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# Structure of Ag(410) and Cu(320)

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We present results of calculations of atomic relaxations on two stepped surfaces Ag(410) and Cu(320) using interatomic potentials from the embedded atom method. Relaxations are found to extend several layers into the bulk, the most striking feature of which is the nonuniform character in damping magnitudes of interlayer relaxations away from the surface into the bulk. The calculated contractions (with respect to the bulk) of 11.6, 5.3, and 9.9 % for the top three interlayer separations of Ag(410) are followed by expansion of 2.1 and 6.7% for the subsequent two interlayer spacings. For Cu(320) contractions of 13.6 and 9.2% of the first two interplaner distances are followed by expansion of 2.9%, contraction of 8.8%, and expansion of 10.7% for the next three. These results are compared with the recent low energy electron diffraction data. Moreover, characteristics in the atomic relaxations around the steps are traced to the changes, relative to the bulk, in the local force fields in these vicinities.

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## I. INTRODUCTION

Structural properties of regularly stepped (so-called vicinal) metal surfaces have been the focus of a broad range of theoretical and experimental studies because of the eminent role they play in technologically important phenomena, such as thin film growth, epitaxial layer formation, and catalysis. The microscopic structure of a vicinal (a high Miller index) surface differs from that of a flat (a low Miller index) surface in that it consists of an array of atomic steps, separating low-index terraces. The presence of such defects ( steps on a surface) is expected to induce a substantial local rearrangement of electronic and ionic structure in their vicinity. As a consequence, the force fields in the region around steps might be modified which in turn may result in local structural relaxation of atoms around steps. Also, knowledge of atomic relaxations in the equilibrium positions near the step and kink sites is the first step towards understanding the novel vibrational and electronic properties of vicinal surfaces.

With advances in atomic scale experimental techniques, there has been a surge in investigations of the structure of vicinal surfaces in the recent years. While a variety of possible experimental methods are now available,[1] the brunt of the experimental data have come from the low-energy electron diffraction (LEED) technique. These studies have, however, been confined to vicinal surfaces whose bulk interlayer spacing is greater than 1 Å, because of computational limitations in analyzing the experimental data.[2,3] Recently, Jona *et al.* have introduced an updated version of a computer program to overcome the difficulty of handling experimental data for interlayer spacings smaller than 1 Å.[4] In two separate papers they have applied this program to analyze quantitative LEED data to determine the structure of Ag(410) and Cu(320) for which the bulk interlayer spacing $d_{bb}$ are 0.496 and 0.501 Å, respectively.[4,5] These two surfaces of fcc metals are interestingly different: fcc(410) is a vicinal of the (100) surface having a (110)-microfacetted step edge, while the fcc(320) is a vicinal of the (110) surface with a (100)-microfacetted step edge. A comparative study of these two surfaces of fcc metals provides an opportunity for comparing the effect of differences in the local geometries of atoms in regions of low coordination. Since experimental data for multilayer relaxation is available on Ag(410) and Cu(320), we have found it opportune to carry out calculations for the same two surfaces. From our previous work[6] on vicinal surfaces, we expect similarity in the relaxation patterns of corresponding vicinal surfaces of Ag and Cu. A comparison of the results obtained here for Ag(410) with our earlier study of Cu(410) will provide further test for their structural similarity.

