ICTP School on Synchrotron Radiation and Applications 2008
Surface Science, Photoemission and Related Techniques
Fadley, Goldoni

<u>No. 1—Student background questions and study questions from the lectures</u>.
Continue on the back side if needed.

Name:_____Country of origin:_____

Educational level: Ph.D._____M.S._____Graduate Student_____

Field of academic study:_____

Major current research subject:
    Atomic and molecular physics_____
    Condensed matter physics_____
    Materials science_____
    Chemistry (please specify)_____
    Biological Sciences (please specify)_____
    Engineering (please specify)_____

Have you had a course in solid state physics or materials physics/chemistry previously?
    Yes: _____

Possible use you will make of synchrotron radiation in the future:

_____

_____

Brief study questions from today's lecture:
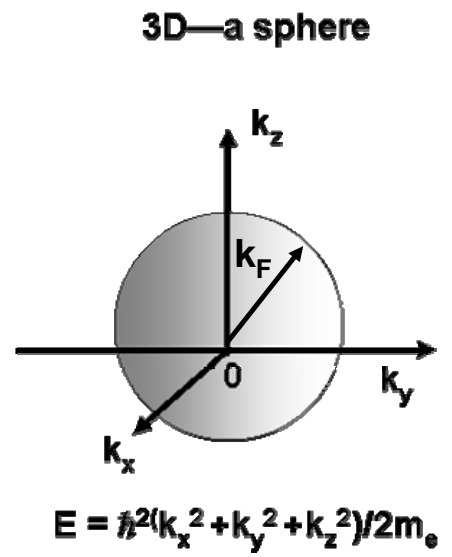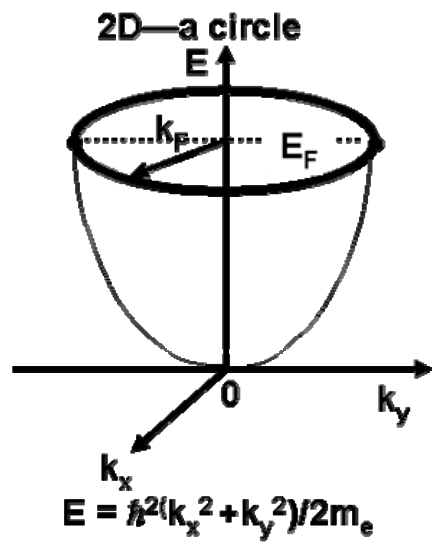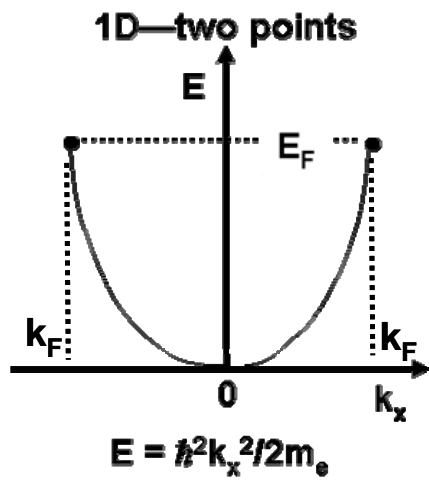

1. What is Moore's Law?
**It is an empirical law which states that the number of transistors on a single IC double about every 18 months.
Actually the rate was to double about every 24 months until the last 10 years, over which it has doubled every 12 months.**

2. What fraction of atoms are on the surface of a <u>two-nanometer</u> cube? See slide from lecture for one method of calculating this, with L = side of cube and D = atomic diameter $\cong$ 0.2 nm which gives

$$\textit{Fraction on surface} = \frac{L^3 - (L-2D)^3}{L^3} = \frac{2.0^3 - (2.0 - 2(0.2))^3}{2.0^3} = \frac{3.904}{8} = 48.8\%$$

3. Why are electrons particularly useful as surface probes? The primary reason is that electrons in the roughly 30 eV to 1500 eV range have very short inelastic attenuation lengths, in the 5-20 Å range. Therefore, any technique which uses such electrons is limited in sensing depth to the surface and near-surface region.

4. Sketch schematically the Fermi surfaces of a 1D, 2D and 3D <u>free-electron</u> gas (use back side if necessary)

1D—two points

$$E = \hbar^2 k_x^2 / 2m_e$$

2D—a circle

$$E = \hbar^2(k_x^2 + k_y^2)/2m_e$$

3D—a sphere

$$E = \hbar^2(k_x^2 + k_y^2 + k_z^2)/2m_e$$

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No. 2--Brief Study questions from the lectures. Continue on the back side if needed.

Name:_____Country of origin :_____

Useful references: X-Ray Data Booklet-- http://xdb.lbl.gov/
X-Ray Properties and X-Ray Optical Calculations-- http://www-cxro.lbl.gov/optical_constants/
General properties of the Elements and Their Compounds-- http://www.webelements.com
Photoelectric cross sections of the elements—
    http://ulisse.elettra.trieste.it/elements/WebElements.html
Calculated inelastic attenuation lengths for the elements (TPP-2M model)—
    http://www.ss.teen.setsunan.ac.jp/e-imfp2.html

1) State Koopmans' Theorem and indicate how it is related to the true binding energy for a given electronic state ?

Koopmans' Theorem states that, if we assume that the (N-1) « passive » electrons that are left behind in a photoemission process do not relax their one-electron orbitals when a given k-shell hole is formed, then the binding energy of the electron that has been ejected is equal to the negative of the Hartree-Fock eigenvalue for its orbital. That is,

$E_{b,KT}(k) = -\varepsilon_k.$

In fact, the other orbitals do relax, and so there will always be a relaxation correction δE_{relax} (taken to be a positive no.), such that the true binding energy will be given by :

$E_{b,TRUE}(k) = -\varepsilon_k - \delta E_{relax}$ **(+ other corrections due to relativity and electron correlation**

2) (a) Write down the expressions for coulomb and exchange integrals and discuss how they differ in their effect on electronic energies.

Coulomb integral :
$$J_{ij} \equiv \langle \phi_i(\vec{r}_1) | \hat{J}_j | \phi_i(\vec{r}_1) \rangle = \iint \phi_i^*(\vec{r}_1)\phi_j^*(\vec{r}_2)\frac{1}{r_{12}}\phi_i(\vec{r}_1)\phi_j(\vec{r}_2)dV_1 dV_2$$

Exchange integral :
$$K_{ij} \equiv \langle \phi_i(\vec{r}_1) | \hat{K}_j | \phi_i(\vec{r}_1) \rangle = \iint \phi_i^*(\vec{r}_1)\phi_j^*(\vec{r}_2)\frac{1}{r_{12}}\phi_j(\vec{r}_1)\phi_i(\vec{r}_2)dV_1 dV_2$$

Be careful of notation here, as exchange often written as J_{ij} in the solid-state literature.

Coulomb integral always increases electron energies due to « uncorrelated » Coulombic repulsion. Exchange integral (always positive in sign but multiplied by minus one), always acts to lower electron energy,

in effect correcting the coulomb integral for the effects of spin-parallel-electron correlation due to the anti-symmetry of the electron wave function and the resulting « Fermi hole » in which each electron moves.

