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AN OVERVIEW OF SEXAFS DURING THE PAST DECADE

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ABSTRACT

The evolution, accomplishments, and impact of the surface extended x-ray absorption fine structure (SEWS) technique are presented. Critical evaluations of previous studies and current assessments of experimental methodology, data analysis procedures, and inherent and practical limitations of the method are discussed. Previously unreported correlations are found between simple concepts of ionicity and SEWS-measured surface bond lengths and coordination numbers. Emphasis is placed on advancing and improving directions of SEXAFS study using present and future synchrotron sources.

I. INTRODUCTION

Ten years ago the idea of measuring the structure of surface atoms with EXAFS was suggested in the literature [1,2], and since that time the technique of surface-EXAFS, or SEXAFS [3,4], has been reviewed seven times [5-11]. A clear absence of need thankfully relieves the call for another SEXAFS review here, but on this 10th anniversary it seems appropriate to take a slightly different view of the technique's evolution, accomplishments, and impact in the field of surface structural study. Aside from historical interest, this overview is intended to highlight the ongoing development of the method as well as to draw attention to its inherent and practical limitations. A current assessment of these factors, particularly against the background of past work, is aimed at forecasting and stimulating directions for future study.

Some comments about the content and format of this article are in order. No discussion of the complementary data obtained in the near-edge x-ray absorption fine structure (NEXAFS) regime [8, 9, 10], \(< 30\) eV above the absorption edge, is given here since this falls outside the realm and analysis of SEXAFS. Similarly, little discussion is given to routine analysis or measurement procedures of SEXAFS, since these have already been adequately described elsewhere [11,12]. On the flip side of this approach towards brevity is the attempt to cover, in one way or another, essentially all of the published work dealing with the subject of SEXAFS. There are two reasons for this seemingly irrational choice. First, from a practical point of view, there are fewer original articles (defined below) than one might have imagined, particularly on the scale of other EXAFS-related applications, and choosing which ones to omit in discussing the development of SEXAFS is more difficult than simply including all of them. Second, from a philosophical point of view, it is beneficial to comment on not only those studies which have provided definitive results but also those which, in the author's view, have not. Taking a sampling from an already small number of papers would not suit this task. It should be emphasized, incidentally, that those studies which may not have been initially successful in their goals are not at all intended to be viewed negatively, for they have clearly helped define what could and could not be accomplished at that time and what future approaches should be taken in order to overcome those difficulties.

That most of the early experimental difficulties have indeed been overcome and that the success of the technique is well established can be judged in a variety of ways. During the
last 10 years invited talks on SEXAFS have been presented almost every conference which had as its theme either surface structure, synchrotron radiation applications, electron spectroscopy, or EXAFS. Numerous facsimile techniques have emerged in that time whose goals of comparably accurate surface structural determination and/or methods of data analysis are specifically geared to match or approximate those of SEXAFS. These include NPD, OPD, and AXPD (normal, off-normal, and azimuthal x-ray photoelectron diffraction), ARXPS and ARPEFS (angle-resolved x-ray photoelectron spectroscopy and angle-resolved photoelectron fine structure), and SEELFS (surface extended energy loss fine structure). The use of SEXAFS for identifying adsorption sites is now almost taken for granted, and recent SEXAFS reports of surface bond lengths falling outside the uncertainty range of ±0.02 Å are usually accompanied with qualifying explanations. SEXAFS experiments are currently being set up or actively carried out by groups at every synchrotron facility in the world, with the number of groups at each facility continuing to expand.

Perhaps the most straightforward gauge for evaluating the utility of an experimental method is the number of published papers which report its use, but here the results require some interpretation. Fig. 1(a) shows the total number of original SEXAFS articles published per year, where original article is defined as one reporting new work on a particular system or group of systems. Reviews and follow-up papers contain the essential work reported in the original articles and so are not included in this category. By the standards of most established experimental methods the numbers in Fig. 1(a) are not large, the total being 48. Subtracting from this total the 7 theoretical papers, indicated by open bars, and the 19 experimental papers whose findings are viewed here as not definitive, indicated by thin lines and discussed in the Appendix, leaves 22 original SEXAFS experimental papers. The actual number of different systems studied with SEXAFS exceeds this value, since some of these remaining papers report on more than one system (a change in substrate, crystal face, adsorbate, coverage, or temperature constitutes a different system). Adding these extra 10 systems, indicated by hatched bars in Fig. 1(b), brings the total number of reliably studied systems as of this writing to 32.

What do these numbers imply? It might be argued that ten years is a long time for so few systems to have been studied by an experimental technique, but a broader perspective suggests otherwise. Recall that until 1976 only one surface structural probe existed — LEED
and this, despite its utility, requires extensive computer analysis to interpret. The clear need for other surface structural methods has since brought about a wide range of approaches in addition to the SEXAFS-facsimile techniques mentioned above. These include ion scattering (low-, medium-/high-energy), diffraction (high-energy electron-, low-energy He atom-, and glancing-angle x-ray-), ion desorption (electron- and photon-stimulated), and microscopy (transmission electron-, field ion-, and scanning tunneling-) [13]. Comparing the relative merits of these different techniques is obviously beyond the scope of this article, but in simple terms of number of systems studied by any one of these methods, reliably or otherwise, only LEED has been more "productive" than SEXAFS. This accomplishment for SEXAFS is particularly noteworthy considering the conditions and effective time in which it was done: much of the last ten years was spent in developing methodology when only a single, partly dedicated and limitedly available synchrotron facility was in existence. Viewed in this light, then, SEXAFS is similar to many of the other structural probes in that it is still comparatively young and thus still in the process of evolving.

In deciding upon a format for presenting the evolutionary part of this article, no truly satisfactory one emerged. By default, therefore, the original articles shown in Fig. 1 are treated chronologically, with their follow-up papers and related work to be published also cited for completeness. Only an overview of the most important developments is presented in the Evolution section of the text. The actual descriptions and critical comments of the original articles responsible for these developments are given in the Appendix. The descriptions are brief and do not cover the details that can be found in the original publications. The comments are geared to the apprentice or active practitioner in the field and emphasize points about the papers which are particularly important, which may not have been known or appreciated at the time the papers were written, which may have been overlooked in recent reviews, or which deserve further study in light of our present understanding. Discussions and comparisons based on these comments, much of which is not published elsewhere, comprise the remaining sections of this paper.

II. EVOLUTION

A number of factors were essential in setting the stage for SEXAFS. In 1971, the recognition that bulk EXAFS data could be Fourier analyzed to give straightforward qualitative information in even complex systems stimulated a great deal of interest in the field [14]. Theoretical treatments of EXAFS in terms of single scattering mechanisms were published in 1975 which significantly simplified interpretation of the data [15,16], and in that same year the experimental advance of synchrotron radiation was applied to EXAFS which reduced typical data accumulation times from bulk-like systems by as much as five orders of magnitude [17]. The following year the procedure of phase-shift transferability was established for empirically obtaining bond lengths to within ±0.02 Å in bulk systems [18], and the use of fluorescence detection for measuring EXAFS from very dilute systems was introduced [19]; combined, these studies opened up the possibility for considering new applications of EXAFS with very high accuracy. The recognized need for a surface structural probe which was both easily interpretable and comparably accurate to bulk structural techniques provided the final ingredient for suggesting the SEXAFS experiment.

A summary of the most important developments in SEXAFS since 1976 is given in Table I. Brief descriptions of each of the articles responsible for and leading up to these developments are found in the Appendix. Since so many of these articles reported on results that were new at the time, an attempt has been made in the Appendix to play down hyperbole, e.g.,... for the first time..., and to emphasize the scientific impact of the articles and developments instead. This is the first time such an attempt has been made in an Appendix [80].

The individual advances made using SEXAFS and represented by most of the references cited in Table 1 fall roughly into one of two general categories, methodology and application (a single article, can, of course, contain contributions in both). Under methodology, the prototypical studies [4, 30, 33, 36, 37, 54, 59] for determining reliable bond lengths and
adsorption sites by SEXAFS were characterized by comparably reliable sample characterizations and data analysis procedures. Essential to this development was the progress made in SEXAFS data quality, which resulted from improvements in detection techniques [3, 23, 29, 57, 70], monochromators [3, 21, 36, 54], insertion devices [37], and the overall performance of synchrotron facilities [28, 30, 44, 75]. In addition to more reliable measurements of bond lengths and adsorption sites, improved data quality also opened up for study generic questions about the effects of adsorbates on substrate reconstruction [28, 75], the effects of anharmonic Debye-Waller factors on bond lengths [78], and the effects of anisotropic electron escape depths [28] and/or Debye-Waller factors [77] on amplitudes. Under the category of application, the earlier studies of high-Z [3], low-Z [29], and intermediate-Z [36] halogens or chalcogens adsorbed in ordered structures on close-packed metal surfaces were followed by investigations of adsorbed metals [40, 49, 50, 74] and molecules [66, 68], disordered structures [40, 49, 50, 78], substrates of reconstructed semiconductors [37, 47], amorphous semiconductors [45], more open metal surfaces [54, 75, 81], and even clean surfaces [63]. Systematic studies as a function of substrate crystal face [30, 42, 81], adsorbate coverage [33, 41, 40, 49, 50, 53, 59, 60, 70, 74, 77, 78], and temperature [33, 60] all have been carried out to advance our limited understanding of surface bonding.

Summaries of the knowledge gained from the different SEXAFS studies on methodology and application are respectively included in Sections III and IV.

III. CURRENT ASSESSMENT

This section, based on the findings and evaluations of articles described in the Appendix, as well as on personal experience, assesses the current status of the SEXAFS technique in the form of three questions: What information does SEXAFS provide? What are the best approaches for carry out a SEXAFS experiment and analyzing the data? What structural information cannot be obtained using SEXAFS? In keeping with the general intent of this
overview, details found in the original articles or described in the Appendix are, for the most part, not presented here. Emphasis is placed, rather, on information that is most noteworthy, current, or not mentioned elsewhere.

A. WHAT CAN BE LEARNED AND HOW ACCURATELY

SEXAFS is ideally suited for determining bond lengths and positions of adsorbates on single crystal surfaces. Additional information related to the substrate, such as the nature of its reconstruction induced by an adsorbate, or its structure prior to being covered by an adsorbate, i.e., clean, has recently been obtained and will be discussed in Section IV. The main focus of this subsection deals with adatom structure.

Provided there is a single first-neighbor shell of substrate atoms surrounding an adsorbate with a second-neighbor shell of atoms separated $\geq 1\ \text{Å}$ from the first, an adsorbate-substrate first-neighbor bond length can routinely be determined to an accuracy of at least $\pm 0.02\ \text{Å}$ using a simple single-shell analysis. Long-range order is not at all required and no theoretical calculations enter into the analysis. If the second-neighbor shell is $<1\ \text{Å}$ from the first, a multishell analysis can provide the same level of accuracy; in some favorable cases even a single-shell analysis can suffice. The number of adsorbate-substrate systems meeting the above criteria are actually many, and they comprise the main body of surface crystallographic work from which almost all surface bonding trends and unifying principles will be or are being derived. Those systems not falling into this category are no less important or interesting (arguably, they may even be more so), and these will be treated in section C. The simple point to be made here, however, is that the determination of adsorbate-substrate bond lengths in a large body of well-studied systems can be obtained using SEXAFS in a direct, theory-independent manner with very high accuracy.

While on the subject of accuracy, it is important to distinguish between the precision of a measurement and this often-misused term. Related to this clarification is the need to discuss the accuracy of the EXAFS phase-shift-transferability procedure. Precision simply reflects experimental reproducibility, and the precision for most submonolayer SEXAFS bond length measurements is typically $\leq 0.01\ \text{Å}$. Accuracy reflects the absolute reliability of the value in question and requires an independent and comparably accurate measurement with which tests for possible systematic errors can be made. Numerous comparisons between EXAFS-derived bulk bond lengths and those determined from electron- and x-ray diffraction studies have established that the combined EXAFS measurement technique and the methods of its data analysis provide distances that are accurate to within $\pm 0.01\ \text{Å}$. The bulk data are, of course, of high signal/noise quality and extend $\geq 300\ \text{eV}$ above the edge. In addition, all of the data analyses rely upon the procedure of phase-shift transferability, whereby the appropriate phase shifts empirically derived from bulk model systems are transferred into "unknown" systems whose environments are often chemically very different, e.g., gas versus solid, ionic versus covalent, even first- versus second-nearest neighbor. The transferability procedure works so well because it is based on the fundamental notion that core-electron scattering is independent of valence-electron scattering; so long as the two scattering regimes are separated, which is insured by extracting phase information only from data with $k \geq 4\ \text{Å}^{-1}$, there simply will be no problem. It should be obvious that the concept of transferability not only has nothing to do with the chemistry of the scattering atoms, but it also has nothing to do with the atomic number of those atoms or the distance between them. These latter two factors may indeed affect the accuracy of theoretically calculated phase shifts (e.g., type of potential used, plane versus spherical waves, etc.) but this too is irrelevant to the validity of the procedure itself. Succinctly stated, then, only some theorists may have difficulty transferring their EXAFS phase shifts; experimentalists using empirically derived values do not.

