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College Of Pharmacy

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جامعة البصرة

كلية الصيدلة

Review *Project*

On

Theory and application on using X-ray diffraction studies

5th stage

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Subjects:

Why study X-ray

What is X-ray Diffraction (XRD)

History of X-ray discovery

Production of X-rays

Basics of Crystallography

Applications of XRD

Instrumental Sources of Error

*Why XRD?

1. Measure the average spacings between layers or rows of atoms

2. Determine the orientation of a single crystal or grain

3. Find the crystal structure of an unknow material

4. Measure the size, shape and internal stress of small crystalline regions.

X-ray crystallography (**XRC**) is a technique used for determining the atomic and molecular structure of a crystal, in which the crystalline structure causes a beam of incident X-rays to diffract into many specific directions. By measuring the angles and intensities of these diffracted beams, a crystallographer can produce a three-dimensional picture of the density of electrons within the crystal. From this electron density, the mean positions of the atoms in the crystal can be determined, as well as their chemical bonds, their crystallographic disorder, and various other information.

Wilhelm Röntgen discovered X-rays in 1895, just as the studies of crystal symmetry were being concluded. Physicists were initially uncertain of the nature of X-rays, but soon suspected (correctly) that they were waves of electromagnetic radiation—in other words, another form of light. At that time, the wave model of light—specifically, the Maxwell theory of electromagnetic radiation—was well accepted among scientists, and experiments by Charles Glover Barkla showed that X-rays exhibited phenomena associated with electromagnetic waves, including transverse polarization and spectral lines akin to those observed in the visible wavelengths. Single-slit experiments in the laboratory of Arnold Sommerfeld suggested that X-rays had a wavelength of about 1 angstrom. However, X-rays are composed of photons, and thus are not only waves of electromagnetic radiation but also exhibit particle-like and their properties **are:**

1-Travel in straight lines

2-Are exponentially absorbed in matter with the exponent proportional to the mass of the absorbing material

3-Darken photographic plates

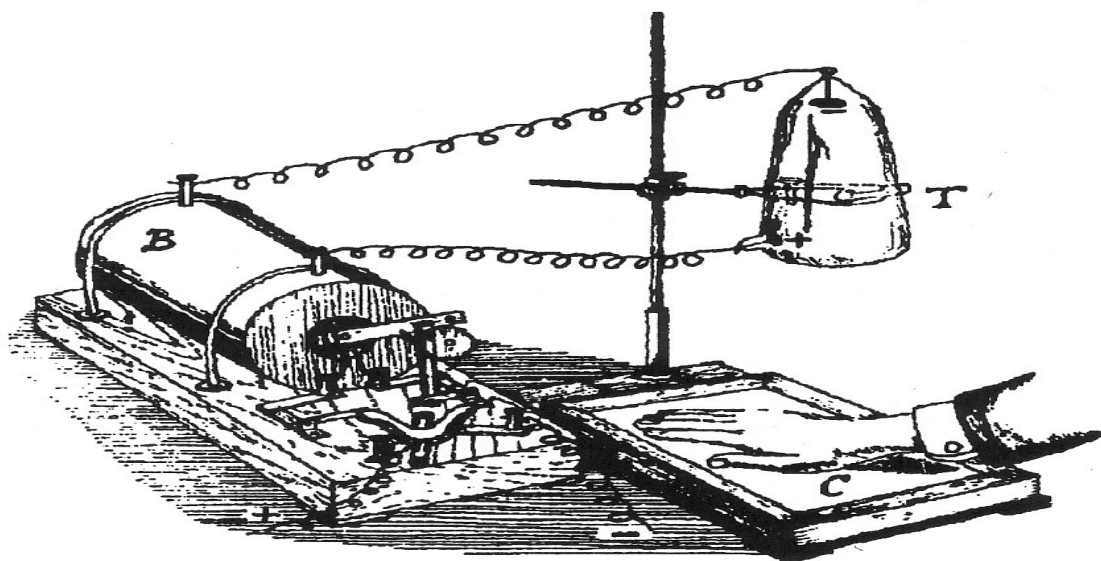4-Make shadows of absorbing material on photosensitive paper

Fig. 1.1. Röntgen's experimental apparatus in 1895: B, Ruhmkorff induction coil; C, photographic plate; T, Hittorf-Crookes evacuated tube.

Theory:

X-rays are a type of electromagnetic radiation. Other types of electromagnetic radiation are radio waves, microwaves, infrared, visible light, ultraviolet, and gamma rays. The types of radiation are distinguished by the amount of energy carried by the individual photons. All electromagnetic radiation consists of photons, which are individual packets of energy. For example, a household light bulb emits about 1021 photons of light (non-ionizing radiation) per second. The energy carried by individual photons, which is measured in electron volts (eV), is related to the frequency of the radiation. Different types of electromagnetic radiation and their typical photon energies are listed in the table below

X-Rays are part of the spectrum of electromagnetic radiation occupying the region between the ultraviolet and gamma rays.

X-rays fall in the range of wavelengths from 10^{-9} to 10^{-1} meters with photon energies 10^3 to 10^5 eV. The wavelengths of X-radiation commonly used for x-ray diffraction lie between 0.7 and 2.3 Å. Cu Kalpha1 is 1.54Å. The more penetrating radiation used for medical x-rays (and most industrial x-ray radiography) has a smaller wavelength.

an angstrom (Å) is 10^{-10} meters

a nanometer (nm) is 10^{-9} meters

a micrometer (μm) or micron is 10^{-6} meters

a millimeter (mm) is 10^{-3} meters

In X-ray crystallography, d-spacings and X-ray wavelengths are commonly given in angstroms.

Max von Laue theorized that if X-rays were waves, the wavelengths must be extremely small (on the order of 10^{-10} meters. If true, the regular structure of crystalline materials should be "viewable" using X-rays. His experiment used an X-ray source directed into a lead box containing an oriented crystal with a photographic plate behind the box
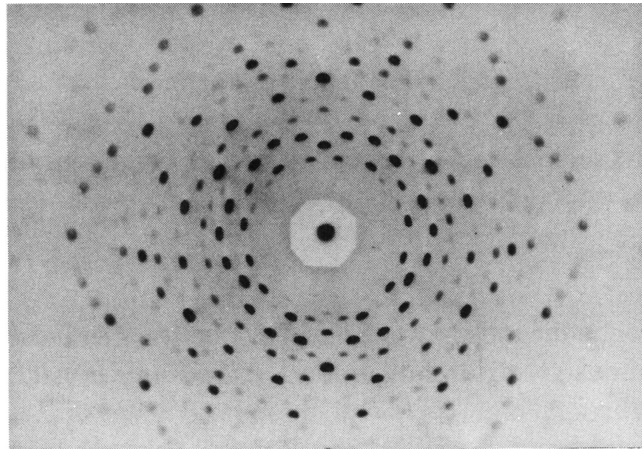
The image created showed:
1-The lattice of the crystal produced a series of regular spots from concentration of the x-ray intensity as it passed through the crystal.
2-Demonstrated the wave character of the x-rays.
3-Proved that x-rays could be diffracted by crystalline materials.

English physicists Sir W.H. Bragg and his son Sir W.L. Bragg developed a relationship in 1913 to explain why the cleavage faces of crystals appear to reflect X-ray beams at certain angles of incidence (theta, q). The variable *d* is the distance between atomic layers in a crystal, and the variable lambda l is the **wavelength** of the incident X-ray beam; n is an integer. This observation is an example of X-ray **wave interference** (Roentgen strahlinterferenzen), commonly known as X-ray diffraction (XRD), and was direct evidence for the periodic atomic structure of crystals postulated for several centuries.

