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Oscillatory Relaxation of the Cu(110) Surface

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Complementary studies of the Cu(110) surface have been carried out by means of low-energy electron diffraction and high-energy ion scattering. The results obtained from the use of the two techniques are in acceptable agreement and indicate that the interlayer spacings in the Cu(110) surface exhibit a damped, oscillatory deviation from the bulk value, in qualitative agreement with the predictions of Landman, Hill, and Mostoller.

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In this Letter, we present briefly the results of complementary low-energy electron-diffraction[1] (LEED) and high-energy ion-scattering[2] (HEIS) studies of the surface structure of Cu(110). Both studies lead to the conclusion that the structure exhibits an oscillatory relaxation of the interlayer spacings in the surface, in qualitative agreement with the results of recent calculations of Landman, Hill, and Mostoller.[3]

Previous LEED studies of unreconstructed metal surfaces have indicated that the most significant deviation from bulk geometry occurs for bcc (100) and fcc (110) planes, where contractions of the first interlayer spacing of up to 10% of the bulk value have been reported.[4,5] The general nature of these results has been reproduced in some recent model calculations of surface-interlayer spacings.[3,6] An interesting additional feature of these calculations is the prediction that the deviation from bulk geometry is not limited to the first interlayer spacing but extends in a damped, oscillatory fashion into the bulk. This possibility does not appear to have been widely examined in the interpretation of experimental measurements of surface structure, and in the case of clean, unreconstructed metal surfaces, we are aware of only two systems where a relaxation (Δd_1 and Δd_2) of both first and second interlayer spacing has been reported. For Re($0\bar{1}01$), Davis and Zehner[7] obtained $\Delta d_1 = -17\%$ and $\Delta d_2 = +1$ to 2%. (The values are given as percentages of the bulk value. The minus sign indicates a contraction.) For V(100), Jensen *et al.*[8] obtained $\Delta d_1 = -7\%$ and $\Delta d_2 = +1\%$. In neither case, however, was the expansion of the second interlayer spacing regarded as being sufficiently large in comparison with the estimated uncertainty to be taken as conclusive evidence of an oscillatory relaxation of the interlayer spacings.

For the Cu(110) surface, Davis and co-workers[9-11] have considered the possibility of a relaxation of both the first (d_1) and second (d_2) interlayer spacing in their analyses of LEED data but have concluded that $\Delta d_2 = 0 \pm 2.5\%$, whereas $\Delta d_1 = -10 \pm 2.5\%$. The LEED results and interpretation presented in the present article are in reasonable agreement with those of Davis *et al.*, except that it has proved to be possible to establish the existence of a relaxation of both d_1 and d_2. This conclusion is confirmed and given extra weight by the complementary HEIS measurements, particularly in view of the fundamental differences between the LEED and HEIS techniques.

LEED study of Cu(110).—After preparation of

a clean Cu(110) surface via Ar^+ bombardment and annealing, LEED intensity-energy spectra were measured at room temperature for nine symmetry-inequivalent beams at normal incidence in the energy range 20–360 eV.

A detailed comparison of experimental and calculated energy spectra will be presented elsewhere.[1]

Intensity-energy spectra were calculated by means of Pendry's[12] layer-doubling algorithm, with the use of modified versions of the computer program of Van Hove and Tong.[5] Ten phase shifts calculated from the potential of Moruzzi, Janek, and Williams[13] were used. Control calculations using the potentials of Chodorow[14] and of Snow and Waber[15] yielded virtually identical results. The calculation of interlayer multiple scattering involved the use, at the highest energy, of 155 beams, reduced by the symmetry of normal incidence to 46 symmetry-inequivalent beams. The nonstructural variables of the calculations, namely the inner potential V_0, the inelastic-damping strength V_{im}, and the Debye temperature θ_D, were taken to be energy- and layer-independent parameters with values to be fixed by R-factor comparison with the experimental spectra.

The R factor[16,17] used in comparing experimental $[I^{expt}(E)]$ and calculated $[I^{calc}(E)]$ intensity-energy spectra is defined as

$$R_2 = \sum_{i=1}^{N} (I_i^{expt} - wI_i^{calc})^2 / \sum_{i=1}^{N} (I_i^{expt})^2,$$

where w is a scaling factor. Parameter optimization was carried out by use of an average R factor $\hat{R}_2$ obtained by averaging R_2 over the nine diffracted beams. $\hat{R}_2$ was assumed to depend quadratically upon the calculational variables in the vicinity of its global minimum value.[17]

In the first stage of the R-factor analysis, plots of $\hat{R}_2(\partial\hat{R}_2/\partial V_0 = \partial\hat{R}_2/\partial d_1 = 0)$ vs θ_D and V_{im} were used to determine optimum values of these variables. The plots were based on intensity spectra calculated for a range of values of d_1, θ_D, and V_{im}, and the optimization process was iterated to convergence.

In the final stage of the analysis, refinement of the values of d_1 and d_2 was carried out using intensity spectra calculated for a range of values of these variables, with θ_D and V_{im} fixed at their previously determined optimum values.

