

Medium-energy ion-scattering study of the temperature dependence of the structure of Cu(111)

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We have studied the surface structure and vibrations of Cu(111) at temperatures between 300 and 1180 K using medium-energy ion scattering. At 300 K, first and second interlayer spacing contractions of -1.0% and -0.2% , respectively, relative to the bulk spacing are found. Above 1040 K, the first interlayer spacing expands significantly more rapidly than the bulk spacing, so that at 1180 K a $+4.3\%$ expansion is found. This expansion is smaller than the one previously determined for Ag(111), in agreement with predictions. Monte Carlo simulation of spectra show also that the vibration amplitudes of the Cu(111) surface atoms are enhanced by $\sim 30\%$ below 910 K, and $\sim 100\%$ at 1180 K, with respect to their bulk values. [S0163-1829(96)02843-3]

I. INTRODUCTION

Since translational crystal symmetry is broken along the surface normal and the coordination number of the atoms is lower at the surface, the geometric structure and vibrations at the surface are different from those in the bulk. Surface atoms are expected to relocate and reconfigure to a different lowest-energy state, and the vibration amplitudes of surface atoms may be significantly enhanced relative to the bulk atoms. In particular, anharmonic terms of the interaction potential should become more significant for atoms in the surface layer. The anharmonicity of the potential leads to a number of dynamic and static effects which are especially pronounced at high temperatures such as, for example, enhanced surface vibrations,¹⁻⁴ changes in phonon energies and lifetime,⁵⁻⁸ thermal expansion of the surface layers,^{1,9,10} and surface premelting.¹¹⁻¹⁴

In a recent medium-energy ion-scattering (MEIS) study of the clean Ag(111) surface,¹ it was reported that this surface, which is contracted at room temperature, becomes expanded at elevated temperatures. Specifically, the first interlayer spacing increased in a nonlinear fashion from a slightly contracted value relative to the bulk value of -2% at room temperature to being strongly expanded by $+10\%$ at 1150 K. Additionally, the amplitude of the atomic vibrations in the surface layer was found to be enhanced with respect to the bulk value by $\sim 40\%$ for all temperatures studied below 670 K, with the enhancement reaching $\sim 100\%$ at 1150 K. The onset temperature for this additional enhancement was the same (670 K) as the onset temperature for the dramatic changes in the interlayer spacing.

The anomalous thermal expansion of the Ag(111) surface was recently studied theoretically by Narasimhan and Scheffler with an *ab initio* total-energy calculation.¹⁵ They showed that the anomalous surface expansion is related to the softening of a vibrational mode *parallel* to the surface, and also predicted a significant chemical dependence on this softening. Specifically, calculations performed for Cu(111) and Al(111) show that these surfaces behave differently from Ag(111).¹⁵ The Cu(111) surface, also contracted at room temperature, was predicted to become expanded at higher temperatures, but the effect is predicted to be much smaller

than on Ag(111). On the other hand, the Al(111) surface is not predicted to expand significantly for any temperature up to the melting point. Our recent experimental studies show that the thermal behavior of surfaces is indeed material dependent. For example, Ni(111) does not exhibit a significant surface relaxation, and remains nearly bulk terminated for temperatures in the range 430–1100 K.²

In this study, we present MEIS results for the temperature dependence of the interlayer separation, and the rms vibrational amplitude of Cu(111) at temperatures between 300 and 1180 K. Our results are in good agreement with the prediction by Narasimhan and Scheffler, and serve to validate their results.¹⁵

II. EXPERIMENTAL PROCEDURES

The surface structure was determined using MEIS with channeling and blocking.¹⁶ The ion-scattering experiments were carried out with a 97.2-keV proton beam. A collimated proton beam was incident along a high-symmetry channeling direction, the [110] direction, and the backscattered ions were collected around the [001] direction, over an angular range of 22° in the scattering plane, using a high-resolution electrostatic toroidal energy analyzer. The backscattered yields were corrected for the Rutherford cross section, and normalized into atoms in a row visible to the detector as discussed elsewhere.¹⁶

