Enhanced multilayer relaxation at high-index stepped Cu surfaces

Masatake Yamaguchi and Hideo Kaburaki
Center for Promotion of Computational Science and Engineering, Japan Atomic Energy Research Institute, Tokai-mura, Naka-gun, Ibaraki 319-1195, Japan

Arthur J. Freeman
Department of Physics and Astronomy, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3112, USA
(Received 18 June 2003; revised manuscript received 30 October 2003; published 22 January 2004)

Multilayer relaxation at high-index Cu(hkl) (hkl=511, 320, and 410) stepped surfaces were determined by the first-principles all-electron full-potential linearized augmented plane-wave method within the framework of the local-density approximation and the generalized gradient approximation. The calculated relaxation of the interlayer distances, obtained by a geometry optimization procedure that minimizes the force on each atom, were compared with low-energy electron-diffraction (LEED) analysis of experimental data. In the case of Cu(511), the calculated results are in good agreement with the LEED analyses. On the other hand, for Cu(320) and Cu(410), there are large differences that may be understood from the fact that the LEED analyses of experiments consider up to only three or four layers from the surface, and that whereas even the fifth or sixth layers show large relaxation in our calculations, our results suggest a reanalysis of the LEED data with the inclusion of more layers.

DOI: 10.1103/PhysRevB.69.045408 PACS number(s): 68.35.Bs

I. INTRODUCTION

High-index stepped surfaces have properties and applications that have attracted great interest among both basic and applied scientists. High-index surfaces can be made by cutting a crystal along a plane at a small angle with respect to a principal (low-Miller-index) direction. Such a surface consists of a sequence of flat low-Miller-index terraces separated by monoatomic or diatomic steps. Generally speaking, the smaller the angle of the cut, the larger the width of the terrace and the shorter the interlayer distance. For this reason, a high-index surface is also called a ''stepped surface'' or a ''small-interlayer-spacing surface.''

In the case of metals such as Cu, the two-dimensional symmetry of the surface does not change from that of the bulk-terminated surface. This is confirmed by the fact that the low-energy electron-diffraction (LEED) pattern is the same as that produced from the unrelaxed (bulk-terminated) 1×1 surface structure.[1] However, multilayer relaxation and registry shifts occur as a result of the different environment around surface atoms compared to that around bulk atoms—and cause different intensity spectra of the diffracted beams from the spectra expected for the simple bulk-terminated surface. Thus, a quantitative analysis of these intensities using scattering theory can give information about multilayer relaxation and registry shifts at the surface.

Steps affect a number of properties such as morphology, reactivity, relaxation, etc., which in turn affect crystal growth, oxidation, catalysis, and corrosion. The determination of the location (relaxation) of the atoms at the stepped surface is a starting point to study these properties. However, there are some difficulties in determining the multilayer relaxation of high-index surfaces: the shorter the interlayer spacing, the more difficult the analysis of LEED intensity spectra, as discussed by Zhang *et al.*[2] About ten small-spacing interlayer surfaces have been studied to determine multilayer relaxation.[1] Recently, a quantitative analysis of LEED data was successfully carried out to determine the multilayer relaxation at a very high-index Cu(320) surface.[3]

On the theoretical side, systematic studies of multilayer relaxation for surfaces, including high-index ones, were carried out by empirical potential methods such as the embedded atom method (EAM).[4–6] Recent progress in computer power has been so remarkable that large scale calculations have gradually become affordable, and so first-principles studies have also been carried out for Cu(n11) (n=2,5,7,9) and Cu(331),[7] and Cu(211 and 331) surfaces.[8]

Previously, using the same full-potential linearized augmented plane-wave (FLAPW) (Ref. 9) code, some discrepancies between first-principles calculations and the LEED analysis were reported for high-index Fe surfaces such as Fe(310).[10] Similarly, the disagreement between LEED determinations and first-principles calculations of the surface multilayer relaxation of reactive transition metals has been a subject of recent interest. LEED measurements and analysis on Ti(0001), Zr(0001), Ru(0001), Mo(110), W(110), and Rh(001) give considerably smaller surface contractions than first-principles calculations predict.[11] With an enlarged data set and greater variational freedom in the LEED analysis, however, Arnold *et al.*[12] obtained a substantial surface relaxation of W(110), in good agreement with their first-principles FLAPW calculations. This result was confirmed by another independent LEED study by Teeter *et al.*[13] New LEED results that agree well with first-principles calculations were also obtained by Teeter and Erskine in the case of Rh(001) and Ti(0001). Considering these situations, we expect that a reconsideration of LEED analysis would be urged by our FLAPW calculations where the results disagree with the LEED analysis.

