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Rietveld Refinement Using GSAS  
Program:  
Some Special Application

Presented by:

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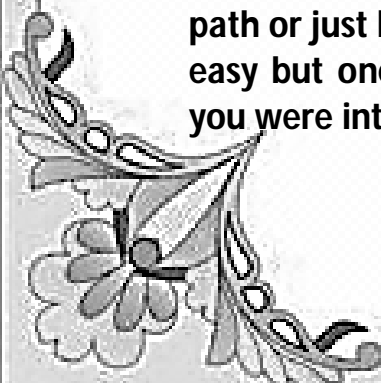
First and foremost praises and thanks  
to the God.

Almighty, for his showers of blessing  
throughout my research work to complete it successfully.

I would like to express my deep and sincere gratitude to my supervisor "Dr. BOUHDJER LAZHAR" for giving me the opportunity to do it and providing invaluable guidance throughout this experience. His dynamism, vision, sincerity and motivation have deeply inspired me. He has taught me the methodology to carry out the research and to present it as clearly as possible, and also I am grateful to my juries "PR. BEN ABBAS ABDERAHIM" and "DR. TOUKA NASSIM" who helped me to accomplish my path.

I am truly blessed to have such wonderful parents. Thank you mom and dad, everything I have and everything I am, I owe it to you. Thank you, my two life lines, getting parents like you by my side makes me what I am today. Thank you so much for supporting me unconditionally.

This achievement is dedicated to all those who have been part of my journey to this point in time. For my sisters, my light, my family and friends who've loved and supported me through the many years of work it took to arrive at this milestone, to my earliest teachers who first inspired a desire for lifelong learning. This milestone is also dedicated to those who may be starting to navigate a long path or just began dreaming about it -you can do it! It is not easy but one day you will arrive at the destination where you were intended to be.



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## General introduction

The Rietveld method for the “XRD” patterns tends to determine the phase contents and to extract detailed structural information from the powder diffraction data. Rietveld worked-out computer-based analytical procedures to make use of the entire powder pattern and putted them to the public domain by publication of two seminal papers (1967, 1969). In the Rietveld method the least squares are carried until the best fit is obtained between the observed and the calculated patterns, as we are going to see in the following chapters. We will apply this refinement method on the x-ray powder data.

X-ray powder diffraction analysis makes it possible to identify the crystalline phases present in the analyzed materials and offers the possibility of confirming their chemical composition. It also gives the possibility to evaluate their degree of crystallinity and to highlight the morphology of the crystallites which constitute them and possibly estimates their dimensions. The X-ray diffraction presents the advantage of being a non-destructive analysis method and accommodates with small samples in various forms.

The objectives of the upcoming subjects are:

- To have a brief vision on the X-ray diffraction method.
- To understand the Rietveld method and the different steps of the refinement procedure.
- To practice the acquired knowledge of the previous objective on some examples.



# CHAPTER 1

## **Introduction**

Powder X-ray diffraction is a decisive tool in identifying polycrystalline materials by their unique diffraction patterns, and is one of the best common analytical techniques for characterizing solid state materials. There are many sources and many detectors of X-rays but the purpose is one. This method can be used for phases identification, quantitative analysis, cell parameter determination, or even full crystal structure analysis using the powerful RIETVELD refinement method. The RIETVELD refinement is a technique dedicated to characterize crystalline materials, using the least squares procedure and evaluated by the criteria of fit with its precision goodness. The X-ray diffraction of powder samples results in a pattern characterized by peaks of intensity, at certain angles. RIETVELD refinement involves the fitting of a calculated profile and background to experimental data.

### **A. X-ray diffraction**

#### **Introduction**

X-rays were discovered in 8 November 1895 by the German physicist Wilhelm Conrad Roentgen, and they were so named (Roentgen) because their nature was unspecified at that time. Unlike ordinary light, these rays were invisible, but they traveled in straight lines and affected photographic film in the same way that light did. Unlike visible light, X-rays were much more penetrating and could easily put to use to study the internal structure of objects that seemed transparent to them and opaque to ordinary light. Until 1912, the main limitation in this period was the source, but that didn't prohibit the introduction of X-rays into medicine and engineering going along with a progress in both the theoretical understanding of the interaction of X-rays with the matter, and in our knowledge of how exploit them experimentally.[1][2][3]

#### **1. Definition**

Radiation may be defined as energy, it might take the form of waves and particles, emitted from its source through space in straight lines, however, electric and/or magnetic field can carry away the rays in the form of charged particles from its linear course. All types of radiation have a dual nature, where the discrimination of properties will be done by giving the best explanation in terms of particles or in terms of waves.[3]

X-ray are defined as electromagnetic waves possessing the same nature of light but with a very much shorter wave length between  $10^{-2}$  to  $10^2 \text{ \AA}$  , produced by deceleration of high-energy electrons or electron transitions in the inside orbits of atoms. These waves are situated between gamma and ultra-violet rays in the complete electromagnetic spectrum. The waves lying nearly in the range  $0.5\text{-}2.5 \text{ \AA}$  are used in diffraction, since they are in the same order of magnitude of the shortest interatomic distances in organic and inorganic materials .[4][5]

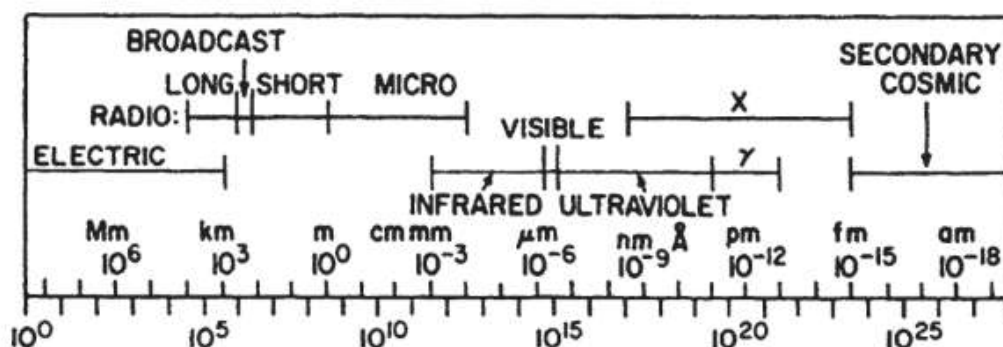


Figure1.1: Electromagnetic spectrum

## 2. Properties

The following up are the main properties of X-rays and the application of each in spectro-chemistry. X-rays propagate with the velocity of light ( $c = 3 \times 10^8 \text{ m/s}$ ), with wave length  $\lambda$  and frequency connected to each other by[4]:

$$\lambda = \frac{c}{\nu} \quad (1.1)$$

X-rays as continuous non-characteristic spectra or as straight lines undeflected by electric or magnetic fields, experience differential absorption in matter and they produce characteristic absorption spectra, so it demonstrates a wave-particle duality and we get to understand those properties when we consider the beam of X-rays as stream of photons which are characterized by their energy  $E$  and their momentum  $p$ , related to  $\lambda$  and  $\nu$  [4][5]:

$$E = h\nu \quad (1.2)$$

And:

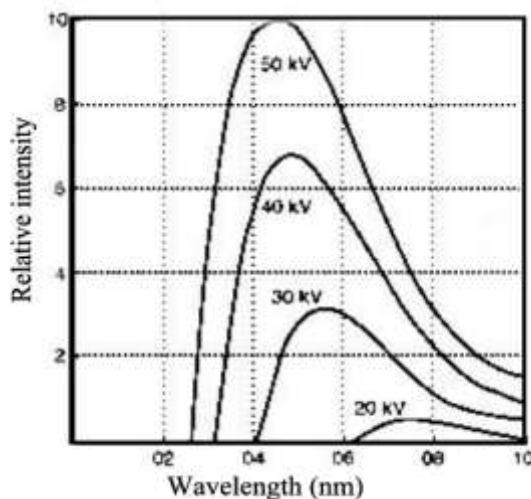
$$p = \frac{h}{\lambda} \quad (1.3)$$

X-rays might cause[4]:

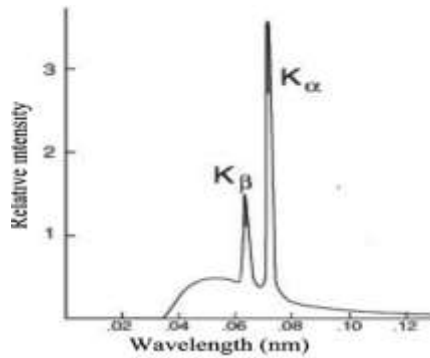
- Ionization in gases, liquids and solids
- Permanent physical damage and damages in genetic change in biological tissue.
- Stimulate photolysis with temporary or permanent effect.
- Excite photo-Auger and Compton-recoil electrons in matter.
- Excite visible and ultraviolet luminescence in certain materials.

### 3. X-rays sources

X-rays are produced when any electrically charged particle of enough kinetic energy decelerates rapidly. We use commonly electrons for this purpose; the radiations will be generated in an X-ray tube which is combined of a source of electrons and two metal electrodes. The high voltage maintained across these electrodes, carries the electrons fast to the anode, or to the target which they strike with really high velocity, Then electrons transmit their energy to the atoms of the target and they return to a more stable energy level passing by a series of electronic transitions, this process named braking radiation: the X-ray radiations do not have a specific wavelength and the emission spectrum is continuous and it intensity grows up with the acceleration voltage.[2][6][7]



a) Braking radiation.



b) Characteristic radiation

**figure3.1:** Emission spectrum of a molybdenum anode bombarded with an electron beam

The most applied source of the X-rays is the X-ray tube, which has many types for several applications. Any X-ray tube must contain a source of electrons (anode), a high accelerating voltage and a metal target (cathode), which must be water-cooled to protect it from melting because the ultimate of the kinetic energy of the electrons is transformed into heat. X-ray tubes are divided into two basic types depending on the way that electrons are provide: Crooks tubes in which electrons are produced when a small quantity of gas is ionized in the tube, and Coolidge tubes in which the source is a hot filament.[2][7]

a) Crooks tubes

This kind of tubes was the one used by Rontgen, who discovered X-rays in 1895. The tubes is attached to a pumping unit, which take in a gas at a very low pressure, between the two electrodes situated inside the tube exists an electrical discharge, the trauma of the positive ions against the cathode results the emission of electrons. These electrons bombard the anticathode which itself emits de-excitation X-rays.[7]

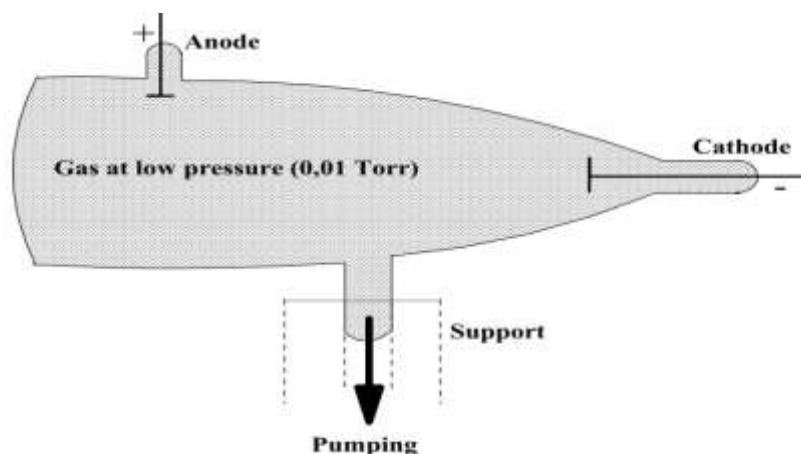
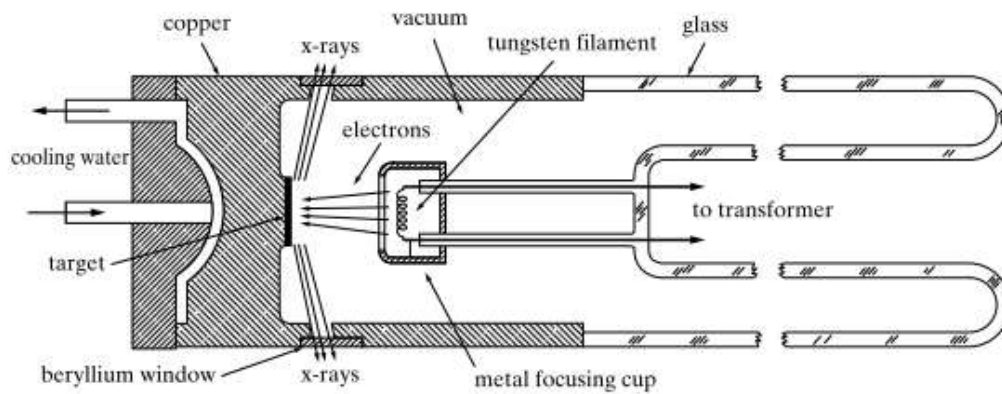


Figure 3.2: Schematic view of a crooks tube

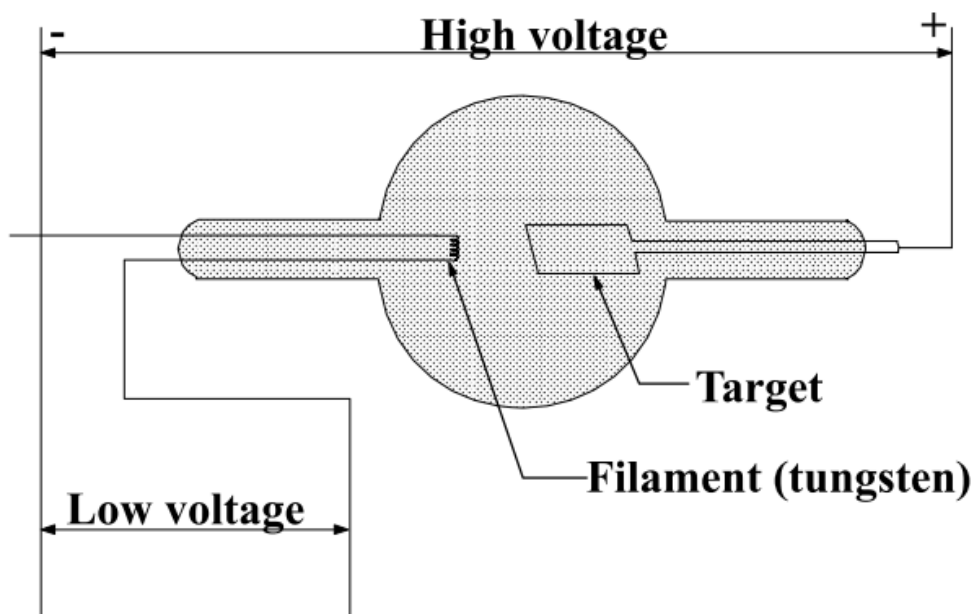
The flows of this types of tubes , is that the intensity of the discharge current inside of it is highly depending on the gas pressure and the anticathode's life is short; but as a benefit the surface of it is pure so that results pure emitted X-rays. These tubes are no longer in use.[7]

### b) Coolidge tubes

Invented by Coolidge in 1913 as another source of X-rays and yet the vastly used. They are formed of an evacuated glass envelope which separates the anode from the cathode, the cathode is a tungsten filament heated by the joule effect and based on the Edison effect, this filament diffuse electrons going under an electrical field and will hit the anticathode which a water-cooled block of copper (desired target as an insert at the one end), the impact will give birth to the X-rays emission.[7][6]



**Figure 3.3:** Cross section of sealed X-



**Figure3.4:** Schematic view of a Coolidge

### c) Synchrotron Radiation

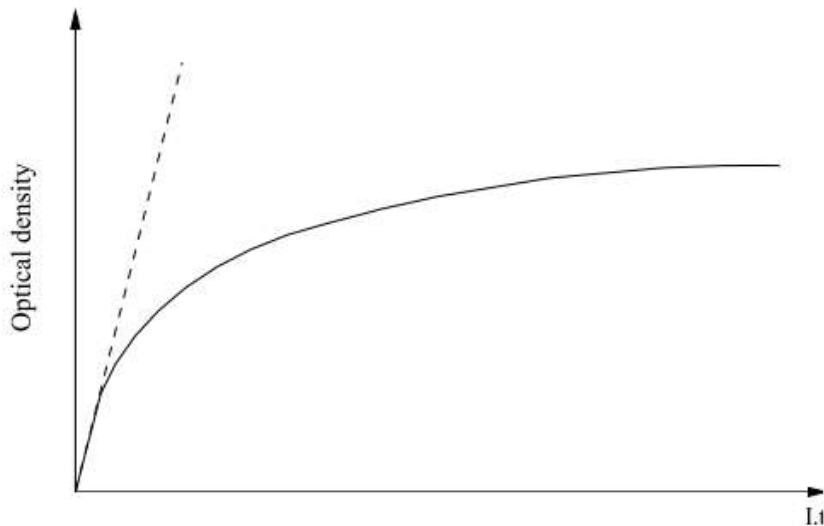
It occurs when the electrons or positrons with relativist velocities adapt a curved trajectory under the effect of a magnetic field, results a continuous spectrum, and for many purposes it is the best source of X-rays , including diffraction.[6]

## 4. X-ray detectors

The detector do transform the individual X-ray photons into voltage pulses that are calculated and/or integrated by the counting tools, authorizing diverse forms of visual indication of X-ray intensity to be achieved. Detectors used in typical X-ray powder diffractometers have a common thing, they depend on the ability of X-rays to ionize matter; by following three specific properties which are: quantum counting efficiency, linearity, and proportionality.[8]

### a) Photographic detectors:

These films were the first X-rays detectors, used by Rontgen to show the being of the X radiations. In the same as light, X-rays reduces silver halides with the ability of producing images on photographic film. The darkening of this latter is related to the intensity of the X-ray beam.[7]



**Figure 4.1:** Darkening of film according to the intensity of the beam that irradiates it.

### b) Gas detectors

The way that these detectors work based on the fit of electrical current coming of the ionization of the atoms in a gas irradiated by an X-ray beam.[7]

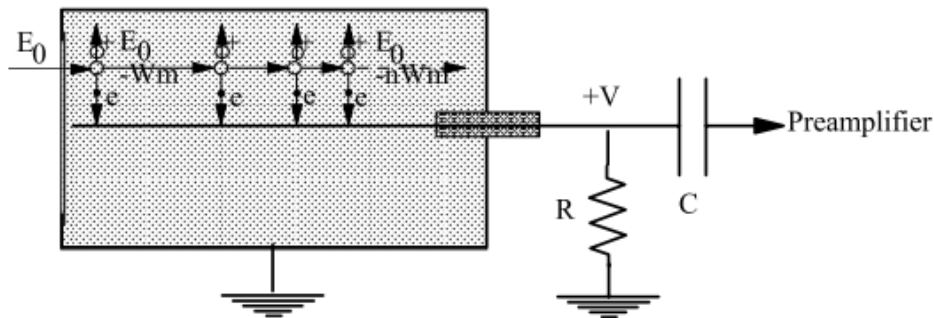


Figure 4.2: how a gas detector works

### c) Solid detectors

It contains:

- Detectors that uses fluorescence in the visible spectrum:

Some bodies can emit light radiation when they are irradiated with electrons or X-rays. As it is the concept of Luminescence as the emission of seen electromagnetic waves coming out of a non-thermal origin.

- Semiconductor detectors:

A diode of a semiconductor single crystal of silicon, or Germanium doped with lithium absorbs the X-ray waves, so the out coming electrons stimulate electronic transitions in the valence and conduction bands of the silicon atoms.[7]

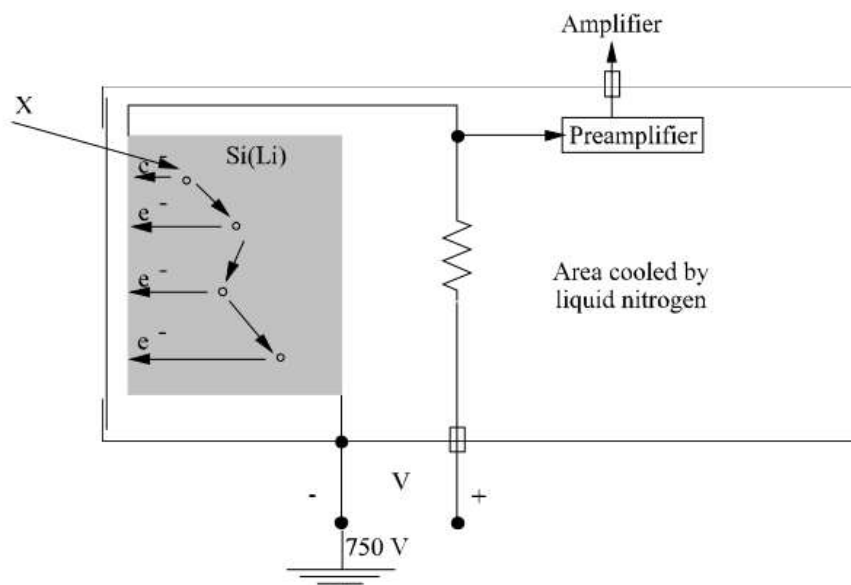


Figure 4.3: Diagram of how a semiconductor detector works



## 5. Techniques of X-rays

These analytical methods give us qualitative and quantitative details on the precise compositions of materials. Among these techniques, there are: XRF technique, PIXE and RX.[9]

### a) XRF:X-ray Fluorescence spectrometry

Is a non-destructive technique used to identify elements and determine their concentrations in solid, powdered and liquid samples. This technique has inherent design borders, which led to a reduction of sensitivity to lower atomic number elements. It's based on X-ray emission theory.[9]

### b) PIXE: Particle induced X-ray emission spectrometry

Defined as a powerful technique used to determine the elemental composition of a solid, liquid, thin film, and aerosol filters samples; it is based on the analysis of the energy spectra of X-rays emitted by the de-excitations of the atoms in the sample bombarded with high-energy protons with the aid of a suitable energy dispersive detector.[9]

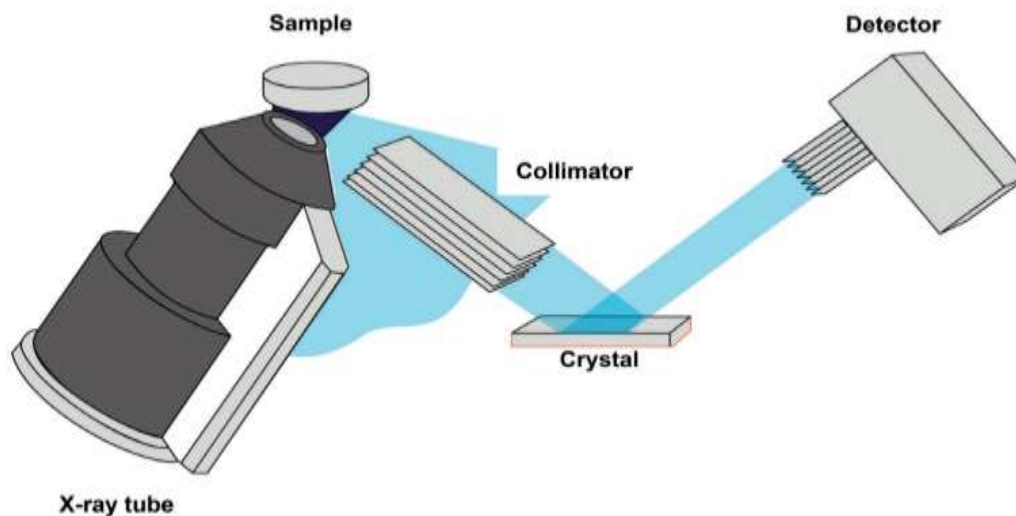


Figure 5.1: X-ray fluorescence spectrometer set-up

### c) XRD: X-RAYS Diffraction

Analytical technical technique to generate X-rays, the scattering is established when a material sample is exposed to radiation, in cylindrical or pellet form. The morphology of the sample defines the nature of scattering and can be coherent or incoherent. Different crystalline phases are identified and quantified in powdered and solid samples, this method includes diffraction on single crystal and powder diffraction[9],

- **Powder diffraction**

Used in the refinement of structure characteristics, identification of unknown solid-state materials and determination of the particle size of phases. and that we will see it farther in chapter 2.

- **Single crystal**

It provides fundamental knowledge of structural nature of the sample , and gives the best tools to understand atomic positions and compositions.[9]

## B. RIETVELD refinement

### Introduction

The last stage of structure determination is the Rietveld method. To determine the unknown structures, we go through a chain of hypotheses of lattice, space groups, atomic structure, each of which is subject to upcoming affirmation, so this method is the least examination of the authenticity of a structure.

