Chemistry 832: Solid State Structural Methods

Outline Notes[1] for the Spring 2000 Class

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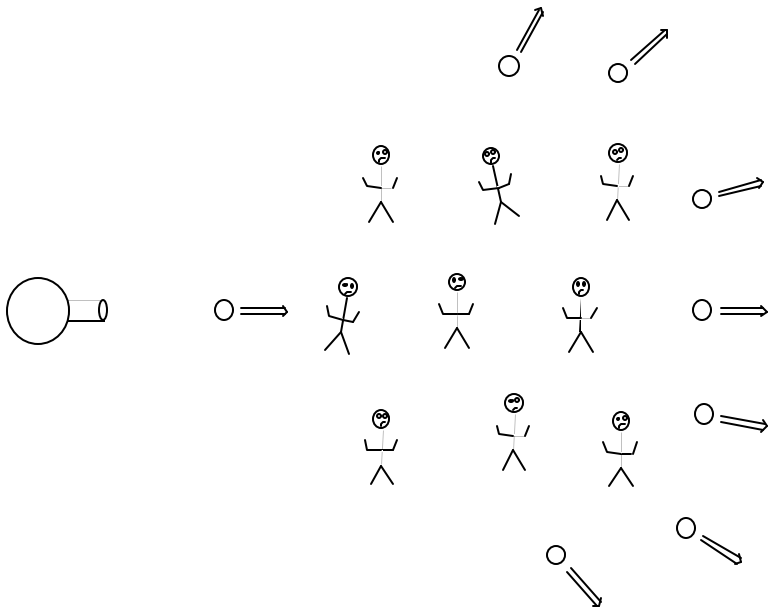


[1] Based partially on the text: Crystal Structure Analysis for Chemists and Biologists by J. P. Glusker, M. Lewis, and M. Rossi, VCH Publishers, New York, NY, ©1994. Unless otherwise noted, chapter and page references are to this text.

Table of Contents

Section 01: Table of Major Topics

Section 02: Complete Table of Contents

Topic I: Introduction to Chemistry 832

- Based primarily on:
  - Chapter 1 (G, L, & R, pages 1-31)
  - A. D. Hunter's YSU Structure Solution Manual
  - Other materials available (or referenced) on my WEB Site

- Chapters 1 and Chapter 2 of G, L, & R need to be read on your own by the next class

Ask Students: What do you know about the Application of Diffraction Methods to Solving Chemical Problems?

Section 01: What is Chemistry 832?

Part a: Chemistry 832 Goals and Objectives

- See the Chemistry 832 Goals and Objectives Handout, available on my WEB Site

Part b: Chemistry 832 Syllabus

- See the Chemistry 832 Syllabus for Spring 2000, available on my WEB Site

Part c: Chemistry 832 Resources

- Texts and Monographs
  - See the list of reference materials: Crystallography-Diffraction Methods Texts List, available on my WEB Site

- The Lab Manuals
  - Copes are available in the Diffraction Lab or may be borrowed from Dr. Hunter

- The Structure Solution Guide
  - Copies are available as .pdf files for those who want their own, one is kept in each of the Diffraction Lab and NT Labs, and may be borrowed from Dr. Hunter

- The NT Lab
  - This lab is equipped with a dozen Windows NT computers, each loaded with all of the software needed for this course. It is available to Chemistry Majors (and other privileged undergraduates) and Graduate Students. To use this lab, you need to get an NT identity and password from Ray.

- The WEB
  - Numerous excellent teaching materials on diffraction methods are available on the WEB, I will place links to some starting sites on my WEB page.

- The Diffractometer Lab
  - This lab is equipped with two Bruker AXS P4 Diffractometers. The southern instrument is equipped with a Cu X-Ray source and is usually used for powder studies. The northern instrument is equipped with a Mo X-Ray source and is our main single crystal instrument. The two PCs in this lab each control one of the diffractometers

Section 02: What Can Diffraction Methods Tell Us

- Diffraction methods can tell us much useful information about crystalline samples, including:
  - The size and shape of the repeating unit (unit cell) of the crystal
  - Overall molecular structures
  - Bond lengths, angles, torsions, etc.
  - Atomic motion and disorder
  - Intermolecular interactions

Section 03: Speed and Cost

- One generation ago, a single crystal study could take up most of a PhD and consequently was a rarely used technique
- Now, a *routine* single crystal study is both quick and relatively inexpensive
  - 1 second to 1 week for data collection
  - 1 hour to several days to solve the data
  - A few hundred to a few thousand dollars for a small molecule, about ten to a hundred times more for a *routine* protein

Section 04: What is a Single Crystal and Why is it Important?

Part a: Single Crystal

Graphics from Text: Figure 1.3, page 5; single crystals of Quartz and Ammonium Dihydrogen Phosphate (NLO material)

- Growing crystals is typically slowest and most unpredictable part of experiment
- Long distance order from one side to the other
- Defects in th crystal effect quality of data

Part b: Unit Cell

- Repeating motif of crystal
- Bricks in the wall
- Includes both dimensions and symmetry
- Made up of "imaginary" lattice points
- Contains complete unique part(s) of molecules (sometimes more than one copy)

Part c: Unit cells and diffraction data

- The more unit cells in the crystal the better the data quality

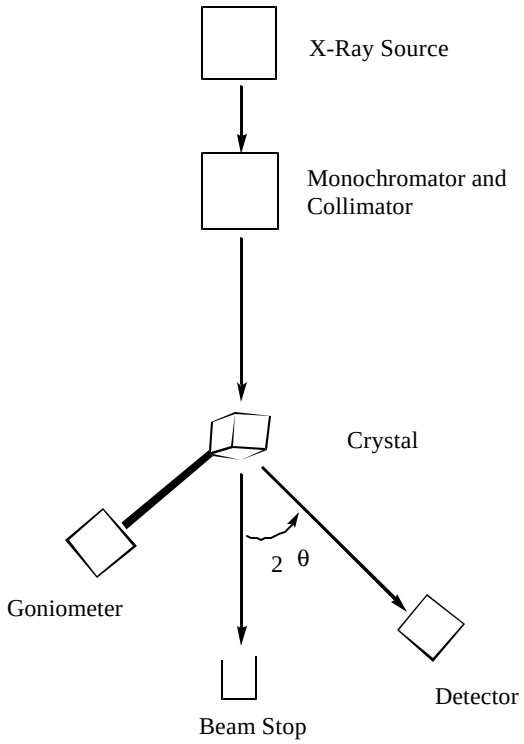
- The less disorder the better the data quality

Graphics from Text: Figure 1.6, page 14; Unit cells of NaCl and KCl

Graphics from Text: Figures 1.7 and 1.8, pages 17 and 18; Crystal structures of Diamond and Graphite

Graphics from Text: Figures 1.9 - 1.11, pages 19 - 21; Crystal structures of Hexamethylbenzene, Hexachlorocyclohexane, and Steroids as representative examples of early diffraction results

Section 05: Block Diagram of an X-Ray Diffractometer



Graphics from Text: Figure 1.5, page 11; Text's diagram of an X-Ray Diffractometer

Section 06: X-Ray Generator

- Needs to produce intense X-ray beam
- Needs to produce monochromatic X-ray beam
- Needs to produce collimated X-ray beam

Part a: Goniometer

- Allows one to place a sample at a precisely controlled orientation in 3D space
- Under computer control

Part b: Detector

- Allows one to measure the intensity of diffracted X-ray beams as a function of diffraction angle

Section 07: Basic Steps in X-Ray Diffraction Data Collection

- Grow Single Crystal
- Mount Single Crystal on Diffractometer
- Evaluate Crystal Quality
- Collect Unit Cell information and Space Group information
- Collect Diffraction Data
- Collect Absorption Data

- Solve Structure

Graphics from Text: Figure 3.11, page 89; Relationship of Crystallographic Data to Structural Data

- Prepare Structural Data for Publication

Section 08: Basic Steps in X-Ray Diffraction Data Analysis

Part a: Data Analysis can be quite routine through impossibly difficult

- Quality of Raw Data Advances?
- Theory Advances
- Software Advances
- Computer Advances
- Synergy of these changes

Part b: The Phase Problem

- Which is more important, Knowing the Intensities or Knowing the Phases of the Diffracted beams?
- Data ↔ Solution Relationship

Experiment ⇒ Intensity Information + Phase Information

↓↑

Results ⇒ Atomic Positions + Atomic Sizes/Shapes

Section 09: Main Steps in Data Analysis

Part a: Procedural Steps

- Process the Raw Data (XPREP)
  - Determine Space Group
  - Do Absorption Corrections

