

ICTP School on Synchrotron Radiation and Applications 2010

Surface Science, Photoemission and Related Techniques

Fadley, Goldoni

No. 1—Student background questions and study questions from the lectures.

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?

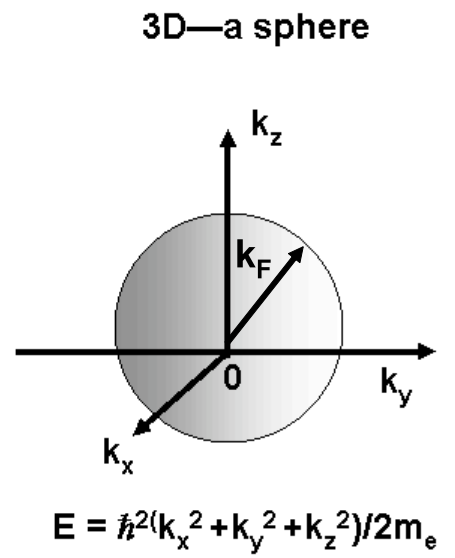
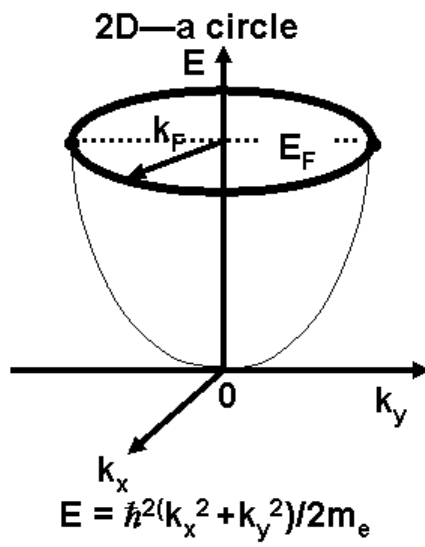
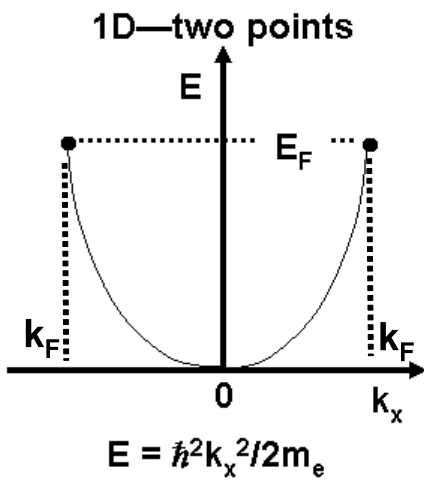
It is an empirical law which states that the number of transistors on a single IC double about every 18 months. Actually the rate was to double about every 24 months until the last 10 years, over which it has doubled every 12 months.

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

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

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 free-electron gas (use back side if necessary)



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Surface Science, Photoemission and Related Techniques

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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,

$$E_{b,KT}(\mathbf{k}) = -\epsilon_{\mathbf{k}}$$

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 :

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

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

Coulomb integral :

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

Exchange integral :

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

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? $\uparrow\uparrow\downarrow\downarrow$ or $\uparrow\uparrow\uparrow\downarrow$ or $\uparrow\downarrow\downarrow\downarrow$ or $\uparrow\uparrow\uparrow\uparrow$?

Let the electrons be labeled 1234. Then all four configurations above have coulombic repulsion due to $4 \times 3/2 = 6$ 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:

$\uparrow\uparrow\downarrow\downarrow$: $K_{12}, K_{34} = 2$ energy-lowering exchange integrals