#### 1. Definition

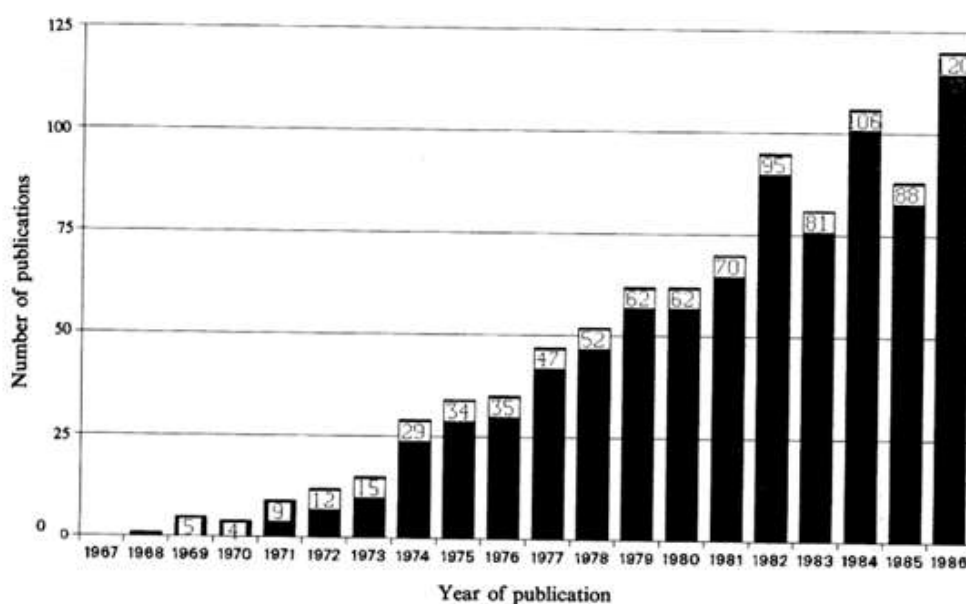
The Rietveld method is a complicated downsize process, it is not an activated appliance for ab initio crystal structure examination, it counts on outer former knowledge and can modestly edit a prejudged paragon created by using the step intensity  $Y(i)$ , where each datum is taken as an observation. The onset parameters for such a paragon need to be near to the final values. Moreover, the order into which the various parameters are being refined must be attentively studied.[10]

The quantity of structural detail that we can receive ordinarily from powder diffraction pattern has greatly enlarged by the Rietveld method, where we adjust structural parameters such as atom coordinate, thermal motion, and site occupation parameters in a least-squares refinement process until the best fit is obtained between entire calculated and observed powder diffraction patterns, as a whole.[11]

This method gives a benefit the efficient reduction or elimination of improprieties arising from preferred orientation, particles statistics, micro absorption, peaks overlapping, and the tracing shapeless phase and trace phases.[12]

## 2. Historic

The Rietveld method had its first appearance at the I.U.C.R. Congress in Moscow in 1966, but the answer to it was in 1969 after the full package of the method was released and published. At this time, the refinement was based on the neutron diffraction, until 1977 the refinement method was used for X-ray powder diffraction as well. This method brought a fixed wavelength and fixed angle, where it credits goes to the Rietveld genuine paper which was published in the science citation index and been developed and approved by to many other authors, therefor the method improved and got acceptance.[13]



**Figure 2.1:** Number of publications between 1967 and 1986 with references to the publications by Rietveld (1967 - 1969) and/or the presence of the name Rietveld in the title.

### 3. The method

#### a) Mathematical aspects of the Rietveld refinement

- The method of least squares:

The least squares method is powerfully used to estimate the values of the adjustable parameters in a model,  $\mathbf{M}(\mathbf{x})$ , it predicts values of a set of observable quantities,  $\mathbf{y}$ . One seeks the minimum, as a function of  $\mathbf{x}$ , of the quadratic form.[13]

$$Q = [\mathbf{y} - M(\mathbf{x})]^T W [\mathbf{y} - M(\mathbf{x})] \quad (1.1)$$

$\mathbf{W}$  is a weight matrix that should be defined as a positive, the singular observations,  $\mathbf{y}_i$ , are being drawn randomly from a population whose means  $\mathbf{M}(\mathbf{x})$  when  $\mathbf{x}$  is a correct unknown value, otherwise said,  $\langle \mathbf{y} \rangle = \mathbf{M}(\mathbf{x})$ , if the model is linear, so that  $\mathbf{y} = \mathbf{A}\mathbf{x}$ , then  $\hat{\mathbf{x}}$  the set of parameters that minimizes  $Q$ . [13]

$$\hat{\mathbf{x}} = (\mathbf{A}^T \mathbf{W} \mathbf{A})^{-1} \mathbf{A}^T \mathbf{W} \mathbf{y} \quad (1.2)$$

It is known as the least squares estimate.

It is an estimate because it is based on random variables taken from a population with a mean and a variance, if the mean of this population is equal to the correct value, if  $\langle \hat{\mathbf{x}} \rangle = \mathbf{x}_c$  then the estimate is said to be unbiased [14]. For the least squares estimate:

$$\begin{aligned} \hat{\mathbf{x}} &= \langle (\mathbf{A}^T \mathbf{W} \mathbf{A})^{-1} \mathbf{A}^T \mathbf{W} \mathbf{y} \rangle = (\mathbf{A}^T \mathbf{W} \mathbf{A})^{-1} \mathbf{A}^T \mathbf{W} \langle \mathbf{y} \rangle \\ &= (\mathbf{A}^T \mathbf{W} \mathbf{A})^{-1} \mathbf{A}^T \mathbf{W} \mathbf{A} \mathbf{x}_c = \mathbf{x}_c, \end{aligned} \quad (1.3)$$

So that the least squares estimate is unbiased irrespective of the choice of  $\mathbf{W}$ .

If, however, the joint probability density function of the populations from which the observations,  $\mathbf{y}_i$ , are drawn has variance-covariance matrix  $\mathbf{V}_y$ , and  $\mathbf{W} = \mathbf{V}_y^{-1}$ , then the variance of the population distributions for the elements of  $\hat{\mathbf{x}}$  can be shown to have the lowest values that they can have for any choice of  $\mathbf{W}$ , the certain least squares estimate[14]:

$$\hat{\mathbf{x}} = (\mathbf{A}^T \mathbf{V}_y^{-1} \mathbf{A})^{-1} \mathbf{A}^T \mathbf{V}_y^{-1} \mathbf{y} \quad (1.4)$$

Equation (1.4) is the best unbiased of  $\mathbf{x}$ .

The models for many important phenomena are non-linear. So the usefulness of least squares method to these models is to find numerical methods, as set of parameters values  $\mathbf{x}'$  close enough to a point at which the gradient of  $Q$  vanishes for the approximation[14]:

$$M_i(x) = M_i(x') + \sum_{j=1}^p (x_j - x_j') \frac{\partial M_i(x')}{\partial x_j} \quad (1.5)$$

to be a good one.  $A_{ij}$  is then equal to  $\frac{\partial M_i(x')}{\partial x_j}$  and the least squares estimate is:

$$\hat{\mathbf{x}} = \mathbf{x}' + (A^T W A)^{-1} A^T W [y - M(\mathbf{x}')]. \quad (1.6)$$

Because the approximation in equation (1.5) is mostly valid when  $\mathbf{x}' = \mathbf{x}$ , it is usual to repeat until full convergence. It is important to distinguish between  $\mathbf{x}'$  which is arbitrary and  $\hat{\mathbf{x}}$  which is a random variable drawn from a population whose mean is  $\mathbf{x}'$ . [14]

- **The Rietveld model**

The observations are the raw data, the amount of X-ray photons or neutrons counted at a point is a powder diffraction pattern. [14] The Rietveld model is:

$$M(S_i, x) = b(S_i, x_b) + \sum_{k=k_1}^{k_2} I_k(x_s) \phi(S_i - S_k, x_p) \quad (1.7)$$

Where  $\mathbf{x}_b$ ,  $\mathbf{x}_s$  and  $\mathbf{x}_p$  are background, structure, and peakshape parameters, respectively, and  $S_i = 2 \sin \theta_i / \lambda_i$ . Either  $\theta_i$  or  $\lambda_i$  can be under control experimental variable. [14]

The background function is represented by the term  $b(S_i, x_b)$ , where  $I_k(x_s)$  is the integrated intensity of the  $k$ th Bragg reflection,  $\phi(S_i - S_k, x_p)$  is a peakshape ('profile') function settled so that the total over the range of the peak 1, and the totality is over the reflections that may participate to the intensity at  $S_i$ . [14]

A main side of Rietveld's contribution was the recognition that when  $\phi$  is known, the contained information is overlapping peaks aren't totally lost only if they exactly coincide.[14]

- **Background**

Background is a smooth function that runs slower with  $S$  than does with diffraction pattern. It might have diffraction patterns of additional

phases with known structure. The smooth part might be illustrated by a polynomial, or a sum of polynomials, each term of which has a linear scale factor. The presentation of the impurity phase part is a pattern dignified from a pure sample of that phase, or calculated from its structure as if it had measured, under the conditions of the experiment, multiplied by a scale factor. The coincident refinement of two or more phases of unknown structure is controversial.[14]

### **b) Rietveld with X-ray powder diffraction**

At first Rietveld's method work was applied on neutron diffraction then he expended his work to X-ray data, but he didn't really applied it because there were a lack of an actual problem, but found it way into X-ray data much later and more slowly. The scientists hesitation was based on considerable complex profiles in X-ray patterns, because these profiles were different from the Gaussian profiles in neutron diffraction, and they do vary strongly with the scattering angle. [10]

The new Rietveld's program can solve any scattering problem in the X-ray data, it is written by FORTRAN IV and contains about 5000 FORTRAN statements, built in a direct applicability with all space groups and scattering factors for all elements, either numerical or as coefficients of an exponential description, plus anomalous scattering corrections and also nuclear scattering lengths when used with data from thermal neutron scattering. The program then generates the multiplicities. [10]

### **c) Computer programs**

As a start the computer programs for X-ray Rietveld analysis were modified from the original program. Lately, many new programs have been written. In the case of the X-ray angle dispersive, the programs and their characteristics are represented in table 2. The non being of any check mark at any data it means that we don't know if this program have it and doesn't mean the lack of it.[17]

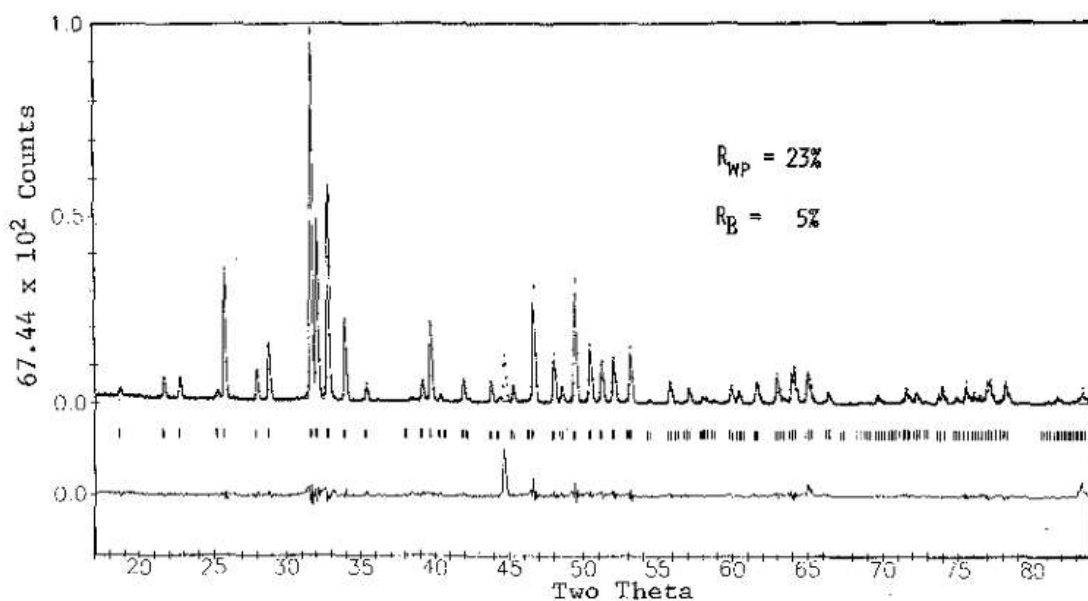
FEATURE	PROGRAM							
	RMT	RHVM	RKC	RWSMT	AI	BH	DBW 2.9	TOR
ALL SPACE GROUPS					✓		✓	✓
SINGLE PASS							✓	✓
MODULAR					✓		✓	
ANSI					✓		✓	
MULTIPHASE				✓			✓	
GEN. COORD.					✓			
CONSTRAINTS		✓			✓	✓	✓	
ANOM. DISPERSION		✓					✓	
R's IN SHELLS					✓			
DATA TYPE	1	2	3	1	2	2	2	2
USED BY OTHERS	✓	✓					✓	
BACKGROUND					✓		✓	✓

**Table1:** programs for Angle

In this table, 'all space groups' refers that program is directly applicable with no additional programming required for any space group. 'single-pass' is access with no preparatory programs in need, get in the program with the data and get out with the refinement results. 'generalized coordinates' are variables resulting from the application of the constraints in such a way as the reduction of the size of the normal matrix. 'R's in shells' indicates that the program can provide separate R factors for different spherical shells in reciprocal space. [17]

#### d) Criteria of fit

A visual informative criterion of fit is a composite plot. As in the upper part, the dots with vertical lines show the examined data. The continuous curve in the calculated pattern obtained from the refined model. The series of short, gives the positions of possible Bragg reflections. The lowest curve refers to the difference between calculated and observed patterns. [17]



**Figure 3.1:** X-ray (CuKa) powder diffraction pattern-fitting (refinement R168)

for hydrothermally prepared OHAp.

The main benefit of this comparison then seeing a good fit is that the information conveys about details about details in the remaining misfit. [17]

#### **e) Precision**

The precision in structural parameters reviewed by Young (1980) for X-ray Rietveld refinements are being ranged from  $10^{-4}$  to  $10^{-2}$  of the cell edge with an average of  $10^{-3}$ , which can be compared to an average of  $\sim 10^{-4}$  for good single-crystal work. [17]

## **CONCLUSION**

The structural determination and its refinement of poly-crystals are being routinely carried out using X-ray powder diffraction with crystallographic software based on the RIETVELD method, at large, structure determination from X-rays powder data and single crystal data may not be the new approach. However, handling the X-ray powder data to identify the unknown stone by determining its molecular structure through RIETVELD method could be the beginning of the history of Forensic science.



# CHAPTER 2

## **INTRODUCTION**

In the previous chapter, we talked about the X-rays diffraction. In this chapter we will briefly introduce the X-rays “Powder” diffraction case instead of the “single crystal” case. It begins by understanding the origin of powder and how it affects the data parameters; next, these later will be analyzed in the second part of the chapter by the GSAS analysis and by using the “EXPEDIT” software.

### **A. powder diffraction**

#### **1. What's powder ?**

The word powder does not earn the same meaning in powder diffraction field as in common language, in powder diffraction it may mean a solid substance divided to very small pieces, or also a solid block or even a thin film or liquid, because in the powder diffraction experiment the powder is defined by the important parameters as the numbers and size of particular crystallites as much as they are small and arbitrary oriented as more are perfect for the experiment.[10]

#### **2. What's and why powder diffraction**

Powder diffraction is one the strongest methods for studying the atomic structure of real materials. It is a very quick and a very multi-skilled analytical method.[10,15]

It is used in the identification of crystalline phases for quantitative determination of their volume fraction in mixed-phase sample. And more often used to solve problems of structure definition and refinement that have long time been the exclusive domain of single crystal diffraction and it describes the composition, the structural discover, microstructure of any crystalline material.[16]

There are many reasons why we use the powder diffraction analysis instead of single crystal analysis. Very often single crystals are not reachable, at least not in the required quality or size for single crystal work. Second, polycrystalline samples can be delivered under “extreme” conditions, as high and low temperature in or out of high pressures without too much hardness. Third, minor impurities are not a severe problem, and finally exposure times can be very short, even in terms of  $\mu\text{s}$ . [10]

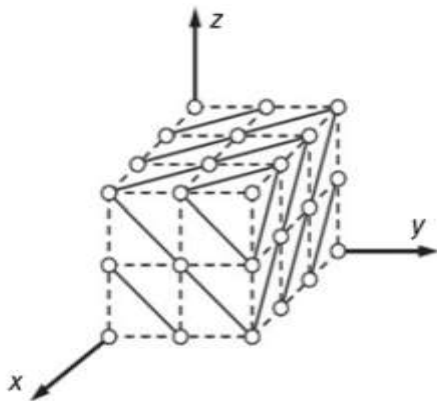
The method has been applied longer and more widely on neutron data, but lately it is affirmed to be more effective with X-ray data. Earlier methods of using X-ray powder patterns of structure analysis have been useful and sometimes innovative.[11]

### a. The Bragg equation

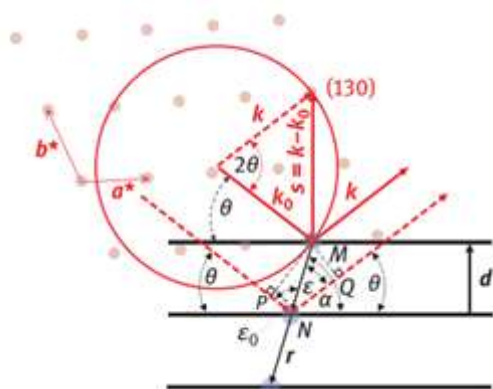
The easiest access to the structural details in powder diffraction is through the well-known Bragg equation, which describes the precept of X-ray diffraction in terms of a reflection of X-ray by sets of lattice planes. [17, 15]

Lattice planes defined as crystallographic planes, recognized by the miller indices  $hkl$ . The parallel planes have the identical indices and spaced evenly, separated by the distance  $d_{hkl}$ . [17]

Bragg analysis treats X-rays like visible light being reflected the surface of a mirror, with the X-rays being reflected specularly at the lattice planes. The X-rays penetrate deep inside the material where additional reflections occur at thousands of consecutive parallel plane. Since all X-rays are reflected in one direction, superposition of the dispersed rays occurs. [17]



**Figure 2.1:** Schematic drawing of a set of parallel lattice planes (111) passing through all points of the cubic lattice.



**Figure 2.2:** Schematic illustration of the geometry required to derive Bragg's law.

Even this isn't a well pictured of what is going on physically, it can be related to the Ewald approach given above using Figure (2.2) [15].

The non-even lengths of X-rays/neutrons emerged from atoms in different planes results a phase shift. [15]

$$\begin{aligned}\Delta &= PN + NQ = (MN) \cos \varepsilon_0 + (MN) \cos \varepsilon \\ &= (MN)[- \cos(\alpha + \theta) + \cos(\alpha + \theta)] \\ &= (MN)[2 \sin \alpha \sin \theta]\end{aligned}\quad (2.1)$$

With

$$d = (MN) \sin \alpha \quad (2.2)$$

For constructive interference,  $\Delta$  must be a multiple  $n$  of the wavelength  $\lambda$ , which tight away takes us to the Bragg equation:

$$n\lambda = 2d \sin \theta. \quad (2.3)$$

For the benefit,  $d$  is usually divided by  $n$  so:

$$\lambda = 2 \frac{d}{n} \sin \theta = 2d_{h\bar{h}\ell} \sin \theta. \quad (2.4)$$

Bragg's law can be presented in vector notation (Figure 2.2). Where the scattering vector  $\mathbf{s}$  is always perpendicular to the scattering plane, and the difference between the wave vectors of the incoming and outgoing beams given by  $\mathbf{K}_0$  and  $\mathbf{K}$ , respectively:

$$\mathbf{s} = \mathbf{K} - \mathbf{K}_0 \quad (2.5)$$

By setting the magnitude of  $\mathbf{k}_0$  and  $\mathbf{K}$  to  $1/\lambda$  (the radius of the Ewald sphere) brings it to the Bragg equation in the side of the aspect of the magnitude of the scattering vector  $\mathbf{s}$ :

$$s = d_{h\bar{h}\ell}^* \quad (2.6)$$

The appearance of the Bragg's law is defined as sharp spots of high intensity that stand out from the crystal-lite in particular directions presented by the Bragg equation, where between the bragg spots and each set of crystallographic planes exists a one-to-one correlation. Each Bragg spot is therefore categorized by the same setoff miller indices,  $h\bar{h}\ell$ , as the set of planes that led to it. The orientation averaging that created the Debye-Scherrer cone is becoming a sharp peak in one dimensional powder pattern.[15]

In powder patterns of real samples, peaks will invariably be enlarged. We can estimate one widening source by calculating the total derivate of the Bragg equation with the d-spacing as the topic, by applying the chain rule, we get:

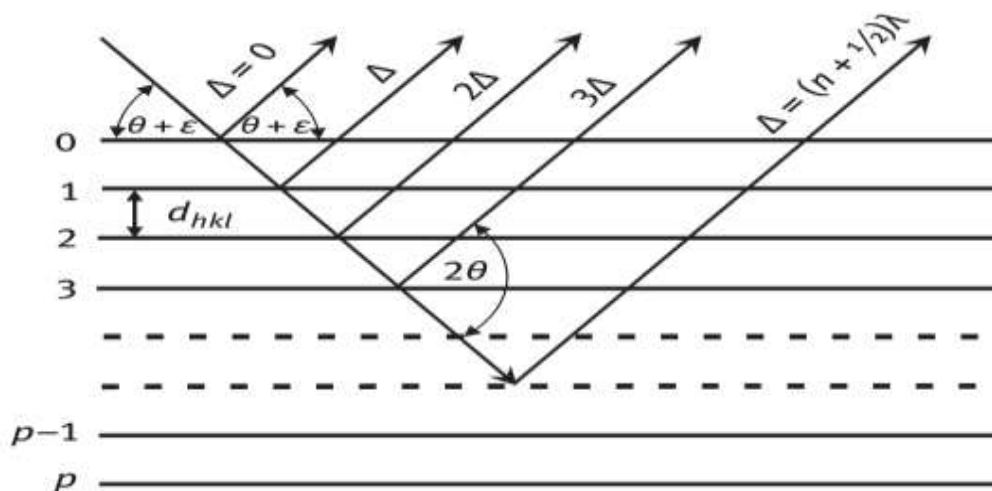
$$dd = \frac{\partial d}{\partial \theta} d\theta + \frac{\partial d}{\partial \lambda} d\lambda = \frac{n\lambda}{2 \sin \theta} \frac{\cos \theta}{\sin \theta} d\theta + \frac{n}{2 \sin \theta} d\lambda \quad (2.7)$$

Which it simplification is:

$$\frac{dd}{d} = \frac{d\theta}{\tan \theta} + \frac{d\lambda}{\lambda} \quad (2.8)$$

The dimensionless quantity  $\frac{dd}{d}$  can be a microscopic stain as interpretation. Any contrast in the d-spacing within a crystallite will rise up a strain peak broadening  $d\theta$ .

Limited crystalline domain size is a second source of broadening. If there is an assumption of infinite pile of lattice planes, the Bragg equation gives the position of  $\delta$ -function Bragg peaks. If the angle between the incoming beam and the lattice plane  $\theta$  is different by an amount  $\epsilon$  from the Bragg condition, there will be a lattice plane for which the heaped up extra path length produces a phase shift of  $(n+1/2)\lambda$  causes a destructive interference (figure 2.3). For a thick crystal this will happen for an arbitrarily tiny  $\epsilon$ , this is the explanation why Bragg reflection are sharp. [15]



**Figure 2.3:** path length difference of the scattered ray versus the depth of the lattice plane in the crystal (adapted from Dinnebier & Billinge (2008) with permission from The Royal Society of Chemistry).

If the size of crystallites is restricted, the situation changes; and in this case, for small  $\epsilon$  the plane for which  $\Delta$  holds may not be illustrated in the crystal, this is getting us to an intensity divisions over some small angular range in  $\theta$ . This is called size expansion and is illustrated by the Scherrer equation (Klug and Alexander, 1974). We can get the Scherrer equation by considering the crystallite in (Figure 2.5), which will have a thickness in the way perpendicular to  $p+1$  lattice planes of separation  $d_{hkl}$  (Figure 2.3) of

[15]:

$$L_{hkl} = p d_{hkl} \quad (2.9)$$

The additional beam path  $\Delta$  between successive lattice planes at the angle  $\theta + \varepsilon$  is:

$$\begin{aligned} \Delta &= 2d \sin(\theta + \varepsilon) = 2d(\sin \theta \cos \varepsilon + \cos \theta \sin \varepsilon) \\ &= n\lambda \cos \varepsilon + 2d \cos \theta \sin \varepsilon \approx n\lambda + 2d \varepsilon \cos \theta. \end{aligned} \quad (2.10)$$

The difference in the phase is then:

$$\varphi = 2\pi \frac{\Delta}{\lambda} = 2\pi n + \frac{4\pi \varepsilon d \cos \theta}{\lambda}. \quad (2.11)$$

The difference in the phase  $\varphi_L$  between the top and the bottom layer  $p$  is as follow:

$$\varphi_L = p \frac{4\pi \varepsilon d \cos \theta}{\lambda} = \frac{4\pi \varepsilon L_{hkl} \cos \theta}{\lambda}. \quad (2.12)$$

If  $a$  is the amplitude of a wave diffracted at a solo lattice plane, then according to Klug and Alexander (1974), as result the amplitude of all diffracted waves is [17]:

$$A = a p \frac{\sin(\varphi_L/2)}{(\varphi_L/2)} \quad (2.13)$$

When the amplitude is at maximum  $A_0 = a$  at  $\varepsilon = 0$ . Half ultimate intensity is then:

$$\frac{A^2}{A_0^2} = \frac{1}{2} = \frac{\sin^2(\varphi_L/2)}{(\varphi_L/2)^2} \quad (2.14)$$

It would be satisfied for:

$$\frac{\varphi_L}{2} = 1.4 \quad (2.15)$$

We can deduce the approximation of the misalignment angle at half maximum intensity the use of eq. (2.16)

$$\varepsilon_{1/2} = \frac{2.8\lambda}{4\pi L_{hkl} \cos \theta}. \quad (2.16)$$

The width of measured angular fwhm<sub>hkl</sub> between the two points of half maximum intensity on a  $2\theta$  scale leads to the Scherrer equation [17]:

$$\text{fwhm}_{hkl} = 4\varepsilon_{1/2} = \frac{0.89\lambda}{L_{hkl} \cos \theta}. \quad (2.17)$$

Due to the finite particle size this measures the peak width in radians. The

prefactor is based on the grain's shape but it's also close to the unity. We take as note that this equation isn't valid for very small or very large crystallites because for the large ones the peak width is ruled by the coherence of the incident beam and not by the particle size. In other hand for the nano-scale crystallites, the Bragg's law is not satisfied and it has to be replaced by the Debye Equation, as we can see in the next section.

