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Barton, J.J.

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DIRECT DETERMINATION OF SURFACE STRUCTURES
FROM PHOTOELECTRON DIFFRACTION

J.J. Barton, C.C. Bahr, Z. Hussain,*
S.W. Robey, L.E. Klebanoff, and D.A. Shirley

Materials and Molecular Research Division
Lawrence Berkeley Laboratory

and
Departments of Chemistry and Physics
University of California
Berkeley, California 94720

I. Introduction

Photoelectron diffraction causes the intensity of photoemission peaks to vary with electron energy or exit angle. Recently,^{1,2} dramatic progress has been made in analyzing photoelectron diffraction data to give surface structure information. This paper summarizes our recent work with particular emphasis on the variety of information one can derive from energy-dependent photoelectron diffraction measurements.

The possibility of observing the diffraction of photoelectrons originating from adsorbate atoms, and of deriving structural information from this phenomenon, was suggested by A. Liebsch in 1974.³ The effect was reported independently by three groups in 1978.⁴⁻⁶ Normal photoelectron diffraction, (NPD), in which the photoelectron

intensity was measured in the direction of the surface normal as a function of electron wave number k , has been used to determine a number of adsorbate geometries.^{7,8} In NPD the diffraction-modulated intensity, $I(k)$, was compared to curves predicted by a LEED-like "quasikinematic" theory developed by S. Y. Tong and co-workers.⁹ The perpendicular distance $d_{\perp}$ between the adsorbate overlayer and the substrate is the parameter to which $I(k)$ is most sensitive, and NPD results were usually expressed in terms of $d_{\perp}$.

The NPD approach to surface structure determination yielded accurate structural parameters, but it suffered from two drawbacks. First, it depended upon an implicit theoretical analysis, much like LEED, albeit simpler. Second, it appeared to emphasize the single parameter $d_{\perp}$, rather than showing approximately equal sensitivity to several structural parameters.

An apparently successful attempt¹⁰ was made to remedy the first deficiency, by using Fourier-transformation analysis. Several peaks appeared in the Fourier transform of theoretical curves at distances near those predicted from interplanar spacings (in reality they actually corresponded to path-length differences, as discussed later).

The second problem was addressed by studying off-normal $I(k)$ curves collected in directions normal to low Miller index planes that were not parallel to the crystal surface.

The goal in these experiments was to perform a complete structure determination by Fourier transforming $I(k)$ data taken in several directions, thereby obtaining d_l values relative to several planes. Initial attempts along these lines failed to yield any new structural information,¹¹ but more recent experiments¹ using sulfur-1s photoelectrons have succeeded beyond all expectations, leading to a new method for adsorbate structure determinations: angle-resolved photoemission extended fine structure (ARPEFS).

There are two major differences between NPD and ARPEFS. First, NPD concentrates on low kinetic energy photoelectrons, 30-150 eV, while ARPEFS works in the higher range 100-500 eV. In the lower range, NPD gains from the high photoemission cross-section near threshold, but it suffers because quasi-kinematic calculations are required for surface structure identification. Although ARPEFS is more difficult to measure, it can be analyzed with analytic single scattering theory. The second difference between these diffraction methods is the energy range. For NPD, a large energy range is only modestly valuable in improving the confidence of structure assignment. For ARPEFS, the range must be as large as possible to give high-resolution Fourier transforms. As we will discuss below, the advantages of direct analysis justify the more intensive measurements required by the ARPEFS approach.

In this paper we will summarize our recent work using ARPEFS. The experimental method is outlined in Section II. The physical model and a simple formula for single scattering of photoelectrons are developed in Section III. In the remainder of the paper, the sensitivity of ARPEFS modulations to three geometrical parameters is described. Section IV analyzes $c(2 \times 2)S/Ni(100)$ measured along $[110]$ to show how atomic geometries can be inferred from path-length differences directly available in the ARPEFS Fourier transform. Section V discusses the use of the photoemission final state angular distribution to obtain structural information. Section VI reports preliminary work on a method for measuring the scattering angle.

