LEED study of the potassium-induced reconstruction of Cu(110)

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Abstract

We have used low-energy electron diffraction (LEED) to determine the adsorption geometry of the ordered p(2×2) potassium overlayer on the (potassium-induced) (1×2) missing-row reconstruction of Cu(110) at 47 K. The K adsorption site in this ordered structure is substitutional, whereby the K atoms occupy half of the Cu sites which are vacated in the missing-row reconstruction. The distance between the K atom and its nearest neighbours (in the second Cu layer) is 3.24 ± 0.05 Å. We observed very little, if any, lateral displacement of the second-layer Cu atoms, but a significant buckling in the third layer. The effect of this buckling is to pull the rows of third-layer Cu atoms which are directly beneath the K rows toward the surface, thus increasing the effective coordination of the K atoms.

1. Introduction

Small amounts of adsorbed alkalis induce reconstructions on certain fcc (110) surfaces such as Cu, Pd and Ag [1]. The structures of these reconstructions are of the 'missing row' type, similar to those found for other clean (110) surfaces such as Au, Pt and Ir [1]. The K-induced reconstruction of Cu(110) has been studied by many techniques, including low-energy electron diffraction (LEED) [2], scanning tunnelling microscopy (STM) [3] and photoelectron diffraction [4]. The LEED study, carried out for a low K coverage and at room temperature (disordered K) determined that the (1×2) reconstructed structure is indeed the missing-row structure for this system. The STM study showed that the reconstruction is driven by a local mechanism which at very low coverages creates strips of missing-row structure which organize themselves into long-range missing-row structures at higher K coverages [3]. This supported an earlier calculation which suggested that the driving force for the reconstruction is the greater adsorption energy for the K on the reconstructed (as opposed to flat) surface. The photoelectron diffraction study went on to show that the adsorption site of the K atom in the disordered overlayer is in fact a substitutional site, with the K atoms occupying sites

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which would have been occupied by missing-row atoms. This substitutional site finding was interesting, given that substitutional sites have been observed for alkalis on many other surfaces, including close-packed surfaces [5].

The structural parameters found in the previous LEED and photoelectron studies are given in table 1. The LEED study was carried out at room temperature and at a coverage of 0.15, where the K atoms are disordered (coverage is defined as the ratio of the number of K atoms to the number of Cu atoms in a bulk Cu(110) layer). Therefore no information was obtained about the K adsorption geometry from that study. However, it confirmed that the reconstructed substrate structure was indeed a missing-row structure, and it produced parameters for the interlayer spacings, lateral relaxations and vertical rumpling of the substrate. The photoelectron diffraction study was carried out at 100 K and a coverage of 0.20, where the K atoms had no long-range order, but were localized in adsorption sites. An adsorption site geometry was obtained for the K atoms, which includes the lateral relaxation and vertical rumpling of the nearby Cu atoms. Some discrepancies between the rumpling parameters found in this study and those found in the earlier LEED study were noted. These were attributed to the fact that the LEED study was averaging over the entire substrate, including regions where K atoms were not in substitutional sites, whereas the PhD study was specific to the environment around the K atoms localized in sites.

Table 1. Structural parameters for K on Cu(110), determined by an early LEED study at room temperature [2], a photoelectron diffraction study [4] and this LEED study. Also shown are the results of an embedded-atom method (EAM) calculation for the (1×2) missing-row structure of Cu(110). The structural parameters are defined in figure 1. 'rms' refers to the root-mean-square vibrational amplitude. 'perp' and 'par' refer to the rms vibrational amplitudes perpendicular to and parallel to the surface, respectively.

Parameter	LEED [2]	PhD [4]	LEED (this study)	EAM [14]
T	300 K	100 K	47 K	300 K
Coverage	0.15	0.20	0.25	—
Energy range	1095 eV	—	4853 eV	—
NN_{K-Cu2}	—	3.27 ± 0.27 Å	3.24 ± 0.05 Å	—
d_{K-Cu3}	—	3.60 ± 0.04 Å	3.58 ± 0.05 Å	—
$d_{Cu1-Cu2}$	1.13 Å	—	1.20 ± 0.03	1.19 Å
$d_{Cu2-Cu3}$	1.28 Å	—	1.30 ± 0.05	1.26 Å
$d_{Cu3-Cu4}$	—	—	1.24 ± 0.05	1.26 Å
$\partial 2x$	—	-0.06 ± 0.16 Å	0.00 ± 0.07 Å	—
$\partial 2y$	0.05 Å	-0.04 ± 0.11 Å	-0.01 ± 0.09 Å	0.02 Å
$b3$	0.02 Å	0.05 ± 0.05 Å	0.11 ± 0.06 Å	0.00 Å
K rms (perp)	—	0.07 Å	—	—
K rms (par)	—	0.1 Å	—	—
K rms (isotropic)	—	—	0.3 Å	—
Cu1 rms	—	—	0.09 Å	—
Cu2 rms	—	—	0.08 Å	—
Cu3 rms	—	—	0.045 Å	—
Cu_{bulk} rms	—	—	0.045 Å	—

