7 - MODELLING

The interpretation of neutron scattering data requires powerful modelling tools. These last years, the understanding and modelling at a finer level has triggered the development of more and more elaborate analysis tools. In this section we present recent development of these numerical tools that have been developed to reduce, model and interpret neutron scattering data.

The capacity of understanding neutron data is strongly correlated with the progress made in various fields of modelling. These modelling efforts can be separated in several categories:

- Understand the physical phenomena at the very deepest level (1-4)
- Accurate modelling of physical systems (SIMBO, CCSL, MOLECULAR DYNAMICS)
- Write fitting programs based on these models (FULLPROF, SIMULREFLEC)
- Develop more efficient fitting methods (CRIME)
- Provide efficient User Interfaces to fitting programs for neutron users (FULLPROF, SIMULREFLEC)

Efforts are being made in all these directions at the LLB.

POLYMERS, COMPLEX SYSTEMS AND BIOLOGY

- ***Theory and simulations of ultrafast electronic transfer:***

Electronic transfer is the elementary process of all chemical reactions the dynamics of which can be very fast and very complex at the same time. Ultrafast dynamics can now be studied in details, thanks to the availability of femtosecond laser sources and powerful spectroscopic techniques, complementing the standard neutron spectroscopy that works currently in the Gigahertz-Terahertz regime. The whole bunch of spectacular results starting to emerge call for sophisticated theories and simulations that go beyond adiabatic approximations and thermally activated processes (see "***highlight***" 1).

- ***Modelling the SANS from Nanocomposites:***

Data analysis often focuses on prominent features in the Small Angle Neutron Scattering (SANS) spectra, like correlation peaks, power laws, or the Guinier regime. Sometimes, data fitting with analytical expressions can be done, but it is possible only for simple geometries (spheres, rods, etc.). However, the power and flexibility of contrast matching methods can give access to the detailed organisation of selected parts of complex systems. In this framework, new tools to model and interpret SANS data measured on complex nanostructures are being developed (see "***highlight***" 2)

- ***Molecular dynamics simulations in Life Sciences:***

An increased effort will also be made in the field of molecular dynamics. A team from the "Centre de Biophysique Moléculaire" will join our laboratory in order to combine in an efficient way Molecular Dynamics and experimental neutron scattering data in Life Sciences. A more detailed description can be found in the following pages (see "***highlight***" 3)

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Polarised neutron reflectometry

The "Magnetism and Superconductivity" chapter has described the experimental results obtained in the field of polarised reflectometry and has detailed the related technical developments, i.e. the magnetic surface diffraction and GISANS methods. To complement these experimental efforts, a new user-friendly program SIMULREFLEC has been developed for the fitting of polarised reflectivity neutron data, obtained for example on the PRISM reflectometer (see "***highlight***"4)

Crystallography and data reduction in diffraction

- In the field of crystallography, new fitting methods are being developed. The new program CRIME CRYSTALLOGRAPHIC **I**maging using **M**aximum **E**ntropy can be used to reconstruct 3D electron and scattering densities from **X-R**ay and **P**olarized/**U**npolarized **N**eutron diffraction data. It provides a very significant gain with respect to the widespread conventional Fourier Imaging. The state of the art of CRIME is illustrated in the following "***highlight***" 5 via two examples pertaining to two typical neutron examples: a spin-density study and a proton density determination. The next pages present the new improvements that have been made in the modelling of magnetic structures by taking into account local magnetic anisotropy.
- Other progress is being made in the modelling of magnetic structure. Two new computing programs, SIMBO and ENERMAG (SEE "***highlight***" 6), provide an invaluable help to interpret experimental magnetic structures occurring in real systems. These programs decipher the crystal structure and the related topology of the magnetic exchange interactions of either well-known or completely new materials and facilitate the detection of new frustrating topologies of interest in magnetism. They allow the possibility of *a priori* predictions about the magnetic ordering in new materials when estimated values of the exchange interactions are available.
- Steady and continuous progresses are also being made in the field of power diffraction. The last FULLPROF version not only allows the treatment of even more complex problems but the user interface has also been improved. Further progress is planned within a European project in which new people, working at ISIS, will collaborate with our team.

