

**Physics 243A--Surface Physics of Materials: Spectroscopy
Final Examination**

December 16, 2014

(3 problems, 100 points total, open book, open notes and handouts)

Name: _____

[1] (50 points), including Figures 1-6

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 WO_2 and WO_3 (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 $A_0\Omega_0D_0$, 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 ~ 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 $d = 1.58 \text{ \AA}$ 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 [Xe noble gas] $4f^{14}5d^46s^2$.

(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.]

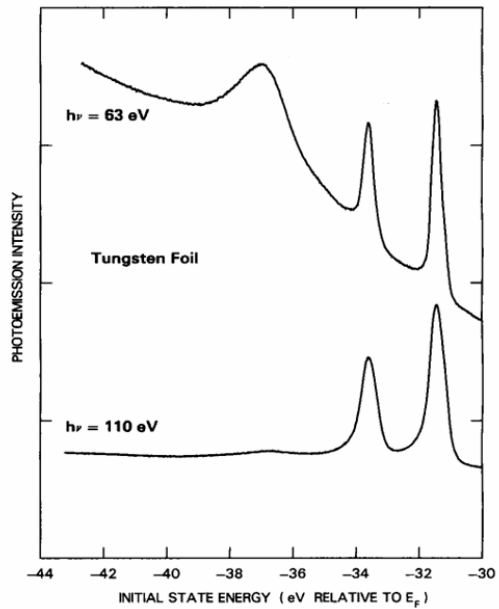


Figure 1

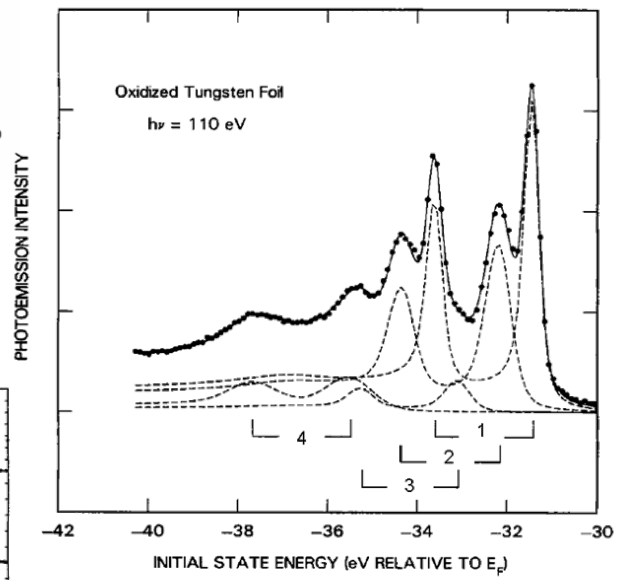


Figure 2

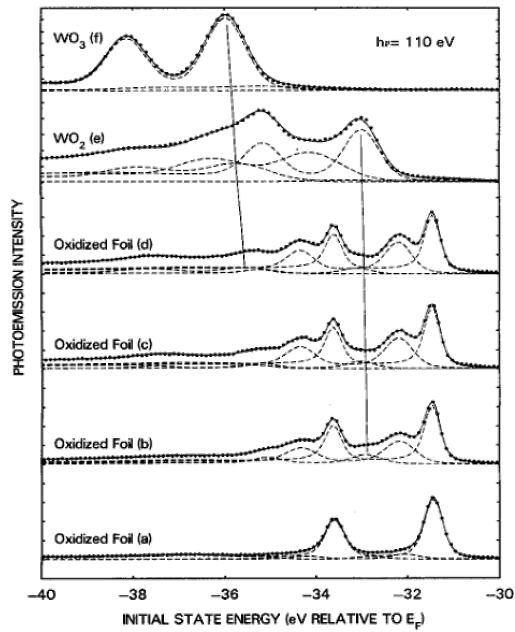


Figure 3

Atomic Calculation of Photoionization Cross-Sections and Asymmetry Parameters

Return to [periodic table](#)

