CHEM 3030 Introduction to X-ray Crystallography

X-ray diffraction is the premier technique for the determination of molecular structure in chemistry and biochemistry. There are three distinct parts to a structural determination once a high quality single crystal is grown and mounted on the diffractometer.

1. Geometric data collection – the unit cell dimensions are determined from the angles of a few dozen reflections.
2. Intensity Data Collection – the intensity of several thousand reflections are measured.
3. Structure solution – using Direct or Patterson methods, the phase problem is cracked and a function describing the e-density in the unit cell is generated (Fourier synthesis) from the measured intensities. Least squares refinement then optimizes agreement between Fobs (from Intensity data) and Fcalc (from structure).

The more tedious aspects of crystallography have been largely automated and the computations are now within the reach of any PC. Crystallography provides an elegant application of symmetry concepts, mathematics (Fourier series), and computer methods to a scientific problem. Crystal structures are now ubiquitous in chemistry and biochemistry. This brief intro is intended to provide the minimum needed to appreciate literature data.

FUNDAMENTALS

1. The 7 crystal systems and 14 Bravais lattices.
2. Space group Tables, special and general positions, translational symmetry elements, screw axes and glide planes.
3. Braggs law. Reflections occur only for integral values of the indices hkl because the distance traveled by an X-ray photon through a unit cell must coincide with an integral number of wavelengths. When this condition is satisfied scattering contributions from all unit cells add to give a net scattered wave with intensity I_{hkl} at an angle Θ_{hkl}. Otherwise destructive interference results.
4. The intensity of a reflection depends on the constructive and destructive interference of waves scattered by each atom in the crystal/unit cell (more precisely the electrons in each atom). The intensities of thousands of reflections I_{hkl} each diffracted at an angle given by Bragg's law provides a "coded" picture of molecular structure accessible only when the phase problem is solved.
5. Fourier series are periodic functions suited to describe the e-density pattern in a crystal which repeats with a period given by the unit cell dimensions a,b, and c in the directions x, y, and z. This Fourier series consists of a sum of thousands of sine and cosine terms whose coefficients are the structure factors F_{hkl} .
6. Structure Factors $/F_{hkl}/$ are proportional to the square root of I_{hkl}. A simple description of a structure factor is that it gives the fraction of the total electron density in the cell which is scattered in phase at angle Θ_{hkl}. If all electrons were located at the corner of a unit cell then F_{hkl} would = total number of electrons. Since matter is spread out in the unit cell some atoms are scattering out of phase with others depending on the angle theta given by Bragg's law. The intensity of every reflection hkl depends on the location of every atom in the cell.
7. Phase Problem. Only the magnitude of F_{hkl} is obtained experimentally. In centrosymmetric crystals F is real and either + or - . More generally F is a complex number (a + bi) with a phase angle between 0 and 2π.

GOALS

1. Learn crystallographic symmetry and be able to use space group tables.
2. Use the SHELX software to solve a structure in the lab. (Expt # 5)
3. Handcrank through some computations for simple structures NaCl, CaF_2 etc.
4. Read, understand, and use crystallographic data in the scientific literature.

BASICS

1. Bragg's Law $n\lambda = 2d \sin\Theta$ (Mo radiation $\lambda = 0.71073$ Å , Cu radiation $\lambda = 1.542$ Å)
   for an orthorhombic crystal $1/d^2 = (h^2/a^2 + k^2/b^2 + l^2/c^2)$ and $\Theta = \sin^{-1}(\lambda/2d)$
   Given a,b, and c you could compute 1000 angles and d spacings hkl on your PC in a minute by running the indices h,k, and l from -10 to + 10. For h = -10 to 10 , next h etc for programmers)

The number of reflections and their angles depend only on the dimensions of the unit cell and the wavelength of the X-rays used and they are independent of the contents of the unit cell.
The intensity of the reflections depends upon how the electron density is spread throughout the unit cell, i.e. the location of atoms. The intensities provide information about the molecular structure (unit cell contents).

The 14 Bravais Lattices – consist of the 7 basic unit cell shapes (crystal systems) plus various types of centering.

