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Surface Structure Determination with ARPEFS

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Abstract

We describe a method of surface structure determination based on oscillations in core-level photoemission intensity—Angle-Resolved Photoemission Extended Fine Structure—with particular emphasis on the use of Fourier transformation. Qualitative comparisons of Fourier power spectra reveal adsorption sites and shortcomings in theoretical calculations; quantitative backtransformation analysis allows accurate bond lengths and bond angles to be determined. Examples are drawn from these similar atomic adsorption systems: c(2x2)S/Ni(100), p(2x2)S/Cu(100) and c(2x2)S/Ni(110).

1. Introduction

Recently [1,2], we introduced a new approach to determining surface structures: Angle-Resolved Photoemission Extended Fine Structure (ARPEFS). This technique is based on photoelectron diffraction: the interference between the direct and ion-core scattered paths for a photoelectron to enter an angular resolving detector. The key features of ARPEFS which recommend it for structure work are:

i) Chemical Specificity: The structural signal is contained in core-level partial cross-section oscillations. By selecting the core level observed, we select the element or even oxidation state of an element to study.

ii) Surface Sensitivity: Using photoelectrons in the 100-500 eV energy range gives good surface sensitivity.

iii) Large Oscillation Amplitude: The detected interference is between direct and scattered waves, giving typical oscillations of 20-50 percent.

iv) High Angular Sensitivity: Each different emission direction yields a different view of the structure; each different combination of polarization direction and crystal orientation gives different emphasis to the scattering atoms.

v) Simple Theoretical Model: The above four experimental considerations combine to greatly simplify curved-wave, multiple-scattering calculations.

vi) Direct Fourier Analysis: The Fourier transform amplitude maps out scattering power versus geometrical path-length difference. The Fourier transform provides a means of displaying the structure

information directly from a measurement.

In this proceedings, we give a brief overview of ARPEFS measurement and interpretation, with an emphasis on structure determination with the Fourier transform.

2. Experiment

We will discuss three atomic surface structures here, c(2x2)S/Ni(100), p(2x2)S/Cu(100), and c(2x2)S/Ni(110). The first system has become the prototypical chalcogenide surface structure, and it serves to verify our methods of analysis. We reported the structure of the S/Cu system in Ref. [1]. The c(2x2)S/Ni(110) system provides an interesting correspondence to the S/Ni(100) system which we discuss below.

All three surfaces were prepared by exposing clean single crystal metal samples to $H_2S(g)$ and warming to 200°C to produce ordered overlayers.

The ARPEFS is derived by measuring a series of S(1s) core-level angle-resolved photoemission spectra for photon energies ~ 2575-3000 eV, typically in steps of 3 eV. The "partial cross section" is derived as the photopeak area normalized for photon flux versus the photopeak energy position. All measurements were made at the Stanford Synchrotron Radiation Laboratory's soft X-ray double crystal monochromator [3] with an electron spectrometer previously described [4].

The fractional oscillations are derived by fitting smooth curves [1] through the partial cross section, I(E), assigning the smooth curve to I_0, and forming

$$\chi(E) = \frac{I(E)-I(E_0)}{I_0(E)} . \qquad (1)$$

To calculate a Fourier spectrum from the $\chi(E)$ curves, the abscissa is converted to momentum (k) where

$$k = \sqrt{\frac{2m}{\hbar^2}} \sqrt{E-E_0} \qquad (2)$$

with E_0 = 11 eV typically. The $\chi(k)$ curve is weighted by k, extrapolated with autoregressive prediction, multiplied by a Gaussian weight and Fourier transformed as described in Ref. [5].

The $\chi(E)$ curves for c(2x2)S/Ni(100) along the [110] (45° polar angle) and [100] (normal emission) crystal directions are shown in Figure 1. Notice the large oscillation size and dramatic difference in character for the two emission angles.

Fourier spectra of these curves are shown in Figures 2 and 3; they are discussed below.

