

Physics 243A - Surface Physics of Materials

Final Examination

December 6, 2016

(100 points total, open laptop and/or books, notes, and class downloads at the 2016 website)

Name: \_\_\_\_\_ **SUGGESTED ANSWERS** \_\_\_\_\_

Student number: \_\_\_\_\_

**Affirmation: I will not make use of any hardcopy or online material from prior versions of this course that is not posted at the 2016 course website.**

Signature: \_\_\_\_\_

[1] (30 Points)

The following are a series of unrelated short questions, to be answered with a sentence or two and/or a sketch or equation.

(a) (5 points) At equilibrium, write down the equation that describes a first-order Langmuir adsorption isotherm, defining all relevant symbols.

As derived in lecture, and discussed in Zangwill, this is:

(9.4) assumes the form known as *Langmuir's isotherm*:

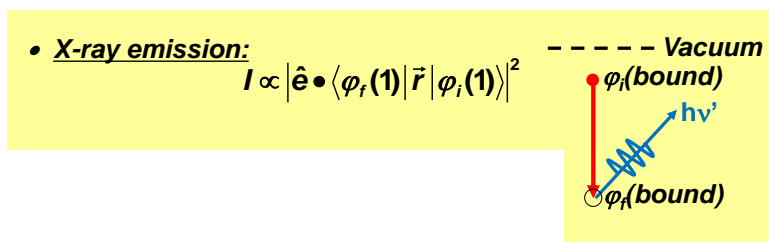
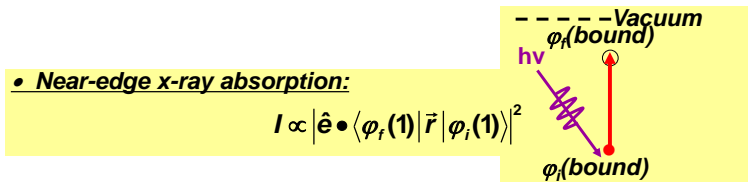
$$\Gamma = \Gamma_0 \frac{P}{P + P_{1/2}(T)}, \quad (9.6)$$

where  $\Gamma_0$  corresponds to saturation coverage ( $P \rightarrow \infty$ ) and  $P_{1/2}(T)$  is the pressure that yields half coverage,

Any similar rendition of this, or the basic equating of forward and backward rates that was discussed in lecture, is full credit here.

(b) (5 points) Which two of the several x-ray techniques we have discussed are the most appropriate for studying unoccupied bound electronic structure? Illustrate your answer with simple electronic energy level diagrams.

Anything equivalent to the things below, but also RIXS and shake-up, shake-off were also counted for full credit. XPS, UPS do not measure unoccupied bound states, and several people fell into that trap.



(c) (10 points) Suppose that a photoelectron is ejected from the very deep W 1s level. Assume that we can now, in the presence of this hole, measure the binding energy of the W 4f<sub>7/2</sub> level. Use the equivalent-core model and your binding energy tables to predict the change in binding energy caused by the hole.

1s hole is deep inside the W atom, so a perfect case for the equivalent core approximation and

$$Z = 74 \text{ for W} \rightarrow Z+1 = 75 \text{ for Re}$$

$$E_b(4f_{7/2}) = 31.4 \text{ eV} \quad 40.5 \text{ eV}$$

And the binding energy shift is  $\Delta E_b(4f_{7/2}) = 40.5 - 31.4 = 9.1 \text{ eV}$

As a second part of your answer, how would you calculate this change in binding energy from first principles via coulomb and exchange integrals, and which precise integrals would be involved? Would coulomb or exchange be expected to be more important?

Since W 1s and W 4f<sub>7/2</sub> really don't overlap at all, the exchange integral  $K_{1s,4f} \approx 0$ , and

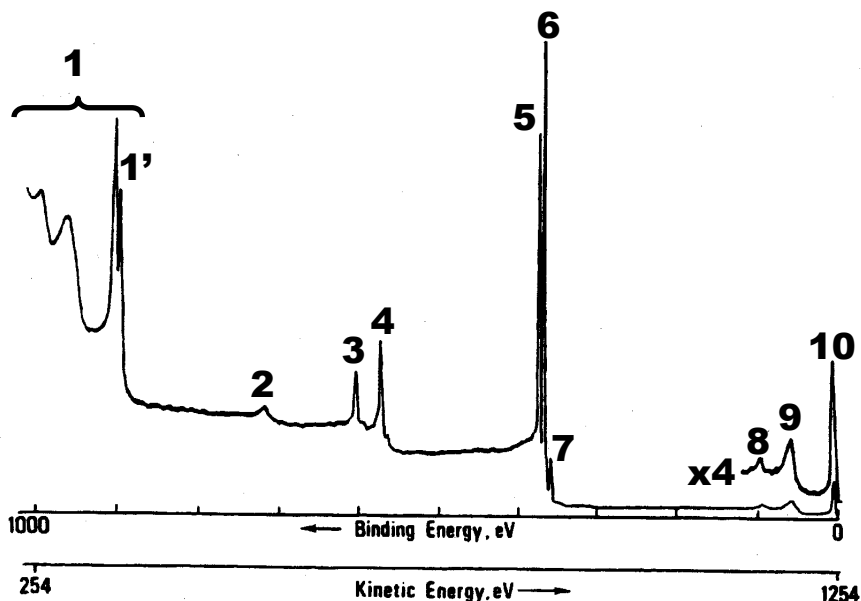
$$\Delta E_b(4f_{7/2}) \approx \iint \phi_{1s}^*(\vec{r}_1) \phi_{4f}^*(\vec{r}_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \phi_{1s}(\vec{r}_1) \phi_{4f}(\vec{r}_2) dV_1 dV_2$$