1. Cubic a=b=c all angles 90 P, F , I
2. Tetragonal a=b ≠ c all angles 90 P, I
3. Orthorhombic a ≠ b ≠ c all angles 90 P, I, F, (A,B,C)
4. Monoclinic a ≠ b ≠ c only β ≠ 90 P, C
5. Triclinic a ≠ b ≠ c no angles 90 P
6. Rhombic a = b = c no angles 90 P
7. Hexagonal a =b ≠ c α =β = 90 and γ = 120 P

P = primitive - object only at (x,y,z)
I = body centered -objects at (x,y,z) and (½ + x , ½ +y, ½ + z)
C = C centered -objects at (x,y,z) and ((½ + x , ½ +y, z)
For A centered extra object is on A face (x, ½ + y, ½ + z), and for B centering, on the B face.
F = face centered - objects at (x,y,z), (½ + x , ½ + y , z), (x, ½ + y, ½ + z), (½ + x, y, ½ + z)

Counting atoms. Z = (# inside cell) + 1/8 (number on corners) + ½ (# on faces) + ¼ (# on edges).
In NaCl Fm3m 8 Na at each corner X 1/8 + 6 on each face X ½ = 4 in Fm3m Wycoff position a
12 Cl on edges X ¼ + 1 in middle = 4 For NaCl Z =4. in Fm3m Wycoff position b
or vice versa since which is which merely depends on where you choose to put the origin.

SPACE GROUPS

Crystallographic space groups include all the symmetry elements from point groups E, C_2, S_2, I, σ etc. except we use different symbols : C_2 is 2, S_2 is -2 , inversion is -1 , and mirror plane is m.
Adding translational elements gives space groups.

1. Translation : For every object Q at (x,y,z) another Q is found by a full unit cell translation in any direction (x+1,y,z), (x,y+1,z), (x+1, y+1, z) etc. The unit cell repeats itself in all 3 dimensions ad infinitum.

2. Screw axis 2_1 rotation by 360/2 and translation ½ unit cell along it in a, b or c direction.
For 2_1 along a (xyz) → (½ + x, -y, -z) A 4_1 would rotate 90 and translate ¼ etc.

3. Glide Plane a,b,c,n, or d reflect through a plane and then translate in a direction parallel to it.
a glide perpendicular to b (xyz) → (½ + x ,-y, z)

There are exactly 17 possible space groups in 2 dimensions and 230 in 3D. Space group Tables are given in the International Tables of Crystallography. Examples are given in figures and below. With a little effort you can quickly become comfortable with them and make effective use of them.

The origin is at the upper left with x running down and y across and z directed above the plane of the paper
The diagram on the left shows the location of objects. The diagram on the right shows the location of symmetry elements. Listed below are the general and special positions with the imposed symmetry and coordinates.
A general position is any arbitrary location (x,y,z)
A special position is a location sitting directly on a symmetry element.
Each symmetry element takes an object at xyz and creates an identical one at a location related by that element.

Cm In Cm a mirror along the b direction takes (xy) to (-x,y). The centering creates another object at (1/2 + x , ½ +y). The two operations together produce a third symmetry element- glide planes parallel to b at x = ¼ and x = ¾. Note that if we apply the glide to (x,y) → (½-x, ½ +y) and then apply the mirror at x= 1/2 we get (½ + x, ½ + y) which is the same as applying the centering to (x,y). Continuing to apply all operations eventually leads to only 4 objects in the cell. Closure is a requirement of a group!

An object may be anything you like. It could be a Mickey Mouse, it could be his ear, it could be a C atom, it could be a myoglobin molecule. Inverted objects are denoted with a comma in the circle.
Asymmetric unit – is the minimum set of objects needed to generate the entire unit cell contents.
Objects placed on special positions MUST possess at least the symmetry at that site. You cannot put d-glucose on a mirror as it lacks a mirror. There are no constraints in a general position.

