

# EXTENDED ABSORPTION FINE STRUCTURE ANALYSIS OF SURFACE STRUCTURE

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Extended absorption fine structure (EXAFS) techniques provide excellent probes of interatomic spacings in both ordered and disordered systems. This review emphasizes applications to surfaces. Various analysis procedures are described, with attention to the importance of good data range and the ultimate limitations due to phase shifts. X-ray beam techniques used are EXAFS, fluorescence EXAFS, PSD, and especially SEXAFS, with various electron-energy detection systems. High and lower energy electron beam methods are EXELFS and EAPFS, respectively, the latter having several different modes. Many comparisons are included, both among these methods and between them and LEED and ion scattering.

## 1. Introduction

Extended absorption fine structure analysis provides a means of deducing directly the spacings between a specified element and its near neighbors, regardless of whether long-range order exists. As such, it provides enormous insight into the structure of surfaces and thin films. It offers a way to probe the structure of clean, and irregular surfaces that play important roles in technology. This exposition has the following purposes: (1) to explain the process in physical terms, (2) to show thereby the unique capabilities of this approach, (3) to discuss how surface sensitivity can be achieved, (4) to describe various actual experimental techniques employed to date, and (5) to compare critically their capabilities. The orientation is pedagogic and heuristic, with no attempt at completeness beyond applications to surfaces of solids. An excellent comprehensive review has recently appeared detailing the background and applications of X-ray induced extended fine structure [1].

## 2. Features of extended absorption fine structure (EXAFS)

Very general features of photon absorption or inelastic electron scattering by an atom are familiar. For energetic incident particles, the dominant loss (or absorption) mechanism is the excitation of electrons into unbound

. The one-electron wave functions of these final states can be viewed for present purposes as spherical waves. When we examine the interaction cross-section as a function of incident  $\nu$ , we find sharp jumps at the threshold for excitation of a particular level, followed by a smooth fall. If the atom is half of a diatomic molecule, however, there is fine structure superimposed on this. For core-level excitation, we again imagine that the final state is basically a spherical wave. Now, however, there is backscattering from the other atom which leads to some interference at the excited state depending essentially on the ratio of the final state wave length to the interatomic spacing. As the final state energy increases, the wave length changes, and one alternates between enhancement and reduction of the excitation probability. As we shall see explicitly below, for energies greater than about 100 eV measured relative to the threshold, the oscillations are sinusoidal in the square root of energy. The idea that interatomic spacings might modify the cross-section is not new to those familiar with resonances in molecules [4]; there, however, the lowest order standing wave is involved. In a metal there are not only far more neighboring atoms but also the background electron gas. It is important to recall two famous curves. First is the "universal" curve of electron mean free path versus  $\nu$  (relative to the Fermi energy) [5]. For energies below about 20 eV, the mean free path is greater than several atomic spacings (viz. 10 Å). An electron thus samples the periodic potential of a crystal, and the dispersion function accordingly reflects the (bulk) band structure. Above about 600 eV, the same holds except that here one encounters high Fourier components of the potential, generally quite small, resulting in small gaps and essentially free electron wave functions. In the intermediate regime, the electron senses only a short distance coherently. For an outward-propagating final state electron in this regime, it is irrelevant whether there is long range order in the material. Second is the differential cross section (or magnitude squared of the scattering factor) versus scattering angle [6]. Scattering is strongly peaked in the forward direction, with 75% of the scattering within a cone with about 20° half-width in the forward direction. There is also some peaking in the backward direction and (for intermediate Z atoms) weak intermediate structure, which decrease with increasing energy. In any case, when the outgoing final-state wave encounters a nearby atom, most of the wave will continue forward with only a moderate fraction being backscattered. More significantly, only a small fraction will be scattered backwards. Hence multiple scattering within the shells of nearby atoms followed by return to the excited state is at least "second-order improbable" and is usually a negligible effect. (The exception is backscattering from a "shadowed" atom, one for which another atom lies between it and the central atom. Then the forward scattering from this intermediate atom contributes significantly.) The upshot is that at energies greater than 50-100 eV, the extended (to distinguish from lower energy, near-edge) fine structure is due to a

ular spacing is due to a single kind of backscattering event. Ultimately, this spacing can be deduced directly from a Fermi surface, rather than by the trial-and-error fits required by LEED. (Even if multiple scattering were to contribute, the most noticeable effect would be a phase shift in the oscillations, with little effect on near neighbor spacings [7]; spurious peaks would appear at spacings equal to the sum of the scattering path lengths [8]).

With the physical picture of extended absorption fine structure (EAFS) in hand, we now point out some of the differences between LEED and EAFS. In LEED, a (modified) plane wave impinges on the sample and reflected beams are detected. Only beams belonging to a (two-dimensionally) ordered array will be detected. There are many forward scatterings with at least one back scattering before an electron leaves the sample [9]. Thus, the multiple scattering complications are inevitable in LEED. In EAFS, the excited atom serves as both source and detector. Moreover, both source and detector are essentially isotropic; the intrinsic angular-average removes much extraneous structure. In LEED one probes all atoms simultaneously; the interference between elements comes from their different atomic scattering factors and their possibly belonging to different two-dimensional nets. In EAFS, one singles out specific elements by looking at fine structure associated with particular core levels. There is the concomitant difficulty that if a system contains two elements with core levels close together in energy, the peaks associated with each may overlap (and hence obscure one another) in the detected spectrum.

