JOINT INSTITUTE FOR NUCLEAR RESEARCH

Frank Laboratory of Neutron Physics

REPORT ON THE INTEREST PROGRAMME

Introduction to neutron scattering experiments at large scale facilities

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1. Introduction

1.1. Neutrons

Neutrons are subatomic particles with no net electric charge, unlike other particles such as protons and electrons, which have an intrinsic electric charge. It has a mass equal 1.67×10^{-27} kg. This is distinction that makes the interaction between neutrons and matter particularly interesting when compared to proton-matter or electron-matter interactions. It together with protons constitutes nuclei of an atom. Protons and neutrons are attracted to each other via the strong force. and also, protons repel each other via electrostatic force. Therefore, neutrons within the nucleus act like nuclear glue. They attract each other and protons which helps offset the electrical repulsion between protons. While the latter interactions are dictated by Coulomb forces involving strong charge repulsion or attraction, charge-free neutrons can move through matter undeterred by these factors. This translates to neutrons generally possessing the ability to penetrate deeper into matter than other subatomic particles. When contemplating the application value of this trait, one can imagine that by evaluating the properties of neutrons scattering from matter, information can be gathered about the bulk characteristics of that matter that cannot be gained from the scattering of other subatomic particles with shorter penetration depths.

1.2 X-ray scattering

X-ray and neutron scattering can be used to investigate a wide range of substances, such as semiconductors, poly and single crystals, metals and alloys, solids, liquids and synthetic polymers etc. These two methods are complementary.

The x-rays are scattered by electrons within the sample, this means the more electrons, the more scattering, meaning that heavier elements with many electrons are often highly suited for scattering experiments. Another consideration is contrast, in this case contrast works based on differences in electron density within a sample. A desirable sample would be highly electron-dense, and surrounded by a sparse medium, so there will be significant contrast and the sample can be easily analysed. Matrices with a similar electron density to the sample should be avoided, such as imaging silicon particles in a silica gel, many scattering experiments can submerge samples in solution to enhance contrast.

The scattered x-rays from electrons within a sample will interfere, in electron dense areas of the sample, meaning that detectors are typically analysing and

characterising scattering that has undergone constructive interference within the sample, allowing for identification of electron location and other structural information.

X-ray scattering techniques can be broadly divided into elastic or inelastic scattering. With elastic scattering, the scattered x-rays have the same energy/wavelength as the incident x-rays, whereas with inelastic scattering, the scattered x-rays have a different energy/wavelength.

1.3. Neutron scattering

Recently, neutron scattering experiments are thought to be a unique technique to investigate the structure of materials. Neutron scattering is the technique of choice for condensed matter investigations in general because thermal/cold neutrons are non-invasive probes; they do not change the investigated sample since they do not deposit energy into it. Neutrons interact through nuclear interactions. Electron beams interact through electrostatic interactions. Light interacts with matter through polarizability and is sensitive to fluctuations in the index of refraction. For this, neutrons have high penetration (low absorption) for most elements making neutron scattering a bulk probe. Neutrons have the right momentum transfer and right energy transfer for investigations of both structures and dynamics in condensed matter.

Contrary to X rays, neutrons are not scattered appreciably by electrons. Neutron scattering experiments measure the number of neutrons scattered by a sample as a function of the wavevector charge (Q) and the energy change (E) of the neutron. They interact mainly with the nucleus. Wavelength of neutrons is determined by equation $\lambda = h/mv$ where m and v are mass and velocity of neutron and h is the Planck constant. When the neutron beam passes through the moderator at temperature T, the mean-square velocity of the neutrons v^2 satisfies the relationship

$$mv^2/2 = 3k_BT/2$$

k_B is the Boltzmann constant. The maximum intensity of the thermal neutron spectrum is at wavelength:

$$\lambda_{max} = (h^2/3mk_BT)^{1/2}$$

Dimensions of the nucleus are much smaller than the neutron wavelength so the scattering length for thermal neutrons will be isotropic.

The experimental scattering of neutrons can basically be part into two categories:

elastic neutron scattering (also known as neutron diffraction) and inelastic neutron scattering. Both techniques have their own unique purposes and methods of implementation.

Elastic Neutron Scattering (Neutron Diffraction)

The basis of elastic neutron scattering is fundamentally no different than that of other diffraction processes such as the various forms of light diffraction. Just like all other quantum particles, neutrons can be described from both a particle and wave-like perspective. In this case, the wave-like behaviour of neutrons allows it to experience the phenomenon of diffraction typically associated with light, which is more naturally thought of from a wave point of view. Elastic neutron scattering consists in measuring the scattered intensity with varying scattering angle. This is a way of resolving the scattering variable $Q = (4\pi/\lambda) \sin(\theta/2)$ where λ is the neutron wavelength and θ is the scattering angle. This is performed by either step-scanning or using a position-sensitive detector. The main types of elastic scattering instruments are diffractometers (either for single-crystal, powder diffraction or for diffuse scattering from amorphous materials), reflectometers and SANS instruments. Diffractometers probe the high Q range (Q > 0.5 Å-1) whereas reflectometers and SANS instrument cover the low-Q range (Q < 0.5 Å-1). They all investigate sample structures either in crystalline of amorphous systems.

