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## Photoelectron diffraction investigation of the local adsorption site of N on Cu(111)

R L Toomes<sup>†</sup>, J Robinson<sup>†</sup>, S M Driver<sup>†</sup>, D P Woodruff<sup>†</sup>, P Baumgärtel<sup>‡</sup>,  
T Geißel<sup>‡</sup>, R Lindsay<sup>‡§</sup>, O Schaff<sup>‡</sup> and A M Bradshaw<sup>‡</sup>

<sup>†</sup> Physics Department, University of Warwick, Coventry CV4 7AL, UK

<sup>‡</sup> Fritz-Haber-Institut der MPG, Faradayweg 4-6, D14195 Berlin, Germany

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**Abstract.** Scanned-energy mode photoelectron diffraction has been used to investigate the local structure of N adsorbed on Cu(111). The results favour an N-induced pseudo-(100) reconstruction as proposed previously, but indicate that this comprises *two* reconstructed Cu layers. The N atoms occupy hollow sites approximately coplanar with the outermost pseudo-(100) layer at a height of about 2 Å above a Cu atom from the underlying pseudo-(100) layer; the N atoms thus have fivefold co-ordination.

### 1. Introduction

There is growing evidence for a significant number of systems in which adsorbate-induced reconstruction of fcc metal (111) and (110) surfaces produces an outermost layer which adopts a geometry similar to that of the (100) surface of the same material [1]. In a few cases, such as the (2 × 3)-N structure on Cu(110) [2–5], these pseudo-(100) reconstructions give rise to relatively small surface meshes which make them amenable to full quantitative structure determination. In many cases, however, the pseudo-(100) overlayers are either incommensurate or have very large coincident surface meshes making quantitative structural analysis difficult. An example of this type is the pseudo-(100)c(2 × 2)-N structure formed on Cu(111).

The adsorption of N on Cu(111) followed by annealing gives a sharp but complex low energy electron diffraction (LEED) pattern. This pattern was attributed by Higgs *et al* [6] to three rotational domains of a (100)-like overlayer with dimensions closely similar to those of the Cu(100)c(2 × 2)-N structure (in which adsorbed N atoms are believed to occupy near-coplanar hollow sites [7, 8]). From the splitting of the spots in the LEED pattern it was deduced that the overlayer was distorted relative to that of an ideal (100) layer with primitive translation vectors of  $1.04 d_{Cu-Cu}$  and  $1.01 d_{Cu-Cu}$  in the  $\langle 110 \rangle$  and  $\langle 112 \rangle$  substrate directions respectively, where  $d_{Cu-Cu}$  is the bulk Cu–Cu nearest-neighbour spacing. Two recent STM studies have provided direct evidence for the formation of such a pseudo-(100)c(2 × 2) overlayer [9, 10], one of these imaging both the periodicity of the N adsorbate and that of the reconstructed Cu layer [10]. These STM studies revealed a significant corrugation perpendicular to the surface in the reconstructed layer which was attributed to variations in registry with the underlying (111) layer, and in one of these investigations [10] the periodic corrugation was shown to be consistent with a  $(25 \times 7\sqrt{3})$ rect. coincidence mesh.

§ Present address: Chemistry Department, University of Manchester, UK.

Here we present the first investigation of the local adsorption geometry in the N-induced pseudo-(100) reconstruction phase on Cu(111) using a method capable of providing quantitative structural information. The technique which we have used is scanned-energy mode photoelectron diffraction (PhD) [11]. This technique provides an element-specific way of probing the local environment of an adsorbate with high sensitivity to the location of the substrate near neighbours.

In PhD the intensity of an adsorbate core level photoemission peak is measured as a function of kinetic energy in a variety of emission directions. Modulations in the intensity arise from coherent interference between the directly emitted component of the photoelectron wavefield and components which are elastically scattered from neighbouring atoms. For many common substrates, such as Cu, there is a local maximum in the scattering cross-section for  $180^\circ$  scattering; in emission directions corresponding to this backscattering from a nearest-neighbour substrate atom one therefore observes strong modulations of long period associated with this dominant scattering path. This effect commonly allows us to perform a direct inversion of the experimental PhD spectra to determine the approximate position of the nearest-neighbour substrate atoms using the so-called projection method [12, 13]. A full quantitative structural determination can then be carried out by comparing the experimental data with the results of multiple-scattering spherical-wave simulations [14, 15] and iterating the structural parameters to obtain the best theory–experiment agreement. These simulations include the influence of the finite energy and angular resolution of the experiment as well as the role of thermal vibrations of the emitter and scatterer atoms.

