

Photoelectron-diffraction measurements of sulfur and selenium adsorbed on Ni(001)

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Photoelectron-diffraction data are presented for the systems sulfur-Ni(001) and selenium-Ni(001). A combination of all normal emission data leads to a clearer understanding of photoelectron diffraction from an adsorbate core level as a two-step process. Experimental observation of diffraction effects from low-coverage, disordered overlayers of selenium demonstrates that the diffraction is clearly due to backscattering off the nickel substrate, and also that normal photoelectron diffraction is potentially quite useful in the study of disordered systems. Certain criteria are established which any photoelectron-diffraction technique must satisfy to be a viable tool for studying surface structure. A comparison of $c(2 \times 2)$ sulfur and selenium data and presentation of off-normal data for the selenium system leads to the conclusion that normal photoelectron diffraction satisfies these criteria. Normal photoelectron diffraction was observed for the nickel $3p$ shell and valence band, showing that both diffraction and multiple-scattering processes affect angle-resolved photoemission intensities.

I. INTRODUCTION

The possible use of final-state scattering effects in angle-resolved photoemission from adsorbate orbitals to determine adsorbate-surface structure has been the subject of several recent theoretical investigations.^{1,2} The basic idea is that the photoelectron's de Broglie wavelength would be comparable to interatomic distances, leading to diffraction phenomena. Photoelectron diffraction has recently been observed in several systems, in two experimental modes; normal and azimuthal photoelectron diffraction. In normal photoelectron diffraction (NPD),^{3,4} energy-analyzed photoelectrons from a specific adsorbate level are collected in "normal" geometry, i.e., perpendicular to the substrate surface. The photon energy is swept through a wide range and an electron intensity-versus-energy curve is thereby generated. Azimuthal photoelectron diffraction (APD)^{5,6} consists of rotating the sample about its normal and recording the intensity of the energy-analyzed adsorbate core-level photoelectron peak while holding the photon energy constant. Both NPD and APD have some experimental advantages, but neither has as yet been shown to be a generally useful technique for adsorbate-structure determinations, although in an earlier study³ we implied that this might well be the case for NPD. In this paper we present further evidence which indicates that NPD is in fact of general applicability. In the course of the paper we answer several questions that were left open before.

In our earlier study,³ normal photoelectron diffraction was observed in the $c(2 \times 2)$ Se-Ni(001) system. Remarkably good agreement was found between peak positions in the Se($3d$) intensity

measured normal to the surface as a function of photon energy and recent calculations by Tong and Li.² The data supported conclusions from low-energy electron diffraction (LEED)⁷ that selenium sits in a fourfold hollow site on Ni(001). However, we also noted an equally remarkable correspondence of the peak positions to those observed in the LEED (00) beam. If the Tong-Li calculations had not been available, our results might have been interpreted as indicating that NPD measures essentially the LEED (00) beam. These two observations actually lead to contradictory conclusions: The LEED (00) beam peak positions are often quite insensitive to the adsorbate-substrate interplanar spacing d_{\perp} , whereas d_{\perp} was in fact the crucial parameter in the Tong-Li calculations.

Recent azimuthal studies, on the other hand, have also not definitively shown APD to be sensitive to d_{\perp} . Indeed calculations by Tong and Li on the Se-Ni(001) system tend to show that, for this system at least, the azimuthal studies are not very sensitive to d_{\perp} . Scattering mechanisms within the adsorbate overlayer itself are emphasized, and essentially the same azimuthal variations of intensity were obtained, independent of d_{\perp} .⁸ However, other calculations⁹ indicate that pronounced variations in the azimuthal dependence on d_{\perp} are present for selected kinetic energies. We leave the subject of APD at this point, noting that more work is needed to establish the magnitude of its sensitivity to d_{\perp} .

Clearly any photoelectron-diffraction technique must satisfy at least two closely related criteria before becoming a viable method for adsorbate-structure determination. First, the dominant scattering process must be off the substrate and

must manifest itself as easily measurable variations in differential cross section. Second, the mechanism must be sensitive to adsorbate registry through d_{\perp} or some other useful parameter. In this paper we describe experiments designed to test the extent to which NPD does indeed satisfy both of these requirements.