Inelastic Neutron Scattering

The inelastic scattering of neutrons, as the name of the technique implies, involves processes in which neutrons incident on a sample experience an exchange of energy with the matter, resulting in a shift in energy/wavelength of the exiting neutrons relative to the incident ones. Inelastic neutron scattering consists in monochromatic, collimation, scattering from a sample, analysis of the neutron energies then detection. Inelastic scattering corresponds to energy transfers around zero, whereas inelastic scattering corresponds to finite energy transfers. The main types of inelastic spectrometers are the triple-axis, the time-of-flight, and the backscattering spectrometers. These instruments cover the meV to meV energy range. They investigate sample dynamics and structure.

2. Neutron/X-ray data manipulation

2.1 Fullprof

The program *FullProf* has been mainly developed to perform Rietveld analysis [1] of neutron or X-ray powder diffraction data collected at constant, or variable, step in scattering angle 2θ or using the technique of neutron time-of-flight (TOF). Single Crystal refinements can also be performed alone or in combination with powder data. However, the program has some "structure determination" capabilities by using the Simulated Annealing method for global optimization.

Two versions of the source code exist at present. The first corresponds to a source written in standard FORTRAN 77 (F77) language, and is organised as to be easily adapted to different computers. This version is that running in multiple platforms. The second version of the source code has been developed from the previous one, and it has been totally re-written in a subset (ELF90) of the new standard Fortran 95 (F95). It uses the new syntax and features of Fortran 95. This last version has many more options that the F77 version, which is no more developed (Version 3.5d - Oct98).

There are some of the most important features of FullProf which summarised below:

X-ray diffraction data: laboratory and synchrotron sources. • Neutron diffraction data: Constant Wavelength (CW) and Time of Flight (TOF). • One or two wavelengths (eventually with different profile parameters). • The scattering variable may be 2θ in degrees, TOF in microseconds and Energy in KeV. • Background: fixed, refinable, adaptable, or with Fourier filtering. • Choice of peak shape for each phase: Gaussian, Lorentzian, modified Lorentzians, pseudo-Voigt, Pearson-VII, Thompson-Cox-Hastings (TCH) pseudo-Voigt, numerical, split pseudo-Voigt, convolution of a double exponential with a TCH pseudo-Voigt for TOF. • Multi-phase (up to 16 phases). • Preferred orientation: two functions available. • Absorption correction for a different geometries. Micro-absorption correction for Bragg-Brentano set-up. • Choice between three weighting schemes: standard least squares, maximum likelihood and unit weights. • Choice between automatic generation of hkl and/or symmetry operators and file given by user. • Magnetic structure refinement (crystallographic and spherical representation of the magnetic moments). Two methods: describing the magnetic structure in the magnetic unit cell of making use of the propagation vectors using the

crystallographic cell. This second method is necessary for incommensurate magnetic structures. • Automatic generation of reflections for an incommensurate structure with up to 24 propagation vectors. Refinement of propagation vectors in reciprocal lattice units. • hkl-dependence of FWHM for strain and size effects. • hkl-dependence of the position shifts of Bragg reflections for special kind of defects. • Profile Matching. The full profile can be adjusted without prior knowledge of the structure (needs only good starting cell and profile parameters). • Quantitative analysis without need of structure factor calculations. • Chemical (distances and angles) and magnetic (magnetic moments) slack constraints. They can be generated automatically by the program. • The instrumental resolution function (Voigt function) may be supplied in a file. A microstructural analysis is then performed. • Form factor refinement of complex objects (plastic crystals). • Structural or magnetic model could be supplied by an external subroutine for special purposes (rigid body TLS is the default, polymers, small angle scattering of amphifilic crystals, description of incommensurate structures in real direct space, etc). • Single crystal data or integrated intensities can be used as observations (alone or in combination with a powder profile). • Neutron (or X-rays) powder patterns can be mixed with integrated intensities of X-rays (or neutron) from single crystal or powder data. • Full Multi-pattern capabilities. The user may mix several powder diffraction patterns (eventually heterogeneous: X-rays, TOF neutrons, etc.) with total control of the weighting scheme. • Montecarlo/Simulated Annealing algorithms have been introduced to search the starting parameters of a structural problem using integrated intensity data.

Input files have different extensions :

• FILE.pcr – Input control file. It will be called sometimes PCR-file. It must be in the current directory to run the program. This file contains the title and crystallographic data and must be prepared by the user with the help of a file editor

• FILE.dat – Intensity data file, its format depends on instrument. This corresponds to the profile intensity of a powder diffraction pattern.

