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Direct Comparison of Core-Electron Binding Energies of Surface and Bulk Atoms of Ti, Cr, and Ni[†]

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A direct comparison has been made of electron-excited soft–x-ray appearance potentials, which are surface sensitive, and photon-excited Auger-electron appearance potentials, which are more characteristic of bulk atoms. A single tungsten emitter served as a reference for both measurements. The "surface chemical shifts" thus obtained for the $2p_{3/2}$ levels of Ti, Cr, and Ni are in reasonable agreement with predictions based on a muffin-tin approximation of overlapping one-electron potentials.

Atoms in the outermost layer of a metal reside in a different chemical environment from their bulk counterparts simply by virtue of their reduced coordination. The resulting modification of the atomic potentials should produce a "surface chemical shift" in the core levels of the atoms. This has been invoked[1,2] to account for the fact that threshold energies for core-level excitation by electron bombardment[1-4] are consistently lower than tabulated x-ray energy levels.[5] The differences are, however, of the same order as the uncertainties in the determination of absolute binding energies. In this paper we present the first direct experimental evidence of a "surface chemical shift" for Ti, Cr, and Ni, and demonstrate that this shift is in reasonable agreement with calculations based on overlapping effective one-electron potentials. These materials span the spectrum of properties of the $3d$ transition metals: Ti is hcp and nonmagnetic, Cr is bcc and antiferromagnetic, and Ni is fcc and ferromagnetic.

When atoms come together to form a solid, the effective atomic potentials overlap appreciably, resulting in a drastically modified potential as seen by the higher-lying electronic states. The deep-lying core levels, however, see a potential only slightly changed in shape and thus essentially are just shifted in energy relative to their free-atom positions. The size of this shift is determined primarily by the superposition of the potentials centered on nearby sites. Since a surface atom has fewer neighbors at any given distance than an atom in the bulk, its core levels experience a smaller shift relative to their free-atom positions. Hence we expect a "surface chemical shift" between bulk- and surface-atom core levels.

We can obtain a theoretical estimate of the magnitude of the "surface chemical shift" from the same potential construction techniques as used in the calculation of the bulk electronic properties of solids. Specifically, we use the muffin-tin approximation as specified by Loucks. Relativistic free-atom charge densities[7] are overlapped and an average constant potential, V_0, is determined in the neighborhood of a particular atom. The "best" effective local atomic potential is determined relative to V_0 in the usual way.[8] The Slater local exchange approximation[9] is used throughout with the exchange parameter being set equal to the Kohn-Sham[10] value of $\alpha = \frac{2}{3}$. We then determine the position of the core level relative to V_0 by numerically solving the radial Dirac equation.[7,11] The calculated chemical shift for a surface atom is then given by

$$\Delta = (V_0 + E_c) - (V_0' + E_c'), \tag{1}$$

where E_c denotes the position of the core level relative to V_0 and the primed quantities refer to the surface atoms as shown in Fig. 1. Agreement to within a few percent of the tabulated x-ray values[5] is obtained in regard to both the positions of the levels and the $2p_{3/2}$-$2p_{1/2}$ splitting. However, here we are concerned with the *difference* in the level positions between the bulk and surface atoms, and the validity of the model for this purpose can be assessed only by comparison with experiment.

In Table I we show calculated values of Δ for the $2p_{3/2}$ levels of surface atoms on the closely packed faces of Ti, Cr, and Ni. Also shown are the calculated shifts of the corresponding free-atom energy eigenvalues relative to their bulk values. In making the calculations, bulk lattice constants at 300°K were used with the muffin-tin radii set equal to $\frac{1}{2}$ the nearest-neighbor distances. Any change in lattice spacings at the surface will, of course, change these values somewhat. Calculations of the chemical shifts for the second atomic layer yield values less than 0.1 eV for all three materials. To gain some idea of the variation from face to face, Δ was also calculated for the (110) face of Ni, and this value is included in Table I.