In this paper, we determined the multilayer relaxation for Cu(hkl=511, 320, and 410) surfaces by the first-principles FLAPW method [within both the local-density approxima-

tion (LDA) and generalized-gradient approximation (GGA)] to investigate the high-index surface interlayer relaxation and compare the results with the experimental LEED analysis. We find good agreement with the LEED analyses for Cu(511), but large differences for Cu(320) and Cu(410) that may follow from the fact that the LEED analyses of experiments consider up to only three or four layers from the surface whereas even the fifth or sixth layers show large relaxation in our calculations.

II. CALCULATIONS

We calculated the electronic structures and multilayer relaxation for high-index fcc Cu surfaces within the framework of the LDA and the GGA. For LDA and GGA, we use the Hedin-Lundqvist formula[14] and the Perdew-Burke-Ernzerhof (PBE96) formula,[15] respectively. In our calculations, the *film* version of the FLAPW (Ref. 9) method is used to calculate the electronic structure of free-standing (isolated) slabs. This method includes no shape approximation for the charge densities, potentials, and matrix elements.

Our film code has advantages compared to other calculations made with bulk codes where the slab model is repeated with a large vacuum space between adjacent slabs in order to have three-dimensional periodicity. Now, since the size of the vacuum region should be large enough to reduce the interaction between the repeated slabs, the large vacuum region needs a large plane-wave basis set, which makes the calculations heavy. On the other hand, the film-code treats an isolated slab, and so does not have any possible interactions with other slabs. In addition, the vacuum region beyond the surface can be greatly reduced compared to the repeated slab model, and thus the size of the plane-wave basis set is greatly reduced.

The cutoff of the plane-wave expansion is 16 Ry, and the cutoff of the star function expansion is 140 Ry. The muffin-tin sphere radii for Cu is chosen as 2.0 a.u. Within the muffin-tin spheres, lattice harmonics with angular momentum l up to 8 were adopted to expand the charge density, potential, and wave functions.

Using the above parameters, we determined theoretically the lattice constants for bulk fcc Cu in both the GGA and LDA cases. For fcc Cu, GGA, and LDA calculations give 6.83 a.u. (0.0%) and 6.64 a.u. (-2.8%), respectively. (The value in parentheses is the percentage difference from the experimental lattice constant.) These lattice constants are used as in-plane lattice constants in our film calculations. The Cu(511), Cu(320), and Cu(410) surfaces are simulated by 19-layer, 21-layer, and 21-layer slabs, respectively. The total number of k points in the two-dimensional Brillouin zone is 36, 32, and 24 for the (511), (320), and (410) cases, respectively.

The geometry optimization was carried out by minimizing the atomic force on each atom. We chose the bulk-terminated one for the starting initial geometry. The surface cell is taken as 1×1, i.e., no reconstruction is considered as in the experimental analysis. The equilibrium structure is assumed when the atomic force on each atom becomes less than 0.002 Ry/a.u.

III. RESULTS AND DISCUSSIONS

The interlayer relaxation and registry shift are expressed as $\Delta d_{i,i+1}$ and $\Delta r_{i,i+1}$, respectively, between the ith and $(i+1)$th layers from the surface. They are defined as follows:

$$\Delta d_{i,i+1}=(d_{i,i+1}-d_{bulk})/d_{bulk}\times 100, \tag{1}$$

$$\Delta r_{i,i+1}=(r_{i,i+1}-r_{bulk})/r_{bulk}\times 100. \tag{2}$$

Here, $d_{i,i+1}$ means the interlayer distance between ith and $(i+1)$th layers from the surface, $r_{i,i+1}$ is the distance parallel to the surface along a mirror plane, and d_{bulk} and r_{bulk} are nonrelaxed bulk values determined from the theoretical lattice constant.

A. Cu(511)

The calculated results, obtained using GGA and LDA and full geometry optimization for Cu(511) are summarized in Table I. PP (LDA) indicates the result from the pseudopotential calculations using mixed basis (plane waves and local orbitals) with LDA by Heid *et al.*[7] Experimental analyses by LEED (Ref. 16) and x-ray[17] diffraction are also given.

