X-ray Energy Spectroscopy (XES).

X-ray fluorescence as an analytical tool for element analysis is based on 3 fundamental parameters:

A. Specificity: In determining an x-ray emission energy E → certainty of presence of element A

B. Sensitivity: Given the presence of element A → what is the concentration of A.

C. Detection limit: The smallest amount or concentration that may be ascertained.

Characteristic emission, X-ray fluorescence

a) Simplified image of the atom as a spherical shell structure (the N. Bohr model, Fig.1)

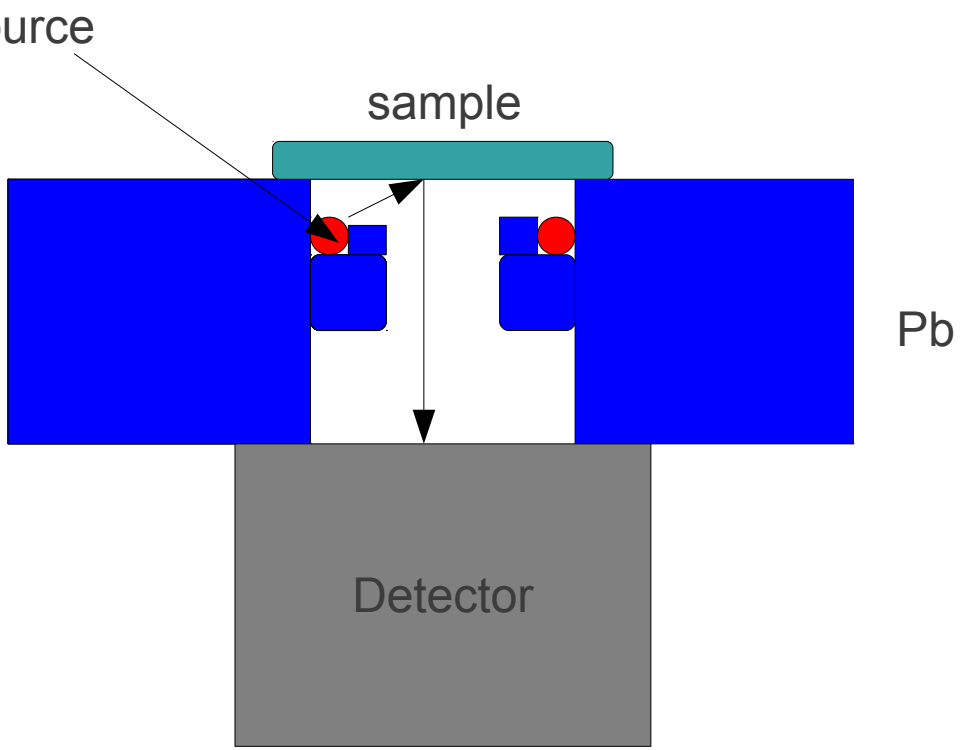
- electrons occupy shells labeled K(n=1), L(n=2)
- M(n=3), N(n=5), O(n=6) etc.; n-principal quantum number

b) Each electron shell has specific binding energy of the electron: K_{ab} , L_{lab} , etc. - absorption edge, the minimum energy required to lift an electron free. Characteristic energy (b.e.) $\leftrightarrow$ Z

Cont. of XES

c) Fluorescencs, or the generation of secondary radiation from an atom after removal of an electron out of its shell – excitation of the atom → emission of electromagnetic radiation $E\gamma = E_i - E_f$ where i and f are the initial and final energies of the elektron undergoing the transition.

This aspect forms the basis for x-ray energy spectroscopy .



Schematic representation of radioisotope excitation system with direct irradiator

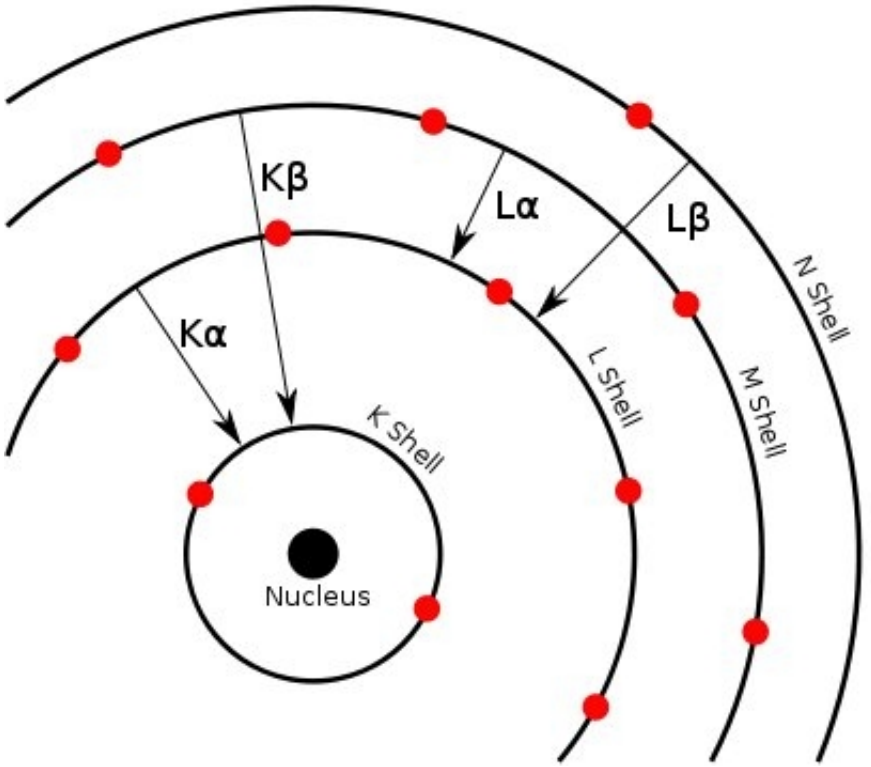
Four basic quantum numbers:

The first, n, describes the electron shell, or energy level. The value of ranges from 1 to "n", where "n" is the shell containing the outermost electron of that atom. For example, in cesium (Cs), the outermost valence electron is in the shell with energy level 6, so an electron in cesium can have an value from 1 to 6.

The second, l, describes the subshell (0 = s orbital, 1 = p orbital, 2 = d orbital, 3 = f orbital, etc.). The value of l ranges from 0 to n-1. This is because the first p orbital (l=1) appears in the second electron shell (n=2), the first d orbital (l=2) appears in the third shell (n=3), and so on. A quantum number beginning in 3,0,... describes an electron in the s orbital of the third electron shell of an atom.

The third, m_l, describes the specific orbital within that subshell.The values m_l range from -l to l. The s subshell (l=0) contain only one orbital, and therefore the m_l of an electron in an s subshell will always be 0. The p subshell (l=1) contains three orbitals, so the m_l of an electron in a p subshell will be -1, 0, or 1. The d subshell: 5 orbitals etc..