In the context of this model the surface core-level eigenvalues are intermediate between the free- and bulk-atom values. Renormalized atom calculations[12] give the conduction-band *d* levels in transition metals lying higher than their free-atom counterparts, but to our knowledge no calculations of the core-level positions have been made using this approach.[13] Our calculation is by no means applicable to the higher-lying electronic states which presumably are more greatly affected by going to self-consistency than the core levels.[14]

The "surface chemical shift" can be determined experimentally through excitation *threshold* measurements which give the core-level positions relative to the lowest unoccupied state to which the core electrons are excited. In metallic systems the lowest unoccupied state is at the Fermi level, which lies within a partially filled band. Although the conduction-band width may change at the surface due to the reduced coordination number,[15] the position of the Fermi level relative to some fixed energy (such as the vacuum level) remains constant (see Fig. 1). Here we report measurements of the surface core-level positions using electron-excited soft–x-ray appearance potentials and of the bulk core-level positions using photon-excited Auger-electron appearance potentials. These measurements are *in situ* and use the same tungsten thermionic emitter as a reference. Hence the difference between the threshold positions provides a direct measurement of the "surface chemical shift."

The soft–x-ray appearance potential technique depends on the fact that, for many materials, the total x-ray emission, plotted as a function of bombarding electron energy, exhibits distinct structure corresponding to the core-level-excitation probabilities superimposed on a bremsstrahlung background. The excitation thresholds can be sensitively detected in the energy derivative of the current from a metal photocathode[16] using the potential modulation technique.[17] Surface atoms make a significant contribution (~ 20%) to the observed spectrum because of the high probability that electrons penetrating more than a few angstroms will lose energy to excitations of the valence electrons. If core electrons of the surface atoms are less tightly bound, this will result in an early onset of the spectrum. For shifts of the order of an electron volt, the surface contribution will not be resolved from the main peak. We therefore take the initial break in the spectrum to correspond to the excitation of

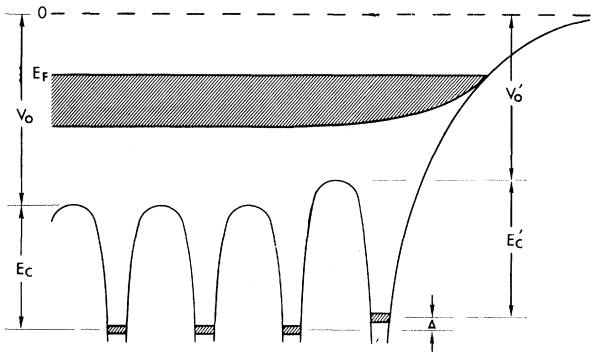

FIG. 1. Schematic diagram of the electronic structure in the surface region of a metal showing the shift Δ of a core level.

TABLE I. Core-level shifts in electron volts of $2p_{3/2}$ binding energies relative to bulk atoms.

	Calculated energy eigenvalue shifts Free atom	Surface atom	Measured polycrystalline surface
$_{22}$Ti (hcp)	1.7	(0001) 0.5	0.7 ± 0.2
$_{24}$Cr (bcc)	2.8	(110) 0.8	1.1 ± 0.2
$_{28}$Ni (fcc)	1.5	(111) 0.4	0.9 ± 0.2
		(110) 0.6	

a surface core level.

Core-electron binding energies can also be determined from the total photoelectron current from a sample plotted as a function of the energy of incident soft x rays. At photon energies just sufficient to excite electrons from a core level to the Fermi energy, there is a sudden change in the photocurrent resulting from Auger recombination of the core holes. Using synchrotron radiation, Gudat and Kunz[18] have recently shown the photoelectron yield of the $2p$ levels of Si to be essentially identical to the extreme ultraviolet absorption measurements of Brown and Rustgi.[19] Almost all of the photoelectrons making up these edges are low-energy secondaries and thus represent photoabsorption events occurring well below the surface. The surface contribution should be too small to detect above the background.

