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Surface extended x-ray absorption fine structure in the soft-x-ray region: Study of an oxidized Al surface

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The extended x-ray absorption fine structure (EXAFS) above the oxygen K edge ($h\nu \approx 535$ eV) has been investigated for an oxidized Al surface. The spectra were obtained using monochromatized synchrotron radiation in the 500–800-eV range and detecting the secondary electron yield from the sample. Pronounced EXAFS was observed extending at least 300 eV beyond the edge. Experiments of the present kind appear to have great applicability for the study of the oxidation and catalytic activity of surfaces.

The interaction of oxygen or oxygen-containing molecules with solid surfaces is one of the most important problems in catalysis and surface science. From previous studies of bromine chemisorbed on graphite[1] it is clear that the extended x-ray absorption fine structure (EXAFS) above the adsorbate K or L absorption edge can provide unique information on the adsorbate-substrate system. However, EXAFS studies of the most important adsorbates *carbon and oxygen* have been impeded in the past by lack of monochromatic photon radiation in the 250–1000 eV range. Furthermore, the study of these elements as adsorbates is complicated by the *background* introduced by the substrate. The purpose of the present paper is to demonstrate that such measurements are feasible using monochromatized synchrotron radiation as the excitation source and electron yield spectroscopy as the detection technique.

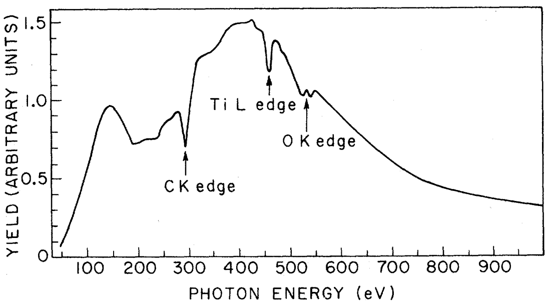

FIG. 1. Photon flux emerging from the monochromator measured as the photoyield of a gold foil in the range $50 \leqslant h\nu \leqslant 1000$ eV. The curve has not been corrected for the (energy-dependent) quantum efficiency of Au. The intensity modulations at 280, 460, and 540 eV are due to C, Ti, and O contaminants on the optical surfaces.

Previously, studies in the photon energy range above the C K edge (~280 eV) suffered from low intensity and unwanted scattered-light background. In order to reduce these problems new optical elements were recently installed in the grazing incidence monochromator "grasshopper"[2] at the Stanford Synchrotron Radiation Laboratory (SSRL). Figure 1 shows the photon flux emerging from the monochromator measured as the photoyield of a Au target as a function of photon energy in the range 50–1000 eV. There is good flux over the entire energy range. Particularly remarkable is that the flux is only slightly modulated at the C K edge. This is attributed to the cleanliness of the freshly installed optical elements. Absorption experiments on thin-film samples furthermore showed that the scattered-light background was small over the above energy range.[3] The spectral bandwidth of the monochromator at the time of the measurement was about 0.2 Å.

EXAFS measurements of surface effects are complicated by the background originating from the bulk. This is especially true for the low-Z adsorbates C and O since their atomic cross sections in the range of interest (300–1000 eV) are of the same order of magnitude as that of the atoms constituting the substrate.[4] Thus opposite to the previously studied system, Br_2 on graphite,[1] where the atomic cross section ratio of adsorbate and substrate atoms above the bromine K edge is ~10^3, measurements on low-Z adsorbates cannot be carried out in the conventional transmission mode. Even with the thinnest pinhole-free substrate films available, the signal-to-background ratio will not exceed ~10^{-2}. Fluorescence detection of the EXAFS above low-ZK edges can be excluded because fluorescence yields are extremely small (~10^{-3}).[5] One is left with one of the various electron yield detection techniques. Recently, monitoring the intensity of the adsorbate Auger line corresponding to the core excitation of interest has been discussed as a possible way to carry out surface EXAFS experiments.[6] However, for C and O as adsorbates this technique cannot be applied since the measured Auger-electron signal is strongly modulated by the core electrons photoemitted from the substrate. With increasing photon energy above the adsorbate K edge, substrate core lines of binding energy in the 10–500 eV range and their inelastic tails will be successively swept through the energy window of the KVV Auger transition. The resulting intensity modulations are usually much stronger than the EXAFS wiggles due to the adsorbate, and it appears impossible to subtract them out reliably.

