chem 5390

# Advanced X-ray Analysis

## LECTURE 3

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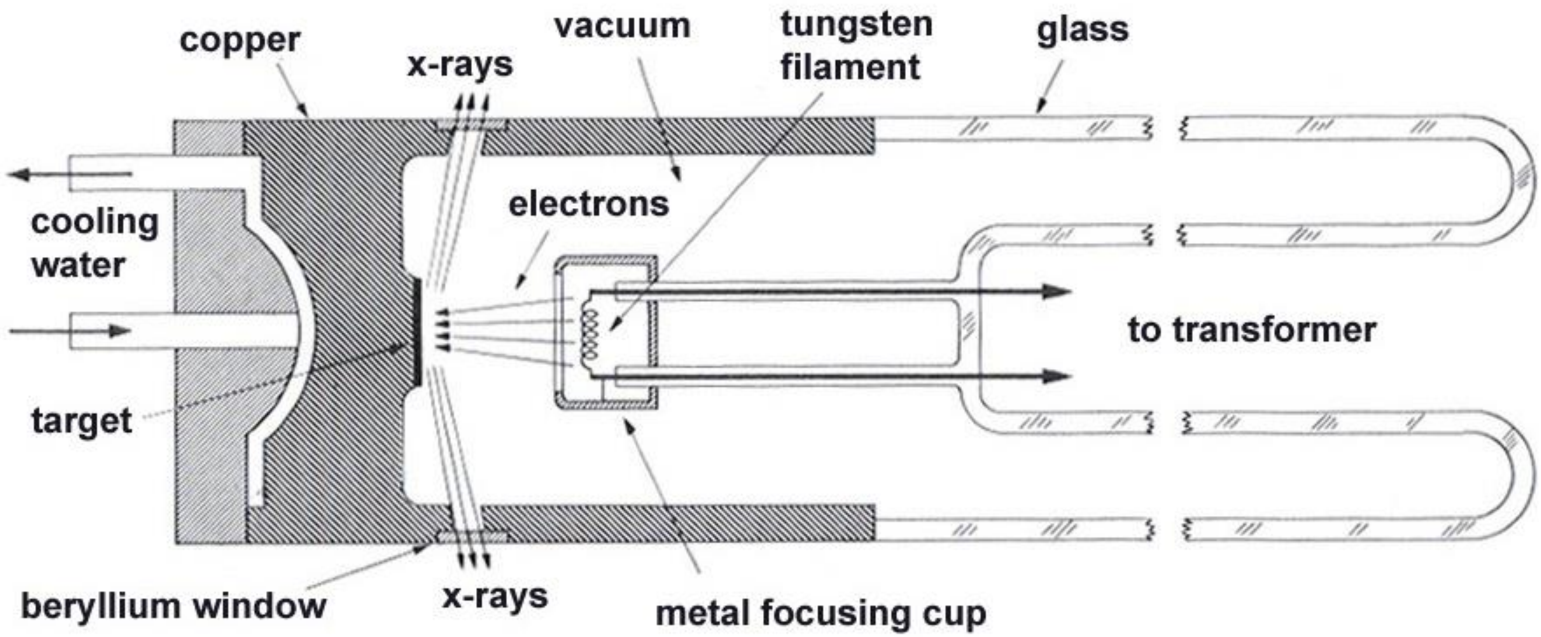
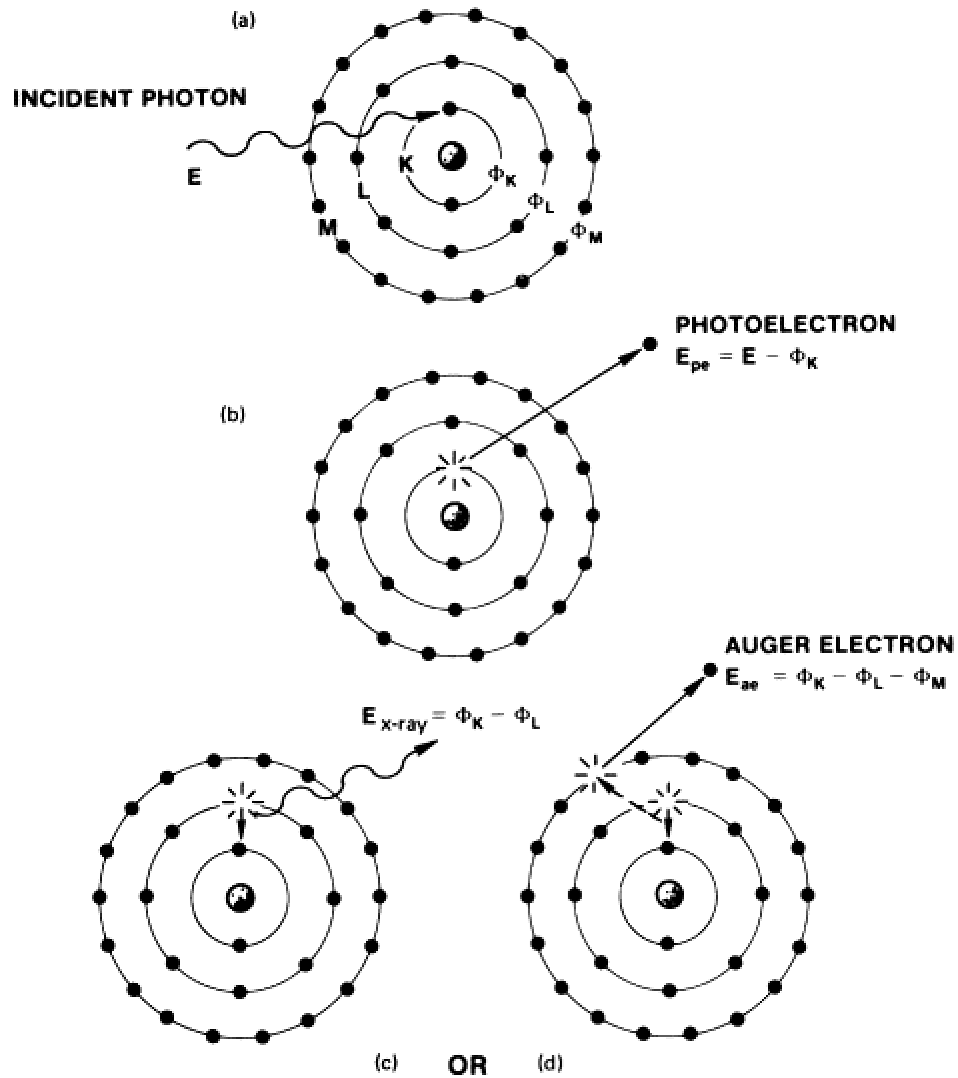
**Department of Chemistry**

