



CHEMISTRY 5570

Advanced Analytical Chemistry

X-ray Diffraction

Lecture 1

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Advance X-Ray Diffraction

Reading:

X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials, H.P. Klug and L.E. Alexander, Wiley, 1974, ISBN 0-471-49369-4

Elements of X-ray Diffraction, B.D. Cullity and S.R. Stock, Prentice Hall, 3rd edition, 2001, ISBN 0-201-61091-4

X-ray Diffraction, C. Suryanarayana and M. Norton, 1998, ISBN 0-306-45744-X

Introduction to X-ray Powder Diffractometry, R. Jenkins and R. Snyder, John Wiley & Sons, 1996, 0-471-51339-3

Advance X-Ray Diffraction

Class Website:

https://sites.chemistry.unt.edu/~tgolden/courses/course_downloadsFall24.xhtml

Readings:

Given at the end of each powerpoint lecture. The books are on reserve at the Willis library under CHEM 5390 (X-ray Diffraction).

Homework Assignments:

Given at the end of each powerpoint lecture. I do not accept assignments by email – all assignments must be turned in during class.

Exams:

There will be an exam in class on Tuesday, December 10th, 8:00 - 10:00 a.m.

History of X-rays

A. Discovery of X-rays

Wilhelm Röntgen discovered x-rays on November 8th, 1895 in Wurzburg Germany.

While experimenting with Crookes tubes, he noticed that some BaPtCN material smeared on thin cardboard and covered with black paper a distance away began to glow.

History of X-rays

Discovery of X-rays





History of X-rays

Discovery of X-rays

Soon he noticed other objects, i.e., wood, books, and metal sheets were penetrated by x-rays.

He then x-rayed his wife's hand and noticed the flesh was transparent but the bones were opaque.

History of X-rays

Discovery of X-rays

In 1901, Wilhelm Röntgen won the Nobel prize in Physics for his discovery.



History of X-rays

Following Röntgen discovery, 3 major branches of science have developed using this radiation.

- ❖ **X-ray radiography (function of average atomic number and density of matter)**
 - **Diagnostic methods – medical and industrial - relies on the relationship between density of materials and absorption of x-rays.**
- ❖ **X-ray crystallography (structure analysis)**
 - **Single crystal and Powder - relies on the dual wave/particle nature of x-rays to discover information about the structure of crystalline materials.**
- ❖ **X-ray spectroscopy (elemental analysis)**
 - **Fluorescence - relies on characteristic secondary radiation emitted by materials when excited by a high-energy x-ray source and is used primarily to determine amounts of particular elements in materials.**

History of X-rays

The nature of these x-rays however took many years to uncover.

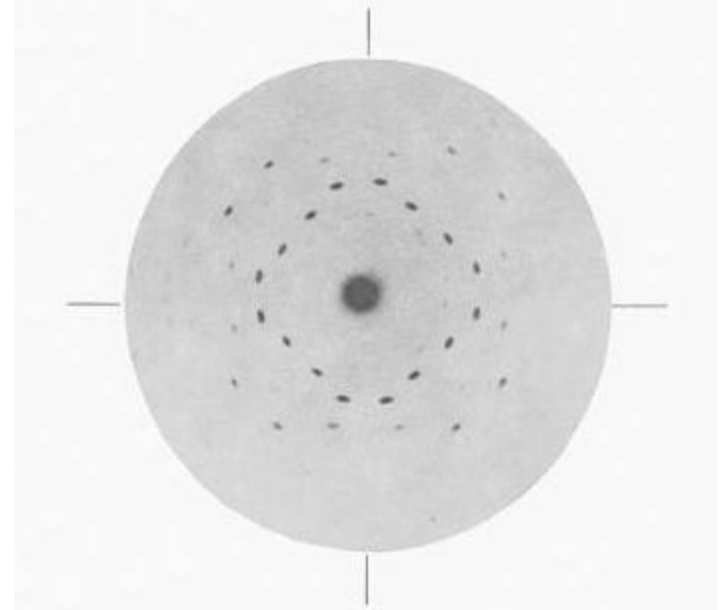
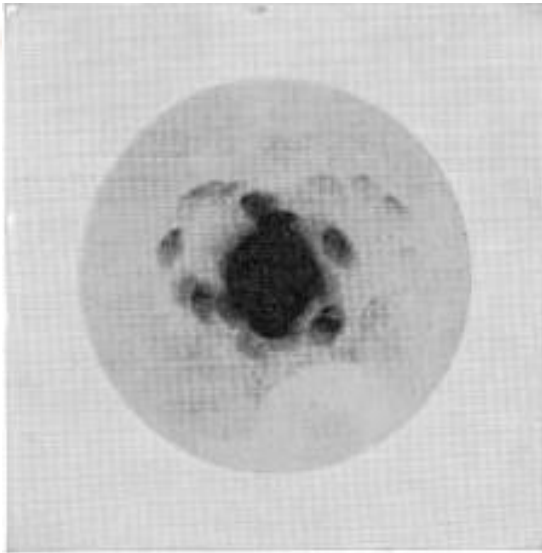
- Röntgen tried unsuccessfully to produce interference effects with x-rays (i.e. visible light and law of optics).**
- Thomson and Rutherford's experiments showed x-rays behaved as waves with very small wavelength.**
- Bragg's experiments interjected the particle theory. In 1912 suggested a theory was needed to explain both waves and particles.**

History of X-rays

Crystallography

In 1912 M. von Laue and P. Knipping obtained the first diffraction pattern of a crystal using X-rays.

Awarded Nobel prize in 1914.



History of X-rays

Important for Calculations

In 1914, the father and son team of English physicists, William Henry Bragg and William Lawrence Bragg determined the atomic structure of a simple inorganic substance, salt (NaCl), and deciphered the mathematical relationships between crystal structure and the associated diffraction pattern.

$$n\lambda = 2d \sin \theta$$

where n is an integer

λ is the wavelength of the x-rays

d is the interplanar spacing in the specimen

θ is the diffraction angle

Bragg Equation

History of X-rays

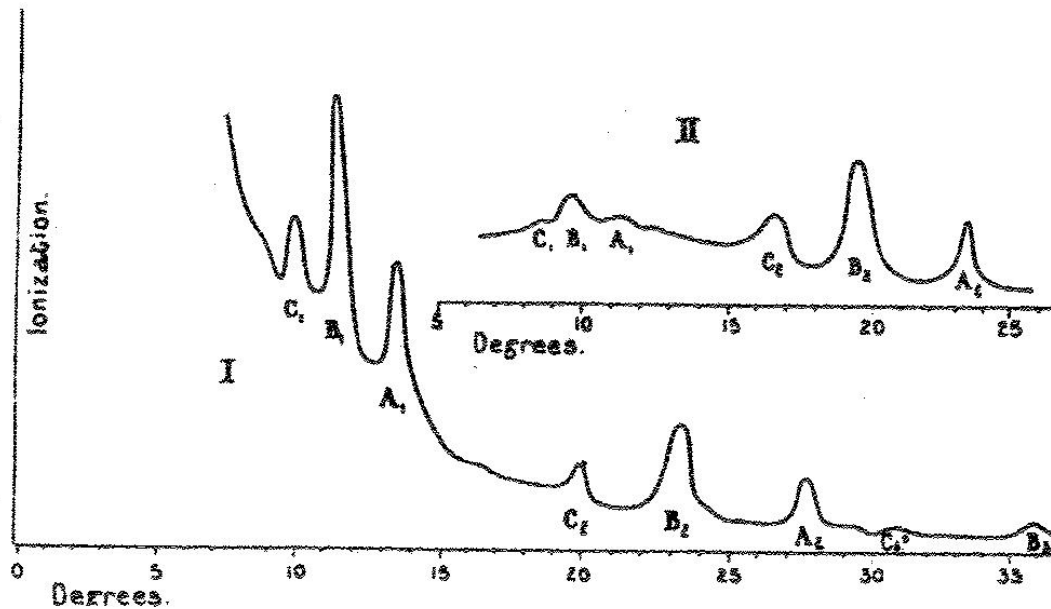


Figure 6. Diffractograms produced by W.H. and W.L. Bragg with sodium chloride crystals. I: diffractogram obtained with a crystal cleaved along the (100) planes, II: diffractogram obtained with a crystal cleaved along the (111) planes

History of X-rays

Crystallography

Rosalind Franklin collected X-ray diffraction data on Na salt of DNA. In 1953, the structure of DNA was solved by J. Watson, a biologist, and F. Crick, a physicist, thanks to the use of X-rays.