From the analysis of the QLEED data for Ag(410), Jona *et al.* concluded that there was no measurable relaxation of the first interlayer spacing with respect to that in the bulk solid. However, in our previous study on atomic relaxations of Cu(410) we found a contraction of 12.67% for $d_{12}$,[7] where $d_{ij}$ is the spacing between layers $i$ and $j$. Since we have reasons to believe that Ag and Cu surfaces have similar trends in surface relaxations,[8] we find QLEED results for Ag(410) puzzling. In contrast to the null relaxation of the first interlayer spacing, the same QLEED data analysis show 36% contraction for $d_{23}$ and 18% expansion for $d_{34}$. On the other hand, QLEED measurements on Cu(320) revealed 24% contraction for $d_{12}$ and 16% for $d_{23}$, followed by 10% expansion of the third interlayer spacing. While the inward relaxation of the step atoms on vicinal surfaces of fcc metals appears to be a standard phenomenon,[9] in a set of theoretical and experimental studies of the vicinals of Cu(100) and Cu(111),[10] it is found that the relaxations of atoms in the top layers are such that all terrace atoms move inwards, except for the corner atoms which move outwards, to preserve the smoothing of the electronic charge density. These conclusions have been further corroborated by recent *ab initio* calculations[11] of Pd(320) and Pd(551)—both vicinals of Pd(110)—which point to an outward relaxation of the atoms in the fifth layer, coupled with inward relaxations of the atoms in other top layers. The positive enhancement of $d_{34}$ for vicinals of fcc(100) and of $d_{56}$ for vicinals of fcc(110) is particularly interesting from consideration of local coordinations of these atoms. On these two types of vicinals with 3-atom-wide terraces the third and fifth layer atoms on the respective surfaces are the least undercoordinated with respect to those in the bulk. Together, the results on vicinals of Cu(111), Cu(100), Pd(111) and Pd(110) thus imply that the most striking increase in spacing is between the least undercoordinated atom and its bulk neighbor. In view of the implications of these theoretical results, and the above mentioned differences in the experimental results on multilayer relaxations of Ag(410) and Cu(320), we present in this work an atomistic study of the structural properties of these two surfaces, using the vastly tested and reliable many-body interaction potentials extracted from embedded atom method (EAM). A related examination of the modifications in the force fields around the steps provides further insights into the relaxation trends. The rest of this paper is organized as follows. In Sec. II, the system geometries are presented together with some computational details. Section III contains the structural features of the associated surfaces. Concluding remarks are presented in Sec. IV.

## II. SURFACE GEOMETRIES AND COMPUTATIONAL DETAILS

The fcc(410) surface is a vicinal of (100) constructed by slicing the crystal at an angle of 14.04° away from the (100) plane and towards the [010] direction. The compact step notation for this surface is 4(100)×(110), which conveys the information that the four-atom-wide (100) terraces are separated by (110) microfacetted steps as shown in Fig. 1. On the other hand, the fcc(320) surface is a vicinal of (110) fabricated by cutting the crystal at an angle of 11.31° away from the (101) plane and towards the [001] direction. It consists of (100) monoatomic steps separating three-atom-wide (110) terraces as shown in Fig. 2. As indicated in Figs. 1 and 2, the $x$ and $y$ axes lie in the surface plane and are, respectively, perpendicular to and along the step edge, while the $z$ axis is along the surface normal. We label the four chains of atoms on the terrace of Ag(410) as corner chain (CC), second middle chain (2MC), first middle chain (1MC), and step chain (SC). The respective coordinations of these atoms are 9, 8, 8 and 7. The chain just underneath the step chain is called a sub step chain (SSC) and has atomic coordination of 11. These five chains comprise the set of five undercoordinated sites on fcc(410) and are also the top five layers on this surface. Bulk coordination begins with the sixth layer (BNN), making the fifth layer (SSC) atoms the least undercoordinated. Similarly, the three chains on Cu(320) terraces are labeled as corner chain (CC), middle chain (MC), and step chain (SC), with respective coordinations of 9, 7, and 6. On this surface, atoms in the next two chains (layers) are also undercoordinated (coordination of 11) and exposed to the vacuum. The fourth layer is labeled as subterrace chain (STC). As with fcc(410), bulk coordination on fcc(320) begins with layer 6 (BNN). Our calculations for Ag(410) and Cu(320) are performed using a 90-layer and a 72-layer super cell, respectively. In the simulations, periodic boundary conditions are applied along the $x$ and $y$ directions, while no such constraint is imposed along the $z$ direction.