The fourth, m_s, describes the spin of the electron within that orbital. Because an orbital never contains more than two electrons, m_s will be either ½ or -½ , corresponding with "spin" and "opposite spin".



Atomic model, showing electron transitions that may follow electron vacancies.

Characteristic X-ray transitions

- K-series
- $K_{\alpha 1} = K - L_{III}$
- $K_{\alpha 2} = K - L_{II}$
- $K_{\beta 1} = K - M_{III}$
- $K_{\beta 3} = K - M_{II}$
- $K_{\beta 2} = K - M_{II,III}$

- L-series
- $L_{\alpha 1} = L_{III} - M_{V}$
- $L_{\alpha 2} = L_{III} - M_{IV}$
- $L_{\beta 1} = L_{II} - M_{IV}$

Radiationless transitions, the Auger effect, the Fluerescence Yield, some complications ..

- This is an internal atomic process that reduces the characteristic x-ray output or yield relative to predictions from photoelectric (p-e) cross sections.
- If a K-shell vacancy has been created the x-ray photon that follows is energetic enough to create vacancies by ejecting electrons from higher shells in the same atom (next Fig). In this case, 2 vacancies are created in the L-shell, as secondary internal p-e absorption ejects an L electron – known as an Auger electron. Barring subsequent Auger processes in still higher shells, the net result will only be the emission of L and M x-rays.

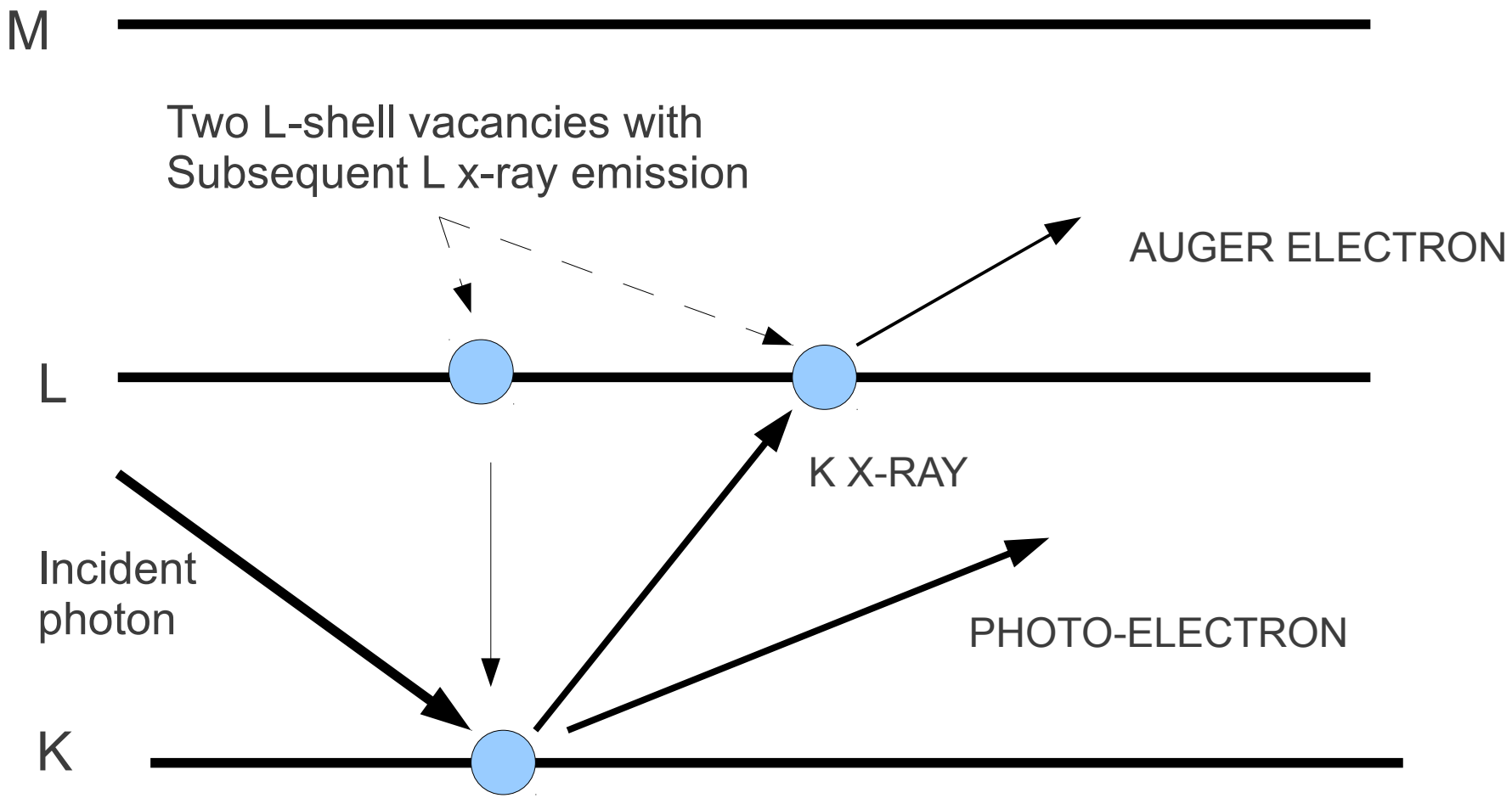
- This competitive effect to characteristic x-ray emission introduces a factor termed fluorescence yield ω , which may be defined as the ratio of emitted x-rays to the number of primary vacancies created. It is a function both of atomic number, and of the location (shell) of initial vacancy.

- Another complication of XES spectra is Elastic Scattering – process where photons of the fluorescing radiation are scattered by atomic electrons that are so tightly bound to the atom that no ionization or excitation is possible. The collision is, therefore, effectively with the atom as an entity – with no energy loss ! The Z dependence of elastic scatter is approximately as Z^2 in the region of interest for XES analysis.