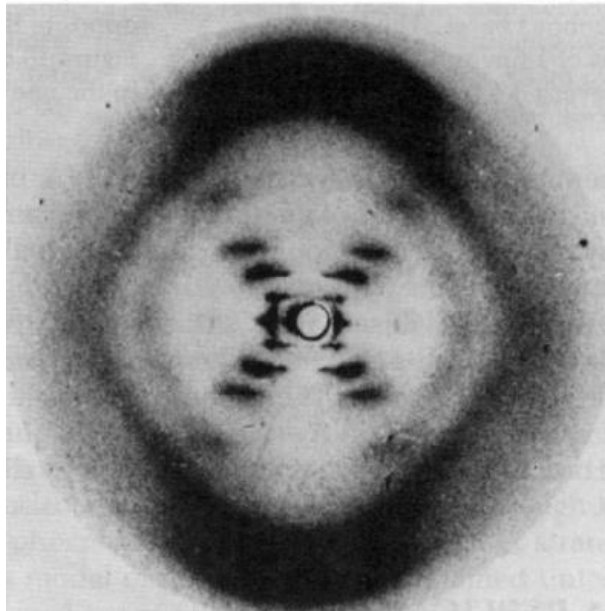
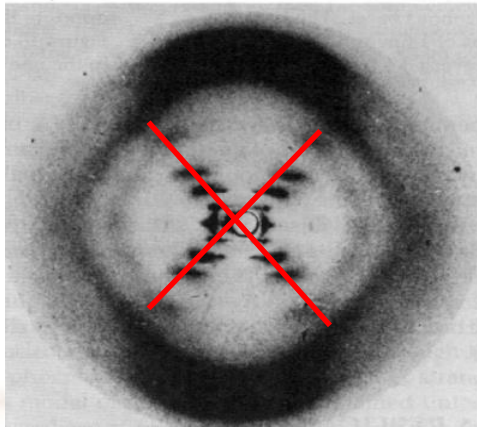


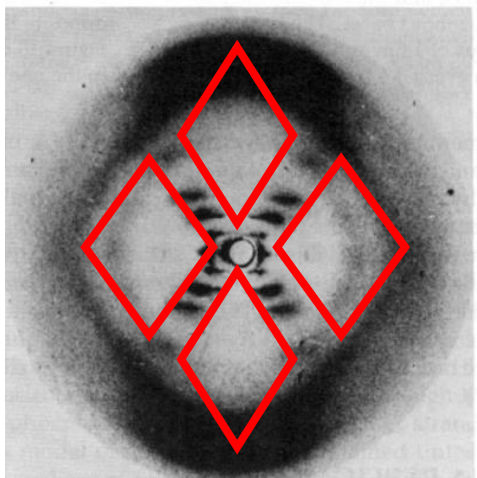
Photo 51- The x-ray diffraction image that allowed Watson and Crick to solve the structure of DNA

