Observation of surface to bulk interatomic Auger decay from Ta(100)

E. Jensen
Department of Physics, Brandeis University, Waltham, Massachusetts 02254

R. A. Bartynski
Department of Physics, Rutgers University, Piscataway, New Jersey 08855

M. Weinert
Department of Physics, Brookhaven National Laboratory, Upton, New York 11973

S. L. Hulbert, E. D. Johnson, and R. F. Garrett
National Synchrotron Light Source, Brookhaven National Laboratory, Upton, New York 11973
(Received 29 November 1989)

Core-valence-valence (*CVV*) Auger spectra from Ta(100) taken in coincidence with bulk and surface-shifted $4f_{7/2}$ core-level emission are presented. These data are compared with self-convolutions of calculations of the *d*-band densities of states for the surface and subsurface layers of a nine-layer slab. Agreement of the bulk spectrum with the calculation is good; agreement for the surface spectrum is very poor. These data are explained by proposing an interatomic surface to bulk Auger decay mode for the surface core hole that is competitive with the conventional *CVV* decay process.

Auger-electron emission is the dominant decay process for shallow core holes in solids. Core-valence-valence (*CVV*) spectra, wherein a valence electron fills the core hole and a second valence electron is emitted, can sometimes be simply interpreted as the self-convolution of the valence-band density of states (SCDOS), thus revealing important information about the valence-band electronic structure.[1] We have employed the technique of Auger-photoelectron coincidence spectroscopy[2,3] (APECS) in conjunction with the phenomenon of surface-shifted core-level binding energies[4] to study the *CVV* Auger spectra of Ta(100) associated with surface and bulk core-hole excitation, independently. In the simplest interpretation, one would expect to observe differences characteristic of the different valence SCDOS at the surface and in the bulk. Instead, we find evidence for a new type of Auger decay, where the surface core hole hops into the bulk before undergoing conventional *CVV* Auger decay. We present calculations of the bulk and surface SCDOS for comparison to the Auger spectra. We also calculate the probability of this interatomic process, and find that it is indeed competitive with the intra-atomic transition rate. This additional decay mode, introduced to explain the APEC data, also explains the anomalously large width of the surface-shifted $4f$ line, first observed by Spanjaard *et al.*[4] We discuss the importance of this new decay mode to other spectroscopies and other materials.

In the APEC technique, two electron-energy analyzers are focused on one x-ray- or uv-illuminated sample. One analyzer is tuned to the energy of a core photoelectron and the other is tuned to an appropriate Auger decay energy. An event is recorded only when electrons are received in each analyzer simultaneously. This is interpreted to mean that both electrons are associated with the same photoexcitation-decay event. Some experimental details have been published;[3] others will be provided in another paper.[5] Briefly, the 80-eV light, from the National Synchrotron Light Source uv ring, was monochromatized by the U14 beamline Plane Grating Monochromator.[6] Commercial double-pass cylindrical mirror analyzers[7] were set to 60-eV pass energy. One, the photoelectron analyzer, was fixed at either the surface-shifted $4f_{7/2}$ photoelectron energy (22.39-eV binding energy)[4] or the bulk $4f_{7/2}$ photoelectron energy (21.65-eV binding energy).[4] This analyzer identifies the initial core-hole site. The total-energy resolution (electron plus photon) in this system was 0.4 eV. This relatively high resolution is required so that the two core lines are well resolved. We estimate that interference of the bulk line in the surface APECS spectrum is less than 1%.[8] The other, or Auger analyzer, was swept through the *CVV* Auger-energy spectrum, 9.5–24.5-eV kinetic energy, with a total-energy resolution of 1 eV. Each coincidence spectrum required approximately two days of counting (about 1000 sweeps of 64 channels at 1 s per channel dwell). The peak count rate was near 0.2 Hz, with 1:1 true to accident ratio. Accidental coincidences have been subtracted from all spectra.

