chem 5390

Advanced X-ray Analysis

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Department of Chemistry

Advance X-Ray Diffraction

Lecture: TTh 8:00 a.m. – 9:20 p.m. CHEM 352 and CHEM 271

Instructor: Dr. Teresa D. Golden

Office hours: 8:00 - 9:00 a.m. MW, CHEM 279, 565-2888, tgolden@unt.edu

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. Synder, John Wiley & Sons, 1996, 0-471-51339-3

Advance X-Ray Diffraction

Exams:

There will be exams, homework assignments, a research project and a final exam. Dates for each exam will be announced in class.

The final will be Tuesday, December 10th, 8:00 - 10:00 a.m.

Project:

The research project can include the student's graduate research related to x-ray analysis or an assigned topic. Abstract for research topic is due September 26th. Outline due October 24th. Research Paper due December 3rd, 2024.

Advance X-Ray Diffraction

Lecture Topics: CHEM 253

I. Production and Properties of X-rays
II. Basic Crystallography
III. Diffraction Theory
IV. Instrumentation for X-ray Diffraction
V. Crystallographic Databases
VI. Qualitative Analysis
VII. Quantitative Analysis

Advance X-Ray Diffraction

Practicum Topics: CHEM 253/271

1: Safety and Sample Prep
2: Basic Instrument Operation
3: Intro to Software, ICDD JCPDS
4: Crystal Structure Determination - Cubic
5: Crystal Structure Determination - Hexagonal
6: Determination of Precise Lattice Parameters
7: Determination of Crystallite Size and Strain
8: Phase Diagram Determination
9: Quantitative Analysis
10: Advanced Software, jPowd, Rietveld

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

X-ray radiography

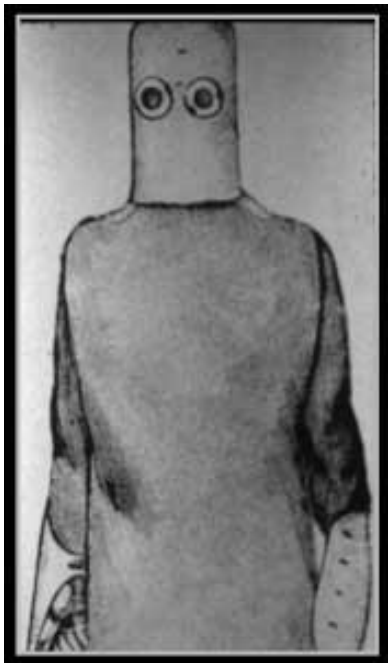
In 1896, the public started to x-ray objects, people, animals, etc… not realizing the health effects.

Herbert Jackson of King's College began developing tubes to focus x-rays in 1896.

That same year Thomas Edison began experimenting with x-ray "lamps" but abandoned the research when his assistant became sick and died.

History of X-rays

By 1910, x-ray operators started to wear protective clothing and using shielding on equipment. (Lead)



History of X-rays

X-ray Therapy

Around 1913, medical doctors began using x-rays to treat ringworm and other ailments.

History of X-rays

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.

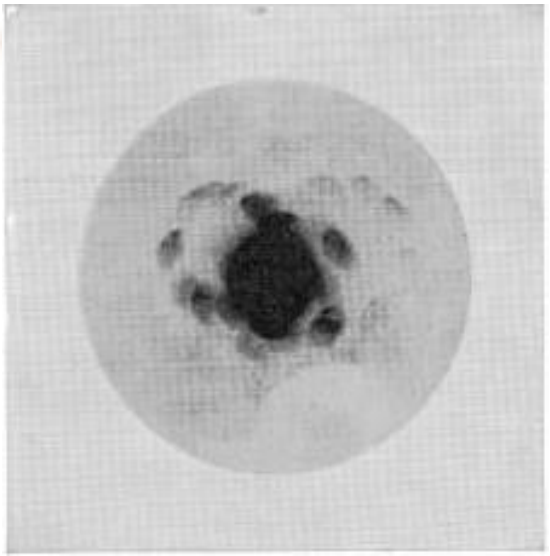
- Bragg's experiments interjected the particle theory. In 1912 suggested a theory was needed to explain both waves and particles.