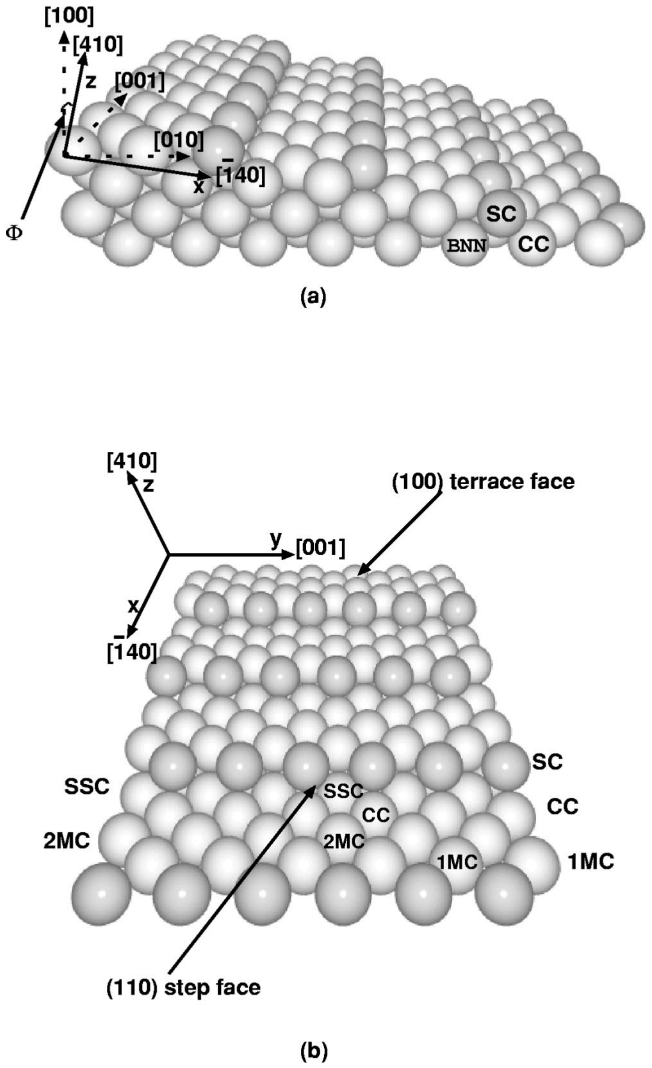

FIG. 1. (a) Side and (b) top views of fcc(410). Here $x$, $y$, and $z$ are the Cartesian coordinate axes. $\phi$ is the miscut angle. The interlayer spacing along [100] is $d=a/2$, $a$ being the lattice parameter.

The embedded atom method (EAM) is used to describe the interactions between the atoms in the model systems. The interaction potential is semiempirical and many body in nature and has proved to be reliable in describing a variety of properties in the bulk and at surfaces for six fcc metals Cu, Ag, Ni, Pd, Pt, and Au.[12] We have also found the EAM potentials to be reliable for examining the temperature dependent structure and dynamics of Cu and Ag flat surfaces and describing the energetics and structures of Cu vicinal surfaces.[13] The model system is constructed in its bulk terminated geometry and the standard conjugate gradient method is used to minimize the total energy of the system and thus to relax the atoms in the systems to their 0 K equilibrium configuration. Atomic force constants are then obtained from analytical expressions for the partial second derivatives of EAM potentials.[12]

