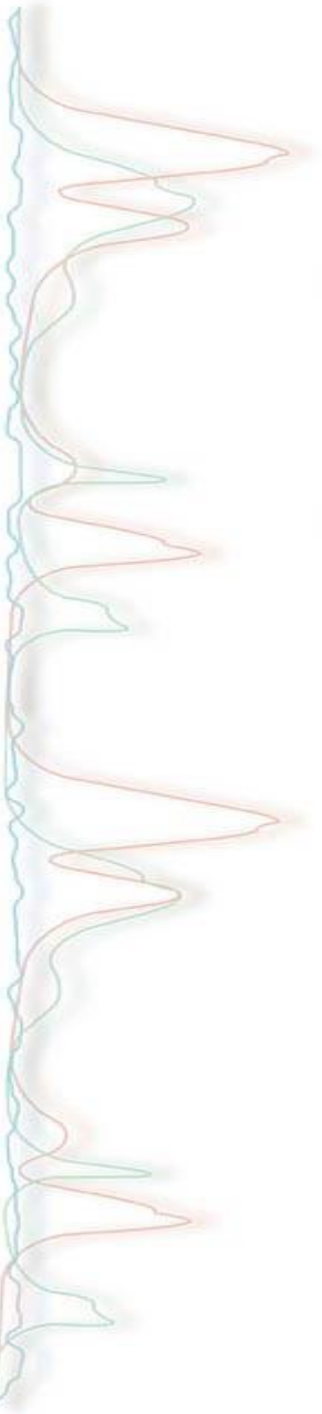


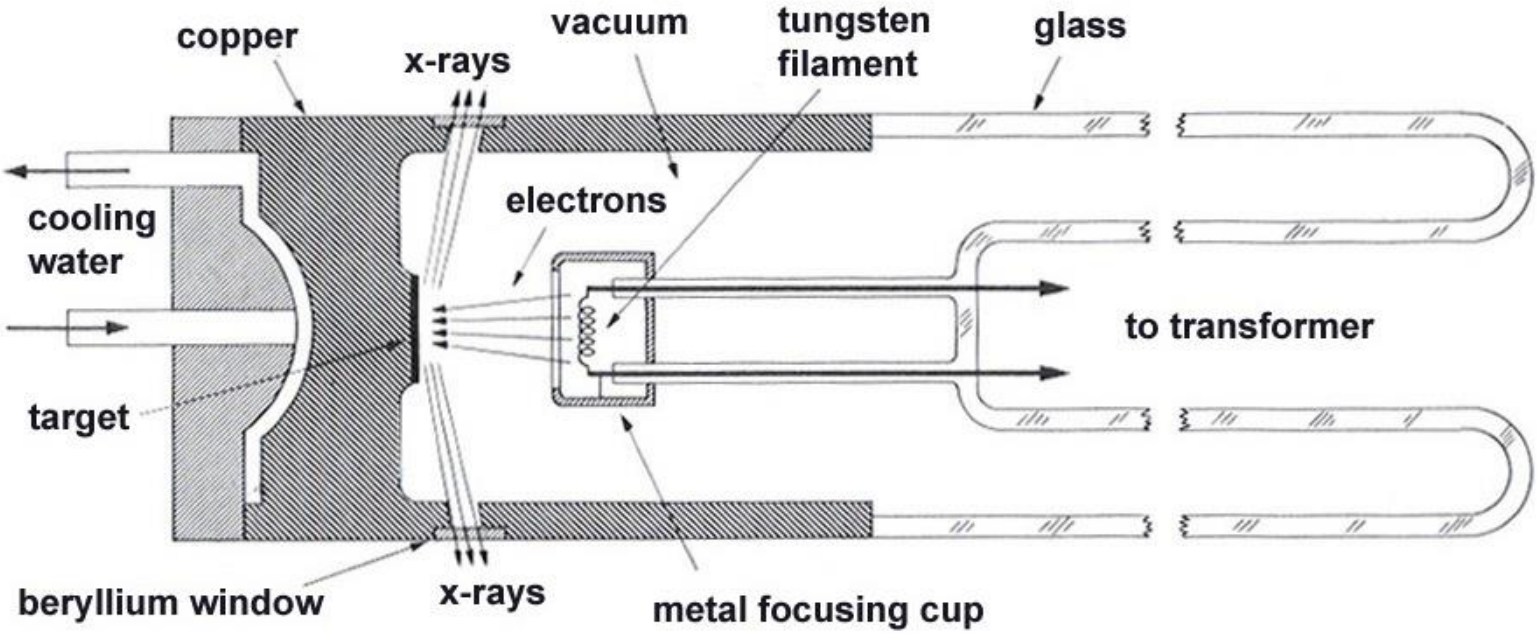
chem 5390

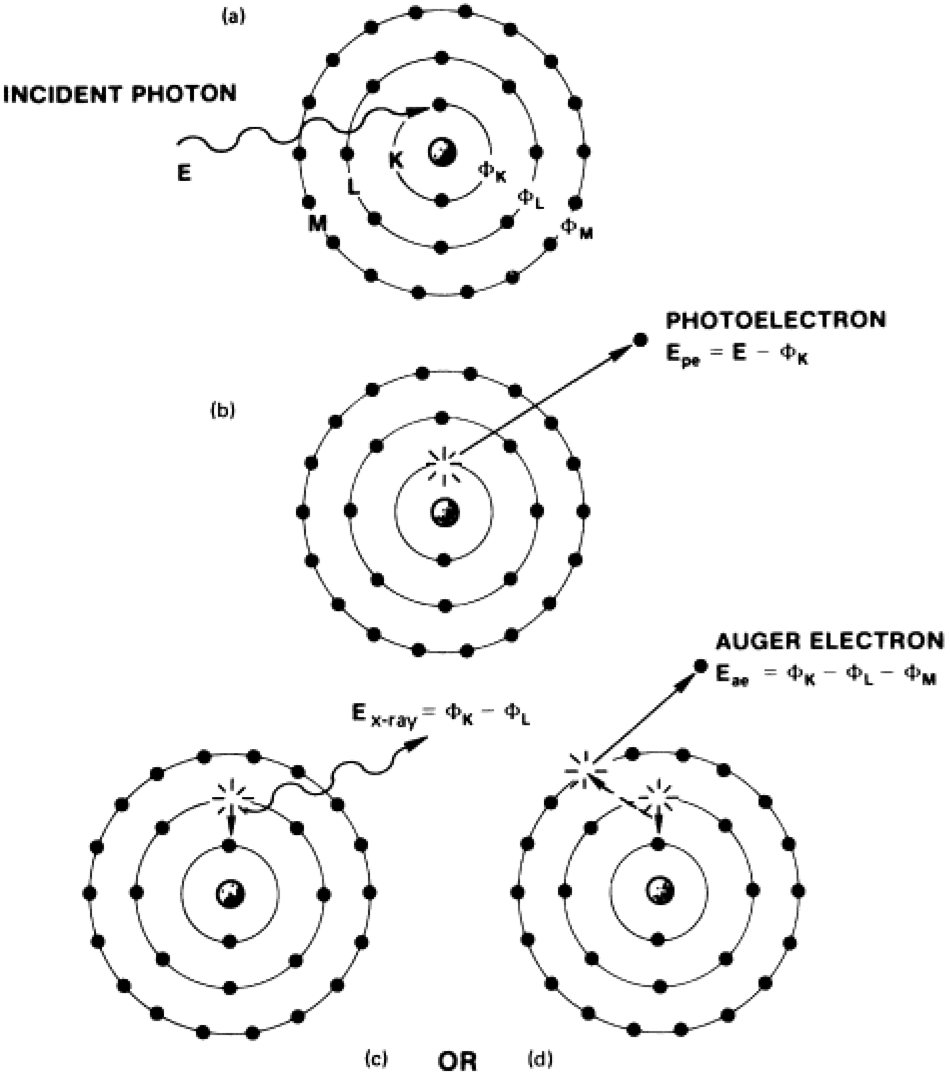
Advanced X-ray Analysis

LECTURE 4

Dr. Teresa D. Golden
University of North Texas
Department of Chemistry

Filament tube

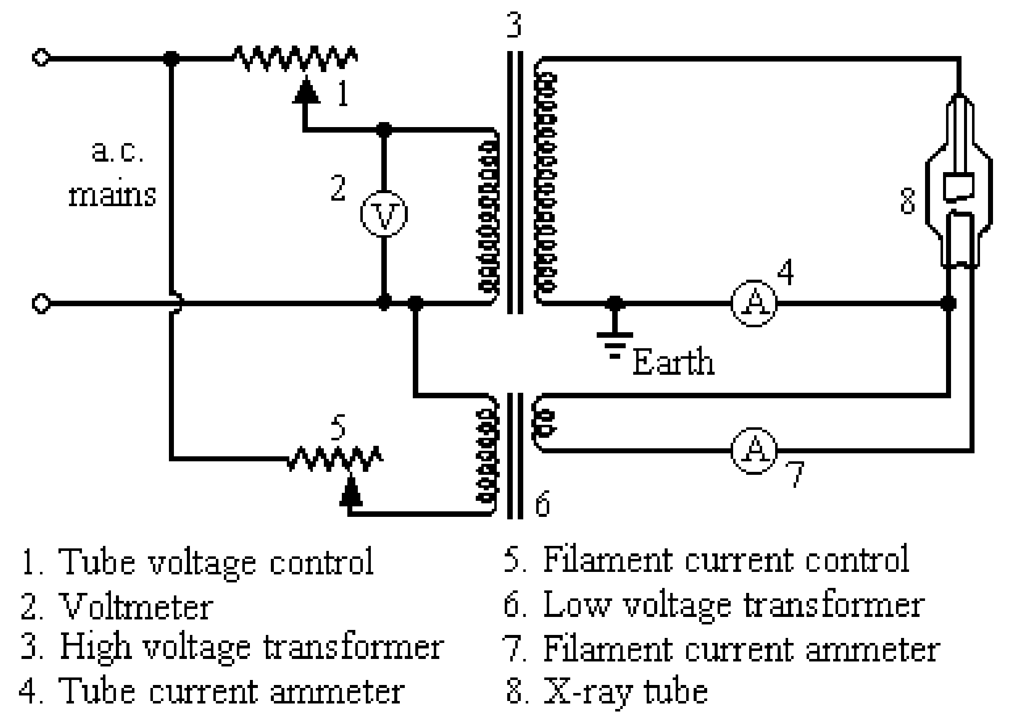



(a)
INCIDENT PHOTON
E
K
L
M
Φ_K
Φ_L
Φ_M
PHOTOELECTRON
$E_{pe} = E - \Phi_K$
(b)
AUGER ELECTRON
$E_{ae} = \Phi_K - \Phi_L - \Phi_M$
$E_{X\text{-}ray} = \Phi_K - \Phi_L$
(c)
OR
(d)

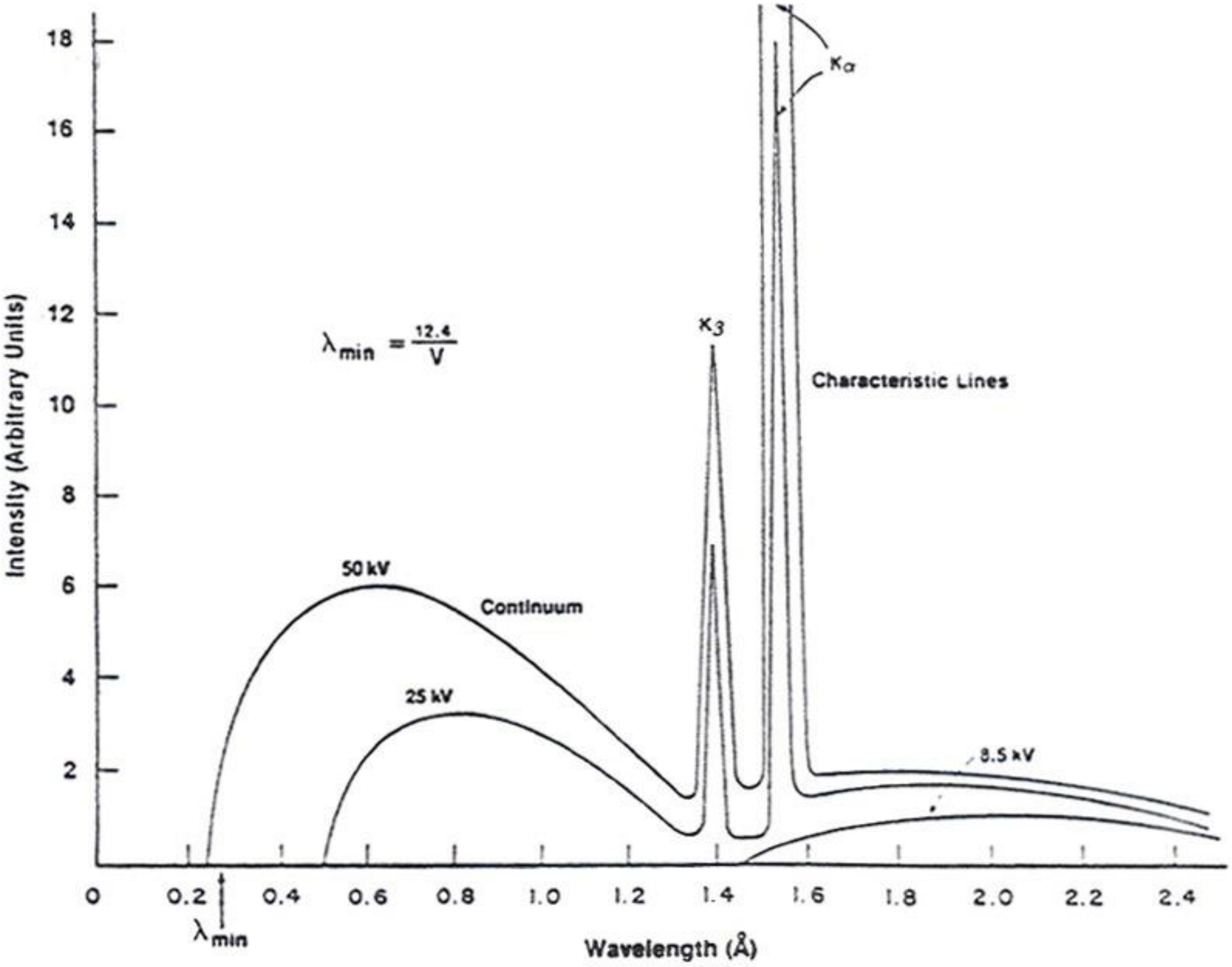
Production and Properties of X-rays

Generating X-rays for Diffraction

HV Power Supply



- In most systems, the anode (at top in 8) is kept at ground
- #2 (KV) and #7 (mA) are what is adjusted on the power supply with #1 and #5
- Our lab, only routinely adjust filament current (#5) from operating (35 mA) to “idle” (10 mA) levels


Intensity (Arbitrary Units)
18
16
14
12
10
8
6
4
2
$\lambda_{min} = \frac{12.4}{V}$
50 kV
Continuum
25 kV
Kβ
Kα
Characteristic Lines
8.5 kV
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
λ_{min}
Wavelength (Å)

Production and Properties of X-rays

Characteristics of Common Anode Materials

Material	At. #	$K\alpha_1$ (Å)	$K\alpha_2$ (Å)	Char Min (keV)	Opt kV	Advantages (Disadvantages)
Cr	24	2.290	2.294	5.98	40	High resolution for large d-spacings, particularly organics (High attenuation in air)
Fe	26	1.936	1.940	7.10	40	Most useful for Fe-rich materials where Fe fluorescence is a problem (Strongly fluoresces Cr in specimens)
Co	27	1.789	1.793	7.71	40	Useful for Fe-rich materials where Fe fluorescence is a problem
Cu	29	1.541	1.544	8.86	45	Best overall for most inorganic materials (Fluoresces Fe and Co $K\alpha$ and these elements in specimens can be problematic)
Mo	42	0.709	0.714	20.00	80	Short wavelength good for small unit cells, particularly metal alloys (Poor resolution of large d-spacings; optimal kV exceeds capabilities of most HV power supplies.)

