

# Quantitative determination of Cu(117) multilayer surface relaxations by LEED

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The relaxation of the first seven atomic layers of Cu(117) was determined by quantitative low-energy electron diffraction (LEED). Intensity versus energy spectra,  $I(E)$ , were measured for the primary beam at near-normal incidence to the (001) terraces. The data collected cover a cumulative energy range of 3200 eV. Computation of  $I(E)$  spectra was performed in the angular momentum representation by considering the surface as a single atomic slab. For the variation of parameters, tensor LEED was applied. The experimental spectra are well reproduced over the entire energy range even for regions of low intensity. The first four layer spacings relax in a way to smooth the surface corrugation, whereby the relative changes  $\Delta d/d_0$  amount (from top) to  $-13\%$ ,  $-2.0\%$ ,  $-10\%$ , and  $+7\%$ . This leads to a reduction of the vertical distance between step and corner atoms by  $0.13 \text{ \AA}$ . Comparison with experimental results for Cu(115) shows that this modification of the step shape is rather independent of the terrace width. Comparison to theoretical results exhibits, however, some discrepancies with respect to both the expansion/contraction sequence and the amplitudes of the layer relaxations.

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## I. INTRODUCTION

Almost all low-index metal surfaces exhibit the phenomenon of multilayer relaxation, i.e., the change of spacings between surface parallel layers compared to the bulk value. This is due to the reduced coordination of surface atoms, and accordingly the relaxation amplitudes increase with increasing openness of the surface.<sup>1,2</sup> For surfaces with higher values of Miller indices it is suitable to use the picture of a stepped surface that is made from microscopic low-Miller-index faces. Generally, different atoms within these low-Miller-index faces are differently coordinated and so will relax differently, changing the microscopic shape of the steps. This must be expected to modify step-related phenomena as, e.g., crystal growth, the enhanced chemical reactivity at steps, the stiffness of step edges and their energy barriers with respect to atomic migration, the step-step interaction, or the lifetime of surface states. Because *real* surfaces exhibit steps as defects on the mesoscopic scale, investigations of relaxations in stepped surfaces as in the present paper are also of general importance with respect to the properties of surfaces. Yet, due to methodological difficulties intrinsic to quantitative experimental structure determination of stepped surfaces (see below) only few such investigations exist (e.g., Refs. 3–12 for fcc surfaces).

We concentrate on a regularly stepped Cu(117) surface, which results by cutting a (001)-oriented Cu single crystal off normal at  $11.4^\circ$  tilted in the  $(1\bar{1}0)$  plane. As displayed in Fig. 1 the surface consists (assuming bulk truncated geometry) of microscopic (001)- and (111)-oriented faces. The (001)-oriented terrace is made from two inside terrace atoms (T1, T2), a corner atom (C), and the step atom (S). Their distance in the  $[117]$  direction, i.e., the spacing of (117) layers, amounts to  $d_0 = 0.506 \text{ \AA}$  (again for bulk truncation geometry). The terraces are separated by steps made up of (111), i.e., close-packed, faces of single-atom height with the edge running along the  $[1\bar{1}0]$  direction. The lateral distance be-

tween steps is  $9.13 \text{ \AA}$  in the  $[77\bar{2}]$  direction, corresponding to a regular terrace width of three atomic diameters. To the best of our knowledge this is up to now the largest terrace width in stepped surfaces of fcc crystals investigated in experimental quantitative structure determination. By comparison to recent structural investigations of the Cu(115) surface<sup>11</sup> (step spacing  $6.64 \text{ \AA}$ ) we can show that the structural influence of the terrace width on the step shape is rather small. Comparison to theoretical work for (117) and (115) surfaces of Cu and Al (Refs. 13–20) exhibits discrepancies with respect to the expansion/contraction sequence of the layer relaxations as well as to their absolute values.