$\uparrow\uparrow\uparrow\downarrow$: $K_{12}, K_{13}, K_{23} = 3$ integrals

$\uparrow\downarrow\downarrow\downarrow$: $K_{23}, K_{24}, K_{34} = 3$ integrals

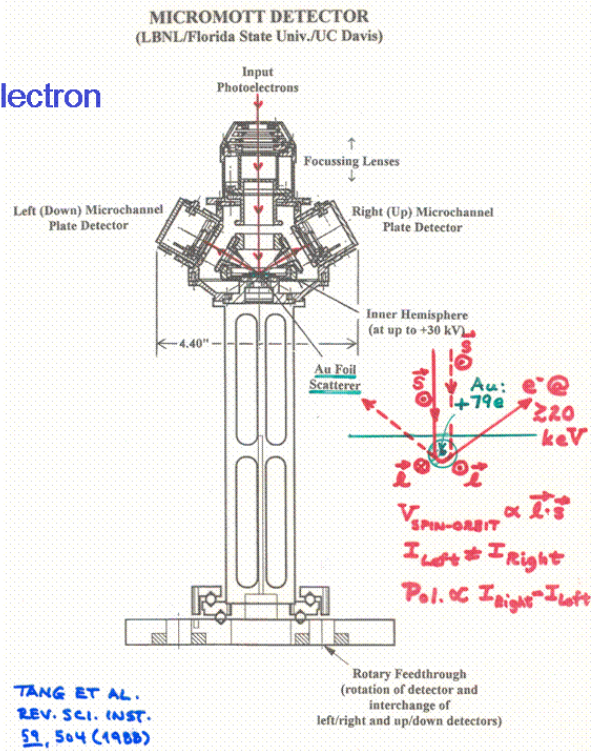
$\uparrow\uparrow\uparrow\uparrow$: $K_{12}, K_{13}, K_{14}, K_{23}, K_{24},$ and $K_{34} = 6$ integrals

So $\uparrow\uparrow\uparrow\uparrow$ will be lowest in energy.

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

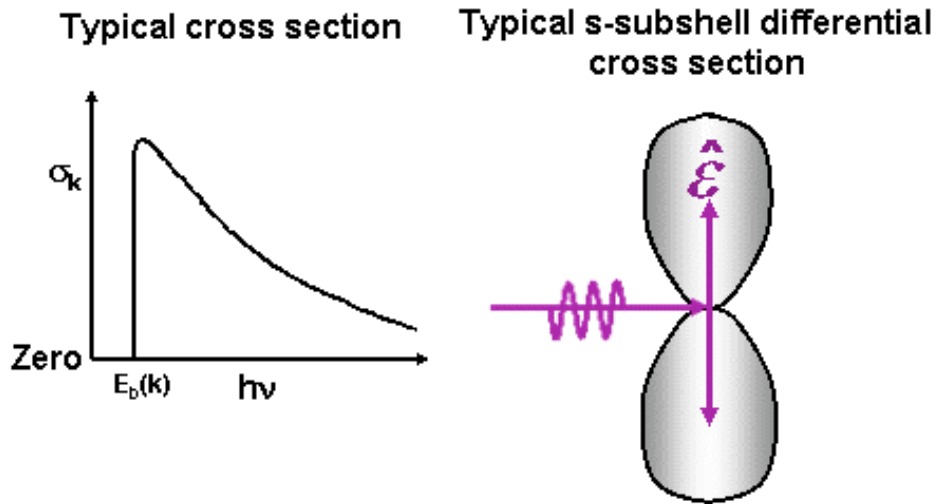
Electrons at high energies of 20-100 keV are scattered from a heavy-atom target such as Au ($Z = 79$), or even Th ($Z = 90$) or passivated U ($Z = 92$). The relativistic spin-orbit interaction means that, since the orbital angular momentum has a different sign for scattering to the left and to the right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

The MicroMott Electron Spin Detector



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.



