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# Extended appearance potential fine structure analysis of oxidized metal surfaces

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Like EXAFS, extended appearance potential fine structure (EAPFS) probes the immediate neighborhood of a particular element and thus, unlike most other structural probes, does not require long-range order. Furthermore, the use of low-energy electron makes the technique surface sensitive. Because no dipole selection rules apply to electron excitation, explicit calculation must determine the angular momentum of the outgoing final-state electron and thus the feasibility of Fourier inversion of the data. For excitation of the O 1s core, we find the outgoing electron is overwhelmingly s-wave. Reaction of Al(100) with about 1-1/2 equivalent monolayers of oxygen disorders the surface completely (i.e., extinguishes the LEED pattern). For this surface, analysis of the O 1s edge gives an O-Al distance of  $1.98 \pm 0.05$  Å, the longer of the two Al-O spacings in bulk Al<sub>2</sub>O<sub>3</sub>, which indicates that the oxygen goes under the top layer of Al. For a thick oxide layer on Ni(100), diffraction effects precluded use of the O 1s edge. From Ni 2p data, for which the angular momentum selection is weaker, we can extract the bulk Ni-O distance by using plausible phase shifts.

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## INTRODUCTION

A principal ingredient in the characterization of surfaces is the distance from any kind of atom to its near neighbors. Most surface structural techniques, such as LEED and ion backscattering, can provide this information only for systems having long range order, and even then the analysis is often tedious and indirect. In contrast, the extended fine structure is appearance potential spectra is produced by backscattering from close neighbors of the excited atom, and thus probes only very short-range order. Moreover, a Fourier transform procedure gives directly interatomic spacings in the surface region. In the second section of this paper, we discuss the measurement of this fine structure and its theoretical interpretation. In the third section, the technique is applied to two oxidized surface systems of scientific interest and technological importance. In the final section, we discuss prospects for our methods.

## METHOD

Appearance potential spectroscopy measures the probability for electronic excitation of a core level as a function of incident electron energy.<sup>1</sup> For electron beams with energy under a few keV, the short mean free path<sup>2</sup> for inelastic scattering renders this approach surface-sensitive. The excitation of the level can be monitored in several ways. The most widely used technique is to measure the derivative of the total soft x-ray yield as a function of the incident electron energy.<sup>3</sup> While differentiation enhances the sharp increase in x-ray emission at the core-excitation threshold, the low probability of radiative recombination for weakly-bound cores<sup>4</sup> and the

low quantum efficiency of most x-ray detectors impede the measurement of small systematic variations in the yield. Therefore, two other ways of monitoring the excitation probability have been employed. By plotting a derivative of the total electron yield as a function of incident electron energy, one can detect an increase above threshold ultimately due to Auger recombination.<sup>5</sup> Using this technique, some of us have previously measured interatomic spacings in the surface region of several light transition metals (Ti, V, Fe) and found good agreement with the known bulk nearest-neighbor distances.<sup>6,7</sup> The elastic yield decreases at threshold due to the opening of the new inelastic channel. Therefore, the appearance potential measurement can also be made by plotting the derivative of the elastic yield as a function of incident electron energy.<sup>8</sup> We use this latter scheme in the work reported here.

Measurement techniques utilizing the electron yield contain many extraneous inflections<sup>9</sup> absent from the x-ray yield spectrum and rooted in diffraction effects which change the elastic backscattering coefficient.<sup>10</sup> To observe the extended fine structure one must filter the data to remove the low frequency background due to these diffraction features. Our particular digital filtering scheme is described in more detail elsewhere.<sup>7</sup>

To measure the elastic yield, we use an ordinary LEED hemispherical retarding analyzer. The accelerating potential of the electron gun is ramped, and the retarding grid potential set a few volts positive with respect to the gun; thus only electrons elastically and quasielastically scattered are accepted by the collector. To obtain derivatives of the elastic yield (needed to enhance the appearance potential edges and the

fine structure) the primary energy must be modulated with a small oscillation. By superimposing this oscillation on the sample potential rather than the gun potential, we eliminate characteristic loss features, which would otherwise obscure the appearance potential spectrum.<sup>10,11</sup>

The component of the elastic yield varying at the modulation frequency is proportional to the derivative of the elastic yield with respect to incident electron energy.<sup>12</sup> To further enhance the fine structure, we in practice measure the second harmonic, which is proportional to the second derivative. This information is convoluted with an instrument response function that accounts for the broadening introduced by the finite modulation amplitude.<sup>1</sup> We use an oscillation amplitude of 2 V rms, which is small compared to the fine structure variations of interest and large enough to provide excellent sensitivity.

