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MATERIALS SCIENCE & APPLICATIONS

LABORATOIRE LÉON BRILLOUIN

MATERIALS SCIENCE & APPLICATIONS

Introduction

Materials Science activity at the LLB covers a variety of research fields including metals, alloys, polymers, geological materials, nanocomposites, organic materials, thin films... They are at the frontier of chemistry, physics and engineering sciences. The objectives of these studies are to understand and predict how parameters such as the chemical composition, the atomic structure and the microstructure determine the properties measured in materials at the macroscopic scale. Most of these studies have direct applications in technology and industry. This interdisciplinary activity addresses several of the main challenges of this beginning of century: advanced materials for energy storage and nuclear energy, new materials for information technology, aeronautics. A large number of the materials science research performed at the LLB is funded by companies and by research contracts.

Neutron scattering provides a wide range of tools to perform such studies:

- **Small Angle Neutron Scattering (SANS) and reflectometry** are key tools to study materials at the nanoscale: thin films, precipitates, pores, cavities, meso and nano porous structures…ranging in size between 1 and 100 nm.
- **Texture and strain scanning:** the strong penetration of the neutrons allows an analysis in volume, and thus to obtain information representative of the whole material.
- **Inelastic neutron scattering spectroscopy**, owing to the large incoherent neutron scattering cross-section of the ^{1}H nucleus, is a unique tool, able to provide a global view of the dynamics of highly protonated systems (water, H_2, CH_4, polymers) in bulk or under confinement.

New technologies for Energy - Energy storage

The energy system in the foreseeable future will probably be a combination of multiple renewable and non-renewable energy sources as well as reversible and non-reversible energy conversion devices. Among these, **lithium batteries** and hydrogen-based storage such as **fuel cells** are prime candidates. During the last two years, a significant body of work has been devoted to these fields at the LLB. The studies have been conducted either as an in-house activity, or as collaborations or as external users performing experiments. This activity is in increasing evolution.

FUEL CELL RESEARCH

Among all the emerging possibilities for storing energy, hydrogen is the ideal fuel and H-cells are one of the most attractive energy conversion device. In principle, hydrogen fuel-cell technology can be highly efficient and powerful in energy conversion, scalable and modular in engineering construction, clean, quiet, and safe in operation. However, formidable challenges exist in the present R&D stage. The major obstacles include the high cost in catalyst loading, corrosion, poisoning of electrodes and severe demands on the properties of electrolytes.

Since it drives the performances of the whole system, the management of water within the polymer electrolytes (Nafion) is another major issue. Inelastic Neutron Scattering spectroscopy has been used in combination with NMR relaxometry to track down the dynamical behavior of water within the porous structure of a Nafion membrane. **[*H1*, J.-C. Perrin]**. It has been shown that, when the membrane is sufficiently hydrated, there is no significant decrease of the water diffusion coefficient between the nanometric and the micrometric scales. Though, at lower hydration, the lamellar structure of the Nafion at the nanometric scale is responsible for a striking decrease of the water mobility.

The economic viability of fuel cells being mostly limited by the cost of the noble metal catalyst, a significant activity is devoted to rationalize its use, for example by a significant increase of the catalyst specific surface **[*C1*, G. Carrot]**. Grafting polymers from platinum nanoparticles permits : (i) to control the dispersion because polymer-grafted nanoparticles give very homogeneous Langmuir films where the distance between particles may be adjusted with the surface pressure. (ii) to improve both the compatibility of the particles with the membrane and the deposition onto gold electrodes.

Another approach consists in using solid electrolytes. Part of the LLB in house research has recently focused on a neutron-scattering study of the dynamics of protons in yttrium-doped barium cerate (BCY) [*H2*, N. Malikova]. BCY shows a high proton conductivity at ~ 800°C, a temperature range acceptable for industrial power generation for onboard vehicle applications. This relatively high operation temperature facilitates the dissociation of hydrogen molecules at the anode-electrolyte interface and the suppression of peroxide intermediates at the cathode without using noble metal catalysts. The experimental approach capitalizes on the exceptional sensitivity of neutron to hydrogen for proton-diffusion study and the high contrasts among the elements in BCY for structural characterization of the electrolyte under different atmospheric and temperature conditions. So far, we have shown that the onset of proton mobility, and therefore conductivity, is closely related to a phase change within the BCY matrix. Work is underway for a global assessment of the detailed dynamics. This work is supported by the Outgoing Marie-Curie International Fellowship granted to Natalie Malikova. This is a joint research program between Argonne Nat. Lab/IPNS and LLB.

REVERSIBLE ENERGY SOURCES: LI BATTERIES RESEARCH

Besides fuel cell, a possible route to the industrial production of viable high specific energy/power energy sources for non-polluting vehicles and portable devices are batteries. The ionic conductivity performances of an electrolyte, *i.e.* the ionic macroscopic transport, are intimately linked to the dynamics and topological properties of the medium in which the ions migrate.
PEO (polyethylene oxide) complexed by Li salts is currently used in lithium solid polymer electrolyte batteries. The ionic conduction mechanism in bulk is now well understood: the polymer local segmental dynamics at short time (ps to the ns) drives the lithium transport properties. Ionic conduction preferentially takes place in the amorphous fraction of the polymer. Inducing polymer amorphisation by confinement makes it possible to increase the conduction performances. Porous alumina membranes, also referred as AAO (Anodic Aluminum oxide) are macroscopically highly ordered confining systems made of oriented parallel cylindrical channels. During the first year of her PhD, K. Lagrené (LLB) has focused on the synthesis, the customizing of the topology of AAO membrane and the confinement of PEO within the pore network [*C2*, K. Lagrene]. These steps have been highly successful and the work will now continue to characterize the PEO+Li conductivity under this highly anisotropic confinement.
The LLB is also involved in the LISSIL project, recently funded by the ANR (PNANO call 2006, Jean Le Bideau, CMOS/ Montpellier & IMN/Nantes). The studied system is Ionogel, a recently patented (CNRS) ionic liquid confined by sol-gel methods in a silica matrix. We will study and correlate the charges migration phenomena, the structuration and the dynamics of these highly confined ionic liquids. The strategy is to use complementary time and space multi-scales techniques (TOF, NSE, NMR relaxometry and confocal spectroscopy). Here again, the target application are lithium rechargeable batteries.

OIL INDUSTRY ORIENTED RESEARCH

During the first stages of the oil extraction process, instead of pure oil, the gross output of a derrick comes as a very stable water-oil macro-emulsion. While the focus is supposed to be set on oil itself, one has to deal with non negligible undesired amount of water. Understanding the stability mechanism of that macro-emulsion is therefore a key issue for the oil industry.
A collaboration between IFP (Institut Français du Pétrole) and LLB (see Highlight **J. Jestin**, in the Soft Matter chapter) has led to the development of an original method using SANS to characterize the structure and composition of interfacial films of asphaltenes (a system usually used as a model for "crude oil") in water/oil macro emulsions. The correlations made between the molecular organization at the local scale and the macroscopic properties of the emulsions offer new perspectives to investigate stability mechanisms during oil production.
This widening gap between demand and supply is leading several major oil companies to consider unconventional resources. Among these, "Tight Gas Reservoirs" (TGR), usually sandstone or carbonate rocks, are already discovered but are not in active production yet, due to technological inefficiency to produce at economical rates. The key issues for the TGR production enhancement are related to the control of the liquid / gas phase transitions under confinement.
This kind of TGR systems are also prime candidates for the underground storage of green house gas such as CO_2. LLB is part of the teams applying for a CO_2. In this framework, neutron scattering is a perfect tool offering:
(i) High penetrating power for working at high temperature (up to 400°C) and high pressures (up to 5 kbar) corresponding to the actual TGR environment.
(ii) Isotopic substitution which can be used to unambiguously separate the contributions of the matrix, the liquid or the gaseous phase.
The following questions could be assessed: what is the structure of the porous material, what is the fluid inside the porous material, what is diffusivity of liquids inside such material…

Materials for the nuclear energy – New composite materials

A significant share of the materials science activity at the LLB deals with the development of advanced materials for the nuclear industry (new fuels or new steels). The LLB has taken part for the last ten years in the research projects concerning the ageing of nuclear reactor materials. SANS brings a characterisation of the microstructure evolution of materials constitutive of the Pressure Water Reactor primary circuit, subjected to important requests (irradiation, thermal ageing, hydridation etc.). Thus, the precipitation of solute atoms or of defects induced by the neutron irradiation were highlighted in ferritic alloys (vessel, piping etc.), and Zr alloys (fuel cladding guide-tube materials). The clusters formation has direct effects on the mechanical properties. The prediction of these materials behaviour in-service conditions requires the knowledge of the mechanisms of precipitation. Also the research in new composite materials (metallic alloys and reinforced polymers) has been very active during the last two years.

ADVANCED MATERIALS FOR THE NUCLEAR INDUSTRY

The last fifty years have shown how much the development of civil nuclear reactors (both prototype and industrial) required a considerable effort of R&D in the field of materials. The severe environment associated with nuclear reactors (high temperature and pressure, irradiation, corrosion, thermo-mechanical stresses, chemical compatibility) asks numerous questions in materials science.

New alloys are being developed in collaboration with the CEA/DEN (Direction de l'Energie Nucléaire), primarily with Service de Recherche de Métallurgie Appliquée SRMA (Y. de Carlan, JL Bechade, J. Henry, A. Alamo) and with the Service de Recherche de Métallurgie Physique SRMP (L. Chaffron, F. Legendre). Strong and fruitful collaborations exist with these two groups since 10 years.

In particular, the ODS (Oxide Dispersion Strengthened) martensitic or ferritic alloys **[*H3*. M.H. Mathon]** have been widely studied in order to understand the relationships between the fabrication process, the obtained microstructure and the mechanical behavior. SANS experiments have shown that the way to introduce the yttrium oxides for the mechanical alloying could be a key point to obtain a very fine distribution of nano-oxides after consolidation. The highest performances of some ODS steels are related to an oxides size of about 2 nm.

The effects of the milling conditions and the evolution of the oxides under annealing are under study. In the near future, we will focus on the behavior of these materials under external solicitation such as irradiation, thermal ageing or friction stir welding. Furthermore, the 9CrW martensitic steels - candidates for the internal structure of future generation reactors or spallation sources – are always the object of various works such as helium bubbles precipitation under irradiation or the influence of the chemical composition on the nanometric carbide formation.

A major long run issue for nuclear based energy is the safe management of the nuclear waste. This issue has been addressed by collaboration between the LI2C group of Univ. Pierre et Marie Curie (Prof. P. Turq) and the LLB. In this framework, the ANDRA has funded the PhD thesis of Natalie Malikova **[*C3*, N. Malikova]**. Diffraction, time-of-flight (ToF), Neutron Spin-Echo (NSE) and Molecular Dynamics (MD) simulations have been combined to provide fine information, at a quantitative level, on the behavior of water and ions in clays (particularly Cs^+ a potential radionuclide).

