Chapter 2

# Crystallography Under Extreme Conditions: State of the Art and Perspectives

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http://dx.doi.org/10.5772/48608

## 1. Introduction

Sir William Henry Bragg and his son William Lawrence Bragg were the pioneers of crystallography (Bragg, W. H., 1912, 1913a, 1915a, 1915b; Bragg, W. L., 1920). In 1913, they published several articles, notably *The reflection of X-rays by crystals* (Bragg, W. H., 1913b) and *The structure of diamond* (Bragg, W. H. & Bragg, W. L., 1913) were they wrote: "We have applied the new methods of investigation involving the use of X-rays to the case of the diamond, and have arrived at a result which seems of considerable interest. The structure is extremely simple". Two years later, they were jointly awarded the Nobel Prize in Physics for their works in the analysis of crystal structure by means of X-rays.

A century after the first crystallographic experiment, new computing facilities, modern technologies and new diffraction sources (synchrotron, neutron sources…) offer a large range of possibilities and opportunities for crystallographers to probe matter. Crystallography appears nowadays as a new science.

Performing structural analyses at ambient conditions or at low temperature (i.e. above 100 K using nitrogen jet-stream) is very common and popular in laboratories to obtain the structure of powder and single-crystal materials. To understand the mechanisms governing the behaviour of materials it is essential to well know the close relations between the structure and the physical and chemical properties. First, X-ray diffraction is a unique tool to obtain routinely a detailed description of atomic structure and thermal vibrations by analysing the diffracted intensities $I_{hkl}$ of the crystallographic *hkl* reflections:

$$I_{hkl} = S.C_{hkl}.\left|F_{hkl}\right|^2 \tag{1}$$

$$F_{hkl} = \sum_{j=1}^{n} f_j.T_j.\exp(2i\pi(h.x_j + k.y_j + l.z_j)) \tag{2}$$

where S is a scale factor, $C_{hkl}$ is an experimental corrections term (including absorption, extinction, Lorentz-polarization correction…), $F_{hkl}$ is the structure factor of a *hkl* reflection which depends of $f_j$ the form factor of the atom j with ($x_j$, $y_j$, $z_j$) coordinates in the cell and of $T_j$ the Debye-Waller factor given in the case of isotropic harmonic vibrations by:

$$T_j = \exp\left(-B_j \frac{\sin^2\theta}{\lambda^2}\right) = \exp\left(-8\pi^2 \left\langle U_j^2 \right\rangle \frac{\sin^2\theta}{\lambda^2}\right) \tag{3}$$

where $\left\langle U_j^2 \right\rangle$ is the mean square atomic displacement of the atom j.

If one wants to increase the data quality, the best choice, without consideration about crystal quality or particular experimental conditions, is to perform a low temperature measurement, usually at 110 K, to reduce the atomic displacement parameters which affect the value of the atomic structure factor. In those experimental conditions, if high resolution X-ray diffraction measurement is performed up to large momentum transfers ($\sin\theta/\lambda > 1$ Å$^{-1}$) the electron density distribution of a molecule can be determined thanks to the Hansen-Coppens pseudo-atomic multipolar expansion (Hansen & Coppens, 1978):

$$\rho(\vec{r}) = \rho_{core}(r) + P_{val}\kappa^3 \rho_{val}(\kappa r) + \sum_l \kappa'^3 R_{nl}(\kappa' r) \sum_{m=0}^{l} P_{lm\pm} y_{lm\pm}(\theta,\varphi) \tag{4}$$

where $\rho_{core}(r)$ and $\rho_{val}(r)$ are spherically averaged core and valence electron densities calculated from Clementi Hartree-Fock wave functions for ground state isolated atoms (Clementi & Roetti, 1974). $\kappa$ and $\kappa'$ are contraction-expansion parameters and $P_{val}$ is the atomic valence shell electron population. The deformation of the valence electron shell is projected on real spherical harmonics $y_{lm\pm}(\theta,\phi)$ times Slater-type radial functions $R_{nl}(r)$. $P_{lm\pm}$ are the multipole population parameters.

In the later case, the accuracy of the results is highly dependant of the experimental conditions (Destro et al., 2004; Zhurov et al., 2008) and particularly of the crystal quality and the measurement temperature which must be chosen to reduce at the maximum the thermal vibrations of the atoms. These *usual experiments* at static low temperature give basic structural properties, and their variations as a function of temperature can reveal particular behaviour of matter as phase transition for example with changes in structural, electronic, optical and/or magnetic properties. But, in a general consideration, performing crystallographic measurements under external perturbations is of prime importance. Nowadays, experiments at different temperatures or hydrostatic pressures can be done almost routinely and exotic sample environments are more and more used to explore materials properties. If we just consider for the moment experiments involving temperature or pressure variations, a Web of Science search for "high pressure", "low temperature" and "high temperature" in the field of X-ray and neutron diffraction between the years 2005 and 2012 gave about 3500 experiments performed in 2005 but nearly 5000 in 2011 (figure 1). Two comments can be done observing figure 1. First, a large amount of the extreme conditions (temperature and pressure) experiments are carried out using X-ray diffraction compared to neutron diffraction. This difference is of course due to the

large number of X-ray diffractometers available in laboratories, which are more and more outstanding in terms of source power and detector efficacy, combined with numerous sample environments especially designed for laboratory equipments. But this is also due to the building of several 3rd generation of synchrotron sources which offer the possibility to conduct very quick measurements on a very small quantity of matter, allowing the measurement of materials under non ambient conditions, particularly in the domains of chemistry and biology sciences (neutron diffraction experiment demands more matter quantity, in general at least some $mm^3$). The second observed aspect on figure 1 concerns the evolution of the cumulative number (neutron and X-ray) of publications during the considered period: about 300 supplementary published papers per year appear between 2005 and 2009, but in the years 2009-2011, a distinct decrease of this number is noticed. This effect is directly related to the number of synchrotron radiation facilities over the world. One can count about 69 particle accelerators and accelerator laboratories in 2005 and about 76 in 2012 (including about 40 synchrotrons in 2011), with most of the new facilities operative in 2006-2008.

As said before, crystallography under extreme conditions is now more and more used and plays a key role as it offers helpful understanding of the physical, chemical and mechanical properties of the solid state. The term *extreme conditions* was first used to define non ambient thermodynamical conditions of pressure or temperature. It is also now employed when out-of-equilibrium conditions are applied such as light irradiation, external magnetic or electric fields, specific chemical environments (e.g. under liquid or gas flux…) or applied strain. In situ measurements can also be considered as extreme conditions, for examples in the cases of time-resolved experiments (picosecond diffraction…) or chemical kinetic reactions (dehydrogenation reaction, diffusion process, decomposition pathway…). The present challenge is to combine two or more extreme conditions to explore new states of matter and new material properties, taking advantage of last generations of high brilliance sources (synchrotron and neutron sources) (figure 2).

