

***Ab initio* calculations of multilayer relaxations of stepped Cu surfaces**Rolf Heid,<sup>1</sup> Klaus Peter Bohnen,<sup>1</sup> Abdelkader Kara,<sup>2</sup> and Talat S. Rahman<sup>2,3,\*</sup><sup>1</sup>*Forschungszentrum Karlsruhe, Institut fuer Festkoerperphysik, 76021 Karlsruhe, Germany*<sup>2</sup>*Department of Physics, Cardwell Hall, Kansas State University, Manhattan, Kansas 66506*<sup>3</sup>*Fritz Haber Institut der Max Planck Gesellschaft, 4-6 Faradayweg, 14195 Berlin, Germany*

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We present trends in the multilayer relaxations of several vicinals of Cu(100) and Cu(111) of varying terrace widths and geometries. The electronic structure calculations are based on density-functional theory in the local-density approximation with norm-conserving, nonlocal pseudopotentials in the mixed basis representation. While relaxations continue for several layers, the major effect is concentrated near the step and corner atoms. On all surfaces the step atoms contract inward, in agreement with experimental findings. Additionally, the corner atoms move outward and the atoms in the adjacent chain undergo a large inward relaxation. Correspondingly, the largest contraction (4%) is in the bond length between the step atom and its bulk nearest neighbor (BNN), while that between the corner atom and the BNN is somewhat enlarged. The surface atoms also display changes in registry of up to 1.5%. Our results are in general in good agreement with low-energy electron-diffraction data including the controversial case of Cu(511). Subtle differences are found with results obtained from semiempirical potentials.

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**I. INTRODUCTION**

Structural properties of regularly stepped 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, nanostructuring of materials, and catalysis.<sup>1</sup> According to crystallographic notation, these surfaces are denoted by high Miller indices, and are called vicinals of their low Miller index counterparts (flat surfaces). The presence of arrays of atomic steps separated by flat terraces creates regions of differing local coordinations, and makes the microscopic structure of a vicinal surface distinct from that of a flat surface. According to Smoluchowski's idea of charge smoothing,<sup>2</sup> for example, electronic charge densities are expected to rearrange in the vicinity of the steps, thereby causing the ion cores to relax to new configurations. The modified electronic structure may also be expected to impact the reactivity and the nature of the force fields in the region around the steps. A knowledge of atomic relaxations in the equilibrium positions near the step and kink sites is thus a step toward understanding the vibrational and electronic properties of vicinal surfaces.

Fortunately, with advances in atomic scale experimental techniques, there has been a surge in investigations of the structure of vicinal surfaces in recent years. The majority of the experimental data have undoubtedly come<sup>3,4</sup> from the low-energy electron diffraction (LEED) technique, which is now capable of detecting changes even for interlayer spacings smaller than 1 Å.<sup>5</sup> For some surfaces the x-ray-scattering technique has provided much needed complementary structural data.<sup>6</sup> An impressive number of theoretical calculations of multilayer relaxations<sup>7-11</sup> has also helped in bringing several issues related to the characteristics of vicinal surfaces to the forefront. Of particular interest here are experimental and theoretical studies of a set of vicinals of Cu(100) and Cu(111), which addressed the question of the

impact of local coordination on the structural and dynamical properties of a surface. In an earlier paper,<sup>10</sup> a comparative study of the local structural and vibrational properties of Cu(211), Cu(511), and Cu(331) was performed using empirical potentials from the embedded atom method (EAM).<sup>12</sup> This study found that the first two surfaces displayed similar local characteristics, while the third surface was somewhat different. An explanation provided for this behavior was the similarity in the local environment of the (211) and (511) surfaces of fcc metals [a combination of (100) and (111) terrace geometry and the step face], and its consequent difference from that of the (331) surface [a (111) terrace geometry and a (111)-microfaceted step face]. The issue of the local geometry was further raised in a joint theoretical and experimental study of the vibrational dynamics of Cu(211) and Cu(511) together with those of the kinked surface Cu(532).<sup>13</sup> Experimental data from electron-energy-loss spectroscopy found modes above the bulk band on Cu(211) but not on Cu(511) [or on Cu(17,1,1), which has the same step geometry as Cu(511)], but theoretical calculations based on EAM potentials predicted modes (slightly) above the bulk phonon spectrum for each of these surfaces. While the similarity between the calculated structural relaxation patterns of Cu(211) and Cu(511) argues in favor of a similarity in the local vibrational dynamics of these two surfaces, the disagreement between the experimental and theoretical results for the high-frequency modes on Cu(511) [and Cu(17,1,1)] remains unreconciled. For Cu(211) the agreement of EAM-based results with available structural data from LEED (Ref. 14) and with *ab initio* calculations for both the structure and the dynamics<sup>15</sup> provides considerable confidence in its predicted properties. The case of Cu(511) is not as simple, due to a lack of calculations based on potentials more accurate than EAM, and because of conflicting conclusions from the analysis of experimental data from LEED (Ref. 16) and x-ray-scattering measurements.<sup>6</sup> The most striking difference in these two sets of data is the relaxation pattern for the