Although this established procedure has proved successful in a large number of applications of the method, it is most effective for the simplest case of an adsorbate occupying a single high-symmetry site. In the case of low-symmetry adsorption sites averaging over symmetry-equivalent directions relative to the substrate suppresses the dominance of the backscattering pathways and renders the direct inversion far less effective. Multiple adsorption sites similarly reduce the effectiveness of the projection method and make structure determination more difficult and potentially less incisive. Furthermore, the number of structural parameters which need to be fitted is greater while the need to average over a number of emitter sites and/or symmetrically equivalent domains considerably increases the computational effort required for each individual multiple-scattering calculation. The current investigation of N in the incommensurate (or  $(25 \times 7\sqrt{3})$ rect. coincidence mesh) pseudo-(100) phase on Cu(111) is the most complicated study yet undertaken and we were unable to obtain a definitive, fully quantitative description of the structure. Nevertheless, we were able to determine unambiguously the local adsorption geometry of the N and obtain important insight into the nature of the reconstruction.

## 2. Experimental details

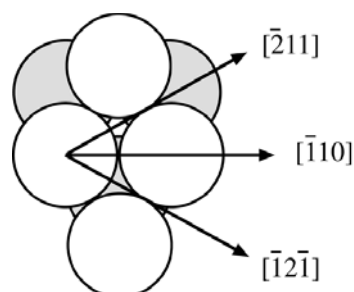
The experiments were performed in a purpose-built UHV system installed on the high-energy toroidal grating monochromator beamline (HE-TGM 1) at the BESSY synchrotron radiation facility in Berlin. The UHV system consists of an upper and lower chamber linked by a gate valve. The upper chamber is used for sample preparation and is equipped with an ion gun, LEED optics, a mass spectrometer and gas dosing system. The lower chamber is used for photoemission measurements using radiation from the synchrotron and is equipped with a VG Scientific concentric spherical sector electron energy analyser (mean radius 152 mm) which is fitted with three parallel channeltrons. The analyser is fixed at an angle of  $60^\circ$  to the direction of the incident radiation and lies in the same (horizontal) plane as the major polarization vector of the light. The direction in which photoemission is measured can be changed by rotating

the sample about the vertical axis of the manipulator (which changes the polar angle) and by rotating the sample about its surface normal (which changes the azimuthal angle). The sample can be heated to high temperature by electron bombardment and cooled to 120 K using a copper braid connection to a liquid nitrogen reservoir. The sample temperature is measured by a chromel–alumel thermocouple inserted into a hole at the side of the crystal.

The Cu(111) crystal was cleaned *in situ* by cycles of Ar ion bombardment followed by brief annealing at 820 K. The surface cleanliness was checked with soft x-ray (synchrotron radiation) photoelectron spectroscopy while the surface order was checked with LEED. The N adsorbate structure was prepared by bombarding the clean Cu(111) surface with 500 eV nitrogen ions for 180 s in an atmosphere of  $3 \times 10^{-5}$  mbar of N<sub>2</sub> followed by annealing at 600 K. This treatment produced a very sharp, complex LEED pattern identical to that previously reported by Higgs *et al* [6]. The N structure was very stable and inert so that several PhD spectra (each taking about one hour) could be recorded after one preparation. The sample was cooled to 120 K during the PhD measurements to reduce the effects of thermal vibrations.

To obtain a scanned-energy photoelectron diffraction (PhD) spectrum in a specific, fixed emission direction, short photoelectron energy distribution curves (EDCs) centred around the N 1s photoemission peak were measured with the photon energy incremented by 2 eV between successive scans. In the set of EDCs comprising one PhD spectrum the kinetic energy of the N 1s photoemission peak covered a range of 60 eV to 464 eV. Each of the EDCs was integrated by fitting a step-Gaussian function and a template background. The resulting peak area versus kinetic energy curve was normalized, using a smooth spline to model the non-diffracted intensity, to obtain the PhD modulation spectrum which is used in data analysis [11].

