Normal Photoelectron Diffraction of the Se $3d$ Level in Se Overlayers on Ni(100)

S. D. Kevan, D. H. Rosenblatt, D. Denley,[a] B.-C. Lu, and D. A. Shirley
Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720, and Department of Chemistry, University of California, Berkeley, California 94720
(Received 18 September 1978)

Modulations of up to a factor of 2 were observed in the Se $3d$ photoelectron intensity normal to the surface, for selenium overlayers on Ni(100), as the photon energy was varied from 90 to 240 eV. Excellent agreement of peak energies with predictions by Tong and Li was obtained for both the $c(2\times2)$ and $p(2\times2)$ structures, using the hollow-site geometry. Normal photoelectron diffraction appears to have promise as a surface structural method.

Large modulations in the Se $3d$ photoelectron intensity with photon energy have been observed in normal emission from both $c(2\times2)$ and $p(2\times2)$ selenium overlayers on a Ni(100) crystal face. The kinetic energies at which the oscillations peak show excellent agreement in each case with calculated predictions[1,2] for the fourfold "hollow" site geometry of Se adsorbed on Ni, and disagree with predictions for the "atop" geometry. These results provide the first experimental evidence that normal photoelectron diffraction from adsorbate core levels is a large effect,[2] and indicate that it has promise as a quantitative structural tool for determining adsorbate geometries.

The relationship of the photoemission final state to the time-reversed low-energy electron diffraction (LEED) state has long been recognized.[3-5] Indeed, the advantages of using photoelectrons for diffraction studies have been discussed in some detail.[6,7] Experimentally, both normal and off-normal photoelectron diffraction was observed earlier for the valence levels of CO on Pt(111),[8] and recently azimuthal variations of adsorbate core-level intensities have been reported,[9,10] but in neither case was quantitative interpretation carried out. Tong and Li have emphasized the great advantage of measuring photoelectron intensities of adsorbate *core* levels *normal* to the substrate crystal face, while varying the photon energy. The energies of the diffraction peaks produced in this manner can readily be analyzed to give $d_\perp$, the interplanar spacing, rather directly. Quite often $d_\perp$ is a crucial parameter in a surface-structure determination, as we shall discuss below.

The photoemission experiments were performed during dedicated beam time on the 4° branch of beam line I at the Stanford Synchrotron Radiation Laboratory. A wide range of photon energies is available on this branch, from $h\nu = 32$ to $h\nu = 280$ eV. A wide energy range is important for these experiments, which extended to 240 eV. The spectrometer, which will be described elsewhere, employs a 5.40-cm-mean-radius hemispherical analyzer with independent two-circle rotation. The analyzer energy resolution was set at 0.40 eV, while the monochromator resolution increased from 0.07 eV at $h\nu = 90$ to 0.50 eV at $h\nu = 240$ eV. Angles were adjusted so that p-polarized radiation was incident on the sample at $\theta = 60°$ from the surface normal in a plane containing the [100] and [001] axes (see the inset, Fig. 1). Photoelectron spectra were collected in a cone of 3° half-angle, normal to the Ni(100) surface. The nickel crystal had been cut and polished to within 1° of the (100) face, etched, and cleaned *in situ* by cycles of ion bombardment and annealing. Auger analysis showed no surface impurities, nor did the photoelectron spectra up to 240 eV, and sharp LEED patterns indicated on ordered (100) surface. Ordered $c(2\times2)$ and $p(2\times2)$ selenium overlayers were produced by exposing the clean crystal at 200°C to H_2Se, following Hagström and Becker.[11] Complete photoemission spectra were collected, rather than peak intensities only, to facilitate data reduction, including background subtraction and peak area measurement. Normalizations were also made for photon flux and the analyzer efficiency.

