D2AM, status, highlights and plans for upgrade of the French anomalous CRG beam line at ESRF.

presented by Nathalie Boudet and Jean-François Bérar

April 17, 2009

This document is the collective work of all those participating in the beam line. They are to be thanked for their written contributions and for their help and comments in preparing this booklet.

Contents.

List of insets.

1 Introduction

The CRG BM2-D2AM was one of the very first beam lines to be opened at the ESRF. It was designed for X-ray diffraction, small angle X-ray scattering and for bio-crystallography with the aim of performing multi-wavelength anomalous scattering experiments. Subsequent to the implementation of the bio-crystallography FIP beam line in 1999, the D2AM beam line is now devoted entirely to Materials Science. Some documents can be found on the beam line web site[1] including the report to the 2004 review panel.

Thanks to the different communities involved in the development of the beam line, it still covers a broad range of **materials science studies** such as : nanostructured semi-conductors, quasi-crystals, magnetic dots, polymers, electrolytes, metallic alloys, ... In 2005-2008, 137 experiments were accepted by the ESRF and CRG review commitees. The high level scientific activity is attested by a similar number of publications, almost 197 in the same period among which are :

journal	2001 2004	2005 2008	journal	2001 2004	2005 2008	journal	2001 2004	2005 2008
Nature Mat.	-	2	Acta Materialia	1	7	Macromolecules	2	10
Phys. Rev. Let.	3	5	Appl. Phys. Let.	2	2	Biomacromol.	-	5
Phys. Rev. B	5	11	J. Appl. Phys.	-	9	Langmuir	5	5
J. Appl. Cryst.	6	8	Polymer	2	7	Carbon	-	3

D2AM is widely involved in training activities (HERCULES, ...) and at least 17 PhD theses based on experiments at the beam line were defended since 2005. Over the same period more than 12 invited lectures at international conferences were directly related to experiments carried out at D2AM.

After a brief presentation of the beam line, selected experiments that are representative of results (page 7) obtained at D2AM in recent years are brought to the attention of the 2009 ESRF review panel. A selection of significant papers are reprinted in the appendix, they are representative of the various scientific topics in which the beam line is involved : from soft condensed matter to semi-conductor nano materials.

The new scientific goal for the beam line will be detailed (page 21) in the context of the ESRF upgrade and the starting operation of the synchrotron SOLEIL. Our project takes into account the expertise at D2AM and responds to developments in materials science. Its aim is to reinforce the means of characterizing samples in a way that is adapted to their function and engineering:

- It concentrates on a D2AM strong point, **Diffraction Anomalous Fine Structure** spectroscopy for the characterisation of strains and composition of nano-objects.
- It improves access to **higher energies** (30-40 keV) to reach more K-edges and penetrate thick samples.
- It allows both in plane and out of plane **Grazing Incidence** studies of **in-situ nano-objet** sets.

This project has been split into a small number of work packages for which funding requests are expected to be positive.

[1] http://www.esrf.fr/UsersAndScience/Experiments/CRG/BM02/

2 D2AM : a French CRG beam line

2.1 Presentation

At the beginning of the ESRF, the CEA and the CNRS decided to create the French-CRG beam lines in order to facilitate access of the French community to synchrotron experiments. This project received strong financial support from the local authorities to help it to achieve completion. Laboratories in the Grenoble area became deeply involved in the CRGs, bringing in committed research workers.

The D2AM beam line was dedicated to anomalous scattering and studies of diffuse scattering at small or wide angles. The optics were designed to satisfy the common requirements of the groups involved : the project leaders, *J.-P. Simon (CNRS)* and *M. Roth (CEA)* paid particular attention to the signal-to-noise ratio.

The beam line was among the first at the ESRF to open to users in September 1994. It is now fully dedicated to materials science with two instruments sharing the beam time.

- a small angle camera (responsible *J.-P. Simon*)
- a 7-circle goniometer (responsible *N. Boudet*)

The mean annual budget allocated by the CNRS and the CEA in last years is about 150 k€. This budget does not include staff salaries but takes into account all charges incurred to the ESRF, running costs and small investments, including part of our detector development program. Considerable effort is now directed towards finding other/new financial sources to allow the beam line to develop towards "modern materials" and their applications, at the same time as adapting the instrument characteristics to the improvements in the ESRF X-ray source. This project will be more detailed in a dedicated section.

2.2 Staff and associated laboratories

For CRG beam lines, management, local contacts and technical supports rely exclusively on CNRS and CEA personnel. Only very specific tasks are supported by the ESRF through the CRG-coordination staff.

The day-to-day activity is supported by 4 permanent CNRS employees of Institut Néel:

S. Arnaud	*J.-F. Bérar*	*N. Boudet*	*B. Caillot*
technician	responsible	scientist	engineer

In addition, research workers from laboratories in Grenoble are involved through their own ongoing activities in development, support of external users and in-house research. About 10 scientists participate in these activities on a part-time basis, that is about 2-3 full-time equivalent staff members. The participation of these laboratories enables the staff to cover various scientific topics, some examples of which are given in the following table.

NEEL	Institut Néel - CNRS-UJF	J.-L. Hodeau, E. Dooryhee	crystallography of functional materials
SIMaP	Science et Ingénierie des Matériaux et Procédés - Grenoble-INP	M. de Boissieu, F. Bley, M. Maret, J.-P. Simon	physics of metal and engineering
LMGP	Laboratoire des Matériaux et du Génie Physique - Grenoble-INP	H. Renevier	nano materials
CERMAV	Centre de Recherche sur les Macromolécules Végétales - CNRS	C. Rochas	soft condensed matter
LSP	Laboratoire de Spectrométrie Physique - UJF	E. Geissler, I. Morfin	soft condensed matter
INAC	Institut Nanosciences et Cryogenie - CEA	V. Favre-Nicolin	nano materials

2.3 User access to the D2AM beam line and training activities.

User access to the D2AM CRG beam line is allocated by different review committees : the ESRF committees for 1/3 of the time and the French CRG committee for the remaining 2/3. The ratio between requested and allocated shifts (or proposals) is about 2-2.5.

	Total†	*BLC*	*IHR*	*Users**	*ESRF users*		*CRG users*	
year	shifts	shifts	shifts	shifts	shifts	proposals	shifts	proposals
2004	648	32	190	420	123	11	297	24
2005	651	51	150	441	141	11	300	24
2006	678	48	153	456	132	10	297	25
2007	669	36	120	498	102	9	354	28
2008	690	30	153	486	195	11	291	19

Beamtime allocation throughout the year : total (†including teaching and industrial shifts), commissioning (BLC), in-house (IHR) and allocated to users by ESRF and CRG **review committees** , the Users' total (*) includes shifts allocated to users on "reserve" lists.

Each year, about 5 days are allocated for teaching practicals for European advanced schools (HERCULES, ESONN) and for University graduate students (UJF, Grenoble-INP). Last year, a 3 further days were devoted to a dedicated school on GISAXS organized by the CNRS. In previous years, 2 to 3 days were devoted to a GDR for cultural heritage materials and to HERCULES Specialized Courses. Out of this time, one or two shifts each year are used by industrial companies under contract with the ESRF. Commissioning, maintenance and in-house research share the remaining time.

The CRG scientific topics are similar those of the ESRF review committees. The following figure represents the activity in 2008 divided into the main scientific fields.

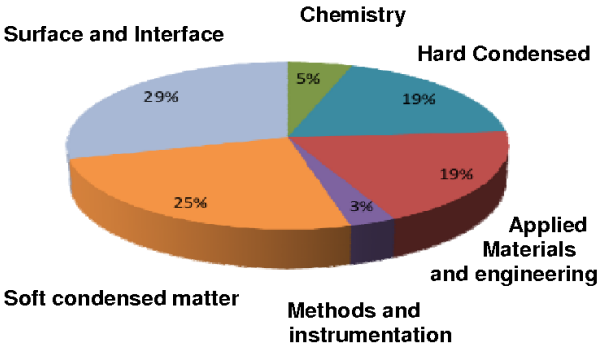

Figure 1: Scientific fields of activities.

During these years very few experiments were interrupted by beam line failures (motors, cryostat) and any lost time was replaced in the following months by using beamtime reserved for maintenance.

Following the opening of the SOLEIL synchrotron, the 2007 CRG-"Conseil d'Administration" decided to establish a common review committee for the French community, so that all French proposals could be "treated" on equal terms. As well as a single review committee, this also implies reimbursement for users coming to a CRG at the ESRF, which is not the case at present for CRG users.

2.4 Optics and instrument overview

The beam line is located on the BM02 bending magnet and uses the 0.85 Tesla source with a critical energy of 20.6 keV. For better energy resolution combined with focussing capability, the D2AM optics is symmetrical, with a double monochromator situated between two mirrors.

2.4.1 Optics

At the entry to the optics hutch, a primary collimator accepts up to 3 mrad of the horizontal divergence. Primary slits located upstream of all the optical components are used to define the effective vertical and horizontal divergence. The first mirror, a platinium-coated silicon single crystal, acts as a low pass filter and focuses the beam in the vertical plane. These first elements lie in a very high vacuum (10^{-9} mbar without beam, 10^{-7} mbar with beam) that extends up to the last Beryllium window. The beam is then processed by a double crystal monochromator equipped with Si(111), or occasionally, to reach higher energies, with Si(311). This monochromator has a bandwidth $\Delta E/E$ of 10^{-4} and focuses the beam sagittally in the horizontal plane.

A second mirror, similar to the primary one, provides focusing in the vertical plane. Rear slits, located just after the second mirror and also near the instruments, reduce spurious signals from optical aberrations.

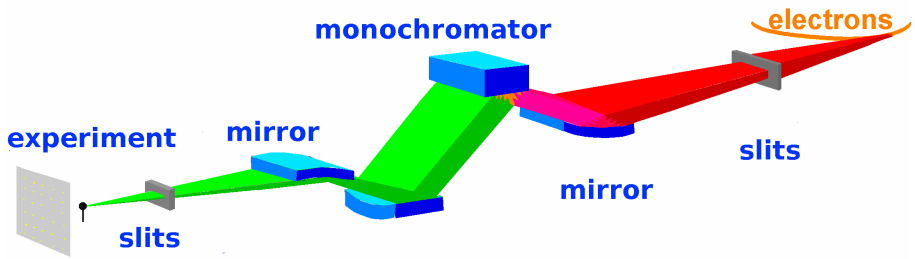

Figure 2: Overview of the optical arrangment.

This whole symmetrical arrangement acts with fixed exit optics and should yield a 3:1 demagnification of the source (2:1 for the SAXS camera). An exhaustive description has been published[2]. It delivers photons from 5 to 25 keV (35 keV using Si(311)) to the experimental hutch in a spot of a few hundred microns. Spots of $70 \times 100\,\mu m^2$ can be attained for experiments requiring very small beam sizes.

2.4.2 Instruments

The optics employs two instruments located in a common experimental hutch. Both instruments share detectors : scintillators/photomultipliers and CCD cameras. The most commonly used 2D-detector at present is a fibre optic coupled CCD ($60 \times 50\,mm^2$) : Roper Scientific FOC CCD 1340×1300.

A "7-circle" goniometer, consists of an Euler cradle for the sample, a detector arm that can move in the vertical polarization plane up to 120^o and up to 75^o in the horizontal plane. All angles are driven by step motors with a resolution of better than 0.001^o. Various analysers can be used on the detector arm, depending on experimental requirements : a two circle analyser using Si or Ge crystal is available for high resolution experiments (ΔE lower than $5\,eV$), e.g., certain powder diffraction measurements; the same settings are also used with curved graphite crystals (ΔE in the range $100 - 300$ eV at 10 (250-700 eV at 30 keV) for experiments that resolve fluorescence lines or Compton scattering, such as amorphous radial distributions; a polarization analyser has also been built. As an increasing number of experiments has been devoted to surface layers, a supplementary circle can be installed, which will facilitate working in grazing incidence geometry. Attention has been paid to ancillary equipment : evacuated sample holder cell, displex, furnaces, ... are available.