Local Magnetic Anisotropy Axes And Atomic Site Susceptibility Tensors In Polarised Neutron Diffraction

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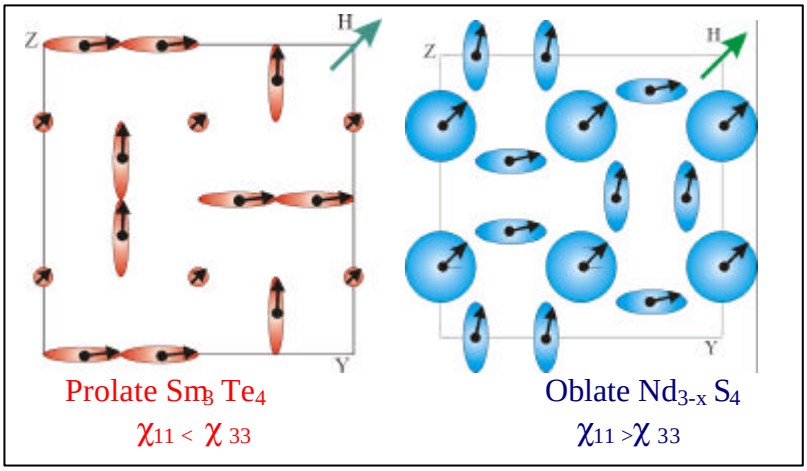
The anisotropy due to the local environment of magnetic atoms can give rise to the appearance of different magnetic moments on equivalent crystallographic positions when the magnetization is induced in the paramagnetic region by an applied magnetic field. Polarized neutron diffraction provides information about the magnetization density of each individual crystallographic site. Here, the role of the atomic site susceptibility tensor χ_{ij} accounting for the magnetic response of individual atoms to an external magnetic field is discussed. The symmetry of this tensor is very similar to that of the tensor u_{ij} describing the thermal motion of atoms. By analogy with the atomic displacement parameters (ADPs), atomic susceptibility parameters (ASPs) can be introduced [1]. The six independent atomic susceptibility parameters can be determined from polarized neutron flipping ratio measurements and visualized *as magnetic ellipsoids*, which are analogous to the thermal ellipsoids, obtained from ADPs. If the local anisotropy is small these magnetic ellipsoids approximate to spheres with diameters proportional to the induced magnetization. In other cases *anomalous* (elongated or flattened) ellipsoids will occur. The ASPs have been determined in the compound Nd_3S_4 that has the Th3P4 structure. They correspond to strongly oblate magnetic ellipsoids.



In contrast in the isomorphous compound Sm3Te4 the magnetic ellipsoids are found to be prolate. Hence in the case of Nd_3S_4 the local tetrahedral axis may be thought of as a *local hard magnetization axis* and the moment induced on the Nd site has a tendency to turn away from it if the magnetic field is not parallel to the tetrad axis. Other examples demonstrate that the anomalous elongation of the magnetic ellipsoids can be considered as a precursor of the low temperature magnetic order [2].

[1] A. Gukasov and P. J. Brown. *J. Phys. ; Condens. Matt.* **14** (2002) 8831
[2] A. Gukasov, P. Rogl, P. J. Brown, M. Michalik and A. Menovsky. *J. Phys.; Condens. Matt*. **14** (2002) 8841

Diffraction Data Analysis: CRYSFML, WINPLOTR and FULLPROF

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WINPLOTR and FULLPROF

In the last few years we have been working in the development of computing tools for data analysis of powder and single crystal diffraction. The public distribution of the programs **WINPLOTR** and **FULLPROF** [1-3] has allowed the introduction of substantial and progressive improvements, thanks to the feedback from the users. At present, the combination of **WINPLOTR** and **FULLPROF** constitutes one of the most popular Rietveld suites and they are used worldwide for the analysis of powder diffraction data. The treatment of incommensurate magnetic structures is one of the areas of expertise of **FULLPROF** that other programs cannot handle [4, 5].

In last few years many improvements have been performed on aspects of the **WINPLOTR** and **FULLPROF** programs concerned with their user friendliness and the treatment of even more complex problems [2, 3]. The task of improving the programs and creating new tools to simplify their use will be reinforced in the forthcoming future. **WINPLOTR** is a Windows-based application that is presently the most used GUI to **FULLPROF** and cannot be easily ported to Linux or other Unix systems.

A re-arrangement of the code and the use of a new library to access the Windows, or X/Motif, API are needed to make it independent of the platform. This will be done using *Winteracter*, as is the case of **GFOURIER** and **EDPCR**. Improvements in the capabilities of **WINPLOTR** are already continued in an incremental way through feedback with the user community. Concerning the improvement and development of **FULLPROF** itself it is important to emphasize that the program can handle flipping ratio measurements from polarized neutrons. Multipolar and wave-function refinements can now be performed from single crystal flipping ratio data.

