

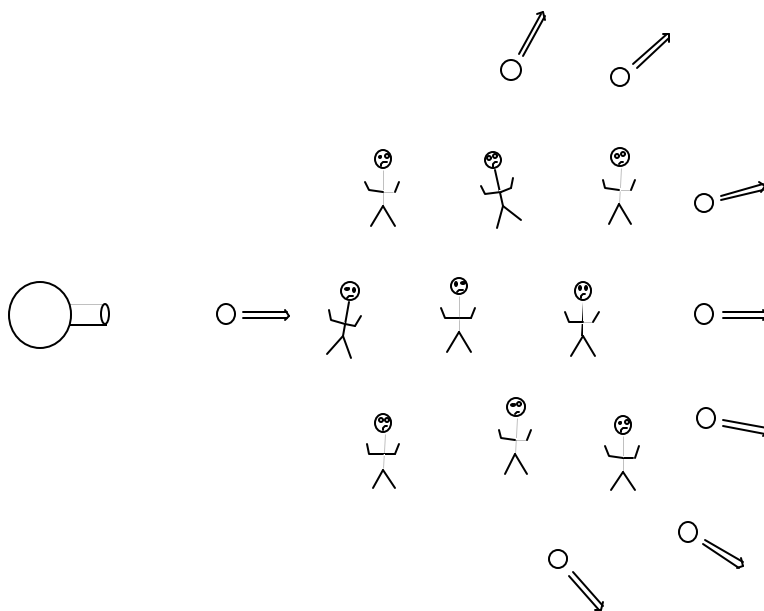
Chemistry 832: Solid State Structural Methods

Outline Notes¹ for the Spring 2000 Class

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March 14th, 2000 Edition of Notes



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

<u>Chemistry 832: Solid State Structural Methods</u>	<u>1</u>
<u>Table of Contents</u>	<u>2</u>
<u>Topic I: Introduction to Chemistry 832</u>	<u>13</u>
<u>Topic II: X-Ray Diffractometers</u>	<u>30</u>
<u>Topic III: Single Crystals</u>	<u>45</u>
<u>Topic IV: Diffraction by Crystals</u>	<u>76</u>
<u>Topic V: Symmetry</u>	<u>107</u>
<u>Topic VI: Physical Properties of Crystals</u>	<u>117</u>
<u>Topic VII: Image Generation from Diffracted Waves</u>	<u>122</u>
<u>Topic VIII: Amplitudes of Diffracted Waves</u>	<u>133</u>
<u>Topic IX: Phases of Diffracted Waves</u>	<u>141</u>
<u>Topic X: Electron Density Maps</u>	<u>150</u>
<u>Topic XI: Least Squares Refinement</u>	<u>155</u>
<u>Topic XII: Crystal and Diffraction Data</u>	<u>161</u>
<u>Topic XIII: Atomic Coordinates and Molecular Structures</u>	<u>163</u>
<u>Topic XIV: Absolute Structures</u>	<u>171</u>
<u>Topic XV: Crystallographic Publications: Preparation and Analysis</u>	<u>176</u>
<u>Topic XVI: Special Topics</u>	<u>180</u>
<u>Index of Topics and Vocabulary</u>	<u>181</u>

Section 02: Complete Table of Contents

<u>Chemistry 832: Solid State Structural Methods</u>	<u>1</u>
<u>Table of Contents</u>	<u>2</u>
Section 01: Table of Major Topics	2
Section 02: Complete Table of Contents	3
<u>Topic I: Introduction to Chemistry 832</u>	<u>13</u>
Section 01: What is Chemistry 832?	14
<u>Part a: Chemistry 832 Goals and Objectives</u>	<u>14</u>
<u>Part b: Chemistry 832 Syllabus</u>	<u>14</u>
<u>Part c: Chemistry 832 Resources</u>	<u>14</u>
Section 02: What Can Diffraction Methods Tell Us	17
Section 03: Speed and Cost	18
Section 04: What is a Single Crystal and Why is it Important?	19
<u>Part a: Single Crystal</u>	<u>19</u>
<u>Part b: Unit Cell</u>	<u>20</u>
<u>Part c: Unit cells and diffraction data</u>	<u>21</u>
Section 05: Block Diagram of an X-Ray Diffractometer	22
Section 06: X-Ray Generator	23
<u>Part a: Goniometer</u>	<u>24</u>
<u>Part b: Detector</u>	<u>24</u>
Section 07: Basic Steps in X-Ray Diffraction Data Collection	25
Section 08: Basic Steps in X-Ray Diffraction Data Analysis	27
<u>Part a: Data Analysis can be quite routine through impossibly difficult</u>	<u>27</u>
<u>Part b: The Phase Problem</u>	<u>27</u>
Section 09: Main Steps in Data Analysis	28
<u>Part a: Procedural Steps</u>	<u>28</u>
<u>Part b: Flow Chart for a Typical Structure Solution</u>	<u>29</u>
<u>Topic II: X-Ray Diffractometers</u>	<u>30</u>
Section 01: What are X-Rays?	31
<u>Part a: Wavelengths of X-Rays</u>	<u>31</u>
<u>Part b: Why are these Wavelengths chosen?</u>	<u>31</u>
Section 02: X-Ray Generators	32

Part a: X-Ray Lasers	32
Part b: Conventional X-Ray Tubes	32
Part c: Rotating Anode Generators	33
Part d: Synchrotron Sources	34
Section 03: X-Ray Monochromators	35
Part a: Foil Filters (Ni foil)	35
Part b: Crystal (Graphite) Monochromators	35
Part c: Focusing Mirrors	35
Section 04: X-Ray Collimators	36
Part a: Graphite Crystal Monochromators and Pin Holes in Tubes	36
Part b: Focusing Mirrors	36
Section 05: Goniometers	37
Section 06: Low Temperature System	38
Section 07: X-Ray Detectors	39
Part a: Serial Detectors	39
Part b: Film Based Area Detectors	40
Part c: Multi-Wire Area Detectors	41
Part d: CCD Detectors	42
Part e: Imaging Plate Detectors	43
Section 08: X-Ray Absorption in the Diffractometer	44
Part a: Air	44
Part b: Windows	44
Part c: Sample, Glue, Fiber & Capillary	44
Topic III: Single Crystals	45
Section 01: Perfect Crystals?	46
Section 02: Growing Single Crystals	47
Part a: General principles of growing single crystals	49
Part b: Proven Methods for growing crystals	52
Part c: What to do when proven methods fail	64
Section 03: The Unit Cell	69
Section 04: Crystal Shapes	70
Part a: Crystal Growth and Shapes	70
Part b: Indexing Crystal Faces	74

Part c: The Crystal Lattice	75
Topic IV: Diffraction by Crystals	76
Section 01: Waves	77
Part a: Generic Waves	77
Part b: Water Waves	78
Part c: Light Waves	83
Section 02: Diffraction in Two Dimensions	84
Part a: Diffraction Pattern from a Single Slit	84
Part b: Diffraction Patterns from Two or More Slits	85
Part c: Diffraction Patterns from Arrays of Slits	86
Part d: Diffraction by Slits vs. Diffraction by Objects	87
Section 03: Diffraction in Three Dimensions	88
Part a: Laser Light Show	88
Part b: The Influences of Object Patterns	89
Part c: Quantum Mechanical Basketball	90
Part d: The Influences of Objects, Periodicity, Array Size, and Disorder on Diffraction Patterns	91
Section 04: X-Ray Diffraction	93
Part a: What Diffracts X-Rays?	93
Part b: The 180° Phase Shift for X-Rays	93
Part c: Atomic Scattering Factors for X-Rays	94
Section 05: Neutron Diffraction	97
Part a: What Diffracts Neutrons?	97
Part b: Atomic Scattering Factors for Neutrons	97
Section 06: Bragg's Law	98
Part a: The Experimental Truth	98
Part b: The Myth Taught in General Chemistry	99
Part c: The Truth About Bragg's Law	100
Part d: Which planes are we talking about?	101
Part e: Getting Unit Cell Parameters from Interplanar Spacings	103
Section 07: Anomalous Scattering	104
Part a: The Origins of Anomalous Scattering	104
Part b: Anomalous Scattering and Neutrons	105

Part c: Anomalous Scattering and X-Rays	105
Section 02: The Ewald Sphere	106
Topic II: Symmetry	107
Section 01: Introduction to Symmetry	108
Part a: Origin of the Unit Cell	108
Part b: Symmetry Operations	108
Part c: Point Groups	108
Part d: Space Groups	108
Section 02: Point Symmetry Operations	109
Part a: Rotation Axes	109
Part b: Mirror Planes	109
Part c: Inversion Centers	109
Part d: Rotary Inversion Axes	109
Section 03: Hermann-Mauguin vs. Schoenflies Symbols	110
Part a: Rotation Axes	110
Part b: Rotation + Perpendicular Reflections	110
Part c: Rotation + Plane(s) Through the Axis	110
Part d: Rotary Inversion	110
Part e: Rotation (n) + n Perpendicular 2 Fold Axes	110
Part f: Rotation (n) + n Perpendicular 2 Fold Axes + Perpendicular Reflections	110
Part g: Rotation (n) + n Perpendicular 2 Fold Axes + Perpendicular Reflections + Diagonal	110
Part h: Cubic Space Groups	111
Section 04: Symmetries of Regularly Repeating Objects	112
Section 05: Crystal Systems \Rightarrow Space Groups	113
Part a: The 7 Crystal Systems	113
Part b: The 14 Bravais Lattices	113
Part c: The 230 Space Groups	113
Section 06: Three Dimensional Symmetry Operations	114
Part a: Translations	114
Part b: Screw Axes	114
Part c: Glide Planes	114
Part d: Review of Crystal Systems & Space Groups	114