How do these considerations of accuracy apply to surface systems? Certainly the differences in chemical environment cited above between bulk model and bulk unknown systems are more extreme than between bulk and surface atoms, but the die-hard skeptic could still insist
that independent comparisons with comparably accurate surface measurements have not been made. Alas, this is true. With only two exceptions, all existing surface structural probes are simply not accurate enough to make these bond length comparisons (some users of other methods are in the habit of quoting small errors, but these errors merely reflect precision). The two surface techniques which can, in principle, provide comparably accurate values are glancing-angle x-ray diffraction and medium-energy ion scattering. The former technique measures distances within the surface plane very well, but much less so in the normal direction. A common system for comparison involving adatom-adatom distances has not yet been studied. With ion scattering there has been only one system with which a SEXAFS result can be compared, namely Ni(110)c(2x2)-S. The first-neighbor S-Ni bond length from ion scattering [82], derived from a measured perpendicular lattice distance, is $2.18 \pm 0.03$ Å, while a recent SEXAFS study [81] reports a direct bond length measurement of $2.19 \pm 0.02$ Å. This lone example does not, of course, establish the accuracy of the SEXAFS technique so much as it serves to support the more compelling evidence from the many other bulk EXAFS studies that the method is indeed accurate. Potential limitations in the accuracy of a given SEXAFS measurement due to data length, data quality, and other factors are treated below in section C. Examples of why it is so important to measure bond lengths with such high accuracy are given later in section IV.

The other essential structural parameter provided by a SEXAFS measurement is the adsorption site. The three methods for obtaining this information use either surface and bulk absolute amplitudes, ratioed (relative) polarization-dependent surface amplitudes, or higher-neighbor adsorbate-substrate distances. The factors determining the applicability of each of these methods are summarized in sections B and C below. The same general statement as above regarding SEXAFS bond length measurements from single first-neighbor systems applies here to SEXAFS adsorption site assignments: they are straightforward, theory-independent, and very reliable.

**B. EXPERIMENTAL METHODOLOGY AND DATA ANALYSIS**

Fortunately, this section falls under the heading of current assessment. Had it been written several years ago, it might have begun: A SEXAFS experiment will require finding a synchrotron, young collaborators, beds, food, espresso, and probably a therapist or divorce attorney. Today, while a synchrotron is still required and the conditions for using it may not seem entirely different at some places, overall the situation is far more civilized and still improving. These changing conditions, added to the stockpile of knowledge gained from previous studies, now allow a SEXAFS experiment to planned, executed, and analyzed in an increasingly thorough and deliberate fashion.

1. **Planning**

The two most important criteria involved in planning a SEXAFS experiment are the accessible range of data above the absorption edge and the required signal/noise. Both strongly depend on the choice of detection scheme. While valuable discussions have appeared in the literature about what factors enter into making this choice, some have not been entirely accurate or complete. An attempt here to cover this subject more thoroughly is made in Table 2, where Auger electron yield (AY), total electron yield (TY), partial electron yield (PY), and fluorescence x-ray yield (FY) are judged in several different areas. The evaluation of FY shown in Table 2 applies to low-Z atoms; for mid- to high-Z atoms the positions indicated by the dashed arrows apply.

The criterion of accessible data range, which for a typical SEXAFS experiment should ideally be at least 300 eV above the edge, is addressed in part by the two columns entitled photopeak and standing-wave interference. The former refers to the limitation of data range imposed by a substrate or adsorbate photoemission peak being swept through the detector window with increasing photon energy. The assignments of FY and TY being the best choices of SEXAFS detection to avoid this problem and AY being the worst are obvious; PY can go either way depending on the effective energy resolution of the retarding grids. If the
resolution is poor, e.g., [66], the data range will be unaffected because the photopeak will be
smeread out, while if the resolution is too good, e.g., [68], it will not. Standing-wave interference

Table 2. Comparison of different SEXAFS detection schemes. $A =$ Auger electron
yield, $P =$ partial electron yield, $T =$ total electron yield, and $F =$ fluorescence x-ray yield. Descriptions of various categories are given in the text.

<table>
<thead>
<tr>
<th>PHOTOPEAK</th>
<th>STANDING-WAVE</th>
<th>SURFACE</th>
<th>ABSOLUTE</th>
<th>COST/</th>
<th>NON-</th>
</tr>
</thead>
<tbody>
<tr>
<td>INTERFERENCE</td>
<td>INTERFERENCE</td>
<td>SENSITIVITY</td>
<td>SENSITIVITY</td>
<td>DIFFICULTY</td>
<td>UHV</td>
</tr>
<tr>
<td>BEST</td>
<td>$F,T$</td>
<td>$A$</td>
<td>$A$</td>
<td>$F,T$</td>
<td>$T$</td>
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<td></td>
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<td></td>
<td>$P$</td>
<td>$T$</td>
<td>$P$</td>
<td>$T$</td>
<td>$F_T$</td>
</tr>
<tr>
<td>WORST</td>
<td>$A$</td>
<td>$T,P$</td>
<td>$F$</td>
<td>$T$</td>
<td>$P_A$</td>
</tr>
</tbody>
</table>

refers to the alteration of the adatom photoabsorption caused by a change in the x-ray
standing-wave fields generated in the single crystal substrate. The fields arise from
interference between coherent incident and Bragg-diffracted x-ray waves and move normal to
the surface with changing Bragg angle or incident energy. The altered adatom
photoabsorption is manifest in the same ways SEXAFS is monitored, namely fluorescent x-
rays, Auger electrons, or secondary electrons, but the unusual shape of the alteration,
sometimes referred to as a Bragg "glitch", varies with substrate and angle and need not be
derivative-like or small [83]. These standing-wave peaks are least problematic in AY because
the reduced solid angle of collection allows small polar or azimuthal rotations of the sample to
shift the peaks out of the energy range of interest. FY applied to low-Z adatoms also does
not exhibit problems with these peaks because of poor wavelength matching between the
incident x-rays and the substrate lattice planes. However, for atoms of $Z \geq 18$ this is no
longer true, as is indicated by the dashed arrow in Table 2. TY, PY, and FY measurements
stand to suffer most from standing-wave peaks because of the large collection angles of the
detectors, but sample rotations as in AY are still worth trying. The final consideration for
determining the accessible data range is the interference created by other substrate or
adsorbate absorption edges. This factor is not included in Table 2 because all the detection
methods are affected by this problem and there is little that can be done about it. If
possible, choosing $L_2$ rather than $L_3$ edges [40] can extend the data range because the $L_2 - L_1$
energy difference exceeds that of $L_3 - L_2$; sometimes even the weaker and broader $L_1$ edge
can be used [61].

The criterion of signal/noise is addressed in part by the two columns entitled surface and
absolute sensitivity. The former refers to the ratio of the surface-layer thickness to the
effective sampling depth of the detected electrons or x-rays. Obviously, when the electrons or
x-rays originate solely from atoms adsorbed on the surface this ratio is unimportant because the
measurements are inherently surface sensitive, but if the absorbing atoms are distributed
within the substrate due to migration and/or compound formation [29, 33, 40, 48, 49, 50, 52] the
choice of detection mode can be important in optimizing the signal/background. Two
examples include identifying the depth of Ni migration in Si(111) and Si(100) using TY versus
AY [52] and isolating the effective surface-atom layer of clean amorphized Si from the bulk Si
atoms using AY from two transitions with different escape depth [63]. As an approximate
guide, effective sampling depths (which, recall, are more than twice the value of the effective
escape depths) for electrons with kinetic energy of 2, 10, 50, 500, 1000 and 5000 eV are
approximately (within factors of 2) 200, 20, 5, 10, 20, and 50 Å, respectively. X-rays with $\lambda
<40$ Å can travel microns in most materials. The absolute sensitivity refers to the measured
signal/background, which is the edge jump divided by the signal before the edge. As it turns out, the intensity of the actual signal, i.e., the height of the edge jump in counts/sec, measured by the different detection schemes exhibits a trend exactly opposite to the one shown in Table 2 for absolute sensitivity. Thus, if the background signal were purely statistical, it would be this latter trend which would determine the detection scheme for maximizing the signal/noise. However, structures in the beamline optical elements which are not completely removed in the normalization process are non-statistical and these can show up in studies of low adsorbate concentrations, i.e., small actual signals. In this case, it is the trend in absolute sensitivity which should determine the method of choice. An example of this latter case was cited in [70] for studying an equivalent coverage of \( \sim 0.08 \) ML of S on Ni(100).

For completeness, the factors of cost/difficulty and applicability to non-UHV environments are included in Table 2. TY is clearly the easiest and least expensive detection scheme; an electron multiplier is not even needed. Simply take a piece of metal, e.g., a spoon, a 9 volt battery for accelerating the secondaries, and a picomammeter to measure the drain current. AY detection is not difficult if commercial equipment is used, but this is usually costly, while FY detection is somewhat less expensive but also requires user fabrication for low- to mid-Z atoms. The long sampling depths of FY and TY detection are advantageous for studying non-UHV systems or absorbing atoms that are buried \( \geq 100 \) A below the surface. FY applied to bulk systems in atmosphere is, of course, routine, but only recently has TY been successfully applied under similar circumstances [84].

The information in Table 2 can be summarized with a few generalizations. The most obvious one is that no single detection scheme is ideal for all systems. For low-Z absorbing atoms \( (Z \leq 10) \), the interference of photopeaks prohibits use of AY, making FY appear to be most desirable on the basis of absolute sensitivity. However, practical limitations due to synchrotron fluxes and other factors, discussed below in section C, may force the use of FY. TY is best suited only when coverages or photon fluxes are high and when unwanted photopeaks are a problem. For UHV and surface systems the strong advantages of FY all but disappear for mid- to high-Z absorbing atoms. In most of these latter cases, AY is the method of choice.

2. Performing

The proper execution of a SEXAFS experiment involves a variety of details which all affect the final measurement. Many of these have been treated elsewhere, e.g., [11], and so will not be discussed here, but there are some that merit additional attention.

One of these is the energy resolution required for a typical SEXAFS measurement. It is usually not high, \( \leq 5 \) eV, and only for some near-edge structures are improvements desirable. However, at higher photon energies, \( E \geq 6 \) keV, the natural beam divergence \( \Delta \theta \) and the lower Bragg angles of the monochromating crystal all conspire to degrade the resolution, viz., \( \Delta E = E \Delta \theta \cot \theta \); this washes out higher-neighbor distances (see discussion of [42]). Use of monochromator crystals with higher index planes, e.g., Si(311) in [77], is one solution, while another is the use of a collimating mirror.

Sample preparation and characterization procedures are other topics for comment. These procedures have assumed a particularly important role as more refined studies are being carried out in systems where multiple distances, adsorption sites, and phases may be present or coexist. The absence of appropriate characterization has, in fact, been responsible for some of the non-definitive results described in the Appendix. In addition to in situ measurements of LEED and Auger electron spectroscopy, ancillary photoemission, e.g., [33], thermal desorption, e.g., [66], and work function measurements should soon become part of standard sample characterization. The same holds true for gentle annealing ( \( \leq 400 \) °C) of most adsorbate-covered surfaces, e.g., [37, 42, 43, 70, 75], which often assures removal of impurities or weakly bound adsorbate species in minority sites. Cooling adsorbate-covered samples to near-liquid-nitrogen temperatures e.g., [4, 28, 30, 44, 70, 75, 78], not only
improves data quality by reducing the effect of the Debye-Waller factor, but in some, albeit, special cases [44, 78] this procedure is essential (very good vacuum and passivated surfaces are also needed).

Two final areas worth mentioning are the measurement of bulk model compounds and of surface systems using different polarization directions. Whenever possible, model compound data should be independently obtained by different groups in order to check for possible systematic errors. For example, nonstoichiometric samples, thickness effects, and most importantly, analysis procedures (see section C) all can contribute to such errors (the former two problems are unlikely for TY data obtained from standard materials). Measurements of the model compound at different temperatures can also provide information about possible anharmonic Debye-Waller effects in the related surface system [78]. Polarization-dependent SEXAFS measurements are invaluable cross-checks for adsorption site assignments, bond length anisotropies, and sample inhomogeneities due to coverage, surface imperfections, or coexisting phases. Changing the sample orientation, however, gives rise to two practical problems. At glancing incidence, i.e., $\theta \leq 30^\circ$, the beam invariably hits the substrate edges. Adjustable x-ray beam slits and phosphor decoration on Ta clips along the sample perimeter [30] or a phosphor screen positioned behind the sample [11] are used to remove this problem. Standing-wave peaks, discussed above, can interfere with a SEXAFS scan, particularly for large solid angles of detector collection. In situ azimuthal (as well as polar) rotation of the sample will usually solve this problem.

3. Analyzing

Analysis of SEXAFS data is in all respects identical in spirit and approach to that for bulk EXAFS data. The fact that SEXAFS data are polarization-dependent is actually an advantage, but this is often balanced out by the shorter data length and higher noise level. Some analysis procedures for optimizing the reliability of the SEXAFS results and some cautionary comments for avoiding potential systematic errors can therefore be useful.

Data accumulated by averaging many scans over long periods of time should be checked for time-dependent non-reproducibilities due to beam motion, monochromator drift, or sample degradation. A simple method for doing this is to compare different fractions, e.g., the first and second halves, of the averaged data.

Use of model compound EXAFS data is essential for reliable SEXAFS bond length determinations, but two points are worth noting here. One is that empirical data can be slightly modified with differences of theoretical phase shifts in those cases where the surface backscattering or absorbing atoms differ in Z by $\leq \pm 2$ from those in a more convenient or reliable model compound. These corrections are usually small, and any systematic errors in the theoretical phase shifts are even smaller due to cancellation. Examples of this procedures are given in [37, 74, 85]. The second point is that care should be exercised in using linearly parameterized phase shifts [11], even if derived from empirical model compound data. The reason [61] is that the small differences in phase between surface and bulk systems at low k, i.e., $4 \, \AA^{-1} \leq k \leq 6 \, \AA^{-1}$, which arise from approximations in the parameterization process (phase shifts are not exactly linear), are given more weight in the analysis procedure of [86] where phase differences are first divided by k and then $E_\sigma$ and R are adjusted. Comparison of results obtained from independent groups using the actual model compound phase shifts and using alternate analysis procedures would determine the size or existence of such possible errors.