The Cu(111) single crystal was prepared by standard procedures involving cycles of ion sputtering (Ne^+ , 0.5 keV, $2 \mu\text{A}/\text{cm}^2$, 30 min) and UHV annealing (1100 K, 30 min) for a prolonged period of time to reduce the impurity concentration in the bulk and surface. The sample was heated radiatively by a tungsten filament. Experiments were performed in the temperature range between 300 and 1180 K. At high temperatures a calibrated optical pyrometer was used for temperature measurements, while at temperatures below 840 K a chromel-alumel thermocouple was used. The temperature gradient over the sample surface was a few percent, while the temperature variation of the sample during measurements was less than 5 K.

The surface cleanliness was monitored by MEIS. MEIS spectra taken at all but the highest temperatures showed no

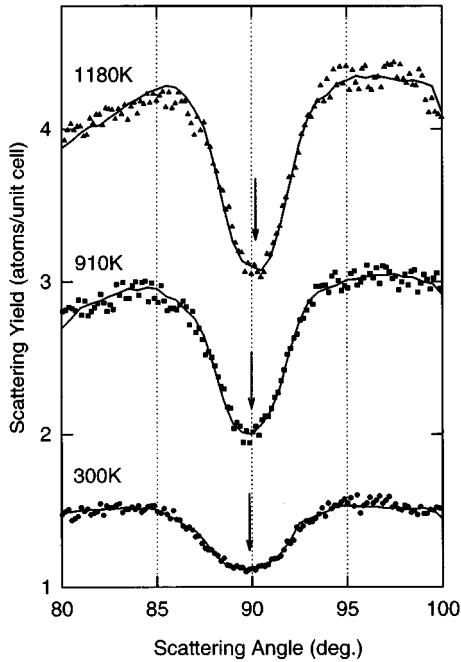


FIG. 1. Angular spectra of backscattered ions from Cu(111) taken at 300, 910, and 1180 K, showing the shift of the blocking dip with temperature. The solid lines are the results of the best-fit simulations. The ion energy was 97.2 keV; the ions were incident in the [110] direction and collected around the [001] direction.

evidence of impurity segregation to the surface. After 2 h of annealing above 1000 K, the surface was found to be contaminated with sulfur corresponding to a coverage of 0.1 ML. Spectra containing less than 0.05 ML of sulfur were therefore used for analysis at this temperature.

III. RESULTS AND DISCUSSION

Figure 1 shows typical angular spectra of backscattered ions taken from the Cu(111) surface at 300, 910, and 1180 K. For a rigid bulk-terminated crystal surface, since subsurface atoms are hidden by the shadow of the surface atom, only the first atom of each row will be visible to the incident ion and involved in the scattering event. Thermal vibrations and/or relaxation will increase the visibility of the subsurface atoms, and result in an increase of the backscattering yield. Some ions backscattered from subsurface atoms will be blocked on their way to the detector by the surface atoms. This blocking leads to a blocking dip in the angular distribution of the backscattered ions. The position of the blocking dip directly reflects the atomic coordinates of the surface atoms. In our scattering geometry, a bulk-terminated surface has a blocking dip at 90° . As the surface layer is contracted or expanded, the blocking dip shifts toward lower or higher scattering angles, respectively. The data in Fig. 1 show that at room temperature the surface blocking dip is shifted very slightly toward lower scattering angles corresponding to a small surface contraction. As the temperature increases, the blocking dip shifts toward higher scattering angles, which indicate that the surface becomes expanded. Also, the absolute yields of backscattered ions increases, which shows that the vibrational amplitudes have increased with temperature. For more accurate information about the surface structure