NEW COMPOSITE METAL ALLOYS

For industrial applications, metallic materials must, more and more often, show very good mechanical properties at high temperatures (250-400°C). A way of improving the mechanical performances of steels (Fe-5%Cr) at high temperatures consists in modifying the secondary precipitation by introducing alloying elements. In collaboration with D. Delagnes et al. **[*H4*, D. Delagnes]** of the Ecole des Mines d'Albi, a study of tool steels has been performed by SANS. This work shows a strong correlation between the secondary carbides precipitation, the mechanical resistance at high temperature and the Charpy impact energy.

In response to the need to reduce the energy consumption and the carbon dioxide emissions, the industry of transport, in particular aeronautics, seeks steels with very high mechanical characteristics. American research and industry have developed a

production process of new steels by designing a microstructure reinforced by a double precipitation of nanometric carbides and intermetallic phase. The principle of this double reinforcement opens the way to new families of materials. With the same aim, the AMARAGE project, funded by the ANR call "Matériaux et Procédés" undertakes this research on martensitic steels alloyed with C, Cr, Mo, Ni, Al, Co or V hardened by simultaneous precipitations of carbides of Mo and intermetallic Ni-Al. This project runs from 2006 to 2009. It is coordinated by Aubert&Duval and networks five research laboratories (CROMeP/Ecole des mines d'Albi, CEMES/Toulouse, LSG2M/École des Mines de Nancy, LLB, GPM/Rouen).

NEW COMPOSITE POLYMER MATERIALS

The LLB is involved in an ANR (with J.P. Salvetat/ CRMD Orléans) dedicated to the study of the mechanical reinforcement of polymer matrix charged with carbon nanotubes (BIONANOCOMP, a "white project" of the 2005 ANR call, funded from 2005 to 2008). A potential application is the production of biocompatible artificial tendons. LLB neutron beams will be used to check the aggregation states of the nanotubes within the matrix. Inelastic neutron scattering experiments are also scheduled to check potential modifications of the polymer local dynamics as a function of the nanotubes loading.

FUTURE TRENDS

A collaboration with DEN/LMPC (J. Lechelle) aims at reducing the heterogeneous character of the distribution of plutonium in microstructure MOX (reduction of the hot points). For that, sintering additives (TiO_2, Cr_2O_3, S) can be added to the MOX. It allows a more important grain growth. When the introduced quantity is higher than the limit of solubility of chromium in the solid solution $(U,Pu)O_2$, chromium can precipitate in the form of $PuCrO_3$ and pin the grain boundaries. The size distribution of the pores is thus modified in the presence of Cr. SANS experiments should allow to characterize the porosity evolution during the sintering. Also, texture measurements will be performed to determine if the crystallographic texture can be modified during the grain growth in the presence or not of additives.
The studies relating to materials of nuclear interest carried out in collaboration with the DEN (SRMA B. Marini) should be extended to the stainless steels used for the internal structures of PWR reactors. These steels present an embrittlement under irradiation probably induced by the formation of defect clusters or of dislocation loops. The analysis by SANS would make it possible to define and quantify these objects. These materials being subject to very strong amounts of irradiation, an important lapse of time was necessary after irradiation so that the radioactivity allows the handling of the samples.

Advanced materials for Information technology

SPIN ELECTRONICS

A large amount of work is dedicated to the study of the magneto-electronic properties of multilayer systems of nanometric thickness. This field is now referred to as *"spin electronics"* and aims at using the magnetic properties of some materials to create a new generation of electronic devices.
In this field, a large part of the materials science research of the last 3 years has been devoted to the search of new materials in the form of thin film suitable for spin-electronic devices. A number of these materials have been characterized by polarized neutron reflectometry at the LLB. We can mention materials such as Fe_3O_4 and $CoFe_2O_4$ (DRECAM/SPCSI), MnAs (INS Paris), GaMnAs, Fe/Ge (Acad. Science Pologne), SiC:Fe (LPM, Univ. Poitier **[*C4*, A. Declemy]**), ZnO:Co (UMR CNRS –Thalès). Polarized neutron reflectometry allows to characterize the magnetization depth profiles (thickness of the films, magnetization orientations in the different layers of spin-valve systems).
Another large field of research deals with magnetic oxides which offer a wealth of properties. Recently, a very active field topic has been the search for magneto-electric materials in which the magnetic behavior can be controlled by an electrical field. Materials such as $BiFeO_3$ are presently being studied in collaboration with the UMR CNRS-Thalès.

RECORDING MEDIA

Rewritable DVD disks use some complex tellurium based covalent alloys. These alloys display some optical properties that depend strongly on the atomic arrangement. Writing or erasing a bit is achieved by amorphizing or recrystallizing a small zone of a thin layer through a laser pulse. The recrystallization process is the time limiting step. In order to find some more efficient alloys, it is necessary to understand what drives both the optical contrast and the recrystallization kinetics. Different classes of Te-alloys have been investigated in the liquid state by neutron diffuse scattering on the 7C2 diffractometer. Some general features have been extracted from neutron scattering characterization of the liquid state : there is a relation between the structure of the liquid, the number of valence electrons per atom and the phase change ability [*H5* **J.P. Gaspard**].

FUTURE TRENDS

The growth of thin films structures and multilayers is now well mastered. Even though there is still a large number of material combinations to be studied, the interest is now shifting towards nano-particles and nano-patterns. The confinement of the magnetic properties does not anymore take place only in one direction (thickness of the film) but in 3 directions.
The fabrication of such nano-objets can be performed either by a top-down approach (use of electronic lithography or alumina membranes) or by a bottom-up approach in which the systems self-organize in nanostructures : formation of magnetic stripe domains in materials such as MnAs (INS Paris) or FePd (DSM/DRFMC, Grenoble), formation of nanoclusters of Co in an insulating matrix (SiO_2 or TiO_2) during a sputtering process. Most of these materials exhibit strange or at least anomalous transport properties. The knowledge of the organization of these materials is thus of great interest since the detailed organization of the nanoparticles controls the electrical transport properties. A number of studies combining polarized neutron reflectometry and SANS have been undertaken in such systems.
In particular we are studying magnetic nanowires synthesized by a chemical route (ITODYS/G. Viau). This bottom-up approach allows to build very clean magnetic objects. It might be possible to implement them in electronic devices such as HF filters or antennas. This topic is the PhD Thesis subject of Thomas Maurer who has joined the LLB at the end of the year on a BDI contract.

Metallurgy - Engineering

RESIDUAL STRESSES – STRAIN SCANNING

Internal and residual stresses in materials have a considerable effect on material properties, including fatigue resistance, fracture toughness and strength. The weak absorption makes neutron diffraction a unique non-destructive tool to determine the complete tensors of the residual stresses in crystalline materials and to establish 3D cartographies. The principle of the technique, called Neutron Strain Scanning, is to use crystal lattice as an atomic strain gauge to measure strain distributions with a sub-millimeter spatial resolution. The stresses are thus calculated from the measured strains using elasticity laws.
Since 1989, the LLB has a diffractometer devoted to the characterization of the residual stresses. This instrument continuously evolved in order to meet the needs of the industrial partners (determination of three-dimensional cartographies of the stress field in massive parts weighing up to 500kg) as to those of the scientific community based on a finer analysis of deformation heterogeneities.
The engineering activity is currently funded by industrial partners and has been reinforced during the last years. Among the main industrial collaborations, we can mention the recent work carried out with CETIM (Centre Technique des Industries Mécaniques), which has consisted in the determination of residual strains in two cylinder heads of boat engines (weight of 150kg).

Very recently, an important collaboration was re-initiated with Dassault Aviation, following preliminary validation measurements carried out successfully in 2003. LLB is now involved in a large research program aiming at characterizing the residual stress fields in a part of a Mirage 2000 fighter wing at different steps of its conception, by coupling neutron diffraction measurements and finite elements calculations.
The development of a compact tensile machine [*C5*, **V. Klosek**] in collaboration with the LPMTM (Laboratoire des Propriétés

Mécaniques et Thermodynamiques des Matériaux) generates new fundamental studies. This machine adapted on the Euler's cradle of the G5.2 and 6T1 diffractometers gives the possibility of following "in situ" the evolution of the residual stresses and texture under uniaxial loading. The deformation mechanisms, the heterogeneities of deformation, the stress induced phase transformations or the local mechanical behaviours of heterogeneous materials are new research field opened to study.
In collaboration with V. Ji from the LIM (Laboratoire d'Ingénierie des Matériaux) at ENSAM Paris, measurements were performed on «duplex» steel (50% ferrite and 50% austenite) to analyze in situ, by neutron diffraction, the evolution of local macro-stresses in each phase as a function of the applied strain. Diffraction peaks for both phases could be recorded simultaneously. The method was validated and will be applied on other kind of materials.

CRYSTALLOGRAPHIC TEXTURE

A large part of the activity was dedicated to the recrystallization phenomena study in copper alloys **[*C6*, S. Jakani]**. A detailed study of bronze and brass alloys is also in progress. Measurements of diffraction of the neutrons highlighted that the distribution and the values of the stored energy according to the crystallographic orientations vary with the added element. Moreover, the "in situ" recrystallization studies allow to evaluate the activation energy for each material. The activation energy decreases with the deformation rate but increases with the content of alloy element. This work will be coupled to a microstructural analysis.
The description and the prediction of the mechanical properties of materials require an analysis of the mechanical behaviour on the grain scale. The polycrystalline materials can be regarded as multiphase materials, each phase being associated with a crystallographic orientation and thus a mechanical behaviour. The "in situ" studies of elastic and plastic strain under uniaxial load will make it possible to quantify these heterogeneities of deformation. The first studies performed on a CuSn 9% alloy showed significant differences between the crystallographic orientations. This type of study will be carried out on various FCC materials such as copper alloys, steels...

FUTURE TRENDS IN METALLURGY STUDIES

In the near future, two new scientific themes will be developed at the LLB in collaboration with ENSAM/Paris.
The first one is the study of memory-shape alloys (MFA). MFA alloys undergo a martensitic phase transformation which leads to a change in macroscopic form following a temperature variation. This phase transformation is characterized by a weak volume variation and an important shearing according to a crystalline plan and a well defined crystalline direction. Any manufacturing treatment can induce this transformation. It is of primary importance to control the impact of a deformed state on the phase transformations. Thus, this process will be applied to Cu-Al-Be and Cu-Zn-Al alloys for which one will endeavour to understand the evolution of the microstructural and mechanic state under mechanical solicitation.
The second one is the study of the martensite transformation under load in steels. "In situ" neutron diffraction measurements under load will allow to obtain a description of the stress state as well as the phases in presence according to the loading. This work will be undertaken in collaboration with the DEN/SRMA.

MATERIALS SCIENCE & APPLICATIONS

H1. QENS study of water dynamics in the Nafion membrane.
J.-C. Perrin, S. Lyonnard, F. Volino, A. Guillermo

H2. Proton Conduction in yttrium doped barium cerate.
N. Malikova, J.-M.Zanotti, C.K. Loong

H3. Small angle neutron scattering investigation of ODS martensitic steels.
M.H. Mathon, Y. de Carlan, P. Olier, L. Chaffron, C. Cayron, S. Ukai, A. Alamo

H4. Influence of alloying elements on nanometric carbides precipitation in 5% chromium martensitic steels.
P. Michaud, D. Delagnes, P. Lamesle, M.H. Mathon

H5. Rewritable DVD, RAM memories: between the electronic structure and the recording ability, neutron scattering shed some light.
J.-P. Gaspard, V. Coulet, C. Bichara, C. Steimer, M. Wuttig, B. Beuneu

[*C1.* G. Carrot] Self-assembling via Langmuir-Blodgett films and SANS characterisation of polymer-grafted platinum nanoparticles: a possible application in fuel cells.