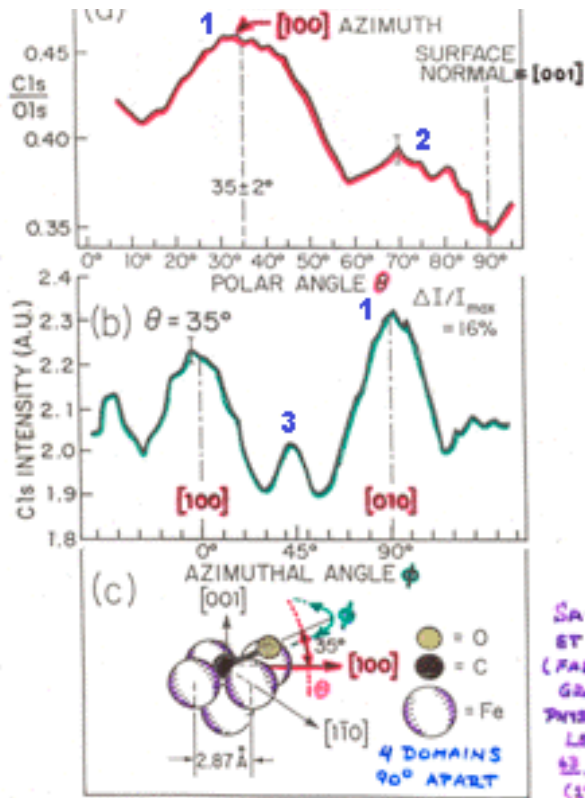
5) At about what photon energy do you expect to see the strongest resonant effects? Reason by analogy with Mn, and look up appropriate binding energies in the X-Ray Data Booklet or some other source.

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 Fadley lectures:



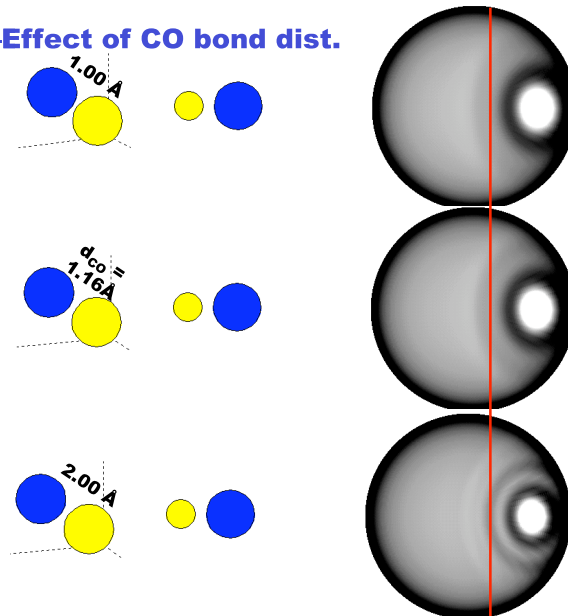
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"Study of Surface Structures..."
Figure 9

(b) Or bond distances?

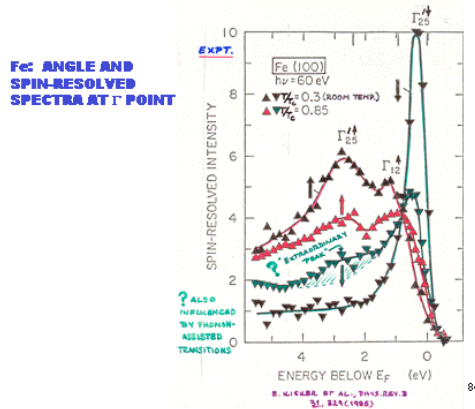
Interference peaks of 1st, 2nd, 3rd, ... order can be used to determine bond distances, including those arising from back scattering at lower kinetic energies. E.g. see theoretical calculations for a single CO molecule below, and cases discussed in Osterwalder lectures and computer tutorial on PD:

CO/Fe(001)—Effect of CO bond dist.



