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Threefold-coordinated hollow adsorption site for $c(4\times2)$-NO/Ni(111): A surface-extended x-ray-absorption fine-structure study

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Surface-extended x-ray-absorption fine-structure studies on the $c(4\times2)$-NO/Ni(111) system yield a nearest-neighbor O-Ni distance of 2.68 ± 0.05 Å and show that NO adsorbs in threefold-coordinated hollow sites. This result casts doubt on the generally used method of absorption site determination via molecular vibrational frequencies, which for this system led to an assignment of a twofold bridge site.

The adsorption of nitric oxide on Ni(111) has been widely studied.[1-14] Below room temperature NO adsorbs molecularly on Ni(111) and forms a $c(4\times2)$ structure at a coverage of 0.5 monolayers (ML).[5] There is strong evidence[5,12,14] that the NO molecules in the $c(4\times2)$ layer are oriented perpendicular to the surface and this orientation has also been found to hold at lower coverages.[13,14]

Early electron-energy-loss spectroscopy[3] (EELS) and more recent reflection absorption infrared spectroscopy[9] (RAIRS) studies showed that the $c(4\times2)$ structure is correlated with the observation of a single NO stretching mode at 1580 cm^{-1}. By comparison with NO stretching frequencies for nitrosyl complexes containing NO bound to different numbers of metal atoms, this mode has been assigned to NO adsorbed on Ni(111) in an upright configuration at twofold bridge sites.[3,9]

The general applicability of the widely used method of adsorption site assignment via molecular vibrational frequencies has already been questioned for the system $c(4\times2)$-CO/Ni(111).[15] This result then stimulated structure determinations for NO adsorption on the same Ni(111) surface. A quite recent photoelectron diffraction (PED) experiment[14] has indicated a threefold hollow adsorption site for NO coverages between 0.1 and 0.5 ML. In this Rapid Communication we present the results of a surface-extended x-ray-absorption fine-structure (SEXAFS) study of $c(4\times2)$-NO/Ni(111). It is shown that NO adsorbs in a threefold hollow site in agreement with PED (Ref. 14) and again in conflict with the adsorption site assignment based on vibrational frequencies.[3,9]

The experiments were conducted at the electron storage ring BESSY in Berlin with the grazing-incidence plane grating monochromator SX-700 IV.[16] The SEXAFS data were taken above the oxygen K edge in the partial electron yield mode at normal ($\theta=90°$, E vector parallel to the surface) and near-grazing ($\theta=20°$) x-ray incidence. They were analyzed by the conventional Fourier-transform method and by a curve-fitting procedure.[17] In both cases the slightly modified empirical O-Ni phase shift of Ref. 18 was used. The Ni(111) crystal was cleaned by successive cycles of argon-ion bombardment, annealing at 650 K, and heating to 800 K. It was characterized by Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED). Nitric oxide

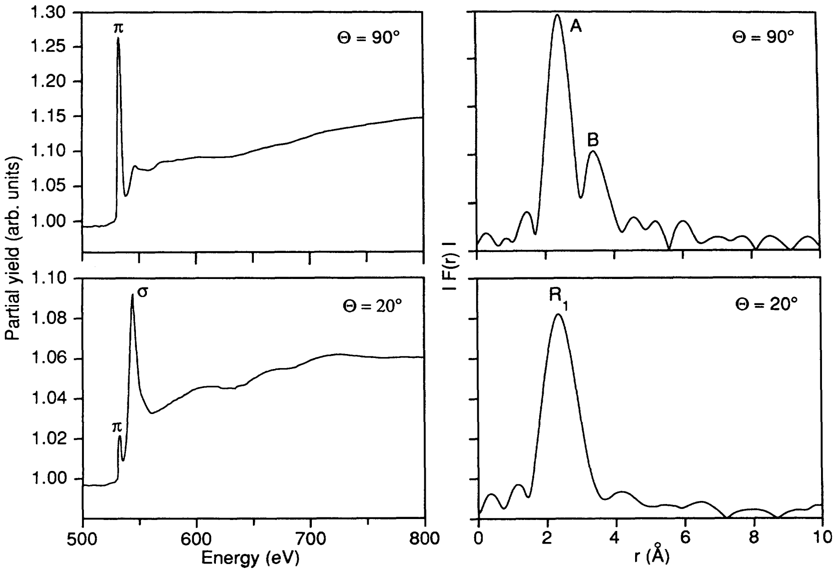

FIG. 1. Oxygen K-edge SEXAFS spectra (left) for $c(4\times2)$-NO/Ni(111) taken at normal ($\theta=90°$) and near-grazing ($\theta=20°$) x-ray incidence and their Fourier transforms (right).

exposures and SEXAFS measurements were performed at 120 K. A high-contrast $c(4\times2)$ LEED pattern was obtained after an NO exposure of about 4 L.