[*C2.* K. Lagréné]Dynamics of a polymer confined in macroscopically monodisperse oriented pores.

[*C3.* N. Malikova] Dynamics of water and ions in clays: a concurrent TOF, NSE and MD study.

[*C4.* A. Declémy] Ferromagnetic Fe-implanted SiC: New results towards a Diluted Magnetic Semiconductor.

[*C5.* V. Klosek] A compact tensile machine for in situ neutron diffraction study of materials under external loading.

[*C6.* S. Jakani] Deformation and recrystallization mechanisms of CuSn alloys (bronze).

H1. QENS STUDY OF WATER DYNAMICS IN THE NAFION MEMBRANE

JEAN-CHRISTOPHE PERRIN, SANDRINE LYONNARD, FERDINAND VOLINO, ARMEL GUILLERMO

UMR SPrAM 5819 DRFMC/CEA Grenoble

Proton Exchange Membrane Fuel Cells are electrochemical devices developed for energy systems able to offer a competitive and clean alternative to standard oil based power suppliers. The key element of the cells is the ionomer membrane that must allow for proton transport from the anode to the cathode. The ionic conductivity insured by the acidic functionalities (SO_3^- groups) strongly depends on the hydration state of the membrane. Since the swelling state of the membrane can vary under operative conditions in a fuel cell, the hydration level appears as a crucial parameter for optimizing the performances. Moreover, proton conductivity and water dynamics are strongly coupled. In this work, we focused on the confinement effects on water mobility at the molecular level, as a function of the water loading in the Nafion. For this purpose, we have used QuasiElastic Neutron Scattering (QENS) to investigate the nano to picosecond molecular dynamical behaviour of the water adsorbed in the membrane.

Experiments. The QENS experiment were performed at 25°C on the time of flight (TOF) spectrometer Mibemol of the LLB with incident wavelengths λi = 5.2 Å and 8 Å corresponding to an elastic resolution of ΔE = 140 μeV and 40 μeV FWHM respectively. The time scale has been extended to the nanosecond range by a complementary backscattering (BS) experiment performed on IN16 of ILL (λi = 6.27 Å; ΔE= 1 μeV).

Sample preparation. The membrane samples have been prepared from almost dry to fully hydrated. The combination of sorption measurements and SANS experiments allowed us to know with precision the quantity of water in each sample. We characterize this quantity by the parameter λ, which corresponds to the number of water molecules per ionic SO_3^- group.

Data analysis. In this work, local diffusion in confined geometry, long-range diffusion and atomic granularity are accounted for in a single model in the full *Q*-range ($0.34 < Q < 2.25 Å^{-1}$). The raw data analysis shows that the spectra needs to be analysed in terms of the superposition of two kinds of dynamics in the water-swelled Nafion that necessarily corresponds to the existence of two types of protons that are not exchangeable within the longer time-scale of the experiments (~600 ps). As a consequence, the experimental intermediate scattering function has been written as the sum of two components witch correspond respectively to "fast" (few ps) and "slow" (>100 ps) motions[1]:

$$I_{\exp}(Q,t) = Amp \times [N_{fast} \times I_{fast}(Q,t) + N_{slow} I_{slow}(Q,t) + I_{el}(Q)] \times R(t) \quad (*)$$

N_{fast} and N_{slow} correspond to the number of mobile protons involved in the corresponding dynamics, $I_{el}(Q)$ is the elastic contribution of the polymer matrix, $R(t)$ is the temporal resolution function and and $I_{fast}(Q,t)$ and $I_{slow}(Q,t)$ are the intermediate scattering functions written as:

- $I_{fast}(Q,t) = I_{loc}(Q,t) \times I_{lr}(Q,t)$, where

$$I_{loc}(Q,t) = \exp\left[-Q^2\sigma^2\left(1-\exp\left[\frac{-(D_t/\sigma^2)t}{(1+2D_tQ^2\tau_{mi})}\right]\right)\right]$$

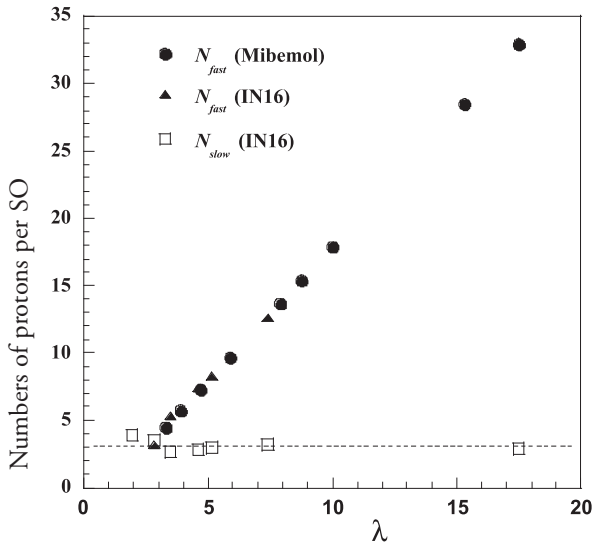
accounts for localized translational diffusion (with a diffusion coefficient D_t and a microscopic jump time τ_{mi}) inside a volume of typical size 2σ and $I_{lr}(Q,t)=exp(-D_{lr}Q^2t)$ accounts for long range diffusion[2].

- $I_{slow}(Q,t) = (1-a(Q)) + a(Q) \times \exp(-t/\tau_{slow})$,

where $a(Q)=exp(-Q^2\sigma_{slow}^2)$ is the EISF of the slow motion (characteristic time tslow and characteristic distance $2\sigma slow$). The quasielastic spectra have been calculated by numerical Fourier transform calculations of expression (*).

Results. The proton population of the "slow" motion is found to be constant over all the swelling range at the value N_{slow}~3 (Figure 1), whereas the "fast" population N_{fast} increases almost linearly with the total number of water molecules λ.

Figure 1



This result pleads in favour of the existence of the hydronium ion as a long life-time entity in the Nafion. This picture is supported by the evolutions of the residence times τ_{mi} and τ_{slow} (Figure 2) and the characteristic confinement domains (2σ and $2\sigma_{slow}$) (Figure 3) which show that the 3 "slow" protons are diffusing ~50 times slower than the "fast" protons, in a confinement domain of almost identical size.

Figure 2

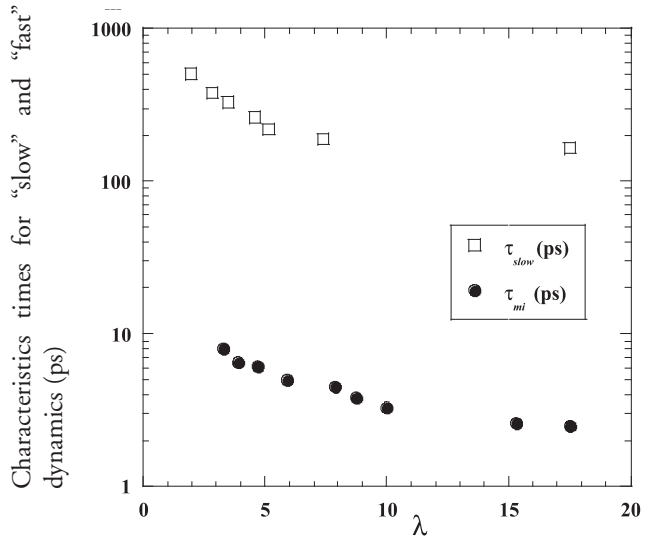
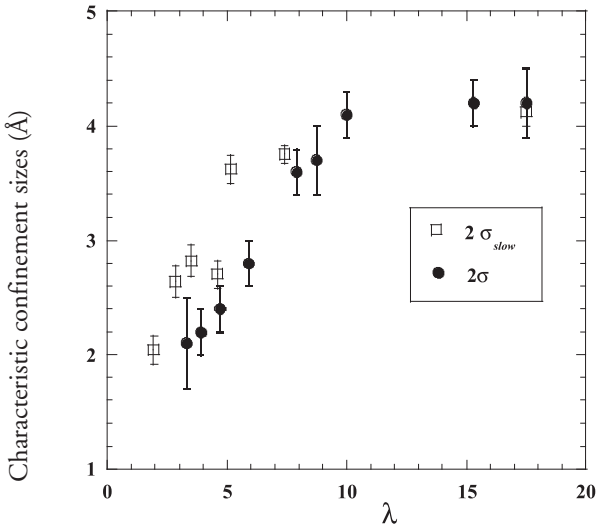
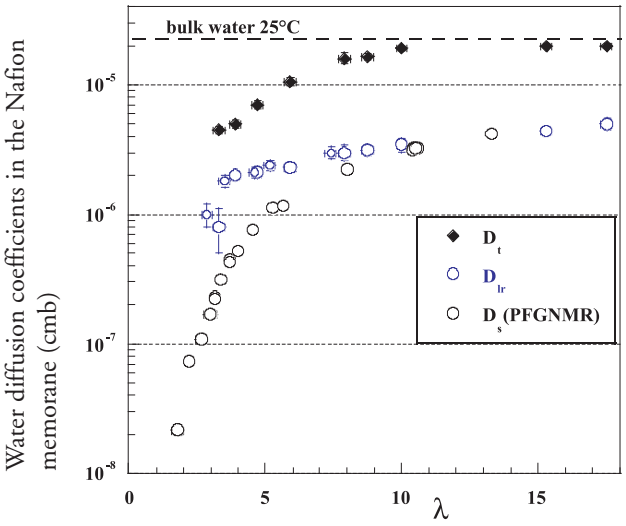


Figure 3



The evolution of these parameters, together with that of the local and the long-range diffusion coefficients (Figure 4) illustrates the progressive acceleration of the water dynamics when hydrating the membrane. For the highest hydration states, the local behaviour is very close the one observed in bulk water. Moreover, as soon as λ~3, a long-range diffusion coefficient must be introduced in order to fit the quasielastic spectra in both experiments. The water can thus diffuse at largerdistances than 2σ for very small amount of water.

Figure 4



Above λ~10 the long-range diffusion coefficient is equal to the self-diffusion coefficient measured by pulsed field gradient NMR at the micrometer scale. This remarkable property of the membrane tells us that there is no slowing down of the diffusion between the nanometric and the micrometric scales when the membrane is sufficiently hydrated. At low hydration, the difference between the two diffusion coefficients can be attributed to the lamellar structure of the Nafion at the nanometric scale as revealed by NMR relaxometry experiments[3].

(1) Perrin, J.-C.; Lyonnard, S.; Volino, F. *J. Phys. Chem B, accepted for publication.*
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(3) Perrin, J.-C.; Lyonnard, S.; Guillermo, A.; Levitz, P. *J. Phys. Chem B* **2006**, 110, 5439.

