Surface vibrations and relaxation effects in Cu(001) studied by x-ray diffraction

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A highly precise surface x-ray-diffraction study of the uncovered Cu(001) surface kept at 160 K was carried out. Based on two independent experiments we find that the first (d_{12}) and second (d_{23}) interlayer spacings are contracted by $1.4 \pm 0.4\%$ and expanded by $0.3 \pm 0.4\%$ relative to the bulk value ($d_b = 1.808$ Å), respectively. The root-mean-square (rms) isotropic vibrational amplitude of the top layer atoms (0.095 Å) is enhanced by 80% over the bulk, rapidly decreasing to 20% and 5% for the second and third layers (average values). The rms amplitude top layer vibrations are isotropic within the experimental uncertainty of about 0.02 Å.

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The uncovered crystal surface represents one of the most important objects in surface science, since it forms the basis for the study of epitaxial systems. For this reason, the precise knowledge of the structure of clean crystal surfaces is of paramount importance for the understanding of more complex systems in general.

In contrast to semiconductor surfaces which often reconstruct, low-index metal surfaces represent seemingly simple substrates. A large number of investigations on the geometric structure of metallic surfaces have been carried out in the past. For an overview we refer to Refs. 1–3. In general, an oscillatory relaxation sequence is observed for the interlayer spacings in which the first interlayer distance (d_{12}) is contracted by several percent, while the second one (d_{23}) is expanded.

In contrast, the precise analysis of the structural disorder in terms of the thermal atomic vibrations is relatively scarce. This can be attributed to the fact that for many well established *k*-space analysis tools such as low-energy electron diffraction (LEED), surface-extended x-ray-absorption fine structure, and photoelectron diffraction,[2,3] the displacement amplitude of the atoms in the near-surface region is not an easily accessible quantity. Thermal vibrations induce only tiny modifications of the scattered intensities and the measurement of very precise intensities is required.

At temperatures far below the melting point, thermal disorder can be described in the harmonic approximation using the Debye model leading to the well-known temperature factor $T(q) = \exp(-Bq^2/4)$. Here, $B = 8\pi\langle u^2\rangle$ is the Debye parameter containing the mean-square amplitude of the vibrations ($\langle u^2\rangle$), and $q = |\mathbf{q}|$ represents the amplitude of the momentum-transfer vector $\mathbf{q}$ (see Ref. 4).

In this context, the Cu(001) surface was also a subject of several experimental and theoretical studies; to some of them we refer to Refs. 5–9. For instance, the LEED study by Davis and Noonan[5] provided experimental evidence for the multilayer relaxation. They found a contraction of the first interlayer distance by $\Delta d_{12} = -1.1\%$ and an expansion of d_{23} by $\Delta d_{23} = +1.7\%$. Using spin-polarized LEED experiments, Lind *et al.*[6] derived $\Delta d_{12} = -1.2\%$ and $\Delta d_{23} = +0.9\%$.

Later, using medium-energy ion scattering (MEIS) Jiang *et al.*[7] and Fowler and Barth[8] analyzed the surface layer root-mean-square (rms) vibration amplitude ($V_1 = \sqrt{\langle u^2\rangle}$). Here and in the following the rms vibration amplitude is labeled as V_i, where the subscript refers to the layer number beginning with $i = 1$ from the surface. Depending on the temperature (107–685 K) a 60%–100% enhancement of V_1 as compared to the bulk was determined. Additionally, both studies revealed an anisotropy of V_1, in which the in-plane amplitude ($V_{1\parallel}$) is *larger* than the perpendicular one ($V_{1\perp}$) by 11%–37%.[7,8] This result is at variance with the molecular-dynamics (MD) study of Yang *et al.*,[9] who derived an isotropic top layer rms amplitude, enhanced by 40% over the bulk at 150 K ($V_1/V_{\mathrm{bulk}} = 0.078$ Å$/0.055$ Å). Presently, this issue is not yet resolved. Moreover, an earlier theoretical study[10] suggested that the out-of-plane vibrations are larger than the in-plane ones by about 50% and discrepancy also exists for other systems such as Ni(001), where isotropic (Ref. 11) and anisotropic surface vibrations with a larger perpendicular amplitude were reported (Ref. 12).

