Absolute $2p_{3/2}$ core binding energies and work functions of 3*d* transition-metal surfaces

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Absolute threshold energies for inelastic electron scattering from the $2p_{3/2}$ core states and absolute work functions have been obtained for 3d transition-metal surfaces using a field-emission source. Core binding energies are conventionally determined either from the kinetic energies of ejected core electrons that have absorbed a known amount of energy as in x-ray photoelectron spectroscopy (XPS), or from the threshold energy for excitation of the core state as in appearance-potential spectroscopy (APS). In the XPS measurements a correction must be made for the effective work function of the spectrometer. In APS, a correction is normally required for the emitter work function. Using a field-emission electron source, however, the threshold energy for core excitation is given directly by the product of the emitter-sample potential and the electronic charge without correction for emitter work function. The thresholds are identified as abrupt changes in the secondary electron yield. Iterative deconvolution was used to correct for instrumental and core-lifetime broadening. The binding energies measured in this way are consistently lower than those measured by x-ray photoelectron spectroscopy. Absolute work functions were measured by the field-emission retarding-potential technique.

I. INTRODUCTION

Although the inner-shell electrons of atoms do not directly participate in chemical bonds, their binding energies can be measurably shifted by redistribution of the valence electrons. This has provided the motivation for increasingly accurate measurements of core-electron binding energies in the surface region of solids. Binding energies are determined either from the threshold energies for excitation of a core state, as in x-ray absorption and appearance-potential measurements, or from the kinetic energies of ejected core electrons that have absorbed a known amount of energy, as in x-ray photoelectron spectroscopy and characteristic energy-loss measurements.

The first extensive table of core-electron binding energies, published by M. Siegbahn,¹ relied on x-ray absorption measurements to establish a reference level for each element. For Z > 51, Siegbahn used the $L_3(2p_{3/2})$ edge as a reference because of its intrinsic sharpness. For lower-Z elements he used the K edge. The energies of the remaining levels were calculated from x-ray emission wavelengths. Siegbahn's table was revised and expanded in 1952 by Hill, Church, and Mihelich² using more accurate values of the physical constants. Subsequent tabulations of binding energies by Bearden and Burr³ and by K. Siegbahn et al.⁴ have relied on x-ray photoelectron measurements rather than absorption edges to establish the reference scale wherever possible. The x-ray photoelectron measurements were not, however, taken under the ultraclean conditions generally regarded as necessary for surface-sensitive techniques. These

compilations are therefore unlikely to be representative of clean-surface values.

More recently, Shirley *et al.*⁵ have determined new values of core-level binding energies of the 3*d* transition metals based on x-ray-photoemission spectroscopy (XPS) measurements on clean surfaces under ultra-high-vacuum conditions. However, the measured kinetic energies of the photoejected core electrons, from which the binding energies are calculated, represent the energy of the ejected electrons relative to the vacuum level of the spectrometer.⁶ Thus, the effective work function of the spectrometer must be known in order to determine the binding energy directly. The spectrometer work function, unfortunately, is a poorly defined quantity.

An alternative approach to the measurement of core-electron binding energies is to measure the threshold energy for electron scattering from a core state. This approach, which is termed appearance-potential spectroscopy, has the advantage that no dispersive analyzer is required. The resolution is therefore limited only by the spread in incident electron energies. This technique was used by Park and Houston⁷ to measure the L-shell binding energies of the 3d transition elements. In a direct comparison of binding energies determined by appearance-potential spectroscopy (APS) and XPS, Webb and Williams⁸ concluded that, within the accuracy of the experiment, both methods gave the same result. They pointed out, however, that the neglect of core-hole lifetime broadening by Park and Houston was unjustified. The principal uncertainty in these measurements, however, was the work function of the thermionic electron source,

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which must be added to the potential difference between the emitter and the sample to obtain the incident electron energy.

In the present paper, we report the first appearance-potential measurements of $2p_{3/2}$ core binding energies of the 3d transition metals using a fieldemission electron source. Since the field-emitted electrons tunnel through the potential barrier at the emitter surface, no correction for work function is required. In addition, we have taken explicit account of the lifetime broadening of the core state, by means of a deconvolution program. These are believed to be the first absolute measurements of core-electron binding energies.