[2] *Ferrer et al.*, J. Synchrotron Rad. **5** (1998) pp 1346-1356

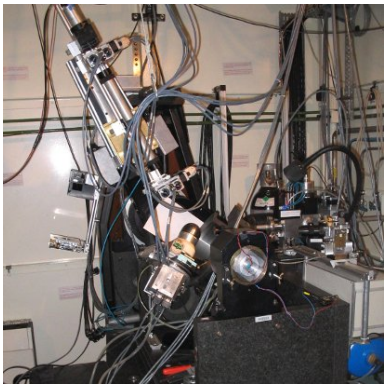
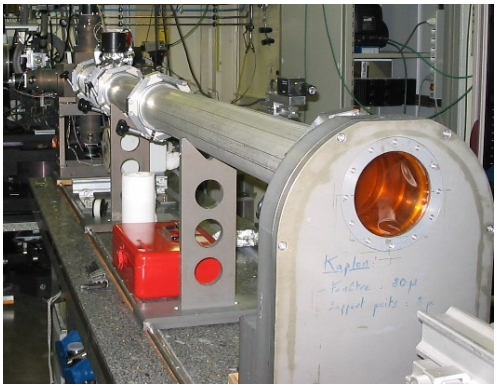

Figure 3: The goniometer and the small angles camera .

The small angle camera is situated at the rear of the same experimental hutch and receives the incoming beam through an evacuated pipe passing through the goniometer. The camera itself[3], on a single granite bench, consists of antiscattering slits, sample holders, exchangeable vacuum pipes up to the beam stop and a CCD detector. The sample-detector distance ranges from 0.3 m to 2 m, with a normal Q range between 3.10^{-3} Å^{-1} and 1 Å^{-1} between 8 and 15 keV. Ultra small angle scattering has attained 4.10^{-4} Å^{-1}, thus providing complete overlap with standard visible light scattering.

Experiments at high pressures or high temperatures need harder X-rays and their Q range extends to wider values, 2 Å^{-1} at 20 keV. The flexibility of the camera has been put to advantage in several in-situ experiments in materials science and engineering.

The Grazing Incidence SAXS setting uses this camera with a dedicated vessel that allows for sample alignment and orientation. The vessel, working under secondary vacuum, can be connected to a UHV suitcase with sample transfer by means of a wobble stick. Sensitive specimens, maintained under vacuum from a laboratory preparation chamber to the GISAXS camera, can thus be investigated.

The beam line design takes advantage of the horizontal aperture of the bending magnet to increase the flux at the sample position. Practical values range from $1.5\,10^{10}$ (10 keV) to $2.3\,10^{10}$ ph/s (20 keV) for a beam selected by 1 mm^2 entrance slits at a current of 200 mA. The whole aperture can reach 90×6 mm^2, but the resolution needed in crystallographic experiments often restricts the aperture to the range 0.1 to 0.5 mrad, yielding flux values of a few 10^{11} ph/s on the sample. Similar values are attained in SAXS experiments, where the optical requirements limit the practical horizontal divergence to 0.04 mrad.

[3] *Simon et al.*, J. Appl. Cryst. **30** (1997) pp 900-904

3 A materials science beam line : scientific results

3.1 Structures and related

The properties of materials depend on the way the constituent atoms combine with each other into crystalline or disordered solids, liquids or glasses, and on the microstructural arrangement of the grains in a bulk material. Synchrotron X-ray radiation provides some of the most powerful tools to study these structures and thereby gain an understanding of why materials behave as they do, and how properties can be tailored and improved for specific applications. The examples presented below cover only the very tip of the iceberg as far as materials research at D2AM is concerned.

The first example involves quasicrystals. Since their discovery[4] in 1984, the question 'where are the atoms?' has been a puzzle to scientists. Recently, bi-atomic quasicrystals have been produced, allowing this question to be answered and giving insight into their cluster structure (*see inset page 8*).

The second example has to do with catalysts: the properties of zeolites depend strongly on the location of the ions that favour the insertion of specific gases. However the small amount of such ions (a few percent) contributes weakly to the diffraction signal. Anomalous diffraction can identify the location of the ions and allows their variation within the zeolite structure to be followed.

The last example in this part focuses on ill ordered structures, ranging from amorphous to liquid solutions. An example concerns amorphous metallic alloys. The knowledge of the structure of such solids requires the scattering to be recorded over a large Q range, up to $10\,\text{Å}^{-1}$ at low energies, $25\,\mathring{A}^{-1}$ at Cd edge (27 keV).

Other amorphous systems that require a wide Q range involve soft matter, notably polymer solutions. In the small Q-range ($10^{-3}\,\text{Å}^{-1} \leq Q \leq 0.5\,\text{Å}^{-1}$), characteristic distances of the inter-chain ordering can be determined. In the higher Q range structural properties on the nanometre scale, such as solvent and intra-chain polymer structures, are investigated, as well as molecular solvation. Furthermore, in polyelectrolyte solutions, studies of counter-ion binding of cations have been performed using the anomalous scattering capability of the beam line. The example highlighted as an inset in page 10 is a study of how the mean distance between neighbouring chains in a polyelectrolyte solution varies as a function of the degree of ionization, i.e., of the strength of the electrostatic repulsion.

3.1.1 Quasicrystal

Quasicrystals, which are long-range ordered aperiodic structures, were investigated by the SIMaP in collaboration with three Japanese teams (Prof. A.P. Tsai, Tohoku University, Prof. T. Ishimasa, Hokkaido University, Prof A. Yamamoto, NIMS, Tsukuba). These fascinating materials still puzzle scientists[5]. In particular their atomic structure has until recently remained controversial. The recent discovery of the CdYb icosahedral phase has been a breakthrough leading to a detailed understanding of their atomic structure (see inset page 8). The stability of the beam line, the number and the high dynamic range of the measured integrated Bragg peak intensities (measured with a point detector), together with a sophisticated 6D analysis have been key elements for the success of the structural solution.

We have also carried out a detailed analysis of diffuse scattering. Aperiodic long range order introduces new specific long wavelength diffusive excitations called phason modes. Phason modes lead to a characteristic signature in the diffuse scattering intensity. It can be computed by generalized elasticity theory, using phason elastic constants, in a very similar way to that achieved for phonon modes (leading to thermal diffuse scattering, TDS). Phason mode diffuse scattering is located close to the Bragg peaks, with a $1/Q^2$ decay: it therefore requires good Q resolution and high dynamic range to be measured properly. Moreover, as was done previously, we carried out measurements on an absolute scale: this is a crucial point which allows different quasicrystals and the 'amount' of diffuse scattering to be compared, but also yields the value of the phason elastic constants[6]. These are key

[4] *Shechtman et al.*, Phys. Rev. Lett. **53** (1984) 1951
[5] *Janssen et al.*, From modulated phases to quasicrystals, Oxford Univ. Press (2007)
[6] *de Boissieu et al.*, in Handbook of Metal Physics : Quasicrystals, Elsevier Science 2008

parameters in the longstanding debate on the mechanism that stabilizes the quasiperiodic long range order.

Atomic structure of the binary icosahedral Yb-Cd quasicrystal

Quasicrystals are extremely well-ordered structures whose atomic arrangement is nonperiodic. This shows up in their diffraction pattern, which displays sharp Bragg reflections (a signature of long range order) but with a 5-fold rotational symmetry, incompatible with lattice translation. The discovery of the icosahedral phase of $Cd_{5.7}Yb$ by Tsai and co-workers[a] was a breakthrough. Indeed this is the first binary quasicrystal, which greatly simplifies structural analysis. The structure of the approximant crystals is described by a periodic packing of a large structural unit with icosahedral symmetry, whose external shell is a triacontahedron (Figure 1). This forms an atomic cluster that is chemically extremely well ordered, with Yb atoms sitting on the vertices of an icosahedron. The clusters are densely packed and connected along the 2-fold and 3-fold axes, where they interpenetrate.

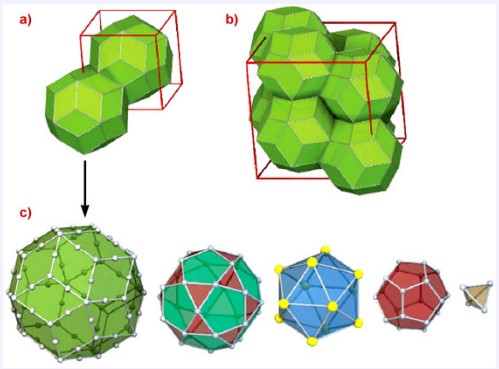

Fig. 1: Packing of the triacontahedral unit in the 1/1 (a) and 2/1 (b) cubic approximant with lattice parameters b=1.57 nm and τb=2.53 nm respectively[b]. (c) the different shells and their atomic decoration (Yb atoms are in yellow, Cd in grey)

The structure of the icosahedral CdYb quasicrystal was solved using X-ray diffraction data collected on the D2AM beam line (BM02). Our model was refined against the experimental data by using a 6-dimensional analysis, which included a phase reconstruction procedure, and this in combination with the information obtained from the approximant structure. The large number of Bragg peaks (more than 5000) and their dynamical range (almost eight orders of magnitude) put a severe constraint on the modelling, which nonetheless resulted in a very good R factor of 0.096. The CdYb quasicrystalline structure is described as a quasiperiodic packing of the triacontahedral cluster, with connections along 2- and 3- fold axis as observed in the approximant: 94% of the atoms belong to such clusters. Other local environments, unique to the quasicrystal, are also present. The model also yields a description of the hierarchical packing of the clusters, illustrated in Figure 2: the clusters are packed together to form a 'cluster of clusters' shown as a yellow disk in the left panel. In turn this 'cluster of clusters' also forms a larger cluster whose characteristic length inflate with τ^3. This inflation property continues to infinity and might be used to explain the physical properties of the quasicrystal.

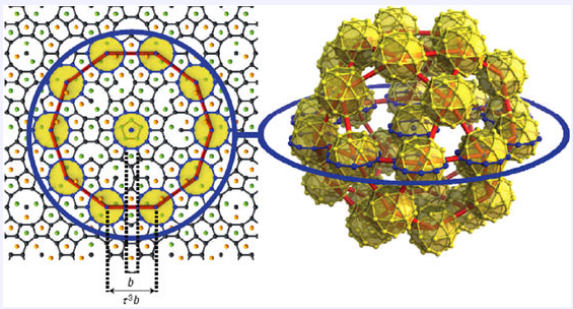

Fig. 2: Illustration of inflation properties in the quasicrystal. The left panel shows the distribution of cluster centres (black dots) in a 5-fold plane. The yellow disk is a trace of a cluster of clusters shown in the right panel. They form a larger unit as highlighted by the blue circle, shown on both panels. The edge of the left panel is equal to roughly 34 *nm*.

Now that this model has been firmly established, it paves the way for further investigation into the stability and physical properties of quasicrystals.

Principal Publication and authors:

H. Takakura, C.P. Gómez, A. Yamamoto, M. de Boissieu, A.P. Tsai, Nature Materials **6**, 58-63 (2007).

[a] *Tsai at al.*, Nature **408**(2000) p537
[b] τ = 1.6168 is the golden mean

A detailed comparison of the absolute scale diffuse scattering measured in the ZnSc 1/1 approximant and the icosahedral ZnMgSc quasicrystal (both isostructural to CdYb) gave two important results[7]: i) the phason diffuse scattering is only measured in the quasicrystal as a signature of quasiperiodic long range order; ii) the amount of phason diffuse scattering is about 4 times smaller in the i-ZnMgSc than in the i-AlPdMn phase, demonstrating that the phason mode fluctuations are system-dependent[8]. This nevertheless strongly suggests that phason modes and the configurational entropy they generate is one of the stabilizing 'ingredients' of quasicrystals.

