Valence Photoelectron Diffraction and Direct-Transition Effects

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(Received 7 October 1991)

We have measured the temperature dependence of valence and core x-ray photoelectron intensities for W(110). At 295 K, valence spectra are very sensitive to emission direction due to direct-transition effects, and *energy-integrated* valence and core photoelectron diffraction curves are similar in form, but with significant differences in fine structure. At 803 K, valence spectra are by contrast very insensitive to direction due to increased zone averaging, but valence and core diffraction curves retain differences due to the atomic-orbital character of the initial and final states involved.

PACS numbers: 79.60.Cn

Valence electron emission for kinetic energies ≤ 100 eV and at ambient temperature or below is usually dominated by the scattering and diffraction processes that are responsible for wave-vector selection rules (direct transitions). At higher energies ≥ 1000 eV characteristic of x-ray photoelectron spectroscopy (XPS) and/or higher temperatures, however, two effects can allow transitions to average over much of the Brillouin zone so that simple wave-vector selection rules are no longer strong: phonon-mediated nondirect transitions (more important at both higher energies and elevated temperatures) and the angular acceptance of the analyzer (more important at higher energies) [1]. One can also ask how the *energy-integrated* intensity over the valence spectral region varies with direction, a valence analog of core-level x-ray photoelectron diffraction (XPD) [2]. In early studies, such integrated XPS valence intensities were found to behave very similarly to those of core-level intensities at nearby kinetic energies for the systems NaCl [3] and Au [4] with highly localized valence levels and/or complete zone averaging [1(a)].

More recently, such valence photoelectron diffraction effects from Al(001) (a nearly-free-electron metal for which zone averaging in XPS should be complete [1(a)]) have also been shown to exhibit intensity modulations essentially identical to the XPD effects from the Al 2*s* core level [5]. In this study, we ask how general this similarity of core and valence diffraction curves is and attempt to understand these phenomena more fully by studying an intermediate case in which direct-transition effects can be selectively suppressed by increasing temperature. In particular, we compare valence and core diffraction patterns obtained at high angular resolution (≤ ±1.5°) from W(110) as a function of temperature. For W at room temperature, it is well known that zone averaging in XPS is not complete [1].

As first pointed out by Shevchik [6], a correct model of valence photoemission spectra at high photon energies or temperatures must include the influence of both direct transitions (DT's) and phonon-assisted nondirect transitions (NDT's). Shevchik's analysis was based on the assumption of uncorrelated lattice vibrations and was similar to that used in x-ray-diffraction theory. Although inadequacies in this model have been discussed in later work [1(b),7], this simple approach nonetheless permits estimating approximately the relative contributions of DT's and NDT's to spectra. Specifically, the temperature dependence of the photocurrent at a given kinetic energy $I(E,T)$ can be approximated as a sum of temperature-independent DT and NDT components modulated by factors involving the Debye-Waller factor $W(T) = \exp[-g^2U^2(T)/3]$. Here g is the magnitude of the reciprocal-lattice vector involved in the direct transition, $U^2(T)$ is the three-dimensional mean-squared atomic displacement, and the resultant expression for the photocurrent is $I(E,T) = W(T)I_{\mathrm{DT}}(E) + [1 - W(T)]I_{\mathrm{NDT}}(E)$. Hence, $W(T)$ at this level of approximation provides an estimate of the fraction of transitions which are direct, and for the temperatures of 295 and 803 K at which we have studied W the resulting values are 0.55 and 0.20, respectively.

The measurements were performed on a Vacuum Generators ESCALAB5 spectrometer modified for high-resolution automated angle scanning, as described elsewhere [8]. Al $K\alpha$ radiation was used for excitation. The angular acceptance cone was precisely limited to ≤ ±1.5° by the use of tube arrays [8(a)]. The high-symmetry directions of the crystal were located to within ±0.3° using strong low-index XPD peaks, and the surface was periodically cleaned using standard methods [1]. During all of the runs, the base pressure was 1.0×10^{-10} torr or lower and total contaminant levels were kept below 10% of a monolayer.

Valence spectra were taken as a series of energy scans at a constant polar angle θ defined with respect to the surface and over the azimuthal range of $\phi = 0°$ ([001] azimuth) to 90° ([1$\bar{1}$0] azimuth). Temperature-dependent energy-integrated core and valence-band intensities were also measured. These data were taken as azimuthal scans at a constant polar angle; a 200° ϕ range covering the [001] to [00$\bar{1}$] azimuths was scanned in 1.8° steps, such that all structures present can be seen twice due to a mirror plane at the [1$\bar{1}$0] azimuth. A simple linear background was subtracted from each spectrum to measure intensity.

