

Geometric structure and surface vibrations of Cu(001) determined by medium-energy ion scattering

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We have investigated the geometric structure and the vibrational properties of Cu(001) with medium-energy ion scattering. The surface structure follows the common trend for metal surfaces. The surface relaxation is found to be small and oscillatory with a top-layer contraction (Δd_{12}) of -2.4% and a second-layer expansion (Δd_{23}) of $+1\%$. In addition, we find that the surface vibrational amplitude is enhanced (as is usually the case) by $\sim 80\%$. A detailed analysis of our data shows an unexpected anisotropy of the vibrational amplitude, such that the out-of-plane vibrational amplitude is 30% smaller than the in-plane vibrational amplitude. This anisotropy can be removed by adsorbing $\frac{1}{4}$ monolayer of sulfur on the surface. Our results are discussed in the context of surface stress and surface contractions.

I. INTRODUCTION

When a crystal is cleaved, a charge redistribution occurs in the surface region. This effect causes atoms at the surface to relocate and form another lower-energy atomic configuration, resulting in a surface relaxation and/or reconstruction. Since the (001) surfaces of fcc metals are close-packed surfaces, the charge redistribution and atomic rearrangement on these surfaces are expected to be small. This has been demonstrated previously for Cu(001),¹⁻⁴ although the exact magnitudes of the surface relaxations vary from experiment to experiment. In this paper we report results for the changes of the first two interplanar separations using medium-energy ion scattering (MEIS) in the channeling and blocking configuration. Our results show that the surface relaxations of Cu(001) follow the expected trend for metal surfaces in that a small oscillatory relaxation exists. More unexpectedly, our data also show that the surface vibrational amplitudes exhibit an unusual anisotropy.

Medium-energy ion scattering is a quantitative technique for the analysis of surface structure and morphology.⁵ The angular distribution of the backscattered flux, and in particular the positions of surface blocking directions, contain direct information about the surface atomic structure. The technique measures the total hitting probability of atoms encountered by the incoming protons along a row of atoms in a high-symmetry crystallographic direction. In channeling, atoms in the first layer of the crystal will shadow atoms in deeper layers. If all the atoms are frozen at their bulk sites, the deeper-layer atoms along the row will be completely shadowed by the surface atom. However, in the presence of thermal vibrations, atoms in deeper layers will have a chance to be exposed to the incident ions. The hitting probabilities of deeper-layer atoms are a function of the vibrational amplitude of the surface atoms. Therefore, MEIS is also sensitive to surface vibrations. By varying the angle of incidence of the ion beam, one can in principle probe the anisotropy of the surface vibrational amplitude.

In most cases studied by ion scattering, both by us⁶⁻⁸ and others,⁹⁻¹⁴ it has been found that the surface vibra-

tional amplitudes are significantly larger than in the bulk by as much as 50% or sometimes even more. In the simplest picture, this is due to the reduced coordination of surface atoms so that the atoms are bound more loosely at the surface than in the bulk. Furthermore, the most significant change in the surface region is in the normal direction, along which the bonds from the other half of the crystal are missing. This effect, it is often argued, may result in an extra softening of the vibrations along the normal direction. Therefore, in this simple picture we expect that the out-of-plane vibrational amplitude should be larger than the in-plane amplitude. This expectation is supported by a large body of experiments,¹⁰⁻¹⁴ as well as some theoretical calculations.^{15,16} Our data for Cu(001) show, on the other hand, that the in-plane vibrational amplitude on this surface is larger than the out-of-plane amplitude.

The plan of this paper is as follows. We describe the experimental procedures in Sec. II and demonstrate the procedure for extracting information about the surface relaxations and surface vibrations in Sec. III. We discuss our results and the origin of the vibrational anisotropy in Sec. IV and finally summarize in Sec. V.

II. EXPERIMENT

The ion-scattering experiments were carried out with a 100-keV proton beam. The backscattered ions were measured over an angular range of 24° in the scattering plane with a high resolution electrostatic toroidal energy analyzer. The ratio of the charged particle flux to the total number of particles exiting the target crystal ($P+$) was measured (using a surface-barrier detector) to be 0.77 at 100 keV. The experiments were performed at room temperature with a base pressure $\sim 10^{-10}$ Torr.