In Cm for example only half of mickey mouse would be needed if mickey lies on the mirror. The mirror would generate his other half. If mickey is put in a general position , the unit cell will contain 4 mickeys. If he is placed on the mirror there will by 4 half mickeys but only 2 full Mickeys. If we want 8 Mickeys we need only put one at (xyz) and the other at (x'y'z') and the symmetry will do the rest. We could have 6 Mickeys in Cm but there is no way to have 1,3,5, or 7 Mickeys in Cm.

Table 1 Symmetry operations on (x,y,z) for elements on coordinate axes[a] with symbols[b]

Inversion centre	O	-1	-x,-y,-z			
Rotation axis	↔ ()	2	∥a x,-y,-z	∥b -x, y,-z	∥c -x,-y, z	rotation flips two coordinates
Screw axis	→ ()	2_1	∥a x+ ½,-y,-z	∥b -x, y + ½ , -z	∥c -x,-y, ½ + z	
Mirror plane	____	m	⊥ a -x, y, z	⊥b x, -y, z	⊥ c x, y, -z	mirror flips one
Glide planes	------	a glide	⊥b x + ½, -y, z	⊥c x + ½, y, -z		
	-----	b glide	⊥a -x, y + ½ , z	⊥c x , y + ½ , -z		
	------	c glide	⊥a -x, y, z + ½	⊥b x , -y , ½ +z		
	.-.-.-	n glide	⊥a -x, y + ½ , ½ + z			translates along the diagonal

a) coordinates will differ if the element is off axis. A 2 ∥a at y = 1/4 generates (x, ½-y, -z).
b) symbols differ if parallel or perpendicular to plane of projection.

Fractional Coordinates The edges of the unit cell are taken as the coordinate axes. Locations are expressed as fractions of the unit cell dimensions (x/a, y/b, z/c). Thus (1/2,1/2,0) is located at the centre of the C face . The distance between two points is given by the law of cosines. For all 90^o angles the cosine terms below are zero.

$$D^2 = \Delta x\ ^2a^2 + \Delta y^2b^2 + \Delta z^2\, c^2 + 2ab\ \Delta x\ \Delta y \cos\gamma + 2ac\ \Delta x\ \Delta z \cos\beta + 2\ bc\ \Delta y\ \Delta z \cos\alpha$$

SYSTEMATIC ABSENCES. The presence of translational symmetry elements which produce symmetry equivalents at x+1/2 or y+1/2 or z+1/2 results in reflections with zero intensity for certain reflections with h, k, or l odd . These conditions are listed in the space group tables. Centering, screws and glides give rise to systematic absences. Inversions, reflections, and rotations do not. The space group is determined by examining the reflection intensities for these systematic absences. For example in $P2_12_12_1$ absences occur for (h00), (0k0) and (00l) for h, k, and l odd. A C centered lattice has identical objects at (xyz) and (½ + x , ½ +y, z) giving absences for (hkl) h+k odd . You can prove this using EQ2 below.

EXERCISE : Consult the space group tables for $P2_12_12_1$, Pbcn, and Pnnm . Identify which crystal is consistent with each space group
Crystal 1 020 120 130 040 013 023 present 050 absent
Crystal 2 020 130 040 023 present 120 050 013 absent
Crystal 3 020 120 130 040 013 present 050 023 absent

SOLVING A STRUCTURE.

The structure solution boils down to two fundamental equations.*
The electron density in the unit cell at a point (x,y,z) is given by EQ 1 (electrons/cubic Angstrom)
for a centrosymmetric case or a sum of sin and cos terms for noncentrosymmetric cases –see below.

EQ 1 $\rho(x,y,z) = 1/V \sum\sum\sum F_{hkl} \{\cos(2\pi(hx + ky + lz))$ sum over all hkl

F_{hkl} are the structure factors..

The structure factor is given by EQ 2. For Centrosymmetric structures the sine terms vanish.

EQ 2 $F_{hkl} = \sum f_i\,(i, hkl)\,\{\cos(2\pi(hx_i + ky_i + lz_i) + i \sin(2\pi(hx_i + ky_i + lz_i))\}$ summed over all atoms, i.