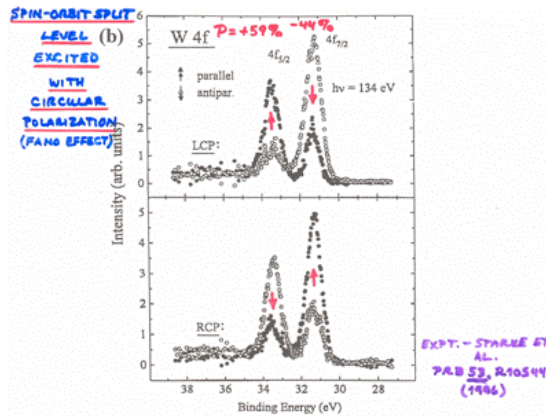
7) Give three ways in which spin-polarized electrons can be emitted from a specimen.

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

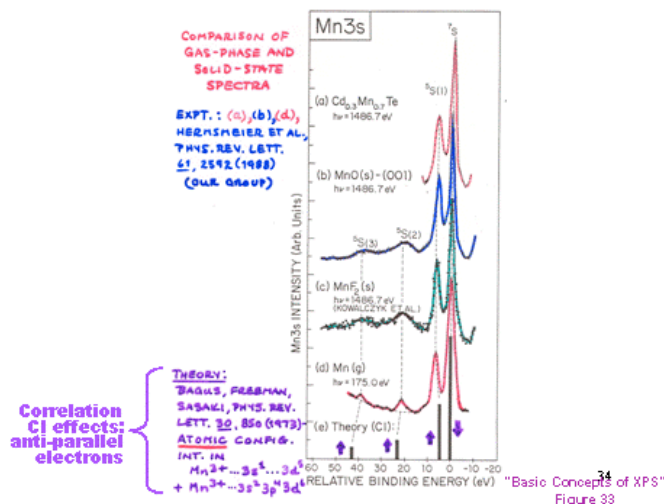


2. Excitation of a spin-orbit-split core level with circularly polarized radiation : e.g. W 4f : referenced to the direction of incidence of the circularly polarized radiation.

Spin polarization in core photoelectron spectra—expt.



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.