The sample was prepared by standard sputtering and annealing cycles until a sharp (1×1) low-energy electron diffraction (LEED) pattern appeared. The cleanliness was monitored by Auger electron spectroscopy (AES) using a double-pass cylindrical mirror analyzer. No detectable impurities were observed. The spectra were inspected carefully for evidence of beam-induced surface dam-

age. No effect was found even with a beam dose one order of magnitude higher than that used below.

III. DATA ANALYSIS

The ion-scattering experiments were performed in three scattering geometries including both the (010) and (110) scattering planes. The scattering geometry and experimental data around the $[10\bar{1}]$ blocking dip (90° scattering angle) for the $[10\bar{1}]$ incidence direction in the (010) zone are shown in Figs. 1(a) and 1(b), respectively. Based on the scattering geometry displayed in Fig. 1(a), simple trigonometry tells us that a blocking dip should occur exactly at 90° if the surface atoms were in their bulk lattice sites. However, the data show some asymmetry about 90° with lower yields on the left side. The shift of the spectrum towards smaller angles is $\sim 0.5^\circ$, implying that the Cu(001) surface is slightly contracted.

To extract detailed structural parameters, the measured spectra should be compared to computer simulations for different surface structural arrangements. Since the ion-surface interaction potential is well known in the energy range we are working in,¹⁷⁻¹⁹ both experiments

and Monte Carlo simulations can be done in absolute units. In favorable cases (for ideally terminated surfaces, such as the one studied here), the structural parameters can be extracted to an accuracy of a few hundredths of an angstrom by a reliability (R) factor analysis. The R factor is defined as

$$R = \frac{100}{N} \left[\sum_{i=1}^N \left(\frac{wY_{\text{expt}} - Y_{\text{calc}}}{wY_{\text{expt}}} \right)^2 \right]^{1/2},$$

where Y is the (experimental or calculated) yield, N is the number of scattering angles, and w is a scaling factor.²⁰ The R factor is a measure of the quality of fit between the experimental yields and a Monte Carlo simulation for a trial structure. The factor of 100 renormalizes the R factor to more convenient size. R factors obtained in MEIS and LEED cannot be compared directly. By varying the trial structural parameters, a minimum R factor can be obtained, which signifies the optimal surface structure. The scaling factor w puts the emphasis of the fit to the angular spectrum on the overall shape rather than on the absolute scattering yield. For a good fit, w is equal to or very close to 1, which is the case in our analysis.

As the incoming protons probe relative atomic vibrations only, the correlation of vibrational motion between adjacent atoms^{21,22} has to be taken into account. We use an effective vibrational amplitude U' which is obtained by rescaling the one-dimensional vibrational amplitude U : $U' = U\sqrt{1-C}$.^{7,8} Here, C is the correlation coefficient between adjacent atoms along the incident-beam direction. Both U and C are calculated in the Debye model. We have used this procedure earlier successfully in analysis of other ion-scattering data.⁶⁻⁸ The correlation coefficient C depends upon the distance between adjacent atoms along the incident-ion beam direction. In the Debye model, C is calculated to be 0.37 and 0.17 for ions incident along $[10\bar{1}]$ and $[30\bar{1}]$ in the (010) plane, respectively, and 0.19 for ions incident along $[1\bar{1}\bar{2}]$ in the (110) plane. The bulk thermal vibrational amplitude is also calculated in Debye model to be 0.083 Å, using the bulk Debye temperature of 320 K found in a previous ion scattering study.²³ The enhanced part of the vibrational amplitude is allowed to decay into the bulk by a factor of 2 between adjacent layers.

