Low energy electron diffraction structure determination of the Ni(110)c(2 × 2)–CN surface phase

C. Bittencourt 1, E.A. Soares 2, D.P. Woodruff *

Department of Physics, University of Warwick, Coventry CV4 7AL, UK

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Abstract

The structure of the Ni(110)c(2 × 2)–CN surface phase has been determined by quantitative low energy electron diffraction (LEED). Contrary to earlier suggestions that relatively intense fractional order LEED beams imply that adsorbate-induced Ni surface reconstruction occurs, the results confirm previous findings by scanned-energy mode photoelectron diffraction and medium energy ion scattering that no significant reconstruction occurs. The C–N axis is oriented along an open-packed \( \{100\} \) azimuth, with the molecule lying above a second layer Ni atom; the intramolecular axis is tilted by \( 23.7 \pm 4.5^\circ \) relative to the surface plane. The adsorption does lead to a substantial \( (9 \pm 4\%) \) outward relaxation of the outermost Ni layer spacing and small distortions of the outermost layers of the Ni substrate.

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1. Introduction

The interaction of cyanogen, \( \text{C}_2\text{N}_2 \), with Ni(110) is known to lead to an ordered cyanide adsorption phase, Ni(110)c(2 × 2)–CN [1–5], but this has only recently been the subject of quantitative structural investigations. The properties of CN adsorbed at metal surfaces appears to be somewhat unusual in that at the metal–electrolyte interface it seems to have been accepted that the molecule bonds end-on to the surface like CO, but at metal–vacuum interfaces experiments show the molecular axis to be more nearly parallel to the surface. In the case of Ni(110)c(2 × 2)–CN, the results of the early spectroscopic studies, supported by cluster calculations, were taken as evidence that the C–N bond axis lies parallel to the surface plane, aligned in the close-packed [110] azimuth such that the C–N axis lies parallel to the close-packed atomic ‘ridges’ and ‘troughs’ of this surface [2]. However, the first full quantitative experimental structural analysis using scanned-energy mode photoelectron diffraction (PhD) concluded that the adsorption geometry is quite different, with the adsorbate molecular axis aligned instead in the [001] azimuth; this azimuthal orientation was
confirmed by near-edge X-ray absorption fine structure [5]. This PhD study determined the local adsorption site of the CN to be above second layer Ni atoms such that both the C and N atoms are approximately threefold Ni coordinated, and concluded that a surprisingly large (14.8 ± 9.6%) expansion of the outermost Ni layer occurs as a result of the adsorption. This may be compared with a contraction of this layer spacing on the clean surface of approximately 8%.

One feature of the Ni(1 1 0)c(2 × 2)–CN phase which was remarked upon in the early characterisation work was the relatively intense appearance of the fractional order low energy electron diffraction (LEED) beams which, in view of the relatively weak scattering cross-sections of the C and N atoms of the adsorbate, might imply that the CN induces some form of c(2 × 2) reconstruction of the Ni(1 1 0) surface. The PhD investigation of this surface found no evidence for such a reconstruction, but the technique is primarily sensitive to the location of the nearest neighbour substrate atoms relative to the C and N photoelectron emitters; this is reflected in the low precision of the outermost layer expansion found in this study. More recently medium energy ion scattering (MEIS), using 100 keV H+ ions, has been applied to this surface [6]. This technique is somewhat complementary to PhD in being primarily sensitive to the relative locations of the more strongly scattering Ni atoms and only weakly influenced by the C and N adsorbate atoms. The main conclusion of the MEIS investigation was confirmation of the large outermost Ni layer spacing expansion, specifically finding an even larger (but formally consistent) value of 21.2 ± 1.6%. Of course, the quantitative LEED technique (in which diffracted beam intensity–energy (I–E) spectra are compared with the results of multiple scattering calculations for different model structures) is also very sensitive to substrate reconstruction. Indeed, in view of the fact that it was a qualitative evaluation of the LEED patterns which led to the suggestion that there may be a CN-induced reconstruction of this surface, quantitative LEED seems ideally suited to provide a final resolution of this question.