second layer, which is inward in LEED and outward in the x-ray data. The oscillatory pattern found in the x-ray data is also in disagreement with the conclusion from a series of previous experimental and theoretical findings on stepped surfaces. Based on these studies,<sup>8-11,17</sup> there is a definite symmetry in the relaxation patterns of stepped surfaces. All terrace atoms, save for the corner one, display inward relaxations. EAM-based calculations<sup>9</sup> further predicted this oscillatory relaxation pattern to continue into the bulk with a damping in the amplitude.<sup>19</sup> Thus the expected relaxation pattern for the (211), (511), and (331) surfaces, each with three-atom-wide terraces, would be  $(- - + - - + \dots)$ , although questions have been raised whether Cu(331) follows this rule.<sup>10</sup> Similarly, the patterns for (711) and (911) surfaces with, respectively, four and five atoms on the terrace, would be predicted to be  $(- - - + - - - + \dots)$  and  $(- - - - + - - - - + \dots)$ . The LEED data on the first three surfaces follow these predicted trends in relaxations, at least for the top three layers. Very recent LEED data<sup>18</sup> for Cu(711) also display the pattern  $(- - - +)$  for the top layers, in good agreement with EAM-based predictions. However, a small discrepancy in the sign of the relaxation is found for both Cu(711) and Cu(511), for a particular layer separation [ $d_{56}$  for Cu(511) and  $d_{78}$  for Cu(711)],<sup>18</sup> beyond that expected from the error bars. Arguably the actual numbers involved in these comparisons are small, but the systematic nature of the discrepancies, and the fact that it negates the prediction of a periodicity in the oscillatory relaxation pattern,<sup>9,19</sup> raise interesting questions about the complexities of the atomic displacements in these systems. Given the above uncertainties arising from experimental observations, it is opportune to carry out more accurate calculations of these relaxation patterns using techniques which are capable of revealing the accompanying changes in the surface electronic structure. It is with this goal in mind that we have carried out *ab initio* electronic structure calculations of the surface geometry and interlayer spacing for this set of vicinals of Cu(100) and Cu(111). In addition to Cu(211), Cu(331), and Cu(511), which help to address the question of the influence of the local geometry on the structure, we have extended the investigation to Cu(711) and Cu(911) to examine the influence of increasing terrace width of the relaxation pattern. Of course, for all surfaces a comparison with available experimental data is of prime concern.

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 results and their discussion. Concluding remarks are presented in Sec. IV.

## II. SURFACE GEOMETRIES

Vicinal surfaces can easily be constructed by cutting the crystal at an angle slightly away from the lower-index crystal planes [i.e., (100), (111), and (110)]. For reasons discussed above, here we are interested in the vicinals of the (100) and (111) surfaces of fcc metals, for which the most tightly packed steps are along the  $\langle 110 \rangle$  direction. In the case of a (111) surface, however, the  $\langle 110 \rangle$  direction is not parallel to

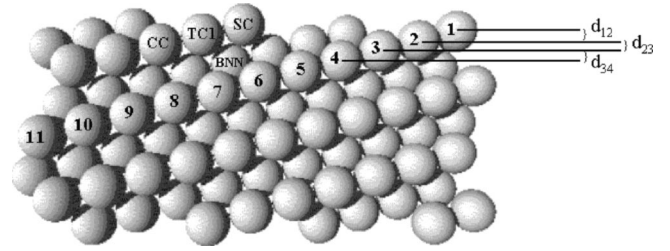


FIG. 1. Sideview of a fcc(511) surface showing the interlayer separations, and the labeling of the atoms and the layers.

any plane of symmetry and there are two different ways of generating monoatomic stepped surfaces. In one type of such vicinals, the step edge has a (100) microfacet, while the other has a (111) microfacet (these are the so called *A* and *B* types, respectively). In standard nomenclature, the vicinals of a fcc(111) surface with monoatomic steps and (100) step edges are denoted by  $(n, n, n+2)$ , while those with (111) step edges are labeled as  $(n, n, n-2)$ , where  $n$  is the number of atoms on the terrace. The *B*-type vicinal Cu(331) considered here is named accordingly, while the *A*-type vicinal Cu(211) seems to be a misnomer. Similarly, vicinals of a fcc(100) surface consisting of monoatomic step edges with a (111) microfacet are labeled  $(2n-1, 1, 1)$ . The Cu(111) vicinals considered here are created by cutting the crystal at angles of  $19.5^\circ$  and  $22^\circ$  away from the (111) plane toward the  $[2\bar{1}\bar{1}]$  and  $[\bar{2}11]$  directions to produce (211) and (331) surfaces, respectively, whereas the three vicinals of (100), (511), (711), and (911) surfaces are constructed by slicing the crystal at angles of  $15.8^\circ$ ,  $11.4^\circ$ , and  $8.9^\circ$ , respectively, from the (100) plane toward the  $[011]$  direction. To facilitate the discussion we have also labeled the atoms that play the dominant role in our calculation.<sup>10</sup> For surfaces consisting of three chains of atoms on the terrace, we label them as corner chain, a terrace chain (TC1), and a step chain (SC). The chain just underneath the step chain is called a bulk nearest-neighbor (BNN) chain. The other two surfaces, Cu(711) and Cu(911), contain, respectively, one and two extra chains of terrace atoms, labeled accordingly as TC2 and TC3. In our notation the  $x$  and  $y$  axes to lie in the surface plane, the  $x$  axis perpendicular to the step, the  $y$  axis along the step, and the  $z$  axis along the surface normal. In Fig. 1, we display a side view of the (511) surface, with an appropriate labeling of the atoms and interlayer spacing.