The scattering factor (small f_i) is equal to the number of electrons in that atom (6 for C , 92 for U) at low angles but drops off at higher Θ_{hkl} for reasons explained elsewhere. These scattering factors are tabulated for each element vs. $\sin\Theta_{hkl} / \lambda$ in International Tables for easy look-up. They have units of electrons

* RHO must be real. From Friedel's Law $I_{hkl} = I_{-h,-k,-l}$. From EQ2 F hkl = A + iB and $F_{-h,-k,-l} = A - iB$ but magnitudes = $(A^2+B^2)^{1/2}$ are equal. Summing over hkl and –h,-k,-l in EQ 1 the imaginary terms drop out and rho = Acos + Bsin . (Note cos (x) = cos (-x) but sin (x) = -sin (-x) . (A and B are the cos and sin terms)

You should notice that while EQ1 and EQ2 look alike, EQ1 is a function of x,y,z and is computed with no knowledge of structure from the structure factors (derived from intensities and phases). EQ2 is a number with units of electrons, not a function, and is computed from the exact locations of each atom. (x.y.z).

Remember that at the outset we have NO knowledge of atom locations so we can't make use of EQ2 but we do have the magnitude of each F_{hkl} from intensities but not the phase or sign of each F_{hkl}. We could of course simply work through all possible combinations of + or – for each F but this would give us say 2^{2000} possibilities or 10^{602}. Impossible! We are thus left with a lot of useless X-ray diffraction intensities unless we can come up with the phases.

Patterson showed in 1935 a somewhat complicated way of getting phases if a heavy atom was present. This allowed the solution of most inorganic structures and even proteins like hemoglobin.

Hauptmann and Karle showed a way of making good guesses by a process known as Direct methods. This relates the phases of the selected more intense reflections to others by various sign relationships such as :
S hkl = S h'k'l' S h-h',k-k',l-l') whose probability of being correct increases as a function of its E value. We won't go into how to pick reflections with high E values here. An electron density map which uses E's instead of F's for coefficients in EQ 1 is called an E-map. (BIG E in E-map does not stand for electron). E(hkl)'s are based upon specially selected reflections for which the direct methods are most likely to be correct. Generally the heavier atoms in a structure are evident in the initial E-map and these locations give good estimates of F(hkl) calculated via EQ2 even if all of the atoms are yet to be located.
Both Patterson and Direct methods have been programmed into crystallographic software. In the lab you will use the SHELX software. Neither method leads automatically to a correct solution without intelligent human intervention. This is where you come in. See lab manual for more.

EXERCISES with EQ 2.

1. Prove that the sin terms drop out of EQ 2 if for every atom at xyz there is an identical one at –x,-y,-z. (Centrosymmetric) .
2. Prove that a 2_1 parallel to a will give rise to absences h00 h = odd.

3. Prove that a C centered lattice gives rise to absences (hkl) h+k = odd.

FOURIER SERIES

EQ1 is a Fourier series describing the electron density in the cell. It should be noted that the Fourier series is periodic in the lattice dimensions a, b , and c as it must be. The cyclical process of examining a preliminary electron density map based upon a limited number of terms to locate additional atoms and then using these to generate better coefficients Fhkl and using these to improve the e-density map is called Fourier synthesis. It may be noted that to digitally generate the electron density map for 2000 reflections one must compute 2000 cosines and 2000 sines at every 0.01 increment of x/a , y/b, z/c – that's 10^6 points and this is repeated for each cycle of Fourier synthesis and least squares refinement. The non-linear least squares refinement seeks to minimize the R factor $R = \Sigma(|F_{obs}| - |F_{calc}|)/|F_{obs}|$ by varying positional and thermal parameters. Nevertheless, any PC or laptop will complete this is a minute or two. 30 years ago it took several months to complete this using boxes of punch cards or paper tape.

THERMAL PARAMETERS. The reflection intensities also depend on the vibrational amplitude of each atom. At room temperature atoms vibrate about their nuclear positions. This smears out the electron density. In an isotropic refinement the vibration adds a fourth parameter to the 3 positional parameters x, y, and z. . For N atoms we require 4N + 1 parameters. An anisotropic refinement uses 6 vibrational parameters which define an ellipsoid of vibration. That makes 9N + 1. A good rule of thumb in least squares is to have at least 10 observations for every parameter. The more complicated the structure, the more intensities you need.