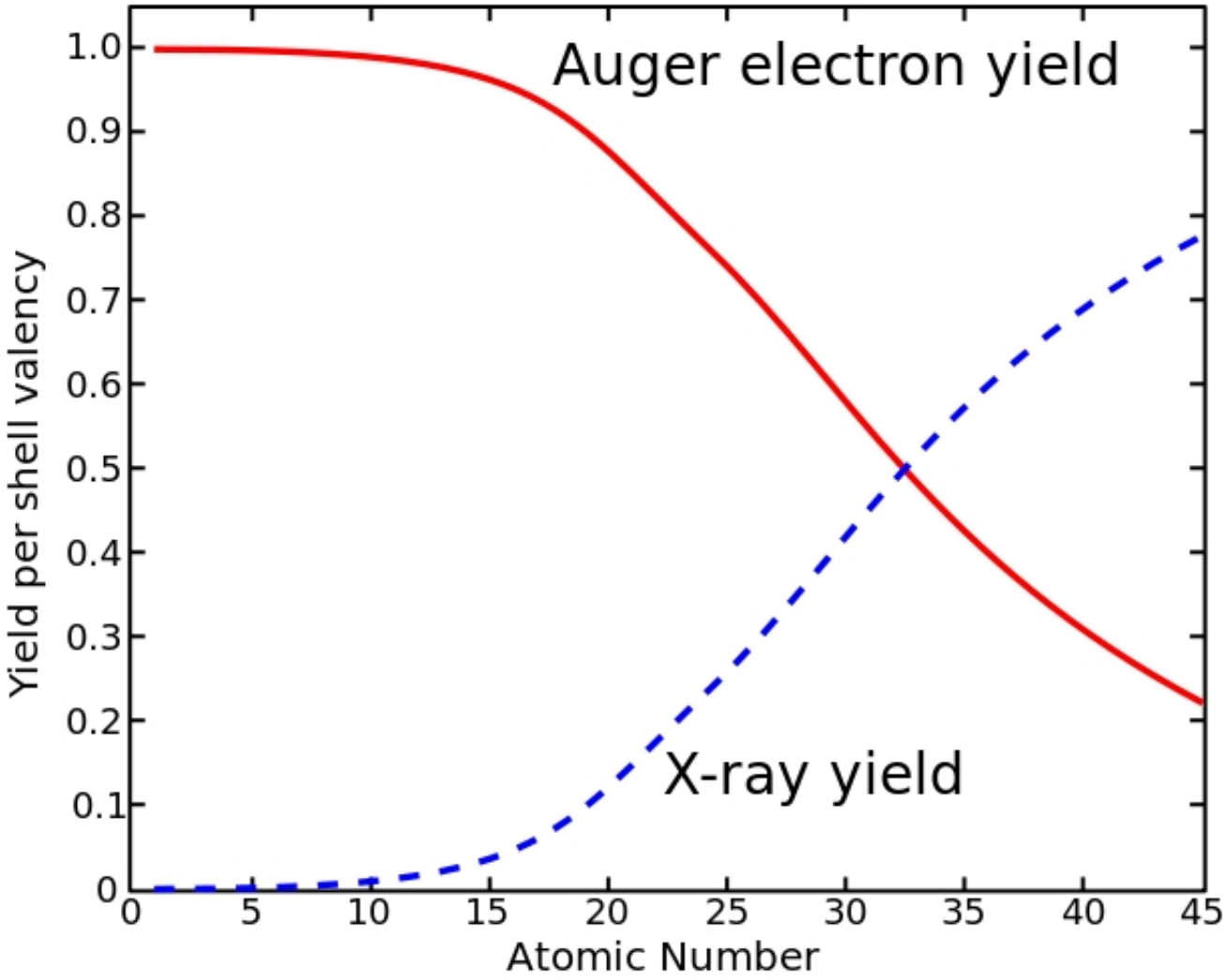
- The importance of the inelastic sctatter to the practical analysis is connected to the appearance of sctattered photons of lower energy than the incident photon beam (well separated for e.g. ^{241}Am when the ~60 keV elastic and ~49 keV inelastic scattering are clearly visible, see Fig.17)

The Escape Peak – another effect related to the detector efficiency

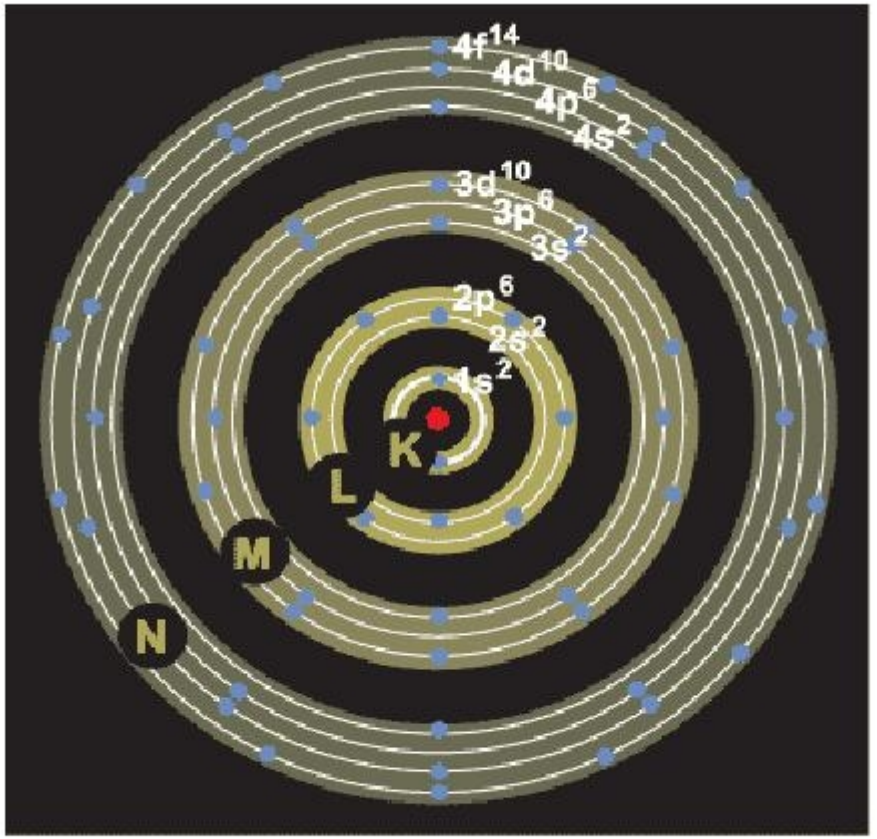
- The energy transfer in the detector is in part through photo-electric absorption, creating Si or Ge x-rays which are being reabsorbed.
- Si escape energy is E-1.74 keV
- Ge more serious problem E-9.97($K_{\alpha 1}$)



Schematic representation of the Auger Effect KLL



Fluorescence and Auger electron yields as a function of atomic number for K shell vacancies. Auger transitions (red curve) are more probable for lighter elements, while X-ray yield (dotted blue curve) becomes dominant at higher atomic numbers. Similar plots can be obtained for L and M shell transitions.