*Bragg's "Extensions" of Diffraction:

Lawrence Bragg and his father W.H. Bragg discovered that diffraction could be treated as reflection from evenly spaced planes if monochromatic X-radiation was used
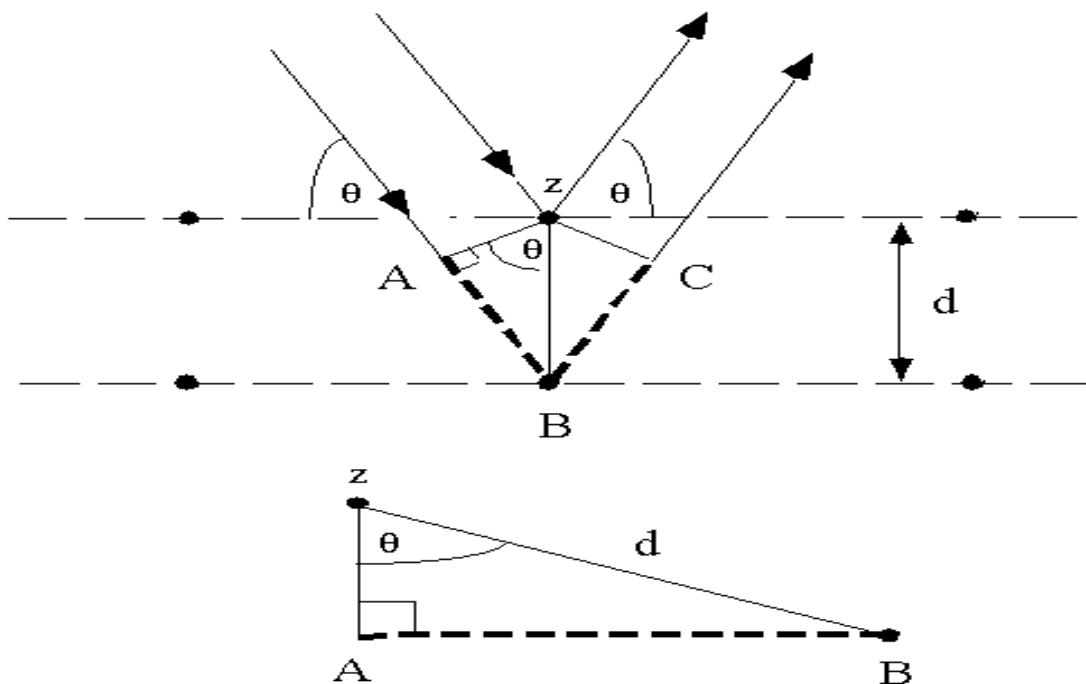
Bragg's Law: $n\lambda = 2d \sin\theta$

where n is an integer

λ is the wavelength of the X- radiation

d is the interplanar spacing in the crystalline material and
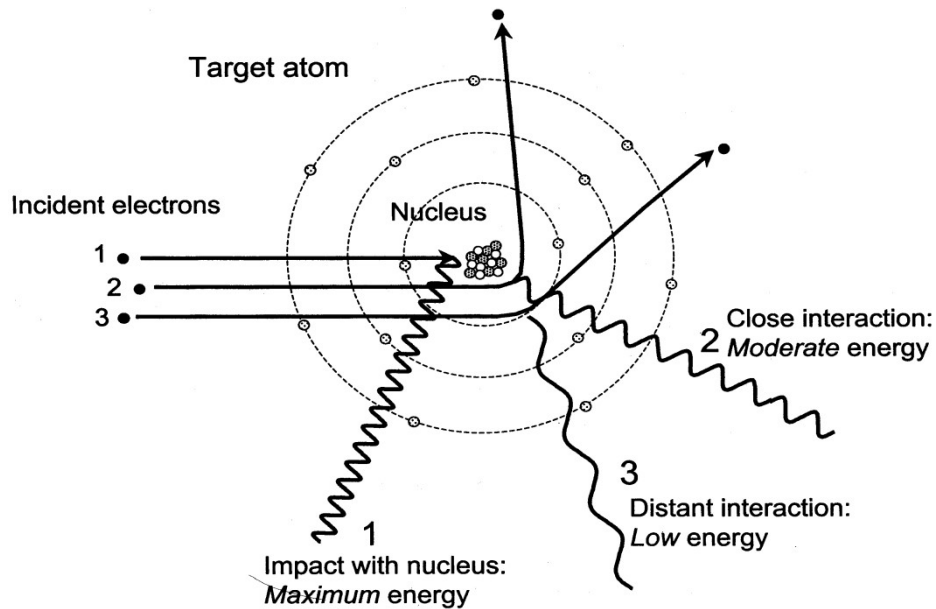
θ is the diffraction angle

The Bragg Law makes X-ray powder diffraction possible

*Bragg's Law /n Λ=2dsinθ:

The Braggs were awarded the Nobel Prize in physics in 1915 for their work in determining crystal structures beginning with NaCl, ZnS and diamond. Although Bragg's law was used to explain the interference pattern of X-rays scattered by crystals, diffraction has been developed to study the structure of all states of matter with any beam, e.g., ions, electrons, neutrons, and protons, with a wavelength similar to the distance between the atomic or molecular structures of interest. When X-rays pass through any material, some will be transmitted, some will be absorbed, and some will scatter.

The proportions depend on the photon energy, the type of material and its thickness. X-rays can scatter off a target to the surrounding area, off a wall and into an adjacent room, and over and around shielding. A common mistake is to install thick shielding walls around an X-ray source but ignore the roof; X-rays can scatter off air molecules over shielding walls to create a radiation field known as skyshine. The emanation of X-rays through and around penetrations in shielding walls is called radiation streaming. Enclosed analytical X-ray systems are typically designed by the manufacturer to shield areas outside the enclosure from scattered X-Rays.

Target atom

Incident electrons

Nucleus

1

2

3

Close interaction:
2 *Moderate* energy

3

Distant interaction:
Low energy

1

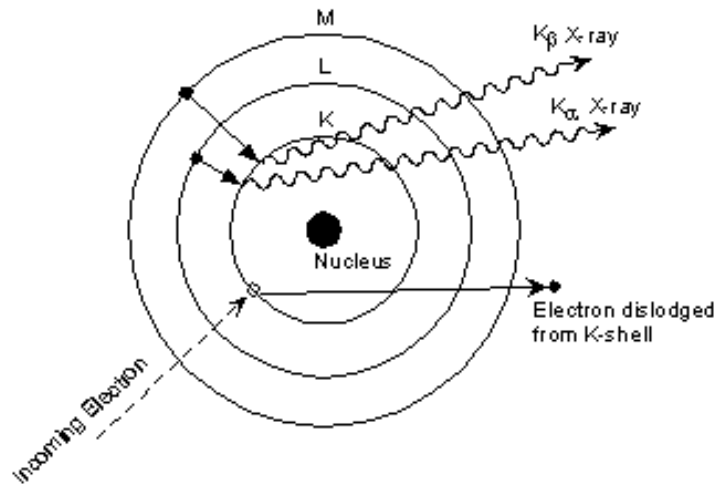Impact with nucleus:
Maximum energy

*Generating Characteristic Radiation:

The photoelectric effect is responsible for generation of characteristic x-rays. Qualitatively here's what is happening:

An incoming high-energy photoelectron disloges a k-shell electron in the target, leaving a vacancy in the shell. An outer shell electron then "jumps" to fill the vacancy. A characteristic x-ray (equivalent to the energy change in the "jump") is generated.

**L-shell to K-shell jump produces a Kα x-ray**

M-shell to K-shell jump produces a Kβ x-ray

Diagram showing atomic shells M, L, K, Nucleus, with Incoming Electron, Electron dislodged from K-shell, K_β X-ray, K_α X-ray.

*Production of X-Rays:

-X-rays are produced by the conversion of the kinetic energy (KE) of electrons into electromagnetic (EM) radiation.