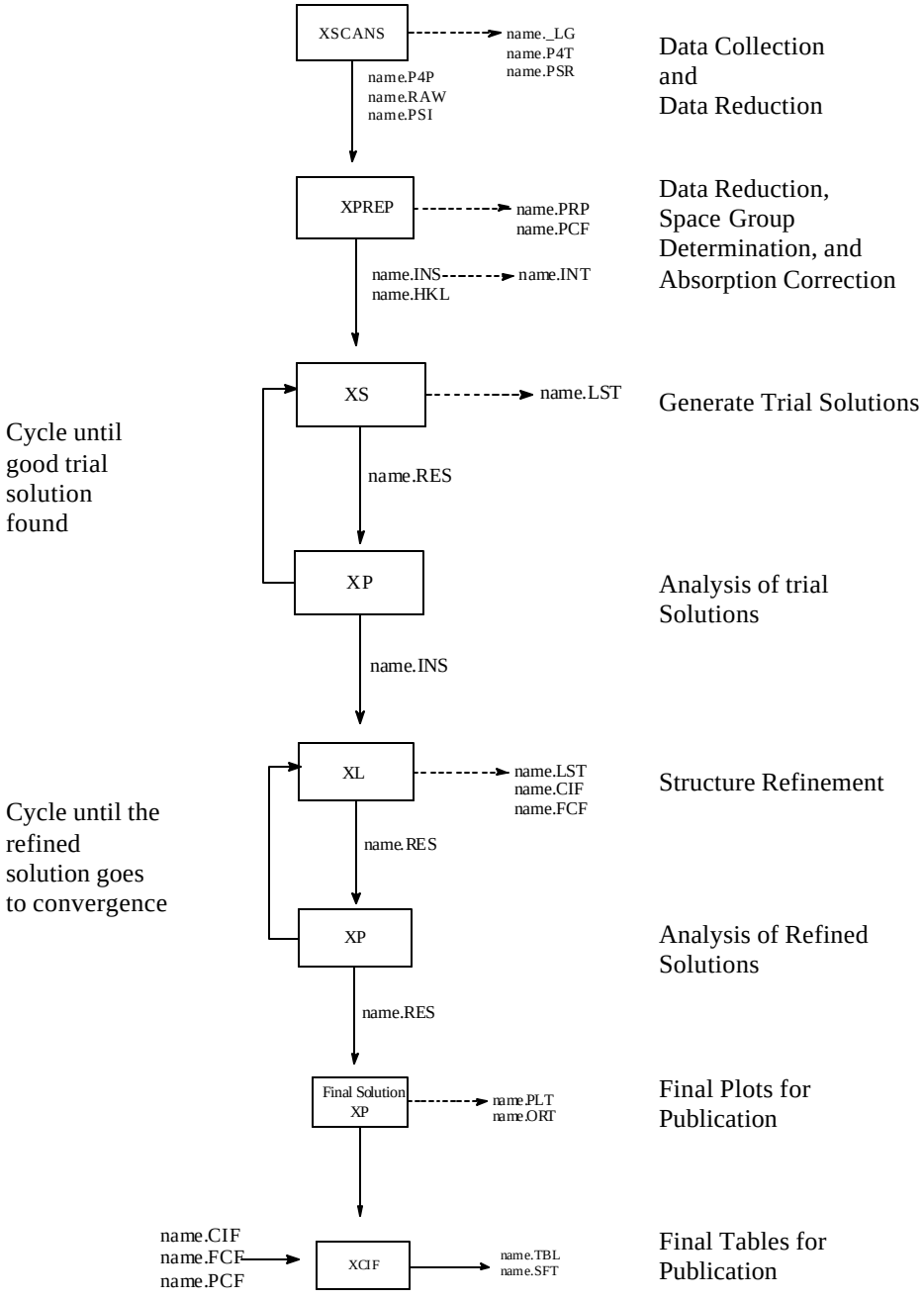
- Determine an Initial Starting Solution (XS)
  - Use one of the "tricks" to find at least one atom at near its actual position
  - This will give you the first phase information

- Evaluate the Trial Structure(s) (XP) and Refine the Trial Structure(s) (XL)

- Evaluate the Final Answer

- Prepare the Data for Publication

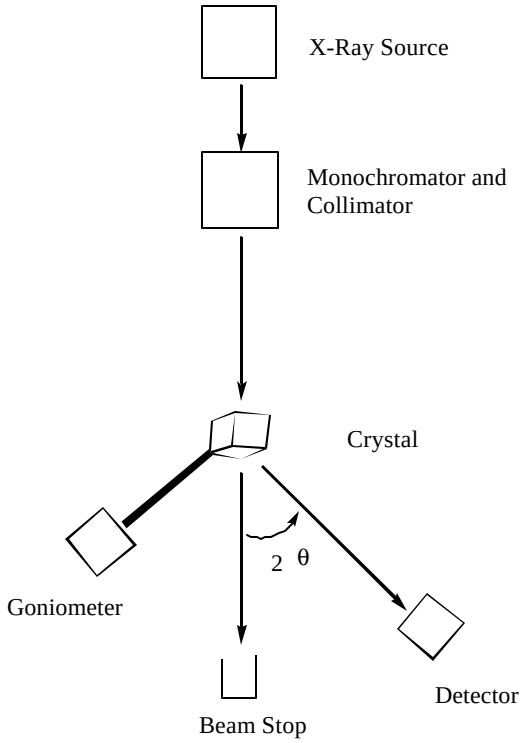
Part b: Flow Chart for a Typical Structure Solution



Topic II: X-Ray Diffractometers

- Based primarily on:
  - Chapter 7 (G, L, & R, pages 225-279)
  - Other materials available (or referenced) on my WEB Site
  - A. D. Hunter's YSU Structure Solution Manual
  - The Instruments in the Diffraction Lab.

Ask Students: What do you know about X-Ray Diffractometers?



Section 01: What are X-Rays?

Part a: Wavelengths of X-Rays

- Typically 0.5 to 2.0 Å
- Limited by X-Ray Generation Capabilities (i.e., target metal)
- Limited by Available X-Ray Flux
- 1.54 Å for Cu Targets
- 0.71 Å for Mo Targets
- 0.49 Å on Ag Targets
- Tunable Wavelengths on Synchrotron Sources

Part b: Why are these Wavelengths chosen?

- They match intermolecular distances

Section 02: X-Ray Generators

Part a: X-Ray Lasers

Part b: Conventional X-Ray Tubes

- Cathode (Tungsten Filament)
  - Provides electrons
  - Slowly boils off Tungsten Vapor and this contaminates Metal Target and leads to filament breakage
- Accelerator Plates
- Metal Target (Anode)
  - Determines Wavelength distribution of X-Rays
  - Must be an excellent conductor of heat
    - Up to 3,000 Watts
- Cooling System
  - Limiting variable on tube output
  - Causes most operating problems
  - Transports heat to a heat sink

Part c: Rotating Anode Generators

- Designed to overcome the cooling limitations of Conventional Anodes

- Their Anode is a Rotating Cylinder of the Target Metal

- Rated Power Limits typically 12 to 18 kW
  - Normally run at 6 to 10 kW to reduce maintenance

- Maintenance Problems
  - Seals have to deal with high voltages, high vacuum, and high speeds
  - Filaments need to be changes every couple of months

- Vacuum System maintenance
- Purchase and Operating Costs

Part d: Synchrotron Sources

- National Level Facilities costing hundreds of millions or even a Billion Dollars

- Rely on "wasted" energy of rotating particle beam
  - Early machines collected stray radiation from bending magnets (broad band)
  - Current machines also use Wiglers to generate tunable radiation

- Advanced Light Source, ALS, at the National Lab in Berkeley

- Advanced Photon Source, APS, at the National Lab in Chicago

Section 03: X-Ray Monochromators

- Needed to reduce radiation to a single wavelength without unduly reducing the intensity

Part a: Foil Filters (Ni foil)

- Ni foil

Part b: Crystal (Graphite) Monochromators

- Large Graphite Single Crystal

Part c: Focusing Mirrors

- Highest Photon Yields
  - Catch a larger "spread" of X-rays from the tube

Section 04: X-Ray Collimators

Part a: Graphite Crystal Monochromators and Pin Holes in Tubes

Part b: Focusing Mirrors

- Much higher photon yields

Section 05: Goniometers

- Manual Goniometers on "Picker Machines"

- Automated Goniometers
  - 4 Circle Goniometers on our P4s
  - Kappa Geometry Goniometers
  - Serial Detectors vs. Area Detectors
  - Full computer control

- Extremely precise machining
  - Digital stepper motors

- Goniometer Heads

Section 06: Low Temperature System

- Why low temperatures?
  - Data intensity at high angles
  - Smaller Displacement Parameters
  - Slower crystal decomposition
    - Decomposition from X-Ray Beam
    - Decomposition from heat
    - Decomposition from air

- Limitations
  - Icing
  - Liquid N_2 Systems to ≈ -150 °C
  - Liquid He Systems to ≈ 15 - 20 K

Section 07: X-Ray Detectors

Part a: Serial Detectors

- Scintillation Counters
- Excellent dynamic range
- Low cost
- Highly reliable
- Only one reflection at a time and therefore long data collection times
- The Multiplex Advantage

Part b: Film Based Area Detectors

- Oldest type of X-Ray Detector
- Multiple layers of film
- Visual estimation of intensities using Densiometer
- Modern automated intensity readings