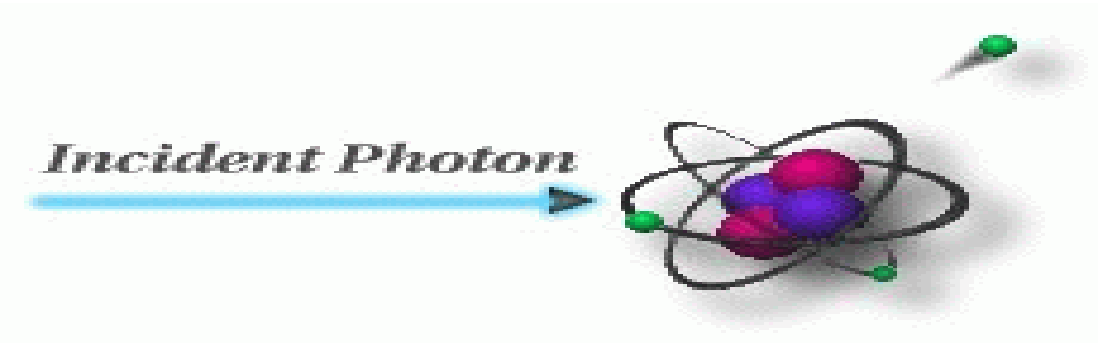
$2(2l+1)$

2 for s; l=0
6 for p; l=1
10 for d; l=2
14 for f; l=3

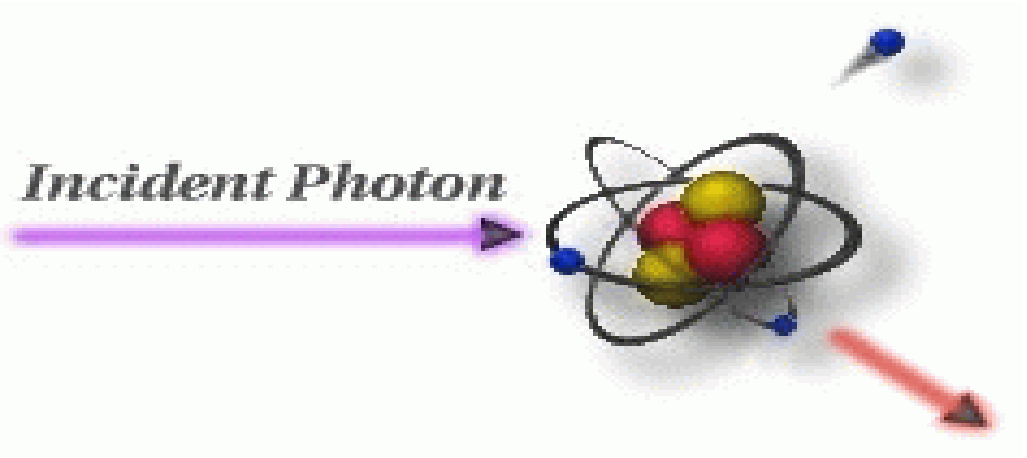
Example: $_{60}Nd \rightarrow 1s^2, 2p^6 2s^2, 3d^{10} 3p^6 3s^2, 4f^{14} 4d^{10} 4p^6 4s^2$

There are at least 4 modes through which electromagnetic radiations interact with atom: i.e., photoelectric absorption, Compton scattering (inelastic scattering), elastic scattering and pair production.

Photoelectric (PE) absorption of x-rays occurs when the x-ray photon is absorbed, resulting in the ejection of electrons from the outer shell of the atom, and hence the ionization of the atom. Subsequently, the ionized atom returns to the neutral state with the emission of an x-ray characteristic of the atom. This subsequent emission of lower energy photons is generally absorbed and does not contribute to (or hinder) the image making process. Photoelectron absorption is the dominant process for x-ray absorption up to energies of about 500 KeV. Photoelectron absorption is also dominant for atoms of high atomic numbers.

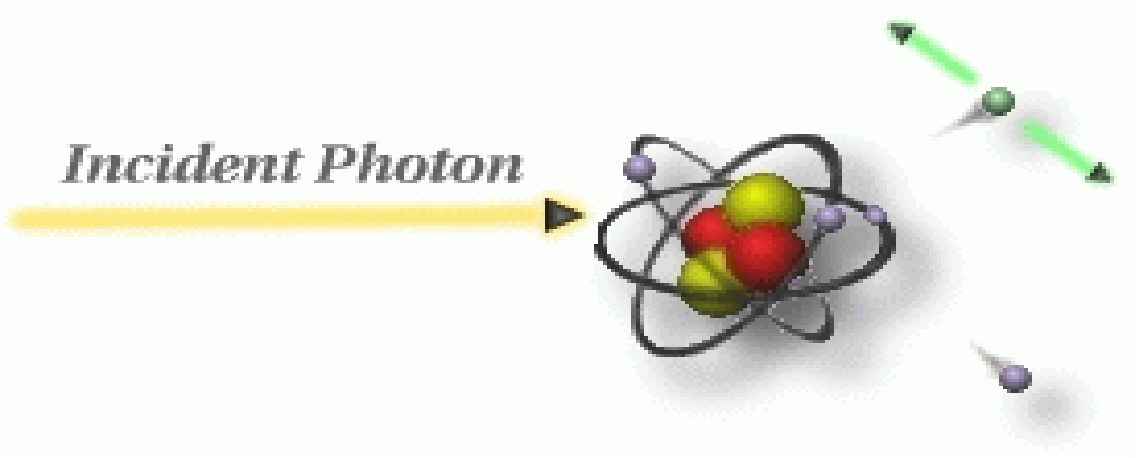


Compton scattering (C) occurs when the incident x-ray photon is deflected from its original path by an interaction with an electron. The electron gains energy and is ejected from its orbital position. The x-ray photon loses energy due to the interaction but continues to travel through the material along an altered path. Since the scattered x-ray photon has less energy, it, therefore, has a longer wavelength than the incident photon. The event is also known as incoherent scattering because the photon energy change resulting from an interaction is not always orderly and consistent. The energy shift depends on the angle of scattering and not on the nature of the scattering medium.



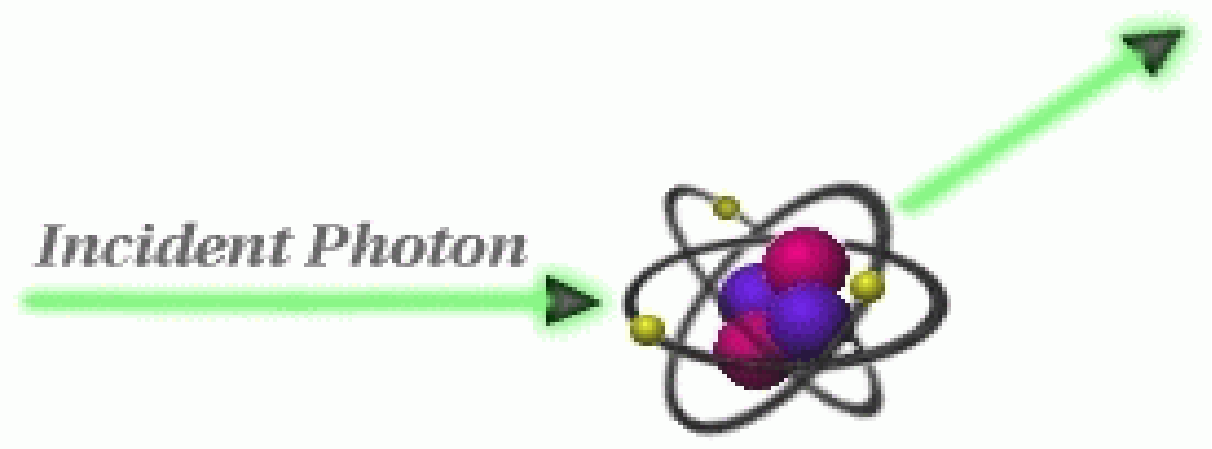
Compton-Incoherent or Inelastic σ ~ Z (compton escape continuum -detector effect)