We present here the results of such a quantitative LEED investigation of the Ni(1 1 0)c(2 × 2)–CN surface. An important conclusion is that we find no evidence of any substantial adsorbate-induced substrate reconstruction. The results also provide independent confirmation of the CN adsorption geometry and of the existence of a significant outermost Ni layer expansion in excellent agreement with the results of the earlier PhD study.

2. Experimental and computational details

The experiments were performed using a standard ultra high vacuum (UHV) chamber equipped with the usual range of facilities for sample preparation and surface characterisation together with a computer controlled LEED optic. The base pressure of the chamber was typically (1–2) × 10−10 Torr. A Ni(1 1 0) crystal disc approximately 12 mm diameter by 2 mm thickness from a single crystal boule was initially prepared by X-ray Laue alignment (to within approximately 0.5°), spark erosion and mechanical polishing prior to being placed in the UHV surface science chamber. The crystal was cleaned in situ by repeated cycles of bombardment with 1 keV Ar+ ions and subsequent annealing to 650 °C until a clean and well-ordered surface was obtained as judged by X-ray photoelectron spectroscopy and qualitative LEED. The Ni(1 1 0)c(2 × 2)–CN surface was prepared using similar procedures to those of the earlier investigations of this phase, exposing the clean Ni(1 1 0)-(1 × 1) surface at a temperature of 298 K to C2N2 gas generated by heating an evacuated glass ampoule of AgCN to 593 K, after which the sample was briefly annealed to around 450 K. This procedure resulted in the appearance of a sharp c(2 × 2) LEED pattern. The structure in the LEED I–E spectra appeared insensitive to annealing conditions in the temperature range 360–600 K or more, but there were some changes in the background intensity.

LEED diffracted beam intensities were measured using incident electron beam energies in the range approximately 50–350 eV at room temperature, using an Omicron video-LEED system at nominal normal incidence. Careful checks, comparing the I–E spectra of symmetry-equivalent
diffracted beams, were undertaken to ensure that a
graph was extremely close to normal incidence was
achieved. \(I - E\) spectra were collected for both the
the clean \(\text{Ni}(1\ 1\ 0)(1\times 1)\) surface and for the \(c(2\times 2) -
\text{CN}\) surface phase. For the clean surface nine in-
tegral order beams were measured over a total
energy range of 2836 eV. In the case of the
\(c(2\times 2) - \text{CN}\) surface, eight integral order and five
fractional order beams with a total energy range of
3100 eV were measured. In both cases these were
used in the subsequent structure analysis.

The structure determination was effected by the
usual approach in LEED of simulating the dif-
fracted beam \(I - E\) spectra for a range of model
structures, comparing these with the experimental
data with the aid of the Pendry \(R\)-factor (reliability
factor) \(R_P\) [7]. The LEED calculations were per-
fomed using the Barbieri/Van Hove Symmetrized
Automated Tensor LEED computer codes with
their associated programs to calculate the muffin-
tin potential and scattering phase shifts [8,9]. In
particular, a self-consistent Dirac–Fock approach
was used in order to compute the self-consistent
atomic orbitals for each element. The muffin-tin
potential was then computed following Mattheis’
prescription and a set of 11 relativistic phase shifts
\(l_{\text{max}} = 10\) were evaluated by numerical integra-
tion of the Dirac equation. In all of the models
tested, the surface atoms were allowed to fully
relax under the provision that they maintain the
symmetry of each structural model. Notice that
because the point group symmetry of all the ad-
sorbate structures considered is lower than that of
the substrate, averaging of diffracted beams related
by the substrate point group operations was nec-
essary to simulate the effects of domain averaging
in the experiment. The real part of the inner
potential was simultaneously optimised with the
structural parameters. For the best structural
model, the Debye temperatures of the CN mole-
cule \((\Theta_{\text{CN}})\) and of the first Ni layer atoms \((\Theta_{\text{Ni}})\)
were optimised by running calculations on a grid
of values. For each value of \(\Theta_{\text{CN}}\) and \(\Theta_{\text{Ni}}\), a full
optimisation of the atomic coordinates was carried
out. All the calculations were performed on a
Pentium III 600 MHz, running Linux.