We apply quantitative low-energy electron diffraction (LEED) for the structure determination of Cu(117). This is demanding both experimentally and theoretically. On the experimental side one has to face that  $I(E)$  spectra on the energy scale separate into regions with maxima at the usual level (up to the order of 10% of the primary beam) and

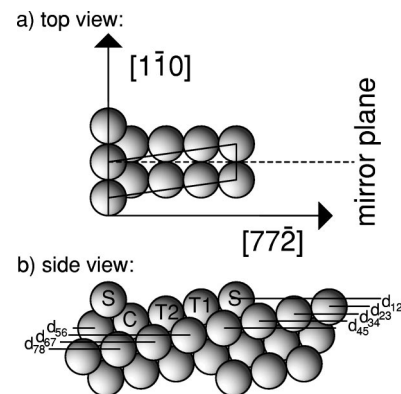


FIG. 1. Hard sphere model of the ideal, i.e., bulk truncated Cu(117) surface. (a) Top view as projected on the (117) plane with the unit mesh and the mirror plane indicated. (b) Side view as projected on the  $(1\bar{1}0)$  plane with the first 8 layers indicated (bulk spacing  $d_0 = 0.506 \text{ \AA}$ ). The distance between step edges is  $9.13 \text{ \AA}$ .

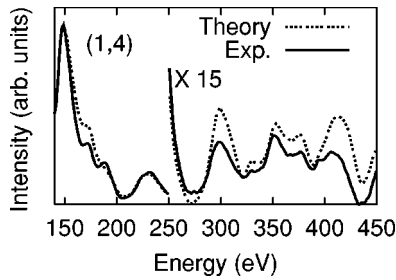


FIG. 2. Experimental and calculated spectra of the (1,4) beam (intensities above 250 eV are multiplied by a factor of 15).

regions with maxima more than an order of magnitude smaller. The reliable measurement of the latter is rather difficult. A similar situation exists in surface x-ray diffraction (XRD) as the intensities along surface truncation rods away from the Bragg points are very weak. Yet, for LEED there is an additional obstacle coming from the full-dynamical calculation necessary for the data analysis. The usual procedures for the stacking of layers break down as they apply plane-wave representations of the electron wave function, an approach inappropriate when layer spacings are as small as in stepped surfaces, i.e., much below 1 Å. We show that both difficulties can be overcome. In the next section we concentrate on experimental details while Sec. III describes the dynamical intensity analysis. The results are discussed in the last section.

## II. EXPERIMENT

The copper crystal ( $\pm 0.5^\circ$  orientational accuracy) was mechanically polished and cleaned *in situ* by repeated cycles of  $\text{Ar}^+$  sputtering and annealing until impurities were below the Auger detection limit. The azimuth of the sputter beam was directed along the step edges, possibly favoring the formation of straighter steps by preferentially exposing kink sites to the ion beam. The resulting LEED pattern is characterized by a low background and sharp diffraction spots with only little broadening of their wings (see Fig. 4). For LEED intensity measurements the sample was cooled to liquid nitrogen temperature (cooling rate  $\approx 50$  K/min) in order to reduce thermal diffuse scattering. For the data collection a computer-controlled video-based measurement technique was applied<sup>21</sup> allowing fast data acquisition to minimize residual gas adsorption. Additionally, the technique provides automatic background subtraction and fast multiple measurement of spectra in order to reduce noise by averaging. This is particularly important for stepped surfaces because—as mentioned above—their spectra consist of regions with high and very low intensities. Clearly, in the latter region intensity peaks are rather small and so generally difficult to be measured reliably. It has been pointed out<sup>10</sup> that the inclusion of such regions in the intensity analysis leads to high values of the reliability factor ( $R$  factor) for the theory-experiment comparison when an  $R$  factor sensitive to the location of intensity extrema is used, as, e.g., the Pendry  $R$  factor  $R_p$ ,<sup>22</sup> which we apply in the present investigation. Yet, we demonstrate in Fig. 2 that the intensities can be measured reliably