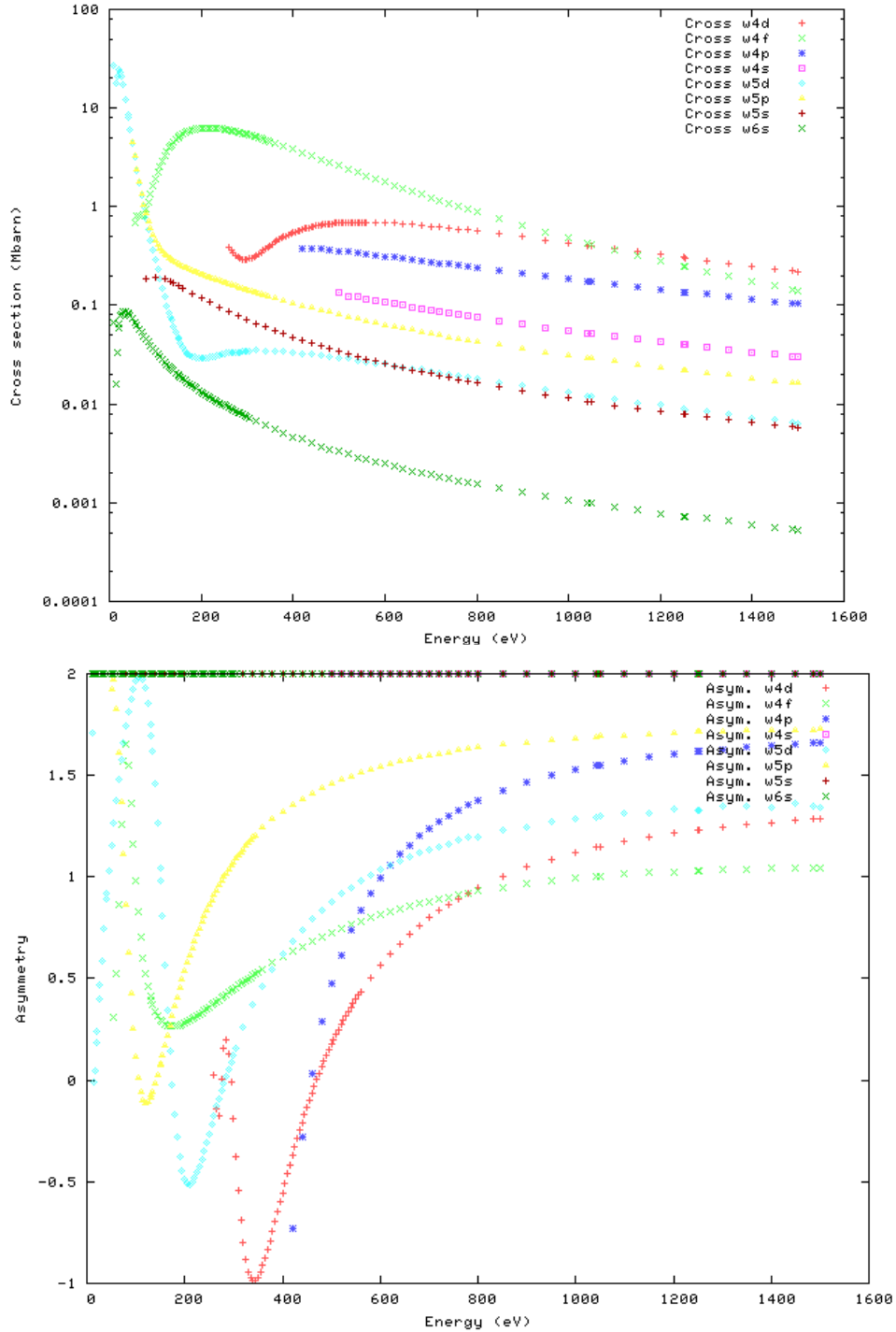


Figure 4

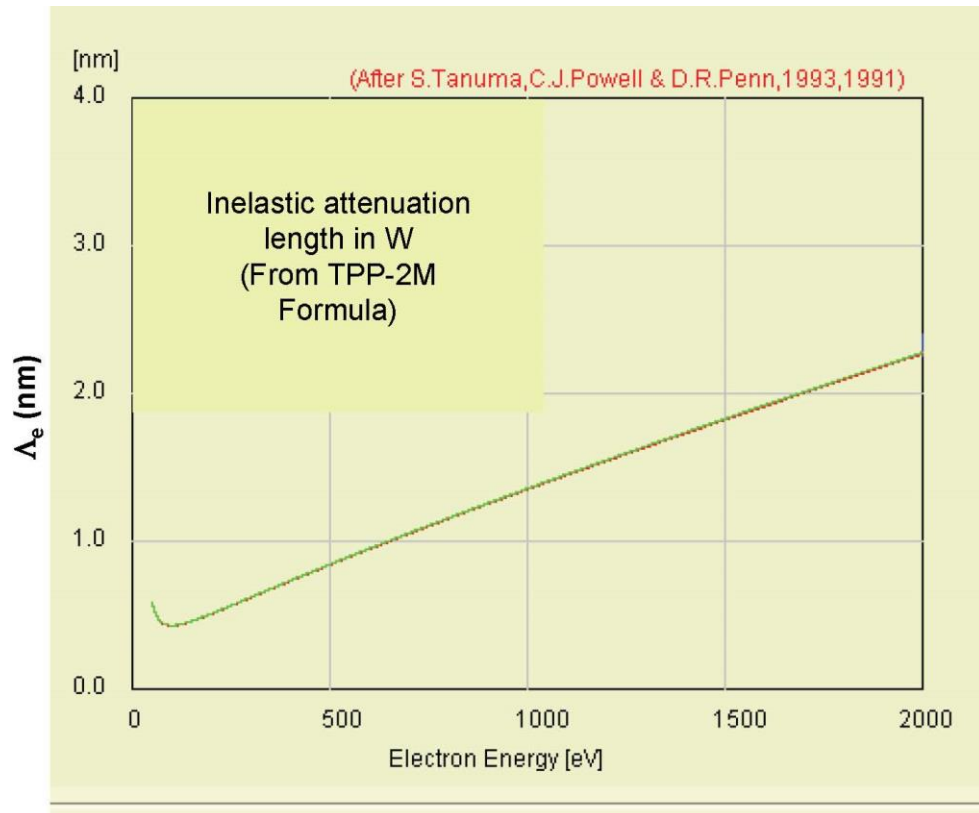


Figure 5

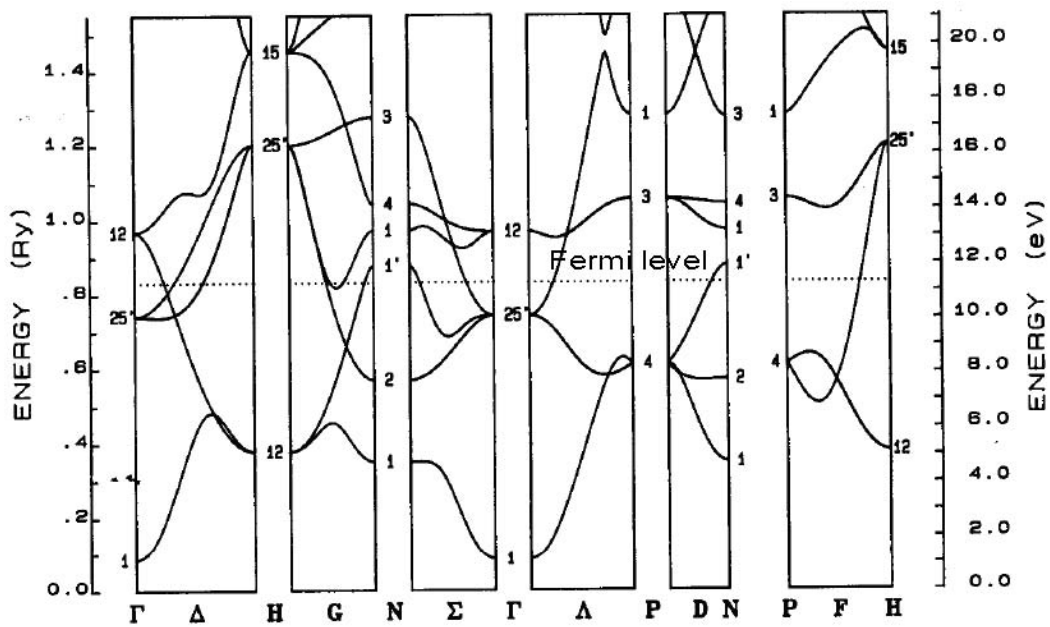


Figure 6

[2] (25 Points) Including Figures 7 and 8

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 WO_3 , 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.

CALCULATED W 4f PHOTOELECTRON DIFFRACTION PATTERN

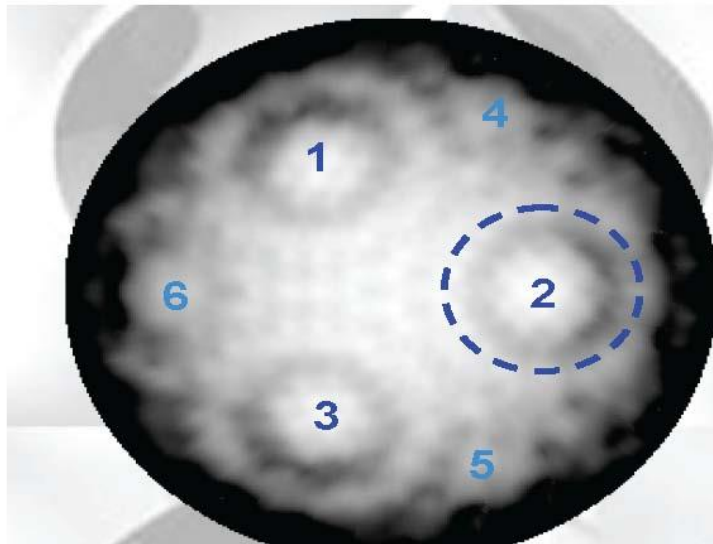
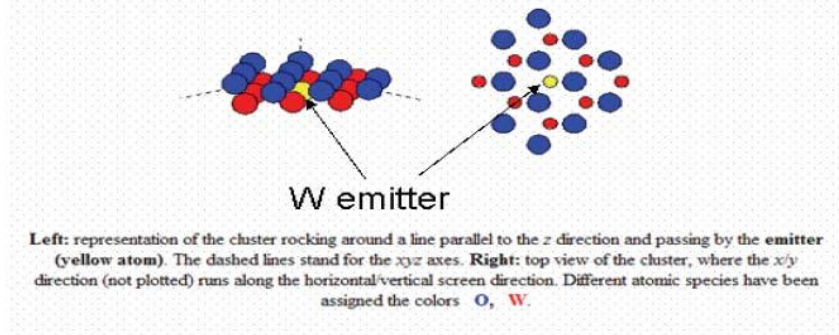