II. Experimental Observations

We will discuss results from two adsorbate systems, $c(2 \times 2)S/Ni(100)$ and $p(2 \times 2)S/Cu(100)$. Both systems were prepared by exposing atomically clean (as checked by Auger measurements) single crystals to H_2S gas at room temperature. Heating to $200^\circ C$ produced LEED order.

Our 2-axis electron analyzer provided control of the emission direction. The nominal angular resolution of the analyzer is $\pm 3^\circ$; the angular resolution increases at high kinetic energy. Rotation of the analyzer in tandem with the

crystal allows independent control of the polarization vector orientation.

The photoemission spectra were measured on Beam Line III-2 at the Stanford Synchrotron Radiation Laboratory (SSRL), using the JUMBO two-crystal monochromator,¹² equipped with Ge(111) crystals. This arrangement provided a soft x-ray beam of intensity $\sim 10^{10} \text{ sec}^{-1}$ in an area of 2 mm x 4 mm, monochromatized to 2-3 eV FWHM at energies between 2000 eV and 3000 eV. It was thus possible to produce photoelectrons from the sulfur K-shell at kinetic energies from threshold (at $h\nu = 2472 \text{ eV}$) to several hundred eV above threshold.

For each kinetic energy from 80 eV to 420 eV, the elastic photopeak intensity was measured as the area of a Gaussian peak fitted to our photoemission spectra. After normalization for photon flux and analyzer transmission, the intensities oscillate as shown in Figure 1.

The normalized intensities were then processed by the methods developed¹³ for EXAFS. A quadratic function of energy approximating the atomic cross-section, $I_0(E)$, was fitted to each intensity curve, $I(E)$. Then the proportional changes, $\chi(E)$, were calculated by

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

The electron kinetic energy, E , was converted to electron wavenumber, k , by the de Broglie relation

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

The energy offset, E_0 , was derived empirically by the back transformation method of Martens.¹³ As we discuss in the next section, this energy should be approximately equal to the metal inner potential.

The χ curves for the measurements we will discuss are shown in Figure 2. The size of the oscillations and the apparent dominance of sinusoidal signals support our assignment of their physical origin given in the next section.

III. Single Scattering Theory

Photoelectron diffraction is caused by the interference between direct photoelectron waves and waves which have scattered from ion cores surrounding the photoemitter. A simple treatment for the direct and scattered waves predicts the important physical effects. We give a brief version of the simple plane wave scattering model here; more complete treatments are available.^{5b,14-16} Orders and Fadley² have discussed many features of the single scattering model.

Figure 3 illustrates the scattering geometry. We set our origin at the photoemitter and label each scattering

center by an index "j". The bond vector $\vec{r}_j$ runs from the emitter to the scatterer; its length, $|\vec{r}_j|$, is the bond length. The photon polarization unit vector, $\hat{\epsilon}$, makes an angle β_j with the bond vector:

$$\beta_j = \cos^{-1} \frac{\hat{\epsilon} \cdot \vec{r}_j}{|\vec{r}_j|} \quad (3)$$

The scattering angle, α_j , is defined as the angle between the bond vector and the direction to the detector $\vec{r}_d$,

$$\alpha_j = \cos^{-1} \frac{\vec{r}_j \cdot \vec{r}_d}{|\vec{r}_j| |\vec{r}_d|} \quad (4)$$

Figure 4 gives a schematic view of the scattering.

In our analyzer we measure a continuum wavefunction intensity $\psi_f^* \psi_f$. This wave function contains contributions from a direct photoelectron wave, ψ_0 , and a photoelectron wave scattered into the detector, ψ_j :

$$\psi_f = \psi_0 + \sum_j \psi_j \quad (5)$$

The direct wave for a 1s core level is a spherical p ($l=1$) wave:

$$\psi_0 = M(k) \cos \gamma \frac{e^{ikr}}{kr} \quad (6)$$

Here the matrix element for photoemission, $M(k)$, serves as an

uninteresting scale factor, while γ measures the angle between the observation direction and the photon polarization direction.