Thus, a complete picture of the near-surface structure has not yet evolved. To this end we have carried out precise surface x-ray-diffraction (SXRD) measurements, which—apart from the analysis of the multilayer relaxation—provides a layer resolved quantification of the rms vibrational amplitudes of the Cu atoms down to the third layer. Two independent data sets were collected at different third generation storage rings, namely, at the APS (Argonne, USA) and at the ESRF (Grenoble, France). In the following we label these as "APS" and "ESRF," respectively. Thus, our study also provides an estimate for the reproducibility of SXRD derived structure parameters in general. This appears especially important with regard to the so-called soft parameters such as the thermal vibration amplitudes. The results presented in this Brief Report are encouraging: Layer spacings are reproducible to within 0.01 Å and rms vibration amplitudes to within about 0.025 Å. At present these values are hardly improvable using standard surface structure analysis tools.

The Cu(001) surface was prepared by repeated cycles of Ar^+-ion sputtering and annealing at 900 K. This procedure leads to an atomically clean surface characterized by terraces several hundreds of nanometers wide as revealed by scanning tunneling microscopy.

The SXRD measurements were carried out *in situ* at a sample temperature of 160 K. Integrated intensities were col-

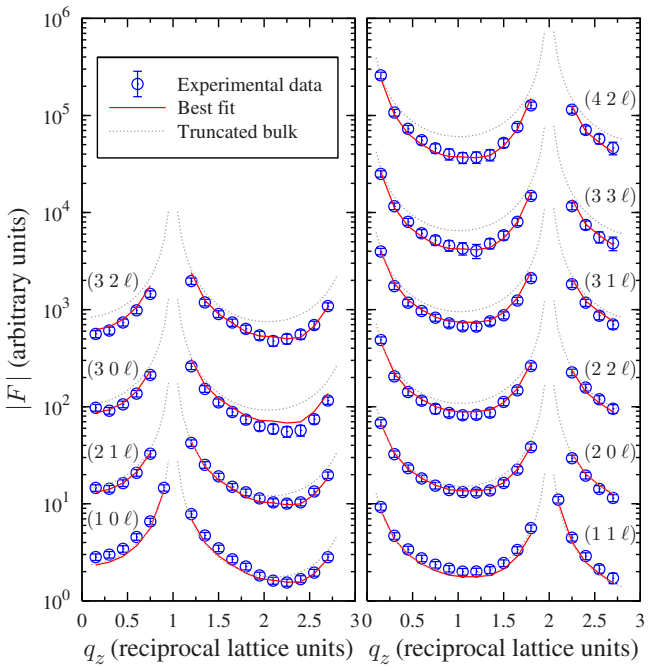

FIG. 1. (Color online) Measured (circles) and calculated (lines) structure factor amplitudes for clean Cu(001). Solid (red) lines correspond to the best-fit model; dotted (gray) lines are calculated for the bulk-truncated crystal. Curves are shifted vertically for clarity.

lected along the integer-order crystal truncation rods (CTRs) (Ref. 13) by rotating the crystal about its surface normal. The structure factor amplitudes $F(q)$ were derived from the integrated intensities by applying geometrical correction factors as described in detail in Ref. 14.

Figure 1 shows the data collected at the ESRF using an x-ray wavelength of 0.62 Å. The detailed comparison with the APS data and the corresponding results is provided by Table I. In total 162 symmetry independent reflections along 10 CTRs were measured. The indexing of the rods is according to the primitive setting of the surface unit cell. Standard deviations (σ) of the $F(q)$ were derived on the basis of the reproducibility of symmetry equivalent reflections.[15,16] Due to the high count rate [e.g., peak intensity $\approx 10^5$ counts/s at the (1 0 0.15) reflection] the contribution of the counting statistics to σ is negligible. For σ we find 5% (APS) and 7% (ESRF), values, which can be considered as excellent.