• FILE.bac – Background file. The program uses this file to calculate the background at each value of the scattering variable. There are two types of formats for this file:

1. The first format is the same as that of FILE.dat for Ins=0:

2. The second format is the is adapted to the case were there is no fixed step in the scattering variable.

- FILE.hkl – Set of files with the reflections corresponding to phase n
- FILE.irf – File describing the instrumental resolution function
- FILE.shp – File providing a numerical table for calculating the peak shape and its derivatives.
- FILE.cor – User-defined intensity corrections. Two types of corrections may be applied.
    1- In the first case the corrections are applied to the integrated intensities as a multiplier constant.
    2- In the second case the correction is applied to the profile intensities. The format depends on a number of variables.
- FILE.int – Single integrated intensity file when the program is used for refining

As a result of calculations related to these files one can get results summarized in different output files:

- CODFIL.out - the main output file that contains all control variables and refined parameters. Its content depends on the values of flags set by the user.
- CODFIL.prf – Observed and calculated profile: to be fed into visualisation programs. This file is used automatically by WinPLOTR. In case of multiple pattern refinements a file CODFIL_p.prf is created for each patern, where p is the ordinal number of the diffracttion pattern.
- CODFIL.rpa – Summary of refined parameters. Short version of CODFIL.sum. This file has the "append" attribute, so if it exists the new output is appended. It is useful when running FullProf in cyclic modes
- CODFIL.sym – contains list of symmetry operators
- CODFIL.sum – Parameter list after last cycle: summary of the last parameters, their standard deviations and reliability factors.
- CODFIL.fou – contains different information about structural factors and can be used for (G)FOURIER and FOURTK programs
- CODFIL.ins – template of the input control file for the program SHELXS • CODFIL.inp – template for (G)FOURIER input file
- CODFIL.hkl – list of reflections and can be input or output file
- CODFIL.sav – contains list of reflections between two selected angles and can be output file if an interval in the scattering variable is given
- CODFIL.dis – contains list of distances and angles for specific phase
- DCONSTR.hlp – list of strings containing eventual distance and angle constraints for phase n. This file with fixed name, DCONSTR, is generated automatically when the user asks for angle/distance calculations.

• CODFIL.mic – contains microstructural information

• CODFIL.sim – contains a simulated diffraction pattern. Can be renamed as a DAT file and used for refinement in simulation work.

• CODFIL.sub – contains calculated profile corresponding to the phase n

• CODFIL.atm – depending on a parameter Jdi it contains information about presence of magnetic phase, magnetic atom positions and can be used as input file for MOMENT program that calculates everything concerned with magnetic structures

• CODFIL.sch - files suitable as input files for programs Schakal and Struplo

• CODFIL.int – files suitable as input files for integrated intensity refinements and contains a list of overlapped reflections obtained by adding integrated intensities from profile matching refinement when they belong to a cluster.

As it was mentioned in the explanation of output files, there is a relationship between FullProf and many other programs. So information obtained from FullProf calculation can be used as an input files for programs like WinPLOTR, (G)Fourier, MOMENT, STRUPLO, VESTA etc.

2.1.1. WinPLOTR

WinPLOTR is a software used for visualization and analysis of powder diffraction patterns. It can be used to plot raw or normalized data files coming from neutron and X-ray diffractometers as well as Rietveld files created by Rietveld type refinement programs . There are many other features in WinPLOTR, such as: one can choose different X space, automatic peak search; automatic background points search; do different calculations like difference, background substraction, profile fitting, microstructural analysis etc.