<u>Section 07: Symmetry in the Diffraction Pattern</u>	<u>115</u>
<u>Part a: Friedel's Law</u>	<u>115</u>
<u>Part b: Symmetry of Packing \mathcal{P} Symmetry of Diffraction Pattern</u>	<u>115</u>
<u>Part c: Laue Symmetry</u>	<u>115</u>
<u>Section 08: Space Group Determination from Diffraction Data</u>	<u>116</u>
<u>Part a: Systematic Absences \mathcal{P} Centering</u>	<u>116</u>
<u>Part b: Systematic Absences \mathcal{P} Translational Symmetry</u>	<u>116</u>
<u>Part c: Cell Parameters and Crystal Systems</u>	<u>116</u>
<u>Part d: Laue Determination</u>	<u>116</u>
<u>Part e: Bravais Determination</u>	<u>116</u>
<u>Part f: Space Group Determination</u>	<u>116</u>
<u>Topic III: Physical Properties of Crystals</u>	<u>117</u>
<u>Section 01: Mechanical Properties of Crystals</u>	<u>118</u>
<u>Part a: Hardness of Crystals</u>	<u>118</u>
<u>Part b: Cleavage of Crystals</u>	<u>118</u>
<u>Section 02: Optical Properties of Crystals</u>	<u>119</u>
<u>Part a: The Nature of Light</u>	<u>119</u>
<u>Part b: Isotropic and Anisotropic Crystals</u>	<u>119</u>
<u>Part c: Pleochromism</u>	<u>119</u>
<u>Part d: Refraction of Light</u>	<u>119</u>
<u>Part e: Birefringence of Light</u>	<u>119</u>
<u>Part f: Polarization of Light</u>	<u>119</u>
<u>Part g: Optical Activity and Crystals</u>	<u>119</u>
<u>Section 03: Electrical Effects of Crystals</u>	<u>120</u>
<u>Part a: Piezoelectric Effects</u>	<u>120</u>
<u>Part b: Pyroelectric Effects</u>	<u>120</u>
<u>Part c: Non-Linear Optical Phenomemom</u>	<u>120</u>
<u>Section 04: Chemical Effects of Crystal Form</u>	<u>121</u>
<u>Part a: Crystal Forms and Chemical Reactivity</u>	<u>121</u>
<u>Part b: Different Faces Different Reactions</u>	<u>121</u>
<u>Part c: Crystal Forms and Explosive Power</u>	<u>121</u>
<u>Topic IV: Image Generation from Diffracted Waves</u>	<u>122</u>

<u>Section 01: Waves</u>	<u>123</u>
<u>Part a: Amplitudes of Waves</u>	<u>123</u>
<u>Part b: Lengths of Waves</u>	<u>123</u>
<u>Part c: Phase Angles of Waves</u>	<u>123</u>
<u>Part d: Summing Waves</u>	<u>123</u>
<u>Section 02: Fourier Series</u>	<u>124</u>
<u>Part a: Periodic Electron Density in Crystals</u>	<u>124</u>
<u>Part b: Baron Fourier's Theorem</u>	<u>124</u>
<u>Part c: Fourier Analysis</u>	<u>124</u>
<u>Part d: Fourier Synthesis</u>	<u>124</u>
<u>Section 03: Electron Density Calculations</u>	<u>125</u>
<u>Part a: Electron Density is Periodic</u>	<u>125</u>
<u>Part b: Equation for Electron Density as a Function of Structure Factors</u>	<u>125</u>
<u>Part c: hkl values and Crystal Planes</u>	<u>125</u>
<u>Section 04: Fourier Transforms</u>	<u>125</u>
<u>Part a: Equation for Structure Factors as a Function of Electron Density</u>	<u>125</u>
<u>Part b: Relationship Between Real and Reciprocal Space</u>	<u>125</u>
<u>Part c: Summary of the Diffraction Structure Process</u>	<u>125</u>
<u>Section 05: X-Ray Scattering Factors of Electrons in Orbitals</u>	<u>126</u>
<u>Part a: Electron Distribution Curves for Orbitals</u>	<u>126</u>
<u>Part b: Electron Scattering Curves for Orbitals</u>	<u>126</u>
<u>Section 06: Neutron Scattering Factors of Nuclei</u>	<u>127</u>
<u>Section 07: Kinematic and Dynamic Diffraction</u>	<u>128</u>
<u>Part a: Mosaic Blocks</u>	<u>128</u>
<u>Part b: Kinematic Diffraction</u>	<u>128</u>
<u>Part c: Dynamic Diffraction</u>	<u>128</u>
<u>Section 08: Extinction</u>	<u>129</u>
<u>Part a: Primary Extinction</u>	<u>129</u>
<u>Part b: Secondary Extinction</u>	<u>129</u>
<u>Part c: Renninger Effect and Double Reflections</u>	<u>129</u>
<u>Section 09: Structure Factors</u>	<u>130</u>
<u>Part a: Structure Factor Amplitudes</u>	<u>130</u>
<u>Section 10: Displacement Parameters</u>	<u>131</u>

Part a: Vibration of Atoms in a Lattice	131
Part b: Disorder of Atoms and Molecules in a Lattice	131
Part c: Isotropic Displacement Parameters	131
Part d: Simple Anisotropic Displacement Parameters	131
Part e: Quadrupole Displacement Parameters and Evaluations of the Shapes of Electron Clouds	131
Section 11: Anomalous Scattering	132
Part a: Absorption Coefficients as a Function of Wavelength	132
Part b: MAD Phasing of Protein Data	132
Part c: Anomalous Scattering	132
Topic V: Amplitudes of Diffracted Waves	133
Section 01: Intensities of Diffracted Beams	134
Part a: Equation for Intensities of Diffracted Beams	134
Part b: Lorenz Factor	134
Part c: Polarization Factor	134
Part d: Absorption Factor	134
Part e: Effects of Wavelength of Measured Intensities	134
Section 02: X-Ray Sources	135
Part a: X-Ray Spectrum of an X-Ray Tube	135
Part b: Monochromatic X-Rays	135
Part c: X-Ray Sources	135
Section 03: X-Ray Detectors	136
Part a: Scintillation Counters	136
Part b: Beam Stop	136
Part c: Area Detectors	136
Section 04: Automated Diffractometers	137
Section 05: Effects of Temperatures on Collected Diffraction Data	138
Section 06: Peak Profiles	139
Section 07: Data Reduction	140
Topic VI: Phases of Diffracted Waves	141
Section 01: Electron Density Distributions vs. Structure Factors and Phases	142
Part a: Flow Diagram	142
Part b: With Known Structures	142

Part c: Non-Centrosymmetric Space Groups	142
Part d: Centrosymmetric Space Groups	142
Section 02: Common Methods for Estimating Phase Angles	143
Part a: The Role of Advances in Computers, Theory, and Software	143
Part b: Direct Methods	143
Part c: Patterson Methods	143
Part d: Isostructural Crystals	143
Part e: Multiple Bragg Diffraction	143
Part f: Shake and Bake	143
Section 03: Direct Methods	144
Part a: Statistical Tools	144
Part b: Mathematics of Phase Relationships	144
Part c: Inequalities	144
Part d: Where Works Best	144
Section 04: Patterson Methods	145
Part a: The Patterson Function	145
Part b: Patterson Maps	145
Part c: Where Works Best	145
Part d: Heavy Atom Methods	145
Section 05: Isomorphous Replacement	146
Part a: Proteins: The Problem Structures	146
Part b: Metal Salts	146
Part c: Unnatural Amino Acids	146
Part d: Related Protein Structures	146
Section 06: MAD Phasing of Proteins	148
Section 07: Shake and Bake	149
Topic VII: Electron Density Maps	150
Section 01: Electron Density Function	151
Section 02: Electron Density Maps	152
Part a: General Features of Maps	152
Part b: P(obs) Map	152
Part c: F(calc) Map	152
Part d: Difference Electron Density Maps	152