H2. PROTON CONDUCTION IN YTTRIUM DOPED BARIUM CERATE

N. MALIKOVA[1,2], J.-M.ZANOTTI[1] & C.K. LOONG[2]

[1]Laboratoire Léon Brillouin, CEA-Saclay, 91191 Gif-sur-Yvette
[2] Argonne National Lab., Intense Pulsed Neutron Source, Argonne, il, USA

One of the major challenges in the development of hydrogen fuel cells remains the choice of electrolyte. Severe demands exist on a number of its properties including very high ionic and very low electronic conductivity, high thermal and chemical stability and durability. Yttrium doped barium cerate (BCY) meets many of the above requirements. It has been studied intensively since the first observation of its high proton conductivity at elevated temperatures (> 600°C) [1]. Barium cerate has a perovskite-type structure, in which substitutions of Ce^{4+} by Y^{3+} cause the formation of oxygen vacancies. The doped material is hygroscopic, it absorbs water dissociatively resulting in the formation of hydroxyl groups (see Figure 1). At temperatures above 400-500°C, hydrogen atoms in the structure become mobile, leading to proton conductivity (20% yttrium doping necessary for optimal conductivity). While the ultimate interest is the macroscopic motion of H atoms under an applied electric field, the understating of the mechanism itself requires the knowledge of the local proton environment. It is studied here using a combination of inelastic and quasi-elastic neutron scattering, taking advantage of the complementary techniques available on pulsed (IPNS, ANL) and continuous (LLB, Saclay) neutron sources. The experimental data are to be complemented with microscopic simulation at a later stage.

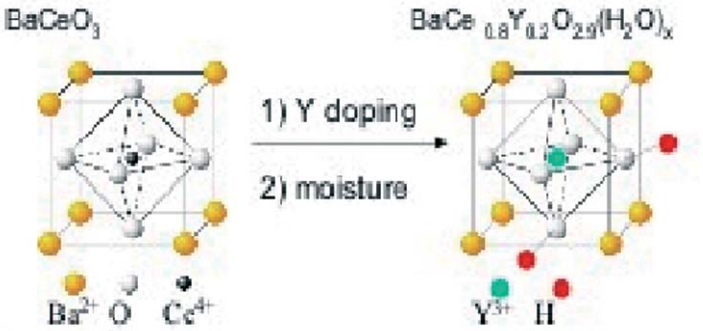

Figure 1: Idealised (cubic) structure of barium cerate and its yttrium-doped counterpart containing hydroxyl (OH) groups.

In recent neutron diffraction experiments, the structural phase transitions of the underlying perovskite network, as a function of temperature and water uptake, have been highlighted as a crucial factor determining the behaviour of H atoms [2]. A monoclinic (I2/m) phase has been identified as a phase accommodating the H atoms in the structure at room temperature. Furthermore, our measurements on the QENS spectrometer at IPNS, providing concurrent structural and dynamic information, give evidence for a link between the disappearance of the monoclinic (I2/m) phase at around 400 °C and a change in the proton dynamics as indicated by the mean-squared displacement determined from the Debye-Waller factor (see Figure 2).

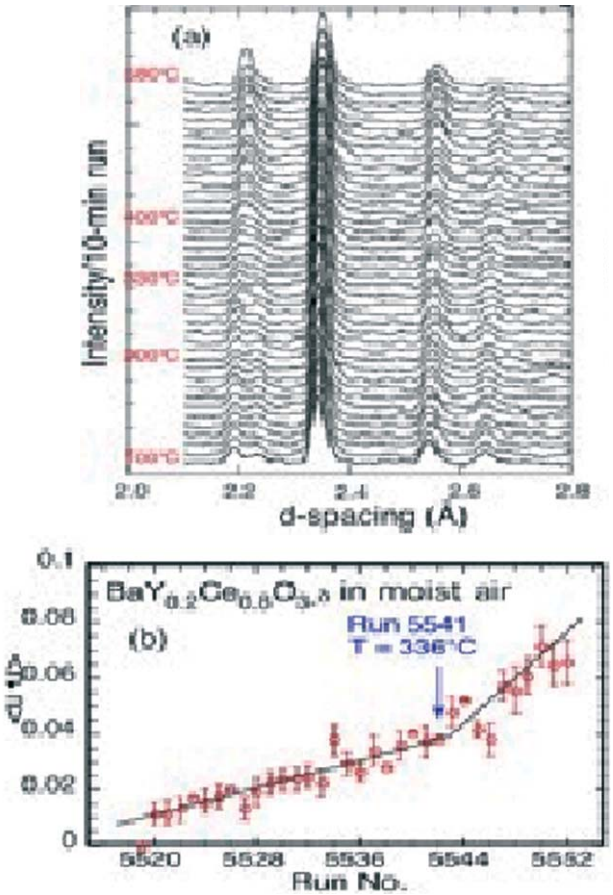

Figure 2: Concurrent data collection of the diffraction patterns of BCY and the hydrogen atom mean-square displacements (QENS spectrometer, IPNS).

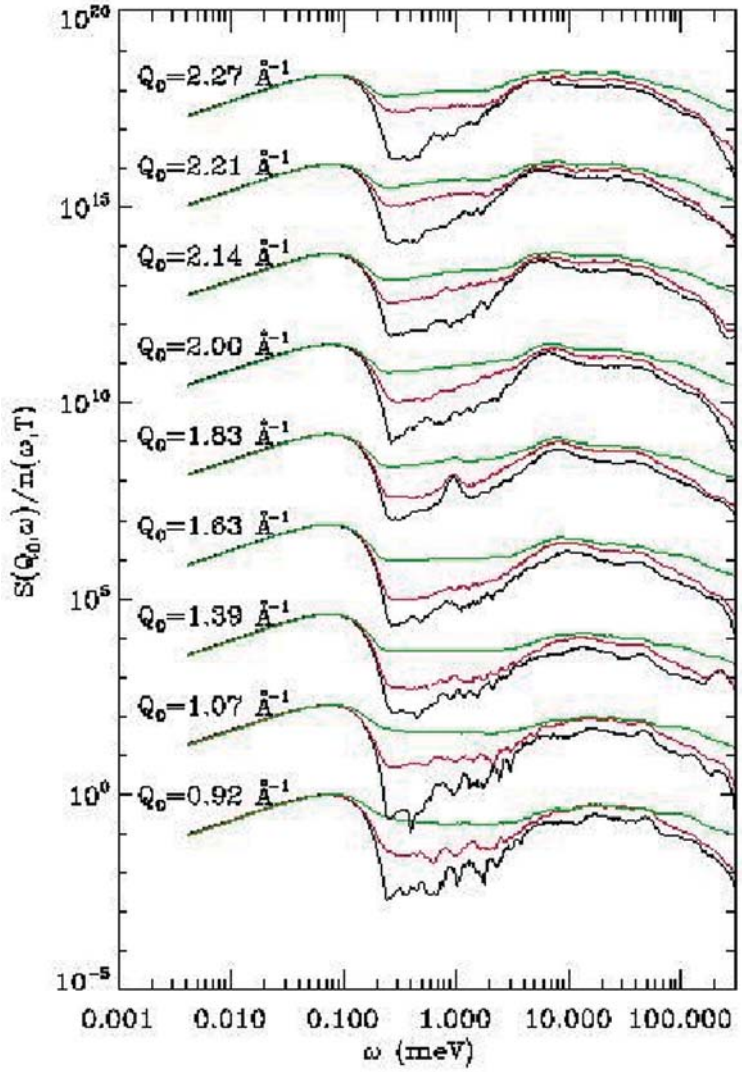

Figure 3: Susceptibility representation of low-resolution quasi-elastic data (650°C, MIBEMOL) on wet BCY (green), dry BCY (red), background (=quartz tube, black).

We are currently complementing the existing quasi-elastic neutron data with more detailed measurements, at varying resolutions, to elucidate the Q-dependence of the observed hydrogen motion.

Using a flow-cell set-up, allowing in-situ hydration and dehydration of the BCY system, we have collected both low- and high-resolution data, at the MIBEMOL spectrometer (LLB, resolution (FWHM) of 150 μeV) and IRIS spectrometer (ISIS, resolution (FWHM) of 18 μeV) respectively.

Susceptibility representation of the low-resolution data (Figure 3), indicates increased signal in the region 0.3-2 meV upon hydration of the BCY sample as well as around 100 meV. The observed quasi-elastic broadening is reproduced well using a trans-rotational model, giving rise to a narrow and broad component. In agreement with previous quasi-elastic neutron scattering studies, the Q-independent rotational broadening is of the order of 1-2 meV (HWHM). However, in the Q range studied (0.8 - 3.0 Å-1), the translational broadening shows rather a weak Q dependence. Data in a lower Q region are probably necessary in order to determine the corresponding diffusion coefficient.
Aside from quasi-elastic spectrometers, the pulse-source HRMECS spectrometer (IPNS, ANL) provides a very wide dynamic range (up to E=600 meV in energy transfer over a large Q-range). High-energy transfers are essential to probe the phonon and local modes involving hydrogen and the surrounding heavier atoms. Experimental phonon density of states of BCY is to be used as a check in the choice of inter-atomic force fields, the key parts of any microscopic model of the system.

Acknowledgements: Argonne National Laboratory is operated by the University of Chicago for the U.S. Department of Energy. This research is funded by a European Community Marie-Curie Fellowship (N.M.).

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[2] K. Takeuchi *et al*., Solid State Ionics **138** (2000) p.63.

H3. SMALL ANGLE NEUTRON SCATTERING INVESTIGATION OF ODS MARTENSITIC STEELS

M.H. MATHON[1], Y. DE CARLAN[2], P. OLIER[3], L. CHAFFRON[4], C. CAYRON[5], S. UKAI[6], A. ALAMO[2]

[1]LLB(CEA-CNRS), [2]DEN/SRMA, [3]DRT/S3ME, [4]DEN/SRMP, CEA/Saclay, 91191 Gif-sur-Yvette, France
[5]CEA/Grenoble, DTEN/SMP, 17 rue des Martyrs, 38054 Grenoble, France
[6]Nuclear Fuel Research Group, O-arai Engineering Center, JNC 4002, Narita, Ibaraki, 311-1393, Japan

The materials reinforced by oxide dispersion, usually called ODS (Oxide Dispersion Strengthened), have a vast applicability because of their excellent mechanical resistance at medium and high temperatures. In general, ODS alloys are manufactured by mechanical alloying from elementary powders and consolidated by hot extrusion or HIP (High Isostatic Pressure). Iron based ODS could be used for nuclear applications between 550°C and 900°C. Indeed, they present good dimensional stability and excellent resistance to swelling under irradiation due to their body centered cubic structure and also good creep resistance because of the dispersion of nanometric Y_2O_3 oxide particles.

The main objective of this work is to study the evolution of the oxide dispersion during the different stages of the fabrication, that is, after mechanical alloying, consolidation process (extrusion or HIP) and after thermal treatments. For this purpose, Small Angle Neutron Scattering (SANS) experiments were used to characterize the nanometric Y_2O_3 oxide distribution in the matrix. Also, the A ratio of the magnetic and nuclear SANS contrasts between matrix and particles gives information on the chemical composition of the particles.