Several argon sputter and subsequent flash to 2800 K cleaning sequences were required to initially clean the sample and eliminate carbon and oxygen peaks from the electron-stimulated Auger spectra and the valence-band photoemission spectra. The sample was flashed to 2800 K every hour during the bulk data acquisition run, and every half-hour during the surface run. The chamber base pressure was less than 7×10^{-11} Torr. The valence-

band spectrum and the $4f$-surface core-level shift were used as sensitive *in situ* monitors of cleanliness and compared to previous results.[9]

The layer-resolved density of states (LDOS) are from a nine-layer Ta(100) slab calculated using the full-potential linear augmented plane-wave (FLAPW) method.[10] The interlayer spacing of the surface was contracted by 14%, near the calculated value of 13.5%.[11] The changes in the LDOS between the relaxed- and bulk-terminated surfaces are noticeable, but not important to the conclusions of this paper. Details and further results of this calculation will be presented elsewhere.[11]

Figure 1 shows an ordinary photoemission spectrum (subsequently called a singles spectrum) for the kinetic energy range 0–80 eV taken at 80 eV photon energy. All electron binding and kinetic energies are referenced to the sample Fermi level. This kinetic-energy range includes the $4f$ photoelectrons and the $N_{6,7}O_{4,5}O_{4,5}$ ($4f5d5d$) Auger electrons, as well as various other features. The inset shows the 0.74-eV $4f$ surface bulk splitting. The lower kinetic energy peak in each of the spin-orbit split lines is interpreted as emission from the surface layer only; the higher kinetic-energy peak has unresolved contributions from the second and deeper layers.[4] Figure 2 shows APECS data, also taken at 80-eV photon energy. Figure 2(a) is the Auger spectrum taken in coincidence with the bulk $4f_{7/2}$ line (photoelectron analyzer at 58.3 eV). Figure 2(b) is the corresponding surface spectrum (photoelectron analyzer at 57.6 eV). Three significant effects are evident. First, much of the large background under the singles Auger spectrum is removed. This is because the APECS technique is more surface sensitive than ordinary photoemission, and because all secondary electrons not directly associated with $4f$ hole decay are eliminated. Second, the secondary electron distribution under the surface spectrum is smaller than that under the bulk. This is because Auger electrons created at the surface can more easily escape without subsequent inelastic scattering, and will thus have a higher ratio of primary to secondary emission. Finally, the energy threshold for Auger emission from the surface is about 0.7-eV higher than the bulk threshold. This occurs because the surface core level has an 0.74-eV larger binding energy, and provides an extra 0.74 eV of kinetic energy to the Auger electron.

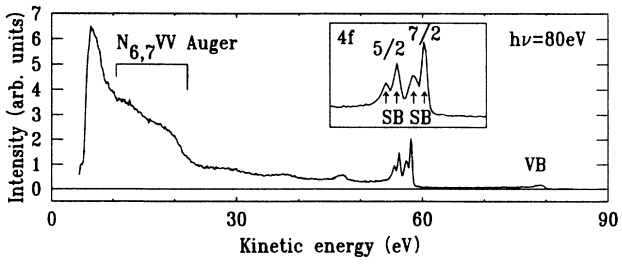

FIG. 1. Wide ordinary photoemission scan through the Ta $4f$ core lines, the Ta $N_{6,7}VV$ ($4f5d5d$) Auger spectrum and the valence-band (VB) region. The inset shows the $4f$ core lines in more detail. *S* and *B* stand for surface and bulk, respectively. The photon energy is 80 eV.