Part e: Deformation Density Maps	152
Section 03: Resolution	153
Part a: Conventional Definition	153
Part b: Effects of Wavelength on Resolution and Intensities	153
Part c: Mo Resolution	153
Part d: Cu Resolution	153
Part e: Ag and Synchrotron Data	153
Part f: Effects of Resolution on the Structure	153
Section 04: Angles of Data Collection and Series Termination Errors	154
Topic VIII: Least Squares Refinement	155
Section 01: What is Least Squares Refinement?	156
Part a: The Mathematics of Least Squares Refinement	156
Part b: Qualitative Picture of Least Squares Refinement	156
Section 02: Precision vs. Accuracy	157
Part a: Precision	157
Part b: Accuracy	157
Part c: Random vs. Systematic Errors	157
Part d: Gaussian Distribution Function	157
Part e: Estimated Standard Deviations	157
Section 03: Constraints	158
Section 04: Restraints	159
Section 05: Global vs. Local Minima in Solution	160
Topic IX: Crystal and Diffraction Data	161
Section 01: The Standard Table	162
Topic X: Atomic Coordinates and Molecular Structures	163
Section 01: Molecular Geometries	164
Part a: From xyz Coordinates to Bond Lengths, Bond Angles, etc.	164
Part b: Vibrational Motion	164
Part c: Fractional Coordinates	164
Part d: Orthogonal Coordinates	164
Part e: Complete Molecules?	164
Section 02: Atomic Connectivities	165
Part a: Derivation of Atomic Connectivity Tables	165

Part b: International Tables for Typical Bond Distances	165
Part c: Bond Lengths	165
Section 03: Molecules in the Unit Cell and Z	166
Section 04: Estimated Standard Deviations	167
Part a: ESD Formula	167
Part b: When are two values different?	167
Part c: ESDs and Reliability of Data	167
Section 05: Torsion Angles	168
Section 06: Molecular and Macromolecular Conformations	169
Section 07: Atomic and Molecular Displacements	170
Part a: Vibration Effects in Crystals	170
Part b: Representations of Displacement Parameters	170
Part c: Effects of Displacements on Molecular Geometries	170
Part d: Uses of Anisotropic Displacement Parameters	170
Topic XI: Absolute Structures	171
Section 01: Chirality of Molecules	172
Section 02: Optical Activity and Chiral Molecules	173
Section 03: Anomalous Dispersion Measurements	174
Section 04: Uses of Anomalous Dispersion	175
Topic XII: Crystallographic Publications: Preparation and Analysis	176
Section 01: Crystallographic Data Bases	177
Section 02: Crystallographic Papers	178
Section 03: Comparing Structures	179
Topic XIII: Special Topics	180
Index of Topics and Vocabulary	181

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 the crystal affect 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

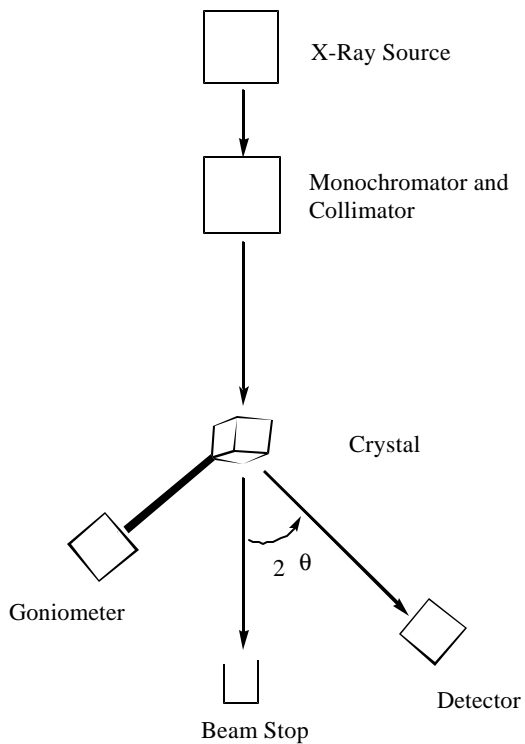
- The less **disorder** the better the data quality

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

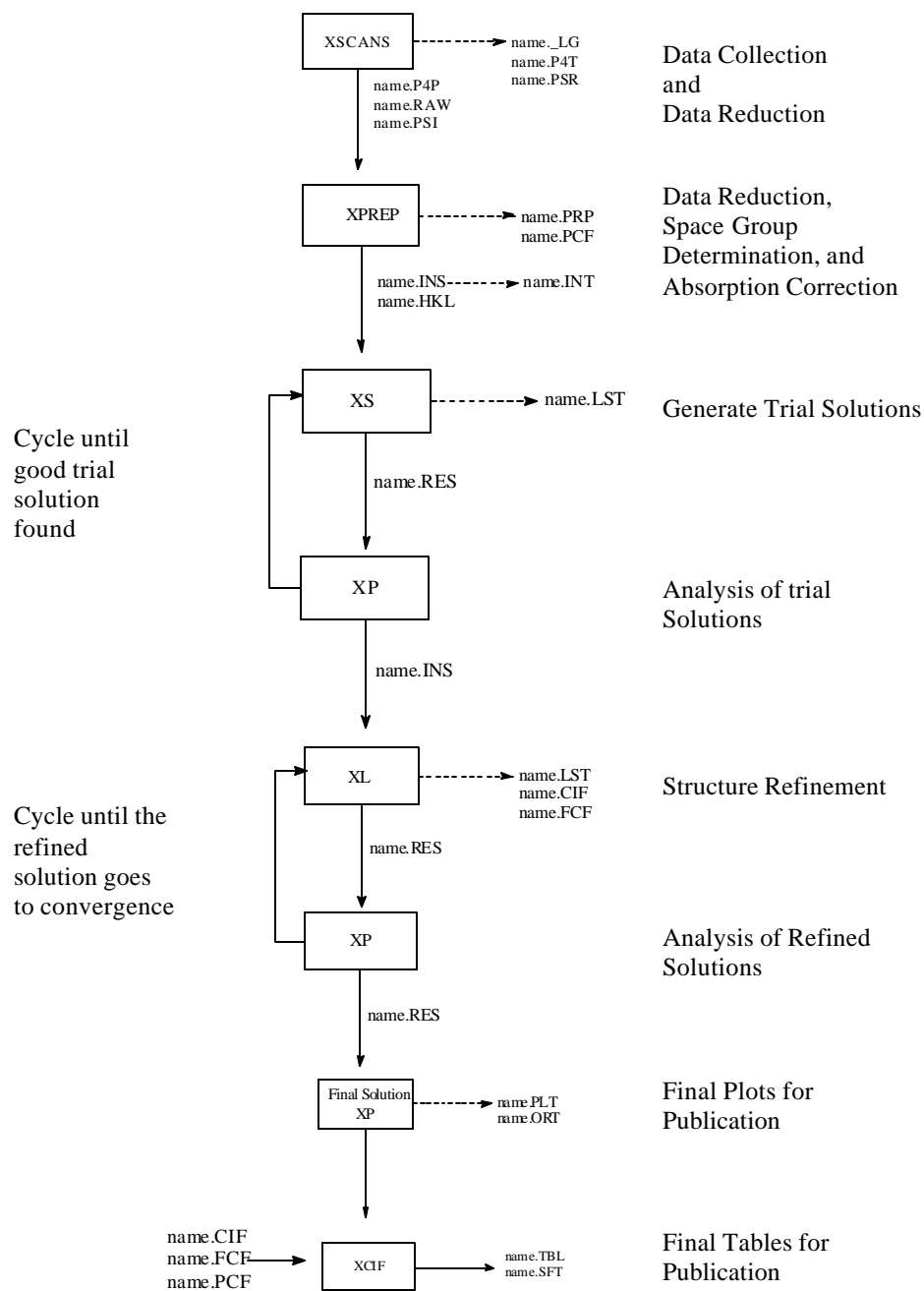
- Determine an Initial Starting Solution (XS)
 - Use one of the “tricks” to find at least one atom at near its actual position
 - This will give you the first phase information

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

- Evaluate the Final Answer

- Prepare the Data for Publication

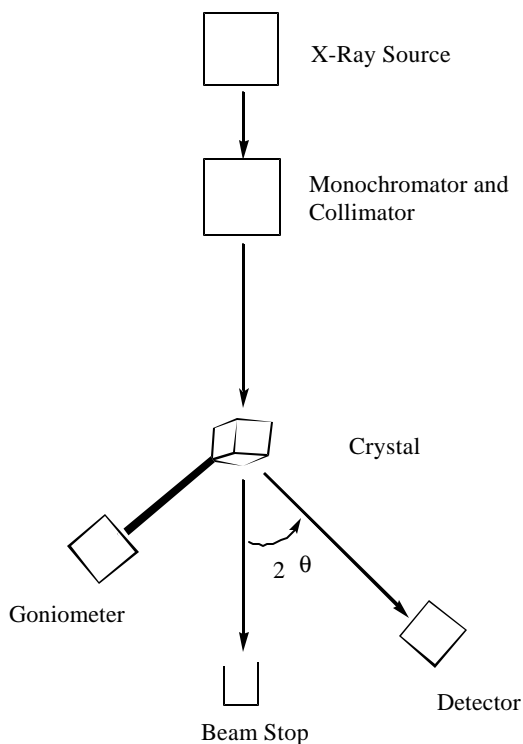
Part b: Flow Chart for a Typical Structure Solution



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 N₂ Systems to ≈ -150 °C
 - Liquid He Systems to $\approx 15 - 20$ 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 Densitometer
- 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:CCrystallization 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 two **immiscible 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 grown 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 convection
 - 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