In Fig. 1 solid (red) lines represent the calculated structure factor amplitudes corresponding to the best-fit structure model. In comparison, dotted (gray) lines represent the structure factor amplitudes calculated for the bulk truncated Cu(001) crystal. In this model the interlayer distances were kept constant at the bulk value ($d_{\mathrm{bulk}}=1.808$ Å) and the rms vibrational amplitude was set for all layers to $V_{\mathrm{bulk}}=0.066$ Å at $T=160$ K. The value for V_{bulk} is calculated using the characteristic Debye temperature $\Theta_D=320$ K for Cu.[17]

Even direct inspection of Fig. 1 allows some qualitative conclusions: (i) There is an inward relaxation of the first layer, which induces an asymmetry in the U-like shape of the CTR profiles. Their minima are shifted to larger q_z values as compared to the CTRs of the truncated bulk model. (ii) The temperature factor $T(q)$ is enhanced over the bulk value, since the deviation between the dotted lines for the truncated bulk model and the experimental data increases with increasing magnitude of the momentum transfer $|q|$, characteristic of the Debye-Waller-type damping.

TABLE I. Comparison between data sets for Cu(001). The bulk interlayer spacing is equal to 1.808 Å.

Interlayer distance (Å)	APS	ESRF
d_{12}	1.788 ± 0.044	1.777 ± 0.028
d_{23}	1.816 ± 0.041	1.806 ± 0.026
d_{34}	1.809 ± 0.040	1.809 ± 0.026
d_{45}	1.807 ± 0.029	1.802 ± 0.018
rms vibrational amplitude (Å)		
V_1	0.090 ± 0.006	0.100 ± 0.013
V_2	0.054 ± 0.008	0.083 ± 0.007
V_3	0.046 ± 0.007	0.073 ± 0.004
V_{bulk}	0.046 ± 0.007	0.066 ± 0.004
Surface to bulk ratio, $\eta_i = V_i / V_{\mathrm{bulk}}$		
η_1	1.95	1.73
η_2	1.17	1.25
η_3	1.00	1.10
rms anisotropic vibrational amplitude (Å)		
$V_{1\parallel}$	0.077 ± 0.015	0.109 ± 0.015
$V_{1\perp}$	0.114 ± 0.015	0.118 ± 0.025
Agreement criterion		
R_u	0.048	0.083
R_w	0.048	0.096
GOF	1.22	1.17
Measurement statistics		
N_{indep}	112	162

The least-squares fitting of the measured structure factor amplitudes included—in addition to an overall scale factor—the first four interlayer spacings $d_{i,i+1}$ $(i=1,2,3,4)$ and the rms displacement amplitudes of the top three layers labeled V_i $(i=1,2,3)$ plus the bulk amplitude V_{bulk}.

An excellent fit could be achieved as represented by the solid (red) line in Fig. 1. The fit quality is quantified by the unweighted residual (R_u) and the goodness-of-fit (GOF) parameter.[18] The results together with the agreement parameters are listed in Table I and can be summarized as follows:

(i) The reproducibility of the interlayer spacings lies within 0.01 Å, somewhat smaller than the standard deviations derived from the variance-covariance matrix (0.02–0.04 Å). For d_{12} we find a contraction of 1.1% (APS) and 1.7% (ESRF). Furthermore, d_{23} is expanded by 0.5% (APS), while for the ESRF data d_{23} is almost equal to the bulk value. Deeper layer spacings are unrelaxed.