(d) (10 points) By considering the electronic configurations of the ionic states, which of the following Cu compounds would be expected to show strong final-state charge-transfer screening satellites in Cu 2p emission and why? CuS, Cu<sub>2</sub>S, CuBr, CuBr<sub>2</sub>.

The Cu atomic electronic configuration is 3d<sup>10</sup>4s<sup>1</sup>. Thus in Cu<sup>+2</sup>S<sup>-2</sup> and Cu<sup>+2</sup>Br<sup>-2</sup> the Cu configuration is Cu<sup>+2</sup> 3d<sup>9</sup> and strong charge-transfer screening of the Cu 2p hole is possible. For Cu<sup>+1</sup>S<sup>-2</sup> and Cu<sup>+1</sup>Br<sup>-1</sup> the Cu configuration is Cu<sup>+1</sup> 3d<sup>10</sup> and charge transfer into the d shell is not possible.

[2] (50 Points)

A specimen of a pure 4d metal has incident on it non-monochromatized Mg x-rays, with the angle between x-ray incidence and electron exit being the so-called "magic angle" of 54.73° at which P<sub>2</sub>(cosθ) = 0. The resulting spectrum is shown below. The group 1 is not found to change in kinetic energy if Al x-rays are used for excitation.



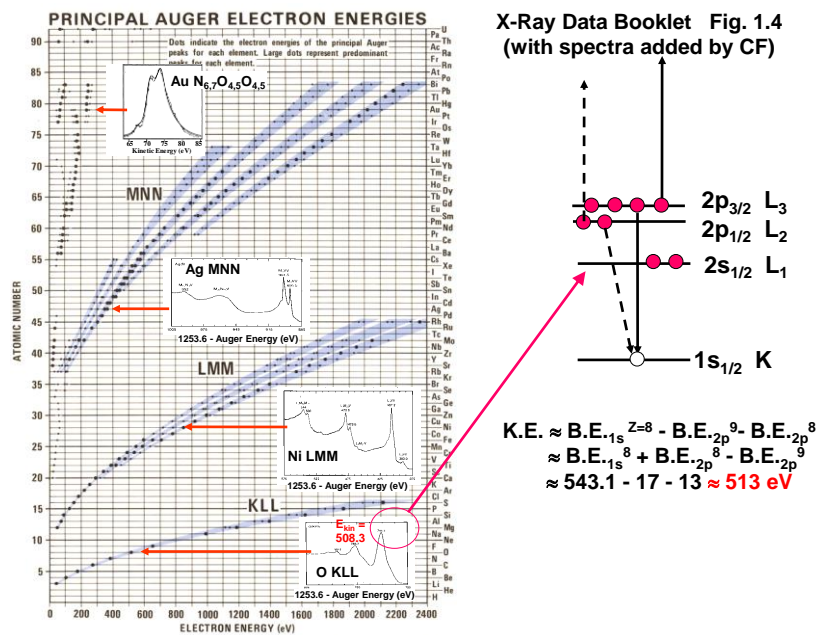
(a) [10 points] Identify the origins of all of the peaks and groups of peaks seen here, thus also identifying the element and its ground-state atomic electron configuration.

(b) [5 points] Do you expect to see multiplet splittings in any of the peaks shown here? Why or why not?

Best answer that 4d shell is filled, so no multiplets, but OK if said that unpaired 5s can lead to them. They would be very small in that case, due to low overlap of core levels and 5s.

(c) [5 points] For the doublet 1', use a tabulated energy plot to identify them and calculate the two energies expected from binding energy tables, finally comparing your answer to experiment.

You can just use this plot (1.4 in X-Ray Data Booklet or Slide 97 from Slide Set 2) to identify them as the highest energy MVV = M<sub>1</sub>V<sub>1</sub>V<sub>2</sub> transitions



See later pages for numbers.

(d) [5 points] Do you see any evidence of the usual types of surface contamination? Explain why or why not.

No C 1s or O 1s visible at ca. 284 eV and 532 eV, so no evidence of usual surface contaminants.

(e) [10 points] If the sample had one monolayer of O-containing contaminant on it, indicate via an equation what the ratio of the O 1s peak intensity to the intensity of peak 4 would be, being as quantitative as you can, and indicating how you have estimated any nos. needed. Two simplifications you can make here are due to the magic angle (cf. Eq. 89 in Basic Concepts) and the fact that O 1s and peak 4 are close enough together in energy for the analyzer factors to be essentially identical.

