LNF-83/59

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OF OXYGEN ON Ni(100)

Surface Extended Energy-Loss Fine Structures of Oxygen on Ni(100)

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Surface electron-energy-loss fine structure above the oxygen K edge and the nickel M_{23} edge has been investigated for several oxygen coverages on a Ni(100) system. In agreement with recent results, it is found that at low coverage the oxygen chemisorbs in the hollow position (0.85 ± 0.05 Å above the nickel plane). On increasing the coverage, islands of nickel oxide are formed. This technique for determining the local geometry of adsorbates is especially useful for light surface species like carbon, oxygen, and nitrogen.

One of the most difficult problems of surface physics is still the determination of the geometry of surface atoms (both on clean surface and on chemisorbed systems). Bond lengths, coordination numbers, and vibration amplitudes are fundamental parameters for understanding surface properties.[1]

Several techniques have been devised for measuring these quantities, like LEED,[2] RBS,[3] SEXAFS,[4-6] HREELS,[7] NPD,[8] and EAPFS,[9] and have been successfully used in recent years.

About one hundred surface structures have been determined up to date by use of low-energy electron diffraction (LEED).[1] This technique requires fairly sophisticated experimental apparatus and lengthy (and costly) calculations for determining bond lengths. Rutherford backscattering (RBS) and surface extended x-ray-absorption fine structure (SEXAFS) both enjoy the use of a rather straightforward analysis for extracting structural information from the experimental data. Both, however, require very sophisticated equipment.

Quite recently we have demonstrated[10] that structural information is contained in the extended loss fine structures which can be observed in reflection energy-loss experiments, above core-level excitations. The surface sensitivity[11] of our technique is provided by the use of low-energy electrons. Similarly to extended appearance-potential fine structure (EAPFS), it involves the excitation of core levels via an electron beam. Also it shares with EAPFS[9] the extreme simplic-

ity of the experimental apparatus. The physical basis underlying the new technique is, however, much more similar to SEXAFS[4,6] (involving the same excitation matrix elements) and it shares with it the simplicity of analysis.

We report detailed surface extended energy-loss fine-structure (SEELFS) measurements on the O_2/Ni(100) system. We demonstrate that it is possible to detect the oxygen position at various stages of oxidation and in particular the transition between the chemisorbed and oxide phases. The technique is indeed so sensitive that it is also possible to detect the variation of the substrate geometry.

A (100) nickel crystal was cleaned by ion sputtering and heating at 1000 °C in a vacuum chamber equipped with a single-pass cylindrical-mirror analyzer (CMA) and LEED. Several oxidation ($P_{O_2} = 10^{-6}$ Torr, $T = 1000$ °C) and reduction ($P_{H_2} = 10^{-6}$ Torr, $T = 800$ °C) cycles were used for eliminating carbon and sulfur contaminants. The clean surface only showed impurities (mainly carbon) well below 1% of a monolayer (ML).

Primary electron energies between 1500 and 2000 eV were used with currents of ~5 μA. No changes were detected in the Ni Auger line shapes or in the SEELFS signal after prolonged beam exposure, showing that the effect of the electron beam was negligible.[11] Peak-to-peak modulation voltages in the CMA of 5–10 V were used, and the signal was detected in the second-derivative mode. In these conditions the spectra were re-

corded in a very short time ($\leq$ 15 min). The crystal was exposed to high-purity oxygen for doses of 25 langmuirs (L) (5×10^{-7} Torr, 50 sec), 70 L, and 120 L. These exposures correspond, respectively, to coverages of 0.3, 0.7, and 1.0 ML, as determined from escape-depth–corrected Auger ratio, in very good agreement with published results.[3,6] A strong $c(2 \times 2)$ LEED pattern was observed at 0.3-ML coverage. At 0.7 ML the LEED pattern changed reflecting the formation of oxide islands. At 1.0 ML the oxide spots were still discernible but the pattern was considerably blurred. The different coverages were reproduced several times, always obtaining identical results.