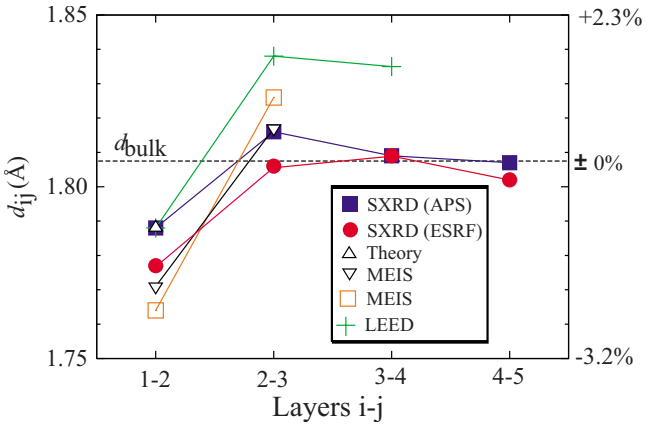

FIG. 2. (Color online) Interlayer distances between layers i and $i+1$. Solid symbols refer to the APS (■) and the ESRF (●) data as indicated, while the other symbols refer to Ref. 5 (+), Ref. 7 (□), Ref. 8 (▽), and Ref. 9 (△). The horizontal dashed line corresponds to the bulk spacing. Error bars are omitted for better overview. Lines are guides for the eye.

(ii) For the (isotropic) rms vibration amplitudes, the reproducibility lies within about 0.025 Å, which is larger than the standard deviations derived from the fitting procedure (≈0.01 Å). Nevertheless, in both data sets there is a clear parallel trend showing an increase in V_i from the bulk (V_{bulk}=0.046 and 0.066 Å) toward the surface (V_1=0.090 and 0.100 Å). This results in an about 10% reproducibility of the surface to bulk ratio $V_i/V_{bulk}=\eta_i$. For η_1 we obtain 1.73 and 1.95, corresponding to a 70%–90% enhancement of the rms vibration amplitude. η rapidly drops for the second layer and almost approaches the bulk value in the third layer (see Table I).

A graphic comparison (APS: solid squares; ESRF: solid circles) is provided in Figs. 2 and 3 for the lattice spacings and the thermal vibrations, respectively. The open symbols correspond to lattice spacings and rms vibrational amplitudes

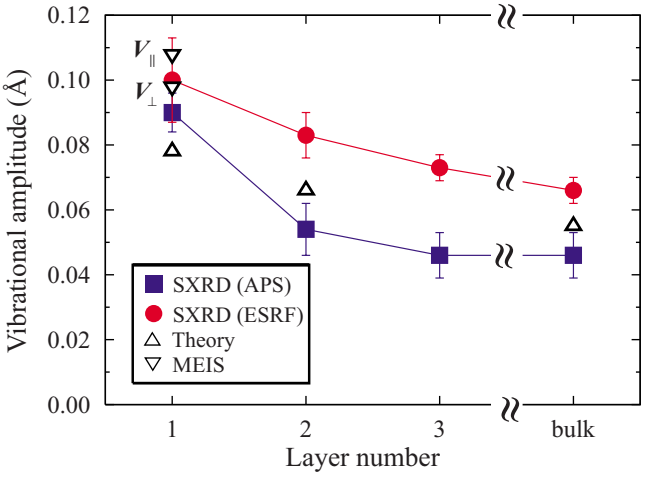

FIG. 3. (Color online) Root-mean-square vibration amplitudes. Solid symbols refer to the APS and the ESRF data as indicated, while the other symbols refer to Ref. 8 (▽) and Ref. 9 (△). Lines are guides for the eye. In-plane and perpendicular vibration amplitudes (Ref. 8) are specified by (∥) and (⊥), respectively.