History of X-rays

Crystallography



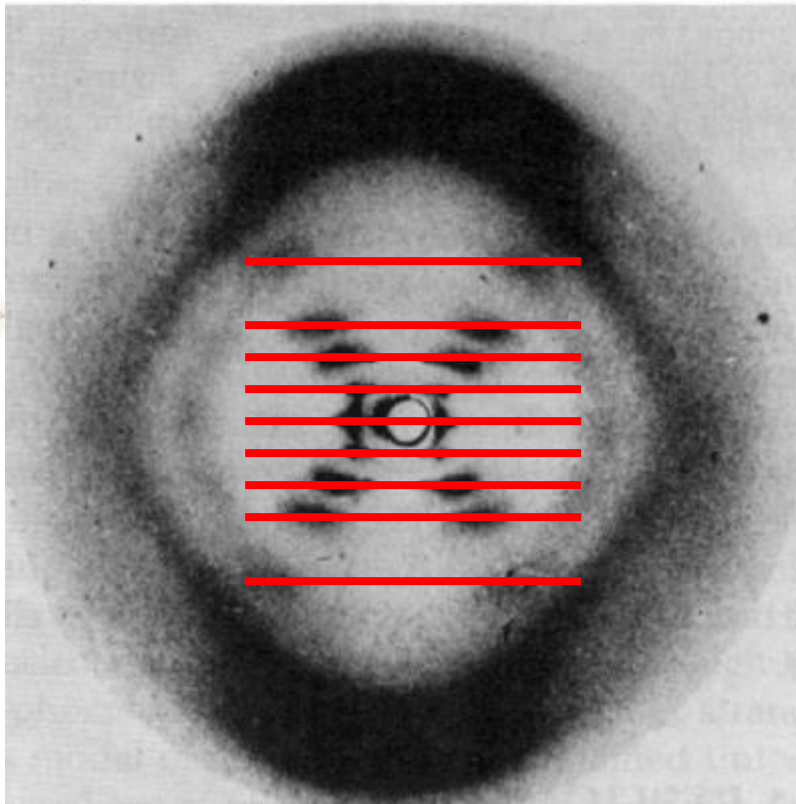
“X” pattern characteristic of helix



Diamond shapes indicate long, extended molecules

History of X-rays

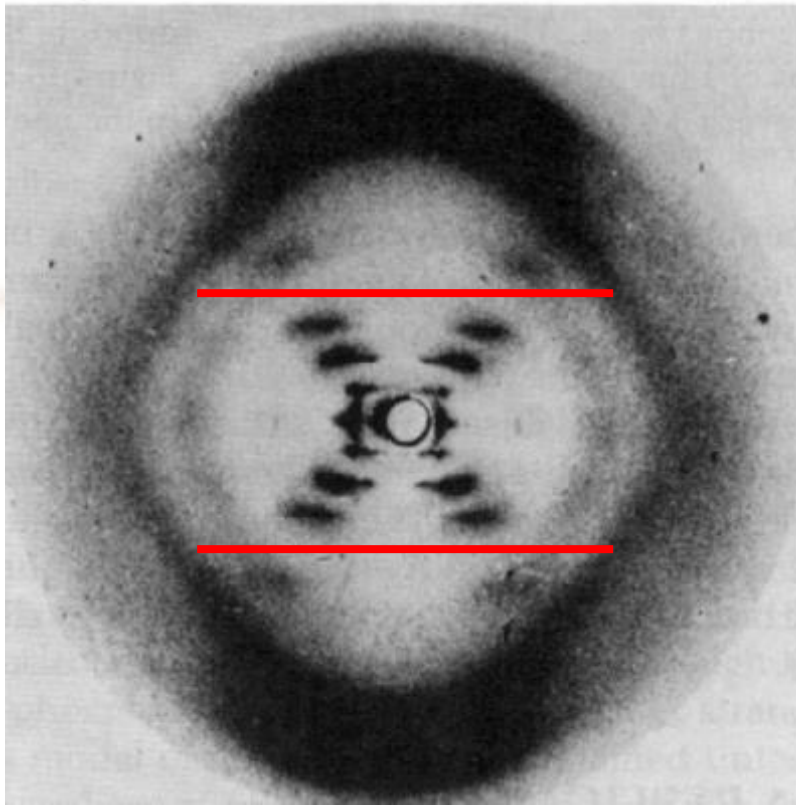
Crystallography



Smear spacing reveals
distance between repeating
structures

History of X-rays

Crystallography



Missing smears indicate interference from second helix

History of X-rays

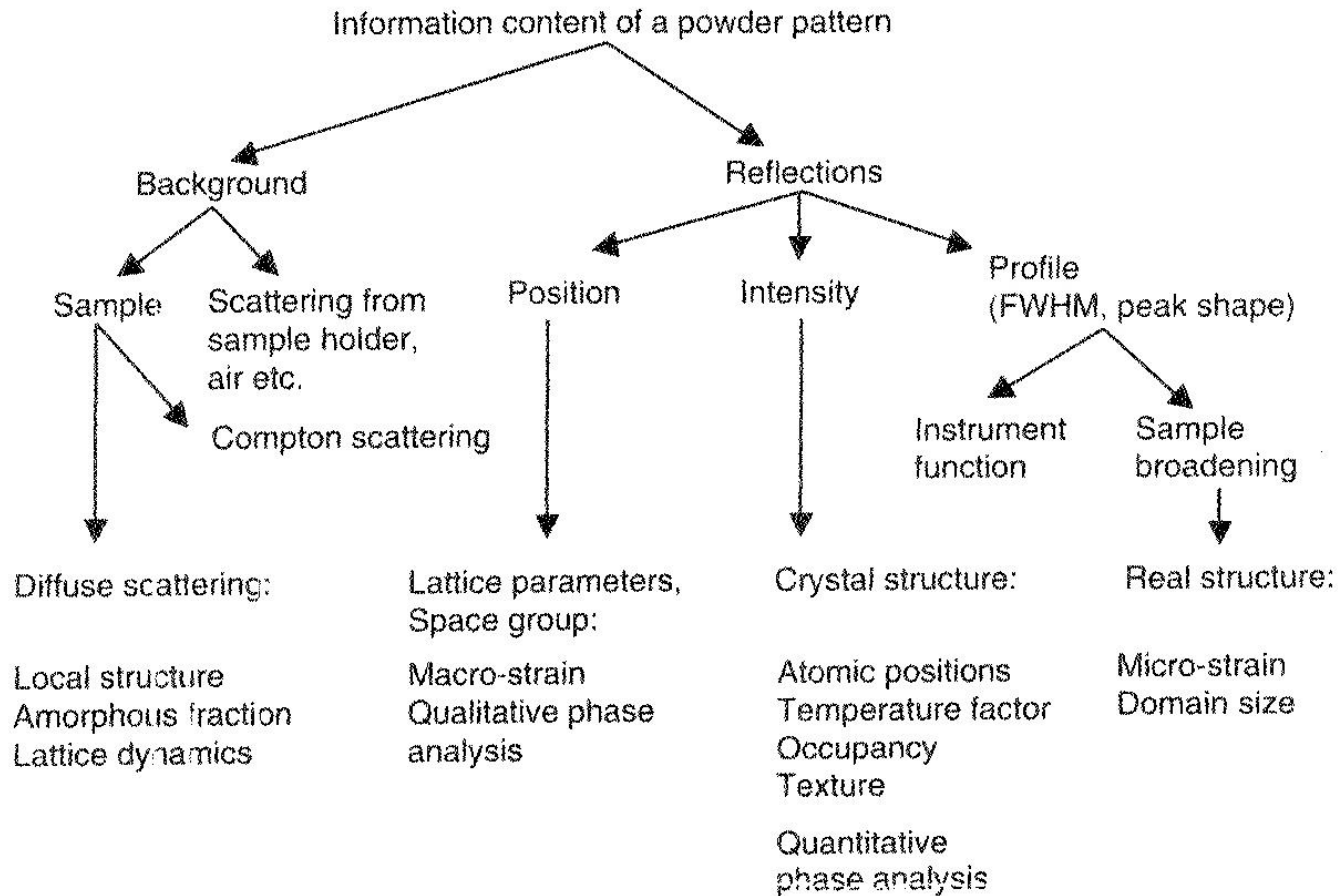


Figure 1 General information content of a powder diffraction pattern.

History of X-rays

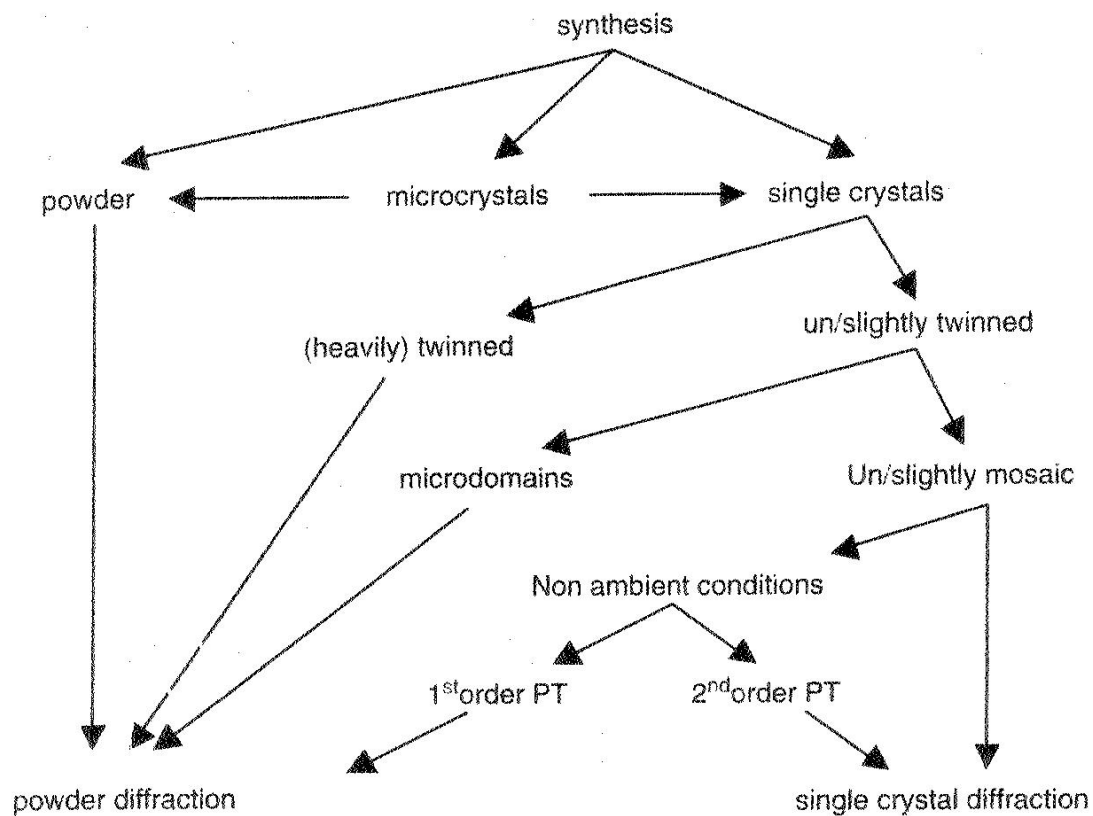
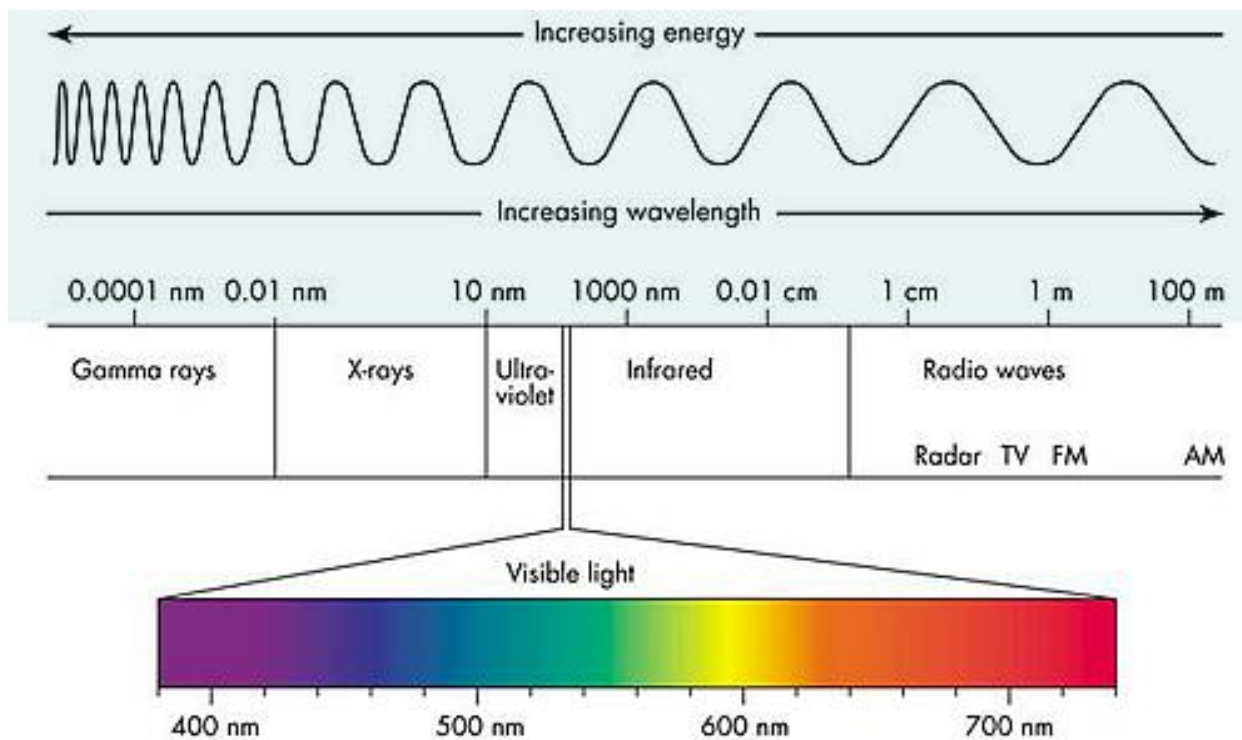


Figure 2 Illustration of the relationship between the domains of applicability of the powder and single-crystal methods in the area of structure solution.