In Sec. II we outline the experimental techniques more explicitly than in our previous paper.³ Section III presents new photoelectron-diffraction data from a series of experiments which answer specific questions about the promise of NPD as a surface structural tool. Conclusions are summarized in Sec. IV.

II. EXPERIMENTAL

All the experiments were performed on the 4° branch of Beam Line I at the Stanford Synchrotron Radiation Laboratory (SSRL). On this line usable photon intensities are available between 40 and 280 eV photon energy. The photoelectron spectrometer employs a 5.40-cm-mean-radius hemispherical analyzer, which can be rotated through 2π steradians of solid angle and which allows for simultaneous analysis of a range of electron kinetic energies via a resistive anode multichannel detection system, thereby enhancing the detection sensitivity by a factor usually between 10 and 100. This latter feature was especially important in the studies reported here, as the ring current was quite low (3–4 mA) throughout our running time, yielding a proportionally low photon flux. In fact, these experiments would have been impossible with a single-channel detection system. A more complete description of the analyzer, drive, and detection system will be published soon.

A high-purity nickel single crystal with a surface orientation to within 1° of the (001) face was mounted in the photoemission spectrometer. Previous treatment of the crystal had largely removed the bulk impurities, so that short cycles of argon bombardment and annealing to 700 °C were sufficient to produce a clean and ordered surface as determined by *in situ* LEED-Auger analysis. Selenium and sulfur coverages were prepared by directing an effusive beam of H₂Se or H₂S at the crystal, which was heated to 200 °C. Exposures roughly equivalent to those reported by Hagström and Becker¹⁰ were required to produce ordered $c(2\times 2)$ overlayers. Low-resolution energy distribution curves of the appropriate adsorbate core level [Se(3*d*) or S(2*p*)] were recorded at photon-energy increments of 3 eV. Figure 1 shows part of the photoelectron spectrum of $c(2\times 2)$ Se-Ni(001) at a photon energy $h\nu=150$ eV. The nickel valence band and 3*p* peak are clearly visible, as is the

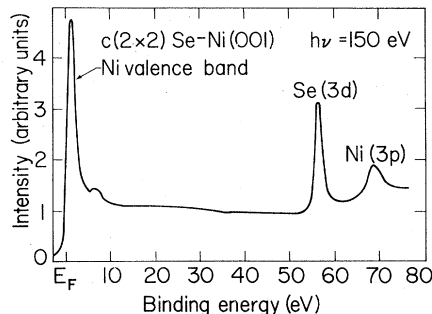


FIG. 1. Normal photoemission spectrum from $c(2\times 2)$ Se-Ni(001) at the photon energy $h\nu=150$ eV, showing the nickel valence band Se(3*d*) and Ni(3*p*) peaks. Note surface sensitivity to one-half monolayer of Se.

Se(3*d*) peak. The surface sensitivity of NPD is exemplified by the fact that this latter peak, which arises from a half-monolayer adsorbate coverage, is of comparable intensity to the bulk-derived nickel peaks. On comparing a series of spectra like that in Fig. 1, but taken at successive photon energies, dramatic variations in the relative intensities of these three peaks were obvious by visual inspection—a convincing demonstration of photoelectron diffraction. To obtain peak intensities, a smooth background was subtracted from the electron distribution curves, the peak areas were calculated, and corrections were made for photon flux and analyzer transmission. These corrections are discussed below.

