Determination of Local Atomic Arrangements at Surfaces from Near-Edge X-Ray-Absorption Fine-Structure Studies: O on Ni(100)

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Near-edge x-ray-absorption fine-structure (NEXAFS) spectra for oxygen adsorption on Ni(100) are found to exhibit pronounced variations with oxygen exposure and x-ray incidence angle. The measured spectra are compared to calculations of the NEXAFS with use of a multiple-scattering formalism. The theory shows considerable sensitivity to changes in the O-Ni coordination and x-ray incidence angle. By comparison of experimental and theoretical spectra NEXAFS is shown to be a new technique for determining the local structure of adsorbates on surfaces.

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X-ray-absorption spectroscopy, in the form of surface extended x-ray-absorption fine-structure (SEXAFS) measurements, has been successfully applied in recent years to determine the structure of adsorbates on surfaces.[1] The weak scattering and short mean free path of the photoelectrons in the EXAFS regime (> 50 eV above the absorption edge) allow an analysis of the data by a single-scattering theory and the derivation of structural parameters via Fourier-transform techniques. The region close to the absorption edge (< 50 eV) is usually ignored in the EXAFS analysis because the strong scattering and longer mean free path of the excited photoelectron give rise to sizable multiple-scattering corrections.[2] It is this region, however, which exhibits the largest modulations of the atomic absorption coefficient and which is therefore most easily recorded experimentally. Previous theoretical efforts to interpret the near-edge x-ray-absorption fine structure (NEXAFS), otherwise referred to as XANES (x-ray-absorption near-edge structure), have dealt with gas-phase molecules,[3] molecular complexes,[4-6] and crystalline[7] and amorphous[8] solids. Here we discuss the first experimental and theoretical NEXAFS study of a chemisorption complex.

In particular, we investigate the case of a periodic atomic adsorbate layer on a single-crystal surface. As our model system we chose O on Ni(100) since it is well established that with increasing O coverage different chemisorption geometries are produced.[9] Another reason for the choice of this system is the existence of a controversy over the structure of the $p(2\times2)$ and $c(2\times2)$ phases.[10] We show that the experimental NEXAFS spectra provide a sensitive fingerprint of structural changes on the surface with oxygen coverage, in particular when recorded for different orientations of the x-ray electric field vector $\vec{E}$ with respect to the surface. We also present a full multiple-scattering NEXAFS calculation which demonstrates for the first time that such an approach can yield sufficiently good agreement with experimental data to distinguish between different possible surface structures. Model calculations show the inclusion of full multiple scattering to be essential, although fortuitously good agreement may be achieved with incompletely converging single-scattering calculations.

Experiments were performed on the grasshopper monochromator on beam line I at the Stanford Synchrotron Radiation Laboratory. The experimental arrangement and sample preparation procedures have been discussed in detail before.[11] NEXAFS spectra were recorded by monitoring the O *KVV* Auger intensity (510 eV) as a function of photon energy near the O *K* edge (~ 530 eV) at grazing ($\vec{E}$ along surface normal) and normal ($\vec{E}$ in surface plane) x-ray incidence with respect to the surface.

Experimental NEXAFS spectra above the O *K* edge for the progressive oxidation of Ni(100) are shown in Fig. 1. Spectra recorded at exposures of 1.5, 10, 20, and 40 L [1 L (langmuir) = 10^{-6} Torr sec] were found to be identical within statistics and to exhibit a pronounced dependence on angle of incidence. The $p(2\times2)$ LEED pattern exhibited maximum contrast around 1.5 L exposure. The $c(2\times2)$ pattern was first visible around 5 L and became clearest around 20–30 L. The NEXAFS features change above 50 L as a result of oxide formation as seen in Fig. 1 for the spectra recorded at 80 L. At 160 L exposure the angular dependence has almost vanished. For 280 L (not shown) the NEXAFS spectrum looks identical to that in Fig. 1(h). It has become completely isotropic and is identical to that for face-centered-cubic bulk NiO. Since the edge fine structure is more easily recorded (collection time ~ 15 min) than a complete SEXAFS spectrum (collection time > 2 h), Fig. 1 represents a nice example of how an unknown system can be characterized first by NEXAFS before addressing certain structural issues by SEXAFS. In the following we shall show that the NEXAFS spectrum itself can yield detailed structural information when compared to an appropriate multiple scattering calculation.