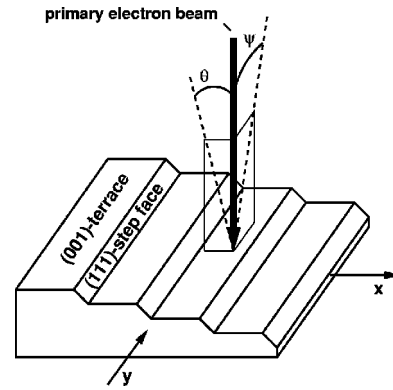


FIG. 3. Degrees of freedom in the adjustment of the primary beam incidence. The mirror symmetry for  $\psi=0$  according to the crystal's mirror plane (see Fig. 1) leads to an equivalent symmetry between beams as indicated in Fig. 4.

over the full energy range even though the low-intensity level is more than a magnitude smaller than the usual level. This is on the one hand due to the low temperature of measurement, which accounts for a comparably low background level. On the other hand, we profit from our measurement technique, which allows both for background subtraction and multiple measurement of intensities, the latter reducing the influence of noise. The figure also shows that there is much intensity variation in the low-intensity region and that this can be well reproduced by theory, i.e., the structural information it carries can be extracted indeed. The incidence of the primary electron beam as displayed in Fig. 3 was adjusted exploiting the  $(1\bar{1}0)$ -oriented mirror plane of the crystal (see Fig. 1). To make the mirror symmetry appear in the LEED pattern, the primary beam incidence must fall within the  $(1\bar{1}0)$  plane ( $\psi=0$ ). Then certain beam pairs such as, e.g.  $(1,1)=(-1,0)$ ,  $(1,2)=(-1,1)$ ,  $(1,3)=(-1,2)$ , etc., are degenerate, i.e., their spectra are identical. This was used for the adjustment for  $\psi=0$  by comparing the spectra of nominally equivalent beams using  $R_p$  as a quantitative measure (in the best alignment  $R_p$  was below 0.04 for all beam pairs). For the eventual data set, the influence of residual misalignment was further reduced by final averaging of equivalent spectra. The polar angle of incidence ( $\theta$  in Fig. 3) could not be adjusted by comparison of spectra because of the lack of symmetry. So, the incidence could be set normal to the (001) terraces only approximately. This was done using a second crystal with (001) orientation mounted on the same sample holder. Adjusting first normal incidence for Cu(001) leads to near-normal incidence to the terraces when assuming almost parallel orientation of the (001) directions in both crystals. The precise value of the polar angle was determined in the course of the intensity analysis where it was made to enter as a free fitting parameter (see below). Due to the procedure described only a small range of angles had to be tested. The resulting database included 15 symmetrically inequivalent beams with spectra covering a total energy width of 3200 eV.

## III. LEED INTENSITY ANALYSIS

The structural analysis of the measured intensities is complicated by two intrinsic properties of stepped surfaces. First,

the structural model displayed in Fig. 1 is an idealization in the sense that the step arrangement is strictly regular with only a single terrace width present and the step edge being straight. In reality, however, there is a distribution of different terrace widths around the ideal value and the step edges can be irregular, which for the surface under investigation was investigated quantitatively by scanning tunneling microscopy (STM).<sup>23–27</sup> Fortunately, around room temperature the surface morphology of Cu(117) is dominated by the ideal terrace width (50%), with one atom broader or smaller terraces of much lesser weight (20%) and others practically negligible.<sup>23–25</sup> With decreasing temperature the weight of the ideal terrace width increases even more. Fortunately also, the step edges become irregular only above room temperature.<sup>26,27</sup> As in the present investigation LEED intensities were taken with the sample at liquid nitrogen temperature, we can assume a regular step arrangement with straight step edges for our model calculations as a good approximation.

