Bharathidasan University
Tiruchirappalli – 620 023, Tamil Nadu

6 Yr. Int. **M.Tech.** Geological Technology & Geoinformatics programme

Course Code: MTIGT0306

CRYSTALLOGRAPHY AND MINERALOGY

UNIT–2 : CRYSTAL PROPERTIES

Georgius Agricola, 'Father of Mineralogy'

German scientist '**Georg Bauer**' - named by birth;
his *First book on Mineralogy was published during* 1530
entitled : *'Bermannus, sive de re metallica dialogus'*
(A description of the ore mountain-Ergebrge, Silver mining district)

René Just Haüy (1743 –1822)
"**Father of Modern Crystallography**"

French (Paris) Mineralogist generally known as **Abbé Haüy**

Prepared by
Dr. K.Palanivel
Professor, Department of Remote Sensing

MTIGT0306: THEORY – CRYSTALLOGRAPHY AND MINERALOGY 4 credits

1. **Elements of Crystallography**: Crystalline and Amorphous forms - Symmetry and Classification of Crystals - System of Crystal Notation - (Weiss and Millerian) - Forms and Habits. Crystal Systems (Isometric, Tetragonal, Hexagonal, Orthorhombic, Monoclinic, Triclinic, Twinning - Crystalline Aggregates – Columnar, Fibrous, Lamellar, Granular - Imitative shapes and Psudomorphism.   **12 Hrs.**

2. **Crystal Properties:** Space Symmetry Elements- Translation – Rotation- Reflection - Inversion Screw and Glide-point groups and Crystal classes - Derivation of 32 Crystal classes based on Schoenflies notation - Bravais lattices and their Derivation - An outline of Space Groups. X-ray Crystallography.   **12 Hrs.**

3. **Physical Mineralogy**: Physical Properties: (Colour – Structure – Form – Luster - Transparency – Streak – Hardness – Specific Gravity – Tenacity – Feel – Taste – Odour) - Electrical, Magnetic and Thermal properties-Determination of Specific Gravity (Jolly's spring balance, Walker's steel yard, Pycnometer methods) - Empirical and Structural formula of minerals – Isomorphism, Polymorphism and Psudomorphism - Atomic substitution and Solid solution in minerals - Non Crystalline minerals - Fluorescence in minerals - Metamict state.   **16 Hrs.**

4. **Optical Mineralogy:** Optical Properties (Colour – Form – Cleavage - Refractive Index - Relief – Alteration – Inclusions – Zoning – Pleochroism – Extinction - Polarization colours – Birefringence) – Twinning - Optic sign (Uniaxial and biaxial)- Interference figures - Primary and Secondary Optic axes - Optic axial angle measurements – Optic Orientation – Dispersion in Crystals - Optic anomalies.   **12 Hrs.**

5. **Mineral Groups:** Ortho and Ring Silicates (Olivine group - Garnet group). Alumino silicates (Epidote group - Zircon – Staurolite – Beryl - Cordierite and Tourmaline). Sheet Silicates (Mica group - Chlorite group and Clay minerals) - Chain Silicates (Pyroxene group - Amphibole group and Wollastonite). Frame work Silicates (Quartz -Feldspar - Feldspathoid - Zeolite and Scapolite groups) - Non-silicate (Spinel group, Carbonates and Phosphates).   **12 Hrs.**

6. Current Contours: (Not for Exam, only for Discussion): Preparation of Field Kit for testing and identifying minerals during field survey; preparation of mineral and crystal samples for making thin sections, x-ray crystallographic studies. Learn how minerals together form different types of rocks.

Text Books:
1. Dana, E.S, A Text Book of Mineralogy, Wiley Eastern, 1955.
2. Flint, Y, Basic Crystallography, Mid Publishers, 1970.
3. Phillips, F.C. Longman, An Introduction to Crystallography, 1956.
4. Bloss.F.B., Crystallography and crystal New york 1971
5. Read, H.H, Rutley's Elements of Mineralogy, CBS Publishers & Distributors, Delhi, 1984.

References:
1. Berry Mason, L.G,Mineralogy, W.H. Freeman & co - 1961.
2. D. Perkins, (2002), Mineralogy, 2nd Edition, Pearson Education (Singapore) Pte. Ltd, Delhi, 483pp, ISBN 81-7808-831-2
3. W. D. Nesse, (2000), Introduction to Mineralogy, Oxford University Press, ISBN 0-19- 510691-1
4. Naidu, P.R.J,. Optical Crystallography.
5. Wahlstrom, E.F, Optical Crystallography, John wiley, 1960.
6. Azaroff, L.V,Elements of X-ray Crystallography, 1968.
7. Deer, W.A, Howie, R.A and J.Zussman, LongmansAn Introduction to the Rock Forming Minerals, 1966.
8. Alexander N.Winchell,Elements of Optical Mineralogy, Part I and II,Wiley Eastern (p) Ltd, 1968
9. Ernest, E.Walhstrom, Optical Crystallography, John Wiley & Sons.1960.
10. Kerr B.F,Optical Mineralogy. Mc Graw Hill, 5 th Edition, New York-1995.
11. Mitra, S,Fundamentals of Optical Spectroscopic and X-ray Mineralogy.

Course outcomes:

After the successful completion of this course, the students are able to:

- Gain knowledge about the source minerals as raw materials for anything on the Earth and for the survival of life
- Independently able to classify the crystals based on symmetrical elements and face indices
- Understand various physical, chemical and optical properties of minerals so as to discriminate them
- Provide ideas about the major existence of rock forming silicates at the surface of the Earth
- Understand the various properties of mineral groups
- Know the crystal and mineral forms and their habits

Unit-2 Crystal Properties:

2. Crystal Properties: Space Symmetry Elements- Translation – Rotation- Reflection - Inversion Screw and Glide-point groups and Crystal classes - Derivation of 32 Crystal classes based on Schoenflies notation - Bravais lattices and their Derivation - An outline of Space Groups. X-ray Crystallography.

-12 Hrs.

Space Symmetry Elements - Space Lattice

◉ Atoms or groups of atoms have regular arrangements throughout a crystal

◉ With this arrangement, a three dimensional pattern is repeated many times

◉ The array of points at which the pattern repeats constitute a SPACE LATTICE

◉ i.e., the arrangement of points in space – Bravais 1848

◉ The unit of pattern is called 'Unit Cell', E.g. NaCl Cube

◉ There are 7 types of unit cells, crystallographic axes and Axis ratios:

1. Cubic, 2. Tetragonal, 3. Hexagonal, 4. Trigonal / Rhombohedral, 5. Orthorhombic, 6. Monoclinic, & 7. Triclinic.

LENGTH AND ANGULAR RELATIONS IN CRYSTAL SYSTEMS

Crystal System	#	Cell Parameters
Cubic	1	$a_1 = a_2 = a_3$; $\alpha = \beta = \gamma = 90°$
Tetragonal	2	$a_1 = a_2 \neq c$; $\alpha = \beta = \gamma = 90°$
Hexagonal: Hexagonal & Hexagonal: Rhombohedral	2	$a_1 = a_2 = a_3 \neq c$; $\alpha = \beta = 90°$, $\gamma = 120°$ -do- Horiz.&Vert. = 90°; Amongst Horiz.=120°
Orthorhombic	3	$a \neq b \neq c$; $\alpha = \beta = \gamma = 90°$
Monoclinic	4	$a \neq b \neq c$; $\alpha = \gamma = 90°$, $\beta \geq 90°$
Triclinic	6	$a \neq b \neq c$; $\alpha \neq \beta \neq \gamma$

- Number of differences in axis by length & angle (uniquenesses)
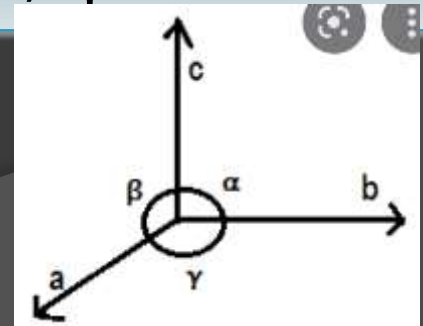
The 32 Point Groups

- 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:

  - *Translation, Reflection, Rotation, Inversion, Improper Rotation*

  The German Mathematician **Arthur Moritz Schoenflies**, devised a notation primarily used to specify point groups in three dimensions –known as "**Schoenflies Notation**"

- *Translation,* is the movement of face from one point to another point along a vector

- *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 co-ordinate 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.