### b. The Debye equation

Totally, diminishing the size of a crystal leads to a rise in Bragg's peaks width as we have seen in the last part. Where the size of the crystallites goes very small, the width of the Bragg peaks is so large that they expand and over-lap and it won't make sense any longer to use  $\delta$ -function Bragg peaks as the beginning point for the analysis. Even though the coherent diffraction is shown in nature and distributed through reciprocal space at this point, it still earns useful structural information. [15]

Under the postulate that only elastic scattering occurs and the photon are being scattered once for each, then for an ensemble of  $n$  atoms at fixed positions without periodicity the structure amplitude is given by [17]:

$$A(s) = \sum_{j=1}^n f_j(s) e^{2\pi i s \cdot x_j} \quad (2.18)$$

With the conjugate complex as follow:

$$A^*(s) = \sum_{j=1}^n f_j(s) e^{-2\pi i s \cdot x_j} \quad (2.19)$$

The intensity would be calculated as follow:

$$I(s) = |A(s)|^2 = A(s)A^*(s) = \sum_{j=1}^n \sum_{k=1}^n f_j(s) f_k(s) e^{-2\pi i s \cdot r_{jk}} \quad (2.20)$$

Where  $r_{jk} = x_k - x_j$  is the vector between the atoms  $j$  and  $k$ . for a simple diatomic molecule (Figure 2.4), it would be:

$$\begin{aligned} I(s) &= f_1(s)^2 + f_2(s)^2 + f_1(s)f_2(s)e^{-2\pi i s \cdot r_{12}} + f_1(s)f_2(s)e^{2\pi i s \cdot r_{12}} \\ &= f_1(s)^2 + f_2(s)^2 + 2f_1(s)f_2(s)\cos(2\pi s \cdot r_{12}) \end{aligned} \quad (2.21)$$

Eq. (2.24) gives simplification for the homonuclear diatomic molecule with  $f_1(s) = f_2(s)$  to:

$$I(s) = 2f_1(s)^2(1 + \cos(2\pi s \cdot r_{12})) \quad (2.22)$$

For example, the  $O_2$  gas, scattering from an individual molecule will be coherent but doing it from different molecules will be incoherent. So in this situation we will notice scattering sum from all the present molecules, which its orientation is relative to the beam with same probability.

It is the necessity of choosing the average of the scattering taking us to

spherically averaged intensity. The outcome is the Debye equation, which its derivation is as below:

According to the first step of eq. (2.21), eq. (2.22) can be rewritten as:

$$I(s) = \sum_{k=1}^n f_j(s)^2 + \sum_{j=1}^n \sum_{k=1, k \neq j}^n f_j(s) f_k(s) e^{2\pi i s \cdot r_{jk}}. \quad (2.23)$$

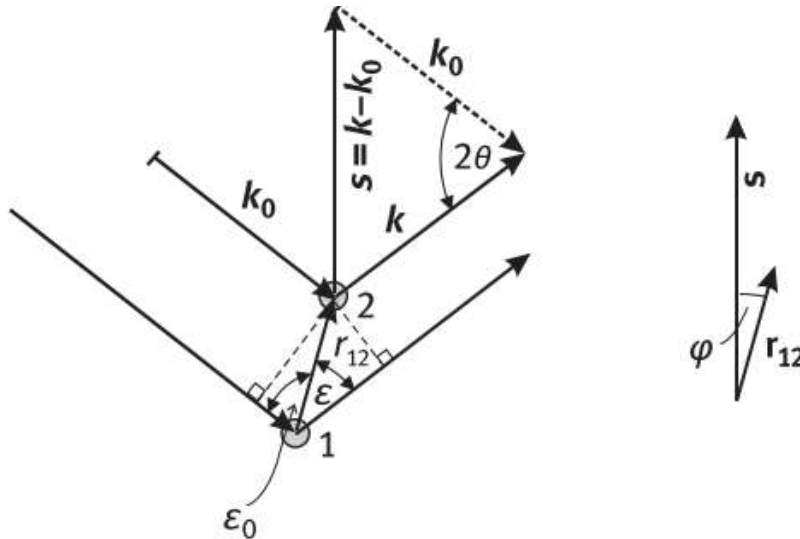
The double sum in eq.(2.27) has  $n(n - 1)$  addends, which can be gathered into  $\frac{1}{2}n(n - 1)$  pairs of addends describing the exact atom-atom pair with the distance vectors  $r_{jk}, r_{kj} = -r_{jk}$ . Subsequently the hence corresponding pairs of addends are complex conjugates. The division of each addend can be rewritten as follow:

$$I(s) = \sum_{k=1}^n f_j(s)^2 + \sum_{j=1}^n \sum_{k=1, k \neq j}^n f_j(s) f_k(s) \cos(2\pi s \cdot r_{jk}) \quad (2.24)$$

Let's see it as a random addend of the double sum, and suppose that the angle  $\varphi$  between the scattering vectors and the direction vector  $r_{jk}$  between two atoms j and k. (Figure 2.4):

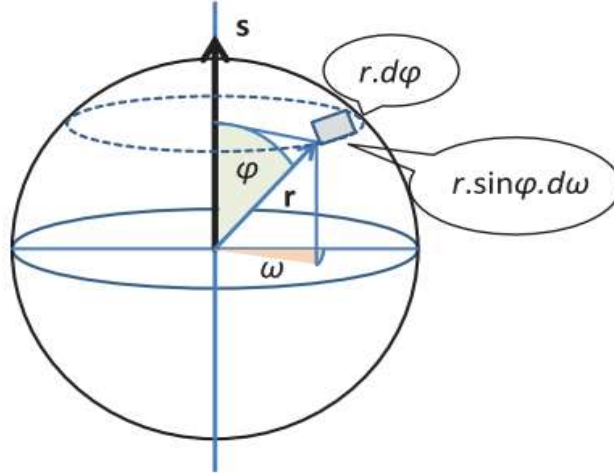
$$s \cdot r_{jk} = s r_{jk} \cos \varphi \quad (2.25)$$

The direction average of the cosine of that particular addend then becomes the integral over the surface of the radius  $r_{jk}$  (Figure 2.5) splitted by the area  $4\pi r_{jk}^2$  of that sphere:



**Figure 2.4:** Scattering by an object consisting of two scatterers 1 and 2, separated by the vector  $r_{12}$ .





**Figure 2.5**  
Definition of a volume element in spherical coordinates.

$$\cos(2\pi s \cdot r_{jk}) = \frac{1}{4\pi r_{jk}^2} \int_{\text{surface of sphere}} \cos(2\pi r_{jk} \cos \varphi) ds \quad (2.26)$$

The illustration in (Figure 2.5) the area element  $ds$  is calculated by:

$$dS = r_{jk}^2 \sin \varphi d\varphi d\omega \quad (2.27)$$

By using the convenient limits of integration, the result is:

$$\cos(2\pi s \cdot r_{jk}) = \frac{1}{4\pi r_{jk}^2} \int_0^\pi \int_0^{2\pi} \cos(2\pi s r_{jk} \cos \varphi) r_{jk}^2 \sin \varphi d\omega d\varphi \quad (2.28)$$

The integration over  $\omega$  simply yields  $2\pi$ . The second integration over  $\varphi$  can be achieved by exchange using  $z = \cos \varphi$ ,  $d\varphi = -dz/\sin \varphi$  and adaption of the integration limits to give:

$$\cos(2\pi s \cdot r_{jk}) = \frac{\sin(2\pi s r_{jk})}{2\pi s r_{jk}} \quad (2.29)$$

The direction rate is taking us to Debye equation

$$I(s) = \sum_{k=1}^n f_j(s)^2 + \sum_{j=1}^n \sum_{k=1, k \neq j}^n f(s) f(s) \frac{\sin(2\pi s r_{jk})}{2\pi s r_{jk}} \quad (2.30)$$

The intensity must be multiplied by the number of particles  $N$  (molecules, nano-crystalline grains and so on) that engages in the scattering.

### 3. Factors effecting different parameters

#### a. Peak position

The scattering angle  $2\theta_s$  of a Bragg reflection in a dispersive powder pattern can be deduced from the corresponding d-spacing by the Bragg equation be corrected by aberrations  $\Delta 2\theta_{corr}$  due to different misalignment [15], as follow:

$$2\theta_s = 2 \arcsin \left( \frac{\lambda}{2d_s} \right) + \Delta 2\theta_{corr}. \quad (2.31)$$

Giving a set of lattice parameters  $(a, b, c, \alpha, \beta, \gamma)$  or their reciprocal counterparts  $(a^*, b^*, c^*, \alpha^*, \beta^*, \gamma^*)$  and the unit cell volume  $V$ , all the possible reflections shad positions that can be calculated [6] as follow for the triclinic case:

$$\begin{aligned} \frac{1}{d_s} &= \frac{1}{V} \sqrt{\frac{h^2 b^2 c^2 \sin^2 \theta + k^2 a^2 c^2 \sin^2 \beta + l^2 a^2 b^2 \sin^2 \gamma +}{2hkabc^2(\cos\alpha\cos\beta - \cos\gamma)} + 2kla^2bc(\cos\beta\cos\gamma - \cos\alpha) + 2hlab^2c(\cos\alpha\cos\gamma - \cos\beta)} \\ &= \sqrt{h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} + 2hka^*b^* \cos \gamma^* + 2hla^*c^* \cos \beta^* + 2klb^*c^* \cos \alpha^*} \end{aligned} \quad (2.32)$$

This equation becomes simpler for by rising the lattice symmetry, as the case for the orthorhombic, tetragonal and cubic system:

$$\frac{1}{d_s} = \sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}} \quad (2.33)$$

- **Correction of the peak position**

The sample and the instrument give a series of contributions that effects in a linear or nonlinear way the position of the Bragg reflection. By evaluating the exact differential of the Bragg equation we can define the absolute error in the interplanar spacing  $\Delta d$  as a function of the measured diffraction angle for a constant wavelength data [15]:

$$\Delta d = \left( \frac{\lambda \cos \theta}{2 \sin^2 \theta} \right) d\theta + 2d \cos \theta d\lambda \quad (2.34)$$

A strong nonlinear increase of  $\Delta d$  at low diffraction angles occurs when we neglect the error in the wavelength even for tiny errors.

Each flat sample whose surface deviates from the focusing circle results the  $\cos \theta$  dependent peak shift which is the common nonlinear correction for the angular dispersive Bragg-Brentano geometry, and it is known as the height error  $c$  in mm:

$$2\theta_{corr}/^0 = -2 \left( \frac{180^0}{\pi} \right) \frac{\cos \theta}{R_{DS}} c. \quad (2.35)$$

In Debye Scherrer geometry the displacement of capillary away from the center of the goniometer causes a nonlinear shift in angular position. The correction function that suits here is:

$$\Delta 2\theta_{corr} = \arcsin \left( \frac{d_L}{R_{DS}} \sin(2\theta) \right) - \arcsin \left( \frac{d_V}{R_{DS}} \cos(2\theta) \right) \quad (2.36)$$

For capillary samples it exist another type of peak shift in angular dispersive powder diffraction experiment caused by the  $\theta$  dependent absorption. An empirical expression given as:

$$\begin{aligned} \Delta 2\theta_{corr}/^0 &= 2A\theta^B (90 - \theta)^C \\ A &= 0.000033\mu_{eff}R \\ B &= 1.168 - 0.22\mu_{eff}R + 0.0168(\mu_{eff}R)^2 \\ C &= 1.155 + 0.2054\mu_{eff}R - 0.0224(\mu_{eff}R)^2 \end{aligned} \quad (2.37)$$

## b. The intensity of a Bragg reflection

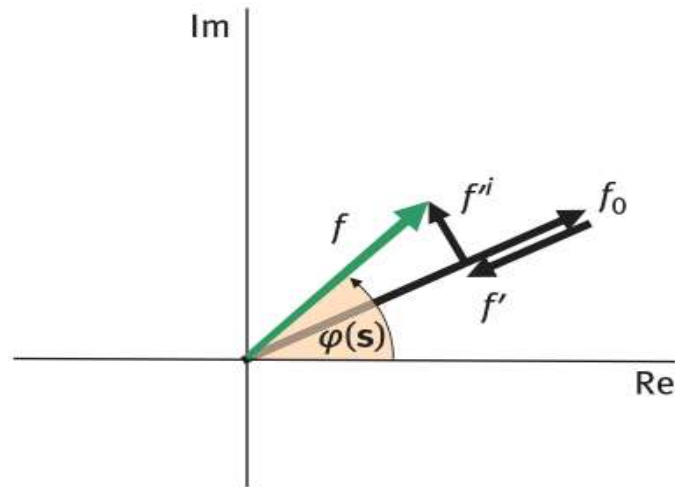
The integrated intensity of the bragg reflection is proportional to the squared complex factor that in the flesh is the vector sum of complex atomic form factors or coherent atomic scattering lengths weighted by additional complex phase factors.

- **THE atomic form factor**

The scattering power of an atom or an ion as a function of the scattering vector length  $s$  is described by the atomic form factor, as it is the case X-rays the form factor  $f_j$  depends on  $s$  with marked decrease at higher values; noting that most explicit parameterization of  $f_i$  and others are formulated as a function of  $\tilde{s} = \frac{s}{2} = \frac{\sin \theta}{\lambda}$  and not of  $s$ . The form factor is decomposed of two parts, a wavelength independent part and the other part is a complex wavelength dependent which is shown below:

$$f_j(\tilde{s}) = f_j^0(\tilde{s}) + \Delta f_j'(\lambda) + \sqrt{-1\Delta f_j''(\lambda)} \quad (2.38)$$

The complex part of the anomalous scattering factor has a phase shift of  $90^\circ$ , while the real part has a phase shift of  $180^\circ$ .



**Figure 3.1:** vector representation of the complex atomic scattering factor  $f$  with normal scattering ( $f_0$ ) and real ( $f'$ ) and complex parts of anomalous scattering.

- **Displacement parameter**

The atoms do vibrate about their equilibrium position at any temperature. We can separate the isotropic displacements from the anisotropic ones, for the entire crystal structure, groups or atoms, the displacement factor in the isotropic case is:

$$t = e^{-B\bar{s}^2} \quad (2.39)$$

Where we define  $B$  as the isotropic displacement parameter and  $t$  is used in the structure factor calculation.

$B$  can be defined physically as:

$$B = 8\pi^2 u^2 \quad (2.40)$$

$u^2$  is the mean square deviation from the equilibrium position of the atom or the atomic group. Where for inorganic compounds a range of  $0.1\text{\AA}^2 \leq B \leq 1.5\text{\AA}^2$  is normal, while for the coordination compounds  $B \leq 3\text{\AA}^2$  is acceptable. Larger values usually indicate errors or severe disorder in the crystal structure, as for the negative values that represent systematic errors in the intensities.

- **The structure factor**

The structure of a Bragg reflection is defined as a complex sum over all atoms

j in the unit cell when the anomalous scattering is ignored, so:

$$F(s) = \sum_j (t_j f_j(s) e^{2\pi i s \cdot x_j}) \quad (2.41)$$

With the positional vector  $x_j$  of an atom in the unit cell defined by the fractional crystal coordinates:

$$x_j = \begin{pmatrix} x \\ y \\ z \end{pmatrix} \quad (2.42)$$

### c. Intensity correction factors:

To calculate the integrated reflection intensities observed experimentally in powder diffraction pattern, a series of correction factors have to be done over the squared structure factors, where a list of the most common correction factor is given by the product:

$$Corr(s) = M(s)LP(s)A(s)PO(s)E(s) \dots, \quad (2.43)$$

And this equation contains: the multiplicity  $M(s)$ , the Lorentz-polarization factor  $LP(s)$ , the absorption correction  $A(s)$ , a correction for primary extinction  $E(s)$ , a preferred orientation correction  $PO(s)$ .

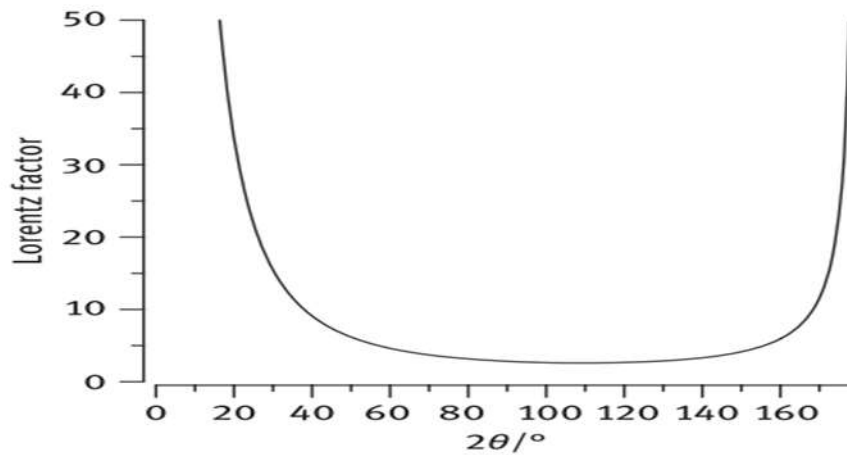
- **The multiplicity**

Is the total number of reflections due to the overlap of Friedel pairs, where the intensity is always doubled. Additionally for symmetries higher than triclinic, reflections with equivalent indices have identical intensity and overlap completely.

- **Lorentz-polarization factors**

They are purely geometric factors with an additional geometrical factor in the case of powder diffraction which normalizes the different radii of Debye-Scherrer rings. The diffraction cone factor is at maximum at low angles and very high angles and is proportional to  $1/\sin \theta$ . So the Lorentz factor in powder is:

$$L = \frac{1}{\cos \theta \sin^2 \theta} \propto \frac{1}{\sin \theta \sin(2\theta)} \quad (2.44)$$



**Figure3.2:** Lorentz factor for angle dispersive data as a function of the scattering angle.

The polarization factor originates from partial polarization of the scattered electro-magnetic wave; the intensity between the diffracted and the primary beam:

$$p = \frac{I}{I_0} = \frac{1 + \cos^2 2\theta}{2}. \quad (2.45)$$

The more general equation is used when a primary or secondary beam monochromator is present, and is valid for unpolarized radiation from a laboratory X-ray tube:

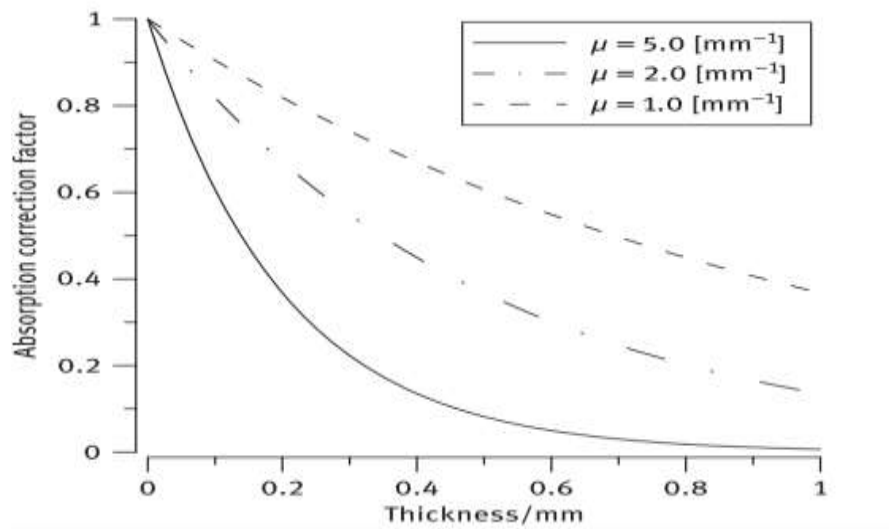
$$P = \frac{1 - \cos^2 2\theta \cdot \cos^2 2\theta_m}{2} \quad (2.46)$$

Where  $2\theta_m$  is the Bragg angle of the reflection from the monochromator.

- **Absorption correction**

The absorption affects the intensities of experiment in powder diffraction, so for the solid material the transmitted intensity  $I$  by respecting the initial intensity  $I_0$  depends on the thickness of the material  $x$  and on the linear absorption coefficient  $\mu$ :

$$I = I_0 e^{-\mu x} \quad (2.47)$$



**Figure 3.3:** intensity corrections factor required for solid samples in transmission geometry with different absorption coefficients.

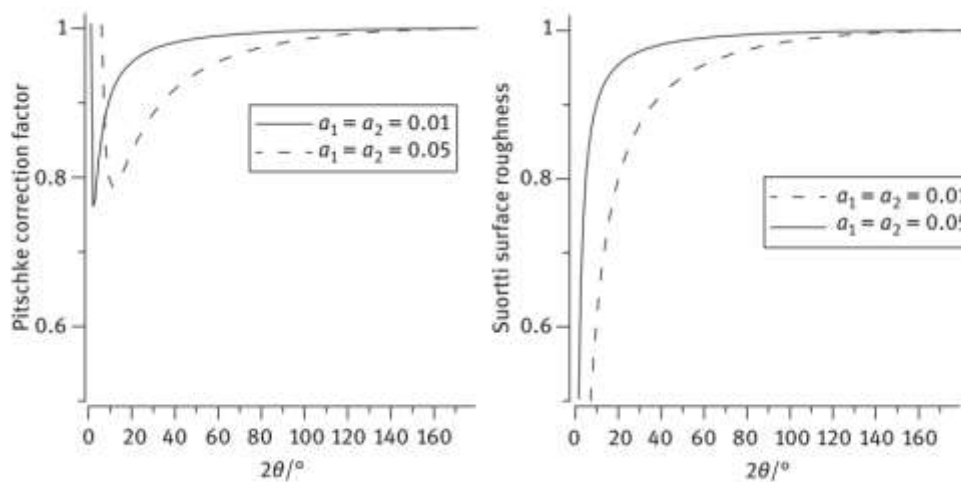
- **Surface roughness**

Created when the density in Bragg-Brentano geometry varies with depth, where the most common corrections, by pitschke:

$$A = \frac{1-a_1 (1/\sin \theta)^{-a_2}/\sin^2 \theta}{1-a_1(1-a_2)} \quad (2.48)$$

And the other is by Suortti:

$$A = \frac{a_1+(1-a_1)e^{a_2/\sin \theta}}{a_1+(1-a_1)e^{-a_2}} \quad (2.49)$$



**Figure 3.4:** correction factor for porosity effect in Bragg-Brentano geometry according to Pitschke (left) and Suortti (right) as a function of diffraction angle.

- **Overspill effect**

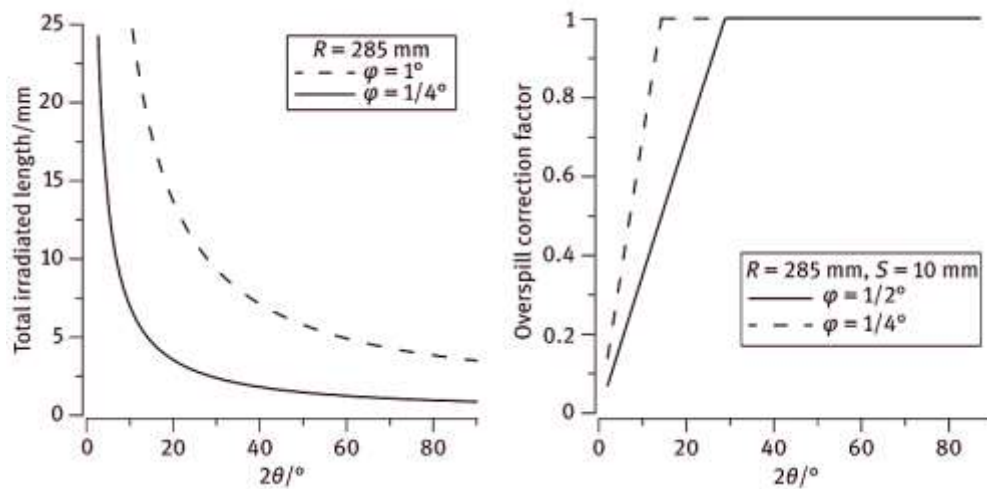
In the goal of keeping the constant illumination volume condition we need to keep the incident beam smaller than the sample area in diffraction pattern. As the importance of it is shown in the Bragg-Brentano geometry, at low angles generally the irradiated area becomes greater than the area covered by the sample on the sample container and this reduces the intensities up to the diffraction angle. The irradiated length for divergent beam Bragg-Brentano geometries with a tube opening angle  $\varphi$  is calculated as follow:

$$L = l_1 + l_2 = \frac{R \sin \frac{\varphi}{2}}{\sin(\theta + \frac{\varphi}{2})} + \frac{R \sin \frac{\varphi}{2}}{\sin(\theta - \frac{\varphi}{2})} \cong \frac{R\varphi[\text{rad}]}{\sin \theta} \quad (2.50)$$

With R is the goniometer radius.