The graphic has been created with Fortran 95.There are different formats of data input files that can originate from diffraction pattern, Rietveld files or microstructural files (Figure 1). After adequate choice, for example .xy file, we get a diffraction pattern that was obtained experimentally in Figure 2.
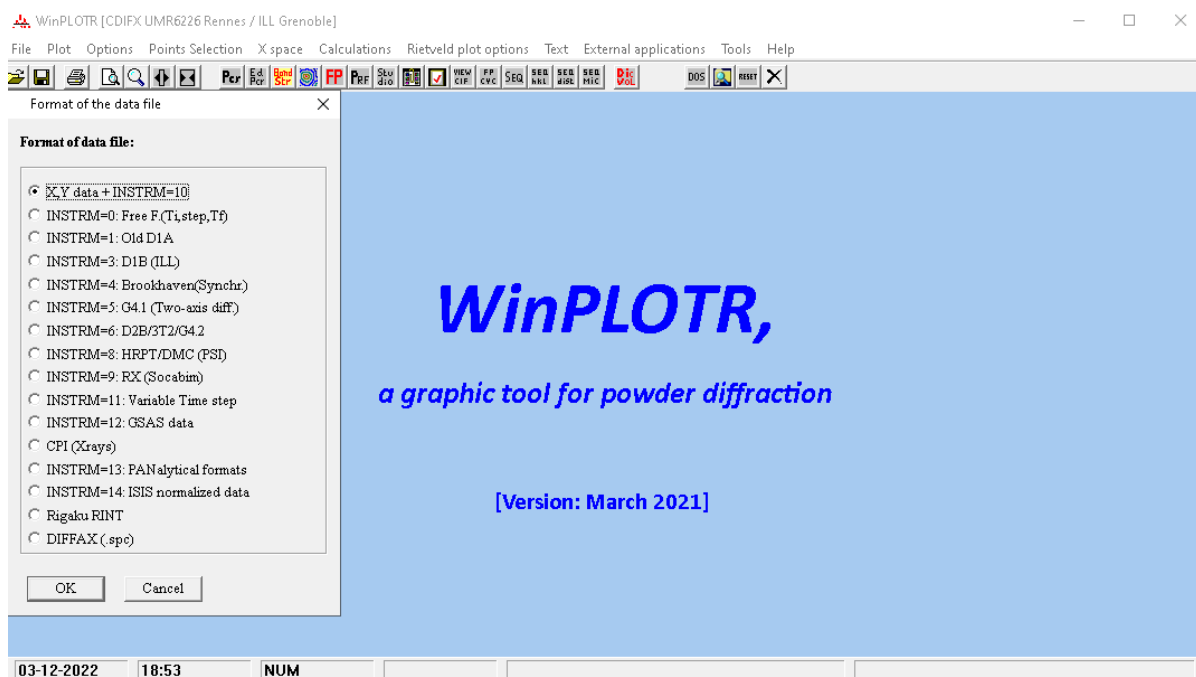
Figure 1. Different formats for input files in WinPLOTR
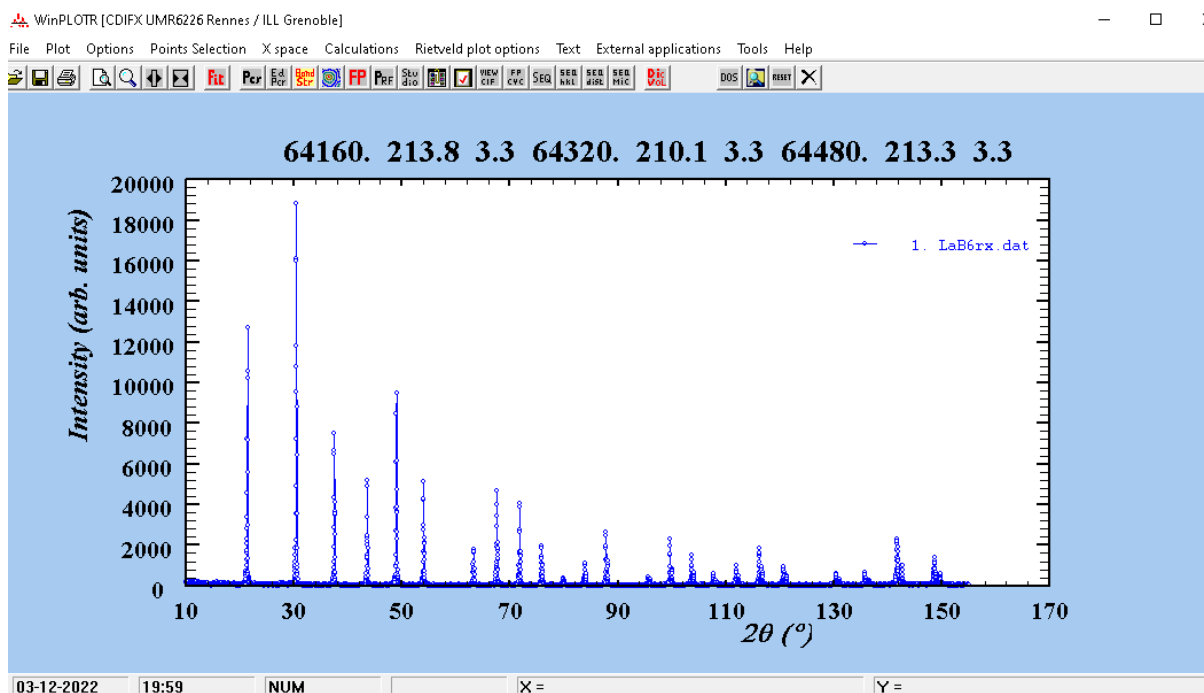

Figure 2. Diffraction pattern

Because WinPLOTR is a program for the visualization of different patterns, as a result of this, it can manipulate with visual features of plots. So that, you can change text font, text colour, legend and text positions and graduations in the menu Text. And also, using in Plots menu, we can create different options for