This same wave also propagates into the substrate. Electrons with kinetic energies in the range 50-1000 eV scatter primarily from the highly localized ion core region. Thus a scattered wave appears to emanate from the position of the substrate atom at $\vec{r}_j$:

$$\psi_j \sim \frac{e^{ik|\vec{r}-\vec{r}_j|}}{k|\vec{r}-\vec{r}_j|}. \quad (7)$$

The scattered wave must be proportional to the amplitude of the original photoelectron wave in the region of the ion core. This amplitude is

$$\psi_0(\vec{r}_j) = M(k) \cos \beta_j \frac{e^{ikr_j}}{kr_j} \quad (8)$$

where β_j is the angle between direction $\vec{r}_j$ and the polarization vector and $r_j = |\vec{r}_j|$.

The outgoing scattered wave is also proportional to the scattering power $k|f(\alpha_j, k)|$ of the ion core for the scattering angle, α_j , between the original propagation direction and the detector direction. The scattered wave is shifted in phase by a small amount ϕ_j by the potential of

the ion core, giving finally

$$\psi_j = M(k) \cos \beta_j \frac{e^{i(kr_j + \phi_j)}}{kr_j} k |f(\alpha_j)| \frac{e^{ik|\vec{r} - \vec{r}_j|}}{k|\vec{r} - \vec{r}_j|} \quad (9)$$

Near our detector the difference between a spherical wave at the origin and a spherical wave at $\vec{r}_j$ appears only as a phase shift equal to $-r_j \cos \alpha_j$. (We can derive this by expanding the shifted spherical wave or by examining Figure 4). Therefore we write the scattered wave at the detector (position r_d) as

$$\psi_j = M(k) \cos \beta_j \frac{|f(\alpha_j)|}{r_j} e^{ik(r_j - r_j \cos \alpha_j) + \phi_j} \frac{e^{ikr_d}}{kr_d} \quad (10)$$

Now we calculate, to first order, the ratio of the interference term to the direct term:

$$\chi = \frac{I - I_0}{I_0} = \frac{\psi_0^* \psi_0 + \sum_j \psi_0^* \psi_j + \sum_j \psi_j^* \psi_0 - \psi_0^* \psi_0}{\psi_0^* \psi_0} \quad (11)$$

$$\chi = \sum_j \frac{\psi_0^* \psi_j + \psi_j^* \psi_0}{\psi_0^* \psi_0} .$$

The direct term is simply:

$$\psi_0^* \psi_0 = M^*(k) M(k) \frac{\cos^2 \gamma}{k^2 r_d^2} , \quad (12)$$

and the cross terms are

$$2\text{Re} \left\{ M(k)M^*(k) \cos \gamma \cos \beta_j \frac{e^{ik(r_j - r_j \cos \alpha_j) + \phi_j}}{r_j} \frac{|f(\alpha_j)|}{k^2 r_d^2} \right\} \quad (13)$$

The cross-section and $1/r_d^2$ dependence are lost when the ratio is found:

$$\chi(k) = 2 \sum_j \frac{\cos \beta_j}{\cos \gamma} \frac{|f(\alpha_j)|}{r_j} \cos(k(r_j - r_j \cos \alpha_j) + \phi_j) \quad (14)$$

This is the ARPEFS formula for 1s photoemission.

Actual measurements of ARPEFS must use a kinetic energy scale, not a wavenumber scale. The de Broglie relation,

$$k = \sqrt{\frac{2m}{\hbar^2}} \sqrt{E - E_0} \quad (15)$$

connects the kinetic energy, E , and the wavenumber k . The parameter, E_0 , adjusts the energy scale measured in the spectrometer to the energy scale in the crystal during the scattering. This parameter should be close to the metal inner potential, but approximations in our simple theory may be partly compensated^{17,22} by adjusting E_0 .