(b) Based on your answer above, which spin state of four electrons in a $3d^4$ configuration is lowest in energy and why? ↑↑↓↓ or ↑↑↑↓ or ↑↓↓↓ or ↑↑↑↑ ?

Let the electrons be labeled 1234. Then all four configurations above have coulombic repulsion due to 4x3/2 = 6 integrals: J_{12}, J_{13}, J_{14}, J_{23}, J_{24}, and J_{34}.
For exchange, which only exist between spin-parallel electrons we have:

↑↑↓↓: K_{12}, K_{34} = 2 energy-lowering exchange integrals

↑↑↑↓: K_{12}, K_{13}, K_{23} = 3 integrals

↑↓↓↓: K_{23}, K_{24}, K_{34} = 3 integrals

↑↑↑↑: K_{12}, K_{13}, K_{14}, K_{23}, K_{24}, and K_{34} = 6 integrals

So ↑↑↑↑ will be lowest in energy.

3) Explain briefly how a Mott detector works. On which fundamental relativistic interaction does it depend?

Electrons at high energies of 20-100 keV are scattered from a heavy-atom target such as Au (Z = 79), or even Th (Z = 90) or passivated U (Z = 92).   The relativistic spin-orbit interaction means that, since the orbital angular momentum has a different sign for scattering to the left and to the right in the figure below, any difference of the left and right intensities is indicative of, and proportional to, the spin polarization of the incoming flux of electrons.

MICROMOTT DETECTOR
(LBNL/Florida State Univ./UC Davis)

The MicroMott Electron Spin Detector

TANG ET AL.
REV. SCI. INST.
59, 504 (1988)
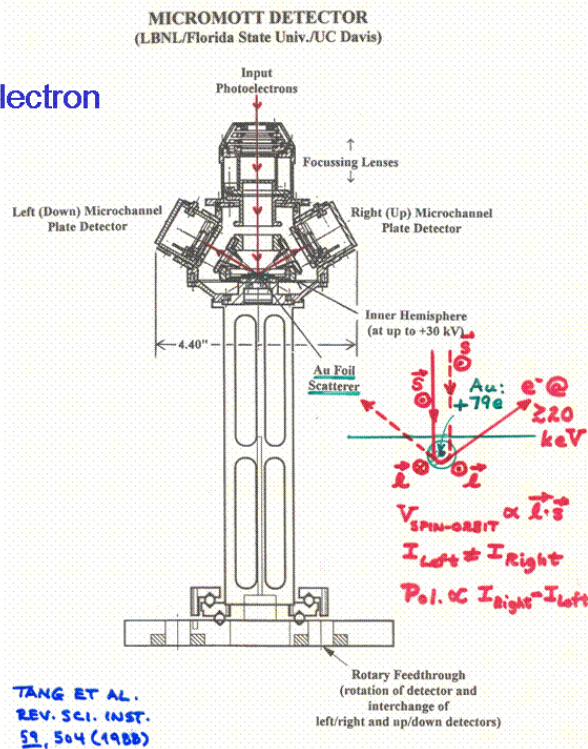
4) Sketch the typical variation of a total cross section with photon energy, and of a 1s differential cross section with angles.

Subshells of s symmetry never show Cooper minima, since they only have one outgoing p photoelectron channel and no interference is possible in the final state. Thus, the energy dependence is as shown below, with a sharp onset at the absorption a little below the 1s binding energy, and a slow decrease above that. Also, all s subshells have an asymmetry parameter of 2, so that, with linearly polarized light, the cross section looks like a p-orbital, with the "dumbbell" shape shown below.

Typical cross section   Typical s-subshell differential cross section
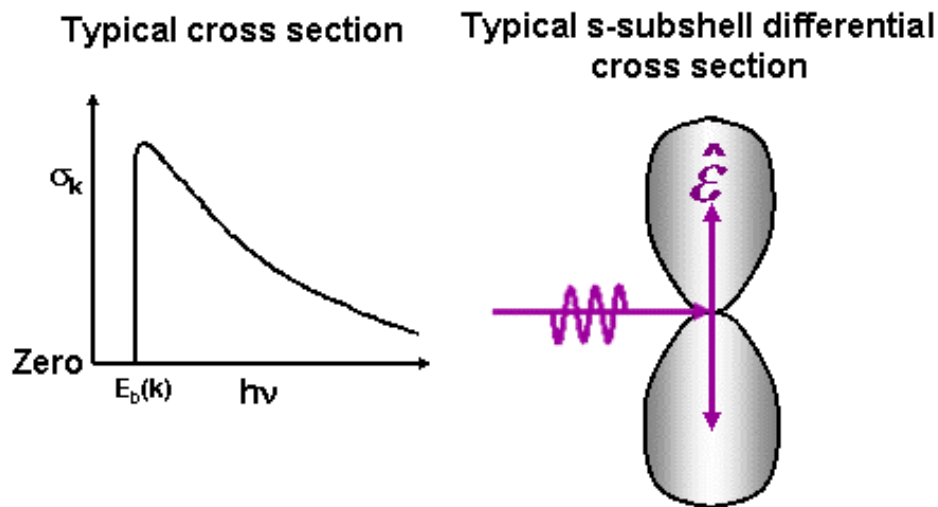
5) At about what photon energy would 3d photoemission from an Fe atom be expected to show the strongest resonant effects? Reason by analogy with Mn, and look up appropriate binding energies in the X-Ray Data Booklet or some other source.

For Mn, we discussed Mn 3d photoelectron emission in resonance with Mn 3p-to-Mn 3d excitation, so for Fe, it will be Fe 3d photoelectron emission in resonance with Fe 3p-to-Fe 3d excitation. Thus, the relevant Fe 3p absorption edge energy will be just below the Fe 3p binding energy, or about 53 eV.

6) What feature in photoelectron diffraction can directly yield:

(a) Information on bond direction?

Forward scattering in small adsorbed molecules (like CO on Ni and CO on Fe) or along low-index directions in crystals, can be used directly to determine the orientation of the molecule on a surface. Example shown below, and others discussed in Osterwalder and Fadley lectures:

SAIKI
ET AL.
(FADLEY
GROUP)
PHYS. REV.
LETT.
62, 283
(1989)
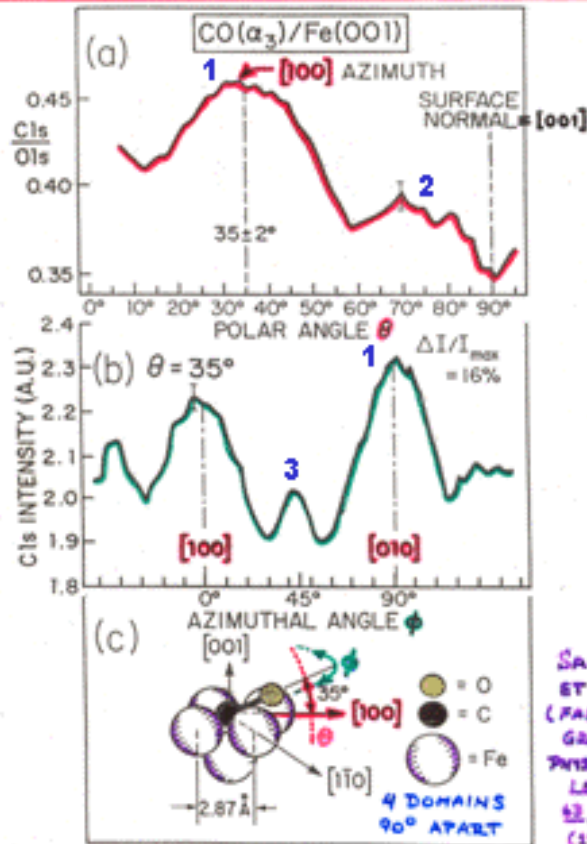
97
"Study of Surface Structures..."
Figure 9