Figure 7

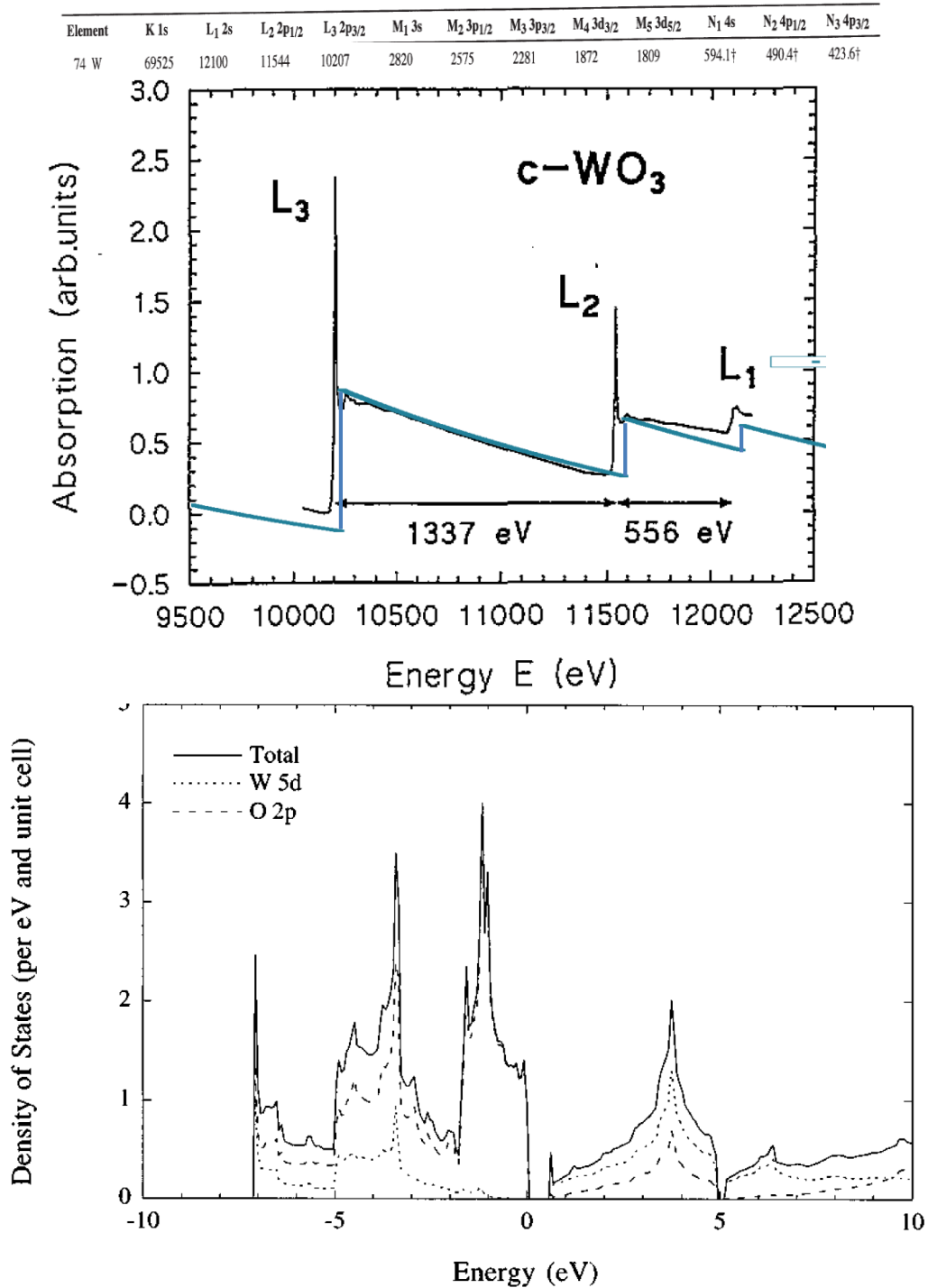


Figure 8

[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 $K\alpha_1$ 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 $3d^9$ 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?

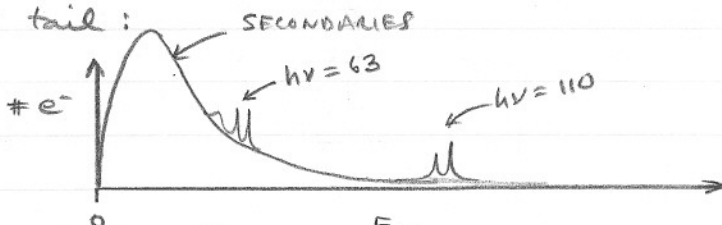
--END OF EXAM--

**Physics 243A--Surface Physics of Materials:
Spectroscopy
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Suggested Answers**

[1]

- (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 e^- peaks are beginning to ride up on secondary e^- tail:

K.E. ranges are:
 $h\nu = 110 \text{ eV} : \sim 62 - 76 \text{ eV}$
 $h\nu = 63 \text{ eV} : \sim 15 - 29 \text{ eV}$



- 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 $W 4f_{5/2}$, $4f_{7/2}$, as seen from nos. in the photoelectric cross section plots on following page:

Cross section σ_{5p}/σ_{4f} @ $h\nu =$

From Yeh + Lindau tables:	40.8 eV - 0.8920	← [NOTE ABOUT DROP SOMEWHERE HERE]
	80.0 eV - 0.0722	
	120.0 eV - 0.0512	

EXTRA COMMENTS:

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

$$\sigma_{5p_{3/2}} = \left(\frac{4}{4+2}\right) \times \sigma_{5p} = \frac{2}{3} \sigma_{5p}, \quad \sigma_{5p_{1/2}} = \left(\frac{2}{4+2}\right) \sigma_{5p} = \frac{1}{3} \sigma_{5p}$$

$$\sigma_{4f_{7/2}} = \left(\frac{8}{14}\right) \times \sigma_{4f} = 0.571 \sigma_{4f}, \quad \sigma_{4f_{5/2}} = \left(\frac{6}{14}\right) \sigma_{4f} = 0.429 \sigma_{4f}$$

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

The Yeh/Lindau tables show $E_b^V(W 4f) = -E_{4f} = 53.9 \text{ eV}$ compared to $E_b^V(W 4f_{5/2, 7/2})$ from experiment of $\sim 32.5 \text{ eV} + \phi_s^V(W) = 32.5 + 4.5 = 37.0 \text{ eV}$. The difference of 16.9 eV must be due primarily to relaxation effects. $-E_{4f}$ has no intraatomic relaxation in it. Also, in W metal, there will be extraatomic relaxation that will further lower the observed E_b^V . So both types of relaxation must add up to $\sim 16.9 \text{ eV}$.