Production and Properties of X-rays

Characteristic Wavelength values (in Å) for Common Anode Materials

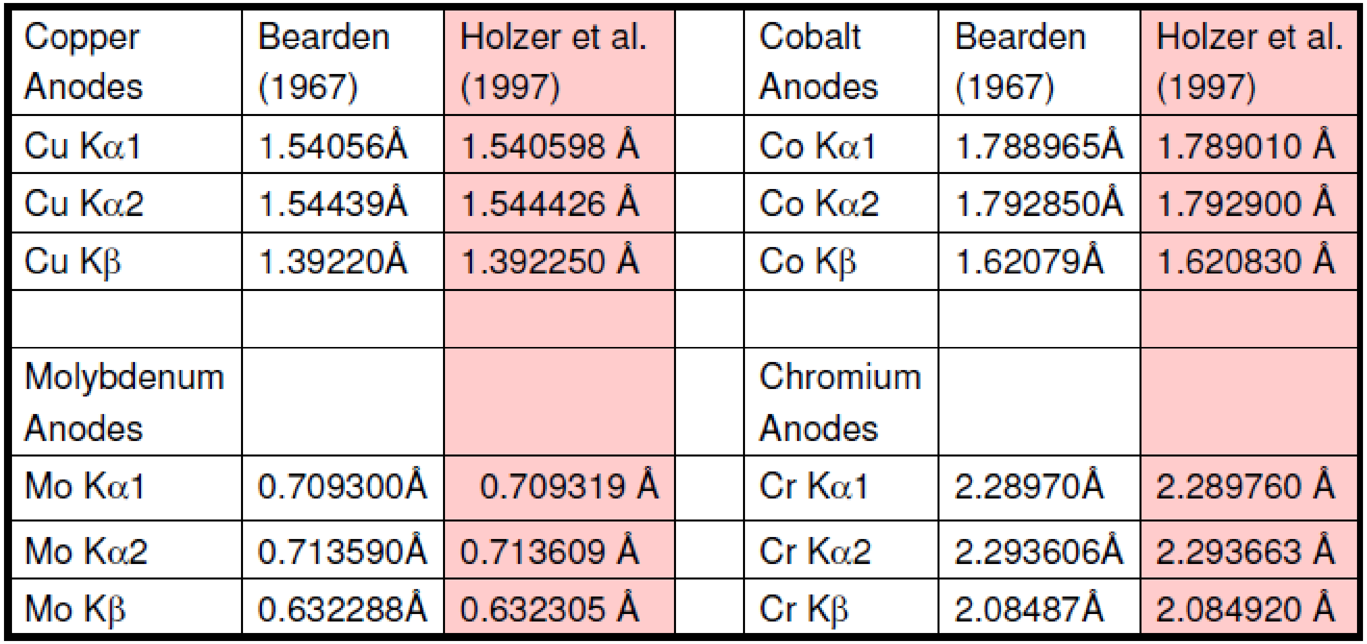
Anode	$K\alpha_1$ (100)	$K\alpha_2$ (50)	$K\beta$ (15)
Cu	1.54060	1.54439	1.39222
Cr	2.28970	2.29361	2.08487
Fe	1.93604	1.93998	1.75661
Co	1.78897	1.79285	1.62079
Mo	0.70930	0.71359	0.63229

*** Relative intensities are shown in parentheses**

Production and Properties of X-rays

B. Properties of X-rays

Wavelengths for X-Radiation are Sometimes Updated



Copper Anodes	Bearden (1967)	Holzer et al. (1997)		Cobalt Anodes	Bearden (1967)	Holzer et al. (1997)
Cu Kα1	1.54056Å	1.540598 Å		Co Kα1	1.788965Å	1.789010 Å
Cu Kα2	1.54439Å	1.544426 Å		Co Kα2	1.792850Å	1.792900 Å
Cu Kβ	1.39220Å	1.392250 Å		Co Kβ	1.62079Å	1.620830 Å
Molybdenum Anodes				Chromium Anodes		
Mo Kα1	0.709300Å	0.709319 Å		Cr Kα1	2.28970Å	2.289760 Å
Mo Kα2	0.713590Å	0.713609 Å		Cr Kα2	2.293606Å	2.293663 Å
Mo Kβ	0.632288Å	0.632305 Å		Cr Kβ	2.08487Å	2.084920 Å

Production and Properties of X-rays

Making Monochromatic X-rays

X-rays coming out of the tube will include the continuum, and the characteristic Kα1, Kα2, and Kβ radiations

A variety of methods may be used to convert this radiation into something effectively monochromatic for diffraction analysis:

- Use of a β filter
- Use of proportional detector and pulse height selection
- Use of a Si(Li) solid-state detector
- Use of a diffracted- or primary-beam monochromator

Production and Properties of X-rays

β Filters

There are two types of absorption of x-rays.

- -Mass absorption is linear and dependent on mass
- -Photoelectric absorption is based on quantum interactions and will increase up to a particular wavelength, then drop abruptly

By careful selection of the correct absorber, photoelectric absorption can be used to select a “filter” to remove most β radiation while “passing” most α radiation

Production and Properties of X-rays

B. Properties of X-rays

2. Characteristic X-ray spectrum

X-Ray Absorption and Fluorescence

When X-ray photons interact with matter, some of the photons are absorbed. Extent of absorption depends on the distance travelled through the substance.

One way to measure this is by using the proportionality constant, μ, also called the <u>linear absorption coefficient</u> of the substance.

μ/ρ is a constant for a given material and is called the <u>mass absorption coefficient</u>.

Production and Properties of X-rays

B. Properties of X-rays

2. Characteristic X-ray spectrum

X-Ray Absorption and Fluorescence

The interaction of x-rays with matter can be represented by plotting the mass absorption coefficient of a substance versus the wavelength of radiation.

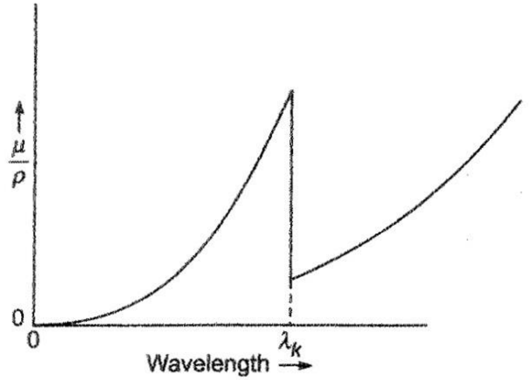


Fig. 3.9 X-ray absorption characteristics of an absorber (schematic)

The longer the wavelength of radiation, the greater is the amount of absorption. Shorter the wavelength, the greater the penetration power of the radiation.