Based on the external symmetry, the 32 crystal classes are grouped into 6 crystal systems:

1. **Triclinic System** has only 1-fold or 1-fold rotoinversion axis.

2. **Monoclinic System** has only mirror plane(s) or a single 2-fold axis.

3. **Orthorhombic System** has only two fold axes or a 2-fold axis and 2 mirror planes.

4. **Tetragonal System** has either a single 4-fold or 4-fold rotoinversion axis.

5. **Hexagonal System** has no 4-fold axes, but has at least 1 6-fold or 3-fold axis.

6. **Isometric System** has either 4 3-fold axes or 3 4-fold rotoinversion axes.

32 Point Groups or Crystal Classes

Sl.No.	Crystal systems	#classes
1.	Cubic / Isometric	**5**
2.	Tetragonal	**7**
3.	Hexagonal-Hexagonal	**7**
	Hexagonal-Rhombohedral	**5**
4.	Orthorhombic	**3**
5.	Monoclinic	**3**
6.	Triclinic	**2**
	Total	**32**

Crystal Classes in TRICLINIC System

Sl.	Xal. Class	Type	Fold Symmetry
1.	**Normal Class** - Axinite type –		-nil-
2.	**Assymmetric class** - Calcium Thiosulphate type -		- nil-

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Crystal Classes in MONOCLINIC System

Sl.	Xal. Class	Type	Fold Symmetry

1. **Normal Class** – Barite type — **-** b xl. Ax.-2

2. **Hemimorphic Class** - Tartaric Acid Type **-** b xl. Ax.-2

3. **Clinohedral Class** - Clinohedrite Type **-** -nil-

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Crystal Classes in ORTHORHOMBIC System

Sl.	Xal. Class	Type	Fold Symmetry
1.	**Normal Class**	- Barite Type	- 3 Xl. Ax.-2
2.	**Hemimorphic Class**	- Calamine Type	- Vert. Ax. -2
3.	**Sphenoidal Class**	- Epsomite Type	- 3 Xl. Ax.-2

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Crystal Classes in HEXAGONAL System

A. Hexagonal Division

Sl.	Xal. Class	Type	Fold Symmetry
1.	**Normal Class**	**- Beryl Type**	**– 1 ver.-6, 6 hor.-2**
2.	**Hemimorphic Class**	**- Zincite type**	**– 1 ver.-6**
3.	**Tripyramidal Class**	**- Apatite type**	**– 1 ver.-6**
4.	**Pyramidal Hemimorphic Class**	**- Nephelite type**	**– 1 ver.-6**
5.	**Trapezohedral Class**	**- β-Quartz type**	**– 1 ver.-6, 6 hor.-2**
6.	**Trigonal class**	**- Benitonite type**	**– 1 ver.-6, 3 hor.-2**
7.	**Trigonal Tetartohedral class**	**- Disilverortho-phosphate type**	**– 1 ver.-3**

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Crystal Classes in HEXAGONAL System
B. Hexagonal – Rhombohedral Division

Sl.   Xal. Class   Type   Fold Symmetry

1. **Rhombohedral Class** - **Calcite Type (Trigonal Dipyramidal / Trigonal Equatorial class)** - Vert. ax.-3, 6 Hor. Ax.-2

2. **Rhombohedral-hemimorphic Class** – **Tourmaline Type (Ditrigonal Pyramidal / Trigonal Hemihedral Hemimorphic / Ditrigonal Class)** - Vert. ax.-3

3. **Tri-rhombohedral Class** – **Phenacite Type (Rhombohedral / Trigonal Rhombohedral / Rhombohedral Tetartohedral / Hexagonal Alternating class)** - Vert. ax.-3

4. **Trapezohedral Class** – **α-quartz Type (Trigonal Trapezohedral / Trapezohedral Tetartohedral / Trigonal Holoaxial class)** - Vert. ax.-3

5. **Trigonal Tetartohedral Hemimorphic Class** – **Sodium Periodate Type (Trigonal Pyramidal / Trigonal Polar class)** - Vert. ax.-3

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Crystal Classes in TETRAGONAL System

1. Normal Class - Zircon type   **- 1 xl.-4, 4 hor.ax.-2**

2. Hemimorphic Class - Iodosuccinimide Type **- 1 xl.-4**

3. Tripyramidal Class - Scheelite type   **- 1 xl.-4**

4. Pyramidal-hemimorphic Class - Wulfenite Type (Tetragonal

   Pyramidal / Hemihedral Hemimorphic/Tetragonal Polar class) **- 1 xl.-4**

5. Sphenoidal Class - Chalcopyrite Type (Tetragonal sphenoidal,

   Sphenoidal Hemihedral, Didigonal Scalenohedral or Ditetragonal

   Alternating class)   **– 3 xl.-2**

6. Trapezohedral Class – Nickel Sulphate type (Tetragonal

   Trapezohedral / Trapezohedral Hemihedral / Tetragonal Holoaxial class)

                                                          - 1 xl.-4, 4 hor.ax.-2

7. Tetartohedral Class (Tetragonal Bisphenoidal / Sphenoidal

   Tetartohedral, Tetragonal Alternating class)   **- 1 xl.-2**

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Crystal Classes in CUBIC System

Sl.	Xal. Class	Type	Fold Symmetry

1. Normal Class – **Galena type**   - 3 xl.-4, 4 diag.-3, 6 diag.-2

2. Pyritohedral Class – **Pyrite type** - 3 xl.-2, 4 diag.-3

3. Tetrahedral Class – **Tetrahedrite type** - 3 xl.-2, 4 diag.-3

4. Plagiohedral Class – **Cuprite type**- 3 xl.-4, 4 diag.-3, 6 diag.-2

5. Tetartohedral Class – **Ullmannite type** - 3 xl.-2, 4 diag.-3

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Crystal System	Symmetry	Sl.No.	Name of Class	# Classes
Triclinic	none	1	Pedial	**2**
	i	2	Pinacoidal	
Monoclinic	$1A_2$	3	Sphenoidal	**3**
	1m	4	Domatic	
	i, $1A_2$, 1m	5	Prismatic	
Orthorhombic	$3A_2$	6	Rhombic-disphenoidal	**3**
	$1A_2$, 2m	7	Rhombic-pyramidal	
	i, $3A_2$, 3m	8	Rhombic-dipyramidal	
Tetragonal	$1A_4$	9	Tetragonal- Pyramidal	**7**
	$1A_4$	10	Tetragonal-disphenoidal	
	i, $1A_4$, 1m	11	Tetragonal-dipyramidal	
	$1A_4$, $4A_2$	12	Tetragonal-trapezohedral	
	$1A_4$, 4m	13	Ditetragonal-pyramidal	
	$3A_2$, 2m	14	Tetragonal-scalenohedral	
	i, $1A_4$, $4A_2$, 5m	15	Ditetragonal-dipyramidal	
Hexagonal	$1A_3$	16	Trigonal-pyramidal	**12**
	1_3	17	Rhombohedral	
	$1A_3$, $3A_2$	18	Trigonal-trapezohedral	
	$1A_3$, 3m	19	Ditrigonal-pyramidal	
	1_3, $3A_2$, 3m	20	Hexagonal-scalenohedral	
	$1A_6$	21	Hexagonal-pyramidal	
	1_6	22	Trigonal-dipyramidal	
	i, $1A_6$, 1m	23	Hexagonal-dipyramidal	
	$1A_6$, $6A_2$	24	Hexagonal-trapezohedral	
	$1A_6$, 6m	25	Dihexagonal-pyramidal	
	1_6, $3A_2$, 3m	26	Ditrigonal-dipyramidal	
	i, $1A_6$, $6A_2$, 7m	27	Dihexagonal-dipyramidal	
Isometric	$3A_2$, $4A_3$	28	Tetaroidal	**5**
	$3A_2$, 3m, 4_3	29	Diploidal	
	$3A_4$, $4A_3$, $6A_2$	30	Gyroidal	
	3_4, $4A_3$, 6m	31	Hextetrahedral	
	$3A_4$, $4A_3$, $6A_2$, 9m	32	Hexoctahedral	

Where,

i   - rotoinversion
m - mirror plane
A - axis/axes

The 14 Bravais Lattices

- When the crystal systems combined with the various possible **lattice centerings**, the **Bravais lattices** are arrived.

- They describe the geometric arrangement of the lattice points and thereby the **translational symmetry** of the crystal.

- In three dimensions, there are 14 unique Bravais lattices which are distinct from one another in the translational symmetry they contain.

- All crystalline materials recognized until now (not including quasicrystals) fit in one of these arrangements.

- There are fourteen three-dimensional lattices, classified by crystal system.