Name: _____

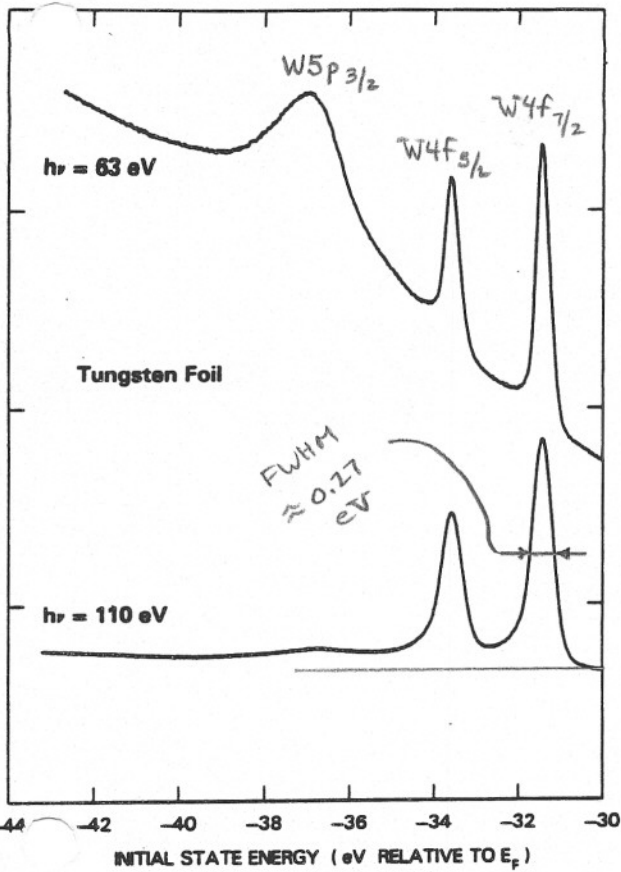


Figure 1

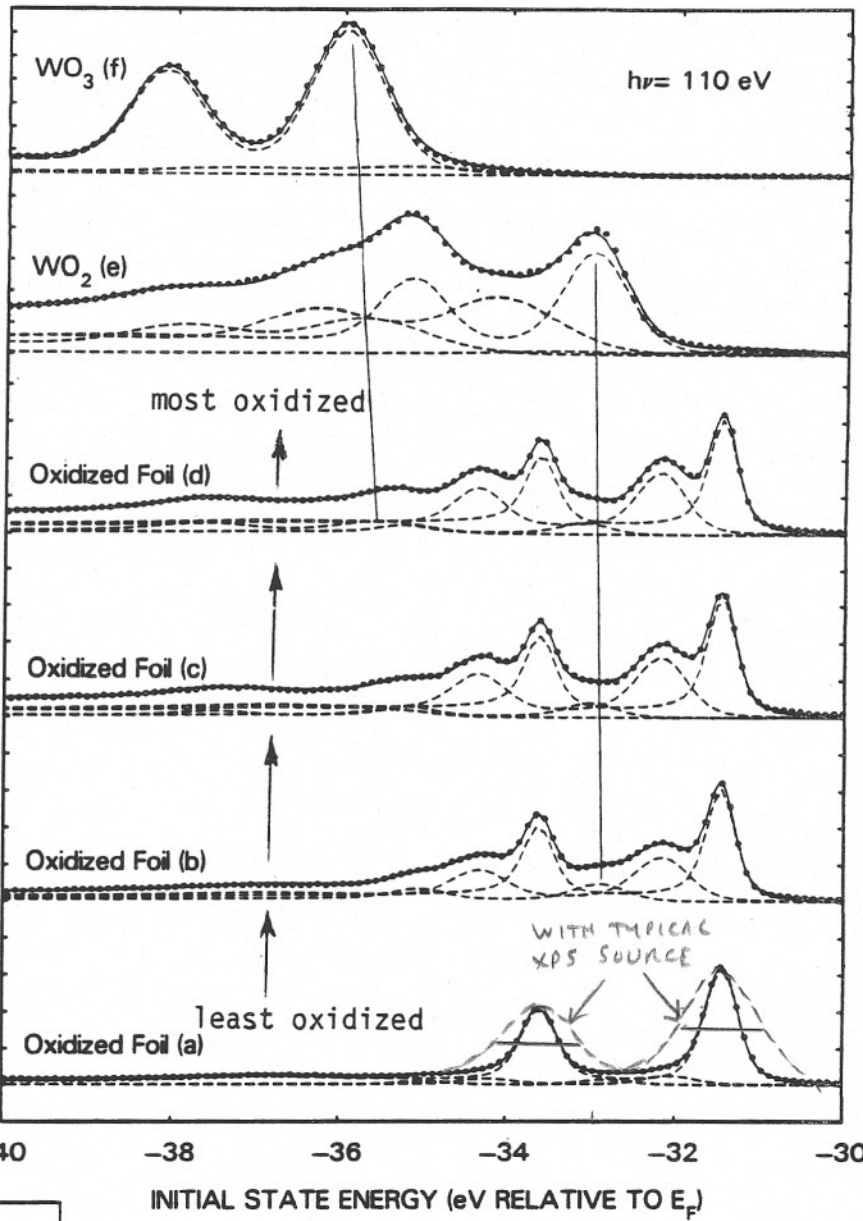
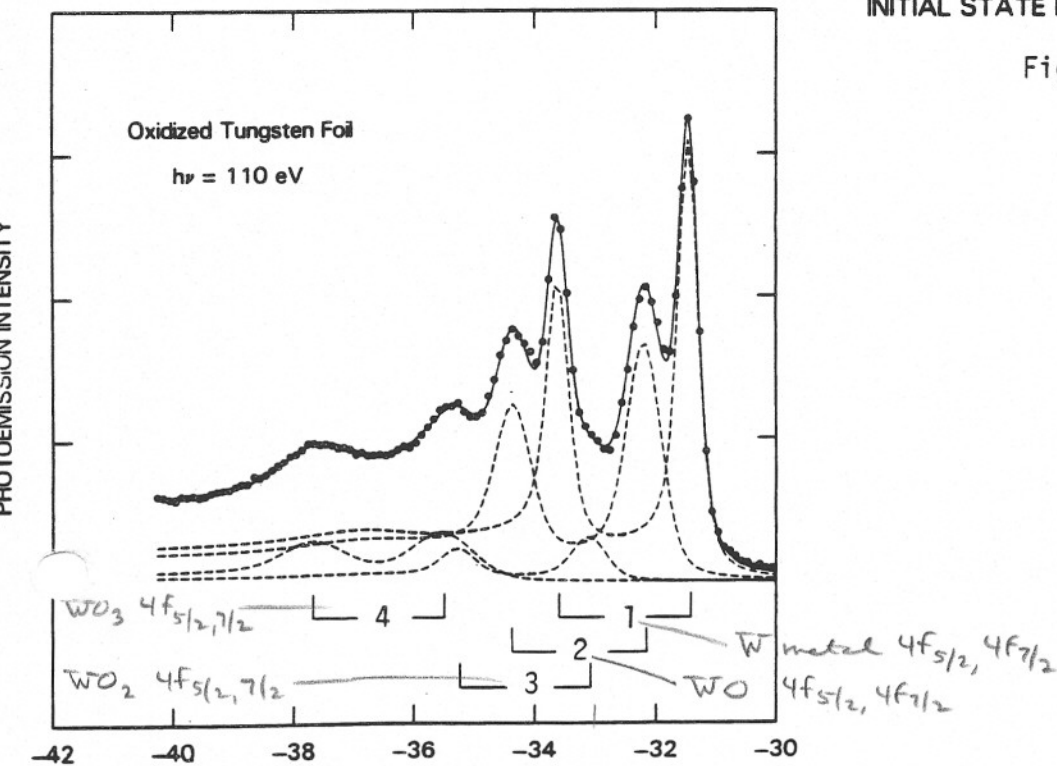