A search for the best fit parameters with R -factor analysis has been done for the geometry displayed in Fig. 1(a) by varying the change in the first- to second-layer spacing (Δd_{12}) and the change of the second- to third-layer spacing (Δd_{23}) until a global minimum was found. In Figs. 2(a) and 2(b), we show the final R -factor curves versus Δd_{12} and Δd_{23} , respectively. In Fig. 2(a) a clear minimum is found at $\Delta d_{12} = -2.4\%$, while in Fig. 2(b) a minimum is found at $\Delta d_{23} = +1\%$. Figure 2(c) shows the R -factor curve as a function of the normalized surface vibrational amplitude (η , the ratio of surface to bulk vibrational amplitudes). In this plot the minimum is found to be at $\eta = 1.86$, which corresponds a vibrational amplitude of 0.15 Å. Taking correlation into account, the effective vibrational amplitude is found to be 0.12 Å.

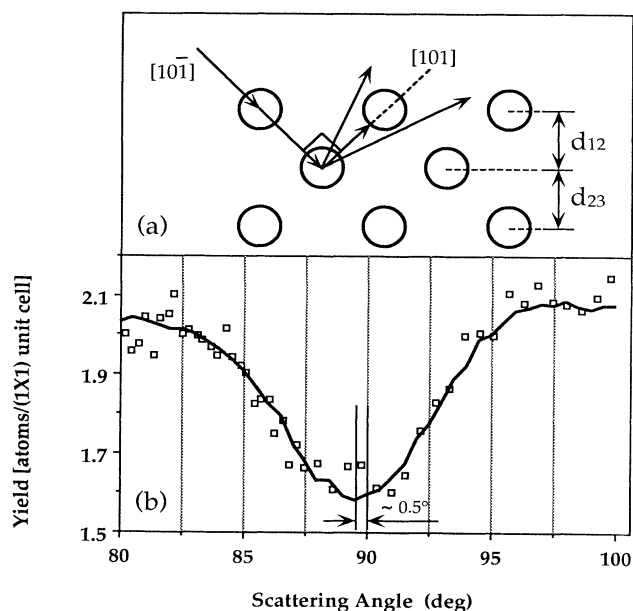


FIG. 1. (a) Scattering geometry for ion-scattering experiments with the beam incident along the $[10\bar{1}]$ direction and detected around the $[101]$ direction. (b) Experimental backscattered yield (open squares) and Monte Carlo simulation (solid line) as a function of scattering angle for 100-keV proton scattering. The vertical lines, distributed symmetrically about 90° , are helpful for observing the asymmetry of the spectrum.

The data from the other scattering geometries agree quite well with the above parameters. The best structure for all of our data sets is therefore obtained for $\Delta d_{12} = (-2.4 \pm 0.8)\%$, and $\Delta d_{23} = (+1 \pm 1)\%$.