XRD Safety and Hazards





XRD Safety and Hazards

Hazards

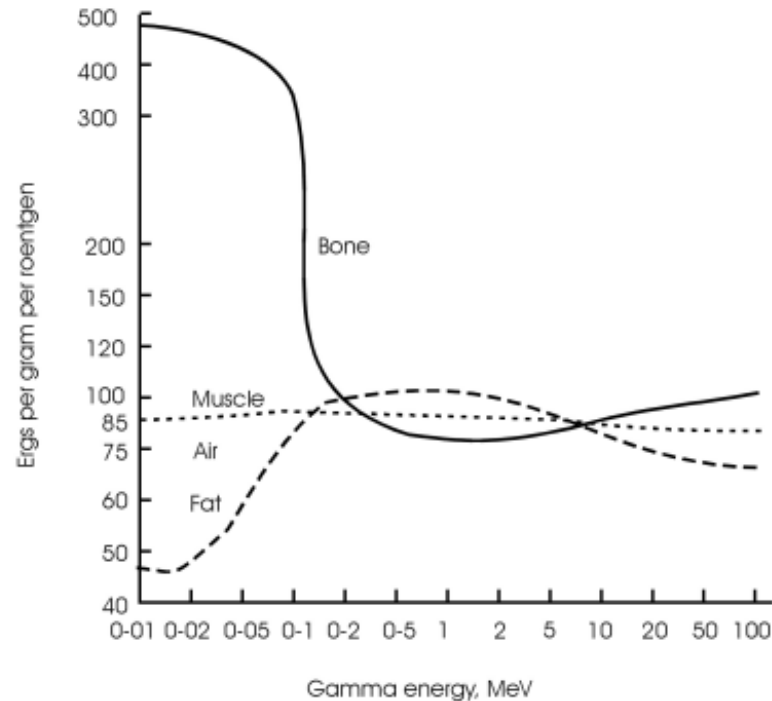
X-Ray Absorption in Human Tissue

When X-ray photons interact with matter -- human tissue in this discussion - some of the photons are absorbed by the tissue. Many analytical x-ray machines produce X-rays up to 50 or 60 kV. Over this energy range, bone absorbs roughly five times the energy that muscle absorbs and about ten times that of fat. This is significant since the hands are mainly muscle and bone. They are therefore more susceptible to X-ray injury.

XRD Safety and Hazards

Hazards

The figure shows the absorption characteristics for bone, muscle, and fat, as a function of the gamma (or X-ray) energy.



Energy absorption per roentgen of various tissues.
(From O. Glasser, *Medical Physics*, Vol. II)

XRD Safety and Hazards

Hazards

Injuries

Injuries are generally characterized by the clinical symptoms manifested (burns, swelling, and so on), and the estimated dose. There are short-term and long-term injuries.

Short-Term Injuries

Short-term injuries are generally manifested by soreness, reddening of the skin, swelling, inflammation, and tissue breakdown characteristic of second and third degree burns. Most often these signs do not begin until several days after the accident.



XRD Safety and Hazards

Hazards

Long-Term Injuries

Many long term injuries are due to the progression of short-term damage. Despite initial treatment of the injury, the tissue may be damaged beyond recovery, sometimes necessitating the removal of the damaged tissue (such as a finger). Cancer and cataracts, in the case of eye exposure, are also considered potential (latent) long-term injuries.

XRD Safety and Hazards

Hazards

Dose Definitions

"Absorbed dose" of any ionizing radiation is the energy imparted to matter by ionizing particles per unit mass of irradiated material at the place of interest. The unit of radiation absorbed dose is the "rad." 1 rad is 100 erg/gram.

"RBE dose" is equal numerically to the product of the absorbed dose in rads and an agreed factor RBE (relative biological effectiveness) whose values for ICRP (International Commission on Radiological Protection). The "rem" (roentgen equivalent [in] man) is the unit of RBE dose.

XRD Safety and Hazards

Hazards

Dose Limits

Maximum Permissible Dose Equivalent for Occupational Exposure

Dose to whole body	5 rem per year
Skin of whole body	50 rem per year
Hands	50 rem per year
Pregnant women	0.5 rems in gestation period
(with respect to fetus)	

[Note that average background radiation in U.S. is 0.36 rem per year.]

XRD Safety and Hazards

Hazards

Minimizing Exposure

How can exposure to radiation be minimized?

There are four physical factors that affect the exposure level in a "radiation field"

- 1. Distance**
- 2. Time**
- 3. Shielding**
- 4. Output factors (kV, mA)**

- Exposure varies as the inverse square of the distance (assuming a point source, as from scattering)**
- Exposure increases linearly with time**
- Exposure is inversely exponential with the thickness of shielding.**
- Exposure increases linearly with current (mA) and as the square of the potential (kV).**

XRD Safety and Hazards

Hazards



Dosimetry

At the University of North Texas, thermoluminescent dosimeters (TLDs) in the form of ring badges and optically stimulated luminescence (OSL) whole-body badges may be issued to operators of analytical x-ray equipment. Thermoluminescent dosimeters contain crystalline materials (for example, CaF_2 with a Mn impurity or LF) that emit light if they are heated after having been exposed to radiation. The whole body badges contain a thin layer of aluminum oxide. After use, the aluminum oxide is stimulated with a laser light and the luminescence is measured. The amount of luminescence is proportional to the amount of radiation exposure.

XRD Safety and Hazards

Hazards

Equipment

The X-ray equipment manufactured today is much safer than that made before the 1970s. Major advances have been in the areas of:

- interlocks
- enclosures
- shutters
- failsafe warning lights
- remote and computer controls

The sealed X-ray tubes and the mechanical goniometers are basically unchanged.



XRD Safety and Hazards

Hazards

Equipment - Interlocks

Interlocks are a set of switches in a series, where EVERY switch must be closed in order for the X-rays to be generated and/or for a shutter to be opened. These switches are connected to doors, panels, and collimators, which if opened or removed, would create a radiation hazard for the user.

If any switch is opened while the X-rays are on or the shutter is open, the X-ray generator will immediately shut off and/or the shutter will close.

XRD Safety and Hazards

Hazards

Equipment - Enclosures

Enclosures are boxes, some having a transparent window, which contain the X-ray instruments so that stray or scattered X-rays do not escape into the room. Enclosures, along with interlocks, also prevent people from encountering the direct X-ray beam.

Equipment - Shutters

Shutters open and close a path for the X-ray beam. When a shutter is properly functioning and closed, no X-rays can pass beyond the shutter.

XRD Safety and Hazards

Hazards

Equipment - Warning Lights, Failsafe

Lights are used to indicate that the X-ray generator is turned on and that a shutter is open. These lights are 'failsafe' so that in the event of a lamp failure (e.g., broken filament) the X-ray generator will NOT turn on and the shutter will NOT open (and, in fact, if on or open, will shut off or close in the event of a lamp failure). Also, the X-ray generator will not turn back on nor the shutter open again without the user first taking action to do so.

XRD Safety and Hazards

Hazards

Equipment - Remote and Computer Controls

Remote and computer controls of X-ray instruments are major safety advances in that the user need not be anywhere near the instrument to operate it. Enclosures, interlocks and warning lights serve to prevent possible radiation exposure to anyone in the vicinity of the instrument.

Equipment - Safety Over-Rides

Any mechanical or electrical system can, by deliberate action, be made unsafe (e.g., using a key to over-ride the interlock system, using jumper wires to bridge an open switch, and/or mechanically opening or removing something). Such actions are reserved for service personnel in the repair or alignment of the instrument. Such actions should NEVER be done by users.



XRD Safety and Hazards

Hazards

Equipment - Repairs

Users are NEVER to attempt repairs or make non-trivial adjustments to instruments. If there is a problem, inform the instrument supervisor. Depending on the severity of the problem, in the absence of the supervisor, users should label the instrument as "down" and power it off. For lesser problems, if deemed safe to do so, label it and walk away.

If users encounter an instrument being repaired, stay back and do not touch it!



XRD Safety and Hazards

Hazards

Normal Operating Procedures

'Normal Operating Procedures' mean operating procedures for conducting suitable for analytical purposes with shielding and barriers in place. These do not include maintenance but do include routine alignment procedures. Routine and emergency radiation safety considerations are part of these procedures.

Normal operating procedures shall be written and available to all analytical x-ray equipment workers.



XRD Safety and Hazards

Hazards

One of the major causes of X-ray accidents has been taking short cuts in attempts to complete work more quickly. Most of these involved defeating interlocks, or modifications to the instruments, but still one must think through every task and procedure to recognize and avoid hazards.