*X-rays Tube Schematic:

SCHEMATIC CROSS SECTION OF AN X-RAY TUBE
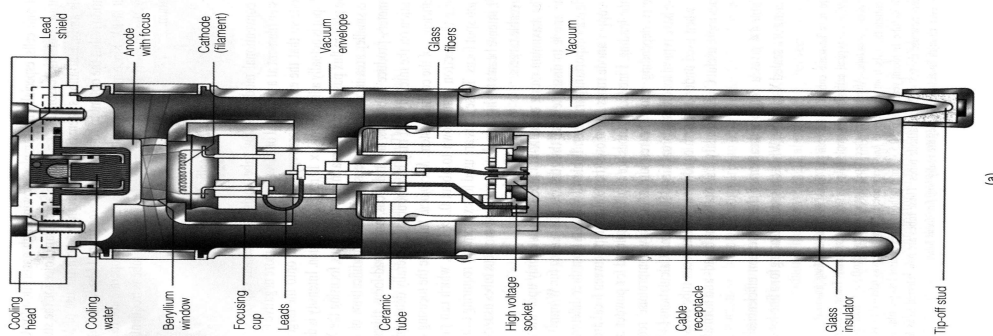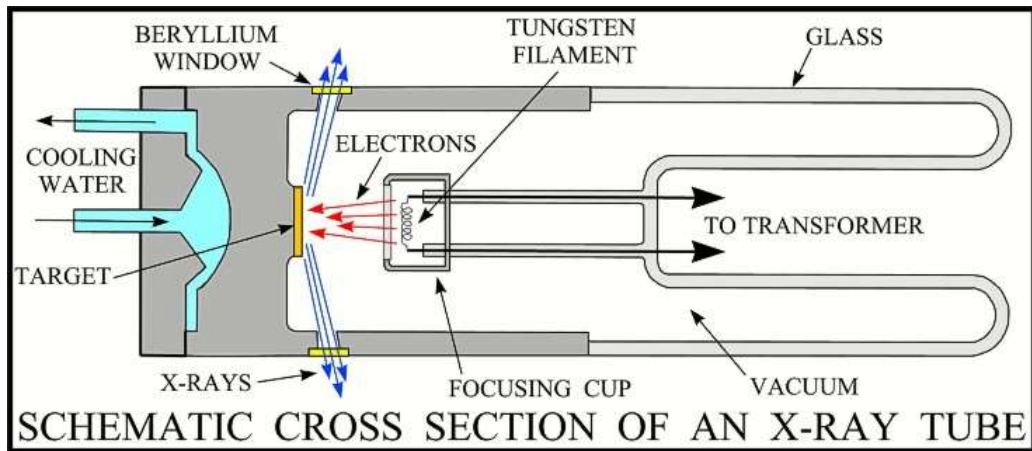
Schematic cross section of an X-ray tube as used in our lab. The anode is a pure metal. Cu, Mo, Fe, Co and Cr are in common use in XRD applications. Cu is used on our Scanting system Cu, Co and Mo will be available on our new systems. The tube is cooled by water and housed in a shielding aluminum tower.
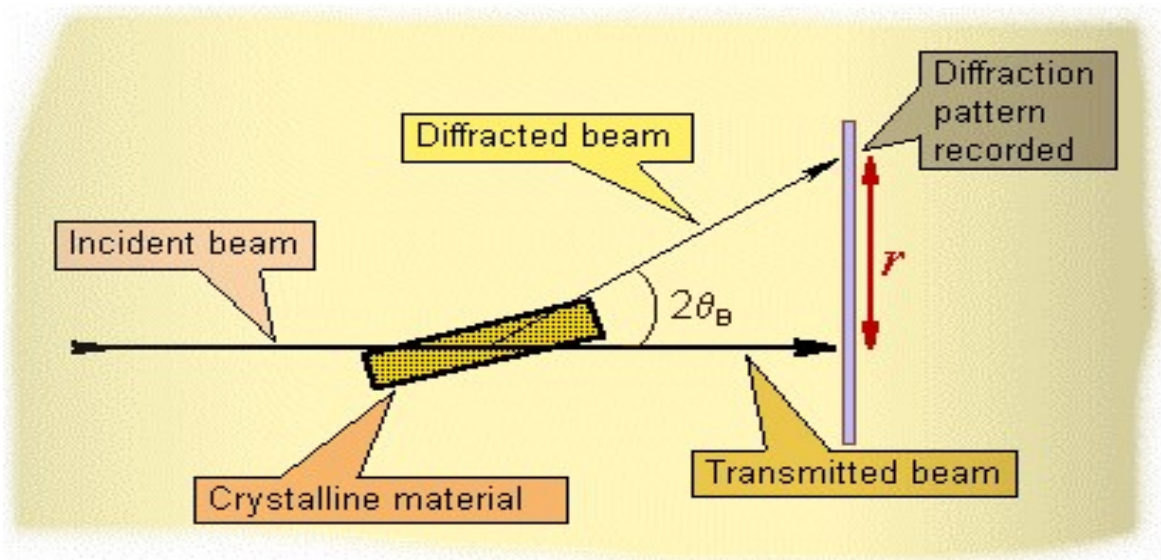
*Generating X-rays for Diffraction:

To get an accurate picture of the structure of a crystalline material requires X-radiation that is as close to monochromatic as possible. The function of the x-ray tube and associated electronics is to produce a limited frequency range of high-intensity x-rays. Filters, monochromators, specially tune detectors and software are then used to further refine the frequency used in the analysis.

4-Circle Goniometer (Eulerian or Kappa Geometry)
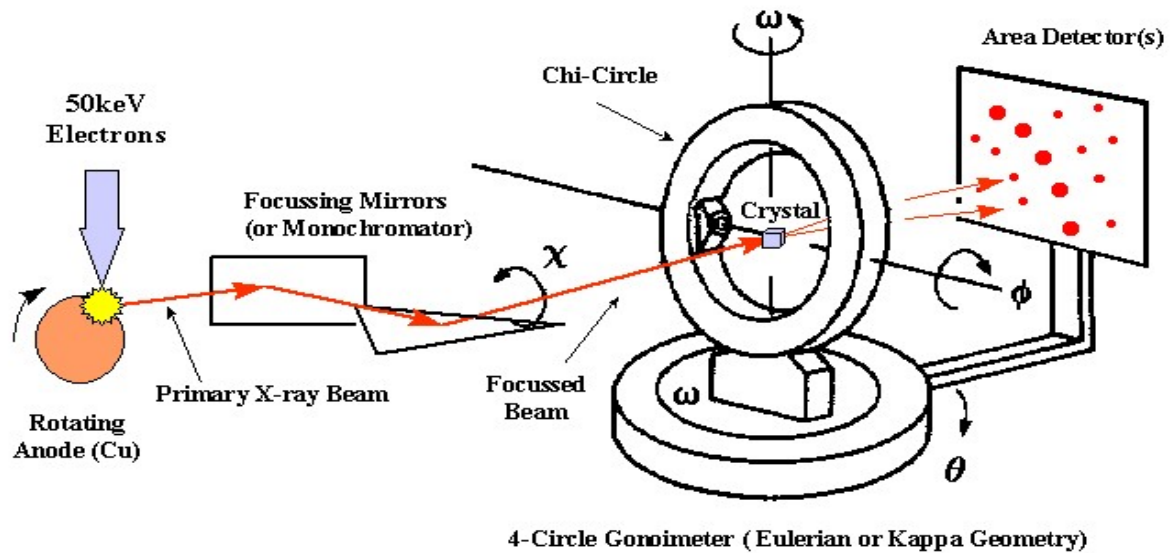
X-rays are produced whenever high-speed electrons collide with a metal target. A source of electrons – hot W filament, a high accelerating voltage between the cathode (W) and the anode and a metal target, *Cu*, Al, Mo, Mg. The anode is a water-cooled block of Cu containing desired target metal.

*Continuous and Characteristic Spectrum:

The minimum wavelength (λ in angstroms) is dependent on the accelerating potential (ν in KV) of the electrons, by the equation above. The continuum reaches a maximum intensity at a wavelength of about 1.5 to 2 times the λ_{min} as indicated by the shape of the curve.