Part c: Multi-Wire Area Detectors

- X-1000 Multi-Wire Detector on Cu Machine in Lab
  - Grid of wires (512 by 512 or 1024 by 1024)
  - Xe gas ionization
  - Be Windows
- Poor Dynamic Range
- Low Cost
- First major automated route for collecting Protein data
- Good for collecting Powder Data

Part d: CCD Detectors

- Developed by DOD and Astronomers
- The current State of the Art for Small Molecules and Synchrotron data
- Chip sizes range from 1k x 1k to 4k x 4k pixels and several cm on an edge
- Fiber Optic Taper normally used to increase data collection area to about 10 cm x 10 cm
- Data collected for 30 seconds to several minutes per frame and then read out to computer (this almost instantly)
- A Phosphor (tailored for the wavelength(s) of interest) converts the impinging X-rays to multiple visible light photons (what is counted by the CCD chip)
- Moderately expensive but price coming down rapidly
- Significantly more maintenance than a serial detector
- Good dynamic range
- CCD chip needs to be "cryocooled" to function

Part e: Imaging Plate Detectors

- The detector of choice for most current protein diffraction studies
- Very large data collection areas, typically 30 cm x 30 cm
  - This is especially important for large unit cells
- X-rays strike a large Storage Phosphor (frame times can be up to tens of minutes)
- Data read out by training an IR laser onto each pixel which causes optical photons to be released
  - Data read out times can be several minutes as this is done in a serial fashion
  - In compensation, many Imaging Plate systems have two phosphor screens and one is collecting data while the other is reading it out
- Prices similar to CCD systems
- Dynamic range smaller but data collection area larger

Section 08: X-Ray Absorption in the Diffractometer

Part a: Air

- Not a problem for short wavelength radiation such as Mo or Ag
- A significant problem for Cu, especially with large unit cell parameters where crystal to detector distances are large
- Use a He beam path

Part b: Windows

- Typically use Be windows on detectors and X-ray tubes
- May also use plastic films around He beam paths, etc.

Part c: Sample, Glue, Fiber & Capillary

- Larger samples with heavy atoms can absorb significantly
- Glue used to mount the sample, any beam that passes through the mounting fiber, and any capillary glass can absorb significantly, especially for Cu radiation

Topic III: Single Crystals

- Based primarily on Chapter 2 (G, L, & R, pages 33-71).

- Crystal Growth Strategies based primarily on Chapter XIV in Allen Hunter's YSU Structure Analysis Lab Manual, SALM, page 240 - 247

Ask Students: What do you know about Single Crystals

Section 01: Perfect Crystals?

- Single Crystals
  - Have long range order
  - Like bricks in a wall

- One distinct orientation
  - Typically a single degree or so of disorder across macroscopic dimensions

Graphics from Text: Figures 2.1 - 2.3, pages 34 - 36; Electron Micrograph pictures of three Virus Crystals

Graphics from Text: Figure 2.4, page 37; Scanning Tunneling Microscope, STM, images of Gallium Arsenide, GaAs, Single Crystals

Section 02: Growing Single Crystals

- Stages of Crystal Growth
  - Nucleation
    - The key step
  - Deposition on Surfaces of Individual Molecules
    - Requires a Saturated Solution
    - Requires that surface have similar metric parameters to the molecules being deposited

Graphics from Text: Figure 2.6, page 42; Sites of crystal growth on a crystal surface

Graphics from Text: Figure 2.8, page 48; Some methods of growing single crystals

- Crystal Growing Strategies from Chapter XIV in Allen Hunter's YSU Structure Analysis Lab Manual, SALM, as a Separate Handout available from:

You Must Print out this Handout
Modified Chapter XIV of ADH's
Structure Analysis Lab Manual, SALM:
Growing Single Crystals Suitable for Diffraction Analysis:
In Color: 137KB.doc, 63KB.pdf
Black and white: 143KB.doc, 62KB.pdf

Part a: General principles of growing single crystals

- General view: Art rather than Science
  - Green Thumb
- Rational approach informed by understanding

Part i: Rates of Crystal Growth

- Slower is better
  - Typically takes days to a week

Part ii: General Conditions for Crystal Growth

- Best Conditions
  - Constant temperatures
  - Minimal vibration
  - Dark (often seems to help, especially avoid direct sunlight)

- Impatience is the Enemy
  - Convection is bad and should be suppressed
    - Viscous solvents
    - Low Thermal Expansion Coefficient, dependence of density on temperature
    - Narrower tubes
  - Don't check crystallizations too often

Part iii: Solvent Properties and Saturated Solutions

- Grow crystals from Saturated Solutions
  - Like a bear's porridge, concentration at saturation must be just right
  - Systematically explore solubility

Part iv: Master Several Favorite Methods

- Success increases with experience
  - One learns to read subtle signals
  - Find a few methods and master them

Part b: Proven Methods for growing crystals

- The most common methods

Part i: Crystallization by Slow Evaporation

- Most popular method
- Works most easily with air stable materials
- Slow solvent evaporation is the key

Part ii: Crystallization by Cooling

- My personal favorite, alone or in combinations
- Solubility typically decreases with temperature
- Cool saturated solution of sample
  - Freezer for organics/inorganics
  - Furnace for extended solids

Part iii: Crystallization Using Mixed Solvents and Solvent Diffusion in the Gas Phase

- Use a mixture of solvents to obtain the correct level of solubility
- Mixed Solvents
  - One solvent is moderately good for the compound
    - Contains dissolved sample near saturation
  - One solvent is moderately bad for the compound
  - The two solvents must be fully miscible
  - The sample is fully dissolved in the better solvent and then through various means the concentration of the second, poorer, solvent is increased

- Allow the two solvents to mix using a very slow solvent pump or dropwise solvent addition

- Allow the better solvent to evaporate out of the system

- Allow one or both of the solvents to diffuse into the other via the gas phase
  - Typically takes longer and requires a moderately volatile solvent

Part iv: Crystallization by Solvent Layering

- Solvent Layering
  - One solvent is moderately good for the compound
    - Contains dissolved sample near saturation
  - One solvent is moderately bad for the compound
  - The two solvents must be fully miscible
  - Layer one on top of the other

Part v: Crystallization by Diffusion Through Capillaries and Gels

- Diffusion through a narrow capillary, constriction in the tube, or a gel
  - One solvent is moderately good for the compound
    - Contains dissolved sample near saturation
  - One solvent is moderately bad for the compound
  - The two solvents must be fully miscible
  - The sample is fully dissolved in the better solvent and then through various means the concentration of the second, poorer, solvent is increased

Part vi: Crystallization From Melts

- Requires that the sample be thermally stable at the requisite melting point of the Melt

- Used industrially to grow single crystals used in the electronics industry, e.g.
  - Single crystal Silicon, Gallium Arsenide, etc.

- Used to grow single crystals of high temperature extended solids, e.g.
  - Minerals such as Diamond and Quartz in nature
  - Metal oxides in Dr. Wagner's group

- Some work has been done on using low temperature ionic liquids (which may melt near room temperature) to apply this approach to less thermally stable ionic materials

Part vii: Crystallization by Sublimation

- The compound must be sufficiently volatile at accessible pressures (vacuums)
  - Can be assisted by using heating of the sample and cooling of the receiver

- Works best with the most volatile materials (typically quite nonpolar), e.g.
  - Naphthalene
  - Ferrocene
  - $Cr(CO)_6$

Part viii: Crystallization Using Combinations

- In Terminator II, Judgement Day, the boy is trying to teach Arnold Swartzenager, the Terminator, how to act more human
  - He first teaches him individual colloquial expression
  - He then tells him he can, like, use combos
  - Arnold gets the idea and comes up with “Hasta La Vista - Baby” (forgive my Spanish)

- Like Arnold, don’t be afraid to use combinations, combos, that your experience and intuition suggest, e.g.
  - My favorite method is to layer the solution and then place it in the freezer

Part ix: Syntheses In Situ

- Reactions at the Interface of Two Solutions
  - Can be at a boundary between to imiscible layers
  - Can be at a capillary junction between the same solvent
  - The starting materials are each dissolved in one solution
  - The product is insoluble in neither
    - It precipitates at the solution boundary
    - Works even for thermally unstable materials

- Can be done with an electrochemical source as one “reagent”

Part x: The Magic of NMR Tubes

- An amazingly large number of single crystals are grow in NMR tubes so always check them before cleaning.