One example in which a $\sim 0.02 \, \AA$ bond length error did result from the use of the procedure of [86] occurred in a simulated L_{2,3}-edge SEXAFS spectrum analyzed with a simulated L_{2,3}-edge EXAFS phase shift [46]. This was due to the $(p \rightarrow d)(p \rightarrow s)$ cross term, present in the SEXAFS but absent in the EXAFS phase shift, which was given unequal k-weighting in the analysis. It was empirically shown [61], however, that at least for I the actual cross-term value is half that of the calculated one and so such bond length errors in experimental data
will be reduced. In general, and apart from using a different analysis procedure, any cross-term effects on the phase of L_{2,3}-edge SEXAFS data from any atom (which, it turns out, will only be important if the atom is in the atop adsorption geometry), can be removed using linear combinations of polarization-dependent data [61].

Related to the above effect on phase is the (p→d)(p→s) cross-term effect on the amplitude of L_{2,3}-edge SEXAFS data. While this effect, too, was empirically shown to be smaller than that calculated for I, it is one that cannot be removed. A general procedure, therefore, which also involves linear combinations of polarization-dependent data, was outlined for determining adsorption sites with a reliability comparably to that using K-edge data.

Regarding adsorption site assignments in general, those systems exhibiting well-defined higher-neighbor distances can usually allow the site to be determined without use of SEXAFS amplitudes. However, such systems are more the exception than the rule, and the additional information provided by studying the polarization dependence of both the phase and amplitude more than justifies the effort. Furthermore, while inherently less reliable due to possible factors affecting non-transferability of amplitudes, the use of absolute amplitudes from either model compounds or even simulated data [61] can give important verification of site assignments. In some cases, notably L_{2,3}-edge data, having such complementary information is a requirement.

Finally, some comments are in order about systems containing distances separated by \( \lesssim 1 \) Å. The first step in analyzing an average of other distances is to recognize its existence in the data. The tell-tale signs are an anomalous amplitude function that contains nodes or that is displaced overall in \( k \) and an anomalously large distance that is also anisotropic. Examples are found in [37, 53, 54, 66, 75, 78, 81]. The need for reliable model compound EXAFS and polarization-dependent SEXAFS data here is obvious. If the difference between only two distances is \( \lesssim 0.2 - 0.3 \) Å, it is possible to get approximate values for each by using simple weighted averages [37, 53, 54]. This procedure can suffer if there are two different damping factors involved or if there are other modifications of one of the distances being averaged, e.g., substrate relaxation, but this is less serious if there is additional anisotropy to isolate the two shell [54, 75, 81]. A more reliable method of obtaining the individual distances is a multishell approach [59, 60, 67, 78], because the damping factors are individually adjustable and more than two distances of any value can be analyzed. In addition, data containing high-Z atoms whose Ramsauer-Townsend resonances can prohibit use of simple Fourier-filtering techniques can usually be analyzed reliably. As with all multi-parameter fitting routines, however, care must be taken to avoid false local minima and overconfidence in possibly unphysical results.

### C. INHERENT AND PRACTICAL LIMITATIONS

An inherent feature of a SEXAFS measurement is that it averages over all configurations of the absorbing atom. It is therefore essential that, whenever possible, the atom or molecule of interest be in a single configuration. This is the underlying reason behind careful sample preparation and characterization procedures; if not adequately carried out, they can only create self-imposed limitations. There are, on the other hand, situations where a distribution of local configurations, i.e., static disorder, is generic to the system itself. Examples include incommensurate overlayers [74], randomly distributed clusters on a surface [40, 48, 74], or inseparable coexistence of multiple phases at higher coverages [29, 40, 48, 49, 50, 52, 62, 64].

A different category of systems exists in which the presence of multiple distances within a single configuration can limit the accuracy of a given bond length. This occurs when the distances are separated \( \lesssim 1 \) Å , which is the approximate practical limit for isolating different shells using conventional Fourier-filtering procedures. Examples of systems with such closely-spaced distance are semiconductor [37, 53] and open metal substrates [54, 75, 81], higher coverages of adatoms [78], and molecular adsorbates occupying low-symmetry sites [66, 67, 68]. As discussed above in section B, a multishell analysis [59, 60, 67, 78] is generally the
most reliable approach, but the degree of reliability clearly depends on the complexity of the particular system and the quality of the data. For example, configurations in which there are only two distances separated \(<0.2\ \text{Å}\) or in which there is azimuthal substrate anisotropy, even a single-shell analysis with appropriate averaging \([37]\) can provide reliable results to \(<0.03\ \text{Å} \) \([54,75,81]\). In systems with more than two distances, or more importantly, with data limited in length or statistics, even a multishell analysis can give results that are reliable to only \(\pm 0.05\ \text{Å} \) \([60, 66, 67, 68, 75]\). By analogy with bulk EXAFS measurements containing multiple distances, it appears that data quality will be the limiting factor in the majority of cases.

Most of the factors affecting data quality in terms of practical or inherent limitations of detection schemes have already been discussed in section B. An important factor affecting all of those considerations, but not specifically mentioned, is the effective total photon flux. If it is too low, requiring too much time for collection of appropriate statistics, systematic errors such as beam motion, monochromator drift, sample degradation, or incomplete beam normalization all can adversely affect the measurement. Typical minimum values required for a SEXAFS experiment are \(\geq 5 \times 10^{10}\) photons/sec within the measured sample area, \(\leq 12\) hr total summed data, and \(\leq 0.3\%\) statistics (\(\geq 10^5\) total counts/pt) in the measured edge jump. Accordingly, SEXAFS measurements from low-Z atoms (\(Z < 10\)) using FY detection still appear to be out of practical reach with presently available fluxes (the reduction in photon flux reaching the sample arises from the ubiquitous C and O absorption on the beamline optical elements). This limitation makes FY the next-best detection scheme for these systems until further improvements in intensity, e.g., use of undulators, have been realized.

In addition to proper statistics, which is a practical limitation, there are two other factors which inherently limit the information content of the data. One is the data length determined by interfering absorption edges (restrictions due to photopeaks and standing-wave peaks were discussed in section B). While this is a problem for all atoms, it is particularly serious for those of low-Z. Many important materials containing C, N, or O usually contain more than one of each, making the lower-Z atom in that system inaccessible for study with SEXAFS. Furthermore, even is no other neighboring low-Z atoms are present, the relatively shorter bond lengths involved reduce the number of complete \(2\pi\) oscillations, and it is this which establishes the overall reliability of the SEXAFS phase. In practical terms, this means that a longer data range will be required (typically 400 eV above the edge) in order to obtain phase information comparable to that from a system with a longer distance. The second inherent factor limiting the information content of the data is the backscattering amplitude. For similar atoms in the same system, e.g., GaAs\([23]\) or Co and Cu\([74]\), it is difficult to distinguish between them without additional information. For high-Z atoms which exhibit Ramsauer-Townsend resonances that overlap neighboring shells in the Fourier-transformed data, a multishell analysis is required \([59, 60]\). For low-Z atoms whose backscattering amplitudes are very weak relative to the other atoms in the system, it is very difficult to determine distances between them. In some favorable cases involving O this problem has been overcome \([28, 29, 75]\), but for C and N it will be much more challenging (H, of course, is out of the question in a SEXAFS measurement). It appears that such information will have to be restricted to low-Z NEXAFS studies and other methods.

A final feature of SEXAFS requiring explicit mention here is its inherent short range nature. This is clearly an asset for studying disordered systems which are inaccessible to other techniques, but it is also a liability if long range information is desired. Even higher-neighbor distances \(<5\ \text{Å}\) are often difficult to determine due to static or thermal disorder. With regard to thermal disorder, however, improvements may be possible. Unlike the \(R^{-2}\) and exponential electron loss terms in the amplitude function which the experimentalist cannot control, the exponential Debye-Waller term is, obviously, temperature dependent. Several recent studies of O on Ni\([110]\) \([75]\), O on Cu\([110]\) \([28]\), and Cl on Ag\([111]\) \([78]\), all taken at near-liquid-nitrogen temperature, gave evidence of higher-neighbor distances up to \(\sim 5\ \text{Å}\).
Of particularly significance is that the Cl-Ag(111) system was also found to exhibit an anharmonic Debye-Waller factor, i.e., the apparent CI-Ag bond length increased with decreasing temperature. This latter effect is undoubtedly an exceptional case since the Ag-Cl bond is known to be unusually ionic and vibrationally soft, but its presence nonetheless underscores an essential message for all SEXAFS experiments. Measurements at lower temperatures are highly desirable, not only for testing anharmonicity, but for improving data quality by including higher distance shells.

IV. ACCOMPLISHMENTS

This section summarizes the variety of results obtained by SEXAFS as of this writing. Rather than presenting a list of bond lengths and other structural findings which may depend on coverage, temperature, sample preparation, etc., the results have been grouped into categories of common theme.

A. RESOLVE PROBLEMS

The direct determination of bond lengths and adsorption sites by SEXAFS has resolved several lively discussions in the literature based on interpretations of various experiments which conflict with each other or with theory. These studies include O on Al(111) [29, 33], O on Ni(100) [41], Cl on Ag(100) [43, 44, 78], Cl on Ge(111) [47], O on Cu(110) [54, 28], and O on Ni(110) [75, 76]. These latter two works also identified the controversial adsorbate-induced reconstructions of the substrates.

B. DISCOVER UNUSUAL GEOMETRIES

From numerous LEED studies of adsorbates on metal surfaces, the general rule has emerged that the highest symmetry site needed to continue the next atomic substrate layer is the one that is usually occupied. This rule has been obeyed in the majority of SEXAFS studies of adsorption sites [4, 30, 36, 37, 42, 43, 47, 64, 69, 78, 81, 88] and is expected to be the case for many more studies to follow. There are, however, exceptions to this rule, pictured in Fig. 2, some of which can even be explained *a posteriori*. For brief descriptions of these explanations, the reader is referred to the Appendix, the original articles cited in the caption, and section C below.

C. IDENTIFY UNIFYING PRINCIPLES

One of the immediate aims of any surface structure investigation is to provide information about a particular system which can then be related to other measurements and calculations. Ultimately, it is the unification of these individual efforts into more generalized theoretical concepts which underlies a major motivation for all of them. The realization of this more estimable goal has simply been frustrated by the difficulty in obtaining surface structural information with sufficient accuracy. The need for high accuracy is that all but the most pathological bond length changes occur within typical limits of ±0.15 Å, so values accurate (not precise) to at least ±0.03 Å are required. Though the overall variations in bond length are small, they are no less significant than the small changes between total energy calculations of two very different structures: both are examples of small differences between large numbers which contain much information and require high accuracy. Some of the difficulty in obtaining this accuracy is becoming history, but on the scale of what structural data are needed, such information is still very meager. With these qualifiers said, an attempt at unifying some of the scant information provided thus far by SEXAFS is given in this section.

A common concept for describing the nature of a bond is its ionicity or covalency. Generally speaking, ionic bonds are characterized by atoms of very different electronegativity with high coordination number to maximize the predominantly coulombic attraction between them. Covalent bonds between atoms of more similar electronegativity are generally shorter and
Fig. 2. Unusual chemisorption geometries found by SEXAFS. Adsorbate atoms are filled circles, substrate surface-layer atoms are open, and substrate second-layer atoms are shaded. Missing atoms in (d) and (e) are dotted. For simplicity, only one adsorbate atom or molecule is shown in each geometry. (a) Ref. 42; (b) Ref. 37; (c) Ref. 37; (d) Refs. 54 and 28; (e) Ref. 75; (f) Ref. 68; (g) Ref. 67 (reanalysis of data from Ref. 66).

more directional as a result of optimizing orbital overlap. So, is the bond between an adatom which occupies a high-symmetry, i.e., non-directional, site on a metal surface with very different electronegativity going to be more ionic than covalent? Is the adsorption behavior of an adatom on a directionally-bonded semiconductor substrate going to be typified more by covalent rather than ionic bonding? Despite this overly simplistic framework for describing the nature of surface bonding, the answers to these question are, for the most part, yes. All generalizations have exceptions (including this one), and it will be seen that the exceptions provide as much useful information as the general rule.

To quantify the degree of covalency or ionicity of a bond in different surface systems, it is useful to have a common basis for comparison. Of several approaches, the simplest one is to calculate the length of a covalent single bond in a bulk-like system and compare it with the measured surface value. The calculated length between an absorbing adatom \( A \) and a backscattering substrate atom \( B \) can be written as [87]

\[
R_{AB}^{(calc)} = r_A + r_B - c |X_A - X_B|,
\]

where \( r_A \) and \( r_B \) are covalent single-bond radii and \( X_A \) and \( X_B \) are electronegativities. \( c \) is an empirical coefficient equal to 0.08 Å if \( A = O \), 0.06 Å if \( B = Si \), 0.04 Å if \( B = Ge \), and zero.
all other times (only those cases needed for this discussion are given here). This expression
and its coefficients represent a hybrid of assumptions made in [87] and, as stated there, is not
without uncertainty. Since it is trends rather than absolute values that are of interest here,
however, the simplicity and consistency of this approach outweigh its other shortcomings.
The basic idea behind the use of covalent single-bond radii, after correcting for electronegativity differences, is that deviations from the calculated values should be indicative of either ionicity or multiple bonding: if $R_{AB}(\text{expt})$ is larger than $R_{AB}(\text{calc})$, then the $A-B$ bond is more ionic, while a smaller $R_{AB}(\text{expt})$ value would suggest greater covalency, i.e., double-bonded character.

Table 3 summarizes the differences $\Delta R = R_{AB}(\text{expt}) - R_{AB}(\text{calc})$, listing them in rows of monotonic adsorbate electronegativity for each substrate ($\chi_B$ is 1.8 or 1.9 for all substrates shown). The quoted errors of the $\Delta R$ entries due to $R_{AB}(\text{expt})$ range from 0.02 - 0.04 Å, with the largest sources of uncertainty coming mainly from the bulk model compound distances; exceptions to this are noted below. Values deviating from trends within a given column or row have been italicized and are separately discussed.