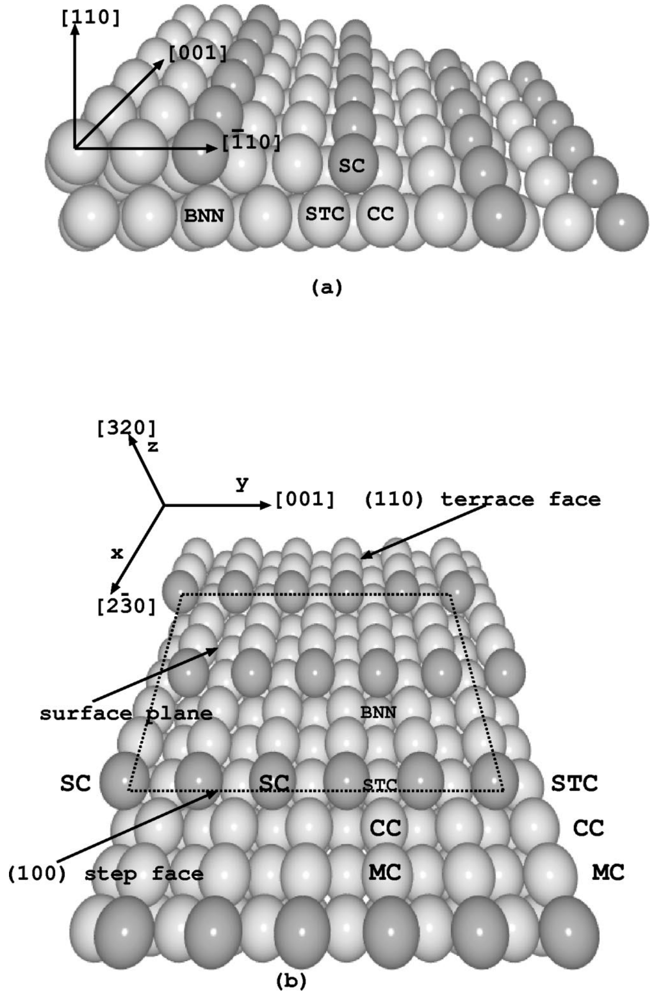

FIG. 2. (a) Side and (b) top views of fcc(320). Here *x*, *y*, *z* are the orthogonal coordinate axes.

## III. RESULTS AND DISCUSSIONS

Unlike flat surfaces, vicinal surfaces relax in both *x* and *z* directions, since the existence of steps at the surface leads to broken symmetry in both of these directions. The relaxations along the *z* direction yield characteristic interlayer separations, while those along the *x* direction provide new registries of atoms (in plane relaxations), as compared to those in the bulk.[9] Relaxations along the *y* direction are symmetry forbidden. Our calculated percentage interlayer spacing and registries for Ag(410) and Cu(320), together with available QLEED data are summarized in Tables I and II. For both surfaces, the largest interlayer relaxation occurs for $d_{12}$. Note that such characteristic behavior in the first interlayer spacing have been reported for several metal vicinal surfaces,[6,9–11] including Cu(410).[7] Results in Table I also predict significant relaxations for several successive interlayer separations which are, however, smaller than the reported QLEED values. It is thus very surprising that the analysis of QLEED data for Ag(410) reveals no measurable relaxation for $d_{12}$.[4] These disagreements may not be a real problem as the authors in the associated work have already recognized the uncertainty in the determination of the interlayer relaxations of Ag(410) because the analysis was based on a limited data base, which was gathered using older techniques.[4] The analysis of the recent QLEED data for the multilayer relaxation of Cu(320) (Ref. 5) is found to be in better qualitative agreement with our calculated values. As seen in Table I, the oscillation of the interlayer relaxations for Ag(410) and Cu(320) are (-,-,-,+,+,-,-) and (-,-,+,-,+,-,-), respectively. It is worth nothing that results from our previous calculations on the surface structure of Cu(410) reveal a similar oscillatory behavior to that of Ag(410).[7] The finding of a striking expansion for $d_{56}$ for both surfaces in Table I [and also for Cu(410)] is indeed very appealing. It agrees with the conclusions of *ab initio* calculations for Pd(320) and Pd(551).[11] As noted above for fcc(320) and fcc(410), the least undercoordinated atoms on fcc(551) are also in layer 5, while those in layer 6 are bulklike. Thus while the step atoms move inwards, these fifth layer atoms adjust their positions to smoothen the charge density in the surface region.