- Why is this true?
  - NMR Tubes are:
    - Typically very clean
    - Have few nucleation sites on their walls (no scratches)
    - Thin and this suppresses convention
    - The plastic caps have a very low permeability to most organic solvents that lets them evaporate out slowly over weeks or months
    - Chemists run at near saturation to get the strongest signal
    - Chemists use their cleanest samples for NMR to get the prettiest pictures for their bosses and themselves

- Chemists, as a Rule, are Lazy
  - They do not clean their tubes for months in dark quiet spot and let them sit around undisturbed in spots the boss can't see and they don't have to look at: perfect crystallization conditions

Part xi: Other Chance Methods

- Don't look a gift horse in the mouth and keep a close watch:
  - dirty old flasks you have been avoiding washing
  - in old bottles of samples
  - in anything that might hold a sample

Part c: What to do when proven methods fail

Part i: Purify Your Material

- Impure materials greatly impede crystallization, especially the formation of single crystals

- If you crystallization doesn't work:
  - Further purify the sample
  - Keep the best solids and use them to start the next round

Part ii: Seed Crystals

- Crystals grow by the addition of individual molecules to a surface having a similar structure

- Crystals can be grown using Seed Crystals of your sample that were too small for diffraction analysis

- Seed crystals are often produced accidentally from solutions splashed on the side walls of flasks

Part iii: The Role of Extraneous Materials

- Interestingly, if one uses too clean of procedures (hard to do in practice) it is much harder for crystals to grow, they typically need a seeding/patterning agent, often provided accidentally

- Dust, dandruff, and grease

- Scratches and defects in the container walls

- Surface treatments of the container walls

Part iv: Try, Try Again

- When All Else Fails, Persistence Pays Off

- Sequential crystal growing strategies

- Systematic approaches to growing single crystals and the exploration of crystallization: the multiplex advantage
  - Learning from Protein Crystallographers

- Make Derivatives
  - They synthetic chemist's best friend

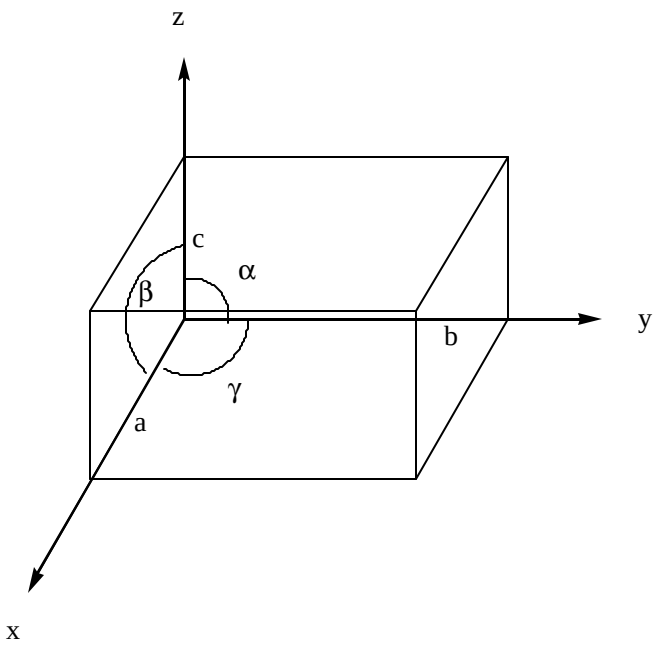
- Solvates and Crystallization Agents
  - Packing / Interacting solvents such as:
    - Water or Alcohols
    - Benzene
    - Chlorocarbons

- Inclusion Compounds and Supramolecular Complexes
  - Thiourea, $SC(NH_2)_2$, Channel Compounds
  - Calix[n]Arenes
  - Cyclodextrins
  - Porphyrins

Section 03: The Unit Cell

Graphics from Text: Figure 2.5, page 38; Unit Cell Axial Lengths and Unit Cell Angles

- Axial naming follows the right hand rule
- The three axial vectors define a Parallelepiped
  - The lengths can be the same or different
    - Range from a few Angstroms to thousands of Angstroms
  - The angle can be the same or different
    - Often are not 90°



Section 04: Crystal Shapes

Part a: Crystal Growth and Shapes

Part i: Crystal Habits and Morphology

- The relative rates that molecules are deposited onto the surface of growing crystals determines the final shape of the crystal

- This final shape for a particular unit cell is referred to as:
  - The Morphology of the Crystal
  - The Habit of the Crystal
  - These external forms are hard to directly relate to unit cell parameters

Graphics from Text: Figure 2.7, page 44; The relationship of crystal faces to the rates of face growth

Part ii: Polymorphism and Isomorphism

- Some molecules are found with several different unit cells (typically because the energies of packing are similar and small changes in crystallization conditions favor one over the others)
  - These different forms are know as Polymorphs and this behavior is know as Polymorphism

Graphics from Text: Figure 2.14, pages 58 - 61; Variations of crystal shapes (crystal habits) from the same cubic unit cells

- Isomorphism occurs when two different molecules crystallize in apparently identical crystals

- Isomorphic Crystals typically have similar:
  - Crystal Shapes
  - Unit Cell Dimensions
  - Similar molecular structures
  - Similar molecular compositions

- With enough similarity can grow mixed crystals via Isomorphic Replacement, e.g.
  - Very common in minerals
  - Mixed isotope compounds
  - $V(CO)_6$ in $Cr(CO)_6$
  - Chromium Alum in Potash Alum
  - Isomorphous Replacement in Protein Diffraction Studies using heavy atom salts, unnatural amino acids, etc.

- Alums, $(M_1)_2(SO_4)\cdot(M_3)_2(SO_4)_3\cdot 24H_20$
  - M_1 = K or NH_4
  - M_3 = Al^{+3} or Cr^{+3}
  - Form large octahedral crystals by evaporating water solutions

- Potash Alum, $K_2(SO_4)\cdot Al_2(SO_4)_3\cdot 24H_20$
  - Colorless
  - Air Stable

- Chromium Alum, $K_2(SO_4)\cdot Cr_2(SO_4)_3\cdot 24H_20$
  - Deep Purple
  - Decays in Air

- Isomorphic Replacement
  - Layered Alums
  - Mixed Alums

Part b: Indexing Crystal Faces

- Very widely done in geology as a way of identifying minerals
  - Contact Goniometer (two hinged straight edges used to measure angles)
  - Graphics from Text: Figure 2.10, page 52; Diagram of a Contact Goniometer

- Indexing Crystal Faces
  - The xyz face of a crystal is
    - Parallel to all of the xyz planes in the crystal
    - Intersects to axes of the unit cell at 1/x, 1/y, and 1/z
    - Examples:
      - 100 Face
      - 134 Face
      - Good Exam Type Question
  - Graphics from Text: Figure 2.11 and 2.12, page 53 and 54; Indexing Crystal Faces

Part c: The Crystal Lattice

- The Crystal Lattice is an imaginary three dimensional array of points, lattice points, that repeats to give the three dimensional order of the crystal

- When convoluted with the unit cell contents, it build the full three dimensional structure of the crystal

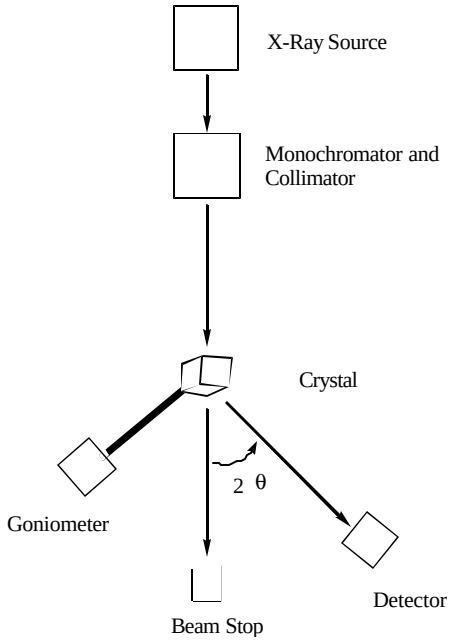
- Graphics from Text: Figures 2.15 and 2.16, pages 62 and 63; The crystal lattice and real crystals

Topic IV: Diffraction by Crystals

- Based primarily on Chapter 3 (G, L, & R, pages 73-103).

Ask Students: What do you know about the Process of Diffraction of Waves?