Starting with the metal substrates, $\Delta R$ generally increases with increasing $\chi_A$, reflecting increasing ionicity. That this rule should be obeyed may not be surprising, but that the measured surface bond lengths are actually observed to obey it is, particularly in view of the sizes of the $\Delta R$ values and their trends. The exceptions to this trend, however, need some discussion. The $\Delta R$ value for O on Cu(100), while positive, is somewhat less so than that for Cl on Cu(100). The deviation is not large and may simply be a breakdown in the simple correlation, but this controversial system may also exhibit a possible dependence of O-Cu(100) distance with surface treatment as has been recently suggested [65]. The $\Delta R$ value for I on Ni(100) is much more positive than even that for O on Ni(100). The difficulties reported in [60] due to overlapping I-Ni and I-I shells in the data are undoubtedly responsible for this. The very large positive $\Delta R$ value for Cl on Ag(111), on the other hand, deduced

---

Table 3. Degree of surface-bond ionicity between adsorbate $A$ and substrate $B$, as measured by $R_{AB}(\text{expt}) - R_{AB}(\text{calc})$ in Å (see text)

<table>
<thead>
<tr>
<th>$B$ $(\chi_B)$</th>
<th>$A$</th>
<th>O</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
<th>S</th>
<th>Te</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(100)</td>
<td></td>
<td>0.05$^a$</td>
<td>0.10$^c$</td>
<td>0.08$^k$</td>
<td></td>
<td>-0.03$^l$</td>
<td></td>
</tr>
<tr>
<td>Ni(100)</td>
<td></td>
<td>0.12$^b$</td>
<td>-0.06$^d$</td>
<td>0.21$^i$</td>
<td>-0.05$^k$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(111)</td>
<td></td>
<td>0.12$^d$</td>
<td>0.05$^k$</td>
<td>0.04$^i$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag(111)</td>
<td></td>
<td>0.27$^e$</td>
<td>0.10$^j$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si(111)</td>
<td></td>
<td>-0.06$^f$</td>
<td>-0.01$^m$</td>
<td></td>
<td>-0.08$^m$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge(111)</td>
<td></td>
<td>-0.09$^f$</td>
<td>-0.02$^m$</td>
<td></td>
<td>-0.13$^m$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Ref. 64 $^b$Ref. 41 $^c$Ref. 43 $^d$Ref. 88 $^e$Ref. 78 $^f$Ref. 47 $^g$Ref. 37
$^h$Ref. 69 $^i$Ref. 30 $^j$Ref. 60 $^k$Ref. 4 $^l$Ref. 36 $^m$Ref. 42
from SEXAFS data which did not encounter such difficulties, clearly reflects the very ionic nature of the surface bond. With perfect hindsight, this result is only to be expected on the basis of the analogous trend observed between the more covalent Ni and Cu halides containing 3- or 4-fold coordinated halogens and the more ionic Ag halides with octahedral NaCl structures (I in the more covalent compound AgI, however, is 4-fold coordinated, of course).

Including the semiconductor substrates and looking down the column for Te, the negative \( \Delta R \) values for Cu(100), Si(111), and Ge(111) are consistent with the small electronegativity differences between A and B and with the likelihood for partial double-bonding character of a divalent chalcogen. That \( \Delta R \) is positive for Te on Cu(111) is consistent with the unusual local adsorption geometry in which Te was found to be 6-fold coordinated, see Fig. 2(a). The correlation of ionicity with high coordination again appears to be obeyed.

The final interesting exceptions to emerge from Table 3 are the negative \( \Delta R \) values for Cl on Si(111) and Ge(111). Compared with either the \( \Delta R \) values for Cl on the metal substrates or those for Te and I on these semiconductor surfaces, a positive \( \Delta R \) would be predicted for such an electronegative and monovalent atom. The suggested partial double-bonding nature of the Cl-Si(111) or Cl-Ge(111) bond was, however, anticipated many years ago in a discussion of chlorosilanes [89]. While the resonance structures written then in terms of hyperconjugation are perhaps more easily understood here in terms of d-orbital occupation, the essential message that strongly covalent partial double-bonding character occurs in these systems is clear. Interestingly, Si-Si double bonds on the Si(111)2X1 surface [90], a highly unlikely concept several years ago, now appears to be accepted lore.

Bulk bond lengths depend on coordination number, and so too should surface bond lengths. Table 4 summaries those values determined by SEXAFS for which an adsorption site has been established on more than one face of a given substrate. The corresponding \( \Delta R \) values for each structure are plotted as a function of coordination number in Fig. 4. An

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>Cl</th>
<th>Te</th>
<th>O</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(100)</td>
<td>2.69(4)(^a)</td>
<td>2.37(4)(^b)</td>
<td>2.62(4)(^d)</td>
<td>1.94(4)(^f)</td>
<td></td>
</tr>
<tr>
<td>(111)</td>
<td>2.66(3)(^a)</td>
<td>2.39(3)(^f)</td>
<td>2.69(6)(^d)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(110)</td>
<td></td>
<td></td>
<td></td>
<td>1.84(2)(^f)</td>
<td></td>
</tr>
<tr>
<td>Ni(100)</td>
<td></td>
<td></td>
<td></td>
<td>1.96(4)(^d)</td>
<td>2.23(4)(^h) (^j)</td>
</tr>
<tr>
<td>(111)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.20(3)(^j)</td>
</tr>
<tr>
<td>(110)</td>
<td></td>
<td></td>
<td></td>
<td>1.85(2)(^j)</td>
<td>2.10(1)(^j)</td>
</tr>
</tbody>
</table>

* only SEXAFS data for which adsorption sites have been determined from different faces of a given metal are quoted

\(^a\)Ref. 30 \(^b\)Ref. 43 \(^c\)Ref. 88 \(^d\)Ref. 42 \(^e\)Ref. 64
\(^f\)Ref. 54 \(^g\)Ref. 41 \(^h\)Ref. 75 \(^i\)Ref. 36 \(^j\)Ref. 81
immediately apparent trend is that, with one exception, the surface bond lengths increase with increasing coordination number. As with the correlation between $\Delta R$ and $\chi_A$ above, this is just what is expected on the basis of increasing relative ionicity, or conversely, decreasing bond order $[91]$. The exception to this trend is Cl-Cu(100) versus Cl-Cu(111), for which no obvious explanation emerges. However, it may be significant that the difference in bond length between these two values is only 0.02 Å and that the individual measurements, quoted to ±0.02 Å, were taken at different laboratories; by contrast, the I-Cu, Te-Cu, and S-Ni data were all taken under identical conditions and referenced to each other (the O-Ni and O-Cu data are sufficiently different so that these considerations are minimal). Of course, there is also the possibility that the simple correlation of bond length with bond order cannot be pushed too far. Further tests of this trend with additional data, as well as with other more refined correlations, are anticipated.

Lastly, in addition to looking at surface bond lengths as a function of adsorbate, substrate, and crystal face, there have been several studies of its variation with coverage. For O on Ni(100) at $\leq$0.2 and $\sim$0.33 ML, giving p(2x2) and c(2x2) structures $[41]$, and for Cl on Ag(111) at $\sim$0.33 and $\sim$0.66 ML, giving disordered and weakly ordered $(\sqrt{3}\times\sqrt{3})R30^\circ$ structures $[78, 79]$, the O-Ni(100) and Cl-Ag(111) bond lengths are unchanged to ±0.03 and ±0.01 Å, respectively. The latter result is particularly intriguing in view of the expected bond-length effect due to the nearest-neighbor Cl-Cl repulsive interactions at 0.66 ML. No change in adsorption site with coverage was reported for the above systems. A small bond length increase of $\leq$0.1 Å was observed $[53]$ at $\sim$0.25 and $\sim$0.5 ML for Te on Si(111) relative to that measured at $<1$ ML $[37]$, which appears to be due to a small distortion of the adsorption site but requires additional analysis to quantify. A unifying principle based on three studies can hardly be meaningful, but a possible (obvious) concept to consider for
testing in future work is that bond length changes with coverage in strongly chemisorbed systems of high symmetry are less probable than those in weakly chemisorbed systems of low symmetry.

D. STUDY OTHER PHENOMENA

The variety of different behavior observed between an adsorbate A with itself and with a substrate B can be approximately categorized into classes based on their relative strengths of interaction at room temperature: (i) physisorption \((B-B \gg A-B \sim A-A)\); (ii) clustering \((B-B \geq A-A > A-B)\); (iii) wetting and epitaxial growth \((B-B > A-A \geq A-B)\); (iv) weak chemisorption \((B-B > A-B > A-A)\); (v) strong chemisorption \((B-B \geq A-B \gg A-A)\); (vi) reactive chemisorption \((A-B > B-B \geq A-A)\). The majority of systems studied with SEXAFS falls into category (v) \([4, 29, 30, 36, 37, 42, 43, 47, 54, 60, 64, 69, 75, 78, 81, 88]\), with some in (iv) \([37, 48, 66, 68]\), two in (ii) and (iii) \([40, 74]\), and one in (i) \([91]\). Category (vi), however, differs from all the others in that the substrate structure is fundamentally altered upon adsorption, i.e., a compound is formed. The destruction of the substrate’s long range order prohibits investigation with most other structural probes, but presents little difficulty with SEXAFS. Examples of such studies include Pd \([40]\), Ni \([49]\), and Pt \([50]\) on Si\((111)\) and Ni on Si\((100)\) \([52]\). In all of these systems transition metal silicides are formed. The work on Ni and Pt involved a wide range of coverages from which information about the initially formed silicide was determined and the nucleation mechanism for compound formation was inferred.

E. REVEAL UNUSUAL SUBSTRATE BEHAVIOR

The inherent surface sensitivity of a SEXAFS experiment involving a uniquely absorbing adsorbate atom is generally absent if substrate absorption is studied. There are, however, two ways to obtain substrate structure. The first and obvious one is to use higher adsorbate-substrate distances from very good statistical and preferably low-temperature data. Two examples are the studies of the Ni\((110)\)2x1-O \([75, 76]\) and Cu\((110)\)2x1-O \([28]\) structures in which the “sawtooth” and “missing-row” reconstructions, respectively, were identified. The second, more difficult way to obtain substrate structure without using an adsorbate is to take linear combinations of AY substrate-edge data measured with two different Auger electrons of different escape depth. An example is the study of clean amorphized Si \([63]\), whose medium range surface structure was found to be very similar to that of the single crystal, i.e., the surface had recrystallized following amorphization. As with the underlying reasons for the different adsorbate-induced reconstructions of Cu\((110)\) and Ni\((110)\), an understanding of this unusual substrate behavior is presently lacking.

V. FUTURE PROSPECTS

If an overview of past and current accomplishments with SEXAFS is made at the right distance, it should be possible to project some of the activity, needs, and directions of future work in the field. Regarding activity, for example, too close a view of Fig. 1 might suggest a levelling off or even a slight decline, but taking a few steps back to the references of this article indicate about a dozen different areas of work actively in progress. A large fraction of this activity is due to the developments and improvements of synchrotron facilities within the last several years. Their greater number and higher quality have been directly manifest in the number and quality of SEXAFS studies from emerging and expanding groups around the world.
The future needs of this burgeoning community are related to the increasingly sophisticated demands of a SEXAFS experiment. Improved synchrotron beam brightness is currently being realized or planned, but with this must come even more beam stability and reproducibility. The additional heat load to the optical elements, particularly the first crystal of a constant-output monochromator, is a problem requiring attention. Towards the higher photon energy end of the spectrum, increased energy resolution will be needed to prevent washing out of higher-frequency structure. The lower end of the spectrum still has to contend with the serious problem of reflected higher-order harmonics from gratings and mirrors. Improved beam intensities with undulators will be an essential requirement for future low-Z SEXAFS studies. More efficient energy analyzers for AY detection will speed up some of the data accumulation time presently limited by some commercial instruments. Also, a more wide-ranged arsenal of sample characterization tools will soon become standard in most systems.

Some future directions for immediate study are obvious from comments on the articles in the Appendix. Other specific areas not yet mentioned but perhaps equally clear are studies of more open metal substrates (bcc) and surfaces with steps. Multiple adsorption sites will undoubtedly occur on these, which could be investigated by taking linear combinations of data and/or analyzed with multishell approaches. Binary semiconductor and insulator surfaces remain to be explored, as do physisorbed and coadsorbed layers. Reconstructed substrates before and after adsorption is an open and challenging direction demanding very high statistics and extended data above an interfering substrate photopeak. Studies of real-time-dependent phenomena presently appear to be several years away, requiring additional improvements in synchrotron facilities and SEXAFS detectors. In view of the accomplishments made since 1976, however, it is difficult not to be optimistic.

ACKNOWLEDGEMENTS

Much of this article is based on personal opinion and experience. For my opinion I take full credit, and blame, but for my experience I am indebted to my collaborators, particularly, Fabio Comin, for having contributed so much to it. I am also grateful to the SSRL staff and administration for their continued support over the years. Finally, I would like to thank Maureen McArdle, who in skillfully typing this impossible article under pressure, has given new meaning to professional endurance under non-synchrotron experimental running conditions.

APPENDIX

Below are brief descriptions of the original articles defined in the Introduction. As stated there, an attempt was made to cover all of the articles published on the subject of SEXAFS. Apologies are therefore tendered to those authors whose work may have been unintentionally overlooked. Theoretical papers are denoted by T, experimental papers by E, and non-definitive papers by N. This latter category includes work which is either preliminary (and may or may not have led to a more complete study) or questionable (for reasons that are discussed). For clarification, descriptions of the sample geometry occasionally refer to the polar angle \( \theta \) defined between the surface normal and the synchrotron polarization direction. Thus, for example, a sample at \( \theta = 90^\circ \) is at normal x-ray incidence with the polarization lying within the surface plane.