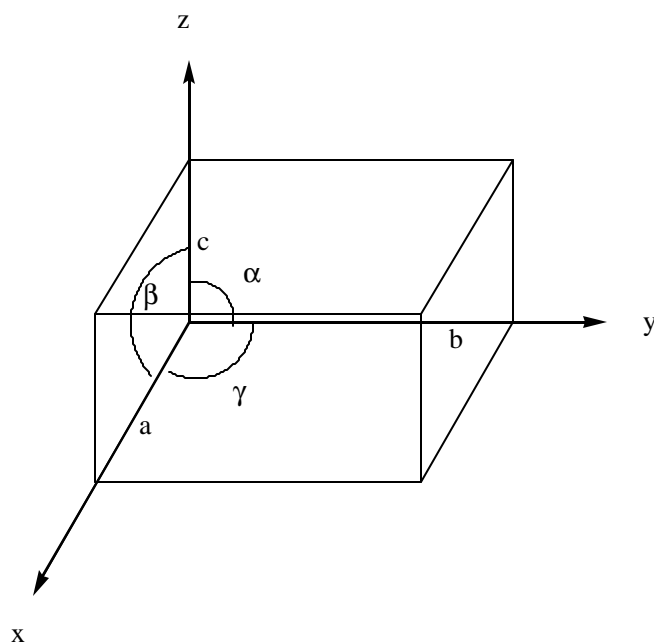
- Solvates and Crystallization Agents
 - Packing / Interacting solvents such as:
 - Water or Alcohols
 - Benzene
 - Chlorocarbons

- 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 known as **Polymorphs** and this behavior is known 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, $(M_1)_2(SO_4) \cdot (M_3)_2(SO_4)_3 \cdot 24H_2O$
 - $M_1 = K$ or NH_4
 - $M_3 = Al^{+3}$ or Cr^{+3}
 - Form large octahedral crystals by evaporating water solutions

- Potash Alum, $K_2(SO_4) \cdot Al_2(SO_4)_3 \cdot 24H_2O$
 - Colorless
 - Air Stable

- Chromium Alum, $K_2(SO_4) \cdot Cr_2(SO_4)_3 \cdot 24H_2O$
 - 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

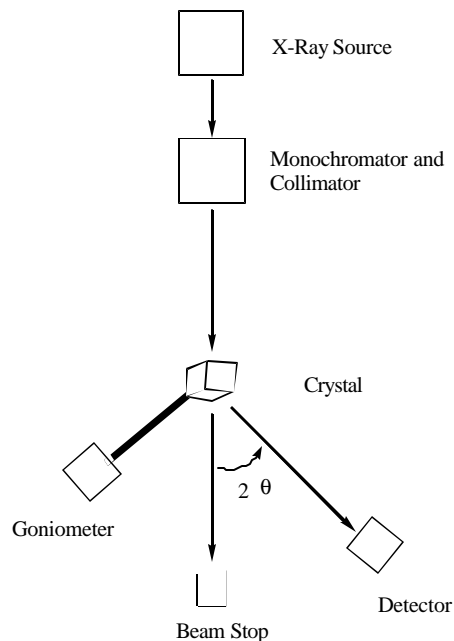
- The **Crystal Lattice** is an imaginary three dimensional array of points, **lattice points**, that repeats to give the three dimensional order of the crystal
- When **convoluted** with the unit cell contents, it build the full three dimensional structure of the crystal
- **Graphics from Text: Figures 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

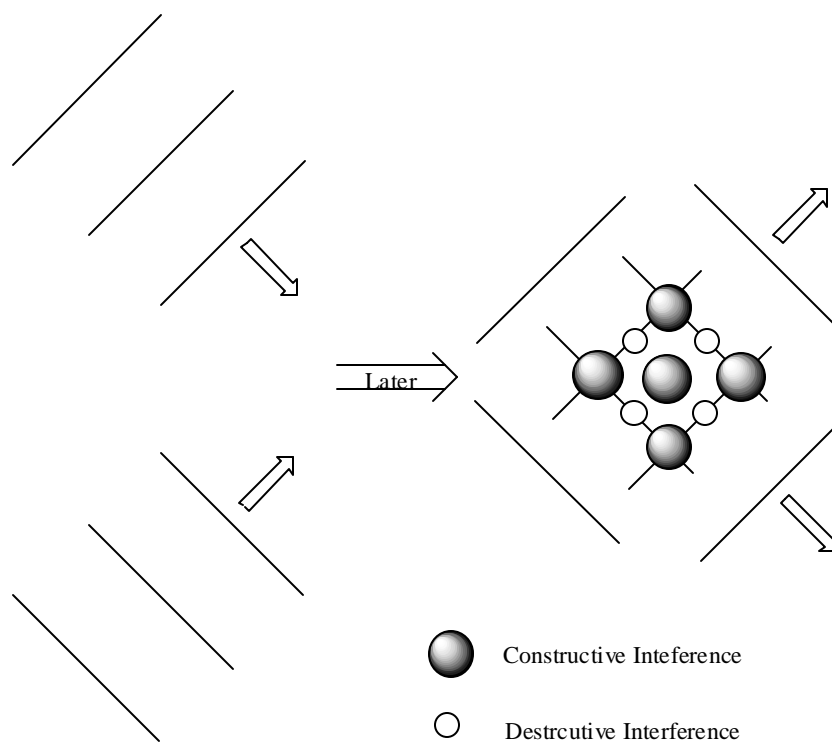
Graphics from Text: Figure 3.1, page 75; The Amplitude, A ,
Wavelength, λ , and Relative Phase, ϕ , of a Sinusoidal Wave

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

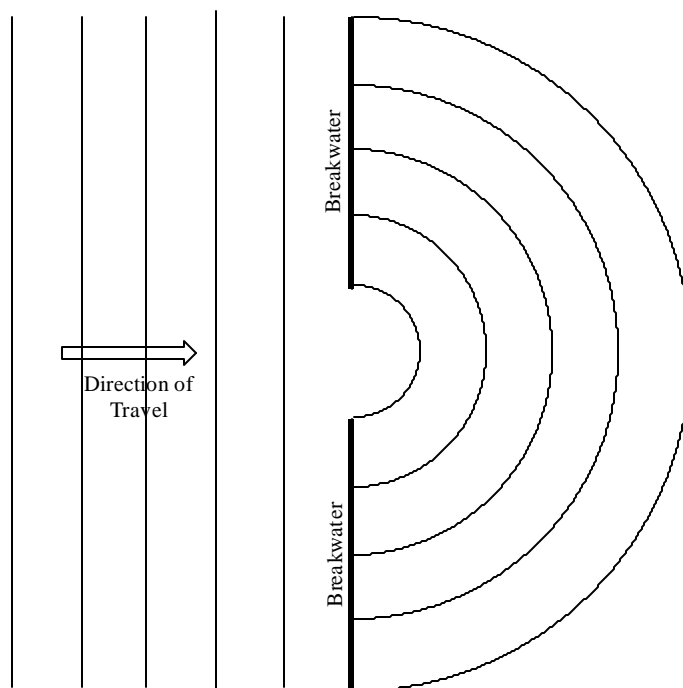
Part i: Non-parallel sets of waves on open water

- 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

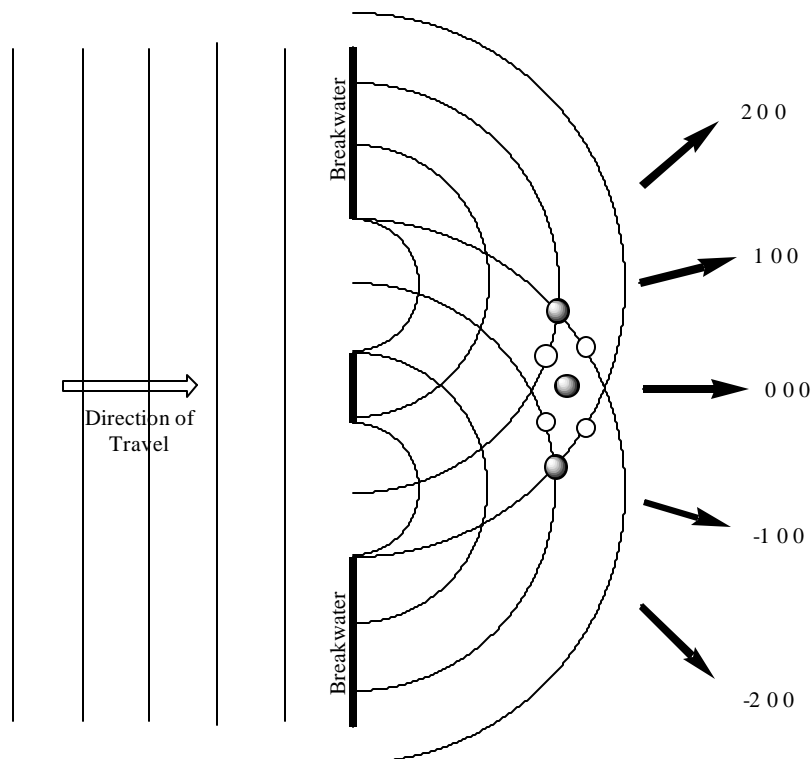
- Areas of unexpectedly high and low amplitudes (can be very dangerous to boats at dock) ⇒
 - Constructive Interference
 - Destructive Interference
- Graphics from Text: Figure 3.2a, page 76; Spreading of Plane Waves passing through a slit