Figures 1(a) and 1(b) show a series of valence-band

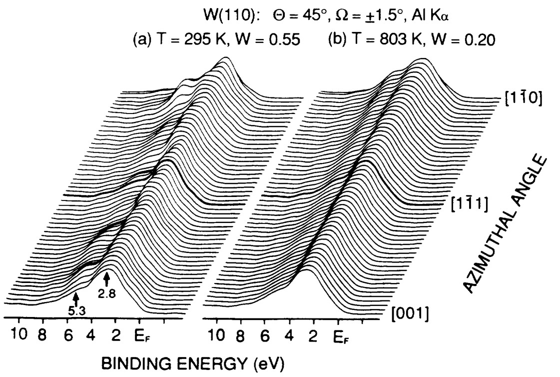

FIG. 1. X-ray photoelectron valence-band spectra obtained at a high angular resolution of ± 1.5° from the W(110) surface at a polar takeoff angle of $\theta=45°$ over the azimuthal range from $\phi=0°$ to 90° in 1.8° steps. (a) Data at ambient temperature (295 K), and (b) data at high temperature (803 K).

spectra obtained at $\theta=45°$ and with 1.8° azimuthal steps from $\phi=0°$ to 90°; data are shown for both ambient temperature (295 K) and high temperature (803 K), respectively. All spectra have been normalized to a constant maximum height for the peak at 2.8 eV, although, in principle, DT effects could cause changes in the relative intensities of all features in the valence spectra. In Fig. 1(a), we see that there is great sensitivity to emission direction for spectra obtained at ambient temperature. For the normalization we have used, the most significant changes are associated with the peak or shoulder located at 5.3 eV. These spectral changes are associated with direct-transition effects in valence emission due to the high Debye-Waller factor of 0.55 at 295 K, and these results are fully consistent with prior XPS studies of this system [1]. In Fig. 1(b), the valence spectra are by contrast found to change very little, if at all, with emission direction, a result of the reduced effect of direct transitions, as indicated by the Debye-Waller factor of 0.20 at 803 K. This behavior with temperature was found to be reversible and reproducible.

Turning now to energy-integrated core and valence intensities, we show in the upper panel of Fig. 2(a) azimuthal scans of the W 4f and valence-band intensities at ambient temperature for a polar angle of $\theta=45°$. The degree of mirror symmetry in both curves across the [1$\bar{1}$0] azimuth indicates the high reproducibility of the fine structure observed. At this high angular resolution, very sharp features can be observed in both the core and valence-band (VB) diffraction patterns, with full widths at half maximum (FWHM's) of as small as 5°. The strongest and also rather narrow peak for $\phi=90°$ is due to forward scattering along a dense [100] row of atoms with nearest-neighbor distances of 3.16 Å. The core and VB diffraction patterns are found to be similar, but significant differences can be observed in the higher-order features away from the forward-scattering peak.

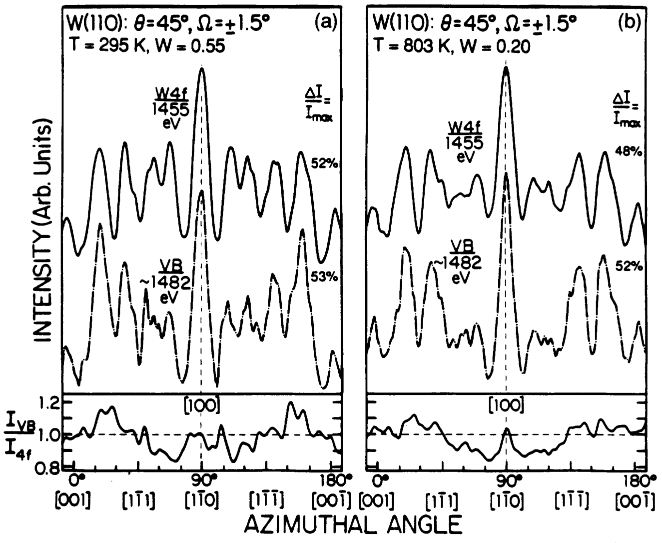

FIG. 2. Azimuthal scans of energy-integrated W 4f ($E_{\text{kin}}=1455$ eV) and valence-band ($E_{\text{kin}}=1487$–1477 eV, where the average energy of ~1482 eV of this range is given in the figure) intensities from the W(110) surface at a polar angle of 45°, together with the normalized ratio of the valence-band intensity to the W 4f intensity. (a) Data at ambient temperature (295 K), and (b) data at high temperature (803 K).