1976

\( T \) "Possibility of adsorbate position determination using final-state interference effects" [1]. The idea of using characteristic Auger electrons of an adsorbed atom to monitor its photoabsorption cross section was introduced. This is the non-radiative analog of the
Fluorescence detection scheme [20]. Emphasis was placed on demonstrating that adsorption sites could be identified by looking at the polarization dependence of the anisotropic amplitudes for test cases of Se on Ni(100), (111) and (110) faces. It was also shown that complete angular averaging of the scattered adatom photoelectrons over 4π sr, rather than the maximum of 2π sr as would be the case in an actual photoemission experiment, is necessary to obtain the exact EXAFS expression. So far, the limits of this theoretical argument have not been experimentally verified.

T "Extended x-ray absorption fine structure-Auger process for surface structure analysis: Theoretical considerations of a proposed experiment" [2]. The main focus of this work was the use of Auger electrons from the clean substrate to study its structure, with surface sensitivity argued to derive from the <10 Å escape depths of those electrons. However, a surface layer is typically ≤5 Å thick, so for escape depths of 5 Å (10 Å) the surface layer would constitute only <40% (<14%) of the total measured signal and would therefore have to be separated from the bulk. [As it turned out, this separation was demonstrated nine years later.] The suggestion of detecting the Auger electron from an adsorbate overlayer, as in [1], was also mentioned.

1977

N "Basic principles of EXAFS applied to simple and complex systems" [3]. The application of Auger electron detection to measure adsorbate structure on a single crystal was demonstrated for I on Ag(111). This system was chosen because the 1/3-monolayer (ML) Ag(111)√3×√3R30°-I structure had been previously studied by LEED, thus providing a basis for comparison, and because the iodine L2 edge at 4.5 keV was compatible for study with the most intense synchrotron radiation beam line at that time (at SSRP a doubly-bent focusing mirror and x-ray double-crystal monochromator, both in He atmosphere, were separated from the UHV chamber by a Be window). In this preliminary report the absence of a LEED apparatus to verify the 1/3-ML overlayer structure prevented direct comparison with the earlier LEED work. Subsequent studies, in fact, confirmed that the overlayer coverage was ≥1 ML and that simply following dosing prescriptions used by other workers with a different vacuum system gives only qualitatively reliable coverages. The acronym SEXAFS was coined.

1978

E "Extended x-ray absorption fine structure of surface atoms on single-crystal substrates: Iodine adsorbed on Ag(111)" [4]. The 1/3-ML Ag(111)√3×√3R30°-I structure was studied using the I(L3M4,5M4,5) Auger electrons as in [3], but here the system was well characterized with LEED. Also, the measurements in [3] were run under parasitic synchrotron operating conditions whereas in [4] small amounts of dedicated beam at SSRP became available. The I-Ag(111) bond length, empirically determined using the bulk AgI phase shift, agreed well with the earlier LEED result but was much more accurate. The uncertainty of ±0.03 Å was limited mainly by statistical noise. The adsorption site was assigned to be the 3-fold hollow using an absolute amplitude comparison with AgI. The amplitude expression used for the L2,3-edge surface data neglected the (p→d)(p→s) cross term, but as shown in later studies this effect is negligible for the 3-fold hollow site.

N "EXAFS in photoelectron yield spectra and optimization of the photon glancing angle" [20]. K-edge EXAFS data from polycrystalline Cu measured by conventional transmission and by total electron yield detection modes were compared in greater detail than previous studies and were shown to be identical in phase but not in amplitude. The equivalence in phase results from the fact that it is mainly the inelastic secondaries created
by the EXAFS-carrying Auger electrons which comprise the total yield (TY) signal. [In a sense, TY is a tertiary measure of EXAFS: photoelectron scattering (primary process) → Auger electrons (secondary decay process) → secondary electrons (tertiary scattering process).] The differences in amplitude were not explained. Although this work dealt primarily with bulk Cu (thus the reason for it being categorized as a non-definitive SEXAFS study), it did emphasize that TY detection from an adsorbate edge could be used as an alternative method to Auger electron detection [1,2].

N "Surface extended x-ray absorption fine structure in the soft x-ray region: Study of an oxidized Al surface" [21]. Partial yield (PY) detection was used to measure O K-edge EXAFS from a 30 Å-thick Al₂O₃ film on Al foil. This particular system was obviously chosen because of convenience, but more generally because the important edges of C, N, and O had not been previously studied (a "grasshopper"-design grating monochromator and mirror at SRRL were used). The pass energy and window width of the analyzer were set to measure inelastic secondaries of ~1-3 eV. These electrons have escape depths >50 Å, so this detection mode is essentially equivalent to TY and is not surface sensitive. Detecting the O(KVV) Auger electrons at ~510 eV could not be done because core and valence photopeaks were swept through the analyzer window with increasing photon energy. Theoretical phase shifts were used to analyze the PY data, giving good agreement with crystalline Al₂O₃ samples. Thus, as with [20], this work described a bulk measurement while emphasizing the possible utility of an alternate detection method for SEXAFS. In addition, it demonstrated the feasibility of obtaining EXAFS data from low-Z atoms.

N "Surface EXAFS studies using electron yield spectroscopy: Oxygen on Ni(100)" [22]. These measurements were obtained using essentially the same PY detection scheme as in [21], but from a smaller amount of oxygen which was exposed to a clean single crystal surface. No LEED apparatus was used for characterizing the clean or O-covered surface. The oxygen coverage was estimated from published dosing prescriptions and corresponded to small NiO-like islands ~3 layers thick. The structure of the islands was found to be qualitatively similar to bulk NiO, but quantitatively the O-Ni distance deduced from calculated phase shifts was reported to be 0.16 Å shorter than in NiO. In a follow-up paper [22] this was corrected to be 0.04 Å shorter. Both [21] and [22] are preliminary studies of bulk-like oxide phases.

1979

N "Surface EXAFS investigation of oxygen chemisorption on GaAs(110)" [23]. Measurements from a cleaved GaAs(110) surface exposed to unexcited oxygen were obtained using PY detection, but with an electron multiplier (rather than an energy analyzer) which only accepted secondary electrons of energy above 325 eV. Although this detection scheme gave a smaller total signal than that using TY or PY of low-energy secondaries (<5 eV), the surface sensitivity of these measurements was enhanced because the higher-energy secondaries have smaller escape depths (the secondaries experience fewer inelastic scattering events). The coverage of this system was not known, but comparison of photoemission data here with that of previous work suggests ~1 ML. The SEXAFS data presented were of very low quality due in part to the smaller detected signal and to unfavorable beam conditions. Published interpretations of them, including a more recent reanalysis [11], are therefore not reliable. Even with present beam conditions, unambiguous analysis of this system would still be challenging for O K-edge SEXAFS owing to the very similar scattering of Ga and As and to the comparatively negligible scattering of O.

N "EXAFS studies of the bonding geometry of oxygen on Si(111) using electron yield detection" [24]. PY detection of 3-eV secondaries was used to study the 2x1 surface of a
cleaved Si(111) crystal exposed to excited oxygen. The resulting system, whose coverage was not known, resembled α quartz in bond length but not in amplitude. The quoted effective coordination number was two times smaller than that in α-SiO₂ and the rms displacement was substantially smaller. The unusual implications of these results and the absence of data at different polarization directions to test for systematic errors (see discussion of [30] below) makes this study questionable. This view, and the recognition [11] that presently available improvements make remeasurement and analysis of this system desirable, have stimulated a recent follow-up study [25].

N  "Al surface relaxation using surface extended x-ray absorption fine structure" [26]. This work addressed the question of whether the surface layer of a clean Al(111) crystal was expanded or contracted in the normal direction. Unlike [2], which proposed detection of elastic Auger electrons, inelastic secondaries with different kinetic energy (4 vs 45 eV), and thus different escape depth, were monitored with PY detection. No separation of bulk and surface contributions was made in the standard EXAFS analysis of the data. Al L₂,3-edge absorption was measured up to 50 eV above the edge in a near-grazing incidence x-ray geometry (θ ≤ 10°) to emphasize absorption along the surface normal. The results of this work are problematic for several reasons. Standard EXAFS analysis of a single oscillation at k < 4 Å⁻¹ is not reliable or justified [12], and L₂,3-edges have a nonisotropic amplitude component which makes absorption within the surface layer (as well as normal to it) important [11]. Even low-escape-depth electrons contain a non-negligible contribution from the bulk which must be removed (see above discussion of [2]), and, most importantly, inelastic secondary electrons, regardless of their ultimate kinetic energy or escape depth, result from scattering processes which originate largely within the bulk (see above discussion of [20]).

N  "SEXAFS studies of iodine adsorbed on single crystal substrates" [27]. Preliminary data for 1/3 ML of I on Cu(111) and 1/2 - 1 ML of I on Cu(110) were reported using the same Auger detection as in [4] but with higher quality due to more available and improved dedicated beam conditions. The I-Cu(111) bond length was 0.03 Å larger than that found in subsequent work [30] due to a non-uniform I coverage (this systematic error is similar to that in [29] discussed below). An effective surface coordination number that was also too large was attributed to slightly different escape depths for surface versus bulk atoms, with the surface values being larger. Such an effect on escape depths has been recently reported for O on Cu(110) [28]. Polarization-dependent measurements of I on Cu(110) for an incompletely annealed surface showed predominantly I-Cu scattering along the surface normal but I-I scattering within the surface. The assignment of adsorbed molecular iodine is unlikely and calls for further study.

E  "Bonding of oxygen on Al(111): A surface extended x-ray absorption fine-structure study" [29]. As in previous work, TY was used to monitor O K-edge absorption, but here a surface coverage of ~1 ML was studied and characterized by LEED and photoemission. The reported data quality demonstrated the feasible application of TY to surface concentrations of low-Z atoms using existing photon sources. Two spectra at different polarization directions (θ = 11° and 45°) gave bond lengths differing by 0.05 Å, which is outside usual reproducibility limits. Also, the 3-fold hollow adsorption site assigned from other studies was not confirmed using the polarization dependence of the SEXAFS amplitudes. Although not mentioned in follow-up papers of this work, disagreement between experimental absolute and relative amplitudes and those calculated for the 3-fold site were observed. Part of the reason for these bond length and amplitude discrepancies is that a surface chemisorbed state and a disordered underlayer oxide-like phase were both present at the oxygen coverages studied. The emphasis of this work was on the average measured O-Al bond length, which was empirically determined using a model compound phase shift. Despite its larger error limits, the SEXAFS bond length distinguished between various theoretical calculations and stimulated re-analysis and correction of previous LEED studies.
E "Adsorption sites and bond lengths of iodine on Cu(111) and Cu(100) from surface extended x-ray absorption fine structure" [30]. An empirical procedure was demonstrated for reliably determining adsorption sites using a combination of absolute amplitudes, as in [4], and polarization-dependent relative (i.e., ratioed) amplitudes. Although the absolute values between surface and bulk systems here agreed well, they need not have because EXAFS amplitudes are not chemically transferable [12]. Also, systematic errors due to sample inhomogeneities (e.g., coverage variations or multiple adsorption sites due to incomplete annealing, crystal defects, etc.) were found to alter absolute SEXAFS amplitudes significantly. Relative amplitudes thus provided an important check for such potential problems. TY detection gave much improved data quality even over [27] and allowed study of the 1/4-ML Cu(100)p(2x2)-I system. Variation of the I-Cu(111) vs I-Cu(100) surface bond lengths were also accurately determined. Inclusion of the (p→d)(p→s) cross term in the calculated absolute amplitudes, made in an erratum, did not alter the 3- and 4-fold hollow adsorption site assignments.

N "Surface extended x-ray absorption fine structure by means of photo-stimulated ion desorption: O on Mo(100)" [31]. Desorbed oxygen ions were used to monitor the L1 photoabsorption from Mo surface atoms on a Mo(100) crystal exposed to ~1 ML of oxygen. The desorption process was assumed to result from an interatomic Auger decay mechanism involving surface Mo atoms rather than from electron impact of inelastic secondaries created in the bulk. If the former mechanism had been the general case, the data would have demonstrated photon stimulated ion desorption (PSID) as being a straightforward detection scheme of SEXAFS for not only surface substrate atoms but possibly other systems as well. However, the puzzling result that surface Mo atoms bound to O (ionically or otherwise) were found to have Mo-Mo bond lengths which were essentially indistinguishable from those in the bulk (desorbed O in minority sites was suggested), and the subsequent finding that the bulk-derived electron-impact mechanism can be an important and even dominant competitive process [32], makes this study open to question. So far, PSID detection has not yet been shown to provide SEXAFS information that is unambiguous in origin and interpretation.

E "Structure models for the interaction of oxygen with Al(111) and Al implied by photoemission and surface EXAFS" [33]. The study of [29] was extended to submonolayer oxygen coverage, and photoemission was used to ensure that only the surface chemisorbed state (A) was produced. The submonolayer oxide-like phase (B), formed upon heating the chemisorbed state, was also studied. The adsorption site in A and the coordination number in B were not determined. The O-Al bond length in A was found to be almost the same (0.01 Å) as that in B, but was 0.05 Å smaller than 3 of the 4 quoted values in the as-deposited (i.e., unheated) monolayer system in [29]. A correlation was made between coordination number and EXAFS-measured bond lengths in a variety of Al oxide systems, from which it was inferred that the O-Al(111) bond in A has covalent character.