Production and Properties of X-rays

B. Properties of X-rays

2. Characteristic X-ray spectrum

X-Ray Absorption and Fluorescence

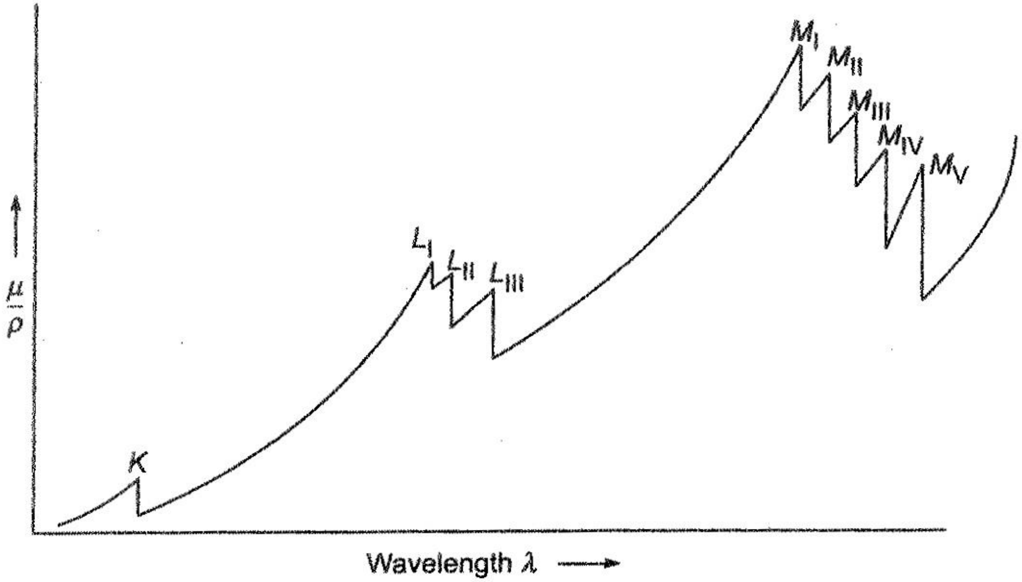


Fig. 3.10 (b) X-ray absorption characteristics (schematic)

Production and Properties of X-rays

B. Properties of X-rays

2. Characteristic X-ray spectrum

X-Ray Absorption and Fluorescence

Use the absorption edge of a material to “filter” x-rays or produce close to monochromatic radiation.

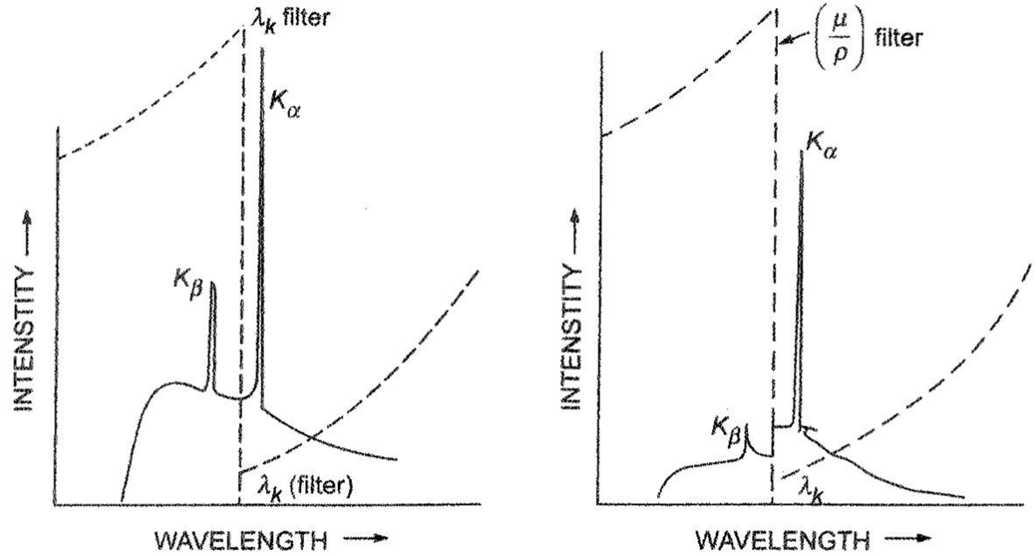


Fig. 3.12 Intensity versus wavelength before and after β-filtering (schematic)

Production and Properties of X-rays

β Filters for Common Anodes

Target	Kα (Å)	β-filter	Thickness (μm)	Density (g/cc)	% Kα	% Kβ
Cr	2.291	V	11	6.00	58	3
Fe	1.937	Mn	11	7.43	59	3
Co	1.791	Fe	12	7.87	57	3
Cu	1.542	Ni	15	8.90	52	2
Mo	0.710	Zr	81	6.50	44	1

Note: Thickness is selected for max/min attenuation/transmission Standard practice is to choose a filter thickness where the α : β is between 25:1 and 50:1

Production and Properties of X-rays

Discriminating with Electronics/Detectors

Pulse-height Discrimination

- Detector electronics are set to limit the energy of x-rays seen by the detector to a threshold level
- Effectively removes the most of the continuum and radiation produced by sample fluorescence
- Particularly effective combined with a crystal monochromator

“Tunable” Detectors

- Modern solid state detectors, are capable of extremely good energy resolution
- Can selectively “see” only Kα or Kβ energy
- No other filtration is necessary, thus signal to noise ratios can be extremely high
- Can negatively impact intensity of signal

Production and Properties of X-rays

Monochromators

Following the Bragg law, each component wavelength of a polychromatic beam of radiation directed at a single crystal of known orientation and d-spacing will be diffracted at a discrete angle

Monochromators make use of this fact to selectively remove radiation outside of a tunable energy range, and pass only the radiation of interest

- A filter selectively attenuates Kβ and has limited effect on other wavelengths of X-rays
- a monochromator selectively passes the desired wavelength and attenuates everything else.

Monochromators may be placed anywhere in the diffractometer signal path

Production and Properties of X-rays

Spectral Contamination in XRD

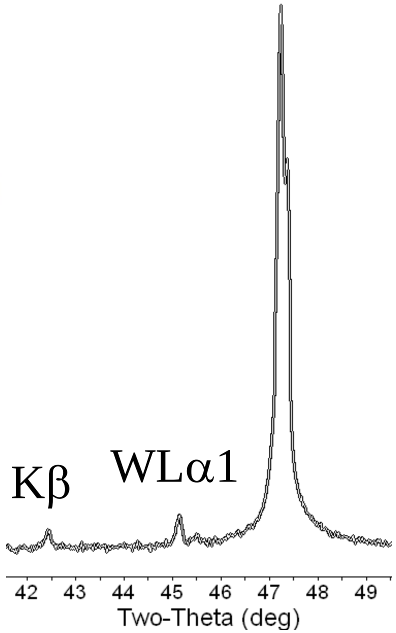
- The Kα1 & Kα2 doublet will almost always be present
    - Very expensive optics can remove the Kα2 line
    - Kα1 & Kα2 overlap heavily at low angles and are more separated at high angles

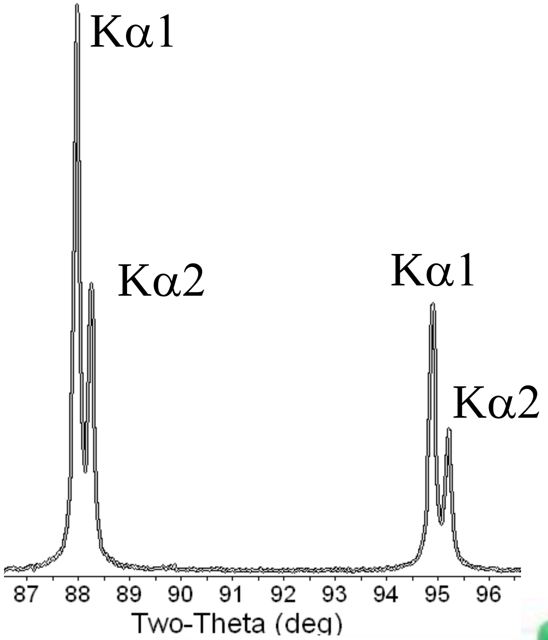
- W lines form as the tube ages: the W filament contaminates the target anode and becomes a new X-ray source