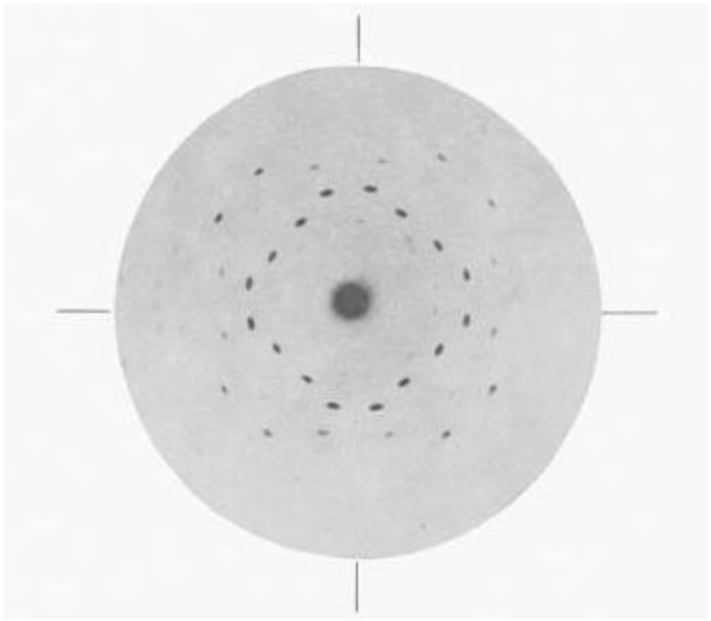
History of X-rays

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

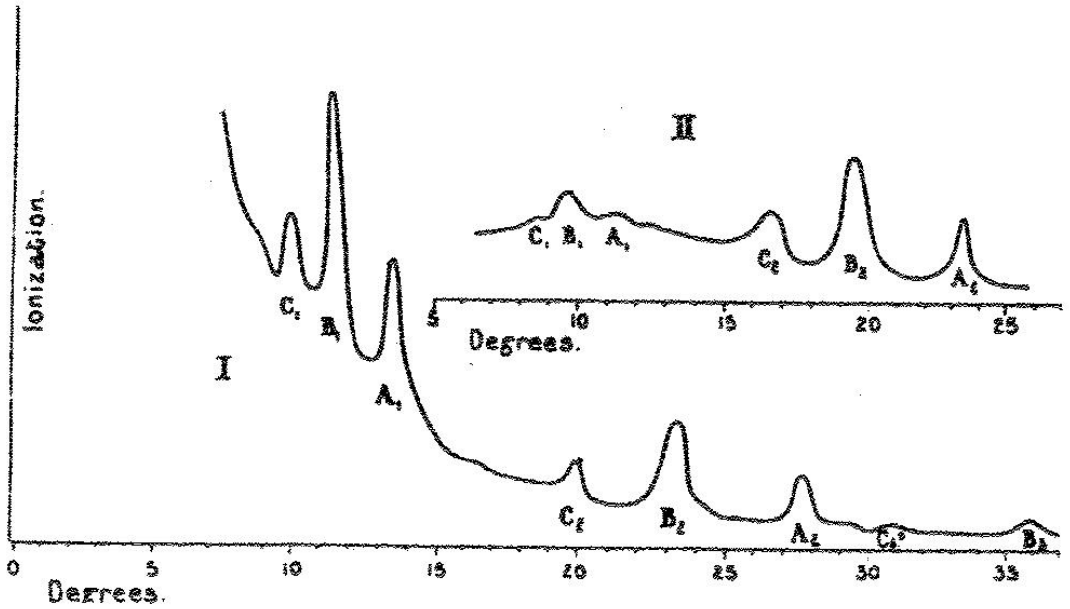


Figure 6. *Diffractograms produced by W.H. and W.L. Bragg with sodium chloride crystals. I: diffractogram obtained with a crystal cleaved along the (100) planes, II: diffractogram obtained with a crystal cleaved along the (111) planes*

History of X-rays

Crystallography

First x-ray powder diffractometer was developed in 1935 by LeGalley – gave poor intensities.

