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Surface extended-x-ray-absorption fine-structure study at the carbon K edge: The $p4g(2\times2)$-C/Ni(100) system

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The surface extended-x-ray-absorption fine structure (SEXAFS) has been studied at the carbon K edge for the $p4g(2\times2)$-C/Ni(100) adsorption system. The results are in good agreement with the fourfold hollow site proposed in a previous low-energy electron diffraction study. The successful measurement of carbon SEXAFS from adsorbed species opens up new possibilities in surface science.

Ordered atomic overlayers on the Ni(100) surface have recently provoked considerable interest because they promise to cast some light on the driving force for adsorbate-induced surface reconstructions.[1] Whereas the $c(2\times2)$ overlayers of sulfur and oxygen leave the nickel surface essentially undistorted,[2] carbon[3] and nitrogen[4] adsorption results in a reconstruction of the outermost layer of nickel atoms. The latter consists of coordinated lateral displacements (alternately clockwise and anticlockwise) of the four nickel atoms around the fourfold hollow site ("distortion"—see Fig. 1) as well as an increase in separation between first and second layers ("relaxation"). Onuferko, Woodruff, and Holland[3] concluded that only a structure of this nature could be responsible for the observation of systematic absences of diffracted beams in low-energy electron diffraction (LEED) from the $p(2\times2)$-C/Ni(100) system. They went on to show in a LEED beam intensity analysis that of the two possible high-symmetry adsorption sites (Fig. 1) only the fourfold hollow site was compatible with the experimental data. A more recent helium diffraction study also favors the fourfold hollow over the so-called "fourfold" bridge site.[5] Such carbidic layers on nickel surfaces are of interest for another reason: Nickel is an important catalyst for the steam reforming and methanation reactions. Even over a Ni(100) single crystal it has been shown that surface carbide forms the active phase in methanation.[6] Recent photoemission studies on $p4g(2\times2)$-Ci/Ni(100) (Refs. 7 and 8) have also been aimed at deriving a clearer insight into the structure and reactivity of this adsorption system. In the present Rapid Communication we report surface extended-x-ray-absorption fine-structure (SEXAFS) data which also clearly rule out adsorption in the fourfold bridge site (as well as underlayer formation) and are in quantitative agreement with the results of the LEED analysis for the fourfold hollow site.

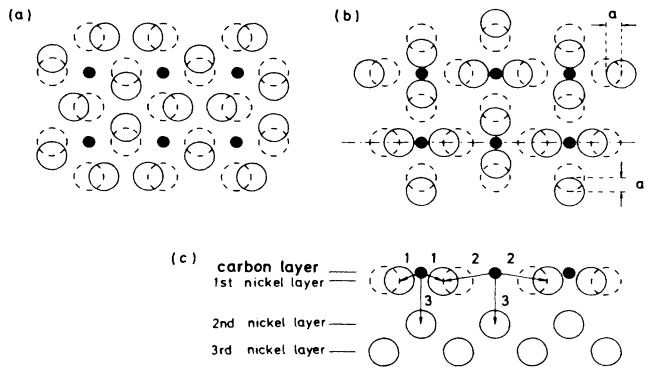

FIG. 1. The two proposed adsorption sites (Ref. 3) on the reconstructed Ni(100) surface induced by a carbon overlayer. The full circles represent the nickel atoms and the dashed circles the unreconstructed surface; (a) the small filled circles are carbon atoms in the fourfold hollow sites and (b) in the "fourfold" bridge site. The lateral movement a of the nickel atoms in the top layer represents the distortion. (c) shows a side view of the fourfold bridge model along the dashed-dotted line in (b). The vectors from the carbon to the nickel atoms represent the "short bridge" distance (1), the "long bridge" distance (2), and the distance to the nickel next-nearest neighbor in the second layer (3).