$$\lambda_{min} = \frac{12.4}{V}$$

Continuous and characteristic radiation for copper.
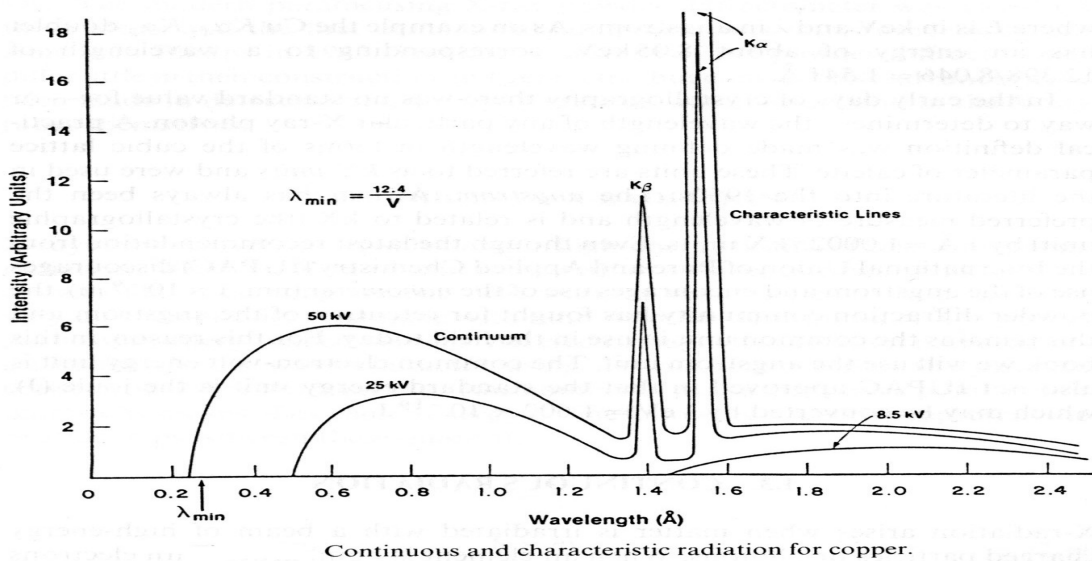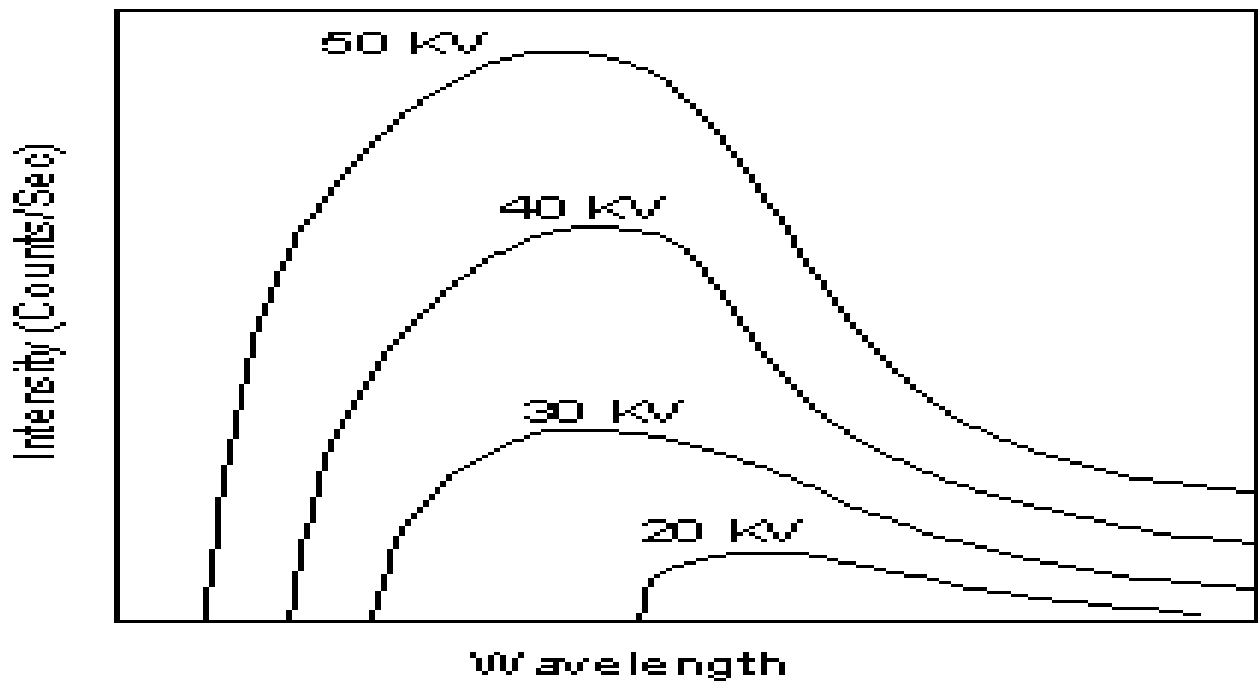
## *Characteristic Spectrum:

Each electron in the target atom has a binding energy (BE) that depends on the shell in which it resides

K shell – highest BE, L shell next highest BE and so on

When the energy of an electron incident on the target exceeds the binding energy of an electron of a target atom, it is energetically possible for a collisional interaction to eject the electron and ionize the atom
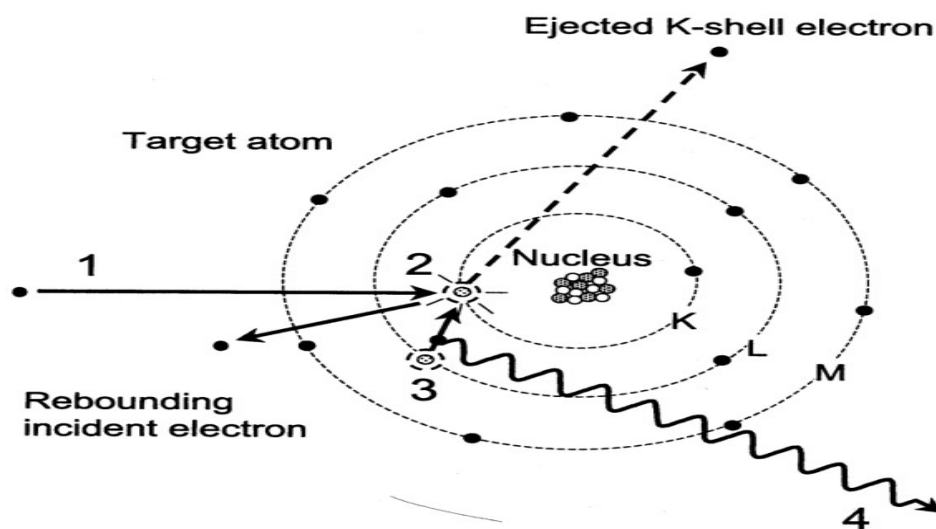
Characteristic x-ray:

from $L \rightarrow K\ e^-$ transition

In a single-crystal X-ray diffraction measurement, a crystal is mounted on a goniometer. The goniometer is used to position the crystal at selected orientations. The crystal is illuminated with a finely focused monochromatic beam of X-rays, producing a diffraction pattern of regularly spaced spots known as *reflections*. The two-dimensional images taken at different orientations are converted into a three-dimensional model of the density of electrons within the crystal using the mathematical method of Fourier transforms, combined with chemical data known for the sample. Poor resolution (fuzziness) or even errors may result if the crystals are too small, or not uniform enough in their internal makeup information.

In the second step, the crystal is placed in an intense beam of X-rays, usually of a single wavelength (*monochromatic X-rays*), producing the regular pattern of reflections. The angles and intensities of diffracted X-rays are measured, with each compound having a unique diffraction pattern.[

As the crystal is gradually rotated, previous reflections disappear and new ones appear; the intensity of every spot is recorded at every orientation of the crystal. Multiple data sets may have to be collected, with each set covering slightly more than half a full rotation of the crystal and typically containing tens of thousands of reflections.

In the third step, these data are combined computationally with complementary chemical information to produce and refine a model of the arrangement of atoms within the crystal. The final, refined model of the atomic arrangement—now called a *crystal structure*—is usually stored in a public database.

The crystal is mounted for measurements so that it may be held in the X-ray beam and rotated. There are several methods of mounting. In the past, crystals were loaded into glass capillaries with the crystallization solution (the mother liquor). Nowadays, crystals of small molecules are typically attached with oil or glue to a glass fiber or a loop, which is made of nylon or plastic and attached to a solid rod. Protein crystals are scooped up by a loop, then flash-frozen with liquid nitrogen.

This freezing reduces the radiation damage of the X-rays, as well as the noise in the Bragg peaks due to thermal motion (the Debye-Waller effect). However, untreated protein crystals often

crack if flash-frozen; therefore, they are generally pre-soaked in a cryoprotectant solution before freezing. Unfortunately, this pre-soak may itself cause the crystal to crack, ruining it for crystallography. Generally, successful cryo-conditions are identified by trial and error.

When a crystal is mounted and exposed to an intense beam of X-rays, it scatters the X-rays into a pattern of spots or *reflections* that can be observed on a screen behind the crystal. A similar pattern may be seen by shining a laser pointer at a compact disc. The relative intensities of these spots provide the information to determine the arrangement of molecules within the crystal in atomic detail. The intensities of these reflections may be recorded with photographic film, an area detector or with a charge-coupled device (CCD) image sensor.

