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# A REVISED LEED DETERMINATION OF THE RELAXATIONS PRESENT AT THE (3 1 1) SURFACE OF COPPER

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Low-energy electron diffraction (LEED) has been used to determine the structural relaxations present at the (3 1 1) surface of copper. Two sets of intensity vs energy curves were measured for normal incidence for 14 beams over a total energy range of 1932 eV. These data were compared with intensities calculated with the layer doubling method for a range of structural models, the comparisons being made with both the Zanazzi–Jona and Pendry $R$-factor schemes. Average values for the first and second interlayer spacings, and percentage changes from the bulk value, are found to be $d_1 = 0.96 \pm 0.02$ Å (– 11.9%) and $d_2 = 1.11 \pm 0.02$ Å (+ 1.8%) respectively. These percentage changes are much closer to the theoretical relaxations (– 12.2% and + 4.4% respectively) calculated by Jiang *et al.* [*Phys. Rev.* **B35**, 7952 (1987)] than those indicated earlier by LEED for the Cu(3 1 1) surface using a 1978 data base.

INTEREST in the relaxations occurring at surfaces of clean metals has been spurred recently by several factors. This topic provides a good testing ground for assessing the abilities of different surface structural techniques to quantify such effects, and in addition theoretical methods are being developed to calculate the relaxations being measured [1]. These relaxations seem most significant for open surfaces [2] which, for a given material, can have appreciably different properties from the closer packed surfaces which have generally been subject to the greater scrutiny by experiment. For example, in surface catalysis, reactivity can change markedly as the surface is varied from one of flat low-index orientation to a stepped surface with higher-index orientation [3]. There is therefore interest in determining the structure of stepped surfaces, and the first such attempt was made with LEED crystallography in 1978 to determine the structure of the (3 1 1) surface of copper [4]. This initial study indicated that the topmost interlayer spacing is contracted by about 5.0% compared with the bulk value (1.09 Å). However, this percentage change from the bulk value appeared small when compared with values subsequently reported for other (3 1 1) surfaces of face centered cubic (f.c.c.) metals including LEED analyses for aluminum (– 13.3%) [5] and nickel (– 15.9%) [6], and a theoretical estimate of – 12.2% [7]. A further reanalysis of the initially measured LEED intensity data for Cu(3 1 1) suggested that the top layer contraction should be increased to 7.3% [8]. Nevertheless, since copper is such an important reference metal, and (3 1 1) provides the simplest stepped surface for a f.c.c. metal, it seemed important to re-examine this system with up-to-date measurement techniques, and that provides the topic of the present report.

The sample used in this work was cut from a high-purity single-crystal copper rod to within 0.2° of the (3 1 1) orientation, and it was cleaned and ordered in an ultrahigh vacuum chamber (base pressure $1 \times 10^{-10}$ Torr) with cycles of $Ar^+$ bombardment and annealing until Auger electron spectroscopy showed no detectable impurities and LEED showed sharp (1 × 1) diffraction patterns with low non-structured background. Throughout, this work followed standard procedures used in this laboratory for cleaning and ordering surfaces of copper [9]. Two independent sets of intensity versus energy curves for normal incidence were measured with a video LEED analyzer [10] for 14 symmetrically inequivalent diffracted beams over a total energy range of 1932 eV. This data base is equivalent to that measured in the LEED crystallographic analysis for the Ni(3 1 1) surface [11], and is approximately twice that in the initial studies for Cu(3 1 1) [4, 8] where only 8 symmetrically inequivalent

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beams could be analyzed. In this work, the multiple scattering calculations were made with the layer doubling method [12] exactly as detailed earlier [8].

The intensity vs energy curves from experiment were compared with those from the multiple scattering calculations using two many-beam $R$-factors, specifically those introduced by Zanazzi and Jona ($R_{ZJ}$) [13] and by Pendry ($R_P$) [14]. Contour plots were made of the $R$-factor values as a function of $d_1$ and $d_2$, the first two interlayer spacings, and $V_{or}$, the real part of the constant potential between the atomic spheres in the conventional muffin tin approximation [12], and this enabled an identification of the conditions for the minimum in each $R$ factor (and hence the best correspondence between calculation and experiment according to that criterion). The differences between the two experimental data sets are extremely small on visual inspection, but a separate optimization was made for each with the individual $R$ factors. The optimized parameters are reported in Table 1. The level of agreement between theory and experiment is high, and that is also confirmed by direct comparison of the intensity curves for the individual beams (some representative examples are shown in Fig. 1).