3. Results

In order to provide a reference check on the
experimental data, the computations, and some of
the non-structural parameters, an analysis was first
conducted on the \(\text{Ni}(1\ 1\ 0)\) clean surface measure-
ments. In this case the only structural parameters
are the outermost few interlayer spacings, and
specifically those of the first-to-second and second-
to-third Ni surface layers, \(z_{12}\) and \(z_{23}\). The open-
packed fcc \((1\ 1\ 0)\) surface generally show quite a
large contraction (of order 10%) of the outermost
layer spacing relative to the bulk value, while
careful investigations reveal a small expansion of
the second layer spacing. Our present analysis
yielded proportional layer spacing changes of
\(-8.0 \pm 1.6\%\) for \(z_{12}\) and \(+3.6 \pm 1.6\%\) for \(z_{23}\), in
excellent agreement with previous determinations
of these parameters (see Table 1). A similar opti-
misation of the third-to-fourth layer spacing, \(z_{34},

Table 1
Comparison of outermost layer spacing changes at the clean \(\text{Ni}(1\ 1\ 0)\) surface, relative to those of an ideally terminated bulk crystal, determined in this and previous studies

<table>
<thead>
<tr>
<th>Reference</th>
<th>Method</th>
<th>Year</th>
<th>(\Delta z_{12}) (%)</th>
<th>(\Delta z_{23}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>van der Veen [16]</td>
<td>MEIS</td>
<td>1979</td>
<td>(-4.0 \pm 0.8)</td>
<td>Bulk assumed</td>
</tr>
<tr>
<td>Feidenhansl [17]</td>
<td>MEIS</td>
<td>1983</td>
<td>(-5.2 \pm 1.6)</td>
<td>(+2.0 \pm 1.6)</td>
</tr>
<tr>
<td>Gauthier [18]</td>
<td>LEED</td>
<td>1984</td>
<td>(-8.4 \pm 0.8)</td>
<td>(+3.1 \pm 1.0)</td>
</tr>
<tr>
<td>Tornqvist [19]</td>
<td>MEIS</td>
<td>1984</td>
<td>(-4.1 \pm 0.8)</td>
<td>Bulk assumed</td>
</tr>
<tr>
<td>Xu [20]</td>
<td>LEED</td>
<td>1985</td>
<td>(-9.8 \pm 1.9)</td>
<td>(+3.8 \pm 1.6)</td>
</tr>
<tr>
<td>Adams [21]</td>
<td>LEED</td>
<td>1985</td>
<td>(-8.6 \pm 0.5)</td>
<td>(+3.1 \pm 0.6)</td>
</tr>
<tr>
<td>Yalisove [22]</td>
<td>MEIS</td>
<td>1986</td>
<td>(-9.0 \pm 1.0)</td>
<td>(+3.5 \pm 1.4)</td>
</tr>
<tr>
<td>Reiner [23]</td>
<td>LEED</td>
<td>1987</td>
<td>(-8.4 \pm 1.6)</td>
<td>(+3.6 \pm 1.6)</td>
</tr>
<tr>
<td>Brown [6]</td>
<td>MEIS</td>
<td>2001</td>
<td>(-4.5 \pm 1.6)</td>
<td>(+1.1 \pm 1.6)</td>
</tr>
<tr>
<td>This work</td>
<td>LEED</td>
<td>Current</td>
<td>(-8.0 \pm 1.6)</td>
<td>(+3.6 \pm 1.6)</td>
</tr>
</tbody>
</table>
yielded a value indistinguishable from that of the bulk. The optimal value of $R_p$ was 0.18, which represents a very good fit as may be seen in Fig. 1. The bulk Debye temperature was taken to be 350 K and the values of this vibrational parameter for the outermost and second layers were optimised at 240 and 260 K respectively.