For small divergence the beam may be considered as quasi-parallel and  $R\varphi$  [rad] is related to the thickness of the beam d. Therefore for a sample length S we can calculate the intensity correction as a function of the diffraction angle:

$$O_V = \frac{S}{L_D} \text{ for } 0 \leq 2\theta[\text{rad}] \leq 2\arcsin\left(R \frac{\varphi}{S}\right). \quad (2.51)$$



**Figure 3.5:** Left: Irradiated length on the surface of a flat place sample in Bragg-Brentano geometry with divergent beam for different opening angles  $\varphi$ . Right: Corresponding intensity correction function for the overspill effect for a sample length of 10mm.



- **Preferred orientation**

The perfect random orientations of the crystallites are experimentally realized in spherical crystallites. The crystallites tend to align in transmission geometry or reflection geometry in one or more preferable way(s). The intensity of the corresponding lattice planes strongly increase if these last are in reflection condition.

The angle between the reciprocal lattice vector  $s$  and the reciprocal lattice vector  $s_{\text{pref}}$  of the preferred orientation is calculated by:

$$\cos\omega = \frac{s_{\text{pref}} \cdot s}{|s_{\text{pref}}| |s|} \quad (2.52)$$

The march-Dollase function can give a correction factor accorded to:

$$T_s = \frac{1}{N} \sum_{i=1}^N (\tau^2 \sin^2 \omega_s^i + \tau^{-1} \sin^2 \omega_s^i)^{-3/2} \quad (2.53)$$

This summation is all over  $N$  symmetry equivalent reciprocal lattice dots, the refined preferred orientation parameter  $\tau$  is defined as the ratio between the correction factors for Bragg peaks perpendicular and parallel to the way of the chosen orientation.

- **Scale factor**

Defined as a linear, phase specific factor that sucks in all the constants in intensity correction factors. it depends on the incident intensity and measuring time. The usefulness of Bragg-Brentano geometry in the a multi-phase of the Rietveld refinement, this factor can be applied full phase analysis by the next equation:

$$X_p = \frac{S_p (ZMV)_p \mu_m^*}{K} \quad (2.54)$$

With  $X_p$  is the relative weight fraction of the phase  $p$  in a mix of many crystalline phases,  $Z$  is the number of formula units of phase  $p$  in the unit cell,  $M$  is the molecular mass of the formula unit of phase  $p$ ,  $V$  is the volume of the unit cell,

$S_p$  is the scale factor of phase  $p$  and  $K$  is a scaling factor.

The weight fraction  $X_\alpha$  of a phase  $\alpha$  is connected to the scale factor in the case of multiphase mixture and it can be introduced as:

$$X_\alpha = \frac{S_\alpha \rho_\alpha}{\sum_p (S_p \rho_p)} \quad (2.55)$$

Where  $\rho_\alpha$  is the density of a single phase and it can be calculated as:

$$\rho_\alpha = \frac{Z_\alpha M_\alpha \cdot 1.66055}{V_\alpha} \quad (2.56)$$

#### d. Peak profile

The profile  $\Phi(X)$  of a Bragg reflection centered at the peak position  $x_0$  can be regarded as mathematical convolution of instrumental resolution function  $IRF(X)$  and from the  $M(X)$  (microstructure of the sample):

$$\Phi(X) = (IRF \circ MS)(X) \quad (2.57)$$

With  $X = x - x_0$ , and  $x_0$  is the observed peak position that it center describes the profile function for the recorded data.

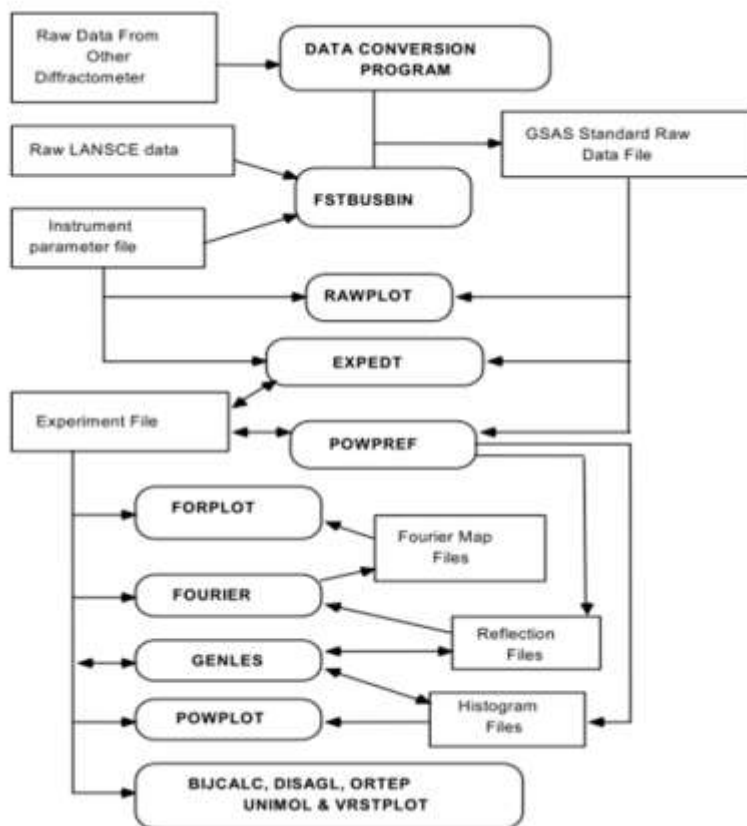
## B. GENERAL STRUCTURE ANALYSIS PROGRAM(GSAS)

### Introduction

**GSAS** is a program that processes and analysis a single crystal data and a powder diffraction data that was produced with X-rays or neutrons. It is able to handle all of these types of data simultaneously for given structural problems.

The **GSAS** program is in FORTRAN language and uses some system callable feature. It is set up appropriately on pc, we give the instructions for obtaining and installing a **GSAS** distribution kit for the Microsoft operating systems and Intel based Linux operating systems via anonymous ftp from the CCP14 web site. [18]

**GSAS** is the gathering of about 50 individual executable, performing various tasks in structure analysis.[19] These programs generate specific files given in single quotes; found in the technical section of this manual. The program layout in **GSAS** and the interconnecting files for powder calculations. [18]



## 1. GSAS Organization

This program contains several tasks and crystallographic calculations listed in an alphabetic way with a short definition of each one of them. All of these programs are being assessable through the **GSAS** shell that is recalled by using the **pc-Gsas** shortcut.[18]

### BIJCALC-Thermal Motion Analysis

Used to print some information extracted from the values on the list file and analyze the anisotropic thermal motion parameters.

### CAD4RD-InputEnraf-Nourius Single Crystal Data

It gives the unit cell information, examines the standard reflections then make corrections for crystal decay after entering it in the reflection file.

### CLLCHG-Unit Cell Transformation Routine

It converts a unit cell and its contents to an unrelated description associated with a.

## **DISAGL-Bond Distance and Angle Computation**

Effects calculations of the inter-atomic distances and angles, and defines estimated standard deviations for these values.

## **EXPEDT-GSAS Editor**

The **EXPEDT** control is thanks to a series of menus with different choices. It contains graphics to display powder patterns, and a training section to get to know the steps of running.

## **EXPNAM-Selection of Experiment Name**

It is attached to the choice of an experiment name for **GSAS**. It is used by **GSAS** to build up a chain of names associated to the current problem.

## **FITSPEC-Fitting of Incident Spectra**

It is used to measure the incident spectra from a certain instrument to a variety of functions.

## **FORSRH-Fourier Peak Search**

It is a routine that lists peak positions and their heights that been found in the Fourier map file and place them after in the experiment file.

## **FORPLOT-Fourier Map Display**

It produces single map slices or interpolated oblique slices of maps on different graphics devices. This program is used also to convert the **GSAS** Fourier format into the **dn6** format.

## **Fourier map calculation**

It is a Fourier map generation program. It produces sections of patterns or maps and numerical map in the list file.

## **GENLES-General Least Squares**

**GENLESES** is a refinement program. For a given structure structural problem, a mixture of powder diffraction and single crystal data can be treated simultaneously. It has also facilities for building linear constraints between parameters, molecular fragments and can involve stereo-chemical observations.

## **GEOMETRY-Calculate Molecular Geometry**

**GEOMETRY** produces the terminal results of many types of molecular geometry calculations on the terminal and the list file.

### **GSAS2CIF-Prepare Crystallographic Information File**

This program creates a Crystallographic Information File, and it is convenient to be published in journals and displayed to the IUCR without mistakes

### **GSAS2PDB-Prepare Protein Data Base File**

This program can be a part of the structure drawing packages by reading the produce file and draw the structure. **EXPEDT** can be applied on this program to read atomic coordinates for macromolecule.

### **HKLSORT-Reflection Lister Publication**

It produces a structure factors list on the list file in the appropriate form to deposit with a journal. This list may contain indices (hkl) with fast or slow running index.

### **HSTDMP-Powder Pattern Lister**

It can calendar parts of the histogram file or produces a list file of the total powder pattern data in a suitable journal for publication.

### **ISTAS-Intensity Statistics**

Mostly it is used to identify the space group.

### **ORTEP-Crystal Structure Plotting**

It witnessed several modifications to be adapted in the **GSAS** program with menu and interactive graphics. It won't plot macromolecular phases.

### **P3R3DATA-Input Siemens P3R3 Single Crystal Data**

It is an interacting routine to read the data such as unit cell information, survey standard reflections and enter it in the reflection file with the necessary corrections; with copies for absorption.

### **POLFPLOT-Pole Figure Plotting**

Displays pole figures on various graphics devices, these figures are generated from spherical harmonic coefficients obtained via **RIETVELD** method of powder diffraction data. **POLFPLOT** can make out axial distribution plots, and convenient pole figure data files.

### **POWPLOT-Powder Pattern Plotting**

It presents powder diffraction pattern on different graphics devices. **POWPLOT** is able to: show calculated, observed and difference curves with reflection markers, produces normal probability plots after examining the weighted differences, and calculates Fourier transform.

### **POWPREF-Powder Data Preparation**

**POWPREF** sets the powder diffraction data for the next least squares analysis. This program connects the position, the step width, incident intensity, refinement weight, and a list of contributing reflections with each powder pattern observation. Also it sets flags for each datum, generates for each kind in the sample the full list of unique reflections. **POWPREF** has a reflection file and a histogram file for each data set.

### **PROFTEST-Display of Powder Profile Shapes and Devices**

For the accessible functions in **GSAS**, **PROFTEST** exhibit calculated powder pattern shapes (related to the profile coefficient and the peak position).

### **PUBTABLES-Preparation of Tables for Publication**

It prepares tables of atomic parameters and structure factors that are appropriate for publication aim.

### **RAWPLOT-Plotting of Powder Patterns**

**RAWPLOT** can provide powder diffraction data in two units: d-spacing and data collection. It contains services for fitting position, intensity and profile shape coefficients as a set of individual reflections.

### **RCALC-Analysis of Structure Factor Residuals**

This program is used to define R-indices of the diverse valence of reflections. Likewise it may be used for generating plots of residual vs. a number of data parameters. It is used for single crystal data and also for powder pattern data in the RIETVELD refinement.

### **REELIST-Reflection Data Lister**

**REELIST** is a listing reflection routine, able to list on the terminal screen or on the listing file; the reflections are associated with each histogram. It can either take out the set of reflections from a single phase in powder pattern after **LeBail** or **RIETVELD** refinement.

### **REF2ASC-Conversion of Reflection File to ASCII**

It transforms **GSAS** reflection files into an **ASCII** form suitable for transmit between PC and UNIX machines. The **nonGSAS** crystallographic software may read the ASCII files.

### **REF2BIN-Conversion of ASCII Reflection File to GSAS Binary**

**REF2BIN** switches **ASCII** files created by the last program back to **GSAS** reflection file format.

### **RDUCLL-Cell Reduction Routine**

It's a cell unit routine that finds the cell traditional representation with detection of any possible pseudo-symmetry.

### **SCABS-Single Crystal Absorption Calculations**

It applies absorption corrections to single crystal data from neutron or X-ray single crystal instrument.

### **SCMERGE-Single Crystal Data Sort and Merge**

It merges single crystal reflection data into a distinctive with unified reflection indices which are entered into a new "**reflection file**". The Friedel related reflections are marked and written in the output file while the space group extinct reflections are deleted.

### **SPCGROUP-Interpretation of Space Group Symbols**

It is defined as an interactive program that explains space group symbols to table the equivalent positions. **SPCGROUP** sets the site symmetry rules for any location in the unit cell. It handles spin flip assignments for magnetic symmetry and establishes a stereo pair drawing to show the out coming results of the pattern.

### **SXTLDATA-General Input of Single Crystal Data**

It is a general routine to insert structure factor, it reads single crystal data from **ASCII** file which will be latter in **GSAS** format.

### **UNIMOL-Assembling of Unique Molecules**

UNIMOL assembles special molecules from the atoms in the "experiment file"; it has the capability of reorganizing the atoms list that replies to their needs.

### **VRSTPLOT-Preparation of Virtual Reality Crystal Structure File**

It arranges a Virtual Reality Modeling Language graphics file. **VRSTPLOT** produces a drawing file of a crystal structure with different representations, it might place in it a single density contour from of the **FOURIER** maps. It provides 3-dimensional view of the crystal structure and won't plot macromolecular phases.

### **Utility Routine in GSAS (UNIX only)**

There are numerous useful routines in UNIX version of **GSAS** that clarify a lot of the routine operations with **GSAS** list files and provides easy entrance to view data files within **GSAS**.

## **ATOM-Display of Atomic Scattering Data**

For a chosen chemical element, the main **ATOM** offers all the information stocked about that element on the file **ATOMDATA.DAT**.

### **ELST, DLST, SLST, TLST- List File Utilities**

**ELST**: modify the list file by the system standard editor, **DLST**: omit the List File, **SLST**: look for the list file, and **TLST**: exhibit the list file on the terminal.

### **PEXP, TEXP, DEXP, SEXP, LSEXP, EDEXP-Experiment File Utilities**

**TEXP**: display the experiment file on the terminal, **DEXP**: omit all files for the experiment except the experiment and raw data, **SEXP**: look for experiment file for a string, **LSEXP**: shows a list of names of all experiment files in the directory, and **EDEXP**: provides manual modification of the experiment file.

### **NEXT-Experiment Selection Utilities**

**NEXT** chooses the following experiment in alphabetical order.

## **2. In put files needed**

- **NABENZO.GDA: Measured intensities.**

For s different types of experiments there are different formats of measured intensities which are listed in the **GSAS** manual. The first line contains the title in free format, the second line contains powder pattern parameters, and the third line contains the measured intensities. [19]

- **NABENZO.BG: Manual background**

It is recommended especially at the beginning of a **Le-Bail/Rietveld** refinement to apply a subtracted back-ground from manually determine background dots. [19]

- **X3B1.PAR: Instrument parameter file**

Describes the parameters of the diffractometer, it is needed for new refinement settings.[19]

- **NABENZO.ATO: List of atoms**

It is token as the entrance to the atom list of **GSAS**. It is therefore appropriate to use the macro option to insert large amount of dummy atoms. [19]

- **NABENZO.MCD: Mathcad file**

It Represents the three dimensional anisotropic strain, which can be derived from the refinement of their half width in the **GSAS** program.[19]

- **NABENZO.EXP: Experiment data file**

It Contain all the information for a **Le-Bail/Rietveld** refinement, built up from scratch only very experienced users should edit this file manually. [19]



### 3. General instructions

- c. Press X to exit to the higher menu
- d. A menu of all options will be established in details by pressing ↵ or? ↵
- e. To leave the programs in the shell we use Q
- f. The <> is for the default answer and will be activated by pressing ↵.
- g. The list file is created by **GSAS** with a lot of useful information, it can be edited using an ASCII editor, and if this latter can't contain it because of its huge size, it would be deleted and rerun last refinement.
- h. The combination of several inputs is accessible in a line separated by at least one space character (L O P L ↵ to).
- i. ASCII format is used for files in **GSAS**, But not with the macro files that are free in the same format. The manually edited files which have length's lines unequal to 80 characters can be converted by Setup! Convert. [19]

### 4. PROGRAM EXECUTION IN GSAS

To execute in **GSAS** you need to be in "foreground" mode, with every execution a 'console' window is created in each routine, when this latter is done an additional carriage is prompt and it will get back to end the run and close the opening window.

#### 1. The Le Bail fit and the RIETVELD refinement

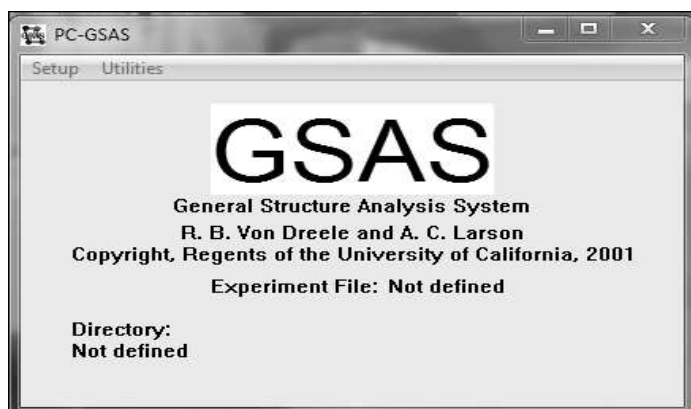
We start in a crystal structure refinement by refining the profile and lattice parameters separately without possessing a structural model, it is what we call the Le Bail fit and when we scroll to the RIETVELD analysis; the profile and the lattice parameters can then be at their refined values. Refinements are easier when there is a clear separation between the powder profile, the background and the crystal structure.[19] For better understanding of some of the instruction basics of **GSAS** program, we will introduce a simple **NICKEL** example that demonstrates the following steps.

#### Introduction to EXPEDT

The principal tool to enter all data, commands and controls included in the processing of diffraction patterns by **GSAS**. It is a multilayer menu interactive editor that takes control of typographical errors and crystallographic insert. [18]

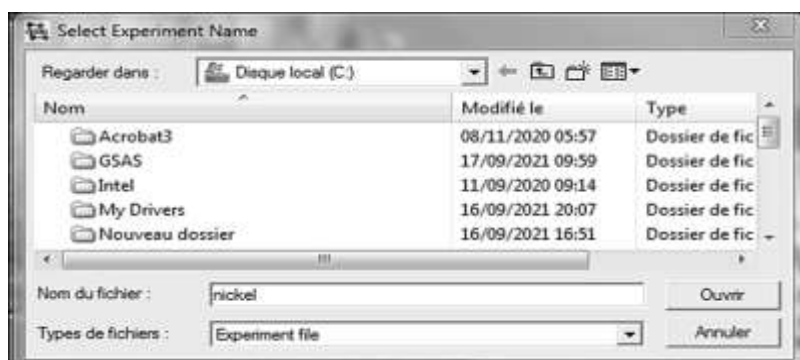
#### STARTING GSAS

For windows version it is obtained by clicking the **PC-GSAS** shortcut and the following screen will appear, where the message in the middle of it refers that **GSAS** flops to find an experiment file in the directory.[18]



**Figure 1.1:** Windows shell of **GSAS** before selecting an experiment name.

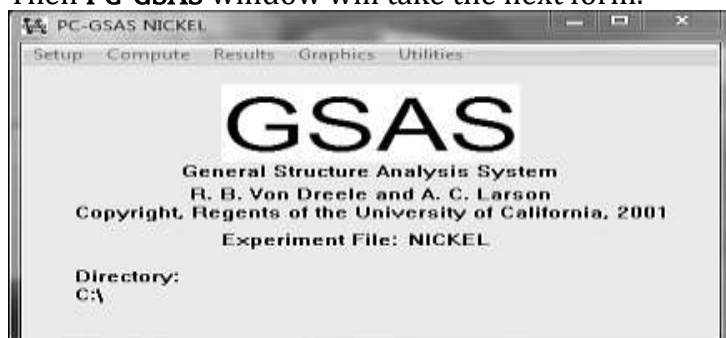
So you have to give a name to the experience by selecting the pull down menu 'setup' and choosing 'EXPNAM'. Then the file's selection window will show up.[18]



**Figure 1.2:** File name selection window.

You enter the file's name 'Nickel' in the File name section then press open, a question about creating this file is displayed , after taking 'yes' as answer, we get our named experiment. [18]

Then **PC-GSAS** window will take the next form.



**Figure 1.3:** Windows shell of **GSAS** after name selection.

Noticing that in the pull down menu more choices are available, and the directory location are now defined.

## Running EXPEDT

By selecting 'Setup' then 'EXPEDT' from the pull down menu, a question about the experiment will be displayed on an MS-DOS opening, informing that the experiment file 'Nickel' do not exist in the existing directory.

```
C:\>echo off
Experiment - NICKEL - was not found in directory
C:\
Do you wish to create it (Y/<N>)? >
```

So that the new file will be created we press 'Y'. After the creation of the file we enter it name 'Nickel'.

```
The new experiment - NICKEL - has been created.
Enter a title for this experiment
>
```

The main title will be displayed with all information and the first menu.

```
Enter a title for this experiment
>nickel

-----
Program EXPEDT Version Win32
A menu driven routine to edit .EXP files
Distributed on Fri Apr 18 09:12:00 2014
-----

-----
Allen C. Larson and Robert B. Von Dreele
Manuel Lujan, Jr. Neutron Scattering Center, MS-H805
Los Alamos National Laboratory, Los Alamos, NM 87545
-----
Copyright, 2000, The Regents of the University of California.
-----

Experiment title:
nickel
EXPEDT data setup option (<?>.D.K.P.R.S.X) >
```

Now EXPEDT illustrates kinds of calculations that can be arranged and they will be explained by pressing '↓'.

```
EXPEDT data setup options:
<?> - Type this help listing
D - Distance/angle calculation set up
K n - Delete all but the last n history records
P - Powder data preparation
R - Review data in the experiment file
S - Single crystal data preparation
X - Exit from EXPEDT
EXPEDT data setup option (<?>.D.K.P.R.S.X) >
```

To prepare a powder diffraction data type 'P'. EXPEDT will carry you through a series of necessary steps to input powder data.

```
EXPEDT data setup option (<?>.D.K.P.R.S.X) >p
You have no phase information
Select editing option for Powder data preparation (<?>.P.T.X)
```

It is shown in the previous window that the file had no phase, so a short menu of options is listed by typing '?'

```
The available powder data preparation options are:
<?> - Type this help listing
P - Phases - lattice & sp. group
T - Change the experiment title
X - Return to the main EXPEDT menu
You have no phase information
Select editing option for Powder data preparation (<?>.P.T.X) >
```

To change the title type 'T', but the main object is to enter phase so type 'P'.

```
There is no phase information present
*** No phase exists ***
Enter phase edit command(<?>,$,I,R) >_
```

To see the options enter '?'

```
Phase editing commands:
<?> - Type this help listing
$ - Enter DGL command
I - Insert new phase
R - Read phase info. from another experiment file
At least one phase must be defined before leaving this menu
*** No phase exists ***
Enter phase edit command(<?>,$,I,R) >
```

To read the information about the phase we select the 'R' option from another experiment file, but to enter a system command we select '\$', while the chosen step now is selecting 'I' for the new phase.

```
Enter identifying name for new phase number 1.
>
```

Give a suitable name to the file, like 'N Powder' ↵

```
No space group information found
Enter space group symbol (ex: P n a 21, P 42/n c m, R -3 c, P 42/m,
R -3 m R for rhombohedral setting) >
```

EXPEDT figures that this phase has no space group and it requires a space group symbol. For our nickel example we enter 'f m 3 m', this step will make EXPEDT interpret the symbol and give all the needed symmetry information.

```
R -3 m R for rhombohedral setting) >f m 3 m
Space group F m 3 m
The lattice is centric F-centered cubic Laue symmetry m3m
Multiplicity of a general site is 192
The symmetry of the point 0,0,0 contains 1bar
The equivalent positions are:
< 1> X Y Z < 2> X Y < 3> Y Z X
< 4> X Y -Z < 5> -Z X Y < 6> Y -Z X
< 7> -Z X Y < 8> -Y -Z X < 9> X -Y -Z
<10> -X Y -Z <11> -Z -X Y <12> X -Y -Z
<13> Y X Z <14> -Z Y X <15> X X Z Y
<16> Y X -Z <17> -Z Y X <18> X X -Z Y
<19> -Z Y X <20> -X -Z Y <21> X X -Z -Y
<22> -Y X -Z <23> -Z -Y X <24> X Y -X -Z
Enter real lattice parameters (Angstroms)
Enter a >
```