To clarify the explicit formalism of EAFS and to see another reason for only analyzing the extended regime, it is helpful to sketch the essence of the relevant formalism. The reader interested in more (or even some) rigor or in greater detail is referred to the literature [1,2,8]. If we determine the excitation probability of a core electron using the Golden Rule formula, the rate  $\Gamma$  is

$$\Gamma = \frac{2\pi}{\hbar} |\langle \psi_f | H' | \psi_i \rangle|^2 \rho(E_f)$$

where  $\psi_i$  and  $\psi_f$  denote the core and final states [10,11], respectively, while  $H'$  is external perturbation producing the excitations in  $\psi_f$ , the final state wave function, that produce the EAFS. Assuming the potential of the excited atom to be local and short-ranged, then beyond some radius a single outgoing spherical wave can be written

$$\psi_f \approx e^{i(kr - Et/\hbar)} Y_{lm}(\theta, \phi)$$

The useful formula relating  $k$  and the electronic kinetic energy  $E_k$  is  $k = \sqrt{2m(E_k - I)}$  (in eV). The radially dependent part  $h_l(r)$  is usually a spherical Bessel function of the first kind. We have assumed here that  $\psi_f$  is in an angular momentum eigenstate with respect to the central atom. This important feature will be discussed more fully below. From the viewpoint of a neighboring atom at distance  $R$  away, the spherical wave crest looks nearly like a plane wave with a wave vector of magnitude  $k$  and direction radial to the central atom to it. The

attering involves going from  $k$  to  $-k$ ; i.e. the scattering vector is  $-2k$  and provides the scattering factor

$$\sim J_{-l} \sim (-1)^l J_l \quad (3)$$

ally seek the component which propagates back to the central atom to rejoin the outgoing spherical wave  $\sim$ . In general we need the component with the same angular momentum as  $\sim$ . (In principle there can be mixing of components that belong to the same irreducible representation of the point group of the backscatterers. This mixing has rarely if ever posed a problem in actual situations.) The problem works out readily in terms of a propagator expanded about the central atom. An incoming spherical wave from the backscatterer  $[h^{(2)}(kR)e^{-i\phi}]$  is deposited (hence complex conjugated) into the outgoing propagating-wave, regular solution  $[lh^{(1)}(kr)]$ , with a factor of  $ik$  corresponding to the (free-electron) density of states for the process. In summary, we have that

$$h^{(1)}(r) \sim 4\pi (l + ikR) [h^{(1)}(kR) e^{i\phi}] I_0(kr) e^{-i\phi}. \quad (4)$$

$A$  is a constant and we have used  $[h^{(2)}]^* = h^{(1)}$ . The correction term is roughly a 2% effect [11]. For  $k \gg 1/R$ , we replace the Hankel function by its asymptotic form to get

$$h^{(1)}(r) \sim 1 + ikR \frac{I_0(kr)}{I_1(kr)} e^{i[2kR + 2\phi + (\pi/2 - \phi)]}, \quad (5)$$

simplification of  $h^{(1)}$  to a single oscillatory term is yet another reason for focusing on the extended rather than near-edge structure. In the extended regime, we can also write  $A I_0(k, 7T) I_1 B/k^2$ , where  $B$  is another constant. Returning now to equation 5 we see that in comparison with the rate  $w_0$  in which no backscattering occurs.

$$\frac{0}{1} (1 - 2B(k^3 R^2) \sim \dots) + i \text{Im} [e^{i(2kR + 2\phi + \dots)} + B^2(k^3 R^2)^{-2}] \\ 1 + B^2(k^3 R^2)^{-2} - 2B(k^3 R^2)^{-1} (-1)^{l+1} \sin(2kR + 2\phi + \dots) \}. \quad (6)$$

aside from a negligible smooth shift, we find that the effect of the backscattering is described by the addition of the following expression

$$\sim -k^3 R \sin(2kR + 2\phi + \dots + (l+1)\pi) \sim r).$$

several shells of differing  $R_j$  contribute (i.e. first neighbors, second neighbors, etc.), this expression generalizes to

$$\sim (-1)^{l-3} \sim i^2 \sin(2kR_j + 2\phi + \dots)$$

write  $\sim j$  in case the shells contain different elements. Likewise the constant  $\sim$  corresponding to  $B$  would vary.  $N_j$  is the number of atoms in the shell, times a J-geometric factor related to beam polarization, which can be extremely helpful

face problems. There are two additional complications often considered. The atoms undergo thermal vibrations, which cause variations in the spacings; a Debye-Waller-like factor  $\exp(-\langle \Delta r^2 \rangle k^2)$  describes this effect. This factor differs from that of x-ray diffraction in that  $\langle \Delta r^2 \rangle$  is the mean-square *difference* of displacements rather than the mean-square displacement [12]. Secondly, inelastic damping of the intensity, noted earlier as making EAFS a local probe, can be described by a factor  $\exp(-2Rj/\lambda)$ , where  $A$  is the inelastic mean free path.

The analysis procedure involves the following steps in some form [13]. Data below 50-100 eV above the edge should be excluded, as well as data at energies so high that the noise overwhelms the signal. Systematic background behavior due to the detector or the collection mode may require removal. Then variations versus  $k$  with "frequency" (less than 1.5  $R$ , or 2-3  $\text{\AA}$   $^{-1}$ ), are smoothly filtered out. Such variations are clearly due to effects other than EAFS. What remains is weighted by  $k^2$  or  $k^3$ , or by a more accurate form accounting for some  $k$ -dependence in  $B$  [14] (which becomes increasingly important as the lower- $k$  cut-off decreases or the  $Z$  of the backscatterer increases [15]). Before the periodicity is sought, the phase shifts must be included. To a reasonable extent, particularly at high  $k$ , the (experimentally relevant combination of)  $\phi$  can be treated as linear in  $k$ —i.e.,

$$\phi = 2\pi(kR + \delta),$$

the simplest way to extract (nearest-neighbor) spacing is to note [16], by comparison with the sinusoidal form of eqs. (7) or (8) that

$$2\pi k(R + \delta) = 2\pi n,$$

where even integers  $n$  correspond to nodes and odd  $n$ 's to extrema. Then a plot of  $n$  versus  $2k$  gives a straight line with slope  $R + \delta$ . Similarly, the magnitude of a (fast) Fourier transform will peak at  $R + \delta$ . Alternatively, one can perform an "optical Fourier transform" by feeding the best estimate of the full ( $k$ -dependent) phase shift into the transform exponent, replacing  $2\pi k r$  by  $2\pi k r + \phi$ , and thereby find the peak at  $R$ . Invariably  $\delta$  is negative; its size is 0.1-0.4  $\text{\AA}$  [17]. Determining  $\delta$  is the major source of error in EAFS analysis, as will be discussed shortly.