3.1.2 Zeolite powders

A dedicated powder beam line exists at ESRF: our effort focuses on the use of anomalous differences to solve problems related to cation occupancy : conventional refinement often cannot identify structural modifications related to cation substitution, which strongly modifies chemical or physical properties. Work on zeolites started in collaboration with the Institut Français de Pétrole[9]. In bicationic zeolite, owing to the partial occupancy of the active cation site, only anomalous refinement can be used to locate cations such as Sr^{++} in one site and Rb^{+} in the other : depending on the energy some lines increase while others decrease. Using this variation, it is now possible to detail the Sr^{++} and Rb^{+} cation distributions on the insertion sites[10].

Using a dedicated reaction chamber, the catalytic process could be approximated by in-situ experiments. The absorption site for xylene molecules in X-zeolite could thus be identified and related to the cation site.

The search for stable dyes, resistant to heat and moisture in particular, places several organic-inorganic hybrids as particularly appropriate and environmentally friendly solutions: the colour can be durably fixed by trapping or encapsulating the organic dye on a mineral or in a clay matrix. In C. Dejoie's PhD work (UJF, 2007-2009), we examine the diffusion and the fixing process of indigo molecules inside the cages and channels of appropriate alumino-silicates such as zeolites. We succeeded in producing a stable composite, whose colour and stability resemble those of the historical Maya Blue pigment. Part of our project is to revisit the structural and spectroscopic features of Maya Blue using the indigo-zeolite complex as a model case. Our new zeolitic analogues are characterized by optical and vibrational spectroscopy, quasi-elastic neutron scattering, and synchrotron X-ray powder diffraction at D2AM. Formation of the hybrid is followed by in situ X-ray diffraction at D2AM. Insertion of the indigo molecules inside the matrix causes a monoclinic-to-orthorombic structural change of the zeolite crystal. Fourier difference syntheses reveal extra electronic density inside the zeolite channels due to the presence of the organic dye. The global organic molecule position in the channel network of the zeolite is obtained by simulated annealing. Further structure refinements complete the structural determination of this new organic-inorganic hybrid.

3.1.3 Solutions and ions

Polyelectrolytes play a central role in living systems, and multivalent ions exert a strong influence on their conformation. In particular, charged biomolecules such as hyaluronic acid, which are present in cartilage and the synovial fluid, must operate without phase separation in solution not only with sodium but also with calcium ions. Anomalous scattering measurements of hyaluronic acid solutions, in which the two ions, Na^{+} and Ca^{++}, are respectively mimicked by Rb^{+} and Sr^{++}, whose thresholds lie within the accessible energy range. The findings show that the monovalent ions form an extended cloud around the polyelectrolyte chain that is consistent with the Poisson-Boltzmann distribution. The divalent ions, however, cluster in a tight sheath round the polymer backbone[11].

[7] *de Boissieu et al.*, Phys. Rev. Let. **95** (2005) 105503
[8] *S. Francoual*, PhD, Univ. J. Fourier (2006)
[9] *H. Palancher*, PhD, Univ. J. Fourier (2004)
[10] *Palancher et al.*, Ang. Chem. Int. Ed. **44** (2005) 1725-1729
[11] *Horkay et al.* , J. Chem. Phys. **125** (2006) 234904

Polymer conformation

Using small angle X-ray scattering, a method allowing the evaluation of the solvophilic/solvophobic character of polyelectrolytes from their conformation in solution is discussed. Analyzed systems are salt-free aqueous solutions of natural co-polysaccharides with controlled chemical structures. Synchrotron Small-angle X-ray scattering diagrams revealed the polymer conformation by a "polyelectrolyte peak".

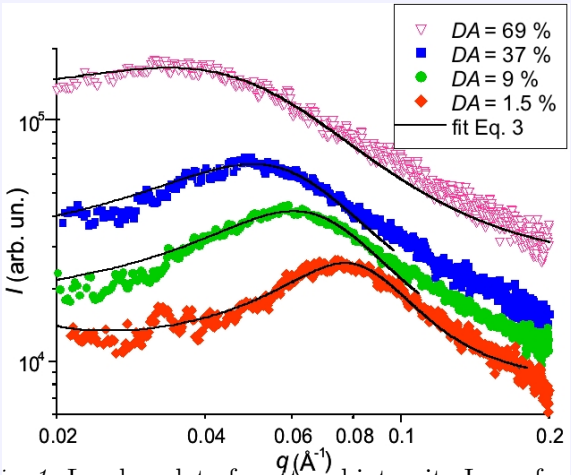

Fig. 1: Log-log plot of scattered intensity I as a function of the scattering vector q for chitosan acetate solutions of different degrees of acetylation (DA), same DPw (3200) and Ip (1.6) and at constant concentration of residues per unit volume of 0.035 mol/l. The scattering curves are shifted vertically for visual convenience.

The study of this peak allowed the determination of c_b, the crossover concentration associated to the transition between the two structural organization regimes predicted by the scaling model of hydrophobic polyelectrolytes developed by Dobrynin and Rubinstein[a]. A structural law of behavior as a function of the chain primary structure is constructed for chitosan, showing an increasingly hydrophobic character when the fraction of N-acetyl-D-glucosamine residues (DA) increases. The variation of the maximum with Q_{max} allows us to separate the string-controlled regime and the bead-controlled regimes according the scaling model. The evaluation of the solvophilic/solvophobic character from the crossover between these two regimes is in agreement with the changes in the different physico-chemical properties of chitosan with DA[b]. In addition, the analysis was applied to other polysaccharide systems (alginates, hyaluronate), showing that this approach is valid for a variety of hydrophobic natural polyelectrolytes.

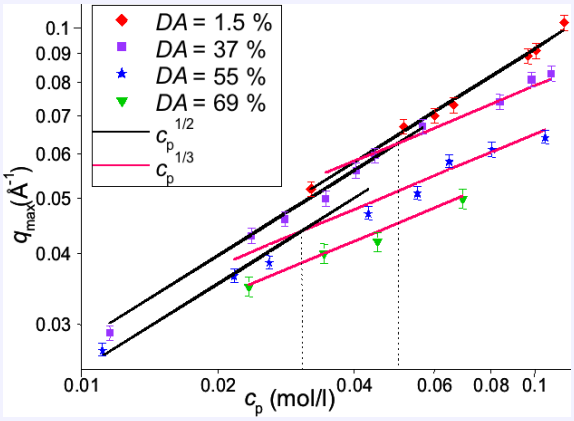

Fig. 2: Variation of Q_{max} (position of the maximum of the polyelectrolyte peak) with the c_p (polymer concentration) in chitosan acetate solutions of different degrees of acetylation (DA). For clarity the values of Q_{max} are shifted vertically.

Principal Publications and authors:

S. Popanita, C. Rochas, L. David, A. Domard, Langmuir, in press 2009
N. Boucard, L. David, C. Rochas, A. Montembault, C. Viton, A. Domard Biomacromolecules **8** 1209-1217 (2007)

[a] Macromolecules **32** (1999) 915-922
[b] *Drogoz et al.*, Langmuir **23** (2007) 10950-10958

3.1.4 Amorphous and bulk metallic alloys

The phenomena of supercooling and glass formation in viscous liquids have been the subject of considerable study in recent years. The structural evolution of the fragile glass-forming liquid $CaAl_2O_4$ was studied[12] during supercooling from the stable liquid phase to the cold glass below T_g. The cooling curve developed a kink at $1.25\,T_g$, indicating a simultaneous change in thermodynamic properties.

[12] *Hennet et al.*, J. Chem. Phys. **126** (2007) 074906, J. Phys. Cond. Mat. **19** (2007) 455210

Following their discovery in the 60's, new families of bulk metallic glasses have recently appeared. Owing to their excellent glass-forming abilities they achieve slow critical cooling rates, lower than $0.1\,K/s$, and can form massive bulk glass more than $40\,mm$ in size. The mechanical characteristics of such glasses are promising as they are not affected by grain boundaries. At the present time, thermodynamic and mechanical properties of Pd-N-Cu-P bulk metallic glasses have been studied systematically, but few fundamental attempts have been made from the view point of the structural and electronic properties to understand why they form glasses so easily. Precise knowledge of these glasses relies on Anomalous X-ray Scattering, which yields accurate values of the distribution functions $g_i(r)$. Such experiments have been commonly carried out on D2AM in the range $8 - 12\,keV$. A new analyser setting using a curved graphite crystal now ensures efficient data collection at the Pd edge (24.34 keV). Data analysis[13] confirms the prediction that such glasses have, at least for the Pd sublattice, a local configuration that differs from the crystalline phases and homogeneous atomic configuration on a long-range scale.

The anomalous scattering experiment on amorphous materials requires high flux and high beam stability, which can be achieved on a bending magnet. At present, very few other beam lines seem suited for such experiments.

3.2 Engineering and in situ materials science.

Materials engineering requires fundamental investigations that characterize samples at atomic and mesoscopic scales. The 2006 SAS conference held in Kyoto (Japan) was opened by J.P. Simon on the "Contribution of synchrotron radiation to small-angle X-ray scattering studies in hard condensed matter"[14].

An example of such studies of alloys is given in inset page 12. It focuses on clustering inside the alloy by coupling stress and temperature. Another inset example, page 13, deals with phase diagrams, the knowledge of which is critical for an understanding of modern production techniques using polymers.

3.2.1 Alloys and related

The performance of metallic materials is improving continuously, by example, the strain in new steels now reaches values that were could not be foreseen from previous materials. To progress further, it is necessary to understand precisely the influence of the composition and the thermo-mechanical treatment on the precipitation path, on the deformation mechanisms, and their interaction. The advantage of the D2AM optics is to provide an X-ray beam with a medium range size and divergence allowing precise measurements with sufficiently good statistics for real materials. X-ray diffraction and small-angle scattering (using, when appropriate, anomalous contrast), are very powerful tools for characterising defects and precipitates, in combination with instruments such as TEM or atom-probe, yielding information on a more local scale.

New generations of high performance steels (TWIP, TRIP) show complex mechanisms of plastic deformation, combining partial dislocations, stacking faults, twinning and strain induced martensitic transformations. Using powder diffraction measured by the 2D detector, we have been able to devise a new method of Bragg peak profile analysis[15] that is able to determine the density of these different crystal defects and also to determine the magnitude of long range internal stresses that develop due to the formation of dislocation pile-ups in these low stacking fault energy materials.

Two main directions have been taken in the characterization of precipitation processes in metallic alloys. The first is to determine in-situ the complex kinetic pathways in multi-constituent alloys. Chemical selectivity is obtained through anomalous studies, and the kinetics of microstructural evolution at the nanoscale is investigated under thermal conditions (isothermal and non-isothermal) and under the combination of temperature and plastic strain (*see inset page 12*).

[13] *Hosokawa et al.*, J. Phys. Conf. S. **144** (2009) 012055
[14] *Simon.*, J. Appl. Cryst. **40**, s1-s9 (2007)
[15] *Collet*, PhD, Grenoble-INP (2009)

Study of precipitation in metallic alloys: in-situ characterization

Precipitation evolution in metallic alloys under the combination of thermal and thermomechanical conditions has been achieved through the use of dedicated sample environments. Notably, a stress/strain apparatus combined with temperature control developed by the SIMaP laboratory specifically for the D2AM beam line allows small angle scattering signals to be monitored, and thus the precipitate microstructure (size and volume fraction of nanoscale particles), during any combination of stress and strain. In-situ thermal studies have been directed towards the study of the kinetic pathway of precipitation in multi-constituent alloys, where the presence of several solute species generates indeterminacy in the intermediate stages of particle composition when the material is moving towards thermodynamic equilibrium. We have for instance ascertained the reason for the exceptional resistance to temperature-induced coarsening of $Al_3(Zr,Sc)$ precipitates by determining the chemically heterogeneous core-shell structure[a].