EXPEDT asks for lattice parameters to describe the unit cell dimensions. Based on it cubic center we type a='3.5234'.

```
Enter real lattice parameters (Angstroms)
Enter a >3.5234
Lattice parameters are
a,b,c = 3.523400 3.523400 3.523400
angles = 90.000 90.000 90.000
volume = 43.741
Lattice symmetry is cubic
Space group symmetry is cubic
Enter phase edit command(<?>,$,D,E,F,M,I,L,R,S,X) >
```

The phase is entered, more phase editing commands are shown up, enter '↵' or '?' to list them

```
Phase editing commands:
<?> - Type this help listing
$ - Enter DCL command
D n - Delete all data for phase "n"
E n - Edit phase data for phase "n"
F n - Enter unit cell contents data for phase "n"
I - Insert new phase
M n - Modify phase type flag for phase "n"
L - List phase names
R - Read phase info. from another experiment file
S n - Enter unit cell sigmas
X - Exit to EXPEDT main menu
At least one phase must be defined before leaving this menu
Enter phase edit command<?>,$,D,E,F,M,I,L,R,S,X >
```

Before the exit of this section, one phase must be entered. For a second phase type 'I', for changing the type of phase enter 'M', but with one phase existing as our case enter 'X'

```
You have no data
Select editing option for Powder data preparation <?>,H,P,T,X >
```

The next step here is to put in some diffraction data, for the helping list type

```
The available powder data preparation options are:
<?> - Type this help listing
H - Select and prepare histograms
P - Phases - lattice & sp. group
T - Change the experiment title
X - Return to the main EXPEDT menu
You have no data
Select editing option for Powder data preparation <?>,H,P,T,X >
```

Choose 'H' for this action to enter some data.

```
Input of histograms and modification of histogram controls:
There are no current histograms
Histogram data editing menu <?>,I,J,X >
```

Two possibilities are present so press '↓', to see what are they.

```
<?> - Type this help listing
I - Insert a new histogram
J - Insert a dummy histogram
X - Return to previous menu
Histogram data editing menu <?>,I,J,X >
```

For real data entrance, type 'I'

```
Enter raw histogram input file name <?>,$,QUIT>
>
```

EXPEDT asks for the file name that has the information about the nickel's powder diffraction scans.

```
This file must be in standard GSAS powder data format
$ - to enter DCL command
/ - for default (if any)
QUIT - to quit program
*** No file name given ***
Enter raw histogram input file name <?>,$,QUIT>
>
```

Enter the file name '/gsas/example/NICKEL.RAW'

```
Header on file:
NICKEL POWDER STANDARD, ROOM TEMP      22:32:50  9/ 8/1984
Is this the correct file <<Y>/N/Q)? >
```

EXPEDT prints the first record from the file and checks if it's the right one, we take it as the correct data and type 'Y'

```
Enter POWDER instrument parameter file name <<?>,$,QUIT>
>
```

Next step is to enter the name that has instrument specific information. Enter '?' for help

```

/
This file must be in standard GSAS format
$ - to run system command
/ - for default (if any)
QUIT - to exit from program
Enter POWDER instrument parameter file name <<?>,$,QUIT>
>
```

Enter the proper file name '/gsas/emapple/inst\_tof.prm'.

```
The raw data file is : /gsas/example/NICKEL.RAW
Enter bank number desired <<0 for list, 0 to quit> >
```

To have a look on the  $2\theta$  values for each bank we enter -1.

```
Available banks of data:
Bank 1 DIFC =      789.51 2-theta =      13.880
Bank 2 DIFC =     4368.97 2-theta =      88.050
Bank 3 DIFC =     5829.29 2-theta =     148.290
Bank 4 DIFC =     5821.89 2-theta =     148.290
The raw data file is : /gsas/example/NICKEL.RAW
```

We will use banks 2 and 3 for this example, so enter 2 to display data.

```
Reading histogram - please wait
Bank 2 DIFC =     4368.97 2-theta =      88.050
Do you wish to preview this histogram <Y/N>? >
```

When we type 'Y' the entire pattern is plotted, predicting that the data is satisfying so enter 'Y'

```

Do you wish to preview this histogram (Y/N)? Y
Editing of histogram information:
Histogram no. 1 Bank no. 2 Two-theta = 88.05
Title: NICKEL POWDER STANDARD, ROOM TEMP      22:32:50  9/ 8/1984
Histogram is not ready to be used in least-squares
Minimum d-spacing must be set before processing by POWPREP
The data compression factor is 1
The data holdout factor is 0
There are 0 channels in the profile
There are 5120 channels in the spectrum
The first 0 channels are not used
Enter histogram data modification command
<<?>.,A,B,C,D,E,F,I,L,M,P,S,T,W,Z) >
```

The title and the description of the first data set and its status are given by EXPEDT, to list the help menu enter '?'

```

Histogram editing commands:
<?> - Type this help listing
A   - Edit sample orientation angles
B   - Edit fixed background
C   - Edit the data compression factor
D   - Set minimum d-spacing - REQUIRED for new histograms
E   - Edit excluded regions
F   - Set phase flags for this histogram
I   - Edit instrumental constants
L   - List histogram title
M   - Modify incident spectrum source
P   - Plot histogram
S   - Edit the RFree sampling factor and seed
T   - Set max 2-Theta or Energy or min TOF (equivalent to D option)
W   - Edit profile params.
Z   - Edit detector azimuthal angle
Enter histogram data modification command
<<?>,A,B,C,D,E,F,I,L,M,P,S,T,W,Z) >

```

It is handy to unveil the powder pattern before the d-spacing is set by 'D' or 'T', to accomplish this step enter 'P'

```

Enter graphic screen option <<?>,A,B,C,D,Z) >

```

To check out the list of supported graphics and select the right one shown, type'?

```

Graphics screen option:
A   black on white graphics always on top
B   white on black graphics always on top
C   black on white graphics not on top
D   white on black graphics not on top
Z   No screen graphics; only hardcopy
Enter graphic screen option <<?>,A,B,C,D,Z) >

```

After the option is chosen a question will be asked for the next option

```

Do you want to save graphics output <Y,<N>?> >

```

If the question had 'y' as it answer the following menu shows up, enter '?' to display the hardcopy options.

```

Enter hardcopy option <<?>,A,B,C,D,E) >

```

```

High resolution hardcopy device:
A   HP Laserjet printer
B   PostScript printer
C   EPS PostScript file
D   Color PostScript printer
E   Color EPS PostScript file
Enter hardcopy option <<?>,A,B,C,D,E) >

```

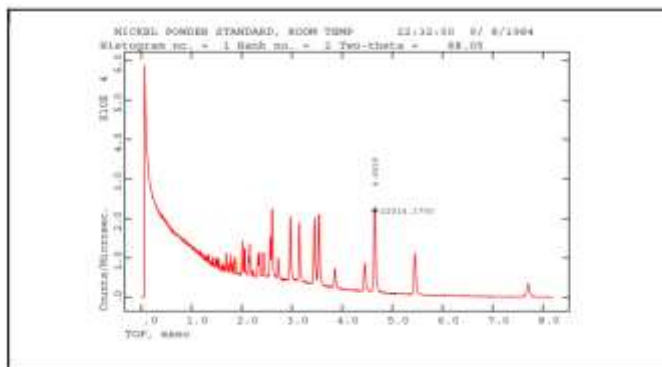
A file called "experiment.device" with the suitable graphic codes is created by the system. After each plot EXPEDT asks whether it is to be added to the file then select which plots to be saved.

After a graphics device is chosen, the following question will be displayed

```
Do you want to set plot ranges for the first plot (Y/<N>)? >
```

By

responding to it with 'Y', EXPEDT will ask for a range in TOF for the primary plot, type '?' to see the full pattern showing up as first plot.



The graphics cursor shows up after the plot is finished. The useful commands of this cursor exist at the bottom of the plot. Type 'X' to exit the cursor mode.

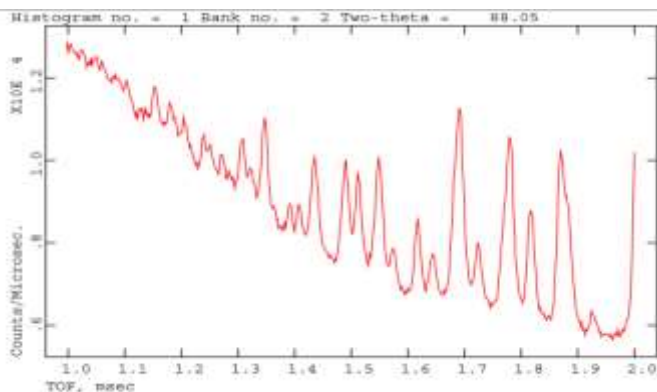
```
Give X-min and X-max for next plot
<default plot="0 0" & <CR> for no plot >
```

The right answer is to give two values covering some part of the total range of the starting plot, the full range will be displayed by entering '0 0', and by typing '12' we will get the shortest TOF part with Bragg peaks, the following line will be shown

```
Type of scaling desired (<?>,A,R,S) >
```

To plot the new plot with the same 'Y' range as the last one answer 'S', if the answer is 'R', EXPEDT will ask for new Y-min and Y-max values.

For the automatic rescale enter 'A' and a new plot is drawn as follow:





Another time the Graphics cursor come up, to exit this mode enter 'X'. The option to view a section of the initiative Plot range will manifest on the console window.

```
Give X-min and X-max for next plot
(default plot="0 0" & <CR> for no plot) >
```

BY entering '?' this menu will show up

```
Enter histogram data modification command
(<<?>,A,B,C,D,E,F,I,L,M,P,S,T,W,Z) >
```

By setting the minimum TOF, the minimum d-spacing is set. To select this option enter 'T'.

```
~ 209 reflections for d-minimum & TOF-minimum of 0.250 A & 1.094 msec
Enter new minimum TOF in msec. (</ if OK) >
```

EXPEDT accepts the new values and progress to the following prompt.

```
Histogram editing commands:
<?> - Type this help listing
A - Edit sample orientation angles
B - Edit fixed background
C - Edit the data compression factor
D - Set minimum d-spacing - REQUIRED for new histograms
E - Edit excluded regions
F - Set phase flags for this histogram
I - Edit instrumental constants
L - List histogram title
M - Modify incident spectrum source
P - Plot histogram
S - Edit the Rfree sampling factor and seed
T - Set max 2-Theta or Energy or min TOF (equivalent to D option)
W - Edit profile params.
Z - Edit detector azimuthal angle
Enter histogram data modification command
(<<?>,A,B,C,D,E,F,I,L,M,P,S,T,W,Z) >
```

The required editing has been performed can be processed by POWPREF.

The compression factor permits you to group adjacent channels into done data point for analysis. To modify the compression factor type 'C'

```
The spectrum has 5120 channels
The current data compression factor is 1
Enter the new data compression factor (<1 to 99>) >
```

Use a compression factor or two so we use 2.

```
The new data compression factor is 2
Enter histogram data modification command
(<<?>,A,B,C,D,E,F,I,L,M,P,S,T,W,Z) >
```

This histogram edition is finished so types 'X'. The coming up window will demonstrate a prompt for a new bank number. The GSAS raw data file name is represented as a reminder.

```
The raw data file is : /gsas/example/NICKEL.RAW
Enter bank number desired <<0 for list, 0 to quit> >
```

Now use the data from the third bank of detectors, type "3".

```
Reading histogram - please wait
Bank 3 DIFC = 5829.29 2-theta = 148.290
Do you wish to preview this histogram <Y/<N>? >
```

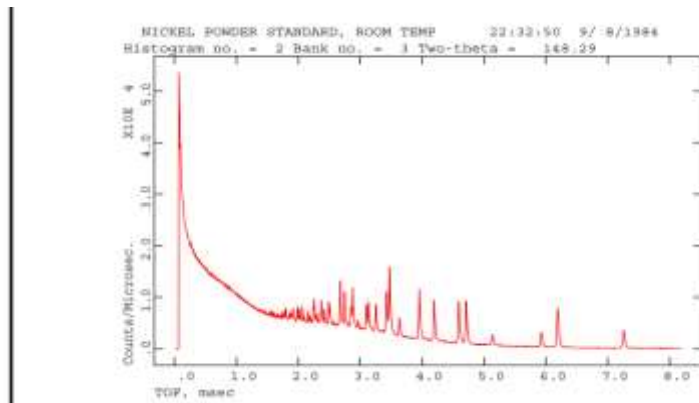
Before letting **GSAS** to use it, you can preview the histogram, type '?'

```
Editing of histogram information:
Histogram no. 2 Bank no. 3 Two-theta = 148.29
Title: NICKEL POWDER STANDARD, ROOM TEMP 22:32:50 9/ 8/1984
Histogram is not ready to be used in least-squares
Minimum d-spacing must be set before processing by POWPREF
The data compression factor is 1
The data holdout factor is 0
There are 0 channels in the profile
There are 5120 channels in the spectrum
The first 0 channels are not used
Enter histogram data modification command
<<?>,A,B,C,D,E,F,I,L,M,P,S,T,W,Z> >
```

When you Type 'P' to plot the pattern, the following request is displayed.

```
Do you want to set plot ranges for the first plot <Y/<N>? >
```

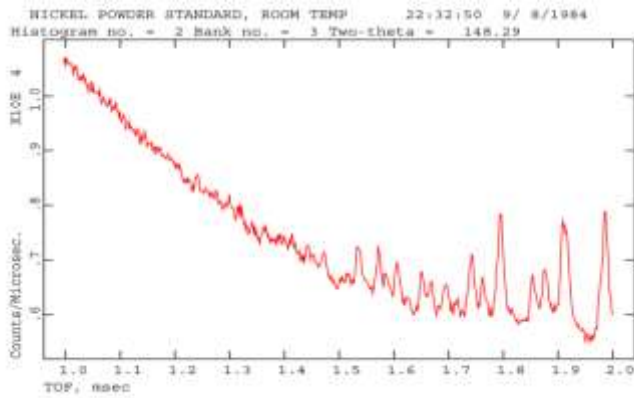
When we type '↓', **EXPEDT** will recognize, the plot will show up directly.



The 'power pulse' is stronger and should be kept out from the next plot, type 'X' to continue.

```
Give X-min and X-max for next plot
(default plot="0 0" & <CR> for no plot) >
```

To accomplish direct scaling type '1 2 a'



Type 'X' to get the next prompt

```
Give X-min and X-max for next plot
<default plot="0 0" & <CR> for no plot >
```

The menu for editing histogram data will be established, to continue type '↓'.

```
Enter histogram data modification command
<(<?>),A,B,C,D,E,F,I,L,M,P,S,T,W,Z >
```

To put the minimum TOF.

```
~ 209 reflections for d-minimum & TOF-minimum of 0.250 A & 1.458 msec
Enter new minimum TOF in msec. </ if OK >
```

The recalculation of the limits and the predestined number EXPEDT and shows an updated prompt.

```
~ 194 reflections for d-minimum & TOF-minimum of 0.257 A & 1.500 msec
Enter new minimum TOF in msec. </ if OK > /
```

The instructions '/' is to accept it. And the following opening will be shown.

```
Editing of histogram information:
Histogram no. 2 Bank no. 3 Two-theta = 148.29
Title: NICKEL POWDER STANDARD, ROOM TEMP 22:32:50 9/ 8/1984
Histogram is not ready to be used in least-squares
Minimum d-spacing must be set before processing by POWPREF
The data compression factor is 1
The data holdout factor is 0
There are 0 channels in the profile
There are 5120 channels in the spectrum
The first 0 channels are not used
Enter histogram data modification command
<(<?>),A,B,C,D,E,F,I,L,M,P,S,T,W,Z >
```

The detector bank at a large 2θ is the source of this powder pattern which has a higher resolution. The instruction 'W' gives access to the Bragg peak shape parameters and related coefficients. To examine these coefficients and modify one of their values types 'W'

```

Change profile parameter values and refinement flags
Histogram no. 2 Bank no. 3 Two-theta = 148.29
Title: NICKEL POWDER STANDARD, ROOM TEMP 22:32:50 9/ 8/1984
Histogram is not ready to be used in least-squares
Histogram needs to be processed by POWPREF

Phase no. 1
Phase name: nickel powder
Aniso. broadening axis 0. 0. 1. Damp 0
Peak profile type no. 1 Number of coefficients: 12
Profile coefficients for Von Dreele, Jorgensen & Windsor convolution function
J. Appl. Cryst., 15,581-589(1982)
Modified by Von Dreele - unpublished (1983).
#1(alp-0) = 0.0000 N #3(bet-0) = 5.5766E-02 N #5(sig-0) = 0.000 N
#2(alp-1) = 0.1374 N #4(bet-1) = 1.3723E-03 N #6(sig-1) = 48.764 N
#8(rstr) = 0.000 N #9(rsta) = 0.000 N #7(sig-2) = 0.000 N
#10(rsca) = 0.000 N #11(slec) = 0.00 N #12(s2ec) = 0.00 N
Cut-off for peaks is 1.00 percent of the peak maximum
Profile editing options - <<?>,$,A,C,L,P,R,W,X) >

```

Each phase and each histogram in a powder data set, there are set of profile coefficient. Type '?' to show the help listing

```

Profile editing options:
<?> - Type this help listing
$ - Enter DCL command
A - Change anisotropic broadening axis
C - Change profile parameter values
L - List the current profile values and their refinement flags
P n - Select new phase "n"
R n - Reset profile coeffs. to default values for type "n"
W - Change the peak cut-off value
X - Exit from this mode
WARNING--- Changes in profile parameters or cutoff
should be followed by rerunning POWPREF
Profile editing options - <<?>,$,A,C,L,P,R,W,X) >

```

In the purpose of establishing new peak limits **POWPREF** must rerun; it is running shortly and peak limits will be set for the first time.

The definition of the width of the peak base as cutoff is when the peak profile function drops below fraction of the peak maximum. Enter '**W 0.5. EXPEDT**' lists the old and new values.

```

The new cut-off is 0.50 percent of peak maximum
Profile editing options - <<?>,$,A,C,L,P,R,W,X) >

```

It is done so type 'X'

```

Enter histogram data modification command
<<?>,$,A,B,C,D,E,F,I,L,M,P,S,T,W,Z,X) >

```

The editing histogram is done so type 'X', the upcoming window shows that it is possible to read another histogram from the data file.

```

The raw data file is : /gsas/example/nickel.raw
Enter bank number desired (<0 for list, 0 to quit) >

```

All the data sets are been examined at this time so type **0**. Trying to reread a data set for new histogram **EXPEDT** will warn you then give you the chance to reconsider.

```
Histogram data editing menu <<?>,E,F,I,J,L,P,R,U,X,Z> >
```

The processing by **POWPREF** can be effected because both histograms are ready, enter '?' to see entire help list

```
Histogram modification options:
<?> - Type this help listing
E n - Edit powder histogram "n"
F - Modify powder histogram weighting factors
I - Insert a new histogram
J - Insert a dummy histogram
L - List histogram titles
P n - Edit phase flags for histogram n
R n - Replace histogram n
U n/n:m - Toggle use of histograms
Z n - Edit zone data for histogram n
X - Return to previous menu
n/n:m - optional histogram numbers:
n - individual histogram number
n:m - range of histogram numbers
ALL - all histograms
Histogram data editing menu <<?>,E,F,I,J,L,P,R,U,X,Z> >
```

There are two options for flagging specific histograms in calculations. The 'U' is preventing **GENLES** from using histograms and would be effective after processing them with **POWPREF** first.

Histogram is finished, type 'X'

```
Select editing option for Powder data preparation <<?>,H,P,T,X> >
```

The main menu of **EXPEDT** will show up next after typing 'X' and some extra entries are available

```
EXPEDT data setup option <<?>,D,F,K,L,P,R,S,X> >
```

The ability to edit the inputs for least squares and Fourier calculations is possible when the data has been introduced to **GSAS**, to show up the possible instructions for it, type '?'

```
EXPEDT data setup options:
<?> - Type this help listing
D - Distance/angle calculation set up
F - Fourier calculation set up
K n - Delete all but the last n history records
L - Least squares refinement set up
P - Powder data preparation
R - Review data in the experiment file
S - Single crystal data preparation
X - Exit from EXPEDT
EXPEDT data setup option <<?>,D,F,K,L,P,R,S,X> >
```

**EXPEDT** will terminate by entering 'X'

```
$TOP EXPEDT terminated successfully statement executed
Appuyez sur une touche pour continuer...
```

To close this window in windows press any key but for Linux the principle **GSAS** prompt will appear as the experiment name **NICKEL**.

## POWPREF program

### Preparation of powder data

The coming step is to preparing the two histograms by running **POWPREF**, it will produce sets according to the space group and lattice parameters with matching it to the powder patterns. In windows this step will start up by selecting '**Compute**' and choose **POWPREF** from the pull down menu.

```
C:\>echo off
Histogram no. 1 Bank no. 2 Two-theta = 88.05
Title: NICKEL POWDER STANDARD, ROOM TEMP 22:32:50 9/ 8/1984
*** Histogram will be used in least-squares
Header on file:
NICKEL POWDER STANDARD, ROOM TEMP 22:32:50 9/ 8/1984
Histogram no. 2 Bank no. 3 Two-theta = 148.29
Title: NICKEL POWDER STANDARD, ROOM TEMP 22:32:50 9/ 8/1984
*** Histogram will be used in least-squares
Header on file:
NICKEL POWDER STANDARD, ROOM TEMP 22:32:50 9/ 8/1984
STOP POWPREF terminated successfully statement executed
Appuyez sur une touche pour continuer...
```

To follow press any button, need to hold on until **POWPREF** ends before going to the next step. This latter will display a listing file "**NICKLE.LS**" containing all line printer output from it.

### Preparation of powder data

The followed manual is to plot observed and calculated patterns in powder diffraction in **GSAS**. It is also used to show the difference curve, to perform an analysis error or mark the reflection positions.

### Running POWPLOT

After running it, it will exhibit a copy right message and ask for a letter to identify the type of terminal to work on.

```
C:\>echo off

-----
Program POWPLOT Version Win32
Powder pattern plotting program
Distributed on Fri Apr 18 09:12:00 2014
-----

-----
Allen C. Larson and Robert B. Von Dreele
Manuel Lujan, Jr. Neutron Scattering Center, MS-H805
Los Alamos National Laboratory, Los Alamos, NM 87545
-----

Copyright, 2000, The Regents of the University of California.

The last history record is :
HSTRY 3 POWPREF Win32 Jan 01 00:37:45 2009
Enter graphic screen option <<?>,A,B,C,D,Z> >
```

**POWPLOT** supports many different graphics terminals, so what's needed is choosing the right code for the terminal.

```
Do you want to save graphics output (Y,<N>)? >
```

To hardcopy the plots, take yes as an answer. In another hand if the answer was no then after typing the experiment name the principle menu is displayed.

```
Experiment title:
NICKEL
Enter command (<<?>,A,B,C,D,E,G,H,I,L,M,N,O,P,R,S,T,U,W,X) >
```

For total listing type '?' or '↓'.

```
POWPLOT Commands:
<?> - Type this help listing
A - ASCII output of plot data
B - Toggle background subtraction control
C - Toggle cursor control
D - Difference curve toggle
E - Plot resolution toggle
G - I or sqrt(I) on Y-axis toggle
H n - Read powder histogram "n"
I - I/I0 or I on Y-axis toggle
L - List histogram titles & plot options
M - Mark reflection positions toggle
N - Read next powder histogram
O - Toggle the observed point plotting mode
P - Plot histogram
R - Plot radial distribution functions
S - Set initial plot ranges toggle
T - TOF/2-theta to D to Q switch for X-axis
U - Enter up to 4 scale ranges for plot
W - Weighted plot toggle
X - Exit from POWPLOT
Enter command (<<?>,A,B,C,D,E,G,H,I,L,M,N,O,P,R,S,T,U,W,X) >
```

The program changes mode and prints a message indicating the current mode each time an option is entered, type 'L' to list the histogram subtitles and the actual case of all the toggles.

```
Histogram no. 1 Bank no. 2 Two-theta = 88.05
Title: NICKEL POWDER STANDARD, ROOM TEMP 22:32:50 9/ 8/1984
**** Histogram will be used in least-squares
Histogram no. 2 Bank no. 3 Two-theta = 148.29
Title: NICKEL POWDER STANDARD, ROOM TEMP 22:32:50 9/ 8/1984
**** Histogram will be used in least-squares

Background will not be subtracted
Difference curves will not be plotted
Plot in low resolution mode (fast)
Reflection positions will not be marked
Y-axis is intensity
Intensities will not be divided by incident spectrum
Unweighted profile will be plotted
Plot will use 2-theta in deg
Full scale plot will be displayed
Observed points will be plotted as "+"
Cursor will not be active
Enter command (<<?>,A,B,C,D,E,G,H,I,L,M,N,O,P,R,S,T,U,W,X) >
```

To begin u need to read an histogram, so type 'H1' or 'N' for it.