In constant-initial-state (CIS) photoelectron spectroscopy the excitation of a given core level of binding energy E_B is followed by varying the kinetic energy at which the photoelectrons are collected to satisfy the Einstein relation

$$E_B = h\nu - E_{\text{kin}}$$

In all CIS studies two corrections are obligatory at each $(h\nu, E_{\text{kin}})$ combination. The first is a correction for the analyzer transmission function which, from elementary optics, goes as E_{kin}^{-1} .¹¹ This form of the correction, which should be a good approximation for our analyzer, has now been applied. In any case, the correction is smooth and will not affect peak positions significantly. The second correction, that of the incident photon flux, is more troublesome, because vacuum ultraviolet monochromator transmission functions are far from smooth. In this work and in our previous study³ we have corrected for photon flux by measuring the photoyield from a gold mesh and assuming that the observed photoyield is proportional to the gold absorption coefficients measured by Hagemann *et al.*¹² The similarity of the transmission thus determined to that measured earlier with a standardized Al₂O₃ photodiode¹³ indicates

that this assumption is reasonable and that any discrepancies, at worst, vary slowly with energy. The advantage of using a gold mesh is that photoyield measurements can usually be made simultaneously with the photoemission experiments, although the low-beam currents mentioned above prevented our doing so in the present work. Instead, the photoyield measurements were carried out before the photoemission measurements and appropriate corrections for beam current were made later. A plot of the resulting corrected intensities produces essentially a constant-initial-state photoemission spectrum. In all cases background subtraction near 62 eV kinetic energy was complicated by a broad nickel Auger peak at this energy. Hence data near this kinetic energy should be treated with caution.

III. RESULTS AND DISCUSSION

In this section we present the results of a series of experiments. Each is discussed in turn and conclusions are summarized in Sec. IV.

Proceeding from the spectra presented in Fig. 1, it is natural to inquire whether the nickel 3*p* and valence-band peaks exhibit photoelectron diffraction, in addition to that shown by the Se(3*d*) peaks, which was documented previously.³ They do indeed. Figure 2 shows the intensity variation of the nickel-derived features, plotted against energy. Peak positions for the Se *p*(2×2) structure lie at the following kinetic energies (relative to the nickel

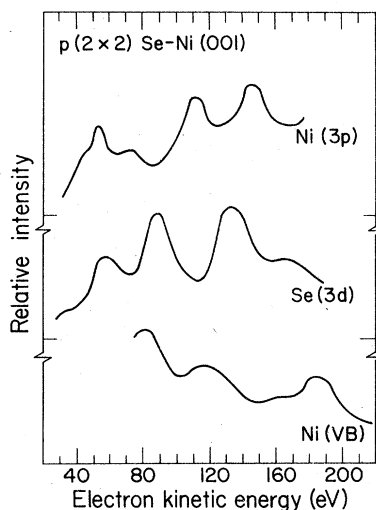


FIG. 2. Normal photoemission intensity vs kinetic energy curves for (a) Ni(3*p*), (b) Se(3*d*), and (c) Ni valence-band electrons from *p*(2×2) Se-Ni(001), plotted as intensity vs electron kinetic energy referenced to the nickel vacuum level. Note diffraction maxima at different energies on all curves.

vacuum level): Ni(3*p*): 54, 73, 111, and 145 eV; Ni(valence band): 82, 119, and 187 eV. We present these results simply to document the effect of photoelectron diffraction from substrate-derived peaks, and will make no attempt at quantitative data reduction. The fact that intensity maxima lie at different kinetic energies for the Se(3*d*), Ni(3*d*), and Ni(3*p*) shells is noteworthy, and it suggests several future lines of investigation, but no unique interpretation. Obviously the nickel data are less amenable to simple interpretation than those from the Se(3*d*) orbitals, because the photo-current originates from several inequivalent layers of lattice atoms. It should be noted that photoelectron diffraction can substantially modulate angle-resolved photoelectron (ARP) intensities from single crystals at the ±30% level. Thus ARP intensity variations cannot be interpreted meaningfully at a higher level of accuracy unless photoelectron diffraction has been taken into account.