In the case of the c(2×2)–CN surface, a significant number of different structural models were tested. For an unreconstructed Ni(110) surface the structures investigated are summarised in Fig. 2. The two principle local geometries are those which were favoured by the earlier experimental PhD investigation [5] and the cluster calculation [2]; in both cases these involved the C–N axis ‘lying down’ (but not necessarily exactly parallel to the surface) in the atomic troughs above second layer Ni atoms. In the PhD study the preferred site was approximately atop a second layer Ni atom with the molecular axis in a ⟨100⟩ azimuth, whereas the earlier cluster calculation favoured a bridging site relative to the second Ni atomic layer with the molecular axis aligned in a ⟨110⟩ azimuth. In addition, adsorption geometries involving end-on adsorption of the CN species in some of the main high-symmetry sites were checked. For each site

![Fig. 1. Comparison of experimental (---) and theoretical (--–) best-fit LEED I–E spectra from clean Ni(110).](image)

![Fig. 2. Schematic plan view of a Ni(110) surface showing the different adsorption geometries explored on an unreconstructed substrate. The C atoms are shown most darkly shaded while the N atoms are unshaded. The C atom is shown larger to allow both atoms to be seen in the standing-up adsorption models.](image)
the influence of different spacings to the substrate of the C and N atoms, and (for the lying-down models) their exact positions parallel to the surface, were explored. These initial searches showed that the local adsorption site involving the CN species above a second layer Ni atom with the C–N axis aligned along a \langle 100 \rangle azimuth ('\langle 100 \rangle trough' of Fig. 1), the local geometry favoured in the earlier PhD investigation, yielded much the lowest \( R \)-factor. The value obtained for this site in this initial search and optimisation was 0.32, while all the other local sites yielded values of 0.60 or greater, well outside the variance defined by the best-fit geometry. This preferred model is shown in Fig. 3. Notice that the fact that the C–N lies down in the surface means that the point group symmetry of this surface phase is significantly less than that (2 \( m \)) of the clean surface, removing both the twofold rotational symmetry and the mirror plane in the \langle 110 \rangle azimuth. This means that quite a number of distortions of the Ni(110) surface layers must be considered, including not only alternate displacements perpendicular to the surface ('rumpling') of even-numbered Ni layers, but also movements parallel to the surface in the \langle 100 \rangle direction for odd-numbered layers and in both azimuths for atoms in even-numbered layers. We will return to the question of the optimised magnitude of these displacements shortly.

In addition to the unreconstructed surface models of Figs. 2 and 3, however, several possible Ni surface reconstruction models which are consistent with the c(2 × 2) translational symmetry were tested. In particular, these included a model in which alternate outermost Ni layer atoms were missing, another in which alternate surface layer Ni atoms in the close-packed \langle 110 \rangle rows were displaced parallel to the surface perpendicular to these rows to produce zigzag Ni atom chains (Fig. 4) and a third model in which alternate Ni atoms in the outermost layers are displaced perpendicular to the surface (rumpled). An important feature of all of these models is that they lower the symmetry of the surface even further in that they remove the mirror plane in the \langle 100 \rangle azimuth, the only remaining point group symmetry operation of the original clean surface. This means that a large number of additional displacement parameters (such as the C and N coordinates relative to the \langle 110 \rangle azimuth—evidently relevant in the model of Fig. 4) must be optimised. All geometries

Fig. 3. Schematic plan view of the Ni(110)c(2 × 2)–CN surface with CN adsorbed in the best-fit \langle 100 \rangle trough sites geometry on an unreconstructed substrate.