Figure 1(a) shows SEELFS spectra above the oxygen K edge for the $O_2/Ni(100)$ system at 0.3, 0.7, and 1.0 ML oxygen coverages. The first curve shows the nickel spectrum before oxygen exposure with the same experimental settings used for recording the other spectra and provides a measurement of the background and noise level. The signal-to-noise ratio is quite good, especially considering the short data acquisition time (15 min).

An important point is the formalism which should be used for analyzing the experimental data and to extract the structural information. For an electron energy-loss process the counting rate of measured electrons $N(E,q)$ which have lost energy E and momentum $\vec{q}$ through the core-level excitation is given by[12,13]

$$N(E) \sim \frac{d^2}{dE\,dq}\, \sigma_{el}(E,\,q)$$

$$\sim q^{-3}\, |\langle \psi_f |\, e^{i\vec{q}\cdot\vec{r}}\, |\psi_i\rangle|^2\, \delta(E_f - E_i - \Delta E), \quad (1)$$

where the matrix element becomes identical to the usual optical matrix element in the small-momentum-transfer limit. We argue in the following that with the typical settings used in a SEELFS experiment the dot product $\vec{q} \cdot \vec{r}$ is still small so that the usual dipole matrix-element approximation holds.

In a SEELFS experiment primary electrons impinging on the sample have a momentum ~ 20 Å^{-1}. The CMA detects electrons which have been scattered by an angle of $40°-50°$. However, most of the momentum change is provided by a surface reciprocal-lattice vector. The momentum transfer with the electronic system is $\hbar q = \hbar(\omega/v)\hat{l} +$ $+ \delta k_{inc}\hat{f}$; for an electron which has lost a few hundred volts it is of the order of 2–3 Å^{-1}, and it is mostly longitudinal. This is because the number of diffracted beams which enter the CMA
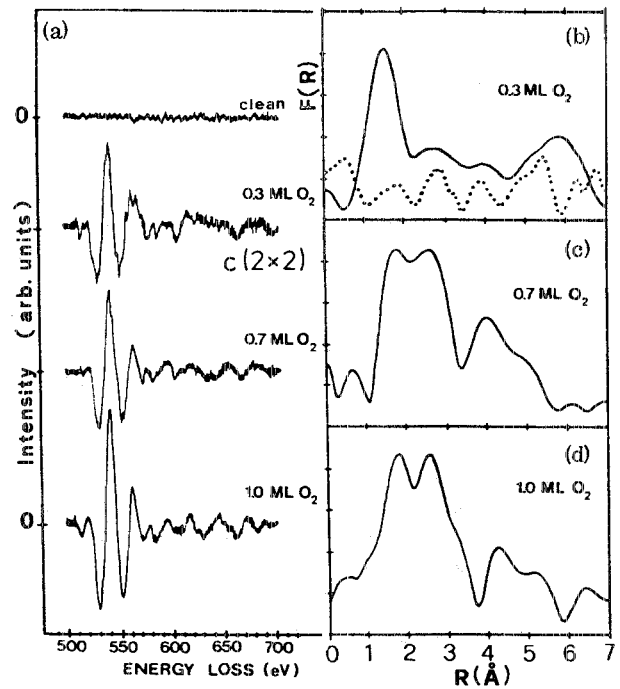

FIG. 1. (a): Reflection energy-loss spectra of Ni(100) obtained before and after exposures of 0.3 monolayer [ML, $c(2 \times 2)$ configuration], 0.7 ML, and 1.0 ML. The primary beam energy was $E_p = 2000$ eV. The surface EELFS oscillations extend up to about 200 eV above the oxygen K edge. (b)–(d): Fourier transform $F(R)$ of the SEELFS signals of (a). The integration limits were $k_{min}=2.0$ Å^{-1} and $k_{max}=7.0$ Å^{-1}. The dotted line of (b) shows the $F(R)$ of the clean nickel spectrum.

is fairly high so that most of the contribution to the measured $N(E)$ comes from electrons in small cones around these diffracted beams.

The effective radius r for a core electron is small (0.1 Å for the oxygen 1s) so that the usual dipole matrix-element approximation still holds. We feel therefore justified in using the usual EXAFS formalism[4,14] for interpreting our data. A more formal justification of course awaits an explicit calculation of the partial-wave character of the outgoing electron.