# Filament tube

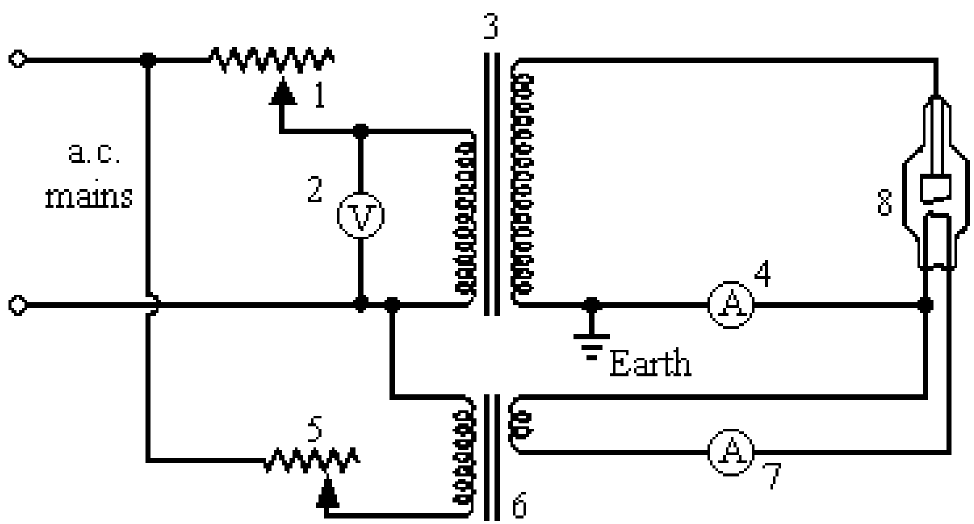



(a)
INCIDENT PHOTON
E
K
L
M
$\Phi_K$
$\Phi_L$
$\Phi_M$
PHOTOELECTRON
$E_{pe} = E - \Phi_K$
(b)
AUGER ELECTRON
$E_{ae} = \Phi_K - \Phi_L - \Phi_M$
$E_{X\text{-ray}} = \Phi_K - \Phi_L$
(c)
OR
(d)