At a potassium coverage of 0.25, it is possible to form a commensurate p(2×2) structure, which means that the entire surface is covered with K atoms which are in equivalent positions. Therefore at this coverage, a LEED study can be performed in which no averaging is required over regions which have different surface geometries. Figure 1 shows a drawing of a commensurate (2×2) structure on Cu(110) and labels the relevant parameters which are listed in table 1. This paper describes a dynamical LEED study of this surface structure at 47 K.
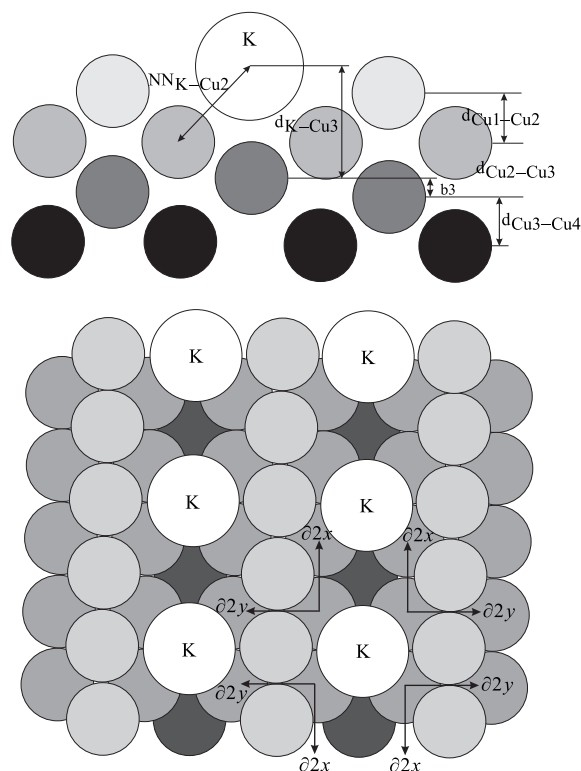
Figure 1. Schematic drawing of the p(2 × 2) ordered K overlayer on reconstructed Cu(110). The top of the figure shows the side view, and the bottom shows the top view. The values for the parameters shown here are given in table 1.

2. Experiment

The Cu(110) crystal wafer was cut from a high-purity single-crystal Cu rod. After orientation of the sample to within 0.5° using Laue diffraction, it was polished on both sides using successively smaller diamond abrasives down to a 1 μm grit size. This procedure resulted in a shiny, mirror-like surface. The sample was further prepared in ultra-high vacuum (UHV) by cycles of Ar$^+$ ion bombardment at ion energies of 500 eV and annealing to 870 K. This preparation produced a well ordered surface as observed from sharp LEED spots accompanied by a low diffuse-elastic background. K was dosed onto the surface using a degassed SAES Getters K source. The sample temperature at dosing was about 50 K, after which the surface was annealed to 200 K and then recooled. The most effective way of monitoring the coverage was the LEED pattern, which indicated an incommensurate structure at coverages above and below 0.25. The cleanliness of the surface was monitored by Auger electron spectroscopy (AES)—no impurities were detected after dosing.

The LEED intensities were measured using a rear-view LEED optics with the incident electron beam normal to the Cu(110) surface, and at a sample temperature of 47 K. The data were acquired using a charge-coupled device video camera interfaced to a personal computer via Data Translation frame grabber and processor boards. At each energy, 50 images were averaged to reduce noise and the averaged image was stored for later data analysis. The $I(E)$ curves were extracted by integrating the spot intensity in circular windows centred on the

diffraction spots. The diffuse background intensity for each spot was determined by fitting a planar background to the perimeter of the window. This background was then subtracted from the integrated intensity. The $I(E)$ curves for symmetrically equivalent beams were averaged and smoothed. The data set consisted of 17 symmetrically inequivalent beams and had a total energy range of 4853 eV.