First, we compare our GGA and LDA results in Table I. There are 3.7%, 2.6%, 3.7%, and 2.5% differences in the first-, second-, third-, and fourth-layer relaxation $(\Delta d_{12},\Delta d_{23},\Delta d_{34},\Delta d_{45})$. However, the overall trend in the layers is similar between the GGA and LDA results.

In the pseudopotential calculations[7] with LDA, Cu$(n11)$ $(n=2,5,7,9)$ and Cu(331) surface relaxations were investigated systematically; the results showed that the step atom (1st layer) contracts inward, the corner atom moves outward, and the atoms in the adjacent chain undergo a large inward relaxation. In other words, if there are $n+1$ rows on a terrace, the first n layers exhibit inward relaxation and the $(n+1)$th layer (corner atom) has an outward relaxation.[3] In the case of Cu(511), the third atom from the surface corresponds to the corner atom. Therefore, Δd_{12} and Δd_{23} show contractions and Δd_{34} shows an expansion, whose trend can be denoted as $(--+)$. Compared to our results, their inward relaxation of the first layer (Δd_{12}) is significantly smaller. However, this trend $(--+)$ is the same as that in our calculations. In deeper layers $(i>3)$, the sign of $\Delta d_{i,i+1}$ is the same between the PP result and our results except for Δd_{67}, where the difference in sign is not so significant since the absolute values are small. The trend of registry shifts $(\Delta r_{i,i+1})$ in the PP results is quite similar to our results.

The analysis of the LEED experiment gives similar results compared to our results and those of PP calculations. However, another analysis from x-ray measurements shows a different result, namely, the second layer (Δd_{23}) shows an outward relaxation and the third layer (Δd_{34}) shows a very small inward relaxation, which is denoted as $(-+-)$.

We compared the total energies of these different geometries: while the total energy of the geometry determined by x-ray diffraction was 127 meV (66.2 meV) lower than the total energy of the bulk terminated surface in the GGA (LDA) case, it is still higher than that of our fully relaxed

TABLE I. Calculated and experimental relaxation for Cu(511). Δd_{ij} and Δr_{ij} are the percentage of relaxation with respect to bulk values (d_{bulk} and r_{bulk}) for interlayer distance and registry shift, respectively. See text.

	This work		PP (LDA) (Ref. 7)	LEED (Ref. 16)	X-ray (Ref. 17)
	GGA	LDA			
d_{bulk}(a.u.)	1.315	1.279	1.311		
Δd_{12}(%)	−17.1	−13.4	−9.3	−13.2	−15.4
Δd_{23}(%)	−13.8	−11.2	−10.7	−6.1	+8.1
Δd_{34}(%)	+11.0	+7.3	+7.2	+5.2	−1.1
Δd_{45}(%)	−7.4	−4.9	−2.9	−0.1	−10.3
Δd_{56}(%)	+0.6	+1.9	+1.1	+2.7	+5.4
Δd_{67}(%)	−0.8	−0.4	+1.7		−0.7
Δd_{78}(%)	−3.7	−2.4	−1.5		−6.9
Δd_{89}(%)	+0.7	+1.8	+1.6		+3.6
$\Delta d_{9,10}$(%)	−1.7	−1.0	−0.5		
r_{bulk}(a.u.)	4.648	4.521	4.637		
Δr_{12}(%)	−0.65	−0.44	−1.17		
Δr_{23}(%)	−1.47	−1.09	−1.21		
Δr_{34}(%)	+2.17	+1.33	+0.98		
Δr_{45}(%)	+0.37	+0.36	+0.25		
Δr_{56}(%)	−0.92	−0.63	−0.31		
Δr_{67}(%)	+0.18	+0.08	+0.01		
Δr_{78}(%)	−0.18	−0.07	0.00		
Δr_{89}(%)	+0.06	+0.04	−0.14		
$\Delta r_{9,10}$(%)	+0.01	+0.02			

geometry by 113 meV (103 meV) in the GGA (LDA) case. Furthermore, the geometry optimization calculations, when started from the x-ray geometry, finally converged to the fully-relaxed geometry obtained from the bulk-termination starting point. For these reasons, the geometry obtained by x-ray diffraction is far from the ground state of this system in our calculations.