## III. SOME DETAILS OF THEORETICAL CALCULATIONS

*Ab initio* electronic structure calculations are performed within a pseudopotential approach to density-functional theory in the local-density approximation.<sup>20</sup> The numerical implementation of the technique is based on a computer code developed by Meyer *et al.*<sup>21</sup> The local-density approximation is applied using a Hedin-Lundqvist form of the exchange-correlation functional.<sup>22</sup> A norm-conserving pseudopotential for Cu, constructed according to a scheme proposed by Hamann, Schlueter, and Chiang,<sup>23</sup> has been used, which was already successfully employed for calculations of the structure and the phonons of low index surfaces of Cu.<sup>25</sup> A mixed

TABLE I. Calculated changes in interlayer separations as percentage of the ideal separation  $d_b$ .

Layer	Cu(211)	Cu(331)	Cu(511)	Cu(711)	Cu(911)
$d_b$	0.736 Å	0.828 Å	0.694 Å	0.505 Å	0.443 Å
$d_{12}$	-12.2%	-12.7%	-9.3%	-7.3%	-11.2%
$d_{23}$	-9.5%	-3.3%	-10.7%	-1.5%	-2.2%
$d_{34}$	+8.7%	+4.5%	+7.2%	-14.8%	+0.6%
$d_{45}$	-2.1%	-2.0%	-2.9%	+8.0%	-13.9%
$d_{56}$	-1.6%	+0.1%	+1.1%	-1.0%	+5.4%
$d_{67}$	+1.5%	-0.1%	+1.7%	-1.1%	-1.3%
$d_{78}$	-0.1%	+0.8%	-1.5%	+1.4%	-4.1%
$d_{89}$	-0.3%	-0.6%	+1.6%	+1.7%	+4.5%
$d_{9,10}$	+0.7%	+0.9%	-0.5%	-1.5%	+3.0%
$d_{10,11}$				-0.40%	-0.5%
$d_{11,12}$				+2.0%	-2.5%
$d_{12,13}$				+0.3%	+1.2%
$d_{13,14}$					+1.6%
$d_{14,15}$					+3.0%
$d_{15,16}$					-2.2%

basis set is applied to represent valence states consisting of five  $d$ -type local functions at each Cu site, smoothly cut off at a radius of 2.3 a.u., and of plane waves with a kinetic energy of 11 Ry. Increasing the cutoff energy to 16 Ry showed no significant effect on the results. A Brillouin-zone (BZ) integration was carried out using a special point sampling technique<sup>24</sup> together with a Gaussian broadening of the energy levels of 0.2 eV. For simulating surfaces we used a supercell approach with cells containing 21–35 atoms (one atom per layer), depending on the surface orientation. The  $z$  dimension of all cells was 47.7155 a.u. The distance between the top and bottom layers of the slabs were thus 31.2761 a.u. for Cu(331), 27.8277 a.u. for Cu(211), 26.2340 a.u. for Cu(511), 25.7715 a.u. for Cu(711), and 25.4390 a.u. for Cu(911). Structure optimization was carried out until forces on all atoms were smaller than  $10^{-3}$  Ry/a.u., which is two orders of magnitude smaller than the forces present on the unrelaxed surfaces. With increasing terrace width, the calculations become increasingly tedious, since the reduction in interlayer spacing makes it more difficult to achieve geometries converged to 1% of the interlayer spacing. We also find that results for terraces with (100) geometry are more sensitive to the number of  $k$  points sampled, as compared to those with (111) geometry. For the latter case 30 points in the BZ are sufficient for a determination of the equilibrium structure, while for surfaces with (100) terraces at least twice as many points are needed to obtain converged results.

#### IV. RESULTS AND DISCUSSIONS

Our results for the multilayer relaxations of Cu(211), Cu(331), Cu(511), Cu(711), and Cu(911) are summarized in Table I. As in previous theoretical studies<sup>9–11,13</sup> of relaxations on stepped Cu surfaces, we find changes in interlayer separations, from bulk-terminated configurations, to persist on all surfaces for a large number of layers. Of course, the

concept of layers is different here from that on flat surfaces (see Fig. 1). The first  $n$  layers, for example, are all exposed to the vacuum, where  $n$  is the number of atoms on the terrace. Correspondingly, the interlayer separations are small, and even large percentage changes in interlayer separations correspond to small numbers in distances. It is important to bear this point in mind when comparing results for a particular surface either with those for flat surfaces or with results from other methods.