In 1945 – Parrish and Gordon developed a Geiger-counter instrument.

Phillips Company (now PANalytical) produced the first commercial instrument in 1947.

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.

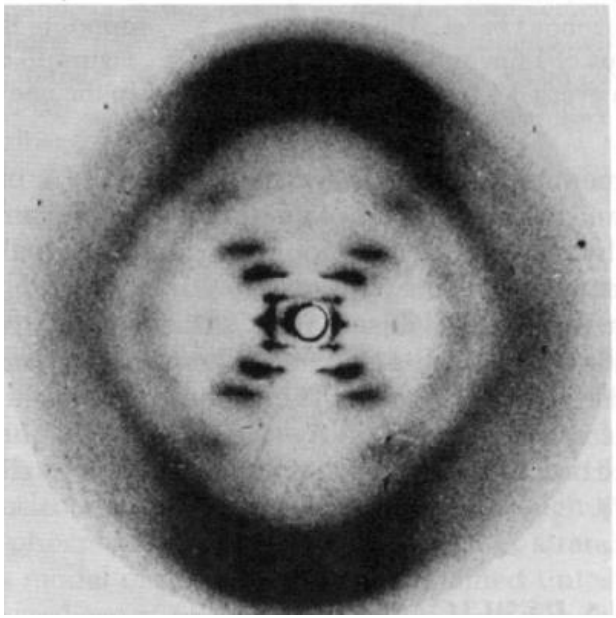
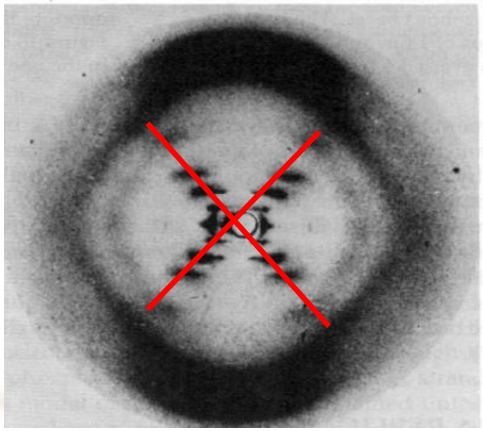


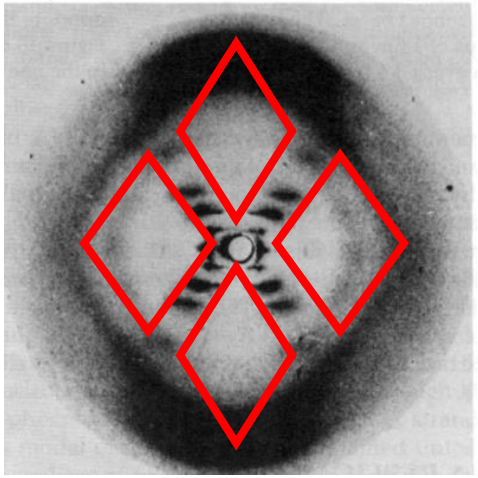
Photo 51- The x-ray diffraction image that allowed Watson and Crick to solve the structure of DNA