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 \Rightarrow Wide patterns
- Wide Slits \Rightarrow 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 spaced 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 \Rightarrow Overall Envelope of Diffraction Pattern
- Slit Spacing \Rightarrow 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

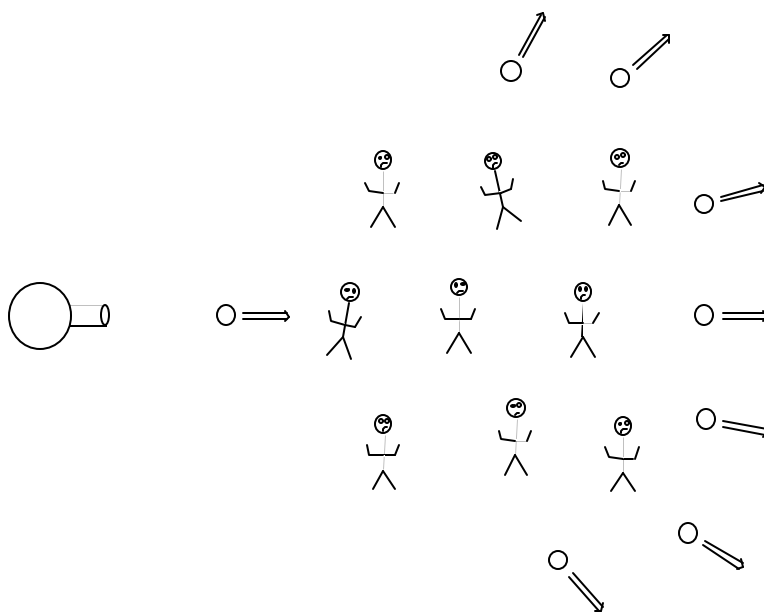
Part b: The Influences of Object Patterns

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

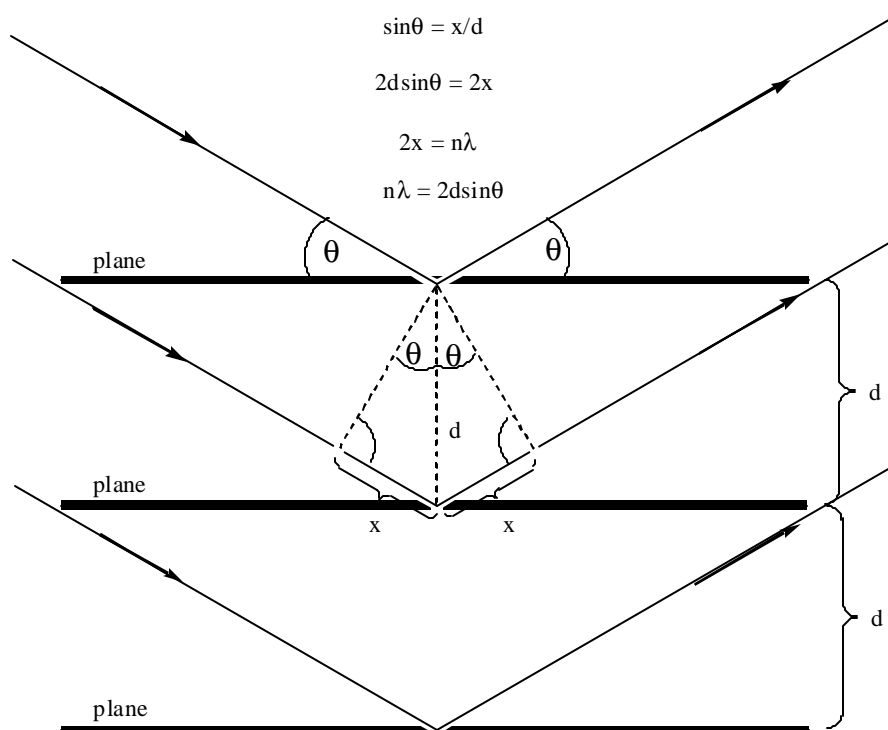
- **Bragg's Law** states for diffraction to occur it is observed experimentally that:

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

- 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)

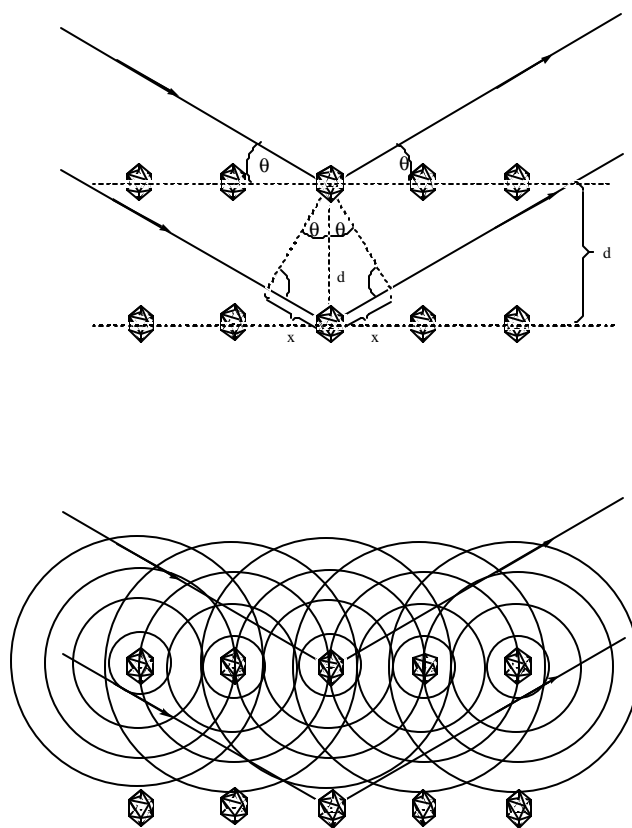


Graphics from Text: Figure 3.10b, page 87; Diffraction off of Planes

Part c: The Truth About Bragg's Law

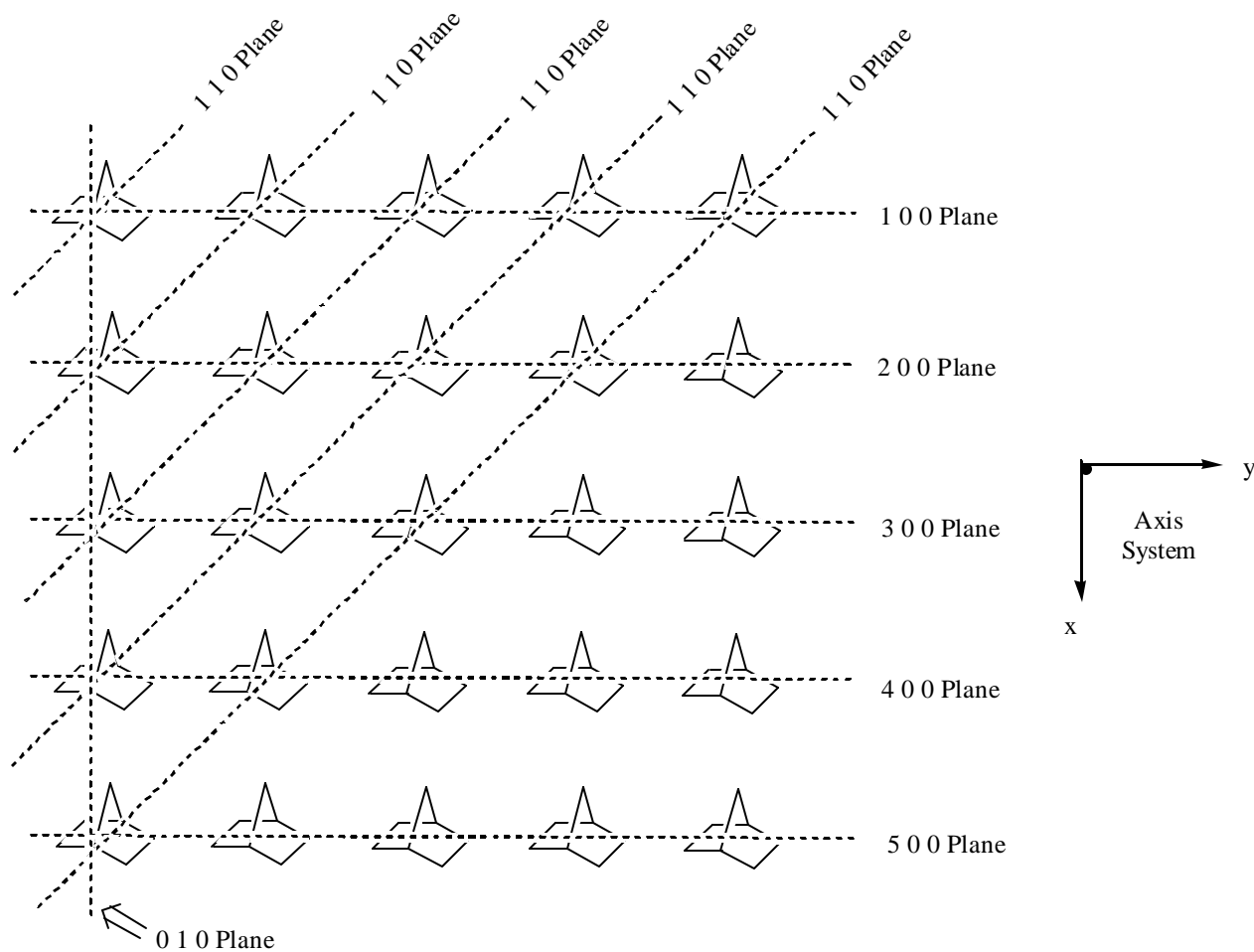
Graphics from Text: Figure 3.9, page 85; Conditions for Diffraction so as to get Constructive Interference - Relating Diffraction Through Slits to Diffraction off of Planes