T "Extra interference effects in SEXAFS" [34]. The question of whether the intensity of elastic Auger electrons is exactly proportional to the photoabsorption cross section was considered theoretically. Two cases were examined wherein similar final states following core hole production could be obtained via different pathways and thus interfere. Significant modifications of experimental SEXAFS amplitudes and distances were predicted to occur as a result of these neglected interferences. To date, these predictions have not been experimentally confirmed.
"Pressure dependent oxidation of Al(111): A photoemission and surface EXAFS study" [35]. An Al(111) surface exposed to similar amounts of oxygen as in [30] but at different dosing pressures was found to give slightly different photoemission spectra. The analysis procedures and quality of the corresponding SEXAFS data were very poor and have been sharply criticized [11].

"Structure determination of c(2x2)S on Ni(100) using polarization-dependent surface extended x-ray absorption fine structure" [36]. The S K edge at 2.5 keV was measured in the well-studied 1/2-ML c(2x2) structure on Ni(100) using S(KLL) Auger electron detection. The SEXAFS data were of higher quality than in [29] and comparable to those in [30] because absence of interfering photopeaks allowed the more surface sensitive Auger detection scheme to be used and because the JUMBO monochromator at SSRL, which opened up the previously inaccessible energy range of 0.8 - 3 keV, provided higher photon fluxes. Absolute and relative amplitudes were shown to identify the adsorption site as in [30], but the greater anisotropy of K-edge amplitudes over those for L_{2,3} edges made site assignments from the relative amplitudes even clearer. In addition, the \( \theta = 90^\circ \) data in this work revealed a higher distance peak in its Fourier transform which was consistent with the 4th neighbor S-Ni shell, thus providing a third and amplitude-independent determination of the 4-fold hollow adsorption site. Both bond length and site agreed well with a variety of earlier results.

"Adsorbate structure on reconstructed semiconductors: Te and I on Si(111)7x7 and Ge(111)2x8" [37]. In a study of bonding trends expected from simple chemical arguments, the application of SEXAFS for determining adsorption sites and bond lengths on semiconductor surfaces was demonstrated for the title systems. The complex and long-range reconstruction of these substrates had made such information unobtainable with other existing methods. The high quality TY data resulted from the enhanced photon fluxes using an 8-pole wiggler. For \( \leq 1 \) ML of I on both Si(111) and Ge(111) surfaces, second-neighbor distances, absolute, and relative amplitudes each identified the 1-fold atop adsorption site. For Te, however, the weaker anisotropy of \( L_{2,3} \)-edge amplitudes and the unresolvable contribution of SEXAFS from nearby Si second-neighbors in the three other high-symmetry sites required the combined use of amplitude and distance information to interpret the data. The sum of first- and second-neighbor contributions was calculated as a weighted average and compared with experiment. Two different and previously unreported sites for a (111) surface were identified, the 2-fold bridge for Te/Si(111) and for Te/Ge(111) the 3-fold hcp hollow, i.e., not the fcc hollow usually found for adsorbates on metal (111) surfaces. Despite its unusual nature, the hcp site assignment was particularly clear owing to the measured anisotropy (0.08 Å) and the anomalously large value (>0.2 Å) of the averaged first- and second-neighbor Te-Ge distances. The I/Si(111), I/Ge(111), and Te/Si(111) results were consistent with a simple picture in which monovalent I or divalent Te saturates the dangling bonds to form a locally unreconstructed (111) surface; in so doing the adsorbates "heal" a clean surface that would otherwise undergo more complex reconstruction. The Te/Ge(111) results do not fall within this picture and still lack an intuitively simple interpretation. Part of the reason for this lack was suggested [37] to arise from adsorbate-induced reconstruction (opposite to the "unreconstruction" due to "healing" in the other systems). Occupation of the hcp hollow has since been calculated [38] and observed [39] to occur in three other systems, with adsorbate-induced reconstruction argued [38] to be the deciding factor. This SEXAFS study showed that unlike adsorption on metals, where bonding is largely nondirectional and occupation of hollow sites is generally the rule, adsorption on semiconductors can exhibit more varied and less predictable behavior.

"Structural studies of Schottky barrier formation by means of surface EXAFS: Pd and Ag on Si(111)7x7" [40]. The application of SEXAFS to metal adsorbates was demonstrated.
The Ag-Si system had been extensively studied by a variety of other surface probes, but structural investigations were lacking in both title systems because depositions of even submonolayer amounts of Ag or Pd removed much of the substrate's long range order. Detecting the L2M4.5M4.5 Auger electrons, SEXAFS from 1.5 ML of as-deposited Pd on Si(111) was seen to give a structure whose Pd-Si distance was very similar to that of bulk Pd3Si. The reduced amplitude of the second-neighbor Pd-Si peak in the Fourier-transformed (FT) data was attributed to the smaller long range order of the Pd3Si islands; the \( \sim 30\% \) reduction of the first-neighbor FT peak was not mentioned. For 2.5 ML of as-deposited Ag on Si(111), Ag metal clusters were identified. Heating 1.3 ML of Ag gave a mixture of Ag clusters and a Ag-Si complex which exhibited polarization-dependent SEXAFS amplitudes and a \( (\sqrt{3} \times \sqrt{3})R30^\circ \) LEED pattern. These preliminary results showed not only the very different behavior of Si with reactive Pd versus non-reactive Ag, but also the utility of providing short range structural information from systems too complex to study with other methods.

E "Structure of p(2x2) and c(2x2) oxygen on Ni(100): A surface extended x-ray absorption fine-structure study" [41]. The dependence of the O-Ni(100) bond length as a function of coverage was studied with PY detection of \( >350 \) eV secondaries to increase the surface sensitivity of the measurements. The motivation for the study came from calculations predicting that the p(2x2) and c(2x2) structures with O in the 4-fold hollow should have very different displacements ( \( >0.6 \) Å) in the normal direction, which in turn should imply different measured bond lengths at \( \theta = 90^\circ (\sim 0.2 \) Å) in the two structures with the shorter bond length also exhibiting a polarization dependence (\( \lesssim 0.2 \) Å). The 4-fold hollow site was identified in the c(2x2) structure using relative amplitudes, but to within \( \pm 0.03 \) Å neither of the bond length predictions was observed in either of the SEXAFS data. These results thus provided definitive evidence for ruling out the proposed theoretical model of different geometries.

E "Unusual chemisorption behavior of Te on Cu(111) versus Cu(100)" [42]. The 1/4-ML Cu(100)p(2x2)-Te and 1/3-ML Cu(111)(2\( \sqrt{3}\times \sqrt{3})R30^\circ \) Te structures were studied with TY and Auger electron detection. In the latter system, Te was found to occupy a novel 5-fold quasi-substitutional site in which Te replaced Cu atoms within the surface layer. With few exceptions involving reactive low-Z atoms, only the highest-symmetry hollow sites had been previously identified, including the Te/Cu(100) system studied here; the large size and comparatively low reactivity of Te make understanding these results particularly intriguing. The SEXAFS data could not account for the doubled unit cell size, i.e., \( (2\sqrt{3}\times \sqrt{3}) \) versus \( (\sqrt{3} \times \sqrt{3}) \). Absence of observed higher-neighbor distances here and in [30] for Te and I on metal surfaces, as opposed to their observation in [36] and [43] (discussed below) for adsorbed S and Cl, was attributed to possible larger vibrational amplitudes of the more weakly bound high-Z atoms. An additional factor not mentioned in [42] could also be the lower energy resolution of the beam at higher photon energies (\( \Delta E = E_{\text{cot}\theta A\theta} \)), which would wash out higher frequencies. These short range limitations of SEXAFS raise the need for further study of the Te/Cu(111) system using more long-range-order probes.

E "Geometry and electronic structures of Cl on the Cu(001) surface" [43]. Motivated by conflicting interpretations of the Ag(100)c(2x2)-Cl structure inferred by a LEED study and by a comparison between calculated and measured photoemission spectra, the analogous Cu(100)c(2x2)-Cl structure was studied using Auger electron detection (Ag was not used because its photopeaks interfered with the Cl(KLL) electrons and because the TY signal gave poor surface sensitivity). In addition to the 4-fold hollow site being clearly identified as in [36], the SEXAFS data also showed the anisotropy of the higher Cl-Cu shells due to an averaging of the 4 third-neighbors in the 2nd layer with the 8 fourth-neighbors in the 1st layer. The SEXAFS structural parameters were used as input to an electronic structure calculation of Cl-Cu(100), which was found to give excellent agreement with detailed
photoemission data. To account for the apparent conflict in the Cl-Ag(100) system, it had been suggested that the Cl-Ag bond length used in the original calculations (obtained from bulk AgCl) was too long by $\geq 0.2 \text{ Å}$, i.e., the Cl-Ag bond on the surface was more covalent than in ionic AgCl. Recent TY SEXAFS data from the Cl-Ag(100) system [44], which overcame the poor surface sensitivity of TY with the higher photon fluxes at the Daresbury synchrotron, did measure a shorter surface Cl-Ag(100) bond, but only by $\leq 0.1 \text{ Å}$, i.e., closer to the largest (and earliest) of the three values previously determined by LEED. Aside from showing that the original Cl/Ag(100) controversy resulted from an incorrect comparison between calculations and photoemission experiments, both Cl/Cu(100) and Cl/Ag(100) SEXAFS studies demonstrated the importance of providing accurate and theory-independent structural information.

1983

"Local structure of Cl on amorphous Si and Ge surfaces" [45]. Chlorine K-edge data were obtained with Auger electron detection from Cl chemisorbed onto silicon and germanium (111) and (100) surfaces which had been extensively Ar$^+$-ion sputtered but not annealed. The surfaces before and after Cl exposure had no long range positional order as evidenced by the absence of either LEED spots or rings. The SEXAFS data, however, were surprisingly anisotropic and closely resembled the K-edge data observed for Cl on well-ordered Si(111)7×7 and Ge(111)2×8 surfaces discussed below [47]. These preliminary measurements of strong bond orientational order on nominally disordered surfaces raised two unexpected possibilities: either the Cl chemisorption process itself was responsible for locally reorienting the disordered surface bonds, or the dangling bonds of the clean amorphized surface had already been reoriented prior to Cl chemisorption. As determined in later work [63], the latter situation was actually the case.

"Polarization-dependent phase and amplitude interference effects in the L$_{2,3}$ surface extended x-ray absorption fine structure" [46]. The effect of the $(p \rightarrow d)(p \rightarrow s)$ cross term on the phase and amplitude of the L$_{2,3}$-edge SEXAFS signal was considered. The study was motivated by the apparent disagreement observed between relative amplitudes of experimental Ag/Si(111) data (see [48] below) and those obtained from simulated data. The latter were generated using calculated phase shifts and a previously used approximation [27, 37, 42] in which the phase of the cross term was taken to be the same as that of the dominant $(p \rightarrow d)$ term, so that the two terms simply add. The approximation was argued to be incorrect because the calculated phases of the two terms were slightly different, resulting in a polarization-dependent change in the net phase and a larger effect on the amplitude. The approximation was further argued to lead to significant bond length errors and erroneous adsorption site assignments for particularly anisotropic geometries, some of which had been identified in the earlier analyses of I and Te L$_{2,3}$-edge data [37, 42]. The conclusions of this study were examined in a later paper [61].

"Direct structural study of Cl on Si(111) and Ge(111) surfaces: New conclusions" [47]. Cl K-edge measurements as in [45] showed that Cl occupied the 1-fold atop site on annealed Si(111)7×7, annealed Ge(111)2×8, and quenched Si(111)$(\sqrt{19} \times \sqrt{19})$ surfaces. The conditions of K-edge absorption from atop adsorption yielded the maximum SEXAFS anisotropy that could be observed, i.e., essentially no first-neighbor SEXAFS at $\theta = 90^\circ$. It was, in fact, these findings which stimulated the attempt in [45] to study a contrasting Cl/(Si,Ge) system that did not exhibit such strong anisotropy. The SEXAFS-determined atop site agreed with theoretical interpretations of earlier photoemission data for the Si(111)7×7 surface and subsequent data for the Ge(111)2×8 surface. However, what provided the initial motivation for this SEXAFS study were the earlier photoemission measurements for Cl on cleaved Ge(111)2×1 and quenched Si(111)$(\sqrt{19} \times \sqrt{19})$ surfaces,
which did not appear to be consistent with atop adsorption; these data are still unexplained. The simplicity of the SEXAFS results for the geometric structure of the Cl-covered quenched system suggests that it is the complexity of its electronic structure which is the problem, while the absence of SEXAFS data for cleaved Ge(111)2x1 keeps open the possibility that different adsorption behavior may occur on that surface. Such studies remain to be performed.

N "Structure of the Ag on Si(111)7x7 interface by means of surface EXAFS" [48]. The preliminary study of [40] was extended to systems of 1/3-ML Ag deposited on Si(111) at room temperature and to 0.6 ML followed by heating to 400 °C. Emphasis was placed on these lower coverage data to minimize the complications of coexisting Ag metal clusters which were readily observed >1 ML. The FT data <1 ML, however, contained sufficiently large noise components at or near distances close to those of Ag metal so that the existence of, and possible interference from, small Ag clusters could not be excluded. The 1/3-ML data were particularly noisy (see discussion of [53] below). The reported anisotropic Ag-Si bond lengths (0.02 Å) and the lack of agreement with calculated relative SEXAFS amplitudes for the 0.6-ML system were both argued to result from the effects of the (p-→d)(p-→s) cross term in the L2-edge data and were taken as supporting evidence for the assignment of an interstitial adsorption site. Absolute amplitudes to confirm this assignment were not reported due to the absence of a model compound. In a later work [61], however, the cross-term effects were shown to be negligible, a procedure for distinguishing between the various sites in question without model compounds was presented, and the potential effects from small Ag clusters were pointed out. The reported bond length and amplitude results from the 0.6-ML Ag-Si system, in which an ordered phase is known to coexist with a disordered one at near-monolayer Ag coverages, is reminiscent of the two phases in the O-Al system discussed above [29]; in an extension of [29] to lower O coverages, photoemission was used to verify the absence of the disordered phase [33]. Further characterization (analogous to [33]) of this Ag-Si system, including higher quality SEXAFS data at lower coverages, is needed for definitive structural identifications of the ordered and disordered phases.