3. Theory

Angle-resolved photoemission extended fine structure (ARPEFS) refers to oscillations in the partial cross section for photoemission due to final state interference. This interference occurs when the photoelectron can find two paths to the detector: the direct path from photoemitter to detector and a path from photoemitter to a nearby atom which can elastically scatter the electron into the

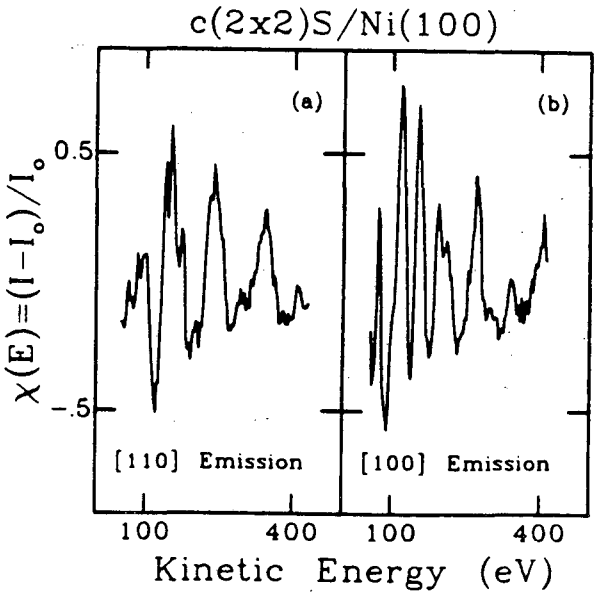

Fig. 1. ARPEFS modulations derived from S(1s) photoemission partial cross-sections. Both curves were measured from the c(2x2)S/Ni(100) system. a) Emission along a [110] direction (45° from normal); b) Emission along the crystal normal.

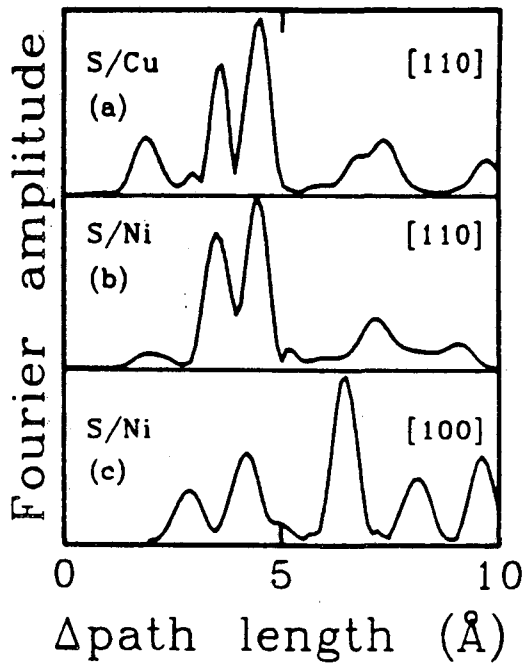

Fig. 2. Autoregressive Fourier transforms of the three ARPEFS curves discussed in the text. Note that a path-length difference of 4.4Å corresponds to a bond length of 2.2Å when $\alpha_j = 173°$. (a) S(1s) ARPEFS from p(2x2)S/Cu(100); detector along [110], $\gamma = 15°$, (b) S(1s) ARPEFS from c(2x2)S/Ni(100); detector along [110], $\gamma = 0°$, (c) S(1s) ARPEFS from c(2x2)S/Ni(100); detector along [100] (normal emission), $\gamma = 20°$. In all curves the intensity below 1.5Å varies with the background function choice and has been disregarded.

