

EXAFS and Near Edge Structure

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Extended Fine Structure in APS *

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With the great success of EXAFS and related X-ray techniques, it is natural to ask why one should bother with a technique that replaces X-rays by incident electrons, sacrificing an intrinsic dipole selection rule and convenient polarization. There are several good reasons for using appearance potential spectroscopy (APS): First, it opens the possibility of absorption fine structure measurement to any modern surface science laboratory. The technique can use single crystal samples, is intrinsically surface sensitive [in most modes of operation], and is ipso facto ultra-high vacuum compatible. The only equipment needed is a low energy electron diffraction system or, better, a cylindrical mirror analyzer (CMA). Second, in a recently developed mode (AMEFS), the Auger decay of a particular element can be selectively monitored. This procedure opens the possibility of studying systems previously inaccessible because fine structure above different core levels overlapped. Third, the excitation matrix element for electron excitation is such that the decay of the fine structure is very slow as a function of energy above threshold. Thus, one obtains excellent data ranges, extending up to 11 or 12 \AA^{-1} . Accordingly, the first 100 eV can be excluded from the analysis, thereby avoiding the regime where calculated phase shifts are least reliable.

In APS, an incident electron with energy 0.5 - 2.0 keV excites a core electron. The final state is essentially a convolution over energy-conserving combinations of these two "active" electrons in unoccupied states. The excitation probability is monitored as a function of incident energy E_i . Because of the sharp onset of unfilled states at the Fermi energy (or at the bottom of the conduction band in the case of semiconductors), we have shown that the derivative of this probability with respect to E_i is dominated by the case of one electron at the Fermi energy and the other electron carrying the remaining energy [1-4]. Traditionally, APS was operated with the "other" electron restricted to within ~ 10 eV of threshold, in order to study the unfilled density of states [5]. This other electron is analogous to the EXAFS final state electron; thus when it has energy 100-500 eV, it has a small EXAFS-like sinusoidal component due to near-neighbor backscattering [6].

In order to obtain the energy dependence of the excitation probability bearing the extended appearance potential fine structure (EAPFS), one collects the electrons (over some specified energy range) or the photons associated with the core decay. The core hole lives long enough so that this yield provides a passive monitor of their number. Four years ago, at the University of Maryland, ELAM et al. [1,7-9] collected the total electron yield ("Auger electron" or AEAPS) and measured EAPFS above the L_3 edges of polycrystalline Ti, V, and Fe. Using a relatively crude analysis, they obtained nearest-neighbor

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spacings consistent with the known values. DENBOER et al. [10] measured the decrease in the elastic yield (disappearance potential spectroscopy or DAPS), thereby directly monitoring the excitation probability. They studied EAPFS above the K edges of O and Al in Al(100) reacted with oxygen. An optical Fourier transform was used, with calculated phase shifts appropriate to the EXAFS-like electron being an s wave. The improved analysis reduced error bars to $\pm 0.05 \text{ \AA}$. Both O and Al K-edge spectra indicated the larger of the two nearest-neighbor spacings of bulk corundum, consistent with other experiments showing that the O bonds between the top and second layers of this face of Al. A thick oxide on Ni was also studied [4]. Since the Ni L_3 -edge lies only 323 eV above the O K-edge, the desired data range could not be obtained above the latter; accordingly EAPFS above the Ni L_3 was examined. The importance of good data range is underscored by JACH and DISTEFANO's [11] DAPS study of EAPFS above the L_3 edges in NiO and Cr_2O_3 ; using data only for $k < 5 \text{ \AA}^{-1}$, they could not extract known spacings. When treating ordered samples, the AEAPS and DAPS modes encounter difficulties due to diffraction. Consequently, MORAR et al. [12] developed a sensitive soft X-ray detector to count core holes by their radiative decay (SXAPS). When applied to the O K-edge of oxidized Si, this scheme obtained the O-Si and the O-O nearest spacing, with spectra at least as good as SEXAFS [13]. While the low probability of radiative core decay required moderately high current (100 μA), excellent signal-to-background limited this problem. Moreover, since the photons are not energy analyzed, relatively low current density (1 $\mu\text{A}/\text{mm}^2$) could be used. The SXAPS spectrometer constructed for these experiments relied on a field emission source that is unfortunately rather temperamental and not commercially available.

Very recently MORAR et al. [14] monitored the excitation probability by tuning a CMA to the Auger line of the central atom core-hole decay. Dubbed AMEFS (Auger-Monitored Extended Fine Structure), this new technique offers the impressive prospect of exploring systems with core levels closely spaced in energy, e.g. the O K-edge in the NiO system mentioned above. In EXAFS-like schemes, Auger detection has been thwarted, for Auger lines below 2 keV, by interference from photoemission peaks passing through the acceptance window [13a]. In AMEFS, a modulation technique is used to distinguish, to leading order, features tied solely to the sample energy levels (viz. Auger lines) from features dependent on the incident energy. AMEFS study of the spectrum above the L_3 edge ($\sim 450 \text{ eV}$) of a single crystal of Ti yields fine structure very similar to that in EXAFS [15]. Optical transformation of simply filtered data gives a nearest-neighbor spacing of 2.93 or 2.91 \AA (vs. a known 2.92 \AA) with s- or p-wave phase shifts, respectively, for the central atom. For a Ti (0001) exposed to 50 L of oxygen, data above the O K-edge (530 eV) is analyzed to show an O-Ti spacing of 1.99 or 1.95 \AA (vs. 1.98 \AA for Ti O_2) with s- or p-wave phase shifts, respectively. The S L_3 edge (165 eV) on this crystal and on Ni (100) is currently being studied. We reemphasize that these experiments were done with a standard commercially available CMA with integral electron gun; the only modification was in the electronics.

A lingering question is the angular momentum ℓ_x of the EXAFS-like final state. Initial calculations of radial integrals using partially orthogonalized wave functions indicated that for deep K levels (e.g. V) the EXAFS-like electron was overwhelmingly $\ell_x = 0$; for shallower K levels, (e.g. O) this monopole behavior still held, though less strongly. For L_3 edges, this approach indicated ℓ_x was below 3, but that the final state could have more than one angular momentum component. We are improving the calculations by taking fully into account orthogonalization, Clebsch-Gordan coefficients, and factors due to antisymmetrization, as well as by performing model calculations to corroborate trends. We are also using wave functions derived from atoms self-consistently embedded in jellium and from SCF- $X\alpha$ programs. Results depend on

the angular momentum of the electron at the Fermi level and are rather insensitive to the energy of the EXAFS-like electron. Detailed exposition requires far more formalism than is appropriate here [16]. A noteworthy result for K edges is that antisymmetrization mutes the $\ell_x = 0$ contribution while angular momentum coefficients enhance the $\ell_x = 1$ part, so that both may play a substantial role. For the low Z elements we have studied, the central atom phase shifts for these two angular momenta have similar slopes over the relevant energy range, with the $\ell_x = 0$ slope a bit greater in magnitude. Thus, analysis with just $\ell_x = 0$, or $\ell_x = 1$ will slightly overestimate or underestimate, respectively, interatomic spacings, bracketing the true value. Such behavior is consistent with our AMEFS results. Note that self-consistent inner potential adjustment tends to diminish the small misestimates, which are a fraction of our error bars.

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