Introduction

Chem 6850/8850
X-ray Crystallography
The University of Toledo

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Course Goals

- To develop an understanding of basic crystallographic concepts
  - Helpful if you ever need to determine a crystal structure yourself

- To be able to interpret the crystallographic data in publications
  - What do the data mean?
  - Does the interpretation make sense?

- To gain an appreciation of the steps involved in a crystal structure determination
  - Enables you to interact with the “black box” if default settings don’t lead to a solution
Crystallography - what and why?

- **What?**
  - Determination of the atomic structure of crystalline solids
  - Location and type of atoms, bond distances/local environment
  - Absolute structure

- **Why?**
  - Materials’ properties are intimately related to their structures
    - Understanding certain properties requires knowledge of atomic arrangement, e.g. piezoelectrics
  - Structural studies of enzyme active sites can allow the rational selection of inhibitors
  - Impact of crystallography can be seen in the large number of Nobel Prizes for work related to crystallography or diffraction
Historical development

- X-rays were discovered by Wilhelm Conrad Röntgen in 1895
  - "Interested in the effects of ultra-violet radiation, he covered a cathode-ray discharge tube with black paper and darkened the room. With the glow from the tube hidden, Röntgen was surprised to see a fluorescent screen two metres away light up. For several weeks, Röntgen hid in his laboratory, finding out more about the mysterious penetrating 'X' rays, produced when the cathode rays hit the end of the discharge tube.” (IUCr history page)

- In 1912, Max von Laue discovered that X-rays are diffracted by crystals
  - Copper sulfate, recorded on film

- In 1913, Sir William Henry and William Lawrence Bragg formulated their famous Bragg law
  - Birth of "crystallography"
Some Nobel Prizes for Crystallography or Diffraction

1901 - Wilhelm Conrad Roentgen for his discovery of X-rays
1914 - Max von Laue for his discovery of the diffraction of X-rays by crystals
1915 - Sir William H. Bragg, William L. Bragg for their services in the analysis of crystal structure by means of X-rays
1927 - A. H. Compton for his discovery of scattering of X-rays by electrons
1929 - Louis-Victor de Broglie for his discovery of the wave nature of the electron
1936 - Peter J. Debye for his contributions to our knowledge of molecular structure through his investigations on dipole moments and on the diffraction of X-rays and electrons in gases
1937 - Clinton J. Davisson, George P. Thomson for their experimental discovery of the diffraction of electrons by crystals
1946 - James B. Sumner for his discovery that enzymes can be crystallized
1954 - Linus C. Pauling for his research into the nature of the chemical bond and its application to the elucidation of the structure of complex substances
1962 - Max F. Perutz, John C. Kendrew for their discoveries concerning the molecular structure of nucleic acid and its significance for information transfer in living material (double helix)
1962 - Francis H.C. Crick, James D. Watson, Maurice H.F. Wilkins for her determinations by X-ray techniques of the structures of important biochemical substances
1964 - Dorothy C. Hodgkin for his studies on the structure of boranes illuminating problems of chemical bonding by X-ray diffraction
1976 - William N. Lipscomb for his development of crystallographic electron microscopy and his structural elucidation of biologically important nucleic acid-protein complexes
1982 - Sir Aaron Klug for his theory of critical phenomena in connection with phase transitions
1985 - Herbert A. Hauptman, Jerome Karle for their outstanding achievements in the development of direct methods for the determination of crystal structures
1988 - Johann Deisenhofer, Robert Huber, Hartmut Michel for the determination of the 3-dimensional structure of a photosynthetic reaction center
1991 - Pierre-Gilles de Gennes for his application of methods for discovering order in simple systems to polymers and liquid crystals
1992 - Georges Charpak for his discovery of the multi wire proportional chamber
1994 - Clifford G. Shull, Bertram N. Brockhouse for their pioneering research in neutron scattering
1996 - Robert F. Curl, Sir Harold W. Kroto, Richard E. Smalley for their discovery of the fullerene form of carbon
1997 - P. D. Boyer, J. E. Walker, J. C. Skou for their elucidation of the enzymatic mechanism underlying the synthesis of adenosine triphosphate (ATP) and their discovery of an ion-transporting enzyme
What is possible today?

- Determination of small molecule structures is routine nowadays
  - This was not true 50 years ago!
  - Takes 6-12 h of data collection in most cases

- Crystal structures of macromolecules can be solved from single crystal data

- Synchrotron radiation can in some cases yield single crystal structures from crystals that are smaller than 10 µm

- Powder methods are becoming more advanced and can in some cases enable full structure determinations, too
How do we determine a structure?

- Oldest methods relied on simple physical observations only
  - Example: Crystal habit
  - Could determine symmetry of crystal, but usually not atomic scale structure

- NMR has become one of the most powerful structural tools for organic molecules
  - Can also be used for amorphous materials
  - Often less straightforward for solids and/or non-standard nuclei

- Crystallographic methods
  - Gives detailed time-averaged picture in 3D
  - Works only for crystalline materials
Electron microscopy

- Electron microscopy is a powerful tool for the visualization of particles and/or lattices (high resolution)
- Electrons can be focused using magnetic lenses
- Gives structural information on a short length scale
  - Provides a 2D image
  - Samples are often damaged by the intense electron beams
  - Only very thin samples can be measured
  - Images can be difficult to interpret
Picking the appropriate probe

- Light scattering can give “structural” information on the length scale of light waves
  - Light microscopy
  - Measurement of particle size distributions by light scattering
- Analysis of atomic length scale ordering requires a probe with the appropriate wavelength
  - Typical bond distances are 1-3 Å
  - X-rays have Angstrom wavelengths
- How do we focus X-rays without appropriate lenses?

Cullity, “Elements of X-ray Diffraction”
How a microscope works

- Light is focused using lenses
Ways of focusing X-rays

◆ There are no refractive lenses for X-rays, as the refractive index in all materials is close to 1
  - Between 0.99 and 0.999

◆ X-rays can be focused using diffraction based optics
  - e.g., a “peak” of X-rays is used as the source

◆ At small incident angles, X-rays can be focused by using X-ray mirrors
  - grazing incidence
  - usually <0.5° for Pt at 10 keV
X-ray cathodes

Cullity, “Elements of X-ray Diffraction”
Typical setup for a diffraction experiment

Specimen C on support table H, can be rotated around axis O; X-ray source S with line focal spot on the target T; A, B and F are defining/focusing slit systems; counter G supported by carriage E, which can also be rotated around O, angular position can be read on scale K. E and H are mechanically coupled so that E rotates twice as far.


Cullity, “Elements of X-ray Diffraction”