TABLE I. Calculated and experimental percentage change in interlayer spacing $d_{i,i+1}$ for Ag(410) and Cu(320). Here $d_{i,i+1} = 100\times[(z_i - z_{i+1}) - d_{bb}]/d_{bb}$ where $d_{bb}$ is the corresponding interlayer distance in the bulk.

| Spacing | Ag(410) (this work) | Ag(410) (QLEED) | Cu(320) (this work) | Cu(320) (QLEED) |
|---|---|---|---|---|
| $d_{12}$ | −11.64% | 0% | −13.63% | −24±6% |
| $d_{23}$ | −5.26% | −36% | −9.19% | −16±12% |
| $d_{34}$ | −9.94% | +18% | +2.88% | +10±6% |
| $d_{45}$ | +2.11% | | −8.78% | |
| $d_{56}$ | +6.69% | | +10.69% | |
| $d_{67}$ | −3.89% | | −6.07% | |
| $d_{78}$ | −3.69% | | −1.63% | |

On vicinal surfaces there is also the issue of readjustments in atomic positions within the layer. These give rise to interlayer registry relaxations, which we have summarized in Table II. We find small percentage changes which may lie well within the experimental error bars. The interlayer relaxations and registries noted above manifest themselves in changes in the *x*, *y*, and *z* components of the interatomic distances between the step atom (SC) and its nearest neighbors, as compared to the corresponding bulk values. For

TABLE II. Calculated percentage change in registries $r_{i,i+1}$ for Ag(410) and Cu(320). Here $r_{i,i+1} = 100\times[(x_i - x_{i+1}) - r_{bb}]/r_{bb}$ where $r_{bb}$ is the corresponding intralayer separation along *x* in the bulk and is 1.984 Å for Ag(410) and 2.506 Å for Cu(320).

| Spacing | Ag(410) (this work) | Cu(320) (this work) |
|---|---|---|
| $r_{12}$ | −2.31% | −0.59% |
| $r_{23}$ | −1.10% | 0.43% |
| $r_{34}$ | 0.28% | 0.37% |
| $r_{45}$ | −0.24% | 0.60% |
| $r_{56}$ | 1.21% | −0.56% |
| $r_{67}$ | 0.09% | 0.15% |
| $r_{78}$ | −0.66% | −0.22% |

TABLE III. Bondlength components in Å along the *x*, *y*, and *z* directions between a step atom and its neighbors for the relaxed and bulk terminated structure of Ag(410). Here $d_s$ and $d_b$ are the bondlength of atoms at relaxed and bulk-terminated configurations, respectively.

| Atoms | Relaxed | | | | Bulk terminated | | | |
|---|---|---|---|---|---|---|---|---|
| | $d_x$ | $d_y$ | $d_z$ | $d_s$ | $d_x$ | $d_y$ | $d_z$ | $d_b$ |
| SC-1MC | 1.938 | 2.045 | 0.438 | 2.851 | 1.984 | 2.045 | 0.496 | 2.892 |
| SC-SSC | 0.563 | 2.045 | 1.861 | 2.822 | 0.496 | 2.045 | 1.984 | 2.892 |
| SC-BNN | 1.445 | 0.000 | 2.390 | 2.793 | 1.488 | 0.000 | 2.480 | 2.892 |

Ag(410) and Cu(320) the bondlength components of the surface atoms are presented in Tables III, and IV, respectively. For both surfaces, shortenings in the bondlength components are more pronounced along the *z* direction, as expected. For Cu(320), the pronounced shortening in the *z* component of the interatomic distance between SC and MC atoms (14%) is followed by the shortenings in the same bondlength components between SC and CC atoms (11%) and SC and STC atoms (7%). Similar is the case for Ag(410), with shortenings of 12, 6, and 4% in the *z* components of interatomic separations between SC and 1MC atoms, SC and SSC atoms, and SC and BNN atoms, respectively. In addition to these shortenings in the *z* components of bondlengths, we also predict a substantial dilation of 14% in the *x* component of the interatomic distance between SC and SSC atoms of Ag(410). Interestingly, our calculations for Cu(320) indicate no such pronounced change (dilation or shortening) in the *x* components of the bond lengths between the SC atom and its neighbors. While there are notable changes in the components of the bondlengths (from bulk values) between step atom and its neighbors, the net change in the bond length between SC and BNN atoms on Ag(410) is -3.4%. This result is indeed surprising because the corresponding calculated changes in bondlengths for vicinals with close-packed step edges such as Pt(331) and Cu(331) are found to be $-4.5$ and $-3.09\%$, respectively.[6,14] One might have expected atoms around steps with non-close-packed edges to be more susceptible to large bondlength changes.