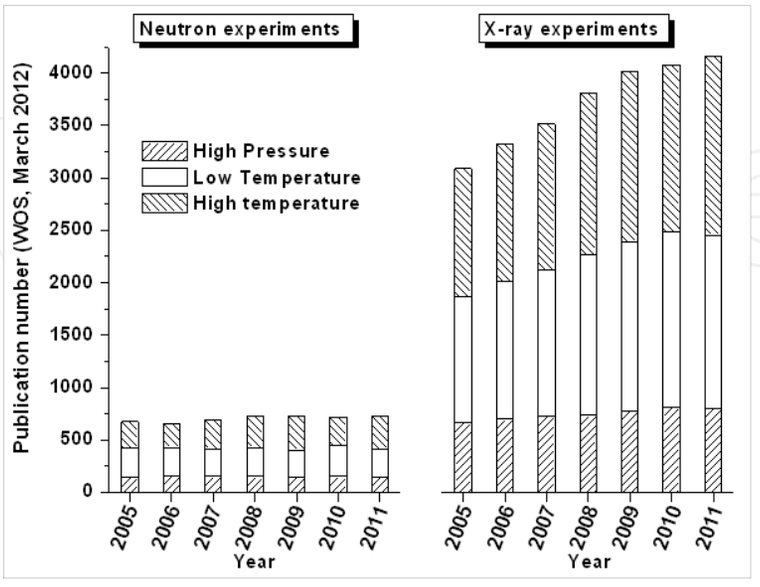


**Figure 1.** Publication number related to neutron or X-ray diffraction experiments under extreme conditions of temperature and pressure during the period 2005-2011 (Web of Science, March 2012).

When extreme conditions are applied to a material, various changes occur. They may involve sample state variations (gaseous, liquid and solid phases), phase transitions (magnetic and structural), electronic structure modifications (the chemical bonds can change from covalent to ionic or metallic) and atomic bond lengths variations (which induce variations of the atomic vibrations, of the coordination numbers, of the diffusion processes…). A large number of the material properties are modified under extreme conditions, leading sometimes to metastable states, which open new investigation opportunities for the crystallographer, but also for all scientist who wants to go deeper in the understanding of the structure-properties relationships in order to design future materials.

**Figure 2.** The neutron source of the Institut Laue-Langevin (ILL) and the European Synchrotron Radiation Facility (ESRF) in Grenoble, France (credit: V. Legrand).

This chapter is reviewing different aspects of the use of crystallography under extreme conditions to investigate the nature, the mechanisms and the dynamics of out-of-equilibrium phase transitions as well as transformations driven by external applied conditions. The part 2. is focus on the advantages of using Large scale facilities around the world and what are now the extreme sample environments available to explore unknown properties of materials. Finally, an overview of perspectives and future developments in diffraction instruments and sample environments are presented in part 3. showing that modern crystallography is in perpetual evolution and that the present century is certainly the one of *crystallography under extreme conditions*.

## 2. Large scale facilities and extreme sample environments

### 2.1. State-of-the-art sample environments at Laboratories

As noticed before, there are more than 5000 publications per year dealing with extreme conditions of temperature and pressure. Nevertheless, those conditions illustrate only 2 of the numberless non ambient thermodynamical and exotic conditions which can be used to probe the close links between structure and properties of materials. Changing the pressure or the temperature in a crystallographic experiment is performed quite routinely in laboratories. But if one wants for examples to apply electric or magnetic fields, to explore

superconductivity properties below 1 K, to perform very fast measurements of transient species or quick chemical reactions, or to understand phase transitions under combined sample environments, the diffractometer performances become overriding and in particular the maximum power of the source, the quality of the beam collimators and the efficacy of the detector. This is very important to obtain exploitable data as the sample environment in those later examples is very bulky and could dramatically affect the beam intensity. Moreover, it is very rare for a laboratory to have sample equipments to perform sub-kelvin, time-resolved or high-magnetic field measurements as these sample environments are very expensive, maintenance demanding and hard to exploit on conventional diffractometers. For a long time, extreme conditions measurements were the privilege of expert laboratories in cryogenic, high fields or high pressures with ability and technical resources to build and to use such devices. Those techniques are nowadays distributed in a larger number of laboratories and, for some of them, take place to semi-industrial devices merchandised by high technology industries. Since ten or so years, apparatus able to be used on conventional diffractometers were punctually developed to respond to the requirement of probing new properties of materials. We can cite some of them. First, to probe the structural and the electronic properties of materials under light irradiation at low temperature, *photocrystallographic* experiments (Coppens et al., 1998; Fomitchev et al., 2000) were developed first to study transient species of transition metal nitrosyl complexes. Coppens et al. (1998) wrote that "the study of photo-induced processes in crystals is a frontier area of crystallographic research, which requires development of novel experimental and computational methods". This is particularly true as the live-time of transient species is in general not related to the time of the experiment required to collect accurate data for structural refinement or experimental electron density modelling. The success of kind experiments consists in in situ laser irradiation of a cryogenically cooled crystal, with a $N_2$ or He gas-flow system for less restricted access than closed cryostat (White et al., 1994), mounted on a diffractometer equipped with a CCD detector for fast data collection (Graafsma et al., 1997; Muchmore, 1999). More recently, Legrand (2005) has developed a crystallographic experimental methodology approach (Legrand et al., 2005; 2007a; 2007b) and shown that it is possible to measure with accuracy photo-induced metastable states and to refine its experimental electron density below 35 K using conventional X-ray sources (Legrand et al., 2006; Pillet et al., 2008).

We can also mention an other development to do pressure measurements using particular pressure cell, up to 3.0 GPa and for T > 9 K (Guionneau et al., 2004) (figure 3). This last device was developed to probe phase transitions and structure-properties relationships in molecular conductor (Chasseau et al., 1997) and spin transition complexes (Guionneau et al., 2001). Doing in situ laboratory pressure investigations is still difficult as the pressure cell induce several perturbations affecting the quality of the data collection. The originality of this high pressure cell is that the X-ray beam goes through the gasket and not through the diamonds, offering a wide diffraction angle of 342° rotation. In this case, Guionneau et al. (2004) indicate that using a CCD area detector to collect Bragg peaks improves data and reduces the measurement time.