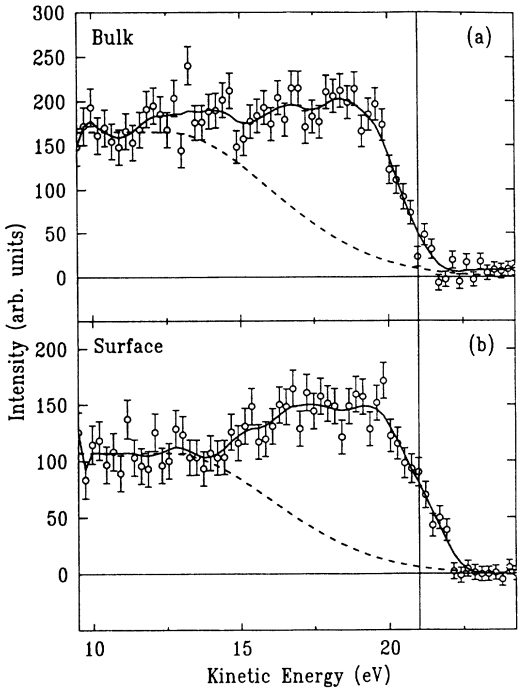

FIG. 2. (a) Ta N_7VV Auger spectrum taken in coincidence with the $4f_{7/2}$ bulk and (b) surface shifted core lines. The data are open circles with error bars; the solid lines are a 1.0 eV full width at half maximum digital smooth to these data. The dashed lines are the assumed secondary electron background to be subtracted in Fig. 3.

A more detailed analysis requires that the inelastic background be removed from the APECS data. A simple approximation to the shape of this background is shown as a dashed line in Fig. 2. The width and height of the background are adjusted so that the remaining peak goes smoothly to zero in the range below 15 eV, where no primary emission is expected. The shape, width, and height of the background can be varied within reason, but the essential features of the remaining peak do not change significantly. The background subtracted data are shown in Fig. 3. These data are compared with the appropriate SCDOS; the top-layer SCDOS is compared to the surface data, while an average of the second through fifth layers is compared to the bulk data.[12] These are shown as dashed lines. It is immediately evident that the bulk data are in reasonably good agreement with the theory; the threshold region is reproduced very well, and the overall width of the data is the same as that of the calculation. There is some discrepancy near 17.5 eV; we assume that this is due to a weak variation in matrix element across the band. This generally good agreement is strong evidence for the validity of the SCDOS description of *CVV* Auger decay, and for our simple background subtraction.

The agreement between surface SCDOS and surface data is much poorer. The threshold behavior is not reproduced by the theory, and the overall width of the

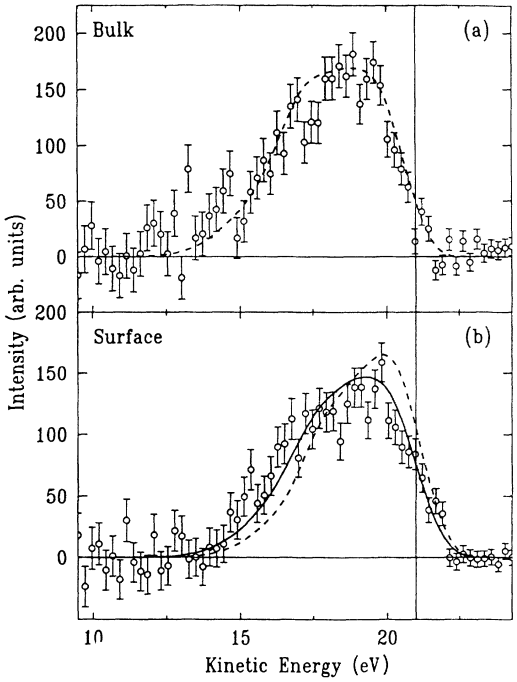

FIG. 3. Background-subtracted data compared with self-convolution of *d*-band density-of-states (SCDOS) theory. The background subtracted data are open circles with error bars. In (a) the bulk data are compared to an average of the second through fifth layer SCDOS (dashed line). In (b) the surface data are compared to the surface layer SCDOS (dashed line), and to an average of the second layer and surface SCDOS in the ratio 0.5 (solid line).

data is much larger than that of the theory. In fact, the surface data are slightly wider than the bulk data, while the SCDOS for the surface is much narrower. Comparisons to earlier calculations by Krakauer[13] showed similar discrepancies. These data clearly show that, while this simple layer-resolved SCDOS picture adequately describes the bulk spectrum, it is inadequate for a description of the surface spectrum, and some important physics is still missing.

Note that the agreement between the surface theory and surface data in Fig. 3(b) would be much improved if there were some way to involve bulk valence electrons in the decay of the surface $4f$ core hole. This would increase the width of the surface Auger spectrum, and round its threshold, exactly what is needed for better agreement with the data. We illustrate this with the solid line in Fig. 3(b); it represents a 50/50 mix of surface and second layer SCDOS. The agreement between theory and experiment is now comparable to that of the bulk spectrum [Fig. 2(a)].