See later pages.

(f) [5 points] If a detector of fluorescent x-ray emission that is sensitive from high energies and down to an energy of 100 eV were situated outside of the sample, where would transitions expect to be seen, and what would be their designations in standard x-ray notation? You may make use of tabulated x-ray energies in doing this part.

See later pages, but the point here is that Mg  $K\alpha$  at 1.25 keV cannot excite anything above that energy, and only one set of x-rays will be seen in the range 1.25 keV to 100 eV. See numbers on later pages.

(g) [10 points] Finally, the band structure of this metal is shown below. Answer the following questions based on this and other data at your disposal:

(i) Is there evidence of bands of free-electron character? If so indicate where they are on the band diagram above.

See later pages.

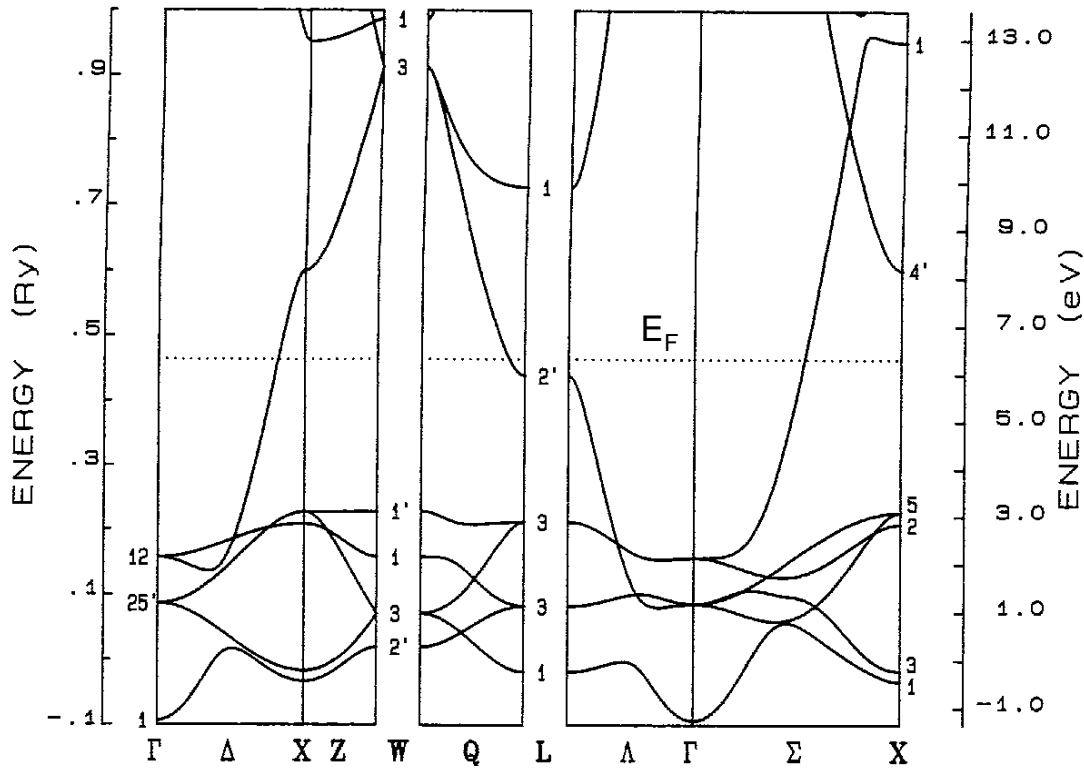
(ii) What are any other types of bands due to? **4d bands**

(iii) If the work function of this material is 4.7 eV, determine the inner potential of this material in eV.

See later pages.

(iv) If an electron is excited from the band at  $X_5$  with a 100 eV photon, what will be its kinetic energy just outside the surface and before entering the spectrometer?