The direct Fourier transformation of the experimental spectra of Fig. 1(a) is shown in Figs. 1(b)–1(d). The integration limits were $k_{min} = 2.0$ Å^{-1} above the oxygen K edge (532 eV) and k_{max} $= 7.0$ Å^{-1}.

The dotted line shown in Fig. 1(b) shows the Fourier transform $F(R)$ of the clean nickel spectrum within the same integration limits and provides the limit of reliability of the observed structures. The solid line in Fig. 1(b) shows the func-

tion $F(R)$ for a 0.3-ML oxygen coverage. The $F(R)$ shows a sharp peak centered at 1.60 ± 0.03 Å. Using an experimental phase shift obtained by a thermally grown NiO film on Ni(100) we determine the O-Ni nearest-neighbor distance to be 1.96 ± 0.03 Å. This value corresponds to a distance of the oxygen atom of 0.85 ± 0.05 Å above the first Ni plane. We find therefore that oxygen, at this coverage, is still sitting above the hollow position of the (100) Ni plane. The value of 0.85 Å is in excellent agreement with the value found in other experiments[2,3,6,8] and confirms that in the $c(2\times2)$ structure the oxygen is still well above the Ni plane. We do not find any evidence instead for the precursor oxide state.[7,15]

The other structures in Fig. 1(b) have the same amplitude of the noise level and we will not discuss them. We just remark that the absence of structure in the high-R range is a clear sign of large amplitudes of vibration of the oxygen atoms.

Figure 1(c) shows that already at 0.7-ML oxygen coverage we have a quite different situation. The function $F(R)$ is now peaked at 1.75 ± 0.03 Å and 2.60 ± 0.03 Å. The phase-shift correction would bring these peaks to 2.10 and 3.00 Å. We interpret these peaks as the nearest-neighbor

distances O-Ni and O-O of nickel oxide, in good agreement with the bulk values.[13]

Figure 1(d) shows that with increase of the oxygen coverage to 1.0 ML the structures in the $F(R)$ function become somewhat sharper but do not change appreciably. It should be noted that at this oxygen coverage the LEED pattern has become very diffuse and fuzzy so that it would be very difficult to obtain detailed structural information from its analysis.

In an attempt to determine the influence of oxygen on the Ni substrate we have performed the SEELFS experiment using Ni core levels. Figure 2(a) shows SEELFS spectra taken above the Ni M_{23} core levels for the same oxygen coverages as in Fig. 1(a). Also the M_1 level at 112 eV is discernible. We note that the atomiclike features (M_{23} and M_1 signals) remain practically unchanged while the EXAFS-like structure changes in an appreciable way at high oxygen coverages.

In the chemisorbed phase (0.3 ML) the SEELFS structure remains practically unchanged: The adsorbate therefore does not noticeably perturb the Ni substrate at this coverage. At high oxygen coverages the Ni substrate is strongly affected especially in the low-K region. This effect is shown also in Fig. 2(b) which gives the Fourier transform of the spectra reported in Fig. 2(a). Indeed the $F(R)$ shown in Fig. 2(b) (0.3-ML coverage) is quite similar to that obtained for a clean Ni sample. The $F(R)$ functions for the oxide phases (0.7 and 1.0 ML) show a shift of the first peak towards higher values of R and a marked broadening (due to the overlap of different Ni-Ni pair distances in the metal and in the oxide phase).