There is a second complication for the full-dynamical intensity evaluation. It originates from the rather small spacing of surface-parallel atomic layers in stepped surfaces. When computing the scattering interaction of the probing electron with the surface, the choice of basis functions is crucial concerning computational efficiency. The usual procedure is to calculate intralayer scattering in the spherical wave representation and to use plane-wave expansions for the scattering between layers, whereby frequently the renormalized forward scattering (RFS) or the layer doubling (LD) scheme is applied.<sup>28,29</sup> Yet, these latter techniques of ‘‘layer stacking’’ either need huge and unpracticable numbers of beams or even fail when the spacing between surface-parallel layers decreases significantly below 1 Å. With a bulk spacing  $d_0 = 0.506$  Å this holds for the present case of Cu(117). A way out of this problem was suggested quite early using a mixed representation in the sense that a certain surface slab of layers is treated in spherical wave representation and the stacking of the remaining layers below accomplished by plane waves.<sup>30–33</sup> However, this generally cannot fully cure the situation, and indeed recent work applying such methods report that at certain (unpredictable) energies in the spectra numerical instabilities develop (e.g., Refs. 8 and 34). They lead to unreliable peaks, unreasonable high intensities or even divergences that have to be eliminated by some trial-and-error procedure through varying the number of beams used. When trying the method for Cu(117) we experienced the same problems in spite of using as much as 560 plane waves.

In contrast, the finally applied use of spherical wave representation in the *full surface*, i.e., treating the surface as a single atomic slab, avoids these problems and therefore is reliable. It has been suggested and successfully tested earlier.<sup>35,6</sup> Of course, one has to pay for this with computer time, as a giant matrix has to be inverted (*giant matrix method*<sup>36</sup>) for which the computational efforts scale with the third power of the number of layers. Yet today’s available computer power can easily handle this problem. Even more, with the powerful perturbation method tensor LEED<sup>37–39</sup> at hand, the calculation can be restricted to a single full-

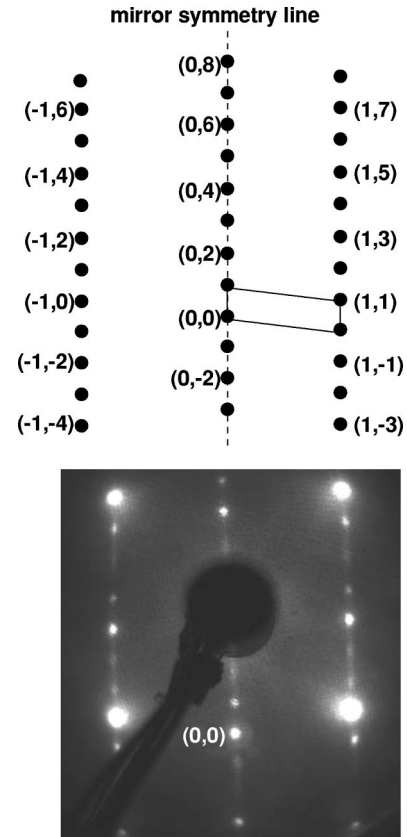


FIG. 4. Top: Schematic LEED pattern of Cu(117) with beam indices, the unit mesh, and the mirror symmetry line given. Bottom: Experimental LEED pattern at 196 eV. Spectra of beams *on* the mirror line were not entered into the analysis since they have no symmetrically equivalents to be averaged with and so are of reduced data quality.

dynamical calculation for a certain reference structure with the matrix to be inverted only once per energy. Then the parameter space can be explored very efficiently using the perturbation scheme. In the present work this exploration was realized through an automated search method<sup>40</sup> which is part of the tensor LEED package used.<sup>41</sup> For both the structural search and the eventual theory-experiment comparison the Pendry  $R$  factor is applied. Its variance<sup>22</sup> is used to estimate error limits for the structural parameters.