See later pages





**[3] (20 Points)**

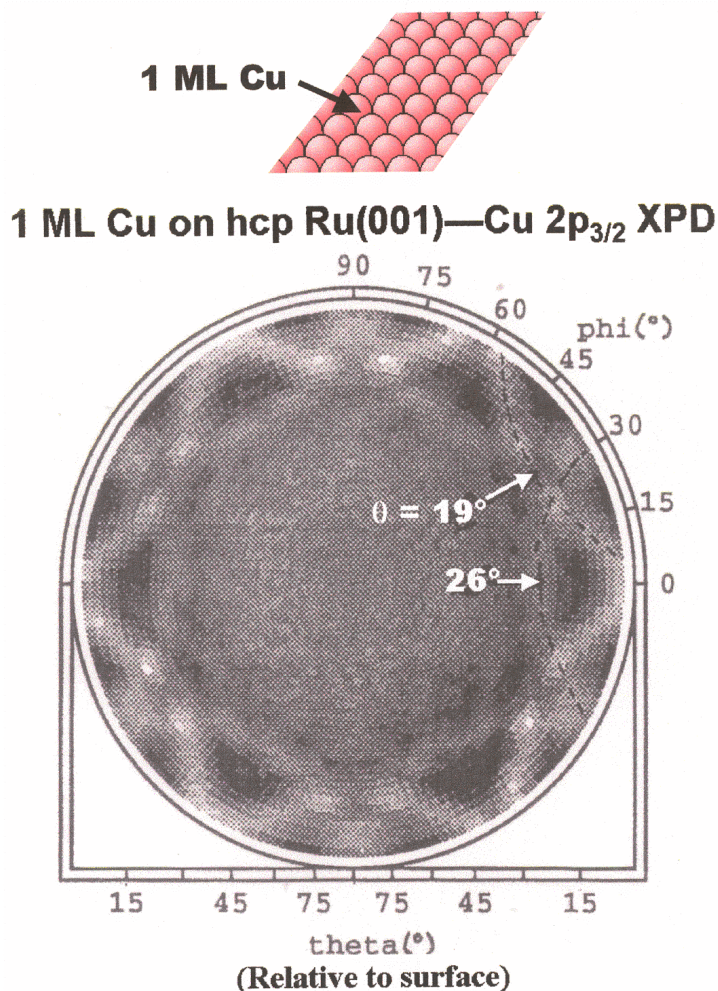
The figure below shows an actual Cu 2p x-ray photoelectron diffraction pattern from a hexagonal-close-packed single monolayer of Cu on a Ru substrate.  $AlK\alpha_{1,2}$  radiation was used for excitation, and the theta and phi angles of emission relative to the substrate are indicated on the figure. Theta is here defined relative to the surface.

- (a) [5 points] In analyzing this data, it has been assumed that the Ru contributes very little to the diffraction pattern. Explain why this is a reasonable assumption in terms of the nature of the electron-atom scattering factor involved at this energy, using a sketch as needed.

See later pages

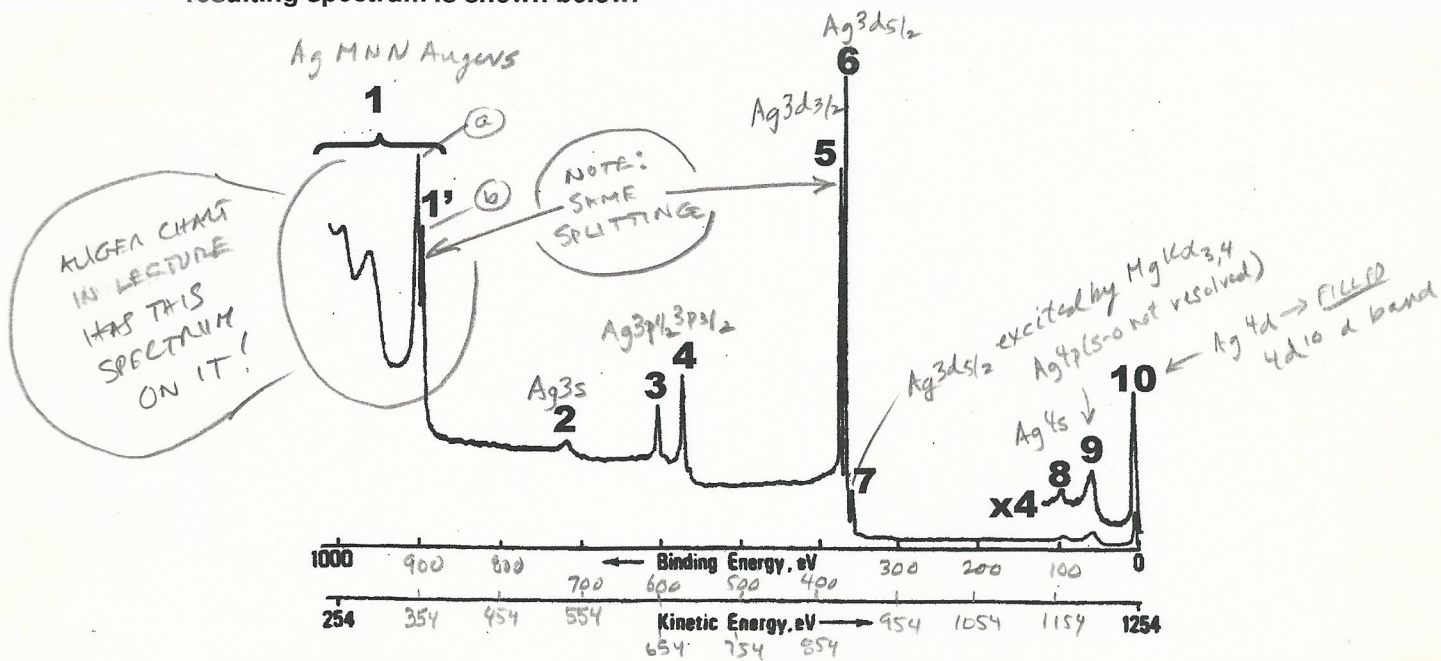
- (b) [15 points] There are two main sets of rings in this diffraction pattern. Associate these with definite types of neighbors in the Cu monolayer, and then use the theta angles at which they appear along the bond direction (as indicated on the drawing) to estimate the distance of these neighbors from a typical Cu emitter. You may assume that the scattering phase shift is zero, and neglect any surface refraction during electron emission due to the inner potential.