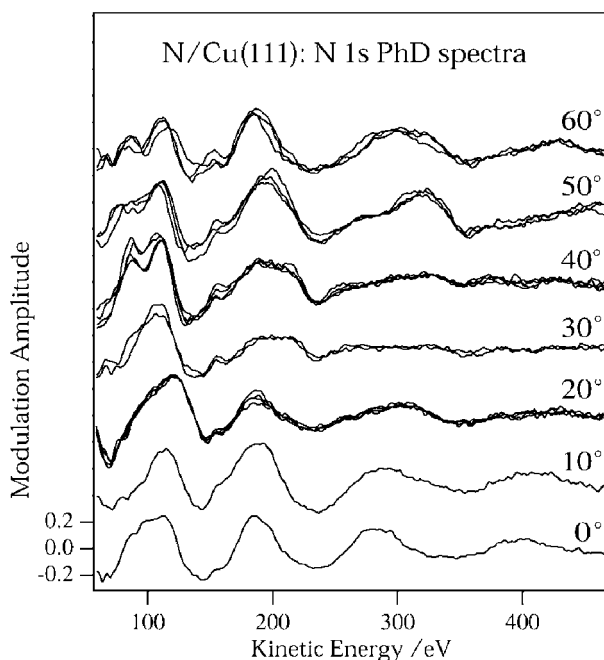
PhD spectra were recorded in a variety of polar emission angles from 0 to 60° (measured from the surface normal) in each of the three principal azimuths of the surface, namely the close-packed  $[\bar{1}10]$  direction and the  $[\bar{2}11]$  and  $[\bar{1}2\bar{1}]$  azimuths at +30 and –30° to  $[\bar{1}10]$  respectively, as shown in figure 1. Additional spectra were recorded at +45° to  $[\bar{1}10]$ , nominally in the  $\langle 010 \rangle$  direction of one of the three rotational domains of the (100)-like surface reconstruction.



**Figure 1.** Schematic plan view of the outermost two layers of a Cu(111) surface defining the high-symmetry azimuths used in the collection of the PhD data.

### 3. Results and discussion

The complete set of experimental PhD spectra obtained for N on Cu(111) is shown in figure 2 with, for each polar angle, the spectra from different azimuths overlaid. It is clear that the spectra depend only on the polar angle and are independent of the azimuthal direction. At polar emission angles of 0 to 10° and 50 to 60° the modulations are dominated by a single



**Figure 2.** Experimental N 1s PhD spectra recorded at different polar emission angles, as labelled, from the Cu(111)/N surface. Spectra for different azimuthal directions at the same polar angles are overlaid.

well defined periodicity and extend to over 300 eV kinetic energy with an amplitude of around  $\pm 25\%$ . At intermediate emission angles, 20 to 40°, the modulations are weak above 150 eV. From these simple observations of the data we can immediately conclude that the surface is reconstructed.

If an adsorbate occupies a single, high-symmetry site on an unreconstructed surface there are well defined, high amplitude modulations in only a few specific emission directions. As discussed in the introduction, these strong modulations arise from backscattering when the emission direction is such that there is a substrate atom directly behind the emitter. Clearly, therefore, the lack of an azimuthal dependence in the strong modulations which are seen at high polar angles is incompatible with the N atoms occupying a single, high-symmetry site on an unreconstructed Cu(111) surface. Several simulations were carried out for multiple occupation of low-symmetry sites, requiring averaging over symmetrically equivalent domains, with various relaxations of the surrounding Cu atoms. All of these simulations retained some azimuthal dependence and gave very poor fits to the experimental data. In particular, it proved impossible to reproduce the strong modulations seen in the experimental data at polar emission angles of 50 to 60°. In general, strong modulations at high polar angles indicate that the emitter atom is near coplanar with the outermost substrate layer; it is not possible for N atoms to be coplanar with the surrounding Cu atoms on the close-packed unreconstructed (111) surface. Thus adsorption on an unreconstructed surface is incompatible with both the lack of an azimuthal dependence in the data and the observed polar angle dependence.

Having dismissed the possibility of the N being on an unreconstructed Cu(111) surface, simulations were carried out assuming three rotational domains of a distorted Cu(100)c(2 × 2)-N overlayer with the close-packed Cu atom rows of this overlayer aligned

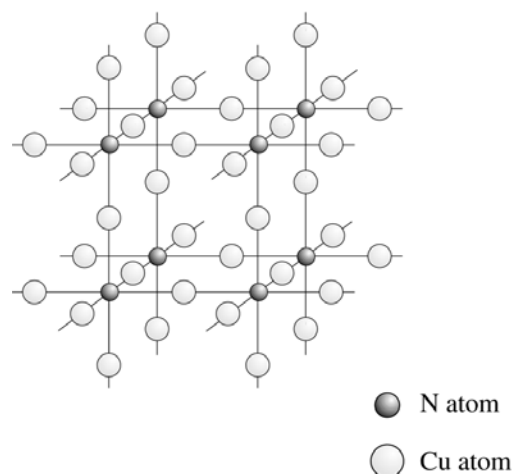
Structure of  $\text{Cu}_3\text{N}$ 

Figure 3. Schematic view of the structure of  $\text{Cu}_3\text{N}$ .

along the close-packed directions of the (111) substrate as originally proposed by Higgs *et al* [6]. It was found that, with the N atoms in symmetric hollow sites, good agreement between experiment and theory could be obtained for the high polar angle PhD spectra provided the N atoms were near coplanar with the surrounding Cu atoms. Furthermore, averaging over the three rotational domains was sufficient to remove almost all azimuthal dependence. Thus the PhD data are consistent with a (100)-like surface reconstruction in which the N atoms occupy hollow sites.