The physical basis of the experiment is as follows: when the incident electron energy equals the core binding energy, an inelastic scattering event can occur, leaving both the incident electron and the ejected core electron in states at  $E_F$ , the Fermi energy. Above this threshold, the electrons can lie in a range of vacant states that conserve energy: the excitation probability reflects the self-convolution of the density of unoccupied states.<sup>1</sup> Because of the discontinuity at the Fermi energy, which is sharper than any structure due to matrix elements or density of states, the derivative spectrum emphasizes the situation in which one electron lies at  $E_F$  while the other carries the excess energy.<sup>13</sup> In an insulator, the lowest unoccupied state lies at the bottom of the conduction band. Presuming that the density of states turns on abruptly, the derivative spectrum is again dominated by the situation in which the two electrons are in the lowest and the highest available states permitted by energy conservation.

Precisely as in extended x-ray absorption fine structure (EXAFS),<sup>14</sup> the higher-lying final-state electron is sensitive only to the local environment of the central atom. Its wave function can be pictured as a spherical wave emanating from the central atom, modified by weak backscattering from nearby atoms. The resulting interference can enhance or diminish the amplitude of the wavefunction near the central atom, depending on the ratio of the interatomic distance to the electron wavelength. Since this wavefunction enters the two-electron matrix element determining the excitation probability, this probability contains small oscillations which depend on the electronic wavevector. The periods of these oscillations are obtained by Fourier transformation of the extended appearance potential fine structure (EAPFS). As in EXAFS, these periods can be simply related to interatomic distances only after phase shift adjustments<sup>15</sup> are made. These phase shifts are due to both the central atom and the surrounding backscattering atoms. They depend on the angular momentum of the outgoing electron wavefunction, and have already been tabulated for many important systems.<sup>16</sup> In EXAFS, photon excitation implies a dipole selection rule, greatly simplifying the determination of this angular momentum and hence of the appropriate phase shift. In EAPFS however, since an electron excites the core, an explicit calculation is required to determine which partial waves are significant.<sup>17,18</sup> Simple inversion techniques are most useful

when just one set of phase shifts need be used to describe the process.

## APPLICATIONS

In this section, we describe the application of the EAPFS technique to two important surface systems with differing long-range order. We first summarize work on oxidized Al, previously reported elsewhere.<sup>19</sup> Small amounts of oxygen disorder the (100) face of Al.<sup>20</sup> An exposure of 120 L (which according to Gartland<sup>21</sup> corresponds to a coverage of  $1\frac{1}{2}$  monolayers of oxygen) completely suppresses the LEED pattern. LEED structural analysis is thus impossible.

Because long-range order is absent, the obfuscating diffraction variations noted earlier are considerably reduced. We find it optimal to measure the oxygen-aluminum distance by studying the EAPFS associated with the oxygen 1s edge at 533 eV.<sup>19</sup> Such fine structure is *ipso facto* sensitive to the overlayer spacing: if the Al 1s edge had been chosen, structure due to the adsorbed region and the first few layers of the Al substrate would have been observed. There are no other edges in this energy range to interfere with the measurement. The Al 2p edge at 73 eV is too low in energy to contribute significant structure above 600 eV, while the Al 1s edge at 1560 eV is well beyond the range of interest.

To further suppress background variations, the second derivative spectrum was measured, a least-squares-fit cubic polynomial was subtracted, and digital filtering was then applied.<sup>7,19</sup> The first 70 eV of data above the O K-edge are excluded to avoid complications produced by multiple scattering. The spectrum is arbitrarily cut off at 450 eV above the edge. As in EXAFS analysis, the data is weighted by the cube of the [outgoing electron] wave vector, to compensate for a decaying envelope.<sup>22</sup> For the excitation of the O 1s core state, the phase shift problem is particularly simple. Our calculation shows the outgoing final state electron is overwhelmingly the  $l = 0$  partial wave.<sup>17</sup> Therefore, only phase shifts appropriate to s-waves need be included in the transform. We use values calculated by one of us (GEL) using an O 1s central atom and