See later pages



**[2] (50 Points)**

A specimen of a pure metal has incident on it non-monochromatized Mg x-rays, with the angle between x-ray incidence and electron exit being the so-called "magic angle". The resulting spectrum is shown below.

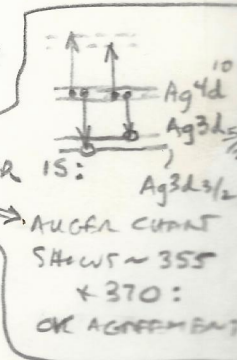


- (a) Identify the origins of all of the peaks and groups of peaks seen here, thus also identifying the element. *SEE ABOVE*
- (b) Do you expect to see multiplet splittings in any of the peaks shown here? Why or why not? *NO. 3d<sup>10</sup> IS FILLED VALENCE SHELL.*
- (c) For the doublet 1', calculate the two energies expected from binding energy tables, and compare your answer to experiment. *MOST ENERGETIC MNN AUGER*  

$$E_{kin}^{(1)} = [374 - \frac{1}{2}[5+11]] \approx 365.5$$

$$E_{kin}^{(2)} = [368 - \frac{1}{2}[5+11]] \approx 361.5$$
- (d) Do you see any evidence of the usual types of surface contamination? Explain why or why not. *NO, SINCE NO C 1s OR O 1s.*
- (e) If the sample had one monolayer of O-containing contaminant on it, indicate via an equation what the ratio of the O 1s peak intensity to the intensity of peak 4 would be, being as quantitative as you can, and indicating how you have estimated any nos. needed. A simplification you can make here is that O 1s and peak 4 are close enough together in energy for the analyzer factors to be essentially identical. *SEE NEXT SHEET.*
- (f) Finally, if a detector of fluorescent x-ray emission sensitive down to an energy of 100 eV were situated outside of the sample, where would transitions expect to be seen, and what would be their designations in standard x-ray notation? *ONLY THE Mg K<sub>α</sub> X-RAYS OF THOSE LISTED WOULD BE SEEN, AS N SERIES TOO LOW IN ENERGY < 100 eV*

5 = AVE. B.E. FOR Ag 4d BANDS  
 11 = AVE. B.E. FOR CALCD CORE LEVELS  
 ⇒ 2+1



SEE FIG. 1-1 IN X-RAY HANDBOOK



(e) TREAT AS NON-ATTENUATING THIN OVERLAY AND USE  
EQN. (120b) FROM "BASCC CONCEPTS --"

$$\frac{N_{O1s}}{N_{Ag3p3/2}} = \left[ \frac{S'_0}{S_{Ag}} \right] \cdot \frac{D_o(E_{O1s}) \rho_o(E_{O1s}) A_o(E_{O1s}) \left( \frac{d\sigma_{O1s}}{d\Omega} \right) d}{D_o(E_{Ag3p}) \rho_o(E_{Ag3p}) A_o(E_{Ag3p}) \left( \frac{d\sigma_{Ag3p}}{d\Omega} \right) \Lambda_e(E_{Ag3p}) \sin \theta}$$

COVERAGE  
IN MONOLAYERS

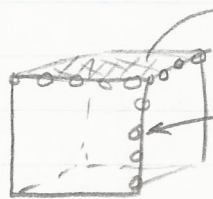
SINCE  $E_{O1s} \approx E_{Ag3p}$ , CANCEL ANALYTICAL FACTORS

SINCE ANGLE "X" = "MAGIC ANGLE",  $\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi}$ , SO CAN LOOK UP

IN YEARY LINDAU TABLES:  $\sigma_{O1s} @ 1253.6 \text{ eV} = 0.063 \text{ Mb}/4\pi$  ← ALLOW FOR S-O SPLITTING  
 $\sigma_{Ag3p3/2} @ 1253.6 \text{ eV} = 0.223 \times \frac{4}{6} \text{ Mb}$   
 $= 0.149 \text{ Mb}/4\pi$

$\Lambda_e(E_{Ag3p3/2}) = \Lambda_e(675 \text{ eV}) \approx 10^{-11} \text{ \AA}$  FROM "UNIVERSAL CURVE"  
 $= 11.1 \text{ \AA}$  ∴ TPP-2M (SEE ATTACHED)

d = AVERAGE SPACING OF PLANES @ Ag SURFACE, CAN BE ESTIMATED  
 SEVERAL WAYS, E.G. FROM  $\rho = \frac{(\text{NO. ATOMS})}{\text{CM}^3} = 5.89 \times 10^{22} \text{ cm}^{-3} = 58.9 \times 10^{21} \text{ \AA}^{-3}$