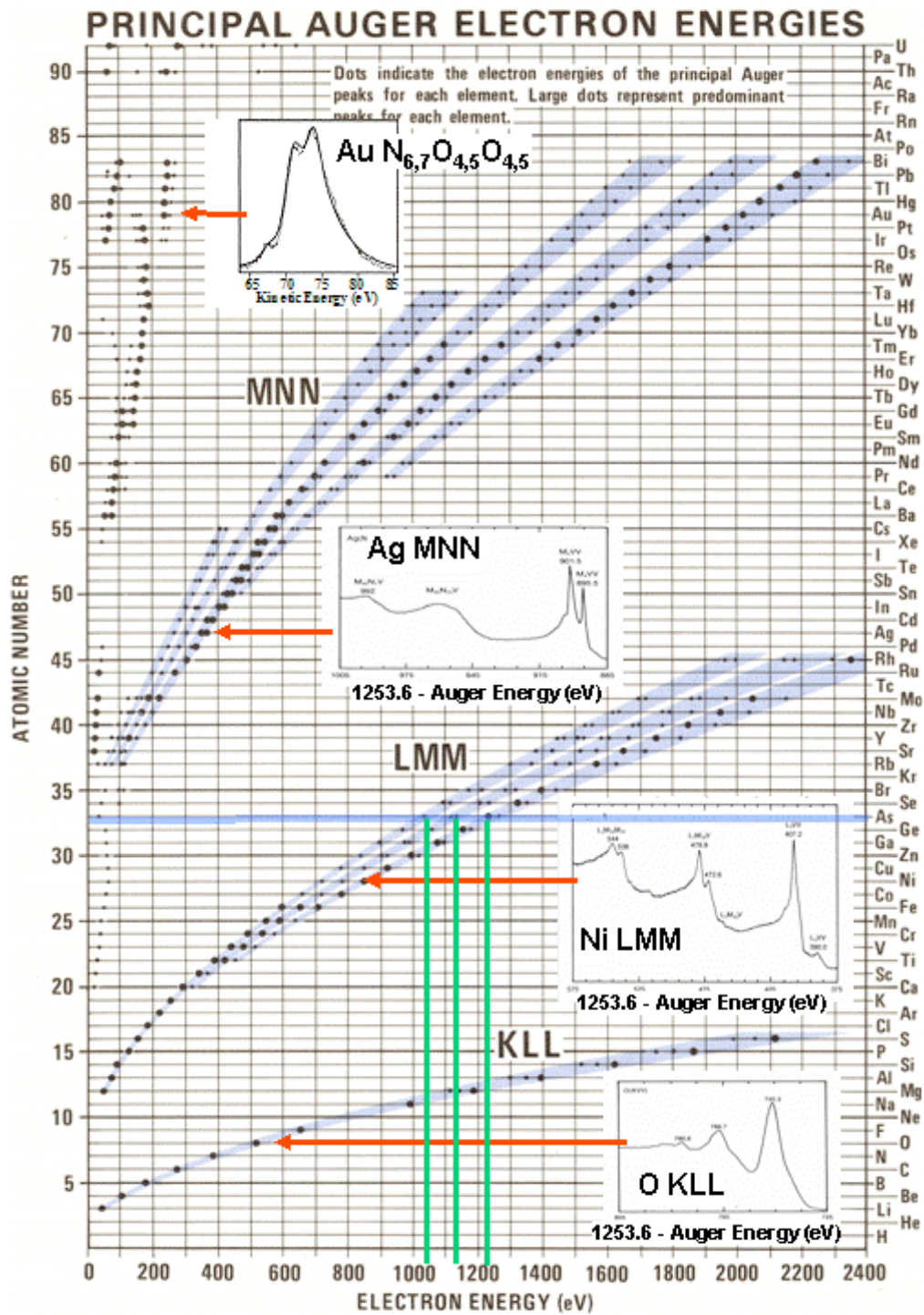
- (a) Are all of the electron binding energies of As present in the table of experimental values in Table 1-1? Explain your answer. The electronic configuration is $[Ar]3d^{10}4s^24p^3$ and from the X-Ray Data Book entries below, we can see that the 4s and 4p valence levels are missing. They will have 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 3n ²	M ₃ 3n ³	M ₄ 3d ⁴	M ₅ 3d ⁵	N ₁ 4s	N ₂ 4n ²	N ₃ 4n ³
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.