(b) *Or bond distances?*

Interference peaks of 1st, 2nd, 3rd,…order can be used to determine bond distances, including those arising from back scattering at lower kinetic energies. E.g. see theoretical calculations for a single CO molecule below, and cases discussed in Osterwalder lectures and computer tutorial on PD:

**CO/Fe(001)—Effect of CO bond dist.**
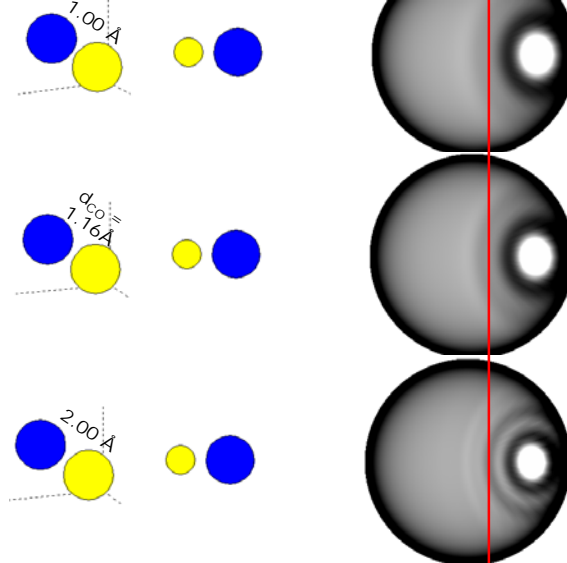
7) Give three ways in which spin-polarized electrons can be emitted from a specimen.

1. **Excitation of spin-split valence bands in a ferromagnet : e.g. Fe(001) or Ni(001) : referenced internally to magnetization of sample.**
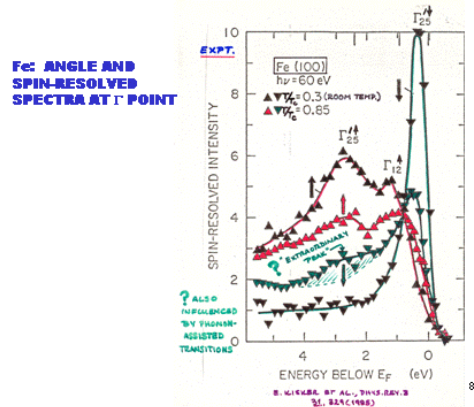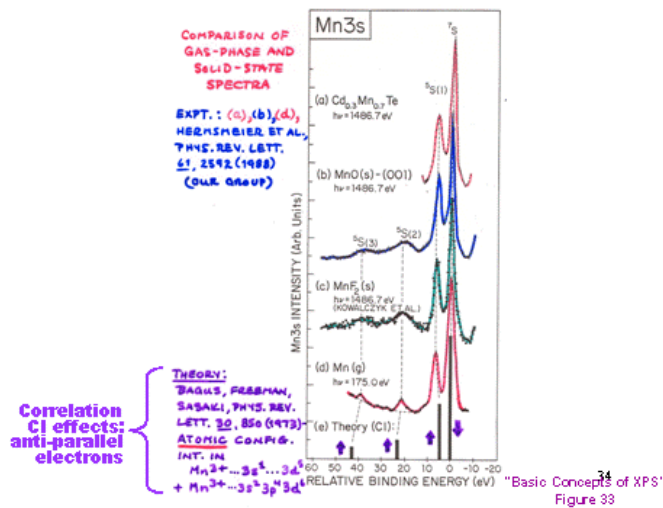

2. **Excitation of a spin-orbit-split core level with circularly polarized radiation : e.g. W 4f : referenced to the direction of incidence of the circularly polarized radiation.**
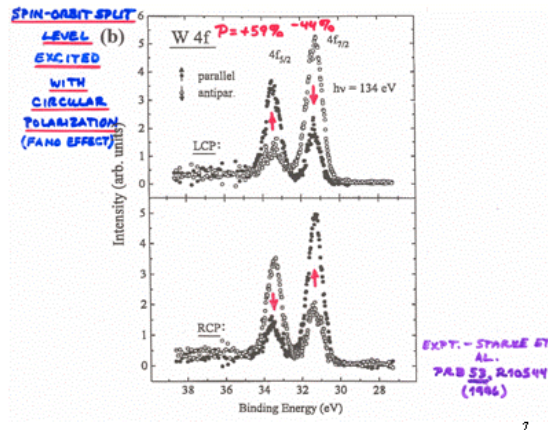
3. **Multiplet-split spectra in atoms/ions with unpaired electrons : e.g. MnO : referenced to the orientation of each Mn^{2+} ion.**

(8) As a more quantitative exercise, consider a sample of arsenic (As), which has a free-atom electronic configuration of $1s^2...4s^24p^3$, that is exposed to incident soft x-rays of 2,000 eV energy. Use the X-Ray Data Booklet available on the web, in particular Table 1-1: electron binding energies, Fig. 1-1: x-ray emission line nomenclature, Table 1-2: x-ray emission energies, Fig. 1-3: energies of most intense Auger peaks, and Table 5.2, which includes electron configurations and other information, to answer the following.

(a) Are all of the electron binding energies of As present in the table of experimental values in Table 1-1? Explain your answer. **The electronic configuration is [Ar]$3d^{10}4s^24p^3$ and from the X-Ray Data Book entries below, we can see that the 4s and 4p valence levels are missing. They will have Fermi-reference binding energies from about 0-10 eV**

Element	K 1s	L$_1$ 2s	L$_2$ 2p$_{1/2}$	L$_3$ 2p$_{3/2}$	M$_1$ 3s	M$_2$ 3p$_{1/2}$	M$_3$ 3p$_{3/2}$	M$_4$ 3d$_{3/2}$	M$_5$ 3d$_{5/2}$	N$_1$ 4s	N$_2$ 4p$_{1/2}$	N$_3$ 4p$_{3/2}$
23 V	5465	626.7†	519.8†	512.1†	66.3†	37.2†	37.2†					
24 Cr	5989	696.0†	583.8†	574.1†	74.1†	42.2†	42.2†					
25 Mn	6539	769.1†	649.9†	638.7†	82.3†	47.2†	47.2†					
26 Fe	7112	844.6†	719.9†	706.8†	91.3†	52.7†	52.7†					
27 Co	7709	925.1†	793.2†	778.1†	101.0†	58.9†	59.9†					
28 Ni	8333	1008.6†	870.0†	852.7†	110.8†	68.0†	66.2†					
29 Cu	8979	1096.7†	952.3†	932.7	122.5†	77.3†	75.1†					
30 Zn	9659	1196.2*	1044.9*	1021.8*	139.8*	91.4*	88.6*	10.2*	10.1*			
31 Ga	10367	1299.0*b	1143.2†	1116.4†	159.5†	103.5†	100.0†	18.7†	18.7†			
32 Ge	11103	1414.6*b	1248.1*b	1217.0*b	180.1*	124.9*	120.8*	29.8	29.2			
33 As	11867	1527.0*b	1359.1*b	1323.6*b	204.7*	146.2*	141.2*	41.7*	41.7*			