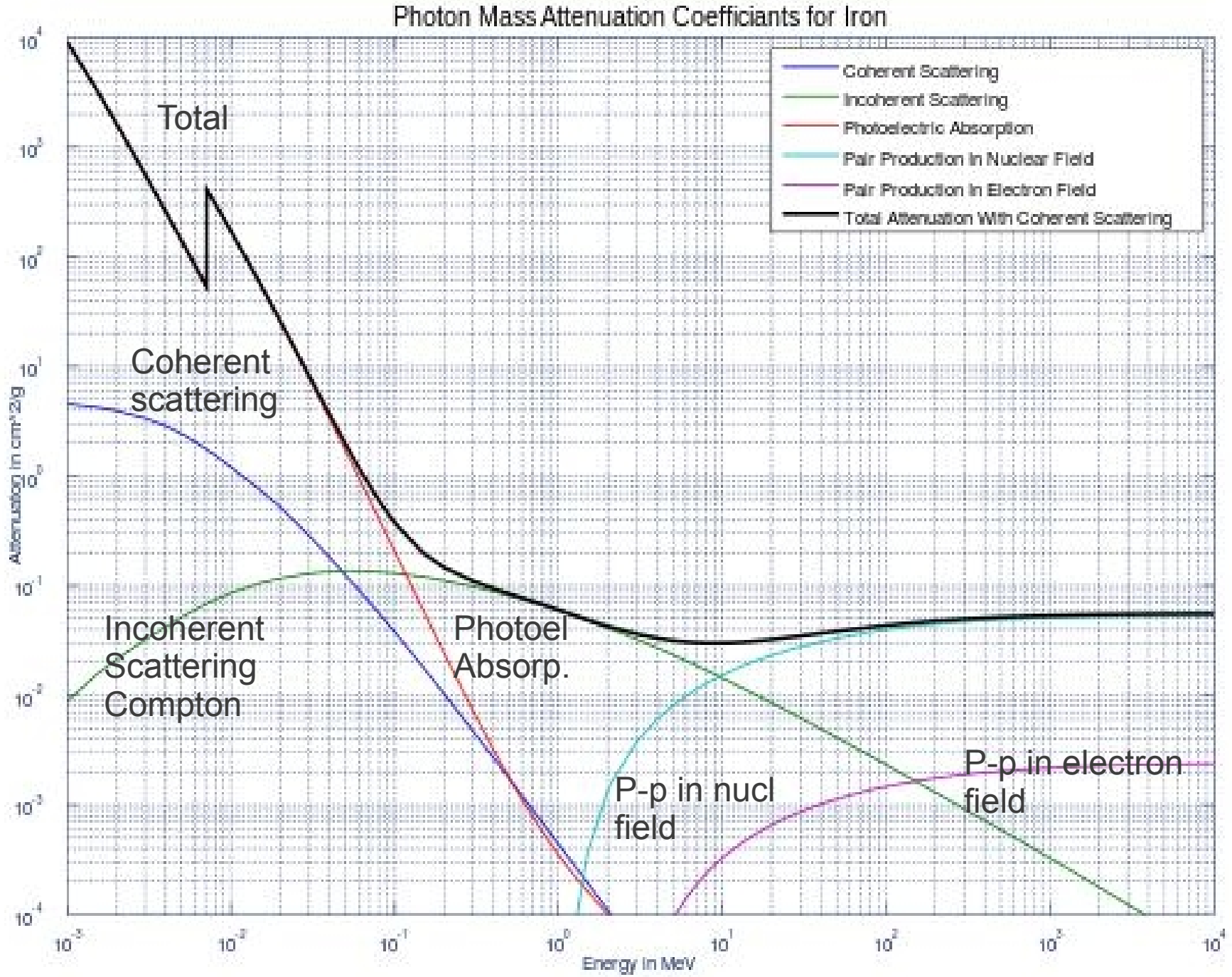
Pair production (PP) can occur when the x-ray photon energy is greater than 1.02 MeV, but really only becomes significant at energies around 10 MeV. Pair production occurs when an electron and positron are created with the annihilation of the x-ray photon. Positrons are very short lived and disappear (positron annihilation) with the formation of two photons of 0.51 MeV energy. Pair production is of particular importance when high-energy photons pass through materials of a high atomic number.