A common feature of all surfaces examined in Table I is that all terrace atoms except those in the corner chain (CC) undergo significantly large inward relaxations. The corner atoms are always found to relax outward. Additionally, atoms in the terrace adjacent to the CC atom exhibit a comparatively large inward relaxation whose magnitude may be larger than that of the step atoms (a SC atom). For example, for Cu(511), Cu(711), and Cu(911) changes, respectively, in  $d_{23}$  (involving a TC1 atom),  $d_{34}$  (involving a TC2 atom), and  $d_{45}$  (involving a TC3 atom), are larger than that of  $d_{12}$ . Thus, in keeping with Schmolkowski's<sup>2</sup> ideas of charge smoothing, the maximum relative change in interlayer separation is focussed around the corner atoms. This is particularly true for the vicinals of Cu(100). The situation with the more close-packed surface Cu(331) is somewhat different. As seen in Table I, the outward relaxation of the corner atom and the inward relaxation of the preceding atom on the terrace on Cu(331) are less than half of that for similar atoms on the other surfaces considered here. Incidentally, this conclusion is in good agreement with results from previous studies which were based on semiempirical potentials.<sup>9,10</sup>

There is, however, a disconcerting difference in the results obtained here from *ab initio* electronic structure calculations and those from semiempirical potentials. An intriguing result for multilayer relaxations of the vicinals of Cu(100) obtained with EAM potentials in Ref. 9 was that the pattern of inward and outward relaxations continued well into the bulk with an exponentially decreasing amplitude. Thus, for Cu(711), the relaxation pattern predicted by the EAM was (- - - +, - - - +, - - - +, . . .) with an eventual damping of the relaxations. The pattern for Cu(711) from Table I is instead (- - - +, - - + +, - - + +). That is, our present calculations do not predict a periodically oscillatory relaxation pattern with a decaying amplitude as we move into the bulk. As we shall see, this particular feature is more in agreement with experimental data, and helps to remove the slight discrepancy between experiment and theory presented by the EAM result pointed by Walter *et al.*<sup>18</sup> Again, it should be recalled that the numbers involved are very small and within the limits of accuracy of *ab initio* calculations. In particular, the small numbers for the relaxations of the inner layers of Cu(911) have to be taken with caution, as our convergence criteria for this surface were not as good as that for the others because of the demands on computational resources imposed by a system as large as this one.

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 these directions. While relaxations along the  $z$  direction yield the characteristic interlayer separations we discussed above, those along the  $x$  direction pro-

TABLE II. Calculated changes in the registries as percentage of that for the ideal surface  $r_b$ .

Registry	Cu(211)	Cu(331)	Cu(511)	Cu(711)	Cu(911)
$r_b$	2.083 Å	2.048 Å	2.454 Å	2.500 Å	2.519 Å
$r_{12}$	-1.22%	-0.10%	-1.17%	-1.37%	+0.99%
$r_{23}$	-0.54%	-1.74%	-1.21%	-0.32%	-0.40%
$r_{34}$	-0.22%	+1.46%	+0.98%	-0.41%	+0.28%
$r_{45}$	+1.50%	+0.62%	+0.25%	+0.77%	-0.60%
$r_{56}$	-0.26%	-0.50%	-0.31%	+0.23%	+0.38%
$r_{67}$	+0.19%	+0.24%	+0.01%	+0.82%	-0.01%
$r_{78}$	0.00%	-0.19%	0.00%	-0.89%	+0.55%
$r_{89}$	-0.11%	+0.23%	-0.14%	-0.01%	+0.16%
$r_{9,10}$				-0.31%	-0.44%
$r_{10,11}$				-0.20%	-0.14%
$r_{11,12}$				+0.11%	+0.40%
$r_{12,13}$					-0.23%
$r_{13,14}$					-0.25%

vide new registries of atoms as compared to those in the bulk. Our calculated percentage intralayer registries for five surfaces are summarized in Table II. As in the observations from EAM calculations, the changes in the registries of the atoms are small. It is thus not useful to make a one-to-one comparison with results from semiempirical calculations. However, the changes in the registries of the atoms are not inconsequential, since they affect the changes in the bond lengths between the atoms in these regions of low coordinations. In Table III, we tabulate our results for the total changes in the distances between the step atoms and their nearest neighbors. For comparison, in parentheses we include the results obtained earlier for the same quantities with EAM potentials.<sup>10,9</sup> The largest changes in the bond lengths (from unrelaxed configurations) are for those between the step atoms and their bulk nearest neighbor (BNN), which lies right below them. The bonds between the CC and BNN show a small enlargement, while all other bonds in Table III are found to undergo shortening. In Figs. 2 and 3, we draw the actual displacements of the atoms on the five surfaces obtained from our calculations. While the sizes of the arrows are exaggerated, it is their relative length and direction that is of consequence. As already noted by Durukanoglu *et al.*,<sup>10</sup> all atoms in low-coordinated sites move to enhance their local coordination. The complex displacement pattern that emerges is thus the net outcome of the competition between the different directions in which the various atoms would

TABLE III. Changes (in %) in bond lengths between the step atom and its nearest neighbors. The results from EAM are in parantheses.