Partial yield spectroscopy,[7] where the electron energy ($E_{\rm kin}$) window of the analyzer is set in the inelastic tail of the spectrum (typically $1 \lesssim E_{\rm kin} \lesssim 10$ eV), avoids this problem as long as the substrate does not have an absorption edge in the energy range of interest (~300–1000 eV). For C and O this criterion is fulfilled for many important substrates. At high photon energies partial yield spectroscopy which collects electrons a few eV above the vacuum level gives results equivalent to total yield spectroscopy which has been shown to image the absorption coefficient.[8,9] The advantage of electron yield spectroscopy over conventional absorption spectroscopy lies in its surface sensitivity.[9] The surface sensitivity is due to the short electron mean free path (L) in solids. Even if electrons a few eV above the vacuum level (i.e., about 5–10 eV above the Fermi level) are collected, L usually does not exceed ~30 Å.[9,10] Thus yield spectroscopy is comparable to a transmission measurement using a substrate film less than 30 Å thick.

The partial yield spectra reported here were recorded with a cylindrical mirror analyzer (CMA). The measurements were carried out in the "constant-final-state" mode with the energy window of the CMA set at $E_{\rm kin} \approx 2$ eV. Operating the detector at a pass energy of $E_p = 50$ eV (i.e., a resolution of $\Delta E = 0.8$ eV) yielded 3×10^4 counts/sec just above the oxygen K edge. The p-polarized light was incident on the sample at a grazing angle of about 10°.

The partial yield spectrum of an untreated Al sample[11] which is known to be covered with a "natural" approximately 30-Å-thick[12] oxide layer is shown in Fig. 2(a) in the energy range $500 \leqslant h\nu \leqslant 800$ eV. The spectrum was recorded in about 20 min. A sharp increase in count rate is observed around 530 eV, corresponding to the oxygen K edge. Above the edge the signal oscillates and 3 maxima and 4 minima can clearly be distinguished. That these oscillations do not arise from modulations of the incident photon flux was carefully checked by measuring the photoyield of samples which do not have any absorption edges in the energy range of interest.[4] As expected for low-Z elements the absorption falls off fairly rapidly above the edge. It appears that the EXAFS oscillations extend to $h\nu > 800$ eV, but unfortunately this energy range was not covered due to experimental difficulties at the time of the measurements. The specific surface sensitivity of the present yield measurements is demonstrated by the fact that we were unable to observe the oxygen K edge by studying a 1500-Å Al film in transmission.[3] Figure 2(b) shows the EXAFS oscillations $\chi = (\gamma - \gamma_0)/\gamma_0$ in more detail. The background function γ_0 which was subtracted from the yield γ was taken to be a spline polynomial.

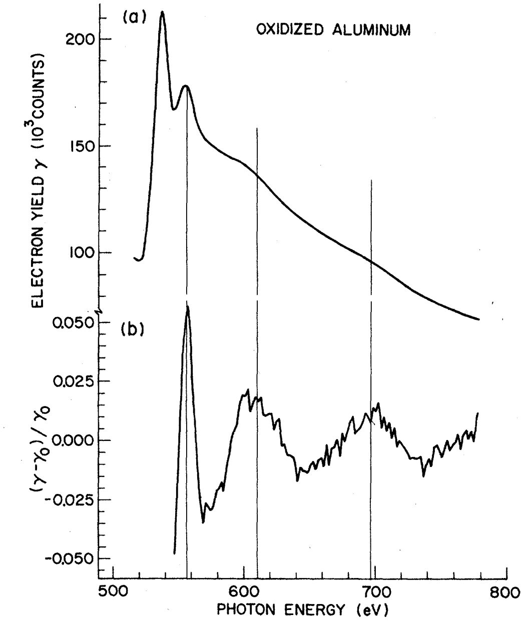

FIG. 2. (a) Partial electron yield spectrum of an untreated Al sample in the energy range 500–800 eV; (b) EXAFS signal obtained from (a) after background subtraction as discussed in the text.

Figure 3(a) shows the function $\chi(k)k$ where the "zero" of the EXAFS energy scale was taken to be at the inflection point of the edge. The Fourier transform of the data in Fig. 3(a) yields the neighbor-shell separations from the O atoms provided that the k-dependent phase shift function $\phi(k)$ is known. Since the present investigation is to our knowledge the first EXAFS measurement above the O K-edge $\phi(k)$ is not known experimentally. We have therefore used the parameterization scheme for the phase shifts and backscattering