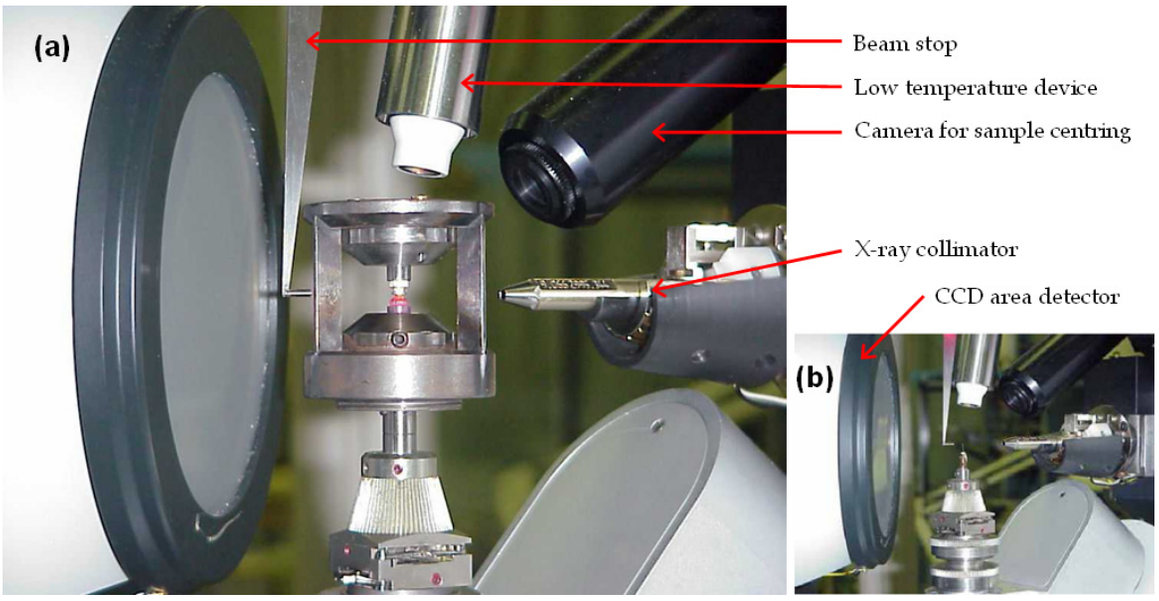


**Figure 3.** The high pressure cell developed by Guionneau et al. (2004): (a) view of the high pressure cell mounted on a 4-circle diffractometer equipped with low temperature device and CCD area detector; (b) comparison of the spatial occupied volume when a conventional goniometer head is used instead of the pressure cell. (Reprinted by permission from IOP Publishing Ltd).

To finish this non-exhaustive description, we can briefly mentioned two device developments in the field of very low temperature measurements. A mini-goniometer for X-ray diffraction studies down to 4 K on a four-circle diffractometer equipped with a CCD area detector (Fertey et al., 2007). The authors used a helium-bath orange cryostat (Brochier, 1977) and added a remarkable evolution: a magnetically coupled two-rotation-axis mini-goniometer permanently installed in the sample chamber of the helium-bath cryostat. This original apparatus was tested with success on organic charge-transfer compounds (Garcia et al., 2005; Garcia et al., 2007). An other low temperature system was developed to analyse Jahn-Teller distortion of $TmVO_4$ using conventional X-ray diffractometer between 0.22 and 3.5 K (Suzuki et al., 2002). The authors used a diffractometer equipped with a counter-monochromator and a scintillation counter, and an X-ray generator with rotating Cu Anode. To perform the ultra-low temperature measurements, a modified $^3$He-$^4$He dilution refrigerator was mounted on the two-fold axis goniometer. In this later case, the study was also a success and the Jahn-Teller effect was fully investigated down to 0.22 K. In their paper, Suzuki et al. mentioned what was noticed above in this section concerning the use of bulky devices: "the x-ray beam generated by a Cu target, which passed through 4 walls of Be 2 mm thick and 4 aluminized mylar walls was reduced to approximately 1/100". This beam attenuation is generally inevitable when doing extreme conditions experiments and to guaranty good data collection, it must be used first class equipments on the diffractometer. Even if a lot of progresses concerning the performances of new diffractometers were obtained last years, extreme conditions measurements are sometimes impossible to perform at laboratories. Then, the best to do is to use Large scale facilities which benefits are now more and more highlighted. The term *Large scale facilities* stands for synchrotron research institutes and neutron facilities (spallation sources and reactors).

## 2.2. Why using large scale facilities in extreme crystallography?

The synchrotron working principle was shown during the Second World War by Oliphant (1943, University of Birmingham, UK). Three years later, it was shown for the first time (Goward & Barnes, 1946; Elder et al., 1947) that it is possible to built synchrotrons providing a satisfactory means of producing high energy electrons and X-rays. Nearly 70 years later, several synchrotrons of 3rd generation are operational throughout the world and are of first necessity for all the scientists communities (Bilderback et al., 2005). The X-ray beam, produces by a synchrotron, is a light beam (electromagnetic wave) which interacts with electrons surrounding the nuclei of heavy elements (Born, 1933, 1935; Born & Schrödinger, 1935). The actual phenomenal success of the synchrotron for performing extreme conditions crystallographic measurements comes from numerous undeniable advantages and particularly it's very intense (brilliance) and focussing beam and it's time structure allowing the measurement of small or ultra-dilute samples at different time scales. Thus, it is possible to study transient species and fast chemical reactions or to perform biological and geological studies using bulky sample environment allowing temperature and pressure changes without affecting the data.

Neutron diffraction also plays a key role in actual crystallographic studies under extreme conditions. The first nuclear reactor was built in 1942 by Enrico Fermi and Leó Szilárd (University of Chicago, USA) (Fermi, 1947). In October 2011, the International Atomic Energy Agency (IAEA) database indexed 241 operational research reactors in the world. Generally, experiments using neutrons to explore the properties of a material are based not only on the intensity of the beam (to exploit this criteria, synchrotron radiation would be preferable) but on the very nature of neutrons. It is a particle beam, allowing interactions with the nuclei and the magnetic moment of unpaired electrons in the sample, scattered by all elements also the light ones like hydrogen and its isotopes, with a deep penetration depth enables bulk studies of materials (Fermi, 1930, 1934, 1940; Szilárd, 1935). As neutrons can penetrate deeper in matter (unless exceptions like cadmium, samarium, europium or gadolinium elements for examples), sample environments requiring to put the sample inside them (e. g. pressure cells, furnaces, gas handling inside a cryostat…) can be used even if further walls, generally in aluminium, must be crossed by neutrons before to hit the sample. This neutron property is very appreciable and neutron facilities now include very well equipped services and highly qualified staff to carry out invaluable experiments as the Services for Advanced Neutron Environment (SANE) at the Institut Laue-Langevin in France, where the Orange Cryostat (Brochier, 1977) and the Cryopad (Tasset, 1989), among others equipments, were invented and built.

Synchrotron and neutron facilities are complementary techniques which allow to analyse structural details of materials at the atomic scale. Microscopic properties are then known and the challenge is to derive the macroscopic ones. To achieve that goal, investigations must concern both surface and bulk phenomena of materials in both dynamic and steady states. Large scale facilities can give fine details on the nuclear structure of materials, on the physical and chemical properties, on the electronic and magnetic structures, they can give

crucial information about surface and interface states. All materials are concerned: metals, alloys, polymers, composites, colloids, glass, cement, biological macromolecules (viruses, enzymes, proteins…), minerals, food products, superconductors… The world-wide scientific community can observe since about ten years state of the art measurements in the above mentioned fields.