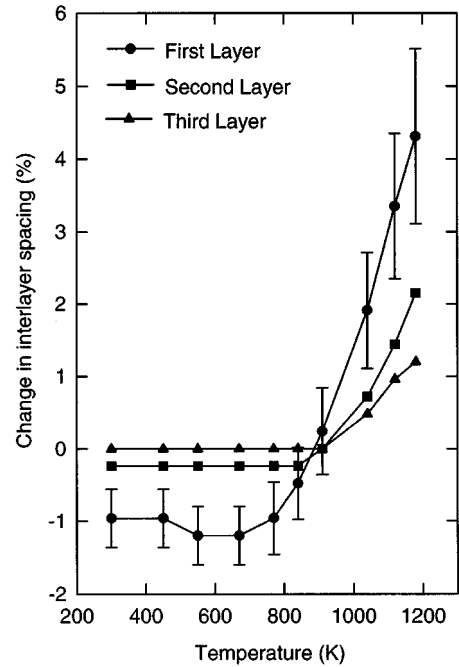


FIG. 2. Change in the surface to bulk interlayer spacing as a function of temperature. Data are shown for the first three interlayer spacings. For clarity only the error bar for first interlayer spacing is shown.

and atomic vibrations, we performed Monte Carlo simulations.¹⁷ The parameters varied were the first three interlayer separations and the corresponding vibrational amplitudes. The bulk vibrational amplitude as well as the nearest-neighbor correlation coefficients used in the simulations were determined using the Debye model. A MEIS reliability R -factor analysis¹⁸ was used to optimize the structural and vibrational parameters. The results of the best fit Monte Carlo simulations are also shown in Fig. 1 as solid lines.

Figure 2 shows the relative change in the surface to bulk interlayer spacing as a function of temperature as derived from the Monte Carlo simulations. Data are shown for the first three interlayer spacing. The error bars shown in Fig. 2 are determined using an R factor that compares the Monte Carlo simulations with the data. For clarity only the error bar for the first interlayer spacing is shown. At room temperature, the surface shows a small contraction of the first and second interlayer spacings of $\Delta d_{12}/d_{\text{bulk}} = -1.0\% \pm 0.4\%$ and $\Delta d_{23}/d_{\text{bulk}} = -0.2\% \pm 0.4\%$, respectively. The error bars here and below reflect only the changes in structural and vibrational properties that would yield statistically inferior fits, and do not include uncertainties of a systematic origin. No significant change was found in d_{34} from the bulk value. The observations disagree with the common trend of oscillatory surface relaxations on metal surfaces. Our results for the Cu(111) surface relaxation at room temperature are summarized and compared in Table I to both experimental results from low-energy electron diffraction (LEED) (Ref. 19) and theoretical values from corrected effective-medium (CEM),²⁰ embedded-atom method (EAM),^{21,22} and first-principles calculations²³ found in the literature. There is an overall agreement that the first and second layers are contracted (or, given the error bars, it is perhaps more appropriate to state

TABLE I. Experimental and theoretical results for surface relaxations of Cu(111) at room temperature.

Method	$\Delta d_{12}(\%)$	$\Delta d_{23}(\%)$	$\Delta d_{34}(\%)$	Reference
MEIS	-1.0	-0.2	0.0	This study
LEED	-0.7			19
CEM	-1.9	0.0		20
EAM	-2.48	-0.04	0.00	21
EAM	-1.39	-0.05		22
First principles	-1.27	-0.64	-0.26	23

that there is a lack of evidence of an expansion of d_{23} and d_{34} . As expected from theoretical calculations,¹⁵ Cu(111) shows a smaller surface relaxation than Ag(111).¹ According to some theoretical calculations, the interlayer force constants are increased by 10–15% for both Cu(111) and Ag(111) from their bulk value,²⁴ while the intralayer force constants are softened relative to their bulk value [by $\sim 8\%$ for Ag(111) and $\sim 13\%$ for Cu(111)].²⁵ The surface atoms in Cu(111) undergo smaller force-constant changes than in Ag(111), in qualitative agreement with our results for the surface relaxation.