Figure 1 shows a plot of the relative Se $3d$ intensity versus electron kinetic energy for the $c(2\times2)$ overlayer. Four distinct peaks are observed; of these, three are well characterized. The peak near 60 eV suffers from interference due to a nickel Auger line and also from multiple scattering, as discussed below. Nevertheless, it was consistent with our interpretation. The modulation is very large,[2] up to a factor of 2, compared to the smaller variations reported in azimuthal studies.[9,10] Also shown in Fig. 1 are the peak energies in the Se $3d$ cross section as calculated by Tong and Li for the $c(2\times2)$ overlayer geometry in both the hollow and atop site registries with the lattice.[1] A time-reversed

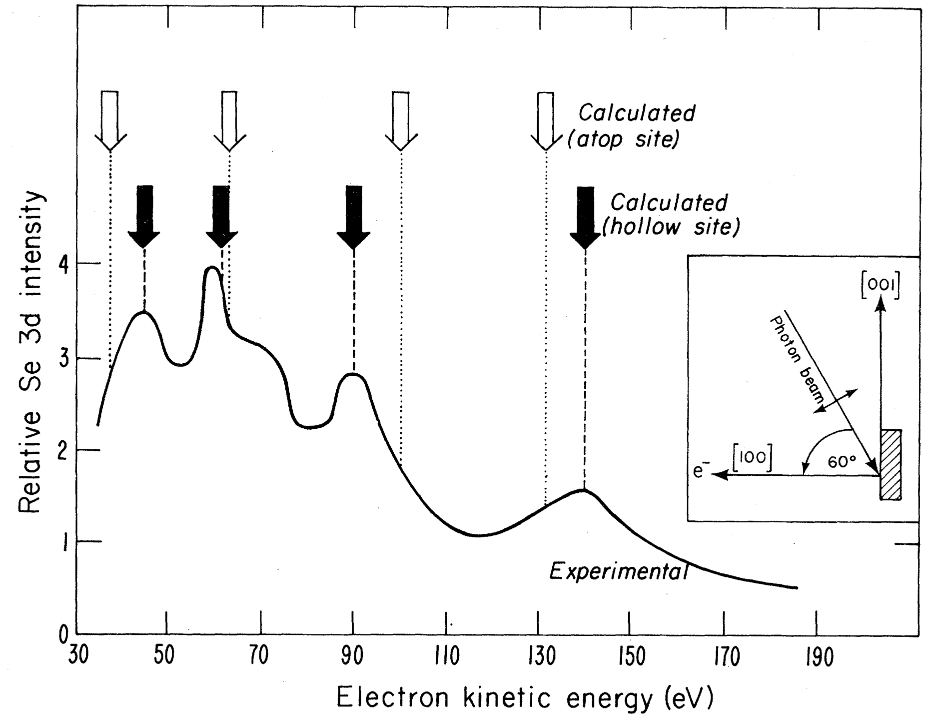

FIG. 1. Plot of the relative Se $3d$ intensity versus electron kinetic energy for the $c(2\times2)$Se + Ni(100) system, and calculated peak energies for the atop and hollow site registries (arrows). The experimental geometry is shown in the inset.

LEED state was used for the photoelectron final state.[3] With the present degree of uncertainty in the scattering potentials, the calculation is not expected to yield accurate peak intensities,[1,12] but the peak energies should be a reliable measure of $d_\perp$, the Si-Ni interplanar spacing. In fact, we find excellent agreement with theory (using the hard-sphere radii) for the hollow-site value of $d_\perp = 1.55$ Å, while the peak positions for the atop-site value of 2.3 Å give poor agreement; the separation between the first and third peaks is 16 eV too large, and that between the third and fourth peaks is 17 eV too small, with a valley coming where a peak would be expected. A series of calculations at several values of $d_\perp$ indicated that even this closeness of the peak positions for the atop and hollow geometries is coincidental; in other systems, the differences are expected to be greater.[1]

In Fig. 2 we show similar results for the $p(2\times2)$ overlayer. Again, the best fit is obtained for $d_\perp = 1.55$ Å, corresponding closely to the hollow site. For both overlayers, a movement of 0.1 Å from $d_\perp = 1.55$ Å produces unacceptable agreement between theory and experiment. This, therefore, provides a rough estimate of the uncertainty in $d_\perp$. Both of these results agree with recent dynamical LEED calculations.[13,14] We conclude that this technique shows promise for surface-structure determination, and emphasize