One field where X-ray and neutron measurements are really complementary is the domain of spin-transition molecular magnetic materials which is highly studied under *exotic environments* since 20 years (Gütlich & Goodwin, 2004; Bousseksou et al., 2011). These materials are especially interesting owing to their bistability properties which give them promising applications as data storage elements, thermal switches or display devices. These materials consist of a $d^4$ to $d^7$ transition metal coordinated to specific containing aromatic ligands whose ligand field is intermediate between weak and strong. Correlatively, the electron configuration of the central metal ion can be driven by several kinds of external perturbations such as pressure, intense magnetic field or light excitation. In the case of iron(II) complexes, the spin conversion is related to the electronic configuration of the ion changing from $t_{2g}^6e_g^0$ in the low spin (LS) state to $t_{2g}^4e_g^2$ in the high spin (HS) state. In addition to this electron redistribution, spin transition complexes present drastic structural variations between both phases, principally observed in the iron coordination sphere: an increase of the iron octahedron distortion and of the Fe-ligand bond length, by typically 0.2 Å, are observed for the LS → HS transition, generating a decrease of the molecular volume by several $Å^3$. Thus, owing to their high electronic and structural contrast, spin transition materials are good candidates for crystallographic studies under extreme conditions especially using Large scale facilities. Pressure dependence of the lattice parameters of several iron(II) complexes were derived from neutron powder diffraction (Legrand et al., 2008) and single-crystal X-ray synchrotron (Legrand, private communication) measurements at ambient and low temperatures. These studies highlight very promising results in the field of spin crossover phenomena under constraint, where crystallographic investigations under pressure are still very rare, especially because experimental conditions are difficult and sometimes not favourable. Concerning investigations under high magnetic field, Goujon et al. (2003) reported the photo-induced magnetization density of the iron(II) spin crossover compound $Fe(ptz)_6(BF_4)_2$ using an experimental setup allowing combined application of light irradiation ($\lambda$ = 473 nm) at low temperature (2 K) and high magnetic field (5 T) (figure 4a). Thanks to this polarized neutron diffraction measurement, the temperature dependence of the magnetization was well described and the thermal relaxation of the photo-induced state well observed.

Moreover, electronic and structural properties of iron(II) spin transition complexes were studied under light irradiation and low temperature (< 15 K) using neutron Laue (Goujon et al., 2006) and X-ray synchrotron (Legrand et al., 2007; Pillet et al., 2008) diffraction (figure 4b). These latter authors notably refined for the first time the experimental electron density of a photo-induced metastable state in a spin transition compound. Finally, probing photo-induced phase transitions in molecular materials can also be performed using ultra-fast measurements at a picosecond time scale (Coppens et al., 2004; Collet et al. 2012a; 2012b).

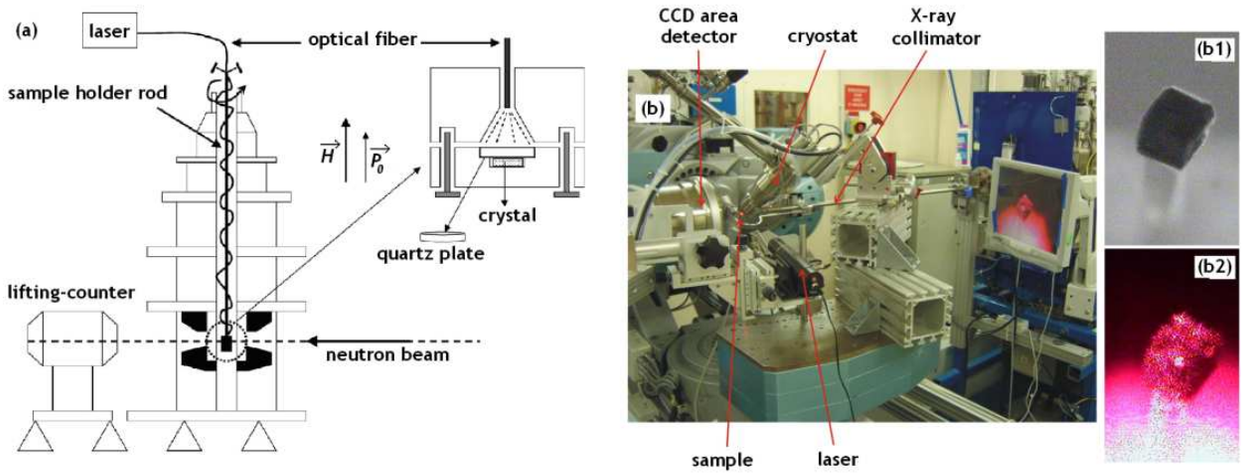


**Figure 4.** (a) Schematic experimental setup of the polarized neutron diffractometer; in the insert, the sample holder allowing light irradiation (Reprinted figure with permission from [Goujon et al., *Phys. Rev. B* 67, 220401(R) 2003]. Copyright 2012 by the American Physical Society). (b) The photocrystallographic experiment used by Legrand et al. (2007) showing the 6-circle diffractometer (BM01 beamline, ESRF - France) equipped with a large CCD area detector, an open flow He cryosystem and a He-Ne laser; inserts show the measured single-crystal (b1) without and (b2) with laser irradiation.

Real time investigation of temporally varying molecular structures during chemical reactions and phase transitions is a great challenge due to their ultrashort time scales. Collet et al. shown that it is possible to track complex reactions by time-resolved X-ray diffraction to temporal and spatial resolutions of 100 ps and 0.01 Å. Kind measurements give access to *molecular movies* during the transformation of matter induced by light irradiation. The authors succeed to describe for the first time the different steps of the dynamical process of several molecular materials and give their thought for the future: "these results pave the way for structural studies away from equilibrium and represent a first step toward femtosecond crystallography".

Other examples using the advantages of synchrotron radiations are numerous in structural biology, geology and materials sciences. The atomic structure of the bluetongue virus core (700 Å in diameter), containing about 1000 protein components self-assembled, was determined at a resolution of 3.5 Å (Grimes et al., 1998). The atomic structure of large ribosomal subunits were refined (Ban et al., 2000; Wimberly et al., 2000) providing a wealth of information about RNA and protein structure, protein-RNA interactions and ribosome assembly. The high brilliance of synchrotron sources in combination with fast detectors was used to perform time-resolved radiography of metal foam formation (Banhardt et al., 2001) (figure 5a). The possibility to have a micro-focus beam was applied to the study of the structure of spider silk (Riekel et al., 1999; Riekel & Vollrath, 2001) (figure 5b). The beam coherence properties enable new imaging techniques to do quantitative phase imaging and holotomography to probe materials with a micrometer resolution (Cloetens et al., 1999).

Nowadays, highlight articles are still numerous and new instrumental and device developments allow unthinkable experiments even ten years ago. Using highly brilliant X-ray beams at the APS (Advanced Photon Source, USA), ESRF (European Synchrotron

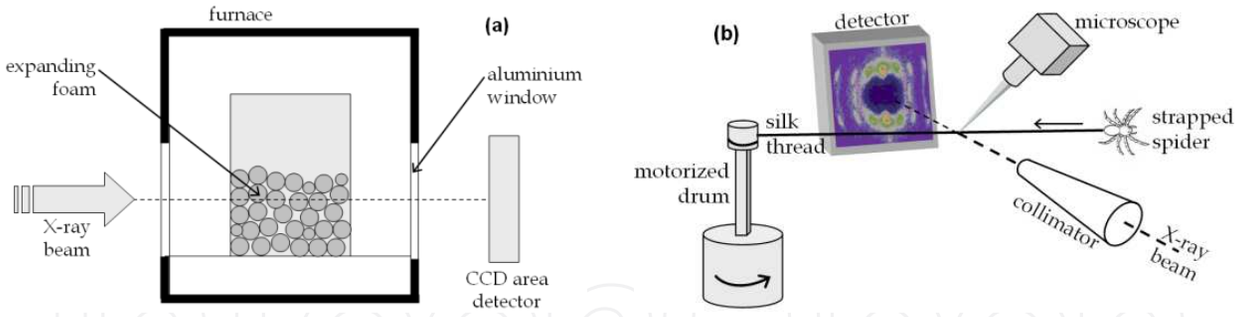


**Figure 5.** Schematic views of the experimental setup for real-time studies (a) of metal foam formation (Banhardt et al., 2001) and (b) of structural properties of spider silk (Riekel & Vollrath, 2001).