For a better understanding of surface structure, we show the top view of the Cu(511) surface in Fig. 1. The radius of each atomic sphere is the same as that of touching spheres in the fcc structure. The number labeled on the sphere indicates the layer number counted from the surface. The area surrounded by dashed lines indicates the two-dimensional unit cell parallel to the surface. From this figure, we can easily understand that there are three atom rows (1, 2, and 3) on the terrace and the third-layer atom, which is the so-called corner atom, is the last atom (layer) exposed to the vacuum.

B. Cu(320)

Our calculated results and the analysis of the LEED experiment for interlayer relaxation for Cu(320) are summarized in Table II. We found that there are two different optimized geometries in the case of LDA: The first, labeled (1), is obtained from the starting geometry in which the interlayer distance is the bulk one. The second, labeled (2), is obtained from the starting geometry that is the same as the experimental analysis. There is a 4.3% difference in Δd_{34}, which corresponds to about a 0.04 a.u. difference. The total energy of case (1) is lower than that of case (2) by 3.3 meV. This difference in the total energy is so small that it is difficult to conclude from first-principles calculations which geometry is the real ground state at this stage. In addition, it should be noted here that this difference might be an artifact due to an insufficient *k*-point sampling. In the case of GGA, the second case of the optimizations from the experimental initial geometries converged to the same geometry as case (1) within a

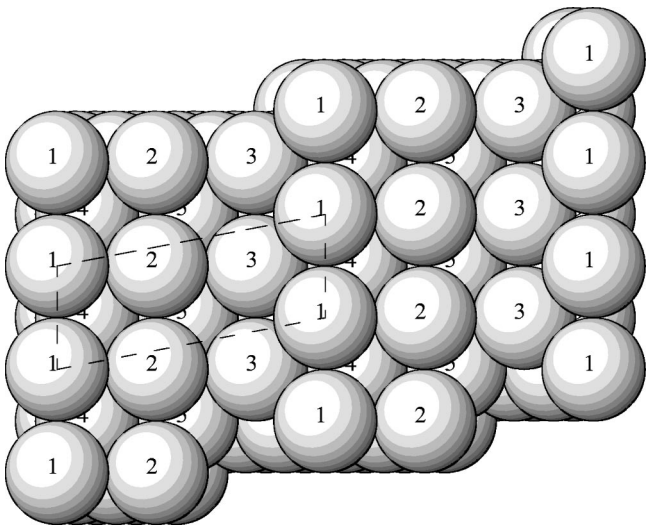

FIG. 1. Top view of the Cu(511) surface. The number on each sphere indicates the layer number from the surface. Nearest-neighbour spheres are shown touching each other. The dashed line indicates the two-dimensional unit cell.

TABLE II. Calculated relaxation of interlayer distance for Cu(320) for the two cases described in the text.

$d_{i,i+1}$	This work (1)		This work (2)	LEED (Ref. 3)
	GGA	LDA	LDA	
d_{bulk}(a.u.)	0.947	0.923	0.923	
Δd_{12}(%)	−16.7	−14.1	−15.3	−24±6
Δd_{23}(%)	−13.8	−13.0	−15.0	−16±12
Δd_{34}(%)	−5.9	−7.1	−2.8	+10±6
Δd_{45}(%)	−7.1	−3.1	−5.0	
Δd_{56}(%)	+16.7	+12.9	+12.2	
Δd_{67}(%)	−4.6	−2.2	−2.9	
Δd_{78}(%)	−1.7	−0.5	−1.6	
Δd_{89}(%)	+0.5	+0.1	+1.3	
$\Delta d_{9,10}$(%)	−5.8	−2.1	−3.0	
$\Delta d_{10,11}$(%)	+2.2	+0.7	+0.5	
r_{bulk}	4.737	4.607	4.607	
Δr_{12}(%)	−0.12	−0.07	−0.08	
Δr_{23}(%)	+0.06	−0.13	−0.20	
Δr_{34}(%)	+0.39	+0.52	+0.52	
Δr_{45}(%)	+0.18	+0.08	+0.04	
Δr_{56}(%)	−1.28	−0.93	−0.91	
Δr_{67}(%)	+0.64	+0.50	+0.60	
Δr_{78}(%)	−0.09	−0.17	−0.12	
Δr_{89}(%)	+0.15	+0.24	+0.16	
$\Delta r_{9,10}$(%)	+0.00	−0.02	0.00	
$\Delta r_{10,11}$(%)	−0.05	−0.04	−0.04	

1% difference in $\Delta d_{i,i+1}$. Among these three cases, there are common features: the first and second layers (Δd_{12} and Δd_{23}) from the surface show a large contraction and the fifth layer (Δd_{56}) shows a large expansion.