In addition, we report absolute-work-function measurements obtained by field-emission retarding-potential method.

II. EXPERIMENT

The apparatus used to obtain the appearance-potential spectra is shown schematically in Fig. 1. It must certainly be the simplest core-level spectrometer ever constructed and may have the highest resolution. The electron source is a tungsten field-emission tip mounted on a heating loop. The tip was deliberately blunted by flashing at progressively higher temperatures until a field-emission current of about 2 μ A was measured at an anode potential of 900 V. A 10⁸- Ω resistor serves as a current limiter.

Electrons passing through a small aperture in



FIG. 1. Schematic diagram of the experimental apparatus used in measurements of absolute core binding energies. Field-emitted electrons passing through an aperture in the anode impinge on the sample with an energy eV. The derivative of the sample current is obtained by the potential modulation technique. That portion of the sample current that varies at the modulation frequency is selected by a tuned circuit. Excitation of a core level is signaled by an abrupt decrease in sample current.



FIG. 2. Energy-level diagram showing the condition for threshold excitation of a core level by a fieldemission source. The binding energy is given by $E_B = eV$.

the anode are retarded, and impinge on the sample surface with an energy eV. Since the sample potential V is kept lower than the anode potential V_o , the anode serves as a collector for secondary electrons. The current measured in the sample circuit is therefore

$$I = I_{p} - I_{s}, \tag{1}$$

where I_p is the primary current and I_s is the secondary emission current from the sample. I_p is independent of the sample potential and variations in sample current as a function of V reflect accurately changes in secondary emission. As shown in the energy-level diagram in Fig. 2, an electron tunneling from the Fermi level of the emitter will impinge on the sample with an energy eV, relative to the Fermi level of the sample. The threshold for inelastic scattering from a core state with binding energy E_B is just

$$eV = E_B, \tag{2}$$

since no electrons will have energy greater than eV.

There is, of course, some spread in the incident electron energy, since electrons may tunnel into the vacuum from any state in the valence band. The tunnel current is a strong function of the barrier width, however, with the result that emission drops off rapidly for states below the Fermi level. Young⁹ has shown that for a free-electron metal the energy distribution of field-emitted electrons



FIG. 3. Instrument-response functions for the spectrometer shown in Fig. 1. (a) Energy distribution of fieldemitted electrons relative to the emitter Fermi level. (b) Semielliptical broadening function associated with potential modulation differentiation using sine-wave modulation. The total instrument response is given by the integral product of (a) and (b).

is given by

$$J(E) = J_{o} e^{E/d} / d(1 + e^{E/kT}).$$
(3)

where d is a parameter determined by the work function and the applied field.

Tungsten, of course, is not a free-electron metal. For the purposes of an instrument-response function, however, the difference is slight since the transmission coefficient for *d*-band tunneling is reduced over that for s-band tunneling by several orders of magnitude.¹⁰ The electric field. which enters into the coefficient d, was obtained from a Fowler-Nordhiem plot.¹¹ The resulting energy distribution has a width at half maximum of 0.2 eV. This is in good agreement with the measured energy distribution of a nearly identical tip mounted in a field-emission retarding-potential (FERP) gun of the Strayer, Mackie, and Swanson design.¹² In any case, the energy distribution has only a slight effect on the measured threshold for core-level scattering, since the distribution cuts off abruptly at E = 0, with only the thermal spread of the room-temperature Fermi distribution producing a slight tail on the high-energy side, as shown in Fig. 3(a).

As the incident electron energy is increased to just above the binding energy of a core state, two factors can be expected to alter the secondary yield: (a) the elastic yield should decrease as the result of opening a new channel for inelastic electron scattering, and (b) the inelastic electron yield should increase as a result of Auger recombination of the core hole. Clearly these effects are partially offsetting. We find experimentally that for the $2p_{3/2}$ edge of the 3d transition metals, the net effect is for the total yield to increase at the threshold. Most of this increase is the result of low-energy secondaries produced in stopping the Auger electrons.¹³ To enhance the excitation threshold structure, the sample current is differentiated as a function of incident electron energy. Additional broadening results from the necessity of taking the derivative of the sample current as a function of the incident electron energy.