The optimum values of d_1 and d_2 were determined from the minima of contour plots of $\hat{R}_2(\partial\hat{R}_2/\partial V_0 = 0)$ vs d_1 and d_2, as shown in Fig. 1. Sections through the elliptic axes of the contour plot for each of two independent data sets are shown in Fig. 2. It is noted that the correlation between the optimum values of d_1 and d_2 is quite small, as evidenced by the fact that the elliptic axes of the contour plot of Fig. 1 make shallow angles to the d_1 and d_2 axes.

Optimum values of the calculational variables based on $\hat{R}_2$-factor analyses for each of the two independent data sets were found to be

$$d_1 = 1.170 \pm 0.008 \text{ Å}, \quad d_2 = 1.307 \pm 0.010 \text{ Å},$$

$$V_0 = 8.9 \pm 0.3 \text{ eV}, \quad V_{im} = 2.5 \pm 0.3 \text{ eV},$$

$$\theta_D = 335 \pm 14 \text{ K},$$

where the estimated uncertainties are derived from the curvature of plots of $\hat{R}_2$ versus the variables.[1,17]

The global minimum value of $\hat{R}_2 = 0.066$ can be compared to the value of $\hat{R}_2 = 0.023$ obtained by comparing the fit between the *two data sets*.

Ion-scattering study of Cu(110).—The clean Cu(110) surface was prepared as described previously. With an incident beam of 300-keV He^+ ions, the surface-peak yield in the backscattering spectrum was measured in a $\pm 1°$ angular interval around the [101] and [100] axes, respectively, the tilt plane being determined by the axis and the crystal normal. To obtain good statistics, the yield-versus-angle curves were obtained by averaging several independent angular scans.

Calculated surface-peak yields for different structural parameters were obtained by Monte Carlo simulations.[18] A bulk Debye temperature

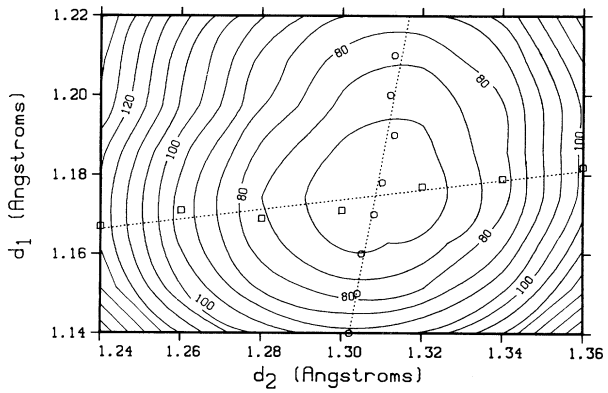

FIG. 1. Contour plot of $\hat{R}_2(\partial\hat{R}_2/\partial V_0 = 0)$ vs d_1 and d_2. Contour levels given on the plot are $1000\hat{R}_2$. Dotted lines represent least-squares fits to computed values (squares) of $d_1(\partial\hat{R}_2/\partial V_0 = \partial\hat{R}_2/\partial d_1 = 0)$ vs d_2, and (circles) $d_2(\partial\hat{R}_2/\partial V_0 = \partial\hat{R}_2/\partial d_2 = 0)$ vs d_1, and define the elliptic axes of the contour plot.

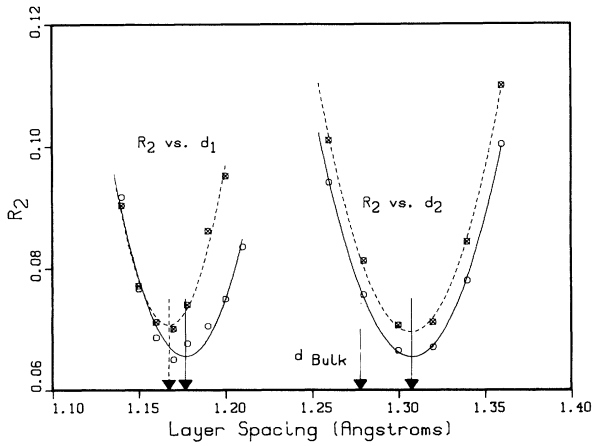

FIG. 2. Plots of $\hat{R}_2(\partial\hat{R}_2/\partial V_0 = \partial\hat{R}_2/\partial d_2 = 0)$ vs d_1 and $\hat{R}_2(\partial\hat{R}_2/\partial V_0 = \partial\hat{R}_2/\partial d_1 = 0)$ vs d_2, corresponding to sections through the elliptic axes of the hypersurface of $\hat{R}_2(d_1, d_2)$. Solid lines, first data set; dashed lines, second data set.