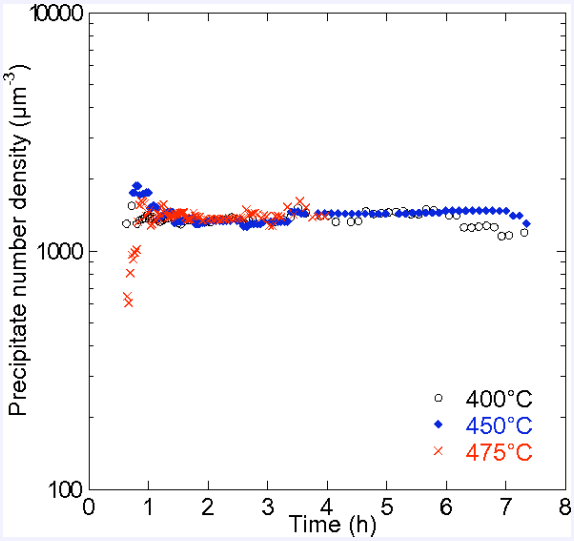

Fig. 1: Stability of Al3ZrSc precipitate number density evidenced in-situ during heat treatments on Aluminium alloys.

Anomalous studies across two edges (Zn and Cu K-edges) during time-resolved experiments at 160 °C on Al-Zn-Mg-Cu allowed us to establish the changes in composition of nanoscale precipitates during their heat treatment. We have shown that the evolution of corrosion resistance during heat treatment of these aerospace alloys was notably related to a progressive incorporation of copper in the precipitates and the corresponding decrease of Cu solute content in the aluminium matrix [1].

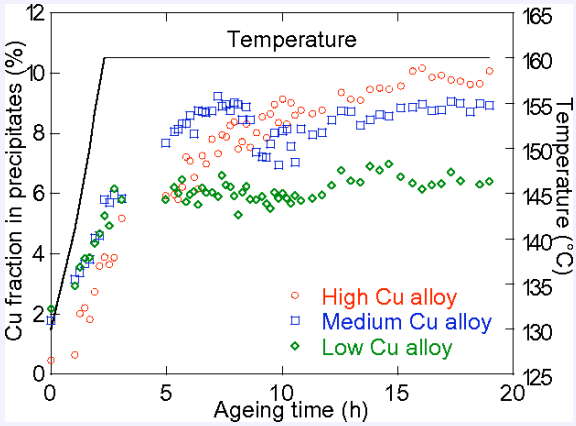

Fig. 1: Evolution of copper content in nanoscale precipitates in three different Al-Zn-Mg-Cu alloys of varying Zn/Cu ratio during heat treatment at 160 °C.

In-situ thermomechanical studies aimed at determining the degree of coupling between the presence of stress and strain and the progress of phase transformation. In particular, we have determined the extent of microstructure evolution under strain (e.g. creep) at moderate temperatures (and thus characterised the stability of microstructures). We have shown that evolution of precipitates was clearly related to the presence of dislocations, as the evolution of precipitates during straining was considerably faster than during simple heating. We also showed that precipitate microstructure could be modified by straining at temperatures where it was otherwise fully stable [2].

Principal Publications and authors:

[1] *T. Marlaud, A. Deschamps, F. Bley, B. Baroux*, 11th International Conference on Aluminium Alloys, vol 1, Wiley-VCH, Weinheim, Germany, Aachen, Germany, 2008, pp. 954-959.
[2] *G. Fribourg, A. Deschamps, Y. Bréchet, J. L. Chemin*, (Keynote lecture),11th International Conference on Aluminium Alloys, vol 1, Wiley-VCH, Weinheim, Germany, Aachen, Germany, 2008, pp. 936-946.

[a] *Clouet et al.*, Nature Materials **5** (2006) 482-488. *Deschamps et al.*, Acta Materialia **55** (2007) 2775-2783

The second direction is to characterise in a quantitative manner heterogeneous microstructures, and, particularly, welds. Several cutting edge welding techniques have been investigated, such as friction stir welding and electron beam welding. The distribution of precipitate microstructures induced by welding and post-welding heat treatment has been mapped (acquisition and interpretation of several thousand SAXS data sets).

3.2.2 Polymers

Polymer-solvent complexes

Nanoporous membranes based on polymer-solvent complexes or intercalates are an important new material with promising applications.
The liberation of solvent molecules from polymer-solvent complexes generates nanoporous structures that have a high storage capacity for small molecules.

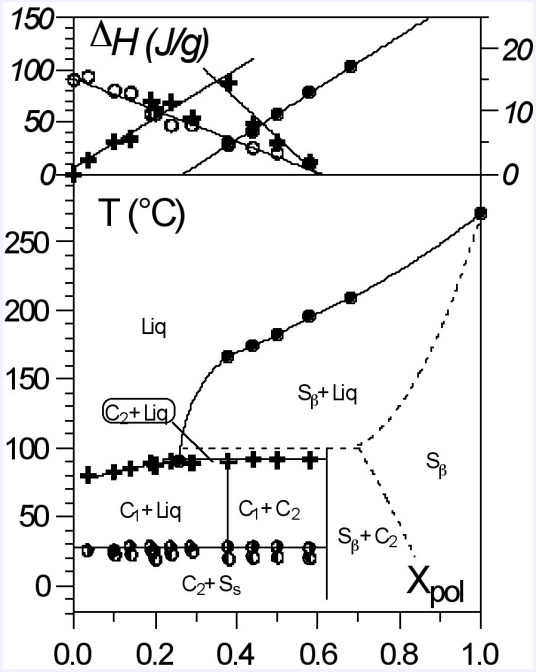

Fig. 1: Temperature-concentration phase diagram (lower) and Tamman's diagram (upper) for sPS/diphenylmethane system. There is a direct correspondence for the data point symbols in each diagram, except for the solvent melting enthalpy which stands for the sum of the enthalpies of the two solvent melting events.

WAXS and SAXS experiments provide rapid and precise information on the phase diagram of these compounds. As an example, the temperature-concentration phase diagram of syndiotactic polystyrene/biphenyl systems is illustrated in figure 1. The occurrence of two compounds is revealed (C_1 and C_2). Application of the Gibbs phase rules (no more than 3 phases for a binary system) implies the existence of a small domain above 90 °C (domain C_2 + liquid the upper limit approximated by a dotted line).
Since DSC experiments at much lower heating rates are unable to resolve the endotherm, no definite conclusion can be drawn about the existence of this domain. Time-resolved X-ray diffraction measurements at the same heating rate as for the DSC experiments confirm the findings obtained from the T-C phase diagram. In figure 2 the occurrence of another crystalline form (reflections shown with arrow at $Q = 6.8 \pm 0.1\,\mathrm{nm}^{-1}$) is clearly visible in the range $90 < T < 110\,^o$C.

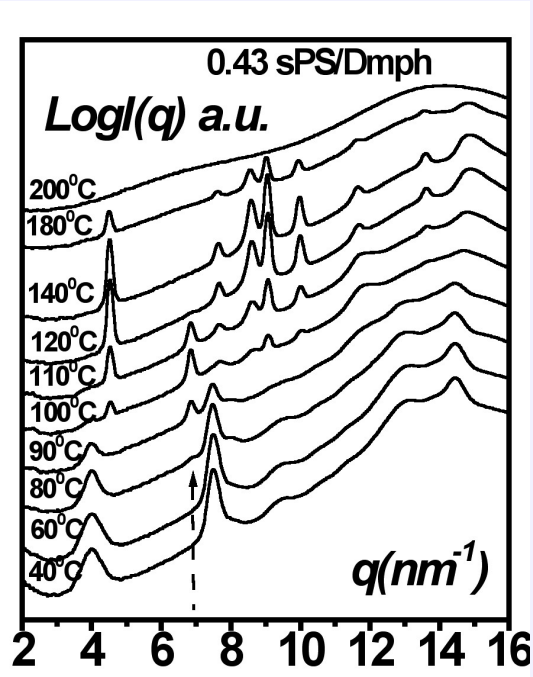

Fig. 2: Time-resolved X-ray experiments as a function of temperature for sPS/diphenylmethane system $C = 0.43$ w/w.

Principal Publications and authors:

Malik S., Rochas C. and J.-M. Guenet Macromolecules **39** (2006) 1000-1007

The properties of filled solid polymers are essentially determined by the structure, the surface chemistry and the nature of the dispersion of the filler. Strong demand for in-situ X-ray characterization of such materials originates both from academic institutions and industry. This is particularly important in modern production techniques in which the filler is formed in situ, thus bypassing the need for mechanical blending. As an example the study of polymer-solvent complexes for which phase diagrams need to be defined is given in page 13. In biological engineering, improvements in the regeneration of natural tissues after injury have been investigated in freshly removed samples of skin in collaboration the Centre de Recherche du Service de Santé des Armées (Grenoble) and Ecole Vétérinaire (Lyon).

3.3 Nanostructures

Recent progress in nanoscience and nanotechnologies leads to new demands for characterization of manufactured objects down to the atomic and mesoscopic scales. This is especially the case for devices made of semiconductor heterostructures but also oxide multilayers appearing for specific properties.

3.3.1 Strain and composition of semiconductor nanostructures by grazing incidence Diffraction Anomalous Fine Structure spectroscopy

Since the last BLRP in 2004, much effort has been devoted on beam line BM2 to improve grazing incidence Diffraction Anomalous Fine Structure spectroscopy, to focus on nano-object structural properties. A knowledge of the strain, chemical composition, atomic inter-mixing and ordering, is mandatory for understanding the growth mechanism as well as the electronic and optical properties of as-grown or encapsulated nanostructures[16]. Capping plays a decisive role in the physical properties by modifying the strain and, in some cases, by inducing atomic inter-mixing.

Recently, two techniques, grazing incidence Multi-wavelength Anomalous Diffraction(MAD) and grazing incidence Diffraction Anomalous Fine Structure spectroscopy (DAFS), have been combined to address the issue of structural properties of as-grown or encapsulated nanonostructures. By measuring diffraction at different energies close to an absorption edge, the scattering amplitude of the resonant atoms can be extracted and their mapping determined using MAD (chemical selectivity). This gives information on the average strain, composition and size of resonant atom containing iso-strain volumes. DAFS gives information on the local environment of resonant atoms located in an iso-strain volume selected by diffraction (fixed Q, spatial selectivity). The combination of these two techniques, together with Monte Carlo atomistic simulation to analyse the data, has proved to be a unique and powerful approach to obtain the most reliable values of strain and composition within nano-islands.

In the past few years, grazing incidence MAD and DAFS has been applied to materials of high technological interest, such as InAs/InP(001) quantum wires[17], GaN/AlN(001) quantum dots[18]. The case of GeSi/Si(001) is discussed page 15.

A recent review can be found in chapters 10 and 11 of the book "Characterization of Semiconductor Heterostructures and Nanostructures"[19].

3.3.2 Nano object morphology and arrangement studied by Grazing Incidence SAXS

The strong development of nanotechnologies in the Grenoble area induce us to offer new experimental possibilities on the beam line : a GISAXS instrument. This set-up has been used in numerous collaborations involving the SIMaP (Grenoble-INP) : LETI-CEA (Grenoble), University of Poitiers, University of Konstanz.