The effect of vibration on an atom's scattering power is given by the equation

$f = f_o\ e^{-X}$ where $X = B((\sin^2(\theta))/\lambda^2$ and $B = 8\pi^2\ u^2$ where u^2 = mean square amplitude of vibration. A typical value of u^2 at 298 K = 0.05 Å^2. This corresponds to a root mean square vibrational amplitude of 0.22 Å.

Cubic space group structures solved by inspection.

CsCl crystallizes in Pm3m , Z =1, a = 4.123 Å NaCl in Fm3m, Z =4, a= 5.6 Å

EX-1 Obtain the densities of each and the ionic radii of the cations given that for Cl^- = 1.81 Å.

EX-2 $Ru(NH_3)_6I_2$ crystallizes in Fm3m with Z = 4 and a = 10.84. If Ru-N = 2.14 Å obtain all heavy atom locations.

EX-3 Compute F_{100}, F_{200} and F_{111} for CsCl, NaCl, and $Ru(NH_3)_6I_2$. (Assume f_i = atomic number of atoms)

BRAGGS LAW AND DIFFRACTION .

Reflection from Planes is typically presented to explain X-ray diffraction and Bragg's Law. What do planes and lattices have to do with it and why are some reflections more intense than others?

Diffraction is a result of the scattering of X-rays by electrons. The Bragg condition arises because scattering intensities are large only when multiple scatterers contribute cooperatively. The repeating unit cell is the key as it leads to uniform spacing between same–atom locations in different cells. All objects with the same uniform spacing scatter in phase with each other at the Bragg angle for that spacing.

To simplify the problem first consider all the e-density in the unit cell to be located at the cell origin. This leads to a lattice of points. In 2 dimensions we can draw lines connecting lattice points. (In 3D these would be planes). For instance over (y) 1 down (x) 2 gives a (2,1) plane, over 4 down 2 gives a (2,4) plane. The Miller indices (hkl in 3D) for each set of planes are the reciprocals of the intersections of the planes on the x,y, and z axes.

Note that for a 2D stickman , the spacing of lines through the lattice points are exactly the same as lines through heads, arms, hands, or toes. For molecules- through identical atoms in the structure. Each atom in a structure scatters in proportion to its number of electrons*. Thus f = 6 for Carbon and 92 for Uranium. The structure factor F(hkl) is simply the sum of all contributions. At the Bragg angle for each reflection hkl , all electrons would scatter in phase and F = sum of electrons in cell. * f also decreases with increasing angle (increasing hkl).

Now consider reality in which atoms are spread throughout the unit cell- not just piled at the origin. Atoms not at the origin will scatter slightly out of phase with those at the origin. Thus each atom in the cell will contribute somewhat differently at each angle and the net intensity will be the sum of contributions from all atoms in the cell. Thus F(hkl) will be less than F(000) and the reduction in intensity depends entirely on where atoms are in the cell and how many electrons they contain. This destructive interference is easily seen in cases of systematic absence. The structure factors, F(hkl,) are proportional to the square root of the intensity I(hkl) of each reflection. The phase problem arises in that we can only measure the magnitude of I, not its phase (or sign).

SCATTERING FACTOR DROPS OFF WITH ANGLE.

If you examine an x-ray photograph or intensities in an hkl file you will notice that as the angle θ increases (as hkl increases) the reflection intensities drop off becoming very weak at high angles. This is a consequence of the finite size of atoms. The electrons scatter the X-rays and they are spread out over the atomic diameter. The result is that scattering from e-density at the top of an atom is slightly out of phase with that at the bottom of the atom and this becomes more pronounced as the angle θ increases. This is easy to prove with a simple Bragg's law figure with the atoms drawn as large circles instead of a planes or points. If all the electrons were located at the atom's centre the

intensities would not decrease with angle. The scattering factors for atoms are tabulated in the International Tables vs. angle and imbedded in software for calculating structure factors.