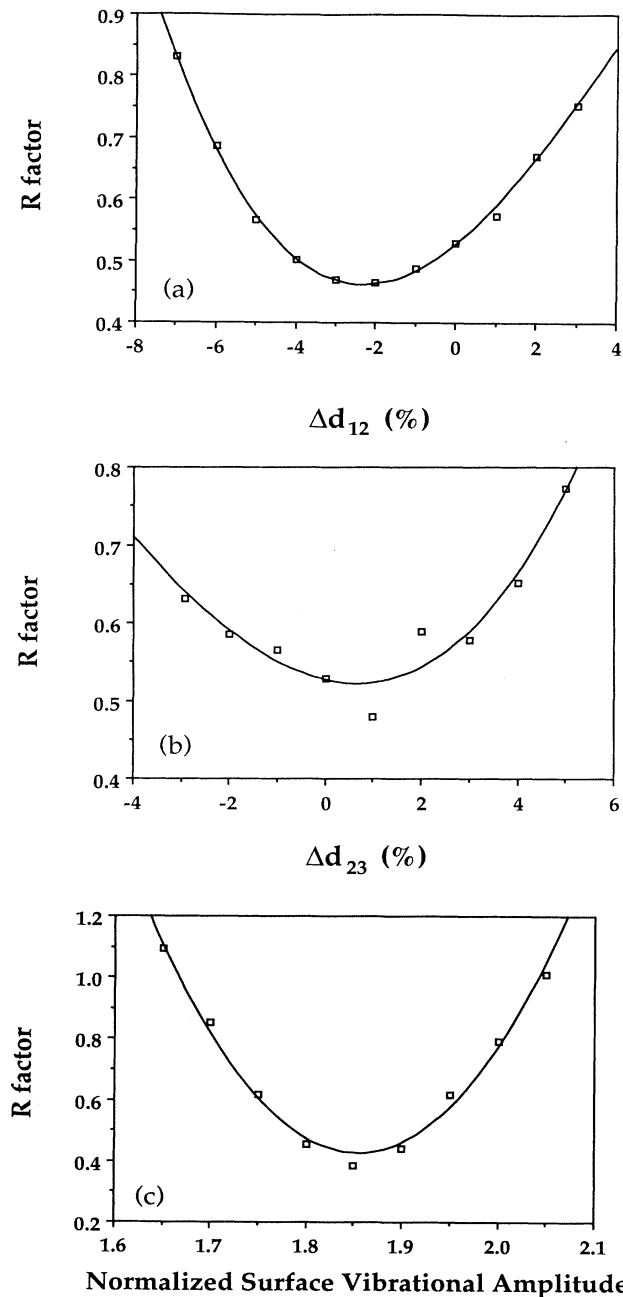


FIG. 2. R -factor plots for the data in Fig. 1(b) as a function of (a) the change of the first- to second-layer spacing (Δd_{12}), (b) the change of the second- to third-layer spacing (Δd_{23}), and (c) the surface vibrational amplitude (normalized to the bulk value). In each case, results are shown with the optimal values for the other two parameters.

One advantage of MEIS is that the technique measures absolute cross sections, and there are no arbitrary fitting parameters involved in the analysis. We find that although the geometric structure converges to the same parameters for data taken in different geometries, the vibrational amplitudes do not. In other words, isotropic vibrations do not explain the data. We can see this effect in Figs. 3(a) and 3(b), in which our experimental data and simulations using both isotropic and anisotropic vibrations are shown for scattering in the $[1\bar{1}\bar{2}]$ and $[30\bar{1}]$ incident directions, respectively. In the isotropic model, the normalized vibrational amplitude of 1.86 measured at 45° incidence is used. It is clear that the simulation using anisotropic vibrations fits our data better. The difference is more pronounced in Fig. 3(b) as the incidence angle there (71.6°) is further separated from 45° than that of Fig. 3(a) (35.3°).

An R -factor analysis with Monte Carlo simulations searching for the best-fit vibrational amplitudes has been carried out. Figures 4(a) and 4(b) show the R factor as a function of the normalized surface vibrational amplitudes

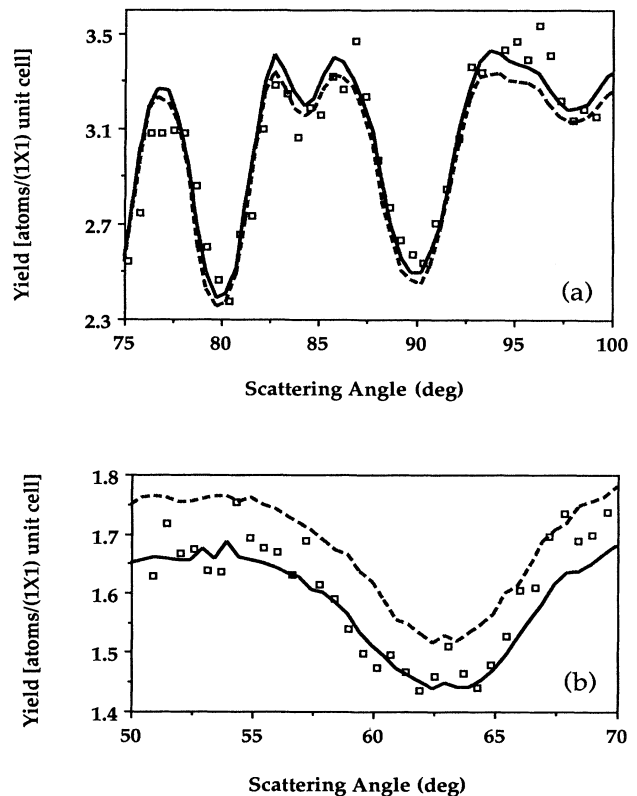
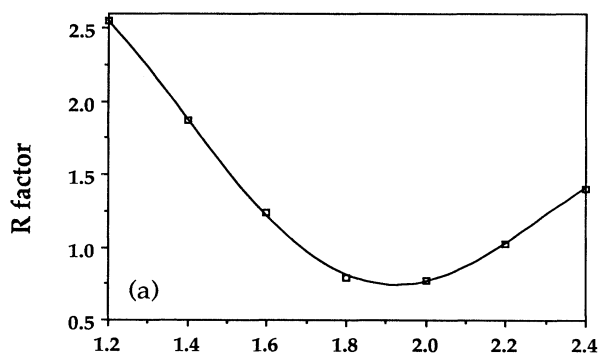