(b) Predict the kinetic energies of all photoelectron peaks that would be observed in the range from 0 to 2050 eV, assuming a spectrometer work function of 4.0 eV and noting that the relativistic spin-orbit interaction splits any non-s ($l \neq 0$) subshell binding energy into two components: $j = l \pm 1/2$. **Just calculate for each binding energy k of As from 2s downward the following: $E_{kin} = 2000 - E_b^F(As,k) - 4.0 = 1996 - E_b^F(As,k)$, where we have noted that the binding energies tabulated are referenced to the Fermi level. So you get:**

2s   2p$_{1/2}$ 2p$_{3/2}$ 3s   3p$_{1/2}$ 3p$_{3/2}$ 3d$_{3/2}$ 3d$_{5/2}$ 4s,4p

469.9 636.9   672.4   1791.3 1849.8   1854.8   1954.3 1954.3 ~1986-1996

(c) From Fig. 1-3 in the Data Book, where would you also expect to find Auger peaks in the photoelectron spectrum? How would the photoelectron peak energies and the Auger peak energies change if the photon energy is changed from 2000 to 2200?
From the figure below (green lines), we expect peaks at about 1040 eV, 1130 eV, and 1220 eV.

PRINCIPAL AUGER ELECTRON ENERGIES
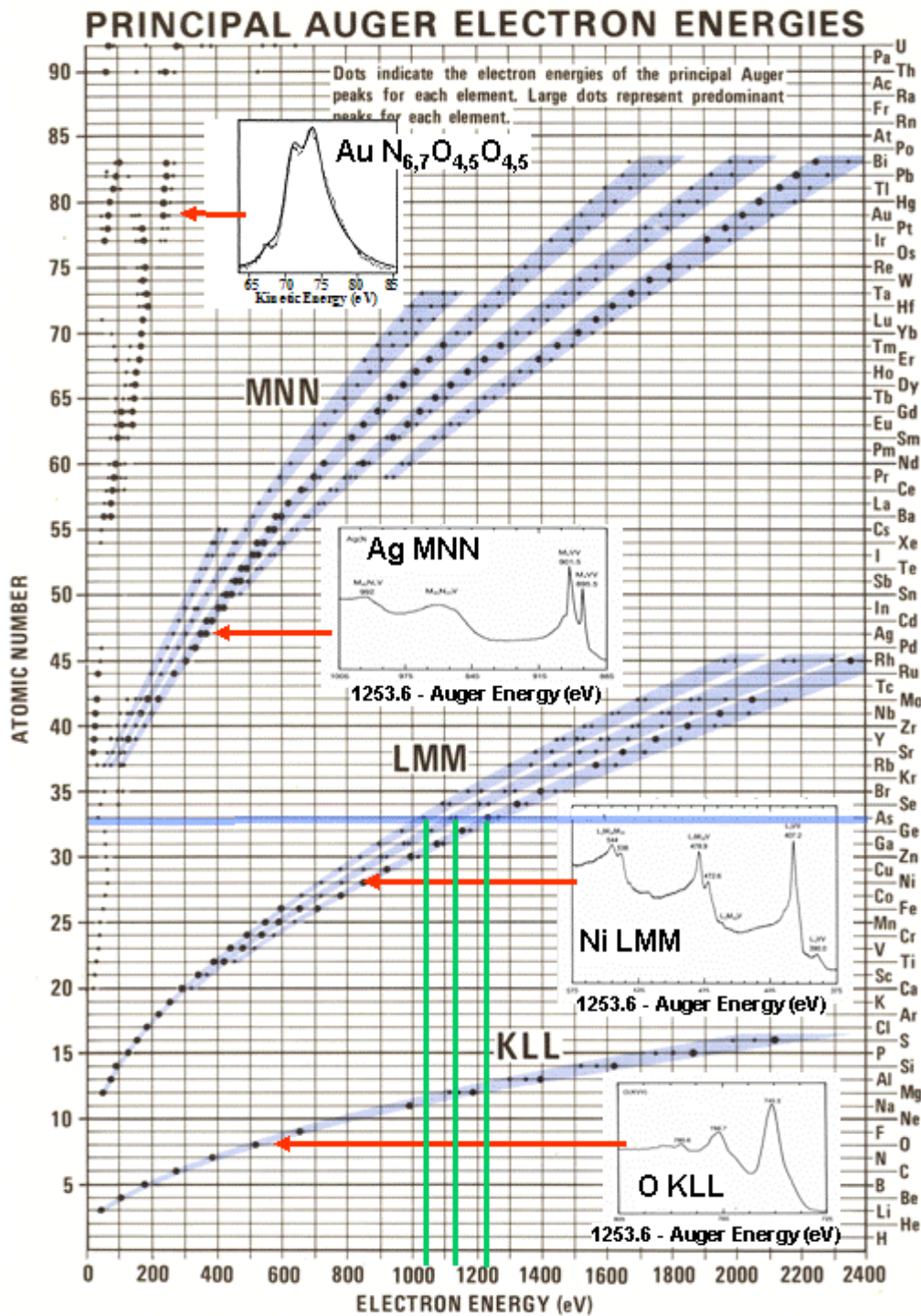
(d) Use appropriate binding energies to calculate the $K\alpha_1$, $K\alpha_2$, and $L\beta_1$ x-ray emission energies for As, and compare your answer to those given in the handbook in Table 1-2.

$E(As\ K\alpha_1) = E_b(A\ 1s) - E_b(A\ 2p_{3/2}) = 11867 - 1323.6 = 10543.4$ (compare 10543.7 from XDB)

$E(As\ K\alpha_2) = E_b(A\ 1s) - E_b(A\ 2p_{1/2}) = 11867 - 1359.1 = 10507.9$ (compare 10508.0 from XDB)

$E(As\ L\beta_1) = E_b(A\ 2p_{1/2}) - E_b(A\ 3d_{3/2}) = 1359.1 - 41.7 = 1317.4$ (compare 1317.0 from XDB)

Very close!

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No. 3--Computer-based tutorials on x-ray optics and photoelectron diffraction :
Below are several problems to explore with the Berkeley CXRO website (http://www-cxro.lbl.gov/optical_constants/) and the photoelectron diffraction program EDAC (http://maxwell.optica.csic.es/).

Elemental and compound properties can be obtained from several slides in Fadley Slide Set 1 or the X-Ray Data Booklet or http://webelements.com, and inelastic attenuation lengths for any element, via the TPP-2M formula, are available from: http://www.ss.teen.setsunan.ac.jp/imfp.html.