COMPLEX NUMBERS , ANOMOLOUS DISPERSION, and CHIRALITY

Structure factors for non-centrosymmetric space groups are complex numbers of the form :

$F(hkl) = A + iB$ where $A = \Sigma f_i \cos(Q)$ and $B = \Sigma f_i \sin(Q)$ where $Q = 2\pi(hx+ky+lz)$

sum over all atom locations (x,y,z) .

The atomic scattering factors have a complex component. $f_i = f_{real} + i f'$

The f' is the anomolous scattering factor and is small for light atoms but not insignificant for heavier atoms where the incident X-ray photon may have an energy near that of a core transition of the atom in question. It can be easily shown that the structure factors F(hkl) will not equal F(-h,-k,-l) in this case. (Friedel's law says F(hkl) = F(-h,-k,-l) In other words the intensity does not depend on whether the X-ray beam comes from the right or left. This is not true for chiral crystals. By examining F calc for a structure and its inverted one (replace every (x,y,z) with (–x,-y,-z) one can determine the absolute configuration of chiral molecules. At least one heavy atom must be present in the structure to produce significant differences in Friedel pairs. It may be noted that f' , unlike f_{real} is largely independent of angle because only the inner core electrons are involved in anomalous scattering . Thus the weakest reflections show the greatest contributions from f' and are the most useful in determining chirality.

HYDROGENS Since H has only 1 electron it doesn't contribute much to X-ray diffraction intensities and can only be seen in high quality data. Precise hydrogen locations are obtained by neutron diffraction (neutrons are scattered by the nucleus.) In X-ray studies one typically takes account of H scattering by computing the theoretical location of hydrogens and letting them "ride" on the carbon they are bound to using a C-H distance of 0.95 A for tetrahedral carbon. It should be noted that this distance is shorter than the actual C-H distance because the X-ray data uses the position of the centre of the H electron density which is not the same as that of the hydrogen nucleus. The "riding" approach improves the fit of the e-density without adding extra parameters in the least squares calculations.

AUTOMATED STRUCTURE DETERMINATION ON A SINGLE CRYSTAL

1. Select and mount single crystal and center it in the X-ray beam. Cease further human intervention until step 9.
2. Diffractometer rotates crystal and detector looking for strong reflections. It needs about 10 to obtain crude unit cell dimensions and 40 for accurate parameters. It indexes these and OUTPUTS a,b,c, α , β , γ
3. Computer computes angles for all reflections hkl and rotates detector to measure their intensities. OUTPUT I(hkl) . Uses Bragg's law and lab geometry info.
4. Computer makes Lorentz, polarization and absorption corrections to raw data and outputs HKL file of 2000 to 3000 intensities.
5. Computer scans reflection file for systematic absences, examines Laue symmetry and finds space group.
6. Computer applies direct methods to select some 500 E values and obtain phases, plugs these into EQ 1 to create Emap, then searches this map for e-density maxima and assigns the lumps to atoms. OUTPUT – 10 to 50 atom locations. (May need help here to tell a Carbon from a nitrogen etc.)
7. For each hkl, Computer calculates $(\sin\theta_{hkl})/\lambda$, obtains $F(hkl)_{obs}$ from I_{hkl} , computes $F(hkl)_{calc}$ using EQ2 and table of scattering factors f_i , and atom locations (x_i,y_i,z_i). OUTPUT $F(hkl)_{calc}$, and new phases.
8. Using Fcalcs and EQ 1 compute e-density MAP 1. Using Fobs and EQ1 compute another e-density map 2. Now examine the DIFFERENCE MAP = MAP2 – MAP 1 . Peaks correspond to new atom locations, holes correspond to incorrect locations or atoms. (Fourier synthesis)
9. A chemist looks at this output to identify what makes sense. Reprocess atom locations until all atoms are located and then obtain the locations and thermal parameters which minimize the R factor (Least Squares routine)
10. Compute bond lengths and angles and output an ORTEP picture of the structure.

CRITERIA FOR A QUALITY STRUCURE DETERMINATION.