A final analysis question with physical impact is how to choose the zero of  $k$ : the final state propagates relative to some potential rather than the Fermi level (i.e. the excitation threshold). While calculations of phase shifts [18] give estimates of the inner potential as a byproduct, one can best let the system determine this number self-consistently. The procedure, suggested by Lee and Beni [16], is to adjust the inner potential until a peak corresponding to a particular shell is at the same position in both the imaginary part and the absolute value of the optical Fourier transform. A separate determination is needed for different shells when they consist of different elements. Another note regarding the preceding discussion is that when the signal is poor, as in semiconductors

molecules, the state  $\sim$  is a Coulomb wave rather than a simple Bessel function. Stern [2] notes that the difference is important for  $k \gg 2 \text{ \AA}^{-1}$ , i.e. in the extended regime.

The general comments are appropriate though awkward on the delicate, emotionally charged question of the accuracy of EAFS. Some LEED aficionados maintain that EAFS techniques are no more accurate than LEED's 0.05-0.1  $\text{ \AA}$  [20]. Some proponents insist it can be (under optimal bulk conditions) nearly an order of magnitude better [1,19]. The truth is probably somewhere in between. There are two sorts of error in the analysis. The first, due to limits in the analysis procedure (limited data range, etc.), is relatively minor, typically about  $\pm 0.02 \text{ \AA}$  for most surface studies but  $\pm 0.01 \text{ \AA}$  or better in case of outstanding (bulk) data. The second, that due to phase shifts, is the larger and more controversial. An early study [21] in the form of eq. (9) suggested an uncertainty in  $\delta$  of about 0.03  $\text{ \AA}$ , roughly 10%. A subsequent more sophisticated approach concluded that phase shifts were largely independent of chemical environment and so values of  $\delta$  from some known system can be applied to another (involving the same atoms in the excitation and backscattering) with errors of order 0.02  $\text{ \AA}$ . To determine the phase shift from a "standard" with known nearest neighbor distance  $R_1$ , one places a narrow window around the transform at  $R_1$ , zeroing out the negative  $-r$  spectrum (or what amounts to it in the discrete procedure), and then transforms; the resulting complex function in  $k$ -space has (up to terms of  $q \sim 1/2$ ) the phase  $2kR_1 + 2\delta + \pi$ , from which the shift emerges (once the zero of  $k$  is specified) [1,23]. (This general procedure can also be used effectively as a noise filter for unknown  $R_1$  [23,24].) For highest quality data, it is now claimed first shell distances of  $\pm 0.01 \text{ \AA}$  are achievable and it is often necessary (but rarely desirable) to use calculated phase shifts and in the most sophisticated calculations these are as good as experimental ones [19]. Relying on transferability, quadratic fit parameters [25] as well as extensive numerical calculations for  $k > 4 \text{ \AA}^{-1}$  have been tabulated for various elements as central atoms and (separately) as backscatterers. To assess the dependence of  $\delta$  on calculational procedures, Laramore [18] recently considered  $\text{Br}_2$ . Various self-consistent potentials gave values, i.e., phase shift slopes (at  $8 \text{ \AA}^{-1}$ ), agreeing to better than  $\pm 0.01 \text{ \AA}$  and to about  $\pm 0.02 \text{ \AA}$  with those of non-self-consistent potentials, the experimentally extracted [22]  $\delta$  differed by 0.04  $\text{ \AA}$  but was reduced to  $\pm 0.02 \text{ \AA}$  when inner potentials were considered. The theoretically based  $\delta$  [15] differed by twice as much, but no attempt was made to see how adjusting the energy zero would improve matters. Further studies of this problem are warranted.

With this global view of the problem in hand, we now turn to specific realizations, with illustrations and comparisons. Two different schemes are distinguished by whether the incident beam is photons or electrons, whether a transmission or reflectance mode is chosen, and what is measured to monitor excitation probability. Almost each scheme has acquired its own acronym.

presence is always the same: to determine the excitation probability as a function of the wave vector of the excited electron.

## Extended X-ray absorption fine structure (EXAFS)

The earliest scheme to analyze EXAFS, EXAFS, measured the X-ray absorption coefficient of thin films: a beam of X-rays impinges on the sample and the number passing through is counted as a function of photon energy. Clearly defined oscillations have been observed persisting until well above 1 keV over threshold, e.g. in Cu and Ge crystals up to  $k = 17 \text{ \AA}^{-1}$  in Br<sub>2</sub> till nearly  $k=21 \text{ \AA}^{-1}$ . Even fifth-neighbor peaks were seen in the (optical) Fourier transforms. With the inner radius determined as noted above, nearest neighbor spacings were found to agree with known values to within 0.02 Å in Cu and to within, 0.01 Å in half of them [19], leading to the cited confidence in EXAFS capabilities.

Upon photoexcitation of K-edges, the momentum transfer  $q$  is  $\sim \hbar k$  and the radial extent of the  $1s$  wave function is of order  $a_0/Z$ , where  $a_0$  is the Bohr radius. The well-known dipole approximation is valid when the expansion parameter in the interaction potential in the interaction,  $qa \sim Za \sim Z/137$ , is much less than unity [26]. (Here  $\alpha$  is the fine structure constant.) Thus, with the possible exception of very heavy atoms, we can use dipole selection rules to determine the angular momentum of the final state wave function,  $l$ . For a K-edge,  $l$  is obviously one. For an L<sub>2,3</sub>-edge, the rule permits both 0 and 2 for  $l$ . Explicit calculations [15] and experimental measurement [27,28] show, however, that the matrix element for  $p \rightarrow d$  is 5 times as great as for  $p \rightarrow s$ , making the first process the more probable by a factor of 50 and the second hence negligible. This result is in contrast to the result for optical studies that  $l \rightarrow l \pm 1$ . The physical bases are that the lower- $l$  state is orthogonalized to the core states (and hence highly oscillatory in the core region) and that the higher- $l$  state is more confined by the angular momentum barrier [29].