Radiation Facility, France) and SPRING-8 (Super Photon ring-8 GeV, Japan), teams uncovered subtle details of how cyan fluorescent proteins store incoming energy and retransmit it as fluorescent light (Goedhart et al., 2012), or investigated structure-properties relationships of biological mesocrystal in the adult sea urchin spin (Seto et al., 2012). Combination of in situ synchrotron X-ray absorption techniques and molecular dynamics simulations were used to determine the density range of primitive lunar melts at pressures equivalent to those in the lunar interior (4.5 GPa and 1800 K) (Van Kan Parker et al., 2012): these extreme conditions were generated with tiny samples heated thanks to high electric current while squashing them in a press (figure 6); knowing the attenuation of the synchrotron X-ray beam through both the solid and molten parts of the sample, the density at high pressure and high temperature could be measured. High pressure in situ X-ray diffraction and specific volume measurements on isotactic poly(4-methyl-1-pentene) melt have uncovered abrupt changes in the pressure dependence of microscopic structure as well as that of macroscopic density (Chiba et al., 2012). It was proved another time that pressure has an essential role in the production and control of superconductivity (Sun et al., 2012): it is reported that in the superconducting iron chalcogenides, a second superconducting phase suddenly re-emerges at a critical temperature Tc reaching 48.0 K and above 11.5 GPa, after the Tc drops from the first maximum of 32 K at 1 GPa. Metallic liquid silicon at 1787 K was investigated using X-ray scattering (Okada et al., 2012): the results show persistence of covalent bonding in liquid silicon and provide support for the occurrence of theoretically predicted liquid-liquid phase transition in supercooled states. To finish, it can be pointed out the crystallographic structure refinement of a protein, PthXo1 (which is a transcription activator–like, TAL, effector), encoded by an important group of harmful plant pathogens (Mak et al., 2012): understanding DNA recognition by TAL effectors may facilitate rational design of DNA-binding proteins with biotechnological applications.

Using neutron diffraction on reactors and spallation sources, researchers also push back the limits of measurements as for examples in the observation of a roton-like excitation in a monolayer of liquid $^3$He, a Fermi liquid (Godfrin et al., 2012). A new class of magnetic ionic liquid surfactants showing remarkable effects on surface and interfacial tension and allowing access to magneto-responsive emulsions and new methods of separation, recovery, catalysis, and potential magnetophoretic applications were analyses by small-angle neutron scattering (SANS) (Brown et al., 2012). Using neutron diffraction studies, along with

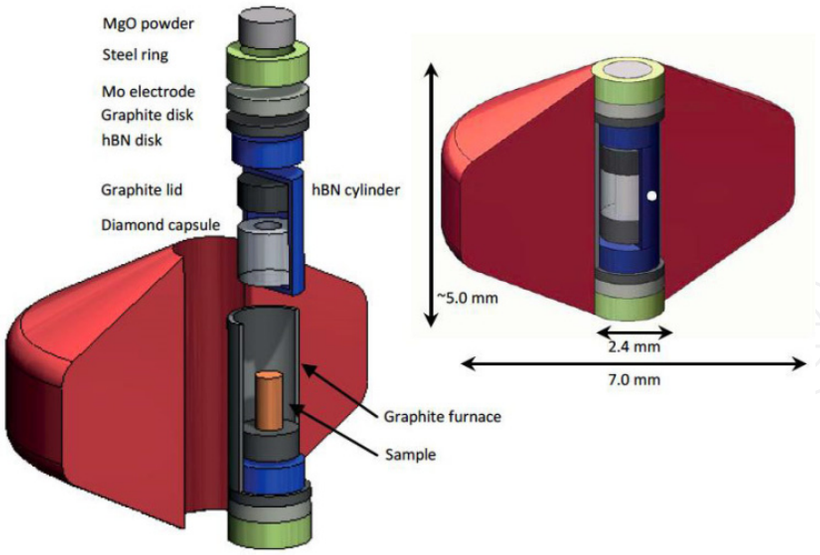


**Figure 6.** Drawing of the high-pressure cell assembly for the synchrotron X-ray experiments used to study the density range of primitive lunar melts (Van Kan Parker et al., 2012). The artificial moon rock samples (orange) were placed inside the ring-shaped, natural diamond sample holder (grey) which in turn was surrounded by a large, disk-shaped container (red). (Reprinted by permission from Macmillan Publishers Ltd: *Nature Geoscience*, copyright 2012)

computational chemistry, the mystery of lead oxide, the battery anode material of lead-acid batteries, was solved (Scanlon et al., 2011): oxygen vacancies give metallic behaviour by freeing up electrons to carry electrical current, neutron experiment put in evidence that commercial lead oxide powder is oxygen deficient by showing that oxygen sites were 1.6% vacant. Using high resolution neutron diffraction under high temperature and high magnetic field, it was shown that the thermal evolution of the helimagnetic state in CoMnSi is accompanied by a change in interatomic distances of up to 2%, the largest ever found in a metallic magnet (Barcza et al., 2010); this important result could lead to more efficient fridges and cooling systems.

The above overview has to remain incomplete with a number of fields left out. However, one can realize the wealth of extreme condition experiments which can be performed nowadays at laboratories and, particularly, using Large scale facilities which benefit of the last innovations in terms of sample environments.

## 2.3. Crystallographic experiments: advances in sample environments

Sample environment equipments like pressure cells, cryostats, etc, are essential adjuncts to perform with success the analysis of materials into a state or a phase with special behaviours and properties. This section is a brief overview of the most employed stately sample environments available mainly on Large scale facilities. The technical points of the discussed devices are not detailed here and the reader could find further information in the references given through section 2.3 and in specific reviews as written by Bailey (2003) or Mignot (2008). Specific Information is also related in reviews from the Workshop "sample

environments in neutron and X-ray experiments" held at the Institut Laue-Langevin (France) in 1984 (Vettier et al., 1984). There are various ways of tuning materials properties. In this section, the most employed sample environments are described, but the possibilities are miscellaneous and it is not possible to make an exhaustive list. *Exotic* sample environments like, among others, electric fields (Guillot et al., 2002; Hansen et al., 2004) or in situ reactions using gas handling (Walker et al., 2009; Price et al., 2010), as well as experiments performed with time resolved methods (Gembicky & Coppens, 2006; Nozawa et al., 2007) are not discussed. The investigations using these increasingly sophisticated experimental methods contribute enormously to the understanding of structural properties and progress in solid state physics and chemistry, biology and in geosciences. Advances in sample environments help to perform crystallographic experiments in extreme conditions and extend current areas of investigations.