1. R factor below 10% and preferably below 5%. Data/parameter ratio > 10.
2. Anisotropic thermal parameters do not go weird on you.

3. Bond lengths and angles have not gone weird.
4. Residual electron density in the difference map below 0.5 e/Å^3

UPDATES-
Area detectors which became available around 1995 measure hundreds of intensities at the same time.
Synchrotrons (now 1 in Canada) provide wavelength tunable high intensity X-rays for protein work.
PROTEIN STRUCTURES – Unit cells are large and the number of atoms/cell is huge. This necessitates much more intense X-ray beams to measure very weak reflections. One also treats amino acids as semi-rigid groups of known geometry with a few parameters to deal with rotations about bonds etc. There is quite a bit of interplay between molecular mechanics –energy minimization- to arrive at trial structures which improves R.

In 2009 the Chemistry Nobel Prize goees to Ramakrishnan, Seitz, and Yonath for ribosome xray structure
S30 structure In $P4_12_12$ Z =8 a= b = 406 c = 173 90 90 90 .
consisting of a 1540 nucleotide RNA strand bound to 21 proteins.
The Physics prize goes to Boyle from Bell Labs for charge coupled devices which dramatical altered detection methods for X-ray crystallography and also digital photography.

Resolution You will see reports such as Myoglobin at 2.1 Å resolution. This does not mean that anything smaller than 2.1 Å can't be resolved. It refers to the minmum interplanar d spacing corresponding to the Bragg angle θ out to which reflections were measured. For Cu radiation $d = \lambda / 2 \sin(\theta)$ so a 2.1 Å resolution would correspond to $\theta = \sin^{-1}(1.54/4.2) = 21.5^{o}$. If Mo radiation then $\theta = \sin^{-1}(0.71/4.2) = 9.7^{o}$. The diffractometer angle between beam and detector is 2θ. Depending on the quality of the data, the bond length standard deviations even at 2.1 Å resolution may be as small as 0.05 Å.

WEB SOURCES of free software for academic users.
SHELX manual on line http://www.doe-mbi.ucla.edu/People/Software/Shelx97_2_doc/manual.html
WINGX free software for solving structures http://crick.chem.gla.ac.uk/~louis/wingx/download.html
Mercury graphic package from Cambridge http://www.ccdc.cam.ac.uk/products/csd_system/mercury/
Protein Data Bank . rasmol / etc. PDB Lite http://www.pdb.bu.edu/oca-bin/pdblite

Crystallography Problem Set

CaF_2 crystallizes in the cubic space group Fm3m with Z =4, a=5.4638 A.

1. Obtain the density.
2. Use the space group tables to identify the location of all atoms in the unit cell.
3. Compute the Ca-F bond length and the shortest Ca-Ca distance.
4. Compute the following structure factors F(000), F(100), F(200), F(111), F(123) assuming scattering factors f_{ca} = 20 and f_F = 9.

5. Using the structure factor expression prove that a 2_1 along the b axis results in systematic absences (0,k,0) for k odd.

6. Give the coordinates of the points generated by the sequence of operations

X,Y,Z (2_1 along b) _____ (Mirror in xz plane) _____ c glide in xz plane

X,Y,Z (2 along b) _____ inversion at origin _____ mirror in xy plane _____

7.a) Provide diagrams for the rectangular 2 dimensional space group Cmm. Mirrors are located along both the x and y axes and half way between. As in the handouts one figure shows object locations and the other symmetry elements. Identify the locations of a C2 axis and glide planes also generated. Provide the coordinates of the 8 general positions.

B) Diagram a stickman in flatland space group Cmm with Z =4

C) Which of cis or trans dibromoethylene or tetrabromoethylene could crystallize in the 2D space group Cmm with Z = 2? Sketch the unit cell.

8. Show how $[Cu(NH_3)_4][NO_3]_2$ $5H_2O$ could crystallize in the two dimensional space group Pmm with Z =1. Use a small square to denote the Cu cation, a triangle for the nitrate ion and a O for the waters. Ignore H's. All moieties lying within or on the edge of the cell must be shown.