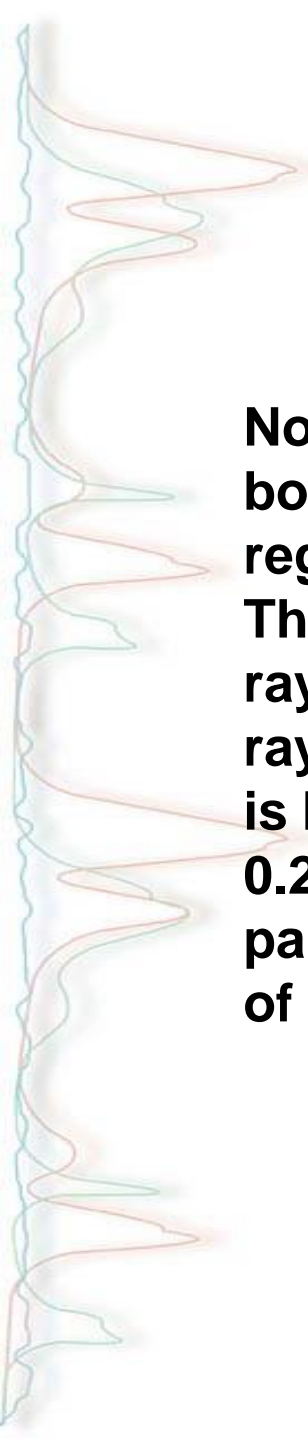
Work smart!



Properties of X-rays

Properties of X-rays

X-rays are part of the electromagnetic spectrum and exhibit a dual nature, behaving as waves and particles.



**Part of the
electromagnetic
spectrum.**

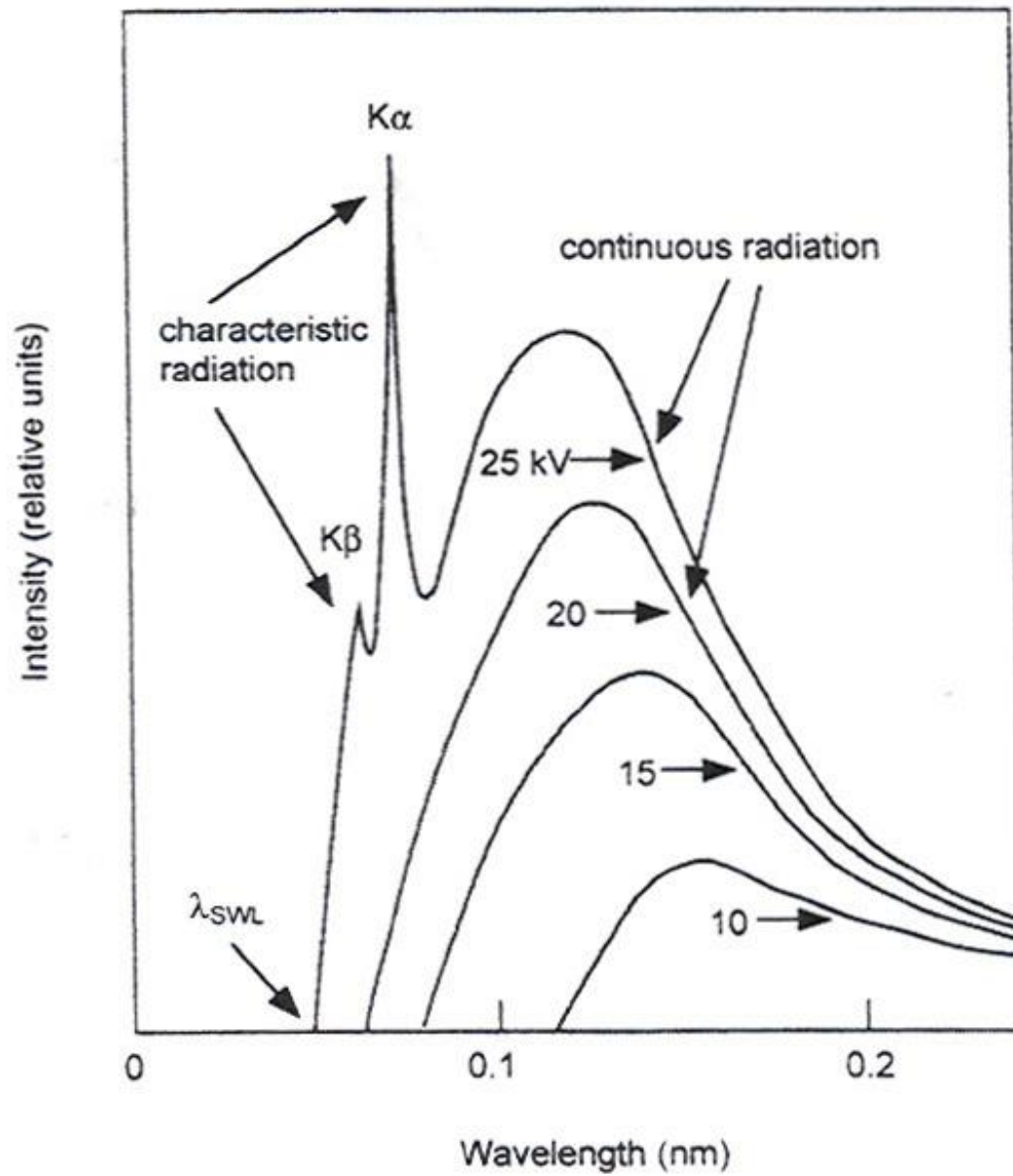
**Note that the
boundaries between
regions are arbitrary.
The usable range of x-
ray wavelengths for x-
ray diffraction studies
is between 0.05 and
0.25 nm (only a small
part of the total range
of x-ray wavelengths).**

$h\nu$ [eV]	ν [Hz]	λ [nm]	Radiation
			infrared
1	10^{14}	10^3	visible
10	10^{15}	10^2	ultraviolet
10^2	10^{16}	10	
10^3	10^{17}	1	x-rays
10^4	10^{18}	10^{-1}	
10^5	10^{19}	10^{-2}	
10^6	10^{20}	10^{-3}	
10^7	10^{21}	10^{-4}	γ -rays
10^8	10^{22}	10^{-5}	



Properties of X-rays

X-ray spectrum composed of a line spectrum of intense single wavelengths superimposed on a continuous background.





Properties of X-rays

Characteristic X-ray spectrum

Instead of a loss of energy by deceleration, the electrons ionize the target atoms.

The resulting spectrum is characteristic lines superimposed on the continuous spectrum.