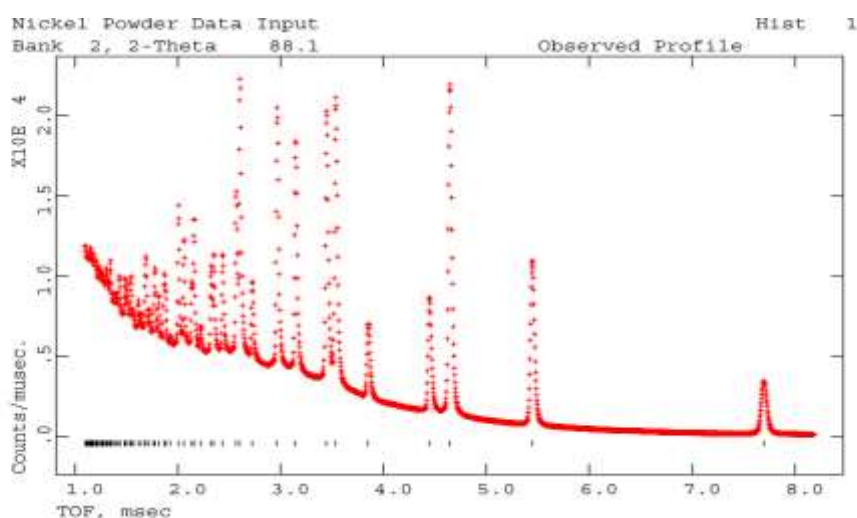
```

The selected histogram is:
Histogram no. 1 Bank no. 2 Two-theta = 88.05
Title: NICKEL POWDER STANDARD, ROOM TEMP 22:32:50 9/ 8/1984
*** Histogram will be used in least-squares
Reading histogram - please wait
Enter command (<<?>,A,B,C,D,E,G,H,I,L,M,N,O,P,R,S,T,U,W,X) >

```

The information shown in the upper section gives access to the histogram and then u can trough it identify the current selected pattern.

The routine would mark the reflection positions and use **TOF** in msec as the X-axis. When u type '**M T**', the new state of the appropriate toggle will be mentioned in the next message:



```

Reflection positions will be marked
Plot will use d-spacing in angstroms
Enter command (<<?>,A,B,C,D,E,G,H,I,L,M,N,O,P,R,S,T,U,W,X) >

```

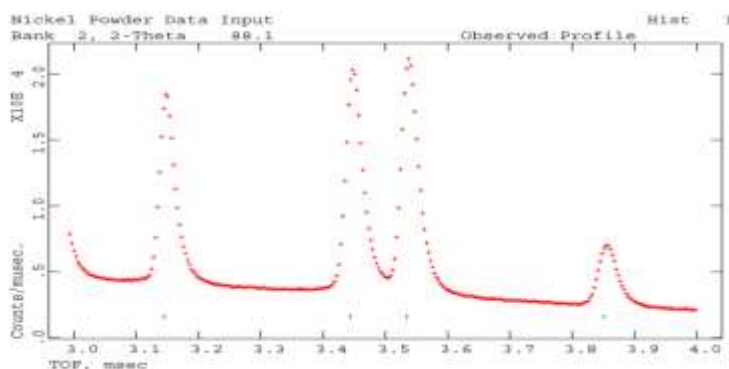
After setting up the appropriate toggles, type '**P**' to draw the plot on the screen. Next on, the following lines will appear on the console screen.

```

Give X-min and X-max for next plot
(default plot="0 0" & <CR> for no plot) >

```

This is utile to see a small part of the plot and runs in the same way as **EXPEDT** does. The '**S**' instruction had been selected above this line would have appeared before the first plot, to look from region '**3 4**' select '**3 4 A**' then a new plot is





You need to be in the main **POW** menu to change the toggle settings, the relationship between the marker positions and the peak tops in this range way clearer according to this plot. The type of approval that is present here is enough, now having the ability to view a part of the plot.

```
Give X-min and X-max for next plot
(default plot="0 0" & <CR> for no plot) >
```

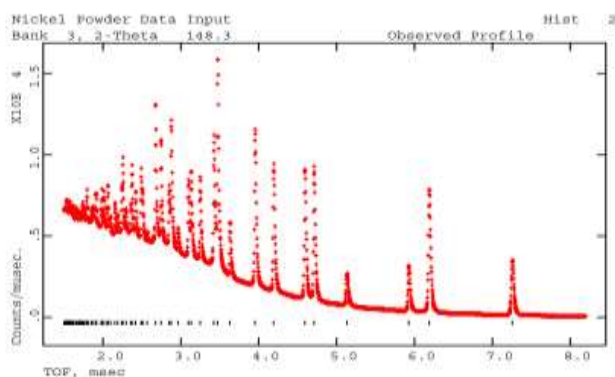
Responding this time with '↓'

```
Enter command <<?>,A,B,C,D,E,G,H,I,L,M,N,O,P,R,S,T,U,W,X) >
```

Now back to the **POW** principle menu, enter '**N**' so that the title and the status of the second histogram will be displayed.

```
The selected histogram is:
Histogram no. 2 Bank no. 3 Two-theta = 148.29
Title: NICKEL POWDER STANDARD, ROOM TEMP 22:32:50 9/ 8/1984
*** Histogram will be used in least-squares
Reading histogram - please wait
Enter command <<?>,A,B,C,D,E,G,H,I,L,M,N,O,P,R,S,T,U,W,X) >
```

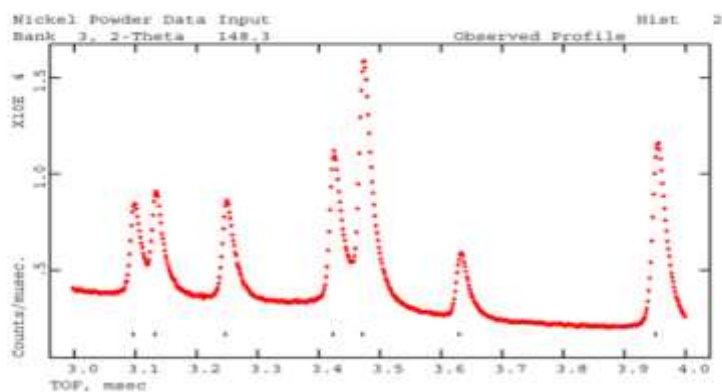
The toggles set for the first histogram are steel valid and to plot this histogram enter '**P**', the next plot is



This line will show up on the console opening

```
Give X-min and X-max for next plot
(default plot="0 0" & <CR> for no plot) >
```

To look at the powder pattern from the region '3-4' enter '**3 4 A**', and it will be plotted as this



When the plot is finished it will be shown on the blinking cursor, the marker positions are kind of close to the peak center positions, the console will show this

```
Give X-min and X-max for next plot
(default plot="0 0" & <CR> for no plot) >
```

Reply with '↓'

```
Enter command <<?>,A,B,C,D,E,G,H,I,L,M,N,O,P,R,S,T,U,W,X >
```

Type 'X' to exit the POWPLOT

```
$TOP POWPLOT terminated successfully statement executed
Appuyez sur une touche pour continuer...
```

### Set up for least squares

It is used to enter the data for the first Rietveld refinement cycles, in this case the example is **NICKEL** so we will introduce the atomic parameters then let the least squares select the refinement.

### Running EXPEDT

According to the previous steps the name **NICKEL** is already given to the experiment and this latter is selected by the **EXPEDT** command. After opening **EXPEDT** a copy right message is displayed with a summary of all previous operation.

```
C:\>echo off

-----
Program EXPEDT Uersion Win32
A menu driven routine to edit .EXP files
Distributed on Fri Apr 18 09:12:00 2014
-----

Allen C. Larson and Robert B. Von Dreele
Manuel Lujan, Jr. Neutron Scattering Center, MS-H805
Los Alamos National Laboratory, Los Alamos, NM 87545

Copyright, 2000, The Regents of the University of California.

The last history record is :
HSTRY 3 POWPREP Win32 Jan 01 00:37:45 2009
Is this the file you wish to use? <<?>,K,Q,R,Y >
```

The name and the version of the last program in **GSAS** are given in the history record with its date and time of modification. Enter '?' To list the options

```
The options here are:
K - Live dangerously. NO NEW COPY, NO BACKUP!
Q - Quit, exit from the program
R - Review the data in this file
Y - Create a copy of this file and edit it
Is this the file you wish to use? <<?>,K,Q,R,Y >
```

If it isn't desired to make a copy of the experiment file before starting with the editing enter 'K'. And if it is desired to own a copy enter 'T'. A new version (**nickel**) of the experiment is created and the former one is called '**nickel.001**'.

```
The last history record is :
HSTRY 3 POWPREP Win32 Jan 01 00:37:45 2009
EXPEDT data setup option <<?>,D,F,K,L,P,R,S,X >
```

The title of the experiment is the one introduced in the **EXPDET**, to have a look at the list of options enter '?' Or '↓'

```
EXPEDT data setup options:
<?> - Type this help listing
D - Distance/angle calculation set up
F - Fourier calculation set up
K n - Delete all but the last n history records
L - Least squares refinement set up
P - Powder data preparation
R - Review data in the experiment file
S - Single crystal data preparation
X - Exit from EXPEDT
EXPEDT data setup option <<?>,D,F,K,L,P,R,S,X >
```

The **EXPEDT**'s menu lists all types of calculations possible for a crystal structure analysis, for least squares data enter 'L', this line will show up

```
Select editing option for Least Squares calculation
<<?>,A,B,F,H,L,O,R,S,T,X >
```

Above is the least squares calculation menu, type '?' to see the help options

```

The available options are:
<?> - Type this help listing
A - Edit atom parameters
B - Edit rigid body constraints
F - Edit atom form factor parameters
H - Edit Pawley extraction controls
L - Edit least squares controls
O - Edit overall parameters
R - Review some of the EXP file data
S - Edit soft constraint data
T - Change the experiment title
X - Exit to main EXPEDI menu
Select editing option for Least Squares calculation
<<?>,A,B,F,H,L,O,R,S,T,X >

```

The listed options are necessary for the least squares set up, it provides editing atom parameters and overall parameters, set the least squares control and finally examine the records. For title editing enter 'T'

```

Enter title editing command <<?>,L,T,X >

```

To list the choices enter '?'.

```

Experiment title editing menu
L - List current title
T - Experiment title
X - Exit from this menu
Enter title editing command <<?>,L,T,X >

```

The right option to enter is 'T'

```

Old Experiment title
NICKEL
Enter new Experiment title(</ for no change > )

```

The next set of titles reflect the status of the problem 'NICKEL POWDER REFINEMENT'

```

Enter title editing command <<?>,L,T,X >

```

To return to the main least squares menu enter 'X'

```

Select editing option for Least Squares calculation
<<?>,A,B,F,H,L,O,R,S,T,X >

```

Insert now the nickel's atom, type 'A'

```

Phase No. 1; Phase has      0 atoms; Title: NICKEL POWDER
Give atom editing command <<?>,$,I,S,X >

```

This window will inform you that there are no inserted atoms for the nickel powder phase, to list the options enter '?'

```
Atom editing commands:
<?>      - Type this help package
x <?>    - To give details on command x
$        - Enter DCL command
I s      - Insert one atom or read atoms from a file
$        - Modify the space group and unit cell data
X        - Exit from editing atoms
Where "t" is an atom type, "s" is an atom sequence number, "s1:s2" refers
to a range of atom sequence numbers, and "codes" are specific to the
command; see the individual help listings for specific instructions
Phase No. 1; Phase has      0 atoms; Title: NICKEL POWDER

Give atom editing command <<?>,$,I,S,X >
```

There are two available choices when there are no inserted atoms: the first is to insert one and the second is to exit. To enter the one nickel atom needed enter 'I1', now will be induced for some information about atom 1

```
Enter TYPE, X, Y, Z, FRAC or <?> for help
>
```

First of all we will enter the atom's **TYPE**, **EXPEDT** uses this chemical symbol to look for the atom data file and place it in the experiment file, the main computational programs such as least squares program **GENLES** use the atom **TYPE** to restore scattering factor data or other need data. A type can also be used to determine ion specific information and to select isotope. The following three numbers to type in are the crystallographic fractional coordinates. For the multiplicity and site symmetry are controlled by the **GSAS** program.

Type 'NI 0 0 0 1' to enter the right values for the **NICKEL**.

```
Enter optional name </ for default = NI1 > >
```

An optional name will be chosen for the reference by **EXPEDT**, by assuming that it is ok enter /

```
Enter FLAG (I or A) and U's <<?> for help) >
```

The demanded **FLAG** is to enter an 'isotropic' or 'Anisotropic' temperature factor, for this example enter one single isotropic value '10.004' then the atom data is listed as follow

```
SER TYPE X Y Z FRAC NAME UIISO CODE STSYM MULT FXU
1 NI 0.00000 0.00000 0.00000 1.00000 NI1 0.00400 I M3M 4 000
Phase No. 1; Phase has 1 atoms; Title: NICKEL POWDER

Give atom editing command
<<?>,$,C,D,E,F,I,K,L,M,S,T,U,V,X,+,-,*,/, >
```

The atom data is listed in the same order as it was input. The extra spaces after I in the column '**CODE**'. It is the atom parameters codes place, **GSAS** handles the symmetry refinement rules for these parameters. The instructions **MULT**, **STSYM** and **FXU** give the number of the equivalent positions, point symmetry

and the damping factors for each of these classes of atom parameters. The editing menu became larger and too have a look at it options enter'?'

```
Atom editing commands:
<?> - Type this help package
x <?> - To give details on command x
$ - Enter DCL command
+,-,*, or / - Modify num. atom parameters
C t/s/s1:s2 codes - Change atom parameters
D t/s/s1:s2 codes - Modify atom damping factors
E t/s/s1:s2 - Erase atoms
F - Fix specific atom parameters
I s - Insert one atom or read atoms from a file
K - Set atom parameter constraints
L t/s/s1:s2 - List atoms, if none specified all atoms will be listed
M - Edit magnetic moment data
S - Modify the space group and unit cell data
I t/s/s1:s2 M U - Transform atom parameters by matrix "M" and vector "U"
U t/s/s1:s2 codes - Convert atom thermal factors
U t/s/s1:s2 codes - Modify refinement flags
X - Exit from editing atoms
Where "t" is an atom type, "s" is an atom sequence number, "s1:s2" refers
to a range of atom sequence numbers, and "codes" are specific to the
command; see the individual help listings for specific instructions
Phase No. 1; Phase has 1 atoms; Title: NICKEL POWDER
Give atom editing command
<<?>.$C.D.E.F.I.K.L.M.S.T.U.V.X.+.-.*./>
```

With each command followed by'?' it gives the help listings, each atom is entered it has a special sequence number in the range **1-999**, and this number is retained for all subsequent manipulations. After inserting one atom, subsequent atoms can be added by typing 'IN', where 'N' is an integer. Now after entering the necessary NICKEL atom, type 'X' to get back to the least squares main menu

```
Select editing option for Least Squares calculation
<<?>A,B,F,H,L,O,R,S,T,X >
```

To examine the controls (of the least squares) enter 'L

```
Maximum number of cycles is 3
Enter L-S control editing option <<?>A,B,C,D,E,J,L,P,T,U,V,X >
```

For the Rietveld's refinement we need to accomplish the required least squares control which is based on the number of least squares cycles to be performed.

```

A a - Maximum atom position shift
B b - Matrix band width (0 full matrix)
C n - Maximum number of cycles
D d - Marquardt factor
E - Change powder data Fobs extraction flags
J - Toggle Conjugate-Gradient vs Gauss-Newton minimization
L - List current settings
P - Select options for the output listing
T - Apply Tukey Robust/Resistant powder diffraction weighting
U - Force restraint weight factor modification
U n - Convergence criterion
Z - Set RMS random atom displacement before each cycle
X - Exit from editing least squares controls
Enter L-S control editing option (<<?>,A,B,C,D,E,J,L,P,T,U,X) >

```

The instruction 'E' gives access to the observed structure factors from Rietveld refinement in **GENLES** and the 'P' option is for requesting additional information farther on the printed default in **GENLES** list output, enter 'X' to go back to the main menu

```

Select editing option for Least Squares calculation
(<<?>,A,B,F,H,L,O,R,S,T,X) >

```

To check the overall parameters enter 'O'

```

Enter overall parameter to be edited (<<?>,A,B,C,D,E,H,L,O,P,S,X) >

```

The following menu lists the different classes of overall parameters, type '?' to see them

```

Overall parameters editing options:
<?> - Type this help listing
A - Absorption coefficients
B - Background coefficients
C - Diffractometer constants
D - Diffuse scattering parameters
E - Extinction parameters
H - Histogram scale factors
L - Lattice parameters
O - Preferred orientation parameters
P - Profile coefficients
S - Phase and element fractions
X - Exit from editing overall parameters
Enter overall parameter to be edited (<<?>,A,B,C,D,E,H,L,O,P,S,X) >

```

As to be noticed each kind of overall parameter has its own editing option and its own refinement flag, now to see how it works with the background and the scales editing options type 'B'

```

Editing of background parameters
Histogram no. 1 Bank no. 2 Two-theta = 88.05
Title: NICKEL POWDER STANDARD, ROOM TEMP 22:32:50 9/ 8/1984
**** Histogram will be used in least-squares
Power series in Q**2n/n! function (#4)

Background parameters:
Refinement flag = Y Damping flag = 0 Full background (Y)
0.100000E+01 0.000000E+00 0.000000E+00 0.000000E+00
Give background parameter edit command (<<?>,B,C,D,F,G,H,K,L,N,U,X) >

```

The background information of the first histogram is displayed along with its title and characteristic data. These background coefficients will be refined by

the least squares program, and for the **GSAS** it allows the use of 36 background coefficient, to list the help menu type '?'

```
Background edit commands:
<?> - Type this help listing
B - Modify the full background refinement flag
C - Change background function type, number of terms and their values
D n - Enter refinement damping factor "n" (n = 0 to 9)
    The applied shift is (10-n)*10% of the computed shift, n = 0 for full shift

F - Fix specific background parameters
G - Global setting of refinement flags
H m - Select histogram "m"
K b - Set constraints for background coeff. "b"
L - List the background parameters and refinement flag
N - Select next powder histogram
U - Toggle background refinement flag
X - Exit to overall parameter menu
Give background parameter edit command (<?>,B,C,D,F,G,H,K,L,N,U,X) >
```

Each option delivers an operation to be performed on the background parameters. The two options that exist to switch histogram are '/H' and 'N', the last one is more preferable, now enter 'N' to move to histogram two after knowing that histogram '1' is ok.

```
Histogram no. 2 Bank no. 3 Two-theta = 148.29
Title: NICKEL POWDER STANDARD, ROOM TEMP 22:32:50 9/ 8/1984
**** Histogram will be used in least-squares
Power series in Q**2n/n! function (#4)

Background parameters:
Refinement flag = Y Damping flag = 0 Full background (Y)
0.100000E+01 0.000000E+00 0.000000E+00 0.000000E+00
Give background parameter edit command (<?>,B,C,D,F,G,H,K,L,N,U,X) >
```

The information for histogram '2' are the same as the ones for histogram one and they are being satisfactory then type 'X' to return to the overall parameter editing menu

```
Enter overall parameter to be edited (<?>,A,B,C,D,E,H,L,O,P,S,X) >
```

To examine the scale factors of both histograms enter 'H'.

```
Editing histogram scale factors
Histogram no. 1 Bank no. 2 Two-theta = 88.05
Title: NICKEL POWDER STANDARD, ROOM TEMP 22:32:50 9/ 8/1984
**** Histogram will be used in least-squares

Histo. scale = 1.0000 Refine Y Damping flag = 0
Histogram scale editing options - (<?>,C,D,G,H,K,L,N,U,X) >
```

The scale factor for the first histogram is displayed and by default it is set to '1.000' and the refinement **FLAG** is set, to display the helping list enter '?'



```

Histogram scale editing options
<?> - Type this help listing
C - Change histogram scale
D - Change the histo. scale damping factor
G - Global setting of refinement flags
H m - Select new histogram "m"
K - Set histo. scale constraints
L - List the current histo. scale and refinement flag
N - Select next histogram
U - Toggle refinement flag
X - Exit to overall parameter editing menu
Histogram scale editing options - <<?>,C,D,G,H,K,L,N,U,X> >

```

The scale factors are satisfying for the first histogram, now we move on to the second by typing 'N'

```

Histogram no. 2 Bank no. 3 Two-theta = 148.29
Title: NICKEL POWDER STANDARD, ROOM TEMP 22:32:50 9/ 8/1984
**** Histogram will be used in least-squares
Histo. scale = 1.0000 Refine Y Damping flag = 0
Histogram scale editing options - <<?>,C,D,G,H,K,L,N,U,X> >

```

For the second histogram, It has the default scale set as '1.000' as the first one, this is ok, enter 'X' to go back to the overall parameters menu

```

Enter overall parameter to be edited <<?>,A,B,C,D,E,H,L,O,P,S,X> >

```

All the needed overall parameters are examined, enter 'X' to go back to the least squares menu

```

Select editing option for Least Squares calculation
<<?>,A,B,F,H,L,O,R,S,I,X> >

```

This least squares editing refinement is complete, enter 'X' to get back to the EXPEDT menu

```

EXPEDT data setup option <<?>,D,F,K,L,P,R,S,X> >

```

All needed data is settled up so enter 'X' to exit the EXPEDT and the GSAS prompt will display

```

TOP EXPEDT terminated successfully statement executed
ppuyez sur une touche pour continuer...

```

Now back to the POWPLOT main menu, enter 'N' so that the title of the second histogram and its status will be displayed.

## Refinement of powder data-program GENLES

To refine the selected parameters for the 'NICKEL' problem, to be specific: the two scale factors and eight background parameters, we need to run **GENLES**.

**GENLES** is the longest running program within the **GSAS** suite, its improvement is presented in a brief summary of statistical information for each cycle of refinement.

```
Restraint data statistics:
No restraints used

Powder data statistics
Bank Ndata Sum(w*d**2) Fitted wRp Rp -Bknd wRp Rp Dwd Average
Hstgm 1 PNT 2 2215 44353. 0.0427 0.0330 0.0441 0.0336 0.173 0.987
Hstgm 2 PNT 3 4181 24413. 0.0378 0.0286 0.0455 0.0329 0.212 0.994
Powder totals 6396 68766. 0.0408 0.0312 0.0446 0.0333 0.187
Cycle 3 There were 6396 observations.
Total before-cycle CHI**2 (offset/sig) = 6.8766E+04 < 5.5197E+02>

Reduced CHI**2 = 10.77 for 10 variables
Histogram 1 Type PNT Nobs = 105 R(F**2) = 0.1976
Histogram 2 Type PNT Nobs = 97 R(F**2) = 0.1172

CPU times for matrix build 0.11 sec; matrix inversion 0.00 sec
Final variable sum((shift/esd)**2) for cycle 3: 0.00 Time: 0.11 sec
Convergence was achieved and
STOP GENLES terminated successfully statement executed
Appuyez sur une touche pour continuer...
```

The payoff the least squares cycle are shown above.' "Restrain data statistics" is empty because none is used in this refinement. The following box shows results from fitting the two powder histograms as the residuals from the comparison between the calculated and the extracted structure factors while the Rietveld refinement, the running time and the convergence for the cycle are given. Enter any key to close the window.

**PLOOTING RESULTS-Program POWPLOT**To examine the results of the first least squares refinement, plot the observed and calculated powder pattern intensities for the two histograms then spot the differences and all it can be done by **POWPLOT**.