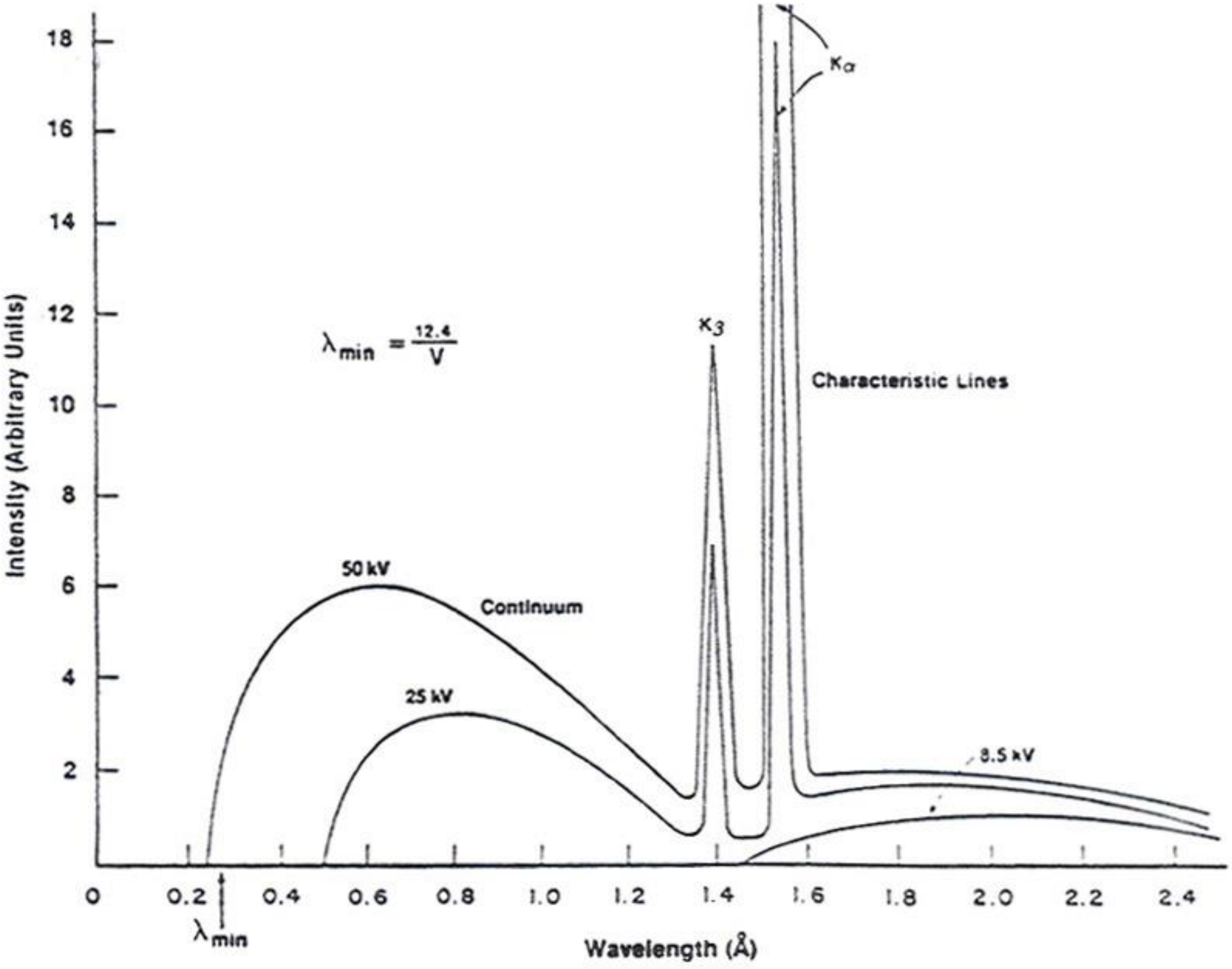
- W and Kβ lines can be removed with optics

Production and Properties of X-rays

Spectral Contamination in XRD

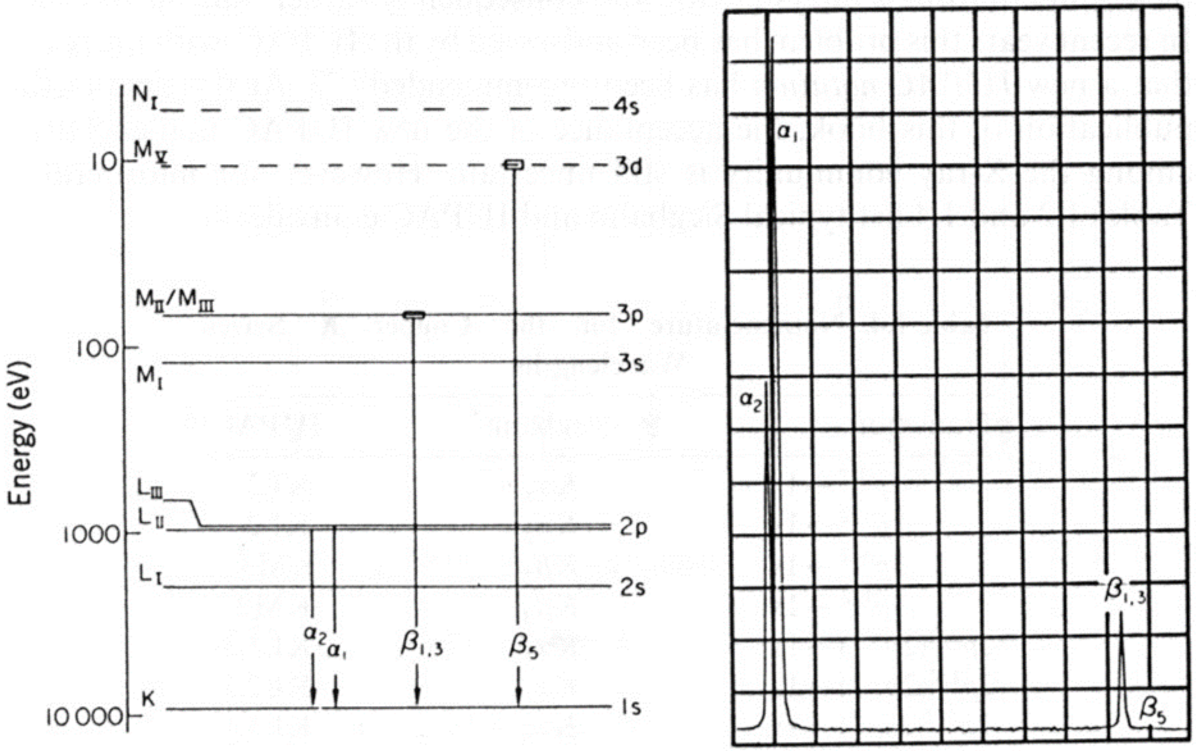





18
16
14
12
10
8
6
4
2
Intensity (Arbitrary Units)
$\lambda_{min} = \frac{12.4}{V}$
50 kV
Continuum
25 kV
Kβ
Kα
Characteristic Lines
8.5 kV
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
λ_{min}
Wavelength (Å)

Production and Properties of X-rays

The Copper K Spectrum



The copper *K*α spectrum.