Fig. 4. Schematic plan view of one possible reconstruction model of the Ni(110)c(2 × 2)–CN surface involving alternate \langle 100 \rangle displacements of the outermost Ni atoms to produce zigzag chains. Notice that this removes the mirror symmetry planes in the \langle 100 \rangle azimuth which are present in the unreconstructed model of Fig. 3.
based on the missing Ni atom reconstruction model also gave large $R$-factor values of 0.6 or more. In this initial search, the addition of surface Ni layer rumpling or zigzag distortions did lead to a small decrease in the $R$-factor to 0.28. However, the size of the displacements associated with these structural distortions was very small (typically 0.05 Å) whilst the number of structural fitting parameters associated with these models is significantly increased. Under these circumstances it is important to apply further tests to establish the significance of this improvement in the fits to the experimental data. Such a test is that devised by Hamilton [10] for conventional X-ray diffraction and recently adapted for use in LEED [11,12]. This is ultimately an empirical criterion which considers the magnitude of the improvement in the $R$-factor relative to the amount of information contained in the experimental data (determined by the total energy range of the $I$–$E$ LEED spectra used and the intrinsic width of peaks in such spectra (the measure used to establish the variance of the Pendry $R$-factor) and the size of the increase in the number of structural parameters. The Hamilton ratio ($H$) between the unreconstructed (10 fitting parameters and $R_p = 0.32$) and the reconstructed surface solutions (25 fitting parameters and $R_p = 0.28$) models was found to be $H = 2.6$. In ideal statistical conditions, the Hamilton ratio $H$ should exceed 3 to indicate real improvements, while values below 1 indicate merely a better fit. However, these numbers 1 and 3 also assume knowledge of the number of independent experimental data points, which in LEED is ill-defined; strictly this means that the applicable ratio scale applicable to LEED is formally uncertain. Nonetheless, the limited experience of applying this test in LEED [11,12] suggests that the value 3 is a good criterion in LEED as well, if each peak in the $I$–$E$ spectra is counted as a data point. Therefore, according to this test, the (very slightly) reconstructed surface models are not significantly better than the unreconstructed model.

Following this first stage of structural optimisation, however, a second stage of optimisation of the non-structural parameters, notably the scattering phase shifts (which were recalculated for the optimised structural models), the Debye temperatures $\theta_{\text{CN}}$ and $\theta_{\text{Ni}}$, and the real and imaginary parts of the inner potential, was conducted. The optimised values of $\theta_{\text{CN}}$ and $\theta_{\text{Ni}}$ for the preferred structure (see below) were 325 and 225 K, respectively. Somewhat surprisingly the imaginary part of the potential, $V_\text{is}$ was found to have an optimum value of 7 eV, significantly larger than the 4–5 eV more typical of other studies of Ni surfaces. However, the dependence of the $R$-factor on this parameter was relatively weak, and we should note that the inelastic scattering mean-free-path varies only as the square root of $V_\text{is}$, so our optimum value is not too unreasonable and our structural results are not sensitive to this parameter. Most significant in this second stage of optimisation was the effect of recalculating the scattering phase shifts; the set used in the original stage of site identification were obtained from a structure model involving CN adsorbed in a standing-up geometry. In the second stage of optimisation phase shifts were calculated for the best-fit versions of each structural model to yield a procedure which is formally more self-consistent. This led to a lowest $R$-factor value for the unreconstructed surface of 0.26. The generally quite good agreement reflected in this value for a complex adsorption system is confirmed in the visual comparison of the experimental and theoretical $I$–$E$ spectra shown in Fig. 5. Using these optimised non-structural parameter values, the slightly reconstructed structural solutions found in the earlier stage actually led to increased $R$-factors of almost 0.30. The new value of the Hamilton ratio was $-2.1$, the minus sign arising because the $R$-factor for the model with the larger number of fitting parameters is higher than that for the model with a smaller number of parameters to adjust). It appears that the slightly lower $R$-factor obtained for the reconstruction model in the first stage of optimisation resulted from a fortuitous combination of the wrong phase shifts and the wrong model. Our final conclusion is therefore not only that the reconstruction model is not to be preferred on the basis of the Hamilton test, but actually leads to a slightly worse $R$-factor. It is also important to recognise that in this optimised reconstruction model the Ni atom movements which characterise the reconstruction are extremely small.
It is therefore very clear that we can formally exclude the idea that the Ni(1 1 0)c(2 x 2)–CN structure involves significant substrate reconstruction.