Surface	SC-TC	SC-CC	SC-BNN	CC-BNN
Cu(211)	-1.78 (-1.27)	-2.27 (-2.67)	-3.22 (-2.10)	+0.61 (+0.7)
Cu(331)	-1.36 (-0.45)	-2.39 (-1.86)	-3.66 (-3.09)	+1.42 (+0.5)
Cu(511)	-1.80 (-2.29)	-1.42 (-0.98)	-3.13 (-2.30)	+1.49 (+1.5)
Cu(711)	-1.59 (-2.16)	-1.36 (-1.11)	-2.88 (-2.26)	+1.06 (+1.8)
Cu(911)	-1.22 (-2.08)	-1.47 (-1.06)	-3.06 (-2.31)	+0.51 (+1.93)

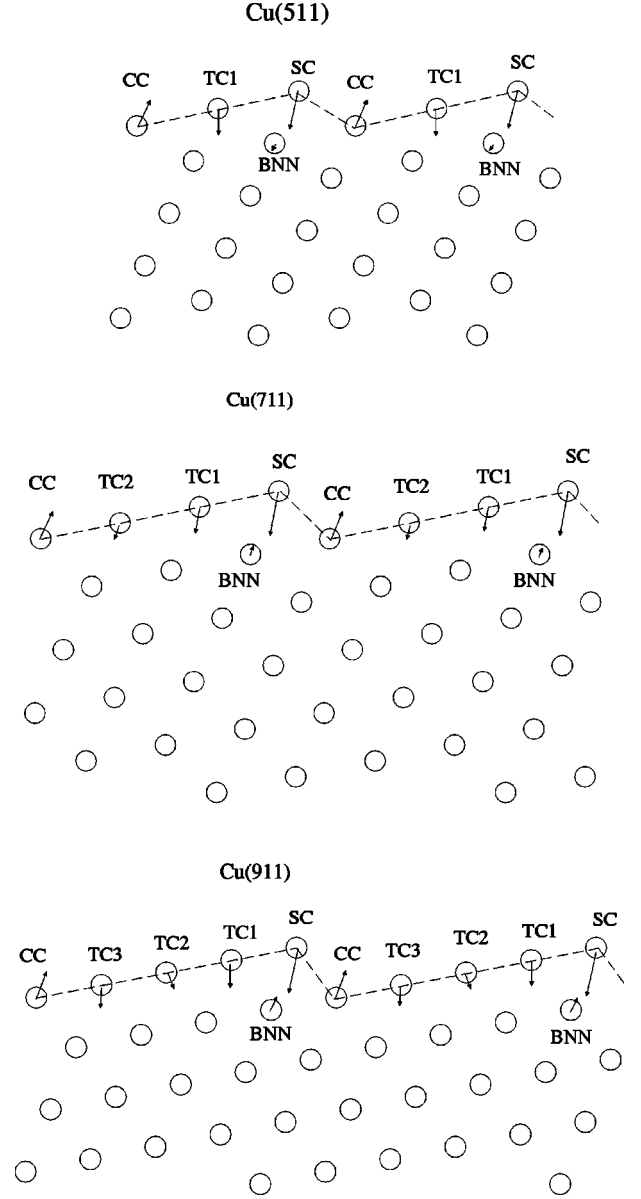


FIG. 2. Schematic representation of displacements of atoms during the relaxation process for Cu(511), Cu(711), and Cu(911).

“like” to relax to enhance their own coordination. For readers who are interested in the exact positions of the atoms on the relaxed surfaces, we summarize them in Table IV. The unusual behavior of the Cu(331) terrace atom is more apparent from this table than the earlier one



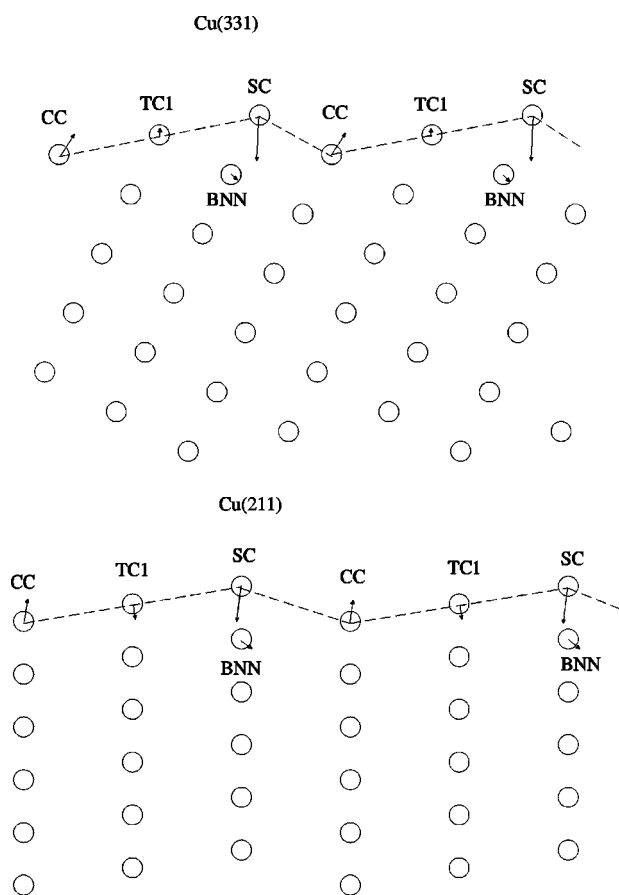


FIG. 3. Schematic representation of displacements of atoms during the relaxation process for Cu(331) and Cu(211).