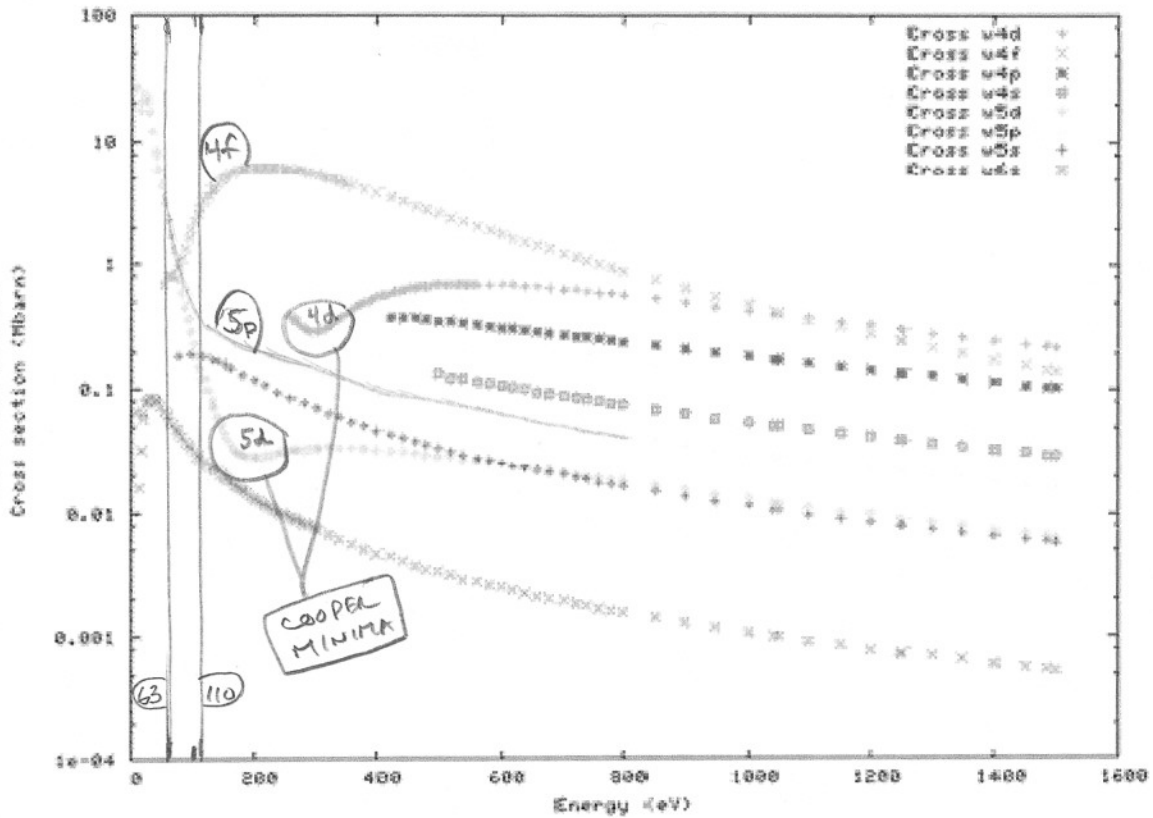
Figure 2



PHOTOEMISSION INTENSITY

-42 -40 -38 -36 -34 -32 -30

W cross sections



W asymmetry parameters

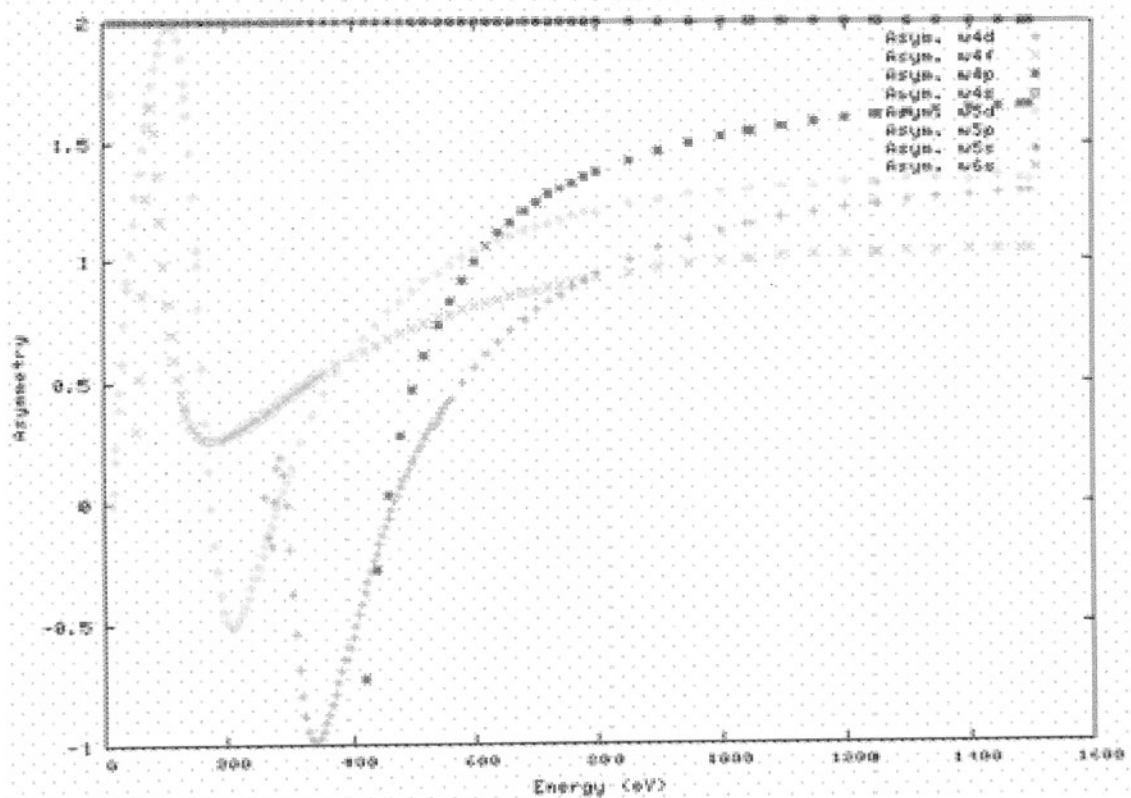


FIGURE 4

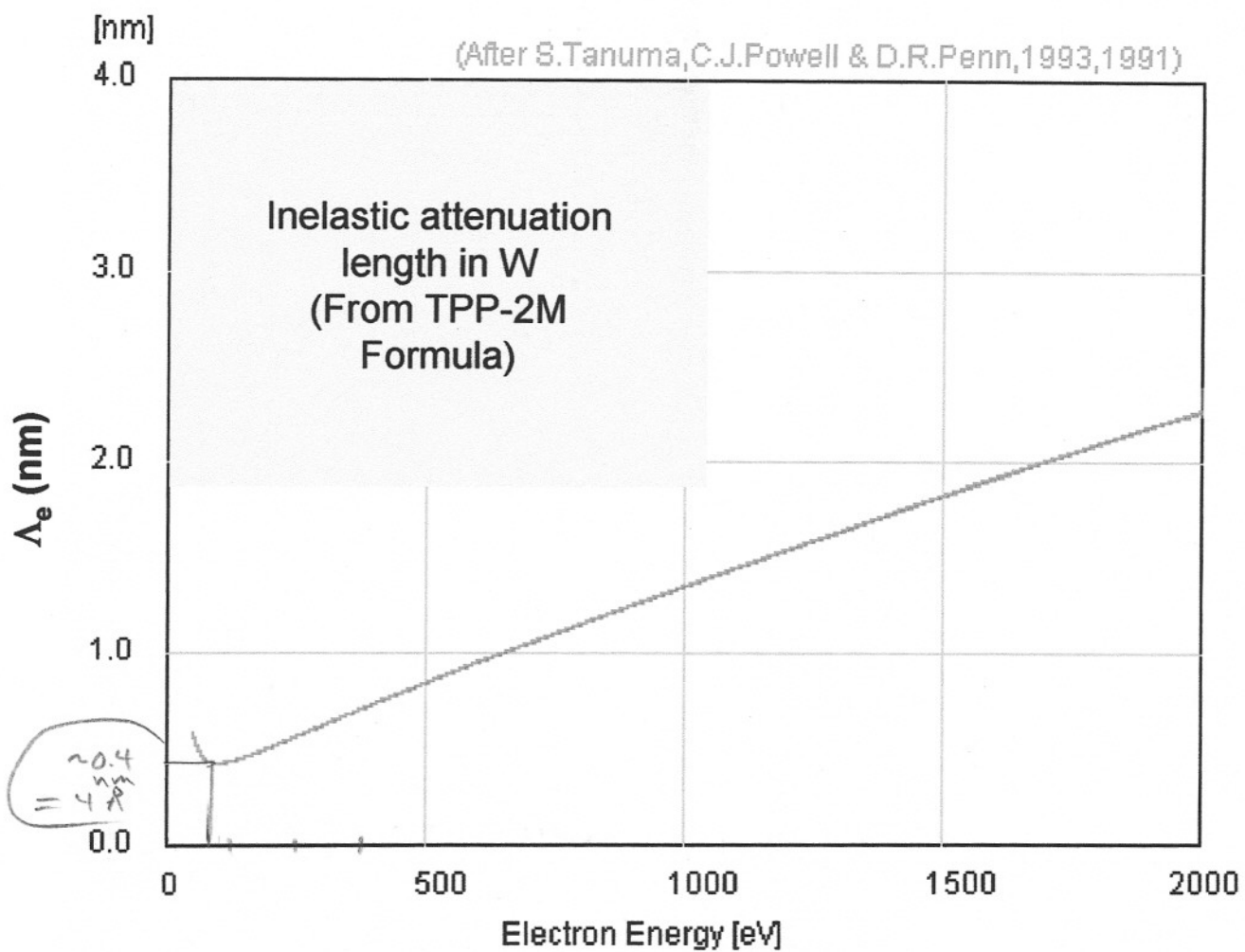


FIGURE 5

[1] (cont'd)

(d) See Fig. 3 on prior page: W, WO, WO_2, WO_3 . OF W

0	+2	+4	+6	= "OXIDATION STATE"
"	"	"	"	
1	2	3	4	

[The rather broad WO_2 spectrum of Fig. 2(e) suggests it may be changing state through further oxidation, but it nonetheless provides a useful doublet reference - 33 eV for the +4 state.]

(e) For an assumed non-attenuating overlayer the relevant equation for photoelectron intensity ratios is (Eq. (120b) in "Basic Concepts of XPS"):

$$\frac{N(\text{states 2+3})}{N(\text{state 1})} = \frac{\Omega_0 A_0 D_0 (d\sigma_{2+3}/d\Omega) d}{\Omega_0 A_0 D_0 (d\sigma_{1}/d\Omega) \Lambda_e \sin\theta} \left[\begin{array}{l} \text{FRACTIONAL MONOLAYER} \\ \text{COVERAGE} \\ \text{III} \\ \text{F.M.C.} = \frac{S'}{S} \end{array} \right]$$

Exact cancellation since peak kinetic energies are so close.

Rearranging

$$\text{F.M.C.} = \frac{N(2+3)}{N(1)} \cdot \frac{\Lambda_e \sin\theta}{d} \quad (1)$$

We desire coverage in oxygen atomic concentration, so note that state 3 = WO_2 has 2 O atoms/W atom.
 $\therefore N(2+3)/N(1) = [0.098 + 2(0.060)] / [1.00 - 0.098 - 0.060]$
 $= 0.218 / 0.842 = 0.259$.

At $E_{kin} = h\nu - E_b^F - \phi_s = 110 \text{ eV} - 33 \text{ eV} - 4.5 \text{ eV} = 72.5 \text{ eV}$,