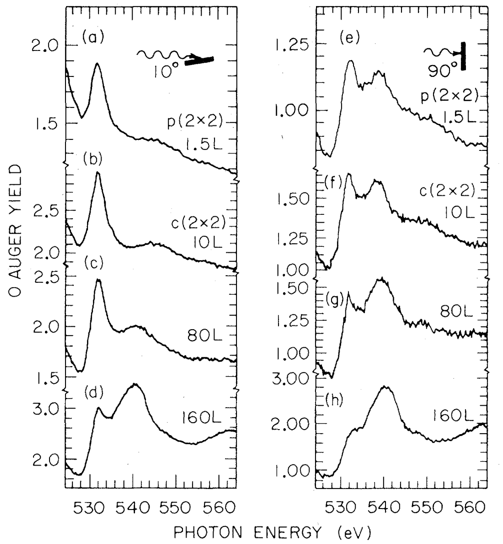

FIG. 1. NEXAFS spectra around the O *K* edge for increasing oxygen coverage on Ni(100) and two different x-ray incidence angles θ. For $\theta = 10°$ the $\vec{E}$ vector makes an angle of 10° with the surface normal and it lies in the surface plane for $\theta = 90°$. Note that the strong polarization dependence vanishes at high coverage as a result of cubic NiO formation.

The NEXAFS calculations were performed with use of the computational scheme described in detail elsewhere.[12] Full multiple scattering is included and the scheme is based on a cluster method. The calculation proceeds by first dividing the cluster into shells of atoms around a central (absorbing) atom. The scattering properties of each shell are described by a set of scattering phase shifts and the multiple-scattering equations are solved consecutively within each shell. The final step is the calculation of multiple scattering between shells and the assembly of the whole cluster. The size of the scattering matrices is reduced by the use of any symmetries (mirror or rotational) of the cluster. Only those components of the angular momentum expansion are used which can be coupled by a Hamiltonian possessing those symmetry elements. When combined with an atomic matrix element linking the core and excited electron states, the reflection matrix so obtained gives the NEXAFS cross section exactly in one-electron theory. Many-body processes which limit the lifetime of the core hole and photoelectron are included as a complex (absorptive) potential whose effect is to broaden spectral features on the appropriate scale.

For the O/Ni(100) system the phase shifts and matrix elements were calculated from one-electron muffin-tin potentials, constructed according to the Mattheiss prescription[13] for bulk Ni and for the O atoms in a specific surface arrangement. The Fermi level was calculated from this potential relative to the muffin-tin zero and all the theoretical densities of states have been convolved with the Fermi function at room temperature to produce the presented curves. All of the calculations were performed with a constant imaginary part of the energy of 0.7 eV, thus broadening features by this amount. This is smaller than the experimental resolution (~ 2.5 eV). The computational codes contain the facility for use of an energy-dependent broadening so that a mean free path may be mimicked; but we have not done so here as the exact form of variation of the mean free path with energy is not known for any particular system, and we were anxious to perform calculations with no variable parameter. The NEXAFS calculations included around 30 atoms to a distance > 5.0 Å from the central O atom and were fully tested for convergence in the number of scattering atoms and in angular momentum components.

In Fig. 2 we compare the experimental data for a $c(2\times2)$ O overlayer on Ni(100) with our NEXAFS calculation assuming different chemisorption sites.[14] The O-Ni nearest-neighbor (NN) distance was fixed to 1.98 Å for all but the fourfold hollow site with an adsorbate-substrate layer spacing of $d_\perp = 0.2$ Å. This latter $d_\perp$ value demands a reduced NN distance of 1.78 Å if the surface Ni layer remains unreconstructed as found by medium-energy ion scattering.[15] For the hollow site with $d_\perp = 0.9$ Å the peaks in the calculated spectra appear at energies within ~ 2 eV of the experimental ones and the relative peak intensities are also in good agreement. The fit is considerably worse for the hollow site with $d_\perp = 0.2$ Å and for the twofold bridge site. The calculated spectra for the atop site show the poorest agreement with experiment.