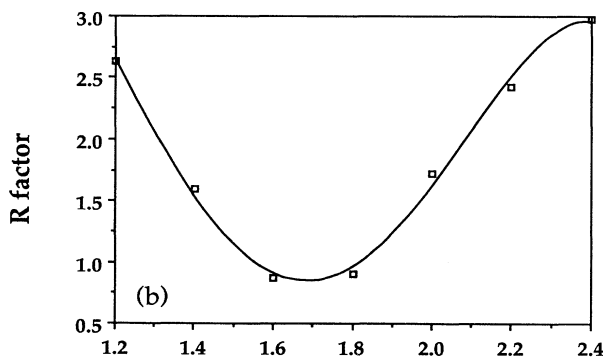
FIG. 3. The experimental yield (open squares) and Monte Carlo simulations using anisotropic (solid lines) and isotropic vibrations (dashed lines) (a) for $[1\bar{1}\bar{2}]$ incidence (35.3° off normal) in the (110) plane and in (b) for $[30\bar{1}]$ incidence (71.6° off normal) in the (010) plane.

for $[1\bar{1}\bar{2}]$ and $[30\bar{1}]$ incidence, respectively. The normalized surface vibration (η) corresponding to the lowest R factor in these two curves is 1.93 for $[1\bar{1}\bar{2}]$ incidence (35.3° off normal) and 1.70 for $[30\bar{1}]$ incidence (71.6° off normal). The values η are greater than one for all the incident angles, which implies that surface atoms vibrate in all directions with an amplitude greater than the bulk value. The vibrational amplitude gets *smaller* as the incident beam is rotated *away* from normal. Since we probe vibrations perpendicular to the ion-beam direction, this leads to the conclusion that the out-of-plane vibrational amplitude is *smaller* than the in-plane vibrational amplitude.

If we picture the surface vibrational amplitudes as an ellipsoid instead of a sphere, with η_{\parallel} lying in the surface plane, and η_{\perp} perpendicular to the surface, the normalized surface vibrational amplitudes extracted from different geometries can be fit by an ellipsoid with $\eta_{\parallel}=2.02$ and $\eta_{\perp}=1.35$ (corresponding to vibrational amplitudes of 0.17 and 0.11 Å, respectively). The anisotropic vibrations correspond to an anisotropic surface Debye temperature with an in-plane magnitude of $\Theta_{\parallel}=160$ K



Normalized Surface Vibrational Amplitude



Normalized Surface Vibrational Amplitude

FIG. 4. R -factor plots vs surface vibrational amplitude (normalized to the bulk value) for (a) $[1\bar{1}\bar{2}]$ incidence in the (110) plane, and (b) $[30\bar{1}]$ incidence in the (010) plane.

and an out-of-plane value of $\Theta_{\perp}=230$ K.

A detailed comparison between our data in the two scattering geometries and Monte Carlo simulations for our optimal structure including the vibrational anisotropy is given in Figs. 5(a) and 5(b). By the standards of MEIS, the simulations agree very well with the data.