Above 550 K the first interlayer spacing contraction appears to increase slightly to $\Delta d_{12}/d_{\text{bulk}} = -1.4\% \pm 0.5\%$. We note that a recent MEIS study on the Cu(100) surface³ reported a slightly larger contraction of that surface above 520 K. At 910 K, the first layer atoms have moved out slightly, so that the surface is nearly bulk terminated. Above 1040 K, all the first three interlayer spacings expand, so that at 1180 K the expansions of the first three interlayer spacing are found to be $\Delta d_{12}/d_{\text{bulk}} = +4.3\% \pm 0.8\%$, $\Delta d_{23}/d_{\text{bulk}} = +2.2\% \pm 0.8\%$, and $\Delta d_{34}/d_{\text{bulk}} = +1.2\% \pm 0.8\%$. The first interlayer spacing changes with temperature are in a good agreement with the recent theoretical study of anomalous thermal expansion for the Cu(111) surface.¹⁵

The surface thermal expansion coefficients can be estimated from the slope of the individual lines in Fig. 2. Figure 3 shows, on a logarithmic scale, the temperature-dependent thermal-expansion coefficients for Cu(111) surface and bulk Cu.²⁶ The surface thermal-expansion coefficients in Fig. 3 were calculated by averaging the change of the first three interlayer spacings to eliminate noise. Below 670 K, the surface thermal-expansion coefficients are similar to the bulk value. At temperatures higher than 670 K, the surface thermal expansion coefficient increases dramatically, so that at 1180 K it becomes some six times the bulk value. Figure 3 also shows the thermal-expansion coefficients for Ag for comparison. The surface thermal-expansion coefficients of Ag(111) are calculated from our previous MEIS data.¹ The surface thermal-expansion coefficients of Ag(111) also increase significantly, so that at 1150 K they become 11 times the bulk value. Clearly, if one were to plot the layer-resolved thermal-expansion coefficients, even more dramatic differences would be observed. Since the thermal expansion is an anharmonic effect, the anharmonicity of the interaction potential is more important in the surface, and becomes more significant as the temperature increases. In Fig. 3, one can see that the onset temperature of Ag(111) is lower than that of Cu(111).

Together with the lattice expansion, an increase of the

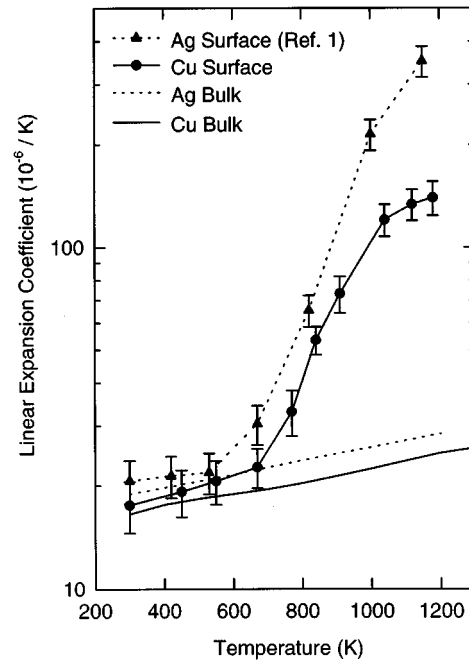


FIG. 3. The thermal expansion coefficient for the Cu(111) surface and bulk Cu. The surface thermal-expansion coefficients were calculated by averaging the changes of the first three interlayer spacings. Also shown for comparison are data for Ag from Ref. 1.

vibrational amplitudes is observed. As shown in Fig. 1 the backscattering yields increase, and the full-width half-minimum of the blocking dip decrease with increasing temperature. These are consequences of the enhancement of the surface vibrational amplitude, which lead to less effective shadowing of subsurface atoms and blocking of the surface atoms at elevated temperatures. Figure 4 shows rms values of the surface vibrational amplitudes normalized to the bulk values *at the same temperature*. At temperatures below 910 K, the rms values of vibrational amplitudes for the first layer are larger than the corresponding bulk values by 20–30%. Above 910 K, the rms values of vibrational amplitudes increase significantly, so that at 1180 K the surface vibrational amplitude become twice that of the bulk value. Just as for Ag(111), the onset temperatures in Figs. 2 and 4 are the same. There are smaller relative enhancements of the second and the third layer vibrational amplitudes. This trend is quite similar to what was observed on Ag(111) (Ref. 1) and Ni(111).² The simultaneous changes in the structural parameters and vibrational amplitudes indicate that the anharmonic term in the interaction potential plays an important role in the lattice expansion, and becomes more significant as the temperature increases.