# Production and Properties of X-rays

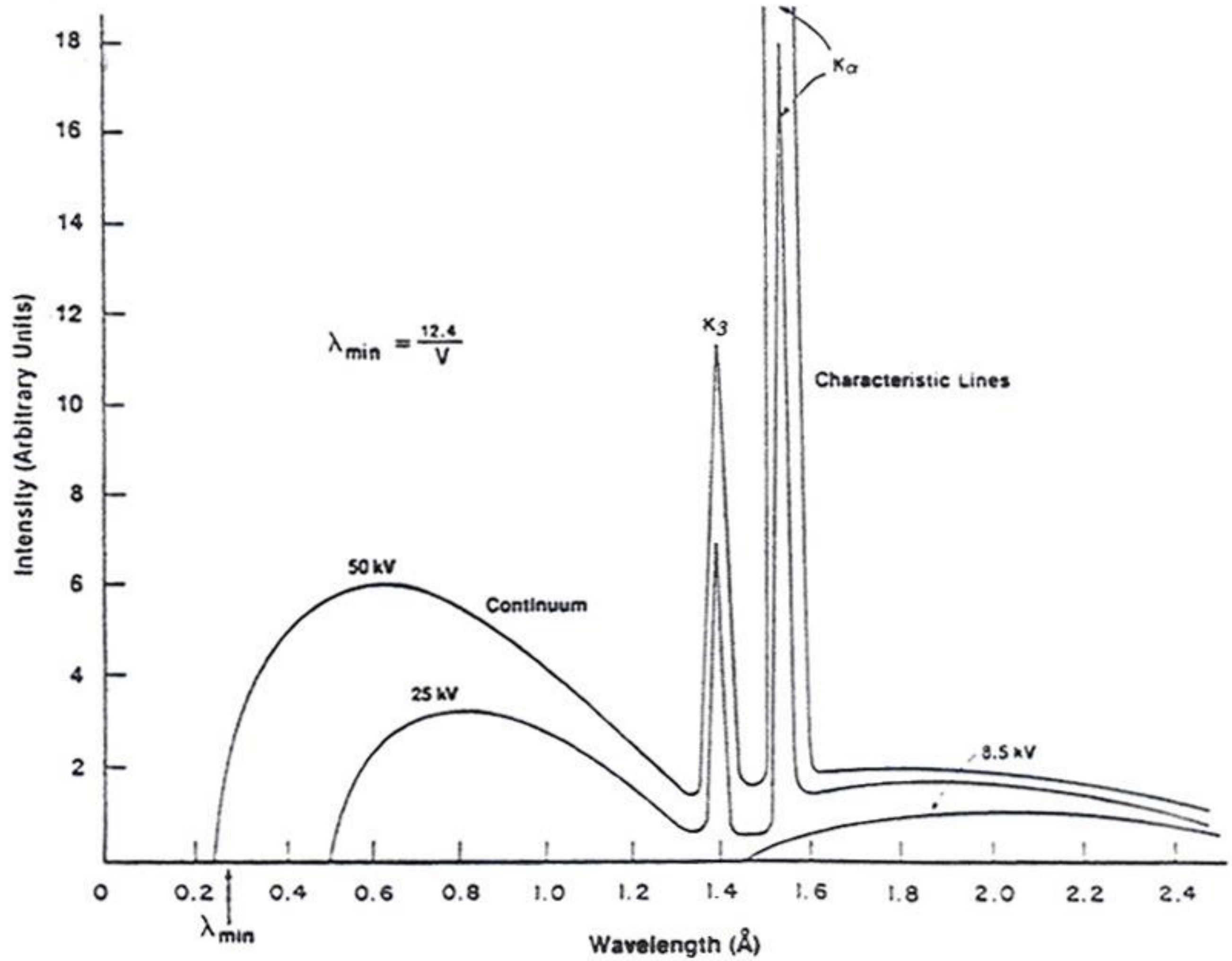
## Generating X-rays for Diffraction

### HV Power Supply




1. Tube voltage control
2. Voltmeter
3. High voltage transformer
4. Tube current ammeter
5. Filament current control
6. Low voltage transformer
7. Filament current ammeter
8. X-ray tube

- 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


18
16
14
12
10
8
6
4
2
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
Intensity (Arbitrary Units)
Wavelength (Å)
$\lambda_{min} = \frac{12.4}{V}$
$\lambda_{min}$
50 kV
25 kV
8.5 kV
Continuum
Characteristic Lines
$K_\beta$
$K_\alpha$

# 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 Kα 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 K$\alpha$1 | 1.54056Å | 1.540598 Å | | Co K$\alpha$1 | 1.788965Å | 1.789010 Å |
| Cu K$\alpha$2 | 1.54439Å | 1.544426 Å | | Co K$\alpha$2 | 1.792850Å | 1.792900 Å |
| Cu K$\beta$ | 1.39220Å | 1.392250 Å | | Co K$\beta$ | 1.62079Å | 1.620830 Å |
| | | | | | | |
| Molybdenum Anodes | | | | Chromium Anodes | | |
| Mo K$\alpha$1 | 0.709300Å | 0.709319 Å | | Cr K$\alpha$1 | 2.28970Å | 2.289760 Å |
| Mo K$\alpha$2 | 0.713590Å | 0.713609 Å | | Cr K$\alpha$2 | 2.293606Å | 2.293663 Å |
| Mo K$\beta$ | 0.632288Å | 0.632305 Å | | Cr K$\beta$ | 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 $K\alpha 1$, $K\alpha 2$, and $K\beta$ radiations

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

- Use of a $\beta$ 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

## <u>β Filters</u>

**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, $\mu$, also called the <u>linear absorption coefficient</u> of the substance.**