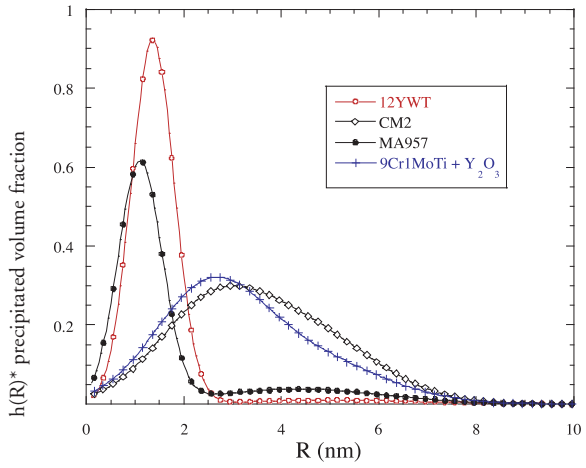


Figure 1 : Y_2O_3 clusters size distribution in consolidated ODS alloys.

In the present study, several commercial or experimental ODS martensitic/ferritic materials have been investigated at consolidated state: MA957 manufactured by INCO metal and the Japanese steel 12YWT (12%Cr) produced by Kobe containing 12% of chromium, and two experimental martensitic alloys presenting a lower chromium content (9%). The SANS experiments show the existence of nanometric (<10 nm) oxides in all materials but their volume fraction depends strongly of the alloy (see figure 1). The ferritic alloy 12YWT which presents exceptional creep-rupture properties, contains the most homogeneous and fine oxide distribution. For the MA957, the volume fraction of very small oxides (radius of 1 nm) is lower. Concerning the low Cr material, the size distribution is larger in relation with their worse creep properties.

In the aim to be able to reproduce and improve the 12YWT steel, different mechanical alloying conditions and thermal treatments were tested.

The volume fraction of small oxides observed after ball milling is higher if the yttrium oxides are introduced as a mixture of Fe_2O_3 and Fe_2Y intermetallics than as Y_2O_3 micro powder. Those small oxides could be the first step of a new precipitation of nano-phases or "the residues" of the mechanical alloying (MA). A heat treatment during 1 hour at 850°C and at 1100°C, induces the precipitation of new nano-oxides with a different chemical composition from the one observed in the MA powder. This result proves that the mechanical alloying produces a partial solid solution super-saturated in yttrium, titanium and oxygen and that a new precipitation occurs during the consolidation treatment. After 1h at 1100°C, the size distribution is quite similar to the Y12WT one…

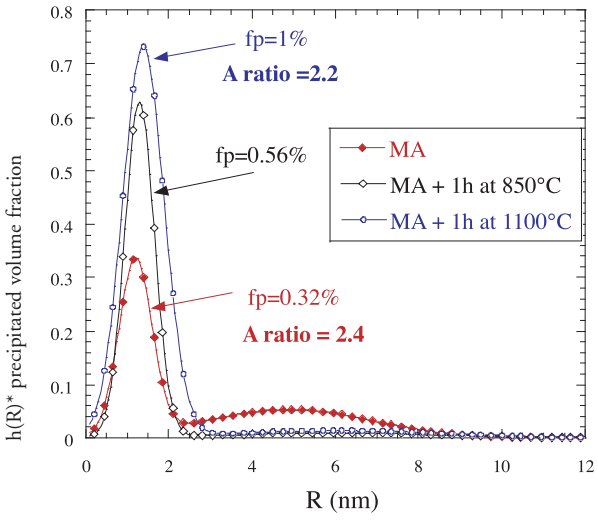


Figure 2 : Y_2O_3 size distribution evolution under thermal treatment.

H4. INFLUENCE OF ALLOYING ELEMENTS ON NANOMETRIC CARBIDES PRECIPITATION IN 5% CHROMIUM MARTENSITIC STEELS

P.MICHAUD [1,2], D.DELAGNES [1], P.LAMESLE [1], M.H.MATHON [3]

[1] Ecole des Mines d'Albi-Carmaux, CROMeP, Campus Jarlard, route de Teillet 81013 Albi, France
[2] Aubert & Duval, 63770 Les Ancizes, France
[3] Laboratoire Léon Brillouin (CEA-CNRS), CEA Saclay, 91191 Gif-sur-Yvette, France

Tempered martensitic steels containing 5% chromium, mainly used for forging and high-pressure die casting tools show a limited lifetime due to the severe thermo-mechanical working conditions. The resistance to stress at high temperature of these steels is directly related to the stability of alloyed carbides which are formed above 450°C during tempering. In order to improve high temperature mechanical properties, the more relevant route is to modify the secondary precipitation by introducing alloying elements. Consequently, carbide forming elements (W, Mo, V, Nb) as well as elements influencing the precipitation kinetics (Co, Ni) were added to a low-silicon AISI H11 steel previously studied, the well known Aubert & Duval steel : ADC3 (reference) [1]. The characterization of carbides formed during the heat treatment was carried out using techniques such as X-ray diffraction and Transmission Electron Microscopy (TEM). However, these techniques were not efficient enough to evaluate parameters of the population of small carbides with an average size lower than 5 nm. Thus, in order to evaluate the size distribution and the volume fraction of the secondary precipitates of nanometric size, small angle neutron scattering (SANS) experiments were performed. Also, the A ratio of the magnetic and nuclear contrasts between matrix and particles gives information on the chemical composition of the particles.

In this study [2], twelve grades of steel with different alloying additions were compared to the reference. Alloying additions corresponding to each grade is presented in table 1.

The neutron scattering experiments were performed at Léon Brillouin Laboratory on PAXE small angle instrument. Measurements were performed at room temperature, under a saturating magnetic field H=2 Teslas perpendicular to the incident neutron beam direction, in order to separate the magnetic and nuclear scattering cross-sections.

Reference	ADC3
Mo	Ref + 1.8%Mo
MoMo	Ref + 3%Mo
MoMoCo	Ref + 3%Mo + 3%Co
V V	Ref + 1%V
Ni	Ref + 1.5%Ni
NiNi	Ref + 3%Ni
Co	Ref + 3%Co
W	Ref + 1.6%W
Nb	Ref + 0.06%Nb
NiMo	Ref + 1.5%Ni + 1.8%Mo
NiV	Ref + 1.5%Ni + 0.7%V
NiW	Ref + 1.5%Ni + 1.2%W

Table 1: Alloying additions (in weight percent)

Volume fraction evaluated by SANS have shown that the number of small carbides (d < 5 nm) are about 100 times higher than the number of carbides with an average radius of 15 nm. Actually, this population of small carbides (d ~ 3 nm) will be more efficient in pinning dislocations and improving mechanical properties. The results have shown that a significant modification of the volume fraction and chemistry of nanometric precipitation are observed only for Mo, V and Ni additions (figure 1). The figure 1 shows green bars for the beneficial effect of Mo and V additions, whereas red bars represent detrimental effect of Ni addition on the volume fraction of small carbides.

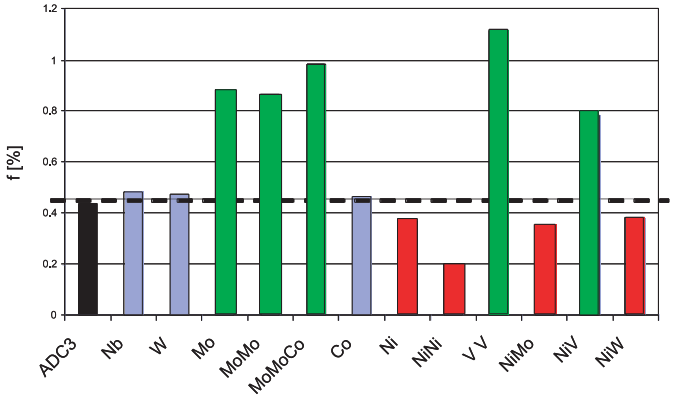


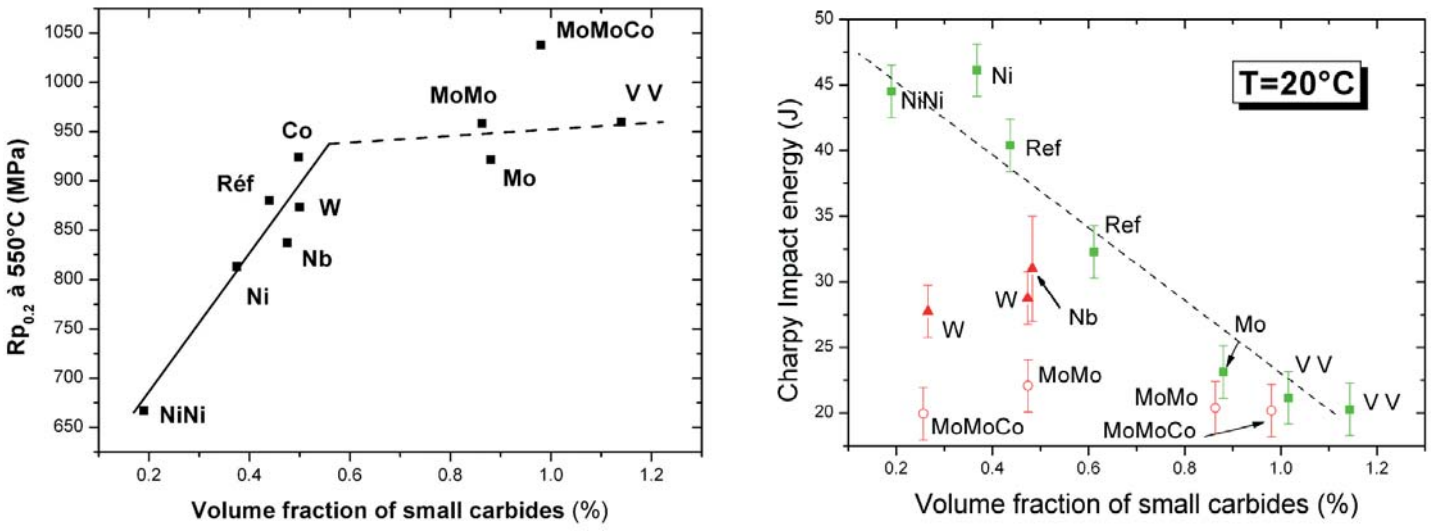
Figure 1: Influence of elements on the volume fraction of small carbides (d ~ 3 nm)

Moreover, results of mechanical properties showed that the volume fraction of small precipitates (VC in all grades and Fe_3Mo_3C in molybdenum grades) directly influences the mechanical resistance at high temperature (figure 2.a) but results in a detrimental effect on Charpy impact energy (figure 2.b). Red points on figure 2.b illustrate the influence of coarse carbides on Charpy impact energy.

In addition, above a volume fraction threshold (~ 0.6%), a saturation of the yield strength is observed. Two different mechanisms dealing with interaction modes between dislocations generated during the quench and precipitates are presented in [2] to explain the saturation.

The first hypothesis considers that increasing number of carbides in addition to the heterogeneity of precipitation can induce formation of Orowan Islands [3]. In that case, increasing the volume fraction of precipitates only increases the heterogeneity of the distribution, the "mean free path" of dislocations between Orowan Islands remaining constant [2].