As an alternative to counting photons transmitted out the back of the sample, it is possible to monitor the core excitation probability (and hence the EXAFS) from the front by collecting the secondary photons emitted as the core-hole decays radiatively [30]. This fluorescence approach is preferable, from a signal-to-noise criterion, for examination of a low- $Z$  atom in a high- $Z$  material [1,30], for example.

It is important that the reader recognize that it is *not* possible to obtain EXAFS by collecting the photoemitted electron. Even if there would be many forward scatterings possible, a simple single-scattering approach would be unrealistic. Even fundamentally, EXAFS assumes a full spherical average at the "detector", i.e. the photoexcited atom; in photoemission spectroscopy the best one can do is a hemispherical average. (Lee [1,31] gives a detailed discussion.)

In recent years EXAFS has been applied with dramatic success to a vast

of systems of interest to physicists, chemists, material scientists, and even biologists. With increasing ambition, researchers have looked at systems with few neighbors in each shell and/or with few atoms of the particular element whose excitations are being probed. To obtain an adequate signal in a reasonable time, it has often become necessary or desirable to use a high-intensity source of photons, particularly the synchrotron radiation from an electron storage ring. An unfortunate fact is that experimenters cannot then do the measurement in their own labs but must take their samples to a major synchrotron and face the familiar tribulations of a high energy physicist. Good fluxes have been generated with rotating-anode sources, making EXAFS in a laboratory possible for non-dilute samples [31-35]. The cost is still substantial [35].

When the goal is to examine very thin films or adsorbed atoms on surfaces, the weak interaction between radiation and matter poses a severe problem. This difficulty can be overcome when it is possible to stack samples while maintaining a viable thickness. For example, a grafoil (exfoliated graphite) substrate was used in an investigation of bromine adsorption [36].

### **Surface EXAFS (SEXAFS)**

In general, it is not possible to model a surface process with a sample that is essentially all surface. To make the EXAFS measurement surface sensitive, it is easiest to involve an electron with energy in the range 20-600 eV (recall second paragraph). By analogy to the EXAFS fluorescence technique, one can also measure from the front of the sample secondary electrons associated with the deexcitation of the core hole, i.e. either Auger electrons [37] or part of the associated lower energy (secondary) cascade. Even when surface sensitivity is automatic, as when EXAFS associated with a characteristic edge of adsorbed atoms is sought, counting of electrons rather than fluorescent photons is usually preferable for levels that are not very deep, since the probability of Auger decay is two to four orders of magnitude greater than soft X-ray fluorescence [38]. Electron detection schemes require that the sample and detector be in a high vacuum; this requirement is also a prerequisite for a well characterized surface. However, there are problems associated with the incident synchrotron radiation. The crystal monochromators traditionally used in these energies require decoupling from the storage ring via window photoabsorption varies approximately as  $Z^4A^3$ , a low-Z window, generally Be, is highly desirable. However, for energies  $\sim 3$  keV, no window is satisfactory [1]. A recently developed double crystal monochromator (JUMBO) is vacuum compatible, permitting use in the previously difficult 1-4 keV range [39]. Experiments in which EXAFS is measured by counting Auger electrons emitted during the core-hole decay have been performed for Fe, Ni, and Cu [40].



r, Hewitt and Kincaid [1,23,24,40]. Specifically, they have studied the EXAFS associated with the excitation of the I of iodine adsorbed on Ag(111), Cu(111), Cu(100) and Si(111) by counting the 3300 eV L<sub>2,3</sub>M<sub>4,5</sub>V<sub>1</sub>M<sub>2</sub>V<sub>1</sub> Auger electron cylindrical mirror analyzer. Iodine was chosen for its suitability for study with the then-available monochromator and grating mirror at the Stanford Synchrotron Radiation Lab (SSRL), along with the existence of LEED data [40]. A windowing scheme was used to obtain precise bond lengths by comparison with analogous bulk iodides. With phase shifts obtained from AgI, for which the nearest neighbor spacing is known, the I-Ag nearest neighbor spacing in the adsorbed (~ X ~)R30° I(111) overlayer was determined with reported accuracy of + 0.03 Å to be 2.87 Å [23], in agreement with less precise earlier work [41]. The I-Cu bond lengths were determined to be 2.66 + 0.02 Å for (~ X ~)R30° I/Cu(111) and 2.69 + 0.02 Å for I/Cu(100) [24].

Beyond the instrumental difficulties, an intrinsic problem has prevented the use of Auger SEXAFS for such low-Z atoms as C and O, which are of greatest practical interest in adsorption systems. In these cases as the photon energy is varied, adsorbate photoemission peaks and their satellites pass through the analyzer window set around the Auger line. This problem is avoided by collecting the total secondary yield [42]. Such a scheme has long ago been used to measure the X-ray absorption coefficient [43]; the direct proportionality in the soft X-ray range was established by Gudat and Kunz [44]. Because of the small solid angle of acceptance of the CMA, this alternative has a better signal-to-noise ratio than the Auger approach even for low-Z atoms and has led to Citrin et al [17] to claim accuracies of 0.01 or 0.02 Å for iodine-substrate atom spacings. An alternative is to collect only a certain energy range of this inelastic secondary electrons. For instance, Stohr et al. [45-47] found it convenient to use a conventional photoemission electron analyzer, collecting electrons <2-5 eV above vacuum (or <7-10 eV above EF' the Fermi level). The underlying idea, of course, is that all three techniques are proportional to each other (cf. De Vries [48]) and are passive monitors of the absorption probability. Because of the very low electron energies, we note that a low-energy partial yield technique is not intrinsically surface sensitive. On the other hand, a high energy partial yield technique is more surface sensitive than total yield [49]. The prescription is to set the low-energy cutoff as high as possible consistent with the photoemission threshold for the edge being examined, all photoemission peaks from core levels with lower binding energy (so that they all spring into the analyzer window as energy increases). Although this scheme optimizes the signal-to-background ratio, the total yield procedure optimizes overall signal-to-noise [42], and is presently the method of choice for SEXAFS [24,42]. (The signal-to-noise improvement over Auger is a factor of 25 [24].)