**Please turn in a 1-2 page hardcopy summary of each of your results for these computer exercises.**

## Photoelectron diffraction : http://maxwell.optica.csic.es/

Note of caution : **Think carefully about the setup of the experimental geometry, including the radiation polarization and whether you scan the sample, or the analyzer. Scanning the sample only with a fixed photon-electron geometry is the most typical experimental setup, and an angle of 90° between photon and electron is special in aligning linear polarization with the electron emission direction in what is called p polarization. But if you set the polarization so that the detector is in a node of the differential cross section, you won't get any electrons ! You have to use s polarization carefully from this point of view as well.**

[1] Calculate the full hemisphere photoelectron diffraction pattern for C 1s emission with 1487 eV excitation from tilted and upright CO on Fe(001): C in a fourfold hollow site, five Fe atoms (4 in plane, 1 below). See Fadley lecture slides for details. Vertical distances and other inputs are given in slides, but additional useful reference nos. are: the C-O distance can be taken to be 1.18 Å and the body-centered cubic Fe lattice constant is 2.87 Å.

Inputs for the tilted case are directly from the lecture notes in fact, and yield typical patterns as below:
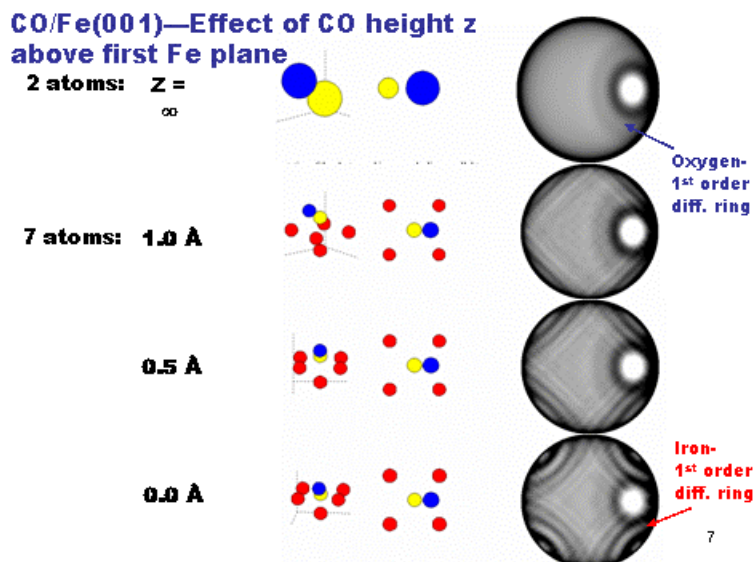
For the vertical case, the O is just above the C atom, and this yields for 1.0 Å spacing of C above Fe plane:
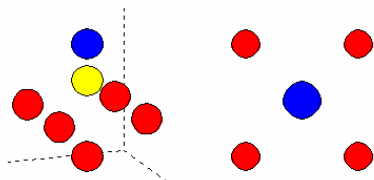
Left: representation of the cluster rocking around a line parallel to the *z* direction and passing by the **emitter (yellow atom)**. The dashed lines stand for the *xyz* axes. **Right:** top view of the cluster, where the *x/y* direction (not plotted) runs along the horizontal/vertical screen direction. Different atomic species have been assigned the colors **O**, **Fe**.
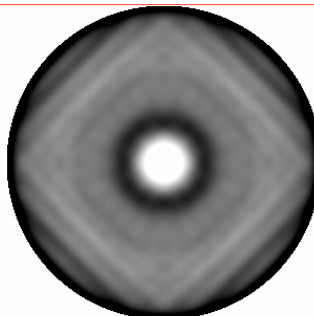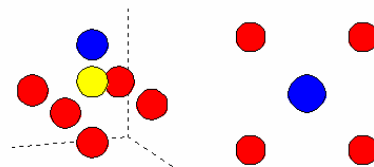
Polar scan of photoemission intensity (logarithmic scale). White/black regions correspond to high/low intensity. The orientation is the same as in the top-view of the cluster. The distance to the center of the figure is proportional to the polar angle θ. The polar angle range is (0.0, 89.0) (in degrees).

Parameters used in the calculation:

N=7 atoms
Iteration order=4
l_{max}=25
V_0=12.4 eV
Photoelecton energy=1202 eV
p-polarized light
z_0=1.435 Å
Recursion iteration method
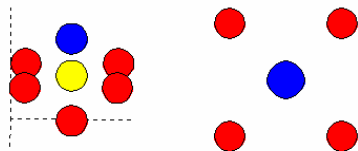
And for 0.5 Å spacing:

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 *xyz* axes. **Right:** top view of the cluster, where the *x/y* direction (not plotted) runs along the horizontal/vertical screen direction. Different atomic species have been assigned the colors **O**, **Fe**.
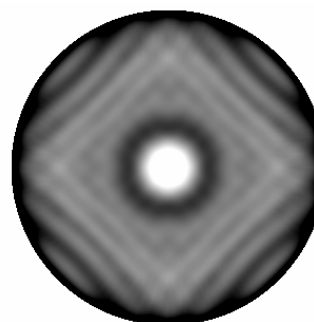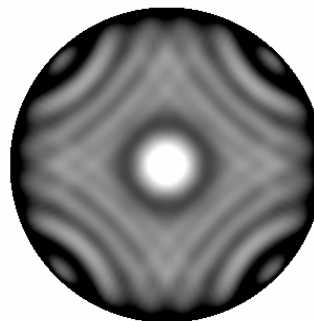
Polar scan of photoemission intensity (logarithmic scale). White/black regions correspond to high/low intensity. The orientation is the same as in the top-view of the cluster. The distance to the center of the figure is proportional to the polar angle θ. The polar angle range is (0.0, 89.0) (in degrees).

And for 0.0 Å spacing:

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 *xyz* axes. **Right:** top view of the cluster, where the *x/y* direction (not plotted) runs along the

Polar scan of photoemission intensity (logarithmic scale).

[2] Calculate the full hemisphere photoelectron diffraction pattern for O 1s emission with 1253 eV excitation from O on Rh(111), with O sitting in a threefold hollow site and three Rh atoms underneath it, varying the height of the O above the Rh plane to check sensitivity. Rh has a face-centered cubic crystal structure with a = 3.90 Å.