- Graphics from Text: Figure 1.2, page 4; Image Generation in Optical Microscopy and X-Ray Diffraction



Section 01: Waves

Part a: Generic Waves

- Parameters that define a wave:
  - Wavelength, λ
    - In Diffraction is typically near 1 Å
  - (Frequency, ν (remember: $C = \lambda \nu$))
  - Amplitude, *A*
  - Relative Phase, ϕ

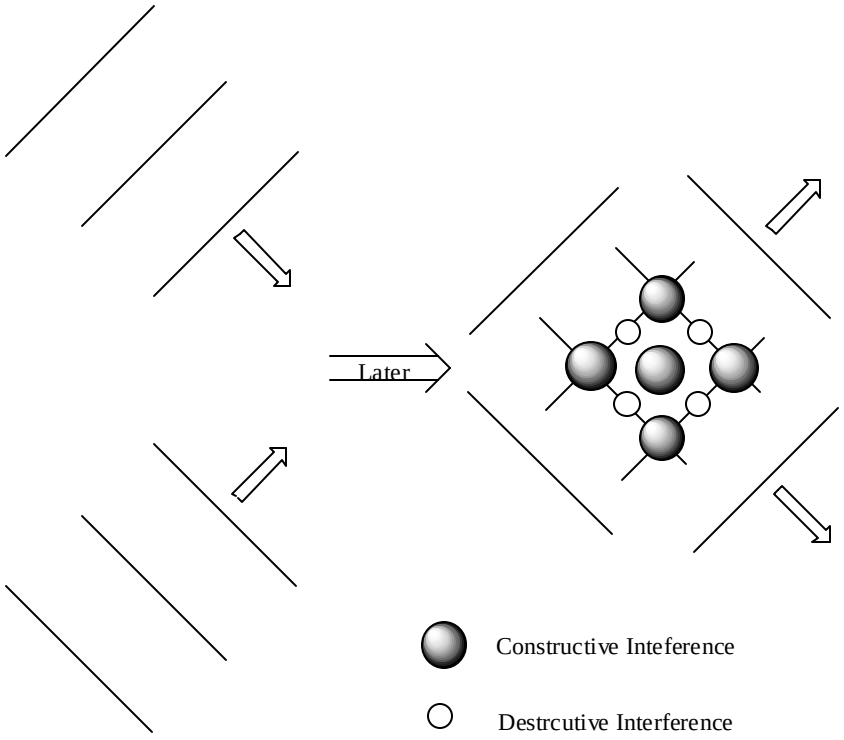
Graphics from Text: Figure 3.1, page 75; The Amplitude, *A*, Wavelength, λ, and Relative Phase, ϕ, of a Sinusoidal Wave

Part b: Water Waves

- Apply your intuition/real world experience/Physics to thinking about planar waves, such as water waves, moving through holes in a barrier (breakwater)
  - Note: The same thing happens when they go through a field of poles in the water

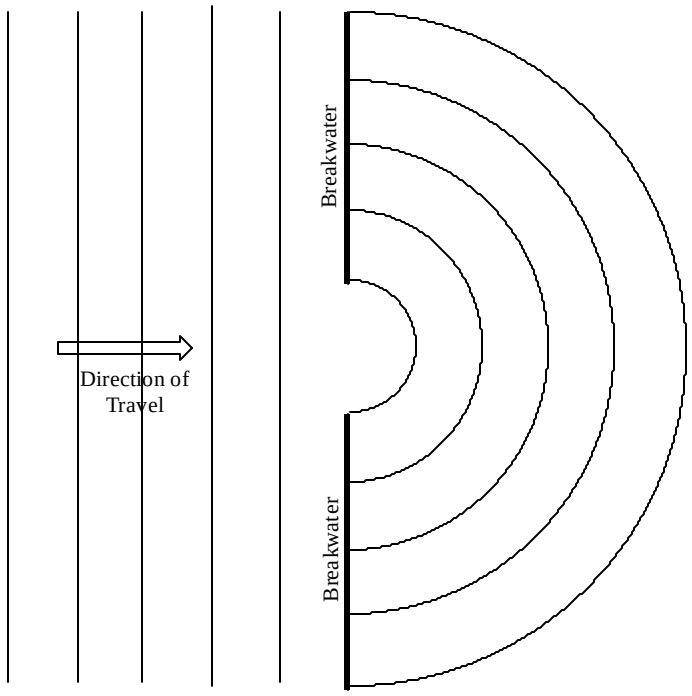
Part i: Non-parallel sets of waves on open water

- Areas of unexpectedly high and low amplitudes (can be very dangerous to boaters) ⇒
  - Constructive Interference
  - Destructive Interference



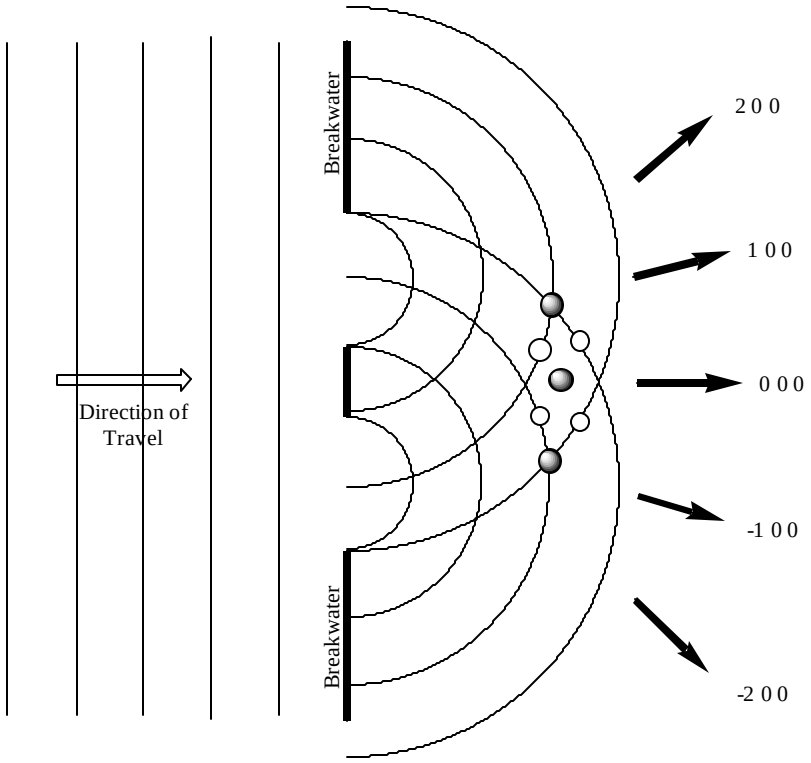
Part ii: Parallel waves passing through a hole in a breakwater

- Areas of unexpectedly high and low amplitudes (can be very dangerous to boats at dock) ⇒
  - Constructive Interference
  - Destructive Interference
  - Graphics from Text: Figure 3.2a, page 76; Spreading of Plane Waves passing through a slit



Part iii: Parallel waves passing through two holes in a breakwater

- Areas of unexpectedly high and low amplitudes ⇒
  - Constructive Interference
  - Destructive Interference
  - Graphics from Text: Figure 3.2b, page 76; Spreading of Plane Waves passing through two slits



Part iv: Parallel waves passing through two holes of varying spacings

- The further apart the slits are the closer together will be the sites of constructive and destructive interference
  - Graphics from Text: Figure 3.2b and c, page 76; Effects of slit spacing on interference pattern

Part c: Light Waves

- Graphics from Text: Figure 1.4, page 9; Diffraction of light through a fine metal mesh sieve

- Note the wavelength does not change

- Constructive Interference and Destructive Interference

- Graphics from Text: Figures 1.1 and 3.3, pages 3 and 77; Constructive and Destructive Superposition of Waves

Section 02: Diffraction in Two Dimensions

Part a: Diffraction Pattern from a Single Slit

Part i: Influence of Slit Width on Diffraction Pattern

- Narrow Slits ⇒ Wide patterns
- Wide Slits ⇒ Narrow patterns
- Note: the inverse relationship characteristic of diffraction

Graphics from Text: Figure 3.5, page 79; Diffraction Patterns of a Single Slit

Part ii: Reason for the Observed Diffraction Pattern Shapes

- Constructive and Destructive Interference from light coming through different parts of the slit

Graphics from Text: Figure 3.6, page 80; Reason for the Diffraction Patterns of a Single Slit

Part b: Diffraction Patterns from Two or More Slits

- Much like with water waves, pairs of slits give rise to interference patterns.

Part i: Influence of Slit Spacing

- Wide spacing of slits leads to closely spaced maxima
- Close spacing of slits leads to widely space maxima

Graphics from Text: Figure 3.6, page 80; Diffraction Pattern Spacing from Larger and Smaller Spacings of Slits

Part c: Diffraction Patterns from Arrays of Slits

- The overall influences of slit width and pattern are a convolution of the influences of slit width and slit spacing
  - Slit Width ⇒ Overall Envelope of Diffraction Pattern
  - Slit Spacing ⇒ Spacing of Maxima within that Envelope

Graphics from Text: Figure 3.6, page 80; Diffraction Pattern Spacing from Arrays of Slits

Part d: Diffraction by Slits vs. Diffraction by Objects

- These discussions have focused on models of slits in walls

- They also work equally well with objects that cause the bending, for example:
  - A field of Telephone Poles planted in a lake for water waves
  - A pattern of glass or plastic rods for light waves

Section 03: Diffraction in Three Dimensions

Part a: Laser Light Show

- Diffraction patterns form by shining light through two dimensional patterns and projected onto a screen

Laser Light Show: Laser Pointer and ICE Slides

Graphics from Text: Figure 3.7, page 82; Diffraction Patterns from Arrays of Points on a Slide