In Fig. 1 oxygen K-edge SEXAFS spectra for $c(4\times2)$-NO/Ni(111) (left-hand side) taken at $\theta=90°$ (above) and $\theta=20°$ (below) are shown together with their Fourier transforms (right-hand side). The near-edge region of the spectra is dominated by the π and σ resonances, which have maximum intensities at normal and grazing x-ray incidence, respectively. A careful π resonance intensity analysis yields an angle of $0\pm10°$ for the N-O axis orientation with respect to the surface normal in agreement with x-ray photoemission spectroscopy,[5] AES,[12] and recent near-edge x-ray-absorption spectroscopy[14] results. The Fourier transforms of the SEXAFS oscillations are dominated by a peak which after phase-shift correction yields an O-Ni distance of 2.68 ± 0.05 Å for $\theta=90°$ (peak A) and 2.67 ± 0.05 Å for $\theta=20°$. Peak B ($\theta=90°$) corresponds to an O-Ni distance of 3.7 Å. Due to the polarization dependence of the SEXAFS oscillations,

$$\chi^{(k)}=\sum_i \frac{N_i^*}{kR_i^2}F_i(k)e^{-2R_i/\lambda}\exp(-2\sigma_i^2k^2) \times\sin[2kR_i+\psi_i(k)]\,, \qquad (1)$$

$$N_i^*=3\sum_{i=1}^{j}\cos^2\alpha_{ij},\ \ \alpha_{ij}=\measuredangle(\mathbf{E},\mathbf{r}_{ij})\,,$$

where N_i^* is the effective coordination number of the ith shell, and α_{ij} is the angle between the $\mathbf{E}$ vector at the absorbing atom site and the vector $\mathbf{r}_{ij}$ from the absorbing atom to the jth atom in the ith shell, and due to the geometry of the Ni(111) surface the measured distance for $\theta=20°$ must correspond to the nearest-neighbor (NN) O-Ni distance (R_1). The assignment of the peaks in the Fourier transform for $\theta=90°$ depends, however, on the type of the NO adsorption site. We consider three different high-symmetry sites: on-top, twofold-coordinated bridge, and threefold-coordinated hollow sites. For on-top adsorption the NN O-Ni distance should not be observed with $\theta=90°$ in conflict with experiment.

We are therefore left with bridge and hollow sites. For the latter site, peaks A and B would correspond to the NN and next-NN (NNN) O-Ni distance, respectively, whereas for a bridge site due to limited resolution the NN and NNN O-Ni distances would overlap and create peak A, so that peak B then would correspond to the third-nearest-neighbor O-Ni distance.

To distinguish between bridge and hollow adsorption sites we simulated our spectra according to Eq. (1). Backscattering amplitudes $F_i(k)$ were taken from McKale *et al*;[19] the mean free path was set at $\lambda=5$ Å,[20] and the Debye-Waller-like term properly adjusted. In Fig. 2 a characteristic simulation for a bridge site (solid line) is compared with experiment (dashed line). From the corresponding Fourier transforms (Fig. 2, middle) it is seen that due to the overlap of the NN and NNN O-Ni distances, the resulting peak A in the simulation is much broader than the experimental one. Also, peak B is not reproduced at the correct position. No reasonable fit of the χ function (Fig. 2 left) is thus possible. The single-shell analysis shown in the right panel of Fig. 2 depicts the relative contributions of the NN (curve 1), NNN (curve 2), and third-nearest-neighbor (curve 3) O-Ni distances to the overall simulation. Changing these does not improve the fit. A good fit of the experimental data is obtained, however, by a simulation assuming a threefold hollow adsorption site. This is shown in Fig. 3. Peaks A and B now correspond to the NN and NNN distances and they are well reproduced.