Differentiation of an experimental curve necessarily involves the use of smoothing to suppress high-frequency noise. The form of the smoothing function depends on the technique used in differentiation. In these measurements the derivative was taken by the potential modulation technique, in which case the first derivative instrument response is given by¹⁴

$$T(E, e_o) = (2/\pi) \left[1 - (E/e_o)^2 \right]^{1/2}, \tag{4}$$

where e_o is the modulation amplitude. For the measurements reported here, a modulation of 0.15 V rms was used.

The total instrument response function corresponds to the convolution product of the broadening terms in Eqs. (3) and (4). The width of this function at half maximum is about 0.4 V. This relatively narrow response makes this perhaps the highest-resolution core-level spectroscopy in use. Moreover, since the instrument-response function is fairly accurately known, some additional resolution can be realized by using deconvolution techniques.

In the first derivative of the sample current, the appearance potential edges are observed on a large background. Therefore, small variations in the primary electron current could completely obscure the spectrum. As a result of small instabilities in the field-emitted current it was necessary to scan the spectrum many times and average the separate spectra.

The long periods required to obtain the spectrum placed stringent requirements on the vacuum. The ion gauge on the ion-pumped fast cycle vacuum system registered less than 2×10^{-10} Torr during measurements. To ensure that no significant contamination took place, spectra were taken rapidly at somewhat higher primary currents using a thermionic emitter, before and after the field-emission measurements. No change in the spectra could be detected in this time.

Ultrapure polycrystalline samples of the metals



FIG. 4. Field-emission retarding-potential curve for a polycrystalline chromium surface. The work function is given directly by the product of the onset potential and the electronic charge. Electrons were formed into a parallel beam normally incident on the surface by a gun of the Strayer, Mackie, and Swanson design (Ref. 12).

were obtained from Materials Research Corp. The nickel sample was a (111) single crystal. Surfaces were prepared by mechanical polishing followed by argon-ion sputtering and annealing, with the exception of manganese, which was evaporated *in situ* onto a stainless-steel substrate.

In addition to absolute core binding energies, absolute work functions of the polycrystalline samples were obtained by the field-emission retardingpotential method.¹² In such measurements, the sample surface is used as an equipotential momentum analyser. It is therefore necessary that the surface be smooth and flat over a large distance compared to the retarding distance, and that the incident electron beam fall normally on the surface. This is in contrast to the appearance-potential measurements which are determined only by the energy of the incident electrons.

A typical field-emission retarding-potential curve is shown in Fig. 4. When the potential difference between the sample and emitter is just equal to the sample work function, electrons tunneling from the Fermi level of the emitter will just arrive at the sample surface with zero kinetic energy. Thus, the potential difference between the emitter and sample at the threshold for sample current, multiplied by the electronic charge, is an absolute measure of the sample work function.

III. RESULTS AND ANALYSIS: CORE BINDING ENERGIES

As Carley, Joyner and Roberts have shown,¹⁵ the Fermi level of a conductor is the appropriate reference for the measurement of absolute coreelectron binding energies. The work function of the sample is irrelevant. Therefore, the threshold energy for inelastic electron scattering from a core state should correspond to the core-electron binding energy. Several factors contribute to the uncertainty in identifying this threshold: (i) instrumental broadening factors, (ii) the finite core-hole lifetime, and (iii) variations in the transition density near the threshold.

As discussed in the previous section, instrumental factors contribute a broadening of about 0.4 eV. Since the instrument response function is accurately known, however, the actual uncertainty this introduces is much less, since much of the instrumental broadening can be removed by deconvolution.

