The photoelectron spectra from a polycrystalline tungsten surface in the following Figures 1-3 have been obtained with low-energy synchrotron radiation at two energies and with high energy resolution. They are shown for a reasonably clean tungsten specimen (Fig. 1), for tungsten surfaces with various degrees of in situ oxidation (Figs. 2 and 3(a)-(d)), and for reference specimens with clean surfaces of WO₂ and WO₃ (Figs. 3(e)-(f)). Also shown on the pages after that in Figures 4 and 5 are the photoelectric cross sections and asymmetry parameters for tungsten as a function of photon energy, and the electron inelastic attenuation length for W (as calculated with the TPP-2M method). The band structure of W is also shown in Figure 6. The work function of W is 4.5 eV. In answering the following questions concerning these spectra, assume that, over the narrow energy range of these spectra, the spectrometer transmission or response function, as sometimes written $A_\omega \Omega_\omega D_0$, is a constant.

(a) What core levels are responsible for the three photoelectron peaks in Fig. 1?

(b) Why is the background for $h\nu = 63$ eV so much more steeply sloping than that for $h\nu = 110$ eV? [Hint: Calculate the kinetic energy range covered by the two spectra.]

(c) Why is the relative intensity of the peak at $\sim 37$ eV binding energy so much suppressed in going from $h\nu = 63$ eV to $h\nu = 110$ eV?

(d) Assume that only W and O are present and use the results of Figs. 2 and 3 to assign the pairs of peaks 1, 2, 3, and 4 that have been self-consistently resolved from the spectrum of Fig. 3 to definite chemical states or species involved. (Note that W can be bound to 1, 2, or 3 oxygens, and assume that any chemical shift is roughly proportional to this number.)
(e) The authors have determined that, for the least oxidized surface of Fig. 3(a), a total of 15.8% of the intensity is in states of type 2 and 3 (9.8% in 2 and 6.0% in 3). Assume emission at an average angle with respect to the surface of 45° and that the oxidized layer so produced is thin and non-attenuating for emission from the metallic W below. Now make the most quantitative estimate of the number of monolayers of oxygen atoms on the surface. The polycrystalline W foil surface can here be taken to have an average spacing of d = 1.58 Å between its atomic layers.

(f) Is there any evidence for Cooper minima in the cross sections of W? If so, indicate which subshell(s) and the approximate energy/energies.

(g) If the W 5d electrons are those most involved in chemical bonding, what specific coulomb integral would be relevant to interpreting the shifts in Fig. 2 between states of types 1-4? Write out this integral in a clear way.
Consider now the W band structure in Figure 6, and note that the free-atom electronic configuration is \([\text{Xe noble gas}] 4f^{14} 5d^4 6s^2\).

(h) Where in this band structure are free-electron-like states obvious? Indicate also the approximate energy range of the 5d bands.

(i) From the band structure and the work function of 4.5 eV, estimate the inner potential of W.

(j) At what energy might you expect the strongest resonant photoemission effects for the 5d components of the W valence spectrum? [Hint: Reason by analogy with the case of Mn 3d discussed in lecture.]
Continuing with the tungsten/oxygen system, consider that, if we expose W(110) to oxygen for a long time, it forms the periodic structure indicated with the cluster in Figure 7. Also shown in Figure 7 is a photoelectron diffraction pattern for W 4f emission with an excitation energy of 1486.7 eV, p-polarized radiation, and an angle between x-ray incidence and electron exit of 90°. Only the analyzer has moved in this calculation, which was made with the program EDAC.

(a) What would be the Wood notation name for this overlayer and what is the coverage in ML? [W has a body-centered cubic structure.]

(b) What is the origin of the three peaks in the photoelectron diffraction pattern labeled 1, 2, and 3 and their associated fine structure? And of the weaker peaks labeled 4, 5, and 6 and their associated fine structure?

(c) Indicate in a simple equation how you would calculate the distance from W to one of its nearest-neighbor O atoms from the fine structure rings in this diffraction pattern, such as the one indicated by the dotted circle. You may neglect the scattering phase shift, and take the electron kinetic energy to be 1450 eV.

