AXIS 2 Research : Materials and Nanosciences - Fundamental Studies and Applications

<u>Researchers (16):</u>

A. Bataille (CEA), B. Beuneu (CEA), G. Carrot (CEA), A. Cousson (CNRS), M.-H. Mathon (CEA), V. Klosek (CEA), L. Noirez (CNRS), F. Ott (CEA), F. Porcher (CEA), G. Chaboussant (CNRS), B. Gillon (CNRS), F. Cousin (CEA), J. Jestin (CNRS), F. Boué (CNRS), R. Papoular (CEA).

<u>Associated Researchers (5):</u>

O. Castelnau (CNRS), J.-M. Kiat (Ecole Centrale), V. Ji (Univ. Paris-Sud), A. Lodini (Univ. Reims), N. Linder (Univ. Paris-Sud)

<u>PhD Students (5):</u>

T. Maurer (2007-2009), C. Said (2008-2011), A.S. Robbes (2008-2011), S. Zhong (2009-2012), M. Dubois (2009-2012)

<u>Post-doc Students (5):</u>

R. Dakhloui (2008), C. Alves Rezende (2008), M. Perrut (2007-2009), F. Zighem (2009-2010), F. Muller (2009-2011)

<u>Keywords</u>

- Thin films, nanoparticles, nanocomposites, textures, strains, dynamics
- Magnetism, polymers, metallurgy, glasses
- SANS, reflectivity, diffraction, synthesis

Scope

This scientific axis covers the activities related to the research in materials science and more generally in hetero-systems (i.e., interfaces, alloys, composites materials, and confined systems). The topics cover the study of the detailed structure of nano-objects, the interactions between nano-objects, and the role of nanostructures in composite materials. The techniques used for these studies range from diffraction to small angle scattering and reflectivity. Other laboratory characterization techniques are also available, including light scattering, rheology, magnetometry (VSM - SQUID), and x-ray reflectivity.
During the period from 2008 to 2010, 152 publications have been produced on these topics (54 in 2008, 59 in 2009, and 39 in 2010). The presented topics have also been the subject of 21 invited conferences and more than 55 oral communications during the last 2 years. Two *Habilitations à Diriger les Recherches* have been defended during the period (2008-2009). One PhD thesis has been defended and 4 PhD students are presently working in the field of Materials Science.

The research in materials science is supported by a number of research contracts: 1 European contract, 1 transverse program CEA-CNRS/DSM-DEN, 7 national ANR contracts, and 3 regional contracts within the RTRA and C'nano organizations.

Current research

The studies in the fields of materials and nanosciences range from the detailed study of nanoparticles (structural and magnetic properties) to the study of the role of nanoparticles in composites systems (either metallic or polymer) to the study of materials confined at the nanometer scale. In all these different studies, the scales which characterize the properties of the systems range between 1-100 nm.

The following topics are presently developed at the LLB:

- Magnetic nanostructures
  - Oxide epitaxial layers
  - Nanoparticles
- Composite materials
  - Polymer reinforcement by nanoparticles
  - Metallurgical composites
- Metallurgy (both fundamental and industrial)
  - Textures and strain heterogeneities
  - Nuclear materials
- Confined systems
  - Organized guest-hosts systems and microporous materials
- Amorphous materials
  - Disordered systems – glasses
  - Dynamics in amorphous systems

Magnetic nanostructures

We study the structure and properties of magnetic nano-objects using various techniques: diffraction, SANS, and reflectivity. Five researchers in the laboratory have research topics in this field.

Oxide epitaxial layers

Regular studies of these materials are performed in collaboration with other laboratories on systems, such as $La_xSr_{1-x}MnO_3$ (with IRAMIS/SPEC – IEF/Orsay – LPMTM/Paris XIII) and Fe_3O_4 – $CoFe_2O_4$ – $MnFe_2O_4$ (with IRAMIS/SPCSI[1]), primarily by using Polarized Neutron Reflectometry. More recently, a significant instrumental effort has been made to apply 4-circles diffraction to the study of epitaxial thin films[2].

During the period of 2008-2009, a concerted effort was made to greatly extend the range of techniques available for studying magneto-electric materials, such as the $BiFeO_3$ system. This effort was carried out in collaboration with UMR CNRS-Thalès and IRAMIS/SPEC by applying diffraction, as well as reflectivity techniques[3].

Multiferroic materials: $BiFeO_3$

$BiFeO_3$ is a multiferroic material in which ferroelectric and anti-ferromagnetic orders coexist well above room temperature (T_N= 643 K, T_C= 1093 K), with a high degree of polarization (over 100 $\mu C/cm^2$ [4]). We have demonstrated at the LLB, that the magnetization of the material can be modified by the application of an electric field (this was the first direct proof of a magneto-electric coupling). This result opens the way towards implementing this material in spintronic devices in which magnetization might be controlled by a small electrical voltage rather than by currents or magnetic fields.

---

[1] *Artificial antiphase boundary at the interface of ferrimagnetic spinel bilayers.* A. Ramos, S. Matzen, J.-B. Moussy, F. Ott, M. Viret, Phys. Rev. B **79** 014401 (2009).

[2] *Biaxial Strain in the Hexagonal Plane of MnAs Thin Films: The Key to Stabilize Ferromagnetism to Higher Temperature.* V. Garcia, Y. Sidis, M. Marangolo, F. Vidal, M. Eddrief, P. Bourges, F. Maccherozzi, F. Ott, G. Panaccione and V. H. Etgens, Phys. Rev. Lett. **99**, 117205 (2007).

[3] *Mechanisms of Exchange Bias with Multiferroic BiFeO3 Epitaxial Thin Films.* H. Bea, M. Bibes, F. Ott, B. Dupe, X.-H. Zhu, S. Petit, S. Fusil, C. Deranlot, K. Bouzehouane and A. Barthelemy, Phys. Rev. Lett. **100**, 017204 (2008).

[4] D. Lebeugle et al., Appl. Phys. Lett. **91** 022907 (2007)

The first step consisted of a detailed study of high quality $BiFeO_3$ single crystals. We confirmed[5] that the spins of the Fe^{3+} ions form a circular cycloid with a long period of 62 nm (from powder diffraction data, several magnetic structures were possible).

In a second step, an electric field was applied to the crystal, which was in a single ferroelectric domain state with the polarization along [111] (Figure 2.1). When the electric

Organization

LLB nanoscience research benefits from a variety of available neutron scattering techniques:

I. SANS (Small Angle Neutron Scattering) - for studying the structure and organization of nanoparticles.

• The laboratory operates 5 SANS instruments: PAXY, PACE, PAXY, PAPYRUS, and TPA. The latter instrument is specifically used for very small angle scattering studies.

II. Reflectivity - to study thin film structures (polymers, magnetic films, liquid surfaces).

• Two reflectometers are operated: EROS for studies on polymer and liquid systems and PRISM for studies on magnetic thin films.

III. Diffraction - to study the crystalline or the magnetic order of nanostructures.

• The 4-circles spectrometer (6T2) was recently upgraded to be capable of performing diffraction studies on epitaxial thin films.

• The different powder diffractometers are also used to characterize the structural or magnetic properties of nanoparticles.

• Two instruments (6T1 and DIANE) are specifically dedicated to the study of textures and strains in metallurgical materials.

IV. Inelastic scattering - to study dynamic properties of nanosystems.

• The time-of-flight spectrometer, MIBEMOL, is primarily used for these studies.

V. Other characterization techniques are readily available for LLB scientists, including: light scattering, rheology, magnetometry (VSM-SQUID), I.R. spectroscopy, X-ray reflectivity.