Figure 3 shows all of our NPD results on the *c*(2×2) Se-Ni(001) system obtained to date. The top curve repeats our earlier data,³ without an error that was made in correcting for the analyzer transmission function in the earlier study. This gives a significant change in relative peak intensities, but peak positions, which are listed in Table I for all four curves, have changed by at most 1–2 eV. Curves *b*, *c*, and *d* in Fig. 3 show new data on this system. Curve *b* was obtained under the same conditions as curve *a*, and shows remarkably consistent results. Peak positions are identical to within 1–2 eV and the peak intensities are nearly the same. Curve *c* demonstrates the effect of changing the angle of incidence of the light to 80° along the same [100] azimuth, so that

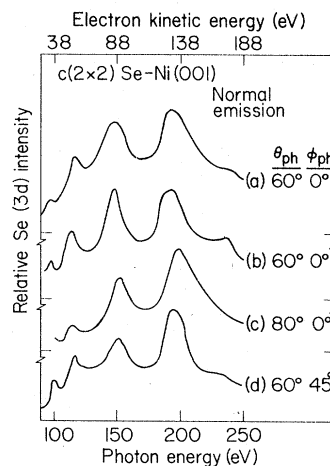


FIG. 3. Normal photoelectron-diffraction curves for Se(3*d*) electrons from *c*(2×2) Se-Ni(001) for different samples and photon polarization vector orientations.

TABLE I. NPD peak energies (in eV) for $c(2 \times 2)$ Se(3d)-Ni(001).

Data set ^a	Peak 1	Peak 2	Peak 3	Peak 4
3a	37 ^b	53	86	130
3b	37	52	86	131
3c	37	52	89	136
3d	37	54	87	130

^aRefers to Curves *a*-*d* in Fig. 3.

^bAll entries are electron kinetic energies referred to the nickel vacuum level.

the \vec{A} vector is only 10° off normal. There is a small shift in peak positions and intensities. Finally curve *d* shows the effect of changing the azimuthal incidence of the light to be along the $[110]$ azimuth. We conclude that, at the level of accuracy with which the NPD curves in Fig. 3 were measured, the peak positions and intensities are quite reproducible and do not depend sensitively on the azimuthal or polar orientation of the photon polarization vector in the range that we have studied.

At this point a preliminary estimate of the accuracy of d_\perp values determined by NPD is of interest. This estimate must be preliminary because only a very limited set of data and of theoretical curves is available. For the same reason it must be conservative. We note the rms peak-energy reproducibility of ± 1.5 eV in Table I and the rms shift of $50 \text{ eV}/\text{\AA}$ in the peak positions calculated by Tong and Li (cited in Ref. 3) between the twofold bridge and fourfold hollow-site peak positions. Division yields $\pm 0.03 \text{ \AA}$; on this basis it is realistic to estimate the error of NPD as $\pm 0.05 \text{ \AA}$ in d_\perp , which compares with LEED accuracies.

There is another pleasing characteristic common to the four curves in Fig. 3. If the diffraction maxima and minima could be eliminated by some sort of averaging process, the remaining curves would have the energy dependence expected for a nodeless initial state. That is, the intensity would rise above threshold to a broad maximum centered about 100 eV above threshold, then decrease. This observation, which was missed in the earlier study³ because of the errant correction for analyzer transmission, supports the view of photoelectron diffraction as a two-step process. There is first an atomlike excitation followed by scattering in the final state, which introduces intensity oscillations with energy. The photoemitting atom acts like an electron gun, with an "emission current" given by the atomic cross section. The observed photoemission intensity can then be taken as a product of an atomic cross-section term and an

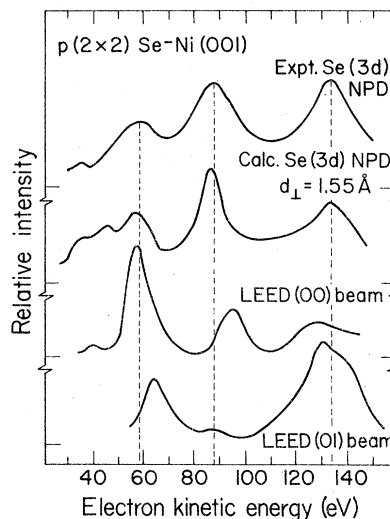


FIG. 4. NPD curve for Se(3d) electrons from $p(2 \times 2)$ Se-Ni(001), compared with theoretical curve by Li and Tong (Ref. 14) and LEED-beam curves by Demuth and Rhodin (Ref. 15).

oscillatory function which describes the final-state scattering. This picture is consistent with recent theoretical predictions¹⁴ that initial states possessing radial nodes exhibit NPD curves with one major sharp peak, the position of which is insensitive to d_\perp . The peak is merely an artifact of a Cooper minimum in the atomic cross section, which sharply attenuates the cross section a few eV above threshold and keeps it at a low value for a long range of energy. Although the diffraction oscillations may be present at higher energies, they will be difficult to observe because the entire elastic peak in the photoemission spectrum is very weak and is obscured by "noise" arising from the inelastic background.