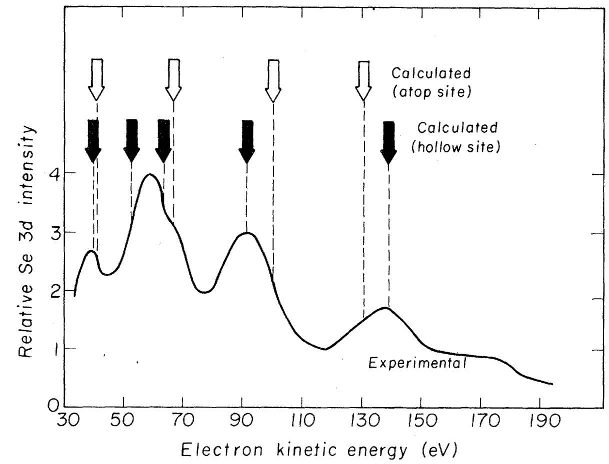

FIG. 2. Plot of the relative Se $3d$ intensity versus electron kinetic energy for the $p(2\times2)$Se + Ni(100) system, and calculated peak energies for the atop and hollow site registries (arrows).

that these results have been obtained using photoemission from a *core* state. This simplifies the calculation significantly, and has the added advantage that spectral subtractions are straightforward, as the photoemission peaks are quite sharp. This last point has been especially important near 62-eV kinetic energy in this study, where a broad nickel Auger peak is added to the background.[15]

Further insight into this diffraction phenomenon is obtained by comparison with LEED I-V curves. If we separate the photoemission process into an atomiclike excitation followed by scattering off the substrate, the relationship between LEED and photoemission becomes quite clear. For normal emission, any part of the outgoing spherical wave centered on the Se atom that impinges on the substrate with $\vec{k}_{\parallel} = \vec{g}_{\parallel}$ may be scattered into the detector. Hence, the photoemission final state is easily seen to be a *coherent* superposition of many time-reversed LEED beams. Because the amplitude of the outgoing wave traveling through the substrate is damped as $r^{-1}e^{-ar}$, one might expect only the lowest-order beams to be significant.

A comparison of our experimental peak positions, Tong and Li's calculated peak positions for the atop and hollow sites, and the experimental peak positions from the 00 and 01 LEED I-V curves[16] for both $c(2\times2)$ and $p(2\times2)$ Se overlayers on Ni(100) is given in Table I. The correspondence is striking; all peaks in the 00 beam have counterparts in our data, shifted by at most 2–3 eV. The peak at 72 eV in the $c(2\times2)$ 01 beam data may account for the shoulder on our second peak in Fig. 1, although this conclusion is tenuous because of the Auger interference mentioned previously. It is interesting to note further that our peak intensities tend to match those given by Demuth and Rhodin[16] for the 00 beam much more closely than they do the calculated intensities. These correspondences provide further evidence that photoelectron diffraction has promise as a quantiative structural tool.

One further conclusion may be drawn from our data. The first, third, and fourth peaks in the 00 LEED beam data in Table I correspond to Bragg peaks. The second is purely a multiple-scattering peak. The fact that we observed a peak at nearly the same energy is strong evidence for multiple scattering in angle-resolved photoemission (ARP). It is unlikely that this peak arises from a Bragg peak in another beam, in light of our previous considerations and the good fit to the 00 beam alone. Clearly, any ARP theory which neglects multiple-scattering effects is incomplete.

This approach, relating photoemission to LEED, provides insight into why the intensity variations are much larger than those observed in either azimuthal studies,[9,10] or surface extended-x-ray-absorption fine structure (SEXAFS).[17] In normal photoelectron diffraction the LEED beams are degenerate in groups of four, whereas in azimuthal studies the degeneracy is significantly reduced. The observed effects should be substantially averaged by this fact alone.[18] In SEXAFS, phase information between the various beams, the major cause of our modulations, is averaged out. Although the nearest-neighbor distance is readily available from SEXAFS, the registry is more difficult to determine. Thus SEXAFS and photoelectron diffraction are complementary.

Photoelectron diffraction has some potential

TABLE I. Kinetic energies of observed and calculated peaks (eV).