The  $\text{Cu}(100)c(2 \times 2)\text{-N}$  outer layer strongly resembles the (100) plane of bulk  $\text{Cu}_3\text{N}$ , shown in figure 3 (albeit with significant lateral strain), a point which was recognized in quite early studies of the properties of the (100) surface itself in the presence of adsorbed N [16]. In view of this structural similarity to the bulk compound, one might ask whether the stability of the pseudo-(100) reconstruction is actually due to the formation of not a single atomic layer of  $(100)c(2 \times 2)\text{-N}$ , but rather of a film of a  $\text{Cu}_3\text{N}$ -like structure comprising several atomic layers. A related question is whether the reconstruction involves subsurface N, especially since the ion bombardment used to create the structure must, at least transiently, form subsurface species. To test for the possible presence of a three-dimensional  $\text{Cu}_3\text{N}$ -like phase, simulations were carried out for a four-layer thick  $\text{Cu}_3\text{N}$ -like film above the  $\text{Cu}(111)$  substrate, with optimization of the interlayer spacings. While the main features of the experimental data could be reproduced, it was found that the presence of the subsurface N in the third layer introduced significant fine structure not present in the experimental data, especially at higher polar angles. Investigations of structures involving a significant number of subsurface N species in the second layer gave even worse fits to the experimental data. Thus we can conclude that, in the surface we prepared, N does not populate a significant number of subsurface sites.

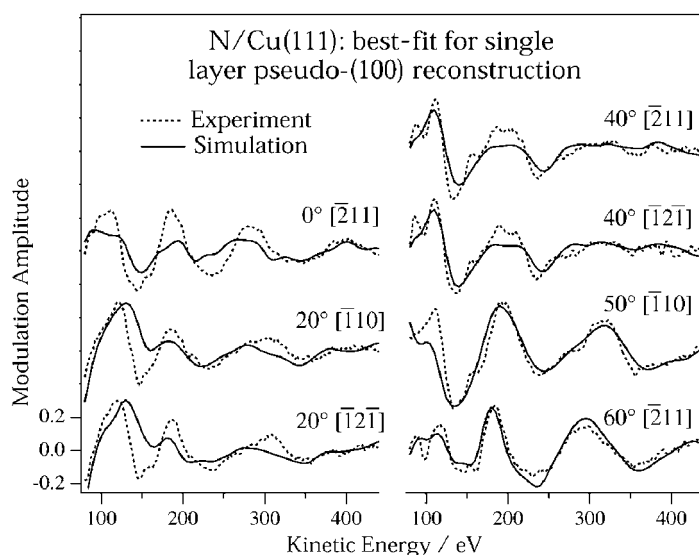
Simulations of the PhD data were found to show only a weak sensitivity to the size of the surface unit mesh vectors defining the  $\text{Cu}(100)c(2 \times 2)\text{-N}$  reconstructed layer, hence the analysis was carried out using the  $(1.04 \times 1.01)d_{\text{Cu-Cu}}$  surface mesh deduced by Higgs *et al* [6] on the basis of the LEED pattern. An incommensurate overlayer greatly complicates even a local structural analysis because there are an infinite number of different local registries of

the emitter atoms in the overlayer to the underlying (111) surface. Even for a commensurate  $(25 \times 7\sqrt{3})$ rect. coincidence mesh [10], which has an almost identical size to that proposed by Higgs *et al*, there are a very large number of emitters in inequivalent registries. An additional complication in modelling this structure is that the mismatch of the pseudo-square overlayer on the hexagonal substrate leads to a strong corrugation in the height of the Cu overlayer atoms above the outermost unreconstructed Cu(111) surface layer. A simple hard-sphere simulation allowing relaxation of the reconstructed layer Cu atoms perpendicular to the surface until they just touch the underlying Cu(111) layer atoms involves a layer spacing variation from 2.08 Å (for atoms in the (111) hollow sites) to 2.55 Å (for atoms which lie atop Cu atoms in the unreconstructed layer). Evidently, the layer spacings of the N emitter atoms which occupy the hollow sites of this corrugated layer will also vary, even if they maintain the same relative positions to the four nearest-neighbour Cu atoms within this layer.