Three structural parameters for each scattering atom appear in the $\chi(k)$ formula: i) the bond length r_j ,

experimentally contained in the path length difference, $r_j - r_j \cos \alpha_j$, ii) the angle between the polarization vector and the bond vector, β_j , and iii) the angle between the bond vector and the emission direction, α_j . In the next three sections we will discuss how structural information can be derived by analyzing ARPEFS measurements for each of these parameters.

IV. Structural Information from the Path-Length Differences

The most obvious manifestation of ARPEFS can be seen in the modulation of the measured photoelectric current. The cosinusoidal dependence on $k(r_j - r_j \cos \alpha_j)$ can be used to derive the bond distances between the photoemitter and surrounding scattering atoms.

The cosinusoidal form for ARPEFS oscillations suggests¹⁴ that a Fourier transform of the experimental curve will be peaked at $r_j - r_j \cos \alpha_j$ for each scattering atom j . The standard Fourier method¹³ involves tapering the data, extrapolating with zeros beyond both ends of the data, and Fourier transforming. Unfortunately, this approach does not provide sufficient resolution for our ARPEFS data: the scattering path lengths are more closely spaced than the Fourier transform of the tapered data will resolve.

To solve this problem, we¹⁸ have adapted an approach used extensively to analyze acoustic and seismic data: the

auto-regressive or maximum entropy spectral analysis method.¹⁹ By modeling the input data with an auto-regressive process and evaluating the resulting model to extrapolate the data, we avoid the unrealistic assumption that the oscillations are identically zero outside the measured range. The AR technique makes it possible to pick out different scattering atoms at similar path-length difference values.

Figure 5 shows the Fourier transform magnitudes of S/Ni(100) ARPEFS in the [110] direction with and without the AR technique applied. The first three peaks in the high resolution spectrum are primarily caused by scattering of the S 1s photoelectrons by its 4 nearest neighbor Ni atoms around the 4-fold hollow site. The other peaks at larger path-length distances can be assigned to scattering from more remote nickel atoms primarily behind the sulfur emitter along [110]. Here we discuss the first three scattering peaks. The role of scattering by other sulfur atoms is unclear. Both simple evaluation of equation (14) without considering sulfur scattering, and the similarity of the Fourier transforms for c(2x2)S/Ni(100) (1/2 monolayer sulfur) and p(2x2)S/Cu(100) (1/4 monolayer sulfur) suggest that sulfur scattering is unimportant.

The first peak is attributed to scattering from the nearest neighbor nickel atom closest to the detector along

the [110] direction, at a scattering angle of 83° . For this atom the path length difference should be $\sim 1.9 \text{ \AA}$. We will discuss the very small amplitude of this peak in the next section.

The second, much larger, peak is caused primarily by scattering from the two equivalent nearest neighbor Ni atoms on either side of the plane containing [100] and [110] (the plane of the page in Figure 3). The scattering angle of $\sim 116^\circ$ corresponds to a path length difference of $3.2 \text{ \AA}$.

The third and largest peak is due to back-scattering from the Ni atom almost directly behind the S atom from the detector. This peak is large partly because the scattering power $k|f(\alpha_j, k)|$ is large for 180° scattering,² and partly because the polarization vector was pointing directly at this atom, giving it the largest incident wave amplitude.