visual features such as focus, add error bars, do 3D plots etc. Examples of those changes are represented in Figure 3.
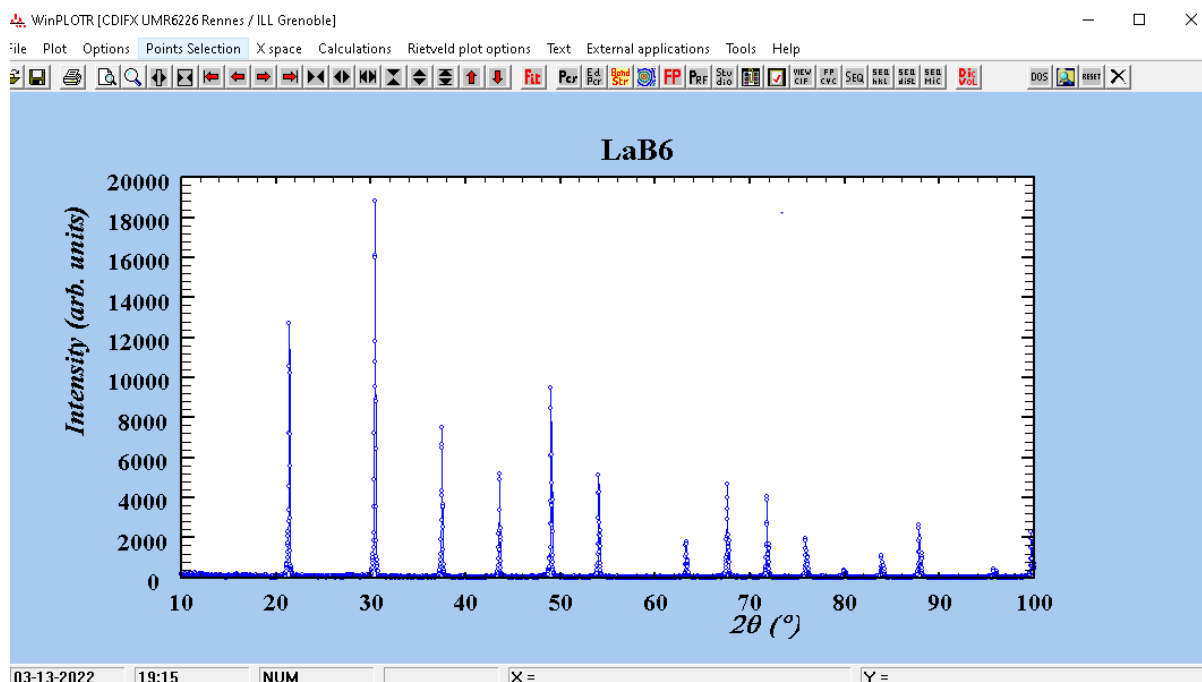

Figure 3. Different visual representation of pattern using Text and Plot menu

Different calculations can be done in WinPLOTR besides visual changes. In the menu Point Selection there is an option for automatic peak and background search. After search, one can add missing peaks/background points or delete the unwanted peaks/background points. Information about peak or/and background positions, intensities and number of peak/background points is automatically pops up in new window. They are presented in Figure 4 and Figure 5.
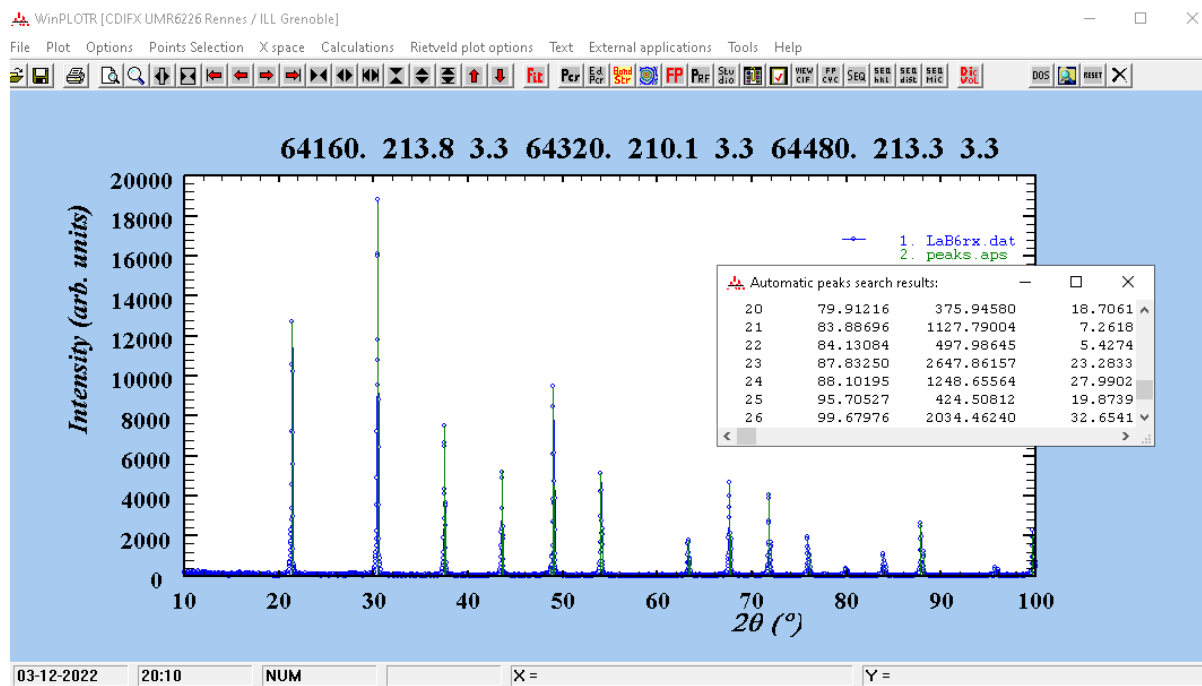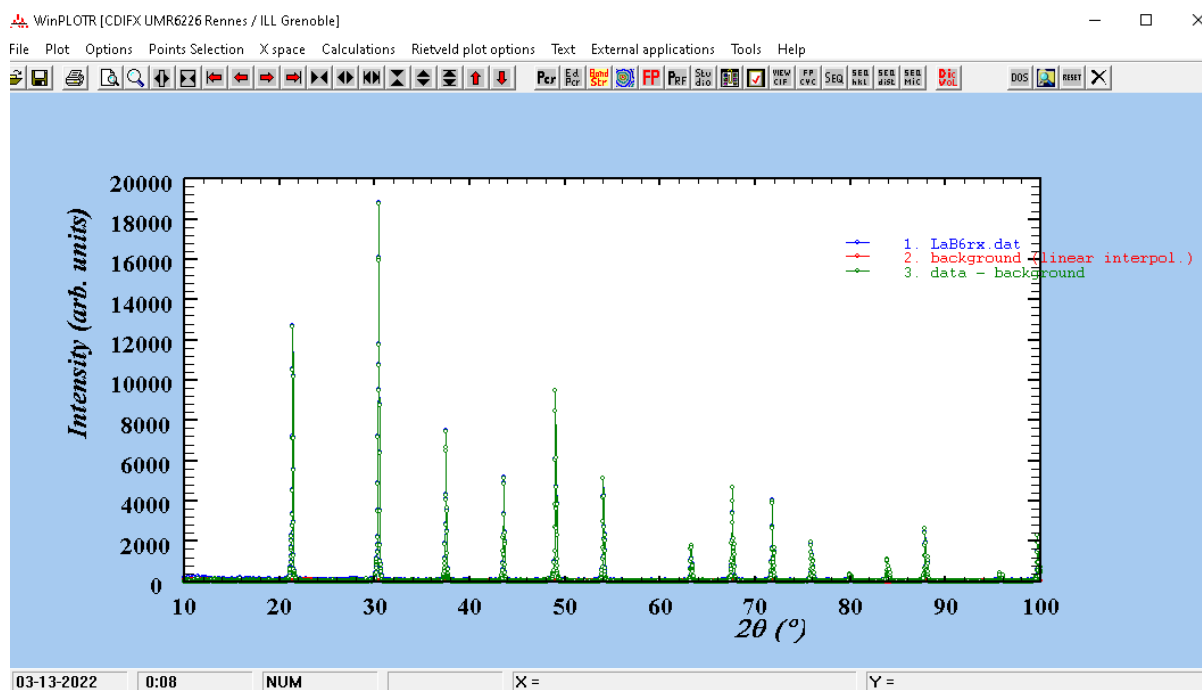
Figure 4. Automatic peak search