The structure you're modeling is shown in 3D below, together with an experimental pattern and some different simulations, due to Osterwalder et al.
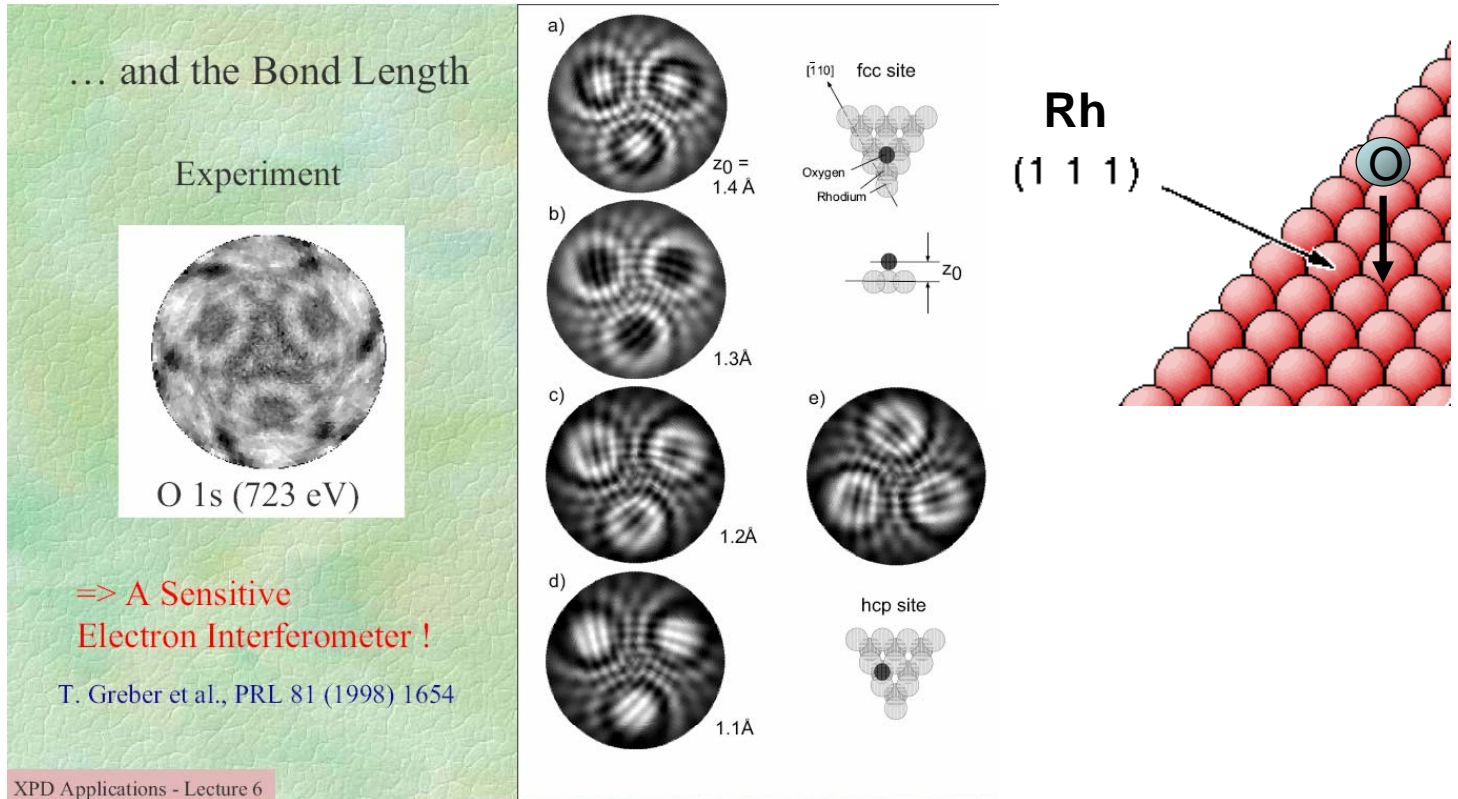
X-ray optics : From the website http://www-cxro.lbl.gov/optical_constants/

[1] (a) Calculate the penetration depth of photons in graphite for incidence angles of 5 and 15 degrees as a function of energy over the photon energy range of 200 eV to 400 eV.

(b) What occurs when you cross the C 1s absorption edge? Why are the results for the two cases different ? (Hint : It may be useful to look also at the optical constant δ and β over this energy range, and to consider also whether there is a significant degree of refraction and reflection from the surface by calculating this for the two angles as well.) See below.

(c) Is the critical angle which is equal to $\sqrt{2\delta}$ and for which the reflectivity rises to about 0.2, obvious in your plot ? Yes, see below.

(d) What is the minimum penetration depth of photons in graphite just above the C 1s edge as judged from another calculation as a function of incidence angle ?

[2] Calculate the reflectivity of a multilayer mirror made of bilayers of 16 Å B_4C and 24 Å W, and with 40 bilayers total, at 900 eV photon energy and as a function of incidence angle from zero upward. Assume that the top layer is B_4C, and that the substrate is SiO_2. It is best to plot this over the full angle range, e.g. from 0° to 90.0°, and to use a linlog plot to be able to see weaker reflectivity features. Also use the maximum no. of points of 500 to be able to adequately see the fine structure.

(a) Do you see evidence of Bragg reflection at different orders ?

(b) Can you relate these to Bragg reflections at specific orders from the multilayer ?

(c) Is there evidence of the onset of total reflection ?

(d) If you now change the bilayers to be 20 Å B$_4$C and 20 Å W, what change do you see in the relative intensities of the different reflection orders? How do you explain this?

(e) Newly added bonus part: Do you see any additional fine structure near normal emission, and does this have any relationship to what are called Kiessig fringes?

Suggested answers to both:

[1]
(a) and (b) The calculations below indicate that the attenuation length drops abruptly when you cross the C 1s edge for both angles. It also increases markedly as the edge is approached from below, probably due to refraction that allows the wave to travel at an angle that is more nearly normal to the surface inside the surface. That is, a change in delta (refraction) precedes the abrupt change in beta (absorption) as energy is increased. The two angles are different in behavior mostly because the attenuation length is measured normal to the surface. So it should go as $\Lambda_x(h\nu)\sin\theta_{incidence}$. Thus, at 15 degrees, you should penetrate about three times as far as at 5 degrees, as observed on the peak. Also, at 5 degrees, there is more refraction, which makes the internal propagation angle lower than the external incidence angle, and reduces the curve for 5 degrees below the resonance by more than a factor of three over 200-300 eV.

(c) Plots below show that the minimum depths just above the C 1s edge are very small, at only about 40 Å…not too much different from electron inelastic attenuation lengths.

(b)Next part involves going beyond attenuation length to look at both optical constants and reflectivity, which show in last two plots that reflectivity does turn on to about 0.2 at the expected value of the critical angle.

C Density=2.2

delta (dash)
beta (solid)

Delta, Beta

Photon Energy (eV)
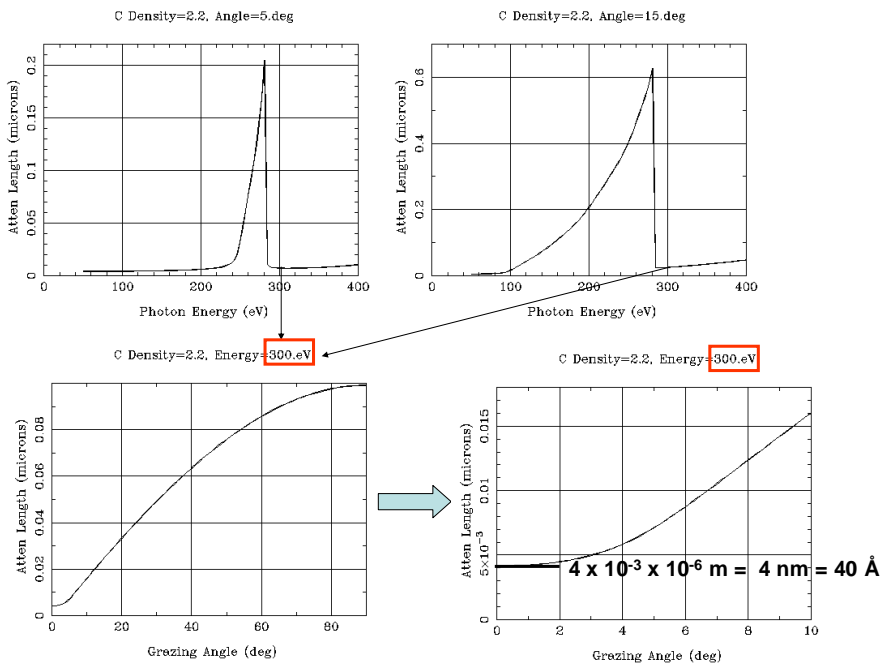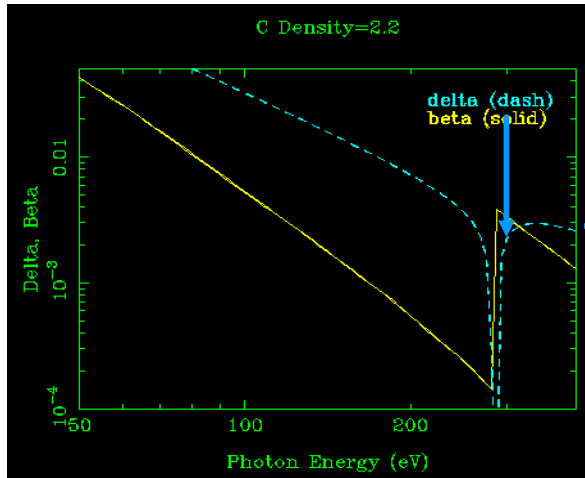
δ= 2.6 x 10^{-3}
∴ critical angle =
$\sqrt{2\delta}$ = $\sqrt{5.2\times10^{-3}}$ =
0.072 radians =
4.1°