 Λ_e from tabulations/graphs is $\approx 4-5 \text{ \AA}$, so we have
 Finally

$$\left[\begin{array}{l} \text{F.M.C.} \\ \text{of O atoms} \end{array} \right] = 0.259 \cdot \frac{[4-5 \text{ \AA}] \sin 45^\circ}{1.58 \text{ \AA}} = \boxed{0.46 - 0.58 \text{ MONOLAYERS}}$$

[At this coverage significantly less than 1.0 monolayer, our assumption of non-attenuation is quite reasonable.]

See curves

[1] (cont'd)

(f) Yes, for $W_{5d} @ \sim 190 \text{ eV}$ and for $W_{4d} @ \sim 280 \text{ eV}$

(g) The Coulomb integral involved would be:

$$J_{4f,5d} = \int \psi_{4f}^*(1) \psi_{5d}^*(2) \frac{e^2}{r_{12}} \psi_{4f}(1) \psi_{5d}(2) d\tau_1 d\tau_2,$$

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

(h) See next page

(i) INPUT. = $10.4 \text{ eV} + 4.5 \text{ eV} = \underline{\underline{14.9 \text{ eV}}}$
 ↑
 From BAND STRUCT.

SEE NEXT PAGE

[1] (j) See text on next page

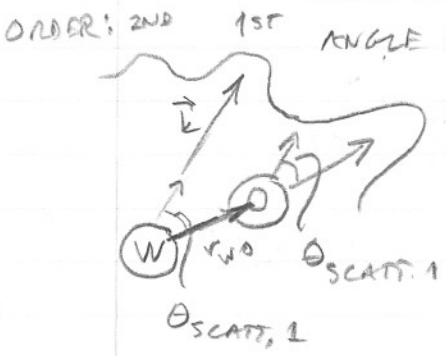
[2]

(a) $W(110) (1 \times 1) - 0 \%$ 1 ML COVERAGE

(b) 1, 2, 3 ARE FORWARD SCATTERING PEAKS FROM THE NEAREST-NEIGHBOR O ATOMS, AS INDICATED ON PRIOR PAGE

4, 5, 6 ARE FORWARD SCATTERING PEAKS FROM THE NEXT-NEAREST-NEIGHBOR O ATOMS, AGAIN AS INDICATED ON **FIGURE 7 on a following page**

(c) SEE **FIGURE 7**, FOR ATOM 2, THE 1ST ORDER DIFFRACTION RING CORRESPONDS TO A SCATTERING ANGLE $\theta_{SCATT,1}$, WHICH CAN BE SUBSTITUTED INTO:



FWD. SCATT.