To allow for these variations in registry and layer spacing, we carried out simulations which incorporated averaging over 144 distinct N sites distributed over a representative portion of the surface. In the simulations it was assumed that all the Cu atoms had a Debye temperature equal to that of the bulk (340 K). Although the surface atoms in the reconstructed layer will almost certainly have a different, but unknown, Debye temperature, we are only sensitive to the *relative* vibrations of these near-neighbour Cu atoms with respect to the N emitter atoms so, to a good approximation, it is sufficient to optimize only the magnitude of the N vibrations. The optimized vibrational amplitudes which we obtain for the N atoms are hence dependent on those chosen for the Cu atoms and the extent of vibrational correlations.

In the initial test structure the heights of the Cu atoms in the pseudo-(100) layer were fixed at values determined by the touching hard-sphere model described above assuming a planar, undistorted (111) layer beneath; the N atoms were placed in fourfold hollow sites within the reconstructed layer at the average height of the surrounding four Cu atoms (i.e. in locally coplanar sites). This model gave a good fit to the high-polar-angle spectra, but the fit at normal emission was very poor. In particular, the random registry and variable height (between 2.20 and 2.48 Å) of the N atoms above the underlying (111) layer led to PhD modulations at normal emission which were weak and ill defined. To maximize the amplitude of these PhD modulations the N atoms were given very a small isotropic mean-square vibrational amplitude of  $0.0005 \text{ \AA}^2$ , effectively leading to a relative N–Cu mean-square vibrational amplitude which is equal to that of a bulk Cu atom ( $0.0024 \text{ \AA}^2$ ); this implies a very strong correlation in the vibrations relative to the second-layer Cu atoms or a very stiff overlayer. To obtain an objective measure of the agreement between experiment and theory we use an *R*-factor defined as the mean-square difference between the theoretical and experimental modulation amplitudes normalized such that a value of 0 corresponds to perfect agreement, a value of 1 to no correlation and a value of 2 to anti-correlation [11, 17]. In previous PhD surface structure determinations using this approach the very best fits have been found to correspond to *R*-factor values of 0.20 or less, while values above 0.4–0.5 are regarded as indicating rather poor levels of agreement. In the present case the multi-spectrum *R*-factor for the initial constrained model was 0.25 but the individual *R*-factor for the normal emission spectrum was 0.59. In order to improve the fit to the PhD spectrum at normal emission, it was necessary to place a significant proportion of the N atoms approximately 2.0 Å above an underlying Cu atom.

The best overall experiment–theory agreement achieved with this model incorporated a reduction in the height of the pseudo-(100)c(2 × 2)-N layer above the (111) bulk by 4% relative to the touching hard-sphere model and an additional lowering of all the N atoms which were within 0.6 Å of being atop a second-layer Cu atom from the locally coplanar geometry to a distance of 2.0 Å above the second layer. The simulated spectra obtained from this model are



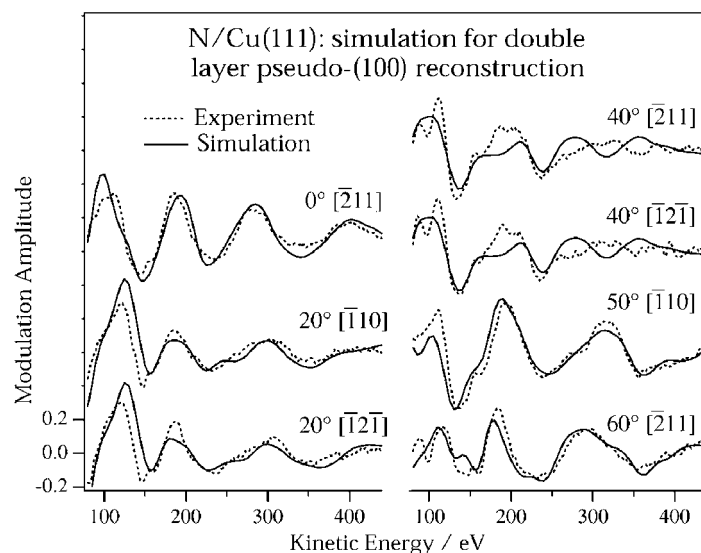
**Figure 4.** Comparison of a subset of the experimental N 1s PhD spectra with the best-fit theoretical spectra obtained assuming only the outer Cu layer is reconstructed to pseudo-(100).