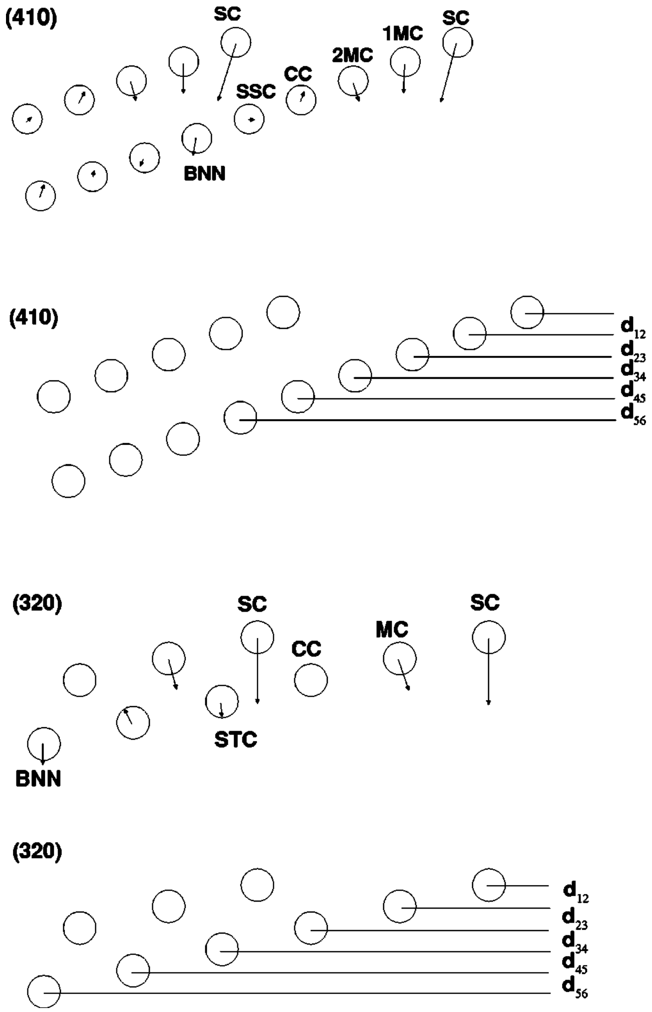

FIG. 3. The relaxation patterns of the atoms at and near the surface and the associated layer definitions for Ag(410) and Cu(320). Here the atomic displacements from the bulk terminated positions are magnified by a factor 20. Arrows indicate the corresponding atomic relaxations.

To better digest the trend in the interlayer relaxations and the change in the bondlengths of the SC atom to its neighbors, we have also examined the relaxations of individual atoms at and near the surface and plotted them together with the associated layer definitions in Fig. 3. The relaxations in the figure are magnified by a factor 20. As seen in the figure, the SC atom relaxes downward the most for both surfaces. On Ag(410), as the SC atom moves inwards, between BNN and SSC atoms, the short range repulsive part of the potential pushes (according to Fig. 3) BNN-atom (the sixth layer atom) downward, yielding a $+6.6\%$ pronounced expansion of relaxation for $d_{56}$, and a SSC atom to the right. It is this trend in the relaxation of the SSC atom that may cause the pronounced 14% dilation in the *x* component of the bond length between SC and SSC atoms of Ag(410). The downward relaxation of the SC atom on Cu(320) leads to a less pronounced expansion of 2.8% on the interlayer spacing of $d_{34}$. From the relaxation of the fifth and sixth layer atoms, we find that while the fifth layer atom moves upward to find the equilibrium position in the relaxed configuration, the latter one moves downward, resulting in an expansion of 10.69% in the interlayer relaxation between the fifth and sixth layers.