The people working on these different topics are organized in groups with specific technical expertise. Each of these groups is in charge of a specific pool of spectrometers (SANS, reflectivity, single crystal diffraction, powder diffraction, or texture/strain). The groups have the duty of operating and upgrading their spectrometers and are in charge of organizing the support for visiting scientists coming to perform experiments at the LLB. This organization allows the laboratory to operate the spectrometers in an efficient way by providing instruments that are constantly upgraded, and by providing a high level of expertise in each technique. These practices strongly benefit our external users.

Though each operational group (see organization chart) has a specific technical expertise, LLB physicists additionally benefit from a variety of different scattering techniques that are available for their research topics. Many of the studies presented here have employed several scattering techniques:

• Magnetic thin film systems have been studied by reflectivity and diffraction techniques.

• Magnetic nanoparticles have been studied by SANS, powder diffraction and inelastic scattering.

• Shape memory alloys are being studied by powder diffraction and on the texture diffractometer.

• ODS steels are characterized by diffraction, texture, and SANS techniques.

field was applied along the [001] direction, the sample switched to a multidomain ferroelectric state. Using neutron diffraction, we showed that the propagation vector was the same as in the virgin state, but that the spins were lying in two different planes. Applying an electric field thus induced a spin flop of the antiferromagnetic sublattice.

---

[5] *Electric-Field-Induced Spin Flop in $BiFeO_3$ Single Crystals at Room Temperature*. D. Lebeugle, D. Colson, A. Forget, M. Viret, A. M. Bataille, and A. Gukasov, Phys.Rev. Lett. 100 227602 (2008).

Integration of multiferroics into spintronic devices requires growing thin films. We thus also studied heterostructures grown by pulsed laser deposition by the group of Agnès Barthelemy at the UMR CNRS/Thales. It was first shown using neutron diffraction that the magnetic structure of the $BiFeO_3$ thin films differs from the bulk one: the cycloidal modulation is not present, and the spins form a simple G-type antiferromagnet[6].

The next step of the study has consisted of investigating the interaction of a $BiFeO_3$ thin film coupled to a ferromagnetic layer (CoFeB in our case). In these heterostructures, the two layers are coupled together via the exchange bias mechanism[7]. Furthermore Malozemoff's model suggests that a net magnetization should be observed in $BiFeO_3$ near the interface with CoFeB. To test this prediction, polarized neutron reflectometry was performed on CoFeB/$BiFeO_3$ bilayers on the PRISM spectrometer (Fig. 2.2). The data are well reproduced by taking into account a 2 nm thick layer carrying a 1 μ_B per formula unit magnetic moment. This is far larger than the surface magnetic moment predicted by Malozemoff's model, and suggests that unpinned spins exist in $BiFeO_3$ near the interface along with the pinned moments predicted by the model. As the ferroelectric domain structure can be easily controlled by an electric field, these results open the route to the electrical manipulation of magnetization at room temperature, in $BiFeO_3$-based, exchange-bias heterostructures.

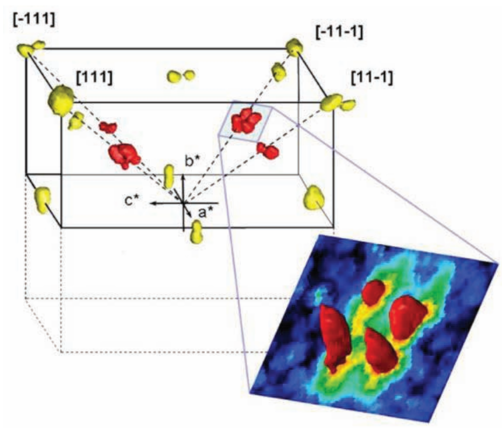

Figure 2.1 *Mapping of the neutron intensity in the reciprocal space, showing the effect of an electric field on a $BiFeO_3$ single crystal. The magnetic peaks (red spots) are split because of the presence of a magnetic cycloid.*

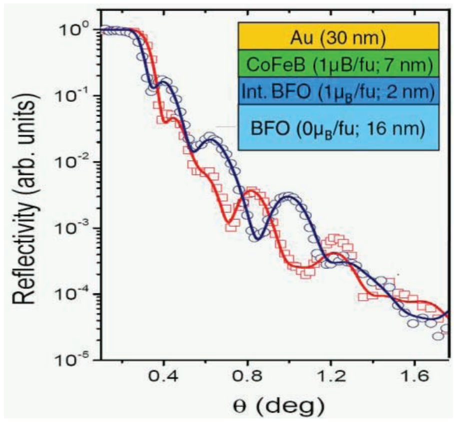

Figure 2.2 *Polarized neutron reflectivity on a CoFeB/$BiFeO_3$ heterostructure showing the presence of an induced magnetization in the interfacial BFO layer.*

This work benefits from the financial support of the RTRA Triangle de la Physique and C'nano, which supported the building of an octupole magnet to perform measurements with arbitrary field directions.

Nanoparticles

Besides magnetic films, we are also studying the magnetism of objects with even more reduced dimensions, such as magnetic nanomolecules whose magnetic properties in the crystalline state can be studied by diffraction, and small magnetic particles such as nanobeads and nanowires, which can be studied by SANS or powder diffraction. The latter topic was the subject of a PhD thesis by T. Maurer (2007-2009).

Molecular magnets

Polarized neutron diffraction allows the exact nature of the magnetic interactions that give rise to the ground state in complex molecular magnets to be determined without any ambiguity contrary to SQUID measurements. Such information is important for optimizing the building of new clusters with the highest spin as possible. Tools are also available to reconstruct magnetization density distribution in the molecules from the diffraction data (acquired on the 5C1 spectrometer).

---

[6] *Structural distortion and magnetism of $BiFeO_3$ epitaxial thin films: A Raman spectroscopy and neutron diffraction study.* H. Béa; M. Bibes, S. Petit, J. Kreisel,,A. Barthélémy, Philos. Mag. Lett. **87**, 165 (2007)

[7] *Mechanisms of Exchange Bias with Multiferroic $BiFeO_3$ Epitaxial Thin Films.* H. Bea, M. Bibes, F. Ott, B. Dupe, X.-H. Zhu, S. Petit, S. Fusil, C. Deranlot, K. Bouzehouane and A. Barthelemy, Phys. Rev. Lett. 100, 017204 (2008).

High-spin molecular clusters

The study of the nature of the spin ground state and interaction mechanisms in paramagnetic molecular clusters is the subject of long time collaborations among the GDR MCM (Montpellier, Lyon)[8,9] and the European network MAGMaNet (Bern, Firenze, Barcelona). Single molecule magnets, such as the Fe_8 cluster[10], possess high spin in the ground state and strong anisotropy, which produce a high energy barrier to magnetization reversal and behave as magnetic nanoparticles at low temperature.

The octacyanometallates, such as $[M'(CN)_8]^{3+}$ (M'^{V} = Mo^V, W^V), have been used in Bern to synthesize a family of high spin $M_9M'_6$ clusters, some of which display single molecule magnetic behavior. The $M_9M'_6$ core consists of a centered cube of M^{II} ions with M'^{V} ions capping its six faces (Fig. 2.3). A diffraction study on single crystals had unambiguously demonstrated the AF nature of the Mo^V-CN-Mn^{II} magnetic interactions in the $Mn^{II}_9Mo^V_6$ cluster (S = 35/2). The experimental induced magnetization density in the (S = 12) ground state of the Ni_9W_6 cluster (Fig. 2.4) confirms the ferromagnetic nature of the [W...Ni] interaction through the CN bridge predicted by calculations based on DFT (Density Functional Theory)[11]. However, the observed strong spin delocalization from the W^V ions towards the CN bridges, as reflected by the positive spin density carried by the N atoms, is underestimated by DFT calculations. This delocalization is at the origin of the strong efficiency of the CN groups to transmit magnetic interactions by super-exchange.

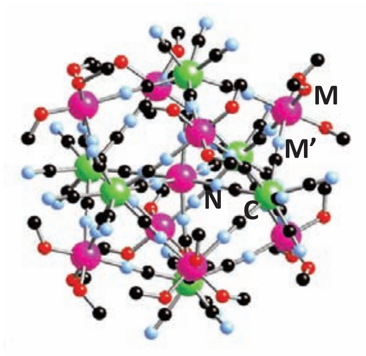

Figure 2.3*. A cyano-bridged $M_9M'_6$ molecular cluster.*

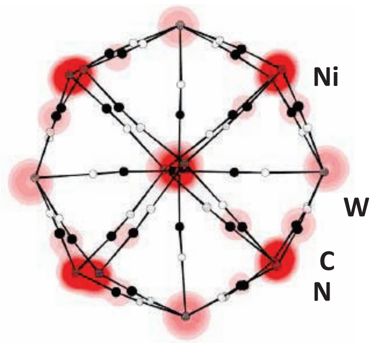

Figure 2.4*. Induced magnetization density (1.5K, 5T) in the Ni_9W_6 cluster (S = 12) integrated along a diagonal of the W_6 octahedra (isodensity levels: 0.0 to 0.90μ_B/Å^2)*

Magnetic nanoparticles

These types of magnetic nano-objects form a part of the basis of the work on composite materials combining hard nanoparticles and polymer materials. We have performed extensive studies of the magnetism of anisotropic magnetic particles.

Magnetic properties of metallic nanowires

The work on this topic began in 2007 with a PhD thesis. Further support was obtained via the ANR contract MAGAFIL (2008-2010) which permitted the hiring of F. Zighem as a post-doc for 2 years (2009-2010). The MAGAFIL network is gathering expertise from various fields, including chemistry at ITODYS Paris VII and LPCNO at INSA Toulouse; magnetism at the LLB; and metallurgy at the LPMTM Paris XIII.

---

[8] E. Ruiz, G. Rajaraman, S. Alvarez, B. Gillon, J. Stride, R. Clérac, J. Larionova, S. Decurtins, Angew. Chem. Int. Ed. **44** (2005) 2711-2715

[9] *Structure, Magnetic Properties, Polarized Neutron Diffraction and Theoretical Study of a copper(II) cubane.* C. Aronica, Y. Chumakov, E. Jeanneau, D. Luneau, P. Neugebauer, A.-L. Barra, B. Gillon, A. Goujon, A. Cousson, J. Tercero, E. Ruiz, Chem. Eur. J., **14** (2008) 9540-9548.

[10] *Experimental spin density in the high spin ground state of the Fe_8pcl cluster*. B. Gillon, C. Sangregorio, A. Caneschi, D. Gatteschi, R. Sessoli, E. Ressouche, Y. Pontillon, Inorg. Chim. Acta, **360** (2007) 3802-3806

[11] *Experimental and Theoretical Study of the Spin Ground State of the High-Spin Molecular Cluster $[Ni^{II}\{Ni^{II}(CH_3OH)_3\}_8(\mu\text{-}CN)_{30}\{W^V(CN)_3\}_6]\cdot 15CH_3OH$ by Polarised Neutron Diffraction and Density Functional Theory Calculations.* B. Gillon, J. Larionova, E. Ruiz, Q. Nau, A. Goujon, F. Bonadio, S. Decurtins,' Inorg. Chem. Acta, **361**(2008) 3609-3615.

After some initial work on the bulk properties of the systems, which showed the potential utility of these nanowires[12] (Fig. 2.5), the work has since focused on revealing their detailed properties. Complex exchange bias properties have been observed[13] (Fig. 2.6), and because of the specific dimensionality of these systems (1D versus 2D for thin films and 3D for nanoparticles), we have been able to demonstrate a key role for oxide shell superpamagnetic fluctuations in these wires. This work combined powder diffraction measurements, for characterizing the magnetic properties of the oxide shell, with magnetization measurements and micro-magnetic calculations.

Further work has been performed on the detailed micro-magnetic modeling of these nanowires in order to optimize their properties for applications. The magnetic properties of the wires as a function of the detailed shape of the objects (e.g., sphere, rods, cylinders, diabolos, and dumb-bells) have been assessed[14]; and nanowire assembly behavior has been modeled[15].

This work was a part of the PhD thesis of T. Maurer.

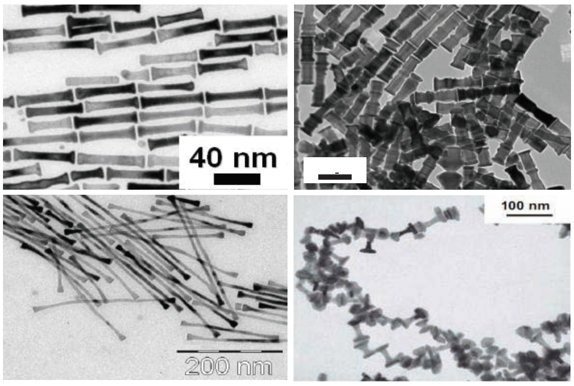

Figure 2.5. *Magnetic nanowires of Co_xNi_{1-x} alloys.*

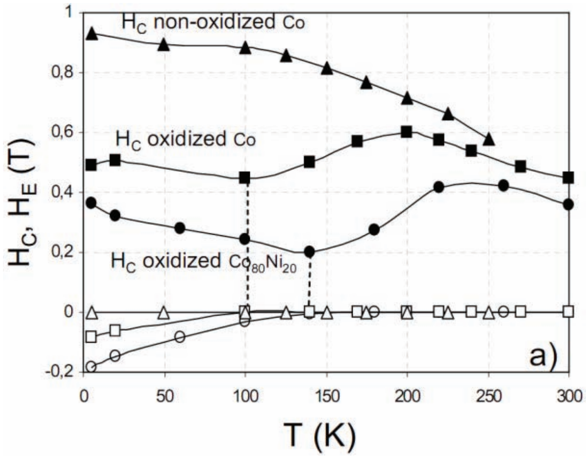

Figure 2.6. *Evolution of the coercive and exchange field in different types of nanowires.*

Composite materials

This field of research deals with the combining of several base ingredients in order to create new materials that have properties which are improved over their initial ingredients. Neutron scattering techniques, such as the Small Angle Neutron Scattering for bulk materials and reflectometry for thin film structures, allow us to understand the structures of these new materials at the nanometer scale.

Polymer reinforcement by nanoparticles

This field of research is a natural extension of the expertise of the LLB in the field of polymer science (see LLB Axis 3: Soft Matter). We benefit from the expertise acquired in the physics of dispersion in a polymer melt, the chemistry of grafting, and rheology. Several types of systems are being investigated at the laboratory.

Mechanical properties of grafted nanoparticles dispersed in a polymer melt[16].

As shown in LLB Axis 3, dispersions of small ramified aggregates were obtained that were homogenous at scales larger than 1 micron. Under uniaxial elongation, the tensile stress versus

[12] *Magnetic nanowires as permanent magnet materials.*
T. Maurer, F. Ott, and G. Chaboussant, Y. Soumare and J.-Y. Piquemal, G. Viau, Appl. Phys. Lett. **91**, 172501 (2007).
Selected for Virtual Journal of Nanoscale Science & Technology **16**(19) (Nov. 5, 2007 issue); News in www.nanotechweb.org.

[13] *Exchange bias in Co/CoO core-shell nanowires: Role of antiferromagnetic superparamagnetic fluctuations*
T. Maurer, F. Zighem, F. Ott, G. Chaboussant, G. Andre, Y. Soumare, J.-Y. Piquemal, G. Viau and C. Gatel, Phys. Rev. B **80**, 064427 (2009).

[14] *Effects of the shape of elongated magnetic particles on the coercive field.*
F. Ott, T. Maurer, G. Chaboussant, Y. Soumare, J.-Y. Piquemal and G. Viau Journal of Applied Physics **105**, 013915 (2009).

[15] *Dipolar interactions in arrays of ferromagnetic nanowires: a micromagnetic study.*
F. Zighem, T. Maurer, F. Ott and G. Chaboussant, to appear in Journal of Applied Physics (arXiv: http://arxiv.org/abs/1008.0172)

[16] *Direct small-angle-neutron-scattering observation of stretched chain conformation in nanocomposites: More insight on polymer contributions in mechanical reinforcement.*
N. Jouault, F. Dalmas, S. Said, E. Di Cola, R. Schweins, J. Jestin, F. Boué, Physical Reviews E 2010, **82**, 031801.

strain curves (elongation ratio λ) displayed an important reinforcement (Fig. 2.7). After an initial jump in low λ regime, the curves appear as though the pure matrix curve is shifted by a constant value depending on the silica concentration. This agrees with the fact that the chain deformation remains unaffected by the presence or absence of nanofillers (see LLB Axis 3). Subtracting the pure matrix contribution, we observed that the remaining stress was constant with λ (Fig. 2.7). This implies that existing reinforcement models may need to be revised. Unless they concern only a very small fraction of chains, two main models fail *in our system*, because they both assume that some chains experience a stronger deformation, either by:

(i) a direct elastic connection of the fillers by the chains[17], or

(ii) the existence of a fraction of glassy chains (glassy layer or glassy paths) that would explain reinforcement dependence on T - T_g[18].

Therefore, confinement effects do not dominate. The important reinforcement must be due to the response of the filler structure to a combination of filler orientation[19] (along the stretching direction) and filler displacement[20], which ultimately induces a continuous locking-unlocking process of fillers associations.

This work was a part of the PhD thesis of N. Jouault.

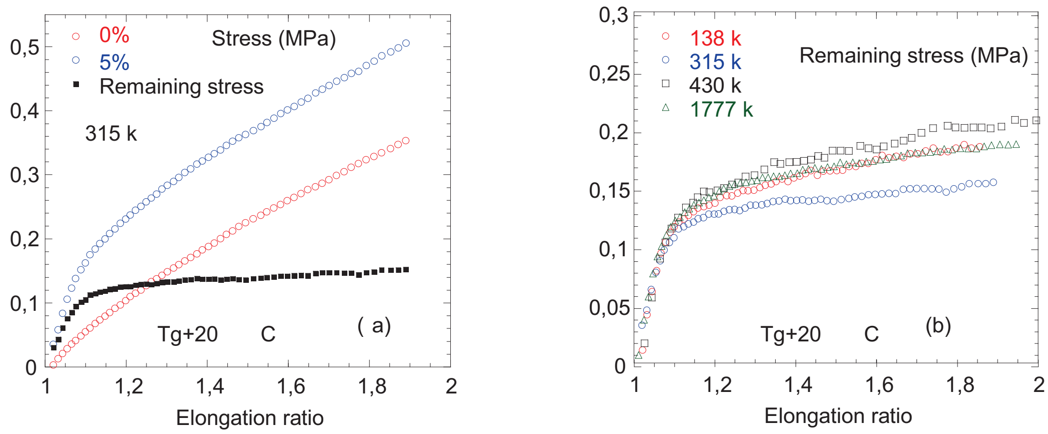

Figure 2.7. *(Left) Stress-strain (elongation ratio λ) for unfilled polymer (red) and 5% filled nanocomposite (blue) for M_w = 315 k. The remaining stress after subtraction of unfilled polymer stress (black) reaches a plateau above λ=1.1. (Right) Remaining stress versus λ for four molecular weights (from 138 k to 1777 k) at same silica volume fraction 5% v/v.*

Natural rubber-clay nanocomposites: mechanical and structural properties[21]

This project relates the mechanical properties of non-vulcanized natural rubber-clay nanocomposites to the morphological and structural aspects of the smectic clay, using TEM and SANS, while paying special attention to the role of non-rubber constituents. Natural rubber latex, apart from polyisoprene, contains non-rubber molecules such as phospholipids, proteins, and a host of inorganic metallic cations, all of which contribute to auto-reinforcement. Pristine natural rubber therefore shows outstanding mechanical properties, with exceptionally high tensile strain and strength at rupture. We have shown that this auto-reinforcement effect is suppressed when non-rubber components are removed by dialysis. On the contrary, for natural rubber-clay nanocomposites, the performance of clay as a reinforcement agent is significantly higher in dialyzed rubber due to the clay' s excellent exfoliation and dispersion characteristics during nanocomposite preparation (i.e., the mixing of pre-exfoliated aqueous dispersions of clay with rubber latex). The reinforcement factor of

---

[17] P.G. Maier, Gummi Kunstst. **2000**, 53. A.S. Sarvestani, Eur. Pol. J. **2008**, *44*, 263-269.

[18] D. Long, *Eur. Phys. J. E.*, **2001**, *4*, 371-387. J. Berriot, *Europhysics Letters* **2003**, *644*, 50. A. Bansal, *Nature Materials*, **2005**, *4*, 693.

[19] *Anisotropic reinforcement of nanocomposites tuned by magnetic orientation of the filler network.*
J. Jestin, F. Cousin, I.Dubois, C. Ménager, R. Schweins, J. Oberdisse, F. Boué, Advanced Materials**,** 2008, **20**, 2533-2540.

[20] Y. Rharbi, Europhysics Letters 1999, **46**, 472-478.

[21] *Natural rubber-clay nano-composites: Mechanical and structural properties.*
Camila A. Rezende, Fabio C. Bragança, Telma R. Doi, Lay-Theng Lee, Fernando Galembeck, François Boué, Polymer **51** (2010) 3644e3652.

the nanocomposite (from uniaxial deformation) can be modeled by the high aspect ratio of exfoliated clay platelets coupled with immobilized rubber matrix, the latter indicated by SANS and calorimetry data. Correspondingly, the onset of accelerated stiffening of the nanocomposite, attributable to filler network formation, occurs at a very low critical clay concentration that is almost an order of magnitude lower than would be expected for spherical particles. TEM and SANS analyses show completely exfoliated clay lamellae in coexistence with a small fraction of tactoids. Interestingly, the presence of tactoids does not appear to compromise the excellent reinforcement properties of the exfoliated platelet fraction. At high deformations, strain-induced alignment of the clay exhibits anisotropic scattering, with anisotropy increasing with clay concentration and degree of stretching (Fig. 2.8). Thus, enhanced mechanical properties at high uniaxial deformations may also be related to the ordering of the clay network in the nanocomposite.

This work was a part of the PhD thesis of C. A. Rezende and the work of the post-doc fellow T. Doi.

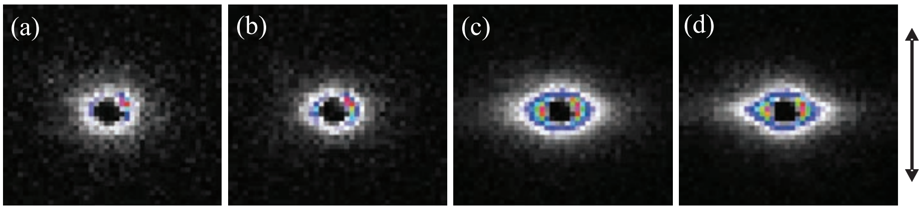

Figure 2.8. *Two-dimensional SANS patterns of natural-rubber clay nanocomposites stretched to λ = 4. Clay concentrations: (a) 0%, (b) 2%, (c) 10%, and (d) 20%. The vertical arrow shows the stretching direction.*

Crosslinked hybrid multilayer (Polystyrenes / Pt Nanoparticles) thin films[22]-[23]

This work has been initiated through collaboration between E. Drockenmuller (Univ. Lyon I) and the LLB, within the ANR " Multiclick" (2007-2009). Organic/inorganic hybrid films made of polymers and inorganic nanoparticles are able to combine two or more desirable properties that can be tuned by particle size, shape and surface chemistry. However, when exposing such hybrid films to solvents, high temperatures, and magnetic or electrical fields, the nanoparticles can undergo aggregation or segregation at the interface. The chemical modification of nanoparticle surfaces, and tuning of the polymer matrix, are therefore of special interest as they enable nanoparticle organization within the thin films to be controlled and directed.

We describe a versatile method of building up well-defined and tunable multilayer thin films based on the combination of polystyrene-grafted platinum nanoparticles with photo-crosslinkable polystyrenes. This approach consists of a straightforward process of sequential spin-coating, UV irradiation, and thermal annealing procedures, which allows the thickness (h = 10-200 nm) and composition (0-50 wt% of PS-grafted Pt nanoparticles) of each layer to be easily tuned as well as providing precise control over their registration and periodicity. Neutron reflectivity experiments performed on pure organic multilayers with alternated hydrido and deuterated layers provide an accurate characterization of layer thickness and of the limited interdiffusion occurring at each polymer/polymer interface in these multilayer architectures. The homogeneity of the resulting multilayer assemblies, and the high level of dispersion for the PS-grafted Pt nanoparticles among hybrid layers, have been confirmed by transmission electron microscopy (TEM; Fig. 2.9). This work represents a powerful method for the versatile and robust elaboration of (hybrid) multilayer architectures and their subsequent stabilization by UV crosslinking, i.e., through covalent binding.

---

[22] *Design of crosslinked hybrid multilayer thin films from azido-functionalized polystyrenes and platinum nanoparticles.* S. Al-Akhrass, F. Cousin, F. Gal, D. Damiron, P. Alcouffe, G. Carrot, E. Drockenmuller, C. Hawker Soft Matter 2009, **5**, 586.

[23] *Polymer-Grafted-Platinum Nanoparticles: From Three-Dimensional Small-Angle Neutron Scattering Study to Tunable Two-Dimensional Array Formation.* G. Carrot, F. Gal, C. Cremona, J. Vinas, H. Perez, Langmuir 2009, **25**, 471.

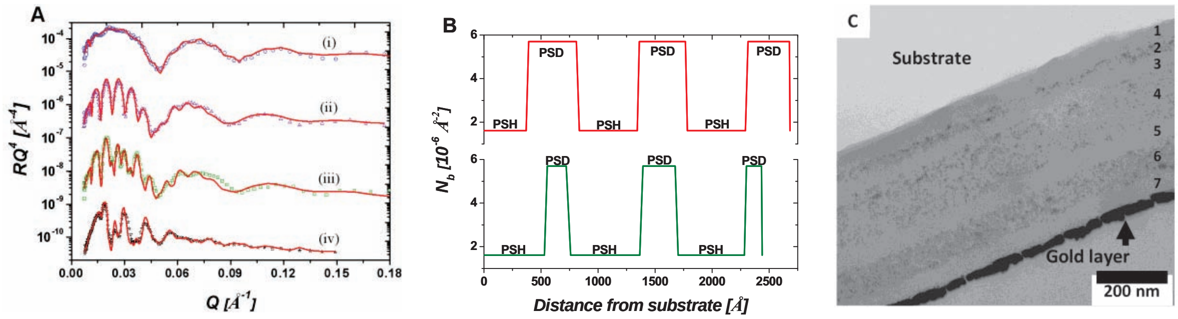

Figure 2.9. *(A) Reflectivity (R.Q^4) vs. Q for PSH/PSD multilayer thin films. (i-iii) correspond to 2, 4 and 6 layers assemblies. The solid lines represent the best fits for each data set. (B) Neutron density length profiles for PSH/PSD multilayers (iii) and (iv). (C) Cross-sectional TEM images of a 7-layer hybrid multilayer assembly with varying layer thickness and a PtH content of 50 wt%.*

Metallurgical composites

In response to industrial needs, steels with very high mechanical characteristics are under continuous development. In particular, the principle of reinforcement, by one or several precipitations of nanometric particles, has attracted considerable interest. The mechanical properties of these composite materials depend strongly on the nature of the nanometer-sized precipitates: i.e., their density, size, and degree of coherence with the matrix. In this research field, Small Angle Neutron Scattering (SANS) allows for very fine characterization of the particles, especially during the first stages of their formation. The LLB is involved in several research contracts for these composite metal alloys.

- **ANR AMARAGE**: Within the framework of this project, the kinetics of the double precipitation of nanometric carbides ($(CrMo)_2C$) and intermetallic phase (NiAl) was studied in martensitic steels intended for the aircraft industry. The SANS analysis, concordant with observations in TEM (CEMES Toulouse) and tomographic atom probe (GPM Rouen) have demonstrated a synergy between the two types of precipitation. Furthermore, the effect of certain alloying elements, such as cobalt, on the kinetics of precipitation has been clearly demonstrated[24].
  This work was performed by M. Perrut (post-doc).
- **ANR AXTREM**: Nanoreinforced steels are being considered for the construction of future nuclear reactors. For higher operating temperatures, Oxide Dispersion Strengthened (ODS) martensitic/ferritic steels exhibit high creep strength as well as potentially high resistance to radiation damage. These materials are being intensively studied with the objective of controlling the evolution of the oxide dispersion during the different stages of the fabrication, which include mechanical alloying, the consolidation processes of extrusion or HIP, and thermal treatments. While these materials are intended for applications up to 1100°C, reinforcement by nitrides is being considered for applications requiring intermediate temperatures (up to 700°C). The development of these new alloys by nitruration at the massive state and in comparison with the ODS, constitutes the AxTrem project. The feasibility of the reinforcement by nitride particles was proved, and nanostructures similar to ODS steels were obtained. Subsequently, correlations with their mechanical properties will be investigated.

Metallurgy from the fundamental to the industrial

The diffractometers associated with metallurgy research activities are DIANE (G52), located in the guide hall, and the 6T1 in the reactor hall. They are respectively dedicated to the analysis of residual strains and to the determination of crystallographic textures. The strong penetrating power of neutrons is used to analyze in-depth metallurgical samples or industrial objects. The instruments are used for both academic and industrial research.

[24] *Small-Angle Neutron Scattering of Multiphase Secondary Hardening Steels.*
M. Perrut, MH. Mathon, D. Delagnes. Acta Mat. (submitted).

Textures and strain heterogeneities

Understanding the macroscopic mechanical properties of polycrystalline materials requires knowledge of the deformation mechanisms at the grain scale. In particular, when a material is subjected to an external macroscopic deformation, the stresses and strains of the crystallites depend on their crystallographic orientation and their environment.

Stress fields in polycrystalline materials.

We have developed a neutron diffraction methodology that associates texture determinations with strain measurements in order to analyze the stress fields within families of crystallites having the same crystallographic orientation in polycrystalline materials[25]. This stress analysis method allows an intermediate approach between a local and a global scale characterization within the bulk of massive samples. It appears promising to use this method in combination with modeling methods that are based on homogenization techniques, due to the statistically representative information it provides. This dual approach has been successfully applied to the vessel steel 16MND5 of pressurized water reactors[26]. The strains measured by *in situ* neutron diffraction during a tensile test (Fig. 2.10) were very heterogeneous among the five analyzed crystallographic orientations (Fig. 2.11). These data were very important for validating a mechanical model developed at CEA/DEN/SRMA, by taking into account both the morphology and crystallography of grains.

Figure 2.10. *Tensile device adapted on the Euler cradle for in situ neutron diffraction measurements.*

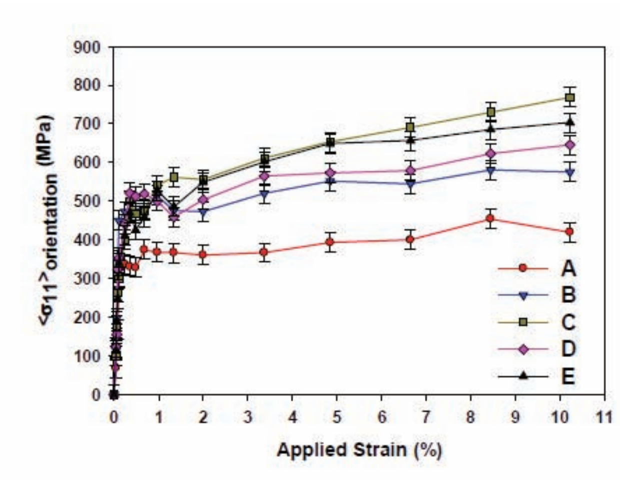

Figure 2.11. *Variation of the axial stresses for different grain families (A to E) vs. applied strain. A significant heterogeneity is highlighted.*

Stress determination in welded materials

Residual stresses in materials can have significant influence on their mechanical properties, including fatigue behavior, resilience, or resistance. Welding processes typically generate important thermal gradients, due to the localized input of intense heat. Frequently, these gradients create large residual stresses around the weld bead, which can reach the yield point value in some cases. During operation of the considered component, these residual stresses will add to applied stresses, possibly resulting in early cracking or fracture. Thus, knowledge of residual stress is critically important for accurately predicting the service behavior of the component, and hence, for optimizing the welding process and the base materials.

Neutron diffraction is an ideal tool for in depth determinations of the residual stresses distributed within welded components, especially because the size of the region probed by the neutrons is relatively small compared to the size of a “classical” weld bead. At LLB during the past several years, numerous experiments have been successfully carried out on welds produced by various processes that utilized different base materials (e.g., steels, aluminum

[25] *In situ analysis of deformation mechanisms of Cu-based fcc materials under uniaxial loading.*
V. Klosek, M.H. Mathon, M.H. Aouni, R. Chiron, V. Ji, Materials Science Forum, **571-572** (2008) 89-94.

[26] *Orientation stress field analysis in polycrystalline bcc steel using neutron diffraction.*
R. Dakhlaoui, V. Klosek, M.H. Mathon, B. Marini, Acta Materiala, Vol. **58** (2010) 499-509.

alloys, magnesium alloys, titanium alloys, etc.)[27-28]. For instance, residual stress fields within the joints of steel pipes designed for PWR (Pressurized Water Reactor) secondary coolant loops or gaseous hydrogen piping were recently determined in collaboration with CEA/DEN[29].

Materials of nuclear interest

Nuclear technologies, such as fission or fusion reactor construction and the storage of accumulated nuclear waste, rely on the development and qualification of advanced structural materials. In particular, the microstructure evolution (precipitation, point defect clusters, etc.) of the materials that constitute the primary water circuit, which must endure important solicitations (e.g., irradiation, thermal aging, hydridation, etc.), is generally responsible for the degradation of their mechanical properties. The knowledge of the aging mechanisms is essential for predicting the behavior of materials under in-service conditions. SANS is a very powerful technique for material characterization and is now usually applied within the framework of research on nuclear materials.

- In Zr alloys (fuel cladding, combustible), the formation of dislocation loops and of β Nb particles induced by neutron irradiation of Zr2.5%Nb alloy, have been revealed in alloys irradiated at different dose rates.
- In martensitic/ferritic alloys, which are candidates for the internal structures of future-generation nuclear reactors, the kinetics of the α' Cr-rich phase precipitation induced by neutron irradiation has been characterized. After a high dose rate, the deduced Cr threshold concentrations in the ferrite agree with models of the binary Fe-Cr equilibrium phase diagram, and attest to a simple irradiation-accelerated precipitation mechanism[30].

Confined systems

Organized guest-hosts systems and microporous materials

This topic was originally developed in CRM2, Nancy, with whom a strong collaboration still exists and where all the single-crystal XRD experiments, and most of sample preparations are performed. Collaborations also involve LMPC (ENSCMu, Mulhouse), LRS (Paris VI) and Chimie Théorique (ENS Paris) for the design and modeling of microporous materials[31-32].

In these studies, diffraction provides the most accurate, though averaged, structural information on the zeolitic system. However, diffraction must also be supplemented by local spectroscopies in order to account for local defects (e.g., " empty zeolites") or disorder (e.g., " guest-host systems"). In the case of good quality single crystals, XRD allows atomic charges to be estimated, and the resulting values compare well with those used in the modeling of adsorption in these kinds of materials. The resulting structure can also be used as a starting point for molecular dynamics/Monte Carlo studies. This approach was applied to X-type zeolites, for which atomic charges were determined in the simple system, dehydrated Na-X. Structural studies on bicationic Na,Co-X were also performed in order to evidence the cation reorganisation induced by dehydration/rehydration[33].

Other structural studies concern guest-host systems built by combining a large-channel zeolite with a small, hyperpolarizable molecule, and then exhibiting Second Harmonic

---

[27] *Study of PM2000 microstructure evolution following FSW process*
M.H. Mathon, V. Klosek, Y. de Carlan, L. Forest, Journal of Nuclear Materials 2009, 386-388, 475.

[28] *Influence of FSSW parameters on fracture mechanisms of 5182 aluminum welds*
S. Bozzi, A.L. Helbert-Etter, T. Baudin, V. Klosek, J.G. Kerbiguet, B. Criqui, Journal of Materials Processing Technology 2010, **210**, 1429].

[29] *Evaluation of residual stresses in dissimilar weld joints*
A. Bonaventure, D. Ayrault, G. Montay, V. Klosek, Materials Science Forum, in press.

[30] *SANS Study of Martensitic Steels and FeCr ODS alloys of Nuclear Interest*,
M.H. Mathon, Y. de Carlan, M. Ratti, S. Zhong, J. Henry, P. Olier, *V. Klosek, V. Ji*, in press in Materials Science Forum.

[31] *Synchrotron powder diffraction characterization of the zeolite-based (p-N,N-dimethylnitroaniline-mordenite) guest-host phase.*
F. Porcher, E. Borissenko, M. Souhassou, M. Takata, K. Kato, J. Rodriguez-Carvajal, C. Lecomte, C. Acta Crystallographica B-Structural Science 2008, **64**, 713.

[32] *Single crystal structure of fully dehydrated partially Co2+-exchanged zeolite X: Comparison with partially dehydrated partially Co2+-exchanged zeolites*
X. E. Borissenko, F. Porcher, A. Bouche, C. Lecomte, M. Souhassou, Microporous and Mesoporous Materials 2008, **114**, 155

[33] F. Porcher, F., Leclercq-Hugeux, F., Lede, B., Kato, K., Takata, M., Hsu, I.-J., Acta Cryst. (2008) **A64**, C504.