An important step in the friendliness for using **FULLPROF** has been the development of **EDPCR** that allows a simple use of the program without knowing all the details of the input control file. Within **EDPCR** stand-alone programs, based in **CRYSFML**, like **BASIREPS**, are accessible with a simple click. There are conversion tools for different formats of crystallographic data and CIF files can be easily imported. A crystallographic calculator will be soon implemented. **EDPCR** is completely interoperable with **WINPLOTR**/**FULLPROF** through a common hidden file collecting run time events: end of a calculation, modifications of a file by one of the applications, etc.

Programs based in CRYSFML

We have developed a set of FORTRAN 95 modules, Crystallographic FORTRAN Modules Library (**CRYSFML**)[6], which may be used in crystallographic and diffraction computing programs. Modern array syntax and new features of FORTRAN 95 are used through the modules. We take advantage of all object oriented programming techniques. The library is entirely written in a subset of FORTRAN 95 called **F**. Compilers for the **F**-language are publicly available for the most important operating systems [7].

The present **CRYSFML** contains procedures for reading files of many different formats, string utilities for handling the reading in free format, generation and reading of CIF files, mathematical modules, modules for generating space groups from their Hermann-Mauguin or Hall symbols for whatever setting. More generic space groups with non-conventional lattice centring vectors can also be built using user-defined generators. Reflection handling modules may be used for generating reflections in selected regions of reciprocal space and for calculating structure factors, etc.

Public programs using **CRYSFML** are **FOURIER**, **GFOURIER**, **BASIREPS** and **EDPCR**.

These programs work on Windows and Linux and are already distributed from the LLB Web site. The first two programs are dedicated to the Fourier analysis of diffraction data. **EDPCR** is a new (still under development) Graphic User Interface (GUI) to **FULLPROF** input control file of extension PCR. **BASIREPS** is a program for calculating basis functions of irreducible representations of space groups. This program is useful for determining magnetic structures and phonon symmetry analysis.

SIMBO, ENERMAG and data-reduction related programs

We dispose of a set of computing programs based on **CRYSFML** that are not yet distributed publicly in the scientific community. A non-exhaustive list is the following:

- **SIMBO and ENERMAG:** Programs for the analysis of the magnetic topology and classical magnetic energy of an arbitrary crystal structure. A more detailed account of these two programs is given in a separate document of this report.
- **SIMILAR:** Program to make conversion of settings for describing crystallographic structures. It determines automatically the splitting of Wyckoff positions on going from a space group to one of their subgroups. Calculate all the *translationengleiche* subgroups of a space group, co-set decompositions, etc.
- **DATARED:** Program for data reduction of single crystal data. It handles twinning and incommensurate magnetic and crystal structures. At present it can read data provided by several integration programs, in particular several versions of COLL5 (LLB and ILL) and prepares files to be read by **FULLPROF** when using single crystals.

The current tasks in course within the project of developing **CRYSFML** include:

i) The implementation of procedures for calculating, using the Blume equations, the scattered polarisation and intensity of reflections of single crystals when using 3D polarimetry.

ii) The implementation of specialised structure factor subroutines for molecules described in the Z-matrix formalism. The free parameters being the distances, bond angles and torsion angles. This last task is extremely useful for structural analysis, based on powder or single data, of molecular pharmaceutical compounds.

References:

[1] "FullProf.98 and WinPLOTR New Windows 95/NT Applications for Diffraction" Juan Rodríguez-Carvajal and Thierry Roisnel, *Commission for Powder Diffraction, IUCr Newsletter* **20**, (1998).

[2] "WinPLOTR: a Windows tool for powder diffraction patterns analysis" T. Roisnel and J. Rodríguez-Carvajal, *Materials Science Forum* **378-381**, 118-123 (2001).

[3] "Recent developments of the program FullProf", Juan Rodríguez-Carvajal, *Commission for Powder Diffraction, IUCr Newsletter* **26**, 12-19 (2001). The complete FULLPROF suite can be obtained from ftp://ftp.cea.fr/pub/llb/divers/fullprof2k/.

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[6] "Crystallographic Fortran Modules Library (CrysFML). A simple toolbox for crystallographic computing programs"J. Rodríguez-Carvajal and J. González-Platas, *Acta Cryst.* A**58** (Supplement), C87; see also: *Computing Commission, IUCr Newsletter* **1**, 50-58 (2003), this document is freely accessible via the Internet at http://www.iucr.org/iucr-top/comm/ccom/newsletters/2003jan/.[7] All free F-compilers can be downloaded from the site: *ftp://ftp.swcp.com/~walt/pub/F*.

See also *http://www.fortran.com* for information about FORTRAN 95 and ELF90.