TABLE IV. Bondlength components in Å along the *x*, *y*, and *z* directions between a step atom and its neighbors for the relaxed and bulk terminated structure of Cu(320). Here $d_s$ and $d_b$ are the bondlength of atoms at relaxed and bulk-terminated configurations, respectively.

| Atoms | Relaxed | | | | Bulk terminated | | | |
|---|---|---|---|---|---|---|---|---|
| | $d_x$ | $d_y$ | $d_z$ | $d_s$ | $d_x$ | $d_y$ | $d_z$ | $d_b$ |
| SC-MC | 2.492 | 0.000 | 0.433 | 2.529 | 2.506 | 0.000 | 0.501 | 2.556 |
| SC-CC | 1.508 | 1.807 | 0.888 | 2.516 | 1.503 | 1.807 | 1.002 | 2.556 |
| SC-STC | 1.008 | 1.807 | 1.404 | 2.501 | 1.002 | 1.807 | 1.504 | 2.556 |

These calculated changes in the interatomic distances are also reflected in the modifications in the local force fields

TABLE V. Force constant matrices between a step atom and its neighbors for the relaxed surface (surface) and the corresponding ones in the bulk (bulk) for Ag(410). Force constants are in eV/Å$^2$/unit mass.

| Atoms | | Surface | | | Bulk | | |
|---|---|---|---|---|---|---|---|
| | | $x$ | $y$ | $z$ | $x$ | $y$ | $z$ |
| SC-1MC | $x$ | −0.762 | 0.767 | −0.383 | −0.697 | 0.766 | −0.191 |
| | $y$ | 0.778 | −0.767 | 0.392 | 0.766 | −0.744 | 0.191 |
| | $z$ | −0.042 | 0.031 | −0.044 | −0.191 | 0.191 | 0.018 |
| SSC-SC | $x$ | 0.025 | −0.239 | 0.185 | 0.018 | −0.191 | 0.191 |
| | $y$ | −0.322 | −0.965 | 0.903 | −0.191 | −0.744 | 0.766 |
| | $z$ | 0.331 | 1.161 | −0.994 | 0.191 | 0.766 | −0.697 |
| BNN-SC | $x$ | −0.564 | 0.000 | −1.106 | −0.373 | 0.000 | −0.696 |
| | $y$ | 0.000 | 0.136 | 0.000 | 0.000 | 0.066 | 0.000 |
| | $z$ | −1.187 | 0.000 | −1.896 | −0.696 | 0.000 | −1.116 |

around the step atoms, as compared to those in the bulk. To illustrate this we have calculated the force constant matrices $k_{\alpha\beta}$, where $\alpha$ and $\beta$ stands for Cartesian components, $x$, $y$, and $z$, between the atoms in the vicinity of the step and compared them with the corresponding bulk values in Tables V and VI, for Ag(410) and Cu(320), respectively. The fact that the force constant matrices at the surface are not symmetric as they are in the bulk echos the broken symmetry along the $x$ and $z$ directions introduced by the existence of the stepped surface. For Ag(410), in Table V, the force constant $k_{zz}$ between the SC atom and its neighbor BNN and SSC atoms is stiffened 70 and 43 %, respectively, which reflects the contraction in the $z$ component of the corresponding bond-length. Existence of steps on surface induces changes not only on the diagonal elements of the force constant matrices between the surface atoms, but also on the off-diagonal elements. For example, $k_{xz}$ and $k_{yz}$ between SC and 1MC atoms on Ag(410) is stiffened 100 and 105 %, respectively. Remember that $k_{xz}$ is the force per unit mass in the $x$ direction on the SC atom resulting from unit displacement of the 1MC atom in the $z$ direction. So when the 1MC atom moves downward during the relaxation process, the SC atom experiences a huge increase in the $x$ component of the force due to the downward motion of the 1MC atom. In addition, the 105% increase in $k_{yz}$ for SC and 1MC atoms does not result in a relaxation along the $y$ direction, as the relaxations along the step edge ($y$) are symmetry forbidden.