Some measures of diffraction quality can be determined at this point, such as the mosaicity of the crystal and its overall disorder, as observed in the peak widths. Some pathologies of the crystal that would render it unfit for solving the structure can also be diagnosed quickly at this point.

*Crystallography:

Is the experimental science of determining the arrangement of atoms in crystalline solids. The word "crystallography" derives from the Greek words *crystallon* "cold drop, frozen drop", with its meaning extending to all solids with some degree of transparency. In July 2012, the United Nations recognised the

importance of the science of crystallography by proclaiming that 2014 would be the International Year of Crystallography. The first crystal structure of a macromolecule was solved in 1958, a three-dimensional model of the myoglobin molecule obtained by X-ray analysis.

* **X-ray crystallography** (**XRC**):

Is a technique used for determining the atomic and molecular structure of a crystal, in which the crystalline structure causes a beam of incident X-rays to diffract into many specific directions. By measuring the angles and intensities of these diffracted beams, a crystallographer can produce a three-dimensional picture of the density of electrons within the crystal. From this electron density, the mean positions of the atoms in the crystal can be determined, as well as their chemical bonds, their crystallographic disorder, and various other.

*Basics of Crystallography:

A crystal consists of a periodic arrangement of the unit cell into a lattice. The unit cell can contain a single atom or atoms in a fixed arrangement. Crystals consist of planes of atoms that are spaced a distance d apart, but can be resolved into many atomic planes, each with a different d spacing. a,b and c (length) and a, b and g angles between a,b and c are lattice constants or parameters which can be determined by XRD.

*CRYSTALLIZATION:

Crystals are regular arrays of atoms, and X-rays can be considered waves of electromagnetic radiation. Atoms scatter X-ray waves, primarily through the atoms' electrons. Just as an ocean wave striking a lighthouse produces secondary circular waves emanating from the lighthouse, so an X-ray striking an electron produces secondary spherical waves emanating from the electron. This phenomenon is known as <u>elastic scattering</u>, and the electron (or lighthouse) is known as the *scatterer*. A regular array of scatterers produces a regular array of spherical waves. Although these waves cancel one another out in most directions through <u>destructive interference</u>, they add constructively in a few specific directions, determined by <u>Bragg's law</u>:

CRYSTALLIZATION are a Process of producing crystals from a homogeneous phase which is obtained from a solution. Capable of producing bioproducts at very high purity and considered to be a polishing step and a purification step.Two different application of crystallization:

1-Crystallization for polishing and purification

2-Crystallization for crystallography

Crystallization is therefore an aspect of precipitation, obtained through a variation of the solubility conditions of the solute in the solvent , as compared to precipitation due to chemical reaction.

Crystal-Structure:

In crystallography, **crystal structure** is a description of the ordered arrangement of atoms, ions or molecules in a crystalline material. Ordered structures occur from the intrinsic nature of the constituent particles to form symmetric patterns that repeat along the principal directions of three-dimensional space in matter

In mineralogy and crystallography, **crystal structure** is a unique arrangement of atoms or molecules in a crystalline liquid or solid. A crystal structure is composed of a pattern, a set of atoms arranged in a particular way, and a lattice exhibiting long-range order and symmetry.
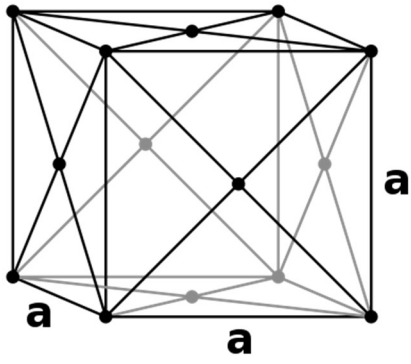
Unit cell:

The crystal structure of a material or the arrangement of atoms within a given type of crystal structure can be described in terms of its unit cell. The unit cell is a small box containing one or more atoms, a spatial arrangement of atoms.
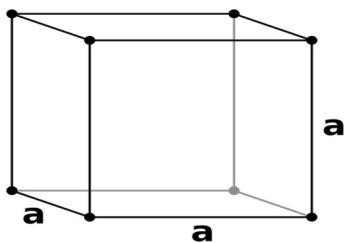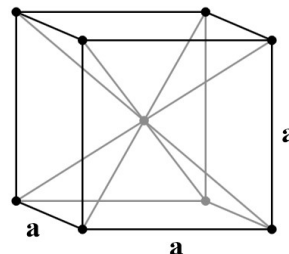
Simple cubic (P)   Body-centered cubic (F)

Face-centered cubic (F)
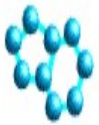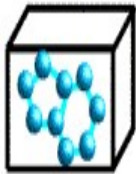
molecule   unit cell   crystal
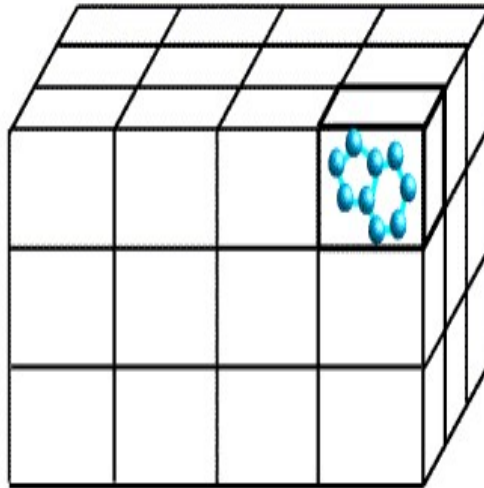
Seven Crystal Systems:

Crystal class	Axis system
Cubic	$a = b = c,\ \alpha = \beta = \gamma = 90°$
Tetragonal	$a = b \neq c,\ \alpha = \beta = \gamma = 90°$
Hexagonal	$a = b \neq c,\ \alpha = \beta = 90°,\ \gamma = 120°$
Rhombohedral	$a = b = c,\ \alpha = \beta = \gamma \neq 90°$
Orthorhombic	$a \neq b \neq c,\ \alpha = \beta = \gamma = 90°$
Monoclinic	$a \neq b \neq c,\ \alpha = \gamma = 90°,\ \beta \neq 90°$
Triclinic	$a \neq b \neq c,\ \alpha \neq \beta \neq \gamma \neq 90°$
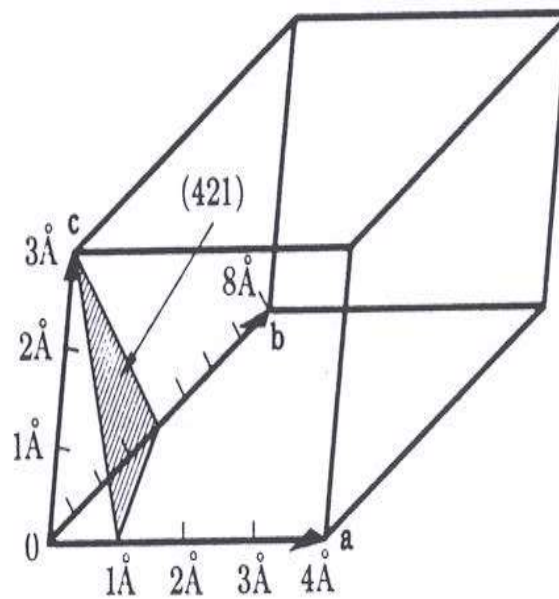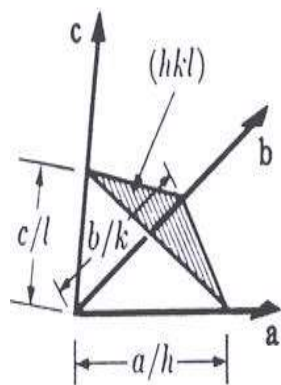
Point groups:

The crystallographic point group or *crystal class* is the mathematical group comprising the symmetry operations that leave at least one point unmoved and that leave the appearance of the crystal structure unchanged. These symmetry operations include

- *Reflection*, which reflects the structure across a *reflection plane*
- *Rotation*, which rotates the structure a specified portion of a circle about a *rotation axis*
- *Inversion*, which changes the sign of the coordinate of each point with respect to a *center of symmetry* or *inversion point*
- *Improper rotation*, which consists of a rotation about an axis followed by an inversion.