compared with the experimental data in figure 4; the multi-spectrum  $R$ -factor is 0.21 and the  $R$ -factor for the individual normal emission spectrum is 0.33. Further improvements to the fit at normal emission could be achieved by introducing large lateral distortions into both the pseudo-(100) layer and the underlying (111) layer to maximize the number of N atoms which were in near-atop registries and which could thus achieve fivefold co-ordination. However, even when allowing the underlying second-layer Cu atoms to relax outwards to the limit of what was deemed physically plausible (up to  $0.2 \text{ \AA}$ ), the increased number of N atoms which had to be moved down away from the locally coplanar geometry to obtain the required layer spacing of  $2.0 \text{ \AA}$  resulted in a significant deterioration in the fit to the higher-polar-angle spectra. Thus, although an  $R$ -factor of 0.19 for the normal emission spectrum could be obtained with physically plausible distortions, the multi-spectrum  $R$ -factor for this model was increased to 0.23. Hence the fit shown in figure 4 with an  $R$ -factor of 0.21 corresponds to the best overall experiment–theory agreement which could be obtained assuming that only the outer layer is reconstructed and that, as indicated by the STM images, all the N sites in the Cu(100)- $c(2 \times 2)$  overlayer are occupied.

A significantly better overall fit to the data, as measured by the multi-spectrum  $R$ -factor, was obtained by additionally reconstructing the layer below the N to pseudo-(100), thereby allowing all the N atoms to achieve fivefold co-ordination. Figure 5 shows a simulation for a double-layer pseudo-(100) reconstruction in which the heights of the Cu atoms have been adjusted slightly from a touching hard-sphere model so that the N atoms are approximately coplanar with the outermost Cu layer whilst being  $2.0 \text{ \AA}$  above the underlying second layer Cu atoms; in particular, the Cu atoms beneath N atoms were lowered by up to a maximum of  $0.1 \text{ \AA}$  and the outermost layer Cu atoms were raised by up to a maximum of  $0.13 \text{ \AA}$ . The multi-spectrum  $R$ -factor for this model is only 0.16 and there are good fits to both the low- and high-polar-angle spectra, although the fit to the  $40^\circ$  spectra is slightly worse than for the single-layer reconstruction. The optimized mean-square vibrational amplitudes for the N atoms in these calculations have reasonable values of  $0.002 \text{ \AA}^2$  parallel to the surface and  $0.006 \text{ \AA}^2$



perpendicular to the surface. There are, however, many slight variations on this model which give comparable overall fits to the experimental data. For example, an alternative model giving a comparable fit is one in which the inner pseudo-(100) layer is placed according to a touching hard-sphere model, the N atoms are placed 2 Å above alternate atoms in this layer and the Cu atoms of the outer pseudo-(100) layer are placed at the average height of the neighbouring N atoms. In view of this ambiguity we are unable to give a definitive, fully quantitative model for the detailed structure of N/Cu(111).

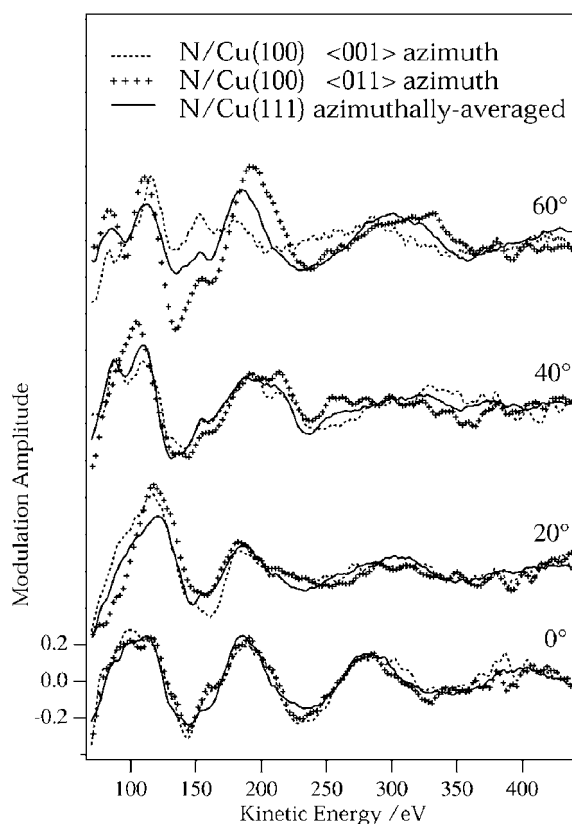


**Figure 5.** Comparison of a subset of the experimental N 1s PhD spectra with theoretical spectra obtained assuming that the two outer Cu layers are reconstructed to pseudo-(100).