Of course the thickness of the surface slab must be carefully checked for convergence. In the present case of Cu(117) a slab consisting of 27 surface-parallel layers equivalent to a thickness of about 14 Å proved to be sufficient, i.e., thicker slabs left the spectra practically unchanged as checked by the  $R$  factor. An energy-dependent real part of the inner potential was used as recently derived for copper<sup>42</sup> and successfully applied to the Cu(100) surface.<sup>43</sup> The imaginary part of the potential was kept constant at 5 eV. The 11 phase shifts applied were computed taking the energy dependence of the inner potential into account<sup>44</sup> and were corrected for isotropic thermal vibrations of atoms. The vibrational amplitudes were taken as free parameters for surface atoms T1, T2, C and S, for deeper atoms they were fixed

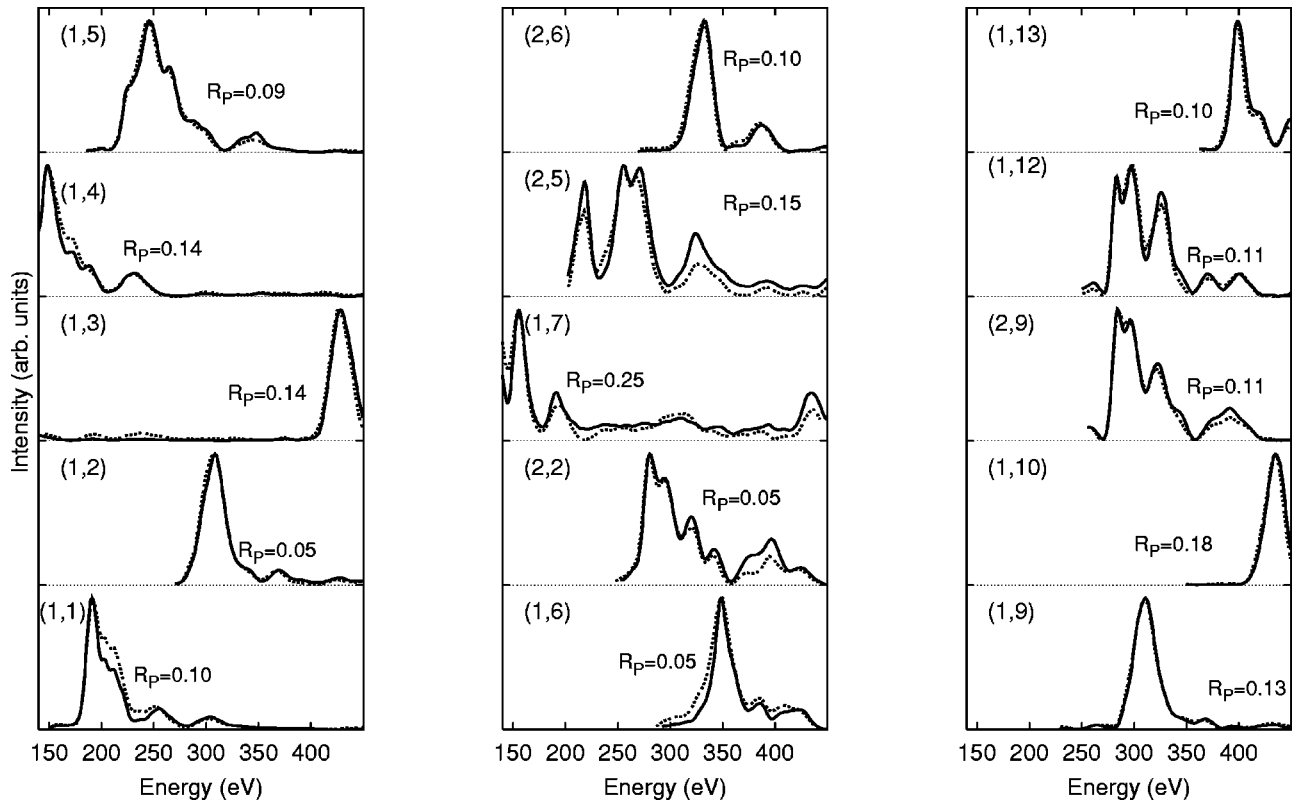


FIG. 5. Comparison of experimental (solid lines) and best-fit calculated spectra (dashed lines) for the beams considered in the analysis. The maxima of spectra are normalized independently, beam indices, and Pendry  $R$  factor values  $R_p$  are given in each case. The sequence of beams corresponds to the length of the  $k$  vector parallel to the surface, it increases from bottom to top and from left to right.