In Figure 8 are shown the W binding energies; the experimental 2p and 2s absorption spectrum of WO₃, overplotted in blue with the imaginary part of the index of refraction β as obtained from the online CXRO database; and the calculated densities of states of the same material, including the projected densities of states for W 5d and O 2p.

(d) Using this data, explain qualitatively why there are sharp “white lines” for the L3 and L2 absorption spectra, and no such features in the blue curve from the CXRO database, nor for the L1 absorption spectrum. For the L1 spectrum, make reference to the dipole selection rules involved in x-ray absorption.
(e) Estimate the peak separations of 1337 eV and 555 eV seen in the x-ray absorption spectrum from binding energies.

Figure 7
[4] (25 points)
Consider processes involving the initial formation of a 1s hole in Cu metal.
(a) What would be the minimum energy required to form this hole?

(b) What will be the most energetic KLL Auger electron resulting from this hole? Make the most accurate estimate you can of its energy, indicating specifically the formula you have used.

(c) After the Auger transition in (a), what type of hole state will be left behind? If we now want to estimate the effect of this hole state on the surrounding outer valence electrons, we might treat the final state as an "impurity atom" in the Cu lattice. Which atom would we choose for the impurity in this case?

(d) Calculate the energy of the Kα1 x-ray that can also be emitted through the filling of this hole, and compare your result to a tabulated value.

(e) Consider Cu 2p photoemission from Cu in CuS with an unfilled 3d⁹ shell, and discuss briefly two extra sources of final state structure in this spectrum that would not be present in Cu 2p photoemission from Cu metal with a filled 3d shell.

(f) Finally, what is one way making use of polarized radiation by which spin-polarized electrons could be emitted in Cu 2p emission, and which effect is involved?

--END OF EXAM--
(a) See Fig. 1 on next page: $W^{5p_{3/2}}, W^{4f_{5/2}}, W^{4f_{7/2}}$.

(b) Background at $h\nu = 63$ is more sloping because photo-electrons are beginning to rise up on secondary $e^-$ tail.

Fermi level ($= E_F$) has been used as reference.

(c) This is due to a rapid change in the relative photoelectric cross sections for $W^{5p_{3/2}}$ compared to $W^{4f_{5/2}}, W^{4f_{7/2}}$, as seen from next page. In the photoelectric cross section plots on following page:

$$\frac{\sigma^{5p}}{\sigma^{4f}} @ h\nu = 4.0 \text{ eV} - 0.8920$$
$$80.0 \text{ eV} - 0.0722$$
$$120.0 \text{ eV} - 0.0512$$

Note about drop somewhere here.

$$\sigma^{5p} = \frac{1}{2} \sigma^{4f}, \sigma^{5p_{3/2}} = \frac{1}{2} \sigma^{4f_{5/2}}, \sigma^{5p_{1/2}} = \frac{1}{2} \sigma^{4f_{7/2}}$$

From Yeh + Lindan tables:

$$G^{5p} = \frac{1}{2} G^{4f}, G^{5p_{3/2}} = \frac{1}{2} G^{4f_{5/2}}, G^{5p_{1/2}} = \frac{1}{2} G^{4f_{7/2}}$$

However, the basic argument can be made on total cross sections.

The Yeh/Lindan tables show $E^V_0(W^{4f}) = - E^{4f} = 53.9 \text{ eV}$ compared to $E^V_0(W^{4f_{5/2}}, W^{4f_{7/2}})$ from examination of

$$32.5 \text{ eV} + \phi(W) = 32.5 + 4.5 = 37.0 \text{ eV}.$$  

The difference of $16.9 \text{ eV}$ must be due primarily to relaxation effects. $E^{4f}$ has no intradotronic relaxation in it. Also, in $W$ metal, there will be extradotronic relaxation that will further lower the observed $E^V_0$. So both types of relaxation must add up to $16.9 \text{ eV}$. 