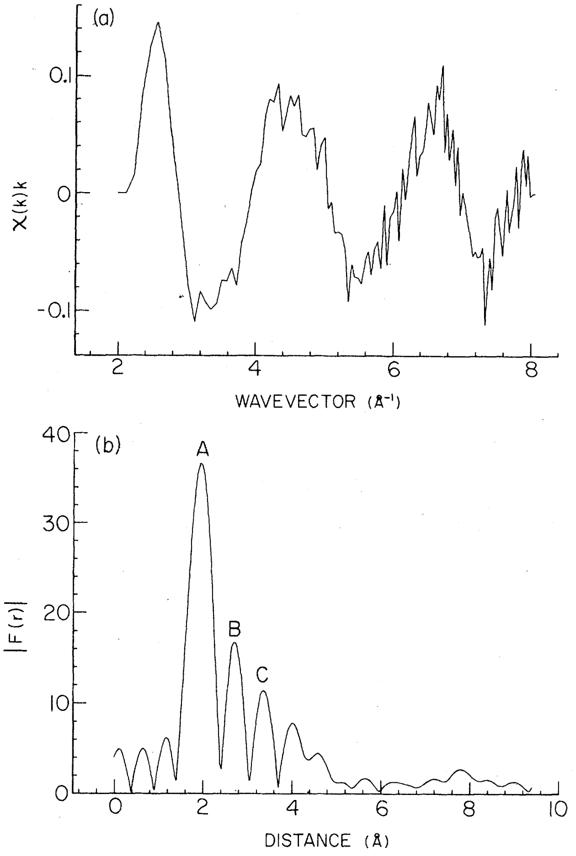

FIG. 3. (a) EXAFS signal $\chi(k)k$ as a function of electron wave vector k. (b) Absolute value of the Fourier transform of the function $F(k)$ defined in Eq. (1).

amplitudes $A(k)$ by Lee *et al.*[13] and Fourier transformed the function[14]

$$F(k) = \chi(k) k e^{-i\phi(k)}/A(k) \tag{1}$$

in the range $2.2 \leq k \leq 8.0$ Å^{-1}. The absolute value $|F(r)|$ of the Fourier transform is shown in Fig. 3(b). The function exhibits three main peaks A, B, and C which are relatively insensitive to the cutoff values of $F(k)$. Raising the lower cutoff to 2.9 Å^{-1} or lowering the upper cutoff to 7.0 Å^{-1} [see Fig. 3(a)] causes a maximum shift of peak A by -0.06 Å, of peak B by $+0.05$ Å, and of peak C by $+0.11$ Å. The peaks in Fig. 3(b) fall at 1.93, 2.70, and 3.36 Å, respectively, when $\phi(k)$ and $A(k)$ are calculated for an Al backscatter. For an oxygen backscatterer $|F(r)|$ looks almost identical and peaks A, B, and C fall at 1.92, 2.67, and 3.33 Å. The peak position of peak A compares well with the *average* O-Al nearest-neighbor distance of 1.915 Å in bulk crystalline Al_2O_3 where each O atom is surrounded by four Al atoms, two at 1.86-Å and two at 1.97-Å separation.[15] The positions of peaks B and C also agree with neighbor-shell separations from the oxygen atoms in Al_2O_3. The second-nearest-neighbor shell consists of oxygen atoms at a mean distance of 2.72 Å and the third-nearest-neighbor shell is formed by Al atoms at a mean distrance of 3.52 Å. In the light of the uncertainty associated with the calculated phase shifts (especially at low k values) the discrepancies of 0.015 Å for the first, 0.05 Å for the second, and 0.16 Å for the third shell are remarkably small. Our findings are consistent with previous soft-x-ray emission[16] and absorption[9,16] measurements which yielded identical spectra for oxidized Al surfaces and bulk crystalline Al_2O_3 samples. Our data do not reveal the bond-length difference of 0.11 Å between the central O atom and the inequivalent Al nearest-neighbor atoms expected for crystalline Al_2O_3. This is not surprising since it is known that the optimal resolution ΔR for which two scattering shells are clearly separated in the Fourier transform of the EXAFS signal is 0.3–0.4 Å.[17]

The accuracy of the present data is limited by the relatively short EXAFS range, by the worsening energy resolution of the monochromator (from ~4 eV at 500 eV to ~10 eV at 800 eV) and by the lack of experimental phase shift information. However, our results clearly demonstrate the feasibility and potential of surface EXAFS measurements on low-Z adsorbates and as such establish it as a technique which will have many applications in catalysis and surface science. Studies of the present kind appear to be even more important in the light of recent multiple-scattering calculations which have shown that *photoemission* studies of adsorbates are quite insensitive to bond lengths.[18] Surface EXAFS experiments are superior to LEED investigations with respect to their higher sensitivity to bonding distances, the simplicity of their analysis, their possible applications to disordered overlayers, and because of the considerably lower probability of radiation damage.

It would be desirable to measure gas-phase EXAFS spectra of carbon- and oxygen-containing molecules[19] in order to obtain more reliable phase shift information. The present technique of studying surface EXAFS can also be improved. By carefully choosing the kinetic energy and emission geometry of the measured electrons the surface sensitivity can be increased.[7,9] The angle of light incidence[9] and the orientation of the electric field vector with respect to the sample[20] are other parameters which should be optimized for a given system. It should then be possible to measure adsorbate coverages of a monolayer or less or look at atoms in the outermost layer of a solid or a liquid. Finally, the development of improved monochromators (throughput, resolution) in the soft-x-ray region[21] will greatly benefit measurements of the present kind.

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