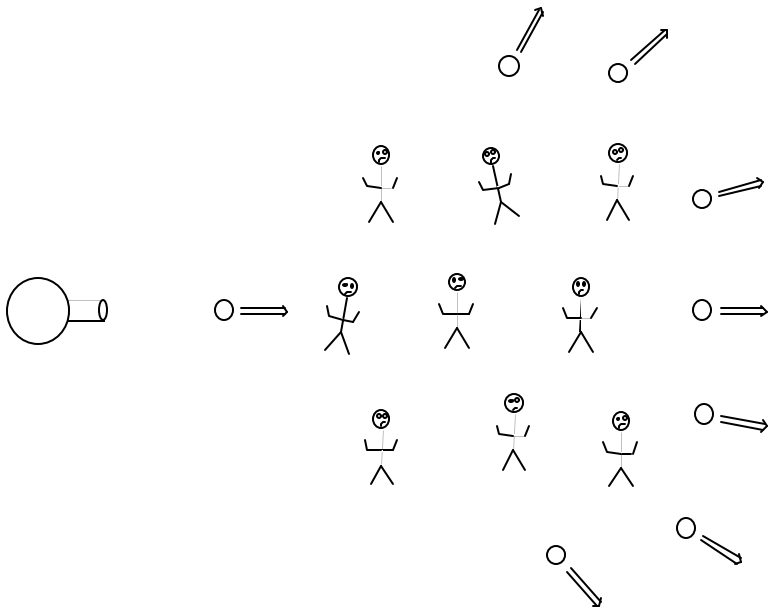
Part b: The Influences of Object Patterns

- It is most apparent that there is a reciprocal relationship between the diffracting array and the observed pattern
  - A square array ⇒ a square pattern
  - A rectangular array ⇒ a rectangular pattern rotated 90°
  - A hexagonal array ⇒ a hexagonal pattern
  - A closely spaced array ⇒ a widely spaced pattern
  - A widely spaced array ⇒ a closely spaced pattern

- Hence the origin of the term Reciprocal Space

Part c: Quantum Mechanical Basketball

- Influences of the patterns on the court on who in the stands will get hit
- Influences of the player orientation, size, and shape on who in the stands will be hit



Part d: The Influences of Objects, Periodicity, Array Size, and Disorder on Diffraction Patterns

Part i: Objects in the Array

- The size, shapes, and orientations or the objects in the array

  ⇒ a continuously varying intensity of diffracted light

  - This is like a topographic map

Part ii: Pattern of the Array

- The periodicity of the pattern determines the angles at which diffracted beams will be observable and hence set a mask over which the continuously varying intensity pattern can be sampled

  - This is like a piece of paper with holes punched out of it through which one looks at a topographic map

Part iii: Size of the Array

- The more objects in the array:
  - the narrower will be each beam of light
  - the stronger will be the total diffracted beam

Part iv: Disorder of the Array

- The more disordered (both dynamically and statically) the array the weaker will be the diffracted beams at higher diffraction angles

Section 04: X-Ray Diffraction

Part a: What Diffracts X-Rays?

- X-rays are diffracted by electrons not the nucleus so an X-ray structure solution tells you where the electrons are in the sample not where the centers of the atoms are

Part b: The 180° Phase Shift for X-Rays

- When a wave is reflected (e.g., a water wave off of a wall or a light wave off of a mirror) that wave gets a 180° phase shift relative to the incoming wave
- The same 180° Phase Shift is typical for X-ray diffraction

Graphics from Text: Figure 3.8, page 84; the Phase Shift during X-Ray Scattering

Part c: Atomic Scattering Factors for X-Rays

- Since X-ray are diffracted by electrons, the size and shape of the electron cloud will influence the diffracted intensity

Graphics from Text: Figure 3.12, page 90; The relationship of Relative Object Size and Wavelength to High Angle Scattering of Waves

Graphics from Text: Figure 3.13a, page 91 and Table 3.2 page 92; Some Atomic Scattering Factors and Atomic Scattering Curves for X-Rays

Part i: Maximum Atomic Scattering Factor, ASF

- More total electrons corresponds to a stronger diffracting ability
  - Thus, the maximum Atomic Scattering Factor, ASF, will follow the order W > Mo > Cr, etc., O^{-2} >O^{-} > O
  - The maximum ASF value for an atom/ion is equal to the total number of electrons
  - Because ASF is determined by the electron cloud and not by the nuclear composition, it is largely independent of the isotope

Part ii: Shapes of the Atomic Scattering Factor Curves

- The size of the atom strongly influences the angular dependence of the diffracted intensity
  - As with slit width effects, this is due to destructive interference between X-rays scattered from different parts of the electron cloud
  - With the same total number of electrons, larger atoms drop off more quickly (i.e., due to Z_{eff})
  - The effects of different orbitals can be calculated to give calculated ASF curves
  - Because atoms are large with respect to the size of X-rays, X-Ray ASF curves drop off fairly rapidly and one tends not to see a lot of diffracted intensity at high angles
  - ASF curves are typically plotted as ASF vs. $\sin\theta/\lambda$ and are thus useful for all X-ray wavelengths

Section 05: Neutron Diffraction

Part a: What Diffracts Neutrons?

- Neutrons are diffracted by nuclei

Part b: Atomic Scattering Factors for Neutrons

- Neutrons used for diffraction have a wavelength of about 1 Å while nuclei have diameters of about 10^{-4} and therefore act a point diffraction objects
  - This means that their scattered intensity is largely independent of angle
  - Because it is nuclei that do the scattering, Neutron ASF values are different for different isotrope
  - However, they are independent of the charge on the atom/ion

Graphics from Text: Figure 3.13b, page 91 and Table 3.2, page 92; Atomic Scatting Factors for Neutrons

Section 06: Bragg's Law

Part a: The Experimental Truth

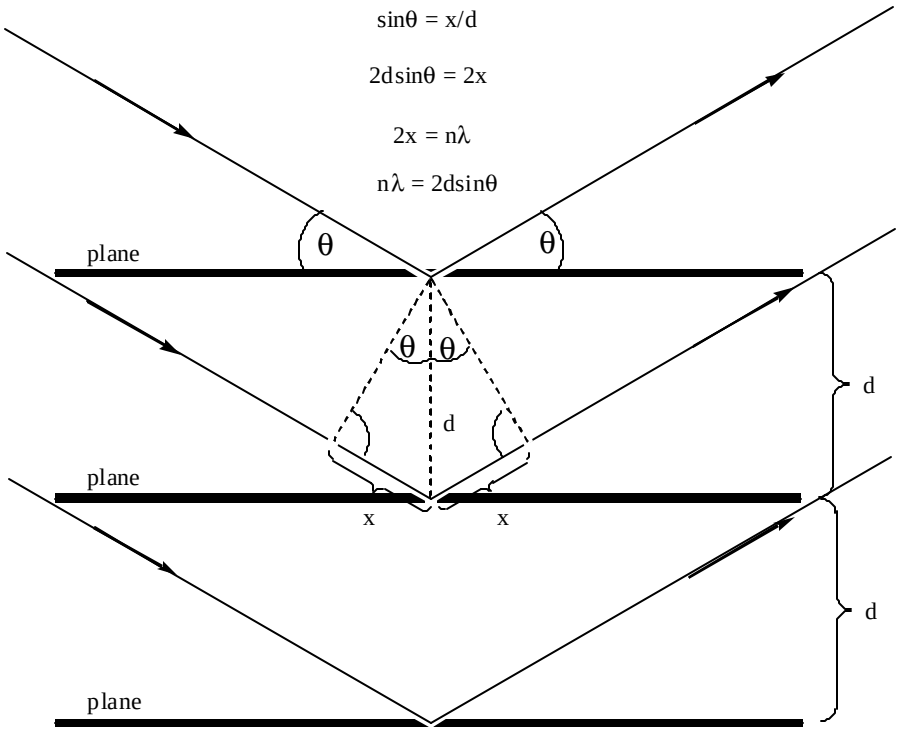
- Bragg's Law states for diffraction to occur it is observed experimentally that:

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

  - Where
    - $n \equiv$ Any integer, 0, 1, 2, 3, 4, etc.
    - $\lambda \equiv$ The Wavelength of Diffracted Light
    - $d \equiv$ The Interplanar Spacing
    - $\theta \equiv$ The Angle between the Incident Ray and the Planes

Part b: The Myth Taught in General Chemistry

- Diffraction Off of Planes gives Bragg's Law (may mention this is due to constructive and destructive interference)

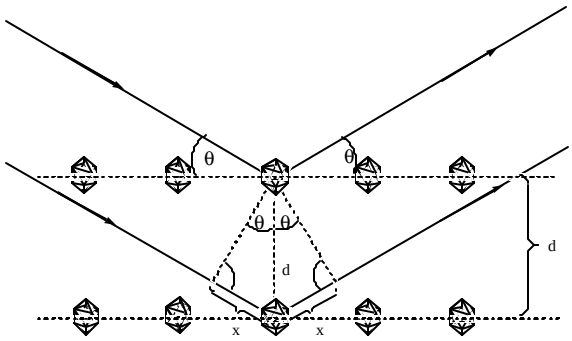


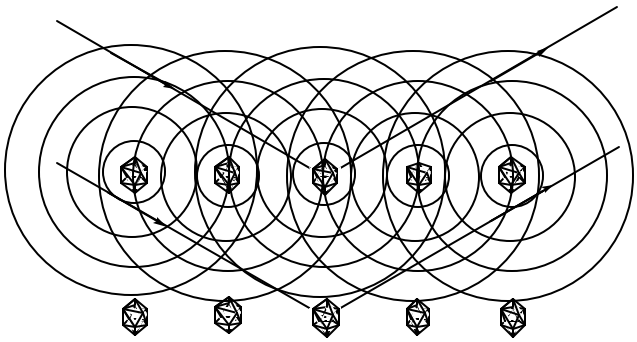
Graphics from Text: Figure 3.10b, page 87; Diffraction off of Planes