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** \Rightarrow reflections off of pairs of planes that are one layer apart and would be the 1 0 0 reflections

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

- The third smallest angle \Rightarrow reflections off to pairs of planes three layers apart and would be referred 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 parallel 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, anomalous 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 ${}^6\text{Li}$

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 $h k l \neq -h -k -l$

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 & 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 & Space Groups

Section 07: Symmetry in the Diffraction Pattern

Part a: Friedel's Law

Part b: Symmetry of Packing P Symmetry of Diffraction Pattern

Part c: Laue Symmetry

Section 08: Space Group Determination from Diffraction Data**Part a: Systematic Absences P Centering****Part b: Systematic Absences P 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

Part a: The Nature of Light

Part b: Isotropic and Anisotropic Crystals

Part c: Pleochromism

Part d: Refraction of Light

Part e: Birefringence of Light

Part f: Polarization of Light

Part g: Optical Activity and 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](#)

#		Anomalous Dispersion Measurements	174
ϕ 77		anomalous scattering	105
(Anomalous Scattering	104, 132
		Anomalous Scattering and Neutrons	105
		Anomalous Scattering and X-Rays	105
$(M_1)_2(SO_4)(M_3)_2(SO_4)_3 \cdot 24H_2O$	73	Application of Diffraction Methods to Solving Chemical Problems?	13
I		APS	34
180° Phase Shift	93	Area Detectors	37, 136
4		Art rather than Science	49
4 Circle Goniometers	37	ASF	95
A		Ask Students:13, 30, 45, 76, 107, 117, 122, 133, 141, 150, 155, 161, 163, 171, 176	
A 77		Atomic and Molecular Displacements	170
absolute structure determinations	105	Atomic Connectivities	165
Absolute Structures	171	Atomic Coordinates and Molecular Structures	163
Absolute Structures of Molecules	171	Atomic motion and disorder	17
Absorption Coefficients as a Function of Wavelength		Atomic Positions	27
	132	Atomic Scattering Factor	95
Absorption Correction	29	Atomic Scattering Factors for Neutrons	97
Absorption Corrections	28	Atomic Scattering Factors for X-Rays	94
Absorption Curves for some representative atoms	104	Atomic Scatting Factors for Neutrons	97
Absorption Data	25	Atomic Sizes/Shapes	27
Absorption Edge	104	Automated Diffractometers	137
Absorption Factor	134	Automated Goniometers	37
Accelerator Plates	32	Axial naming	69
Accuracy	157	axial vectors	69
Advanced Light Source	34	B	
Advanced Photon Source	34	Baron Fourier's Theorem	124
Ag	44	Basic Steps in X-Ray Diffraction Data Analysis	27
Ag and Synchrotron Data	153	Basic Steps in X-Ray Diffraction Data Collection	25
Ag Targets	31	Be windows	44
Air	44	Be Windows	41
Al^{+3}	73	Beam Stop	136
Alcohols	68	bear's porridge	51
Allen D. Hunter	1	bending magnets	34
Allen Hunter's YSU Structure Analysis Lab Manual		Benzene	68
	48	Berkeley	34
ALS	34	Birefringence of Light	119
Alums	73	Block Diagram of an X-Ray Diffractometer	22
Ammonium Dihydrogen Phosphate	19	Bond Lengths	165
Amplitude	77	Bragg's Law	98, 99
Amplitudes of Diffracted Waves	133	Bravais Determination	116
Amplitudes of Waves	123	breakwater	78
Analysis of Refined Solutions	29	Bricks	20
Analysis of trial Solutions	29	bricks in a wall	46
Angles of Data Collection and Series Termination		Bruker AXS	16
Errors	154	Bucknell University	107
angular dependence of the diffracted intensit	96		
Anode	32, 33		

C			
Calix[n]Arenes	68	Costs	33
capillary	44, 56, 60	Cr(CO) ₆	58, 72
Cathode	32	Cr ⁺³	73
CCD chip	42	cryocooled	42
CCD Detectors	42	Crystal (Graphite) Monochromators	35
Cell Parameters and Crystal Systems	116	Crystal and Diffraction Data	161
Centrosymmetric Space Groups	142	crystal decomposition	38
Channel Compounds	68	crystal faces	70
Chapter 1	13	Crystal Forms and Chemical Reactivity	121
Chapter 10	155	Crystal Forms and Explosive Power	121
Chapter 14	171	Crystal Growing Strategies	48
Chapter 16	176	crystal growth	47
Chapter 2	13, 45	Crystal Growth and Shapes	70
Chapter 3	76	crystal habits	71
Chapter 4	107	Crystal Habits and Morphology	70
Chapter 5	117	crystal lattice	75
Chapter 6	122	Crystal Lattice	75
Chapter 7	30, 133	Crystal Quality	25
Chapter 8	141	crystal shapes	71
Chapter 9	150	Crystal Shapes	70, 72
Chapter XIV	45	Crystal Structure Analysis for Chemists and Biologists	1
Chapters 1	13	Crystal Structures	133, 141
Chapters 11 to 13	163	crystal surface	47
Chemical Effects of Crystal Form	121	Crystal Systems ⇒ Space Groups	113
Chemistry 832	1	crystallization	64
Chemistry 832 Goals and Objectives	14	Crystallization Agents	68
Chemistry 832 Resources	14	Crystallization by Cooling	52
Chemistry 832 Syllabus	14	Crystallization by Diffusion Through Capillaries and Gels	56
Chicago	34	Crystallization by Slow Evaporation	52
Chip sizes	42	Crystallization by Solvent Layering	55
Chirality of Molecules	172	Crystallization by Sublimation	58
Chlorocarbons	68	Crystallization From Melts	57
Chromium Alum	72, 73	Crystallization Using Combinations	59
Cleavage of Crystals	118	Crystallization Using Mixed Solvents and Solvent Diffusion in the Gas Phase	53
collimated X-ray beam	23	Crystallographic CourseWare	107
combinations	59	Crystallographic Data Bases	177
combos	59	Crystallographic Literature	176
Common Methods for Estimating Phase Angles	143	Crystallographic Papers	178
Comparing Structures	179	Crystallographic Publications: Preparation and Analysis	176
Complete Molecules	164	Crystallography-Diffraction Methods Texts List	14
Complete Table of Contents	3	Cu 44	
Computer Advances	27	Cu Machine	41
Constant temperatures	50	Cu radiation	44
Constraints	158	Cu Resolution	153
Constructive and Destructive Superposition of Waves	83	Cu Targets	31
Constructive Interference	79, 80, 81, 83, 100	Cu X-Ray source	16
Contact Goniometer	74	Cubic Space Groups	111
Convection	50	cubic unit cells	71
Conventional Anodes	33	Cyclodextrins	68
Conventional Definition	153		
Conventional X-Ray Tubes	32	D	
convoluted	75	d ≡ The Interplanar Spacing	98
Cooling System	32		