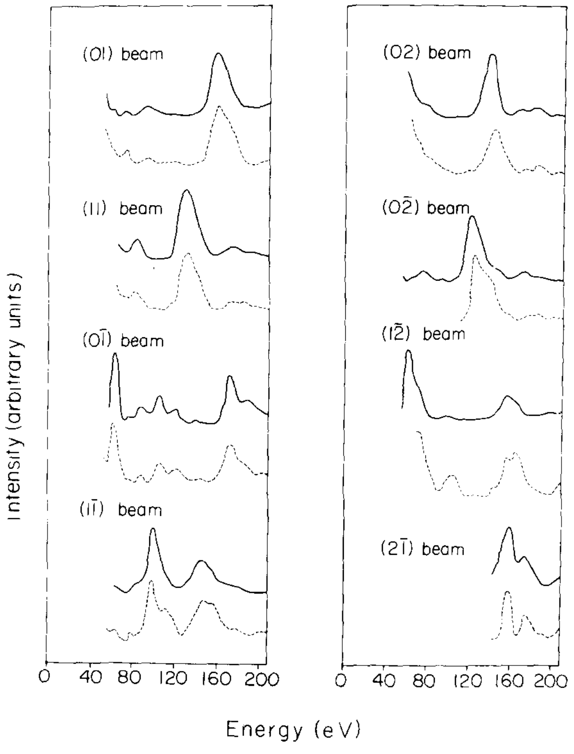

Fig. 1. Comparison of $I(E)$ curves from experiment (dashed lines) and calculation (full lines, with $d_1 = 0.96$ Å and $d_2 = 1.10$ Å) for the diffracted beams designated (0 1), (1 1), (0 $\bar{1}$), (1 $\bar{1}$), (0 2), (0 $\bar{2}$), (1 $\bar{2}$) and (2 $\bar{1}$) according to the notation used in [6].

*Table 1. Values of two interlayer spacings $d_1$ and $d_2$ (in Å) for the* Cu(3 1 1) *surface as indicated by the minimum values of two R factors for two independent sets of experimental LEED intensities*

| *Data set* | *R factor* | $d_1$ | $d_2$ | $R_{min}$ |
|---|---|---|---|---|
| A | $R_{ZJ}$ | 0.953 | 1.10 | 0.123 |
| | $R_P$ | 0.977 | 1.12 | 0.225 |
| B | $R_{ZJ}$ | 0.951 | 1.09 | 0.134 |
| | $R_P$ | 0.978 | 1.12 | 0.204 |

From the information in Table 1, we conclude that the first two interlayer spacings and relaxations for the Cu(3 1 1) surface are $d_1 = 0.96 \pm 0.02$ Å ($-11.9\%$) and $d_2 = 1.11 \pm 0.02$ Å ($+1.8\%$). These values can be compared with the theoretical predictions of Jiang *et al.* [7] which correspond to $-12.2\%$ and $+4.4\%$ respectively. The measured top layer relaxation for the Cu(3 1 1) surface is now also established as being much closer to the values determined by LEED for the Al(3 1 1) ($-13.3\%$) [5] and Ni(3 1 1) ($-15.9\%$) [6] surfaces than was the case for the earlier analyses for Cu(3 1 1) which depended on a less extensive measured intensity base, and probably a less well-prepared surface. The theoretical calculation of Jiang *et al.* assumes that the surface relaxations are dominated by electrostatic forces associated with positive ion cores immersed in a uniformly distributed electron gas, without consideration of more specific chemical bonding interactions which conceivably could also affect these interlayer spacings. Nevertheless, at this point, the differences in the $d_1$ spacings determined by LEED for the (3 1 1) surfaces of copper, aluminum and nickel are barely significant.

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