In a previous study we found that upon adsorption of $\frac{1}{4}$ monolayer of S on Cu(001) [resulting in a $p(2\times 2)$ S/Cu(001) structure], the top layer of Cu is in a bulklike position and there is no vibrational anisotropy.⁸ Since sulfur is more electronegative than Cu, the S atom shifts the electron distribution away from the substrate towards the new solid-vacuum interface. The direction of this charge transfer is approximately in the opposite direction to the charge redistribution which occurs when the crystal is cleaved. This shift in the electron distribution relieves the top-layer contraction that we observe for the clean surface. In addition, we found that the surface vibrations become isotropic with an amplitude of 0.15 Å ($\eta=1.83$).⁸

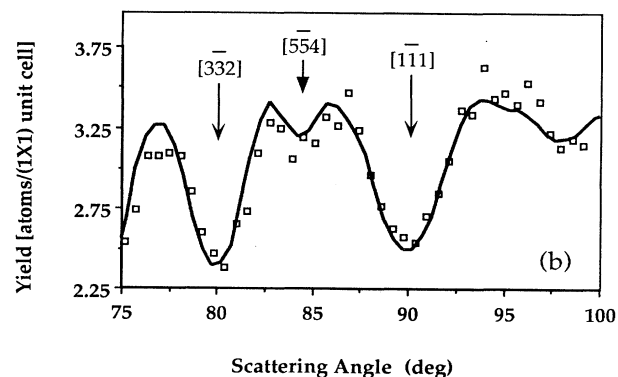
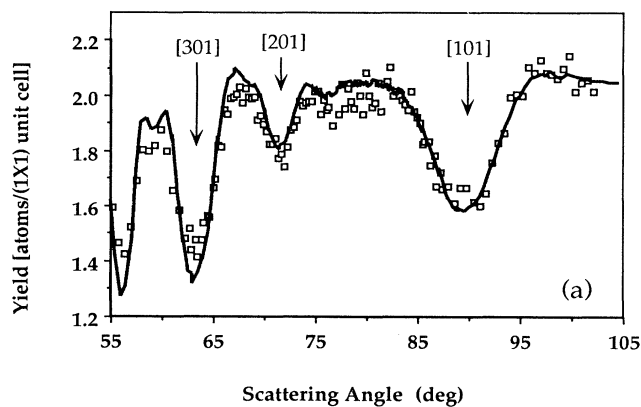


FIG. 5. Experimental data (open squares) and simulations for our optimal structure (solid lines) (a) for protons incident along the $[10\bar{1}]$ direction in the (010) zone, (b) for protons incident along the $[1\bar{1}\bar{2}]$ direction in the (110) zone. The crystallographic direction associated with each blocking dip is indicated in the spectra.

IV. DISCUSSION

Our values for the relaxation of the Cu(001) surface are compared to earlier work in Table I. Theoretical work using the embedded-atom method (EAM) indicated that $\Delta d_{12} = -1.4\%$ and $\Delta d_{23} = -0.3\%$,²⁴ while a first-principles calculation gave $\Delta d_{12} = -3\%$,²⁵ both in good agreement with our findings. From low-energy electron diffraction (LEED) it was concluded that $\Delta d_{12} = -1.1\%$ and $\Delta d_{23} = +1.7\%$,² Spin-polarized LEED (SPLEED) found that $\Delta d_{12} = -1.2\%$ and $\Delta d_{23} = +0.9\%$,⁴ and a previous medium-energy-ion-scattering study (with helium ions as probes) found that $\Delta d_{12} = -2\%$.³ Within an error of $\sim 1\%$, all the studies therefore agree, although there appear to be some minor differences. For example, the earlier LEED study seems to suggest that $\Delta d_{13} > 0$,² while our data imply the opposite.

In a previous medium-energy-ion-scattering study using the same geometry as in Fig. 1(a), an effective vibrational amplitude of 0.12 \AA was found,³ in exact agreement with our results. In addition, low-energy helium scattering experiments (which probe the surface vibrational amplitude in a very different way than MEIS) found the out-of-plane vibrational amplitude to be 0.11 \AA ,²⁶ again in excellent agreement with our results.