dandruff	66	Dynamic Diffraction	128
Data ↔ Solution Relationship	27	dynamic range	39, 42
Data Analysis can be quite routine through impossibly difficult	27	Dynamic range	43
data collection	18	Dynamic Range	41
data collection area	43	<i>E</i>	
data collection areas	43	Edition of Notes	1
Data for Publication	28	Effects of Displacements on Molecular Geometries	170
Data intensity at high angles	38	Effects of Resolution on the Structure	153
Data read out times	43	Effects of Temperatures on Collected Diffraction Data	138
Data Reduction	29, 140	Effects of Wavelength of Measured Intensities	134
Decomposition from air	38	Effects of Wavelength on Resolution and Intensities	153
Decomposition from heat	38	Electrical Effects of Crystals	120
Decomposition from X-Ray Beam	38	electrochemical source	60
Defects in th crystal	19	Electron Density Calculations	125
Deformation Density Maps	152	Electron Density Distributions vs. Structure Factors and Phases	142
Densimeter	40	Electron Density Function	151
Department of Chemistry	1	Electron Density is Periodic	125
Deposition on Surfaces	47	Electron Density Maps	150, 152
Derivation of Atomic Connectivity Tables	165	Electron Distribution Curves for Orbitals	126
Derivatives	67	Electron Micrograph	46
Destructive Interference	79, 80, 81, 83	Electron Scattering Curves for Orbitals	126
Detector	24	electrons	93
d_{hkl} Values	103	Equation for Electron Density as a Function of Structure Factors	125
Diamond	21, 57	Equation for Intensities of Diffracted Beams	134
Difference Electron Density Maps	152	Equation for Structure Factors as a Function of Electron Density	125
Different Faces Different Reactions	121	ESD Formula	167
Diffracted beams	27	ESDs and Reliability of Data	167
diffraction angle	24	Estimated Standard Deviations	157, 167
Diffraction by Crystals	76	evaporate	53
Diffraction by Slits vs. Diffraction by Objects	87	Ewald Sphere	106
Diffraction Data	25, 122	Extinction	129
Diffraction in Three Dimensions	88	<i>F</i>	
Diffraction in Two Dimensions	84	F(calc) Map	152
Diffraction Lab	14, 15	Ferrocene	58
Diffraction of Waves	76	Fiber Optic Taper	42
Diffraction off of Planes	100	Figure 1.2	76
Diffraction Pattern from a Single Slit	84	Figure 1.3	19
Diffraction Pattern Spacing	85	Figure 1.4	83
Diffraction Pattern Spacing from Arrays of Slits	86	Figure 1.5	22
Diffraction Patterns from Arrays of Points on a Slide	88	Figure 1.6	21
Diffraction Patterns from Arrays of Slits	86	Figure 2.10	74
Diffraction Patterns from Two or More Slits	85	Figure 2.11 and 2.12	74
Diffraction Patterns of a Single Slit	84	Figure 2.12	101
Diffraction Through Slits	100	Figure 2.14	71
Diffractometer Lab	16	Figure 2.4	46
diffuse	54	Figure 2.5	69
Direct Methods	143, 144	Figure 2.6	47
disorder	21	Figure 2.7	70
disorder across macroscopic dimensions	46		
Disorder of Atoms and Molecules in a Lattice	131		
Disorder of the Array	92		
Displacement Parameters	38, 131		
dropwise solvent addition	53		
Dust	66		

Figure 2.8	47	Glue	44
Figure 3.1	77	Goals and Objectives Handout	14
Figure 3.10b	99	Goniometer	24
Figure 3.11	26	Goniometer Heads	37
Figure 3.12	94	Goniometers	37
Figure 3.13a	94	Graphics from Text 19, 21, 22, 26, 46, 47, 69, 70, 71,	
Figure 3.13b	97	74, 75, 76, 77, 80, 81, 82, 83, 84, 85, 86, 88, 93,	
Figure 3.17	106	94, 97, 99, 100, 101, 103, 104, 105, 106, 122, 123	
Figure 3.2a	80	Graphite	21
Figure 3.2b	81	Graphite Crystal Monochromators and Pin Holes in	
Figure 3.2b and c	82	Tubes	36
Figure 3.5	84	Graphite Single Crystal	35
Figure 3.6	84, 85, 86	grease	66
Figure 3.7	88	Green Thumb	49
Figure 3.8	93	Grow Single Crystal	25
Figure 3.9	100	Growing crystals	19
Figure 6.23	104	growing single crystals	47
Figures 1.1 and 3.3	83	Growing Single Crystals	47
Figures 1.7 and 1.8	21	Growing Single Crystals Suitable for Diffraction	
Figures 1.9 - 1.11	21	Analysis	48
Figures 2.1 - 2.3	46	H	
Figures 2.15 and 2.16	75	$hkl \neq -h-k-l$	105
Figures 3.10a and b	100	Habit of the Crystal	70
Filaments	33	Hardness of Crystals	118
Film Based Area Detectors	40	He beam path	44
Final Plots for Publication	29	heat sink	32
Final Tables for Publication	29	Heavy Atom Methods	145
Flow Chart for a Typical Structure Solution	29	Hermann-Mauguin vs. Schoenflies Symbols	110
Flow Diagram	142	Hexachlorocyclohexane	21
Focusing Mirrors	35, 36	Hexamethylbenzene	21
Foil Filters (Ni foil)	35	High Angle Scattering of Waves	94
Fourier Analysis	124	high speeds	33
Fourier Series	124	high vacuum	33
Fourier Synthesis	124	high voltages	33
Fourier Transforms	125	hkl values and Crystal Planes	125
Fractional Coordinates	164	I	
Frequency	77	ICE Slides	88
Friedel's Law	115	Image Generation from Diffracted Waves	122
From xyz Coordinates to Bond Lengths, Bond		Image Generation in Optical Microscopy and X-Ray	
Angles, etc.	164	Diffraction	76
G		Imaging Plate Detectors	43
GaAs	46	Imaging Plate systems	43
Gallium Arsenide	46, 57	imiscible layers	60
Gaussian Distribution Function	157	Impatience is the Enemy	50
General Conditions for Crystal Growth	50	Impure materials	64
General Features of Maps	152	incidence angle	102
General principles of growing single crystals	49	Inclusion Compounds	68
Generate Trial Solutions	29	Index of Topics and Vocabulary	181
Generic Waves	77	Indexing Crystal Faces	74
geology	74	Indexing of Crystal Faces	101
Getting Unit Cell Parameters from Interplanar		Inequalities	144
Spacings	103	Influence of Slit Spacing	85
gift horse	63	Influence of Slit Width on Diffraction Pattern	84
Glide Planes	114	Initial Starting Solution	28
Global vs. Local Minima in Solution	160		

Intensities of Diffracted Beams	134	M	
Intensity Information	27	M. Kastner	107
intensity of diffracted X-ray beams	24	M. Lewis	1
Interface of Two Solutions	60	M. Rossi	1
Interference and Bragg's Law	100	MAD Phasing of Protein Data	132
intermolecular distances	31	MAD Phasing of Proteins	148
Intermolecular interactions	17	Main Steps in Data Analysis	28
International Tables for Typical Bond Distances	165	Maintenance Problems	33
Introduction to Chemistry 832	13	Manual Goniometers	37
Introduction to Symmetry	108	mask	91
Inversion Centers	109	Master Several Favorite Methods	51
ionic liquids	57	Mathematics of Phase Relationships	144
IR laser	43	maximum ASF value	95
Isomorphic Crystals	72	Maximum Atomic Scattering Factor, ASF	95
Isomorphic Replacement	72, 73	Mechanical Properties of Crystals	118
Isomorphism	72	Melt	57
Isomorphous Replacement	72, 146	metal mesh sieve	83
Isostructural Crystals	143	Metal oxides	57
isotope	95	Metal Salts	146
isotopes	105	Metal Target	32
isotrope	97	minerals	72, 74
Isotropic and Anisotropic Crystals	119	Minerals	57
Isotropic Displacement Parameters	131	Mirror Planes	109
J		miscible	55
J. P. Glusker	1	Mixed Alums	73
K		Mixed Solvents	53
K 73		mixture of solvents	53
$K_2(SO_4) \cdot Al_2(SO_4)_3 \cdot 24H_2O$	73	Mo	44
$K_2(SO_4) \cdot Cr_2(SO_4)_3 \cdot 24H_2O$	73	Mo Resolution	153
Kappa Geometry Goniometers	37	Mo Targets	31
KCl	21	Mo X-Ray source	16
Kinematic and Dynamic Diffraction	128	Molecular and Macromolecular Conformations	169
Kinematic Diffraction	128	Molecular Geometries	164
Knowing the Intensities	27	Molecular Structure Information	163
Knowing the Phases	27	molecular structures	17
L		Molecular Structures	133, 141, 150
Lab Manual	14	Molecules in the Unit Cell and Z	166
large unit cells	43	monochromatic X-ray beam	23
Laser Light Show	88	Monochromatic X-Rays	135
Laser Pointer	88	Morphology of the Crystal	70
lattice points	20, 75	Mosaic Blocks	128
Laue Determination	116	Mount Single Crystal	25
Laue Symmetry	115	Multiple Bragg Diffraction	143
Layered Alums	73	multiplex advantage	67
Least Squares Refinement	155	Multiplex Advantage	39
Lengths of Waves	123	Multi-Wire Area Detectors	41
Light Waves	83	Multi-Wire Detector	41
Liquid He Systems	38	N	
Liquid N ₂ Systems	38	$n \equiv \text{Any integer}$	98
Long distance order	19	$n \lambda = 2 d \sin \theta$	98
long range order	46	NaCl	21
Lorenz Factor	134	Naphthalene	58
Low Temperature System	38	Narrow Slits \Rightarrow Wide patterns	84
		Narrower tubes	50