$\rho^{2/3} = \text{AVER. SURFACE DENSITY}$   
 $= 1.51 \times 10^{15} \text{ cm}^{-2}$

$\rho^{1/3} = \text{AVERAGE LINEAR DENSITY}$   
 $= 3.88 \times 10^7 \text{ cm}^{-1}$

↓  
 AVERAGE PLANAR SPACING = d  
 $\approx \frac{1}{\rho^{1/3}} = 0.258 \times 10^{-7} \text{ cm}$

$= 2.58 \times 10^{-8} \text{ cm}$

$= 2.58 \text{ \AA}$

[ NOT FAR FROM NEAREST-NEIGHBOR  
 DISTANCE OF 2.89 \AA ]

SO, FINALLY, WITH REARRANGEMENT

$$\left[ \frac{S'_0}{S_{Ag}} \right] = \left[ \frac{N_{O1s}}{N_{Ag3p3/2}} \right] \cdot \left( \frac{\sigma_{Ag3p3/2}}{\sigma_{O1s}} \right) \frac{\Lambda_e(E_{Ag3p3/2}) \sin \theta}{d}$$

$$= \left[ \frac{N_{O1s}}{N_{Ag3p3/2}} \right] \cdot \left( \frac{0.149}{0.063} \right) \cdot \frac{11.1 \sin \theta}{2.58} = \left[ \frac{N_{O1s}}{N_{Ag3p3/2}} \right] 10.2 \sin \theta$$

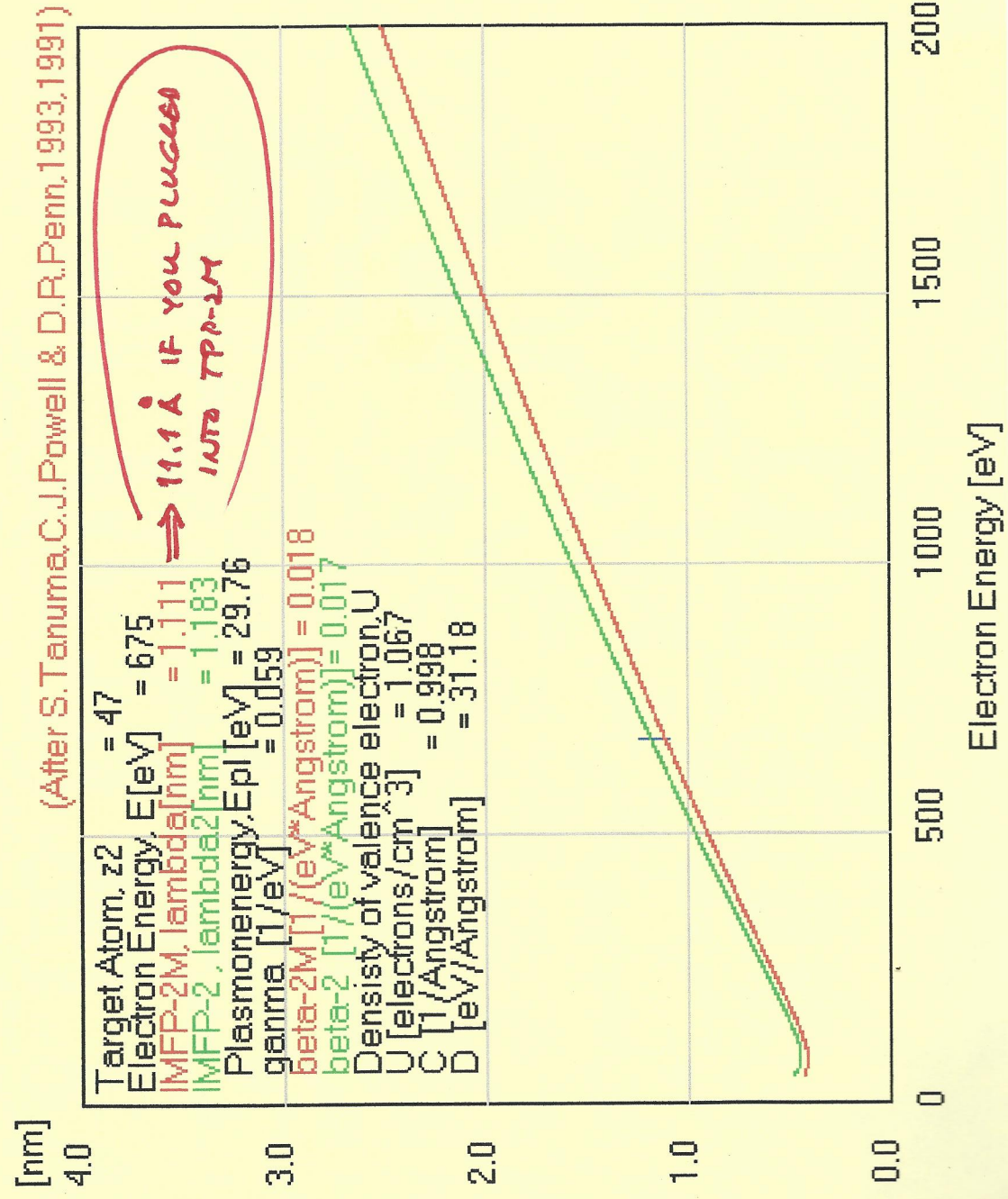
↑  
 NOT  
 KNOWN

DON'T NEED ALL THE NOT. FOR FULL CREDIT.

