Appendix A

X - Ray Crystal Structure Determination

X – ray was the name given to the highly penetrating rays which emanated when high energy electrons struck a metal target. Within a short time of their discovery, they were being used in medical facilities to image broken bones. They are high frequency electromagnetic rays which are produced when the electrons are suddenly decelerated these rays are called bremsstrahlung radition, or braking radiation. X - rays are also produced when electrons make transitions between lower atomic energy levels in heavy elements. X - rays produced in this way have have definite energies just like other line spectra from atomic electrons. They are called characteristic X - ray since they have energies determined by the atomic energy levels. In interactions with matter, X - rays are ionizing radiation and produce physiological effects which are not observed with any exposure of non - ionizing radiation, such as the risk of mutations or cancer in tissue.

X - rays are part of the frequencies : 3 x 10^{16} Hz, Wavelengths : 10 nm, Quantum energies : 124 eV . An X - ray which reflects from the surface of a substance has travelled less distance than an X - ray which reflects from a plane of atoms inside the crystal. The penetrating X - ray travels down to the internal layer, reflects, and travels back over the same distance before being back at the surface. The distance travelled depends on the separation of the layers and the angle at which the X - ray entered the material. For this wave to be in phase with the wave which reflected from the surface it needs to have travelled a whole number of wavelengths while inside the material (Figure 75). Bragg expressed this in an equation now known as Bragg's Law.

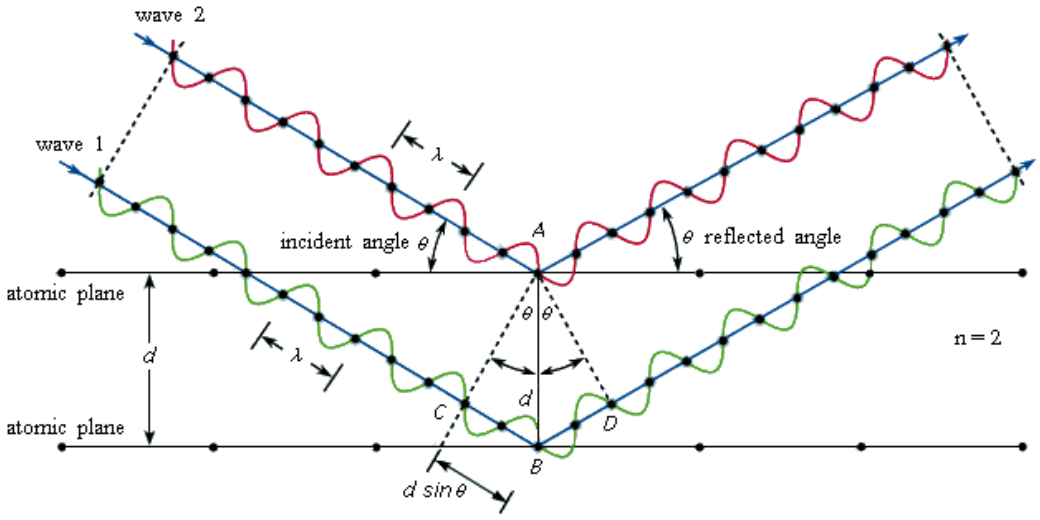

Figure 75. Bragg's Law condition.

Bragg's Law refers to the simple equation :

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

derived by the English physicists Sir W.H. Bragg and his son Sir W.L. Bragg in 1913 to explain why the cleavage faces of crystals appear to reflect X - ray beams at certain angles of incidence (theta, θ). The variable *d* is the distance between atomic layers in a crystal, and the variable lambda , λ, is the wavelength of the incident X - ray beam and n is an integer. This observation is an example of X -ray wave interference commonly known as X - ray diffraction and was direct evidence for the periodic atomic structure of crystals postulated for several centuries. The Braggs were awarded the Nobel Prize in physics in 1915 for their work in determining crystal structures beginning with NaCl, ZnS and diamond. Although Bragg's law was used to explain the interference pattern of X - rays scattered by crystals, diffraction has been developed to study the structure of all states of matter with any beam, e.g., ions, electrons, neutrons, and protons, with a wavelength similar to the distance between the atomic or molecular structures of interest.

SHELTL NT program (version 6.12)

SHELTL NT version 6.12 is an integrated system for the determination of crystal structures from diffraction data. The programs have been highly used to optimize calculations times, memory and disk space requirements. All calculations are valid for all space group in conventional setting, otherwise, there is almost on limit on the number of unique atom is limited to 5,000 for structure refinement and 10,000 or more for all other calculation.