concerning changes in the bond lengths. The TC1 atom of Cu(331) undergoes the least displacement among its counterparts. Its displacement is also smaller than that of a TC2 atom (1.4, 0.0, and  $-2.6$ ) on Cu(711), and of both TC2 (0.8, 0.0, and  $-2.0$ ) and TC3 (0.1, 0.0, and  $-2.3$ ) atoms on Cu(911). The coordinates of the displacements above in parentheses are in the same units as those in Table IV.

We now turn to comparisons of the results obtained here for individual surfaces with those available from experimental measurements. In Table V we show that for Cu(211) the salient features in the trends in the relaxation patterns predicted by our calculations are observed in the experimental data. Apart from the large inward relaxation of the step atoms, the major change occurs at the corner atom and its adjacent terrace atom. Our results are in good agreement with previous density-functional theory (DFT) local-density

approximation calculations,<sup>15</sup> based on the pseudopotential approximation and with results from EAM-based method. Theoretical calculations using the full potential linearized-augmented-plane-wave (FLAPW) method,<sup>26</sup> however, predict a much larger relaxation ( $-28.4\%$ ) of the step atom than any of the previous theoretical or experimental studies. This brings us to the discussion of ionic relaxation on Cu(331) in Table VI for which also we do not get the large relaxation reported in Ref. 26. The present results for Cu(331) are, however, in good agreement with the LEED data.<sup>17</sup> The discrepancy with the results from LEED for  $d_{23}$  should not be taken too seriously, given an error bar of 4% in the analysis of the LEED data. With respect to EAM-based results,<sup>10</sup> we find a noticeable difference for  $d_{34}$ , for which the present results agree better with the LEED data and also preserve the predicted relaxation pattern ( $- - +$ ) for the terrace atoms. This trend is in keeping with what was reported in calculations on Al(331).<sup>8</sup> In trying to reconcile our results with those of Geng and Freeman,<sup>26</sup> we note that the latter predicted an outward displacement of the TC1 atomic chain for both Cu(211) and Cu(331), while we find this not to be the case. As already mentioned, while the changes in the bond lengths of the terrace atoms of Cu(331) are no different from those of the other surfaces, the displacement of a TC1 atom is strikingly smaller than that of the TC atoms on other surfaces.

The case of multilayer relaxations for Cu(511) is interesting because of the differences in the published data from LEED (Ref. 16) and x-ray measurements.<sup>6</sup> These are displayed in Table VII. Except for the displacement of the step atoms, for which all results point to a large inward relaxation, the results from x-ray-scattering measurements are in disagreement with present results and with those from LEED as well as EAM calculations. We do not understand the reasons for this disagreement, except for the notion that x-ray measurements may be very sensitive to the quality of the crystal surface. It should be noted that differences from the x-ray results are both qualitative and quantitative, beyond the established error bars in the experiments and calculations. Because of the controversy in the experimentally determined multilayer relaxations of Cu(511), we have carried out an extensive analysis of the dependence of the theoretical results on the approximations necessary to produce computational feasibility: the choice of pseudopotentials, the maximum kinetic energy of the plane waves ( $E_{cut}$ ), the number of layers in the supercell, and the number of points used to sample the surface Brillouin zone. As already mentioned, changing  $E_{cut}$  to a higher value (16 Ry) for the chosen norm-

TABLE IV. Atomic displacements from bulk terminated to relaxed positions [ $\text{\AA}(\times 10^{-2})$ ].

Surface	SC	TC1	CC	BNN
Cu(211)	( $-1.8, 0.0, -10.9$ )	( $0.7, 0.0, -1.9$ )	( $1.7, 0.0, 5.1$ )	( $2.3, 0.0, -1.4$ )
Cu(331)	( $-0.4, 0.0, -10.0$ )	( $-0.1, 0.0, 0.5$ )	( $3.5, 0.0, 3.2$ )	( $0.6, 0.0, -0.8$ )
Cu(511)	( $-2.5, 0.0, -9.2$ )	( $0.1, 0.0, -2.7$ )	( $2.7, 0.0, 4.7$ )	( $0.2, 0.0, -0.3$ )
Cu(711)	( $-2.8, 0.0, -7.1$ )	( $0.6, 0.0, -3.4$ )	( $2.4, 0.0, 4.8$ )	( $0.5, 0.0, 0.8$ )
Cu(911)	( $-2.7, 0.0, -7.4$ )	( $-0.2, 0.0, -2.9$ )	( $1.6, 0.0, 3.2$ )	( $0.7, 0.0, 1.1$ )

TABLE V. Relaxation of Cu(211): experiment and theory.