**$\mu/\rho$ 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.**

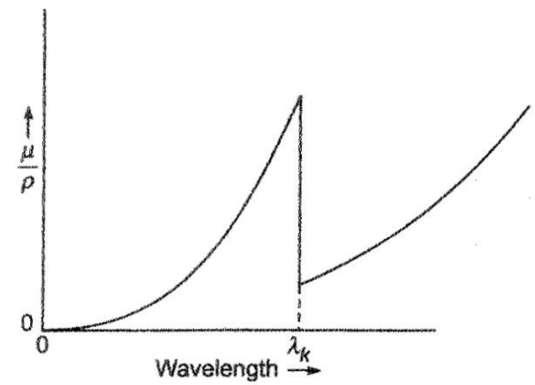



**Fig. 3.9** X-ray absorption characteristics of an absorber (schematic)

**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**

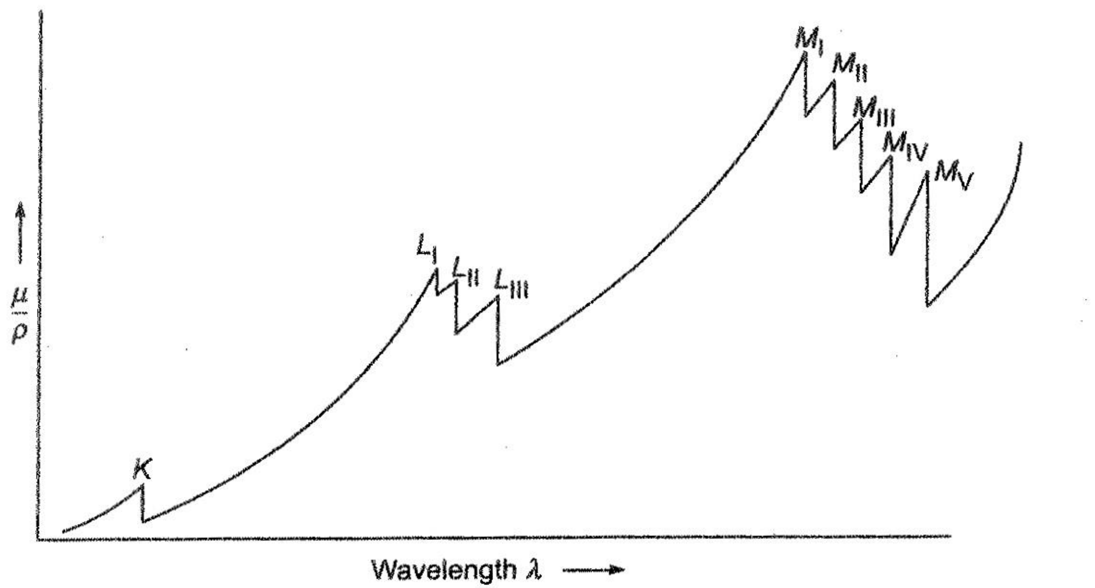



Fig. 3.10 (b) X-ray absorption characteristics (schematic)

# 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.**

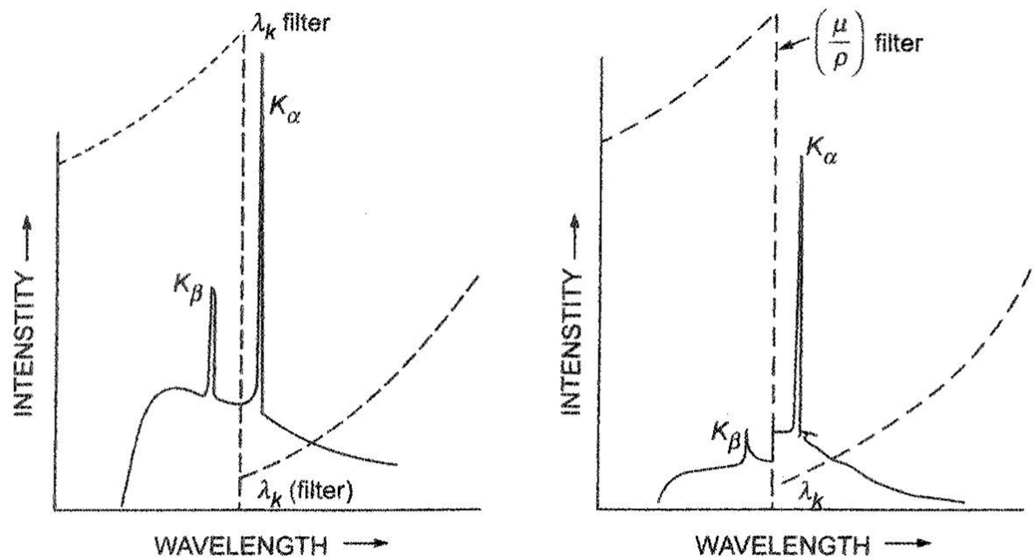



**Fig. 3.12** Intensity versus wavelength before and after β-filtering (schematic)

# Production and Properties of X-rays

## $\beta$ Filters for Common Anodes

| Target | K$\alpha$ (Å) | $\beta$-filter | Thickness ($\mu$m) | Density (g/cc) | % K$\alpha$ | % K$\beta$ |
|---|---|---|---|---|---|---|
| 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 $\alpha$ : $\beta$ 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 K$\alpha$ or K$\beta$ 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