Peak	Calc. (atop)	Calc. (hollow)	Expt.	Expt. LEED 00 beam	Expt. LEED 01 beam
		$c(2\times2)$Se + Ni(100)			
1	37	44	43	42	...
2	63	62	58[a]	58	72
3	98	88	88	91	95
4	131	139	138	137	...
		$p(2\times2)$Se + Ni(100)			
1	40	39	38	37	...
2	64	(51, 62)	58[a]	58	65
3	99	91	92	93	92
4	130	139	138	138	136

[a] See Ref. 15.

advantages over LEED. First, photoemission is nondestructive, facilitating applications to molecular adsorbate systems. Second, photoelectron diffraction does not require long-range order in adsorbate overlayers, and may be used to study low-coverage systems. Finally, photoelectron diffraction is phase sensitive: All the photoelectrons originate from a particular adsorbate level at the same distance from the surface in almost all cases. This facilitates the measurement of $d_\perp$ for adsorbate atoms. Hence photoelectron diffraction, unlike LEED, should be quite sensitive to the bond-axis orientation in molecular adsorbates.

In conclusion, we have observed substantial photoelectron diffraction effects in normal photoemission from the 3*d* core levels of Se adsorbed on a Ni(100) substrate. Comparison with Tong and Li's calculations has established the sensitivity of normal photoelectron diffraction in determining adsorbate registries. Finally, comparison with LEED *I-V* curves has indicated the existence of multiple scattering phenomena in ARP.

We wish to acknowledge S. Y. Tong and C. H. Li for many helpful discussions and for generously providing us with their unpublsihed calculations, which were heavily relied upon in parts of our analysis. We also thank R. F. Davis for his assistance in carrying out the measurements, and Mrs. Winifred Heppler for the preparation of the nickel crystal.

This work was performed at the Stanford Synchrotron Radiation Laboratory, which is supported by the National Science Foundation Grant No. DMR 73-07692 A02, in cooperation with the Stanford Linear Accelerator Center and was done with support from the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy.

[a] Also with Department of Physics, University of California, Berkeley, Calif. 94720.

[1] C. H. Li and S. Y. Tong, Phys. Rev. B (to be published); S. Y. Tong and C. H. Li, Bull. Am. Phys. Soc. 23, 417 (1978).

[2] S. Y. Tong and N. Stoner, J. Phys. C 11, 3511 (1978). This reference gives a detailed analysis of the physical origin of the type of cross-sectional variation reported here.

[3] C. H. Li, A. R. Lubinsky, and S. Y. Tong, Phys. Rev. B 17, 3128 (1978).

[4] I. Adawi, Phys. Rev. 134, A788 (1964).

[5] P. J. Feibelman and D. E. Eastman, Phys. Rev. B 10, 4932 (1974).

[6] A. Liebsch, Phys. Rev. Lett. 32, 1203 (1974), and Phys. Rev. B 13, 544 (1976).

[7] S. Y. Tong and M. A. Van Hove, Solid Solid State Commun. 19, 543 (1976), and references therein.

[8] D. A. Shirley, J. Stöhr, P. S. Wehner, R. S. Williams, and G. Apai, Phys. Scr. 16, 398 (1977).

[9] S. Kono, C. S. Fadley, N. F. T. Hall, and Z. Hussain, Phys. Rev. Lett. 41, 117 (1978).

[10] N. V. Smith, P. K. Larsen, and S. Chiang, Phys. Rev. B 16, 2699 (1977).

[11] H. D. Hagström and G. E. Becker, J. Chem. Phys. 54, 1015 (1971).

[12] Because of the additional complexity of the photoemission process as compared to LEED, one would expect even more difficulty in calculating intensities for this experiment than in the LEED case.

[13] M. Van Hove and S. Y. Tong, J. Vac. Sci. Technol. 12, 230 (1975).

[14] S. Anderson, J. B. Pendry, B. Kasemo, and M. Van Hove, Phys. Rev. Lett. 31, 595 (1973).

[15] Our second peak is the least reliable because of Auger interference.

[16] J. E. Demuth and T. N. Rhodin, Surf. Sci. 45, 249 (1974).

[17] P. H. Citrin, P. Eisenberger, and R. C. Hewitt, Phys. Rev. Lett. 41, 309 (1978); J. Stöhr, D. Denley, and P. Perfetti, Phys. Rev. B (to be published).

[18] A. Liebsch, in *Electron and Ion Spectroscopy of Solids*, edited by L. Fiermans, J. Vennik, and W. Dekeyser (Plenum, New York, 1978), Vol. B32, p. 93.