The experimental analysis by Jona *et al.*[3] considers only three layers for interlayer relaxation and shows that the third layer undergoes a large expansion—in very clear contrast to our results. Both calculated geometries do not show such a large expansion of the third layer (Δd_{34}). As stated above, when we started the second self-consistent geometry optimization from the geometry determined by LEED analysis, we finally got the optimized geometries that are far from the initial LEED geometry.

The compact step notation for the Cu(320) surface is 3(110)(100), which means that (110) terraces with three atom rows are separated by steps in the ⟨100⟩ direction. As stated above, a general rule was found in the Cu(511) case, that if there are $n+1$ rows on a terrace, the first n layers exhibit inward relaxation and the $(n+1)$th layer has an outward relaxation.[3] This rule was also assumed to be valid in the Cu(320) case, where, however, the situation is different compared to other surfaces such as Cu(511).

Looking at the top view of the Cu(320) surface in Fig. 2, we can understand that the terrace on the Cu(320) surface is significantly different compared to the terrace on the Cu(511) surface. For the Cu(511) terrace, the fourth- and fifth-layer atoms are almost completely hidden by first-, second-, and third-layer atoms. The third-layer atom is regarded as the corner atom (the last exposed atom) and the third-layer (Δd_{34}) shows an expansion. On the other hand, for the Cu(320) terrace, the fourth- and fifth-layer atoms are greatly exposed to the vacuum, and so we can no longer say that the third layer is the last exposed. For this reason, we should not regard the third atom but the fifth atom from the surface as the corner atom or the last exposed atom. In this way, it

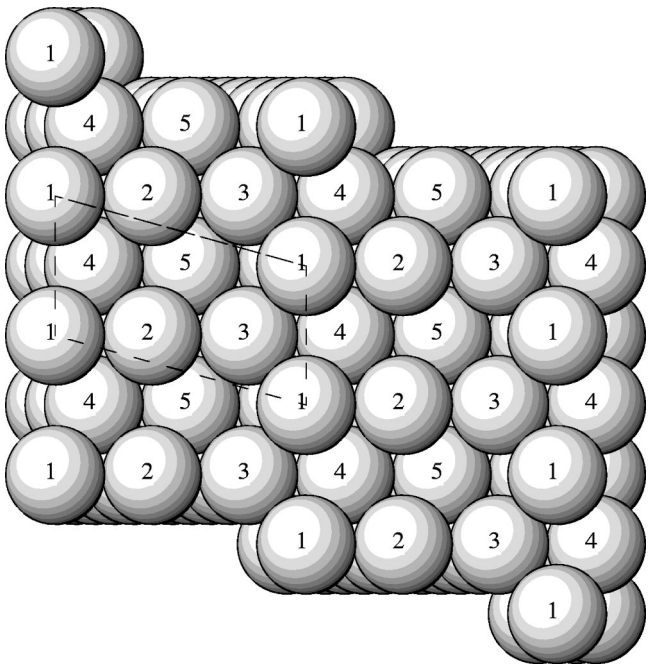

FIG. 2. Top view of the Cu(320) surface; notation as in Fig. 1.