EXTRA

If desired (but not essential), these cross sections could be divided into their $J = l + 1$ components according to occupation numbers, as:

For $G_{5p}$:

$$G^{5p_{3/2}} = \frac{2}{2} G^{5p}, G^{5p_{1/2}} = \frac{2}{2} G^{5p}$$

For $G_{4f}$:

$$G^{4f_{5/2}} = \frac{2}{2} G^{4f}, G^{4f_{7/2}} = \frac{2}{2} G^{4f}$$

But the basic argument can be made on total cross sections.
Figure 1

Tungsten Foil

Figure 2

Oxidized Tungsten Foil

Figure X
Inelastic attenuation length in W
(From TPP-2M Formula)

Electron Energy [eV]

$\Delta_e$ (nm)


**FIGURE 5**
(d) See Fig. 3 preceding page: W, WO, WO₂, WO₃. 

[The rather broad WO₂ spectrum of Fig. 2(c) suggests it may be changing state through further oxidation, but it nonetheless provides a useful doublet reference - 33 eV in the +4 state.]

(e) For an assumed non-attenuating overlayer. The relevant equation for photoelectron intensity ratios is (Eq. (1206) in "Basic Concepts of XPS":

\[ \frac{N(\text{states } 2+3)}{N(\text{state } 1)} = \frac{A_0 \rho_0 (d_{\text{surf}}/d_0) d}{\rho_0 A_0 (d_{\text{surf}}/d_0) \Delta \rho \sin \theta} \]

[FRACtIOnAL MONOLAYER COVERAGE]

Exact cancellation since peak kinetic energies are so close.

Recalling

\[ \text{F.M.C.} = \frac{N(2+3)}{N(1)} \cdot \Delta \rho \sin \theta \]

We desire coverage in oxygen atomic concentration, so note that state 3 = WO₂ has 2 O atoms/W atom.

\[ \therefore \frac{N(2+3)}{N(1)} = \frac{0.098 + 2(0.060)}{1.0c - 0.098 - 0.060} = \frac{0.218}{0.842} = 0.259 \]

At \( E_{\text{Ein}} = h \nu - E_0 - \phi s = 110 \text{ eV} - 33 \text{ eV} - 4.5 \text{ eV} = 72.5 \text{ eV} \), \( \Delta \rho \) from tabulations/graphics is \( \approx 4-5 \text{ Å} \), so we have

Finally

\[ \text{F.M.C. of 0 atoms} = 0.259 \cdot \frac{[4-5 \text{ Å}] \sin 45^\circ}{1.58 \text{Å}} = \frac{0.46 - 0.58 \text{ monolayers}}{ } \]

[At this coverage significantly less than 1.0 monolayer, our assumption of non-attenuation is quite reasonable.]
(4) Yes, for WS\alpha, e = 190 eV and for WH\alpha, e = 280 eV

(9) The Coulomb integral involved would be:

\[ J_{4f, 5d} = \int \psi_{4f}^* (1) \psi_{5d}^* (2) \frac{e^2}{\mathbf{r}_{12}} \psi_{4f} (1) \psi_{5d} (2) d\mathbf{r}_1 d\mathbf{r}_2, \]

as this is the only direct interaction the 4f electrons have with the bonding 5d electrons.

(10) See next page

(i) INTRAPOT. = 10.4 eV + 4.5 eV = 14.9 eV

\[ \text{From the band structure.} \]

[1] (i) See text on next page

[2] FIGURE 7 on a following page

(a) \( 110 \) (1 x 1) - 0% 1 ML coverage

(b) 1, 2, 3 are forward scattering peaks from the nearest-neighbor O atoms, as indicated on previous page

4, 5, 6 are forward scattering peaks from the next-nearest-neighbor O atoms, again as indicated on previous page.

(c) See FIGURE 7, for atom 2, the 1st-order diffraction ring corresponds to a scattering angle \( \theta_{\text{scatt}} \), which can be substituted into:

\[ \text{DIFF. PATTERN} = \frac{1}{(2\pi \cdot \lambda) \cos \left( \frac{1}{2} \left( k - k_{\text{scatt}} \right) \right)} \]

\[ \propto \cos \left[ k_{\text{scatt}} \left( 1 - \cos \theta_{\text{scatt}} \right) + \frac{1}{2} \theta_{\text{scatt}} \right] \]

To 1st order maximum for:

\[ k_{\text{scatt}} \left( 1 - \cos \theta_{\text{scatt}} \right) = 2\pi \]

With:

\[ k = \frac{2\pi}{\lambda}, \quad \lambda = \frac{2\pi}{(20.4)^{1/2}} = 0.288 \text{ Å}, \quad 21.8 \text{ Å}^{-1} \]

So, if we know \( \theta_{\text{scatt}} \), we can calculate \( k_{\text{scatt}} \).
At what energy might you expect the strongest resonant photoemission effects for the 5d components of the W valence spectrum? [Hint: Reason by analogy with the case of Mn 3d discussed in lecture.]