DIFF. PATTERN = $\chi(k)$

$\propto \cos [k r_{WO} (1 - \cos \theta_{SCATT}) + \psi(\theta_{SCATT})]$

\therefore 1ST ORDER MAXIMUM FOR

$$k r_{WO} (1 - \cos \theta_{SCATT}) = 2\pi$$

WITH

$$k = \frac{2\pi}{\lambda_e} = \frac{2\pi}{\left(\frac{120.4}{1450}\right)^{1/2}} = 0.288 \text{ \AA}^{-1} = 21.8 \text{ \AA}^{-1}$$

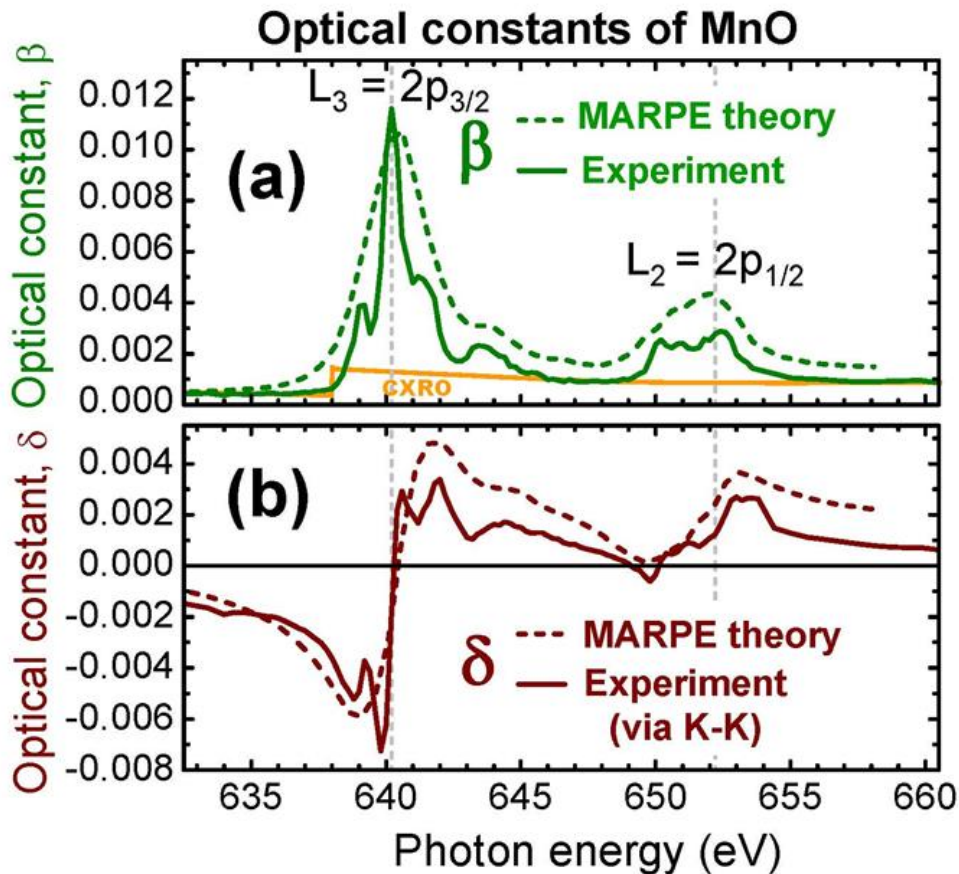
SO, IF WE KNOW θ_{SCATT} , WE CAN CALCULATE r_{WO}

**[1] (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.]**

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.

[2] (e) These are just differences of binding energies in first approximation, so $B.E.(W 2p_{1/2}) - B.E.(W 2p_{3/2}) = 11544 - 10207 = 1337$, and $B.E.(W 2s) - B.E.(W 2p_{1/2}) = 12100 - 11544 = 556$, exactly as found in the experiment