This generally good agreement is maintained by second-layer SCDOS/surface SCDOS ratios in the range 0.4–0.7. Our justification for adding the SCDOS is the following: We propose that the surface core hole sometimes hops into the bulk before conventional *CVV* Auger decay occurs. This process is then followed by ordinary bulk *CVV* Auger decay. In this way the surface shifted $4f$ emission is associated with bulk Auger emission. We require, in order for this picture to explain the data, that the interatomic rate be at least 40% of the intra-atomic rate. The existence of interatomic transitions in elements is a novel idea, and would generally be considered very rare. In fact, the only previously documented interatomic Auger transitions occur in ionic compounds, and these occur primarily because shallow cation core holes have no electrons available for intra-atomic decay.[14] It is therefore necessary to estimate the probability of such an interatomic transition to check that it can, in fact, occur at a rate significant on the scale of the intra-atomic transitions. We do so below.

Within the independent electron picture of conventional Auger decay, the decay rate (linewidths) can be written as[15] (with $\hbar=m=e^2=1$)

$$\Gamma_A=2\pi\int d\varepsilon \sum_{k,k',k_A}(M_A^D-M_A^E) \times\delta(\varepsilon_k+\varepsilon_{k'}-\varepsilon_{k_A})\delta(\varepsilon-\varepsilon_{k_A}) , \quad (1)$$

where k,k' label the (occupied) valence electrons and k_A labels the outgoing Auger electron. The two-electron direct M_A^D and exchange M_A^E matrix element contributions are given by[15]

$$M_A^D=\left\langle\phi_k(1)\phi_{k'}(2)\left|\frac{1}{r_{12}}\right|\chi(1)\psi_A(2)\right\rangle^* \times\left\langle\phi_k(1)\phi_{k'}(2)\left|\frac{1}{r_{12}}\right|\chi(1)\psi_A(2)\right\rangle , \quad (2a)$$

$$M_A^E=\left\langle\phi_k(1)\phi_{k'}(2)\left|\frac{1}{r_{12}}\right|\psi_A(1)\chi(2)\right\rangle^* \times\left\langle\phi_k(1)\phi_{k'}(2)\left|\frac{1}{r_{12}}\right|\chi(1)\psi_A(2)\right\rangle , \quad (2b)$$

where χ is the core-electron wave function. The valence wave functions ϕ_k are obtained in the presence of the core hole, while the Auger wave function ψ_A is determined in the ground state of the system.

In a Coster-Kronig transition, one of the valence electrons is replaced by a core electron with smaller binding energy than the original core-level binding energy ε_c resulting in a final state that again contains a core hole. Our proposed process is similar, but now the surface core hole "hops" to an adjacent (and less tightly binding) bulk site: An on-site valence electron fills the core hole and an off-site core electron is excited into a previously unoccupied valence state on a neighboring site, resulting in a final state with a core hole on the neighboring site—a process distinct from the direct transfer of the core hole (or electron) from one site to another. The direct matrix element contribution is

$$M_H^D=\left\langle\phi_k(1)\chi_b(2)\left|\frac{1}{r_{12}}\right|\chi_s(1)\Phi_{k'}(2)\right\rangle^* \times\left\langle\phi_k(1)\chi_b(2)\left|\frac{1}{r_{12}}\right|\chi_s(1)\Phi_{k'}(2)\right\rangle . \quad (3)$$

Equation (3) can be obtained from Eq. (2a) by replacing the Auger orbital ψ_A with an unoccupied valence orbital Φ and $\phi_{k'}$ by the bulk core wave function χ_b, i.e., this process is contained in the standard Auger decay, but with the k,k' sums in Eq. (1) extended to include all occupied levels, including core states, and with the Auger-electron k_A sum extended to include all unoccupied states. The exchange matrix elements, as well as those corresponding to tunneling of the hole from one site to another, are negligible since they involve the direct overlap of $4f_{7/2}$ orbitals on different sites.