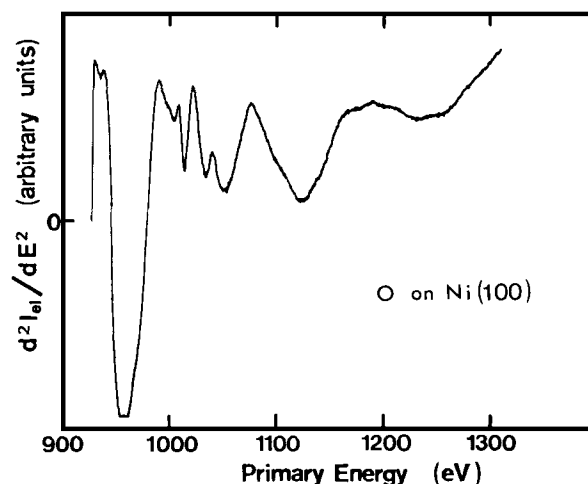


FIG. 1. Second derivative of the elastic yield of the oxidized Ni (100) sample in the primary energy range 925–1315 eV. At 855 eV is the Ni  $2p_{3/2}$  edge and extending several hundred eV above it is the fine structure, which is substantially masked by the slowly-varying background.

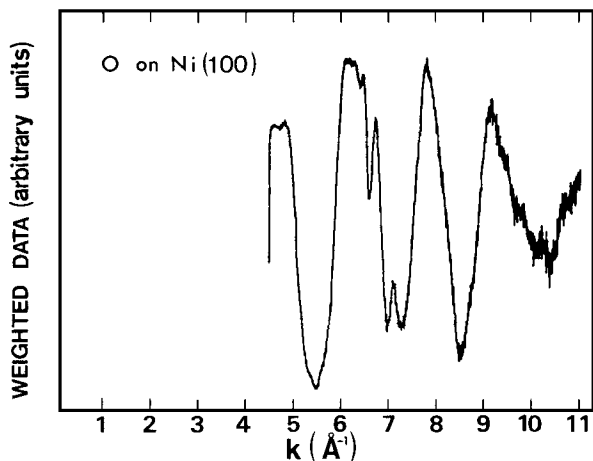


FIG. 2. Data of Fig. 1, filtered<sup>7,19</sup> to remove background variations due to diffraction and ramping the gun potential, then converted to a function of the wave vector of the outgoing electron; the data is weighed by the cube of this wave vector. The kink in the second peak is due to the Ni 2s edge. The periodicity of the fine structure, associated with the Ni 2p edge, is evident.

Al neutral backscatterers. These agree well with tabulated results.<sup>16</sup> The results of this optical transform,<sup>23</sup> with standard weighting, indicate an oxygen-aluminum distance of  $1.98 \pm 0.5$  Å for our thin oxide layer. In bulk Al<sub>2</sub>O<sub>3</sub>, there are two O-Al separations, 1.86 Å and 1.97 Å.<sup>24,25</sup> The larger of the two occurs for oxygen triads lying between two Al atoms, while the smaller happens for oxygen between an Al and a "vacancy" in the chain.<sup>25</sup> Thus, one would expect the smaller number if the oxygen adsorbed on top of the surface and the larger if it penetrated beneath the top Al layer. Our analysis favors the latter picture and had been proposed by others on the basis of work function<sup>26</sup> and SIMS<sup>27</sup> measurements. Similarly, Messmer and Salahub<sup>28</sup> determined the low-coverage O-Al spacing on Al(100) to be 2.02 Å by fitting the energies of photoemission peaks, although their calculations placed the O in a four-fold site above the surface. Using surface EXAFS on a 30 Å natural oxide film on an Al foil, Stohr *et al.*<sup>29</sup> found a spacing of 1.91 Å, the average of the two bulk values. That experiment thus was not sensitive to features distinctly related to the surface.

The other system studied was the (100) face of nickel reacted with oxygen. At low coverage, this oxidized overlayer retains sufficient order to cause diffraction variations in the elastic yield large enough to preclude unambiguous measurement of the fine structure above the oxygen 1s edge. Moreover, the Ni 2p edge at 855 eV would truncate the usable 0 1s fine structure at just 322 eV above the edge. Therefore, we studied the fine structure above the Ni 2p edge. Since such a measurement would not be intrinsically sensitive to only a thin oxygen overlayer, we allowed the oxide coating to reach its limiting thickness, about 12 Å.<sup>30</sup> This distance is fortunately comparable to the inelastic mean free path of electrons of 855-eV energy. Any residual fine structure associated with the oxygen 1s edge extending beyond this 2p level is expected to be relatively small compared to that of the Ni 2p level.