The core-hole lifetime broadening is more difficult to treat. As Webb and Williams⁸ pointed out, the width of the core level cannot be safely ignored in determining the binding energy. Experimental determinations of 2p core-level widths, however, are virtually nonexistent for Z < 65. We were therefore forced to rely on one-electron atomic calculations, ¹⁶ which should be about right for the pure metals. We have assumed the shape of the corelevel function is adequately represented by a Lorentzian. The calculated widths range from 0.24 eV for Z = 22 to 0.61 eV for Z = 28. These widths are solely a consequence of the Auger lifetimes of the core holes, and solid-state effects might be expected to contribute additional broadening. Flynn¹⁷ has calculated the broadening of x-ray edges due to phonon creation by the core excitation for a number of metals. In the case of titanium, the calculated room-temperature phonon broadening is 205 meV, which is comparable to the Auger lifetime broadening. For most transition metals the effect is much smaller, however, and it has not been included in our analysis.

Assuming constant oscillator strengths, the appearance-potential edge should have the shape of the self-convolution of the density of conduction states, broadened by the core-level width. To suppress the large background, however, the spectra were taken in the first derivative. Near the edge the derivative of the self-convolution is a good approximation to its unfold.¹⁸ Thus, near the threshold the spectra of transition metals should reflect the large density of unfilled d states.⁷

The 2p Auger-electron appearance-potential spectrum of vanadium, obtained by the field-emission method, is shown in Fig. 5. The large positive peak at the $2p_{3/2}$ threshold presumably corresponds to the unfilled portion of the 3d band. To extract a core binding energy from this spectrum requires that we understand the effect of the broadening factors, including the core-level width and instrumental effects. Unfortunately, the noise level of



FIG. 5. Auger-electron appearance-potential spectrum of the 2p levels of polycrystalline vanadium, obtained with a field-emission source.

the spectrum makes deconvolution a risky procedure. We therefore employed a less direct method of evaluating the effect of the broadening factors.

The spectrum was taken at a higher primary current (5 μ A) using a thermionic emitter (Fig. 6). Although the spectrum is shifted by the emitter work function, the shape should be nearly the same as that taken by the field-emission method but with a lower noise level. The only significant difference is the less abrupt threshold resulting from the Maxwellian energy distribution of thermionically emitted electrons. This distribution is known fairly accurately for the tungsten emitter. Using the Van Cittert¹⁹ iterative deconvolution method, the instrumental broadening resulting from the thermionic energy distribution and potential modulation, and the core-level broadening were removed from the spectrum as shown in Fig. 6. The rms difference between the predicted spectrum using the deconvolution result and the raw data was used as the criterion for convergence.²⁰ 15-20 iterations were required.

Several features are evident in the deconvoluted spectrum. The threshold is much better defined and shifted to slightly higher energy. In addition, a distinct shoulder is developed on the low-energy side of the spectrum. This is not unexpected. The 3d density of states consists of two maxima corresponding to antibonding and bonding orbitals. In the case of vanadium, the antibonding orbitals are not quite filled and should therefore show up on the low-energy edge of the spectrum. In the spectrum of titanium, which has one less electron, a shoulder corresponding to the antibonding orbitals is evident in the raw data.⁷ For vanadium this feature is not really evident until the broadening factors are removed. Once a "deconvoluted" spec-

trum is obtained, the broadening factors are put back in, this time using the field-emission energy distribution as shown in Fig. 7. It is now possible to assess the effect of the broadening terms on the leading edge of the vanadium spectrum. The energy distribution of field-emitted electrons has the effect of shifting the spectrum to higher energies, since the centroid of the energy distribution is negative with respect to the Fermi level of the emitter. In the case of vanadium, this tends to compensate for the shift in the threshold produced by modulation broadening and core-level width.

It is evident from Fig. 6 that although deconvolution has sharpened the edge, it has not succeeded in producing a discontinuity corresponding to the Fermi level. This is probably evidence that we do not have the shape of the tails correct in the broadening functions. This could involve an asymmetric core-level function resulting from many-body screening effects, or it could be the result of phonon broadening. To test whether the failure to produce a sharp discontinuity at the threshold might be a consequence of using too narrow a core width, we tried progressively wider core widths. This did not result in an appreciably sharper threshold, but eventually began to produce an unphysical dip ahead of the edge. We thus concluded that the calculated core widths were at least of the right order of mag-



FIG. 6. Auger-electron appearance-potential spectrum of the $2p_{3/2}$ level of vanadium taken with a thermionic emitter, and the same spectrum deconvoluted to remove instrumental broadening and a Lorentzian core lifetime broadening of 0.28 eV. The shoulder exposed on the leading edge is evidence of unfilled *d*-bonding orbitals. The threshold shift is due primarily to the Maxwellian distribution of thermionically emitted electrons.