The LEED intensity spectra were calculated using the Symmetrized Automated Tensor LEED (SATLEED) programs of Barbieri and Van Hove [6]. The scattering phase shifts were calculated with the Barbieri–Van Hove phase shift package [6]. Eleven phase shifts were used in the scattering. The imaginary part of the inner potential was optimized to -5.5 eV and the real part of the inner potential was optimized to 10.48 eV. The agreement between calculated and experimental $I(E)$ curves was measured by the Pendry r-factor [7] after both the experimental and theoretical data were smoothed using a weighted three-point smooth. The reference structure was optimized with respect to the geometrical parameters by minimizing the R-factor, and the uncertainties in these parameters were calculated using its variance.

3. Results and discussion

To determine the site for the K atom in the commensurate (2×2) structure, preliminary calculations were carried out for K adsorbed in the substitutional site shown in figure 1, in the long bridge and short bridge sites, and on the top and bridge sites on top of the Cu rows. (While the tops of the rows may seem highly unlikely, it has recently been shown that Xe and Kr atoms do adsorb preferentially on the tops of rows on this substrate [8].) These calculations included both vertical and lateral relaxations of the first three layers of substrate atoms. The result of this preliminary analysis was that the best agreement was for the substitutional site found before, which gave an r-factor of 0.23, and the other structures all had r-factors which were greater than 0.36. Further refinements, including the optimization of the vibrational amplitudes of the K and Cu atoms, further reduced the r-factor to 0.22. The final parameters obtained from this analysis are given in table 1, and the final intensity spectra are shown in figure 2.

The result of this LEED analysis is that the K atoms do occupy substitutional sites in the (2×2) structure, as found in the PhD study for the disordered K overlayer. The K adsorption parameters (K–Cu distances) are almost exactly the same as those found in the earlier PhD study. There was slightly more variation in the substrate parameters, although the results are consistent with each other. In the PhD study, it was noted that the directions of the lateral relaxations found using PhD were opposite to those found by the earlier LEED study. The earlier LEED study was done for a disordered K overlayer and the K atoms were neglected in the LEED calculation. In order to assess the importance of the K atoms to the LEED calculation, we carried out a similar calculation, ignoring the contribution from the K atoms in the calculation and comparing to our (2×2) LEED data. The results of this analysis were remarkably similar to those found in the earlier LEED study. The interlayer substrate spacings, the lateral relaxations and the third-layer rumpling were almost identical to the values found in the earlier LEED study, and rather different from those found when the K atoms were included in the calculation. This indicates that the neglect of the scattering by the K atoms affects the determined structural parameters even if there is no long-range order of the K atoms. In cases like this, the analysis should be performed with a random fractional occupancy of adsorption sites.

We also observe a buckling of the third Cu layer, which has the effect of pulling the row of Cu atoms which is directly beneath the row of K atoms outward, toward the K atom. A similar buckling was observed in the PhD study, although in that case, it was only possible to observe the position of the Cu atom directly beneath the K atom, and not the Cu atoms which
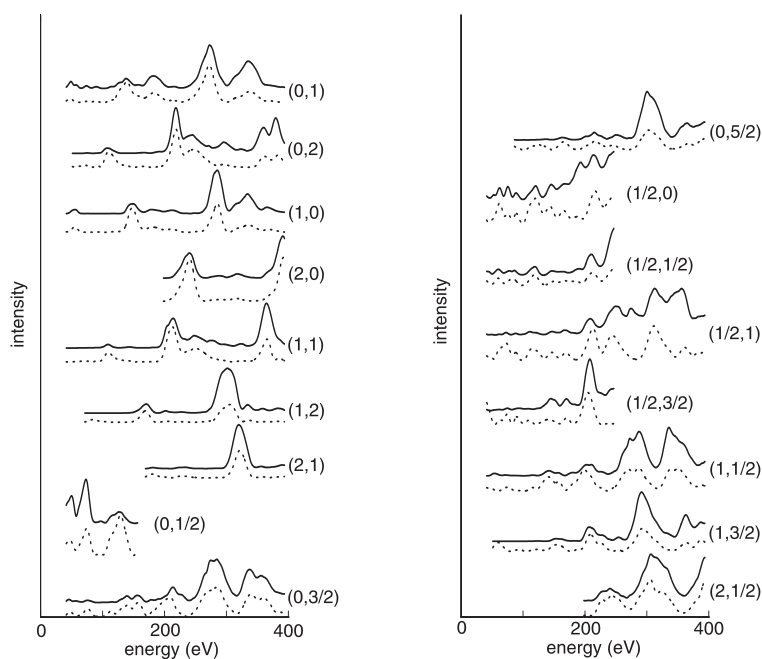
Figure 2. Experimental and best-fit calculated spectra for the structure shown in figure 1. The experimental curves are solid and the calculated ones are dashed. The structural parameters are given in table 1.