The proposed mechanism clearly *must be occurring* since it is not forbidden by symmetry or energy considerations; the question is only if the decay rate is large enough for this decay channel to be important. Conventional wisdom has that in Auger decay the contributions from electrons on other sites is small. If this is true, then it is difficult at first to understand why our proposed mechanism should be important. To address this point, we consider the rates for Auger decay both on site (both valence electrons on the atom with the core hole) and off site (one valence electron on site, the other on a neighboring atom). Starting from Eq. (1) and assuming only a weak energy dependence of the total matrix element ($M_A = M_A^D - M_A^E$), we can write the on-site (Γ_A^0) and off-site (Γ_A^n) Auger rates in terms of the averaged on- (M_A^0) and off-site (M_A^n) matrix elements and the LDOS:

$$\Gamma_A^0 = 2\pi M_A^0 \int d\varepsilon_A \int d\varepsilon \int d\varepsilon' \, g_0(\varepsilon) g_0(\varepsilon') \rho_0(\varepsilon_A) \times \delta(\varepsilon + \varepsilon' - \varepsilon_c - \varepsilon_A) , \quad (4)$$

$$\Gamma_A^n = 2\pi M_A^n \int d\varepsilon_A \int d\varepsilon \int d\varepsilon' \, g_0(\varepsilon) g_n(\varepsilon') \rho_n(\varepsilon_A) \times \delta(\varepsilon + \varepsilon' - \varepsilon_c - \varepsilon_A) . \quad (5)$$

In these equations, $g(\varepsilon)$ is the occupied LDOS and $\rho(\varepsilon)$ is the Auger-electron-continuum density of states. The on-site rate Γ_A^0 is then given as an integral over a self-convolution of the LDOS,

$$\Gamma_A^0 = 2\pi M_A^0 \int d\varepsilon_A \, \rho_0(\varepsilon_A) \int d\varepsilon \, g_0(\varepsilon) g_0((\varepsilon_c + \varepsilon_A) - \varepsilon) , \quad (6)$$

which is approximately proportional to the number of valence electrons on the site (in the presence of the core hole) squared. The off-site rate can be written similiarly:

$$\Gamma_A^n = 2\pi M_A^n \int d\varepsilon_A \, \rho_n(\varepsilon_A) \int d\varepsilon \, g_0(\varepsilon) g_n((\varepsilon_c + \varepsilon_A) - \varepsilon) . \quad (7)$$

Estimates based on the results from the Ta(001) calculation give a ratio $\Gamma_A^n / \Gamma_A^0 \sim 10^{-2}$. Thus, we find that standard off-site Auger contributions are small, in agreement with normal expectations.

The enhancement of our proposed hopping term relative to normal Auger processes can be rationalized by considering a similar analysis as above. The decay rate via this channel can be obtained from the off-site Auger rate, Eq. (5), by substituting the density of states for the bulk core level for off-site valence LDOS [$g_n(\varepsilon') \rightarrow N_c \delta(\varepsilon' - \varepsilon_c^n)$, N_c is the degeneracy of the bulk core level] and by replacing the Auger-continuum LDOS by the unoccupied valence LDOS [$\rho_n(\varepsilon) \rightarrow \bar{g}_n(\varepsilon)$]:

$$\Gamma_H = 2\pi M_H N_c \int d\varepsilon' \, \bar{g}_n(\varepsilon') \int d\varepsilon \, g_0(\varepsilon) \delta(\varepsilon - \varepsilon' + (\varepsilon_c^n - \varepsilon_c^0)) = 2\pi M_H N_c \int d\varepsilon \, g_0(\varepsilon) \bar{g}_n(\varepsilon + (\varepsilon_c^n - \varepsilon_c^0)) . \quad (8)$$

This rate is proportional to an integral over a joint density of states separated by the difference in binding energy of the two core levels. Conservation of energy allows this hopping only when $\varepsilon_c^n - \varepsilon_c^0 > 0$. The ratio of this hopping rate to the off-site Auger rate is proportional to N_c ($=8$ for $4f_{7/2}$ levels) multiplied by valence density of states factors. Note that a large enhancement comes just from the large number of core electrons than can participate in the process. These calculated factors for Ta(001) give approximately a two orders of magnitude increase in the rate for the hopping process compared to the offsite Auger terms.