Figure 5. Background points

The refinement of crystal structures using data in a two-stage method is described. The integrated intensities of the individual reflections are derived by a profile fitting method in which the profile shapes are accurately defined using an experimentally determined instrument function and the
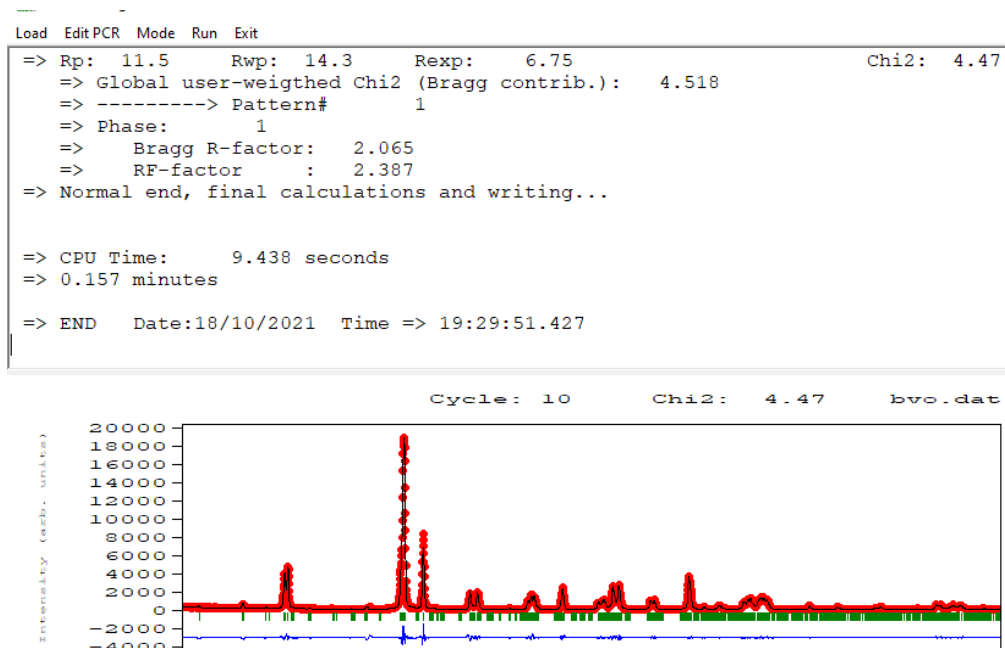
sum of Lorentzian curves.

Figure 6. **Profile fitting after refinement**

Obtained information from Figure 4can be saved in different formats like .dicvol, .ito etc. These files can be used as input PCR files for Rietveld analyisis or profile fitting using FullProf. After uploading this file in PCR editor, Fullprof calculation is started and profile fitting after initial cycle is presented in **Figure 6**. In Figure 6 is presented result with much better fitting X^2 value is 4.47 .Other than X^2 there are also parameters Rp, Rwp and Rexp which also indicate quality of Rietveld refinement. As a result, one can get many output files (which were chosen before calculation) where can be found different crystallographic information.