Neutron ASF	97	photon yields	36
Neutron Diffraction	97	Photon Yields	35
Neutron Scattering Factors of Nuclei	127	Physical Properties of Crystals	117
Neutrons	97	Picker Machines	37
NH ₄	73	Piezoelectric Effects	120
Ni foil	35	Plane Waves passing through a slit	80
NLO material	19	Plane Waves passing through two slits	81
NMR tubes	61	plastic caps	61
Non-Centrosymmetric Space Groups	142	Pleochromism	119
Non-Linear Optical Phenomenon	120	Point Groups	108
Non-parallel sets of waves on open water	79	Point Symmetry Operations	109
NT Lab	15	Polarization Factor	134
Nucleation	47	Polarization of Light	119
nucleation sites	61	Polymorphism	71
nuclei	97	Polymorphism and Isomorphism	71
O		Polymorphs	71
Objects in the Array	91	Porphyryns	68
octahedral crystals	73	Potash Alum	72, 73
Operating Costs	33	Powder Data	41
Optical Activity and Chiral Molecules	173	Precision	157
Optical Activity and Crystals	119	Precision vs. Accuracy	157
Optical Microscope Works	122	Primary Extinction	129
optical photons	43	Procedural Steps	28
Optical Properties of Crystals	119	Process the Raw Data	28
orientation	46	Protein Crystallographers	67
orientation in 3D space	24	Protein data	41
Origin of the Unit Cell	108	protein diffraction studies	43
Orthogonal Coordinates	164	Protein Diffraction Studies	72
Other Chance Methods	63	Proteins: The Problem Structures	146
Outline Notes	1	Proven Methods for growing crystals	52
P		Purchase Costs	33
P(obs) Map	152	Purify Your Material	64
P4 37		Pyroelectric Effects	120
P4 Diffractometers	16	Q	
Parallel waves passing through a hole in a breakwater	80	Quadrupole Displacement Parameters and Evaluations of the Shapes of Electron Clouds	131
Parallel waves passing through two holes in a breakwater	81	Qualitative Picture of Least Squares Refinement	156
Parallel waves passing through two holes of varying spacings	82	Quality of Raw Data	27
Parallelepiped	69	Quantum Mechanical Basketball	90
Pattern of the Array	91	Quartz	19, 57
Patterson Maps	145	R	
Patterson Methods	143, 145	Random vs. Systematic Errors	157
Peak Profiles	139	Rated Power Limits	33
Perfect Crystals	46	Rates of Crystal Growth	49
Periodic Electron Density in Crystals	124	rates of face growth	70
Persistence Pays Off	67	Raw Crystallographic Data	163
Phase Angles of Waves	123	Reason for the Observed Diffraction Pattern Shapes	84
phase information	28	reciprocal relationship	89
Phase Information	27	Reciprocal Space	89
Phase Shift during X-Ray Scattering	93	Refine	28
Phases of Diffracted Waves	141	Refraction of Light	119
Phosphor	42	Related Protein Structures	146
		Relationship Between Real and Reciprocal Space	125

Relationship of Crystallographic Data to Structural Data	26	Slit Width \Rightarrow Overall Envelope of Diffraction Pattern	86
Relative Phase	77	Slower is better	49
Renninger Effect and Double Reflections	129	Small Molecules	42
Repeating motif of crystal	20	Software Advances	27
repeating unit	17	Solid State Structural Methods	1
Representations of Displacement Parameters	170	Solvates	68
Resolution	153	Solve Structure	26
Restraints	159	solvent evaporation	52
Review of Crystal Systems \Rightarrow Space Groups	114	Solvent Layering	55
right hand rule	69	Solvent Properties and Saturated Solutions	51
Rotary Inversion	110	solvent pump	53
Rotary Inversion Axes	109	Space Group	28
Rotating Anode Generators	33	Space Group Determination	29, 116
Rotating Cylinder	33	Space Group Determination from Diffraction Data	116
rotating particle beam	34	Space Group information	25
Rotation (n) + n Perpendicular 2 Fold Axes	110	Space Groups	108
Rotation (n) + n Perpendicular 2 Fold Axes + Perpendicular Reflections	110	Spacings of Slits	85
Rotation (n) + n Perpendicular 2 Fold Axes + Perpendicular Reflections + Diagonal	110	Special Topics	180
Rotation + Perpendicular Reflections	110	Speed and Cost	18
Rotation + Plane(s) Through the Axis	110	Spring 2000 Class	1
Rotation Axes	109, 110	Stages of Crystal Growth	47
routine single crystal study	18	State of the Art	42
S		Statistical Tools	144
SALM	45, 48	stepper motors	37
Sample, Glue, Fiber & Capillary	44	Steroids	21
saturated solution	52	STM	46
Saturated Solution	47	Storage Phosphor	43
Saturated Solutions	51	Structural Data for Publication	26
SC(NH ₂) ₂	68	Structural Information	122
Scanning Tunneling Microscope	46	Structure Analysis Lab Manual	45, 48
Scintillation Counters	39, 136	Structure Factor Amplitudes	130
Scratches	66	Structure Factors	130
Screw Axes	114	Structure Refinement	29
Secondary Extinction	129	Structure Solution Guide	15
Seed Crystals	65	Summary of the Diffraction Structure Process	125
seeding/patterning agent	66	Summing Waves	123
Sequential crystal growing strategies	67	Supramolecular Complexes	68
Serial Detectors	37, 39	Surface treatments	66
Shake and Bake	143, 149	Syllabus for Spring 2000	14
Shapes of the Atomic Scattering Factor Curves	96	Symmetries of Regularly Repeating Objects	112
Silicon	57	Symmetry	107
Simple Anisotropic Displacement Parameters	131	Symmetry in the Diffraction Pattern	115
Single Crystal	19	Symmetry of Packing \Rightarrow Symmetry of Diffraction Pattern	115
Single Crystals	45, 46	Symmetry Operations	108
single wavelength	35	Synchrotron data	42
Sinusoidal Wave	77	Synchrotron Sources	31, 34
sin θ/λ	96	Syntheses In Situ	60
Size of the Array	92	Systematic Absences \Rightarrow Centering	116
slit spacing	82	Systematic Absences \Rightarrow Translational Symmetry	116
Slit Spacing \Rightarrow Spacing of Maxima within that Envelope	86	Systematic approaches to growing single crystals	67
		T	
		Table 3.1	103

Table 3.2	94, 97, 105	V	
Table of Contents	2	V(CO) ₆	72
Table of Major Topics	2	vacuum	58
Tables of Crystal and Diffraction	161	Vacuum System maintenance	33
Telephone Poles	87	VCH Publishers	1
Terminator II, Judgement Day	59	Vibration Effects in Crystals	170
Texts and Monographs	14	Vibration of Atoms in a Lattice	131
The 14 Bravais Lattices	113	Vibrational Motion	164
The 180° Phase Shift for X-Rays	93	Virus Crystals	46
The 230 Space Groups	113	Viscous solvents	50
The 7 Crystal Systems	113	visible light photons	42
The Crystal Lattice	75	Visual estimation of intensities	40
The Ewald Sphere	106	volatile materials	58
The Experimental Truth	98	volatile solvent	54
The Influences of Object Patterns	89	W	
The Influences of Objects, Periodicity, Array Size, and Disorder on Diffraction Patterns	91	Water	68
The Magic of NMR Tubes	61	Water Waves	78
The Mathematics of Least Squares Refinement	156	wavelength	44
The Myth Taught in General Chemistry	99	Wavelength	77
The Nature of Light	119	Wavelength distribution	32
The Origins of Anomalous Scattering	104	Wavelengths of X-Rays	31
The Patterson Function	145	Waves	77, 123
The Phase Problem	27	WEB	15
The Role of Advances in Computers, Theory, and Software	143	What are X-Rays?	31
The Role of Extraneous Materials	66	What Can Diffraction Methods Tell Us	17
The Standard Table	162	What Diffracts Neutrons?	97
The Truth About Bragg's Law	100	What Diffracts X-Rays?	93
The Unit Cell	69	What is a Single Crystal and Why is it Important	19
Theory Advances	27	What is Chemistry 832	14
Thermal Expansion Coefficient	50	What is Least Squares Refinement	156
Thiourea	68	What to do when proven methods fail	64
Three Dimensional Symmetry Operations	114	When are two values different	167
topographic map	91	Where Works Best	144, 145
Torsion Angles	168	Which planes are we talking about?	101
Translations	114	Why are these Wavelengths chosen	31
Trial Structure	28	Wide Slits ⇒ Narrow patterns	84
Try, Try Again	67	Wiglers	34
tunable radiation	34	Windows	44
Tungsten Filament	32	Windows NT computers	15
Tungsten Vapor	32	With Known Structures	142
U		X	
unit cell	17	X-1000	41
Unit Cell	20	Xe gas ionization	41
Unit Cell Angles	69	XL	28
Unit Cell Axial Lengths	69	XP	28
Unit Cell Dimensions	72, 103	XPREP	28
Unit Cell information	25	X-Ray Absorption in the Diffractometer	44
unit cell parameters	103	X-ray are diffracted by electrons	94
unit cells	21	X-ray beam	23
Unit cells and diffraction data	21	X-Ray Collimators	36
Unnatural Amino Acids	146	X-Ray Detector	40
Uses of Anisotropic Displacement Parameters	170	X-Ray Detectors	39, 136
Uses of Anomalous Dispersion	175	X-Ray Diffraction	93

X-Ray Diffractometer	22	Z	
X-Ray Diffractometers	30		
X-Ray Flux	31	Z_{eff}	96
X-Ray Generator	23	I	
X-Ray Generators	32		
X-Ray Lasers	32	λ 77	
X-Ray Monochromators	35	$\lambda \equiv$ The Wavelength of Diffracted Light	98
X-Ray Scattering Factors of Electrons in Orbitals	126	n	
X-Ray Sources	135		
X-Ray Spectrum of an X-Ray Tube	135	ν 77	
X-ray tubes	44	q	
Y			
Youngstown State University	1	$\theta \equiv$ The Angle between the Incident Ray and the Planes	98