Relaxation	This work	FLAPW (Ref. 26)	EAM (Ref. 10)	DFT-PW (Ref. 15)	LEED (Ref. 14)
$d_{12}$	-12.2%	-28.4%	-10.3%	-14.4%	-14.9%
$d_{23}$	-9.5%	-3.0%	-5.41%	-10.7%	-10.8%
$d_{34}$	+8.7%	+15.3%	+7.26%	+10.9%	+8.1%
$d_{45}$	-2.1%	-6.6%	-5.65%	-3.8%	
$d_{56}$	-1.6%	+0.7%	-1.2%	-2.3%	
$d_{67}$	+1.5%	+3.0%	+4.0%	+1.7%	
$d_{78}$	-0.1%		-2.6%	-1.0%	
$d_{89}$	-0.3%		-0.17%	-0.05%	
$d_{9,10}$	+0.7%		+0.0%	+0.0%	

conserving pseudopotential, in the mixed-basis representation, has little effect on the results presented above. To examine the dependence of our results, then, on the choice of the pseudopotentials, we have carried out calculations with two other sets of *ab initio* electronic structure codes employing an ultrasoft, Vanderbilt-type<sup>27</sup> pseudopotential, in the plane-wave representation, using a value of  $E_{cut}$  of 30 Ry (which we find to be adequate). We find our calculated values of multilayer relaxations to have the same behavior, qualitatively, and to lie, quantitatively, within 3% of the ones reported here. One of the plane-wave codes used for the purpose was developed by Baroni *et al.*,<sup>28</sup> and the other by Kresse and Hafner.<sup>29</sup> Thus the choice of the pseudopotential does not appear to influence the results in any significant manner. We also find our choice of supercell size to be adequate. There is, however, a strong dependence of the results on the number of BZ points sampled. For the case of Cu(511) this dependence is illustrated in Table VIII. Calculations performed with a few points could give erroneous relaxations as signified by the case of  $d_{23}$  in Table VIII. An inward relaxation of 1.8% is found with four points, while the converged result is 10.7%. Convergence in the calculated relaxation is reached once the number of points is increased to 24 and beyond. Thus, when comparing results from *ab initio* calculations, one has to keep these technical points in mind. Unless sufficient checks are made for convergence in the reported values, quantities such as the equilibrium positions of surface atoms may differ in different calculations, and lead to a disagreement in the calculated relaxations. It would be worthwhile to clarify whether the differences be-

tween our results and those from the FLAPW method for Cu(211) and Cu(331) could be attributed to  $k$ -point sampling.

Finally, we come to a comparison of our results for Cu(711) with those from experiments [we are not aware of any data on Cu(911), so far]. The LEED data<sup>18</sup> for this surface has been very carefully analyzed and compared to existing calculations. Table IX shows that the *ab initio* results obtained here are in excellent agreement with the data, and that the small differences from the EAM results that the authors<sup>18</sup> noted is removed by the present calculations. As in the case of Cu(511), the largest percentage change in the interlayer spacing is not for  $d_{12}$ . In this case it is for  $d_{34}$  which separates the CC atom from the TC2 atom. As before, there is an outward relaxation of the spacing between the CC and the BNN atoms. The fact that relaxations near the CC atom persist in being strong, even as the terrace width increases, is interesting in itself. This particular argument has not been made in any previous theoretical result to our knowledge. Our calculated values for Cu(911) further support this argument as the largest percentage change is found for  $d_{45}$ , the interlayer spacing between the CC and TC3 atoms (in this case). While these results are intriguing, the main outcome of relaxations that ensue when a surface is created is in the actual displacements of the atoms from their bulk terminated positions to the new equilibrium positions. As already stated, these values are summarized in Table V, and the related patterns are presented in Figs. 2 and 3. Obviously, for stepped surfaces there is a complex rearrangement of most terrace atoms. Our calculations show that de-

TABLE VI. Comparison of multilayer relaxation of Cu(331): experiment and theory.

Relaxation	This work	FLAPW (Ref. 26)	EAM (Ref. 10)	LEED (Ref. 17)
$d_{12}$	-12.7%	-22.0%	-10.4%	-13.8%
$d_{23}$	-3.3%	+1.6%	+1.7%	+0.4%
$d_{34}$	+4.9%	+6.9%	-1.7%	+4.0%
$d_{45}$	-2.0%	-2.4%	-0.3%	-4.0%
$d_{56}$	+0.1%	-0.6%	-0.3%	
$d_{67}$	-0.1%	-0.4%	+0.5%	
$d_{78}$	+0.8%		-0.4%	
$d_{89}$	-0.6%		+0.2%	
$d_{9,10}$	+0.9%		+0.0%	

TABLE VII. Relaxation of Cu(511): experiment and theory.