- The Bravais lattices are sometimes referred to as *space lattices*.

- The crystal structure consists of the same group of atoms, the *basis*, positioned around each and every lattice point.

- This group of atoms therefore repeats indefinitely in three dimensions according to the arrangement of one of the 14 Bravais lattices.

- The characteristic rotation and mirror symmetries of the group of atoms, or unit cell, is described by its crystallographic point group.

The 14 Bravais Lattices

The 7 Crystal systems (From least to most symmetric)

Crystal systems   **Symmetry elements - # folds**

⊙   **I. Triclinic**

     one type   (none) – No any face repeated along an axis

                                                        of rotation, i.e., No fold.

  1.   **Simple Triclinic** – *lattice point only at the corners*

⊙   **II. Monoclinic**

     2 types   (1 diad)

  2.   **Simple Monoclinic** – *lattice point only at the corners*
  3.   **Base Centered**   (Primitive)
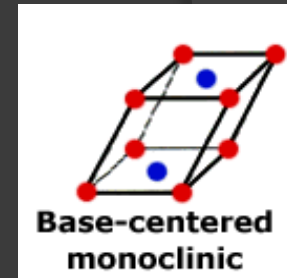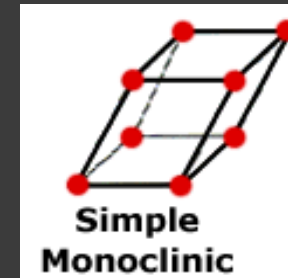
⊙   **III. Orthorhombic**

     4 types   (3 perpendicular diads)

  4.   **Simple Orthorhombic** – *lattice point only at the corners*
  5.   **Base Centered**
  6.   **Body Centered**
  7.   **Face Centered**

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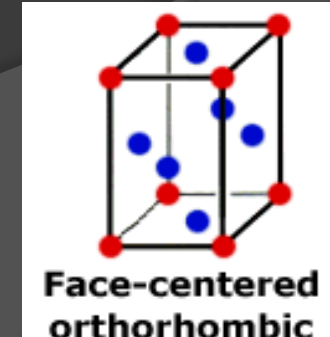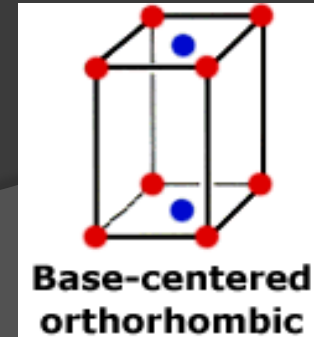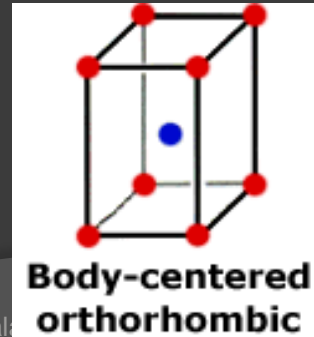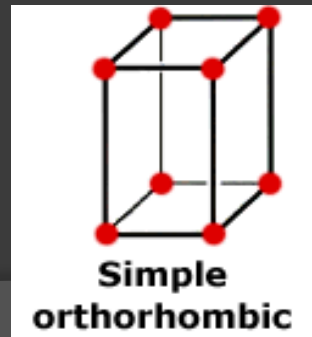
Crystal systems   Symmetry elements - # folds

- **IV. Rhombohedral**
  one type   (aka, trigonal)
                                (1 triad)

  8. **Simple Rhombohedral** – *lattice point only at the corners*

Rhombohedral

- **V. Tetragonal**
  2 types   (1 tetrad)
 9. **Simple Tetragonal** – *lattice point only at the corners*
 10. **B**ody Centered

Simple tetragonal

Body-centered tetragonal
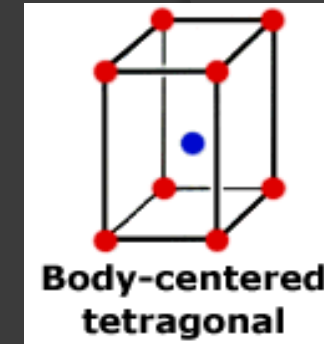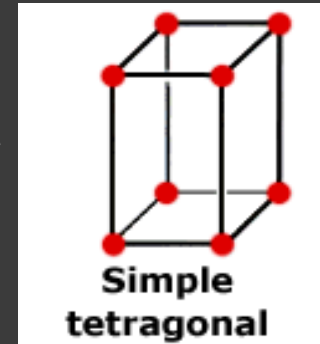
- **VI. Hexagonal**
  one type   (1 hexad)
  11. **Simple Hexagonal** – *lattice point only at the corners*

Hexagonal

- **VII. Cubic**
  3 Types   (4 triads)
  12. **Simple Cubic** – *lattice point only at the corners*
  13. **Body Centered Cubic** - *lattice points at corners & in middle of cube*
  14. **Face Centered Cubic** - *lattice points at corners & in middle each face*

Simple cubic

Body-centered cubic

Face-centered cubic
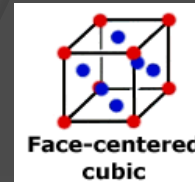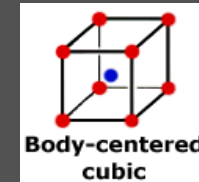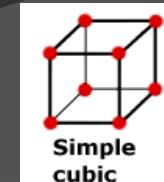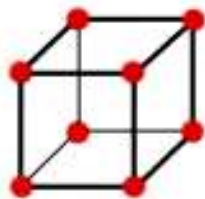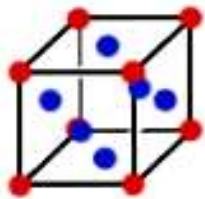
Simple cubic

Face-centered cubic
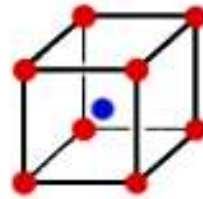
Body-centered cubic
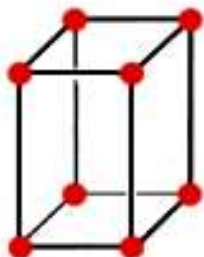
Simple tetragonal
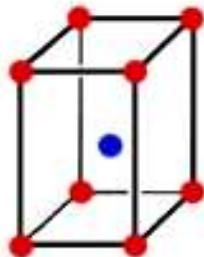
Body-centered tetragonal
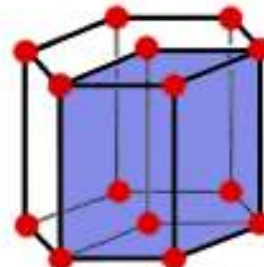
Hexagonal
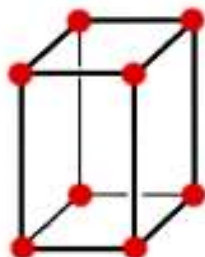
Simple orthorhombic
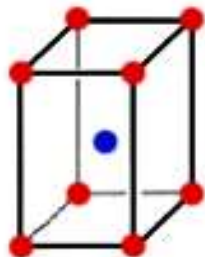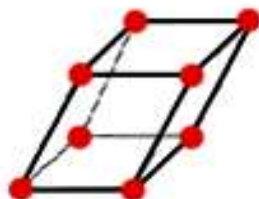
Body-centered orthorhombic
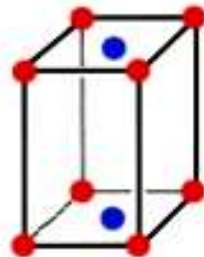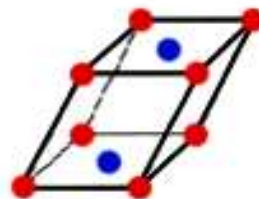
Base-centered orthorhombic
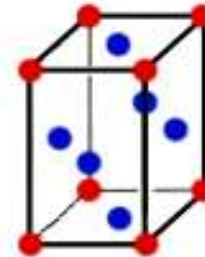
Face-centered orthorhombic

Rhombohedral

Simple Monoclinic

Base-centered monoclinic

Triclinic

The 230 Space Groups

- The **space groups** of the crystal structures are composed of the **14 translational symmetry** operations (latices) in addition to the **32** operations of the **point group**. 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.

X-ray Crystallography

A study of crystals, esp. the atomic structure, bonds, disorders, etc., using the x-ray which has scattered after striking the crystal is known as X-ray Crystallography.