To determine an accurate structure we must remove the phase shift, ϕ_j . Since accurate phase shifts have been published²⁰ for $\alpha_j = 180^\circ$, we use the strong $4.5 \text{ \AA}$ peak ($\alpha_j = 173^\circ$) for this analysis. Our procedure follows Martens.¹³ First the complex FFT was masked to include only the region under the $4.5 \text{ \AA}$ peak. These coefficients were then back-transformed to provide an experimental function $k(r - r \cos \alpha) + \phi_{Ni}$. We then subtracted a nickel scattering phase shift and divided by k . The resulting function should be a constant, $r - r \cos \alpha$, over the region of

k for which we have valid data, but can deviate from a constant for low k values, where the simple scattering picture breaks down. The effective photoelectron wavenumber, k , is determined from the kinetic energy after choosing an inner potential E_0 . With an optimal choice of E_0 , the cosine argument will be most nearly linear in k , so the empirical function $(r-r \cos \alpha)(k)$ will be nearly constant. We derive a path length difference of 4.44 Å giving a S-Ni bond length of 2.23 Å. Our estimate of the uncertainty, 0.03 Å, is shown along with the back-transformed path-length difference in Figure 6.

A similar analysis on the "unknown" system $p(2 \times 2)\text{Cu}(001)$ yields similar results: a fourfold-hollow site with $\Delta R = 4.54$ Å, and $R(\text{S-Cu}) = 2.28(3)$ Å. The structure of $p(2 \times 2)\text{S/Cu}(001)$ is thus determined.

V. Structural Information from the Final-State Symmetry

In addition to the Fourier peak position, we can use the Fourier peak amplitude to derive structure information. The simplest way to extract geometries from the peak sizes exploits the independent control of the polarization vector available in ARPEFS. That is, we rotate the crystal and analyzer together, maintaining a fixed emission direction. Then all the scattering angles α_j , and, of course, the bond lengths, r_j , are fixed, and only the angles β_j and γ

change. Since the path-length differences are fixed, the Fourier peak positions do not change, but their intensities change with $\cos \beta_j / \cos \gamma$.

The manner in which these intensities change is dictated by their physical origin. The factor $\cos \beta_j / \cos \gamma$ is the ratio of the p-wave amplitude in the direction of atom j to the p wave amplitude in the direction of the detector (see Figure 4). Since we will want to keep the photoemission flux high in our detector, we will usually vary γ near 0° : $\cos \gamma$ will remain near 1. A large effect will be seen for $\beta_j \sim 90^\circ$ where a small change in angle gives a large change in the cosine. Thus we expect the scattering intensity of atoms near a final state node to exhibit the most dramatic intensity changes.

We can demonstrate the use of this type of intensity change for verifying Fourier peak assignments by comparing the Fourier transform of $c(2 \times 2)S/Ni(100)$ with that of $p(2 \times 2)S/Cu(100)$, both measured along $[110]$. These surface structures are nearly identical as can be seen from the Fourier amplitudes in Figure 7. The only major difference is the increased intensity for the first peak in S/Cu compared to S/Ni . For the measurement of S/Ni $\gamma = 0^\circ$, and the angle β_j was 83° for the first peak. When S/Cu was measured, the polarization vector was tipped 15° closer to the sample, giving $\gamma = 15^\circ$ and $\beta_j = 68^\circ$ for the first atom peak. The

ratio of the cosine factors for these two cases is 3.2, in agreement with the increase observed experimentally.

The polarization effect for s initial states is particularly simple since only one final state wave, $\ell = 1$, is excited. For higher angular momentum initial core levels, two final state waves will be excited, and a much more complicated angular distribution will result. Fortunately, the higher angular momentum final state usually dominates, and, as illustrated in Figure 8, the major effect will be a change from odd to even final state shape: a d state will change $\cos \beta_j$ in eq.(14) to $\cos^2 \beta_j$. The direction of the final-state node(s) will change, of course, and we should be able to exploit this to determine structures by comparing Fourier intensities from ARPEFS curves with the same photoemission geometry but different initial core levels.

VI. Structural Information from the Scattering Angle α_j

The third method for obtaining structural information from ARPEFS uses an interesting and curious physical effect: at certain energies and certain angles the Ni (or Cu) potential does not scatter electrons. Since we scan energy in the ARPEFS measurement, a dip in the scattering amplitude becomes a signature for a special scattering angle.