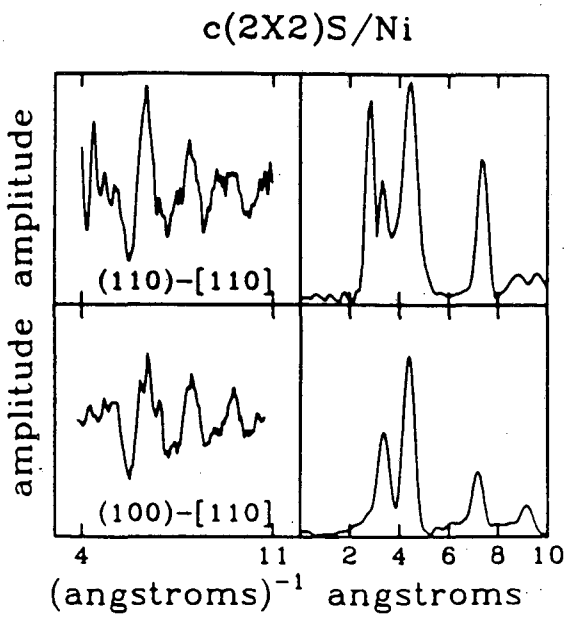

Fig. 3. ARPEFS measurements (left panels) and Fourier amplitudes (right panels) for c(2x2)S overlayers on Ni. Top panels were obtained in normal emission from a (110) crystal. Bottom panels were obtained by measuring along the [110] axis for a (100) crystal surface. The major peaks can be assigned by analogy. Both peaks at 4.4Å are ~180° backscattering: a nearest neighbor Ni for (100) and a second layer Ni for (110). The 3Å features are ~115° scattering: two nearest neighbors for (100) and four nearest neighbors for (110). The 3Å feature for (110) is split by a Generalized Ramsauer-Townsend resonance accentuated by the polarization vector position (~100° to the scattering vector). The 7.5Å features indicate Ni atoms further along [110].

detector.

Consider a (1s) photoemitter at the origin of coordinates with the z axis along the electric vector $\vec{\epsilon}$. If our detector is set at a position labeled $\vec{R}$, then the direct probability amplitude wave will be

$$\psi_o = M(k) \cos\gamma \frac{e^{ikR}}{kR} \tag{3}$$

where M is independent of R and $\cos\gamma = (\vec{\epsilon}\cdot\vec{R})/R$.

If $\vec{a}$ denotes the "bond" vector between the photoemitter and the scatterer, then the scattered wave will be [6]:

$$\psi_{\vec{a}}(\vec{R}) = M(k) \frac{e^{ik|\vec{R}-\vec{a}|}}{ikR} \frac{e^{ika}}{|\vec{a}|} F(\vec{a},\vec{R},\vec{\epsilon},k) \ . \tag{4}$$

Typically, the complex scattering factor, $|F|$, has a large (~.3) amplitude, $|F|$, and small phase, ϕ, so the fractional oscillation is large and has a frequency near the path-length difference, $|\vec{a}|(1-\cos\alpha_j)$:

$$\chi = \sum_j \frac{\psi_o^*\psi_j + \psi_j^*\psi_o}{\psi_o^*\psi_o} = \frac{|F|}{|\vec{a}|} 2\cos[ka(1-\cos\alpha) + \phi] \tag{5}$$

Successful structure determination with ARPEFS relies on this formula. Several physical circumstances collaborate to make this simple form useful for interpreting ARPEFS spectra:

i) The frequency of the cosine is dominated by the geometrical path-length difference. The scattering phase ϕ is usually quite linear with a $d\phi/dk \sim 0.1$Å.

ii) The scattering amplitude $|F|/|\vec{a}|$ (usually) contains little structure.

iii) Among all of the scattering angles which can reflect electrons into the detector, backscattering ($\alpha = 180°$) is strongly favored [7] in the 100-500 eV range. This selectivity is further enhanced by the polarization dependence of the final state.

iv) Multiple scattering is small for all angles except forward scattering [8], where there is little effect on the oscillation frequency.

To the extent that i) and ii) apply, Fourier analysis can contribute to the determination of surface structure; the selectivity iii) insures that the Fourier spectrum will contain predominately a few backscattering path lengths.

An important exception to this simple picture occurs for some scattering angles and energies. At these points—which we refer to as generalized Ramsauer-Townsend resonances [2]—the scattering amplitude $|F|$ falls to zero, and the scattering phase shift ϕ jumps by π. These resonances can complicate the ARPEFS spectrum: the amplitude drop in $|F|$ simulates a beat envelope and can split the Fourier peak for the corresponding path-length differences. On the other hand they may also be a powerful means of determining surface structure. The resonances are sensitive indicators of surface bond angles, as we discuss below.

4. Structure Determination with the Fourier Transform

Given the experimental ARPEFS measurements at a number of emission angles, and an understanding of the physical origin of the oscillation, we must deduce the structure. With these simple atomic surface structures we have been developing the mechanics of the structure determination which should then be applicable to more complex systems.