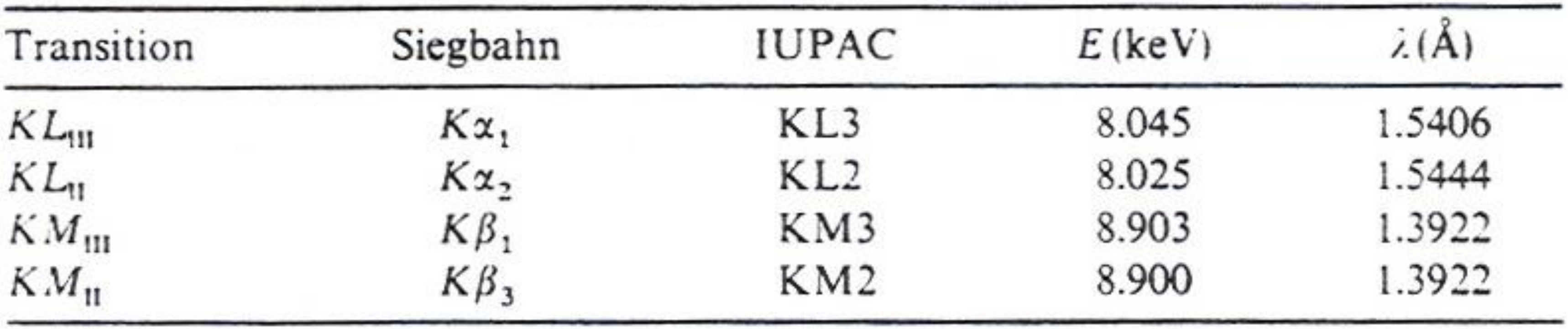
- The diagram at left shows the 5 possible Cu K transitions
- L to K “jumps:
  - **$K\alpha_1$ (8.045 keV, 1.5406Å)**
  - **$K\alpha_2$ (8.025 keV, 1.5444Å)**
- M to K
  - **$K\beta_1$ $K\beta_3$ (8.903 keV, 1.3922Å)**
  - **$K\ \beta_5$**

Production and Properties of X-rays

Siegbahn and IUPAC notations

Siegbahn notation is the original nomenclature system for x-ray wavelengths proposed by K.M. G. Seigbahn in the 1920s. However, there have been a number of lines observed later that have not been classified within this nomenclature, such as the M and N series.

IUPAC notation has been recommended but not widely adopted. This nomenclature is more systematic and simple.



Transition	Siegbahn	IUPAC	E (keV)	λ (Å)
KL_{III}	$K\alpha_1$	KL3	8.045	1.5406
KL_{II}	$K\alpha_2$	KL2	8.025	1.5444
KM_{III}	$K\beta_1$	KM3	8.903	1.3922
KM_{II}	$K\beta_3$	KM2	8.900	1.3922

Production and Properties of X-rays

B. Properties of X-rays

2. Characteristic X-ray spectrum

a. Selection Rules

There are a great number of transitions possible, however, in practice, x-ray spectra are fairly simple.

Three selection rules cover the allowed electron transitions:

- **$\Delta n \geq 1$ (change in principle quantum number) - transition between any shell is allowed.**
- **$\Delta l = 1$ (angular) - transition where $l=0$ is not allowed.**
- **ΔJ (or j) = 0 or 1 (angular and spin)**

Production and Properties of X-rays

B. Properties of X-rays

2. Characteristic X-ray spectrum

a. Selection Rules

n - principle quantum number

l - angular quantum number, if l= 0 (s), l = 1 (p), l = 2 (d)

J (j) - vector sum of the angular and spin quantum numbers.

J (or j) = l + m_s (or s)

m_s - spin quantum number, $\pm 1/2$

For the K shell; n = 1 and l = 0

For the L shell; n = 2 and l = 0, 1

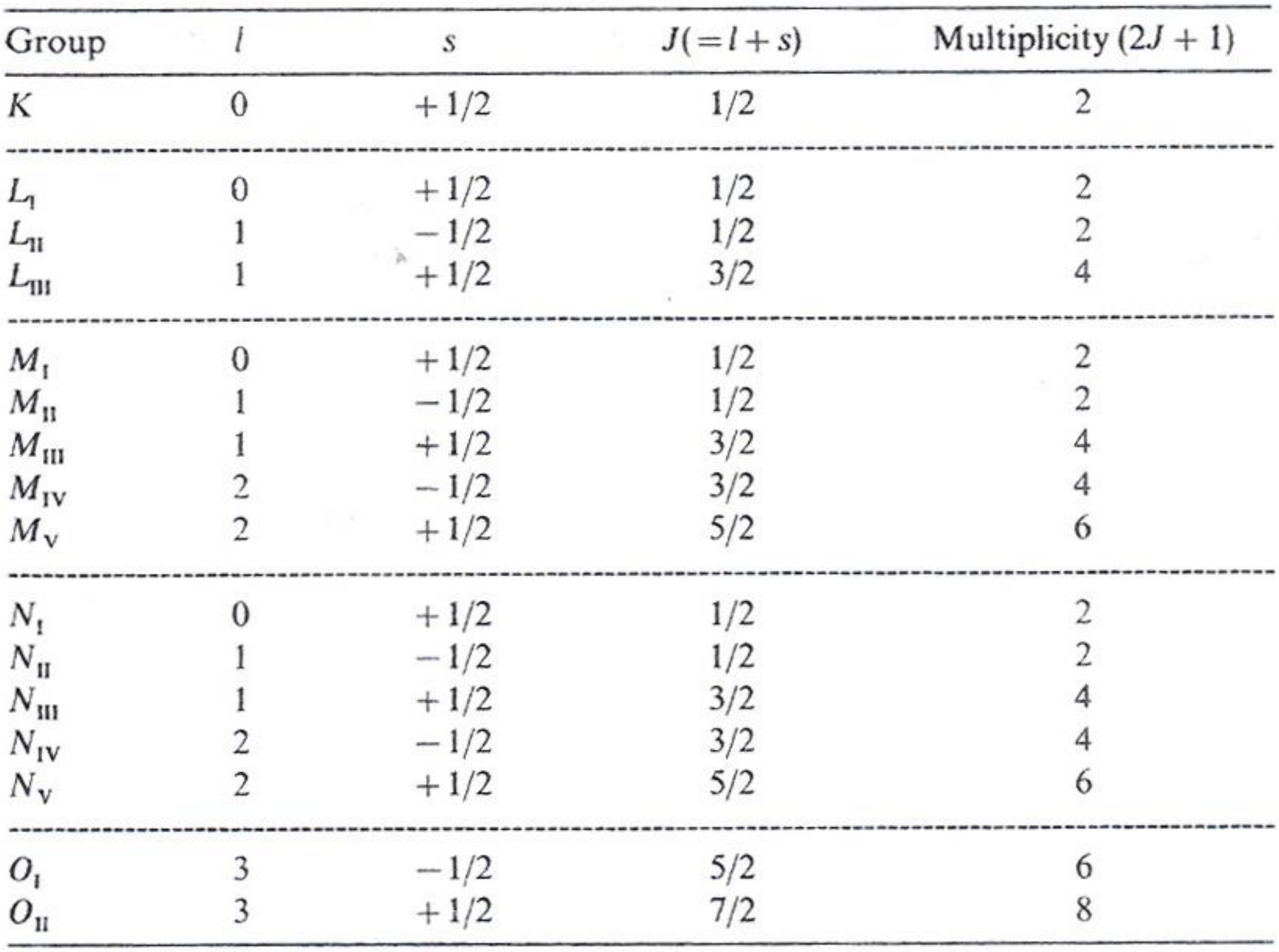
Production and Properties of X-rays

B. Properties of X-rays

2. Characteristic X-ray spectrum

a. Selection Rules

Subshell	n	l	m_s	j
L_I	2	0	+1/2	1/2
L_{II}	2	1	-1/2	1/2
L_{III}	2	1	+1/2	3/2



Group	l	s	$J(=l+s)$	Multiplicity $(2J+1)$
K	0	$+1/2$	1/2	2
L_{I}	0	$+1/2$	1/2	2
L_{II}	1	$-1/2$	1/2	2
L_{III}	1	$+1/2$	3/2	4
M_{I}	0	$+1/2$	1/2	2
M_{II}	1	$-1/2$	1/2	2
M_{III}	1	$+1/2$	3/2	4
M_{IV}	2	$-1/2$	3/2	4
M_{V}	2	$+1/2$	5/2	6
N_{I}	0	$+1/2$	1/2	2
N_{II}	1	$-1/2$	1/2	2
N_{III}	1	$+1/2$	3/2	4
N_{IV}	2	$-1/2$	3/2	4
N_{V}	2	$+1/2$	5/2	6
O_{I}	3	$-1/2$	5/2	6
O_{II}	3	$+1/2$	7/2	8

Construction of transition groups and number of electrons allowed in each state (Multiplicity).