This limiting oxide was grown by exposing the (100) face of Ni to several thousand Langmuir of oxygen at room tem-

perature. By this exposure, the clean (100) Ni LEED beams disappeared, while very broad beams characteristic of NiO emerged, indicating partial order in the oxide layer. The measured Ni spectrum between 70 and 460 eV above the 2p edge is shown in Fig. 1. Subtraction of a cubic polynomial and subsequent digital filtering, to remove the slowly varying background, somewhat enhances the periodic fine structure. This periodicity becomes striking when the abscissa is converted to the wave vector,  $k$ , of the outgoing EXAFS-like electron. Weighting the data by  $k^3$  removes the well-known systematic envelope,<sup>22</sup> thereby producing the rather uniform peak amplitudes. The relatively small Ni 2s edge at  $6.4$  Å<sup>-1</sup>, i.e. 1008 eV (253 eV above the 2p edge), may be ignored in the analysis: the edge itself is too sharp to contribute to the relevant range of the Fourier transform, while its associated fine structure is too weak to significantly affect the measurement. This figure makes it clear that the fine structure is due to excitations of the 2p edge, rather than the 2s edge as had been conjectured earlier.

The exclusion of the first 70 eV of data above the edge to avoid multiple-scattering complications allowed us to neglect the spin-orbit splitting of the 2p levels. Our preliminary calculations<sup>17</sup> on light transition metals suggest that above a 2p edge, the outgoing electron has angular momentum not greater than 2. Using  $\ell = 2$  phase shifts, we obtain a well-defined peak at 2.04 Å, as illustrated in Fig. 3. With  $\ell = 0$  or  $\ell = 1$  phase shifts, the peak lies at 2.27 or 2.21 Å, respectively [Higher partial waves give separations over 0.2 Å smaller than that from  $\ell = 2$ .] Similar results, to well within the experimental accuracy of  $\pm 0.05$  Å, were obtained by Kortan on oxidized Ni(111).<sup>31</sup> Since the bulk O-Al separation is 2.09 Å,<sup>24</sup> it appears that two or three final state partial waves contribute to the fine structure. We are conducting thorough calculations to check the relative weightings of the first few partial waves. While the presence of more than one final state can potentially lead to a richer variety of data, analysis of L edge EAPFS data would seem to require far more theoretical input than K edge spectra.

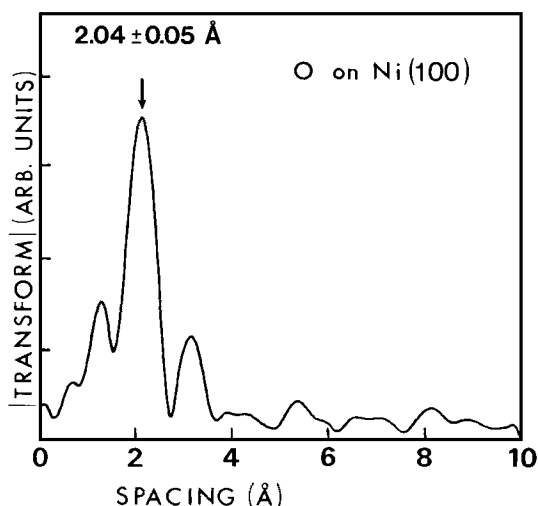


FIG. 3. Optical Fourier transform of the fine structure illustrated in Fig. 2, associated with the Ni 2p edge for a Ni (100) surface reacted with oxygen, for the case of an outgoing electron with  $l = 2$ .

## DISCUSSION

Our treatment of the EAPFS technique has illustrated its remarkable capability for examining surface systems of great current interest. In stark contrast to most traditional structural probes, it thrives on systems lacking long-range order. EAPFS experiments thus do not suffer from stringent requirements of sample regularity and purity, and thereby offer closer contact with realistic systems. In contrast to EXAFS, it can obtain fully adequate signal strength from a relatively thin adsorbate layer, and thus can probe features distinctly characteristic of the surface region. Moreover, EAPFS uses equipment most surface laboratories already have, which makes the option of fine structure measurement widely available.

A desire for intrinsic surface sensitivity and for the ability to use conventional apparatus has motivated us to consider low-binding-energy core states. From the viewpoint of ease of analysis, *K* edges seem optimal. Thus, we are drawn to low-*Z* elements, e.g. C and O, which happily occur in a wide range of important systems. The selection of this energy regime does mean that the diffraction structure noted earlier can impede measurements, particularly on well-ordered surfaces. Because such diffraction features are largely in the elastic beam, they could be reduced by detecting changes in the Auger electron yield, the low-energy electron yield, or the total x-ray yield associated with the excitation of a core level. On the other hand, since recent measurements of the temperature dependence of these diffraction features has revealed intriguing systematics,<sup>10</sup> such structure could probably be exploited to obtain quantitative crystallographic information.

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