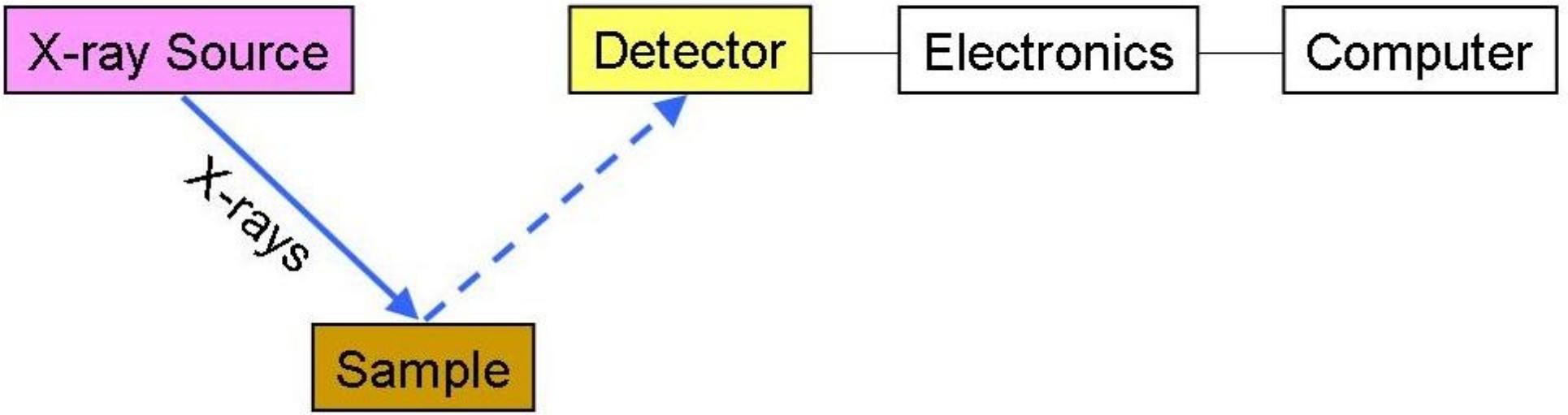


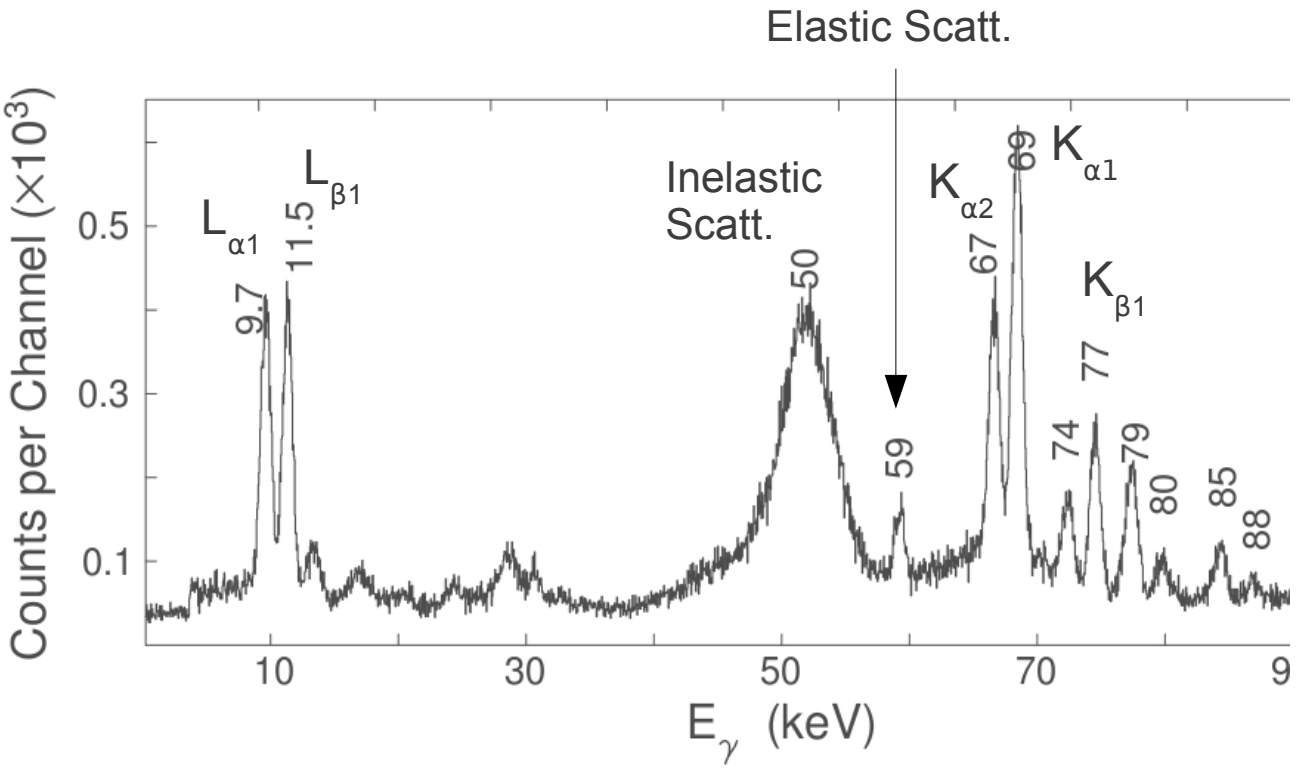
Elastic scattering of γ-rays and X-rays by atoms

Thomson scattering (R), also known as Rayleigh, **coherent**, or classical scattering, occurs when the x-ray photon interacts with the whole atom so that the photon is scattered with no change in internal energy to the scattering atom, nor to the x-ray photon. Thomson scattering is never more than a minor contributor to the absorption coefficient. The scattering occurs without the loss of energy. Scattering is mainly in the forward direction.




Photon Mass Attenuation Coefficiants for Iron
Coherent Scattering
Incoherent Scattering
Photoelectric Absorption
Pair Production in Nuclear Field
Pair Production in Electron Field
Total Attenuation With Coherent Scattering
Total
Coherent scattering
Incoherent Scattering Compton
Photoel Absorp.
P-p in nucl field
P-p in electron field
Attenuation in cm^2/g
Energy in MeV


X-ray Source
Detector
Electronics
Computer
X-rays
Sample



Typical scattering spectrum of 59.9 keV photons by the Au target through ~ 130^{o}.
Most intensive K and L X-ray energies of Au element are marked.

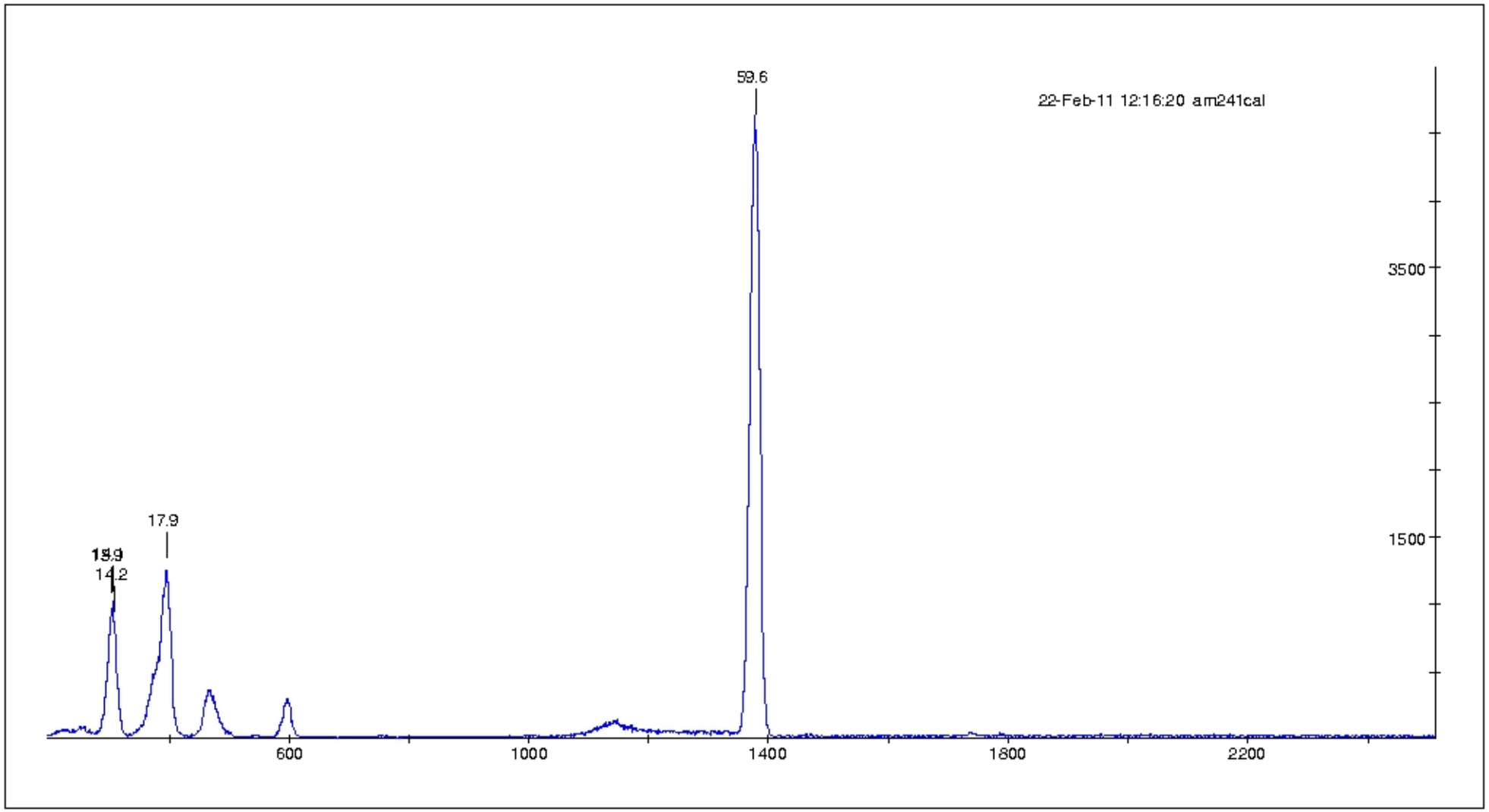

59.6
22-Feb-11 12:16:20 am241cal
3500
1500
17.9
14.2
600
1000
1400
1800
2200

Table 7a. X-ray Energies and Intensities (per 100 K-Shell Vacancies)