History of X-rays

Crystallography



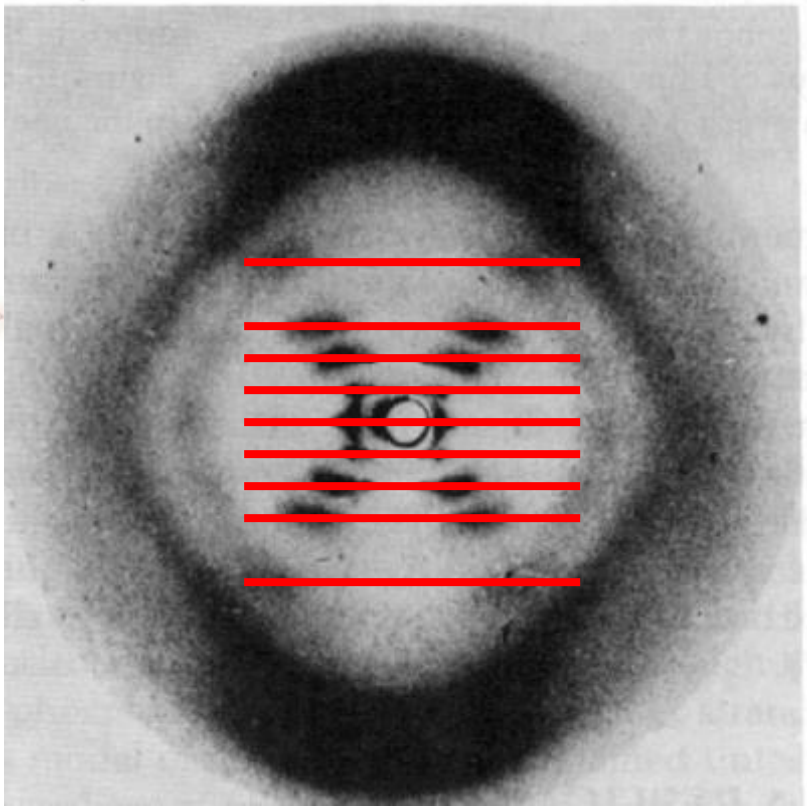
"X" pattern characteristic of helix



Diamond shapes indicate long, extended molecules

History of X-rays

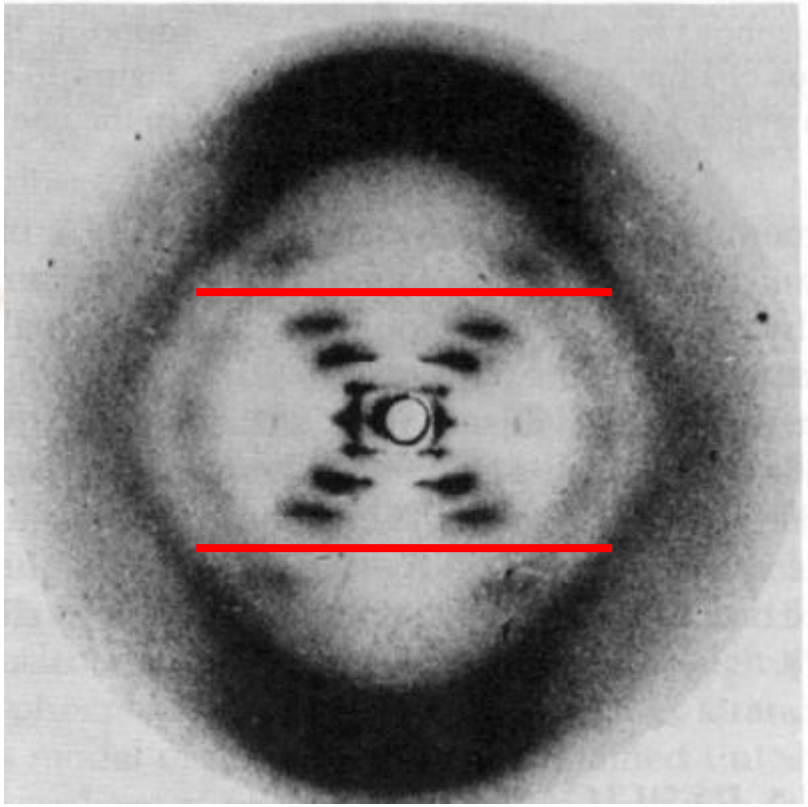
Crystallography