(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.

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

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

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

Very close!

ICTP School on Synchrotron Radiation and Applications 2006

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Fadley, Osterwalder

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://csic.sw.ehu.es/jga/software/edac/a.html>).

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.

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.

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 reflectivity from the surface by calculating this for the two angles as well.) See below.

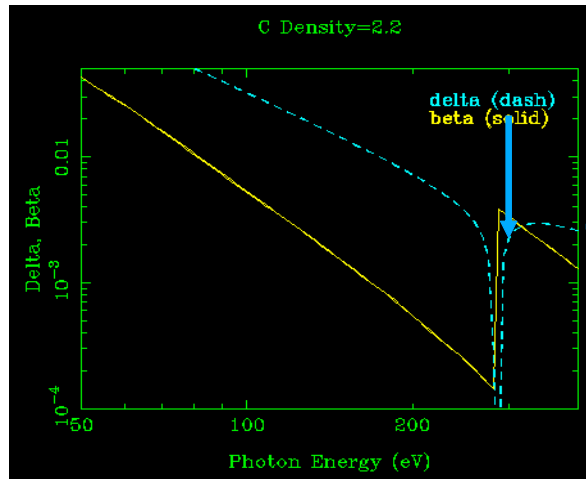
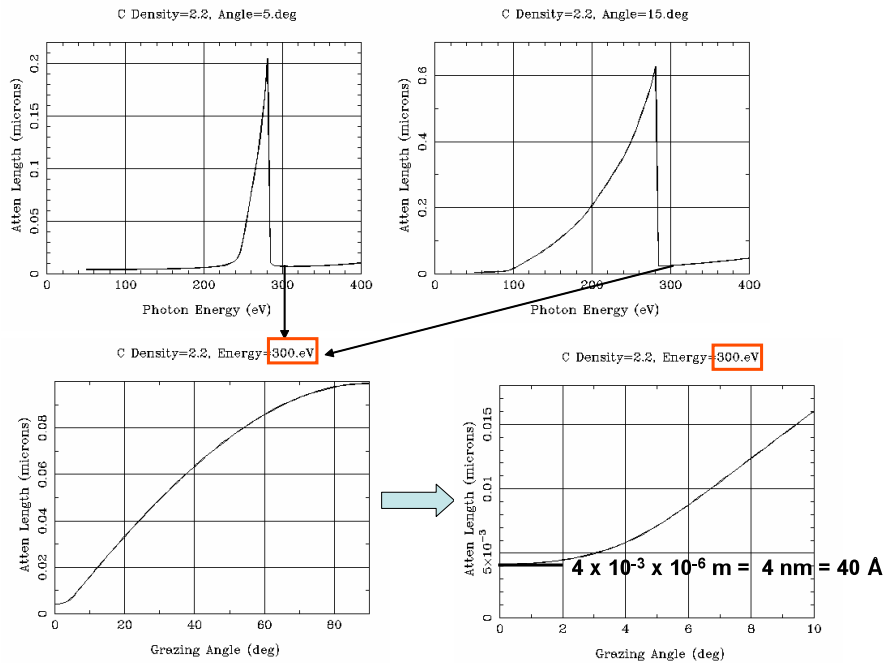
Is the critical angle which is equal to $\sqrt{2}\delta$ and for which the reflectivity rises to about 0.2, obvious in your plot ? Yes, see below.

What is the minimum penetration depth of photons in graphite as judged from another calculation as a function of incidence angle ?

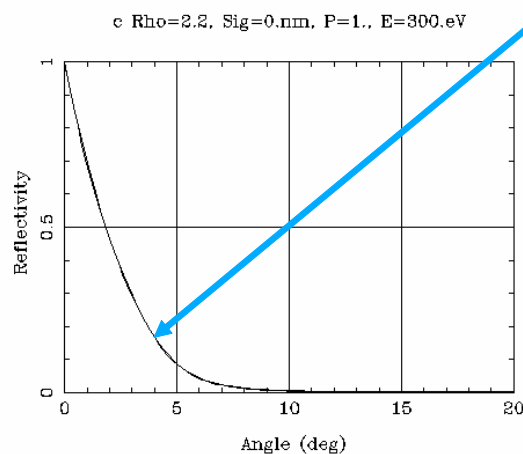
Suggested answers:

Calculations below indicate that : The attenuation length drops abruptly when you cross the C 1s edge for both angles. Next part was meant to focus on the minimum just above the C 1s edge, although OK if you looked at 50 eV and plotted that as a function of angle instead. Minimum depth just above the C 1s edge is very small, at only about 40 Å...not too much different from electron inelastic attenuation lengths.

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.



$\delta = 2.6 \times 10^{-3}$
 $\therefore \text{critical angle} = \sqrt{2\delta} = \sqrt{5.2 \times 10^{-3}} = 0.072 \text{ radians} = 4.1^\circ$



A subsidiary question that arises here is why the penetration depth increases strongly just below the C 1s edge for both incidence angles 5° and 15° , but 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 zero (!), thus increasing the amount of radiation that penetrates the surface.