The Fourier transform of the ARPEFS displays an integrated scattering amplitude versus scattering path-length difference. We must proceed with caution when we interpret the peaks in the transform for a number of reasons:

i) The extended fine structure is only approximately given by a cosine series. The oscillation frequency varies slightly with energy and, more important, the cosine envelope contributes to the Fourier peak shape.

ii) The entire data range contributes to each Fourier coefficient. Inaccurate data points on the end of a spectrum are not ignored by the transform. Care must be taken when comparing two transforms to insure that the transformed range and the weighting functions are identical.

iii) Transforms with different frequency resolution should be compared only with hesitation: when two Fourier peaks with different phases are merged, they need not appear as the sum of two peaks.

iv) The Generalized Ramsauer-Townsend effect (see 4.4 below) can split Fourier peaks.

With these caveats in mind Fourier analysis can be a powerful tool for studying surface structure. In the remainder of this report we discuss four ways the Fourier transform can be used to determine surface structure information from ARPEFS.

4.1 Adsorption Sites from Fourier Spectrum Comparisons

When confronted with an experimental Fourier spectrum our first task is assigning the major features to path-length differences. From the simple theoretical model we expect major peaks for backscattering; these path lengths must be about twice the distance from the emitter to the scatterer. Nearest neighbors scattering through angle further from 180° may also be seen since the photoemitted wave decays very little as it travels towards them. These path lengths must be less than twice a bond length.

Figure 2(b) illustrates such an assignment. The largest peak in the spectrum corresponds to backscattering ($\alpha = 173°$), from a nearest neighbor (path-length difference 4.46Å). At a slightly lower path length (3.2Å), two other nearest neighbors with smaller scattering angles ($\alpha = 135°$) contribute. Two higher peaks signal backscattering Ni atoms further away along [110].

When the adsorption site is unknown, the process of identifying the path-length difference will be more involved (also take note of the Ramsauer-Townsend effect discussed below). A collection of ARPEFS spectra for atomic adsorption will, however, greatly simplify the adsorption site and path-length difference assignment. For example, compare the Fourier spectra in Figures 2(a) and 2(b), both taken along the [110] crystal axis. The striking similarity of the c(2x2)S/Ni(100) and p(2x2)S/Cu(100) spectra eliminates any doubt about the adsorption site of S/Cu. The comparison of the two S/Ni systems in Figure 3 is

novel: the ARPEFS was measured along the same crystallographic direction for two different surfaces. If the local orientation of Ni atoms about S is the same, then the Fourier spectra from the two measurements will be ther same and the site is determined. We deduce that a Ni atom must rest directly below the S on the (110) surface, at a distance close to the S-Ni bond distance for S/Ni(100). Since scattering peaks occur at shorter path lengths, we conclude that this Ni atom must be in the second layer—one atop site would not have shorter path-length distances. Hence we are drawn to the (known) four-fold geometry.

To be sure, these adsorption sites are quite simple, but the principle should apply to more complex systems. Note again two key features of ARPEFS analysis: it is elementally specific and highly angle dependent. We have the potential for measuring a great deal of information about the position of a single constituent of an adsorbate system.

4.2 Comparison of Theory with Experiment in Fourier Space

A second important role for Fourier analysis of ARPEFS is qualitative comparison of theoretical calculations and experimental data. The Fourier transform comparison rapidly reveals over- or under-emphasized path-length differences as an aid to correcting theoretical models. Perhaps more important, by limiting the comparison to short path-length differences, very economical calculations are possible, even for more sophisticated models for electron scattering. Since the angular momentum of the photoemission final state is restricted by dipole selection rules and since multiple scattering is only important in the forward direction, curved wave multiple-scattering calculations can be routinely performed for comparison to experiment.