### Running POWPLOT

For windows it can be run from the 'GRAPHICS' pull down menu, then it will display a copyright message and prompt for a letter that mentions the terminal you are working on

```

C:\>echo off

-----
Program POWPLOT Version Win32
Powder pattern plotting program
Distributed on Fri Apr 18 09:12:00 2014
-----

-----
Allen C. Larson and Robert B. Von Dreele
Manuel Lujan, Jr. Neutron Scattering Center, MS-H805
Los Alamos National Laboratory, Los Alamos, NM 87545
-----

Copyright, 2000, The Regents of the University of California.

The last history record is :
HSTRY 5 GENLES Win32 Sep 24 01:22:20 2021 Sdsq= 0.688E+05 S/E= 0.257E-04
Enter graphic screen option <<?>,A,B,C,D,Z) >

```

After choosing the letter that is related to your terminal, enter 'N' as the respond to the hardcopy question.

```

Experiment title:
NICKEL POWDER REFINEMENT
Enter command <<?>,A,B,C,D,E,G,H,I,L,M,N,O,P,R,S,T,U,W,X) >

```

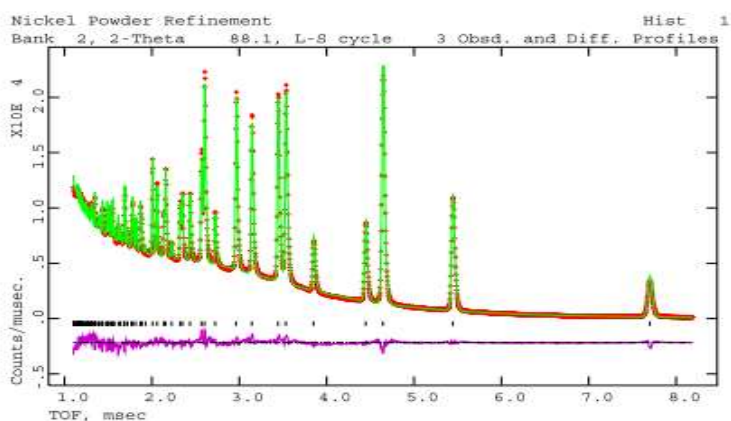
Choose the first histogram by entering 'N' or 'H1'

```

The selected histogram is:
Histogram no. 1 Bank no. 2 Two-theta = 88.05
Title: NICKEL POWDER STANDARD, ROOM TEMP 22:32:50 9/ 8/1984
*** Histogram will be used in least-squares
Reading histogram - please wait
Enter command <<?>,A,B,C,D,E,G,H,I,L,M,N,O,P,R,S,T,U,W,X) >

```

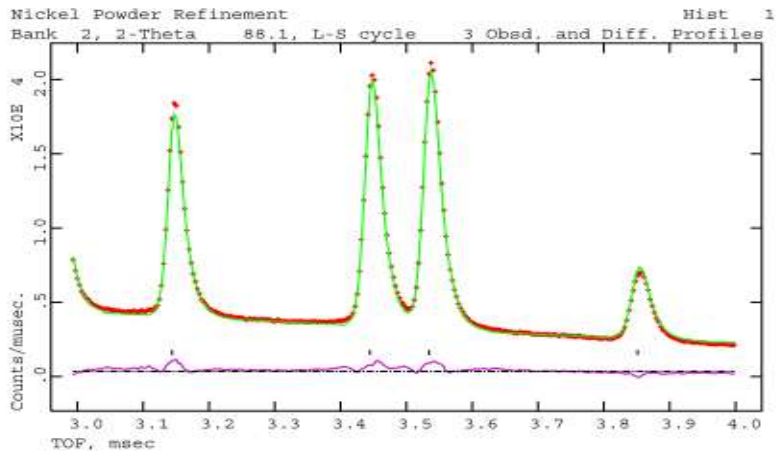
To plot the first histogram, enter different commands in one line such as 'M D T P', a few lines might appear as the diverse toggles are set.



The intensities of the powder pattern are displayed as crosses with the calculated values drawn as a curve. The difference curve is shown near the bottom of the graph with a zero line. The reflection positions are marked. To discover other characteristics existing in the differences, look at a small part of the plot. The next lines will look on the console.

```
Give X-min and X-max for next plot
(default plot="0 0" & <CR> for no plot) >
```

To have a look at the region from '3-4' msec with auto-scaling type '3 4 A'. The new plot would look like this.



There is a satisfying match between the factors. The noticeable difference is a small intensity mismatch for each reflection.

```
Give X-min and X-max for next plot
(default plot="0 0" & <CR> for no plot) >
```

You answer will be '?' This time

```
Do you wish to see error analysis (Y/<N>)? >
```

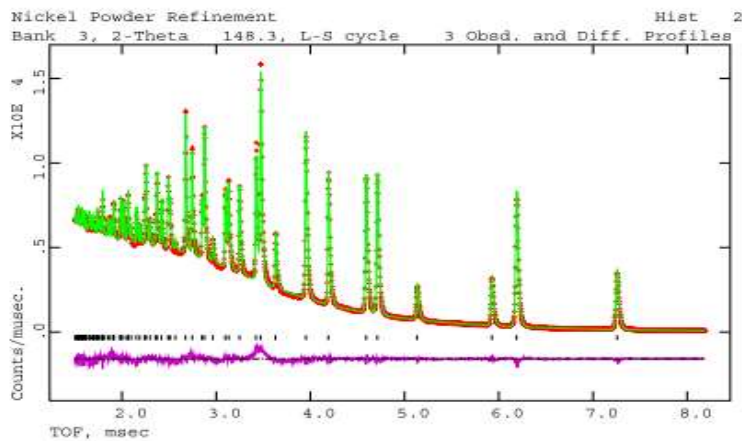
The option of viewing a series of graphs that portray the differences distribution is attached to a set of calculated values for the histogram. As an answer we take 'N' and it will cover the second histogram.

```
Enter command (<?>,A,B,C,D,E,G,H,I,L,M,N,O,P,R,S,T,U,W,X) >
```

Now back to the **POWLOT** main menu and to look at the second histogram enter 'H2' or 'N', certain information about the second histogram will be available.

```
Histogram no. 2 Bank no. 3 Two-theta = 148.29
Title: NICKEL POWDER STANDARD, ROOM TEMP 22:32:50 9/ 8/1984
**** Histogram will be used in least-squares
Reading histogram - please wait
Enter command (<?>,A,B,C,D,E,G,H,I,L,M,N,O,P,R,S,T,U,W,X) >
```

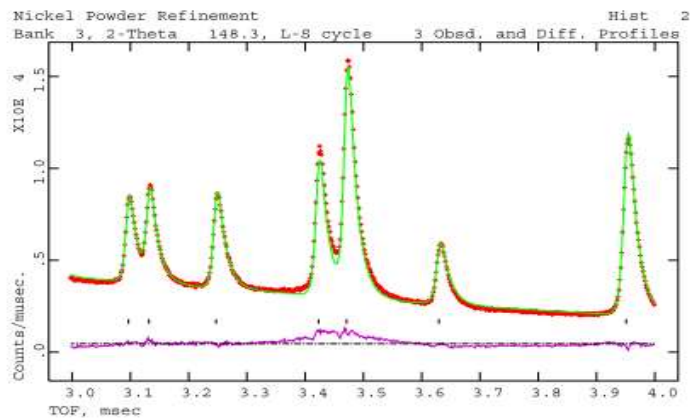
To obtain the plot of this histogram enter 'P' and it should be as follow



For this situation the overall fit is much better and the difference curve is much flatter. The console will display the following message

```
Give X-min and X-max for next plot
<default plot="0 0" & <CR> for no plot> >
```

The powder pattern from '3-4' mscs can be displayed after entering '3 4 A'.



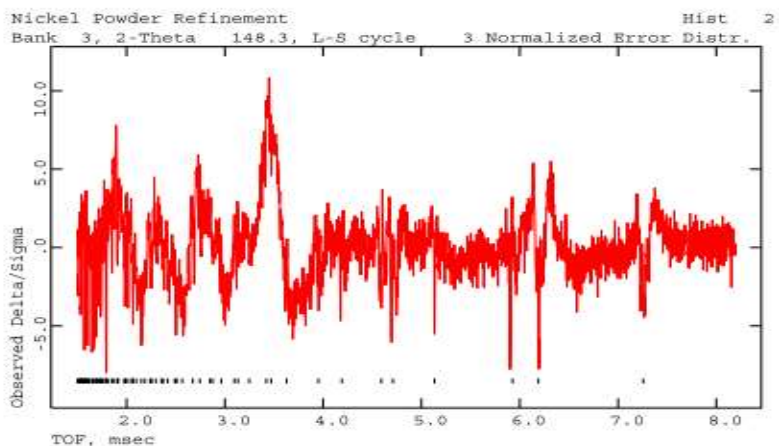
THE (111) reflection offset by one TOF frame is on the console as

```
Give X-min and X-max for next plot
<default plot="0 0" & <CR> for no plot> >
```

Respond with'?

```
Do you wish to see error analysis (Y<N>)? >
```

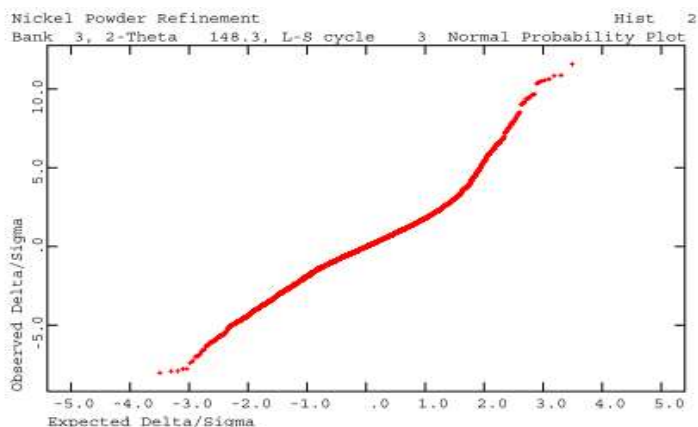
The fit worthwhile doing the error analysis, enter 'Y' then the plot Verses TOF will come after immediately.



The nature of any other systematics in the differences scaled by esd's can be revealed by the close examination of various regions of this plot. The reflection positions are marked accorded to the previous plot.

```
Give X-min and X-max for next plot
(default plot="0 0" & <CR> for no plot) >
```

To continue with this example enter '?' , the following plot is the normal probability plot for this histogram.



This plot gives nearly straight line, expediting the extreme positive end, expediting that certain values are for the most part normally distributed

```
Give X-min and X-max for next plot
(default plot="0 0" & <CR> for no plot) >
```

To examine parts of this plot, type '?' to continue

```
Range of expected deltas to be used for slope/intercept calculation: -2.00 2.00
New values ?(</ to accept) >
```

Next the program will compute the slope and intercept for the distribution, enter/

```
The slope & intercept of the normal probability plot are 2.1124 0.0146
Enter command (<<?>,A,B,C,D,E,G,H,I,L,M,N,O,P,R,S,T,U,W,X) >
```

The slope's high value describes an incomplete refinement, this value will diminish as more the parameters are refined and a better fit is obtained. The main menu **POWPLOT** shows up immediately.

This operation is all done so enter X, **POWPLOT WILL** be closed.[18]

## CONCLUSION

The Rietveld method has contributed to a renewed interest in powder diffraction techniques; in this chapter we introduced the GSAS program which is a program to perform the Rietveld analysis and we implemented the EXPEDT software with the nickel example to get a better view of this program, it demonstrates some the options that can be offered in the determination of structures, calculation of the Fourier maps, and structure refinement along with Rietveld refinement.

# ***CHAPTER 3***

***CHAPTER 3***



## INTRODUCTION

The goal of the Rietveld method is to fit a structural model to powder diffraction data. To accomplish this, we need to determine the structural parameters for the crystalline phases present. In this chapter we will provide tutorial examples of how to use GSAS software package with the EXPGUI interface to perform Rietveld analysis.

### A. EXPGUI

EXPGUI is a graphical interface for the GSAS package, it does two things: allows the modification of the GSAS experiment file with a graphical user interface (GUI), and invokes the programs inside the GSAS package. EXPGUI is written in the Tcl/Tk scripting language, so it is largely independent.

It edits the cell and atomic parameters as well as the damping and the refinement flags. (Phase parameters), provides information about scale factor, background, diffractometer constants, phase fractions, and profile terms. (Histogram parameters) and Controls the number of cycles, the print options and the  $F_{obs}$  extraction parameters (Least-squares options).

In another hand, EXPGUI can't change atoms nature, can't invent or modify soft constraints or many types of hard constraints. It is not applicable on magnetic scattering parameters or on single-crystal histograms.

#### 1. The EXPGUI interface

It contains three sections; the menu bar at the top is used to run all of the various GSAS programs and to select options within EXPGUI. Below the menu bar there is a button bar invokes frequently used menu bar commands. The program documentation includes instructions and examples on how to customize that button bar. The bottom section of the window is to display and modify the contents of the experiment file.

#### 2. EXPGUI UTILITIES

The most significant programs are the LIVEPLOT and the LSTVIEW programs, which are independent Tcl scripts.

- **LIVEPLOT:** a program to display the Rietveld results by plotting an observed and computed diffractogram along with the background curve and the observed-minus-computed differences.
- **LSTVIEW:** used to view the GSAS listing file in a scrolled window

## B. Rietveld refinement by EXPGUI

### 1. Refinement requirements

To perform these tutorials we need the GSAS program and the EXPGUI on the computer, and also three files:

- **The raw data file:** it's an external text file whose records contain data values that are arranged in fields; there filename extensions are .dat. and .txt.
- **The instrument parameter file:** aims to describe an instrument, in particular providing details about those components of the instruments that are critically affecting the observed signal from the experiment.
- **The CIF file (the unit cell and the atomic parameters):** A file constructed by editing a template file or as an output file by a crystallographic software package, considered as a common output option for the Rietveld refinement program.

### 2. Refinement procedure and steps

#### a. Run EXPGUI

Once EXPGUI has been started, a text window and an interface window are opened. The interface window is used to set refinement parameters. Some results will be returned to you in the text window.

#### b. Opening an existing .exp file or Creating a new one

When you first run EXPGUI, the program will instruct you to open an existing file. If EXPGUI is already running, you may open a file using file drop-down menu. If you wish to create a new file, type in the desired name and click the read usa-button.

#### c. Enter crystal structure data for phases in the exp file

To enter structure data, select the phase title, the Space Group, and the unit cell values. Then select the add usa-button. GSAS will then give a symmetry analysis output for you to check to make sure you have entered the space group

correctly. Select continue once you are satisfied with the structure data. This will give the main EXPGUI screen with the cell information but no atoms. Now select the add new atoms usa-button and add in the atom information using the keyboard.

The alternative way to enter phase data is to import it directly from the database as a CIF format like our case.

**d. Open a histogram (powder diffraction data)**

Select the powder tab followed by the add histogram usa-button. Find and add the data file and the instrument parameter file.

**e. Fit the background**

Set the function type to 1 (shifted) and the number to 6

**f. Fit the profile**

In the profile tab, set the profile type to 3. (Pseudo-Voigt with Finger-Cox-Jephcoat peak asymmetry function)

**g. Perform refinements**

For each refinement run **GENLES** using the usa-buttons, preceded by **POWPREF** when specific variables such as peak cutoff, or peak profile, sample displacement, or an instrument parameter is changed (modified). Run **LIVEPLOT** to see the state of the refinement in terms of how well the calculated pattern is fitting the data. The black crosses are the raw data, the red line is the calculated pattern and the blue line below is the difference.

## C. Application of Rietveld refinement on powder samples

### 1. CORINDON GSAS/EXPGUI refinement

For the 'CORINDON' we used the following data parameters:

- Crystallographic information file:  $Al_2O_3.cif$
- The raw data file: 1.gsas
- Instrument parameter file: poudre.prm

After preparing and treating the  $Al_2O_3$  powder sample; we collected the data to refine them by following these refinement steps:

Step\_1: changing the Background function

Step\_2: Refine scale factor and background.

Step\_3: Refine scale factor, zero point and the unit cell parameters.

Step\_4: Refine scale factor and profile shape parameters (LX then LY).

Step\_5: Refine scale factor and Gaussian widths terms (GU then GV then GW)

Step\_6: refine scale factor and asymmetry parameter.

Step\_7: refine scale factor and Coordinates and overall Uiso.

Step\_8: Refine scale factor and the March-Dollase Preferential Orientation.

Step\_9: LX and GU

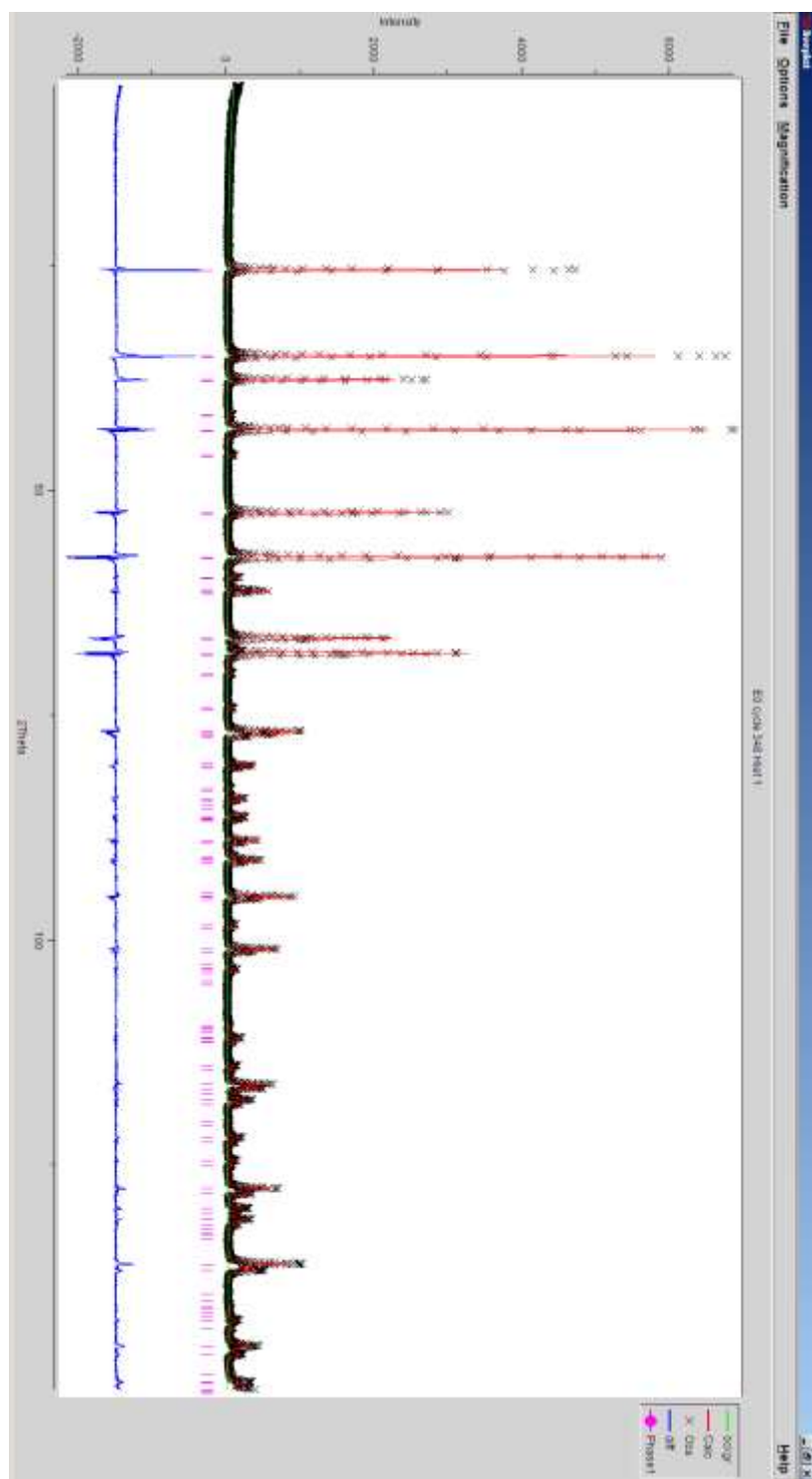
Step\_10: LX and GV

Step\_13: LX and GW

Step\_14: LX and LY

Step\_15: LX and GU and asymmetry parameter.

The out coming plot of observed and calculated pattern was as follow



**Figure 1.1:** Plot of calculated and observed patterns with peaks positions and differences plot of  $Al_2O_3$

- Agreement factors

$R_p$	$R_{wp}$	$CHI^2$
0.1243	0.1585	3.141

- Structural information

A and B	C	$\alpha$ and $\beta$	$\gamma$	System
4.758380	12.990047	90.000	120.000	Hexagonal

- Asym, shft and trns parameters

Asym	Shft	Trns	Space group
7.174E+00	-2.754E-01	5.391E+00	R- 3 C

- Gaussian width parameters

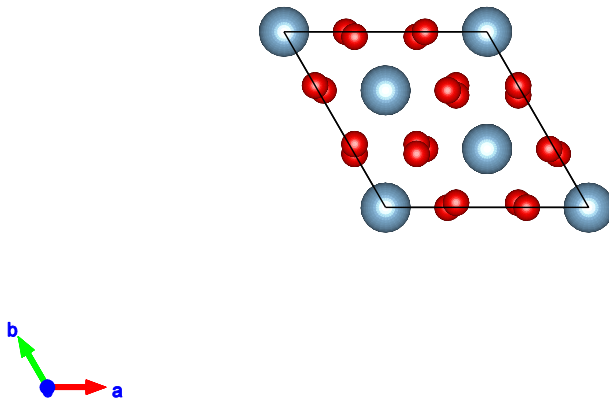
GU	GV	GW
0.000E+00	1.978E+01	1.185E+01

- Laurantsian parameters

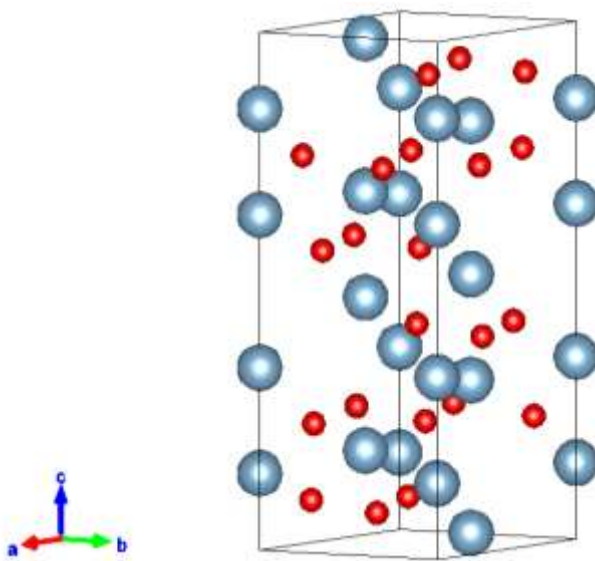
LX	LY
5.396E+00	3.265E+00

- Atoms positions

ATOMS/ POSITION	X	Y	Z	$U_{iso}$	Occ
$Al_2$	0.000000	0.000000	0.352183	0.00517	1.0000
$O_3$	0.305541	0.000000	0.250000	0.00508	1.0000



**Figure1.2:** 2D Structural for  $AL_2O_3$  phase



**Figure1.3:** 3D Structural for  $AL_2O_3$

.ZINCITE GSAS/EXPGUI refinement:

After preparing and treating the “ZnO” powder sample; we collected the data to refine them by following these refinement steps:

Step\_1: changing the Background function.

Step\_2: Refine scale factor and background.

Step\_3: Refine scale factor and zero point.

Step\_4: Refine scale factor and the unit cell parameters.

Step\_5: Refine scale factor, unit cell parameters and the zero point.

Step\_5: Refine scale factor and Gaussian widths terms at once (GU,GV and GW)

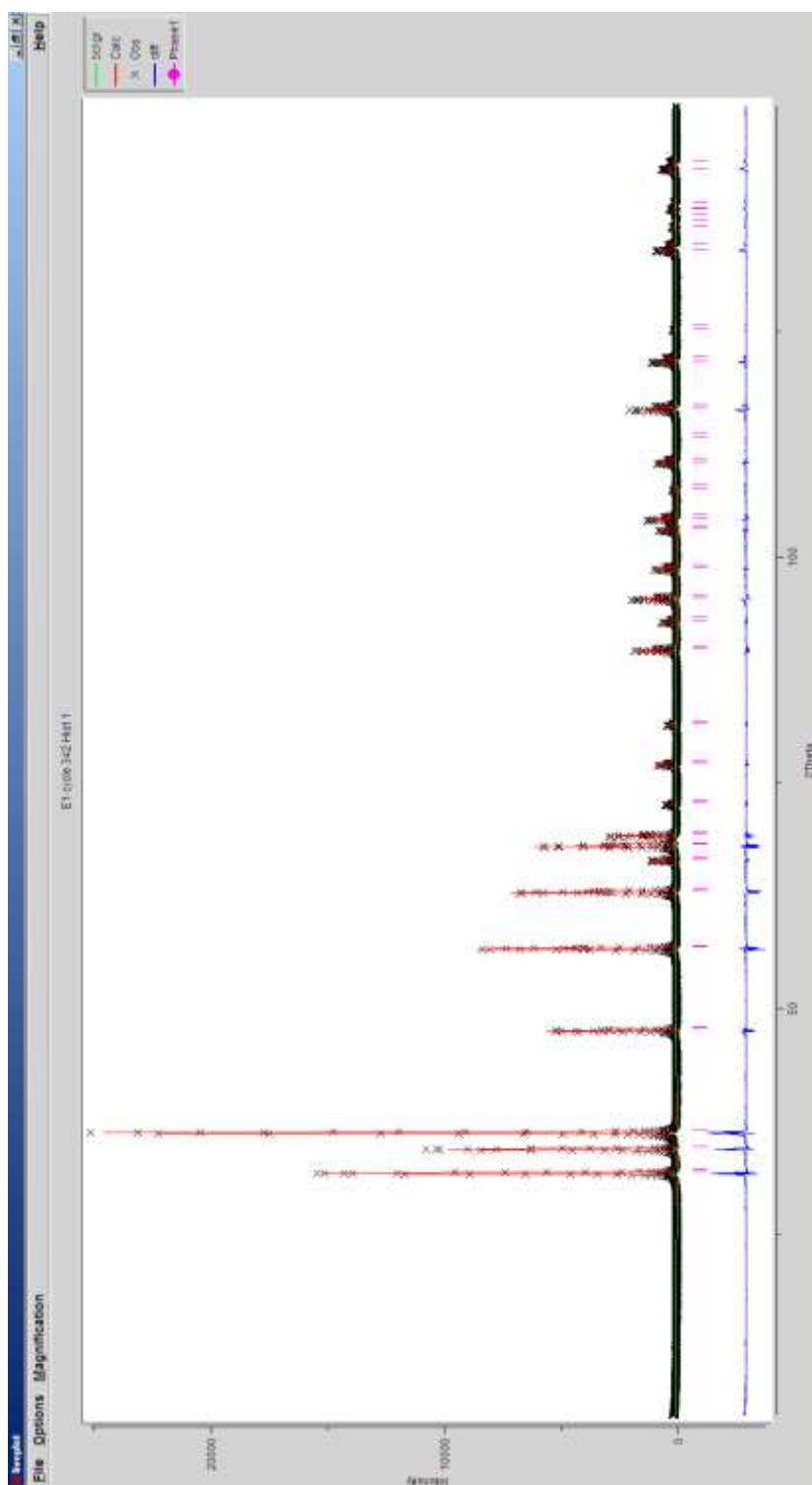
Step\_6: Refine scale factor and profile shape parameters (LX then LY).