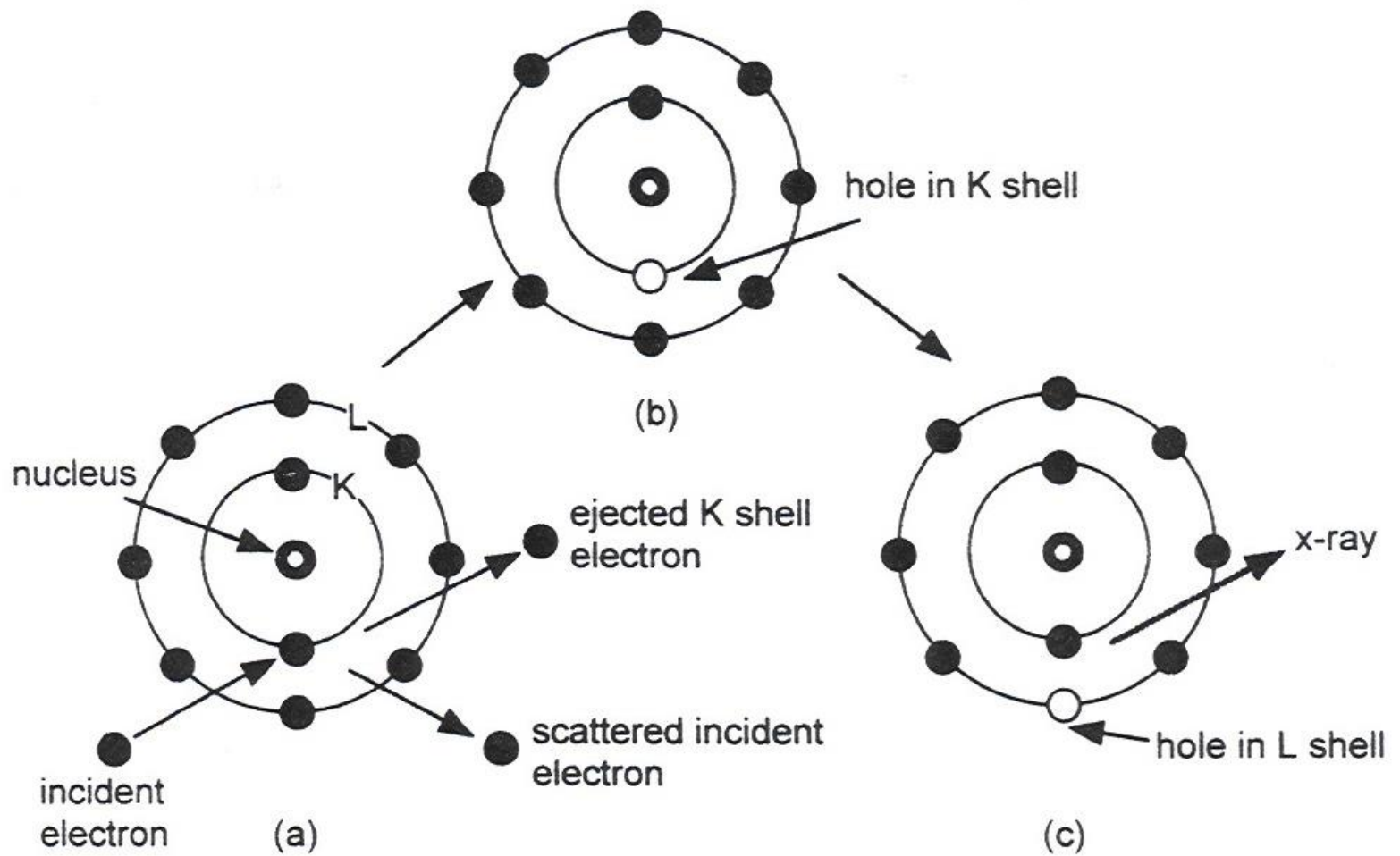
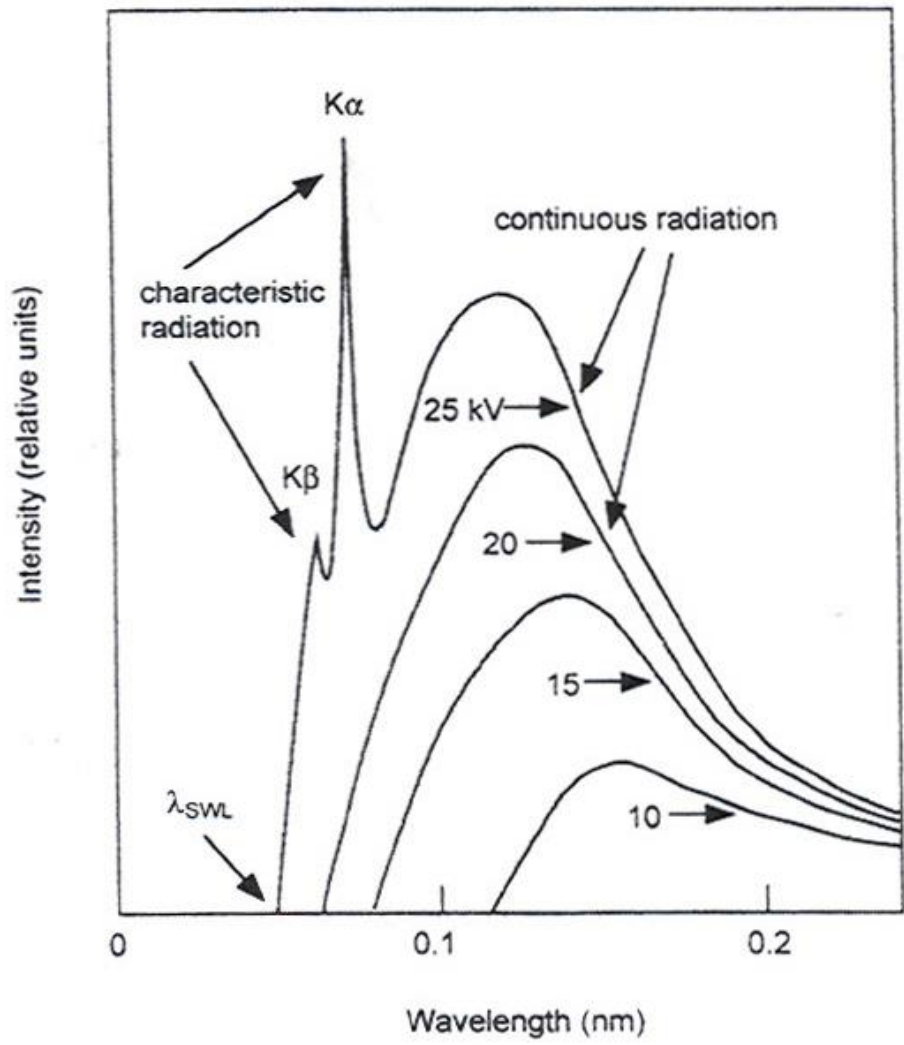


Illustration of the process of inner-shell ionization and the subsequent emission of a characteristic x-ray: (a) an incident electron ejects a K shell electron from an atom; (b) leaving a hole in the K shell; (c) electron rearrangement occurs, resulting in the emission of an x-ray photon.



X-ray spectrum of molybdenum at different potentials. The potentials refer to those applied between the anode and cathode. (The linewidths of the characteristic radiation are not to scale.) .



Properties of X-rays

Characteristic X-ray spectrum

These lines correspond to electron transfer between different energy levels and are classified as K, L, M, etc...

For Mo target, the K lines have a wavelength of $\sim 0.7 \text{ \AA}$, L lines = $\sim 5 \text{ \AA}$, etc... Normally the K lines are the most useful for x-ray diffraction.

Properties of X-rays

Characteristic X-ray spectrum

There are several K lines present, but the most useful are the strongest three, $K_{\alpha 1}$, $K_{\alpha 2}$, and K_{B1} .

For Mo the wavelength's of these lines are:

$$K_{\alpha 1} = 0.709\text{\AA} \quad K_{\alpha 2} = 0.714\text{\AA} \quad K_{B1} = 0.632\text{\AA}$$

the $\alpha 1$ and $\alpha 2$ components are very close and difficult to resolve except at higher angles.