[16] *Stangl et al.*, Rev. Mod. Phys. **76** (2004) 725
[17] *Letoublon et al.*, Phys. Rev. Lett. **92** (2004) 186101
[18] *Coraux et al.*, Phys. Rev. B **73** (2006) 205343, **75** (2007) 235312; Appl. Phys. Lett. **88** (2006) 153125
[19] *Lamberti*, Elsevier Science, Amsterdam (2008)

MAD and DAFS applied to Ge_xSi_{1-x} domes grown on nominal Si(100)

The knowledge of 3D strain and chemical composition, atomic inter-mixing and ordering, is mandatory for an understanding of the growth mechanism, as well as the electronic and optical properties of as-grown or encapsulated nanostructures[a]. Below, we report on one of our most recent works on combining Multiwavelength Anomalous Diffraction and Diffraction Anomalous Fine Structure in grazing incidence to study Ge_xSi_{1-x} domes grown on Si(001). MAD at the Ge K-edge (11.103 keV) was used to map the Ge content in the reciprocal space. Figure 1 shows the Ge content x as a function of the reciprocal lattice unit h near the 400 reflection of the Si substrate. According to Iso Strain Scattering theory[b], an iso-strain region located at height z above the Si surface can be associated with an h value. MAD results show a Ge content of 0.6-0.7 above $5-6\,$nm ($h = 3.97$). Below this h value, the substrate contributes to the diffraction and MAD overestimate the Si content.

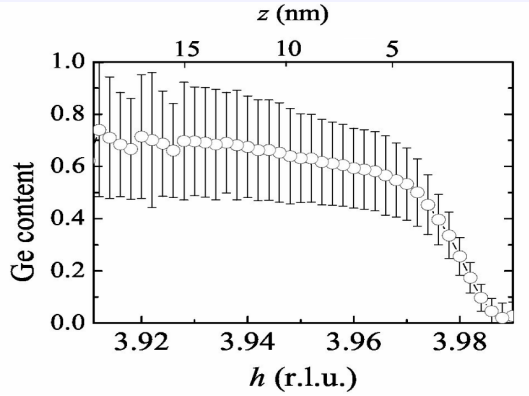

Fig. 1: Ge content as a function of reciprocal unit h and z for GeSi dome shapes grown on a nominal Si(001) surface, where z is the height above the Si surface of the corresponding iso-strain region (see text).

Figure 2 shows an experimental EDAFS spectrum (Extended-DAFS) measured on the Ge_xSi_{1-x} domes at the Ge K-edge. For comparison, theoretical EDAFS spectra obtained by atomistic simulation (Monte Carlo) based on the Tersoff potential, which is known to reproduce the inter-atomic distances in the IV-IV or III-V semiconductors, are also shown. The experimental EDAFS spectrum corresponds to an iso-strain region located at $z = 5 \pm 1\,$nm above the Si surface (Q : $h = 3.97, k = 0, l = 0$). The EDAFS oscillations show remarkable variations according to the composition in the Ge_xSi_{1-x} islands. These are well reproduced by atomistic simulation obtained for a Ge content of about $x = 0.5 - 0.6$, indicating the presence of a $Ge_{0.5}Si_{0.5}$ alloy, in agreement with the MAD results at the corresponding Q value ($h = 3.97$). The next step is to measure EDAFS at higher h values, close to the Si substrate 400 reflection ($h = 3.98$ for instance), to investigate strain and composition at the base of the islands, below $5-6\,$nm, near the island/substrate interface. The technique can also determine the local atomic order inside the diffraction selected iso-strain region. The atomistic simulations clearly show that the EDAFS spectra are very sensitive to the atomic arrangement of atoms (ordering) and composition.

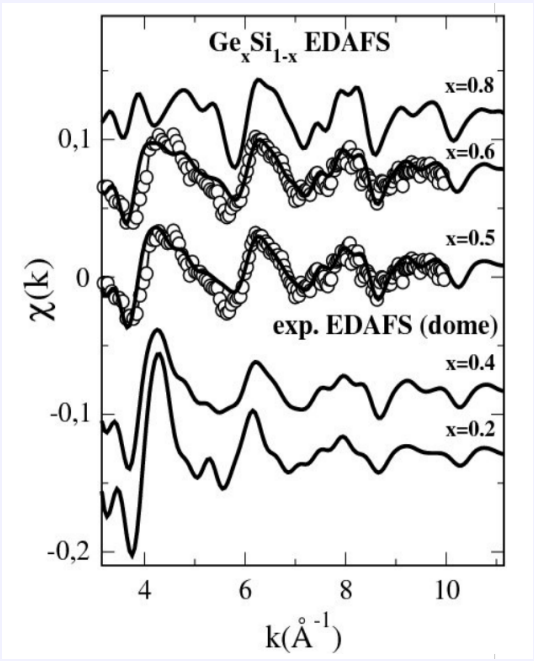

Fig. 2: Background-subtracted EDAFS spectrum of GeSi dome shapes. This corresponds to $h = 3.97$ ($z = 5 \pm 1\,$nm), shown together with theoretical EDAFS spectra obtained by atomistic simulations (MC) of relaxed Ge-Si alloys.

Principal publication and authors

H. Renevier, M.I. Richard, N. Ayape-Katcho, M.G. Proietti, V. Favre-Nicolin, G. Bauer, Eur. Phys. J. Special Topics **167** (2009) 3.

[a] *Stangl et al.*, Rev. Mod. Phys. **76** (2004) 725
[b] *Kegel et al.*, Phys. Rev. B **63** (2001) 035318

An experiment[20] devoted to the methodology of Anomalous GISAXS was performed to ensure that quantitative measurements can be extracted from the weak anomalous signal. Dedicated samples were prepared : nanocomposite films consisting of Au and/or Cu nanoclusters embedded in amorphous carbon matrices. Whenever relative intensities can be measured with precision, we show that AGISAXS, being element specific, is a powerful method for separating the scattering contributions of two types of metallic nanoclusters. The differential method appears to be the most efficient, since it almost suppresses dynamical effects (reflection, absorption and refraction corrections) and it eliminates the non-anomalous contribution, which is the major part of the signal.

Towards organized porosity in Ultra Low K dielectrics characterized by GISAXS

One of the present limitations of integrated circuit miniaturisation is cross-talk between wires through the dielectric barrier. Bulk SiOCH materials have a dielectric constant (k=$\epsilon\epsilon_o$) higher than 3. Pores have to be introduced into the dielectric matrix to decrease k (**U**ltra **L**ow **K** materials). Current attempts with a nearly 30% pore volume fraction reach k values close to 2. Such ULK materials with interconnected and disordered pores are not compatible with integration processes in terms of chemical absorption and mechanical properties.
One idea is to structure the porosity starting from suitable "silicon"-based polymer precursors, both to achieve the best mechanical properties and to have closed pores.
Model systems[a] such as mesoporous silica with well known pore patterns (cylinders, honeycomb, regular arrays of monodisperse spheres, ...) were first studied by GISAXS. A TEOS silica gel was compared with three pore patterns already studied : disordered percolating micropores smaller than a nanometre in size, mesopores of several nanometres and submicronic macropores. All images do not depend on a rotation around the normal to the layer: the samples select the domains that are in diffraction condition with a mosaic around the normal to the surface.

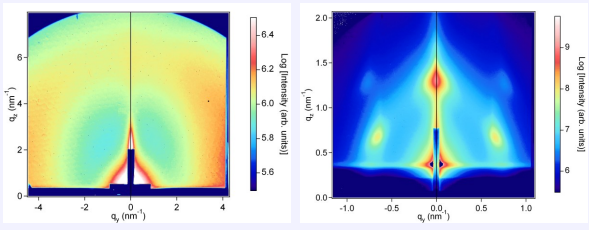

Fig 1: ULK prepared by PECVD, from left to right an unorganized nanoporous silica and an organized mesoporous silica.
Fig.1 left shows micropores (a fit is possible with pores of 0.6 nm of diameter with a $\approx 1\,nm$ correlation); right: mesopores organized in a quasi hexagonal lattice ($d = 5$ nm).
Families of organosilates were then studied, BTSE, a blend of MTSE and TEOS as precursors in different amounts...

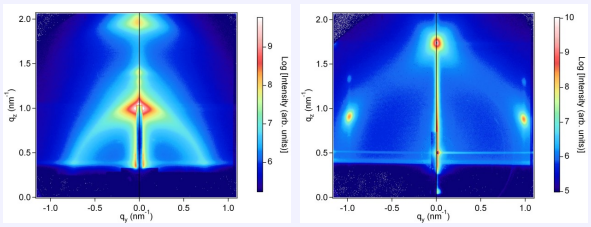

Fig 2: BTSE (layer organization together with distorted amorphous ring) and a blend of (MTSE/Silica (almost periodic hexagonal pattern) obtained for samples dried at 150 ^oC.

In Fig.2 right, two superimposed pore patterns: a pattern in strata that shrank from 6.3nm to 4.9nm by baking and a correlation ring from disordered pores with a preferential mean distance. These GISAXS images reveal pore patterns arranged on a nano-lattice with pseudo Bragg peaks at small angles: with this pattern-porosity description, the comparison between the nanoindentation measurements and the simulation of mechanical properties becomes meaningful.

Principal publications and authors:

V Jousseaume, G Rolland, D. Babonneau , JP Simon, Thin Solid Films, accepted (2009).
JP. Simon, V. Jousseaume, G. Rolland, J. Appl. Cryst., **40** (2007) s363-s366.

[a] ANR "PICSSEL" including CEA-LETI, IEM-Montpellier and SIMaP

[20] *Simon et al.*, J. Appl. Cryst. **42** (2009) 312-322

With long samples (80mm) the footprint of the beam remains well inside the sample, thus allowing comparative measurements of (integrated) intensities, using different grazing angles α_i.

Since 2007 various samples have been studied, such as uncapped magnetic Co_xPt_{1-x} dots prepared on WSe_2 or NaCl low binding surfaces, self organized ZrO_2 dots on Al_2O_3. Some studies have involved bubbles in implanted materials. He or Ne bubbles in SiC is a way of creating porosity, Ar bubbles in UO_2 (Cadarache-CEA) simulate the stress due to gas in nuclear fuel. GISAXS experiments appear to be a very sensitive way to characterize and distinguish the effect of the processing as illustrated on several dielectrics, porous SiOCH (see inset on page 16).

3.3.3 Epitaxial bi-axial strain engineering of ferroelectrics in multilayers.

The integration of perovskite materials, such as $BaTiO_3$ and $SrTiO_3$, into thin films and superlattices has attracted a great deal of attention over recent years due to their properties and the relevant numerous applications[21]. In particular, (001) oriented epitaxial $BaTiO_3/SrTiO_3$ superlattices can exhibit electrical properties[22] superior to those of the solid solution $(Ba/Sr)TiO_3$. First-principle calculations have shown a significant enhancement of the polarization in these superlattices over that of bulk $BaTiO_3$[23]. In such perovskite-based superlattices (SLs), the physical properties are strongly related to strain variation and atomic interdiffusion. Until recently, only a few high resolution diffraction analyses were performed on oxide SLs. Experiments carried out at D2AM[24] in collaboration with C. Dubourdieu, LMGP, showed that the chemical ordering in $BaTiO_3/SrTiO_3$ CVD-grown superlattices can be reliably estimated. [00l] diagrams for l=1 to 8 have been simultaneously simulated using a unique set of parameters describing the stack with a model based on periodic structural and chemical profiles. Accuracies as good as 5% can be obtained regarding the Ba and Sr atomic concentrations. Electron energy loss spectroscopy measurements at the Ba and the Sr edges give very good agreement with the diffusion profiles determined from our X-ray diffraction diagram simulations. In such oxide multilayers, the extracted chemical profile does not fully obey Vegard's law[25].

Another example on how the strain influences the orientation of the polarization in $PbTiO_3$ layers is given in inset, page 18.

3.4 Methods and instrumentation.

With the increasing number of experiments requiring grazing incidence with a small focal spot, imperfections in our optics became a sensitive issue. The bender has been changed to the standard CNRS-ESRF device to ensure better reproducibility of its movement. On this type of bender the anticlastic effect is minimized by ribs at the rear of the crystal. However this system modulates the focal length and all the rays do not converge in the same plane. To improve the convergence, some crystals without ribs in the central region have been tested. They greatly improve the horizontal focus at the price of some degradation in the vertical plane. Optimisation is being pursued to improve this focussing device and to increase the intensity for SAXS and Grazing Incidence experiments.