Part c: The Truth About Bragg's Law

Graphics from Text: Figure 3.9, page 85; Conditions for Diffraction so as to get Constructive Interference - Relating Diffraction Through Slits to Diffraction off of Planes

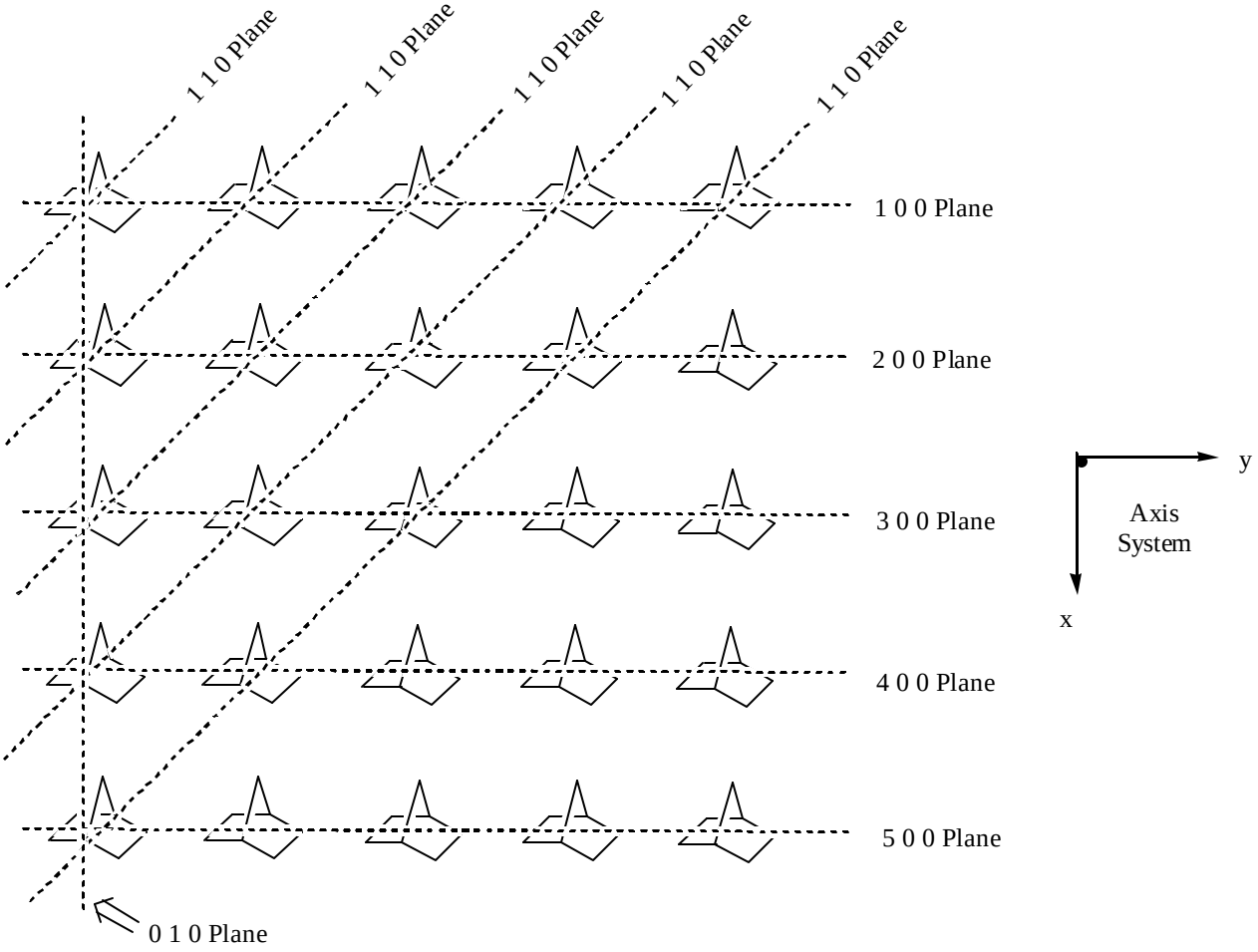
Graphics from Text: Figures 3.10a and b, pages 86 and 87; Interference and Bragg's Law





Part d: Which planes are we talking about?

- Diagram of planes from a section of crystal



- Graphics from Text: Figure 2.12, page 34; the Indexing of Crystal Faces

- The minimum incidence angle ⇒ reflections off of pairs of planes that are one layer apart and would be the 1 0 0 reflections

- The next angle ⇒ reflections off to pairs of planes two layers apart and would be reffered to as the 2 0 0 reflection

- The third smallest angle ⇒ reflections off to pairs of planes three layers apart and would be reffered to as the 3 0 0 reflection

- Thus the 1 0 0, the 2 0 0, the 3 0 0, etc., reflections all come off of a set of parrallel planes that intersect the x axis but not the y and z axes

Part e: Getting Unit Cell Parameters from Interplanar Spacings

- Once one measures the observed angles of a dozen or so reflections, it is an exercise in geometry to calculate the unit cell parameters
  - Obviously the more accurate the angles (and the larger the number) the more accurate will be the unit cell parameters

Graphics from Text: Table 3.1, page 88; Obtaining Unit Cell Dimensions from d_{hkl} Values

Section 07: Anomalous Scattering

Part a: The Origins of Anomalous Scattering

- Upon diffraction from an array of atoms, most of the time the phase shift is approximately 180°

- In the ideal case, the absorption of radiation by an element increases smoothly with increasing wavelength
  - Occasionally, when the incident radiation is similar in energy to the energy required to excite or ionize a bound electron, there will be a spike in the absorption curve called an Absorption Edge
  - Graphics from Text: Figure 6.23, page 219; Absorption Curves for some representative atoms

- If the wavelength of the incident radiation is near the absorption edge of an element then the phase shift is likely to be significantly different than 180°, more later

Part b: Anomalous Scattering and Neutrons

- For neutrons, anomolous scattering is dependent on the isotope one uses and can be used to readily distinguish isotopes in different positions
  - Graphics from Text: Table 3.2, page 92; Atomic Scattering Factor Table including an example of Anomalous Scattering for ^{6}Li

Part c: Anomalous Scattering and X-Rays

- As we will see later, this is very important for X-rays both in helping to estimate phases of complex molecules such as proteins and in absolute structure determinations where anomalous scattering makes reflection h k l ≠ -h -k -l

Section 08: The Ewald Sphere

- The Ewald Sphere is a way of thinking about when a crystal will be at the right orientation for a reflection to occur

Graphics from Text: Figure 3.17, pages 98 and 99, The Origin of the Ewald Sphere

Topic V: Symmetry

- Based primarily on Chapter 4 (G, L, & R, pages 105-141) and on the Software Package: Crystallographic CourseWare (M. Kastner, Bucknell University)

Ask Students: What do you know about Symmetry?

Section 01: Introduction to Symmetry

Part a: Origin of the Unit Cell

Part b: Symmetry Operations

Part c: Point Groups

Part d: Space Groups

Section 02: Point Symmetry Operations

Part a: Rotation Axes

Part b: Mirror Planes

Part c: Inversion Centers

Part d: Rotary Inversion Axes

Section 03: Hermann-Mauguin vs. Schoenflies Symbols

Part a: Rotation Axes

Part b: Rotation + Perpendicular Reflections

Part c: Rotation + Plane(s) Through the Axis

Part d: Rotary Inversion

Part e: Rotation (n) + n Perpendicular 2 Fold Axes

Part f: Rotation (n) + n Perpendicular 2 Fold Axes + Perpendicular Reflections

Part g: Rotation (n) + n Perpendicular 2 Fold Axes + Perpendicular Reflections + Diagonal

Part h: Cubic Space Groups

Section 04: Symmetries of Regularly Repeating Objects

Section 05: Crystal Systems Þ Space Groups

Part a: The 7 Crystal Systems

Part b: The 14 Bravais Lattices

Part c: The 230 Space Groups

Section 06: Three Dimensional Symmetry Operations

Part a: Translations

Part b: Screw Axes

Part c: Glide Planes

Part d: Review of Crystal Systems Þ Space Groups

Section 07: Symmetry in the Diffraction Pattern

Part a: Friedel's Law

Part b: Symmetry of Packing Þ Symmetry of Diffraction Pattern

Part c: Laue Symmetry

Section 08: Space Group Determination from Diffraction Data

Part a: Systematic Absences Þ Centering

Part b: Systematic Absences Þ Translational Symmetry

Part c: Cell Parameters and Crystal Systems

Part d: Laue Determination

Part e: Bravais Determination

Part f: Space Group Determination

Topic VI: Physical Properties of Crystals

- Based primarily on Chapter 5 (G, L, & R, pages 143-183).