Recently, anisotropic surface vibrations have been reported for Cu(001).^{3,18} These results show that the perpendicular vibrational amplitudes are smaller than the in-plane vibrational amplitude. This agrees qualitatively with a theoretical calculation based on the EAM, reporting a 15% softening of intralayer force constant and 15% stiffening of interlayer force constant.⁸ On the other hand, the result of a calculation for Cu(111) (Ref. 27) suggests a smaller in-plane vibrational amplitude relative to the perpendicular vibrational amplitude. To study the anisotropic surface vibrations for Cu(111), an additional series of experiments was per-

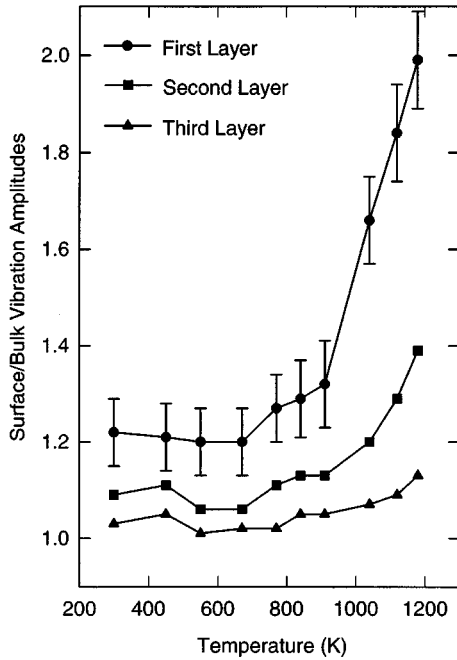


FIG. 4. rms values of surface vibrational amplitudes as a function of temperature. Data are shown for the first three layers. The amplitudes are normalized to the bulk values at the same temperature. For clarity only the error bar for first layer is shown.

formed with the ion beam incident along [111] direction, that is, normal to the surface. In this geometry, the first three layers of Cu atoms are exposed directly to the incident beam, and the backscattering yield is determined mainly by the in-plane vibrational amplitude of the Cu atoms. The backscattered ions were collected around the [001] direction as in the previous geometry. Since the backscattering yield depends only on the in-plane vibrational amplitude in the normal-incidence geometry, the value of the in-plane vibrational amplitude can be determined independently. Then this value of the in-plane vibrational amplitude is used in the Monte Carlo simulation in another geometry in order to determine the perpendicular vibrational amplitude.

Figure 5 shows in-plane and perpendicular surface vibrational amplitudes as a function of temperature. Data are shown for the first layer. The amplitudes are normalized to the bulk values at the same temperature. At room temperature, the perpendicular vibrational amplitude is larger than the in-plane vibrational amplitude by somewhat less than 20%. The ratio of surface to bulk vibrational amplitudes for the in-plane (η_{\parallel}) and perpendicular (η_{\perp}) modes are 1.15 and 1.35, respectively. These values show a good agreement with the result of the embedded-atom-method calculation for Cu(111),²⁷ though the absolute values of vibrational amplitudes themselves are different. There is also quite reasonable agreement if one uses the surface phonon energies calculated by Nelson, Daw, and Sowa²⁴ to calculate the zero-point vibrational mean-square displacement.⁶ The detailed values are listed in Table II. As the temperature increases to 910 K, the ratio of perpendicular to in-plane surface vibrational amplitudes ($\eta_{\perp} / \eta_{\parallel}$) decreases slightly. Above 910 K, the perpendicular vibrational amplitude increases more slightly than the in-plane vibrational amplitude, so that at 1180 K the values of $\eta_{\perp} / \eta_{\parallel}$ becomes ~ 1.3 . It is evident that at all temperatures