TABLE VI. Force constant matrices between a step atom and its neighbors for the relaxed surface (surface) and the corresponding ones in the bulk (bulk) for Cu(320). Force constants are in eV/Å$^2$/unit mass.

| Atoms | | Surface | | | Bulk | | |
|---|---|---|---|---|---|---|---|
| | | $x$ | $y$ | $z$ | $x$ | $y$ | $z$ |
| SC-MC | $x$ | −1.828 | 0.000 | −0.605 | −1.898 | 0.000 | −0.397 |
| | $y$ | 0.000 | 0.017 | 0.000 | 0.000 | 0.104 | 0.000 |
| | $z$ | −0.077 | 0.000 | −0.061 | −0.397 | 0.000 | 0.008 |
| CC-SC | $x$ | −0.702 | −0.863 | 0.346 | −0.622 | −0.859 | 0.484 |
| | $y$ | −0.920 | −1.024 | 0.423 | −0.859 | −0.945 | 0.573 |
| | $z$ | 0.635 | 0.740 | −0.278 | 0.484 | 0.573 | −0.219 |
| STC-SC | $x$ | −0.275 | 0.735 | −0.540 | −0.219 | 0.573 | −0.485 |
| | $y$ | 0.710 | −1.146 | 0.915 | 0.573 | −0.945 | 0.859 |
| | $z$ | −0.665 | 1.173 | −0.817 | −0.485 | 0.859 | −0.622 |

Similarly, for Cu(320), $k_{zz}$ between SC and STC atoms shows a stiffening of 25%. In addition, the $k_{zx}$ element of the force constant matrix for SC and MC atoms is softened by 81%. As it is clear from Fig. 3, the downward relaxation of the SC atom does not induce any change in the position of the CC atom. This might be traced back to the fact that the 28% stiffening of $k_{zz}$ element of the force constant matrix between CC and SC atoms is screened by 29% softening of the off-diagonal element of $k_{xz}$. Furthermore, the force constant $k_{zx}$ for SC and MC atoms is stiffened by 52%. Some force constants for the surface atoms are also found to soften. This is particularly true for those between the SC atoms, which have been found to result in super localized, low frequency modes.[15] While the trends in the deviations in the force constants from bulk values on Ag(410) and Cu(320) are similar, it is difficult to make a direct comparison because of the differences in the local geometries on the two surfaces.

## IV. CONCLUSION

In summary, we have investigated the multilayer and atomic relaxations of Ag(410) and Cu(320), traced these relaxations to the modifications in the local force fields around the step, and compared the calculated multilayer relaxations for both surfaces with the recent quantitative low energy electron diffraction (QLEED) data and available *ab initio* calculations on relaxations of vicinal surfaces. The most striking feature in the calculated relaxation patterns of Cu(320) and Ag(410) is the pronounced expansion of the separation between the fifth and the sixth layer atoms for both surfaces. This trend in the characteristics of the relaxation patterns is in accord with the findings of the previously reported works on vicinal surfaces. Moreover, unlike the QLEED data on the first interlayer spacing of Ag(410), the analysis of our results yield a 11.64% contraction. We look forward to new measurements or newer analysis of Ag(410) data to confirm our findings. On the other hand, our results on the multilayer relaxation of Cu(320) are in qualitative agreement with the more recent QLEED data. We also establish that atomic relaxations are traceable to the changes in local force fields around the associated atoms. A word of caution is that because of the many-body nature of the interactions there is no simple relationship between bondlength changes and modifications of specific force constants. Future work using *ab initio* electronic calculations will be very useful in putting our understanding of the nature in atomic relaxations on these specific types of surfaces on a firmer footing.

## ACKNOWLEDGMENTS

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