3.4.1 Methods

At present, apart from data collection for structural studies, a large proportion of experiments is done using slits, which means that lot of photons are wasted. To improve this situation, further effort is required on 2D detectors, but also on the usability of such 2D data. On D2AM effort has been put on both. Image pre-processing is performed, at a rate that allows changes in the radial distribution to be monitored during in-situ SAXS experiments. This procedure, which includes all the standard corrections (dark, flat field, grid distortions) can also be used in preparing goniometer maps.

[21] *Iijima et al.*, J. Appl. Phys. **72** (1992) 2840; *Gregg et al.*, J. Phys.: Condens. Matter **15** (2003) V11
[22] *Dubourdieu et al.*, Ferroelectrics **268** (2002) 137; *Tsai et al.*, J. Cryst. Growth **284** (2005) 65
[23] *Neaton et al.*, Appl. Phys. Lett. **82** (2003) 1586; *Lee et al.*, Nature **433** (2005) 395
[24] *M. Nemoz.*, PhD, Univ. J. Fourier (2004)
[25] *Nemoz et al.* J. of Appl. Phys. **100**(2006) 124110

Interlayer structural coupling in superlattices

As an example, we report on the characterization of superlattices based on $PbTiO_3$ (PT), a prototypical ferroelectric perovskite which is of great interest for applications such as non-volatile memories, pyroelectric detectors and piezoelectric devices. An intriguing result that clearly merits further pursuit, is the influence of the second constituent of the superlattice on the orientation of the polarization in the PT layers[a]. When PT is layered with a constituent exhibiting a large lattice mismatch, such as the ferroelectric $BaTiO_3$ (BT) or the relaxor $PbMg_{1/3}Nb_{2/3}O_3$ (PMN), the polar axis lies in the plane of the PT layers. However when the mismatch between the two constituents is small, as with the dielectric $SrTiO_3$ (ST), the polar axis is aligned along the growth direction.

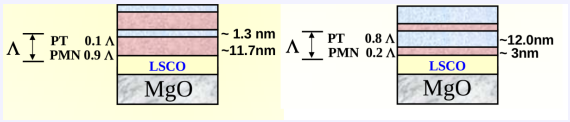

Fig. 1: Varying the relative thickness of layers inside the multilayer.

The understanding of these strain effects on the orientation of PT and its domain structure is very important since strains can induce a reduction of tetragonality (c/a) which can be correlated with the electric polarizability[b]. Strain effects are more intense in superlattices than in thin films, and thus a larger range of c/a values can be reached.

In order to investigate strain effects on PT layers, additional studies were performed on selected BT/PT and PMN/PT superlattices at D2AM (see fig. below for PMN/PT). For a constant superlattice period $\Lambda=\Delta_{PMN}+\Delta_{PT}$, we find that varying the relative constituent thicknesses Δ_{PMN} and Δ_{PT} causes a significant effect on the internal a1/a2 domain structure of the PT layers as well as on the unusual appearance of domains in PMN. In particular, PT imposes its in-plane a1/a2 domain pattern on the adjacent PMN layers when the Δ_{PMN}/Δ_{PT} ratio decreases. This has never, to our knowledge, been previously observed in pseudocubic bulk or thin-film relaxor materials. Moreover, the strain induced in these structures stabilizes the ferroelectric phase in the PT layers, at least up to 873 K, well above the bulk T_c of 765 K. The fact that, depending on the Δ_{PMN}/Δ_{PT} ratio, the PMN and PT layers adopt strikingly different structures highlights the in-plane structural coupling that can take place in superlattice systems. Since the strain effects on the structural patterns can be modulated by adjusting the Δ_{PMN}/Δ_{PT} ratio, this is one way to control the polar axis at a nanoscale level.

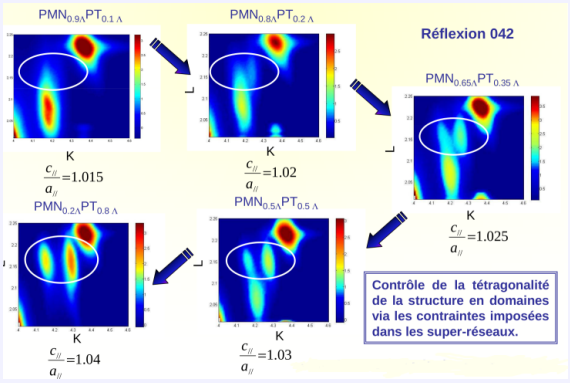

Fig. 2: Dependence of tetragonality from strain states in ferroelectric layers.

Main publication and authors:

Lemee N., Dooryhee E., Bouyanfif H., Le Marrec F., Nemoz M., Hodeau J.-L., Karkut M.G, Phys. Rev. B. 78, 140102 (2008)

[a] *Le Marec et al.* Phys. Rev. B **61** (2000) 6447(R), *Bouyanfif et al.* Phys. Rev. B **71** (2005) 020103(R)
[b] *Cohen et al.*, Nature **356** (1992) 136

On the goniometer, camera scans are used to reconstruct parts of reciprocal space with high resolution: such scans can strongly reduce the number of steps needed to reconstruct an *hkl* map, which increases from n to n^2 when slits are used. However, owing to non-linearity and to the dynamical range of intense peak, the remapping is not obvious. Satisfactory results are now obtained, as illustrated in the example of oxide multilayers.

Camera scans are also needed to obtain high resolution powder patterns. Standard reconstruction programs do not often allow high resolution images to be remapped accurately if they are far from the origin. A dedicated tool available on the beam line allows such reconstructions, and take misalignment

into account. This tool takes advantage of the 2D nature of images and avoids the asymmetric shape characteristic of powder profiles at low angles. The result produces high quality data that can be fitted using standard procedures.

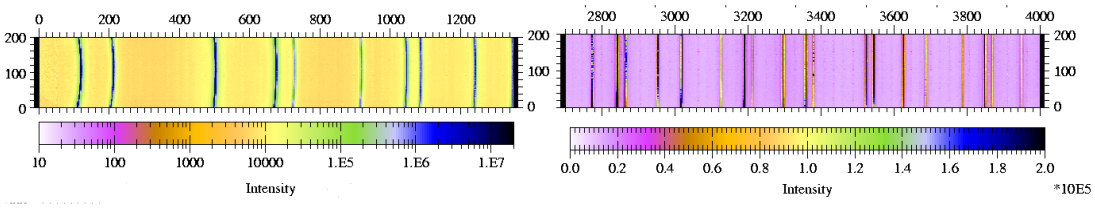

Figure 4: High resolution Debye Scherrer film reconstructed from 600 images taken with steps of 0.1 ^{o} 2θ leading to high quality powder data (right, first 20 ^{o}2θ and left last 20 ^{o} 2θ of a CeO_2 pattern.

3.4.2 Detector development

Third generation synchrotron sources have been of major importance for progress in materials science, but as detector technology has not kept up with advances in sources, a lot of photons are wasted. This situation stimulated beam line staff to become involved in a detector development program. A first phase[26] validated the use of hybrid pixel technology in constructing new modern detectors : they consist of a pixellized (330 μm) sensor bonded to dedicated electronic chips that incorporate both analogue and digital parts.

A real 2D detector composed of 8 modules of 8 chips was built[27], with which we performed a few experiments on multilayered compounds and on powders. As anomalous scattering is one of the concerns of the beam line, it was essential to ensure that the same quality of data could be attained with such 2D detectors. Anomalous high resolution data from the zeolite sample previously studied were collected by scanning the XPAD : data of at least the same quality were obtained, with a collection time that was reduced by a factor of about 12. Further analysis of the data showed that the collection time could have been reduced to one hundredth without degrading the data quality.

The detector, however, did not fulfil all our requirements and, to correct the observed weaknesses of the XPAD, a new chip had to be designed. This situation provided an opportunity to enlarge the cooperation. The SOLEIL detector group joined the project with the goal of achieving broad Si detectors as well as detectors using CdTe diodes that are suitable for high energies. Availability of industrial processing led to a change of design to the 0.25 μm IBM technology, thereby reducing the pixel size to 130 μm. Standard development steps culminated in a single chip detector using a dedicated test card in order to fully characterize it under operational conditions with a beam[28]. Modules were then assembled using $15 \times 76\, mm^2$ Si sensors, 500 μm thick. At the present time a first detector consisting of 8 ladders of 7 chips has been delivered (fig. 5), while two others are under assembly. These are composed of more than 5.10^5 pixels for an overall size of $120 \times 76\,\mathrm{mm}^2$. At the same time, a small CdTe detector ($15 \times 20\ mm^2$) has been tested in the energy range 8 - 40 keV.

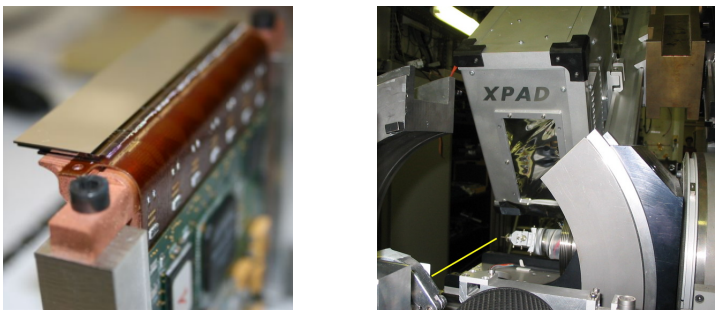

Figure 5: 7 chip ladder with Si sensor and the 8 ladder detector on D2AM goniometer

[26] *Berar et al.*, J. Appl. Cryst. **35** (2002) 471-476
[27] *Basolo et al.*, J. Synch. Rad. **14** (2007) 151-157
[28] *Pangaud et al.*, Nucl. Instr. and Meth. A **591** (2008) 159-162

Test experiments carried both on D2AM and SOLEIL beam lines reveal that these detectors are fully functional and it was decided that future detectors will be produced from them.

One of the major advantages of pixel detectors compared to CCDs is their dynamic range, but, more importantly, also the shape of the response to pulses. Owing to the direct conversion of incoming photons in the measured electron cloud, the point spread function has a very short extension and does not propagate intense signal, as opposed to detectors that use scintillators like X-ray CCDs, in which the PSF has almost Lorentzian tails. This makes pixel detectors the preferred system for measuring peak shapes and diffuse scattering.

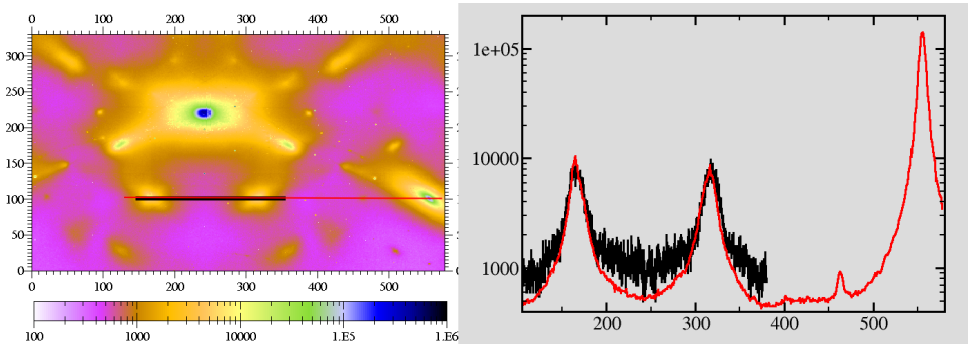

Figure 6: diffuse stattering from a Quasi crystal obtained with XPAD, slice (red) compared to same slice with CCD (black))

Moreover pixel detectors, by virtue of their internal gate, can be used without a mechanical shutter. They can therefore be used for time resolved experiments based on the bunch structure of the beam. This has been proved on a test experiment using the 4-bunch structure of the ESRF.