# Inelastic mean free path for Ag

Atomic Number of Target Atom, Z2=  (1<=Z2<=92)

Cursor Energy





(f) If a detector of fluorescent x-ray emission that is sensitive from high energies and down to an energy of 100 eV were situated outside of the sample, where would transitions expect to be seen, and what would be their designations in standard x-ray notation? (SEE FIRST PAGE.)

(g) Finally, the band structure of this material is shown below. Answer the following questions based on this and other data at your disposal:

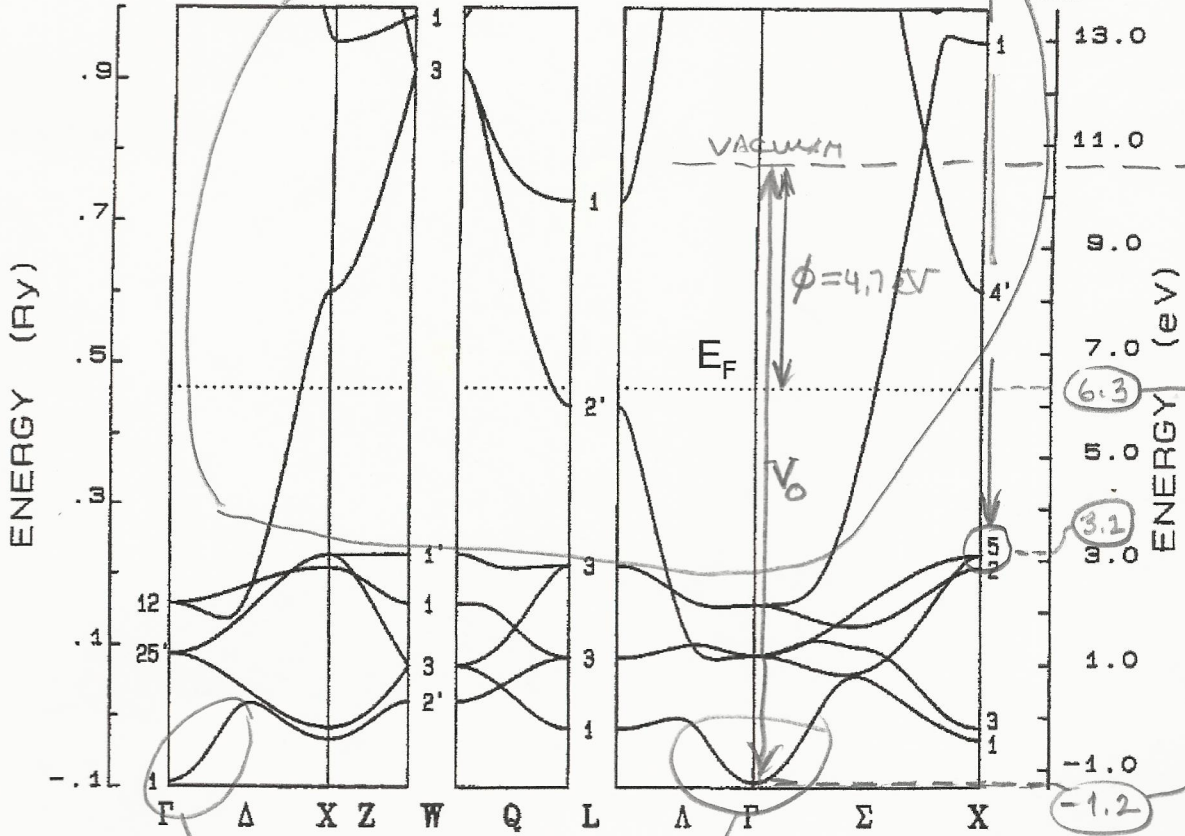
(i) Is there evidence of bands of free-electron character? If so indicate where they are? SEE BELOW.

(ii) What are any other types of bands due to? THE FILLED  $4d^{10}$  BANDS OF Ag

(iii) If the work function of this material is 4.7 eV, determine the inner potential of this material.  $4.7 + 7.5 = 12.2 \text{ eV}$  SEE BELOW

(iii) If an electron is excited from the band at  $X_5$  with a 100 eV photon, what will be its kinetic energy just outside the surface?