### *2.3.1. Low temperature*

Cryogenic conditions are by far the most used sample environments principally to reduce vibrations and thermal motions of atoms, thus the structural refinement is improved. Moreover, phenomena like phase transitions are also generally induced at low temperature. Different devices could be used for low temperature experiments depending the desired temperature range: liquid helium bath cryostat (Orange Cryostat (Brochier, 1977)) for 300 K to 1.5 K; $^3$He sorption systems for 3 K to 300 mK; $^3$He/$^4$He dilution refrigerator systems below 1 K. Of course, there exist many others systems allowing to reach low and very low temperatures as $N_2$ or He gas-flow systems, helium closed cycle refrigerators (Displex), etc.

The Orange cryostat is now regarded as the international standard for low temperature experiments performed above 1.5 K. Some variations exist differing in the sample stick geometry (diameters and length). Cryofurnace and Cryomagnet versions were also developed. Nowadays, more and more experiments are based on combining sample environments. Thus, special versions of the Orange cryostat or Displex were built to meet the demand of users. Among the list of special purposes, it can be noted versions allowing the use of a high pressure cell (even Paris-Edinburgh cell) (figure 7), a gas handling for in situ chemical reactions analysis, an omega rotating for single crystals measurements, a sample changer. Because these cryostats are very common at Large scale facilities and are user friendly, recently improvements were made to have the possibility to do ultra-low temperature measurements using new sample stick inserts including high performance dilution refrigerator with a base temperature of less than 15 mK (Neumaier et al., 1984).

### *2.3.2. High temperature*

Contrary to cryogenic devices, there is no standard high temperature apparatus. The designs depend of the working temperature range, of the type of experiment, of the diffraction beam (X-ray or neutron). However, a typical furnace configuration places a sample into the centre of a thin cylindrical metal foil element, of about 50 μm thick, surrounded by heat shields. According to the chosen metal, the achieved temperature could

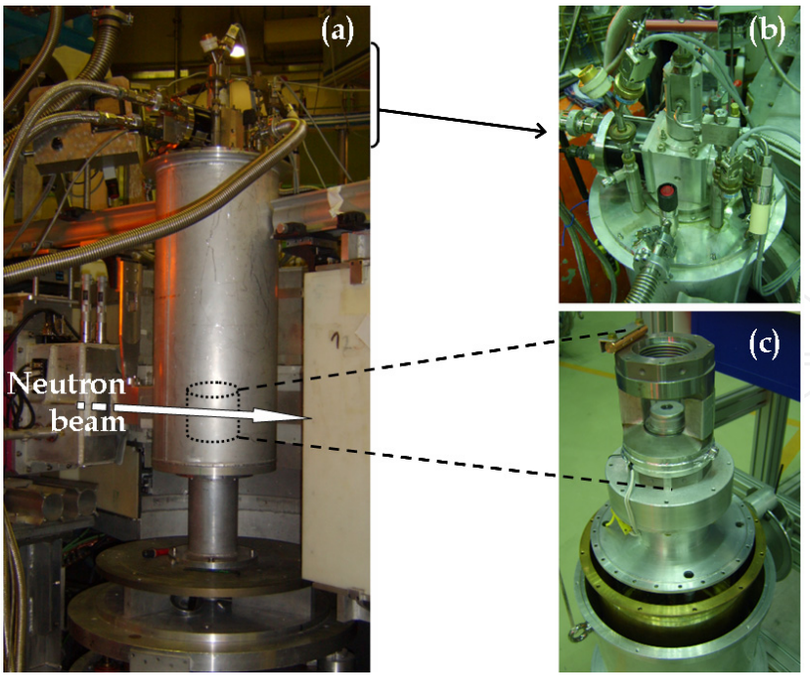


**Figure 7.** (a) Details of the high-intensity 2-axis diffractometer D20 (Hansen et al., 2008) at the Institut Laue-Langevin (France) with a special version of the helium closed cycle refrigerator (Displex) allowing the use of (c) Paris-Edinburgh high pressure cell. Cryostats are now fully self-governed (b) with automated cold valve, pressure transducer which monitors the exhausting helium gas pressure and temperature controller which adjust the liquid helium flow to the set temperature value.

be typically up to 1400-2000 K. Closed-shell furnaces (Kuhs et al., 1993) and mirror furnaces (Lorenz et al., 1993) were developed for powder and single-crystal analysis at high temperature. This last furnace type has the advantage to allow air-operated experiments with no heat shield, thus removing apparatus diffraction. As for cryogenic, variations are developed to combine for example high temperature and high pressure (Falconi et al., 2005). Finally, the last developments concern the design and built of furnace using aerodynamic levitation for reaching ultra-high temperatures up to 3000 K. This technique is well described by Hennet et al. (2007): "A spherical sample (3mm in diameter) is placed on a levitator that contains a convergent-divergent nozzle enabling the diffusion of a regulated gas flow onto the sample from below. This enables the sphere to remain in a stable position without any contact with the nozzle. When the sample levitates, it is heated by two $CO_2$ laser from the bottom through the hole in the nozzle. The temperature is measured with one or two optical pyrometers". Aerodynamic levitation apparatus were optimized for neutron (Hennet et al., 2006) and X-ray (Hennet et al., 2002; Sakai et al., 2005) scattering measurements. They were applied with success for examples to study the liquid states and the solidification of $CaAl_2O_4$ (Hennet et al., 2008) and $Y_2O_3$ (Hennet et al., 2003; Cristiglio et al., 2007).

### *2.3.3. High magnetic field*

Studying materials under high magnetic field could be done ether by X-ray diffraction (Katsumata, 2005) or by neutron scattering (Brown et al., 2002; Givord et al., 2004).

However, one of the advantages of neutrons is their possible interaction with the unpaired electron magnetic field. Thus, magnetic studies deal with a wide proportion of the total neutron diffraction experiments. As magnetic properties variations are generally observed at low temperature, superconductor cryomagnets are used for kind studies, with applied vertical or horizontal fields. The available magnetic field range is wide and nowadays fields around 10 T are commonly obtained, some devices also produce fields between 14.5 T and 17 T (Nietz, 2003). It can finally be noticed that punctual apparatus are developed through the world allowing 1 s pulsed magnetic fields up to 25 T (Nojiri et al., 1998) or 40 T (Grössinger, et al., 2004), in order to achieve fields up to 70 T in the future. Thermal neutrons are thus largely used to refine magnetic structures in addition to the nuclear structure. Hot polarized neutron diffraction is also a very interesting technique used to obtain crucial information about the magnetic form factors (reflecting the state of the magnetic ions) and magnetisation distributions of para-, ferro- and some antiferro-magnetic single-crystal materials if measurements are performed under high magnetic field configuration. On the other hand, one can performed zero-field neutron polarimetry measurements using Cryopad (CRYOgenic Polarization Analysis Device) (Tasset et al., 1999; Lelièvre-Berna et al., 2005; Takeda et al., 2005) to refine complex antiferromagnetic structures or to perform accurate determination of antiferromagnetic distributions.