4 Towards "real materials" in-situ : future and plans for upgrading

In what follows we propose a major upgrade of the D2AM beam line that will give rise to a completely new instrument. It is primarily a response to changes in the requirements of the materials science community. It also responds to the tremendous progress achieved at the ESRF in the quality of the source, the present parameters of which largely outclass the characteristics of our optics, which were designed more than 15 years ago. Furthermore, the coming ESRF upgrade will introduce new optical constraints.

The future plans also take into account the present and future status of synchrotron radiation facilities, with, on one hand, the French source SOLEIL[29] and, on the other, the ESRF upgrade[30], with a major emphasis on nano-diffraction.

Finally, the proposed plans rely on what has been the strength of the D2AM beam line: beam stability, anomalous scattering and spectroscopy, and low background for measuring very weak signals.

One of the goals of present day materials science remains the understanding of the relationship between structure and physical properties, in order, ultimately, to 'tailor' physical properties for specific requirements. Whereas up to recent years studies have been carried out mainly on model systems (single phase, single grain) and the focus was on their atomic structure, several groups are now investigating "real materials" in their operating environment.

Real materials, either produced industrially or naturally found (e.g., geological samples), generally present an extremely complex hierarchical structure, with different length scales, different degrees of long range order, different kinds of disorder and defects, a distribution of strain and heterogeneities. This is well known in the metallurgy of structural alloys, where the size, shape and distribution of precipitates inside a matrix influences their mechanical properties. It is also true for functional materials, such as nano-structured oxides or semiconductors, and where the interfaces, the distribution of defects (dislocations, chemical disorder, vacancies...) largely influence their physical properties. Similar problems are found in polymers, biological materials, natural minerals of geological interest from the earth's mantle, a large number of materials of technological interest (cements, batteries, catalysts, alloys, composites, nanomaterials...), cultural heritage materials.

Such complex materials require an understanding of the structure and microstructure at the various relevant length scales: not only the atomic structure must be determined, but also their crystallinity, defects (dislocations, chemical disorder, short range order, etc.) and the associated strain and spatial distribution must be characterized. At larger scales it is often required to determine the overall mesoscopic organisation, such as grain shape and distribution in polycrystalline materials, density or heterogeneity fluctuations, the distribution of the different building blocks (e.g., in alloys and in polymers), and even their overall organisation.

Amoung these modern materials, there are important needs in the characterisation of nanostructures composed of semi-conducting, metallic or magnetic dots and thin oxide layers. These needs have to be covered at various length scales from the single object to the statistical properties of their assemblies. The purpose of our upgrade plan focuses on this last aspect. The strengths of X-ray techniques are primarily the high resolution in the determination of strain, the capacity to probe all correlation length scales, e.g. morphology and atomic structure, and the ability to average over sizes up to square millimetres : i.e., basically to provide statistically averaged information. Most often, X-ray data can be quantitatively analysed using the simple formalism of single scattering, with no or only a few assumptions. Frequently measurements require no special preparation or sample environment: it is a non-destructive probe and the penetration depth can be varied between a few nanometres to hundreds of micrometres with hard X-rays, thus probing both surface or near-surface structures, as well as the bulk of the sample.

It is also of importance to study materials in situ: this is the case for chemical reactions, the durability of materials while functioning, application of external mechanical stress, solidification processes, temperature dependence. The upgrade therefore also places emphasis on the sample environment

[29] http://www.synchrotron-soleil.fr
[30] http://www.esrf.fr/Upgrade/documentation/purple-book

and time dependent phenomena with characteristic time scales ranging from milliseconds to several minutes.

In order to attain the above targets we propose an important upgrade of the beam line and have defined a scientific case that has been approved by our authorities. Various actions to obtain the requisite financial support have already been started. In the following, the scientific case will, as it is a French document, be summarized, and the upgrade plan will be presented according its financial perspectives. Briefly, **our objective is a 6 to 40 keV sub-millimetric probe for multi-scale materials with the ability of doing spectroscopy measurements and characterizing materials under *operating* conditions** (in-situ anealing, applying a stress, ...). Practically, this means:

- a new monochromator designed for spectroscopy,
- mirrors with up-to-date polishing and curvature,
- a new goniometer suited for heavier and bigger sample environments
- a wider (4 m) SAXS camera

This project, which is based on D2AM specificity and expertise, will attain a new and needed step in modern sample characterization.

4.1 Scientific case

Numerous functional materials are heterogeneous: artificial (nanomaterials) or natural (ores). These "real materials" (i.e., materials as they are used for their functionality) exhibit complex hierarchical organization with graduation in order, disorder and heterogeneity. Their functionality is often due to the association/existence of a few parts (constituents) or of a specific interrelation between them (microstructure). Such hierarchy is found in geological minerals, environmental materials, cultural heritage samples, composites and hybrid materials, in biometric materials, numerous technological product (drugs, cements, alloys, catalysts, composites, nanomaterials, energy storage compounds, ...) and in materials that evolve in severe environments.

To understand better the functions and properties of "real materials", at least a description of their structure at the atomic scale and at the macroscopic/mesoscopic scale is required. The goal of present day materials science studies is to be able to relate the overall properties of the local atomic structures (orientation, strain, structural distortion, grain size,...) to those of their neighbours and thereby deduce the overall macroscopic properties.

The following presents questions related to some materials for which it appears that D2AM beam line expertise can bring new results in their characterization.

4.1.1 Nanostructures

Strains and chemical composition measured by anomalous diffraction : The knowledge of strain, chemical composition, atomic inter-mixing and ordering at the long and short range scales, is mandatory for understanding the growth mechanism as well as the electronic and optical properties of hetero and nanostructures. X-ray scattering/diffraction is a non destructive probe that is known to be highly sensitive to strain. However, determination of absolute strain values in 3 dimensions is a challenge because it is closely related to composition, shape and aspect ratio of the nanostructures, and to the mutual stress that nanostructures, substrate and capping exert on each other. To improve x-ray diffraction efficiency in the study of nanostructures, two complementary methods have been developed at the beamline BM2-D2AM. Both are based on resonant x-ray scattering.

A) Grazing Incidence Multiwavelength anomalous diffraction (GIMAD) allows the scattering amplitude of the resonant atoms (chemical mapping in the reciprocal space) to be extracted. It gives model-free information on strain, composition and size of iso-strain volumes containing resonant atoms, on strain and composition gradients in nanostructures or thin films.

B) Grazing Incidence Diffraction Anomalous Fine Structure (GIDAFS) spectroscopy determines the local environment of resonant atoms (chemical selectivity) located in an iso-strain volume selected by diffraction (spatial selectivity), as shown on page 15.

In the past few years, we have demonstrated the feasibility and, more importantly, the relevance of combining Grazing Incidence MAD and DAFS in the study of nanostructures. We have applied the method to systems of great technological interest, such as, for instance, semiconductor nanostructures (InAs/InP quantum wires, GaN/AlN and GeSi/Si quantum dots, nitride nanowires, ...). Obviously, it could also be easily applied to metallic or oxide nanostructures, thin films, core shell quantum dots, core shell nanowires, ... To provide easier access to the experiment for the wide scientific community it is clear that the beamline optics and the diffractometer must be updated.

Surface morphology and chemistry probed by GISAXS : Generally, coupled with chemical order characterization, GISAXS measurements can provide information on the possible relationships between the type of chemical ordering, size and equilibrium shape as well as the growth direction for epitaxial nanostructures. The BM32-SUV station has been dedicated to the study of the first step of the growth of such particles, but its heavy environment restricts it to very few samples. On the BM2-D2AM beam line, the design of a new GISAXS chamber operating at 10^{-6} torr enables measurements to be made on particles of different types of phases of alloys that have already been prepared elsewhere and to position them in the beam without exposure to air.

The contribution of resonant scattering is also well suited for studying nanoparticles of alloy phases. In these particles one species can segregate at the particle surface and anomalous GISAXS experiments allow the determination of the thickness of particle shell. For example, in CoCr-Pt based recording media, the alloy grains are enriched in Cr at the surface, leading to an increase of the coercivity field.

4.1.2 Electronic and Optoelectronic Devices

The strain states in thin solid films and nanostructures are nowadays used to change the physical properties of a large number of electronic and optoelectronic devices. For example in silicon and silicon/germanium transistor technology, the creation of elastic strain in silicon transistor channels is the most widely accepted method of enhancing the carrier mobility [31]. Two principal ways have been explored up to now : (i) local strain engineering within transistor module optimization through stacking of different materials and/or stressor implantations, and (ii) global strain introduction through the epitaxial growth of silicon on top of a silicon-germanium layer, followed by a layer transfer process to get strained Silicon On Insulator materials (sSOI). For these two methods, the deformations must be checked at the successive preparation steps to understand the strain-engineering of the devices, and for buried objects. This quantitative information can be obtained straightforwardly by grazing incidence X-ray diffraction (GIXRD) in such systems, the main requirements being to have access to a grazing incidence angle goniometer on a high flux beam line. More generally, nano-objects such as quantum dots or quantum wires have been studied with these techniques to obtain average deformation (and also sometimes the shape of the assembly distribution), or interdiffusion estimation with anomalous diffraction measurements. The use of these methods is even enlarged by giving complementary averaged information compared to electron microscopy and has direct application in the fields of:

- Substrate evaluation quality: strained Si, templates obtained by wafer bonding (for example on oxide), dewetting of thin layers, estimation of thermal strained
- Semiconductor heterostructure devices with 0D, 1D, 2D geometry (active part of the device).
- Estimation of high-K or metallic gate deposition on the strain.
- Back-end problems: low K deposition and metallic contacting of the active components.
- MENS and NEMS.
- Defect quantification in crystalline materials (stacking faults, dislocations, bonding defects)

GIXRD techniques will be also useful for understanding the strain evolution by varying the experimental conditions or cycling the materials (under current, thermal annealing, oxidizing atmosphere). It can be performed using a small environmental setup (e.g., a furnace under gas flow).

[31] *Pascale et al.*, Surf. Sci. **600** (2006) 3187-3193

As an example, Ge(TeSb) materials, already used in RW disks, are transparent and conducting in the stable crystalline phase and are opaque and resistive in the amorphous phase: the reversibility from the metastable glassy phase to the stable phase is critical, which requires an understanding of the crystal nucleation and growth mechanism. GIXRD will be a technique of choice[32].

To further decrease cross-talk between wires, low-k SiOCH dielectrics must be porous. Different pore patterns have already been deduced from GISAXS images, some of them with marked anisotropy. One of the dilemmas of back-end technology is the decrease in the mechanical properties: the route to better strength for same pore volume fraction is through selected organized pore patterns.

4.1.3 Oxide Materials

The move to smaller and smaller devices is mostly driven by recent expertise in semiconductor nanostructures. However, many other important functionalities are also required and therefore other types of nanostructure must be manufactured for their magnetic, ferroelectric, ... properties. Growing these structures relies on the growth mecanism caracterisation : atomic diffusion, quality of interfaces, ... Numerous such nanostructures have already been studied at the BM2-D2AM beam line. All require high flux (a small amount of material is often present), good signal-to-noise ratio and sometimes high resolution to measure several orders of magnitude of information and better characterize the state of strain and quality of the interface. When the contrast between atoms is too small, the anomalous effect can be used. It is also a means of obtaining redundant information on multilayers when the growth quality is mediocre and the number of reflections is small. Atomic concentration profiling can also benefit from this method [33].

Regarding the potential applications of ferroelectric materials in numerous electronic, electro-optic and acoustic devices, the fabrication and the investigation of ferroelectric oxide superlattices is a potentially rich field of inquiry. By combining ferroelectric layers with artificially modulated structures, it is possible to explore many of the topics that are of current interest, such as the role that size plays in the ferroelectric transition, ferroelectric coupling through ferroelectric or dielectric layers, and effects of strain on the ferroelectric properties. In superlattice structures for instance, the nature and the nanoscale thickness of the alternating layers control the orientation of the polarization, as recently demonstrated[34]. There is considerable interest in such orientational control in terms of opening up prospects in the electronic and electromechanical domains.