$K_{\alpha 1}$ is 2 times as strong as $K_{\alpha 2}$

$K_{\alpha 1}$ is 5 times as strong as K_{B1}



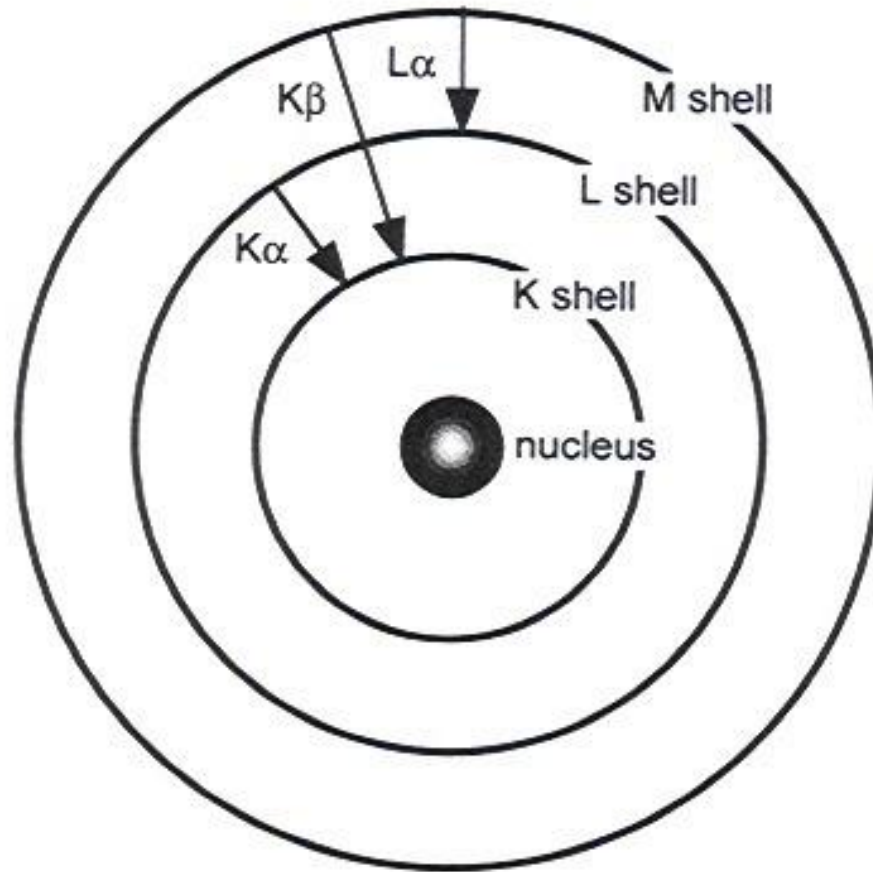
Properties of X-rays

Characteristic X-ray spectrum

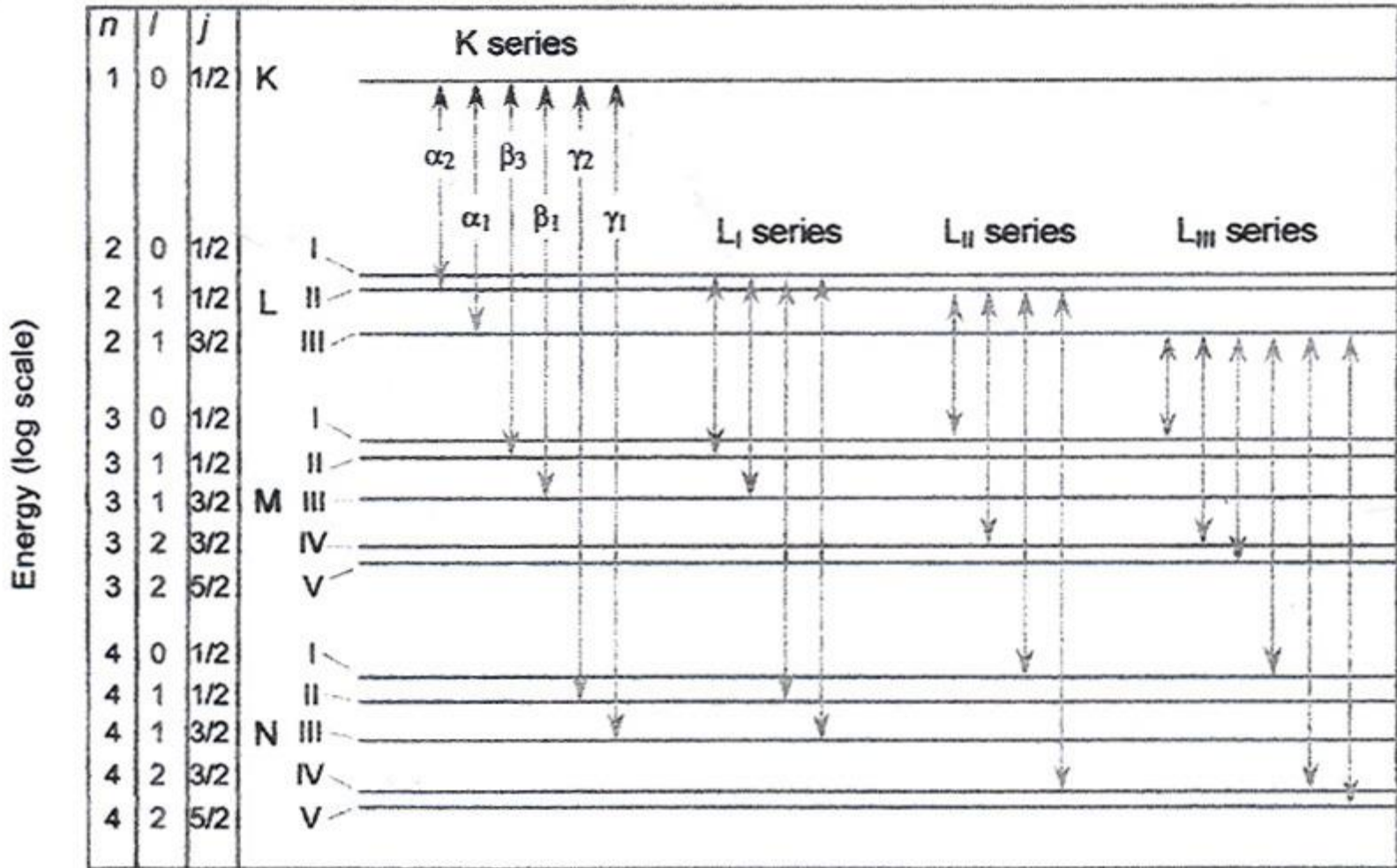
Characteristic lines correspond to electron transitions between different energy levels.

The final resting place of the electron determines the type of radiation.

There are also subshells, i.e. L consist of L_I , L_{II} , and L_{III} .



Electron transitions in an atom, which produce the $K\alpha$, $K\beta$ and $L\alpha$ characteristic x-rays.



Energy-level diagram showing all the allowed electron transitions in a molybdenum atom.

Properties of X-rays

Characteristic X-ray spectrum

So the transition from L_{III} to $K = K_{\alpha 1}$ x-ray radiation and L_{II} to $K = K_{\alpha 2}$ x-ray radiation.

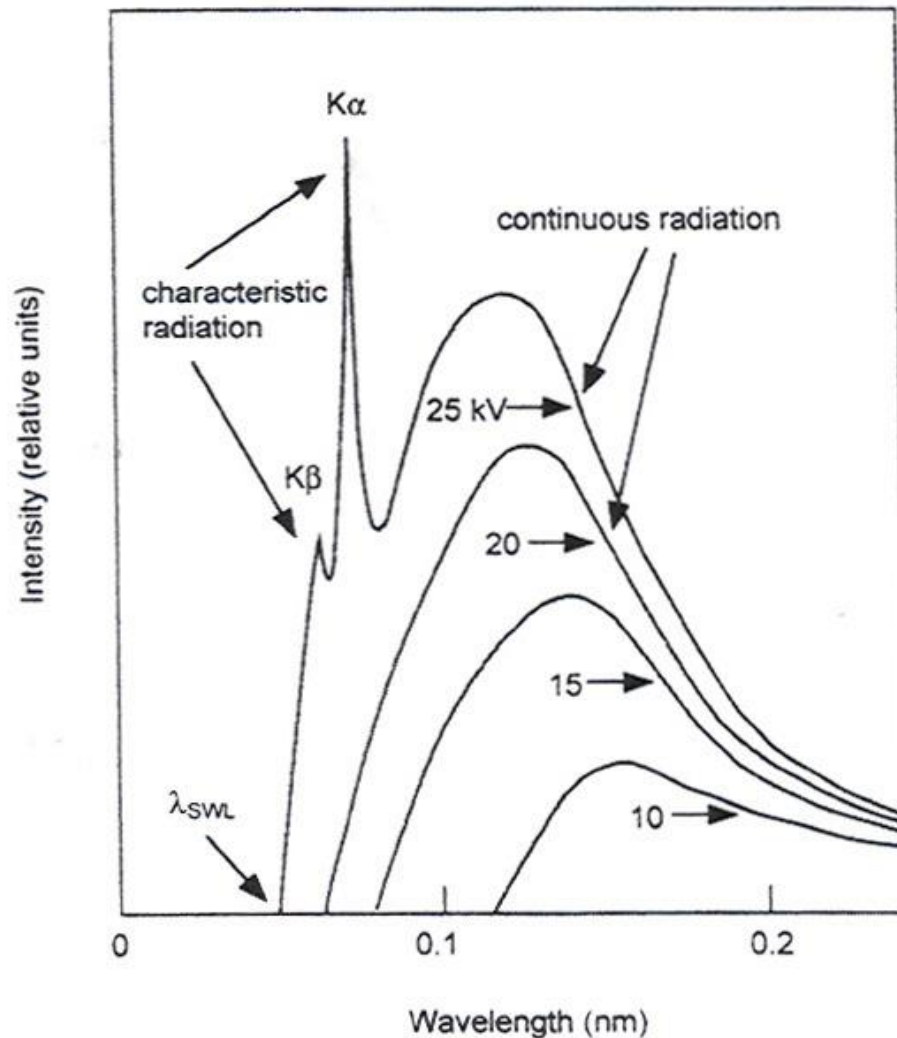
Example: For a Mo target

<u>Level</u>	<u>Energy (KeV)</u>
K	-20.00
L_{II}	-2.63
L_{III}	-2.52

For L_{III} to K transition for Mo $\Delta E = -20.00 - (-2.52) = -17.48$ KeV

$$\lambda = 12.40/17.48 \text{ KeV} = 0.709 \text{ \AA}$$

So, $K_{\alpha 1}$ for Mo = 0.709 \AA or 0.0709 nm



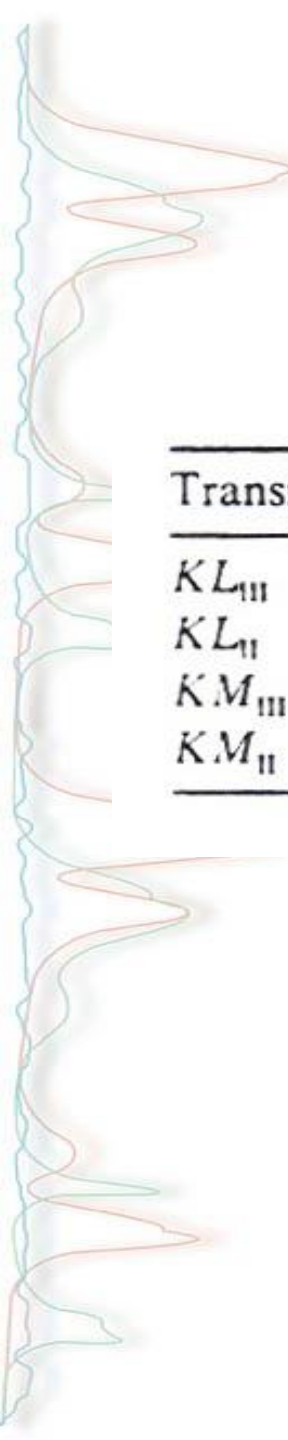
X-ray spectrum of molybdenum at different potentials. The potentials refer to those applied between the anode and cathode. (The linewidths of the characteristic radiation are not to scale.) .