Relaxation	This work	EAM (Ref. 10)	LEED (Ref. 16)	X-ray (Ref. 6)
$d_{12}$	-9.3%	-9.5%	-13.2%	-15.4%
$d_{23}$	-10.7%	-7.9%	-6.1%	+8.1%
$d_{34}$	+7.2%	+8.8%	+5.2%	-1.1%
$d_{45}$	-2.9%	-4.2%	-0.1%	-10.3%
$d_{56}$	+1.1%	-4.0%	+2.7%	+5.4%
$d_{67}$	+1.7%	+3.4%		-0.7
$d_{78}$	-1.5%	-1.7%		-6.9%
$d_{89}$	+1.6%	-1.1%		+3.6%
$d_{9,10}$	-0.5%	+0.0%		

spite this complexity, all terrace atoms except for the CC move inwards.

V. CONCLUSION

In summary, we have performed a comparative study of multilayer and atomic relaxations of five stepped Cu surfaces which are vicinals of Cu(100) and Cu(111) using *ab initio* electronic structure calculations based on density-functional theory and nonlocal, norm-conserving pseudopotentials. The set of three of these surfaces—Cu(211), Cu(331), and Cu(511)—provides a comparison of structural changes from bulk termination, for vicinals of similar terrace widths but differing local geometry. The other set, consisting of Cu(511), Cu(711), and Cu(911) offers a comparative study of relaxation patterns with changing terrace widths. In each case we find the relaxation of the step atoms to be pronouncedly inward, and that of the corner atom to be outward. The other terrace atoms and their nearest neighbors also undergo relaxations following a complex displacement pattern. Subsequently, the bond lengths between all the surface atoms and their nearest neighbors change from the bulk-terminated values; while the bond length between CC and BNN atoms experiences an elongation (about 1%), all other surface bond lengths shrink anywhere from 1% to 4%. Most of our findings are in agreement with previous calculations which were based on semiempirical model potentials, except that we do not find the pattern of inward relaxations of SC, TC1, TC2 atoms, etc., followed by outward relaxation of CC atoms to

continue into inner layers. We also find that the percentage contraction of the spacing between the TC and CC atoms is generally larger than that between SC and TC atoms. While the actual magnitudes of the changes in the spacing considered here are small, there is a systematic trend in the relaxation pattern which points to significant rearrangements in the electronic charge densities near SC and CC atoms. By and large our results are in good agreement with available structural data on these surfaces, except for the case of Cu(511), for which we favor LEED results over those from x-ray-scattering measurements. We believe our results will help settle the issues that have emerged on this particular surface. Our systematic examination of five surfaces also helps to address the question of whether the relaxations on Cu(331) are anomalous. The only striking difference between this surface and the others is in the relaxation of the TC1 atom which is very small. Otherwise the relaxation pattern and the changes in bond lengths are similar to those on the other surfaces.

The main message from these observations is that the important quantity to examine is the displacement pattern of the surface atoms as they relax to their equilibrium positions from their bulk-terminated configurations. The deeper question, of course, is the nature of the accompanying changes in the surface electronic structure. It will be interesting to examine the characteristics of the local electronic densities of states in the different regions of low symmetry that are natu-

TABLE VIII. Relaxation of Cu(511): effect of the number of  $k$  points in the BZ.

Interlayer	65 $k$ pts	44 $k$ pts	24 $k$ pts	4 $k$ pts
$d_{12}$	-9.3%	-9.9%	-10.6%	-15.1%
$d_{23}$	-10.7%	-10.6%	-11.2%	-1.8%
$d_{34}$	+7.2%	+7.3%	+7.9%	+5.4%
$d_{45}$	-2.9%	-3.4%	-4.1%	-0.1%
$d_{56}$	+1.1%	+1.0%	+0.5%	+1.4%
$d_{67}$	+1.7%	+1.7%	+2.7%	+0.2%
$d_{78}$	-1.5%	-1.7%	-2.6%	+1.2%
$d_{89}$	+1.6%	+1.7%	+1.7%	+2.9%
$d_{9,10}$	-0.5%	-0.4%	+0.2%	+2.2%

TABLE IX. Relaxation of Cu(711): experiment and theory.

Relaxation	This work	EAM	LEED (Ref. 18)
$d_{12}$	-7.3%	-10.0%	-13%
$d_{23}$	-1.5%	-5.3%	-2%
$d_{34}$	-14.8%	-9.7%	-10%
$d_{45}$	+8.0%	+13.8%	+7%
$d_{56}$	-1.0%	-4.5%	-1%
$d_{67}$	-1.1%	-4.5%	-4%
$d_{78}$	+1.4%	-4.6%	+7%
$d_{89}$	+1.7%	+8%	0%
$d_{9,10}$	-1.5%	-2%	
$d_{10,11}$	-0.4%	-3%	
$d_{11,12}$	+2.0%	-2%	
$d_{12,13}$	+0.3%	+3%	

rally present on the stepped surfaces considered here. We leave this as an exercise for the future.

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\*Corresponding author. Email address: rahman@phys.ksu.edu, FAX: 785 532 6806

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