### *2.3.4. High pressure*

High pressure condition is certainly the more used sample environment after low/high temperature. This field of research is also one of the most well-informed facing the number of published papers and reviews concerning experimental results or technical information (see for examples Paszkowicz, 2002; Boldyreva, 2008; Katrusiak, 2008; and references therein). Material studies under pressure are nowadays numerous due to the increase capabilities of modern X-ray diffractometer and the making of dedicated instruments on synchrotrons and neutron facilities. At the present time, about 30 synchrotron beamlines in the world (at 11 synchrotrons) allow high-pressure measurements to be performed, with possibility of high temperature too. It could be pointed out that 2012 marks the 35$^{th}$ anniversary of high pressure diffraction at synchrotron (Buras et al., 1977). The application of pressure on a material may induce major structural variations, particularly a modification in the weak intermolecular contacts and reorganization of the electronic structure, but also phase transitions or chemical reactions. Anyway, the application of pressure on a system induces more effects than the application of cryogenic temperatures, which is of interest to physicists, chemists, biologists and geologists. Pressure can give substantial information about structure-properties relationships and new thermodynamic phenomena (phase diagrams, polymorphism, cohesion forces, transformations…). Moreover, temperature variations can now be applied in combination to high pressure due to the high brilliance of modern sources at facilities which can bypass the unavoidable absorption of the beam by the cryostat or furnace and the pressure cell containing the tiny studied sample. Now, it is possible to perform experiments at 100 GPa and further thousands of Celsius degrees (Fiquet et al., 1999; Akahama et al., 2002; Guo et al., 2002; Hu et al., 2002; Orosel et al., 2012)

using synchrotron radiations, this is achieved with the laser heating technique (Bassett, 2001). Due to the relatively large sample volume required for neutron diffraction, high pressure measurement are always a challenge and reached maximum pressures are not so high: it was recently reported a high-pressure single-crystal neutron diffraction to 10 GPa at ambient temperature taking advantage of the neutron diffractometer D9 at the Institut Laue-Langevin (France) (Bull et al., 2011). To succeed those measurements, teams generally use DAC (Diamond Anvil Cell) (Jamieson et al., 1959; Weir et al., 1959), MAC (Moissanite Anvil Cell) (Xu et al., 2002) or LAC (Large Anvil Cell, as Paris-Edinburgh cell) (figure 7c) (Ohtani et al., 1977; Besson et al., 1992; Mezouar et al., 1999; Le Godec et al., 2003) pressure cells. For low and moderate pressures up to about 3 GPa at ambient temperature, there are also piston-in cylinder clamped cells (McWhan et al., 1974) and continuously loaded cells (Paureau, 1975). From the firsts diffraction measurements under pressure (Barnett et al., 1963; Bassett et al., 1966) to the last ones (Basu et al., 2012; Orosel et al., 2012; Tulk et al., 2012) efforts still continue to increase the available pressure range in both static and dynamic conditions, and also to improve instruments (Utsumi et al., 2002) or allow new techniques (Bromiley et al., 2009).

## 3. New instrumental developments at dawn of the third millennium

Using extreme conditions, researchers can consider not only to extend the accessible parameters scale to measure some physical constants or to verify existing theories, but also to point out new behaviours and states which increase our knowledge of materials properties. With progresses in the domains of available sources as 3rd generation synchrotrons or powerful neutron sources and of new sample environment devices as explained in part 2., extreme conditions measurements have known since 10 years a meteoric rise in all scientific fields for fundamental studies, for examples, of complex fluids, high correlated electrons systems, geological and biological materials at the origin of earth or life. However, will this keen interest continue for a long time? Are technological innovations always possible in that scientific area to build more efficient instruments and devices? Could it be possible to go further the actual limits of high pressures, high and low temperatures, applied magnetic fields? Is it really necessary to cross these limits as numerous material properties are still unexplored? All these questions have one simple answer: yes. Going further in the field of crystallography under extreme conditions is also expanding our knowledge of the world and life by probing the matter at the border of the unknown. Scientist needs everyday new challenges and the one to push back those limits is a necessity for him, but mostly essential for mankind.

In this way, *extreme conditions beamline* projects have emerged throughout the world at Large scale facilities. It will be pointed out thereafter some examples of instrumental projects which were, or will be, realized to explore materials properties giving access to new non-ambient conditions. The proposed examples are a non-exhaustive list of the actual developments in crystallography under extreme conditions. These examples are chosen on the most powerful Large scale facilities around the world in terms of the most important parameters (energy, current...): SPring-8 (Japan), APS (USA) and ESRF (France) are the

chosen synchrotron sources (table 1); ISIS (neutron spallation source, UK) and the ILL (neutron reactor, France) are the chosen neutron facilities.

| Name | Location | Energy (GeV) | Perimeter (m) | Current (mA) | Emittance (mrad) | Number of straights |
|---|---|---|---|---|---|---|
| SPRING-8 | Japan | 8 | 1436 | 100 | 3 | 48 |
| APS | USA | 7 | 1060 | 100 | 3 | 40 |
| ESRF | France | 6 | 844 | 200 | 3.8 | 32 |
| SSRF | China | 3.5 | 396 | 300 | 4.8 | 20 |
| ALBA | Spain | 3 | 268.8 | 250 | 3.7 | 24 |
| Australian Synchrotron | Australia | 3 | 216 | 200 | 8.6 | 14 |
| DIAMOND | UK | 3 | 560 | 300 | 2.7 | 24 |
| SPEARS3 | USA | 3 | 240 | 500 | 18 | 18 |
| CLS | Canada | 2.9 | 171 | 500 | 18 | 15 |
| SOLEIL | France | 2.85 | 354 | 500 | 3.1 | 24 |

**Table 1.** The most important parameters of the 10 world-wide most powerful 3rd generation light sources available in 2012.

During the last 10 years, numerous Large scale facilities begun an upgrade of their instruments and installations. This is partly due to the increase demand for high-brilliance X-ray and high-flux neutron beams by user communities requiring always an increase of the instrument performances and of the allocated beamtime. Users want to perform measurements on smaller samples mostly in *exotic* environments. One of the engineering goals for the upgrades is making available advanced sample environments with extreme conditions on the beamlines whilst fitting in the tight space around the sample also detectors and monitoring equipment. The challenge for the facilities will be to commonly supply extreme environments like pressures up to 100 GPa, low temperature below 1 K, high temperature above 3000 K, high magnetic field up to 50 T in pulsed mode and 30 T in continuous mode. To achieve these goals, facilities must also invest in the engineering of new dedicated instruments and particularly in the development of new detectors which have to be more sensitive, more efficient (especially for high-energy X-rays) and faster (notably in the sub-millisecond range to perform time resolved measurements). Upgraded a Large scale facility is difficult, long and very expensive (table 2).

| Name | Type of facilities | | Period | Total cost |
|---|---|---|---|---|
| SPRING-8 | synchrotron | upgrade | 2012-2019 | 375 M€ |
| APS | synchrotron | upgrade | 2010-2018 | 275 M€ |
| ESRF | synchrotron | upgrade | 2008-2017 | 290 M€ |
| DIAMOND | synchrotron | construction | 2002-2007 | 460 M€ |
| SOLEIL | synchrotron | construction | 2000-2006 | 403 M€ |
| ILL | neutron reactor | upgrade | 2001-2014 | 85 M€ |
| ISIS- TS2 | neutron spallation source | construction | 2003-2009 | 200 M€ |

**Table 2.** Estimated time and total cost of the upgrade or construction of some synchrotron and neutron facilities around the world.