4.3 Empirical Backtransformation Analysis

The very close analogy between angle-resolved fine structure, (ARPEFS), and the angle-integrated fine structure, EXAFS, leads to the third use of Fourier analysis: backtransformation analysis. The idea and its justification are drawn directly from the experiences in EXAFS [9]; we applied this method to c(2x2)S/Ni(100) and p(2x2)S/Cu(100) in Ref. 1. The Fourier transform separates the ARPEFS into individual oscillations. By isolating a single backscattering Fourier peak and applying a complex backtransformation, the amplitude and argument of the backscattering cosine can be extracted. Then the scattering phase shift ϕ can be subtracted from the total experimental argument to give a line whose slope is the path-length difference. We have applied this analysis to the main 4.4Å scattering peak in S/Ni(110)-[110], using the scattering phase shift derived experimentally from the main peak in the well-known S/Ni(100) system. Thus we determine that the distance between the S atom and the second layer Ni atom on the (110) surface is the same (2.23Å) as the bond distance on the (100) surface.

4.4 Generalized Ramsauer-Townsend Resonance Analysis

Finally, we have been developing an entirely new method for determining surface structure information which is unique to the analysis of ARPEFS. Here we take advantage of an interesting physical feature of electron scattering: the scattering phase shift as a function of wavenumber can pass through the origin in the complex plane for some scattering angles. At these angles, the scattering amplitude falls to zero for some energy and rises again at higher energy. Simultaneously, the scattering phase angle jumps by pi radians. We call these points Generalized Ramsauer-Townsend resonances [2] and they are useful for determining structure because the shape of the scattering phase argument is strongly dependent on angle.

For Ni, a resonance occurs near $k=7\text{Å}^{-1}$ and a scattering angle of 127° scattering angle. For normal emission from the (100) surface, the four Ni atoms closest to S have a scattering angle of ~127°. As the scattering amplitude dips toward zero at $k=7\text{Å}^{-1}$, the Fourier spectrum for this 3.2Å path-length difference is split into two peaks as shown in Figure 2(c). Isolating both peaks and performing the complex backtransformation give the phase jumps shown in Figure 4. It appears that the scattering angle cannot exceed 127°, nor be lower than 125°.

Some important questions must be addressed before we can apply this method to unknown systems with confidence. As we show in Figure 4, plane wave calculations make substantial errors in the position of this resonance: theoretical calculations must have high accuracy if we rely on them for predicting the resonance. Preliminary work with changing the inner potential (E_0) shows little effect on the angle analysis, but this must be verified. Finally, we must confirm that the Fourier processing does not distort the resonance shape.

5.Conclusion.

Angle-Resolved Photoemission Extended Fine Structure promises to be an exciting new method for examining surface structures. We see its most important early role in furthering our understanding of electron scattering and in clarifying adsorbate geometries which baffle other techniques. For both problems, the high selectivity and direct Fourier analysis features of ARPEFS should recommend its application.

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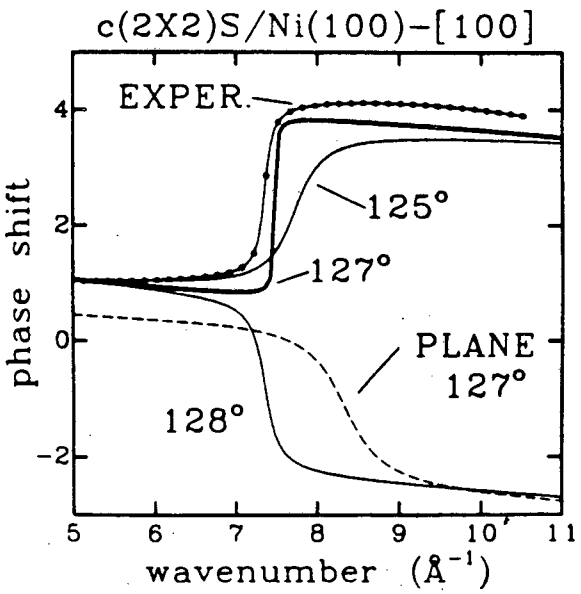

Fig. 4. Phase shifts for scattering from Ni. The dashed line shows the phase shift calculated with plane wave theory $\alpha_j = 127°$. The dotted line is the phase shift from the experimental curve Figure 2c, where the first two Fourier peaks are backtransformed together. The zero crossing jump in phase occurs too high in wavenumber for the plane wave calculation. Solid lines are curved-wave calculations of the phase shift for the indicated scattering angles.

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