As one reason for believing that such a reconstruction might occur was the earlier perception that the fractional order diffracted beams were of relatively high intensity, it is clearly important to compare this quantity in the LEED experiments and theoretical calculations. In this regard it is important to note that in quantitative LEED it is common (although not universal—see, for example, Refs. [13–15]) practice to compare only the relative amplitudes of the intensity modulations of each diffracted beam, using what may be a different experiment/theory normalisation factor for each beam. Indeed, this is implicit in the Pendry R-factor, which compares logarithmic derivatives of the I–E spectra. However, inspection of the experimental and theoretical I–E spectra for different integral and fractional order diffracted beams using a common theory/experiment normalisation factor shows that these relative intensities are in good agreement. As an example, the I–E spectra for the (1 0) and (1/2 1/2) beams using a common scaling factor derived from all the beams used in the analysis are shown in Fig. 6. Clearly the relative average intensities of these integral and fractional order beams are well reproduced by the theoretical calculations.

As remarked earlier, because of the low point group symmetry of the Ni(1 1 0)c(2 x 2)–CN surface, a consequence of the fact that the CN species lies down on the surface and that the two ends of the linear molecule are inequivalent, there are quite a large number of structural parameters which must be optimised, and these include lateral distortions and (for some layers) rumpling in the outermost Ni substrate layers, so presentation of all the relevant structural parameters in a simple form is not possible. The complete set of atomic coordinates does, of course, provide this information, and these are given in Table 2, but the information content is not very transparent. In
order to understand the nature of the lateral distortions of the optimised structure Fig. 7 shows a plan view of the surface with the atoms drawn as filled circles sufficiently small to allow one to discern the relative displacements of successive Ni layers which, in an undistorted structure, would perfectly overlap. The 4th and 5th Ni layer atoms are not displaced from their bulk-terminated positions and thus provide a reference. Of course, many of these optimised distortions are extremely small, and thus not statistically significant. Most significant is the amplitude of the zigzag distortion of the second Ni layer (the difference between the alternate displacements in the y (along $\langle 100 \rangle$) direction which is $0.17 \text{ Å}$ with an estimated precision of $\pm 0.09 \text{ Å}$.

The more significant structural parameters which may be deduced from the coordinates of Table 2 are summarised in Table 3. In this table interlayer spacings are denoted by $z_{AB}$ where A and B are either the atomic element in the case of C or N or the layer number in the case of Ni atoms. For the Ni interlayer spacings these are average values in the case where one layer is rumpled, and the more significant rumplings on the $n$th layer are denoted by $\Delta z_n$. Interatomic distances are denoted by $d$ with similar suffix notation for that of the $z$ values. The angle of the C–N axis relative to the surface plane is $\phi_{CN}$. Also shown in this Table are some of the main parameters measured in the earlier PhD [5] experimental determination of the structure of this surface. The agreement between the two studies by quite different methods is clearly excellent in terms of the adsorption site, the CN geometry (including its tilt relative to the surface plane) and the rather significant outward relaxation of the outermost Ni layer induced by the CN adsorbate. The original PhD study found an expansion of $15 \pm 9\%$ and the current LEED result is $9 \pm 4\%$. On the other hand the MEIS investigation [6] of this parameter found a value of $21.2 \pm 1.6\%$, clearly well outside the value obtained by LEED. The origin of this significant discrepancy is unclear, although we note that the MEIS analysis did

Fig. 6. Comparison of experimental (-----) and theoretical (——) $I$–$E$ LEED spectra for the (1 0) and (1/2 1/2) beams for the best-fit (unreconstructed) model of the Ni(1 1 0)(2 × 2)–CN surface. These two beams are also shown in Fig. 5, but in the present figure the same experiment-theory intensity scaling factor has been applied to both beams using a value obtained from the average of all the beams studied. The absolute intensity scale is still arbitrary, but the relative intensities of the two panels are meaningful. Note the similarity of the average relative intensities of these integral and fractional order beams.
not consider the possibility of lateral distortions of the Ni layers which may also give rise to similar changes in the interatomic blocking directions which form the basis of the MEIS structure determination.

The one area of marginal discrepancy between the results of the LEED and PhD studies evidenced in Table 3 concerns the nearest-neighbour distances between the C and N adsorbate atoms and the near-neighbour Ni atoms. These are parameters which are typically obtained with particularly high precision in a PhD study which is sensitive to the local structure around the adsorbate atoms which provide the source of the outgoing electron wave, and such precision is especially good when the near-neighbour bonds are nearly perpendicular to the surface. The different precision of the two techniques to these parameters is reflected in the error estimates of Table 3. By contrast, of course, LEED is sensitive to subtle distortions of the Ni substrate even for atoms well removed from the adsorbed molecule, and PhD shows very little dependence on these parameters.