At this point we make an interesting qualitative comparison of the NPD spectrum for the $p(2 \times 2)$ Se-Ni(001) system to the published¹⁵ LEED (00) and (01) beams for this system, as well as to the curve calculated by Tong and Li. We commented briefly on this comparison before. All four curves appear in Fig. 4. The close correspondence of peak positions is striking and it supports the prediction that an NPD spectrum should contain a coherent superposition of LEED beams, with the normal (00) beam being emphasized in the NPD spectrum. As noted before,³ the peaks at approximately 37, 88, and 134 eV are Bragg peaks in the (00) beam, while the 58 eV peak arises from multiple scattering, thereby demonstrating the importance of considering multiple scattering in angle-resolved photoemission. Another earlier observation—that the NPD relative peak intensities were close to those in the (00) LEED beam—was incor-

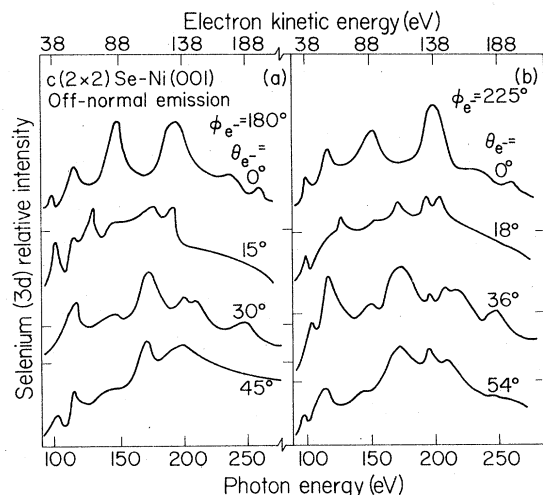


FIG. 5. Off-normal Se(3d) photoelectron-diffraction curves for the $c(2 \times 2)$ Se-Ni(001) system (a) in the $(\bar{1}00)$ mirror plane; (b) in the $(0\bar{1}\bar{1})$ mirror plane. Note similarity of lateral pairs.

rect, in light of the new intensity corrections.

To further characterize constant-initial-state photoelectron diffraction, we also carried out off-normal studies in the $c(2 \times 2)$ Se-Ni(001) system. In Fig. 5(a) we show results for emission into the $(\bar{1}00)$ mirror plane at various polar angles, and in Fig. 5(b) similar data are shown for emission into the $(0\bar{1}\bar{1})$ mirror plane. The curves are rich in structure, and if they could be interpreted quantitatively, they would probably yield a good deal of information. It is also clear that the intensity modulations are not nearly as pronounced off normal as they are at normal emission. Indeed at some angles little structure is observed at all. This can be understood as arising from the reduction in symmetry of the off-normal final state and the consequent removal of degeneracies in the various time-reversed LEED beams contributing to the final state. We discussed this point earlier.³ It is probably also responsible for smaller oscillations being observed in azimuthal spectra (APD). In contrast to the behavior of the LEED (00) beam,¹⁵ there is no obvious systematic shift of peak energies with (polar) emission angle. In fact the curves seem to evolve more by reduction in the intensities of some peaks and by increases in others.