Production and Properties of X-rays

B. Properties of X-rays

2. Characteristic X-ray spectrum

a. Selection Rules

If l =1 and J = 1/2, resulting states are $p^{1/2}$ (2 electrons)

If l= 1 and J = 3/2, resulting states are $p^{3/2}$ (4 electrons)

If l = 0 (i.e. L_{I}) K = 0, then $\Delta l = 0$ and L_{I} ---> K not allowed

Production and Properties of X-rays

B. Properties of X-rays

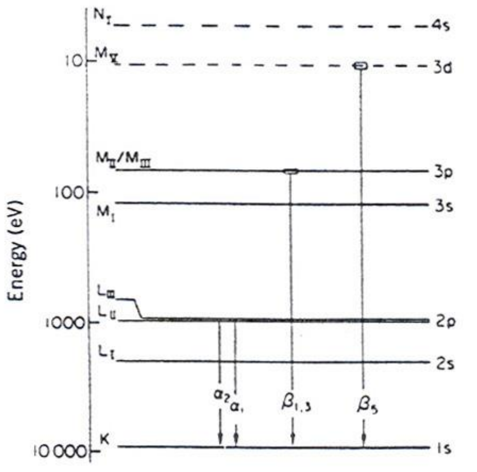
2. Characteristic X-ray spectrum

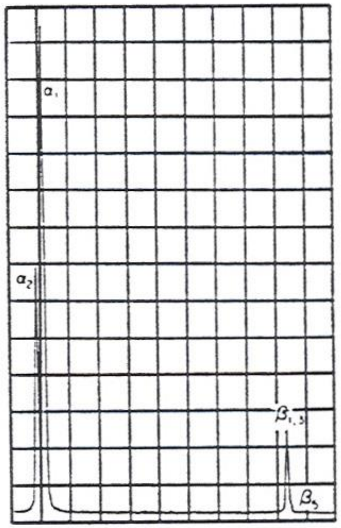
a. Selection Rules

K spectrum is simple for copper:
2 α lines from $2p^{1/2}$ ---> 1s and $2p^{3/2}$ ---> 1s
2 B lines from $3p^{1/2}$ ---> 1s and $3p^{3/2}$ ---> 1s

The relative intensity of these lines are:
$K_{\alpha1}$, $K_{\alpha2}$ > K_{B1}, $_{B3}$ > K_{B2}

For Cu, the intensity ratio is 5:1:0
For Mo, the intensity ratio is 3:1:0.3





Production and Properties of X-rays

B. Properties of X-rays

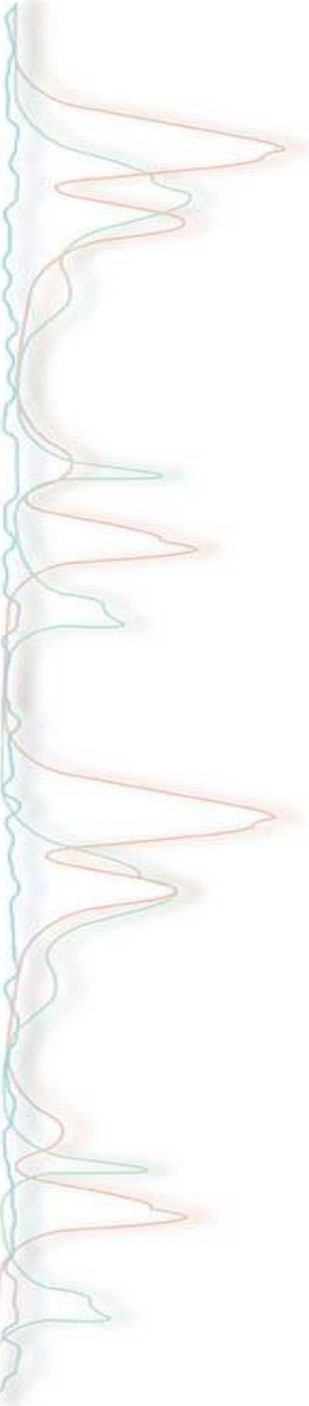
2. Characteristic X-ray spectrum

a. Selection Rules

The <u>relative intensity</u> of the <u>line pairs</u> can be predicted by a simple rule.

<u>Burger-Dorgelo rule</u> - the intensity ratio is equal to the number of electrons that may make the transition.

i.e for $K_{\alpha 1}$:$K_{\alpha 2}$ ---> there are 4 $p^{3/2}$ electrons for $K_{\alpha 1}$ and
2 $p^{1/2}$ electrons for $K_{\alpha 2}$
4:2 or 2:1 ratio



Transition	Siegbahn	IUPAC
$2p^{3/2} \rightarrow 1s$	$K\alpha_1$	KL3
$2p^{1/2} \rightarrow 1s$	$K\alpha_2$	KL2
$3p^{3/2} \rightarrow 1s$	$K\beta_1$	KM3
$3p^{1/2} \rightarrow 1s$	$K\beta_3$	KM2
$2p^{3/2}(2p^{-1}) \rightarrow 1s$	$K\alpha_3$	KL3,3
$2p^{1/2}(2p^{-1}) \rightarrow 1s$	$K\alpha_4$	KL2,3
$2p^{3/2}(2s^{-1}) \rightarrow 1s$	$K\alpha_5$	KL3,1
$2p^{3/2}(2s^{-1}) \rightarrow 1s$	$K\alpha_6$	KL2,1

Production and Properties of X-rays

B. Properties of X-rays

2. Characteristic X-ray spectrum

b. Nondiagram Lines

Other lines can occur outside of the selection rules by special ionization conditions - there are two categories of these types of lines:

forbidden transitions and satellites.

Production and Properties of X-rays

B. Properties of X-rays

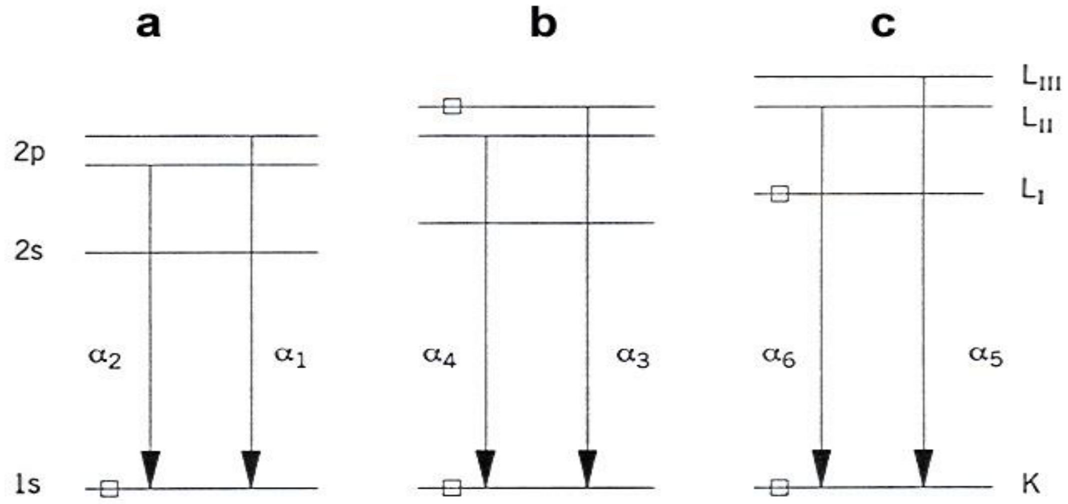
2. Characteristic X-ray spectrum

b. Nondiagram Lines

- Forbidden transitions - arise due to hybridization of outer orbitals (especially for transition metals).