Figure 3 shows the effect of adding O atoms around a central O atom in the fourfold hollow site with $d_\perp = 0.9$ Å to give a $p(2\times2)$ and $c(2\times2)$ surface net. It is seen that scattering off the other adsorbate atoms is nonnegligible, especially when $\vec{E}$ lies in the surface plane (normal incidence). The differences between the $p(2\times2)$ and $c(2\times2)$ calculations are, however, small. The NiO calculation shown at the bottom is in good agreement with the normal-incidence 160-L spectrum in Fig. 1(h) which corresponds to a thin oxide layer on the surface.[15]

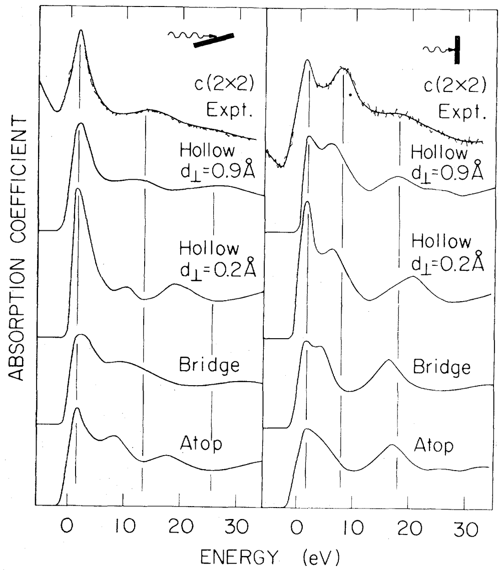

FIG. 2. Experimental and calculated NEXAFS spectra for a $c(2\times2)$ O on Ni(100) overlayer. The calculated spectra assumed different chemisorption sites as indicated.

It has recently been proposed[16] that a good description of the NEXAFS may be obtained within a *single-scattering* formalism by replacing the EXAFS plane-wave approximation by a proper combination of spherical waves. We have investigated the validity of this single-scattering approximation for bulk NiO. Figure 3 shows the result for six shells (eighty scattering atoms) in direct comparison with the respective fully converging multiple-scattering calculation. There is poor agreement. Most importantly, the single-scattering curve is changed considerably by the addition of each successive shell of atoms and has not converged even with ten shells (170 atoms)! Results with fewer shells show fortuitously good agreement with experiment. We conclude that for situations where multiple-scattering effects occur, it *may* be possible to ignore them because they cancel for certain geometries, but it is not possible *a priori* to predict when lesser approximations may suffice.

The present results show that angle-dependent NEXAFS studies provide a sensitive tool to monitor structural changes at surfaces. It is possible to model the experimental data by the presented multiple-scattering cluster approach and in fact discriminate between different structural models. The use of NEXAFS to obtain structural information for *atomic* adsorption on solid surfaces thus appears to be possible. There are

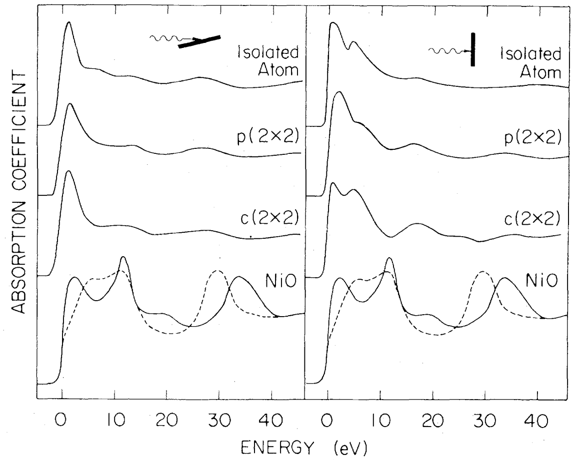

FIG. 3. Calculated NEXAFS spectra for O on Ni(100) with increasing oxygen coverage. Changes in the top three spectra are due to scattering off additional O neighbor atoms. The lowest calculated spectra are for bulk NiO. The dashed line shows the calculated spectrum in the single-scattering, curved-wave approximation.

two advantages with respect to SEXAFS. NEXAFS measurements can be performed for lower adsorbate coverages (~ 1/100 monolayer) and they can be carried out even if absorption edges occur too close together to allow a SEXAFS analysis. From a practical point of view it is a major disappointment, however, that the NEXAFS spectra of *atomic* adsorbates are not dominated by just the NN substrate atoms but rather that the scattering from as many as thirty neighbor atoms has to be included in the calculations before convergence is achieved. This is in contrast to the NEXAFS of *molecular* adsorbates[11,17] where the spectra are dominated by intramolecular scattering with only small or negligible scattering contributions from the surface substrate atoms.

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