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

Properties of X-rays

Characteristic X-ray spectrum

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)

Properties of X-rays

Characteristic X-ray spectrum

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.

$$J \text{ (or } j) = l + m_s \text{ (or } s)$$

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

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

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

Properties of X-rays

Characteristic X-ray spectrum

Selection Rules

<u>Subshell</u>	<u>n</u>	<u>l</u>	<u>m_s</u>	<u>j</u>
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).

Properties of X-rays

Characteristic X-ray spectrum

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_1) $K = 0$, then $\Delta l = 0$ and $L_1 \rightarrow K$ not allowed

Properties of X-rays

Properties of X-rays

Characteristic X-ray spectrum

Selection Rules

K spectrum is simple for copper:

2 α lines from $2p^{1/2} \rightarrow 1s$ and $2p^{3/2} \rightarrow 1s$

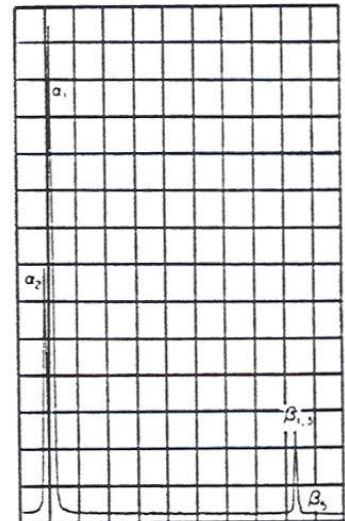
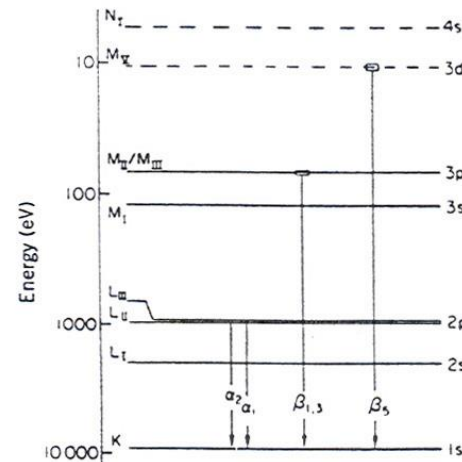
2 B lines from $3p^{1/2} \rightarrow 1s$ and $3p^{3/2} \rightarrow 1s$

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



Properties of X-rays

Properties of X-rays

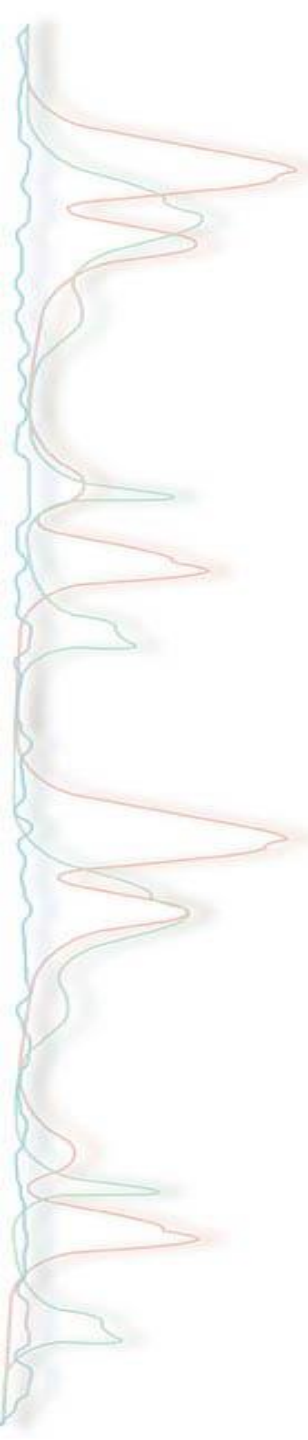
Characteristic X-ray spectrum

Selection Rules

The relative intensity of the line pairs can be predicted by a simple rule.

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

i.e for $K_{\alpha_1} : K_{\alpha_2} \rightarrow$ there are $4 p^{3/2}$ electrons for K_{α_1} and
 $2 p^{1/2}$ electrons for K_{α_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

Assignments

Do UNT Bridge Module:

“Radiation Safety Training”

You must make a copy of your successful completion of this training and give to Dr. Golden by 11-18 (next Monday) in person.

Read this website page and listen to the videos:

<https://www.sciencemuseum.org.uk/objects-and-stories/chemistry/x-ray-crystallography-revealing-our-molecular-world>

Do Homework Assignment 1 – Due Monday 11-18-24 (see slides after this slide)

Read Chapter 1 from the following 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**

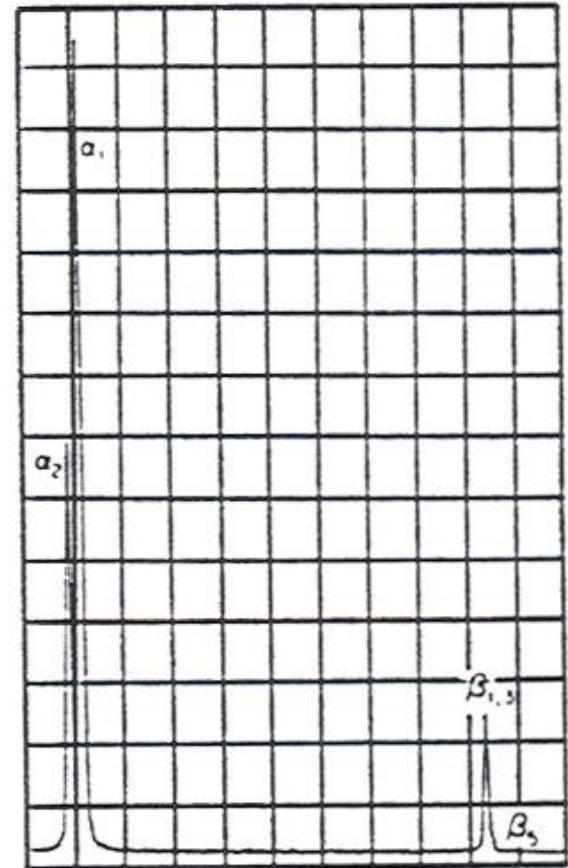
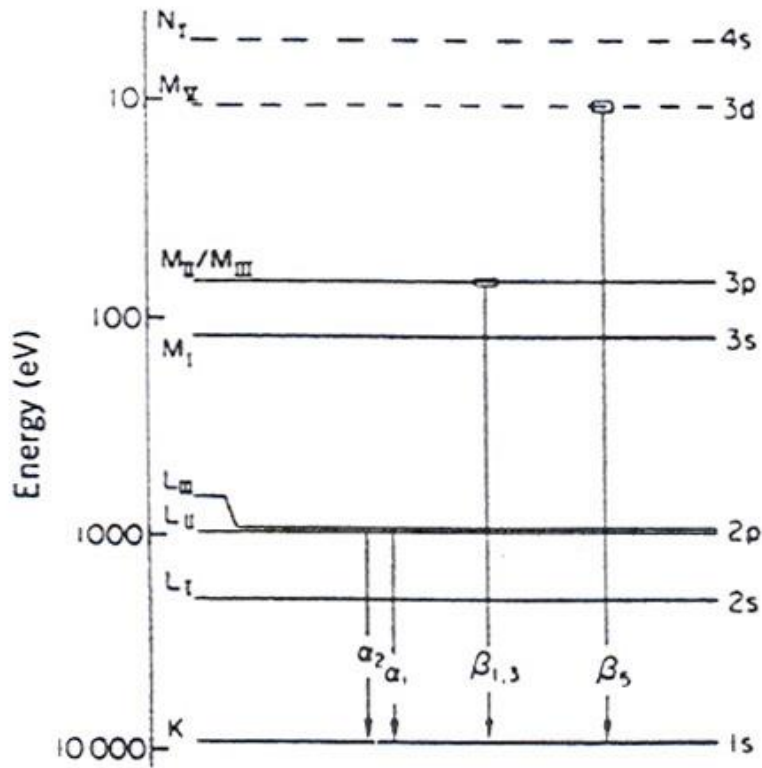
Properties of X-rays

Homework Assignment 1:

Calculate the λ for Cu $K_{\alpha 1}$, $K_{\alpha 2}$, and K_B , and memorize.

(Due next Monday 11-18)

Info For HW 1



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Level	Binding Energy (keV)
K	8.978
L_{II}	0.953
L_{III}	0.933
M_{II}	0.078
M_{III}	0.075