The principal characteristic of instruments for diffraction on pulsed neutron sources is their use of time-of-flight (t.o.f) techniques to allow for optimal use of the white neutron beams produced by the source. These rely on the fact that neutrons with different energies, and hence different wavelengths, from de Broglie's relationship, travel at different velocities:

$$\lambda = h/mv$$

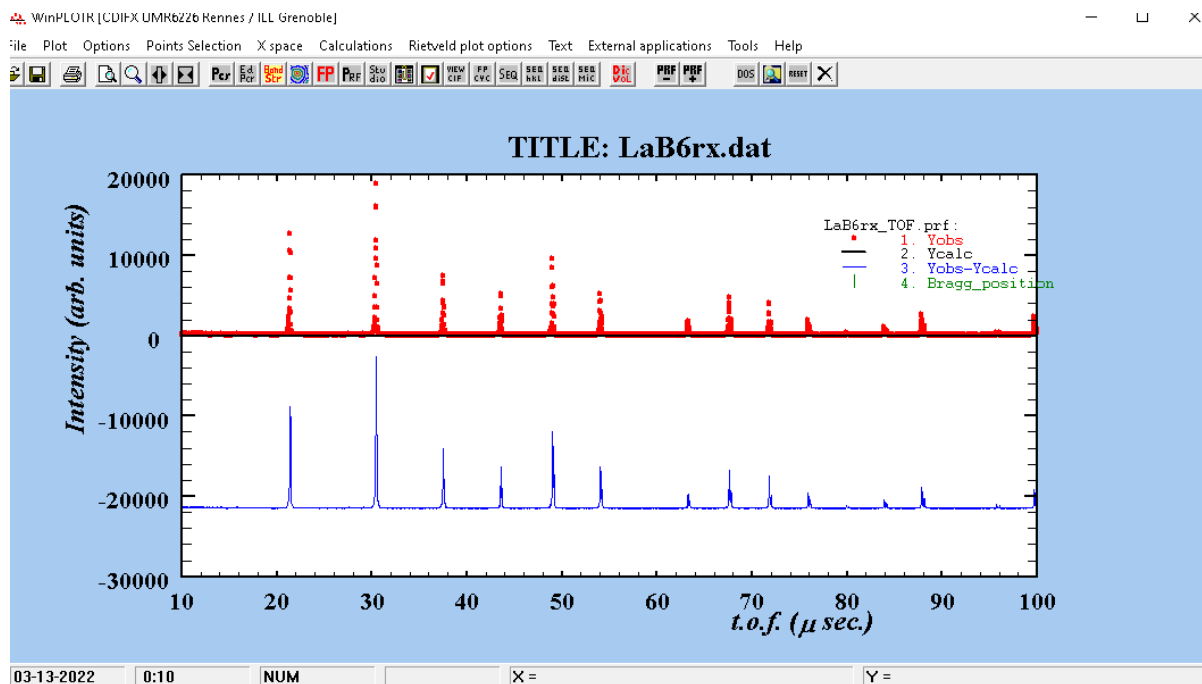where m is the neutron mass and v the neutron velocity

Figure 7. Time of flight neutron diffraction

Thus, since in the spallation process all neutrons in a given pulse are essentially created at the same time, t0, the higher energy, shorter wavelength neutrons travel faster and hence arrive at sample and subsequently at detector, at an earlier time than the lower energy, longer wavelength, slower neutrons. By measuring the time of arrival of a neutron at the detector, and of course knowing its flight path, we can calculate its velocity and hence its wavelength (energy). This is the basis of TOF, which is a genuinely wavelength-s
The peak shape of a neutron diffraction spectrum in Figure 9 includes a combination of contributions from the instrument, from the sizes of ordered domains inside crystalline grains, from residual inhomogeneous elastic microstrain in the crystallites, and from solution inhomogeneity during solidification.

3. The proposal for neutron/X-ray scattering experiment at large scale facilities

3.1. Details of neutron/X-ray experiment
D1B - High intensity two-axis powder diffractometer with incident neutron beam of λ=2.52 nm in the range 10-90 degrees. Temperature scan between 1.5-300 K can be done to investigate thermal phase transitions. Mass of the sample is 1.5 g.

Neutrons with optimal wavelength are very useful because they can give a detailed insight into the crystallographic properties of material. Neutron diffraction was preferred to X-ray diffraction because of the greater sensitivity of neutrons to the oxygen atoms and can give information about bulk properties of material.

Diffraction pattern is collected in 1-5 minutes and complete thermal variation for one sample can be obtained in 3-5 h. There are five different routes of synthesis plus three different dopants for every synthesis which equals 60 h of beam time.

3.2. Aim of the proposed experiment and description of the scientific background

The proposal consist of many parts, such as aim of the proposed experiment and description of the scientific background, results of the previous own work at the facility that proposal was sent, details of the neutron/X-ray experiment (experimental methods with specific information about instrument of interest, justification for the use of neutrons/X-rays, justification of the amount of experimental time needed, any issues related to safety, special technical difficulties), description of the results expected and their scientific relevance, related own publications.