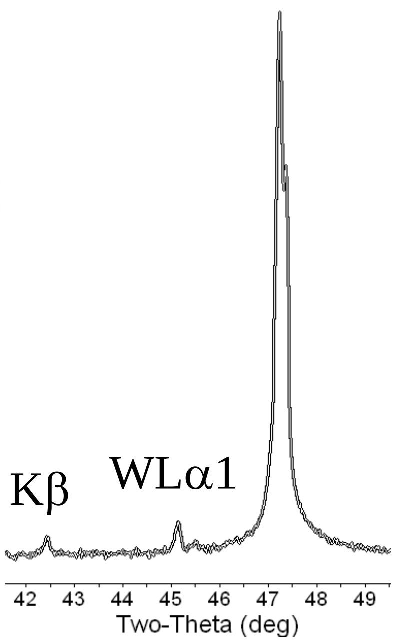
- The $K\alpha1$ & $K\alpha2$ doublet will almost always be present
  - Very expensive optics can remove the $K\alpha2$ line
  - $K\alpha1$ & $K\alpha2$ overlap heavily at low angles and are more separated at high angles

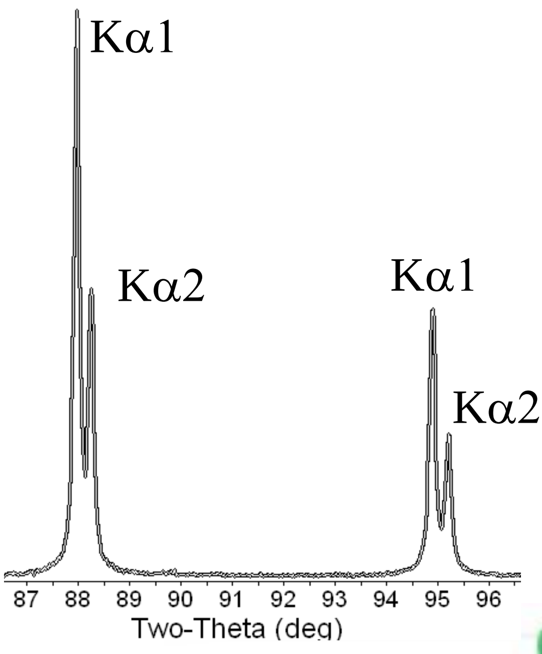
- W lines form as the tube ages: the W filament contaminates the target anode and becomes a new X-ray source

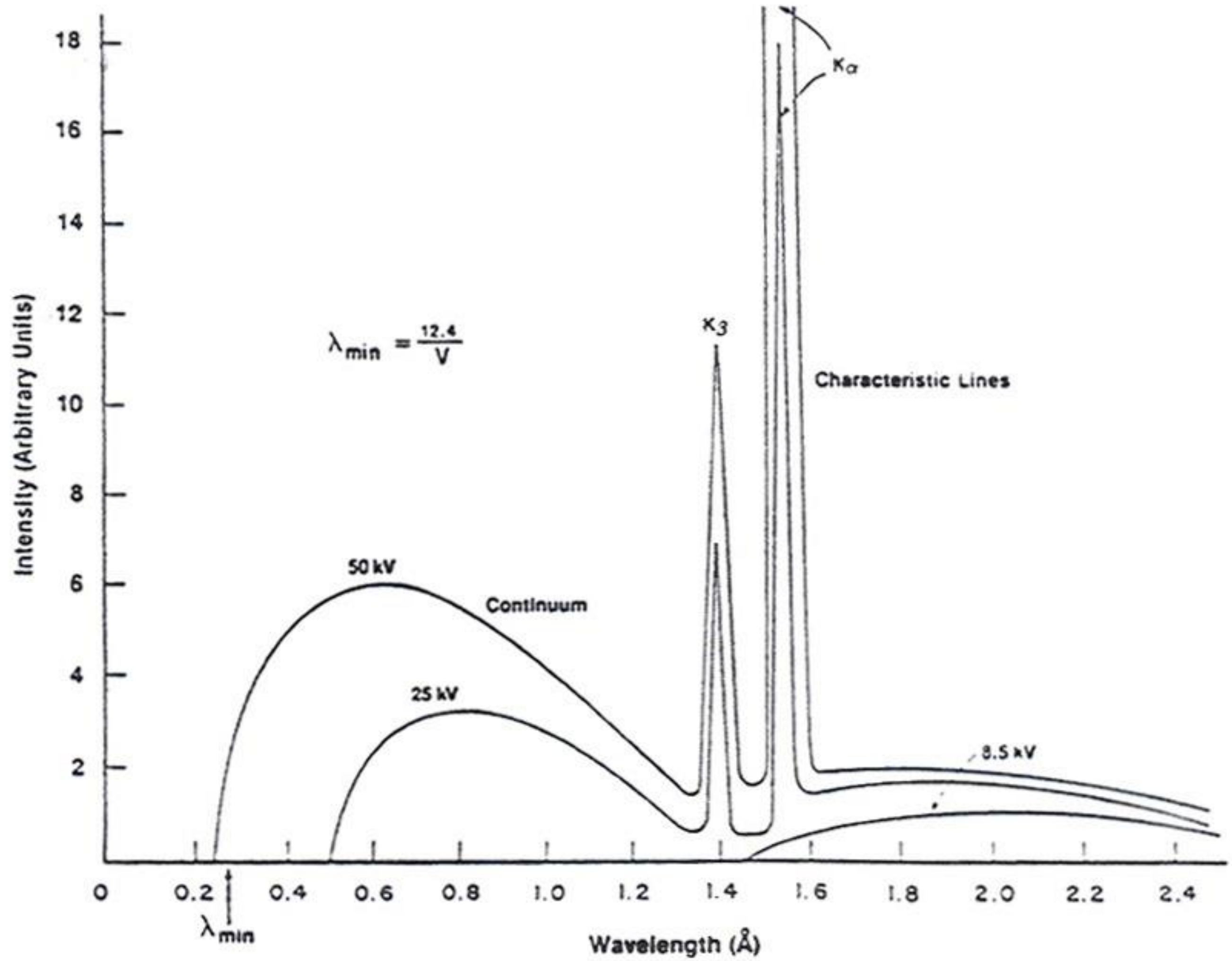
- W and $K\beta$ lines can be removed with optics