at  $0.08 \text{ \AA}$  corresponding to the Cu bulk Debye temperature of 343 K.

For the calculation of the reference intensities a bulk-terminated surface was used. The parameter space explored variations of the topmost seven interlayer distances  $d_{i,i+1}$  on a grid spacing of  $0.005 \text{ \AA}$ . The lateral positions of atoms were kept fixed in view of the results for the related Cu(115) surface according to which parallel atomic movements (registry shifts) are below  $0.01 \text{ \AA}$ .<sup>9</sup> Additionally, the polar angle of incidence had to be varied, too, as mentioned above. Its fit in an early stage of the analysis resulted in  $\theta = 10.5^\circ$  with respect to the  $[117]$  direction, i.e., about  $0.9^\circ$  off the  $[001]$  direction.

As expected, the quality of the comparison between experimental data and intensities calculated for the bulk-terminated reference surface ( $d_{i,i+1} = d_0$ ) is rather limited ( $R_p \approx 0.50$ ). Yet, allowing for the relaxations mentioned the  $R$  factor decreases to  $R_p = 0.12$ , which, to our knowledge, is the best achieved for a stepped surface in a LEED structure determination. This is in spite of the fact that by the use of the Pendry  $R$  factor the very small peaks that are difficult to measure enter the analysis with the same weight as large peaks. The low  $R$  factor is consistent with an equally favorable visual comparison of spectra as demonstrated in Fig. 5. Both the spectral structure and the intensity level are well reproduced in regions of high as well as of low intensities (see also Fig. 2).

#### IV. RESULTS AND DISCUSSION

For vicinal surfaces of the type  $\text{fcc}(11\{2n+1\})$  theory predicts a periodic relaxation pattern repeating every  $n+1$  layers,  $n+1$  being the number of surface atoms with reduced coordination.<sup>15-20</sup> There should be an inward relaxation for the step and terrace atoms and an outward movement of the corner atom leading, e.g., for  $\text{fcc}(115)$  to a periodic sequence  $(- - +, \dots)$  and for the present case of  $\text{fcc}(117)$  to  $(- - - +, \dots)$ . The value of the relative relaxation depends on the chemical species and increases with the openness of the surface.

Our quantitative results largely (though not fully, see below) meet this pattern as given in Table I where they are compared to results experimentally obtained<sup>11</sup> for Cu(115) as well as to theoretical results for the two Cu surfaces<sup>16</sup> and for the isostructural surfaces of Al.<sup>17</sup> For the Cu(117) values we report no figures after the decimal point because error limits for the top three spacings as estimated by the variance of the Pendry  $R$  factor [ $\text{var}(R_p) = 0.013$ ] are in the range 2-3%. This estimate neglects correlations between parameters as well as the approximation made with respect to the uniform terrace width, so the true error should be even larger and will certainly increase for deeper spacings (we recall that an error of 2% corresponds to an absolute error of only about  $0.01 \text{ \AA}$ ). The best-fit (isotropic) vibrational amplitudes are  $0.11 \text{ \AA}$  for the S and T1 atoms,  $0.10 \text{ \AA}$  for T2, and  $0.09 \text{ \AA}$  for the C atom, so there is a gradual and reasonable decrease towards



TABLE I. Relaxations of interlayer spacings  $d_{i,k}$  relative to the bulk value  $d_0$  as experimentally determined for Cu(117) (this work) and for Cu(115) (Ref. 11). Comparison is made to calculated values for both the Cu surfaces (Ref. 16) and the isostructural surfaces of Al (Ref. 17).