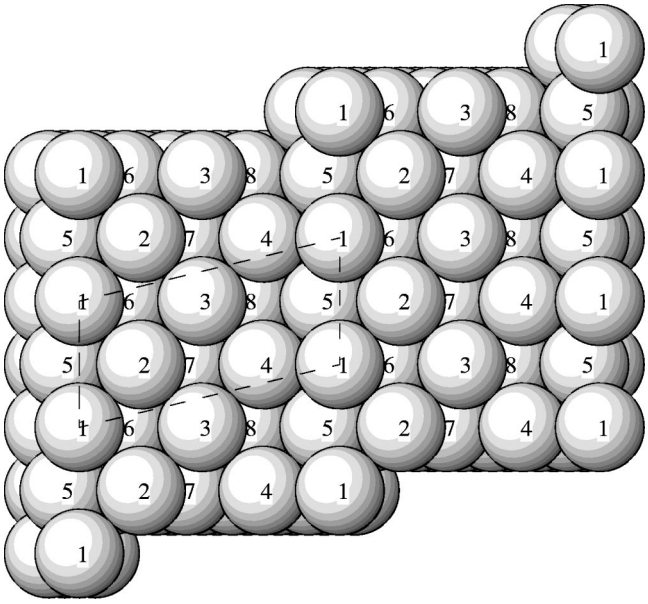

FIG. 3. Top view of the Cu(410) and Ag(410) surface; notation as in Fig. 1.

makes sense that the fifth layer shows an outward relaxation in our results, which now obey the general rule stated above. From this, it appears that experimental analyses should include up to at least the fifth layer in order to properly account for the relaxation.

C. Cu(410)

The top view of the Cu(410) surface shown in Fig. 3 shows that it is a complicated one compared to the other surfaces. We can see that five layers from the surface are greatly exposed to vacuum and that a small portion of even the sixth, seventh, and eighth layers can also be seen from the top—making it a very open surface. For this reason, we can see that experimental and theoretical analyses for relaxation should consider more than five layers from the surface.

The calculated and experimental results for Cu(410) are summarized in Table III. These results were obtained by geometry optimization in which the initial geometry is a bulk terminated one. We tried the other initial geometry that is the same as the experimental analysis for Ag(410),[18] but we did not get a different final geometry.

Another theoretical result by the EAM is shown in Table III. Compared to our results, there is a significant difference. In the EAM case, Δd_{45} shows expansion, whereas Δd_{45} shows contraction in our case. We calculated the total energy of the EAM geometry to be lower than that of the bulk-termination surface by 160 meV (148 meV) in the GGA (LDA) case. However, this total energy is still higher than that of the fully optimized geometries by 109 meV (101 meV) in the GGA (LDA) case. Furthermore, the geometry optimization starting from this EAM geometry converged to our fully optimized geometries stated above. Hence, we can say that the EAM geometry is far from the ground state.

There are two experimental analyses to compare with our results. The first one is the LEED study,[19] which shows almost no relaxation in d_{12}—in complete disagreement with our result. The second is the ion-scattering result,[20] which shows a large contraction in d_{12} in quite good agreement with our result. These results were discussed in previous papers[21] and compared with the calculated result by a modified point-ion model of multilayer relaxation. The result of this model showed large compressions in both Δd_{12} (26.7%) and Δd_{23} (28.2%).

TABLE III. Calculated relaxation of interlayer distances for Cu(410) compared with EAM results. Exp(1) LEED, $\Delta d_{12}=0\%$ (Ref. 19); Exp(2) IS, $\Delta d_{12}=-21.7\pm 6\%$ (Ref. 20), deduced from the value of depression, 0.18 ± 0.05 Å.

	This work		EAM (Ref. 6)
$d_{i,i+1}$	GGA	LDA	
d_{bulk}(a.u.)	0.828	0.806	
Δd_{12}(%)	−16.9	−17.4	−12.7
Δd_{23}(%)	−10.9	−8.1	−8.7
Δd_{34}(%)	−7.3	−10.1	−11.6
Δd_{45}(%)	−3.6	−4.6	+6.2
Δd_{56}(%)	+8.5	+8.4	+9.2
Δd_{67}(%)	−5.4	−3.6	−4.6
Δd_{78}(%)	−2.3	−1.9	−5.5
Δd_{89}(%)	+1.5	+1.2	−3.6
$\Delta d_{9,10}$(%)	+0.3	+0.5	
$\Delta d_{10,11}$(%)	−1.8	+0.5	
r_{bulk}	3.314	3.223	
Δr_{12}(%)	−1.95	−2.04	
Δr_{23}(%)	−0.54	−0.23	
Δr_{34}(%)	−0.13	−0.56	
Δr_{45}(%)	−1.48	−1.80	
Δr_{56}(%)	+3.24	+3.35	
Δr_{67}(%)	+0.46	+0.74	
Δr_{78}(%)	−0.72	−0.81	
Δr_{89}(%)	−0.47	−0.62	
$\Delta r_{9,10}$(%)	−0.23	−0.20	
$\Delta r_{10,11}$(%)	+0.12	+0.12	