# Production and Properties of X-rays

## Spectral Contamination in XRD




Intensity (Arbitrary Units)
Wavelength (Å)
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25 kV
Continuum
8.5 kV
$K_\beta$
$K_\alpha$
Characteristic Lines
0
0.2
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1.8
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2.2
2.4
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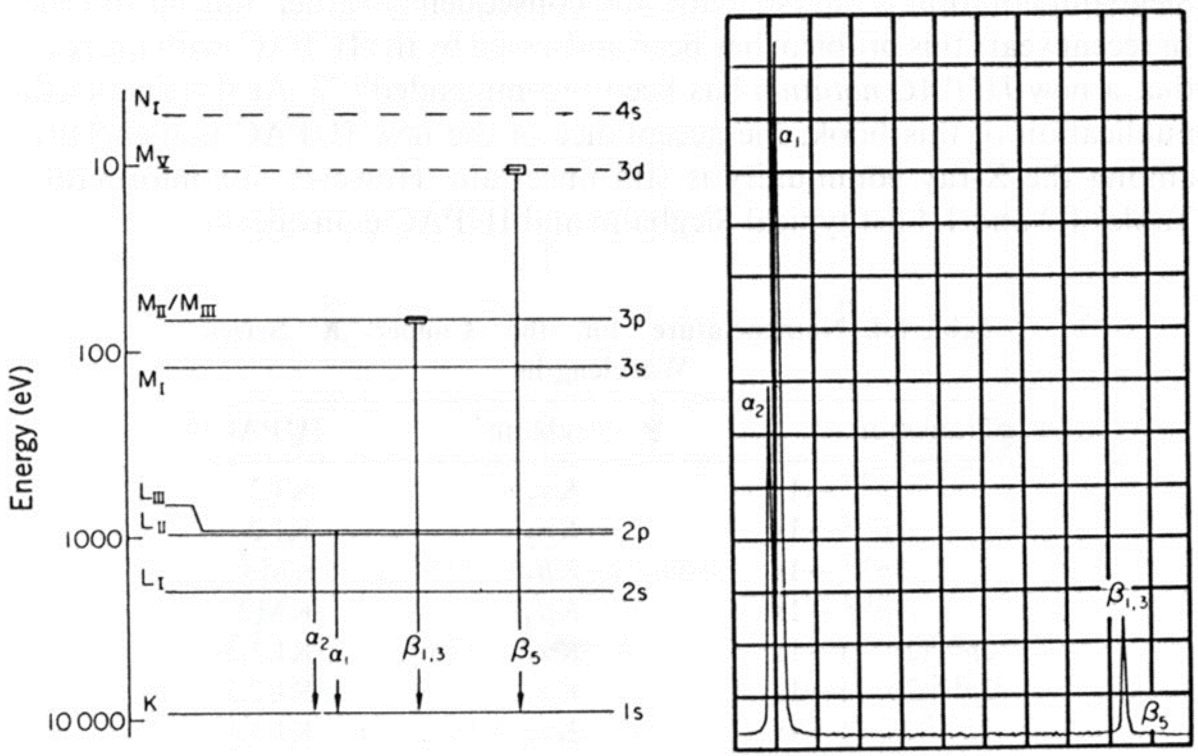
14
16
18

# Production and Properties of X-rays

## The Copper K Spectrum




The copper $K\alpha$ 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) | $\lambda$ (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.**
- **$\Delta J$ (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

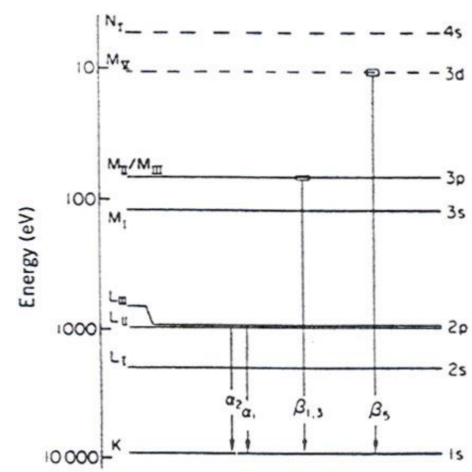
## 2. Characteristic X-ray spectrum

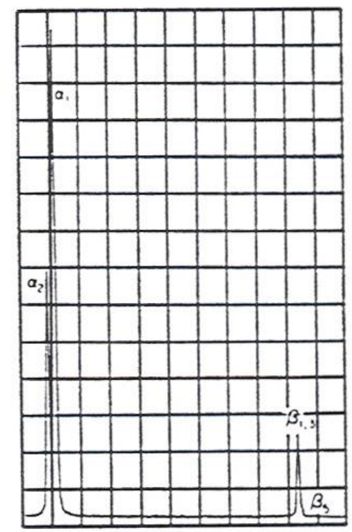
### a. Selection Rules

**K spectrum is simple for copper:**
**2 $\alpha$ 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:**
**$K_{\alpha 1}$, $K_{\alpha 2}$ > $K_{B1}$, $_{B3}$ > $K_{B2}$**

**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 $K_{\alpha1}$:$K_{\alpha2}$ ---> there are 4 $p^{3/2}$ electrons for $K_{\alpha1}$ and**