Physically, this "anti-resonant" zero in the ion-core scattering power resembles a generalized Ramsauer-Townsend

effect. Ramsauer and Townsend observed that argon becomes transparent to electrons at 0.7 eV. The origin of this surprising lack of scattering, suggested by N. Böhr and verified by Faxen and Holtsmark,²¹ follows from the partial wave formula for the (complex) scattering amplitude:

$$f(\alpha_j, k) = \frac{1}{2ik} \sum_{\ell=0}^{\infty} (2\ell+1) P_{\ell}(\cos \alpha_j) (e^{2i\delta_{\ell}} - 1) \quad (16)$$

At very low kinetic energies only δ_0 , the isotropic s wave, contributes to the scattered wave. If, as is the case for Ar at 0.7 eV, the value of the S phase shift were exactly 180° , then even this term goes to zero and the amplitude, $f(\alpha_j, k)$ becomes very small.

Our generalized Ramsauer-Townsend effect is more complicated.²² At higher energies many partial waves contribute to the scattering amplitude. Then only with the proper linear combination of angular factors, $(2\ell+1) P_{\ell}(\cos \alpha_j)$, and energy factors, $(e^{2i\delta_{\ell}} - 1)$, will the scattering amplitude be zero. Thus while the classical Ramsauer-Townsend effect gives zero amplitude at all angles and very low energy based on special behavior by one phase shift, our generalized Ramsauer-Townsend effect occurs at special angles and energies with many phase shifts involved.

Some ideas about the consequences of this effect can be derived from Figure 9. Scattering amplitudes for four

different angles are plotted in the complex plane. For each angle a line represents $f(k, \alpha_j)$ for $k = 4 \text{ \AA}^{-1}$ (60 eV) to $k = 12 \text{ \AA}^{-1}$ (550 eV). The distance from the origin to a point on the line represents the scattering power for that angle and energy; the angle from the real axis to that point gives the wave phase shift caused by the potential.

For $\alpha_j = 180^\circ$ we see the scattering power peaks broadly around $k = 6 \text{ \AA}^{-1}$. From $k = 4 \text{ \AA}^{-1}$ to $k = 12 \text{ \AA}^{-1}$ the phase angle sweeps gently through $\sim 60^\circ$. For $\alpha_j = 130^\circ$, however, the behavior is radically different. Now the scattering amplitude approaches the origin for $k = 8 \text{ \AA}^{-1}$. The amplitude falls nearly to zero here, and the phase angle sweeps rapidly through 180° . The behavior for $\alpha_j = 125^\circ$ is similar, but the phase angle is rotating in the opposite direction. As Figure 10 shows, the phase shift is particularly sensitive to the scattering angle.

Clearly, we have an opportunity to determine the scattering angle α_j if this angle is near to 130° (for Ni) and if we can isolate the scattering phase shift from the cosine argument.

We have observed the generalized Ramsauer-Townsend effect in the ARPEFS from $c(2 \times 2)\text{S}/\text{Ni}(100)$ measured along the surface normal, $[100]$. The Fourier transform of this ARPEFS curve is shown in Figure 7c. A single scattering model can assign the major peak at $6.2 \text{ \AA}$ to five second-layer Ni

atoms. However, no peak appears at $3.6 \text{ \AA}$, the path-length difference for the four nearest neighbors. Instead two small peaks with no path length explanation rise on either side of $3.6 \text{ \AA}$.

These two peaks are in fact due to nearest neighbor scattering, split and shrunk by the scattering amplitude behavior. Figure 11 displays the back transformation of both peaks with the $3.56 \text{ \AA}$ path length removed. Comparing Figures 10 and 11 shows that the nearest neighbor scattering angle must be $\sim 130^\circ$.

