# Azimuthal Anisotropy in Deep Core-Level X-Ray Photoemission from an Adsorbed Atom: Oxygen on Copper(001)

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For oxygen adsorbed on a Cu(001) surface, the O 1*s* x-ray photoelectron intensity is found to exhibit a complex azimuthal anisotropy with an overall amplitude of ~ 26% for a grazing 10° angle of emission. No significant anisotropy is observed at 45°. Several reasons for expecting a direct relationship between such final-state scattering effects and atomic geometry are discussed, and the data are found to be suggestive of a surface-chemisorbed $c(2\times2)$ oxygen overlayer in fourfold coordination.

In studies of adsorbate bonding to single-crystal surfaces, angle-resolved photoelectron spectroscopy of *valence* levels has proven to be a promising technique.[1] Extracting structural information from such data, however, requires calculations of both initial- *and* final-state wave functions using methods closely related to the multiple-scattering theory of LEED (low-energy electron diffraction).[1] Thus, deep core-level emission might also be useful for such studies, as the initial state is simply a spherically symmetric charge distribution that is unperturbed by chemical bonding. For a fixed geometry of radiation source and electron analyzer, any azimuthal anisotropy in core photoelectron intensity with respect to a single-crystal surface must be due to final-state scattering effects, as first discussed by Liebsch[2] in theoretical calculations for ultraviolet excitation energies. An added advantage of core-level emission is that peaks originating in a definite atomic species can be studied. However, prior attempts to observed anisotropies in core emission from adsorbates have not yielded significant effects. Smith, Larsen, and Chiang[3] have studied Cs on W(001) using ultraviolet excitation and observed only a small azimuthal anisotropy for the weakly bound Cs $5p_{3/2}$ core level; the amplitude of these effects as measured by the maximum-to-minimum ratio was ~ 1.12. In this Letter, we report the first observation of larger azimuthal anisotropies of ~ 1.26 for deep-core x-ray photoemission (XPS) from an adsorbate, and comment qualitatively on the potential utility of such measurements for structural determinations.

The system investigated was oxygen chemisorbed on a copper surface oriented to within 0.5° of (001). The experimental geometry has been discussed previously.[4] The polar emission angle $\theta$ as measured with respect to the surface was varied by rotating the specimen about an axis perpendicular to the plane containing the directions of x-ray incidence and electron emission (which were separated by a fixed angle of 72°). The azimuthal angle $\varphi$ was varied by full 360° rotation about an axis parallel to [001] (cf. Fig. 1).

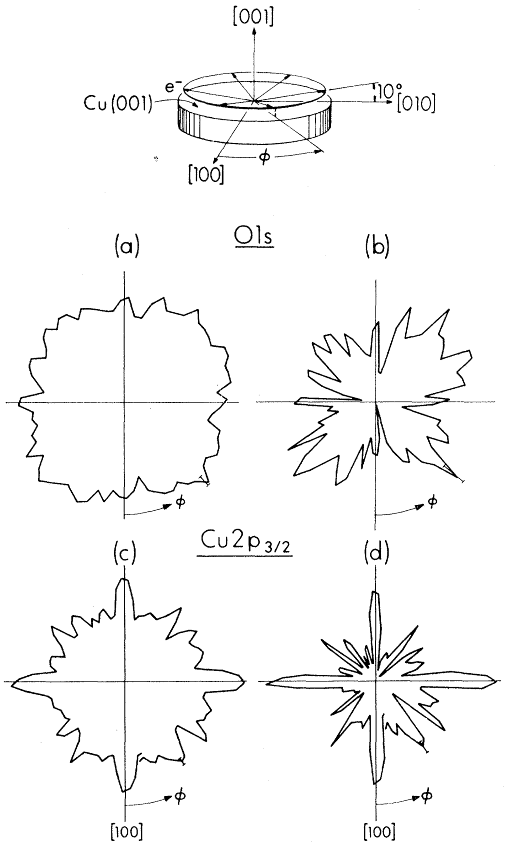

FIG. 1. Azimuthal angular distributions of absolute XPS intensities for the O 1*s* and Cu $2p_{3/2}$ core levels from a Cu(001) surface exposed to 1200 L oxygen (1 L $=10^{-6}$ Torr sec). A polar emission angle of 10° with respect to the surface was used. The O 1*s* data are a sum of three complete scans; Cu $2p^{3/2}$ is one scan. In (b) and (d), the minimum value has been subtracted from the data to amplify anisotropies.