E "Structure and nucleation mechanism of nickel silicide on Si(111) derived from surface extended x-ray absorption fine structure" [49]. Ni(KLL) and Ni(LMM) Auger electron detection was used to study the reaction of 0.5 - 5 ML of Ni deposited onto room temperature Si(111)7x7. This system is like Ag on Si in that it had been previously well studied and still lacked structural characterization, but is more like Pd on Si in that it is an example of reactive chemisorption leading to compound silicide formation. The intensity and shape of the 0.5-ML SEXAFS K-edge amplitude function was found to be almost identical in shape and intensity to that measured in bulk NiSi2. Along with a comparably measured Ni-Si distance, this was shown to establish the local chemisorption geometry of interstitially imbedded Ni. Such a site is similar to the one reported in [48] for 0.6 ML of Ag heated on Si(111) and to the one recently reported for 0.8 ML of Pt on room temperature Si [50]. At higher Ni coverages the intensity of the SEXAFS amplitude function decreased dramatically, and was explained by the creation of anti-site defects i.e., Ni and Si interchanging sites within the NiSi2 structure (the amplitude is reduced because the Ni and Si backscattering phase shifts are almost exactly antiphase). The SEXAFS structure of the as-deposited silicide <1 ML was shown to account for a variety of other measurements which, coupled with the higher coverage data, led to a proposed silicide nucleation mechanism for coverages <5 ML. Recent interpretations of ion backscattering data [51] have challenged the SEXAFS results, arguing instead for thin Ni2Si islands (∼4 Å) whose possible Si-rich skins could have biased the SEXAFS data. These suggestions cannot be valid because even the lower energy Ni(LMM) electrons have escape depths >15 Å , making the SEXAFS data insensitive to such possible effects. Furthermore, recent TY SEXAFS measurements [52] (whose sampling depths are even longer) from samples with up to 20 ML of Ni, along with bulk EXAFS measurements from Ni2Si [52], collectively ruled out the conclusions of [51] and confirmed those of [49].
"SEXAFS studies of adsorbate structure on Si and Ge surfaces" [53]. Interest in determining the possible coverage dependence of the unusual 2-fold bridge site for Te on Si(111)7x7 found in [37] motivated a study of the Si(111)(√3×√3)R30°-Te structure at ~1/4 ML (a mixture of 2x2 and 3x1 structures was formed at ~1/2 ML). The low Te concentration for a 1/4 ML on Si(111), corresponding to ~1/10 ML on a fcc metal (111) surface, required ~10 h of summed data to achieve the reported high signal/noise; Te(L3M4,5M4,5) Auger electron detection and a wiggler beam line were used. For comparison, this system was similar to the 1/3-ML Ag-Si system in [48], but the JUMBO beam line used in that work delivered about ten times less intense beam, thus explaining the difficulty there with noise. In the preliminary study of [53], the 2-fold bridge site was again identified for the 1/14 ML system, but the averaged first- and second-neighbor Te-Si distance was somewhat longer than found for ≤1 ML. Using a simple weighted averaging procedure as in [37] to separate these closely spaced (≤0.2 Å) distances, the bond lengthening was attributed to a slight tilting of the Te. However, this explanation is not unique. To confirm the origin of this effect will require more accurate knowledge (and thus a more refined analysis, e.g., [59]) below) of the distance between Te and the second-neighbor Si atom in the (possibly relaxed) Si second layer.

"Azimuthal- and polar-angle-dependent surface extended x-ray absorption fine structure study: (2x1)O on Cu(110)" [54]. As in [37] and [53] for Te on Si(111), a low symmetry 2-fold bridge site was identified using relative amplitudes of weighted averaged first- and second-neighbors whose distances differed by only ≤0.2 Å. This study for O on Cu(110), however, had a number of noteworthy distinctions. The measured adsorption site along the [100] bridge, which is not the high-symmetry hollow usually found on metals, had been a source of controversy in earlier studies. The low symmetry of the substrate allowed the site to be readily determined not only from the usual polar (i.e., θ) dependence of the amplitude but also by its azimuthal variation. The higher anisotropy of the K- rather than L2,3-edge absorption also allowed the individual first- and second-neighbor distances to be better determined despite the simplicity of the analysis. This study further marked the beginning of SEXAFS measurements outside SSRL. The high quality first- and second-neighbor data from the 1/2-ML system was obtained by detecting the PY of secondaries >400 eV using the new SX-700 monochromator at BESSY. The inability to distinguish between the various models of adsorbate-induced substrate reconstruction, due to the lack of comparably low-noise data at higher distances, has been recently removed by additional experimental improvements [28]. The observation of a fourth-neighbor FT peak without a corresponding third-neighbor peak was taken as strong evidence for a missing-row Cu reconstruction.

"Surface EXAFS of the (2x1) oxygen adlayer on Ag(110)" [55]. This study was similar to [54], but because the Ag(110) substrate limited the data range to ~250 eV above the O K edge and, more importantly, because it contributed a much larger background that did Cu(110) in [54], the data quality was considerably reduced. An anisotropy of ~0.1 Å between the first- and averaged first- and second-neighbor O-Ag distances was quoted for two different azimuthal directions, but this was not obvious by inspection in the reported FT data (the anisotropy was, however, clear in the FT data of [54]). The quoted relative amplitudes were also difficult to determine reliably in view of the low signal/noise. Improved data are desirable for a more definitive determination of this structure.

"Auger and photoelectron contributions to the electron-yield surface extended x-ray absorption fine structure signal" [56]. Auger electron and TY detection modes of SEXAFS were compared theoretically and experimentally, from which the equivalence in phase for the two methods was, as expected, confirmed (see above discussion of [20]). The inelastic and
secondary electrons created by the initial photoelectrons, many of which do not contain EXAFS due to phase incoherence, were shown to contribute an increasing background in the measured TY signal with increasing energy above the edge. This additional background was argued to account for the observed amplitude differences between the transmission and TY EXAFS data in [20], where the background subtraction procedure had been determined by the slope of the data below the edge. Using the slope of the background above the edge, which is the usual subtraction procedure, was shown to avoid this potential difficulty.

"Fluorescence detection of surface EXAFS" [57]. The application of fluorescence detection at glancing angles to enhance surface sensitivity was demonstrated for the concentration equivalent of 1-2 ML of Au evaporated on glass. At CHESS, absorption of the Au L₃ edge at 11.9 keV was measured at atmospheric pressure with three gas ionization detectors which monitored the incident, reflected, and fluorescent x-ray fluxes. Despite the narrow 120 μm entrance slit that defined the incident angle, the use of a high-Z adsorbate on a low-Z substrate minimized the background and yielded ~640 eV of high quality data. Metal agglomeration undoubtedly occurred, but no analysis of the data was reported to confirm this. Some obvious advantages of fluorescence detection, e.g., studying samples in nonvacuum environments and in subsurface (>100 Å) regions, weigh against possible interference of single-crystal-substrate Bragg diffraction peaks produced by standing waves. These peaks become increasingly troublesome for mid- to high-Z atoms because the absorbing photon wavelength more readily matches the substrate lattice planes. The peaks are also more easily detected when the solid angle of collection is large. The problem of standing wave diffraction was avoided in this study by using a noncrystalline substrate.

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"Azimuthal and polar angle dependent SEXAFS of (2x1)O and N₂O or Cu(110)" [58]. Using the same procedures as in [54], molecular N₂O was exposed to Cu(110) until the measured PY intensity of the oxygen edge was comparable to that observed in [54] for the Cu(110)2x1-O structure. Since it was known that molecular N₂O dissociatively adsorbs on Cu(110) leaving only O behind, and since the same LEED patterns and SEXAFS distances, amplitudes, and angular dependences were observed for both O- and N₂O-Cu(110) systems, it was concluded that both chemisorption mechanisms are sufficiently energetic to yield the most stable adsorption site, viz., the 2-fold long bridge site.

"A surface EXAFS study of a surface iodide phase on Ni(100)" [59]. I L₃-edge TY data were measured at the Daresbury synchrotron facility from a 1-2 ML surface iodide phase formed on Ni(100). The SEXAFS data were analyzed two ways, one using conventional filtering procedures around a single Fourier peak, and the other using a curve fitting routine involving model calculations of multiple neighboring-atom shells. The latter approach, which had been applied in some bulk systems [12], is semi-empirical in that the calculated phase shifts were modified to fit model compound data. The SEXAFS data were fitted by a curve generated from two shells corresponding to the Ni first-neighbors and the I second-neighbors in bulk NiI₂ at slightly contracted distances. The so-determined first-shell I-Ni distance was in excellent agreement with that obtained from the Fourier filtering analysis, implying a near equivalence of the two methods for at least the first shell. Recently, however, it was shown [60] that data from the 1/2-ML Ni(100)c(2x2)-I structure, which contained only I-Ni scattering, could not be analyzed with a single-shell approach because part of the FT peak from the second-shell I atoms in the model compound NiI₂ fell within the width of the first-shell window function. Therefore, the good agreement between the two methods in [59] was actually fortuitous since the surface iodide phase contained the same second-shell contributions as in NiI₂. In general, the simple Fourier filtering approach will provide accurate first-neighbor distances so long as the second neighbors are separated ≥ 1 Å and an appropriate model compound is used; if one is not available and/or shorter distances in the surface system are involved, e.g., see [57] below, a multishell approach is required.
Bond lengths and coordination numbers from L₂,₃-edge versus K-edge surface extended x-ray absorption fine structure" [61]. Motivated by the conclusions of [46], the effects of the (p→d)(p→s) cross-term on L₂,₃-edge SEXAFS measurements were considered in detail. The experimental cross-term for I, isolated from the I L₂-edge data in [37], showed that the calculated phase shifts used in [46] predicted a cross-term value too large by about a factor of two. This result explicitly justified previous analyses of experimental data [27, 37, 42] in which the cross-term was approximated to affect only the amplitudes but not the phase, and explained why the amplitudes of simulated data were overestimated in [46]. It was also shown that the calculated cross-term effect on the phase corresponded to only a ∼0.01 Å correction in bond length for the worst-case example of atop adsorption; as a result of the method of data analysis used in [46], this effect too was overestimated. Other adsorption geometries were shown to have negligible effects on the phase. In the absence of empirical cross-term values for other elements, a general procedure for analyzing L₂,₃-edge SEXAFS data was developed which allows structural parameters to be determined for any geometry with a reliability comparable to that using K-edge data.

"Room temperature nickel silicide nucleation on Si(111) and Si(100)" [62]. The measurements of Ni on Si(111) in [49] were extended to Si(100) for coverages of 0.5 - 3 ML. Data from the 0.5-ML Ni-Si(100) system closely resembled those in [49] at 0.5 ML, but at higher coverages a similar progressive growth of anti-site defects was not observed. Recent TY measurements [52] at still higher coverages showed that substantial amounts of Ni diffused into the bulk. Possible substitutional occupation of Ni was suggested since no evidence was found for the six second-neighbor Si atoms in the interstitial "adamantane-like" cage geometry proposed in previous work; however, large static/thermal disorder could not be completely ruled out as an alternate explanation for the observed absence of higher shells. While further work is needed to establish the Ni site and the mechanism of Ni diffusion (substitutional migration vs interstitial hopping), these results have already demonstrated the strong differences between the Ni-Si(111) and Ni-Si(100) reactions.

"Local atomic structure of a clean surface by surface extended x-ray absorption fine structure: Amorphized Si" [63]. Motivated by the unexpected results of [45], the application of SEXAFS to a clean surface (originally proposed in [2]) was demonstrated for amorphized Si, prepared by sputtering a Si crystal with 2 kV rare gas ions. Linear combinations of the ~1600-eV KLL and ~90-eV LVV Auger transitions, both produced from the same Si K-shell vacancy (ls→KLL→LVV) but with each with different electron escape depth (25 Å and 5 Å), were used to separate the contributions of the surface from the bulk. The local structure (up to 3 shells) of the amorphized surface layer was shown, surprising, to be nearly the same as that of the bulk crystal, i.e., the nominally amorphized surface had recrystallized. Since e-beam evaporated amorphous surfaces did not show this behavior, and subsequent work [52] on sputtered amorphous surfaces did not either, the recrystallization process still remains to be explained. Apart from the particular system of amorphized Si, the procedures of this study are general since most elements contain both low- and high-energy Auger transitions. However, only ~90-eV of data had been used in [63] (corresponding to the analyzer window for detecting Si LVV electrons), whereas future studies of clean surfaces will require more extended data for quantitative structural information. Furthermore, surface and bulk distances will undoubtedly need to be different by at least 0.1 Å for reliable determinations.

"Structure of c(2x2) oxygen on Cu(100): A surface extended x-ray absorption fine structure study" [64]. PY measurements as in [41] and [54] were measured at SSRL and BESSY from an unannealed O overlayer chemisorbed on a room temperature Cu(100) surface. This seemingly simple system was very controversial due to the variety of chemisorption geometries which had been proposed using other techniques and due to the reported evidence of two LEED patterns with either c(2x2)(≡(√2x√2)]R45°) or (√2x2√2)]R45° symmetry. From the relative SEXAIFS amplitudes at θ = 90° and 45° and the nearly constant O-
Cu(100) bond length, the 4-fold hollow site was assigned to the system measured; a 30% upper limit was quoted for the possible coexistence of another site. Recently, a LEED study using a sensitive detector gave evidence [65] that the \((\sqrt{2} \times 2\sqrt{2})\{45^\circ\}\) structure for O on Cu(100) does not exist. Since the degree of order of the \((\sqrt{2} \times 2\sqrt{2})\{45^\circ\}\) structure was found [65] to vary strongly with the conditions of surface preparation, further SEXAFS measurements as a function of temperature and coverage, particularly at more grazing angles, are desirable for a more complete picture of this system.