c Rho=2.2, Sig=0.nm, P=1., E=300.eV

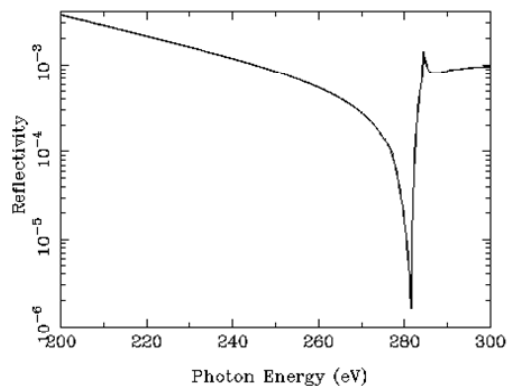Reflectivity

Angle (deg)
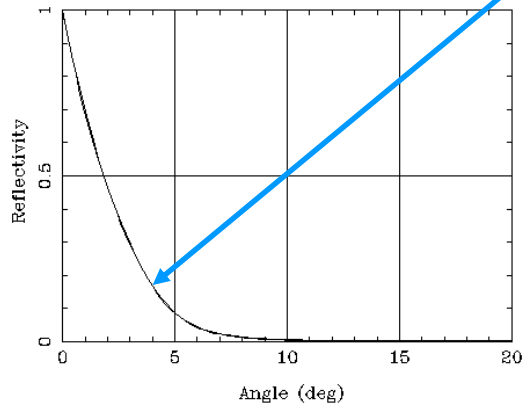
To discuss a little bit more why the penetration depth <u>increases</u> strongly just below the C 1s edge for both incidence angles 5° and 15° , we note from above that δ decreases strongly below the resonance, together with a gradual decrease in β, and that both of these will act to increase the penetration depth : decreasing δ will decrease the refraction toward the surface for the transmitted component, and decreasing β will decrease the strength of absorption, and thus also increase the x-ray attenuation length. We can also see an interesting consequence of this on reflectivity in the plot below of reflectivity as a function of photon energy for the two angles : just below the C 1s edge, the index of refraction is nearest to unity, and so it become more like the vacuum above, and reflectivity goes down, actually to a very small value, thus increasing the amount of radiation that penetrates the surface.

c Rho=2.2, Sig=0.nm, P=1., 5.deg
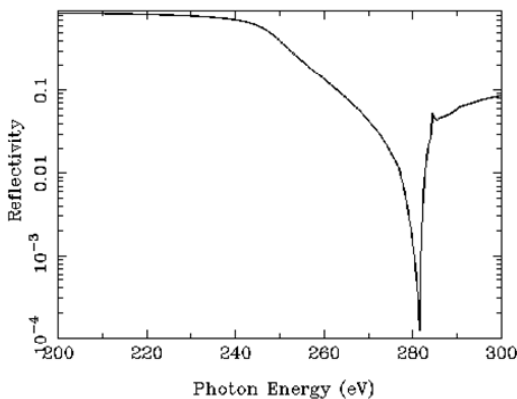
Reflectivity

Photon Energy (eV)

c Rho=2.2, Sig=0.nm, P=1., 15.deg

Reflectivity

Photon Energy (eV)

2) Calculate the reflectivity of a multilayer mirror made of bilayers of 16 Å B_4C and 24 Å W, and with 40 bilayers total, at 900 eV photon energy and as a function of incidence angle from zero up to 90°. Assume that the top layer is B_4C, and that the substrate is SiO_2. It is best to use a linlog plot, and 500 points over the range, so that you do not miss fine structure.

(a) Do you see evidence of Bragg reflection at different orders ? Yes, in a linear-log plot, 1st, 2nd, 3rd, and 4th , and a hint of 5th orders are seen, but with 1st by far the strongest.
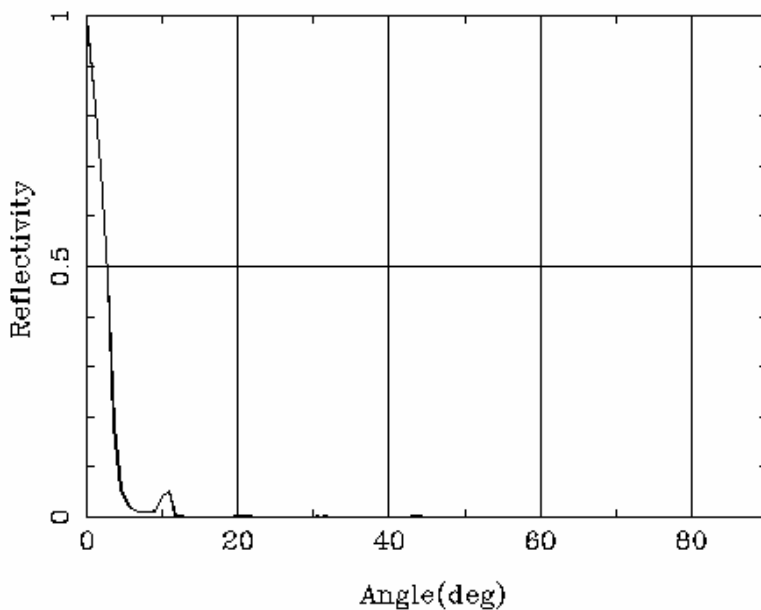
(b) Can you relate these to Bragg reflections at specific orders from the multilayer? Do this by plugging into Bragg formula: $n\lambda = 2D\sin\theta_n$ or $\theta_n = \arcsin[n\lambda/2D]$, which gives with D = 40 Å and $\lambda = 12,398/E_{photon}(eV)$ = 13.77 Å, $\theta_1 = 9.9^0$, $\theta_2 = 20.1^0$, $\theta_3 = 31.1^0$, $\theta_4 = 43.5^0$, $\theta_5 = 59.4^0$. These are in good agreement with the calculations, with only slight shifts between the peaks and the expected Bragg positions.