Strongest interaction for electronic states that are most overlapping with 5d, which is 5p, so resonances expected at the 5p absorption energies, which are: $5p_{1/2} = 45.3$ eV and $5p_{3/2} = 36.8$ eV. You might also mention 5s, or somewhat more removed in energy, 4d.
[2] (d) A two-part answer:

The CXRO tabulations never take the compound-specific “white line” absorption features into account, as illustrated in this slide from lecture for Mn 2p of MnO:

The difference between the L1 absorption edge and the L2 and L3 lies primarily in the dipole selection rule and the available densities of states for x-ray absorption just above the Fermi level, which are predominantly 5d in character. Thus, 2p to 5d transitions are allowed into these states, but not 2s to 5d, much reducing the white-line peak for the L1 absorption edge.
These are just differences of binding energies in first approximation, so $\text{BE}(W 2p\frac{1}{2}) - \text{BE}(W 2p\frac{3}{2}) = 11544 - 10207 = 1337$, and $\text{BE}(W 2s) - \text{BE}(W 2p\frac{1}{2}) = 12100 - 11544 = 556$, exactly as found in the experiment.
FIGURE 6

CALCULATED W 4f PHOTOELECTRON DIFFRACTION PATTERN

Left: representation of the cluster rocking around a line parallel to the z direction and passing by the emitter (yellow atom). The dashed lines stand for the z axis. Right: top view of the cluster, where the w direction (not plotted) runs along the horizontal/vertical screen direction. Different atomic species have been assigned the colors O, W.

FIGURE 7

Polar scan of photoemission intensity (logarithmic scale). White black regions correspond to high/low intensity. The orientation is the same as in the top view of the cluster. The distance to the center of the figure is proportional to the polar angle $\theta$. The polar angle range is (0, 90°) in degrees.
(a) Minimum E is Cu Kβ1 Kβ1 Auger = 8979 eV

(b) Most energetic is Cu KLL 3 + 3:

\[
E_{\text{Auger}} (\text{Cu KLL 3 + 3}) = E_b (\text{Cu 1s}) - E_b (\text{Cu 2p}^{3/2}) - E_b (\text{Zn 2p}^{3/2})
\]

\[
= 8979 - 932.7 - 1021.8 = 7024.5 \text{ eV}
\]

(c) 2 holes in Cu 2p^{3/2} \rightarrow "2+2" atom or \( \text{Cu}^0 \)

(d) Cu KLX 1:

\[
E (\text{Cu KLX 1}) = E_b (\text{Cu 1s}) - E_b (\text{Cu 2p}^{3/2}) = \frac{8046.5 \text{ eV}}{8047.8 \text{ eV}} \text{ (Compared to table value of Cu)}
\]
Consider now Cu 2p photoemission from Cu in CuS (3d^9), and discuss briefly two extra sources of fine structure in this spectrum that would not be present in Cu 2p photoemission from Cu metal (3d^10).

CuS would be like CuO as to chemical family, and so nominally Cu^{+2} 3d^9 in electronic configuration. Two sources of extra structure in the Cu 2p photoelectron spectra will thus be (1) charge-transfer screening of 3d^9 to become 3d^{10}, which produces very strong satellites, and (2) multiplet splittings connected with the peaks that are more d^9 in character. So it would look something like the example shown below, from lecture:
[3] (f) One could excite with circularly-polarized light and take advantage of the Fano effect to yield spin-polarized Cu 2p spectra through spin-orbit coupling. In this case, the spin polarization is referenced to the direction of propagation of the light, and magnetic order in the sample is not required. A slide from lecture illustrating this is below: