PHYSICAL REVIEW B VOLUME 24, NUMBER 10 15 NOVEMBER 1981

Angle-resolved x-ray photoemission and Auger emission from core levels of $c(2\times2)$ S and Se on Ni(001): Diffraction effects and single-scattering theory

P. J. Orders, R. E. Connelly, N. F. T. Hall, and C. S. Fadley
Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822

(Received 17 March 1981)

Azimuthal anisotropies in x-ray photoemission from S $2p$ and Se $3p$ core levels of $c(2\times2)$ overlayers on Ni(001) are found to agree very well with single-scattering cluster calculations for the known geometries of these adsorbates. These results thus further confirm the utility of such analyses for surface-structure studies, although the sensitivity to adsorbate vertical position is not predicted to be high unless $z \lesssim 0.5-1.0$ Å. Analogous anisotropies observed in Se *Auger* electron intensities are found to be identical to those observed for Se $3p$ photoelectrons despite the inherent differences between their respective emission processes.

In several recent studies,[1] it has been suggested that angle-resolved x-ray photoemission (XPS) from adsorbate core levels can be used to provide surface structural information, and that an important simplification possible at XPS electron energies of ~1 keV lies in being able to utilize a single-scattering or kinematical theory. For example, single-scattering calculations have been compared with experimental results for azimuthal scans at grazing emission angles from $c(2\times2)$ O on Cu(001),[1] and this comparison suggests that the oxygen atoms reside in fourfold hollow sites coplanar with the Cu surface atoms. However, the atomic adsorbate overlayers studied to date by this method [O/Cu(001) and O/Ni(001)] have been cases where the bonding geometry has not been well established by other techniques, [1] so that a definitive test of the applicability of a single-scattering analysis is lacking. Here, we report the first XPS study of this kind for two geometrically well-understood chemisorption systems: $c(2\times2)$ S and $c(2\times2)$ Se on Ni(001). Low-energy electron diffraction[2] (LEED) and normal photoelectron diffraction[3] (NPD) studies of $c(2\times2)$ Se on Ni(001) have established that the Se atoms occupy the fourfold hollow sites with z, the Se–Ni interplanar spacing, equal to 1.55 Å. Similarly, LEED[4] and NPD[5] studies of $c(2\times2)$ S on Ni(001) indicate that the S atoms also occupy the fourfold hollow sites, but with z equal to 1.30 Å. These systems thus provide critical tests as to the accuracy of single-scattering calculations in describing such azimuthal XPS data. As a further element of this study, we have measured for the first time the azimuthal dependence of high-energy adsorbate *Auger* electrons (Se $L_3M_{4,5}M_{4,5}$), and compared the results with similar measurements based upon Se $3p$ *photo*electrons.

The experimental apparatus has been described in detail previously.[1] The nickel surface was oriented to within ±0.5° of the (001) face, etched, and cleaned *in situ* by argon-ion bombardment and annealing. LEED patterns indicated a well-ordered (001) surface. The $c(2\times2)$ overlayers of Se were produced following a previously described method.[6] The same procedure was used to obtain $c(2\times2)$ overlayers of S. The $c(2\times2)$ LEED patterns remained sharp and the respective Se $3p$/Ni $3s$ and S $2p$/Ni $3s$ ratios changed by less than the experimental uncertainty of 10% over the course of an azimuthal scan. The polar emission angle θ is measured with respect to the surface and the azimuthal angle ϕ with respect to the [100] crystal axis. Unpolarized Al $K\alpha$ radiation (1487 eV) was used for excitation. Azimuthal scans were made of the core photoelectron peaks Se $3p$ (kinetic energy = 1322 eV) and S $2p$ (1325 eV), and of the Se Auger peak $L_3M_{4,5}M_{4,5}$ (1311 eV) at several polar angles near grazing emission. For the photoemission data, the $p_{1/2}$ and $p_{3/2}$ intensities were summed to improve statistics and simplify data analysis.

One-quadrant Cartesian plots of the S $2p$ and Se $3p$ experimental results are shown as dashed lines in Figs. 1 and 2, respectively. The data have been fourfold averaged over the symmetry-equivalent azimuthal angles ϕ, $\phi+90°$, $\phi+180°$, and $\phi+270°$ so as to reduce spurious sources of intensity variation, although all fine structure in the averaged data was seen also in each quadrant of

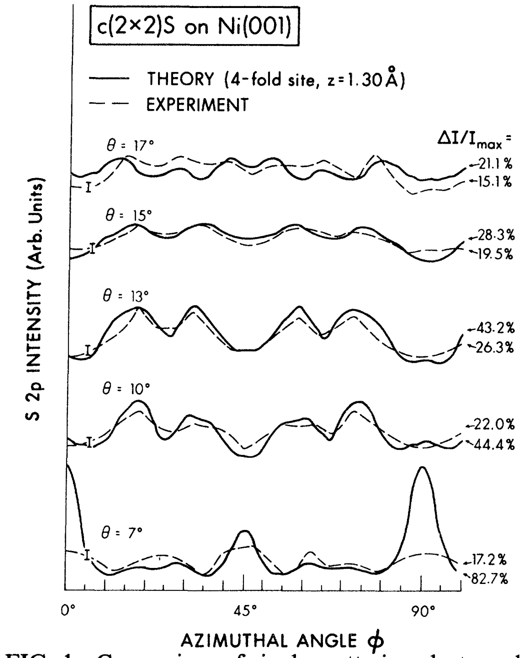

FIG. 1. Comparison of single-scattering cluster calculations with experiment for the azimuthal variation of photoelectron intensities from the S $2p$ core level in $c(2\times2)$ S on Ni(001) at polar angles of $7^\circ \leq \theta \leq 17^\circ$. The experimental curves have been arbitrarily scaled to facilitate comparison with theory. Overall anisotropies $\Delta I/I_{\max}$ are given at right.

the raw data. This procedure does not include averaging over the [110] mirror plane at $\phi = 45^\circ$, and thus the degree of reproducibility of the experimental data about $\phi = 45^\circ$ is an indication of their overall accuracy. Peak positions and widths show a strong dependence on polar angle for both sets of data. The overall anisotropies, defined as $\Delta I/I_{\max} = (I_{\max} - I_{\min})/I_{\max}$, are marked on the right of the figures as percentage values. They range between 15% and 26% for S and between 15% and 35% for Se.

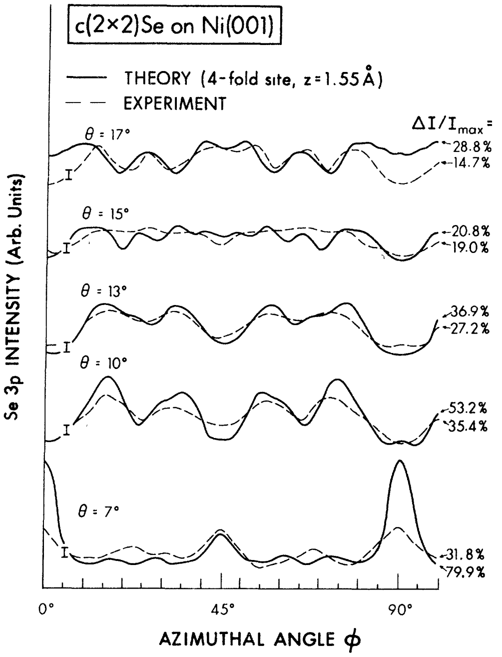

FIG. 2. As in Fig. 1, but for emission from the Se $3p$ core level in $c(2\times2)$ Se on Ni(001).

The single-scattering model employed here has been discussed in detail elsewhere.[1] It is essentially a superposition of the direct or primary wave excited from a given adsorbate site and those waves scattered once by adsorbate or substrate atoms at other sites in a cluster. The clusters used contained approximately 30 adsorbate and 90 substrate atoms. The scattering from the jth atom is described by a complex scattering factor $f_j(\theta_j) = |f_j(\theta_j)| \exp[i\Psi_j(\theta_j)]$, where θ_j is the scattering angle and Ψ_j the overall phase shift. $f_j(\theta_j)$ is determined from 25 partial-wave phase shifts for the appropriate atoms and energies. Attenuation of the measured "no-loss" intensities by inelastic scattering is included by assuming an isotropic exponential decay of wave amplitudes. The effects of thermal vibration are incorporated via Debye-Waller factors. Surface refraction effects are included by assuming that the Ni inner potential is a step function located at 1.24 Å (the Ni hard-sphere radius) above the surface. However, since S and Se are found at greater distances of 1.30 and 1.55 Å, respectively, above the surface, scattering from other adsorbate atoms will not be much affected by the Ni inner potential, even though it might be argued that some nonzero potential could exist in a $c(2\times2)$ overlayer. Furthermore, model calculations suggest that such adsorbate scattering will be the major source of anisotropies in the diffraction patterns of overlayer geometries with rather large z values such as those studied here, and thus, electron refraction effects due to the Ni inner potential should be negligible. The calculations included broadening in both θ and ϕ to simulate the experimental acceptance cone of 3.5° half angle.[1]

The results of such single-scattering calculations for $c(2\times2)$ S on Ni(001) with S in the fourfold hollow sites at $z = 1.30$ Å and for $c(2\times2)$ Se on Ni(001) with Se in the fourfold hollow sites at $z = 1.55$ Å are shown as solid lines in Figs. 1 and 2, respectively. There is, in general, excellent agreement between experiment and theory as to peak positions and relative intensities, with *all* major features being correctly predicted in the theoretical curves. In fact, there exist only a few areas where minor discrepancies can be seen. In Fig. 1 for $\theta = 10°$, a very weak peak at $\phi = 0°$ and the symmetry-equivalent direction $\phi = 90°$ is observed in the theoretical curve but is absent in the experimental data. Considerable very weak fine structure is observed in the $c(2\times 2)$ Se theoretical curve of Fig. 2 for $\theta = 15°$ but remains unresolved in the experimental data. However, both predicted and observed anisotropies are very low in this region, and so it is not surprising that it might be difficult to resolve such features experimentally. A doublet in the $c(2\times 2)$ Se experimental data for $\theta = 7°$ at $\phi = 22°$ and 32° is slightly shifted with respect to the corresponding features in theory at $\phi = 18°$ and 29°, but the relative intensities of the two components are correctly predicted. However, the equivalent doublet for $c(2\times 2)$ S is correctly predicted in position as well as relative intensity. A final point of qualitative discrepancy for both S and Se at $\theta = 7°$ is that the relative intensity of the peak at $\phi = 0°$ and 90°, which can be shown theoretically to result predominantly from simple forward scattering off nearest-neighbor adsorbate atoms along [100]-type directions, is much lower in the experimental data than in the theoretical curves. Theoretical calculations indicate that such discrepancies cannot be fully explained as being due to slight electron refraction at the lowest θ values caused by a nonzero inner potential in the overlayer, even though they tend to diminish at higher polar angles, where the observed and calculated percent anisotropies agree reasonably well, especially for $\theta \geq 15°$. In any case, there are several previously discussed reasons why such theoretical calculations should predict more anisotropy than is observed[1]: (i) surface nonidealities, (ii) nonisotropic inelastic scattering, (iii) scattering factors that are too large in the forward direction due to curved-wave corrections, and (iv) multiple-scattering effects.

Overall, it is thus clear that single-scattering calculations give a very good description of the basic physics of final-state diffraction in angle-resolved XPS from adsorbate core levels. In further utilizing this type of analysis to determine unknown adsorbate geometries there are also certain limitations that should be discussed, however. For adsorbates that reside well above the metal surface, geometric considerations require that the scattering angles from near-neighbor substrate atoms become quite large. Also, at electron energies of ~ 1 keV the scattering factor is strongly peaked in the forward direction, with a full width at half maximum of ~ 10°. Thus, substrate scattering events involving much larger angles will contribute very little to the anisotropy since their relative scattering amplitudes will be much less than those for electrons more nearly forward scattered from adsorbate atoms. Scattered electron amplitudes are also damped by a Debye-Waller factor which will attenuate large-angle interference effects more than those associated with the small angles of forward scattering.[1]

For the two systems studied here with $z = 1.30$ and 1.55 Å, the scattering angles from the near-neighbor Ni atoms that are most significant in producing diffraction effects are large ($\theta_j \approx 23° - 58°$) in comparison with those involved in S or Se adsorbate scattering (where $\theta_j = \theta$ for all atoms). Thus, the resultant modulations caused by scattering from the substrate are negligibly small with with respect to those from the adsorbate. In fact, single-scattering calculations[7] show no noticeable changes in the diffraction patterns from $c(2\times 2)$ S on Ni(001) for z values above ~1.2 Å, while the patterns from $c(2\times 2)$ Se on Ni(001) remain essentially unchanged for z values above ~0.6 Å. A further consequence for such large z values is that the predicted patterns are insensitive to the horizontal registry of the $c(2\times 2)$ Se overlayer with the Ni surface, although they *are* very sensitive to the change from $c(2\times 2)$ to a $p(2\times 2)$ overlayer. Hence, at least with the degree of angle broadening presently involved in theory and experiment, diffraction effects at large z are expected to be rather insensitive to changes in z or coordination site (as fourfold, twofold, etc.), even though the short-range intralayer geometry can be determined. By contrast, for $z \approx 0$ [as appears to be the case with O on Cu(001)], it has been shown that a sensitivity in z of ~ ±0.1 Å can be expected.[1] Thus, the techniques will be best utilized with adsorbates positioned in or near the surface.