SPring-8 light source will be upgraded in order to advance promising science and to support industrial innovations that will improve our life and contribute to a more sustainable society (SPring-8, 2012). This upgrade programme is principally focused on the construction of a new ring in place of the actual one, retaining the existing insertion device beamlines. In 2019, the new ring (SPring-8 II) would produce 1000 times higher brilliance than the present SPing-8 (new stored current of 300 mA instead of 100 mA presently) with a short X-ray pulse option of around 1 ps. The frontiers of science will be definitely opened. Instruments like BL02B1 (designed for analyses of single crystal structures and for investigations of phase transitions under external fields), BL04B1 (dedicated to high pressures and high temperatures researches in geoscience), BL10XU (designed to perform X-ray diffraction structure analyses under high pressure - 300 GPa - and low temperature - 10 K - or high temperature - 3000 K -) or BL40XU (high flux beamline for time-resolved x-ray diffraction) will benefit of new opportunities.

On April 2010, the US Department of Energy approved the Advanced Photon Source (APS) upgrade project (APS, 2011). The upgrade will provide high energy, high brilliance, short pulse, new and upgraded instruments. The objective is to push the stored current to 150 mA, to upgrade 6 beamlines and to build at least 6 new ones between 2010 and 2018 (Mills, 2011). The new beamlines will especially deal with the overarching theme *Real materials under real conditions in real time*. It means an easier access for users to high pressures, low/high temperatures and in situ chemical reactions. One frontier for X-ray science in the 21$^{st}$ century is to combine atomic-level spatial and temporal information, a frontier which would be crossed after the upgrade. For extreme conditions experiments, the APS had plane to upgrade 4 instruments and to build 2 new ones. For examples, the outboard branch of 16-ID will be dedicated to high pressure spectroscopy using sub-µm probes (beam size of 100-500 nm with a flux $\geq 10^{12}$ photons.s$^{-1}$ at sample position).

In this context, the ESRF (ESRF, 2007) has planned an upgrade programme for its instruments, like ID20 (beamline for magnetic and resonant X-ray scattering investigations under extreme conditions; Paolasini et al., 2007), ID22 (micro-fluorescence, imaging and diffraction beamline, Martinez-Criado et al., 2007), ID24 (Energy dispersive X-ray absorption spectroscopy beamline) or ID27 (high pressure beamline; Mezouar et al., 2005). The ID27 source was upgraded to the most recently developed cryogenic or superconducting undulator to obtain the maximum flux from the ESRF machine after its upgrade. This very high flux beamline will provide new approaches to very challenging problems such as the search for a new metallic superfluid state of matter predicted at pressures above 400 GPa, or to perform ultra-high pressure and temperature X-ray emission spectroscopy in combination with X-ray diffraction in the laser heated diamond anvil cells. In addition to this upgrade, the ESRF will build two new dedicated high pressure beamlines for diamond anvil cells and Paris-Edinburgh research. Time-resolved diffraction is also a priority for the ESRF which propose to build a dedicated beamline covering the timescale from 10 picoseconds to seconds in studies of physical, chemical and biological processes. The 4-circle diffractometer of this beamline will include Laue diffraction and classical diffraction, a very intense focused beam, a new 3 kHz chopper which isolates single pulses of X-rays

from the timing modes and a fast readout (0.1 s) Frelon CCD based camera. An other upgrade example concerns the ID20 magnetic scattering beamline with an extend of its experimental conditions in order to provide new research opportunities. It is also planned to build a dedicated station for very low temperatures below 1 K, high magnetic fields up to 17 T and high pressure up to 5 GPa at 1.5 K.

The world's leading spallation neutron source, ISIS, has contributed significantly to many of the major breakthroughs in materials science, physics and chemistry since it was commissioned in 1985. To keep the UK at the forefront of neutron research, it was decided in 2003 to build a second spallation neutron source, ISIS Target Station 2, where three key areas of science are planned to be investigated in priority: soft matter, bio-sciences and advanced materials. ISIS TS-2 project was completed in 2009 on time and to budget. There are currently 7 available instruments (and 4 instruments under building) at ISIS TS-2 which has a capacity for a total of 18 instruments in the future, adding to the 20 instruments already available at ISIS Target Station 1. Concerning the new instruments dedicated to extreme condition measurements, the available WISH instrument (Chapon et al., 2011) is a long-wavelength diffractometer primarily designed for powder diffraction at long d-spacing in magnetic and large unit cell systems, with the option of enabling single-crystal and polarised beam experiments. The WISH sample environments include a dedicated low background cryostat (with ultra-low temperature inserts), a dedicated 13.6 T vertical magnet, but also the standard ISIS furnaces, pressure cells and gas rigs. Futhermore, there is the IMAT instrument (Kockelmann et al., 2007), in design phase and operating in 2015, which will be a neutron imaging and diffraction instrument for materials science, materials processing and engineering. IMAT will offer a unique combination of imaging and spatially resolved diffraction modes for *tomography-driven diffraction*: residual stresses inside engineering-sized samples can be more effectively analysed if the diffraction scans are guided by radiographic data. Finally, the future EXEED instrument (McMillan and Tucker, 2007) will be a neutron time-of-flight diffractometer optimised for extreme environment studies of materials which will complement the capabilities of WISH on Target Station 2 and PEARL on Target Station 1. The experiments will be performed at high pressure, above 50 GPa using diamond anvil cells, under combined very low temperatures (mK), very high temperatures (2000 K, including laser heating in cells) or intense magnetic field, up to 10 T.

Finally, the neutron reactor installations and instruments at the ILL are undergoing a modernisation phase called the *Millennium programme 2001-2014*, 30 years after the first experiments in 1972. During the first phase (2001-2008) of the ILL upgrade, significant advances had been provided. The efficiency of the instruments has been boosted by a factor of 19. Moreover, 6 new instruments were built and 8 others were upgraded. In the second phase (2008-2014), 7 new instruments are planned to be built and 4 actual instruments upgraded. For extreme conditions experiments, it was planned a new neutron diffractometer XtremeD (Rodriguez-Velamazan et al., 2011). This instrument will be optimized for high pressure, up to 30 GPa, and high magnetic field, up to 15 T in continuous mode, studies for both single crystals and powders. The diffractometer,

mainly dedicated to study molecular chemistry and magnetism under extreme conditions, will include a large 2D position-sensitive detector and a radial oscillating collimator to suppress background.

It is clear, with all the above mentioned new instrumental developments at almost worldwide Large scale facilities, that the challenge for crystallography in the next years is to perform non-equilibrium and extreme condition measurements. All the domains of sciences are concerned in order to increase the knowledge and the understanding of materials behaviours and properties under external perturbations. It can be asserted without ambiguity that the present century is the one of *crystallography under extreme conditions*.

## 4. Conclusion

Since the first crystallographic experiment at the beginning of the 20$^{th}$ century, scientists have always whished to push back frontiers of measurements. Obtaining the structure-properties relationships in static and dynamic modes is one fundamental goal to increase our knowledge of materials and verify existing theories. This was largely made possible by the arrival of modern Large scale facilities allowing material investigations under extreme conditions. State-of-the-art crystallographic measurements discussed in this review and recent upgrades achieved at most facilities augur that limits will be increasingly crossed in the next years, giving rise to unsuspected highlight researches in all domains of sciences. The considered perspectives will offer new opportunities in crystallography.

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