Especially in the soft X-ray regime (200-1000 eV), signal has been a major problem. First, the photon flux was much lower than in the hard X-ray regime, two to three orders of magnitude lower [40,45,50]. Secondly, the Grasshopper (grating) monochromator

1] used at low energies is not very efficient and degrades rapidly [45]. (These difficulties have been significantly improved recently. Photon flux has been increased by operation at higher beam current and more substantially by the use of "wiggler" magnets [50]. The JUMBO monochromator which operates down to 500 eV, is over an order of magnitude more intense than the Grasshopper [39].) Nonetheless, Stohr and co-workers have successfully obtained results using SEXAFS measured with the oxygen K-edge (~ 532 eV) for O on a variety of substrates: Ni(100) [46], GaAs(110) [49], Si(111) [45], Al(III) [42,47]. For about 1 equivalent monolayer of O on Ni(100), 3-layer thick islands of NiO form in addition to a chemisorbed background [52]. With theoretical phase shifts, the average O-O nearest neighbor stretched by  $0.08 + 0.05$  Å compared with bulk NiO [46]. For the GaAs substrate, an accuracy of  $+0.05$  Å was again obtainable, but doubts about calculated phase shifts precluded quotation of a spacing [49]. For the Si(III) substrate, calculated phase shifts were calibrated against a bulk EXAFS measurement of SiO<sub>2</sub>; the O-Si spacing for the oxidized sample studied with SEXAFS was slightly ( $\sim 0.03$  Å) expanded and the error bars, though not quoted, seem to be in the  $0.03$  to  $0.05$  Å range. For the Al(111) substrate at exposures (100-150 L), O-Al spacings were consistent with O chemisorbed outside the Al (see the later comments on Ni(100) with EAPFS), namely 1.80 or 1.81 (in one case 1.76) with error bars of  $0.03$ – $0.05$  Å, the O-O spacing was determined with error bars nearly twice this size. (At larger exposure, a spacing consistent with bulk Al<sub>2</sub>O<sub>3</sub>, viz.  $1.88 + 0.05$  Å, was found.)

In all these SEXAFS measurements, the signal stopped at about  $8$ – $9$  Å<sup>-1</sup> (washed out for low Z, interfering with the L<sub>2,3</sub> or I). To obtain an adequate data range for the transform, the lower cutoff is taken at  $2$  Å<sup>-1</sup>. Although the quadratic fit to phase shifts is valid only above  $4$  Å<sup>-1</sup> [25], the form was sometimes extrapolated to the lower cutoff [42,45]. Comparison with standards then suggested that the calculated shifts produced spacings too short by  $\sim 0.05$  Å. This apparent discrepancy from the increase of the (negative) slope of the phase shift at small  $k$ . Naive extrapolation underestimates this slope and (recalling the discussion after eq. (9)), the spacing. Since phase shifts are simpler and more reliably obtainable above  $4$  Å<sup>-1</sup>, it is desirable to have the lower end of the data range above this value. However, a natural requirement is an upper cut-off around  $10$  Å<sup>-1</sup> or higher. Such a range is possible for EXAFS (and for EAPFS, which we will discuss later) but has been achieved only recently with SEXAFS using JUMBO, and then only for Mo [53]. (This relatively high-Z atom provides much stronger scattering than those discussed above [15].) In addition to instrumental limitations, which have been considerable, an important contributing problem is the sharp fall-off in the photo-absorption cross-section (in the case of a K-edge by as fast as  $1/k^3$  above threshold. Note that with a rotating anode source Martens et al. [33] did detect EXAFS in the total yield above the edge up to about  $11$  Å<sup>-1</sup> – it is noisy above  $8$ – $9$  Å<sup>-1</sup>). Their quoted error, based on the above procedure, in determining the nearest neighbor spacing is  $0.02$  Å<sup>-1</sup>.

A distinct advantage of a synchrotron beam is its automatic strong polarization. By varying the polarization vector from perpendicular to parallel to the surface, adatom-adatom spacings can be pulled out. Moreover, since the parameter  $N$ , of eq. 1, depends strongly on polarization [1,31], SEXAFS researchers have been able to deduce binding sites from comparison of studies with different polarization [24] directions when only nearest-neighbor spacing are extracted or extractable [24,40]. I/Cu(100) [24], I/Cu(111) [24], I/Ag(111) [23], and O/Al(111) [42b] were all found to bind to the centered (highest symmetry) site. (The two 3-fold sites on (111) fcc's cannot be distinguished yet, a feat LEED has accomplished [55].)

More continuing, we briefly discuss two apparent but not actual inconsistencies between LEED and SEXAFS. First, a experiment using partial-yield SEXAFS suggested that the Al(111) surface relaxed inward by  $0.15 \pm 0.05 \text{ \AA}$  [56]. However, since the  $k$  range was just 2.5 to 3.5  $\text{\AA}^{-1}$  (due apparently to instrumental problems) [57], this deduction is quite unreliable and indicative of EXAFS capabilities, and thus should not be considered as a substantive contradiction of the careful LEED [58]. Secondly, a LEED study [59] reported an O-Al spacing of  $2.12 \pm 0.05 \text{ \AA}$  on Al(111); very recent work indicates that the oxygen had actually been of a more weakly bound molecular  $\text{O}_2$  adsorbate state found at low coverage [60].