Although the off-normal curves in Fig. 5 were taken at a coarse angular mesh and do not represent as complete a study as would be desirable, being the first of their kind they yield enough information to merit several observations. Clearly the photoelectron-diffraction curves evolve with polar angle θ differently than does a single LEED

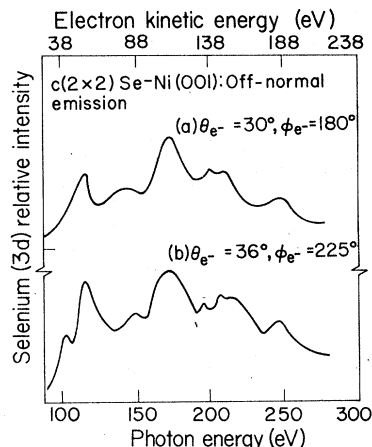


FIG. 6. Direct comparison of the middle pair of off-normal curves from Fig. 5. Note similarity of overall shape and particularly of peaks near kinetic energies of 55, 111, and 184 eV.

beam. This is, by negative inference, consistent with the expectation that the off-normal photoelectron-diffraction curve will be comprised of a coherent superposition of several LEED beams, with the amplitude admixture coefficients varying with θ . Careful theoretical analysis will be required to establish the extent to which these curves can in fact be fitted quantitatively.

One of the original incentives for these off-normal studies was to explore whether the intensity-voltage curves became particularly simple at particular nonzero values of θ . For example, the (θ_{e-}, ϕ_{e-}) combinations of $(45^\circ, 180^\circ)$ and $(54^\circ, 225^\circ)$ correspond to emission normal to the $(\bar{1}01)$ and $(\bar{1}\bar{1}\bar{1})$ planes, respectively. Some sensitivity might be expected in these curves to the d_\perp values of overlayer selenium relative to these two planes, although complicating factors abound (low symmetry, energy-dependent refraction, etc.). In fact we have not noted any obvious relationships between the forms of the off-normal curves in Fig. 5 and the known adsorbate-substrate geometry. This question must be left open pending further experimental and theoretical work. There is, however, one unexpected feature of the off-normal curves that deserves comment. The three lateral pairs of off-normal curves in Fig. 5 show a fair degree of resemblance to one another. This is most pronounced in the middle pair, which is also the off-normal pair showing the largest photoelectron-diffraction modulation. In Fig. 6 these two curves are compared on a common energy scale. Several of the most prominent peaks fall at similar energies, with similar intensities, in the two curves. At this point we can only note this interesting similarity as an empirical fact, to be clarified by

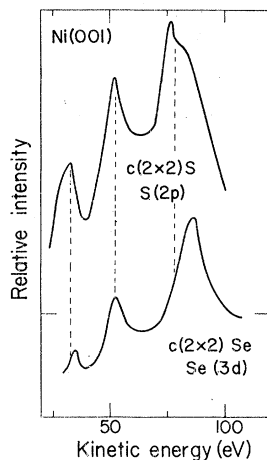


FIG. 7. Comparison of NPD curves for $c(2 \times 2)$ S-Ni(001) and $c(2 \times 2)$ Se-Ni(001).

further research. The pairwise similarity of the curves in Fig. 5 for similar polar but different azimuthal angles suggests in a *very tentative* way that the polar angle alone may be a critical variable in determining the scattering curve. This would be true, for example, if the substrate surface were effectively an isotropic scattering plane.

Perhaps the most conclusive way to show that NPD does not simply measure the (00) LEED beam is to study a different system in which peak energies in the LEED (00) beam are similar to those in the selenium system, but for which peaks in the NPD curve are different. Such a system is $c(2 \times 2)$ sulfur on Ni(100). In Fig. 7 we show NPD results for that system, and for comparison the second curve in Fig. 3, which shows similar data for the $c(2 \times 2)$ Se-Ni(001). The S(2*p*) core level was used as an initial state for the sulfur data. At first glance the curves in Fig. 7 appear remarkably similar. However, as the dashed lines in the figure and the tabulation of peak positions in Table II indicate, there are differences between the two cases which are well outside our experimental error and which cannot be removed by simply

TABLE II. Comparison of NPD and LEED (00) peak energies.

$c(2 \times 2)$ S(2 <i>p</i>)	NPD ^a (eV)	LEED (00) ^b
Peak 1	32	36
Peak 2	52	56
Peak 3	78	92
$c(2 \times 2)$ Se(3 <i>d</i>)		
Peak 1	37	39
Peak 2	52	56
Peak 3	86	91

^aAll NPD data are electron kinetic energies referred to the nickel vacuum level.