Rotation axes (proper and improper), reflection planes, and centers of symmetry are collectively called *symmetry elements*. There are 32 possible crystal classes. Each one can be classified into one of the seven crystal systems.

Space groups:

In addition to the operations of the point group, the space group of the crystal structure contains translational symmetry operations. These include:

- Pure *translations*, which move a point along a vector
- *Screw axes*, which rotate a point around an axis while translating parallel to the axis.
- *Glide planes*, which reflect a point through a plane while translating it parallel to the plane. There are 230 distinct space groups

Arrangement of asymmetric unit in a lattice defines the crystal symmetry. The allowed symmetries are 2-, 3, 4, 6-fold rotational, mirror(m), and inversion (i) symmetry (+/-) translation.

Rotation + translation = screw and Rotation + mirror = glide so by application all of these symmetry element to the 7 crystal systems and 14 Bravais lattice with 32 point groups to get 230 space groups.
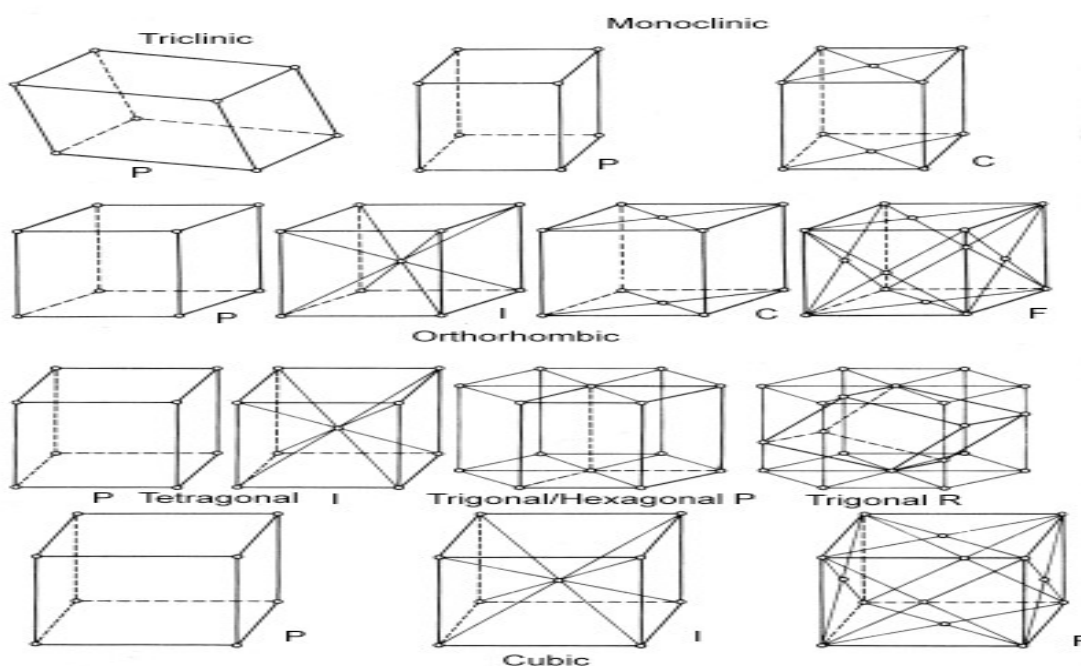
Crystallization:

Crystallization is the (natural or artificial) process of - formation of solid crystals precipitating from a solution, melt or more rarely deposited directly from a gas . Crystallization is also a chemical solid–liquid separation technique, in which mass transfer of a solute from the liquid solution to a pure solid crystalline phase occurs. Once the supersaturation is exhausted,

the solid–liquid system reaches equilibrium and the crystallization is complete.

The crystal Growth:

The *crystal growth* is the subsequent growth of the nuclei that succeed in achieving the critical cluster size. Nucleation and growth continue to occur simultaneously while the supersaturation exists. Supersaturation is the driving force of the crystallization, hence the rate of nucleation and growth is driven by the existing supersaturation in the solution.The crystallization process consists of two major events, *nucleation* and *crystal growth*.

Nucleation is the step where the solute molecules dispersed in the solvent start to gather into clusters, on the nanometer scale (elevating solute concentration in a small region), that become stable under the current operating conditions. An important stage of the precipitation process is the onset of nucleation. The creation of a hypothetical solid particle includes the formation of an interface, which requires some energy based on the relative surface energy of the solid and the solution. If this energy is not available, and no suitable nucleation surface is available, supersaturation occurs.

Precipitation:

Is the formation of a solid in a solution or inside another solid during a chemical reaction or by diffusion in a solid. When the

reaction occurs in a liquid, the solid formed is called the **precipitate**, or when compacted by a centrifuge, a **pellet**. The liquid remaining above the solid is in either case called the **supernate** or **supernatant**.
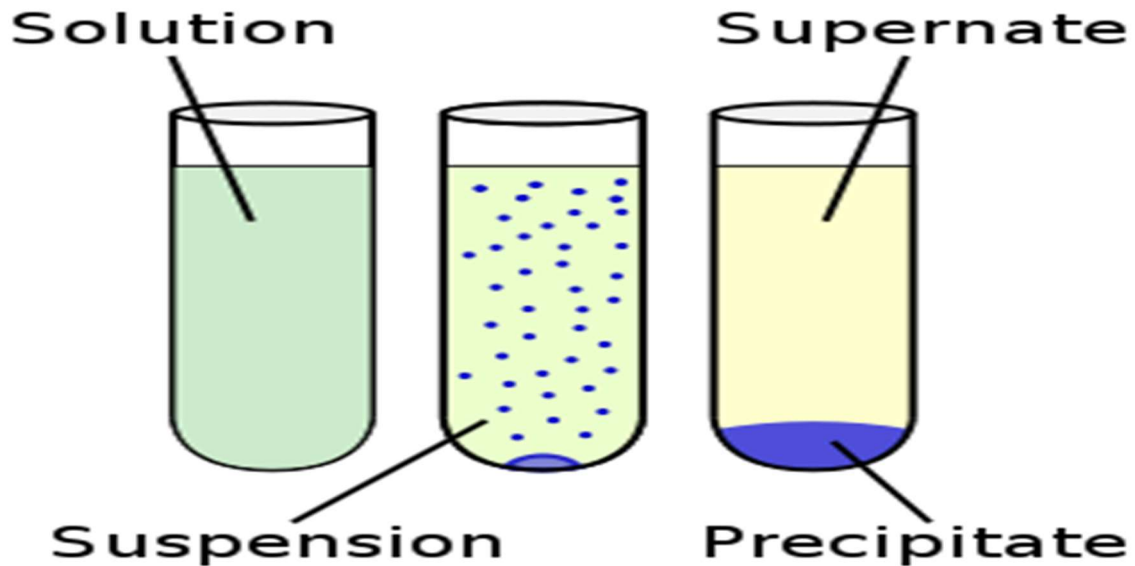
Applications of XRD:

1-To identify crystalline phases and orientation.

2-To determine structural properties.

3-Lattice parameters (10-4 Å), strain, grain size, expitaxy, phase composition, preferred orientation.

4- To measure thickness of thin films and multi-layers.

5- To determine atomic arrangement.

6-Detection limits: ~3% in a two phase mixture Spatial resolution: normally none.

One of the most important uses of XRD:

1-Obtain XRD pattern

2-Measure d-spacings

3-Obtain integrated intensities

4-Compare data with known standards in the JCPDS file, which are for random orientations (there are more than 50,000 JCPDS cards of inorganic materials).

Procedure:

The technique of single-crystal X-ray crystallography has three basic steps.

The first and often most difficult step is to obtain an acceptable crystal of the material under study. The crystal should be sufficiently large (typically larger than 0.1 mm in all dimensions), pure in composition and regular in structure, with no significant internal imperfections such as cracks or twinning.

In the second step, the crystal is placed in an intense beam of X-rays, usually of a single wavelength (*monochromatic X-rays*), producing the regular pattern of reflections. The angles and intensities of diffracted X-rays are measured, with each compound having a unique diffraction pattern. As the crystal is gradually rotated, previous reflections disappear and new ones appear; the intensity of every spot is recorded at every orientation of the crystal. Multiple data sets may have to be collected, with each set covering slightly more than half a full rotation of the crystal and typically containing tens of thousands of reflections.