Anisotropic surface vibrations with $\eta_{\perp} > \eta_{\parallel}$ have been observed in many systems, such as Pt(111),¹¹ Ni(100),¹² Pb(110),¹³ W(110),¹⁴ O/Ni(100),¹² and Ga/Si(111).²⁷ Exceptions have been found in some recent studies on both clean and chemisorbed surfaces.^{28,29} A LEED study found that the in-plane vibrational amplitude of Ni(110) is about 2.4 times the out-of-plane vibrational amplitude above $\sim 500 \text{ K}$.²⁸ A surface extended x-ray-absorption fine structure study of Cu(100) $c(2 \times 2)$ -Cl determined that the vibrational amplitudes of both the Cl and the surface Cu atoms are approximately twice as large along the surface compared to along the normal.²⁹ To our knowledge, ours is the first report of an anisotropy with $\eta_{\parallel} > \eta_{\perp}$ on a clean metal surface at room temperature.

A simple understanding of the vibrational anisotropy can be found with Badger's rule,³⁰ which states that the product of force constant between atoms and the third power of the change in atomic separation is a constant. This rule leads directly to a conclusion that a surface contraction should be accompanied by an interlayer force constant stiffening. This simple argument has been sup-

ported by calculations using the embedded-atom method,²⁴ where the force constants were calculated directly. Based on this calculation,²⁴ the intralayer and interlayer force constants have been softened and stiffened, respectively, by 15%. However, this 30% difference in the relative force constants (k) would produce only a 15% anisotropy in the relative vibrational amplitudes (since $\eta \sim k^{-1/2}$). Therefore, although the EAM is in qualitative agreement with our results, there is a factor of 2 difference in the magnitude of the anisotropy. If this difference is significant, then there must be another mechanism which has a strong effect on surface vibrations. It is interesting to speculate about the relationship between this difference and surface stress.

The lattice spacing of a free standing fcc (100) surface (two monolayers) has also been calculated with the embedded-atom method.³¹ It was found that Cu prefers a smaller unit cell on its free-standing surface than in the bulk. The mismatch on Cu(001) is relatively large, but smaller than the critical value driving a surface reconstruction [as is found for Au(001) (Ref. 32) and Pt(001) (Ref. 33)]. Therefore, a large strain is present in the Cu(001) surface plane. This may result in a considerable tensile stress. Consequently, the atoms at the Cu(001) surface are bound to each other through an attractive force and will prefer to vibrate as a whole. For this collective vibrational mode, in-plane motion will stretch interlayer bonds less efficiently than out-of-plane motion. Therefore the value of the vibrational amplitude in the plane may be larger than out of the plane. Assuming a rigid surface plane vibrating on top of the Cu substrate (bound through springs), we calculate the ratio of the out-of-plane to in-plane vibrational amplitudes to be $\sim 70\%$, close to our measurement.

The frequency of the Rayleigh mode of Cu(001) measured by electron-energy-loss spectroscopy³⁴ was found to be anomalously high at Brillouin zone boundary. In that study, Wuttig, Franchy, and Ibach claimed that the anomalies can be explained by either introducing a surface tensile stress or stiffening the first interlayer force constant by 20% in analogy with our observations.

V. CONCLUSIONS

In conclusion, we have studied the geometric structure and surface vibrations of Cu(001) using medium-energy ion scattering. The relaxation of Cu(001) follows the

TABLE I. Experimental and theoretical determinations of the surface relaxations of Cu(001). The bulk interplanar separation is 1.81 \AA .

Tech.	MEIS ^a	LEED (Ref. 2)	SPLEED (Ref. 4)	MEIS (He) (Ref. 3)	Calc. ^b	Calc. ^c
Δd_{12}	-2.4%	-1.1%	-1.2%	-2%	-1.4%	-3%
Δd_{23}	+1%	+1.7%	+0.9%		-0.3%	

^aResults of this study.

^bCalculated using the embedded-atom method, Ref. 24.

^cCalculated using a first-principles calculation, Ref. 25.

common trends for metals, while the surface vibrations behave in an unexpected fashion, in which the out-of-plane vibrational amplitude is only $\sim 70\%$ of the in-plane vibrational amplitude. The changes in force constants and surface stress may be responsible for this unexpected behavior. Upon adsorbing $\frac{1}{4}$ monolayer of S on the surface, the surface vibrations become isotropic.

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