIG. 1. Structure of the Cu(211) vicinal surface. The surface consists of three-atom (111) terraces separated by single atom (100) steps. The lattice parameters and conventions for our coordinate system are illustrated in the top panel. We model the (211) surface with a film containing 17 Cu sites. The lower panel is a projection of this film on the (011) plane with the atoms in the unit cell identified.

FIG. 2. Atomic displacements in the equilibrium structure of our model thin film for Cu(211). The arrows show the magnified displacements of each atom from its position in the ideal lattice termination to the equilibrium position. For clarity the displacements have been magnified by roughly a factor of 20.
FIG. 3. Vibrational densities of states for the Cu(211) film. The spectra give the densities of states for modes which are even under reflection through the (011) mirror plane. The light curve is a trace over even modes of the expanded film. The bold curve is a trace over the modes weighted by the squares of the normal-mode amplitudes in the surface terrace.

FIG. 4. Vibrational densities of states for the Cu(211) film. The spectra give the densities of states for modes which are odd under reflection through the (011) mirror plane. The light curve is a trace over odd modes of the expanded film. The bold curve is a trace over the modes weighted by the squares of the normal-mode amplitudes in the surface terrace.

FIG. 5. A snapshot of the displacement field for the backfolded Rayleigh mode at 11.5 meV in the surface vibrational spectrum. The amplitudes decay exponentially into the bulk. At the surface, this mode has a standing wave pattern which is “pinched” at the step edges.
FIG. 6. A snapshot of the displacement field for the backfolded longitudinal resonance centered at 24.7 meV. The mode is weakly resonant with bulk excitations. At the surface, the atomic displacements are mainly polarized parallel to the surface.

FIG. 7. A snapshot of the displacement field for the TA2 resonance centered at 11.3 meV. This mode is odd under reflection through the (011) mirror plane, and can be described as a shear horizontal mode polarized parallel to the surface steps and localized at the surface step edge.
frequency (cm$^{-1}$)

density of states (states/cm$^{-1}$/atom)

- surface-projected DOS
- total DOS

TA2 Resonance