In the third step, these data are combined computationally with complementary chemical information to produce and refine a model of the arrangement of atoms within the crystal. The final, refined model of the atomic arrangement now called a *crystal structure* is usually stored in a public database

*Instrumental Sources of Error:

1- Specimen displacement

2- Instrument misalignment

3- Error in zero 2q position

4- Peak distortion due to Ka2 and Kb wavelengths

*Advantage of XRD:

1 -Non-destructive, fast, easy sample prep

2- High-accuracy for d-spacing calculations

3- Can be done in-situ Single crystal, poly, and amorphous materials

4- Standards are available for thousands of material systems.

*References:

1. UN announcement "International Year of Crystallography". iycr2014.org. 12 July 2012

2. *Kendrew, J. C.; Bodo, G.; Dintzis, H. M.; Parrish, R. G.; Wyckoff, H.; Phillips, D. C. (1958). "A Three-Dimensional Model of the*

However, Schönberg, Singer, and Stephan[33] assigned an i.r. band at 1695 cm^{-1} in (L^{Ph}-Se) to a C=Se double-bond. This seems unlikely, as the value is similar to that for ν(C=O) in a urea.

The crystal packing in the unit cell (Figure 4) of (2) is the same as that found in the Te analogue (3).

2.2.c The X-Ray Crystal Structure of the Thiourea EtN(CH$_2$)$_2$N(Et)C=S (1) (abbreviated as L^{Et}-S)

A pale-yellow, air-stable, single crystal of the thiourea (1) was sealed in a thin-walled glass capillary under argon. The sample was prepared from the electron-rich olefin L^{Et}$_2$ and S, equation (7) (R = Et). X-Ray diffraction quality crystals were obtained by cooling a toluene solution to -30 ^{o}C.

$$\left[\begin{array}{c} R \\ N \\ \\ N \\ R \end{array} C = C \begin{array}{c} R \\ N \\ \\ N \\ R \end{array} \right] + 2S \longrightarrow 2 \left[\begin{array}{c} R \\ N \\ \\ N \\ R \end{array} C = S \right] \quad (7)$$

(8)   (1)
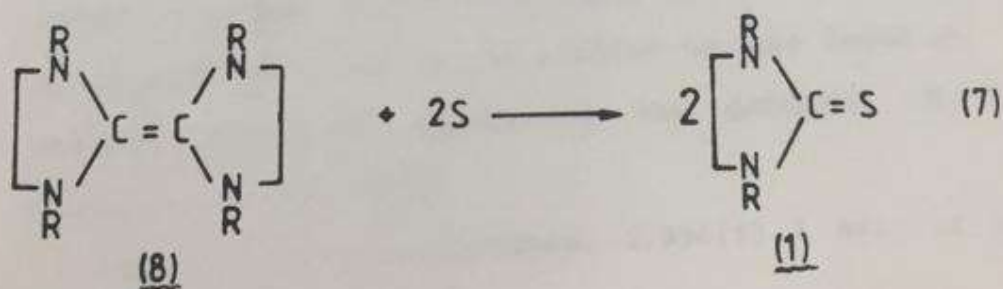
The molecular goemetry and the atom numbering scheme for the thiourea (1) are shown in Figure 5. The crystal packing in the unit cell is illustrated in Figure 6. Fractional atomic co-ordinates, intra-molecular distances and angles, anisotropic temperature factors, and torsion angles are listed in Tables 3a – 3d , respectively. The crystal data and refinement parameters are in Table 4. The least-squares mean planes are in Table 5. Tables of structure factor amplitudes are in Appendix 4.

The thiourea ($L^{Et}-S$) (1) has no crystallograp-hically imposed symmetry. The sum of the angles around the central carbon atom C(1) is 360°. Thus the C(1) environment is planar with sp^2-hybridisation . The sum of the angles at each nitrogen atom is 359.9°. The C_2N_2C framework is planar and this plane also contains the sulphur atom.

The S-C bond distance, 1.670(3) Å, is significantly shorter than the single bond value of 1.81 Å,[27] and longer than the double-bond value of 1.60 Å.[34] The S-C bonding in compound (1) is similar to that found in several molecules possessing the grouping -N-CS-X, where X = N or C.[35-38]

The C(1)-N bond distance, 1.336(1) Å av., is very

close to the value 1.352 Å considered as appropriate for a partial double-bond in certain nitrogen heterocyclic systems,[27] and is similar to that found for 1,3-dimethylimidazole-2(3H)-thione of 1.349(6) Å,[36].

From the S-C and C(1)-N bond lengths in compound (1) we propose that the N_2CS framework is π-delocalised [*cf*., the Se analogue (2)], as illustrated in (33).

(33)
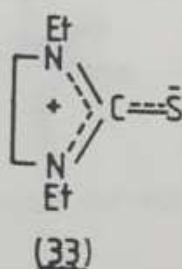
Once again [*cf*., the earlier discussion of the selenourea (2)], our conclusions are in conflict with those based on i.r. data.[31,32] For various compounds containing the functional group YN-CX-NY (X = S or Se) (Y = H, Me, or Et), $\nu(CX)$ was believed to fall below 650 cm^{-1}, as appropriate for a C-S or C-Se single bond.

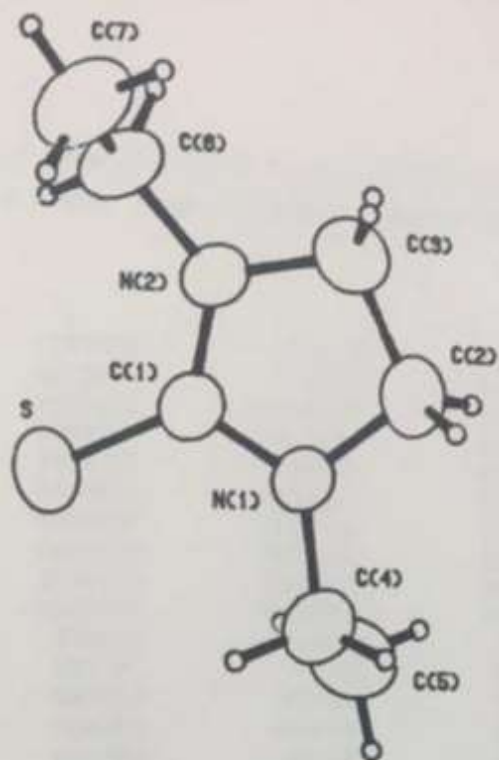Figure 5. *The molecular structure and the atom numbering scheme for* $(L^{Et}-S)$ *(1)*
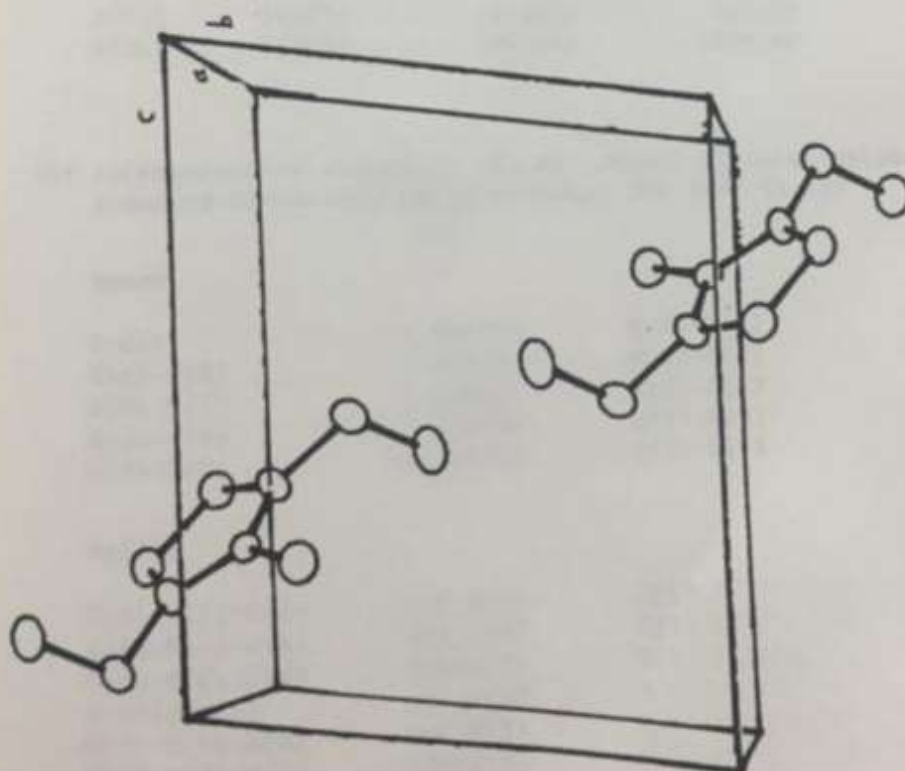