Ask Students: What do you know about the Physical Properties of Crystals?

Section 01: Mechanical Properties of Crystals

Part a: Hardness of Crystals

Part b: Cleavage of Crystals

Section 02: Optical Properties of Crystals

Section 03: Electrical Effects of Crystals

Part a: Piezoelectric Effects

Part b: Pyroelectric Effects

Part c: Non-Linear Optical Phenomenon

Section 04: Chemical Effects of Crystal Form

Part a: Crystal Forms and Chemical Reactivity

Part b: Different Faces Different Reactions

Part c: Crystal Forms and Explosive Power

Topic VII: Image Generation from Diffracted Waves

- Based primarily on Chapter 6 (G, L, & R, pages 185-223).

Ask Students: What do you know about How an Optical Microscope Works?

Ask Students: What do you know about How X-Ray Diffraction Data is Transformed into Structural Information?

Graphics from Text: Figure 1.2, page 4; Imaging object using microscopes and diffraction methods

Section 01: Waves

Part a: Amplitudes of Waves

Part b: Lengths of Waves

Part c: Phase Angles of Waves

Part d: Summing Waves

Graphics from Text: Figure 1.1, page 3; Effect of relative phases when summing waves

Section 02: Fourier Series

Part a: Periodic Electron Density in Crystals

Part b: Baron Fourier's Theorem

Part c: Fourier Analysis

Part d: Fourier Synthesis

Section 03: Electron Density Calculations

Part a: Electron Density is Periodic

Part b: Equation for Electron Density as a Function of Structure Factors

Part c: hkl values and Crystal Planes

Section 04: Fourier Transforms

Part a: Equation for Structure Factors as a Function of Electron Density

Part b: Relationship Between Real and Reciprocal Space

Part c: Summary of the Diffraction Structure Process

Section 05: X-Ray Scattering Factors of Electrons in Orbitals

Part a: Electron Distribution Curves for Orbitals

Part b: Electron Scattering Curves for Orbitals

Section 06: Neutron Scattering Factors of Nuclei

Section 07: Kinematic and Dynamic Diffraction

Part a: Mosaic Blocks

Part b: Kinematic Diffraction

Part c: Dynamic Diffraction

Section 08: Extinction

Part a: Primary Extinction

Part b: Secondary Extinction

Part c: Renninger Effect and Double Reflections

Section 09: Structure Factors

Part a: Structure Factor Amplitudes

Section 10: Displacement Parameters

Part a: Vibration of Atoms in a Lattice

Part b: Disorder of Atoms and Molecules in a Lattice

Part c: Isotropic Displacement Parameters

Part d: Simple Anisotropic Displacement Parameters

Part e: Quadrupole Displacement Parameters and Evaluations of the Shapes of Electron Clouds

Section 11: Anomalous Scattering

Part a: Absorption Coefficients as a Function of Wavelength

Part b: MAD Phasing of Protein Data

Part c: Anomalous Scattering

Topic VIII: Amplitudes of Diffracted Waves

- Based primarily on Chapter 7 (G, L, & R, pages 225-279).

Ask Students: What do you know about How the Amplitudes of Diffracted Waves are Related to Crystal Structures and Molecular Structures?

Section 01: Intensities of Diffracted Beams

Part a: Equation for Intensities of Diffracted Beams

Part b: Lorenz Factor

Part c: Polarization Factor

Part d: Absorption Factor

Part e: Effects of Wavelength of Measured Intensities

Section 02: X-Ray Sources

Part a: X-Ray Spectrum of an X-Ray Tube

Part b: Monochromatic X-Rays

Part c: X-Ray Sources

Section 03: X-Ray Detectors

Part a: Scintillation Counters

Part b: Beam Stop

Part c: Area Detectors

Section 04: Automated Diffractometers

Section 05: Effects of Temperatures on Collected Diffraction Data

Section 06: Peak Profiles

Section 07: Data Reduction

Topic IX: Phases of Diffracted Waves

- Based primarily on Chapter 8 (G, L, & R, pages 281-343).

Ask Students: What do you know about How the Phases of Diffracted Waves are Related to Crystal Structures and Molecular Structures?

Section 01: Electron Density Distributions vs. Structure Factors and Phases

Part a: Flow Diagram

Part b: With Known Structures

Part c: Non-Centrosymmetric Space Groups

Part d: Centrosymmetric Space Groups

Section 02: Common Methods for Estimating Phase Angles

Part a: The Role of Advances in Computers, Theory, and Software

Part b: Direct Methods

Part c: Patterson Methods

Part d: Isostructural Crystals

Part e: Multiple Bragg Diffraction

Part f: Shake and Bake

Section 03: Direct Methods

Part a: Statistical Tools

Part b: Mathematics of Phase Relationships

Part c: Inequalities

Part d: Where Works Best

Section 04: Patterson Methods

Part a: The Patterson Function

Part b: Patterson Maps

Part c: Where Works Best

Part d: Heavy Atom Methods

Section 05: Isomorphous Replacement

Part a: Proteins: The Problem Structures

Part b: Metal Salts

Part c: Unnatural Amino Acids

Part d: Related Protein Structures

Section 06: MAD Phasing of Proteins

Section 07: Shake and Bake

Topic X: Electron Density Maps

- Based primarily on Chapter 9 (G, L, & R, pages 345-387).

Ask Students: What do you know about the Relationship of Electron Density Maps to Molecular Structures?

Section 01: Electron Density Function

Section 02: Electron Density Maps

Part a: General Features of Maps

Part b: P(obs) Map

Part c: F(calc) Map

Part d: Difference Electron Density Maps

Part e: Deformation Density Maps

Section 03: Resolution

Part a: Conventional Definition

Part b: Effects of Wavelength on Resolution and Intensities

Part c: Mo Resolution

Part d: Cu Resolution

Part e: Ag and Synchrotron Data

Part f: Effects of Resolution on the Structure

Section 04: Angles of Data Collection and Series Termination Errors

Topic XI: Least Squares Refinement

- Based primarily on Chapter 10 (G, L, & R, pages 389-411).

Ask Students: What do you know about How Least Squares Refinement Works?

Section 01: What is Least Squares Refinement?

Part a: The Mathematics of Least Squares Refinement

Part b: Qualitative Picture of Least Squares Refinement

Section 02: Precision vs. Accuracy

Part a: Precision

Part b: Accuracy

Part c: Random vs. Systematic Errors

Part d: Gaussian Distribution Function

Part e: Estimated Standard Deviations

Section 03: Constraints

Section 04: Restraints

Section 05: Global vs. Local Minima in Solution

Topic XII: Crystal and Diffraction Data

- Based primarily on Literature References

Ask Students: What do you know about How to Interpret Tables of Crystal and Diffraction Data?

Section 01: The Standard Table

Topic XIII: Atomic Coordinates and Molecular Structures

- Based primarily on Chapters 11 to 13 (G, L, & R, pages 413-571).

Ask Students: What do you know about How one Interprets Raw Crystallographic Data to Get Molecular Structure Information?

Section 01: Molecular Geometries

Part a: From xyz Coordinates to Bond Lengths, Bond Angles, etc.

Part b: Vibrational Motion

Part c: Fractional Coordinates

Part d: Orthogonal Coordinates

Part e: Complete Molecules?

Section 02: Atomic Connectivities

Part a: Derivation of Atomic Connectivity Tables

Part b: International Tables for Typical Bond Distances

Part c: Bond Lengths

Section 03: Molecules in the Unit Cell and Z

Section 04: Estimated Standard Deviations

Part a: ESD Formula

Part b: When are two values different?

Part c: ESDs and Reliability of Data

Section 05: Torsion Angles

Section 06: Molecular and Macromolecular Conformations

Section 07: Atomic and Molecular Displacements

Part a: Vibration Effects in Crystals

Part b: Representations of Displacement Parameters

Part c: Effects of Displacements on Molecular Geometries

Part d: Uses of Anisotropic Displacement Parameters

Topic XIV: Absolute Structures

- Based primarily on Chapter 14 (G, L, & R, pages 573-625).

Ask Students: What do you know about How the Absolute Structures of Molecules are Determined?

Section 01: Chirality of Molecules

Section 02: Optical Activity and Chiral Molecules

Section 03: Anomalous Dispersion Measurements

Section 04: Uses of Anomalous Dispersion

Topic XV: Crystallographic Publications: Preparation and Analysis

- Based primarily on Chapter 16 (G, L, & R, pages 689-729).

Ask Students: What do you know about Using the Crystallographic Literature?

Section 01: Crystallographic Data Bases

Section 02: Crystallographic Papers

Section 03: Comparing Structures

Topic XVI: Special Topics

Index of Topics and Vocabulary

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