^bAll LEED data are from Ref. 15.

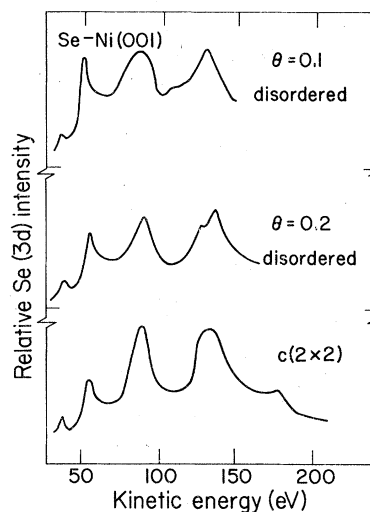


FIG. 8. Comparison of NPD curves for Se(3*d*) in disordered Se on Ni(001) at (a) 0.1 monolayer and (b) 0.2 monolayer with the $c(2 \times 2)$ pattern.

shifting one curve with respect to the other. The curves' similar appearance is probably attributable to the fact that the S(2*p*) and Se(3*d*) radial wave functions are similar; hence the atomic cross-section term discussed earlier will be similar for the two cases. Calculations will be presented in a future paper which will show that the sulfur data can be fitted using a value of $d_{\perp} = 1.3 \text{ \AA}$,¹⁶ the same value reported from LEED⁷ and other photoemission analyses.¹⁷ This result is the clearest indication that NPD is sensitive to d_{\perp} .

The final data set which we wish to present (Fig. 8) is that for disordered, low coverages of selenium on Ni(001). The top curve in Fig. 8 shows NPD data for a coverage of approximately 0.1 monolayer, while the middle curve is for 0.2 monolayer. Neither surface gave an ordered LEED pattern, but both show substantial photoelectron-diffraction effects. Indeed the amplitude of oscillation is nearly as large in these two cases as in the bottom curve, which shows for comparison the $c(2 \times 2)$ curve. The significance of this result should not be underemphasized. It shows first that the dominant scattering mechanism in NPD is definitely off the substrate and not the overlayer itself; otherwise the effect in the disordered overlayer would not be so large. It also confirms the claim made in our earlier paper that NPD, like extended x-ray absorption fine structure, can deal quite effectively with disordered overlayer systems which are common in surface studies (especially in the case of stepped crystals). This is a significant advantage over LEED, in which (00) beam intensity variations are the only changes useful in making a structure determination on dis-

ordered overlayers. A similar experiment using APD is clearly in order, to determine the extent to which APD is sensitive to the substrate-adsorbate overlayer geometry as opposed to the geometry of the overlayer alone.

IV. CONCLUSIONS

In this paper we have reported the results of a series of experiments designed to test the viability of NPD as a surface-structure-sensitive technique. Our principal conclusion is that NPD is indeed structure sensitive and is a candidate technique for adsorbate-structure determinations. Detailed conclusions are given below.

1. Both adsorbate and substrate levels show large NPD oscillations, including multiple-scattering peaks. Thus photoelectron-diffraction effects, including multiple scattering, must be considered in quantitative interpretations of intensities in angle-resolved photoemission experiments.

2. NPD intensity-energy curves are reproducible and peak positions show little sensitivity to the direction of the photon \vec{A} vector.

3. The intensity-energy curves for both sulfur and selenium on Ni(001) behave like atomic cross sections, modulated by photoelectron-diffraction

peaks supporting a two-step mechanism.

4. NPD measures a coherent superposition of LEED beams, and not the (00) beam alone. This follows both from off-normal studies of $c(2 \times 2)$ Se-Ni(001) and from NPD studies of $c(2 \times 2)$ S-Ni(001).

5. NPD is applicable to disordered adsorbate systems.

6. Off-normal curves showed smaller oscillation amplitudes than NPD curves, and somewhat similar evolution with θ for two different values of ϕ .

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