The second hypothesis assumes a modification in main carbides crossing mechanism of precipitates by dislocations when volume fraction is above 0.6% (figure 2.a), changing from Orowan mechanism with formation of dislocation loops to shearing mechanism [2].



a) **b)**

Figure 2: relationship between volume fraction of small carbides and a) yield strength at 550°C. b) the Charpy impact energy.

[1] D.Delagnes, P.Lamesle, M.H.Mathon, N.Mebarki, and C.Levaillant, Mater. Sci. Eng., Vol A394, pp 435-444 (2005).

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H5. REWRITABLE DVD, RAM MEMORIES: BETWEEN THE ELECTRONIC STRUCTURE AND THE RECORDING ABILITY, NEUTRON SCATTERING SHED SOME LIGHT.

JEAN-PIERRE GASPARD[1], JEAN-YVES RATY[1], MARIE-VANESSA COULET[2], CHRISTOPHE BICHARA[3], CHRISTOPHE STEIMER[4] ET MATTHIAS WUTTIG[4], BRIGITTE BEUNEU[5]

[1]Inst. Phys., Université de Liège (Belgique), [2] Laboratoire TECSEN, UMR6122, CNRS- Université Paul Cézanne, Marseille, [3]CNRS/CRMCN/UPR7251, Marseille, [4]RWTH,Inst. Phys., Aachen (Allemagne), [5]LLB

Data storage and memory devices utilizing the optical and electrical properties of phase-change (PC) materials are important for multimedia applications[1]. The pseudo-binary chalcogenide compound $(GeTe)_2$-Sb_2Te_3 ($Ge_2Sb_2Te_5$) is one of the reference materials for commercial DVD-RAM (digital versatile disc-random access memory) because it presents good optical and electrical contrast.

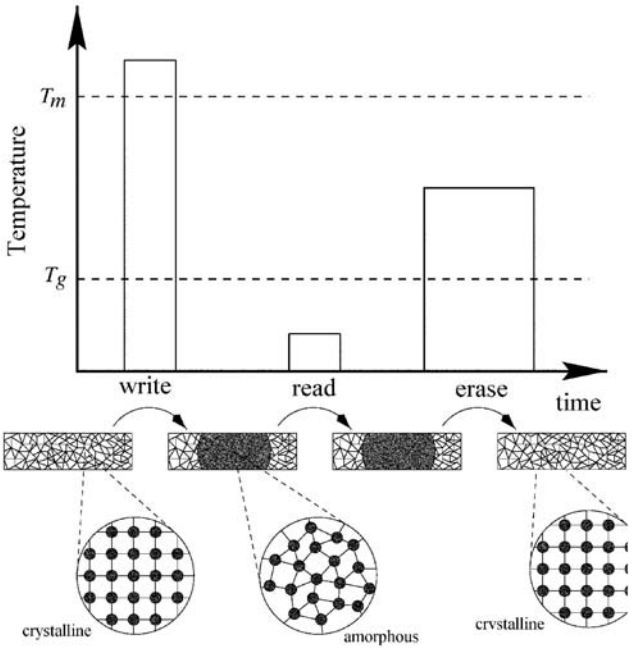

Figure 1: Write, read and erase sequence. T_g is the glass transition temperature and T_m is the melting temperature.

More precisely, the GeSbTe phases have the ability to easily crystallise and amorphise under the action of a laser pulse, basic process of commercial phase-change optical disks. During this reversible process, the crystal is locally melted to obtain an amorphous spot (crystal-liquid-amorphous transitions): this corresponds to the recording process. In a second time, this spot can be recrystallised (amorphous-crystal transition) by using a less intense laser beam, this is the erasing process (Fig. 1). The recrystallisation of the material is the slower process. In order to develop faster phase-change materials, it is necessary to understand the transformation mechanism and the structural origins of the phase change from amorphous to crystal.

A number of new materials for optical and electronic non-volatile pc-storage have been identified by trial and error [1]. Recently, microscopic models of the amorphous and crystalline states have been suggested to explain the working mechanisms of PC-materials [1], [3]. However, much less is known however about the liquid state of these materials despite its prominent role for both amorphization and re-crystallization. Indeed, amorphization is achieved by quenching the liquid, while the fast re-crystallization of amorphous regions takes place above the glass-transition temperature, suggesting that it might proceed through the under-cooled liquid state. Therefore an in-depth knowledge of the structure of the liquid state improves our understanding of both the amorphization and the re-crystallization mechanisms.

Many-ternary Te-based alloys were studied in the liquid state by neutron scattering on the 7C2 diffractometer. The structure of the liquid was shown to depend primarily on the average number of electron per atom.

Using the ratio between the heights of the first two peaks of the total scattering function S(q), two classes of liquids were defined (Figure 2).

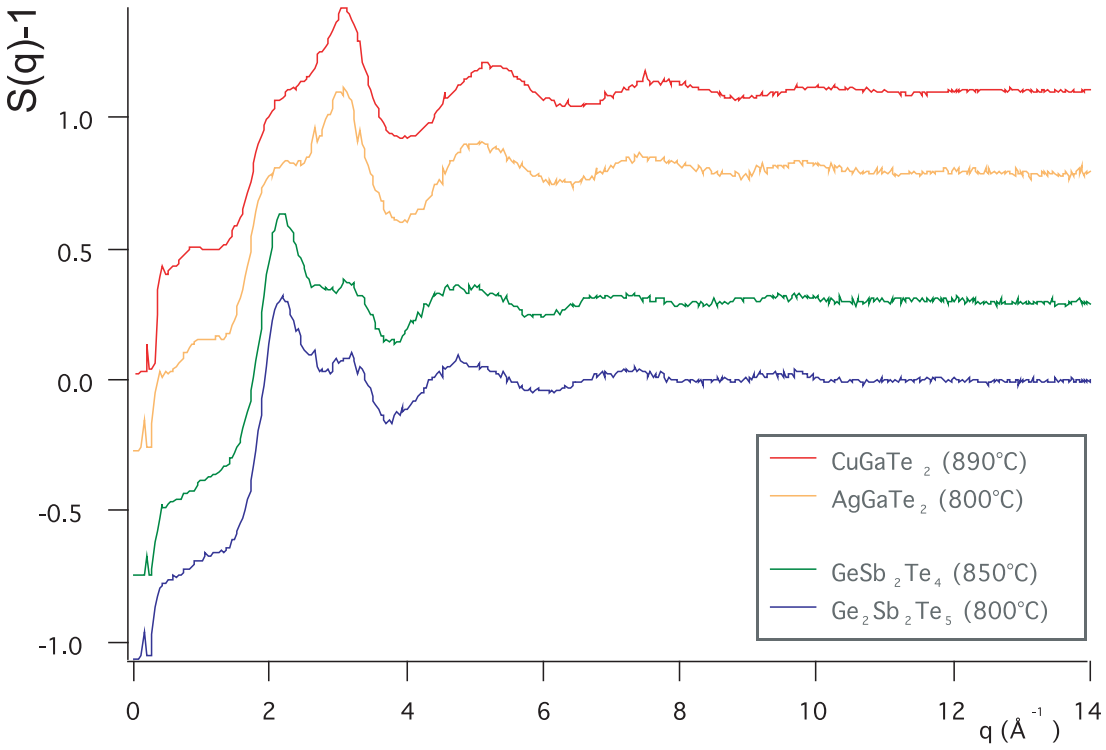

Figure 2: Structure factor of alloys with e/a>4.5 (upper part) and e/a<4.5 (lower part).

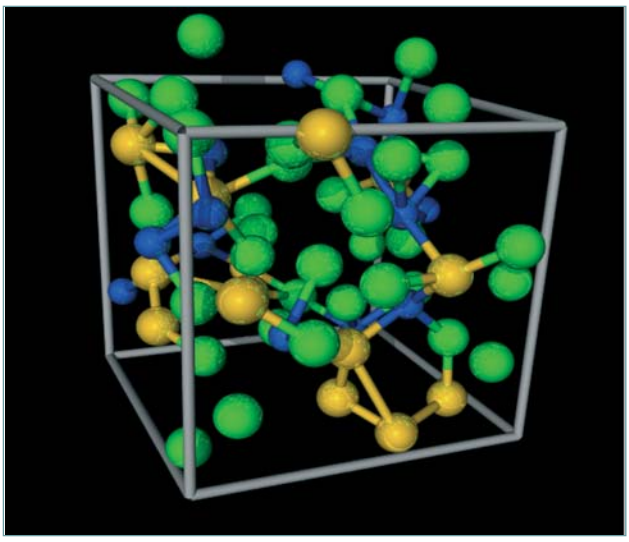

Figure 3: A snapshot of the liquid $Ge_2Sb_2Te_5$ liquid alloy

In the first class with a low number of electrons per atoms ($N_{e/a}$ < 4.5), the structure of the liquid is tetrahedral-like similarly to the solid and the contrast in electrical/optical properties is not sufficient to qualify the material for PC availability. On the contrary, the second class of materials with a higher number of electrons per atoms ($N_{e/a}$ > 4.5) has an octahedral-like local structure and possesses a PC capability.

The local structure of these complex amorphous or liquid materials is largely under discussion ([2], [3], [4]). It cannot be directly extracted from the neutron data only, and other investigations are needed. In parallel to the experimental analyses, computer simulations of the liquid structure are been performed (ab initio molecular dynamics). From these *ab initio* MD experiments, that compare well to the experimental data in the case of $Ge_2Sb_2Te_5$, a detailed analysis of the local order will be made (Figure 3).

It is clear that finding generic features that qualify suitable PC-materials requires a fundamental understanding of the parameters that drive the transition between tetrahedral and octahedral environments. The transition region (around 4.5 electron/atom) will be more closely investigated, as well as the effect of the atomic radii for a given electron/atom ratio.

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[*C1.* G. Carrot] **Self-assembling via Langmuir-Blodgett films and SANS characterisation of polymer-grafted platinum nanoparticles : a possible application in fuel cells.**

We synthesized platinum nanoparticles possessing electrocatalytic properties which are used as catalyst in the reduction of oxygen in fuel cells. The study of their electrical and electrochemical properties is performed after deposition on gold electrodes via Langmuir-Blodgett (LB) films. To improve the dispersion of the particles in the LB film as well as the deposition step, we grafted polymer chains onto the platinum nanoparticles. Well-dispersed LB films can be obtained directly from the polymer-grafted-particles solution and the distance between particles may be adjusted depending on the degree of compression (Figure 1a). We are currently conducting electrical and electrochemical measurements onto these materials and the transfer onto gold electrodes can be done without the presence of fatty acid (Figure 1b). SANS spectra of two polymer-grafted nanoparticles with different molecular weights but the same grafting density are shown in Figure 1c (particle matching). First they show a plateau at small q which attests that the objects are individual and well-dispersed. We used a model of polymer star (chains connected together to a very small core) to fit the form factor. This model permitted us to determine both the number of chains (between 5 and 8, depending on the polymerisation batch), the radius of gyration of the polymer corona and the chain molecular weight.