Currently we are investigating the accuracy of the scattering angle determination by this method. Thus far we have determined, not surprisingly, that the generalized Ramsauer-Townsend effect is very sensitive to the scattering potential calculation. The formula given by equation (16) assumes that the scattering potential lies in the asymptotic region far from the photoemitter. Figure 11 compares this phase calculation to experiment. Equation (16) places the zero crossing $1.5 \text{ \AA}^{-1}$ (88 eV) too high. If, instead, the wavefront curvature and finite size of the potential are included in the calculation of the scattering amplitude, the agreement improves.¹⁶

VII. Summary

Much of the early interest³⁻¹¹ in photoelectron diffraction from surface structure studies focused on the

benefits of the photoemission probe. In addition to the surface sensitivity given by an electron spectroscopy, photoemission is chemically specific. The core-level energies reflect changes in chemical environment; they are narrow features in the emission spectrum, easily identified and followed in energy.

Angle-resolved photoemission adds more attractive features to photoelectron diffraction as a basic tool for surface science. Each position for the detector gives a different diffraction curve, placing nearest neighbor atoms at different path-length differences. Large anisotropy in the atomic partial cross-section leads to "search light" effects as described in Section V.

The diffraction itself gives more than just the path-length difference information. Strong differences in the scattering cross-section with angle boosts the "search light" effect and increases the differences between diffraction curves. The generalized Ramsauer-Townsend effect may lead to accurate bond angle determinations.

Using the ARPEFS energy region and the analytic single scattering theory, direct analysis makes photoelectron diffraction a much more viable structure method. Analysis of the Fourier transforms dramatically simplifies the interpretation of the diffraction information. As we have demonstrated here, the Fourier peak positions correspond to

scattering path-length differences while the peak intensities relate to final state amplitudes and scattering cross sections. Rotation of the detector with respect to the crystal will change the path lengths and hence shift the peaks; rotation of the detector together with the crystal will change the polarization direction and hence change the peak intensities without changing their position.

Clearly, we must also recognize the limitations of this approach to surface structures. The most serious problem remains the lack of a synchrotron radiation facility commitment to comprehensive surface structure studies. Currently this limits ARPEFS measurements to special, particularly important problems unsolvable by the available laboratory methods. We hope that our studies of the simple atomic sulfur adsorption represents a first step toward molecular surface structure measurements--complicated studies to which ARPEFS can uniquely contribute.

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*Department of Physics, University of Petroleum and Minerals, Dhahran, Saudi Arabia.

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Figure Captions

Figure 1. Photoemission partial-cross-section measurements for $c(2 \times 2)S/Ni(100)$. The curve I represents the area of the elastic photopeak, divided by the background emission to correct for photon flux, multiplied by kinetic energy to correct for electron-analyzer transmission, and divided by 100,000.

Figure 2. ARPEFS modulations derived from $S(1s)$ photoemission partial cross-sections. Both curves were measured with the detector along a $[110]$ direction from a (100) surface; a) $c(2 \times 2)S/Ni(100)$; b) $p(2 \times 2)S/Cu(100)$.

Figure 3. Cross-sectional view of a fcc crystal (001) surface showing the experimental geometry and illustrating the parameters of the analytic single-scattering formula. The angle-resolved detector is along the vector labeled e^- ($[011]$ direction); the polarization vector is ϵ . The angle between these two vectors is γ . The vector from the emitter to the scattering atom j makes an angle β_j with the polarization vector and an angle α_j with the emission direction.

Figure 4. Illustration of the scattering process. The direct wave has an angular distribution dependent

upon the initial state ($1s$) and the photon polarization direction, $\vec{\epsilon}$. The scattering from each atomic center depends upon its scattering angle α_j . The scattering amplitude calculated for 300 eV is shown superimposed on the scattering atom. This amplitude is strongly peaked in the forward and backward directions. The geometric path-length difference is also illustrated.