SHELTL is a major rewrite in order to incorporate and exploit modern structure solution and refining algorithms. These programs consist of five major sub programs and XSHELL program, developing to make the interaction with the mouse and menu feather of Windows NT, are as follows :

XPREP : This program is automatically applied for space group determination, absorption correction, scaling and merging of different data sets, index transformations, reflection statistics, reciprocal space plots and contoured Patterson section. There are mainly two stages for operating by XPREP, The first stage, XPREP reads the new data file name.raw or name.hkl (This name is generated by SADABS program, program for absorption correction with the SMART system) and parameter file name.p4p written by diffractometer controlled program. The second stage, XPREP write the crystal data file name.ins and new reflection data file name.hkl used by the XS and XL subprogram. Besides, this program writes log of all operations to the file name.prp and writes a CIF format name.pcf

XS : This program is utilized for solving structure by “phase annealing” direct method or automated Patterson interpretation based on superposition minimum functions. It reads the resulting file of XPREP program (name.ins and name.hkl) and writes the solution in the form of crystal data to file name.res and a listing file name.lst. The module calculated normalized structure factor E_s, performs the Patterson interpretation and use direct method of structure calculation. The structure

factors of all elements (but not ions) are stored internally. The program checks the symmetry data entered by a user. Because of the presence of symmetry elements, the reciprocal domain being studied will have equivalent spots ; the experimental data are survived to enable a set of independent reflection to be selected

XL : This program is used for Least - squares refinements. It reads name.res, obtained by editing the name.res (file from XS program or a previous XL job, e.g. via XP), and write the new result file name.res and new listing file name.lst. Furthermore, this program can produce the CIF format files name.cif crystal data, atoms and requirement result and name.fcf, observed and calculated structure factors.

XP : This program is the old fashion, applied for providing interactive molecular graphic and publication quality diagrams. It reads the file name.res from structure solution and requirement and it can write name.ins for next requirement run. Moreover, XP also calculated plot file (name.plt) save file (name.sav) orthogonal file (name.ort)

XCIF : This program is used for preparation of crystallographic data tables for publication via CIF format. It reads name.cif, name.pcf and name.fcf and write table.

XSHELL : This program is utilized for Least - squares refinements similar to XP, but it is powerful for graphic data or final solution plot for publications. It reads name.res and neme.hkl, obtained by editing the name.res (file from XS program or a previous XL job, e.g. via XP), and wrires the new result file name.res, new listing file name.lst and also name.cif. This program can be used together with previous five program of SHELTL NT 6.12

Xtal System

Xtal has been developed by research workers supported by grants from a wide range of agencies. The names of the program authors are listed at the start of each program description and it is important that acknowledgement is given to the authors in any resulting publications and presentations.

Most Xtal calculations are initiated and controlled from a input line file usually known as the .dat file. The results of a calculation are output to files and a screen device. Xtal calculations use various files to store intermediate and archival data. This strong dependence on files means that Xtal is considered a file - driven archival system rather than an interactive menu - driven system. This is not strictly true because of the interactive graphics programs such as PIG and PREVUE but for most calculations the file - driven approach has been adopted as the Xtal philosophy for the most efficient use of both computing and human resources.

Xtal employs two basic file types : line (character) and binary. Line files are composed of ascii text which may be manipulated with a normal text editor. The two principal line files are the line inputfile (compid.dat) and print file (compid.lst). The former contains data that determines which and how calculations are performed and the latter is the printed results of these calculations. Xtal uses other line files for certain calculations. These include a punch file, formatted sequential files, formatted direct - access files, various ancillary database files (e.g. cifmap, cifdic, symmap) and an error message file. Later there will be a more detailed description of the format of line files.

Binary files are used extensively as working files (ie. Intermediate files for exchanging within and between calculations) and to archive certain types of data. Binary files are more efficient than line files for certain operations because of their compactness and because they do not require decoding or encoding when data is extracted from or transferred to computer memory. A binary file is often referred to in Xtal documentation as a “ bdf ” (binary data file). Xtal binary files are divided

into two categories : archive and auxilliary. Archive bdf's are used as an archive record of accumulated crystal structure data. These files are updated as the analysis progresses. For example, atomic coordinates and reflection intensities are stored in an archive file. The data structure for archive files is carefully defined for all.

Auxilliary bdf's are used to transfer data from one calculation to another. They are created by a calculation for a specific data exchange purpose. Electron density maps are typical of data stored in an auxiliary file. The actual format of these files is similar to the archival files, but their contents are only known to the programs that write or read them.

Most Xtal programs employ two archive binary files ; one for input and one for output. These have filename extensions aa1 and aa2. At the start of an Xtal run the file aa1 is assumed to be the input archive file and this file will be read by the first calculation requiring data from the archive file. If a calculation adds to or changes archive data this will initially be written to the file aa2 so that it contains the latest archive data. At the close of this calculation the nucleus will reverse the roles of the two archive files so that aa2 becomes the input file and aa1 becomes the output file. This interchange process is repeated for every calculation that writes data to an archive file.