are also in the third Cu layer, but between K atoms. Our LEED analysis shows that the vertical displacements of the two types of Cu atoms in the row beneath the K row (i.e. the type which is directly beneath K and the type which is not) are nearly identical (within 0.02 Å). Furthermore, they are pulled up by about 0.11 Å relative to those Cu atoms which are not beneath the K rows. The magnitude of this buckling is twice that determined by the PhD study, but is well within their mutual uncertainties. A smaller buckling was noted in the earlier LEED study, and might be attributed to the lower coverage of K, but again we note that we could obtain essentially the same value if we neglected the presence of K in our calculation, as done in the earlier LEED study. The effect of this buckling is to slightly increase the coordination of the K atom. The nearest-neighbour distance determined in this study, 3.24 Å, gives an effective K radius of 1.96 Å, which is within the range of values observed in other K adsorption systems for fourfold to fivefold coordination [5]. In this case, there are four nearest neighbours (in the second Cu layer), with a fifth (in the third Cu layer) only 0.34 Å farther way. Thus, the nearest-neighbour spacing is consistent with the dependence on coordination observed in other alkali adsorption systems.

From our LEED analysis, the isotropically averaged vibration amplitudes were determined for both the K atoms and the Cu atoms. The root-mean-square vibration amplitude of K was found to be 0.3 Å. This vibration amplitude is similar to values determined in other LEED studies for adsorbed alkalis, i.e. between about 0.2 Å and 0.5 Å. The vibration amplitude of K was also determined in the PhD study, which separated the perpendicular and parallel components, finding that the parallel amplitude (0.10 Å) is larger than the perpendicular amplitude (0.07 Å). Similar anisotropy has been noted in other studies of alkali metal adsorption systems [9, 10]. The difference in the magnitudes of the vibration amplitudes determined in this

LEED study and the earlier PhD study is not particularly shocking since they are measured in rather different ways. In the LEED studies, the vibrational amplitudes are fitting parameters, which primarily are determined by the *k*-dependence of the scattered intensity. There is evidence that LEED at normal incidence is more sensitive to the perpendicular component of the vibration, and that an 'isotropic' vibration amplitude is dominated by the perpendicular component [11]. In PhD, the vibration amplitudes are also fitting parameters, which give the mean-square vibration amplitudes of atoms relative to the emitter. These vibration amplitudes are perhaps determined more explicitly than those in LEED, since the fitting includes the actual scattered intensities, but typically the uncertainties are rather high in both techniques (typically 30 to 50% in LEED). The fact that the LEED result is significantly larger than the PhD result may be at least partly due to correlated vibrations of the K atoms and their nearest neighbours, the neglect of which in the PhD calculations would tend to give a smaller-than-actual amplitude [12]. In any case, the vibration amplitude of the K atom is significantly larger than that of the underlying Cu atoms, as shown in table 1.

4. Conclusions

We have shown that the adsorption site for a p(2 × 2) overlayer of K on the (K-induced) missing-row reconstructed surface of Cu(110) is a substitutional site. This is the same site found by an earlier PhD study at a lower coverage of disordered K on this surface. The K–Cu nearest-neighbour distance is 3.24±0.05 Å. We observed very little, if any, lateral displacement of the second-layer Cu atoms, but there is a significant (0.11 ± 0.06 Å) buckling of the third layer of Cu, which acts to pull the rows of Cu atoms which are directly beneath the K rows upward, toward the surface.

This adsorption geometry is consistent with the earlier observations that indicate that alkali adatoms tend to maximize their coordination, e.g. by pushing deeper in the surface. In this case, the substitutional site increases the coordination over an on-surface adsorption site, and the buckling of the third Cu layer further increases the coordination. The substitutional adsorbates form an ordered array which leads to the missing-row reconstruction of the Cu(110) surface. Similar 'concerted' substitutional adsorbate structures have been observed on Al(111), for example, where $(\sqrt{3} \times \sqrt{3})$R30° structures are formed by substituted alkali adatoms [13]. In the case of K/Cu(110), not every site which is vacated by a Cu atom is filled by a K atom—each K atom replaces two Cu atoms. This rather massive reconstruction is presumably facilitated by the small energy difference between the unreconstructed and the reconstructed surfaces of Cu(110) [14].

Acknowledgments

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