Smear spacing reveals distance between repeating structures

History of X-rays

Crystallography



Missing smears indicate interference from second helix

History of X-rays

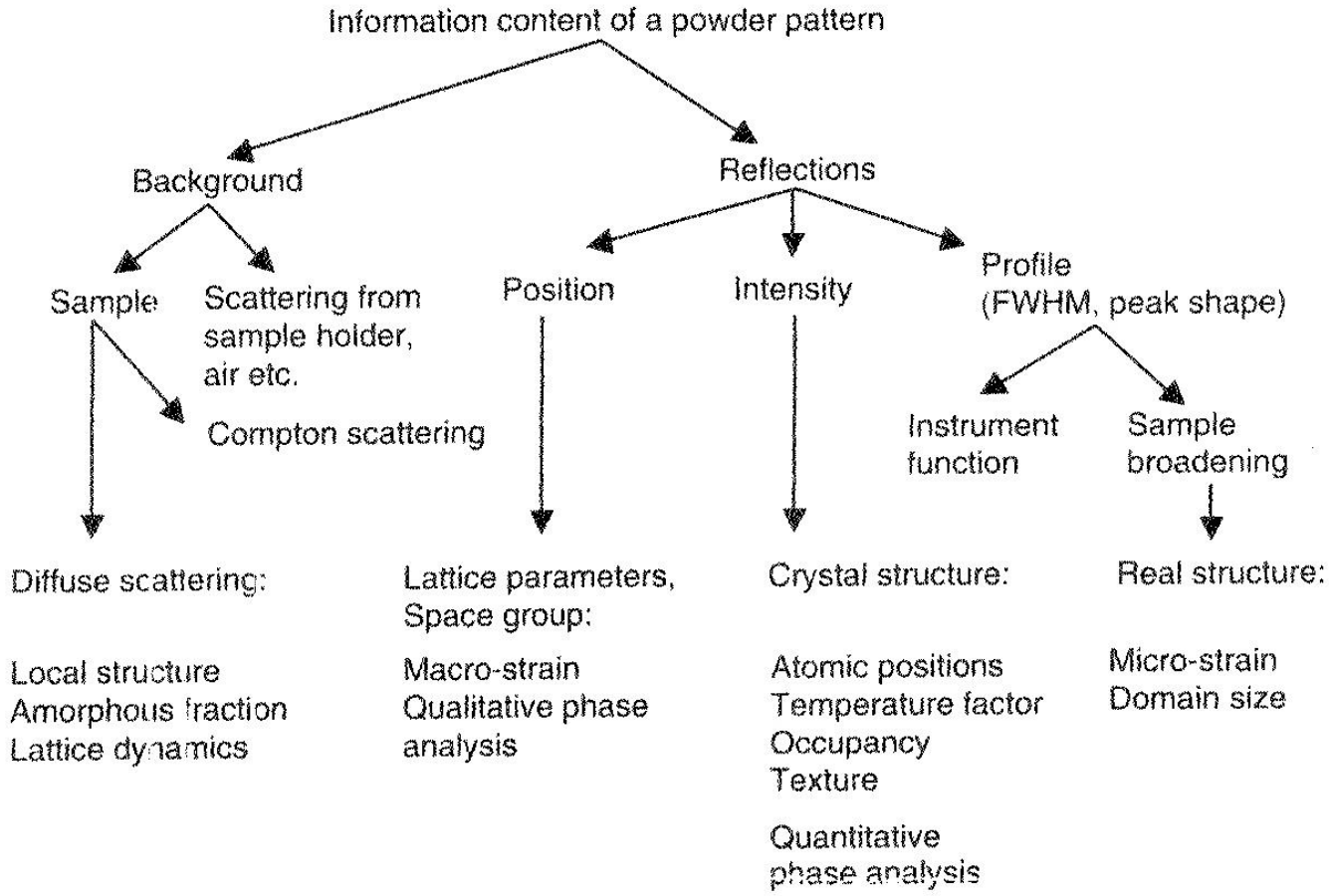


Figure 1 General information content of a powder diffraction pattern.