	$_{5}$B	$_{6}$C	$_{7}$N	$_{8}$O	$_{9}$F	$_{10}$Ne	$_{11}$Na	$_{12}$Mg	$_{13}$Al	$_{14}$Si	$_{15}$P	$_{16}$S	$_{17}$Cl	$_{18}$Ar	$_{19}$K
$K_{\alpha 1}$	**0.183** 0.11 5	**0.277** 0.19 8	**0.392** 0.35 14	**0.525** 0.55 22	**0.677** 0.9 4	**0.849** 1.20 12	**1.041** 1.53 16	**1.254** 2.0 2	**1.487** 2.6 3	**1.740** 3.3 3	**2.010** 4.1 4	**2.308** 5.0 5	**2.622** 6.1 6	**2.957** 7.3 7	**3.314** 8.5 9
$K_{\alpha 2}$	**0.183** 0.056 23	**0.277** 0.09 4	**0.392** 0.17 7	**0.525** 0.28 11	**0.677** 0.43 17	**0.848** 0.60 6	**1.041** 0.77 8	**1.254** 1.00 10	**1.486** 1.29 13	**1.739** 1.64 17	**2.009** 2.04 21	**2.307** 2.49 25	**2.621** 3.0 3	**2.955** 3.6 4	**3.311** 4.3 4
$K_{\beta 1}$									**1.554** 0.0155 16	**1.836** 0.056 6	**2.136** 0.122 12	**2.464** 0.229 23	**2.816** 0.38 4	**3.190** 0.58 6	**3.590** 0.79 8
$K_{\beta 3}$									**1.554** 0.0079 8	**1.836** 0.028 3	**2.136** 0.062 6	**2.464** 0.116 12	**2.816** 0.192 20	**3.190** 0.30 3	**3.590** 0.40 4
$L_{\beta 1}$														**0.251** 0.011 3	**0.296** 0.013 4
$L_{\beta 3}$														**0.310** 0.0038 13	**0.359** 0.0050 17
$L_{\beta 4}$														**0.310** 0.0024 9	**0.359** 0.0010 5

	$_{20}$Ca	$_{21}$Sc	$_{22}$Ti	$_{23}$V	$_{24}$Cr	$_{25}$Mn	$_{26}$Fe	$_{27}$Co	$_{28}$Ni	$_{29}$Cu	$_{30}$Zn	$_{31}$Ga	$_{32}$Ge	$_{33}$As	$_{34}$Se
$K_{\alpha 1}$	**3.692** 9.8 4	**4.091** 11.3 5	**4.511** 12.8 6	**4.952** 14.5 7	**5.415** 16.4 7	**5.899** 18.3 8	**6.404** 20.2 9	**6.930** 22.1 10	**7.478** 24.0 11	**8.048** 26.0 12	**8.639** 28.0 10	**9.252** 29.8 11	**9.886** 31.3 11	**10.544** 32.7 12	**11.222** 34.1 12
$K_{\alpha 2}$	**3.688** 4.93 22	**4.086** 5.68 25	**4.505** 6.4 3	**4.945** 7.3 3	**5.405** 8.3 4	**5.888** 9.3 4	**6.391** 10.2 5	**6.915** 11.2 5	**7.461** 12.2 6	**8.028** 13.3 6	**8.616** 14.3 5	**9.225** 15.2 6	**9.855** 16.1 6	**10.508** 16.8 6	**11.182** 17.6 6
$K_{\beta 1}$	**4.013** 1.02 5	**4.461** 1.22 6	**4.932** 1.42 6	**5.427** 1.64 7	**5.947** 1.84 8	**6.490** 2.14 10	**7.058** 2.40 11	**7.649** 2.65 12	**8.265** 2.88 13	**8.905** 3.10 14	**9.572** 3.39 12	**10.264** 3.70 13	**10.982** 3.98 14	**11.726** 4.25 15	**12.496** 4.54 16
$K_{\beta 2}$												**10.366** 0.0314 11	**11.101** 0.097 4	**11.864** 0.194 7	**12.652** 0.323 12
$K_{\beta 3}$	**4.013** 0.519 23	**4.461** 0.62 3	**4.932** 0.72 3	**5.427** 0.84 4	**5.947** 0.94 4	**6.490** 1.09 5	**7.058** 1.23 6	**7.649** 1.36 6	**8.265** 1.48 7	**8.905** 1.59 7	**9.572** 1.74 8	**10.260** 1.90 7	**10.975** 2.05 7	**11.720** 2.19 8	**12.490** 2.34 8
$K_{\beta 5}$							**7.108** 0.00127 7	**7.706** 0.00188 11	**8.329** 0.00264 15	**8.977** 0.00365 21	**9.651** 0.00504 25	**10.350** 0.0063 3	**11.074** 0.0078 4	**11.826** 0.0095 5	**12.601** 0.0116 6
$L_{\alpha 1}$		**0.396** 0.026 7	**0.452** 0.063 16	**0.511** 0.12 3	**0.572** 0.19 5	**0.637** 0.26 7	**0.704** 0.33 8	**0.776** 0.41 10	**0.851** 0.50 13	**0.929** 0.60 15	**1.012** 0.65 13	**1.098** 0.70 14	**1.188** 0.81 16	**1.282** 0.87 17	**1.379** 0.98 20
$L_{\alpha 2}$		**0.396** 0.0028 7	**0.452** 0.0070 18	**0.511** 0.013 3	**0.572** 0.021 5	**0.637** 0.029 7	**0.704** 0.037 9	**0.776** 0.045 11	**0.851** 0.056 14	**0.929** 0.066 17	**1.012** 0.072 15	**1.098** 0.077 16	**1.188** 0.090 18	**1.282** 0.096 19	**1.379** 0.108 22
$L_{\beta 1}$	**0.350** 0.016 4	**0.400** 0.020 5	**0.458** 0.050 12	**0.518** 0.096 24	**0.581** 0.15 4	**0.648** 0.20 5	**0.717** 0.25 6	**0.791** 0.31 8	**0.868** 0.34 9	**0.949** 0.39 10	**1.035** 0.42 11	**1.125** 0.46 12	**1.219** 0.49 12	**1.317** 0.52 13	**1.420** 0.58 15
$L_{\beta 3}$	**0.412** 0.0062 19	**0.468** 0.0075 23	**0.529** 0.009 3	**0.590** 0.010 3	**0.652** 0.012 4	**0.720** 0.014 4	**0.792** 0.016 5	**0.866** 0.018 5	**0.940** 0.020 6	**1.022** 0.021 6	**1.107** 0.023 7	**1.195** 0.024 7	**1.294** 0.025 7	**1.386** 0.027 8	**1.492** 0.029 9
$L_{\beta 4}$	**0.412** 0.0039 12	**0.468** 0.0048 15	**0.529** 0.0056 17	**0.590** 0.0067 20	**0.652** 0.0079 24	**0.720** 0.009 3	**0.792** 0.010 3	**0.866** 0.012 4	**0.940** 0.013 4	**1.022** 0.014 4	**1.107** 0.015 5	**1.191** 0.016 5	**1.286** 0.016 5	**1.380** 0.018 5	**1.486** 0.019 6
$L_{\beta 6}$		**0.402** 0.0017 4	**0.456** 0.0018 5	**0.513** 0.0022 6		**0.640** 0.0023 6	**0.708** 0.0022 6	**0.779** 0.0022 6	**0.855** 0.0022 6		**1.020** 0.0021 4	**1.114** 0.0027 5	**1.212** 0.0033 7	**1.315** 0.0038 8	**1.424** 0.0045 9
$L_{\gamma 3}$												**1.297** 0.0012 4	**1.412** 0.0042 13	**1.524** 0.0047 15	**1.648** 0.0051 16
L_{η}		**0.353** 0.020 5	**0.401** 0.022 6	**0.454** 0.026 7	**0.510** 0.025 6	**0.568** 0.026 7	**0.628** 0.028 7	**0.693** 0.028 7	**0.760** 0.026 7	**0.831** 0.028 7	**0.907** 0.029 7	**0.984** 0.030 8	**1.068** 0.031 8	**1.155** 0.031 8	**1.245** 0.034 9
L_{l}		**0.348** 0.026 7	**0.395** 0.029 8	**0.446** 0.034 9	**0.500** 0.033 9	**0.556** 0.038 10	**0.615** 0.040 11	**0.678** 0.043 11	**0.743** 0.045 12	**0.811** 0.048 13	**0.884** 0.047 10	**0.957** 0.048 10	**1.037** 0.052 11	**1.120** 0.053 11	**1.204** 0.056 12