IV. CONCLUSIONS

We performed multilayer relaxation of high-index Cu(511,320,410) surfaces by the FLAPW method. In the case of Cu(511), our calculated results are in good agreement with the LEED analysis and a previous theoretical calculation.[7] In the Cu(320) and Cu(410) cases, we found that even the fifth layer from the surface shows a large (outward) relaxation. These optimized geometries show large differences compared with the analysis of LEED experiments which, however, included only a few layers. However, our results are consistent with the general rule: the last exposed layer shows expansion and the other surface layers show contraction. In the case of Cu(320), there are more than one optimized geometries in which the total-energy difference of the two was very small (of order of meV). In addition, the calculated total energy assuming the geometries determined from experimental analyses was significantly

higher than the total energy for the optimized geometries. Hence, we suggest that the experimental analysis should include up to fifth or more layers for interlayer relaxation at very high-index surfaces such as Cu(320) and Cu(410).

Very recently, the calculated results of atomic relaxations on the Ag(410) and Cu(320) stepped surfaces using embedded atom method were published.[22] There are some discrepancies in d_{23}, d_{34}, and d_{45} between theirs and ours. This might be due to the very small energy differences among some possible geometries. However, the most striking feature, the large expansion between fifth and sixth layers (d_{56}), is commonly found.

ACKNOWLEDGMENTS

We thank T. Shishido and Yu-Jun Zhao for helpful discussions.

[1] F. Jona, Surf. Rev. Lett. **6**, 621 (1999).
[2] X.-G. Zhang, P.J. Rous, J.M. MacLaren, A. Gonis, M.A. Van Hove, and G.A. Somorjai, Surf. Sci. **239**, 103 (1990).
[3] Y. Tian, J. Quinn, K.-W. Lin, and F. Jona, Phys. Rev. B **61**, 4904 (2000).
[4] S. Durukanoglu, A. Kara, and T.S. Rahman, Phys. Rev. B **55**, 13 894 (1997).
[5] I.Yu. Sklyadneva, G.G. Rusina, and E.V. Chulkov, Surf. Sci. **416**, 17 (1998).
[6] S. Durukanolu and T.S. Rahman, Surf. Sci. **409**, 395 (1998).
[7] R. Heid, K.P. Bohnen, A. Kara, and T.S. Rahman, Phys. Rev. B **65**, 115405 (2002).
[8] W.T. Geng and A.J. Freeman, Phys. Rev. B **64**, 115401 (2001).
[9] E. Wimmer, H. Krakauer, M. Weinert, and A.J. Freeman, Phys. Rev. B **24**, 864 (1981), and references therein; M. Weinert, E. Wimmer, and A.J. Freeman, *ibid.* **26**, 4571 (1982).
[10] W.T. Geng, M. Kim, and A.J. Freeman, Phys. Rev. B **63**, 245401 (2001).
[11] P.J. Feibelman, Surf. Sci. **360**, 297 (1996).
[12] M. Arnold, G. Hupfauer, P. Bayer, L. Hammer, K. Heinz, B. Hohler, and M. Scheffler, Surf. Sci. **382**, 288 (1997).
[13] G. Teeter, J.L. Erskine, F. Shi, and M.A. Van Hove, Phys. Rev. B **60**, 1975 (1999).
[14] L. Hedin and B.I. Lundqvist, J. Phys. C **4**, 2064 (1971).
[15] J.P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[16] M. Albrechit, R. Blome, H. L. Meyerheim, W. Moritz, and I. K. Robinson (unpublished).
[17] D.A. Walko and I.K. Robinson, Phys. Rev. B **59**, 15 446 (1999).
[18] F. Jona, P.M. Marcus, E. Zanazzi, and M. Maglietta, Surf. Rev. Lett. **6**, 355 (1999).
[19] M. Henzler and E. Suliga, Appl. Surf. Sci. **25**, 179 (1986).
[20] A.J. Algra, S.B. Luitjens, E.P.Th.M. Suurmeijer, and A.L. Boer, Surf. Sci. **100**, 329 (1980).
[21] P. Jiang, F. Jona, and P.M. Marcus, Surf. Sci. Lett. **185**, L520 (1987).
[22] S. Durukanoglu and T.S. Rahman, Phys. Rev. B **67**, 205406 (2003).