X-ray crystallography is a method of determining the arrangement of atoms within a crystal, in which a beam of X-rays strikes a crystal and causes the beam of light to spread into many specific directions. (William Lawrence Brag – Father of X-ray Crystallography).

Importance of X-ray Crystallography

- From the angles and intensities of these scattered 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 disorder and

  - various other information through this method can be derived like the

    - size of atoms,

    - lengths and types of chemical bonds, and

    - atomic-scale differences among various materials, especially minerals and alloys.
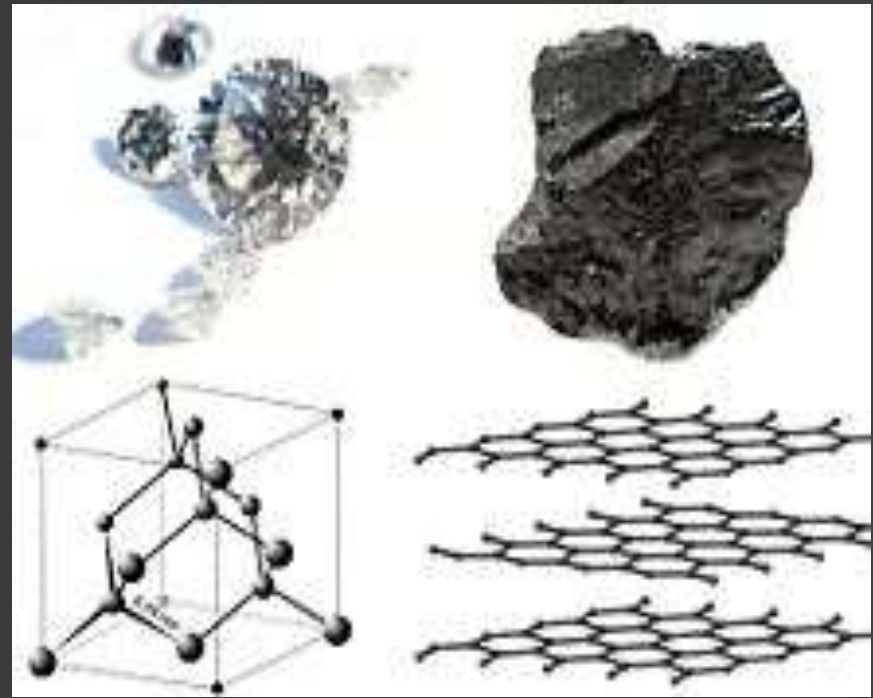
- Although **Diamond** (top left) and **Graphite** (top right) are identical in chemical composition — being both pure Carbon (C) — X-ray crystallography revealed the arrangement of their atoms (bottom), which accounts for their different properties.

- In **Diamond**, the carbon atoms are arranged **tetrahedrally** and held together by **single covalent bonds**, making it strong in all directions.

- By contrast, **Graphite** is composed of stacked sheets, in which the carbon atoms are bonded **hexagonally** by **delocalized bonds** of average order 4/3; there are no covalent bonds between sheets, making graphite easy to cleave into flakes.

Principles : Single-crystal X-ray diffraction

- The oldest and most precise method of X-ray crystallography is **Single-crystal X-ray Diffraction**, in which a beam of monochromatic and collimated X-rays strikes a single crystal, producing scattered beams.

- When they land on a piece of film or other detector, these beams make a **diffraction pattern** of spots; the **strengths** and **angles** of these beams are recorded as the crystal is gradually rotated.

- Each spot is called a **reflection**, since it corresponds to the reflection of the X-rays from one set of evenly spaced planes within the crystal.

- For single crystals of sufficient purity and regularity, X-ray diffraction data can determine the **mean chemical bond lengths** and **angles** to within a few thousandths of an Ångström and to within a few tenths of a degree, respectively.

- The atoms in a crystal are also **not static**, but **oscillate** about their mean positions, usually by less than a few tenths of an Ångström. X-ray crystallography allows the size of these oscillations to be measured quantitatively.   (1 Ångström = 0.1 nm or 10^{-10} m = one ten-billionth of a meter)

- In an X-ray diffraction measurement, a crystal is mounted on a **goniometer** and gradually rotated while being bombarded with X-rays, producing a diffraction pattern of regularly spaced spots known as **reflections**.

- The **two-dimensional images** taken at different rotations 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.

- X-ray crystallography is related to several other methods for determining atomic structures through the **diffraction patterns** produced by scattered electrons or neutrons.

- If single crystals of sufficient size cannot be obtained, various other methods like, **Fiber Diffraction, Powder Diffraction and Small-Angle X-ray Scattering (SAXS)** can be applied to obtain less detailed information.

- If the material under investigation is only available in the form of nanocrystalline powders or **suffers from poor crystallinity**, the methods of **Electron Crystallography** can be applied for determining the atomic structure.

Procedure

Three basic steps:

1. Sufficiently large crystal (typically **larger than 100 micrometres** generally **smaller than a millimeter** across, in all dimensions), **pure** in composition and **regular** in **structure**, with **no** significant internal **imperfections** such as **cracks** or **twinning**.

2. The crystal is placed in an intense beam of X-rays, usually of a single wavelength (**monochromatic** X-rays) and collimated to a single direction, producing the regular pattern of reflections.

   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 reflection intensities.

3. 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.

Data analysis – Crystal symmetry, unit cell, and image scaling

Having recorded a series of diffraction patterns from the crystal, each corresponding to a different orientations of the crystal, the crystallographer must now convert these two-dimensional (2D) images into a three-dimensional (3D) model of the density of electrons throughout the crystal using the mathematical technique of **Fourier transforms**.

Roughly speaking, each spot corresponds to a different type of variation in the electron density.

This is to determine,
- which variation corresponds to which spot (**indexing**),
- the relative strengths of the spots in different images (**merging and scaling**) and
- how the variations should be combined to yield the total electron density (**phasing**).
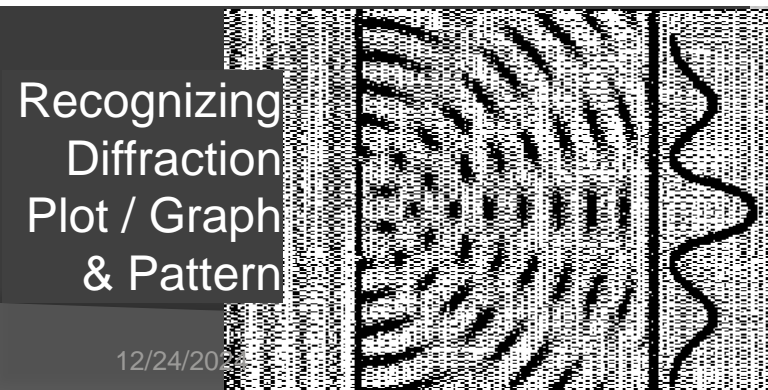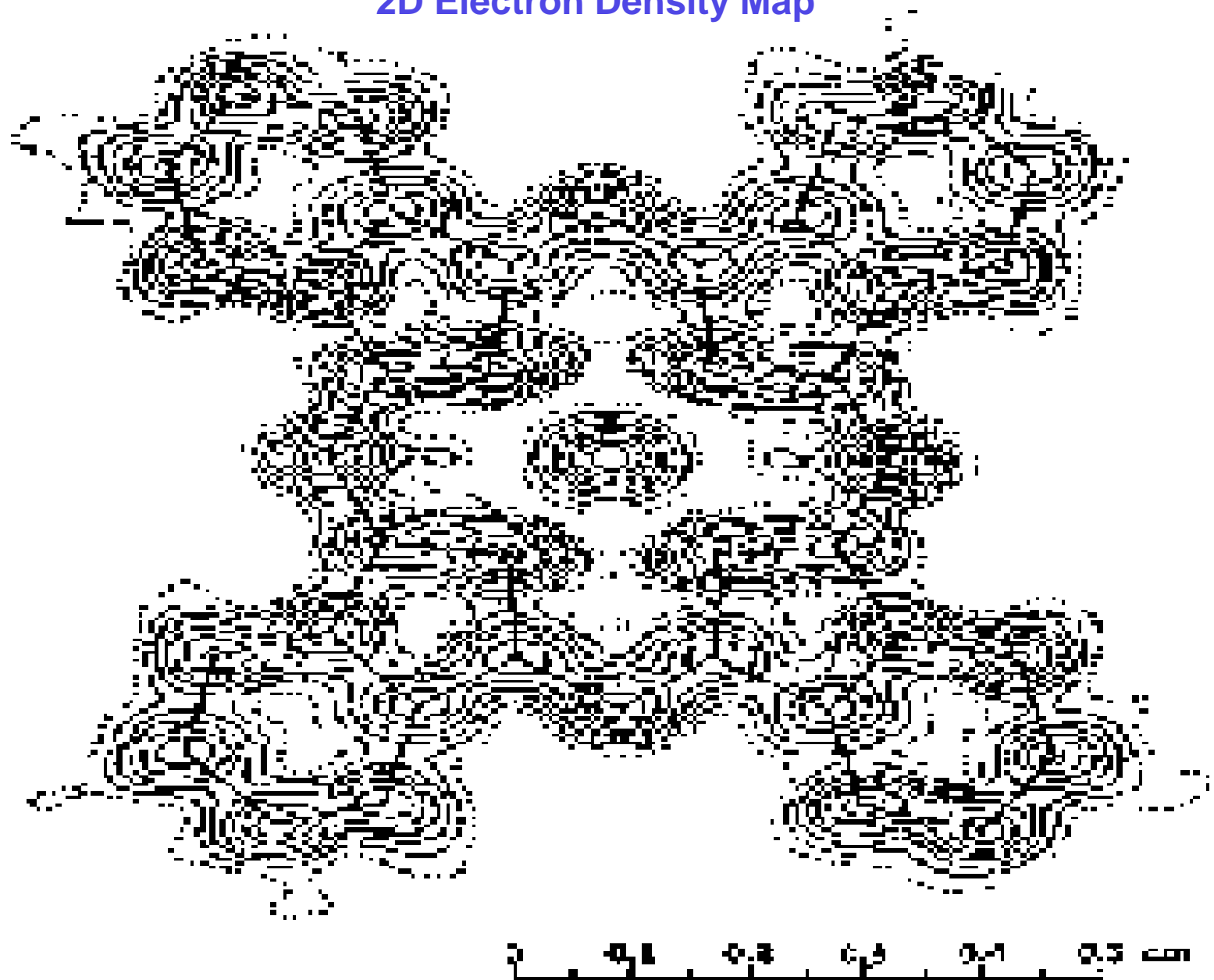
A diffractometer