We can, however, identify key aspects of the structure and can exclude many possible models. Specifically, we show that the important features of the experimental data can be reproduced if all the N atoms are fivefold co-ordinated in a double-layer reconstruction such that they are approximately coplanar with the outer pseudo-(100) layer and are about 2 Å above the atoms of the underlying pseudo-(100) layer. It may be noted that the bondlength between the N and the coplanar nearest-neighbour Cu is about 1.85 Å which is less than the N–Cu bondlength of 1.91 Å in Cu<sub>3</sub>N, while the bondlength between the N and the second-layer nearest-neighbour Cu is, at about 2.0 Å, slightly longer.

If the two outer layers of the Cu(111) surface are reconstructed to pseudo-(100) then the local binding site of the N should be essentially the same as the binding site of N on Cu(100). Figure 6 shows a comparison of the azimuthally averaged PhD spectra for N on Cu(111) with the PhD spectra obtained for N on Cu(100) in the  $\langle 011 \rangle$  and  $\langle 001 \rangle$  azimuths [18]. It is evident that for polar angles below 40° the spectra for N on Cu(111) are identical to the spectra for N on Cu(100). At a polar emission angle of 60° the azimuthally averaged spectrum for N on Cu(111) is intermediate between the spectra in the  $\langle 011 \rangle$  and  $\langle 001 \rangle$  azimuths for N on Cu(100). This provides strong support for the proposition that N occupies near-identical local adsorption sites on Cu(111) and Cu(100).

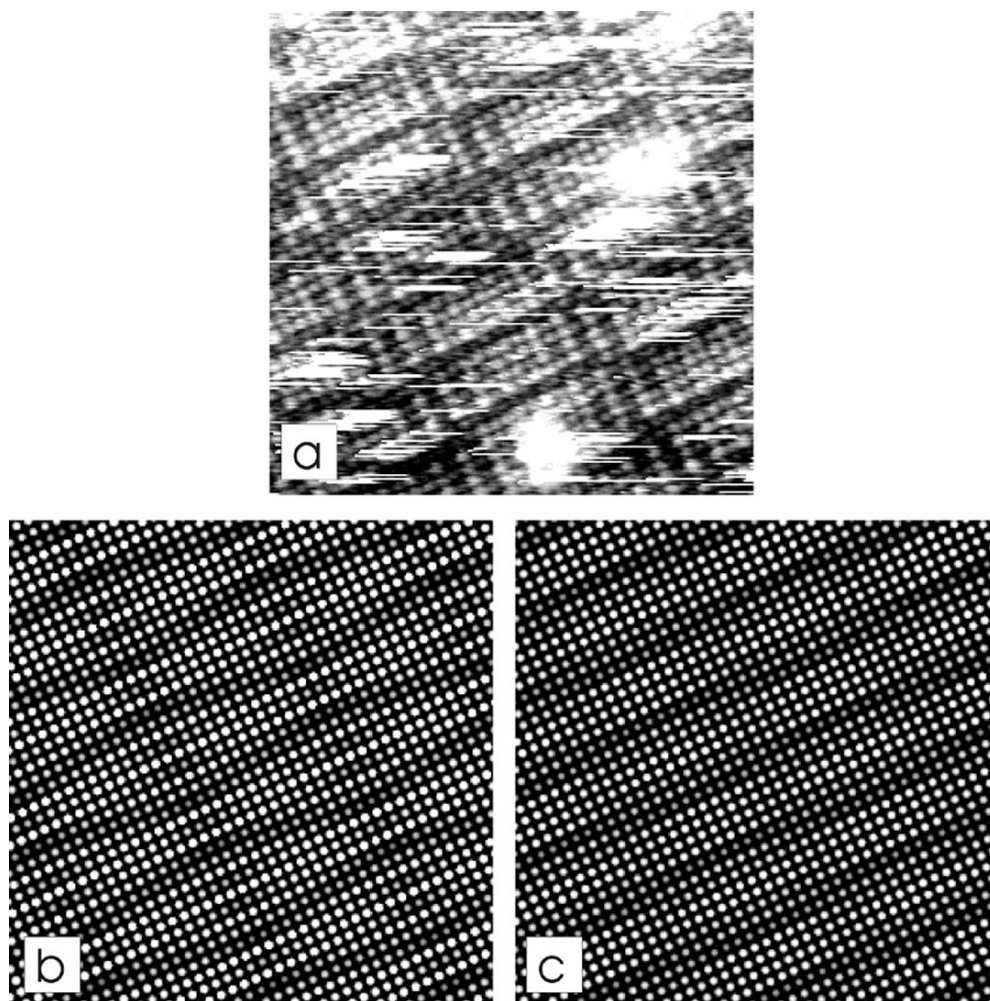
Further evidence in support of a double-layer pseudo-(100) reconstruction is given by the pattern of corrugation seen in the published STM image of the Cu atoms in the outer pseudo-(100) layer [10]. Figure 7 shows the experimental STM image (figure 7(a)) alongside