Electron yield SEXAFS measurements above the carbon K edge at $\sim$285 eV are experimentally difficult for several reasons. (1) There are normalization problems because of the structure due to carbon contamination in the monochromator transmission function. (2) The proximity of the nitrogen and oxygen K edges at $\sim$400 and $\sim$530 eV, respectively, means that only a limited SEXAFS range is available for adsorbates containing these atoms. (3) Using partial electron-yield detection, which has until now been the detection method of choice in the soft x-ray region,[9] the SEXAFS range is limited to about 200 eV, because at higher photon energies the C 1s electrons overcome the retarding voltage of a partial-yield detector. As a result, no carbon K-edge SEXAFS data have been published to date, although quite recently carbon SEXAFS has been observed for linear hydrocarbons adsorbed on Cu(100).[10] Our data presented here for the $p4g(2\times2)$-C/Ni(100) system show that with stable, dedicated electron storage rings like BESSY, normalization problems can be solved. The measurements still suffer, however, from the limited data range resulting in larger errors for the bond lengths obtained and underline the need of fluorescence detection in the soft x-ray region.[11]

The experiments were conducted at the Berlin electron storage ring BESSY with the plane grating grazing-incidence monochromator SX-700 (Ref. 12), using the 1200-1/mm grating. The data were taken in the partial

electron yield mode using a four-grid high-pass filter set to a retarding voltage of -210 V combined with a channel-plate multiplier as a detector. The spectra shown in Fig. 2 represent the ratio of the signals from the clean and covered surfaces. The x-ray incident angle on the sample could be varied from 60° ($\theta=30°$) to normal incidence $\theta=90°$, **E** vector parallel to the surface. The Ni(100) crystal was cleaned by Ar^+ bombardment and O_2/H_2 treatment as described by Paolucci, Rosei, Prince, and Bradshaw.[13] The carbidic overlayer was formed by thermal decomposition of ethylene during exposure of 40 L (where 1 L $=10^{-6}$ Torr sec) at a crystal temperature of $\sim$500 K and gave rise to a LEED pattern identical with that of Onuferko *et al.*[3]

SEXAFS spectra taken for polar angles $\theta=90°$ and 30° are shown in Fig. 2 together with the corresponding Fourier transforms. As no empirical C-Ni phase shifts are available, we determined bond lengths by taking the O-Ni phase shift $\Phi=-0.75k+7.70$ (Ref. 9) as an approximation. The bond lengths calculated from the dominant peaks in Fig. 2 and the corresponding amplitudes are listed in Table I. The large errors of ± 0.05 Å quoted for the bond lengths are only due to the limited SEXAFS range. The error introduced by using the O-Ni phase shift should be much smaller. Since the background fit was performed identically for the three angles measured, however, the relative errors are less than ± 0.02 Å. The increase in bond length observed on decreasing the polar angle θ is therefore real.

As is seen from Table I, experimental k-averaged amplitude ratios and r values are in excellent agreement with calculated values taken for a fourfold hollow site with the carbon atoms sitting 0.1 Å above the distorted and relaxed surface plane. Using the distortion from the LEED analysis ($a=0.35$ Å) a relaxation of 0.1 Å was found to be optimal as opposed to a value of 0.2 Å from LEED.[3] For polar angles of 55° and 30° the contributions of the fifth Ni atom located in the second layer below the adsorbed carbon has been taken into account (see Fig. 1). This C-Ni distance is 1.96 Å and cannot be resolved experimentally. For this reason the measured (average) r value increases for lower θ values. From our data we thus determine a carbon-nickel nearest-neighbor spacing of 1.82 ± 0.05 Å and a separation of 0.2 ± 0.2 Å between the adsorbed carbon layer and the unrelaxed surface in good agreement with the corresponding LEED values of 1.803 ± 0.015 and 0.3 ± 0.15 Å.[3]