N "Evidence for a novel chemisorption bond: Formate (HCO\(_2\)) on Cu(100)" [66]. The application of SEXAFS to chemisorbed molecules was demonstrated at SSRL for the planar, bent formate species O(CH)O\(_2\), produced by dissociation of formic acid on Cu(100). The expected interference of the C 1s photopeak \(\sim 150\) eV above the O K edge was not observed in this work. Instead, the PY detector used with 450 V retardation gave more than 300 eV of data as a result of the detector's low-energy-resolution response which acted to smear out the photopeak and to alter the background only slightly. An averaged first- and second-neighbor O-Cu bond length was reported which was about 0.4 Å larger than any known first-neighbor O-Cu bond; in addition, a small bond-length anisotropy (0.03 Å) was quoted. Comparison of the experimental relative amplitude with that calculated using the measured average bond length led to the assignment of a "cross-bridge" site for the formate species in which the O-C-O plane straddled the Cu-Cu bridge and the O atoms resided almost over the 4-fold hollows. This assignment has been recently challenged [67] as a result of the strong mismatch found between the raw data at \(\theta = 15^\circ\) and simulated data generated from the cross-bridge parameters of [66]. The source of the problem was suggested [67] to be an unphysical change of \(E_o\) (\(\sim 10 - 15\) eV) made between the \(\theta = 15^\circ\) and 90° data in the original analysis. The data were reanalyzed in [67] using a multishell routine, keeping \(E_o\) the same for the two SEXAFS spectra, which is clearly essential, and assigning \(E_o\) to be the same as that in the Cu\(_2\)O model compound, which is arbitrary and likely to introduce some, albeit small (<0.05 Å) errors. A different assignment of a "diagonal-atop" site was made in which C was positioned above a Cu atom and the O-C-O plane lay along the diagonal of two Cu(100) "squares". The revised O-Cu first-neighbor bond length was also found to be \(\sim 0.4\) Å shorter than in [66]. The measurement of an anomalously large average bond length is reminiscent of the hcp hollow site found for Te on Ge(111) in [57], but there a bond length anisotropy had also been observed due to the anisotropic contribution from second-neighbor atoms. An analogous anisotropy is, in fact, apparent in the raw data of [66], but its observation would be obscured in the analysis if \(E_o\) is changed.

E "Structure determination of the formate intermediate on Cu(110) by use of x-ray absorption fine-structure measurements" [68]. An independent study similar to [66] was carried out at BESSY with a Cu(110) surface. As in [54] and [58], the additional use of azimuthal- as well as polar-angle amplitude information significantly simplified the site determination. The formate species was found to occupy an "atop-ridge" site, similar to the recently revised site assignment for Cu(100) in [67] but with the O-C-O plane lying along the ridge of contiguous Cu surface atoms. The averaged first- and second-neighbor O-Cu bond length was found to be close to that determined in [67] and in other formates. The large quoted uncertainty of \(\pm 0.07\) Å was due mainly to the limited range of data above the O K edge (\(\sim 150\) eV) which resulted from the interfering C 1s photopeak in the PY detector. This study, along with [66] and [67], established the feasibility of determining chemisorbed molecular structures while also showing some of the limitations imposed by short data lengths, multiple bond lengths, and electron detection techniques of low-Z atoms.

E "Adsorbate fluorescence EXAFS: Determination of bromine bonding in c(2\(\times\)2)Br-Ni(001)" [69]. As in [57], a grazing incidence geometry was used to study a higher-Z adsorbate on a lower-Z substrate. The poorer signal/noise of the shorter length of data in
this work (~270 eV) compared with that in [57] was due to several factors: an 80 μm entrance slit, an energy dispersive scintillation detector for the fluorescent x-rays with a smaller solid angle of collection, absorption filters, a larger substrate background, and 1/2 ML coverage of adsorbate. The well-ordered Br overlayer was prepared and measured in UHV and was isolated from the detectors by 4-500 μm-thick Be windows. The small solid angle of collection also minimized the likelihood of detecting substrate standing-wave diffraction peaks (see [57]). Analysis of the SEXAFS above the Br K edge at ~ 13.5 keV gave a Br-Ni first-neighbor distance, but no site assignment could be made reliably. Although the quality of these results was not high according to current standards, there were a number of obvious improvements pointed out which could make future studies with this detection scheme more desirable.

"Surface extended x-ray absorption fine structure of low-Z adsorbates studied with fluorescent detection" [70]. The application of fluorescence detection was demonstrated for S K-edge SEXAFS from S and C₂H₄S chemisorbed on Ni(100). These systems were opposite to those in [57] and [69] in that a lower-Z absorbing atom on a higher-Z substrate was studied. The detector, which was a proportional counter isolated from the UHV chamber by a 127 μm-thick Be window with a collection efficiency intermediate between that in [57] and [69], was able to be mounted perpendicular to the incident x-ray beam because the fluorescence yield (FY) background from the substrate was so low. This was a consequence of the comparatively long S Kα wavelength (~5.4 Å) relative to the Ni lattice planes, thereby minimizing substrate Bragg scattering, the large x-ray absorption cross section of the substrate, thereby reducing the scattering volume, and not specifically mentioned in [70] but very important, the absence of interfering Ni Kα fluorescence falling within the ~1-keV energy window of the detector. Direct comparison of SEXAFS data from the 1/2-ML Ni(100)c(2x2)-S structure [36] taken with FY and Auger electron yield (AY) showed improved absolute sensitivity (signal/background) for FY due to the reduced substrate background but no improvement in signal/noise over the AY data. The real advantages of FY detection actually become apparent in two other general cases. The first is studying systems in which Auger and photoemission peaks interfere with one another. This is usually the situation for low-Z adsorbates, but need not be limited to them (see, e.g., Cl on Ag(100) in [44]). The second is studying very low adsorbate concentrations (≤0.2 ML), where data quality is limited not by counting statistics but by systematic errors, e.g., instrumental noise or normalization procedures. FY SEXAFS data from ~0.08 ML of S in C₂H₄S chemisorbed on clean and oxygen-predosed Ni(100) surfaces were cited in [70] as such examples which could not be studied by AY. Unfortunately, FY data collection times and explicit AY data for comparison were not reported (recall that effectively ~0.1 ML of Te had been studied in [53] with AY). It was shown that C₂H₄S on clean Ni(100) dissociated even at 100 K, but it did not dissociate on the predosed surface, presumably because the active 4-fold hollow sites had already been occupied. Recently, using a double differentially-pumped polypropylene window [71] to detect C Kα fluorescence, C K near-edge data from C₂H₄ condensed on Cu(100) were obtained with FY, AY, PY, and TY schemes [72]. This comparison directly showed the improvements in FY due to the lack of normalization difficulties caused by the C absorption on beamline optical elements.

"Multiple bond lengths and short data ranges in SEXAFS and EXAFS" [73]. The effects on the observed phase and amplitude of SEXAFS data containing multiple bond lengths were considered theoretically as a function of differences in bond length and data range. It was shown that unequal contributions to the SEXAFS from atoms at slightly different distances could in some cases lead to apparent bond lengths which fall outside the range of the actual values. This situation, however, is extreme and would probably not go unnoticed in an actual analysis of experimental data. More likely is the case of similar multiple distances leading to anisotropic and anomalously large averaged bond lengths with modified amplitude functions; these have been observed in [37] and [66] and were considered
theoretically in [61]. The important message of this work still remains, though, namely that data of limited range, and particular from molecular species which are likely to occupy low-symmetry sites, cannot be analyzed too carefully.

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E "Crystallographic properties and adsorbate geometries by surface EXAFS" [74]. TY measurements at LURE were obtained from ~1 and ~1/3 ML of Co evaporated on Cu(ll1) surfaces. The motivation was to characterize the structure of a single Co adlayer which had been previously calculated to be magnetically active. The normal incidence Co K-edge data for 1 ML was of high quality and indicative of a two-dimensional Co monolayer with ~6 nearest Co neighbors at distances the same as those in bulk Co, not bulk Cu. Analysis of the grazing incidence data led to a Co-Cu distance which was reported to be 0.04 Å shorter than the Co-Co distance. The measured amplitude function at higher k for the θ = 90° data was suggested to be due to static or thermal disorder, but no definitive distinction could be made. The 1/3-ML data indicated formation of small Co clusters with distances the same as in bulk Co for both polarization directions and coordination numbers of only ~3. Given 3D cluster growth <1 ML and 2D island growth at ~1 ML, and that Co-Co bonding is known to be stronger than Co-Cu bonding, this study demonstrated the dependence of surface wetting as a function of coverage due to the increase in Co coordination (6 versus 3). Unfortunately, the close similarity in Co-Co versus Co-Cu phase shifts makes a more detailed coverage study of this system impractical.

E "Local bonding geometry of O(2x1) on Ni(110): A surface extended x-ray-absorption fine-structure study" [75]. PY data were obtained at BESSY as in [54] using the azimuthal- and polar-angle dependences of the phase and amplitude from O chemisorbed on Ni(110). Experimental improvements led to exceptionally high data quality for the effective ~1/3-ML coverage system. Not only was the long bridge site identified, but the controversial nature of the oxygen-induced reconstruction of the Ni(110) surface was also established. Similar to the observations in a recently improved study of the Cu(110)2x1-0 structure [28], the third-neighbor Ni shell in the FT data was absent; this immediately ruled out the buckled-surface model. However, the fourth-neighbor shell in [75] was approximately half the intensity of that in [28]. This result, supported by relative amplitude information, identified the reconstruction for Ni(110)2x1-0 to be "saw-tooth" in character and also served to confirm the assignment of a "missing-row" reconstruction for Cu(110)2x1-0 [28]. The underlying reasons for the differences in reconstruction remain to be explained. Further refinements of the reconstructed Ni(110)-O surface in terms of tilted O and/or vertically relaxed Ni [75], along with a recent identification of O-O scattering in the data [76], were limited in their reliability due to the shortened range of data from interfering Ni L-edges and uncertainties regarding possible anisotropic electron escape depths (see [28]) and/or Debye-Waller factors (see [77] below).

N "Experimental and theoretical evidence for a strong anisotropy of the surface Debye-Waller factor as determined for a monolayer of cobalt on copper (111) by surface extended x-ray-absorption fine structure" [77]. In an extension of [74], the measurements of the 1-ML 300-K Co data on Cu(111) were repeated at 77K. The value of Δσ² for the θ = 15° data, which reflected only Co-Cu scattering, was ~25% larger than that for the θ = 90° data, which reflected primarily Co-Co scattering. These values, plus those measured from bulk Co and Cu were compared with calculations of Δσ² in bulk Co and Cu and in a model system of an epitaxial monolayer of Co on Cu. On the basis of trends in the calculated and experimental Δσ² values it was argued that the observed difference in Δσ² for the θ = 15° and 90° data resulted from anisotropic force constants between surface versus bulk atoms rather than from differences in bonding between Co-Co versus Co-Cu. The argument is not without ambiguity, however, because not only was the observed Co-Co Δσ² value in the
actual Co/Cu(111) system identical within experimental error to that in bulk Co, but the $\Delta \sigma^2$ value for Co-Cu in Co/Cu(111) was also experimentally indistinguishable from that in bulk Cu. This would simply suggest that the Co-Cu "bond" in Co/Cu(111) is weaker (i.e., softer) than the Co-Co bond. Such an alternate explanation is supported by the findings of [74], where it was found that Co does not, in fact, grow epitaxially on Cu(111) but instead retains the bulk Co-Co distance. This observation, along with the Co clustering found at submonolayer coverage [74], gives direct evidence both for the dominance of Co-Co versus Co-Cu bonding and for the formation of an incommensurate 2D island of Co on Cu(111) whose Co-Cu "bonds" are not simple averages of Co-Co and Cu-Cu (as was assumed in the model calculation of $\Delta \sigma^2$). Additional work is needed for distinguishing more clearly between surface Debye-Waller anisotropy and adatom-adatom versus adatom-bulk bonding.

E "Surface extended x-ray absorption fine-structure: Critical appraisal of a structural tool for adsorbates" [78]. In addition to supplementing some of the preliminary work in [44] for Cl on Ag(100), TY measurements of Cl on Ag(111) were reported for 2/3 and 1/3 ML coverages. These latter data have also recently appeared elsewhere [79]. Anharmonic distortions were observed for the Cl-Ag(111) bond, $\sim 0.06$ Å, similar to that found in bulk AgCl, thereby requiring the Cl K-edge SEXAFS measurements to be made at 100 K. The 2/3-ML system gave a weak $\sqrt{3} \times \sqrt{3}$ R30° LEED pattern, while none was seen at 1/3 ML. A multishell analysis as in [59] was applied to the $\theta = 90°$ data for both coverages. As many as four shells at distances up to $\sim 5$ Å were reported for the 2/3-ML system, including the first- and second-neighbor Cl-Cl distances. A graphite honeycomb structure consistent with the fitted distances was proposed, with Cl occupying the 3-fold hollow sites (unfortunately no other polarization directions were obtained to confirm this site). The 1/3-ML data were fitted using three shells, with the first-neighbor Cl-Cl distance found to be missing and a simple 3-fold hollow occupation again assumed. The first-neighbor Cl-Ag(111) distance was seen to be unchanged with coverage, a surprising result in view of the nearest-neighbor Cl-Cl interactions at 2/3 ML. This low temperature study of a disordered and a weakly ordered system in which multiple distances were identified in both is particularly noteworthy considering that the poorest detection scheme in terms of signal/background, namely TY, was used due to interfering photoemission lines from the substrate.

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