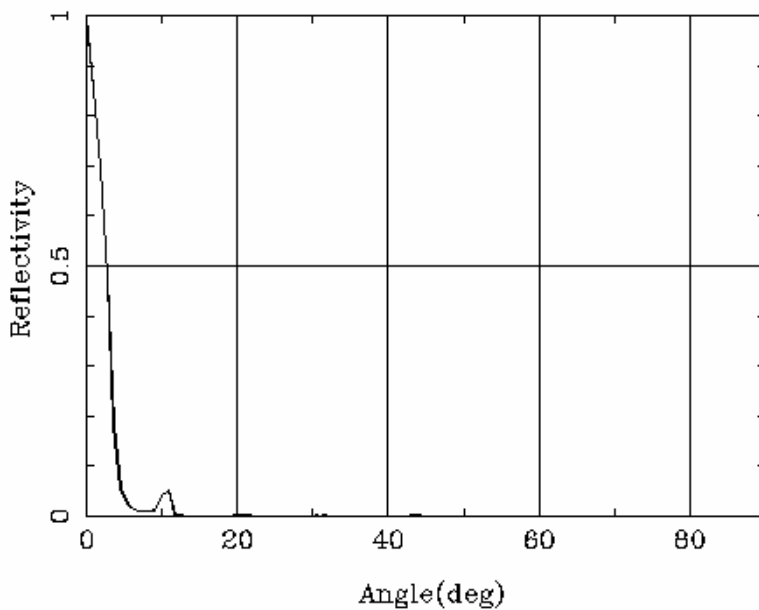
2) Calculate the reflectivity of a multilayer mirror made of bilayers of 16 Å B₄C and 24 Å W, and with 40 bilayers total, at 900 eV photon energy and as a function of incidence angle from zero upward. Assume that the top layer is B₄C, and that the substrate is SiO₂.

Do you see evidence of Bragg reflection at different orders ? Yes, 1st, 2nd, 3rd, and 4th orders are seen, with 1st by far the strongest.

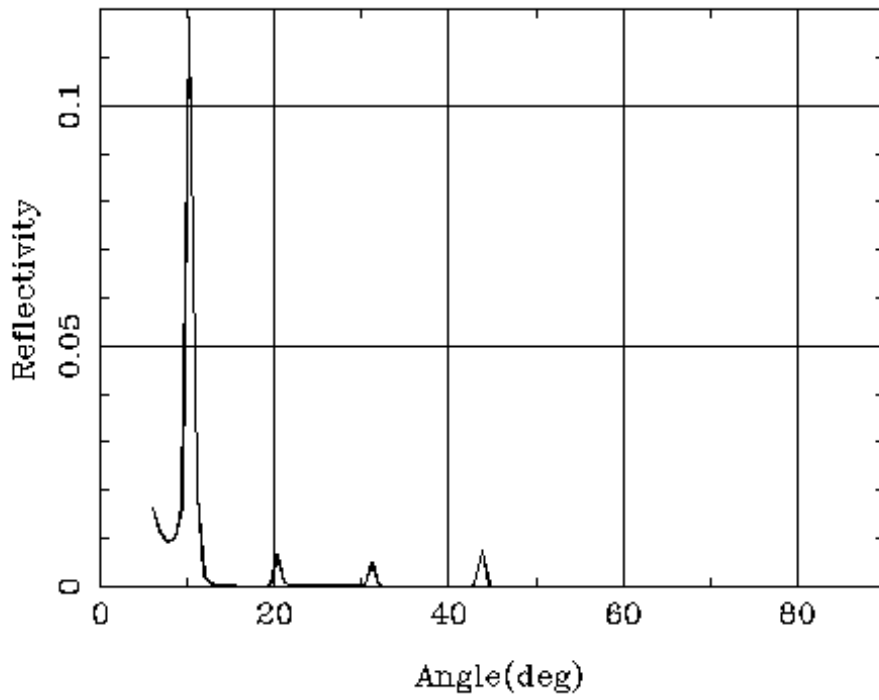
Can you relate these to Bragg reflections at specific orders from the multilayer ? Do this by plugging into Bragg formula: $n\lambda = 2D\sin\theta_n$ or $\theta_n = \arcsin[n\lambda/2D]$, which gives with $D = 40 \text{ \AA}$ and $\lambda = 12,398/E_{\text{photon}}(\text{eV}) = 13.77 \text{ \AA}$, $\theta_1 = 9.9^\circ$, $\theta_2 = 20.1^\circ$, $\theta_3 = 31.1^\circ$, $\theta_4 = 43.5^\circ$.