We used the short-wavelength bremsstrahlung limit of a W x-ray target as a "pseudomonochromatic" source of soft x rays. Near this limit the bremsstrahlung spectrum reflects the density of unoccupied states above the Fermi energy of the W target.[20] Thus the high density of $5d$ states produces a distinct peak which drops to zero at the Fermi energy. This limit was modulated by superimposing a small oscillation on the target potential. The alternating component of the photoelectron current from a sample exposed to this source increases sharply as the target potential is swept across the threshold for a core-level excitation of the sample.[21] For small oscillation amplitudes the shape of the edge approximates the convolution product of the energy derivative of the W bremsstrahlung spectrum and the photoelectric excitation probability of the core level of the sample. The procedure can be considered as a measurement of the excitation probability by an instrument whose response function is just the energy derivative of the bremsstrahlung spectrum. The shape of the spectrum therefore depends as much on the W source as on the sample. The initial break however provides a unique point of comparison with the electron-excited soft-x-ray appearance potential spectrum.

The soft-x-ray appearance potential measurements were made in the usual fashion[2] using an evaporated Au photocathode. The sample temperature was then increased by electron bombardment until a heavy evaporated deposit of the sample material coated the photocathode. Using a carousel arrangement the sample was then replaced with a W target which served as an x-ray source for studies of the photocathode. The Au photocathode was replenished by rotating a Au sample into position and evaporating a fresh Au film.

The resulting $2p$ spectra of Ni are shown in Fig. 2. The shift in the threshold is 0.9 ± 0.2 eV. The results for Ti, Cr, and Ni are summarized in Table I. The widths of the peaks in the electron-excited soft-x-ray appearance potential spectrum in Fig. 2 are a measure of the width of the unfilled $3d$ band broadened by the lifetimes of the $2p_{3/2}$ and $2p_{1/2}$ holes.[2] The peaks in the photoelectron appearance potential spectrum are broader, reflecting the fact that the instrument response function corresponding to the tungsten x-ray source is comparatively broad, as one would expect from the tungsten bremsstrahlung isochromat spectrum.[20] This breadth does not affect the short-wavelength x-ray limit but it does cause the spectrum to turn on less abruptly, which introduces additional uncertainty in determining the threshold.

Although the experimental core-level shifts are somewhat larger than the calculated values, the agreement between the measurements and the model predictions seems quite reasonable.[22] It should be noted that the measurements were made on polycrystalline samples which we assume expose predominantly the most closely packed faces. The presence of less densely packed faces would increase the shifts. An expanded upper layer spacing would also produce larger shifts. A more serious concern is that the bulk and surface measurements were not

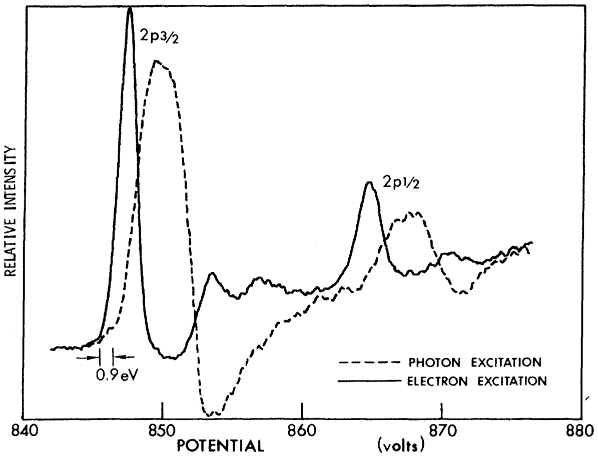

FIG. 2. Comparison of the nickel $2p$ electron-excited soft-x-ray appearance potential spectrum and the photoelectron appearance potential spectrum. The surface chemical shift in the $2p_{3/2}$ threshold is about 0.9 eV.

actually made on the same sample. Experiments are planned to overcome this difficulty and to look for chemical shifts between different faces of the same material.

The agreement between theory and experiment is an indication that the procedures for constructing effective one-electron potentials for bulk solids are valid for the surface region. This is important since the first task in analyzing the electronic properties of the surface region is construction of a reasonable one-electron starting potential.

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