Generation. In (dmpNA-MOR), the guest molecules are disordered over 8 sites, but are aligned in the channels with a moderate tilt angle, as requested for SHG. The diffraction explains the stabilization of the guest molecules via H-bonds with the framework (Fig. 2.12 Left). However, due to disorder, it fails to discriminate between different possible local models. UV-visible spectroscopy (Fig. 2.12 Right) gives complementary insight: the blue shift on the dmpNA reflectance window suggests dipolar $-NO_2..(CH_3)_2N-$ interactions. Hence, the local arrangement of dmpNA molecules in MOR channels is head-to-tail.

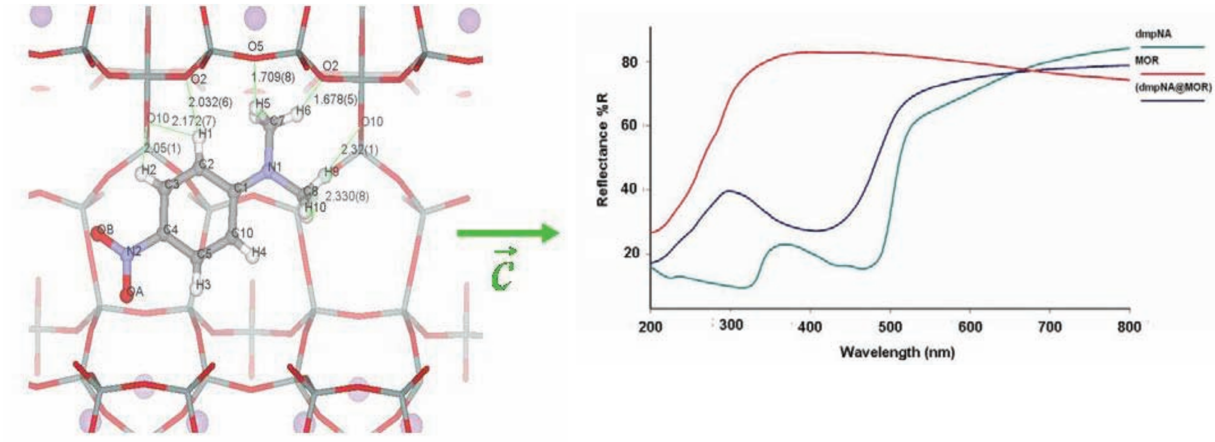

Figure 2.12. *(Left) Interaction of dmpNA molecule with MOR framework. (Right) UV-Visible reflectance spectra of MOR, dmpNA and (dmpNA-MOR) guest-host system.*

Amorphous materials

Disordered systems – glasses

Short-wavelength neutrons from the hot source of the ORPHEE reactor offer a decisive advantage for the characterization of short-range order in noncrystalline materials (i.e., liquids and amorphous materials). The LLB' s 7C2 diffractometer allows structure factors to be measured over a widely scattered vector range and pair distribution functions to be determined, either directly for simple elements (using isotopic substitution for binary compounds), or by combining the neutron structure factor with other measurements (e.g., X-ray diffraction, EXAFS, or NMR) in the framework of a Reverse Monte Carlo simulation that fits all the datasets simultaneously.

There is considerable interest in phase transition in liquids, and some very accurate studies performed at the LLB have concerned the melting of some simple elements. However, the emerging fields of interest for the structure of liquids and amorphous materials are often related to new problems in materials science, such as those presented by the oxide glasses. The study of Phase Change (PC) materials, which will be developed hereunder, is typical of the connection between materials problems and fundamental properties. The search for better PC materials requires investigating the interplay among electronic structure, atomic structure, and thermal anomalies.

In the metallic or metalloid elements of the 14-16 group, some very accurate measurements of their thermal properties and the anomalous thermal behavior of sound velocity in the materials were carried out by an Israeli team, together with very careful measurement and analysis of the temperature dependence of the structure factor (Y. Greenberg, E. Yahel, E. Caspi, B. Beuneu, C. Benmore, M. Dariel & G. Makov). A temperature-driven structural transformation could be evidenced in liquid bismuth, while the sound velocity maximum was correlated with both the structure and rigidity of the two first shells (*Europhys. Lett.,* 86, May 2009, pp. 36004-9; *J. Chem. Phys.,* 133, Sept 2010, 094506)

Phase change alloys

Tellurium-based phase-change materials are among the most promising materials for future data-storage applications, including rewritable DVDs and nonvolatile PC-RAM memories. These alloys display optical (DVD) or electronic (PC-RAM) contrasts between their crystalline and amorphous structures, which permit data storage. A data bit is written by the melting and amorphization of a small zone of a thin layer, while recrystallization erases the bit and is the time limiting step. Improving the properties of the PC-alloys requires an understanding of what drives both the contrast and the crystallization kinetics. Since the liquid state is a precursor to the amorphous state, we have studied by means of neutron scattering, the liquid state of several ternary Te-based alloys, for which the optical contrast had been proven or not, and in which the number of valence electrons (N_{sp}) were varied. The latter variable has been shown to be a crucial parameter[34]. With increasing N_{sp}, the local atomic arrangement changed from a tetrahedral type (bad optical contrast) to an octahedral type. This octahedral atomic arrangement, and its correlation to a pps-type bonding, were also deduced from an *ab initio* molecular dynamics investigation of $Ge_{0.15}Te_{0.85}$ by the sharp distribution of bond angles at approximately 90°[35]. It has been shown previously that this octahedral local environment is generally distorted at low temperature by a Peierls-like mechanism (trigonal distortion).

An interesting connection could be done using parent alloys that display a negative thermal expansion (NTE), such as Te-rich Ge_xTe_{1-x} alloys. All these alloys show an octahedral local structure consistent with their large N_{sp}. An inelastic neutron scattering experiment showed that increased temperatures induced a red shift of the density of vibrational states in the NTE domain due to a gain of vibrational entropy that weakens the Peierls distortion[36].

Dynamics in disordered systems

Finite shear-elasticity in glass formers

On the basis of a Maxwell gas model (1867), it has long been suspected that liquids exhibit a shear elastic effect at sufficiently high solicitation frequencies. Recent experimental improvements carried out at the LLB show that it is in fact possible to reveal shear elasticity at low frequencies. In other words, liquids exhibit long range solid-like correlations at a macroscopic scale away from any phase transition. This result is coherent with studies emerging from different disciplines, such as micro-rheology[37], NMR[38], X-ray photon correlation spectroscopy[39], and voltage effects[40], which have provided evidence for relaxation modes that are much slower than those described by conventional theoretical models. The consideration of this non-negligible macroscopic component is of primary importance in redefining the relevant parameters that will lead to a better understanding of glass and glass former properties, and more generally, of fluid properties. In these experiments, the shear modulus is measured by applying a mechanical stress to the sample (dynamic relaxation). The stress transmitted by the sample is measured by simple contact between the sample and the surface, which is submitted to small mechanical oscillatory solicitations. Up-to-date progress in instrumentation sensitivity allows access to shear moduli over 6 orders of magnitude[41]. Our developments show that it is also possible to improve the measurement by controlling the boundary conditions between the material and the substrate whereby the stress and the measurement are transmitted[42]. Using this method, we enable the detection of subtle properties that would not have been considered previously, such as the identification of a non-zero low frequency shear elasticity in the liquid state. A new (patented) protocol has been established to measure these elastic properties at the sub-millimeter scale in various materials, such as glass formers (Glycerol, PPG, *o*-Terphenyl, and alkanes) and polymer melts (polystyrene, polybutylacrylate, polybutadiene, etc.), which have been so far considered as viscous liquids away from any phase transition[43] (Fig. 2.13). These results contrast with the conventional macroscopic description. The solid-like property is usually not considered since

---

[34] *Characteristic Ordering in Liquid Phase-Change Materials*.
Steimer C., Coulet V., Welnic W., Dieker H., Detemple R., Bichara C., Beuneu B., Gaspard J.-P. Wuttig M., Adv. Mater. **20**, 1-6 (2008).