The unpolarized radiation was at 1486.6 eV and the instrument resolution was 1.0 eV FWHM (full width at half-maximum) for Au $4f_{7/2}$. Pressures during measurement were $5\times10^{-11}$–$1\times10^{-10}$ Torr. Surfaces were prepared by argon-ion bombardment and annealing at ~ 800°K. Pronounced angular anisotropies in copper core-level intensities [cf. Fig. 1(c)] verified the presence of near-surface atomic order.[4] Oxygen exposures were 1200 L (1 L $=10^{-6}$ Torr sec) at $10^{-6}$ Torr and 300°K, LEED measurements in a separate chamber indicated that such exposures resulted in the formation of a $c(2\times2)$ surface structure, as expected from prior studies.[5-8] XPS spectra were obtained for the adsorbate O 1*s* core level (binding energy = 530 eV, kinetic energy = 952 eV) and the substrate core levels Cu $2p_{3/2}$ and Cu 3*s*. No impurity peaks were observed. After inelastic background subtraction,[9] absolute "no-loss" peak areas were determined as a function of $\varphi$ for various constant polar angles $\theta$, as shown in Fig. 1 for a grazing 10° angle of emission. The O 1*s* peaks were all symmetric in shape and rather narrow (FWHM) = 1.3–1.4 eV at $\theta = 10°$), and their shapes and positions were not found to change with emission angle; these results suggest a single, well-defined chemical state. For a given $\theta$ and $\varphi$, the (O 1*s*)/(Cu 3*s*) ratio changed by less than the experimental uncertainty of ~ ± 10% over the course of an azimuthal scan, indicating a stable specimen condition. To minimize spurious instrumental sources of anisotropy, raw data such as those in Fig. 1 have been fourfold averaged by adding intensities at $\varphi$, $\varphi+90°$, $\varphi+180°$, and $\varphi+270°$, as shown in Fig. 2.

The data of Figs. 1 and 2 exhibit fourfold azimuthal anisotropies in both the O 1*s* and Cu $2p_{3/2}$ intensities that are in registry with the (001) surface symmetry. The complex pattern of peaks 5–9 noted for Cu $2p_{3/2}$ is more pronounced than that for O 1*s* (with an overall amplitude of 1.67 compared to 1.26 for O 1*s*), does not change significantly with oxygen adsorption, and is caused by electron scattering in the substrate.[4] For O 1*s*, the raw data in Figs. 1(a) and 1(b) exhibit an overall four-peak pattern with maxima for $\varphi = 45°$, 135°, 225°, and 315°, and weaker, narrower peaks are also suggested for emission with $\varphi = 0°$, 90°, 180°, and 270°. The fourfold-averaged data in Figs. 2(a) and 2(b) confirm all of these features, and also indicate that each of the four main components consists of a triplet of peaks of types 2, 3, and 4. These triplets are also suggested in Fig. 1(b). Peaks 2 and 4 should be equivalent by symmetry, and the fourfold-averaged data are fully consistent with this. All of peaks 1–4 in the O 1*s* data were found to be reproducible on three different crystals, although the relative intensities of peaks and valleys (especially for peaks 2–4) are less certain. There is thus significant final-state scattering when a grazing takeoff angle is used.

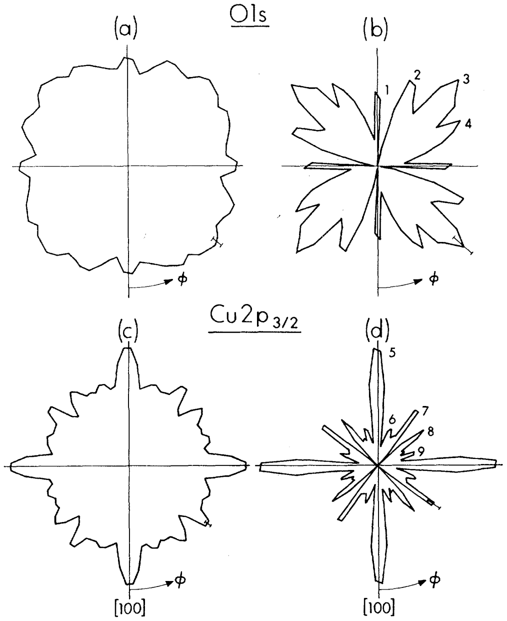

FIG. 2. Same as Fig. 1, but the data have been fourfold averaged to reduce spurious ources of non-fourfold anisotropy.

Azimuthal scans of O 1*s* intensity were also made at a higher takeoff angle of 45°, and the data exhibit essentially no anisotropy, with an amplitude of ~ 1.05 that is not larger than the estimated experimental error. These data thus suggest that large-angle scattering from surface atoms is not significant in producing these effects, but rather that grazing emission involving directions passing close to neighboring surface atoms is necessary.

Although no quantitative theoretical calculations directly related to such XPS adsorbate angular distributions are as yet available, prior analyses of closely related processes[10-16] permit several qualitative conclusions to be made. At electron energies of ~ 1000 eV, the individual electron-atom interactions will lead to *elastic* scattering that is highly peaked in the forward direction.[10-16] Partial-wave analyses of such scattering are cumbersome because of the large number of phase shifts which must be computed,[12,13,16] but it is expected that simpler calculations based upon the Born approximation or other perturbative approaches will provide a reasonable first-order description.[10,12] If the scattering angle is $\theta'$, Born calculations of the differential cross sections $|f(\theta')|^2$ for O 1$s$ photoelectrons at 952 eV scattering from atomic Cu and O yield forward-scattering peaks with FWHM values of only ~10° and ~20°, respectively,[10] in good agreement with a partial-wave analysis for Cu at 680 eV.[13] Forward scattering from Cu is also predicted to be approximately 5 to 10 times stronger than that from O becuase of its higher atomic number.[10,11] Backscattering intensities are also expected to be very weak at such high energies, and to be down by a factor of ~1/100 relative to forward scattering.[10,12-15] Thus, modulation of the photoelectron intensity by coherent backscattering from neighboring atoms to the adsorbate atom [as in EXAFS (extended–x-ray-absorption fine structure)[12-15]] should be negligible in comparison to forward-scattering effects. If atomic vibration is also considered by including a Debye-Waller factor (≡DW) in coherent superpositions,[12,13,15] the short electron wavelengths of ~0.4 Å are expected to further diminish the importance of interference effects that arise in large-angle scattering. For example, for Cu at 952 eV, DW≈0.1 for $\theta'=60°$, whereas DW≈1.0 for $\theta'$ near zero. Finally, single, rather than multiple, scattering should be most important in producing anisotropies at such high energies.[15]

The reduction of no-loss photoelectron intensity by *inelastic* scattering must also be considered. The optical potential most appropriate for this in high-energy photoemission is of the form $V(\vec{r}) = V_1(\vec{r}) + iV_2(\vec{r})$, for which $V_2(\vec{r})$ is nonisotropic to allow for the enhanced possiblity of inelastic scattering near atomic centers (for example, due to the excitation of localized $d$ electrons).[14,17] Inelastic scattering is thus qualitatively predicted to be more pronounced for motion along directions close to atomic centers, while elastic scattering will conversely cause a sharp peaking in scattered intensity for directions immediately forward of each scattering center. Thus, for an adsorbate atom sitting on or in the first atomic layer of the surface, anisotropies should be largely determined by single low-angle scattering events from the first few circles of neighbor atoms along the surface, together with associated interference effects and nonisotropic inelastic scattering. Long-range order should therefore not be essential for observing such anisotropies (by contrast with LEED).

These ideas can be qualitatively used to relate the data of Fig. 2(b) with proposed atomic geometries for $c(2\times2)$ oxygen on Cu(001). Previous theoretical analyses of LEED data have not conclusively determined the structure of this overlayer, although a fully reconstructed oxygen-copper surface layer is somewhat favored over the next most reasonable possibility of fourfold-coordinated oxygen chemisorbed on the copper surface.[7,8] By contrast, a combined LEED/XPS study[6] at various adsorption temperatures concludes that fourfold coordination occurs. Within the framework of the simple assumptions above, the present XPS data also qualitatively suggest the fourfold geometry, as illustrated in Fig. 3, where the O 1$s$ intensity at grazing emission has been overlaid on the approximate atomic structure expected. Broad intensity maxima are found for emission toward "holes" in the Cu surface such as that at $\varphi=45°$. Along such open directions, *inelastic* scattering from neighboring atoms should be diminished, in agreement with the observed increase in no-loss intensity. Superimposed on the general four-peak structure are narrower peaks of types 1–4 that are found at $\varphi$ values very nearly equal to those of certain sets of near-neighbor surface atoms: 1 can thus be

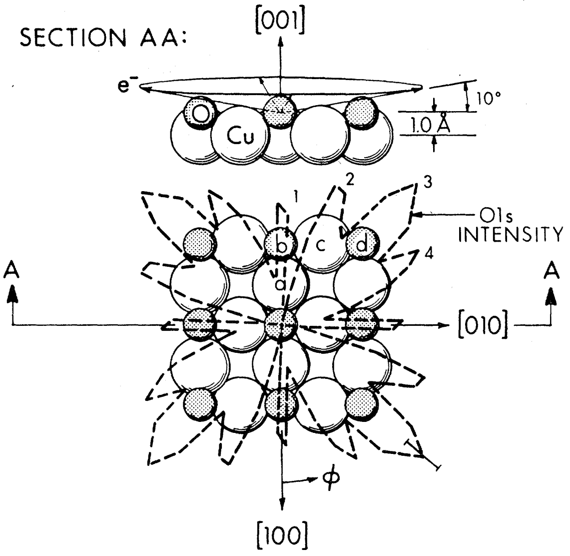

FIG. 3. The O 1$s$ data of Fig. 2(b) superimposed on a fourfold-coordinate atomic geometry for the $c(2\times2)$O overlayer. An O vertical displacement of 1.0 Å has been chosen to be consistent with typical Cu-O bond distances and prior LEED analyses of $c(2\times2)$O on Ni (Refs. 7 and 8).

associated with a set beginning with Cu(a) and O(b) and extending radially outward, 2 and 4 a set beginning with Cu(c), and 3 a set beginning with O(d), as well as with the most open emission direction. The positions of the symmetry-identical peaks 2 and 4 yield an average $\varphi$ of 25.3° that is in good agreement with the 26.6° position of the associated atomic set. Thus, peaks 1–4 can be explained as having strong contributions from forward peaking in the *elastic* scattering from near-neighbor atoms along the surface, with peak 3 also perhaps being enhanced by a reduction in inelastic scattering. The valley-to-valley angular widths of 16° for peak 1, 25° for 2 and 4, and 24° for 3 are also of the same order as those expected from atomic scattering at 952 eV, although we stress that the relative phases of various strongly scattered waves also will have an important influence on both peak widths and relative intensities. For the O position chosen in Fig. 3, the scattering angles $\theta'$ would be Cu(a), 38°; O(b) and O(d), 10°; and Cu(c), 24°. Although that for Cu(a) is rather large, a significant $f(\theta')$ will result because of the higher scattering power of Cu. A similar analysis of the O 1*s* pattern in relation to a reconstructed surface, by contrast, does not yield as good agreement: Overall experimental minima, rather than maxima, occur for emission along open directions; the correlation of peaks 2 and 4 with a near-neighbor atomic set is not as close (25.3° measured versus 18.5° expected); and the set at 18.5° is not as dense in scattering centers as that at 26.6° in the fourfold geometry.

These results thus provide tentative support for a relatively direct relationship between XPS adsorbate core-level anisotropies and atomic structure, as well as for fourfold coordination of $c(2\times2)$O on Cu(001), although further experimental and theoretical study will be required for full confirmation.

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