Recently, a novel and exciting scheme has been reported for measuring surface EXAFS using photon-stimulated desorption [53]. The insight is that, (1) PSD can be precipitated by an intra or inter-atomic Auger process which breaks the adsorption bond (Knotek-Feibelman picture [61]) and, (2) any monitor of the fraction of core holes created as a function of photon energy should show EXAFS. Instead of collecting Auger electrons, one counts desorbed ions. In this case the oxidized Mo(100) was recorded as the photon energy swept above the Mo L1-edge (2866 eV). EXAFS oscillations, recorded for an excellent  $k$  range of 5- 13  $\text{\AA}^{-1}$ , are similar in frequency but about half the amplitude of a total yield SEXAFS experiment of clean Mo(100) over the same range. The factor of a half is consistent with a surface Mo atom having half the nearest neighbors of a bulk Mo. Before Fourier transforming, the data below 7.8  $\text{\AA}^{-1}$  are removed as being contaminated by EXAFS and possibly weak O backscattering. The resulting primary peak is identical to that from the SEXAFS, and is all due to the bulk Mo-Mo. (Both would need large  $Q$ 's.) Since this PSD-EXAFS is manifestly extremely surface sensitive (nearest neighbors of the adatom overlap adequately for interatomic Auger to occur), this result indicates no surface reconstruction (presuming any reconstructed region would continue Knotek-Feibelman desorption). Later work investigates the difficulties and problems of doing PSD above an adatom edge with intra-atomic Auger [62].

## Extended electron-energy-loss fine structure (EXELFS)

With the success of EXAFS, interest developed in doing analogous experiments with an incident electron beam [63,64]. In addition to natural curiosity, a major motivation was the ability to obtain a high intensity and easily controllable source that could be used in a normal laboratory. An obvious difference between electrons and photons is that electrons undergo a variety of energy first-order inelastic loss processes, which for photons would be second-order (absorption and reemission). Instead of measuring the absorption coefficient, it is better to measure the loss function  $\text{Im}^{-1}(\epsilon(q, E))$ , where  $E$  is the energy loss and  $q$  the momentum transfer, and  $\epsilon$  the longitudinal dielectric function. (It is also important that the sample be sufficiently thin so that a series of small losses not be confused with a large loss.) Since  $\text{Im}^{-1}(\epsilon)$  is proportional to the dynamic form factor, it varies as the magnitude squared of the matrix element of  $\mathbf{e} \cdot \mathbf{r}$  between initial and final states [65], we retrieve the EXAFS scenario in the limit that  $q \cdot r \ll 1$  and a dipole expansion is again valid [66]. Since the core radius goes as  $a_0/Z$ , the dipole approximation should again be valid for  $q \sim 1/\lambda$  or so. To get an estimate of the minimum incident energy  $E_j$  needed to create a loss  $E$  with momentum transfer  $q$ , we consider the case of pure forward scattering [67]. It is elementary to show that  $E_j \sim 2/4Eq$ . For  $E \sim 500$  eV and  $Eq \sim 4$  eV,  $E_j \sim 12$  keV. For smaller  $q$  or scattering laterally,  $E_j$  increases substantially. In the experiments [68-74],  $E_j$  ranges from 60 to 300 keV.

The first observation of fine structure in loss spectra appeared nearly a decade ago [68]. Over a half dozen shallow (< 30 eV) edges of various angular momenta were examined. The oscillations were interpreted in terms of unfilled shells of states, but had been done erroneously for EXAFS originally [75]. Here, however, the data range rarely exceeded 50 eV above threshold, making that interpretation reasonable for the lower half of the spectrum. The EXAFS-like nature of the loss data was recognized in an examination of the 100 eV above the Al L<sub>2,3</sub>-edge [69]. Decent agreement was found with prediction from a model calculation, of the energies at which peaks and troughs should occur. No phase shifts were used nor any Fourier transform attempted. In a later study of TTF-TCNQ, this group looked at EXELFS above the S 2p<sub>1/2</sub>-edge and the C 1s edges [70], but only the first 40 eV above threshold were considered. Again the only objective was to confirm that experimental predicted energies. The first attempt to extract spacings from data concerned EXELFS above the Al K-edge in Al<sub>2</sub>O<sub>3</sub>. The mode of analysis involved plotting the  $k$ -value of (selected) maxima versus peak order for the second through fifth, respectively. Without phase shifts and with only the first 140 eV, spacings with two significant figures and a quoted accuracy were obtained. In view of the crudeness of the method, it is amazing the results turned out so well. With modern EXAFS sophistication awaited Kincaid et al.'s investigation

K-edge EXELFS of graphite [72]. Using calculated phase shifts in an optical Fourier transform, with an upper limit  $A^{-1}$ , they obtained the known spacing, 1.42A, the quoted accuracy of +0.02A seems better than might be expected. Resolvable peak due to second and third neighbors was also observed. Discussion indicated that optimal sample thickness [76] (~ 500 A) was comparable with EXAFS. With existing equipment the count rate for both processes were comparable for  $E_j < 1$  keV (the 105 advantage of the SSRL beam being lost in the monochromation), and schemes to boost EXELFS rate by 105 are listed. Work by this group has apparently [1] continued on a variety of edges but has not been published. Csillag et al. [73] have also applied modern techniques to EXELFS studies of graphite, Al, and Al<sub>2</sub>O<sub>3</sub> films. The high sensitivity of EXELFS was recently demonstrated in an investigation again of the C K-edge in graphite, as well as amorphous C on mica and on KCl [74]. The field-emission electron-gun-equipped, scanning transmission microscope focused on a 3 nm<sup>2</sup> area of a 10 nm thick sample: only 104 atoms were probed and data could be obtained in times as little as 4min. Since only a limited k range (1.5-5 A<sup>-1</sup>) was obtained, spacings are quoted to only 2 significant figures. With this sensitivity, studies of adsorbate edges on thin films should be possible. A major drawback of EXELFS is the low upper energy limit, which is understandable in view of the even more rapid decay above threshold than photoabsorption [65,77]. Experiments to look at the surface region directly with EXELFS are also in progress. The idea is to set the incident beam at grazing incidence, with various detection modes proposed. Stray fields and other complications make these experiments very difficult; no results have yet been reported. A curious variant on EXELFS is small-angle inelastic scattering of 2.5 keV electrons to study inner-shell excitation of atoms in small molecules. The following excitations to the continuum were considered: C 1s in CCl<sub>4</sub> and Cl 2p in CCl<sub>4</sub>, CCl<sub>3</sub>, and CH<sub>2</sub>Cl<sub>2</sub>. Analysis involved plots of wave vector versus order of extrema, and the upper limit of k was 6 and 4 A<sup>-1</sup> respectively. Even though no phase shifts were used, deduced spacings were larger (not smaller) than known values, 4 to 0.5 A [78].