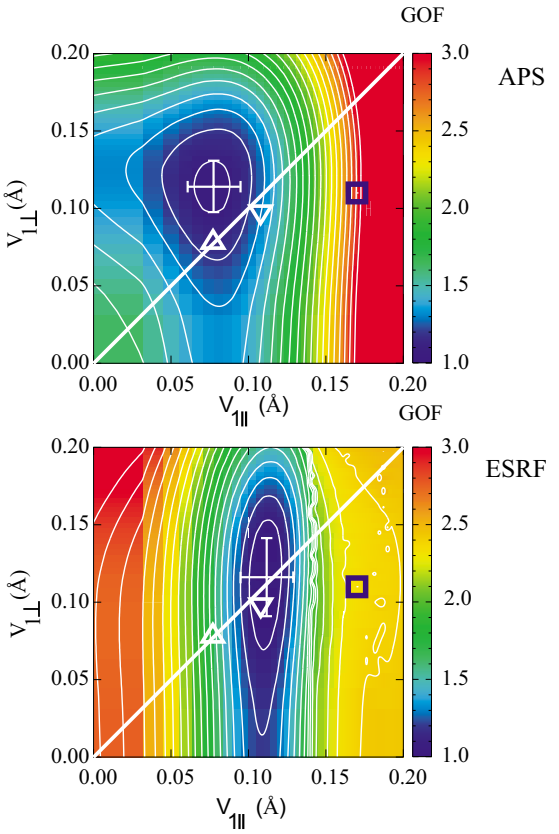

FIG. 4. (Color online) Contour plot of GOF versus $V_{1\parallel}$ and $V_{1\perp}$ for the APS (top) and ESRF (bottom) data. Symbols refer to results of Ref. 7 (□), Ref. 8 (▽), and Ref. 9 (△). The diagonal line represents the condition $V_{1\parallel}=V_{1\perp}$. Contour levels are separated by 0.1 in GOF.

taken from Refs. 5–9. First we discuss the lattice spacings.

In general, the overall agreement between both experimental and theoretical investigations is quite good. The only exception from this rule is the result for $\Delta d_{23}=+1.7\%$ and $\Delta d_{34}\approx+1.5\%$ derived by the early LEED study of Davis and Noonan[5] (+). The expansions appear exceptionally large and were also not reproduced by the later MEIS studies of Jiang *et al.*[7] (□) and of Fowler and Barth[8] (▽). Similarly, the theoretical work of Yang *et al.*[9] (△) is in accord with our findings to within 0.01 Å, corresponding to Δd=0.5%.

Figure 3 compares the results for the thermal vibration amplitudes. In the MEIS study of Fowler and Barth[8] (▽) anisotropic vibrations of atoms in the topmost layer were determined: (i) $V_{1\perp}$=0.084 Å and $V_{1\parallel}$=0.094 Å at 107 K and (ii) $V_{1\perp}$=0.136 Å and $V_{1\parallel}$=0.147 Å at 305 K, i.e., depending on temperature the in-plane vibration amplitudes are about 11%–30% *larger* than the out-of-plane ones. This is at variance with the MD study of Yang *et al.*,[9] who found isotropic vibrations. In Fig. 3 the data of Fowler and Barth[8] and Yang *et al.*[9] are represented by the down (▽) and up (△) triangles, respectively. Note that the data of Fowler and Barth[8] were adjusted to 160 K for comparison with our results by interpolation based on the Debye model. Within 0.015 Å their results are in agreement with our values of V_i.

In order to address the anisotropic surface vibration issue in more detail, we have also carried out calculations allowing

for anisotropic surface vibrations. Figure 4 shows the contour plots of GOF versus $V_{1\|}$ and $V_{1\perp}$ for the APS (top) and the ESRF (bottom) data. All other parameters were also allowed to vary; i.e., parameter correlations are included. From the variance of GOF we estimate uncertainties (1σ level) of $\Delta V_{1\|}=\Delta V_{\perp}\approx 0.015$ Å (APS) and $\Delta V_{1\|}=0.015$ Å and $\Delta V_{1\perp}=0.025$ Å (ESRF), which are represented by the error bars.