So far we concentrated on the $\theta=90°$ data which provide clear evidence for NO adsorption in hollow sites. This assignment is strongly supported by comparing the measured distances for $\theta=90°$ and 20°. For a bridge site the overlapping NN and NNN contributions to peak A ($\theta=90°$) and the vanishing NNN contribution of $\theta=20°$ would lead to peak A being shifted by approximately 0.2 Å relative to peak R_1 which is not observed. Finally, the measured NN O-Ni distance of 2.68 Å implies a NN N-Ni bond length of 1.82 Å if we assume a hollow site and an N-O bond length of 1.15 Å. For a bridge site a NN N-Ni bond length of 1.60 Å is calculated which seems to

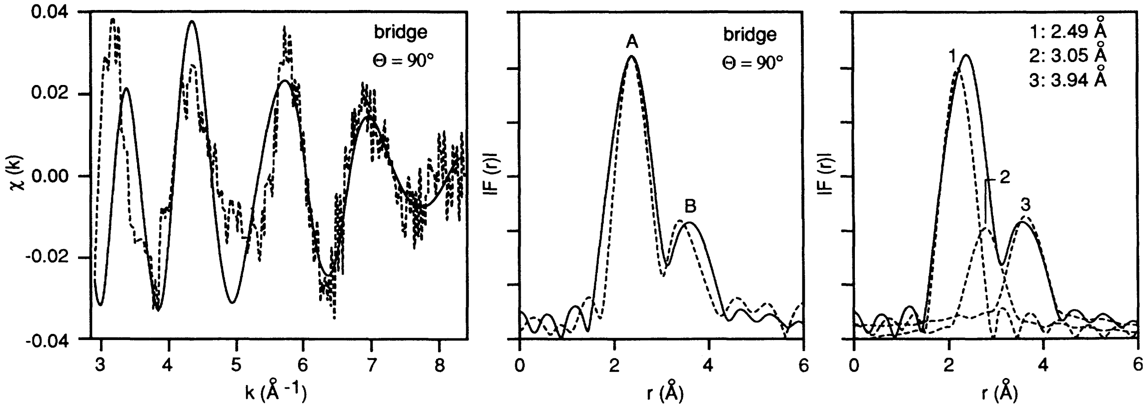

FIG. 2. Left and middle figures: SEXAFS simulation (solid line) for $\theta=90°$ assuming a bridge site compared with experiment (dashed line) and their Fourier transforms. Right figure: Single-shell contributions R_1, R_2, and R_3 (dashed line) to the overall simulation (solid line).

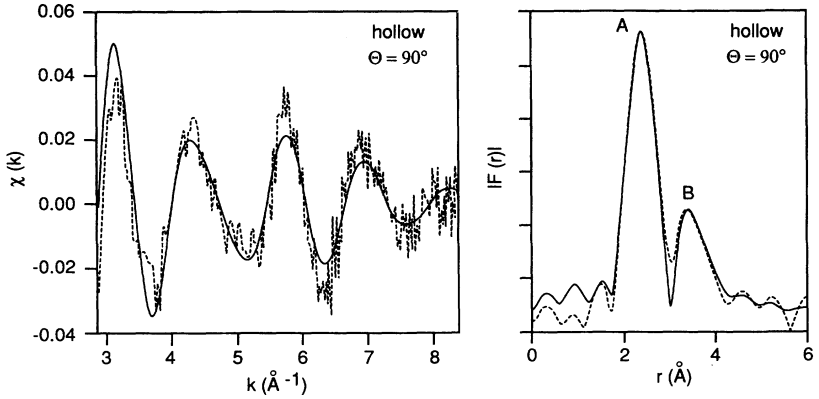

FIG. 3. SEXAFS simulation (left figure, solid line) for $\theta = 90°$ assuming a threefold hollow site compared with experiment (left figure, dashed line) and their Fourier transforms (right figure).

be too low. In summary, our SEXAFS data clearly rule out NO adsorption in bridge sites and suggest hollow site adsorption for the majority phase in complete agreement with the PED (Ref. 14) result.