Ag ...  $5d^{10}4s^2$



$E_{kin}$   
 $= 100$   
 $- 4.7$   
 $- 6.3$   
 $- 3.2$   
 $= 92.2$   
 $\text{eV}$

FILLED e- LIKE

FREE e- LIKE

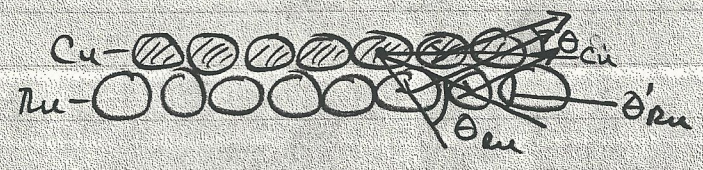
$h\nu = 100 \text{ eV}$

7.5



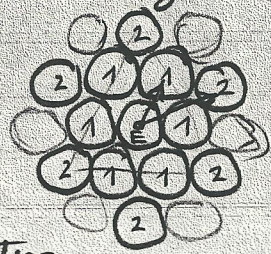
[3] (a)  $E_{kin}^{(JUST\ OUTSIDE\ MONOLAYER)} = h\nu - E_b^r$   
 $= 1486.7\text{ eV} - 938\text{ eV}$   
 $= \underline{548.7\text{ eV}}$

Electron-atom scattering at this energy is very strongly forward peaked. Thus, scattering down to Ru and back out to a detectable angle is much less intense than simple near-forward scattering in the monolayer. The sketch below illustrates this:



$\therefore \theta_{Cu}$  is the same for all Cu atoms, and  $\theta_{Cu} < \theta_{Ru} < \theta_{Ru}$ , so Ru scattering is away from forward direction and  $\therefore$  <sup>much</sup> weaker.

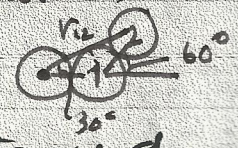
(b) Hexagonal layer looks like:



FROM TABLES FOR Cu + Ru:

$r_{11} = r_{nn} = 2.56 - 2.65 \text{ \AA}$

$r_{12} = r_{nnn} = 2(2.56) \cos 30^\circ = 4.43 \text{ \AA}$

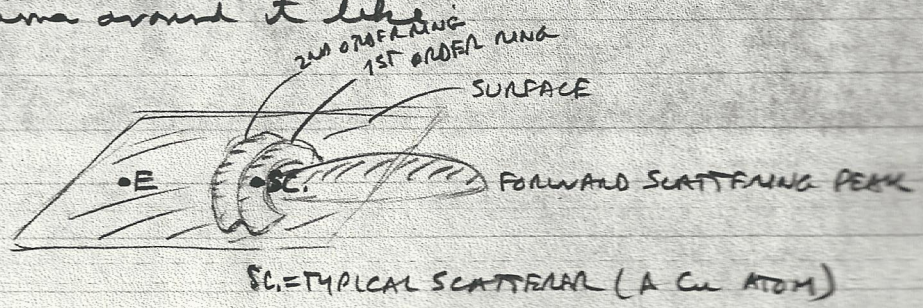


E = emitter

1 = nearest neighbors at distance  $d_1$

2 = next-nearest neighbors at distance  $d_2$

Each atom will have a set of diffraction maxima around it like:





General formula for position of rings is:

$$2\pi n = k r_{sc.} (1 - \cos \theta_{sc.}) + \psi_{sc.}(\theta_{sc.}), \quad (1)$$

so

$$r_{sc.} = \frac{2\pi n - \psi_{sc.}(\theta_{sc.})}{k(1 - \cos \theta_{sc.})} \quad (2)$$

For 1st order,  $n=1$ , and neglecting  $\psi_{sc.}$  gives:

$$\tilde{r}_{sc.} = \frac{2\pi}{k(1 - \cos \theta_{sc.})} \quad (3)$$

USE TO DERIVE IF NEEDED

Now some nos. :  $k(\text{\AA}^{-1}) = 0.512 (E_{kin}(\text{eV}))^{1/2} = \frac{2\pi}{\lambda_e(\text{\AA})} = 2\pi \left( \frac{E_{kin}(\text{eV})}{150.4} \right)^{1/2}$

$$= 0.512 (549)^{1/2}$$

$$= 12.0 \text{\AA}^{-1}$$

So, for 2 angles we have:

$$\tilde{r}_{sc.}^1 = \frac{2\pi}{12.0(1 - \cos(26^\circ))} = 5.17 \text{\AA} \Rightarrow r_1, \text{ NEAREST NEIGHBOR}$$

$$\tilde{r}_{sc.}^2 = \frac{2\pi}{12.0(1 - \cos(19^\circ))} = 9.61 \text{\AA} \Rightarrow r_2, \text{ NEXT-NEAREST NEIGHBOR}$$

THESE NOS. CAN BE COMPARED TO THE  $\sim 2.56 \text{\AA}$  AND  $\sim 4.43 \text{\AA}$  EXPECTED. CONCLUDE THAT THE PHASE SHIFT IS IMPORTANT!!! AND PERHAPS ALSO SURFACE REFRACTION DUE TO  $V_0$ .