Ex: Cu K spectrum has a weak K_{B5} from a 3d ---> 1s transition, this transition gives a $\Delta l = 2$, which is forbidden by selection rules. (this transition is extremely weak).

- Satellite lines - occur from transitions involving removal of more than one electron (dual ionization).

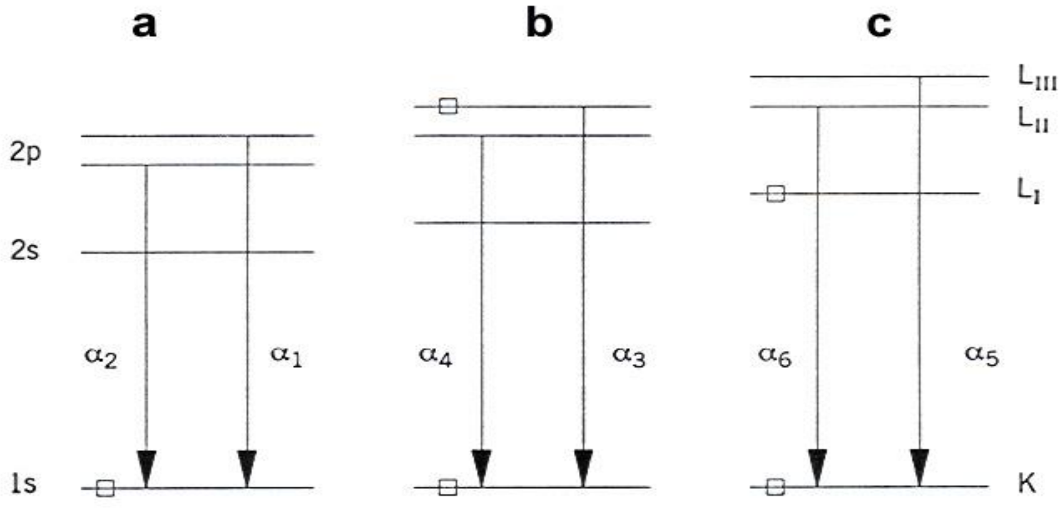


Selection rules allow:

$2p^{3/2} \longrightarrow 1s$

$2p^{1/2} \longrightarrow 1s$

a - is the normal situation for K vacancy giving $K_{\alpha 1}$ and $K_{\alpha 2}$.

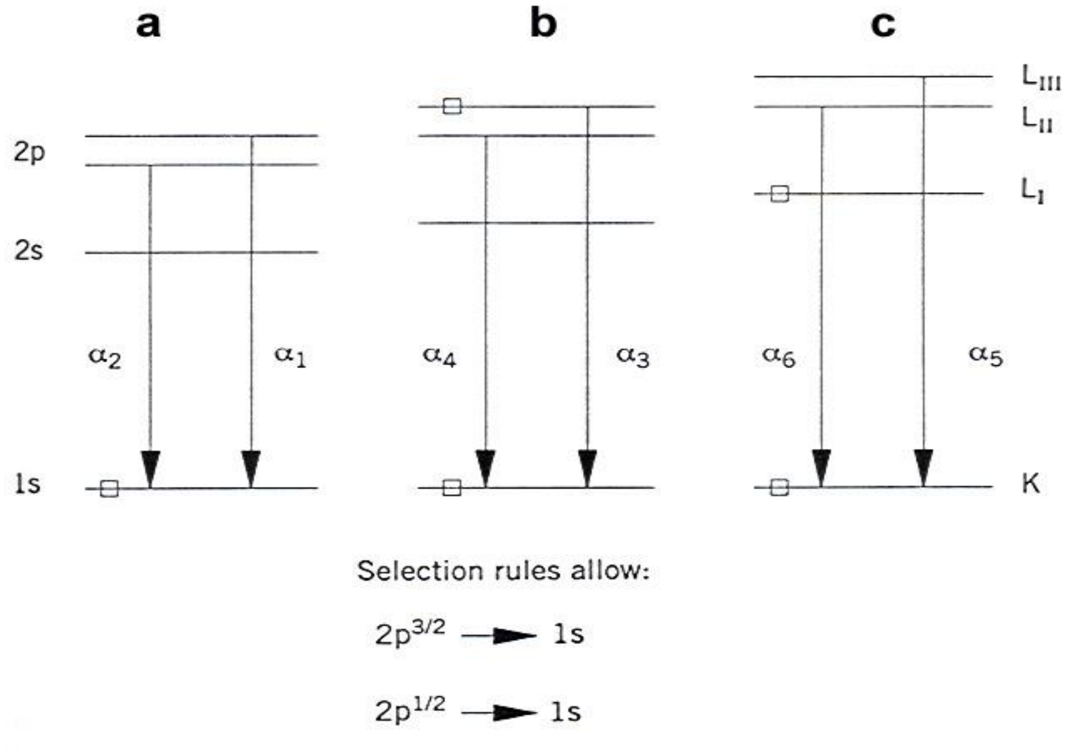


Selection rules allow:

$2p^{3/2} \longrightarrow 1s$

$2p^{1/2} \longrightarrow 1s$

b - has two vacancies (in the K shell and L_{III} level), removal of the L_{III} electron at the same time as the K electron decreases the total electron charge of the atom and thus the attraction of the charge by the nucleus. The energy gap between K and L widens, and a shorter λ transition of α3 and α4 occurs.



c - two vacancies also but in the K shell and L_I level, which gives rise to $\alpha 5$ and $\alpha 6$ lines.

Production and Properties of X-rays

B. Properties of X-rays

2. Characteristic X-ray spectrum

b. Nondiagram Lines

The increase of the energy gap by this process is actually very small and cannot be resolved by normal monochromators.

So the $K_{\alpha1}$, $K_{\alpha2}$ lines in reality are made up of six lines (two triplets).

This does come into play for the profile-fitting programs (i.e. Reitveld), and takes into account some asymmetry in the lines (especially for $\alpha2$).

Production and Properties of X-rays

B. Properties of X-rays

2. Characteristic X-ray spectrum

b. Nondiagram Lines

The largest energy gap within any of the triplets is only about 2.5 eV. The absolute energy resolution of the diffractometer using $\mathrm{CuK}\alpha$ radiation ranges from:

200 eV at $2\theta = 10^{o}$ to about 2.5 eV at $2\theta = 140^{o}$.

So cannot resolve the fine structure of the triplet. For practical purposes, the copper K spectrum is assumed to consist of $K_{\alpha 1}$ and $K_{\alpha 2}$ and the $K_{B1,B3}$.

Assignments:

Read Chapter 1 from textbooks:

-X-ray Diffraction, A Practical Approach by Norton

-Elements of X-ray Diffraction by Cullity and Stock

-Introduction to X-ray powder Diffractometry by Jenkins and Synder