Assuming a threefold-coordinated hollow site, there are two possible arrangements of NO molecules in a $c(4\times2)$ structure on Ni(111) with a coverage of 0.5 ML. These are depicted in Figs. 4(a) and 4(b) together with the widely known model involving twofold bridge sites [Fig. 4(c)]. In model 4(b) NO molecules are either in fcc hollow or in hcp hollow sites at a separation of 2.49 Å, whereas in model 4(a) fcc and hcp sites are mixed and the intermolecular distance measures 2.88 Å. In both models the NO-NO separation is substantially shorter than the corresponding value of 3.29 Å for the bridge model 4(c) which must result in increased lateral interactions within the adsorbed NO layer. These indeed have been indicated by the two-dimensional band dispersion observed with angle-resolved ultraviolet photoemission spectroscopy.[12] A distinction between models 4(a) and 4(b) is not possible from our SEXAFS data. More information is obtained, however, by a careful inspection of the observed LEED patterns. In Fig. 5 a calculated normal incidence LEED pattern for model 4(a) is depicted using kinematic theory (solid circles). Beams which are excluded in single scattering and which result only from multiple scattering are also marked (open circles). The observed LEED patterns are consistent with the predictions for model 4(a). Calculations for models 4(b) and 4(c) show that due to glide symmetry beams $\frac{1}{2}\,\frac{1}{2}$, $\frac{1}{2}\,0$, $0\,\overline{\tfrac{1}{2}}$, $\overline{\tfrac{1}{2}}\,\overline{\tfrac{1}{2}}$, $\overline{\tfrac{1}{2}}\,0$, and $0\,\frac{1}{2}$ are missing for normal incidence in contrast with experiment. The observed LEED patterns thus clearly favor model 4(a).

So far we have concentrated on the $c(4\times2)$-NO/Ni(111) system characterized by an NO coverage of 0.5 ML. To understand fully the adsorption site assignment suggested by vibrational spectroscopy we have to recall the coverage-dependent results. For small NO exposures an NO stretching frequency at 1475 cm^{-1} (1460 cm^{-1}) appears in the RAIRS spectra[9] which for higher coverages shift to 1513 cm^{-1}. As the exposure increases further another band grows in at 1543 cm^{-1} which finally shifts to 1585 cm^{-1} ($\theta = 0.5$). From a comparison of the measured NO stretching frequencies (1475 cm^{-1}, 1543 cm^{-1}) with those for nitrosyl complexes (Ref. 21 and references therein) a bridge site has been proposed with bent (1475–1513 cm^{-1}) and upright standing (1543–1585 cm^{-1}) NO molecules.[3,9] We doubt, however, that an unambiguous assignment is possible in view of the rather limited number of measured NO stretching frequencies for nitrosyls containing NO bound to three metal atoms. In a later vibrational line-shape study[10] it has

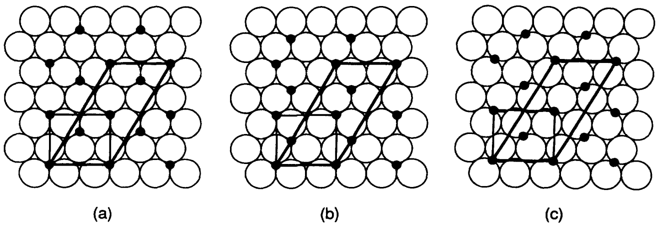
(a) (b) (c)

FIG. 4. Models for $c(4\times2)$-NO/Ni(111) corresponding to a coverage of 0.5 ML. NO molecules (solid circles) are (a) inequivalent (fcc and hcp) hollow sites (NO-NO, 2.88 Å), (b) either fcc hollow or hcp hollow sites (NO-NO, 2.49 Å), and (c) inequivalent bridge sites (NO-NO, 3.29 Å).

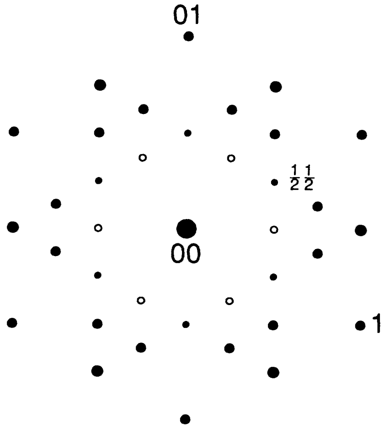

FIG. 5. Calculated LEED pattern for Fig. 4(a) using kinematic theory (solid circles). Beams which are excluded in single scattering and which result only from multiple scattering are marked by open circles.

been shown that it costs very little energy to shift NO molecules continuously between twofold-coordinated bridge and threefold-coordinated hollow sites. Consequently, it has been concluded that at lower coverages NO molecules possibly occupy hollow sites or intermediate sites between bridge and hollow. The PED study[14] finally indicates that the two frequency bands belong to the same hollow adsorption site. In that study the two bands have been explained in terms of dipole-dipole interactions (cf. Refs. 3, 9, 10 , 22, and 23) in the overlayer rather than due to different binding configurations.[3,9,10]

In summary, our SEXAFS study on $c(4\times2)$-NO/Ni(111) has shown that NO molecules occupy threefold-coordinated hollow sites. This result demonstrates that at least for this system an adsorption site assignment based on vibrational frequencies is in error.

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