Step\_6: refine scale factor and asymmetry parameter

Step\_7: refine scale factor and Coordinates and overall Uiso

Step\_8: Lx, GU and asymmetry parameter.

The resulting plot of observed and calculated pattern was as follow



**Figure 2.1:** Plot of calculated and observed patterns with peaks positions and differences plot of **ZnO**.



- Agreement factors

$R_p$	$R_{wp}$	$CHI^2$
0.0899	0.1193	3.088

- Structural information

A and B	C	$\alpha$ and $\beta$	$\gamma$
3.251807	5.209905	90.000	120.000

- Asym, shft and trns parameters:

Asym	Shft	Trns	Space group
862560E+01	0.245421E+02	0.550714E+01	P 63 m c

- Gaussian width parameters

GU	GV	GW
0.0000E+00	0.022625E+02	-0.217307E+01

- Laurantsian parameters

LX	LY
0.466327E+01	0.248388E+01

- Atoms positions

Atoms/postions	X	Y	Z	Uiso	occ
Zn	0.3333	0.66667	-0.002822	0.1134	1.000
O	0.3333	0.66667	0.377823	0.0815	1.000

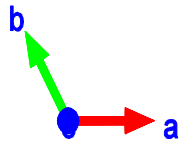
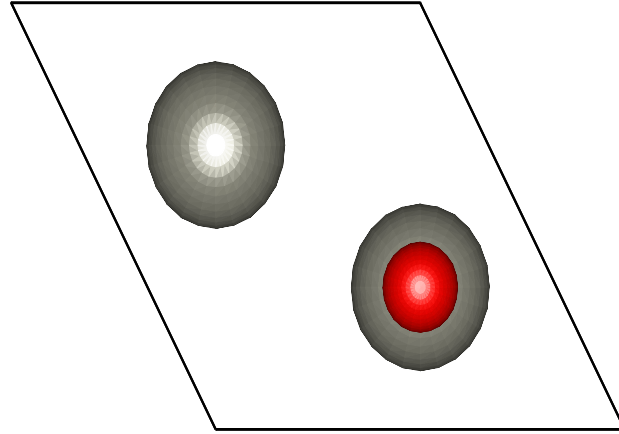


Figure 2.2: 2D Structural for ZnO phase

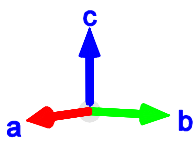
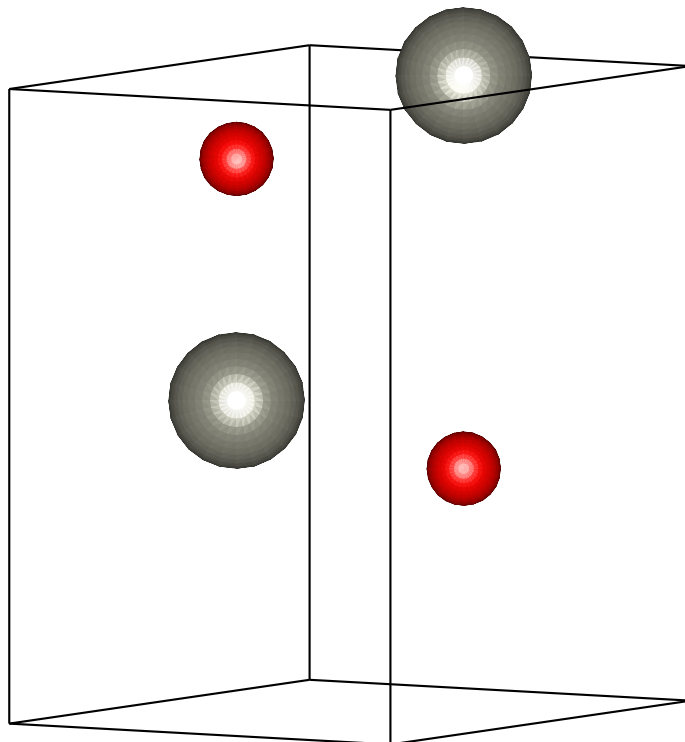


Figure2.3: 3D structural for ZnO phase

## 2. ZIRCON GSAS/EXPGUI refinement

After preparing and treating the  $ZrSiO_4$  powder sample; we collected the data to refine by following these refinement steps:

Step\_1: changing the Background function

Step\_2: Refine scale factor and background.

Step\_3: Refine scale factor, background and zero point.

Step\_4: Refine scale factor and profile shape parameters (LX then LY).

Step\_5: Refine scale factor and Gaussian widths terms (GU then GV then GW).

Step\_6: refine scale factor and asymmetry parameter.

Step\_7: refine scale factor and Coordinates and overall Uiso.

Step\_8: Refine scale factor and the unit cell parameters.

Step\_9: Refine scale factor, unit cell parameters and the zero point.

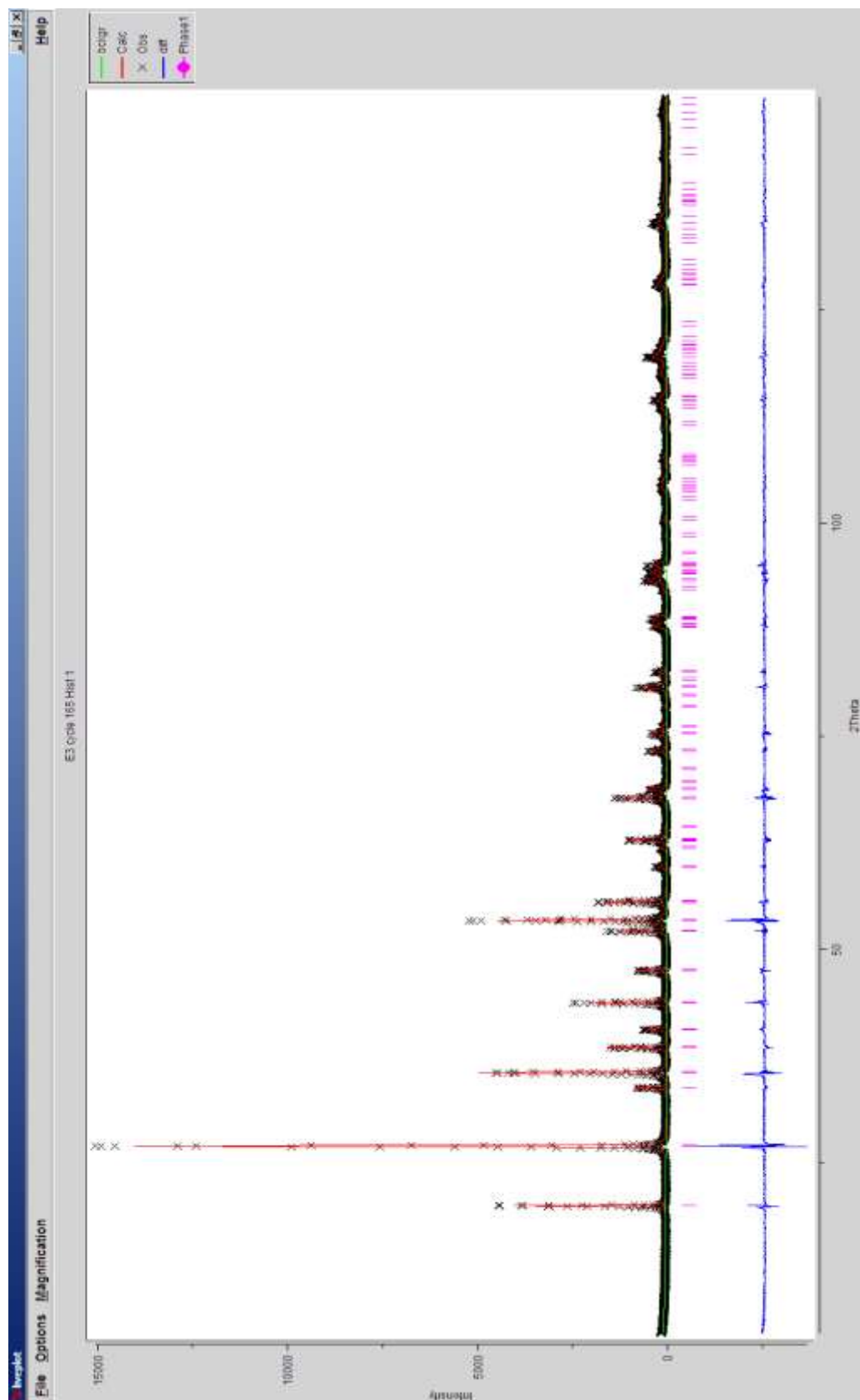
Step\_10: LX and GU

Step\_11: LX and LY

Step\_12: LX and GU and asymmetry parameters

Step\_13: unit cell parameters.

The resultant plot will look like the following:



**Figure3.1:** Plot of calculated and observed patterns with peaks positions and differences plot of  $ZrSiO_4$

- Agreement factors

$R_p$	$R_{wp}$	$CHI^2$
0.1226	0.1547	3.510

- Structural information

A and B	C	$\alpha, \beta$ and $\gamma$	System
6.604012	5.98973	90.000	TETRAGONAL

- Asym, shft and trns parameters:

Asym	Shft	Trms	Space Group
0.620543+01	-0.384920+01	0.585335+01	I 41/a m d

- Gaussian width parameters

GU	GV	GW
0.0000	0.822048	0.500000+01

- Laurantsian parameters

LX	LY
0.116926+01	0.250770+02

- Atoms positions

ATOMS/POSITION	X	Y	Z	U	OCC
Zr	0.0000	0.75000	0.12500	0.007	1.000
Si	0.0000	0.75000	0.62500	0.005	1.000
$O_4$	0.0000	0.06484	0.19677	0.010	1.000

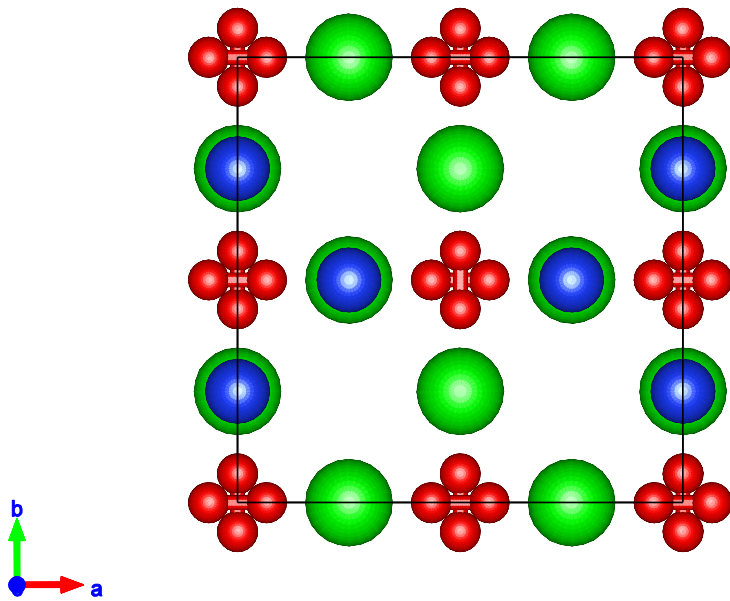


Figure3.2: 2D Structural for  $ZrSiO_4$

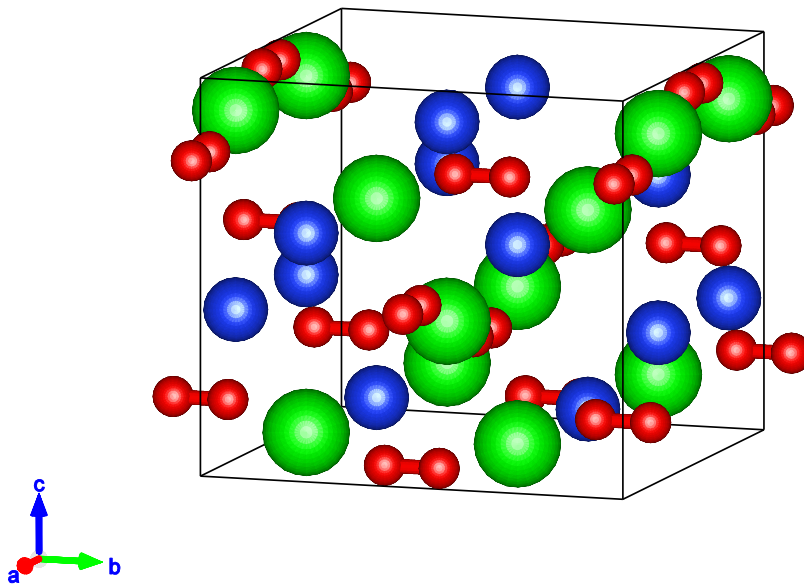


Figure3.3: D Structural for  $ZrSiO_4$

### 3. FLUORINE GSAS/EXPGUI refinement

After preparing and treating the  $CaF_2$  powder sample; we collected the data to refine them by following these refinement steps

Step\_1: changing the Background function

Step\_2: Refine scale factor and background

Step\_3: Refine scale factor and zero point

Step\_4: Refine scale factor and profile shape parameters (LX then LY).

Step\_5: Refine scale factor and Gaussian widths terms (GU then GV then GW)

Step\_6: refine scale factor and asymmetry parameter

Step\_7: refine scale factor and Coordinates and overall Uiso.

Step\_8: Refine scale factor and the March-Dollase Preferential Orientation.

Step\_9: Refine scale factor and the unit cell parameters.

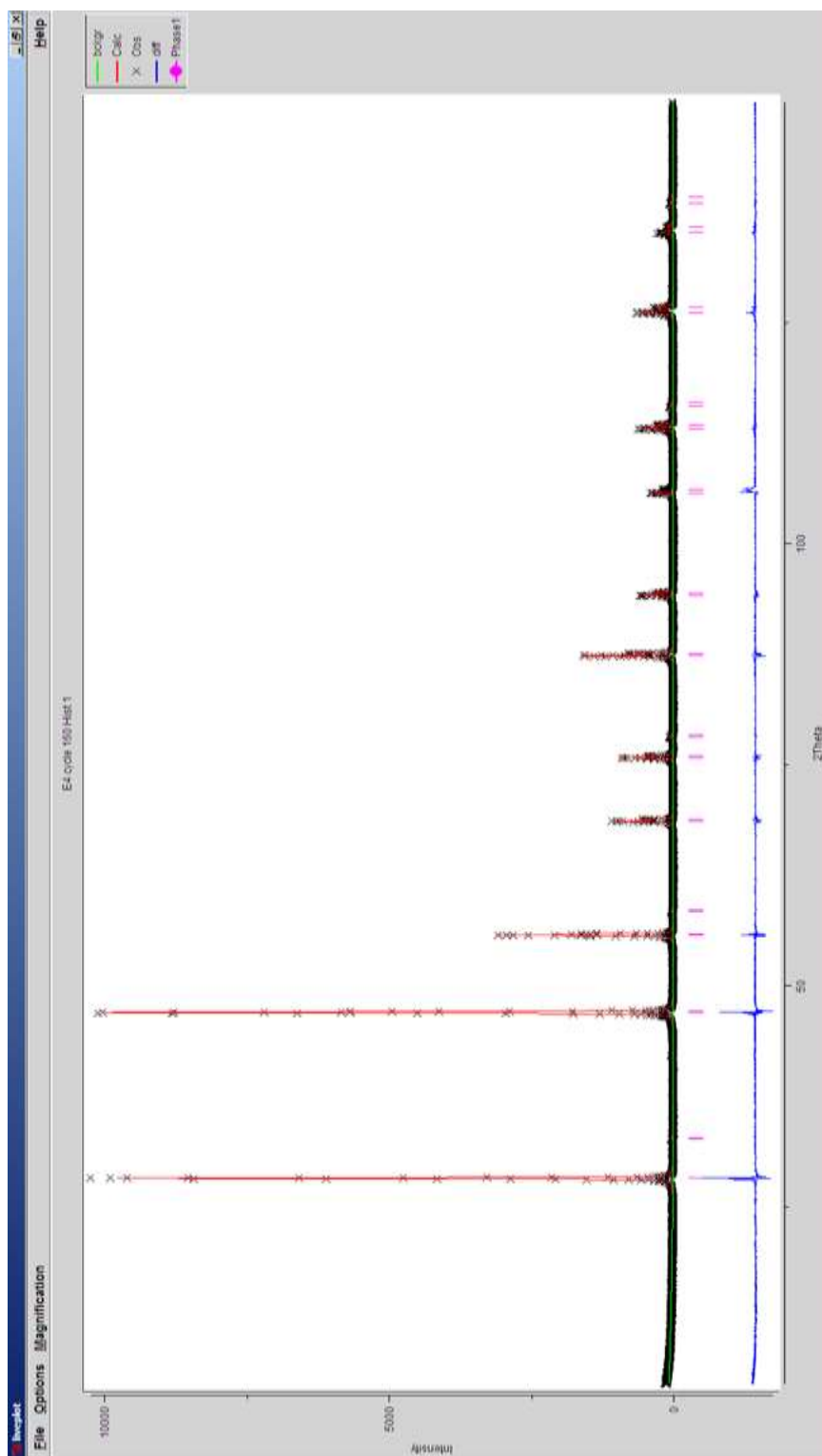
Step109: Refine scale factor, unit cell parameters and the zero point.

Step\_11: LX and GU

Step\_12: LX and GV

Step\_13: LX and GW

Step\_14: LX, LY and asym



**Figure 4.1:** Plot of calculated and observed patterns with peaks positions and differences plot of  $\text{CaF}_2$ .



- Agreement factors

$R_p$	$R_{wp}$	$CHI^2$
0.1186	0.1918	2.372

- Structural information

A,B and C	$\alpha, \beta$ and $\gamma$	System
5.46236	90.00000	cubic

- Asym, shft and trns parameters:

ASYM	Shft	Trns	Space group
0.521713+01	-0.351053+01	0.331411+01	F m -3 m

- Gaussian width parameters

GU	GV	GW
0.505090	0.107866+02	0.417344+01

- Laurantsian parameters

LX	LY
0.365115+01	0.333940+01

- Atoms positions

ATOMS/POSITION	X	Y	Z	U	OCC
Ca	0.00000	0.00000	0.00000	0.010	1.000
F2	0.25000	0.25000	0.25000	0.013	1.000

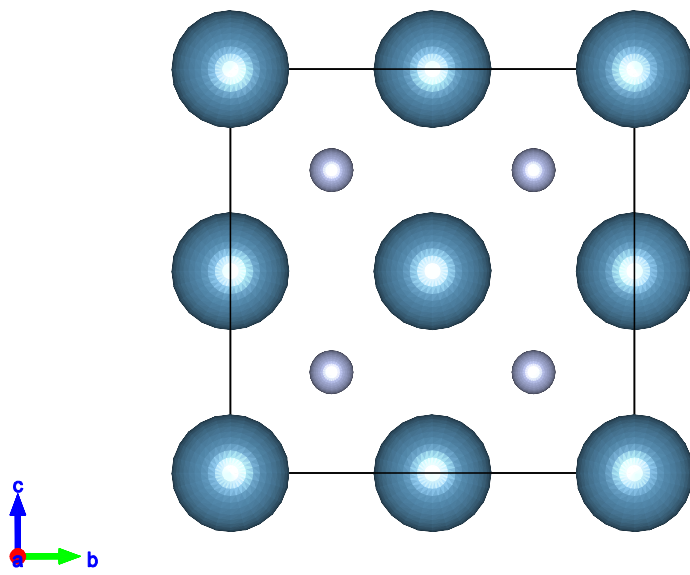


Figure 4.2: 2 D Structural for  $\text{CaF}_2$

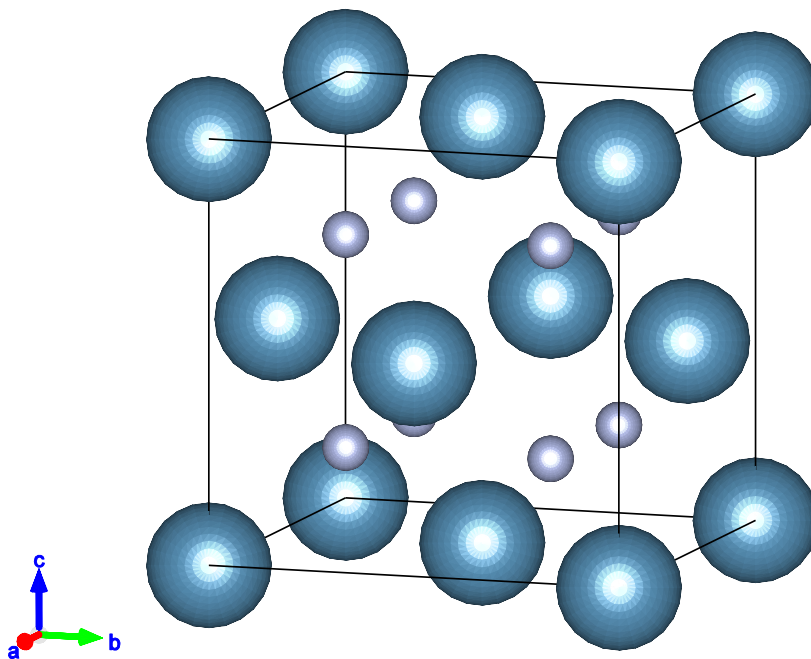


Figure 4.3: 3D Structural for  $\text{CaF}_2$

## CONCLUSION

The main Goal of the Rietveld refinement is to optimize the outcome of the fit until it is close to the ideal (1). In this chapter we tried to refine different X-ray diffraction patterns with single-phase nature, we deduced that the results depend on many variables such as: the Gaussian parameters, the asymmetry parameters, the Laurentian parameters and so go on, which resulted for the cases a variety different analyzing steps.

## **General conclusion**

The Rietveld method found its way to solve the facing problems when we do a powder analysis refinement instead of a single crystal analysis, by modeling the entire powder pattern the minimized the difference between calculated and measured powder pattern has improved which provides sufficient information.

We gave a slight view on the X-ray method and the Rietveld refinement on the first chapter, to illustrate the Rietveld method and its steps and also include the GSAS “EXPEDT” tool (to treat the example of “nickel”) as a running program for the Rietveld refinement. At the last chapter, we applied the introduced the “EXPGUI” software and applied it on several examples to illustrate many structural information on these samples as X-ray powder patterns. All the way of refining different parameters we check the goodness of fit and try to improve it farther to obtain better final results.

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## ABSTRACT

X-ray diffraction (XRD) is an invasive technique in materials science, it is a versatile, non-destructive analytical technique used to extract information about the structural model such as cell parameters and to identify and quantify phases present in powdered and solid samples. For this purpose, the Rietveld method is one of the most famous and successful methods that have been used in materials science. Especially in the case of a sample that contains a phase that does not exist in the database. In this work we will detail some theoretical aspects of the Rietveld method and the GSAS program with their different commands, using some special powder examples.

La diffraction des rayons x (XRD) est une technique invasive en science des matériaux, c'est une technique polyvalente et non destructive utilisée pour extraire des informations sur le modèle structural telles que les paramètres cellulaires et pour identifier et quantifier les phases présentes dans les échantillons en poudre et solides. A cette fin, la méthode de Rietveld est l'une des méthodes les plus célèbres et les plus réussies utilisées en science des matériaux surtout dans le cas d'un échantillon qui contient une phase qui n'existe pas dans la de données. Dans ce travail, nous détaillerons certains aspects théoriques de la méthode Rietveld et du programme GSAS avec leurs différentes commandes, en utilisant quelques exemples spéciales de poudres.

ان انعراج الاشعة السينية هو تقنية اجتاحت علم المواد و هي تقنية تحليلية متعددة الاستخدامات و غير مدمرة تستخدم لاستخراج المعلومات حول النموذج الهيكلي مثل معلمات الخلية و لتحديد و قياس الاطوار الموجودة في عينات المسحوق و الصلب لهذا الغرض تعد طريقة ريتفالد واحدة من اشهر الاساليب المستخدمة و اكثرها في علم المواد خاصة في حالة عينة تحتوي على طور غير موجود في قاعدة البيانات لذلك في هذا العمل سنقوم بتفصيل بعض الجوانب النظرية لطريقة ريتفالد و برنامج كما سنعالج في هذا البحث بعض الأمثلة الخاصة لمساحيق.