Figure 5. Fourier transform magnitudes for the ARPEFS of $c(2 \times 2)S/Ni(100)$ along $[110]$. The upper curve demonstrates the application of the "taper and transform" method; the lower curve benefits from the additional auto-regressive extrapolation (refs. 18, 19).

Figure 6. Path-length determination for the major peak in the Fourier transform of ARPEFS from $c(2 \times 2)S/Ni(100)$ measured along $[110]$. The Fourier peak was isolated and back-transformed to extract the cosine argument. The Ni phase shift for 173° was subtracted, and the resulting numbers were divided by k . The inner potential was adjusted to flatten the curves as much as possible from 6 to $10.5 \text{ \AA}^{-1}$. The three curves demonstrate the insensitivity of the processing to the weighting of $\chi(k)$.

Figure 7. Auto-regressive Fourier transforms of the three ARPEFS curves discussed in the text. Note that a path-length difference of $4.4 \text{ \AA}$ corresponds to a bond length of $2.2 \text{ \AA}$ when $\alpha_j = 173^\circ$. (a) $S(1s)$ ARPEFS from $p(2 \times 2)S/Cu(100)$; detector along $[110]$, $\gamma = 15^\circ$, (b) $S(1s)$ ARPEFS from $c(2 \times 2)S/Ni(100)$; detector along $[110]$, $\gamma = 0^\circ$, (c) $S(1s)$ ARPEFS from $c(2 \times 2)S/Ni(100)$; detector along $[100]$ (normal emission), $\gamma = 20^\circ$. In all curves the intensity below $1.5 \text{ \AA}$ varies with the background function choice and has been disregarded.

Figure 8. ARPEFS of $c(2 \times 2)S/Ni(100)$ along $[100]$ (also called NPD). The top curve is a measurement of $S(1s)$ photoelectrons; the bottom curve, $2p$ photoelectrons. As discussed in the text, switching the initial state angular momentum has the dominant effect of switching the sign of the modulations.

Figure 9. Ni scattering amplitudes calculated in the small atom (plane wave) approximation, eq. 16. Each solid line represents the scattering amplitude for the scattering angle indicated. For each scattering angle the amplitude was calculated for wavenumbers from $5\text{--}12 \text{ \AA}^{-1}$; the labeled tick marks give some indication of the wavenumber

scale. The amplitudes are plotted in the complex plane to illustrate the connection between scattering intensity and phase shift. Note that the scattering intensity is nearly zero for $\alpha_j = 130^\circ$ and $k = \sim 8.5 \text{ \AA}^{-1}$.

Figure 10. Ni scattering amplitude phase shifts using the small atom (plane wave) approximation, eq. (16). Four angles near the generalized Ramsauer-Townsend zero crossing are plotted. All four begin with a phase shift near .5 radians at $4 \text{ \AA}^{-1}$ and end near $\pm 3.1 \text{ rad.}$, but in the region of the resonance the behavior depends strongly on scattering angle.

Figure 11. Phase shifts for scattering from Ni. The solid line shows the phase shift calculated from equation (16) for $\alpha_j = 128^\circ$. The dotted line is the phase shift from the experimental curve Figure 7c, where the first two Fourier peaks are back-transformed together. The zero crossing jump in phase occurs too high in wavenumber for the plane wave calculation. Preliminary calculations (ref. 18) demonstrate that spherical wave formulas place the zero crossing at $7 \text{ \AA}^{-1}$.

SS1W M03

XBL 839-11331

Figure 1

XBL 839-11332

Figure 2

p (2x2) S/Cu(001)

XBL 8212-7380

Figure 3

XBL 831-1157

Figure 4

XBL 8210-2856

Figure 5

XBL 839-11330

Figure 6

XBL 839-11334

Figure 7

XBL 8210-2834

Figure 8

XBL 839-11333

Figure 9

XBL 839-11329

Figure 10

XBL 839-11363

Figure 11

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