	$_{35}$Br	$_{36}$Kr	$_{37}$Rb	$_{38}$Sr	$_{39}$Y	$_{40}$Zr	$_{41}$Nb	$_{42}$Mo	$_{43}$Tc	$_{44}$Ru	$_{45}$Rh	$_{46}$Pd	$_{47}$Ag	$_{48}$Cd	$_{49}$In
$K_{\alpha 1}$	**11.924** 35.6 13	**12.651** 36.8 13	**13.395** 38.0 14	**14.165** 39.1 14	**14.958** 40.1 14	**15.775** 41.0 12	**16.615** 41.8 12	**17.479** 42.6 12	**18.367** 43.3 12	**19.279** 44.0 12	**20.216** 44.6 13	**21.177** 45.1 13	**22.163** 45.6 13	**23.174** 46.1 13	**24.210** 45.3 13
$K_{\alpha 2}$	**11.878** 18.4 7	**12.598** 19.0 7	**13.336** 19.7 7	**14.098** 20.3 7	**14.883** 20.9 8	**15.691** 21.4 6	**16.521** 21.9 6	**17.374** 22.4 6	**18.251** 22.8 6	**19.150** 23.2 7	**20.074** 23.5 7	**21.020** 23.9 7	**21.990** 24.2 7	**22.984** 24.5 7	**24.002** 24.5 7
$K_{\alpha 3}$													**21.708** 0.00100 4	**22.693** 0.00115 4	**23.702** 0.00135 5
$K_{\beta 1}$	**13.292** 4.84 17	**14.111** 5.12 19	**14.961** 5.39 19	**15.836** 5.63 20	**16.738** 5.89 21	**17.667** 6.15 17	**18.623** 6.35 18	**19.607** 6.61 19	**20.619** 6.80 19	**21.657** 6.99 20	**22.724** 7.18 20	**23.819** 7.35 21	**24.943** 7.52 21	**26.095** 7.69 22	**27.276** 7.85 22
$K_{\beta 2}$	**13.469** 0.484 18	**14.311** 0.676 24	**15.185** 0.85 3	**16.085** 1.00 4	**17.013** 1.13 4	**17.969** 1.25 4	**18.952** 1.33 4	**19.965** 1.45 4	**21.005** 1.54 4	**22.074** 1.64 5	**23.172** 1.72 5	**24.299** 1.79 5	**25.455** 1.88 5	**26.644** 1.98 6	**27.863** 2.09 6
$K_{\beta 3}$	**13.284** 2.50 9	**14.104** 2.64 10	**14.952** 2.78 10	**15.825** 2.91 10	**16.726** 3.04 11	**17.653** 3.17 9	**18.607** 3.28 9	**19.590** 3.41 10	**20.599** 3.51 10	**21.634** 3.61 10	**22.699** 3.71 10	**23.791** 3.81 11	**24.912** 3.90 11	**26.060** 3.99 11	**27.238** 4.07 12
$K_{\beta 4}$							**18.982** 0.0010 5	**19.998** 0.0015 7	**21.042** 0.0023 11	**22.115** 0.0032 16	**23.217** 0.0043 21	**24.349** 0.006 3	**25.511** 0.007 3	**26.702** 0.008 4	**27.924** 0.010 5
$K_{\beta 5}$	**13.404** 0.0139 7	**14.231** 0.0162 8	**15.089** 0.0186 9	**15.971** 0.0215 11	**16.880** 0.0244 12	**17.816** 0.0275 12	**18.780** 0.0305 14	**19.771** 0.0341 15	**20.789** 0.0377 17	**21.836** 0.0418 19	**22.911** 0.0446 20	**24.013** 0.0496 22	**25.144** 0.0547 25	**26.304** 0.060 3	**27.493** 0.065 3
$KO_{2,3}$															**27.939** 0.0170 18
$L_{\alpha 1}$	**1.481** 1.09 22	**1.581** 1.20 24	**1.694** 1.3 3	**1.806** 1.4 3	**1.923** 1.5 3	**2.042** 1.66 25	**2.166** 1.8 3	**2.293** 1.9 3	**2.424** 2.0 3	**2.558** 2.1 3	**2.697** 2.3 3	**2.839** 2.4 4	**2.984** 2.5 4	**3.134** 2.6 4	**3.287** 2.8 4