Finally, we consider the azimuthal anisotropies observed in Se Auger intensities at 1311 eV for $c(2\times 2)$ Se on Ni(001). This $L_3M_{4,5}M_{4,5}$ Auger transition is of the core-core-core type. The Auger data is shown as dashed lines in Fig. 3, where it is compared with corresponding Se $3p$ core-photoelectron diffraction patterns at very similar kinetic energy (solid lines). Although quite different in basic origin, the two sets of data are in full agreement to within our estimated experimental accuracy. Little is known about the angular dependences of such adsorbate Auger electrons. Angular anisotropies have been observed in adsorbate Auger intensities for $c(2\times 2)$ S on Ni(001),[8,9] where the transition studied was of $L_{2,3}M_{2,3}M_{2,3}$ or core-valence-valence (CVV) type and was at a much lower energy of 148 eV. However, analysis of such data to derive surface structural information is made extremely difficult by the interaction of angular dependences inherent in the Auger emission process itself and final-state electron diffraction that may include significant multiple-scattering effects. The same complications have also been encountered in similar measurements of low-energy CVV Auger intensities from clean metal surfaces.[9,10] The present data suggest that, despite fundamental differences between the Auger and photoemission processes, at energies of $\sim 10^3$ eV and for Auger and photoelectron emission involving core levels only, final-state diffraction effects are dominant and essentially identical for both cases. A likely reason that anisotropies in the basic Auger emission process are not more important is that the highly forward-peaked nature of the final-state scattering effectively selects a rather narrow cone of emitted waves as being significant in producing both direct and scattered amplitudes, with the primary intensity of Auger emission being very nearly constant over this small angular range.

In conclusion, we have shown that a simple single-scattering cluster model provides a very good description of final-state diffraction effects observed in azimuthal XPS from adsorbate overlayers. It appears then that this technique will be a valuable tool for the determination of overlayer geometries, although the sensitivity to z and coordination site is expected to be high only for adsorption at $z \lesssim 0.5-1.0$ Å. The analogous azimuthal anisotropies observed in core-level Auger emission from an adsorbate are essentially identical to those seen in photoemission and thus, such measurements also hold promise for surface structural studies.

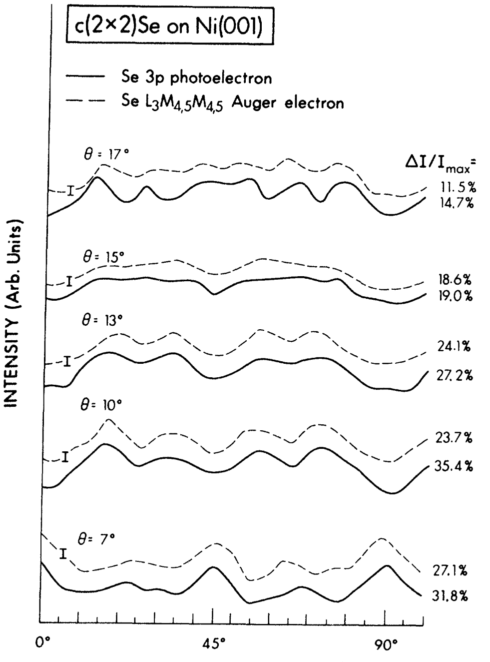

FIG. 3. Comparison of experimental azimuthal data from Se $3p$ photoelectron intensities and Se $L_3M_{4,5}M_{4,5}$ Auger intensities in $c(2\times 2)$ Se on Ni(001) for polar angles of $7° \leq \theta \leq 17°$.

We are indebted to D. A. Shirley for providing us with certain results prior to publication. We also gratefully acknowledge the support of the National Science Foundation (Grant No. 76-24506).

---

[1] S. Kono, S. M. Goldberg, N. F. T. Hall, and C. S. Fadley, Phys. Rev. Lett. 41, 1831 (1978); L. -G. Petersson, S. Kono, N. F. T. Hall, S. M. Goldberg, J. T. Lloyd, and C. S. Fadley, Mater. Sci. Eng. 42, 111 (1980); S. Kono, N. F. T. Hall, and C. S. Fadley, Phys. Rev. B 22, 6085 (1980).

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

[3] S. D. Kevan, D. H. Rosenblatt, D. Denley, B. -C. Lu, and D. A. Shirley, Phys. Rev. Lett. 41, 1565 (1978); Phys. Rev. B 20, 4133 (1979).

[4] J. E. Demuth, D. W. Jepsen, and P. M. Marcus, Phys. Rev. Lett. 32, 1182 (1974).

[5] D. H. Rosenblatt, J. G. Tobin, M. G. Mason, R. F. Davis, S. D. Kevan, D. A. Shirley, C. H. Li, and S. Y. Tong, Phys. Rev. B 23, 3828 (1981).

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

[7] N. F. T. Hall, Ph.D. Thesis, University of Hawaii, 1979 (unpublished).

[8] T. Matsudaira, N. Nishijima, and M. Onchi, Surf. Sci. 61, 651 (1976).

[9] D. Aberdam, R. Baudoing, E. Blanc, and C. Gaubert, Surf. Sci. 71, 279 (1978) and references therein.

[10] L. McDonnell, D. P. Woodruff, and B. W. Holland, Surf. Sci. 51, 249 (1975).