Mounting the crystal in Goniometer

Diffracted rays

X-ray beam

Crystallized molecule

Film

crystal

x-rays

diffraction pattern

phases

refinement

electron density map

fitting

atomic model
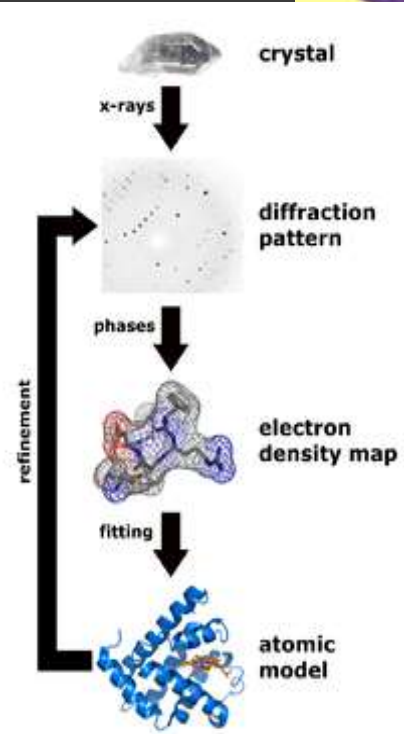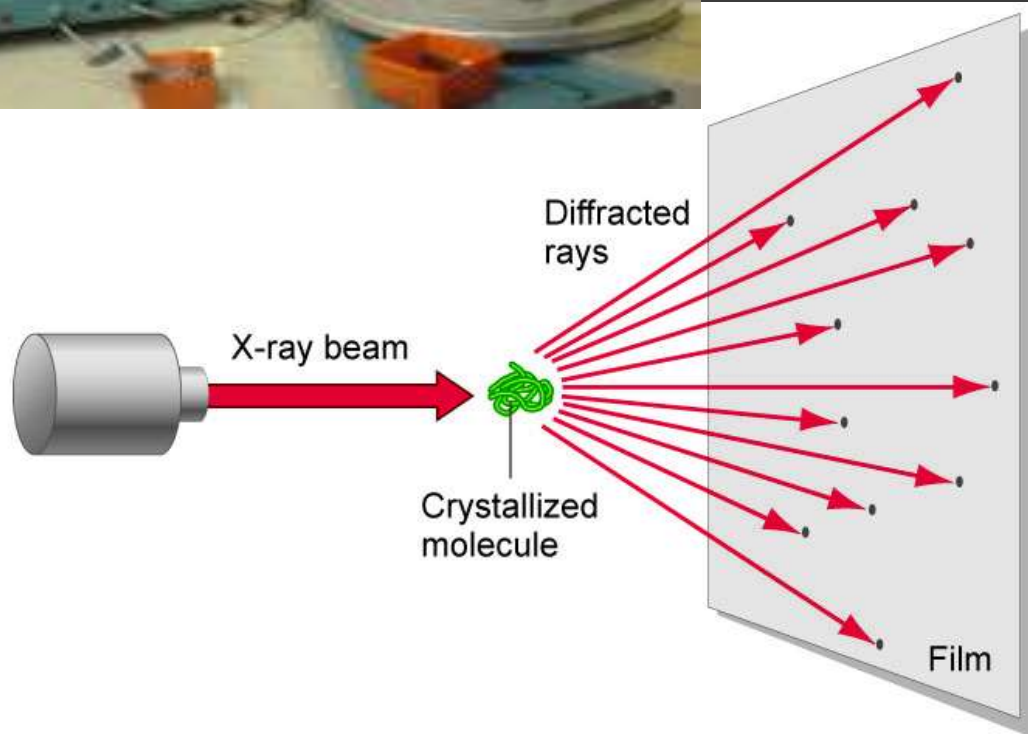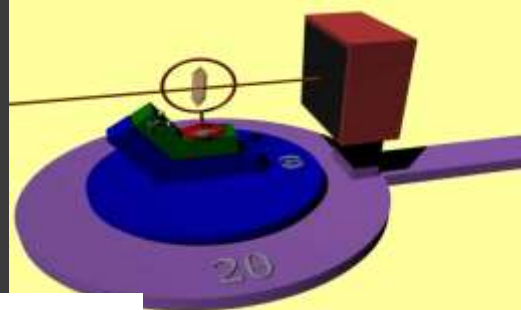
Recording the reflections

Recognizing Diffraction Plot / Graph & Pattern

Mapping of Electron Density

12/24/2024

Dr.Palanivel K, DRS, BDU
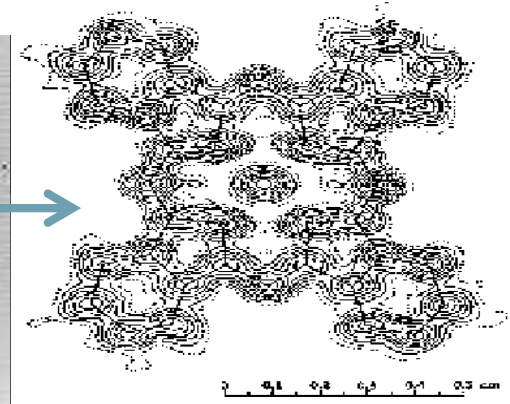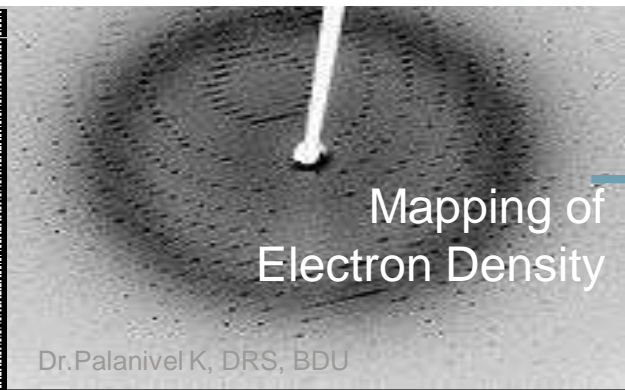
Similar Types of Crystal studies using Spectroscopic methods

- Nuclear Magnetic Resonance (NMR) spectroscopy
- Electron spin resonance (ESR)
- Raman Spectroscopy
- Infra Red (IR) spectroscopy
- Mössbauer spectroscopy
- Atomic Absorption Spectroscopy (AAS)
- Mass spectrometry

1. NMR - Nuclear Magnetic Resonance Spectroscopy

- Nuclear Magnetic Resonance Spectroscopy, most commonly known as **NMR spectroscopy**, is the name given to a technique which exploits the magnetic properties of certain nuclei.