[35] Bichara C., Johnson M., Raty J.Y PRL **95**, 267801 (2005).

[36] *Dynamics of the Negative Thermal Expansion in Tellurium Based Liquid Alloys*
Otjacques C., Raty J.-Y., Coulet M.V., Johnson M., Schober H., Bichara C., Gaspard J.P., PRL **103**, 245901 (2009).

[37] J. Goyon, A. Colin, G. Ovarlez, A. Ajdari, L. Bocquet, Nature, **454** (2008) 84.

[38] U. Tracht, M. Wilhelm, A. Heuer, H. Feng, K. Schmidt-Rohr, H.W. Spiess, Phys. Rev. Lett. **81** (1998) 2727.

[39] Y. Chushkin, C. Caronna, A. Madsen, A., EPL, **83** (2008) 36001.

[40] E.C. Fuchs, P. Baroni, B. Bitschnau, L. Noirez, J. of Physics D, **43** (2010) 105502.

[41] C. Maggi, B. Jakobsen, T. Christensen, N. Boye Olsen, J.C. Dyre, J. Chem. Phys. B **112** (2008) 16320.

[42] Baroni, P., Mendil, H., Noirez, L., Fr. Pat., 05 10988, (2005), P. Baroni, H. Mendil-Jakani, L. Noirez, Techniques de l'Ingénieur, TI Editions, 1 (2010) RE145,

[43] Noirez L., Baroni, P., J. of Molecular Structure, **972** (2010) p.16. Mendil H., Baroni P., Noirez L., Eur. Phys. J. E **19** (2006) 77, L. Noirez, H. Mendil-Jakani, P. Baroni, Polym. Inter. **58** (2009) 962.

this delicate signal, which is observable at low thickness geometry, is hidden in conventional measurements[44].

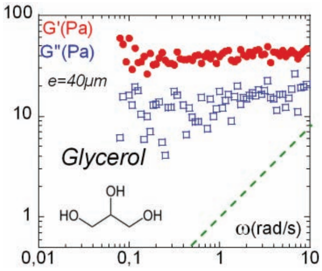

Figure 2.13. *Viscoelastic moduli (G', G'') of Glycerol at room temperature (improved boundary condition, Gap thickness: 0.040mm, 2% strain amplitude). The dotted line (---) corresponds to the expected viscous behavior (J. mol. Struct. 2010).*

[44] J.D. Ferry, Viscoelastic properties of polymers, Wiley 1971; W. Graessley, Adv. Poly. Sci. **16** (1974) 1.

Scientific output

Scientific collaborations

The publications are usually the result of close collaborations with other institutes and university. The main collaborating institutes are listed in Table I.

Collaborators	total
[UNIV PARIS 6 - FRANCE]	12
[ECOLE CENT PARIS - FRANCE]	11
[INST LAUE LANGEVIN GRENOBLE	10
[UNIV PARIS 7 - FRANCE]	10
[UNIV PARIS 11 - FRANCE]	9
[UNIV MONTPELLIER - FRANCE]	7
[INSA - FRANCE]	5
[UNIV TOULOUSE - FRANCE]	5
[UNIV RENNES - FRANCE]	4
[UNIV NANCY - FRANCE]	4

Collaborators	total
[INST CIENCIA MAT MADRID - SPAIN]	7
[UNIV READING - UK]	7
[RES INST SOLID STATE PHYS OPTiCS]	7
[DIAMOND - ENGLAND]	5
[RUTHERFORD APPLETON LAB - UK]	5
[DESY - GERMANY]	5
[UNIV CHEMNITZ - GERMANY]	5
[UNIV TUNIS - TUNISIA]	5
[UNIV TOKYO - JAPAN]	4
[WASEDA UNIV - JAPAN]	4

Scientific contracts

The research in materials science is supported by a number of research contracts.

National support:

- ANR MAGAFIL Magnetic nanowires as permanent magnet materials (2008-2010)
- ANR PROMETFOR Réalisation d' outillage de forge par un matériau à gradient fonctionnel obtenu par projection métallique
- ANR AXTREM Aciers ferritiques/martensitiques renforcés par nanoparticules pour application à haute température en conditions extrêmes (2008-2010).
- ANR AMARAGE Aciers martensitiques alliés de nouvelle génération : vers l'élaboration guidée par la maîtrise de la précipitation secondaire nanométrique (2007-2010)
- ANR NANOHPCUIVRE Recherche Collaborative sur Le Bronze Industriel (2009-2010)
- ANR NSF Structure et Dynamique de Liquides à liaison hydrogène
- ANR BIOSELF Auto-assemblages de nanogels et nano-composites bio-inspirés (2006-2010).

Regional support

- C' nano FILASPIN Filtres à spins (2007-2009)
- RTRA: OCTUOMETRE: Octupole for 4-circle magnetic diffraction

Transverse program of our governing bodies (CEA and CNRS)

- CEA/DSM-DAM: Neutron Irradiations
- CEA/DSM-DEN: SANS measurements on steel samples

Other

- ECO-NET: Magnetic wave guides (2007-2008)

Industrial contracts

- General Electrics: Determination of residual stresses in crankshafts
- Swiss Neutronics: Reflectivity Measurements on Guide coatings

Other

PhD theses defended, and in preparation, during the period 2008-2010

- Thomas Maurer (2007-2009) « Magnétisme de nano-objets anisotropes. »

- Matthieu Dubois (2009-2012) (LLB – Univ. Reims). « Analyse multi-échelle de l’ état microstructural et mécanique d’ un alliage à mémoire de forme cuivreux par diffraction des neutrons. »
- Shengyi Zhong (2009-2012) « Etude des hétérogénéités de déformation en corrélation avec la distribution de nano-renforts dans des aciers ODS. »
- Cynthia Mohamed-Said (2008-2011) (complete supervision – BDI thesis started October 2008)) Structural and optical properties of PNIPAM-coated gold nanoparticles
- A.S. Robbes (2008-2011) (co-tutelle SOLEIL) « Nanocomposites magnétiques : contrôle de la dispersion par greffage et orientation des charges sous champ externe »
- A. L. Fameau (2008-2011) (co-tutelle INRA Nantes) « 'Vers de nouveaux détergents : assemblages d’ acides gras hydroxylés du volume aux interfaces, impact de la structure sur les propriétés moussantes et émulsifiantes’ .

Post-docs working during the period 2008-2010

- Rim Dakhloui (2008) (CEA/DEN/DANS/DMN/SRMA). « Contribution à l’ étude des hétérogénéités des champs mécaniques dans un acier bainitique à l’ aide de la diffraction des neutrons. »
- Francois Muller (2009-2010) l’ ANR BIOSELF « Elaboration de nouveaux biomatériaux à base de celluose »
- Mickael Perrut (2007-2009) Stage post-doctoral dans le cadre des ANR AMARAGE et aXtrem.
- Fatih Zighem (2009-2010). Stage post-doctoral dans le cadre de l’ ANR MAGAFIL «Aimants permanents à base de nanofils. »
- Camila Alves Rezende - funded by DRI-CEA (05/2007-04/2008) "Nano-composites: bulk and surface structural properties."

Habilitation à Diriger les Recherches defended during the period 2008-2010

- Grégory Chaboussant. *Contribution de la diffusion des neutrons à l'étude des aimants moléculaires. (Univ. Paris VI)*
- Frédéric Ott. *Neutron scattering on magnetic nanostructures. (Univ. Paris-Sud XI)*