4. Conclusions

Overall, the present quantitative LEED study of the Ni(1 1 0)c(2 × 2)–CN surface phase leads to conclusions which are in excellent agreement with the earlier PhD study. While one might hope that this would be true as far as identifying the local
Table 3
Summary of the main structural parameters obtained for the Ni(110)(2 x 2)-CN surface phase derived from the coordinates of Table 2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>This work (LEED)</th>
<th>PhD study [5]</th>
</tr>
</thead>
<tbody>
<tr>
<td>z_{CN} (Å)</td>
<td>0.47 ± 0.07</td>
<td>0.48 ± 0.05</td>
</tr>
<tr>
<td>( \vartheta_{CN} ) (°)</td>
<td>23.7 ± 4.5</td>
<td>22.5 ± 3.0</td>
</tr>
<tr>
<td>d_{CN} (Å)</td>
<td>1.17 ± 0.08</td>
<td>1.25 ± 0.12</td>
</tr>
<tr>
<td>z_{C1} (Å)</td>
<td>0.74 ± 0.07</td>
<td>–</td>
</tr>
<tr>
<td>z_{C2} (Å)</td>
<td>2.10 ± 0.09</td>
<td>1.99 ± 0.02</td>
</tr>
<tr>
<td>d_{C1} (Å)</td>
<td>2.00 ± 0.07</td>
<td>1.93 ± 0.07</td>
</tr>
<tr>
<td>d_{C2} (Å)</td>
<td>2.11 ± 0.07</td>
<td>2.03 ± 0.02</td>
</tr>
<tr>
<td>d_{Ni} (Å)</td>
<td>2.01 ± 0.07</td>
<td>1.91 ± 0.07</td>
</tr>
<tr>
<td>z_{12} (Å)</td>
<td>1.36 ± 0.05</td>
<td>1.43 ± 0.12</td>
</tr>
<tr>
<td>( \Delta z_{2} ) (Å)</td>
<td>0.03 ± 0.05</td>
<td>–</td>
</tr>
<tr>
<td>( y_{2} ) (Å)</td>
<td>0.17 ± 0.09</td>
<td>–</td>
</tr>
<tr>
<td>z_{23} (Å)</td>
<td>1.23 ± 0.05</td>
<td>–</td>
</tr>
<tr>
<td>z_{34} (Å)</td>
<td>1.24 ± 0.06</td>
<td>–</td>
</tr>
<tr>
<td>z_{45} (Å)</td>
<td>1.24 ± 0.08</td>
<td>–</td>
</tr>
</tbody>
</table>

As described more fully in the text, \( z_{AB} \) are interlayer spacings, \( \Delta z \), and \( \Delta y \), are rumpling and zig-zag lateral distortion amplitudes and \( d \) are interatomic distances. \( \vartheta_{CN} \) is the angle of the C–N axis relative to the surface plane.

Adsortion site and molecular orientation, the quite different sensitivity of LEED and PhD to other structural parameters, and notably those associated with adsorbate-induced substrate distortions or reconstructions, means that one may not necessarily expect detailed agreement in the overall structural model. Specifically, it had been previously suggested on the basis of rather qualitative LEED observations that CN must induce a substantial reconstruction of the Ni surface not detected in the PhD investigation. The present study shows that this is not the case. Rather subtle (and in many cases marginally significant) distortions of the outermost Ni layers are seen in the best-fit LEED solution, but these do not involve any lowering of the translatinal or point group symmetry, nor do they involve any change in the atomic density of any of the Ni layers. As such, they would not normally be classified as 'reconstruction'. Moreover, the structure obtained in the LEED analysis is capable of reproducing the experimentally-observed relative intensities of the integral and fractional order LEED beams which formed the basis of the original suggestion that the surface is reconstructed.

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