- The principle of NMR usually involves **three** sequential steps:

  - The **alignment (polarization)** of the magnetic nuclear spins in an applied, constant magnetic field B_0 (the main static magnetic field in Tesla unit for MRI-Magnetic Resonance Imaging).

  - The **perturbation / agitation** of this alignment of the nuclear spins by a weak oscillating magnetic field, usually referred to as a **radio-frequency (RF) pulse**.

  - **Detection and analysis** of the electromagnetic waves emitted by the nuclei of the sample as a result of this perturbation.
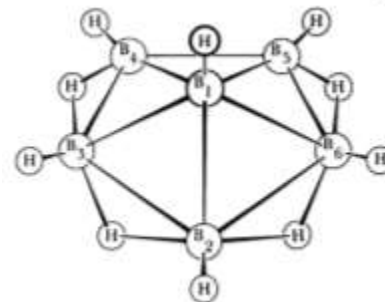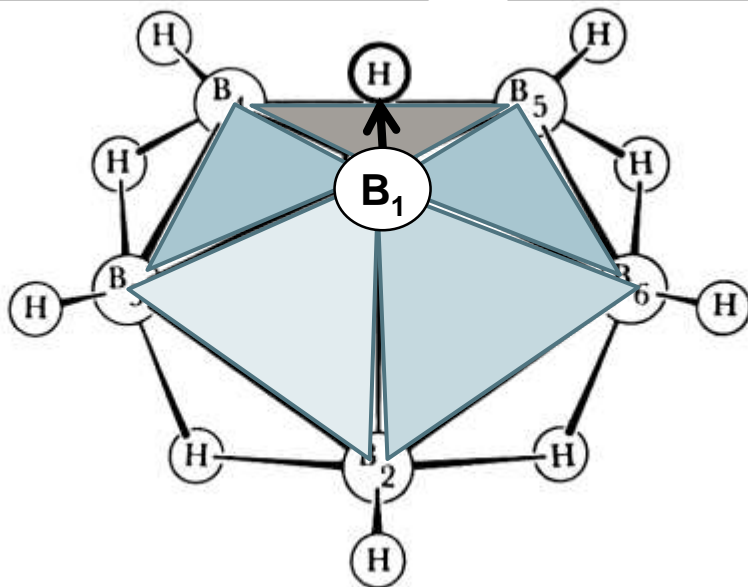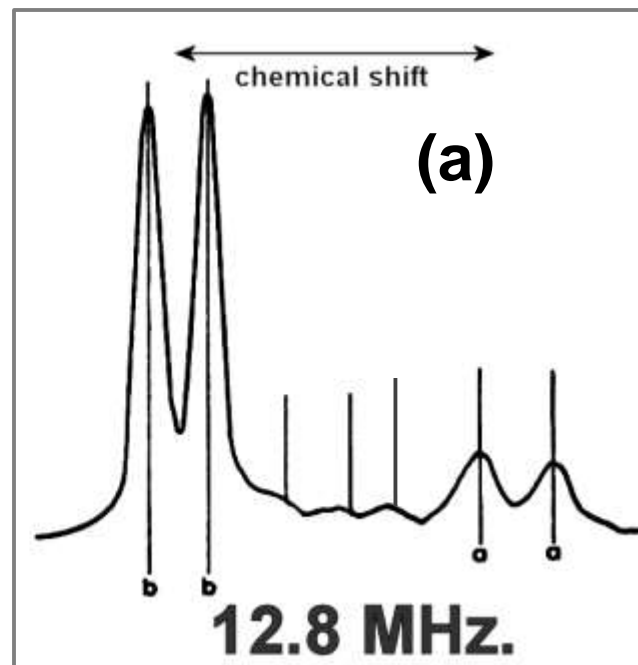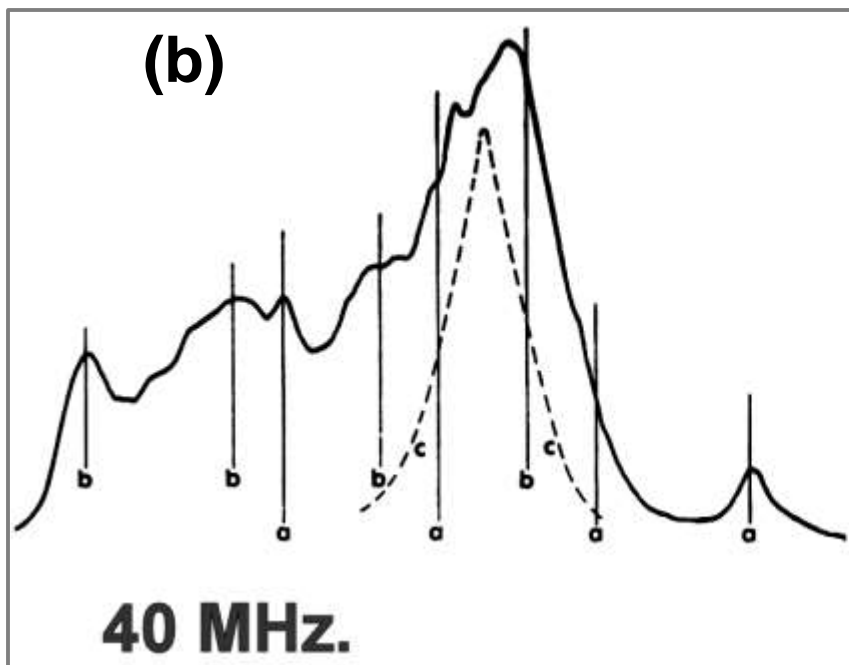
- Since the nucleus is surrounded by electrons, that's why this energy - the **strength** of the electromagnetic field (pulse), **needed for excitation** is changing depending on (first of all) the **structure** of the electron shell of that atom.

- If the atoms are in connection with different atoms in a **chemically bonded molecule** by their outer valence electrons, this new electron distribution also changes the electromagnetic field around the nucleus.

- In this way, the **transition energy** may **change** again since it is the function of the strength of the electromagnetic field around the given nucleus.

- On using a range of wavelengths around the average transition energy, the **absorption patterns** can be seen.

- From the extent of the **shift** and the efficiency of **transmission**, the **type** and **number of atoms** or particles connected directly or the type of environment or chemical surrounding are determined.

- With a suitable computer apparatus, the whole 3D structure can be established.

- A lot of extracted data from the system is useful for more accurate determination of the structure, but not useful for the higher molecular masses.

A typical

$_{13}$C

NMR spectrum
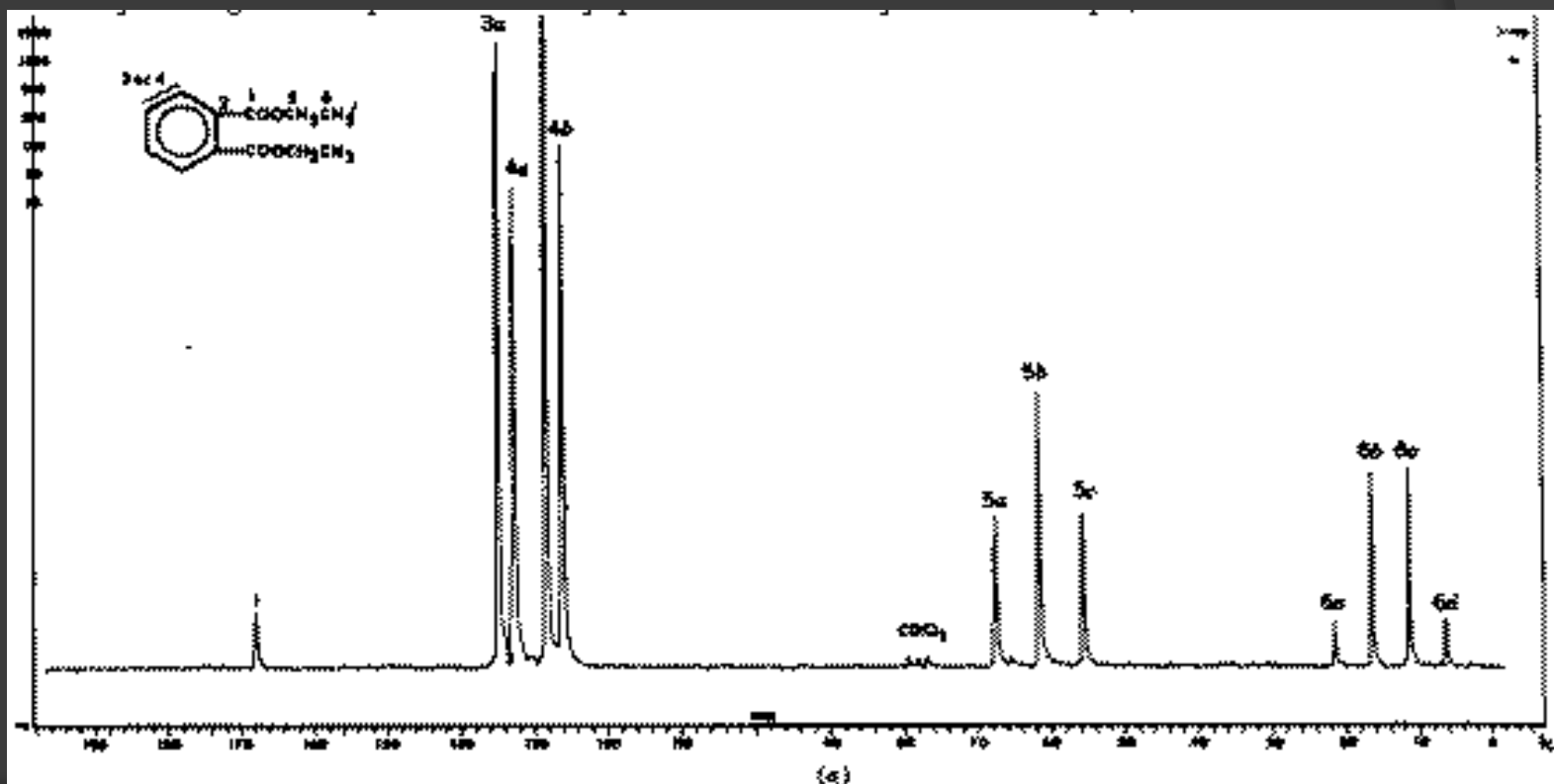
For example, the **NMR spectrum and structure of Hexaborane** B_6H_{10} is shown and described here**:**