Is there evidence of the onset of total reflection ? Yes, by about 3 degrees, it has turned on to about 0.2.

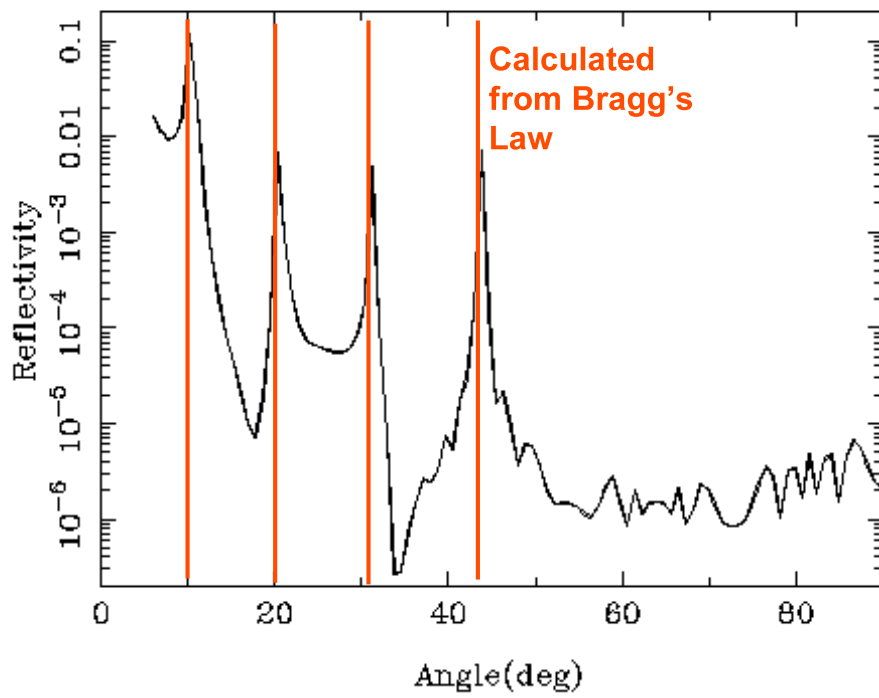
b4c/w d=4.nm s=0.nm N=40 at 900.eV, P=1.



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.

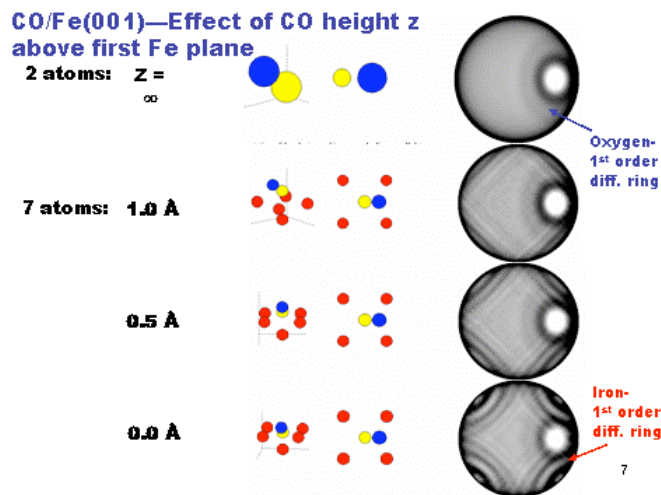


Photoelectron diffraction : <http://electron.lbl.gov/~edac/>—use either the European mirror (faster) or the U.S. mirror

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.

Beginning exercise for everyone—

- 1) 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 are given in slides, but C-O distance can be taken to be 1.18 Å and the body-centered cubic Fe lattice constant is 2.87 Å.



Plus choose one or more problems below for more independent work :

- 2) O 1s emission with 1253 eV excitation from O on Rh(111): O in a threefold hollow site, three Rh atoms, vary the height of the O to check sensitivity. Rh has a face-centered cubic crystal structure with $a = 3.90$ Å. See Osterwalder lecture slides for more details.