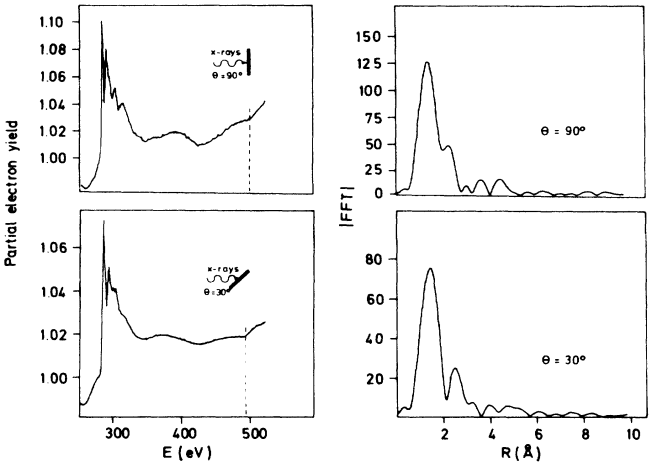

FIG. 2. Carbon K-edge SEXAFS spectra for $p4g(2\times 2)$-C/Ni(100) taken for normal ($\theta=90°$) and oblique ($\theta=30°$) incidence (left) and the corresponding Fourier transforms (right). At a photon energy of about 500 eV (dashed lines) the C 1s electrons overcome the retarding voltage (-210 V) of the partial-yield detector thus limiting the useful SEXAFS range.

So far we have only considered the fourfold hollow site. Are the SEXAFS data compatible with adsorption at the fourfold bridge site? If we assume 1.70 Å to be the shortest possible Ni-C bond length[15] we can calculate the polarization-dependent amplitude ratios for an unresolved peak in which the "short" and "long" bridge distances (see Fig. 1) and the distance to the Ni atom in the second layer overlap. Such calculated ratios do not agree with the experimental data for horizontal distortions greater than about $a=0.10$ Å as is seen from Table I. However, for low distortions $a\leq 0.2$ Å the calculated difference $r(30°)-r(90°)$ is in excess of the experimental value of 0.05 Å (cf. Table I). Using a value greater than 1.70 Å for the lower limit of the Ni-C bond length gives even worse agreement. Carbon adsorption in a fourfold bridge site is thus unambiguously ruled out. Simple arguments also show that underlayer formation—a third possibility briefly considered by Onuferko *et al.*[3]—is also not compa-

TABLE I. Measured and calculated bond lengths and amplitude ratios. The theoretical values were calculated for the fourfold hollow adsorption site (Ref. 3) for a relaxation of 0.1 Å and for carbon atoms adsorbed 0.1 Å above the surface. Because of the lack of experimental data for anisotropy in the surface mean free path and in the surface Debye-Waller factor for nickel, the values determined for copper (Ref. 14) have been used. The theoretical values for the fourfold bridge adsorption site (Ref. 3) were calculated for different distortions a (see text).

	Experiment		Theory					
			Fourfold hollow		Fourfold bridge			
					$a=0.1$ Å		$a=0.2$ Å	
θ (deg)	r (Å)	A/A_{90}	r (Å)	A/A_{90}	r (Å)	A/A_{90}	r (Å)	A/A_{90}
90	1.82 ± 0.05	1	1.82	1	1.79	1	1.85	1
55	1.85 ± 0.05	0.75 ± 0.16	1.84	0.80	1.83	0.83	1.91	0.91
30	1.87 ± 0.05	0.52 ± 0.07	1.89	0.54	1.95	0.61	2.02	0.80

tible with the SEXAFS data.

The weak second feature seen in all Fourier transforms creates a certain problem. It would correspond to a C-Ni spacing of 2.9 Å but cannot be explained in terms of any of the models described in Ref. 3. It is interesting to note that it has approximately the same polarization dependence as the main peak, indicating a C-Ni spacing parallel to the surface. Two explanations spring to mind. There is, first, the possibility that small areas of the surface are covered with a carbide phase where reconstruction occurs in a complicated (and unknown) way. This could not correspond to Ni_3C where the nearest-neighbor and next-nearest-neighbor Ni-C spacings are 1.88 and 3.25 Å, respectively.[16] Alternatively, the model proposed by Onuferko *et al.* could be incorrect and another type of reconstruction occurs, leaving the surface with $p4g$ space-group symmetry. Such a structure is, however, difficult to conceive and, on the basis of both the LEED analysis and the SEXAFS data, somewhat unlikely.

The data reported here are not only significant because of the good agreement with previous LEED work, they also open up the possibility of performing surface EXAFS at the carbon K edge on a large number of carbon-containing, in particular organic, molecules adsorbed on surfaces.

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