(a) NMR Interpretation of hexaborane **12.8 MHz. range** (right) :

- A simple example of the **chemical shift** is the "a" and "b" doublets (pairs of peaks).

- "a" and "b" are two groups of boron atoms in different electronic environments, which place the "a" doublet to the right of the "b" doublet in the spectrum.

- The relative peak heights of the "a" and "b" doublets suggest a 1:5 ratio of borons in one environment to borons in another environment.

- This suggests, combined with the molecular weight of the molecule: 5 boron atoms in one environment ("b") and 1 boron atom in another environment ("a"), which in turn suggests a **pyramidal structure**, which does appear in the atomic diagram.

(b) 40 MHz. range (left) :

- "a" suggests a hydrogen at the apex, which is in the atomic diagram sticking straight up.

- "b" suggests hydrogens bonded to one boron each, which are in the atomic diagram sticking straight out from the edges.

- "c" suggests other bridge hydrogens, which is to say hydrogens in the middle of a boron-hydrogen-boron bonding arrangement like a hydrogen bridge between two boron shores, which are in a ring around the atomic diagram.

Source:https://en.wikipedia.org/wiki/Nuclear_magnetic_resonance_spectroscopy#/media/File:Lipscomb-NMR-hexaborene-B6H10.png
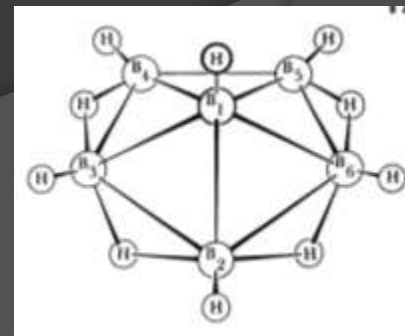
- Since the only one factor which makes difference in the spectrum is the **difference in the strength of the electromagnetic field around the nucleus.**

- **This** offers several types of information from lots of types of experiments with programmed impulses of the magnetic field, such as angles, distances, coupling constants, chemical shifts, rate constants, etc.

A 900MHz NMR instrument with a 21.2 T magnet at HWB-NMR, Birmingham, UK, being loaded with a sample.

Processional orbit – angular momentum ω

Nuclear Magnetic dipole μ

Spinning proton

B_0
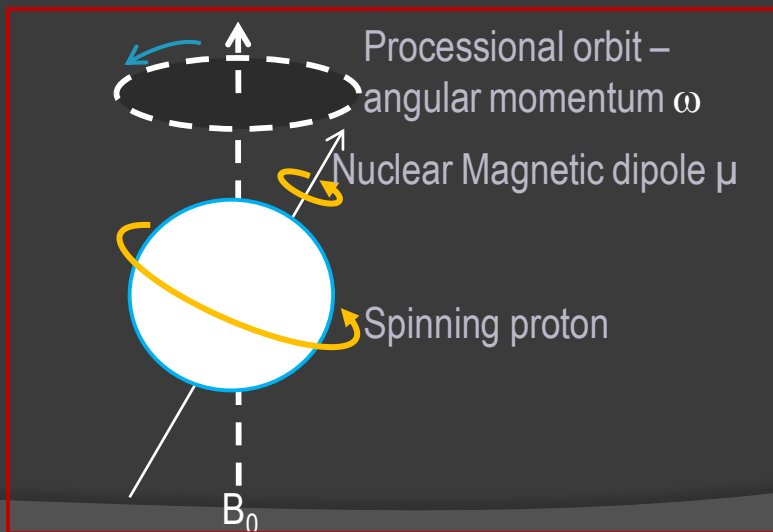
When radiofrequency matches with angular momentum ω, then the energy is absorbed by the nucleus and the spin will invert.

Raman spectroscopy   (Roman Spectroscopy)

- Raman spectroscopy (named after Sir C. V. Raman) is a spectroscopic technique used in condensed matter physics and chemistry to observe vibrational, rotational, and other low-frequency modes in a system.

- It relies on *inelastic scattering, or Raman scattering*, of **monochromatic** light, usually from a **laser** in the **visible**, **near infrared**, or **near ultraviolet** range (photons).
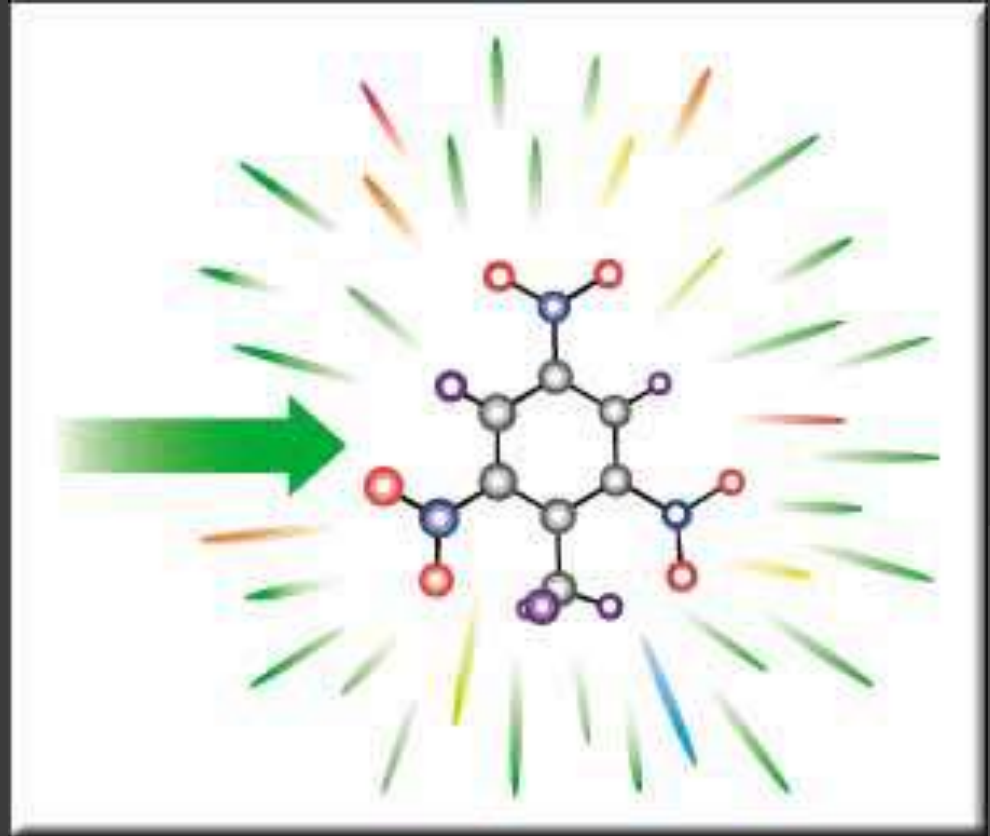
- The laser light interacts with phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. (A *phonon* is a definite discrete unit or quantum of vibrational mechanical energy, just as a *photon* - a quantum of electromagnetic or light energy)

- The shift in energy gives information about the **phonon modes** in the system.