[Collaboration : G. Carrot, LLB, H. Perez, SPAM, CEA-Saclay]

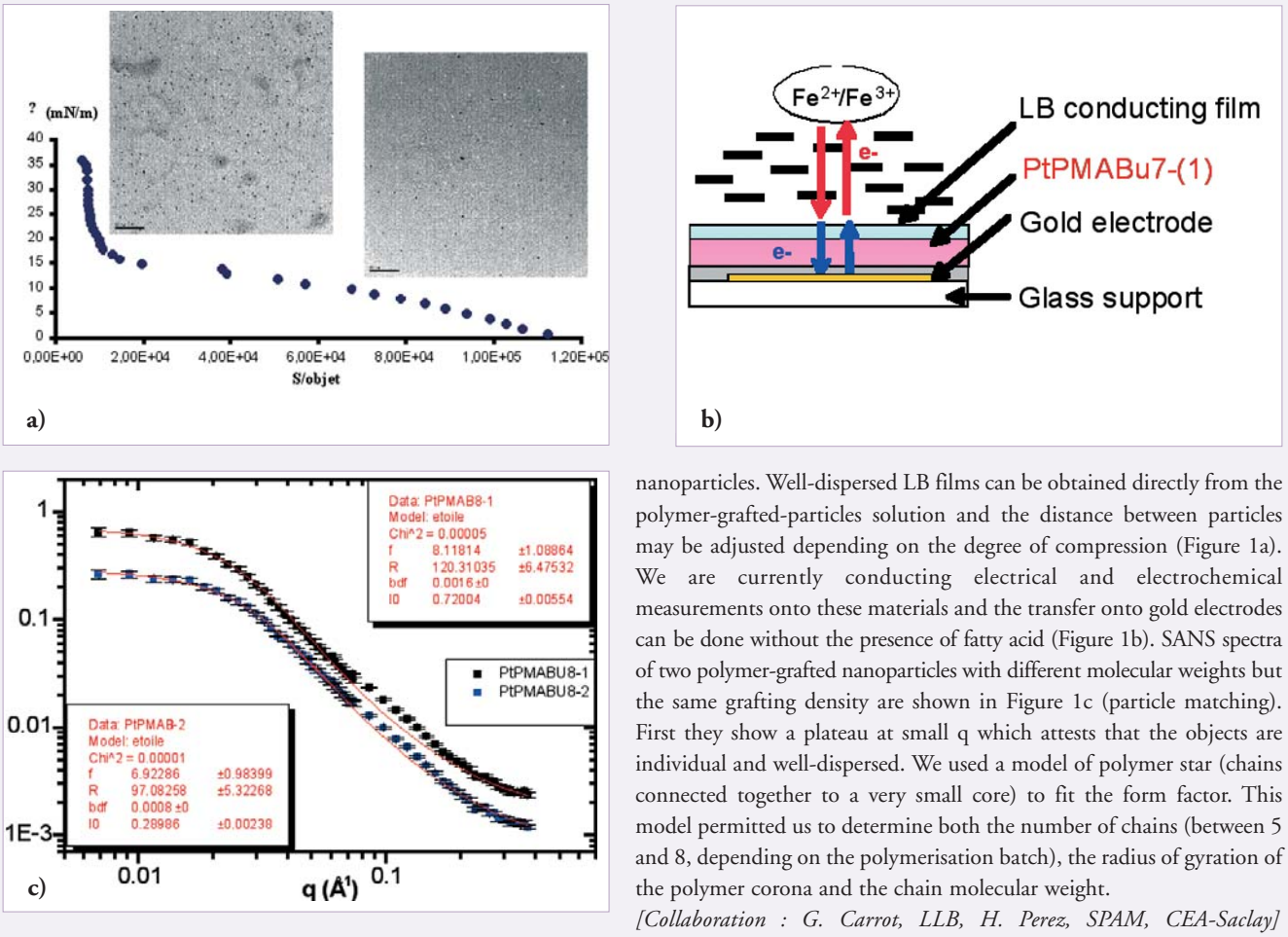


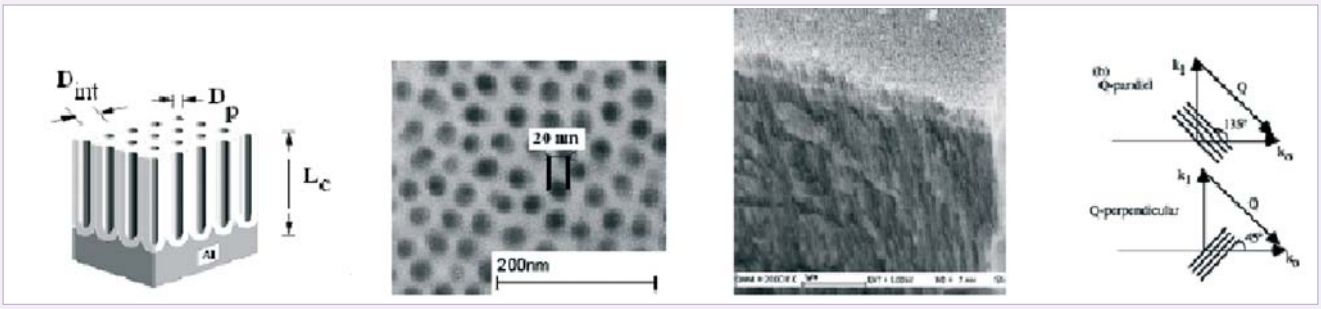
Figure 1: (a) Compression isotherm from polymer-grafted platinum nanoparticles and corresponding TEM images at different degrees of compression (surface pressure, P=2 mN/m (left image); P=26 mN/m (right image)) **(b)** Configuration scheme for electrochemical measurements **(c)** Neutron scattering spectra obtained from the grafted polymer chains at two different polymerisation time (particle matching): fit with a polymer star mode (particle matching).

[*C2.* K. Lagréné] **Dynamics of a polymer confined in macroscopically monodisperse oriented pores.**

Thanks to numerous theoretical developments spanned over few decades, it is now possible to draw a close relationship between polymer rheology in the bulk and polymer dynamics at the molecular level. Nevertheless, numerous technical applications are a step forward of the theoretical developments and already take advantage of the peculiar properties of polymers in interfacial situations or deep confinement. In the scope of my thesis work, we focus on the influence of confinement on hydrogenated polyethylene oxide (^{h}PEO) with high molecular mass 100 000 g/mol (the critical entanglement mass (M_C = 3600)). As confining material, we use Anodic Aluminium Oxide (AAO) membranes. AAO are a class of materials showing an extremely well defined and anisotropic porous structure made of macroscopically aligned micrometers long cylinders with nanometre size diameter (Fig. 1). The isotropic "average out" of the dynamical information occurring in non-oriented systems can then be overcome by proper orientation of the AAO pores axe relative to the beam. The topology is described by the pore

diameter, D_p, the inter-pores distance, D_{int}, and channels length, L_c. We have shown that the topology can be tailored so as to obtain fairly mono-disperse pores with diameter in the range 11 to 45 nm. The Small Angle Neutron Scattering (SANS) contrast matching technique is used to evidence that PEO can be fully and uniformly confined within the AAO porous network. We probe the properties of the confined polymer by differential scanning calorimetry and incoherent quasi-elastic neutron scattering. The ratio R_G / D_p sharply drives the properties of the confined polymer. Upon confinement, for D_p / R_G > 2, a strong depression of the melting point temperature is observed but above the bulk melting point the PEO dynamics is not affected. For D_p / R_G < 2 no melting transition is detected and the PEO protons mean-square displacement is significantly reduced compared to the bulk behaviour.

[K. Lagrené and J.-M. Zanotti, Proceedings of the QENS 2006 conference, MRS Symp. Proc., accepted.]

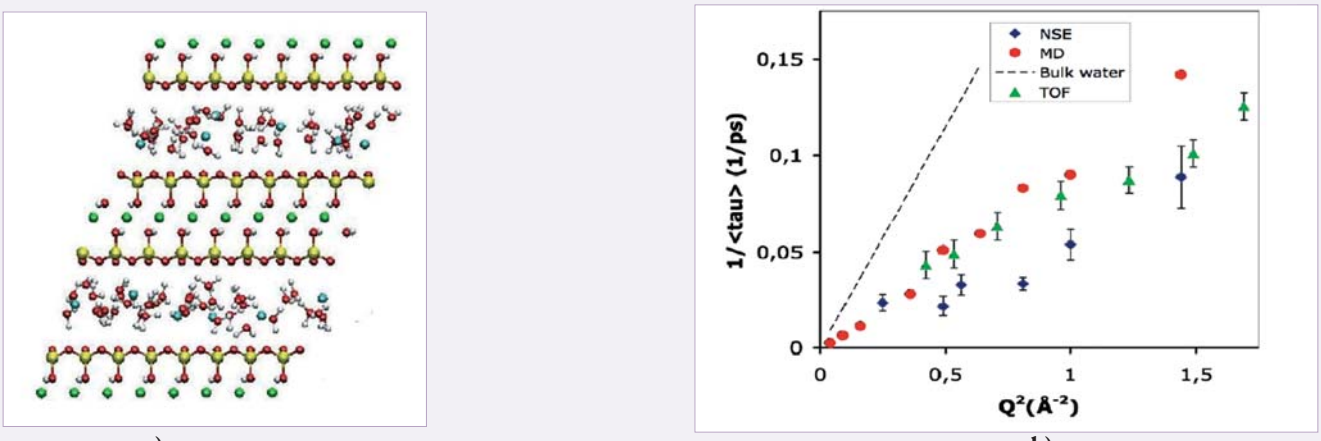


a) **b)** **c)** **d)**

Figure 1. a) Schematic drawing of a porous alumina membrane. **b)** Scanning Electron Microscope (SEM) image of a LLB made AA0 membrane. Here, the pore diameter is 20 nm. **c)** 3D SEM view of an actual LLB made AAO membrane showing the macroscopic alignment of the cylindrical pores in the bulk of the membrane (scale is 1 µm). **d)** Schematic illustration of how relative orientation of AAO samples to the incident beam (k0) and measurement of the intensity scattered in a detector at 2θ= 90° (i.e. along k1), can provide information (sensed along Q) on confined PEO dynamics parallel (top) and perpendicular (bottom) to the AAO cylinders axes.

[*C3.* N. Malikova] Dynamics of water and ions in clays: a concurrent TOF, NSE and MD study

The potential application of clays as components of barriers around underground storage sites of radio-active waste has recently intensified the study of mobility of water and ions (both natural, e.g. Na^+, and potential radionuclides, e.g. Cs^+) in these systems. At a more fundamental level, these investigations shed light onto dynamics of liquids in confined charged media and phenomena at a solid/liquid interface. The dynamics of water in a montmorillonite clay has been investigated here on the picosecond timescale by quasi-elastic neutron scattering (time-of-flight (TOF) and neutron spin echo (NSE) techniques) and classical molecular dynamics (MD) simulations.



a) **b)**

Figure 1. a) Atomic structure of a hydrated clay used in MD. Mobile species: water molecules (white and red), Na^+ / Cs^+ ions (blue). **b)** Inverse relaxation times versus the wave-vector for two-layer hydrate of Na-montmorillonite.