Allowing for anisotropy leads to a 10%–15% improvement of the fit quality based on both GOF and R_u, the latter being independent of the number of refined parameters. While the two independent SXRD studies provide almost identical values for $V_{1\perp}$ (0.114 and 0.118 Å), there is a 30% difference for $V_{1\|}$ (0.077 and 0.109 Å for APS and ESRF, respectively), i.e., the APS data suggest an anisotropy characterized by $V_{1\|}<V_{1\perp}$. The deviation with regard to $V_{1\|}$—albeit within the 1σ level—might tentatively be attributed to differences between the quality and quantity of the data. While on average the APS data set is more accurate in terms of the standard deviations of $F(q)$, the ESRF data set includes more reflections also extending to a larger parallel momentum transfer (the 42ℓ rod was not measured in the APS experiment). To some part this leads to a different profile of the GOF contour plot, which is steeper along $V_{1\|}$ in the case of the ESRF experiment. Nevertheless, within the experimental uncertainty the SXRD derived vibration amplitudes are in agreement with the MEIS results of Ref. 8 (∇ in Fig. 4), the latter suggesting an anisotropy, in which $V_{1\|}$ is *larger* than $V_{1\perp}$, but by 10% only. Thus, while we cannot conclude whether $V_{1\|}$ is smaller or larger than $V_{1\perp}$, the analysis indicates that if there is an anisotropy, it is below about 10%–20% at this temperature. Note that the experiments by Jiang *et al.*[7] ($\square$) were carried out at 320 K.

In summary, we have carried out a SXRD study of the Cu(001) surface at 160 K. Layer relaxations and thermal vibrations are in excellent agreement with recent studies. We find an enhancement of the surface vibrations by about 70%–90% and rapid damping into the bulk. Surface vibrations are isotropic within 20%. These results also show that SXRD data collected with high precision at different third generation x-ray sources are fairly reproducible even with regard to subtle details of the disorder usually not considered in standard surface structure determinations.

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[1] F. Jona and P. M. Marcus, in *The Structure of Surfaces II*, Springer Series in Surface Science Vol. 11, edited by J. F. van der Veen and M. A. Van Hove (Springer-Verlag, Berlin, 1988), p. 90.

[2] M.-C. Desjonquères and D. Spanjaard, in *Concepts in Surface Physics*, Springer Series in Surface Science Vol. 30, edited by G. Ertl, R. Gomer, and D. L. Mills (Springer-Verlag, Berlin, 1993).

[3] G. A. Somorjai, *Surface Chemistry and Catalysis* (Wiley, New York, 1994).

[4] W. F. Kuhs, Acta Crystallogr., Sect. A: Found. Crystallogr. **48**, 80 (1992).

[5] H. L. Davis and J. R. Noonan, Surf. Sci. **126**, 245 (1983).

[6] D. M. Lind, F. B. Dunning, G. K. Walters, and H. L. Davis, Phys. Rev. B **35**, 9037 (1987).

[7] Q. T. Jiang, P. Fenter, and T. Gustafsson, Phys. Rev. B **44**, 5773 (1991).

[8] D. E. Fowler and J. V. Barth, Phys. Rev. B **52**, 2117 (1995).

[9] L. Yang, T. S. Rahman, and M. S. Daw, Phys. Rev. B **44**, 13725 (1991).

[10] S. K. S. Ma, W. F. de Wette, and G. P. Aldredge, Surf. Sci. **78**, 598 (1978).

[11] Y. Cao and E. Conrad, Phys. Rev. Lett. **65**, 2808 (1990).

[12] J. W. M. Frenken, J. F. van der Veen, and G. Allan, Phys. Rev. Lett. **51**, 1876 (1983).

[13] I. K. Robinson, Phys. Rev. B **33**, 3830 (1986).

[14] E. Vlieg, J. Appl. Crystallogr. **30**, 532 (1997).

[15] I. K. Robinson, in *Handbook on Synchrotron Radiation*, edited by G. Brown and D. E. Moncton (Elsevier, New York, 1991), Vol. 3, Chap. 7.

[16] R. Feidenhans'l, Surf. Sci. Rep. **10**, 105 (1989).

[17] J. A. Ibers and W. C. Hamilton, in *International Tables for X-ray Crystallography*, edited by C. H. MacGillavry and G. D. Rieck (Kluwer, Dordrecht, 1985), Vol. III, Sect. 3.3.5.

[18] R_u is defined as $R_u=\Sigma||F^{\mathrm{obs}}|-|F^{\mathrm{calc}}||/\Sigma|F^{\mathrm{obs}}|$, with F^{obs} and F^{calc} as observed and calculated structure factors, respectively. For GOF see Ref. 16.