- Infrared spectroscopy yields similar, but complementary, information.

- Spontaneous Raman scattering is typically very weak and as a result the main difficulty of Raman spectroscopy is separating the weak inelastically scattered light from the intense Rayleigh scattered laser light.

- Historically, Raman spectrometers used **holographic diffraction gratings** and **multiple dispersion stages** to achieve a high degree of laser rejection.

- A **phonon** is a quantum mechanical description of an elementary vibrational motion in which a lattice of atoms or molecules uniformly oscillates at a single frequency. Typically, a sample is illuminated with a laser beam.

- Light from the illuminated spot is collected with a lens and sent through a monochromator.

- Wavelengths close to the laser line, due to elastic Rayleigh scattering, are filtered out while the rest of the collected light is dispersed onto a detector.

- In the past, PMTs (photomultiplier tube) were the detectors of choice for dispersive Raman setups, which resulted in long acquisition times.

- However, modern instrumentation almost universally employs notch or edge filters for laser rejection and spectrographs (either Czerny-Turner, echelle or FT based) and CCD detectors.

- There are a number of advanced types of Raman spectroscopy, including **surface-enhanced Raman**, **tip-enhanced Raman, polarised Raman, stimulated Raman** (analogous to stimulated emission), **transmission Raman, spatially-offset Raman**, and **hyper Raman**.
- Energy level diagram given here shows the states involved in Raman signal.
- The line thickness is roughly proportional to the signal strength from the different transitions.

Energy-level diagram showing the states involved in Raman spectra.
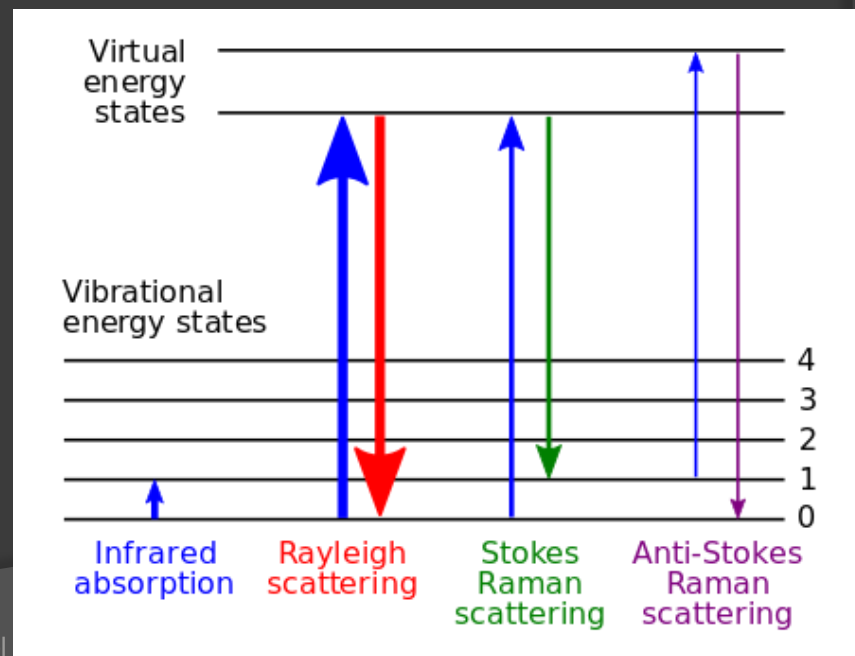
(The magnitude of the Raman effect correlates with polarizability of the electrons in a molecule.

It is a form of inelastic light scattering, where a photon excites the sample.

This excitation puts the molecule into a virtual energy state for a short time before the photon is emitted.)

- Raman spectroscopy provides information about molecular vibrations that can be used for sample identification and quantitation.
- The technique involves shining a sample with a monochromatic light source (i.e. laser) and detecting the scattered light.
- The majority of the scattered light is of the same frequency as the excitation source; this is known as Rayleigh or elastic scattering.

- A very small amount of the scattered light is shifted in energy from the laser frequency due to interactions between the incident electromagnetic waves and the vibrational energy levels of the molecules in the sample.

- Plotting the intensity of this "shifted" light versus frequency results in a Raman spectrum of the sample.

- Generally, Raman spectra are plotted with respect to the laser frequency such that the Rayleigh band lies at 0 cm-1.

- On this scale, the band positions will lie at frequencies that correspond to the energy levels of different functional group vibrations.

- The Raman spectrum can thus be interpreted similar to the infrared absorption spectrum.

Raman offers several advantages over Mid-IR and Near-IR spectroscopy, including:

- Complementary to Infrared Absorption Spectroscopy.

- Little or no sample preparation is required.

- Water is a weak scatterer - no special accessories are needed for measuring aqueous solutions.

- Water and CO_2 vapors are very weak scatterers - purging is unnecessary.

- Inexpensive glass sample holders are ideal in most cases.

- Fiber optics (up to 100's of meters in length) can be used for remote analyses.

- Since fundamental modes are measured, Raman bands can be easily related to chemical structure.

- Raman spectra are "cleaner" & inherently sharper / narrower than mid-IR spectra and useful for more straightforward quantitative & qualitative analyses.

- The standard spectral range reaches well below 400 cm^{-1}, making the technique ideal for both organic and inorganic species.

- Raman spectroscopy can be used to measure bands of symmetric linkages which are weak in an infrared spectrum (e.g. -S-S-, -C-S-, -C=C-).

- The spectra are very specific and chemical identifications can be performed by using search algorithms against digital databases.

- As in Infrared Spectroscopy, band areas are proportional to concentration, making Raman spectroscopy amenable to quantitative analysis.

IR spectroscopy

- Infrared spectroscopy (IR spectroscopy) is the spectroscopy that deals with the infrared region of the electromagnetic spectrum, that is light with a longer wavelength and lower frequency than visible light.

- It covers a range of techniques, mostly based on absorption spectroscopy.

- As with all spectroscopic techniques, it can be used to identify and study chemicals.

- A common laboratory instrument that uses this technique is a Fourier Transform Infrared (FTIR) Spectrometer.

- Infrared spectroscopy exploits the fact that molecules have specific frequencies at which they rotate or vibrate corresponding to discrete energy levels (vibrational modes).

- These resonant frequencies are determined by the shape of the molecular potential energy surfaces, the masses of the atoms and, by the associated vibronic coupling.

- Simple diatomic molecules have only one bond, which may stretch. More complex molecules have many bonds, and vibrations can be conjugated, leading to infrared absorptions at characteristic frequencies that may be related to chemical groups.

- For example, the atoms in a CH_2 group, commonly found in organic compounds can vibrate in six different ways: symmetrical and antisymmetrical stretching, scissoring, rocking, wagging and twisting:
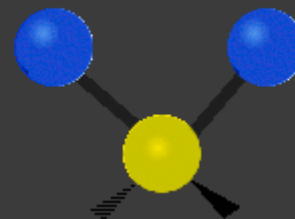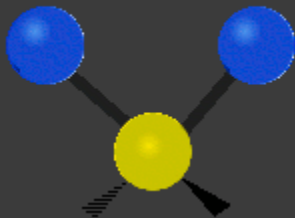
Symmetrical
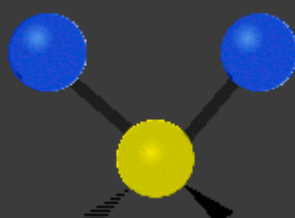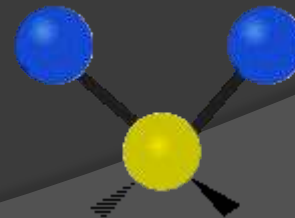stretching
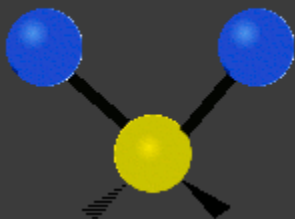
Antisymmetrical
stretching
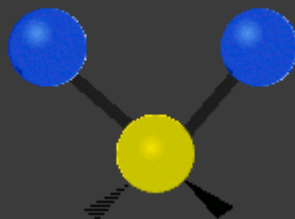
Scissoring

Rocking

Wagging

Twisting

Thank you