FIG. 7. Predicted $2p_{3/2}$ spectrum of vanadium for a field-emission source using the deconvoluted appearancepotential spectrum of Fig. 6, broadened by the instrument response functions shown in Fig. 3 and a Lorentzian core-hole lifetime broadening function. The shift in the threshold is slight in this case.

nitude.

Difficulties were expected at the high-Z end of the series (Co and Ni) since the width of the unfilled portion of the 3d band becomes appreciably less than the core broadening, and we were not disappointed. Under these conditions any noise in the spectrum, or uncertainty in the broadening function, can be expected to prevent the iterative deconvolution from converging. The result for nickel was that continued iteration began to generate oscillations ahead of the edge. Since the spectral features for cobalt and nickel were quite sharp to begin with, however, these artifacts did not introduce much uncertainty into the determination of threshold energies.

Our values for the $2p_{3/2}$ binding energies of elements 22–28 are compared with other compilations in Table I. The data of Park and Houston⁷ were obtained by soft x-ray appearance-potential spectroscopy (SXAPS) using a thermionic emitter. They neglected the width of the core level in their determinations and made only an approximate allowance for instrumental broadening. They used a correction of 4.5 eV for the work function of their pure tungsten emitter. We attempted to test this by measuring the work function of a reference surface by the absolute FERP method¹² and comparing it with the contact potential difference between the reference and a thermionic emitter prepared from

TABLE I. Absolute $2p_{3/2}$ binding energies in eV compared to earlier tabulations.

	AEAPS ^a (field- emission)	SXAPS ^b	XPS °	x-ray ^d
²² Ti	454.2 ± 0.2	453.4 ± 0.5	454 9	455.5 ± 0.4
^{23}V	512.0 ± 0.2	512.6 ± 0.5	513.4	512.9 ± 0.3
²⁴ Cr	574.3 ± 0.2	574.0 ± 0.5	576.0	574.5 ± 0.3
²⁵ Mn	637.4 ± 0.2	638.5 ± 0.5	639.4	640.3 ± 0.4
²⁶ Fe	705.8 ± 0.2	706.3 ± 0.5	707.6	708.1 ± 0.9
²⁷ Co	777.0 ± 0.2	776.9 ± 0.5	781.0	778.6 ± 0.3
²⁸ Ni	851.3 ± 0.2	850.9 ± 0.5	854.2	854.7 ± 0.4

^a Auger-electron-appearance potential spectroscopy.

^b Soft x-ray-appearance potential spectroscopy, Ref. 7. ^c Reference 5.

^d Reference 3.

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the same tungsten stock used by Park and Houston. We concluded that the work function correction used by Park and Houston was about 0.2 eV too high.

The tabulated binding energies of Bearden and Burr³ and Shirley et al.⁵ are based on x-ray photoelectron measurements. Hence, they involve the measurement of momentum rather than energy. Moreover, the ejected core electron is at a high kinetic energy. In the appearance-potenial case both the incident and excited core electrons are in states just above the Fermi energy. It is not clear whether this altered screening could account for different measured binding energies. Certainly no such difference is evident in the measurements of Webb and Williams, 8 who find close agreement between XPS and SXAPS measurements. The tabulated values of Shirley et al.⁵ are referenced to the vacuum level, rather than the Fermi level. In Table I, therefore, we have subtracted the values of work function used by Shirley et al. in presenting their binding energies.

Our binding energies are consistently lower than those reported by Shirley *et al.*⁵ They are closest to the appearance-potential measurements of Park and Houston, ⁷ being in all cases within stated error limits.

IV. WORK FUNCTIONS

Although the Fermi level is the appropriate reference for the core-binding energies of a metal, we have measured absolute work functions under conditions identical to the core binding energy measurements (Table II). For those with an emotional attachment to core binding energies referenced to the vacuum level, the work function should be added to the core binding energies in Table I.