Figure 6. *The crystal packing in the unit cell of* $(L^{Et}-S)$ *(1)*

Table 3

(a) Fractional atomic co-ordinates (x 10⁴) for S, N, and C atoms, and (x 10³) for H atoms, with estimated standard deviations in parentheses for (L^{Et}-S) (1)

	x	y	z
S	2259(2)	1748(2)	7606(1)
N(1)	6115(4)	710(4)	6536(3)
N(2)	4635(4)	-1120(4)	8421(4)
C(1)	4384(5)	415(4)	7516(4)
C(2)	7710(6)	-690(5)	6746(5)
C(3)	6675(6)	-1929(5)	8077(5)
C(4)	6452(6)	2210(5)	5322(5)
C(5)	7465(7)	3642(6)	5761(6)
C(6)	3154(6)	-1904(5)	9653(4)
C(7)	2249(7)	-3438(6)	9253(6)
H(2a)	805(5)	-119(5)	575(4)
H(2b)	895(5)	-17(4)	699(4)
H(3a)	663(5)	-307(4)	777(4)
H(3b)	724(5)	-204(5)	899(4)
H(4a)	511(5)	261(4)	516(4)
H(4b)	727	173	445
H(5c)	864(5)	335(5)	593(4)
H(5b)	652(6)	415(5)	671(5)
H(5a)	780(6)	451(5)	487(4)
H(6a)	216(6)	-97(5)	998(4)
H(6b)	378(5)	-231(5)	1060(4)
H(7a)	325(5)	-441(4)	887(4)
H(7c)	163(7)	-313(6)	837(5)
H(7b)	145(5)	-397(5)	1010(4)

(b) Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses for (L^{Et}-S) (1)

Bonds

S-C(1)	1.670(3)	N(1)-C(1)	1.335(4)
N(1)-C(2)	1.459(5)	N(1)-C(4)	1.459(5)
N(2)-C(1)	1.338(4)	N(2)-C(3)	1.447(5)
N(2)-C(6)	1.439(4)	C(2)-C(3)	1.509(5)
C(4)-C(5)	1.481(7)	C(6)-C(7)	1.490(7)

Angles

C(1)-N(1)-C(2)	112.8(3)	C(1)-N(1)-C(4)	126.0(3)
C(2)-N(1)-C(4)	121.1(3)	C(1)-N(2)-C(3)	111.9(3)
C(1)-N(2)-C(6)	126.6(3)	C(3)-N(2)-C(6)	121.4(3)
S-C(1)-N(1)	125.6(2)	S-C(1)-N(2)	125.6(2)
N(1)-C(1)-N(2)	108.8(3)	N(1)-C(2)-C(3)	102.2(3)
N(2)-C(3)-C(2)	104.2(3)	N(1)-C(4)-C(5)	112.9(4)
N(2)-C(6)-C(7)	113.2(3)		

(c) Anisotropic temperature factors ($\times 10^3$) in the form
$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}ka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$
for (L^{Et}-S) (**1**)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	48(1)	69(1)	76(1)	4(1)	-12(1)	-10(1)
N(1)	43(2)	60(2)	49(2)	-6(1)	-4(1)	7(2)
N(2)	52(2)	44(2)	56(2)	-8(1)	-1(2)	3(2)
C(1)	46(2)	48(2)	39(2)	-11(2)	-9(2)	-9(2)
C(2)	47(2)	65(2)	67(3)	-2(2)	-7(2)	-11(2)
C(3)	67(2)	52(2)	67(3)	1(2)	-14(2)	-6(2)
C(4)	59(2)	75(3)	54(3)	-12(2)	-4(2)	2(2)
C(5)	89(3)	65(3)	105(4)	-20(2)	-30(3)	10(3)
C(6)	77(3)	63(3)	52(3)	-22(2)	-4(2)	3(2)
C(7)	93(3)	73(3)	89(3)	-37(2)	-1(3)	-8(3)

(d) Torsion angles ($^{\circ}$) for (L^{Et}-S) (**1**)

S-C(1)-N(1)-C(2)	179.5(3)
S-C(1)-N(1)-C(4)	-2.7(5)
N(2)-C(1)-N(1)-C(4)	177.7(3)
N(2)-C(1)-N(1)-C(2)	-0.1(4)
C(1)-N(1)-C(2)-C(3)	-1.0(4)
C(4)-N(1)-C(2)-C(3)	-178.9(3)
C(1)-N(1)-C(4)-C(5)	98.9(4)
C(2)-N(1)-C(4)-C(5)	108.6(4)
N(1)-C(2)-C(3)-N(2)	1.7(4)
S-C(1)-N(2)-C(3)	-178.3(3)
S-C(1)-N(2)-C(6)	-1.1(5)
N(1)-C(1)-N(2)-C(3)	1.3(4)
N(1)-C(1)-N(2)-C(6)	178.5(3)
C(1)-N(2)-C(6)-C(7)	104.7(4)
C(3)-N(2)-C(6)-C(7)	-78.3(4)
C(1)-N(2)-C(3)-C(2)	-1.9(4)
C(6)-N(2)-C(3)-C(2)	-179.3(3)

2.3 Comparative Discusion on the Structures of the Chalcogenoureas (L^{Et}-X) (X = S, Se, or Te)

The angles N-C-N (110.7° av.) are significantly different from the 120° expected from a trigonally hybridised carbon atom; this arises from strain in the ring. Similarly, the angles N-C-C (102.1° av.) differ greatly from the tetrahedral value, while the angles X-C-N (124.7° av.) differ slightly from 120°; again, this is a consequence of ring strain.

The shortest intermolecular X...X distances increase in the sequence X = Te, 5.512 Å; X = Se, 5.655 Å; and X = S, 6.136 Å, all of which are greater than the sum of the van der Waals radii. Thus, in none of the three structures is there any indication of X...X interactions.

Within the series L^{Et}-X, the X-ray data show that there is a partial C——X double-bond only for X = O, S, and Se, whereas for X = Te, CX is largly a single bond with correspondingly higher CN_2 multiple bonding.

Table 4

Crystal data and refinement parameters for $(L^{Et}-S)(1)$, $(L^{Et}-Se)(2)$, and $(L^{Et}-Te)(3)$

Formula	$C_7H_{14}N_2S$ (I)	$C_7H_{14}N_2Se$ (2)	$C_7H_{14}N_2Te$ (3)
M	158.96	205.16	253.8
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$	$C2/c$
colour	pale yellow	off-white	pale-brown
$a/\text{Å}$	6.743(1)	13.481(9)	13.660(3)
$b/\text{Å}$	7.629(2)	7.535(5)	7.910(3)
$c/\text{Å}$	8.960(1)	9.071(4)	9.150(4)
$\alpha/^{\circ}$	81.50(1)	–	–
$\beta/^{\circ}$	78.88(2)	100.57(5)	101.03(6)
$\gamma/^{\circ}$	84.39(2)	–	–
$U/\text{Å}^3$	446.19	905.8	970.4
Dc/gcm^{-3}	1.18	1.50	1.74
$F(000)$	172	416	488
μ/cm^{-1}	2.8	43.8	31.2
$\lambda/\text{Å}$	0.71069	0.71069	0.71069
Size/mm	0.20x0.15x0.10	0.35x0.35x0.20	0.30x0.30x0.30
No	699	615	689
$R1$	0.039	0.076	0.117
$R2$	0.041	0.086	0.137
shift/error	0.01	0.01	0.01
$2\theta/^{\circ}$	44	50	40
Z	2	4	4

Abbreviations: M, molecular weight; U, volume of the unit cell; D_c, calculated density; $F(000)$, number of electrons in unit cell; μ, absorption coefficient; R_1R_2, residual indeces; θ, maximum Bragg angle; No, number of reflections used in the structure refinement; and Z, number of molecules in unit cell.

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