These simple arguments show that the decay rate for this process may be of the correct order of magnitude to be important; all other off-site Auger contributions are small. A quantitative determination of the decay rate requires a more detailed calculation including matrix element effects. To this end, the calculated wave functions and LDOS from the Ta(001) film have been used to explicitly evaluate the hopping contribution to the surface core linewidth. Specifically, Eq. (3) is evaluated for M_H^D, and then Γ_H is evaluated from

$$\Gamma_H = 2\pi \int d\varepsilon \sum_{k,k',k_A} M_H^D \delta(\varepsilon_k + \varepsilon_{k'} - \varepsilon_{k_A}) \delta(\varepsilon - \varepsilon_{k_A}) . \quad (9)$$

Note that this equation is nearly identical to Eq. (1), with M_H^D replacing M_A^D, and M_H^E known to be negligible. The calculated value is $\Gamma_H \approx 0.05$ eV.[16] This is of similar magnitude to the observed width of 0.12 eV for the bulk $4f_{7/2}$ line, indicating that this mode is indeed competitive with the conventional *CVV* mode. We believe that this extra decay channel for the surface core hole, together with crystal-field splitting of the surface $4f$ line, also explains the long-standing puzzle of why the surface shifted $4f_{7/2}$ linewidth (0.22 eV) of Ta(001) is so much wider than the bulk.[4] Another very recently proposed mechanism for increasing the surface core width is that the valence electrons in the surface are more localized, enhancing the $4f$-$5d$ overlap. In W, this was shown to be a 0.02-eV effect.[17] In Ta we estimate that the effect is somewhat smaller, approximately 0.01 eV.

This decay mode will be important in other selected materials and spectroscopies. For this mode to be important, one needs a high LDOS near the Fermi level [a large integrand in Eq. (8)] and a large surface core-level shift (large limits on the integral). For Ta(001) these conditions are satisfied. They should also be satisfied for Hf, which is reported to have a 0.34 eV shift of its surface $4f$ core level to higher binding energy for the (0001) face.[18] For metals to the right of Ta in the periodic table, the surface core-level shift is of opposite sign, and this mode should contribute to the first subsurface (bulk) linewidth. For W, this contribution should be smaller than for Ta since the W core-level shift and the bulk W LDOS near

the Fermi level are each smaller than in Ta. In addition, since the surface line should also have some crystal field broadening, the increased width of the subsurface (bulk) line due to the hopping mechanism may be difficult to distinguish from the crystal field splitting of the surface line.

This hopping process will also perturb the surface sensitivity of Auger spectroscopy in a manner that cannot be described by a single mean free path; if the surface core level has a lower binding energy than the bulk level, then Auger emission from the surface layer will be enhanced, while if the surface level has a higher binding energy, surface emission will be suppressed. This will change both the Auger line shape and its secondary background from what would, otherwise, be expected. This decay mode may also have a dramatic effect on some exotic spectroscopies, such as positron annihilation induced Auger spectroscopy[19] and ion stimulated electron emission,[20] since even though the initial core hole produced by these techniques is probably localized to the surface layer, it may move into the bulk before conventional Auger decay occurs.

ACKNOWLEDGMENTS

Support from Analog Devices Corp., the Rutgers University Research Council, the National Synchrotron Light Source staff, and the Division of Materials Science of the Office of Basic Energy Sciences of the US Department of Energy (DOE) under Contract No. DE-AC02-76CH00016 is gratefully acknowledged. We thank David Zehner (Oak Ridge National Laboratory) for use of the Ta(100) sample and for permission to quote unpublished Hf results.

---

[1]Complications to this simple picture arise when, (1) the valence band is highly correlated, or (2) the valence band has significant contributions from more than one angular momentum component. In case (1) the independent electron picture is invalid. The Cu *CVV* spectra are an example of this situation, and detailed explanations are available in M. Cini, Solid State Commun. **24**, 681 (1977), and G. A. Sawatzky, Phys. Rev. Lett. **39**, 504 (1977). In case (2) the assumption of constant matrix element is invalid. A recent discussion of this situation for *sp* band metals can be found in C. O. Almbladh and A. L. Morales, Phys. Rev. B **39**, 3503 (1989). Most of the structure in the Ta valence band comes from the relatively uncorrelated 5*d* electrons, and one therefore expects a *CVV* spectrum resembling the self-convolution of the *d*-DOS.