### **tended appearance potential fine structure (EAPFS)**

When an electron beam with energy two orders of magnitude lower than EXELFS (i.e. ~ 1 keV) is used, the dipole excitation collapses. Moreover, the final state contains two "active" electrons, which can have a wide range of energies  $E_f$  as their sum equals that of the incident electron ( $E_j$ ) plus the excited core electron ( $E_c$ ) which was excited. The ionization probability thus can be written [79-82]

$$dEIM(E_i, E_c; E, E_i + E_c - E) I_2 p(E) p(E_i + E_c - E). \quad (10)$$

$\rho(E)$  is the *unfilled* density of states, essentially the density of states times a unit step function at the Fermi energy  $E_F$ . For two-electron inelastic Coulomb scattering. If we differentiate with respect to  $E_i$ , then  $\frac{d}{dE_i} p(E_i + E_c - E) \sim X \sim (E_i + E_c - E - E_F) \sim$  and we find [67,79-82],  $I(M(E_j, E_c, E_x \sim E_F) \sim P(E_x) p(E_F) \sim$

$E_x - E_i + E_c - E_F$ . (We have neglected a smooth term containing the derivative of  $M$ .) Thus, the derivative of the ion probability is dominated by the situation in which one final state electron lies at the Fermi level while the other carries the energy, which is now well-defined [48-50]. The subscript  $x$  is chosen to indicate that the associated final state is analogous to that in EXAFS. It is thus the *derivative*  $dI/dE_i$  which we expect to be analogous to EXAFS [83]. Fortunately, we take derivatives using electron beams; a small sinusoidal oscillation is superimposed on the ramped  $E_i$ , and the first harmonic is detected synchronously [84].

While  $\sim x$  is comparable to EXAFS, the matrix element is more complicated. The two-electron nature of the process is emphasized by the need to talk of singlet and triplet combinations of the two processes "core  $\sim \sim x$ " and "incident electron  $\sim$ ". Spectra are a relatively inconsequential nuisance. A serious question is whether  $\sim x$  can be described adequately by a single momentum eigenstate. Model calculations were performed using an accurate description of the core wave-function and spherical waves orthogonalized to it for the other three [85,86]. For a  $1s$  core, the conclusion is that the excitation process is largely to an  $l=0$  (rather than  $l=1$ )  $\sim x$  [87]. For a  $2p$  core, the calculation shows  $l$  that  $l=2$  but does not conclusively indicate whether  $s$ ,  $p$ , or  $d$  dominate. (It does suggest that  $l=0$  and  $l=1$  are more important than  $l=2$ .) A more painstaking calculation is in progress to elucidate this important issue [88].

When we actually measure  $I(E_j)$  or  $dI/dE_j$ , one monitors either electrons or  $\sim$ -rays that are emitted as the core-hole de-excites. The

excitation process is independent of the excitation (taking place long after the excitation process is complete) and contains interference with periodicities comparable to the EXAFS. The technique of ramping  $E_j$  with a small superimposed sinusoidal and measuring some emission product at the first harmonic (to obtain a spectrum dominated by final state electrons with well-defined energies) or at the second harmonic (to measure  $d^2I/dE_j^2$  and further enhance subtle variations) is called appearance potential spectroscopy (APS). It has been used extensively with  $E_x$  within 10-15 eV of threshold to study the density of states of a wide variety of materials [89]. For  $E_x > 50$  eV it is plausible to find EXAFS. Collecting soft X-rays (SXAPS) [89] is

y analogous to fluorescence EXAFS while collecting all secondary electrons (Auger electron APS, or AEAPS) [90] is analogous to total yield SEXAFS. In a third mode the decrease in the elastic electron yield above each core-excitation edge is measured [91]. This mode is called disappearance potential spectroscopy (DAPS), and is somewhat analogous to EXAFS. In the two electron-detection modes (AEAPS and DAPS), the second derivative measurement is usually possible.

Three years ago, at the University of Maryland, fine structure was observed to extend several hundred volts above the L<sub>2,3</sub> edge of a polycrystalline V sample in AEAPS and was noted to be analogous to EXAFS [79]. Soon after, with deeper understanding, EAFS over a  $k$  range of 6-12 Å<sup>-1</sup> above the V L<sub>2,3</sub>-edge was crudely filtered and Fourier transformed. The data was then shifted by a mean slope of the phase shifts [a of eq. (9)] [92]. With an improved filter, a similar technique was applied to EAFS above L<sub>2,3</sub>-edges of V, Fe, and Ti polycrystals [93,94]. The nearest-neighbor spacings were consistent with known values; the degree of accuracy was about ±0.1 Å. Meanwhile, other experiments using DAPS (in first derivative mode) looked at EAFS above L<sub>2,3</sub>-edges in NiO and Cr<sub>2</sub>O<sub>3</sub> [95]. Analysis used both Fourier transform and extremum-order- $k$  plot techniques. Only the first 100 eV or so above threshold (i.e.  $k < 5$  Å<sup>-1</sup>) were analyzed. The extracted numbers agree with known spacings, which in retrospect is not too surprising given the host of complications at small  $k$  (particularly for non-low- $Z$  elements).