**Figure 6.** Comparison of the azimuthally averaged experimental N 1s PhD spectra for N on Cu(111) with the experimental N 1s PhD spectra in the  $\langle 001 \rangle$  and  $\langle 011 \rangle$  azimuths recorded from a Cu(100) $c(2 \times 2)$ -N surface.

simulations for a single-layer (figure 7(b)) and double-layer (figure 7(c)) pseudo-(100) reconstruction. The corrugations in the STM simulations are of the actual atomic positions and were determined by undistorted touching hard-sphere models; however, essentially the same patterns are obtained for the distorted models producing the fits to the PhD data shown in figures 4 and 5. It is clear from figure 7 that the corrugation pattern for the double-layer reconstruction gives much better agreement with the experimental STM image than that for the single-layer reconstruction.

The most probable driving force for the proposed N-induced double-layer pseudo-(100) reconstruction of the Cu(111) surface is the preference for N to have fivefold square-pyramidal co-ordination, as in the (100) surface of  $\text{Cu}_3\text{N}$ . The strong preference for N to have fivefold co-ordination is also shown in the  $(2 \times 3)$  N-induced structure on Cu(110). In this case the N atoms also occupy fourfold hollow sites in a  $c(2 \times 2)$  arrangement on a pseudo-(100) reconstructed surface layer. Within each  $(2 \times 3)$  unit mesh there are four N atoms. One of these N atoms is directly fivefold co-ordinated, being atop a second-layer atom, one is above a bridge site and is only fourfold co-ordinate while the remaining two are laterally displaced by  $0.15 \text{ \AA}$  from the ideal pseudo-square mesh which, together with a  $0.05 \text{ \AA}$  lateral displacement of the nearest-neighbour second-layer Cu atom, allows them to achieve fivefold co-ordination [5]. Both STM [19] and LEED [4, 5] studies indicate that the three fivefold co-ordinate sites are



**Figure 7.** Comparison of (a) the experimental STM image of the N-induced surface phase on Cu(111) under conditions which image the Cu atoms (from [10]) with simulations of the expected atomic corrugation assuming (b) single-layer and (c) double-layer pseudo-(100) reconstructions. The simulations are based on touching hard-sphere models.

preferentially occupied and that the  $(2 \times 3)$  reconstruction is stable with only low occupation of the fourfold co-ordinate sites.

If N on Cu(111) does, as proposed, induce the reconstruction of the underlying layer then this indicates that the interaction between the N and the Cu second layer is important despite the rather long bondlength of  $2 \text{ \AA}$ . Evidence that this may be the case is presented in a recent paper by Wiell *et al* [20] which examines the local bonding of N on Cu(100). In this study x-ray emission and x-ray absorption spectra were compared to theoretical calculations using a model in which the N atoms occupy fourfold hollow sites at a height of  $0.4 \text{ \AA}$  above the topmost Cu layer which is relaxed outwards by 4%; this is the structure favoured by a SEXAFS study of this phase [8] although a LEED study places the N more nearly coplanar with the top Cu layer [7]. It was found that the antibonding states derived from the  $\sigma$  interaction of the N  $2p_z$  orbital with the Cu second layer extended above the Fermi level and were only partially occupied.

In contrast, there was full occupancy of both the bonding and antibonding states derived from the interaction of the N  $2p_{xy}$  orbitals with the outermost (near-coplanar) Cu layer. Thus it was concluded that the interaction of the N  $2p_z$  orbital with the second layer could be important for chemisorption energetics despite the bondlength in this model calculation being significantly longer than that found in our analysis of the Cu(111)/N reconstruction phase.

#### 4. Conclusions

Although the complexity of the N/Cu(111) system precludes a detailed quantitative structural determination, we have been able to deduce a significant amount of information on the adsorption site from PhD data. We are able to confirm that the N atoms occupy hollow sites in a pseudo-(100) reconstructed layer as proposed by LEED observations and STM. We have further been able to determine that the N atoms are near coplanar with the outermost pseudo-(100) layer. On the basis of PhD simulations, comparison to PhD data for N/Cu(100) and the pattern of corrugation in the outermost pseudo-(100) Cu layer seen by STM, we propose that the second Cu layer, as well as the outermost layer, undergoes a pseudo-(100) reconstruction so that all of the N atoms have fivefold co-ordination.

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