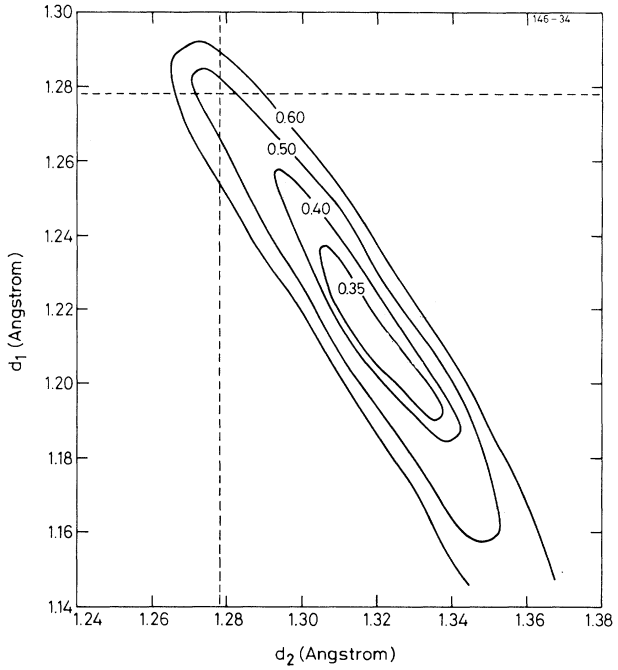

FIG. 3. Contour plot of $\hat{R}_{IS}$ vs d_1 and d_2 for $\theta_B = 320$ K, $\theta_S = 250$ K, and no displacement correlations. Dashed lines correspond to bulk-interlayer spacings.

$\theta_B = 320$ K determined by x-ray diffraction[19] was used throughout. The surface Debye temperature θ_S was varied from 200 to 320 K. Nearest-neighbor displacement correlations could be included in the calculations. Using a Debye model, we estimate the bulk nearest-neighbor correlation coefficient ρ_{12} to be 0.36 along Cu[101] in the high-temperature limit. The effects of a variation of θ_S and ρ_{12} are discussed below.

A procedure similar to an R-factor analysis of LEED data has been adopted in comparing experimental and calculated data. The calculated data points are approximated by a polynomial fit of suitable order. The deviation of the experimental surface-peak yields Y^{expt} from the theoretical curve Y^{calc} is then evaluated as

$$R_{IS} = 100\{\sum_{i=1}^{N}[(Y^{\mathrm{calc}} - wY^{\mathrm{expt}})/NwY^{\mathrm{expt}}]^2\}^{1/2},$$

where N is the number of data points and w a common scaling factor minimizing R_{IS}. This procedure emphasizes the shape and symmetry of the data and reduces the influence of normalization errors.

A detailed description of the data analysis will be presented elsewhere.[2] Here we summarize the main results. The experimental data were analyzed in terms of both a single-layer and a double-layer relaxation model. Acceptable fits (as judged from a visual assessment) to the experimental data could be obtained for both the [101] and [100] axes in the single-layer model, assuming a 1% contraction and a 3% expansion, respectively. These significantly different results reflect the different symmetries in the experimental angular scans and rule out the single-layer model. The analysis in terms of a double-layer relaxation model was based on contour plots of $R_{IS}^{[101]}$ and $R_{IS}^{[100]}$ versus the interlayer spacings d_1 and d_2. In this model, an overlap of the global minima for the two contour plots was observed for $\theta_S = 250$ K.

A contour plot of the average "R factor" $\hat{R}_{IS}$ for the two sets of experimental data is shown in Fig. 3 with a global minimum corresponding to values of $d_1 = 1.21^{+0.03}_{-0.02}$ Å and $d_2 = 1.32 \pm 0.02$ Å. The uncertainties, which are correlated, are based on a visual assessment of the quality of agreement between experimental and theoretical data.

Data analysis with $\theta_S = 200$ K and $\theta_S = 320$ K led to poorer fits and/or failure to obtain acceptable fits of the two experimental data sets for the same values of d_1 and d_2. Inclusion of the nearest-neighbor displacement correlations reduced the calculated surface-peak yields but with little influence on the shape and symmetry of the theoretical curves. Although no systematic variation of θ_S and ρ_{12} has been carried out, we do not

expect any significant change in optimum structural parameters to result from such an investigation.

Summary and discussion.—Analyses of LEED and HEIS measurements for the Cu(110) surface lead to the conclusion that the first two interlayer spacings relax from the bulk value. The determined values are as follows: from LEED, $d_1 = 1.17$ Å (−8.5%), $d_2 = 1.307$ Å (+2.3%); from HEIS, $d_1 = 1.21$ Å (−5.3%), $d_2 = 1.32$ Å (+3.3%), where the values in parentheses give the deviations from the bulk value. The difference between the values determined by LEED and HEIS for d_1 is a little larger than expected from the estimated errors of ± 0.008 Å and ± 0.02 Å, respectively, but it is clear that these estimates do not include possible systematic errors in the measurements or in the model calculations.

We regard the agreement between the two structure determinations as acceptable at the current stage of development of the two techniques and sufficient to be regarded as conclusive evidence for the existence of an oscillatory relaxation of the surface-interlayer spacings.

Finally, we note that although the results reported here are in qualitative agreement with the predictions of Landman, Hill, and Mostoller for Cu(110), they indicate that the relaxations are smaller and more rapidly damped into the bulk than is predicted. This conclusion appears to apply also to the case of Al(110), where a recently completed LEED study by some of the present authors[20] has yielded relaxations of −8.4%, +4.9%, and −1.6%, respectively, for the first three interlayer spacings.

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