(c) Is there evidence of the onset of total reflection ? Yes, by about 3 degrees, it has turned on to about 0.2.
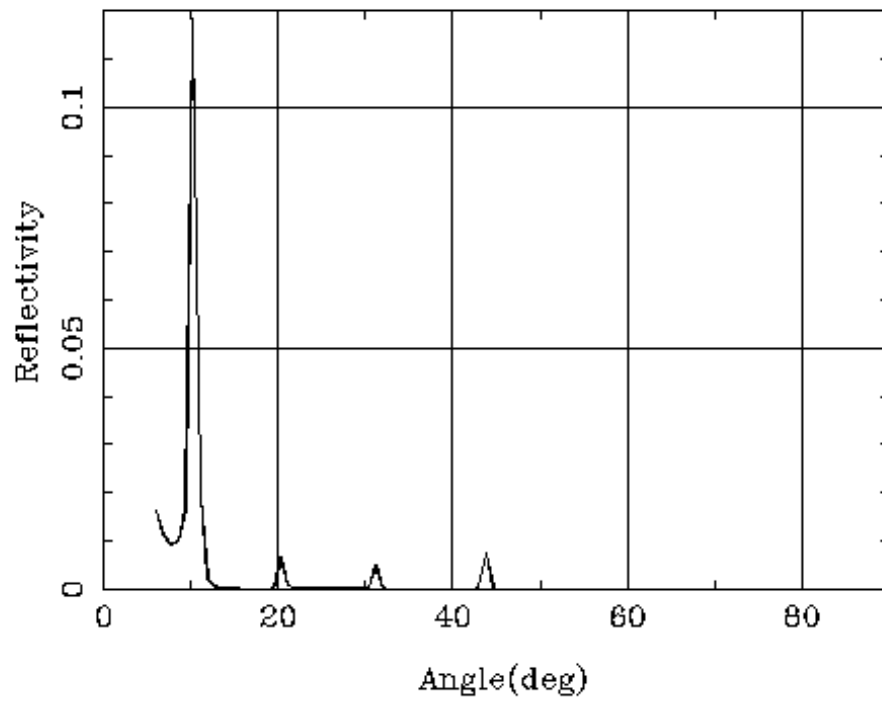
(d) The even orders of diffraction are strongly suppressed when the two layers in the bilayer have equal thickness, since the reflections from the top e.g. B4C/W interface of the bilayer is out of phase with that in the middle W/B4C interface. This suppression has the same origin as the forbidden reflections in fcc and bcc crystal structures.

(e) For angles near normal emission, there is additional fine oscillatory structure. To what is this due? This is due to the so-called Kiessig fringes that arise due to the interference of wave components reflecting from the top surface of the multilayer and from the top surface of the SiO2 substrate on which the multilayer is grown. The last figure superimposes the reflectivity from a single mirror layer on SiO2 that is made of W only, but with a thickness of 40 x 4 nm = 160 nm thickness, and the fringes are clearly there.
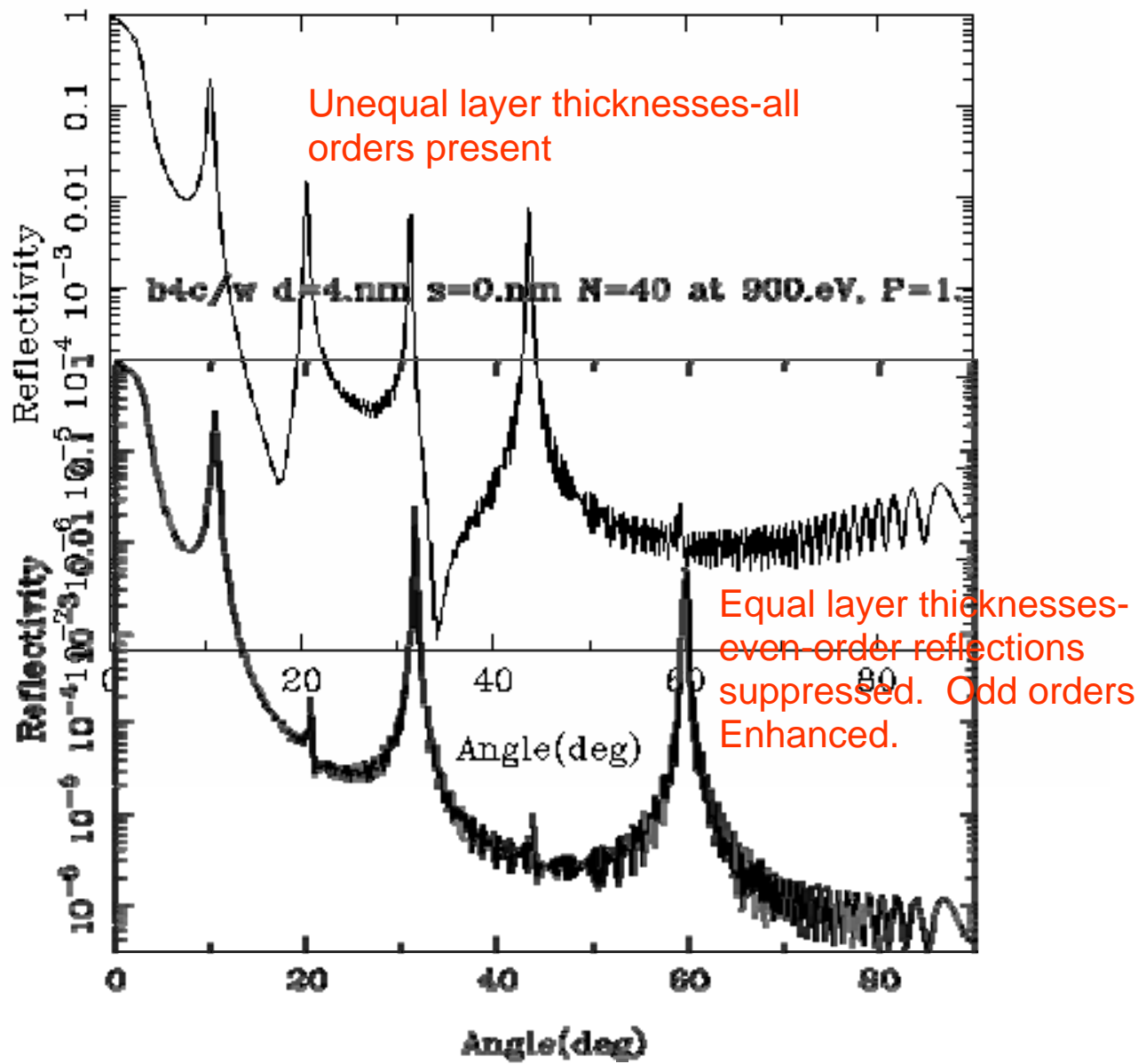

b4c/w d=4.nm s=0.nm N=40 at 900.eV, P=1.

b4c/w d=4.nm s=0.nm N=40 at 900.eV, P=1.

b4c/w d=4.nm s=0.nm N=40 at 900.eV, P=1.

Unequal layer thicknesses-all orders present

b4c/w d=4.nm s=0.nm N=40 at 900.eV, P=1.

Equal layer thicknesses-even-order reflections suppressed. Odd orders Enhanced.

Reflectivity

Angle(deg)

b4c/w d=4.nm s=0.nm N=40 at 900.eV, P=1.

W 130.nm on SiO2 at 900.eV, P=1.

Reflectivity

Reflectivity

Angle(deg)

Angle (deg)