	Cu(117) (This work)	Cu(115) [Expt. (Ref. 11)]	Cu(117) [Theor. (Ref. 16)]	Cu(115) [Theor. (Ref. 16)]	Al(117) [Theor. (Ref. 17)]	Al(115) [Theor. (Ref. 17)]
$d_0$ (Å)	0.506	0.693	0.506	0.693	0.563	0.773
$\Delta d_{12}/d_0$ (%)	-13	-14.2	-10.0	-9.5	-8.3	-8.0
$\Delta d_{23}/d_0$ (%)	-2	-5.2	-5.3	-8.0	-4.9	-5.2
$\Delta d_{34}/d_0$ (%)	-10	+5.2	-9.7	+8.6	-5.9	+8.4
$\Delta d_{45}/d_0$ (%)	+7	-1.2	+13.8	-4.4	+13.1	-3.2
$\Delta d_{56}/d_0$ (%)	-1	+3.2	-4.5	-4.4	-3.6	-3.2
$\Delta d_{67}/d_0$ (%)	-4	-3.1	-4.5	+4.8	-3.1	+4.5
$\Delta d_{78}/d_0$ (%)	+7	-3.3	-4.6	-2.0	-3.3	-1.4

the bulk value (0.08 Å). This is consistent with a recent LEED structure analysis of Cu(001), yielding an amplitude of 0.11 Å for top layer atoms.<sup>43</sup> We did not check for vibrational anisotropy as this should be small at liquid-nitrogen temperature according to calculations for Al.<sup>17</sup>

Both for Cu(117) and Cu(115) the expansion/contraction sequence predicted by theory is not fully met by the experimental results. In both cases the relaxation of the spacing between layers below the corner atom C [ $d_{78}$  for Cu(117) and  $d_{56}$  for Cu(115)] differs in sign from the theoretical prediction. Otherwise the absolute values of the relaxations are in rough agreement with the theoretical predictions given the experimental errors and the theoretical uncertainties involved. Yet, with respect to the ratio of subsequent relaxations as e.g.,  $\Delta d_{12}/\Delta d_{23}$  there are considerable discrepancies between experiment and theory. This together with the discrepancy with respect to the relaxation pattern should trigger some refinement of theory. As judged from the calculations there seems to be no considerable difference between the relaxations in Cu and Al.

As the three topmost layers of Cu(117) relax inward and the corner atom layer outward, the height of the step edge is reduced, i.e., the surface corrugation undergoes some smoothing. The distance between S and C atoms normal to the (001) terrace is contracted by 8.3% with respect to the bulk value, i.e., by  $\Delta D(117)=0.124$  Å. This compares to a 9.7% contraction retrieved for Cu(115),<sup>11</sup> equivalent to an

absolute value of  $\Delta D(115)=0.129$  Å normal to the (001) terrace. Surprisingly in view of the discrepancies with respect to the relaxation amplitudes for the different layer spacings, these values are very close to those derived from the calculations. The difference between the experimental values  $\Delta D(117)$  and  $\Delta D(115)$  is within the error margins of the respective structure. So, apparently the terrace width has no or a negligible influence on the step shape.

In summary, we have shown that the stepped Cu(117) surface undergoes a considerable multilayer relaxation involving a surface slab of at least seven layers. The vertical height of the step edge is reduced by about 0.13 Å, i.e., the surface is smoothed correspondingly. The findings agree very well with experimental results for Cu(115) for which within the limits of error the same value for surface smoothing is reported. Yet, there is only rough agreement [both for the (117) and (115) surfaces] with theoretical predictions. Discrepancies exist with respect to both the expansion/contraction sequence and the amplitudes of the layer relaxations.

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