The capability of obtaining high-quality EAPFS with a simple LEED system [96] was first demonstrated in a study of the structure of Al(100) reacted with 11 equivalent monolayers of oxygen, an amount sufficient to destroy any long-range order, as monitored by LEED spots [86]. DAPS rather than AEAPS was used for technical reasons [95]. After a filtering scheme similar to that used for EXAFS, a  $k$  range of 4-11 Å<sup>-1</sup> (cf. fig.1) was inverted by optical Fourier transform, with calculated phase shifts appropriate to an  $s$ -wave final state (making it impossible to try EXAFS phases for  $d$ -states). A peak due to the nearest neighbor O-Al spacing was easily seen. The spacing deduced, 1.98 ± 0.05 Å, corresponds to the longer of the two O-Al spacings in bulk corundum (1.97 Å), and indicates that the O sits below rather than above the surface. A similar conclusion has been reached with several other techniques [97]. The analysis of the data was subsequently improved to include adjustment of the inner potential and the concomitant need to integrate the data to a first derivative spectrum [98]. As a check, EAPFS above the Al K-edge was also examined [98]. The results are consistent with the O K-edge result, as well as with the suggestion from X $\alpha$  analysis of photoemission that the spacing corresponds slightly to 2.02 Å [99]. EAPFS was also explored in a thick oxide on NiO. Since the Ni L<sub>2,3</sub> falls only 323 eV above the O K, the desired data range could not be obtained by analyzing that edge again. Instead, EAPFS above the Ni L<sub>2,3</sub> was examined and a reasonable transformed [real space] curve obtained [82]. Improvements in the analysis procedure are presently being applied.

unfortunate problem with the electron detection schemes is that any ordering produces diffraction of the incident beam. Surprising that such diffraction would obscure the EAFS oscillations. Both kinds of oscillations are produced by interactions, the wave vector of the incident electron is only a few times (or less) the  $k$  associated with  $\sim x$ , and diffraction is avoided with ordered arrays. Thus, EAPFS studies Si and SiO<sub>2</sub> films or adsorbates on single crystals using DAPS has been hindered. SXAPS mitigates the diffraction problem. One drawback is that the intrinsic surface sensitivity is greatly diminished here is no lower-energy electron collected and  $E_i \sim 1$  keV. A second is that for low-Z elements, core-hole deexcitation is preponderantly by Auger rather than soft X-ray emission [38], as noted earlier. Thus, an extremely sensitive detector array if excessive incident beam intensities are to be avoided. Such a detector has been built [1] - but since it is unshielded it requires a dark source, provided by a field emission array. As it has been difficult to get both operational simultaneously,



preliminary results are available, but these are highly encouraging [98]. The O K-edge was again examined, for a surface exposed to air. The data range again goes up to 11 Å<sup>-1</sup>. In an optical Fourier transform, both O-Si nearest neighbor and O-O second neighbor peaks are clearly seen [98]. The former is consistent with SEXAFS results, the latter with SEXAFS and diffraction numbers for SiO<sub>2</sub> (no SEXAFS value being quoted) [42]. Again, the error bars are not yet as good as better than about ±0.05 Å, but probably twice as accurate results should be achievable once the analysis and equipment are optimized. The question of beam damage also needs further attention. In this study, a current of 100 nA was used on a 1 cm<sup>2</sup> area for 6 h.

It is worth emphasizing that the data range in EAPFS easily extends to 11 Å<sup>-1</sup> and probably could be taken higher (though there is a limit to how much is useful in EAPFS [102]). This significant advantage over SEXAFS may be related to the relative energy independence of the excitation matrix element of EAPFS seen in model calculations [85]. This model is not surprising when one recalls that the electron-impact ionization cross-section (which includes many partial ionization peaks) peaks for  $\sim E_j^{-1} \ln E_j$  and then falls off relatively slowly in  $E_j$  like  $\sim \ln E_j$  [103]. Analogous to the very recent PSD work, it would not be surprising to find EAFS in electron stimulated desorption (ESD) [104]. At least one brief unsuccessful attempt at observation has already been made. Since ESD-EAFS would be a convenient source with extraordinary surface sensitivity, further efforts will undoubtedly be forthcoming.

## Including comparisons

To avoid the risk of oversimplification, some general comparisons are in order after these extended discussions. In systems for which LEED, ion-scattering (IS), and some EAFS mode are all possible, the latter two are likely to give better estimates of neighbor spacings (±0.02-0.07 Å versus ±0.05-0.1 Å) with (much) less effort. LEED, on the other hand, has been most widely applied and accordingly has acquired the greatest lore. Both LEED and IS require long-range order, which is not invariant (or for AEAPS or DAPS, even harmful) for EAFS. By the same token, when there are both ordered and disordered phases on or near a surface (e.g. oxidized Ni, reconstructed or relaxed faces) these methods will focus on the ordered parts while EAFS would mix them together. For the important adsorbate H, IS is most sensitive. Analysis of data is simplest for EAFS. It is also important to note that there are several other spectroscopies, such as photoemission [99] (infrared- and electron-induced) vibrational loss spectroscopies [105], that have been so well refined that spacings can be determined indirectly from measurements.

Within the EAFS group, if we were to single out schemes as best in some

ory, we would suggest PSD-EAFS for surface sensitivity, AEAPS or DAPS EAPFS for simplicity and lowest-cost  
nent, EXELFS for total sensitivity, and SEXAFS for flexibility in determining binding sites. Focusing on the modes  
FS and EAPFS, it is clear that EAPFS has great advantages in terms of cost, convenience, and availability, although  
t problem is being alleviated with the construction of dedicated sources [106]. These new facilities should also lessen  
t problems of beam stability [11]. For K-edges both methods have worked well, though with different final state  
r momenta. How well EAPFS will do for L-edges is not yet clear. Both handle disordered materials well; for ordered  
SXAPS is needed to compete with SEXAFS. SEXAFS has the advantage of readily usable beam polarization. EAPF  
d better signal strength [107], providing a superior data range that enables more convincing use of calculated phase  
The beam may also, however, produce some surface damage in some instances. This aspect deserves further study,  
s calibration of EAFS amplitudes in EAPFS, understanding of which has been very useful in SEXAFS. In summary,  
chniques have relative advantages and ideally should be used in conjunction with each other. EAPFS should soon  
e from the final paragraph of EAFS reviews [1,108]. EAFS in general will play an important role in characterizing  
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