In conclusion, we have shown in this Letter that the EELFS technique in the reflection mode (SEELFS) is highly sensitive to surface geometry. It can be easily used for measuring the geometric structure of adsorbed species in the submonolayer coverage and it seems especially suitable for light elements, like oxygen, nitrogen, and carbon.[16] A comparison of our results with state-of-art SEXAFS data[6] shows that our technique is highly competitive in terms of signal-to-noise ratio. Besides, cumbersome I_0 normalization techniques[5] in the 200–800 eV energy region are not needed. The technique is also extremely attractive since it needs only a CMA and an electron gun and it is therefore within reach of every surface physics laboratory.
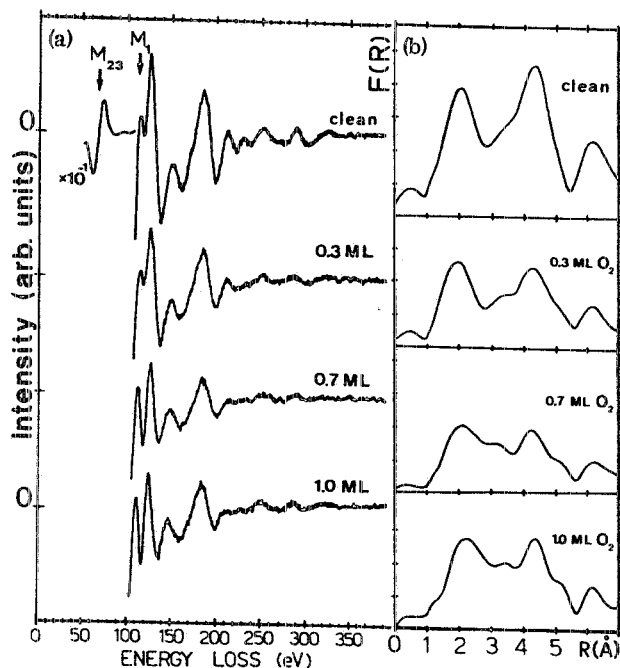

FIG. 2. (a): Surface EELFS signals measured above the Ni(100) M_{23} core level as a function of the oxygen exposure. The primary beam energy was $E_p = 2000$ eV. (b) $F(R)$ of the Ni M_{23} EELFS signals of (a). The integration limits were $k_{min} = 3.0$ Å^{-1} and $k_{max} = 10.0$ Å^{-1}.

[1]M. A. Van Hove, in The Nature of the Surface Chemical Bond, edited by Th. N. Rhodin and G. Ertl (North-

Holland, Amsterdam, 1979), Chap. 4.

[2]P. M. Marcus, J. E. Demuth, and D. W. Jepsen, Surf. Sci. 53, 501 (1975).

[3]R. G. Smeenk, R. M. Tromp, J. W. M. Frenken, and F. W. Saris, Surf. Sci. 112, 261 (1981).

[4]P. H. Citrin, P. Eisenberger, and R. C. Hewitt, Phys. Rev. Lett. 41, 309 (1978).

[5]J. Stöhr, L. Johansson, I. Lindau, and P. Pianetta, Phys. Rev. B 20, 664 (1979).

[6]J. Stöhr, R. Jaeger, and T. Kendelewicz, Phys. Rev. Lett. 49, 142 (1982).

[7]H. Ibach and D. Bruchmann, Phys. Rev. Lett. 44, 36, (1980).

[8]D. H. Rosenblatt, J. G. Tobin, M. C. Mason, R. F. Davis, S. D. Kevan, D. A. Shirley, C. H. Li, and S. Y. Tong, Phys. Rev. B 23, 3828 (1981).

[9]M. L. den Boer, T. L. Einstein, W. T. Elam, R. L. Park, L. D. Roelofs, and G. Laramore, Phys. Rev.

Lett. 44, 496 (1980), and references therein.

[10]M. De Crescenzi, L. Papagno, G. Chiarello, R. Scarmozzino, E. Colavita, R. Rosei, and S. Mobilio, Solid State Commun. 40, 613 (1981).

[11]M. De Crescenzi, G. Chiarello, E. Colavita, and R. Rosei, Solid State Commun. 44, 285 (1982).

[12]B. M. Kincaid, A. E. Meixner, and P. M. Platzmann, Phys. Rev. Lett. 40, 1296 (1978).

[13]R. D. Leapman, L. A. Grunes, P. L. Fejes, and J. Silcox, in EXAFS Spectroscopy, edited by B. K. Teo and D. C. Joy (Plenum, New York, 1980), p. 217.

[14]E. A. Stern, D. E. Sayers, and F. W. Lytle, Phys. Rev. B 11, 4825 (1975).

[15]T. H. Upton and W. A. Goddard, III, Phys. Rev. Lett. 46, 1635 (1981).

[16]R. Rosei, M. De Crescenzi, S. Modesti, F. Sette, C. Quaresima, A. Savoia, and P. Perfetti, Phys. Rev. B (to be published).