History of X-rays

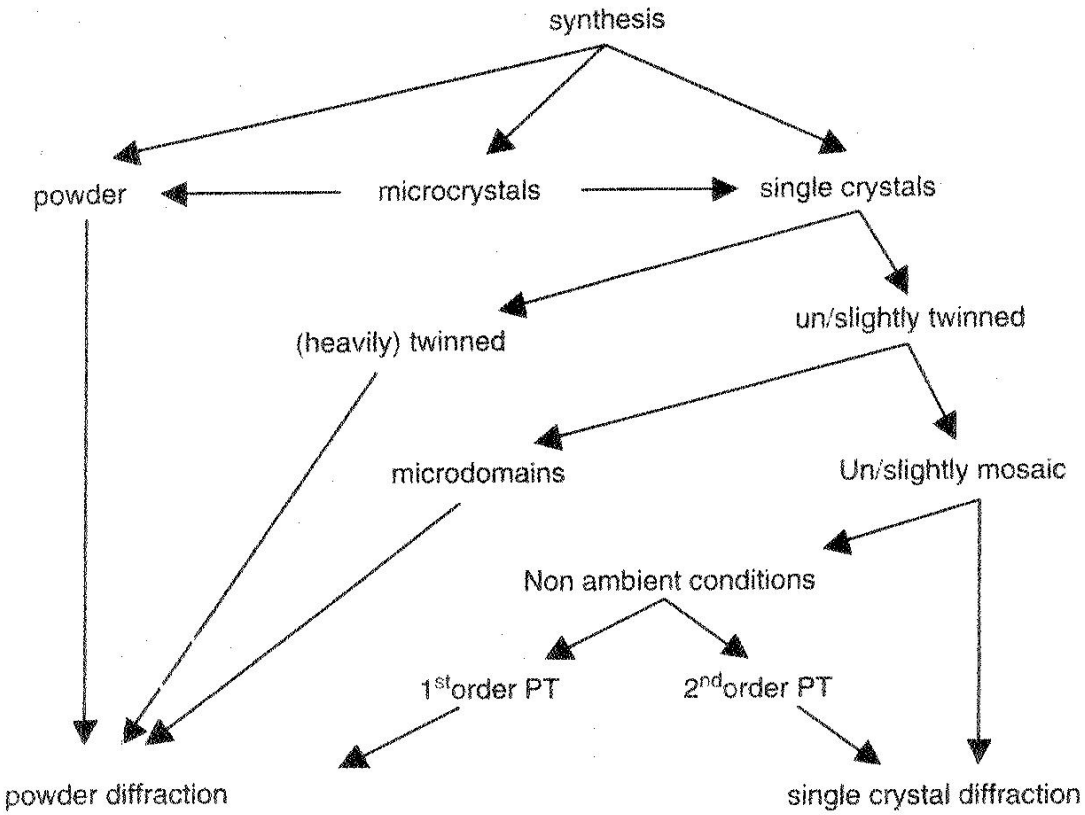


Figure 2 Illustration of the relationship between the domains of applicability of the powder and single-crystal methods in the area of structure solution.

Assignment

Read W. L. Bragg's Nobel Lecture "The diffraction of X-rays by crystals" at class website under "Assignment 1"

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

Read article at following website:

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

Read article at this link:

http://chemistry.unt.edu/~tgolden/courses/Zeitschrift%20anorg%20allge%20chemie%20-%202014%20-%20Etter%20-%20A%20Century%20of%20Powder%20Diffraction%20a%20Brief%20History.pdf