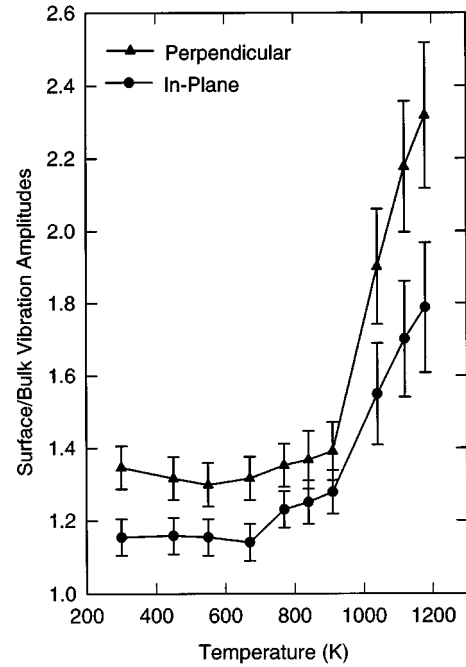


FIG. 5. First-layer in-plane and perpendicular surface vibrational amplitudes as a function of temperature. The amplitudes are normalized to the bulk values at the same temperature.

the in-plane vibrational amplitudes are smaller than the perpendicular vibrational amplitudes. However, there is little change with temperature of the relative size of the two components. For Ag(111), the parallel component increased significantly faster than the perpendicular one, as expected if a parallel vibration is responsible for the anomalous expansion.²⁸ The effect is smaller on Cu(111). Anisotropic surface vibrations with larger perpendicular vibrational amplitude have been observed in many systems, such as Pt(111),²⁹ Ni(100),³⁰ Pb(110),³¹ and W(110).³²

IV. CONCLUSIONS

The structure and vibrations of the clean Cu(111) surface at temperatures between 300 and 1180 K have been studied using medium-energy ion scattering. The surface relaxations and surface vibration amplitudes were determined from comparison of Monte Carlo simulations of the scattering to experimental blocking spectra. At room temperature the sur-

TABLE II. Bulk, perpendicular, and in-plane surface vibrational amplitudes (σ_b , σ_{\perp} , σ_{\parallel}) and the ratio of surface to bulk vibrational amplitudes (η_{\perp} , η_{\parallel}) for Cu(111) at room temperature.

Method	σ_b (Å)	σ_{\perp} (Å)	η_{\perp}	σ_{\parallel} (Å)	η_{\parallel}	Reference
MEIS	0.078 ^a	0.10	1.35	0.09	1.15	This study
EAM	0.084	0.113	1.35	0.098	1.17	27
Phonon data	0.082 ^b	0.119 ^c	1.45	0.088 ^c	1.07	24

^aCalculated using the Debye model.

^bE. C. Svensson, B. N. Brockhouse, and J. M. Rowe, Phys. Rev. **155**, 619 (1967).

^cCalculated from surface phonon calculations from Ref. 24 using the formalism in Ref. 6.

face interlayer spacing changes show an overall agreement with the theoretical calculations. Above 840 K the first surface interlayer spacing begins to increase, and reaches a +4.3% expansion at 1180 K. While Cu(111) therefore shows a transition from contraction to expansion as the temperature is changed, the effect is significantly smaller than for Ag(111). This result is in agreement with predictions of a theoretical calculation.¹⁵ The enhancement of the vibrational amplitudes of the Cu(111) surface atoms increases dramatically with increasing temperatures, as was observed for Ag(111) (Ref. 1) and Ni(111).² This increase of the enhancement of the vibrational amplitude with increasing tempera-

tures implies that the anharmonicity of the surface atomic potential is greater than in the bulk. The spectra taken from different experimental geometries show anisotropic surface vibrations with a larger perpendicular vibrational amplitude than in-plane vibrational amplitude.

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