MD shows that while Na+ ions have no specific adsorption sites on the clay surface, Cs+ ions exhibit a jump diffusion between sites allowing coordination to six oxygen atoms of the adjacent clay layers. In the bulk, on the picosecond-nanosecond timescale, water molecules diffuse by a combination of translational and rotational motion. In the case of clays, this behaviour is necessarily modified by the narrow confinement between two parallel clay layers. Never-the-less, while the water diffusion coefficient in case of a single confined water layer is an order of magnitude lower than in bulk water (1-2 ¥ 10-10 m2/s), in the two-layer clay hydrate the diffusion coefficient is already almost half of the bulk value (1 ¥ 10-9 m2/s, Dbulk=2.3 ¥ 10-9 m2/s). This is seen both in experiment and simulation.
PhD thesis of N. Malikova (LI2C/ANDRA), [Collaboration LI2C (Université P&M Curie, Paris VI, CNRS) and LLB]
Malikova, Cadène, Marry, Dubois & Turq , J. Phys. Chem. B 110, pp.3206-3214, **2006**.

[*C4.* A. Declémy] **Ferromagnetic Fe-implanted SiC: New results towards a Diluted Magnetic Semiconductor**
SiC is a good candidate for diluted magnetic semiconductors which could be used in spin-electronic devices. It has a wide band-gap (3.1 eV), low spin-orbit coupling, excellent transport properties and has reached a mature state of industrial development. In order to create magnetic SiC, substrates have been implanted with Fe ions at the LMP Univ. Poitiers (at doses of the order of $5.10^{16}/cm^3$). After annealing (700-900°C), a ferromagnetic behavior has been observed with a high Curie temperature (up to 700°C). Polarized neutron reflectivity has allowed to probe the magnetization of the SiC:Fe films as a function of the depth. From the PNR reflectivity (Fig. 1), it is possible to reconstruct the magnetization profile (Fig. 2). The complicated shape of the fitted magnetization profile through the depth of the sample is connected to the multi-implantation process. The measured profile corresponds quite well with the implantation profile which can be simulated with SRIM. The fact that we are dealing with a magnetic semi-conductor needs to be confirmed. Until now, EXAFS shows that there are no Fe atoms in the very near Fe environment which excludes the presence of Fe clusters. The possibility of secondary phases such as Fe3Si needs to be checked.
[Collaboration: A. Declémy, M. Drouet, C. Dupeyrat, D. Babonneau, J. Mimault, T. Girardeau, D. Eyidi, M.F. Beaufort, J.P. Eymery, Université de Poitiers, F. Ott, M. Viret, LLB/SPEC Saclay.]

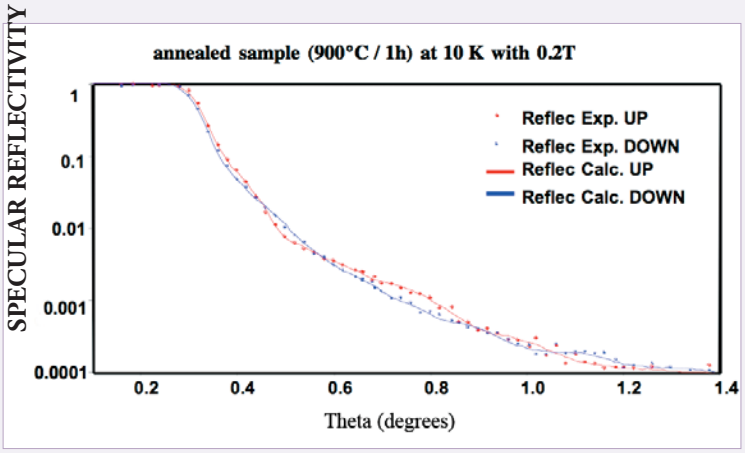


Figure 1: polarized neutron reflectivity of an SiC:Fe sample measured at 10K (fits in solid lines)

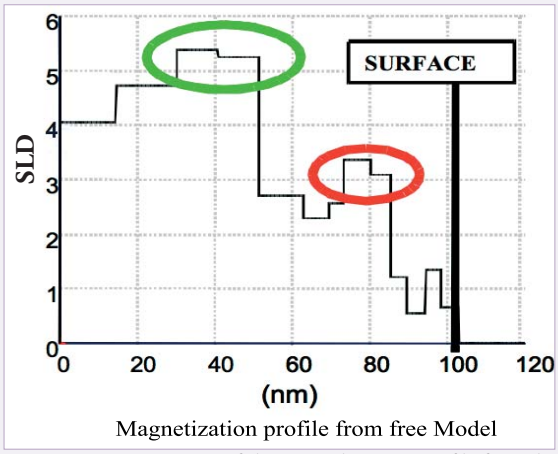


Figure 2: Reconstruction of the Fe implantation profile from the PNR. The fit is very close to the calculated implantation profile

[*C5.* V. Klosek] **A compact tensile machine for in situ neutron diffraction study of materials under external loading**
In order to characterize the behaviour of materials under mechanical loading, a very compact tensile machine was recently developed at LPMTM. This machine is designed to be mounted on the Eulerian cradles of G5.2 and 6T1 diffractometers: to allow a huge variety of sample orientations, its frame consists in two side columns on which are fixed the plates supporting the tensile heads (Fig. 1). It thus now becomes possible to analyse elastic and plastic behaviours of materials during a tensile test by in situ neutron diffraction. This machine is an incomparable tool to study deformation mechanisms under external loading of materials: macro- and micro-strains, texture or stored energy can now be measured as a function of applied load (up to 30 kN). First tests were performed on a brass (Cu-Zn) alloy sample. Figure 2 shows the (111) diffracted peaks recorded on G5.2 at three different loadings, with their corresponding FWHM (λ = 3.03 Å). At low strain, the peak is essentially shifted toward lower angles (elastic deformation mainly). At higher strain, the peak broadens, traducing the plastic deformation of the material.

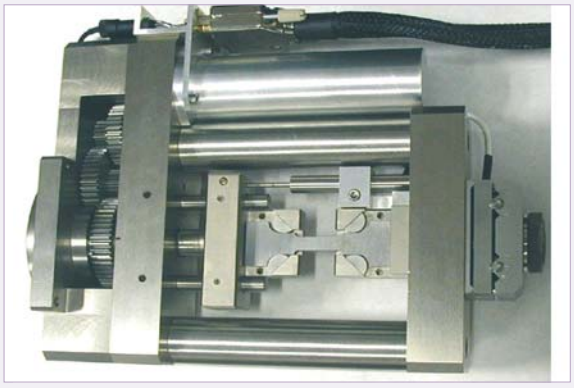


Figure 1: the tensile machine, equipped with a sample

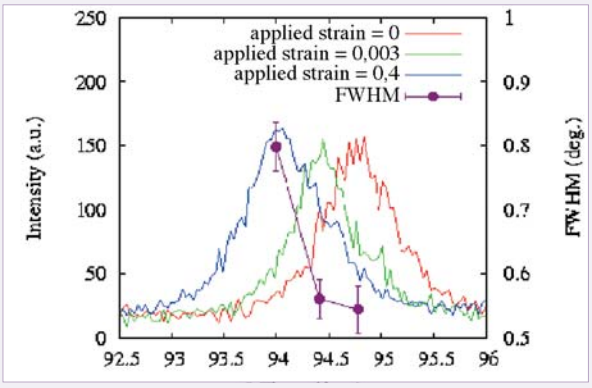


Figure 2: (111) peaks and FWHM recorded on G5.2 for several loadings

[Collaboration: V. Klosek, M.H. Mathon, LLB; V. Ji, LIM-ENSAM, Paris; R. Chiron, LPMTM, Villetaneuse]

[C6. S. Jakani] **Deformation and recrystallization mechanisms of CuSn alloys (bronze)**

The optimization of the macroscopic properties requires the comprehension of the deformation and recrystallization mechanisms. In the case of the copper and of its alloys, the deformation step conditions mainly the mechanisms of recrystallization. Neutron diffraction, performed on 6T1, was used to characterize the deformation texture, stored energy after various rates of rolling (between 0 and 90% of deformation) and the activation energy of recrystallization with "in situ" measurements. The addition of tin (4 to 9%) in pure copper lowers the stacking fault energy. Thus, it is not astonishing to observe a texture of deformation primarily consisted of the a fibre (with the Brass and Goss components). During cold rolling, stored energy increases with the deformation rate but contrary to the case of pure copper and brasses, its distribution is homogeneous between the various crystallographic orientations. A light increase of energy is observable with the tin content. Measurements of kinetics of recrystallization reveal that the energy of activation of the recrystallization process decrease with the deformation rate but remains much more important than in pure copper. The recrystallization is accompanied by the development of the orientations C {112} <11-1> and G {110} <001>. These results show that recrystallization is not only interpretable by stored energy but that the kinetic aspect via the grain boundaries mobility is a prevalent factor in the presence of tin. The presence of an element of addition can then reinforce the energy stored by decreasing the mobility of dislocations and thus act on the dynamic phase of restoration. By the same mechanism, the recrystallization is slowed down. The copper alloys thus present distinct behaviours, a priori depend on the nature of the element of addition which acts differently on the mechanisms of deformation and the mobility of dislocations and the grain boundaries.

[Collaboration: S. Jakani, S. Melusson, M.H. Mathon, LLB]

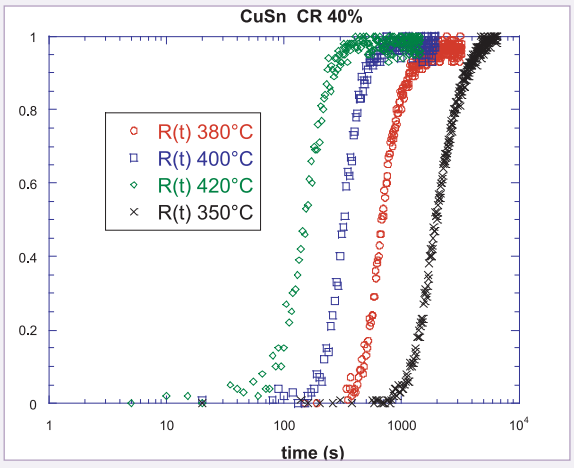


Figure 1: Recrystallization kinetic on the CuSn4% cold rolled up 40%

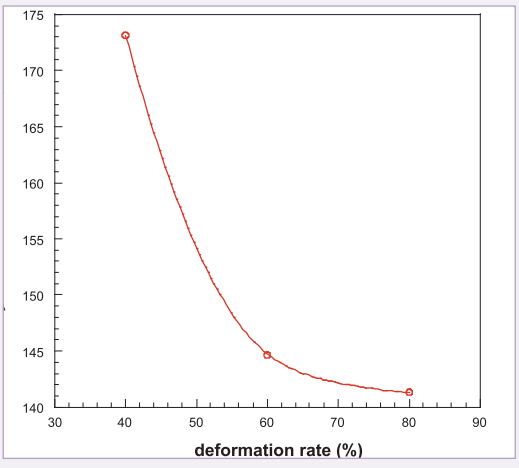


Figure 2: Recrystallization activation energy (kJ/mol) versus the deformation rate.