TUNGSTEN BAND STRUCTURE

5

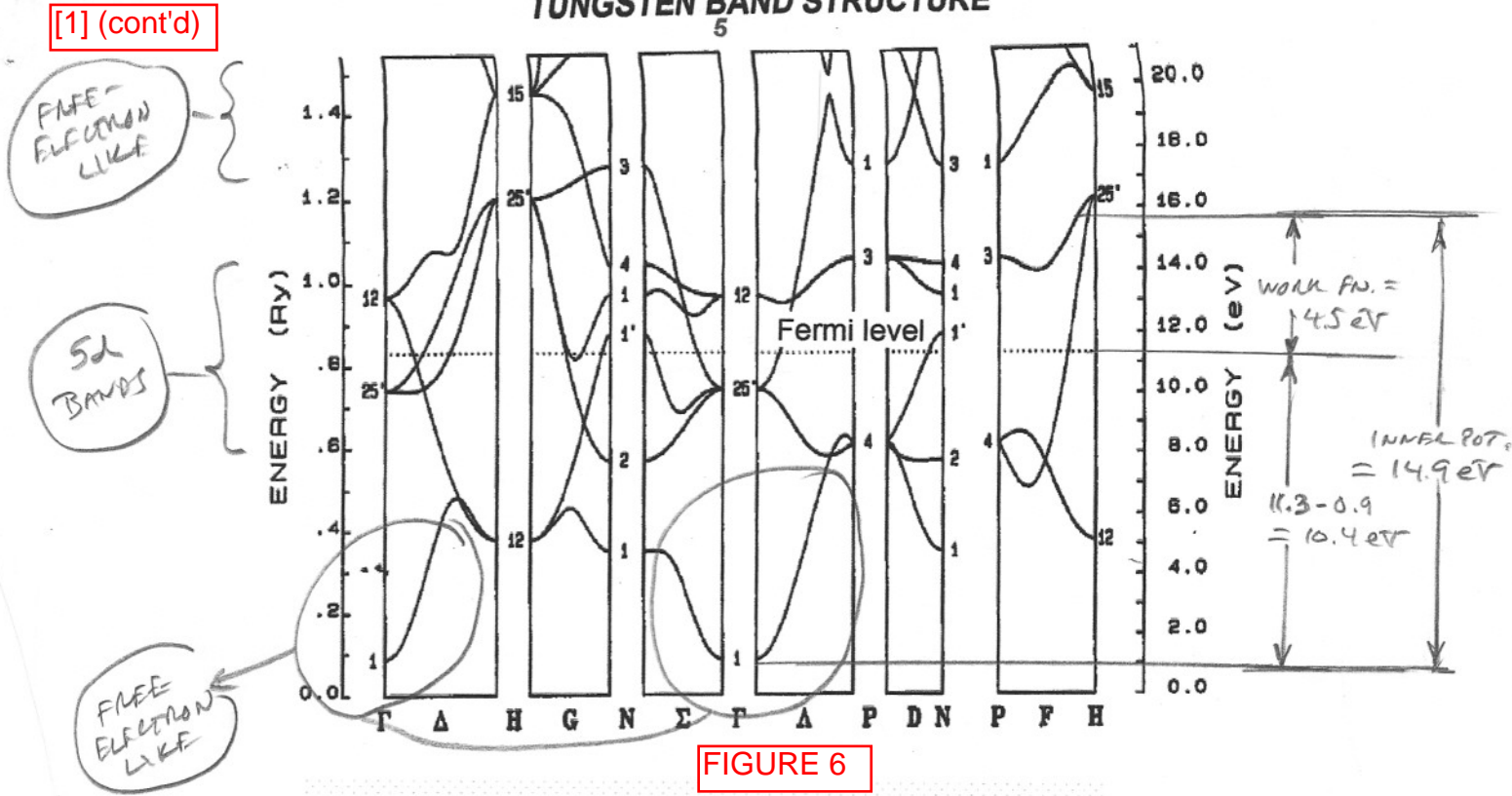


FIGURE 6

[2] (cont'd) CALCULATED W 4f PHOTOELECTRON DIFFRACTION PATTERN

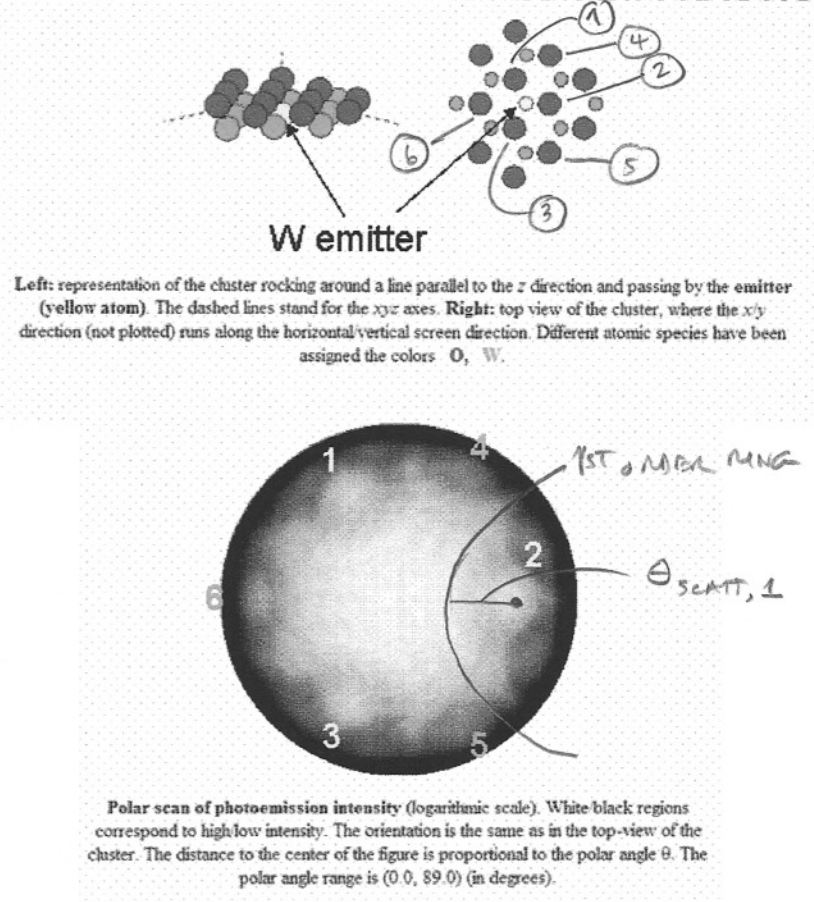
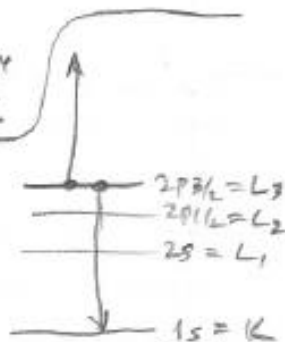


FIGURE 7

[3] (a) MINIMUM E IS Cu's BINDING ENERGY
 $= 8979 \text{ eV}$

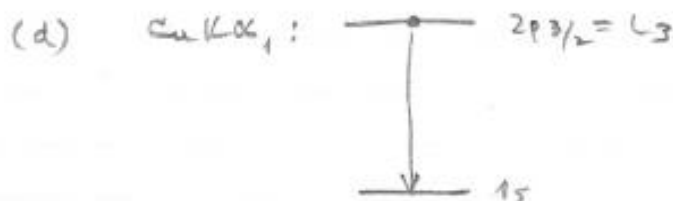
(b) MOST ENERGETIC IS Cu $K L_3 L_3$:



$$E_{\text{min}}(\text{Cu } K L_3 L_3) = E_b(\text{Cu } 1s) - E_b(\text{Cu } 2p_{3/2}) - E_b(\text{Cu } 2p_{3/2})$$

$$= 8979 - 932.7 - 1021.8 = 7024.5 \text{ eV}$$

(c) 2 HOLES IN $\text{Cu } 2p_{3/2} \rightarrow "Z+2" \text{ ATOM OR } \underline{\text{Ga}}$



$$E(\text{Cu } K \alpha_1) = E_b(\text{Cu } 1s) - E_b(\text{Cu } 2p_{3/2}) = 8046.3 \text{ eV}$$

COMPARED TO TABLE VALUE OF $\underline{8047.8 \text{ eV}}$ } VERY CLOSE!

[] (e) 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:

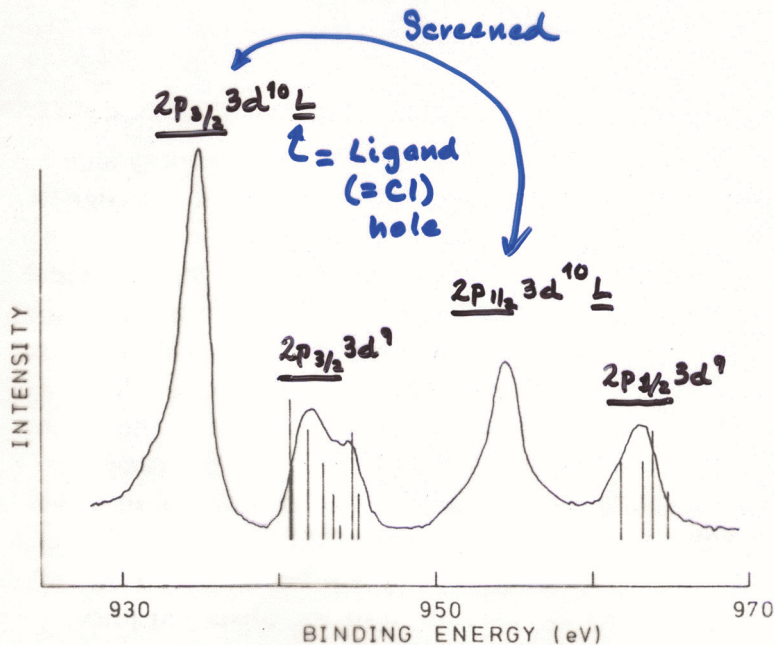


FIG. 2. The Cu 2p spectrum of CuCl₂ together with the expected multiplet splittings, represented by bars, for the $2p3d^9$ level as calculated and discussed in the text.

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ET AL., PHYS.
REV. B 23, 4369
(1981)

[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:

Fano effect and Spin polarization in core photoelectron spectra—expt.