In order to measure more quantitatively the differences between the core and VB data, we have in the lower panel of Fig. 2(a) taken a ratio between the two diffraction patterns, with the two being normalized to have the same *average* intensity over the region $0° < \phi < 80°$ and $100° < \phi < 180°$, that is, away from the principal forward-scattering features. The interval for taking the average intensity is not crucial to any of our conclusions, as the form of the ratio curves will remain exactly the same, but the choice we have made allows for a convenient estimation of the percentage of changes in the diffraction fine structure away from the forward-scattering peaks. The largest changes in relative intensity in this format are seen to be about ± 20%. The most significant differences between the two curves are a reduction of VB intensity in the symmetry-related regions from $\phi=50°$ to 80° and $\phi=100°$ to 130°, and an increase in intensity in the regions from $\phi=15°$ to 35° and $\phi=145°$ to 165°.

Shown in Fig. 2(b) are a similar set of high-resolution azimuthal scans, but at the higher temperature of 803 K. The features look very similar to those in Fig. 2(a), but with the major differences being losses in intensity from $\phi=50°$ to 80° and $\phi=100°$ to 130° in both the 4f and VB curves. A visual comparison of Figs. 1 and 2 indicates some convergence of the 4f and VB curves at higher temperature as to the positions and relative intensities of different peaks. Again a normalized ratio was taken between the valence-band and core diffraction patterns, as shown in the lower panel of Fig. 2(b). In this format, also, the differences between the 4f and VB curves are found to be ~ ± 10%–15% and thus slightly lower than, although still qualitatively similar to, those at ambient temperature. The qualitative convergence seen in these results is consistent with the reduced degree of direct-transition contributions at the higher temperature; that the two curves have not more fully converged could also be due to the estimated 20% DT effect remaining at 803 K.

In order to further assess the possible connection between the direct-transition effects responsible for the variation in relative intensity of the VB peak at 5.3 eV and the differences seen between the VB and 4*f* photoelectron diffraction curves, we show in Figs. 3(b) and 3(c) the relative intensities I_{VB}/I_{4f} and $I(5.3\ \mathrm{eV})/I(2.8\ \mathrm{eV})$ at both 295 and 803 K. Although the 2.8-eV peak also may exhibit DT effects in its intensity, it is in fact found to follow the energy-integrated valence intensities to a high degree, and so we focus on the 5.3-eV peak here. There is no visible correlation between the curve for I_{VB}/I_{4f} at 295 K and that for $I(5.3\ \mathrm{eV})/I(2.8\ \mathrm{eV})$ at 295 K. This might at first be interpreted as indicating that direct-transition effects do not play a role in producing the difference between valence and core photoelectron diffraction curves at ambient temperature. However, focusing only on the ratio $I(5.3\ \mathrm{eV})/I(2.8\ \mathrm{eV})$ as a gauge of DT effects on integrated intensities does not provide the entire picture, since DT selection rules also may affect the intensity of the 2.8-eV peak in a way that cannot be uniquely extracted from the experimental data alone. Comparing the analogous two curves in Figs. 3(b) and 3(c) of I_{VB}/I_{4f} and $I(5.3\ \mathrm{eV})/I(2.8\ \mathrm{eV})$ for 803 K furthermore indicates that, even when the two primary valence components are only very slowly varying with angle (implying that the overall spectral shape is very nearly constant), the normalized I_{VB}/I_{4f} ratio can still exhibit significant differences from unity. The latter data thus finally suggest that, even if DT effects were fully suppressed, there would likely be residual differences in the energy-integrated valence and core photoelectron diffraction curves.

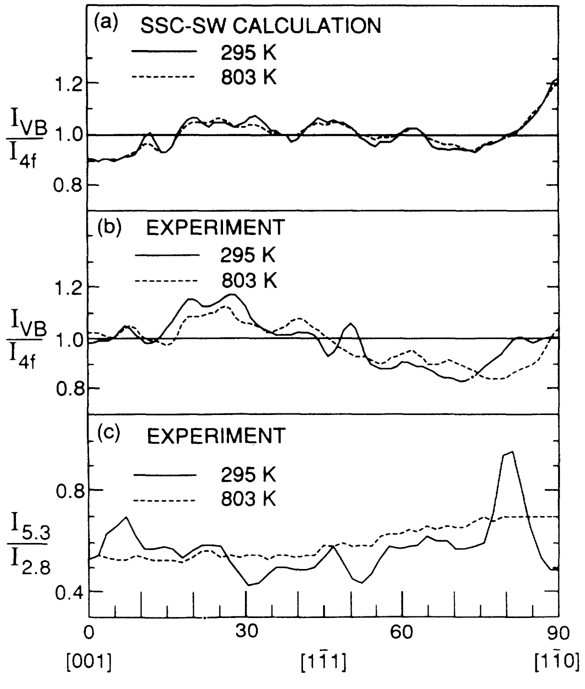

FIG. 3. Comparison of normalized valence-band/core 4*f* relative intensities at 295 and 803 K: (a) as calculated for 5*d* to *p*+*f* and 4*f* to *d*+*g* emission, respectively, and (b) as measured at the same temperatures. (c) The relative intensities of the two main components in the valence spectrum at 5.3- and 2.8-eV binding energies, again for 295 and 803 K.

Since the VB and 4*f* kinetic energies are only ~27 eV apart (1487–1477 vs 1455 eV), these residual differences must be due to some combination of the differences in both the initial state (localized 4*f* versus more delocalized 5*d*/6*s*/6*p* valence) and the final state (interfering *d* and *g* channels versus a more complex state reached in valence emission) of the photoemission process. As qualitative justification for this, Friedman and Fadley [9] have found in model photoemission calculations that simply changing the initial- and final-state angular momenta (e.g., from *s* to *p* to *p* to *s*+*d*) can significantly change both the relative strength of the forward-scattering peaks and the diffraction fine structure away from the forward-scattering directions; it is this fine structure that will in general influence the higher-order diffraction features that are found to be different between the core and VB curves. As more quantitative proof of the importance of such state differences, we show in Fig. 3(a) the I_{VB}/I_{4f} ratio calculated in a simple single-scattering cluster model [9] with spherical-wave scattering and free-atom-like 5*d* to *p*+*f* or 4*f* to *d*+*g* initial and final states, respectively. Atomic radial matrix elements and phase shifts were used to couple the two final-state channels. Comparing the dashed 803-K curves in Figs. 3(a) and 3(b) shows a high degree of agreement as to the peak shapes and positions, as well as overall heights, particularly in view of the simple corelike model assumed for valence emission.

Our results can now be contrasted to those of Osterwalder *et al.* [5], who recently measured diffraction effects from Al(001) for both the highly localized Al 2*s* core level and the highly delocalized nearly-free-electron Al valence band. As noted previously, the core and valence diffraction patterns were found to be essentially identical at ambient temperature, for which the relevant Debye-Waller factor is only 0.03 [1(a)]. These data have been used to qualitatively argue that the similarity of these two *final-state-associated* diffraction patterns provides evidence that the final-state wave functions in both processes are very similar, and thus that the valence hole left behind is, at least on the time scale of photoemission, effectively localized in a manner similar to the hole left in core emission [5]. Our results, however, further show that, for an intermediate case as far as zone averaging is concerned such as W, such energy-integrated core and valence intensity curves are not necessarily identical due to two effects: remnant direct-transition selection rules and the different atomiclike initial and final states involved in the transition. Thus, complete zone averaging due to phonon and/or angular aperture effects is necessary for achieving the near identity of core and valence diffraction curves noted by Osterwalder *et al.* for Al, and even then there may be residual differences if the core and valence excitations involve different angular momenta. The reason for this near identity of Al thus may be that both emission processes have their strongest contributions from s to p photoemission.

In conclusion, for W at ambient temperature, we find that valence spectra change form very rapidly with emission direction, confirming that zone averaging is not complete. Energy-integrated valence photoelectron diffraction intensities are found to be similar to, but significantly different from, analogous core diffraction intensities. Upon heating the crystal to 803 K so as to increase the degree of zone averaging, we find only very small changes in valence spectral form with direction, and that the core and valence photoelectron diffraction patterns are more similar to one another, although still not identical. Full zone averaging is thus essential for comparing the forms of core and valence diffraction patterns in the most direct way; but even in this case, residual differences due to atomic-orbital character may exist.

We gratefully acknowledge the support of the Office of Naval Research under Contract No. N00014-87-K-0512 and Grant No. N00014-90-J-1457, and the Department of Energy under Contract No. DE-AC03-76SF00098.

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