**2 $p^{1/2}$ electrons for $K_{\alpha2}$**

**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

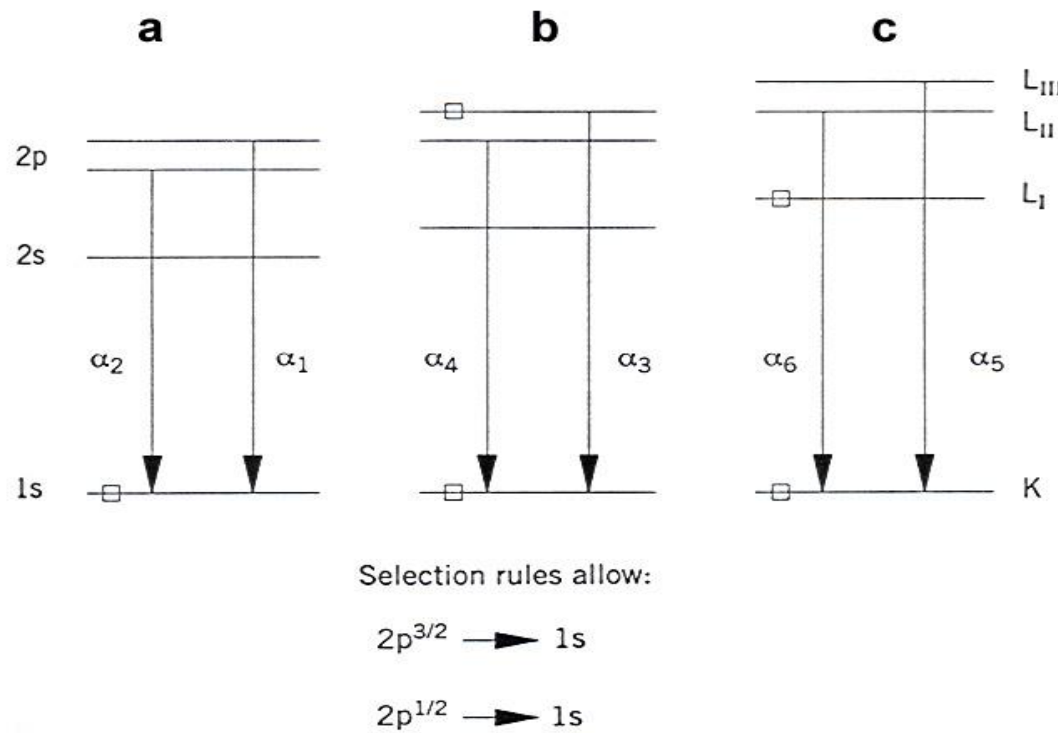
### 2. Characteristic X-ray spectrum

**b. Nondiagram Lines**

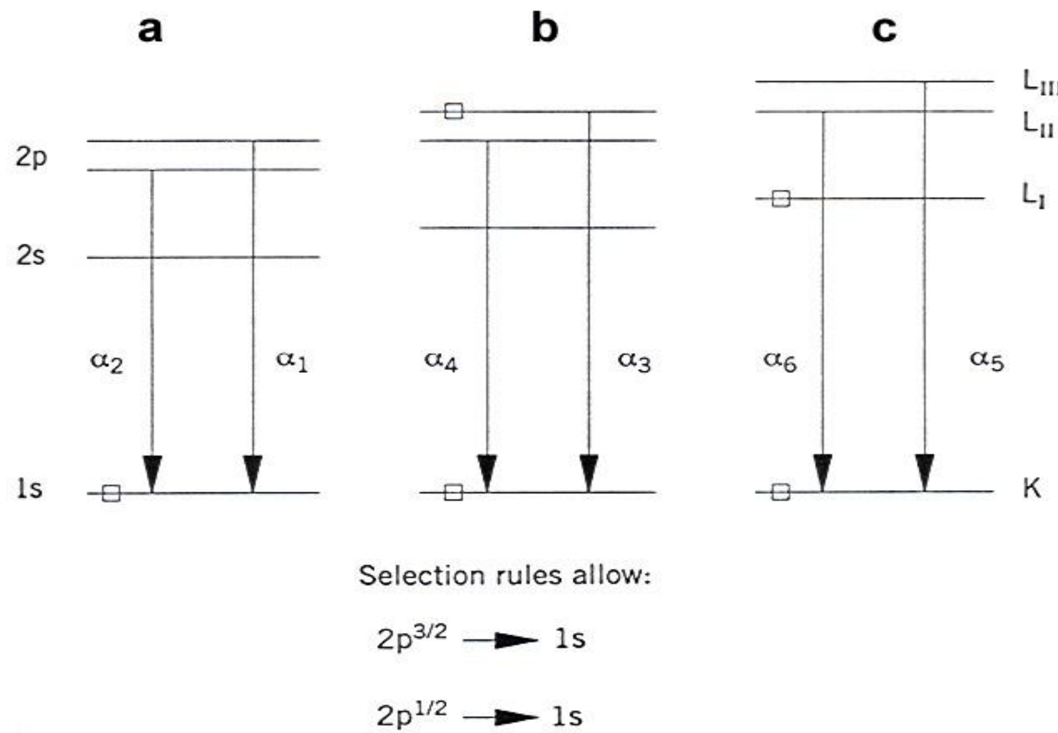
**- Forbidden transitions - arise due to hybridization of outer orbitals (especially for transition metals).**

**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).**

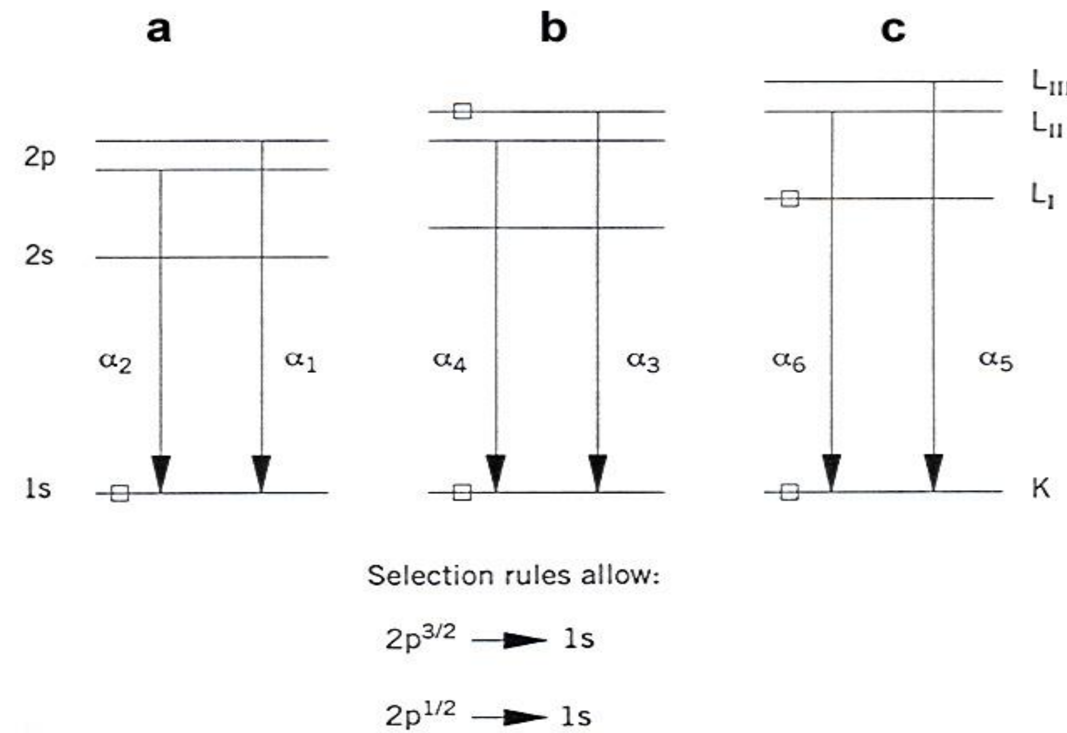
**- Satellite lines - occur from transitions involving removal of more than one electron (dual ionization).**




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




**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 $\lambda$ transition of $\alpha$3 and $\alpha$4 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 $K_{\alpha 1}$, $K_{\alpha 2}$ 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 $\alpha$2).**

# 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 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

Do UNT Bridge Module:
“Radiation Safety Training”