[2]H. W. Haak, G. A. Sawatzky, and T. D. Thomas, Phys. Rev. Lett. **41**, 1825 (1978); H. W. Haak, G. A. Sawatzky, L. Ungier, J. K. Gimziewski, and T. D. Thomas, Rev. Sci. Instrum. **55**, 696 (1984).

[3]E. Jensen, R. A. Bartynski, S. L. Hulbert, E. D. Johnson, and R. Garrett, Phys. Rev. Lett. **62**, 71 (1989).

[4]Daniel Spanjaard, Claude Guillot, Marie-Catherine Desjonqueres, Guy Treglia, and Jean Lecante, Surf. Sci. Rep. **5**, 1 (1985).

[5]E. Jensen, R. A. Bartysnki, S. L. Hulbert, and E. D. Johnson (unpublished).

[6]Gwyn P. Williams, Malcolm R. Howells, Norene Lucas, and Peter Z. Takacs, Nucl. Instrum. Methods **222**, 99 (1984).

[7]Physical Electronics, Eden Prairie, MN, model 15-255*G*.

[8]When Fig. 1 is examined closely, it appears that much more than 1% of the surface line is background from the bulk line. This is an incorrect conclusion, and occurs because the singles scan does not properly illustrate the coincidence process. In the singles spectrum, both lines are broadened by the total-energy resolution of the apparatus, and appear to overlap strongly. In the coincidence process, when, e.g., the photoelectron analyzer is tuned to the surfaceline, the probability of accepting a bulk photoelectron is very small, and is given by the convolution of the kinetic energy resolution function with the photon energy resolution function separated by 0.7 eV. These individual contributions to the total resolution of 0.4 eV are not precisely known; however, independent of how the 0.4 eV is split up, the overlap is much less than 1% of the surface intensity. Additional contributions from line asymmetry and inelastic background are also small, and smaller than they appear in Fig. 1 because the coincidence process has an enhanced surface sensitivity and discriminates against inelastic background.

[9]R. A. Bartynski, D. Heskett, K. Garrison, G. M. Watson, D. M. Zehner, W. N. Mei, S. Y. Tong, and X. Pan, Phys. Rev. B **40**, 5340 (1989).

[10]M. Weinert, E. Wimmer, and A. J. Freeman, Phys. Rev. B **26**, 4571 (1982).

[11]M. Weinert (unpublished).

[12]This average is determined by exponential decay based on an electron mean free path of 6 Å. The resulting simulated spectra are not sensitive to variations of this parameter in the reasonable range of 5–10 Å.

[13]H. Krakauer, Phys. Rev. B **30**, 6834 (1984).

[14]P. H. Citrin, J. Electron Spectrosc. Relat. Phen. **5**, 273 (1974).

[15]C. O. Almbladh, A. L. Morales, and G. Grossmann, Phys. Rev. B **39**, 3489 (1989).

[16]There are explicit approximations made in constructing the one electron orbitals used in Eq. (3) and there are implicit approximations involved in the use of one electron matrix elements to describe Auger decay that together make the value of 0.05 eV linewidth contribution quantitatively uncertain. For example, using ground state valence orbitals, rather than those obtained in the presence of the core hole, reduces the linewidth contribution by about 10%. We consider this value an accurate order of magnitude estimation.

[17]D. M. Riffe, G. K. Wertheim, and P. H. Citrin, Phys. Rev. Lett. **63**, 1976 (1989).

[18]D. M. Zehner (unpublished). Note that this relatively small shift is for the close-packed face. Larger shifts are expected for the more open faces.

[19]A. Weiss, R. Mayer, M. Jibaly, D. Mehl, and K. G. Lynn, Phys. Rev. Lett. **61**, 2245 (1988).

[20]D. M. Zehner, S. H. Overbury, C. C. Havener, F. W. Meyer, and W. Heiland, Surf. Sci. **178**, 359 (1986); T. Aizawa, T. Tsumo, H. Daimon, and S. Ino, Phys. Rev. B **36**, 9107 (1987).