The work functions were measured by the field-

TABLE II. Absolute work functions in eV measured by the field-emission retarding method compared to photoelectric values.

	$e\phi$ (FERP)	$e\phi$ (Photoelectric) ^a
²² Ti	3.96 ± 0.04	4.33 ± 0.1
^{23}V	4.17 ± 0.04	4.30 ± 0.1
²⁴ Cr	5.05 ± 0.04	4.50 ± 0.15
^{25}Mn	3.54 ± 0.04 ^b	4.10 ± 0.2
26 Fe	4.85 ± 0.04	4.50 ± 0.15
²⁷ Co	4.92 ± 0.04	5.00 ± 0.1
²⁸ Ni	5.27 ± 0.04 °	5.15 ± 0.1

^aReference 21, evaporated films.

^b Evaporated and annealed film.

^c (111) single-crystal surface.

emission retarding-potential method first introduced by Henderson.²² Electrons from a fieldemission source are focused into a parallel beam at an arbitrary energy and directed normally at a plane surface of the sample. The external potential between the emitter and sample is adjusted to the threshold for the detection of sample current. Since the most energetic electrons from the emitter will have tunnelled from the emitter Fermi level, the threshold potential, multiplied by the electronic charge, is the direct measure of the "true" work function.

The sharpness of the threshold depends on the momentum distribution of the incident electrons. We have used the electron-optical system of Strayer, Mackie, and Swanson¹² to obtain a parallel beam. A laser alignment technique was used to insure normal incidence. A typical retarding-potential plot is shown in Fig. 4.

The measured work functions are compared in Table II with photoelectric work-function measurements of Eastman.²¹ The agreement is not impressive. Eastman's values were for freshly evaporated films, whereas our measurements were made on bulk surfaces cleaned by argon-ion bombardment and subsequent annealing to remove the damage, with the exception of manganese, which was evaporated and annealed. The surfaces were polycrystalline, with the exception of nickel, which was a (111) oriented single crystal.

It seems likely that most of the differences between our work function values and the photoelectric work function values of Eastman are a consequence of differences in surface morphology. In the case of Ni(111) our work function is in good agreement with the photoelectric work function measurements of Baker *et al.*²³ on Ni(111). In the case of polycrystalline surfaces, however, we can expect surface morphology to play an important role. Besocke and Wagner,²⁴ for example, demonstrate that deposition of partial monolayers of tungsten on clean tungsten substrates can produce changes in work function of more than half an electron volt. It is worth noting that the work functions of our surfaces, prior to annealing out the sputtering damage, were from 0.12 to 0.65 eV lower than the annealed values. Contrary to the experience of Eastman, most contaminants seemed to cause an increase in the work function.

V. CONCLUSIONS

It is clear by this point that the principal uncertainty in the determination of absolute core binding energies by the field-emission appearance-potential technique is the identification of the point on the spectral edge corresponding to the excitation of core electrons to the Fermi level of the sample. This, of course, is precisely the same uncertainty encountered in the use of x-ray-absorption-edge measurements.²⁵ What may not be quite so apparent is that one is confronted by essentially the same problem in attempts to extract binding energies directly from x-ray photoelectron measurements. It is insufficient in such measurements to simply measure the kinetic energy of the ejected core electrons. To directly measure binding energies, it is necessary to take the energy difference between the ejected core electron and the high kinetic-energy limit of the spectrum. This limit corresponds to electrons from the highest occupied level of the sample. In metals this is the Fermi level, but once again it is an edge, with uncertainties introduced by transition probability variations and instrumental factors.

Our binding energies are consistently lower than tabulated XPS values. The values of Shirley *et al.* are $0.3 \pm 0.04\%$ larger than ours except for Ti (-0.15%) and Co (-0.51%). It remains to be determined whether this difference represents experimental error or a difference in the physical processes represented by the two methods.

Our results suggest that work function measurements in the absence of a detailed characterization of the surface structure may not be meaningful. Certainly the wide variation in work functions reported for clean polycrystalline samples would seem to argue strongly against referencing coreelectron binding energies to the vacuum level of the sample.

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