Hexaborides (MB6) can be monovalent metals or semiconductors depending on whether the metal ion M is trivalent or divalent, respectively, because the B6 molecule in them needs two electrons from the metal to stabilize the divalent B6 state. LaB6, a monovalent and nonmagnetic metal, is of great technological importance as thermionic cathodes in electronic devices with high performance characteristics [2]. It is a refractory ceramic material that has a melting point of 2210 °C, and is insoluble in water and hydrochloric acid. It has a low work function and one of the highest electron emissivities known, and is stable in vacuum.

The unit-cell parameter (ao) and atomic position of boron (x) for LaB6 were determined to be 4.1549 (1) A° and 0.1991 (9), respectively (Rwp = 4.26, RBragg = 3.21).
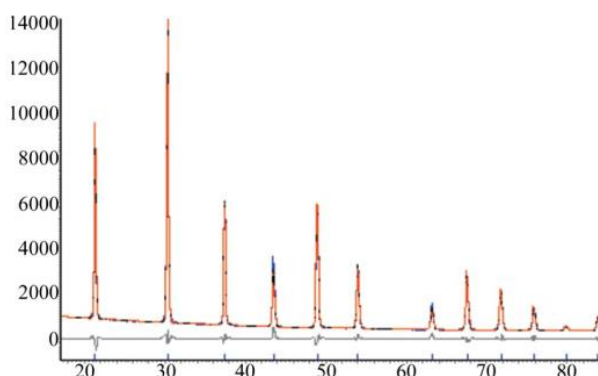
Parameter	Value	Booth et al. (2001)
Zero error	−0.038 (1)	
Absorption (cm^{-1})	18.5 (8)	
Scale factor	0.00575 (2)	
Mass	203.77	
Volume (Å^3)	71.73	
a_o (Å)	4.1549 (1)	4.1561 (1)
B_{iso}(La^{3+})	0.641 (3)	
x position (B)	0.1991 (9)	0.1995 (1)
La−B (Å)†	3.0522 (9)	3.0535 (1)
R_{Bragg} (%)	3.21	
R_{wp} (%)	4.26	
R_{exp} (%)	3.66	
χ^2	1.16	

† The La−B bond length was calculated according to La−B = $a_o(x^2 + 0.5)^{1/2}$, where x is the boron atomic position and a_o is the length of the LaB$_6$ unit cell.

The X-ray pattern is shown in Figure and the refinement results are given in Table. These results compare well with the neutron powder diffraction results of Booth et al. (2001) [ao = 4.1561 (1) Å, x = 0.1995 (1)]. Calculating of Booth's bond length of La—B to be 3.0535 (1) Å.

4. References

1. Structure Analysis by Small-Angle X-Ray and Neutron Scattering, Feigin L.A. and Svergun D.I., New York: Plenum Press

2. Introduction to Neutron Scattering, D.L Price and K. Skold, Methods of Experimental Physics 23A, 1, 1986

3. X-Ray and Neutron Diffraction, The Commonwealth and International Library: Selected Readings in Physics, Author: G. E. Bacon, Editor: D. Ter Haar, ISBN: 9781483158297

4. Small–angle scattering: theory, instrumentation, data and applications, Hamley, I. W., John Wiley and Sons, Chichester, UK, ISBN 9781119768302

5. β-Lactoglobulin associative interactions: a small-angle scattering study, L. Anghel, A. Rogachev, A. Kuklin, R.V. Erhan, (2019), 48(3), 285-295

6. An introduction to the program FullProf – Manual, Juan Rodriguez-Carvajal, Laboratoire Leon Brillouine, France, 2001

7. WinPLOTR, a graphic tool for powder diffraction – Manual, Thierry Roisnel, Juan Rodriguez-Carvajal, Laboratoire Leon Brillouine, France, 2001

8. Crystal-Structure Refinement by Profile Fitting and Least-Squares Analysis of Powder Diffractometer Data by G. Will, W. Parrish and T. C. Huang, J. Appl. Cryst. (1983). 16, 611-62

9. Neutron sources and instrumentation, Bjorn Winkler, Eur. J. Mineral.

(2002), 14, 225-232

10. Neutron cross sections, McLane V., Dubford C., Rose P., New York, Academic Press, 1988

11. Rietveld refinement of LaB6: data from mXRD ,Guangrong Ning and Roberta L. Flemming, Journal of Applied Crystallography, 2005

12. The production and slowing down of neutrons, Amaldi E., Berlin, Springer, 1959

13. Neutrons in soft matter, Imae T., Kanaya T., Furusaka M., Torikai N., John Wiley & Sons, 2011, ISBN: 1118002180

14. Time-of-flight neutron diffraction, C. C Wilson, July 2003, 204

15. Time-of-Flight Neutron Diffraction (TOF-ND) Analyses of the Composition and Minting of Ancient Judaean "Biblical" Coins, Stephen E. Nagler, Alexandru D. Stoica ,Grigoreta M. Stoica , (2019), 1-18

16. Effective Cadmium Cutoff Energies, Stoughton R. W., Halperin J., Lietzke M., Nuclear science and engineering, (1959), 441-447,