The next step is to characterize quantitatively thin oxide films and superlattice microstructures[35] : quality of the interfaces (roughness, inter-mixing), compositional and strain gradients, formation and orientation of polarized domains. A key point is to monitor these microstructures during thermal treatment (i.e., to simulate working conditions). Data acquisition, performed with a 2D detector to allow measurements during annealing and quantitative analysis are innovative and strong points of this project.

4.1.4 Applied Materials and Engineering

Our main interest is to study and correlate microstructures and defaults in industrial alloys with their mechanical properties. Other studies concentrate on the nanostructure of metallic samples, the characterisation of quasi-crystalline phases and also complex metallic alloys. Among all these investigations, the different scales : mean atomic structure, distribution of defects, nano- or microstructures, play a major role in the macroscopic properties, as is encountered in any multi-phase material. It is therefore very important to characterize them as accurately as possible, and in-situ experiments, such as applying a tensile stress, annealing, can bring relevant information.

Complex materials do not depend only on their crystalline structure but more often on grains or phase intermixing. This is well known in metals, the mechanical properties of which rely more

[32] S. Maitrejean (LETI/CENG), F. Hippert (LMGP/Grenoble-INP) submitted at Fondation Nanoscience.
[33] *Dechelette Barbara et al.*, J. Magn. Magn. Mater. **165** (1997) 8791
[34] *Lemée et al.*, Phys. Rev. B **78** (2008) 140102
[35] *Dubourdieu et al.* MRS, Boston (1999)

on domain boundaries than on their simple basic lattice. Spatial arrangement of phases plays a similar role in complex materials such as cements, storage compounds, ... The new tomographic diffraction method[36] allows such spatial relations to be analysed and the strains, compositions, ... of its constituents to be extracted. However, this approach is not restricted to the micron scale as described in original paper, but can be adapted to the sub-millimetre scale, as in the DIFTOMO ANR project.

4.1.5 Soft condensed matter

The studies currently carried out on the D2AM beam line cover a wide variety of systems like : polymers, colloids, biological compounds. These systems are often very complex either because they contain a large number of constituents, or they possess a multi-structured architecture, or they belong to both categories. Studied as solids, gels or in solution, all those systems display organization over a wide range of scales. SAXS experiments are therefore often performed at different resolutions, i.e., at different sample-detector distances, covering a Q range from 10^{-3} to $50\,\mathrm{nm}^{-1}$. These experiments also rely on various sample environments, either to facilitate the characterisation of numerous samples in strictly the same conditions (temperature, hygrometry, beam size) or to be able to modify a parameter such as (very often) the temperature, but also applying a stress.

The X-ray scattering technique has many advantages for this kind of study as it spans the required wide spatial resolution range (from SAXS to WAXS). Another advantage, compared to light scattering or neutron diffraction, is that opaque samples can be studied and also a short acquisition time can be attained for time resolved experiments.

4.2 Planned upgrade

The CRG BM2-D2AM was one of the very first beam lines to be opened at the ESRF in 1994. It was designed for bio-crystallography, X-ray diffraction and small angle X-ray scattering with the aim of performing multi-wavelength anomalous scattering experiments (MAD).

Since this opening, demand for characterisation of nanomaterials is still increasing as a result of the importance of Grenoble in nanoscience. In this perspective, maintaining an expert community in local laboratories and high grade characterisation tools close to them is essential.
The planned upgrade relies in our expertise in :

- thin film and nanostructure characterization,
- bulk crystalline or amorphous characterization,
- in-situ experiments,
- small angle experiments including GISAXS.,
- combination of both wide and small angles using the same samples.

For reasons of funding, the whole project has been divided into a small number of work packages that can be addressed to funding partners. It will maintain the overall optical design, the major qualities of which are a highly stable beam at the sample position and very low diffuse background.

4.2.1 A monochromator to ensure the survival of DAFS spectroscopy

The original design of the beam line optics does not take into account the requirement of X-ray spectroscopy and the diffractometer was not built for grazing incidence diffraction. The feasibility of MAD and DAFS experiments, in grazing incidence, was first demonstrated at BM2-D2AM. However, with the present beamline arrangement, alignment is time consuming and a considerable number of photons is lost : only 0.03 mrad of the X-ray horizontal spread is used out of the available 3 mrd. It is essential to optimize and renew the beamline optics and the diffractometer in order to make this unique tool available to the scientific community. It is important to note that no other beam line at the ESRF offers the possibility of performing DAFS experiments, even though the energy range (5-25 keV)

[36] *Bluet et al.*, Nature Materials **7** (2008) 468-472

is perfectly suited to most elements present in semiconductor nanostructures and is complementary to that already planned on the SOLEIL line SIRIUS (2-10 keV).

The minimum scheme for an upgrade is described below.

The current monochromateur is not optimized for this kind of experiment and, moreover, the out-of-date design and ageing of its mechanics considerably degrades the angular precision and repeatability (the beamline is now 15 years old !). It must be changed for a monochromator such as found on any spectroscopy beamline. We also plan to extend our energy range up to 40 keV to access more chemical elements and reach deeply buried objects and interfaces. Several manufacturers (Oxford, Kozu,. . .) have been contacted, but our preference has gone to adapting the monochromator developed for the French CRG FAME by Alain Prat from our Institute. Part of the financial support will be supplied by the "Fondation Nanoscience". The other part is still being negotiated with the CEA-LETI for the characterisation of their electronic and optoelectronics devices. The monochromator cooling must also be re-designed to benefit fully from the ESRF-upgrade (current soon to be increased to 300 mA, then to 500 mA, compared with 100 mA in 1994, which implies a higher heat load).

A new second crystal without ribs in the central region has been tested and used for DAFS experiments, and has given very encouraging results, namely more photons at the sample position, clean beam profile and stability. Also, SAXS experiments usually performed with a 2 mm horizontal beam (entrance slits S1) could be performed with an opening of 3.5 mm). A new focusing system including a narrower 2nd crystal, and its appropriate bender must now be designed. This study will be launched with the new monochromator.

. . . Furthermore, the use of new mirrors with better polishing (see next section) will substantially increase the flux.

4.2.2 Mirrors suited for smaller and sharper beam in the range 6-40 keV

There is a need to increase the flux delivered at high energy by the beam line optics since anomalous scattering experiments must access a wide range of elements and certain experiments on thick materials have to be done in transmission. Several crystals are therefore required (Si111, 220, 311) but also better polished mirrors (at 25keV with Si111 the incident angle on both mirror is 0.1^o).

Many experiments carried out at the beam line require a "small" beam, i.e., between 50 and 100 μm in both directions, either in SAXS, because very weak signals are to be resolved close to the direct beam, or in grazing incidence techniques, or in sample mapping as in investigations of welding. In all cases, a small beam means also a sharper beam, i.e., long tails that "pollute" the relevant signal must be avoided.

Furthermore, the poor quality of the two mirrors and their benders drastically limits the vertical portion of the useful X-ray fan. Since the delivery of our mirrors, however, dramatic progress has been achieved in surface polishing and coating technology. Financial support has been requested from the "ANR" programme through the DIFTOMO project (coordinator : J.L. Hodeau, Institut Néel) that is meant to develop the 3D structural and texture mapping at sub-millimetric resolution by X-ray Diffraction Computed Tomography. For samples of a few centimetres in size, a need exists for a medium and adaptable probe. Development of the "diffraction-tomography" method on a stable beam line is needed with a square shaped beam like that provided by the bending magnet CRG-D2AM at the ESRF (BM02). The basis of this method does not require the use of a micro beam (the choice made at the ESRF beam lines ID22 and ID15). The micro-beam choice simplifies the approach as the volume sampled is smaller. The chosen beam shape will introduce more restraints in the reconstruction phase.

4.2.3 Instruments

The goniometer For many studies, we want to implement in-situ experiments, implying relatively large sample environments (heating, surface annealing under gas, traction machine, ...). The limiting element is the goniometer : it does not offer enough room around the sample. At the present time, since the motor speeds have been reduced to conserve the required precision, mapping times can

become prohibitive ! We therefore need to purchase a recent KAPPA geometry goniometer such as that implemented on the SOLEIL beam lines. Attention will be paid to still being able to measure during the same experiment **both grazing incidence and out of plane diffraction peaks**.

A project, QMAX (coordinator : R. Guinebretière, SPCTS, CNRS Limoges), was submitted to the ANR-P3N program and should bring financial support for a new goniometer. This project consists in coupling XRD and GISAXS on the goniometer.

X-ray scattering has been broadly used in the past to characterize powder samples, bulk materials and thin films. With the ever-increasing interest in nanostructured materials and devices, size effects become prominent and often strongly complicate any straightforward interpretation of the scattering data, especially when the nanostructures exhibit a significant degree of size and shape dispersity, which is frequently the case in practice. This issue can be partly solved by combining different X-ray scattering methods operating in distinct regimes, namely Grazing Incidence Small Angle X-ray scattering (GISAXS) and High Resolution X-ray Diffraction (HR-XRD). GISAXS is a small angle scattering technique and is hence mainly sensitive to morphological features (shape, size, and spatial distribution of the nanostructures), whereas HR-XRD is sensitive to both morphological and crystallographic features (crystal defects and more generally microstructure). The coupling of both approaches constitutes the core of the present project. We propose to implement an innovative experimental HR-XRD / GISAXS set-up, combining microstructural characterization and high temperature thermal treatment (up to 1500 ^{o}C). The capability of this experimental platform to produce hands-on results (i.e., data reduction and data handling/modelling) directly depends on the availability of new user-oriented numerical tools dedicated to the quantitative characterization of nanostructures. Both the instrument and its accompanying software package will be put at the disposal of the growingly concerned French community. In parallel, this development and its commissioning/testing will be supported by an appropriate scientific issue, focussing on nanostructured compounds epitaxially grown onto oxide surfaces. The general goal of this project is thus to address the problem of the quantitative characterization of nanostructures, and to follow quantitatively the microstructure evolution of nanostructured films as a function of temperature. In many processes and devices, the engineering of the materials (design and properties) are governed in a large part by their (micro-)structural features. Therefore the proposed multi-modal instrument and its accompanying simulation/modelling package should have a significant impact in materials science, from both fundamental and applied points of view.

The SAXS camera For the SAXS station, we want to measure simultaneously small angles (SAXS) but also wide angles (WAXS) because in-situ experiments are often difficult to reproduce in the same way and measuring the small and wide angles separately is more tricky. For this we need to enlarge the SAXS table and the experimental hutch. The wide angle measurements are to be made with the 2D hybrid pixel detector XPAD, developed by our team and soon becoming available. The modular detector concept introduced by the pixel detector enables new 2D detector shapes to be defined in which holes are allowed. It will then be possible to record small and wide angles simultaneously.

4.3 Summary of the planned upgrade

As shown in previous sections, there are common requirements covered by the various techniques encountered. Nonetheless, this project has been launched through diverse actions to spread the load over the different possible financial supports. Its main actions are summarized in the following table :

Monochromator	2009-2010	Fondation Nanosciences + LETI
Mirrors	2010-2012	ANR DIFTOMO
Goniometer	2010-2012	ANR-P3N QMAX (+ part of annual budget)
SAXS	2010-2013	to be defined
pixel 2D Detector	2004-2009	prototype already financed

At the present time, all the financial support has not yet been confirmed. The first step, however, i.e., the new monochromator, received a positive answer from the Fondation Nanoscience and will be started as soon as the LETI agreement is finalized.

It has to be noted that this project will require human resources and that the beam line responsible and one engineer will soon retire. To ensure proper transfer of knowledge and smooth running of the beam line at least one new scientist is necessary to reinforce the staff before these retirements take place.

The common objectives of these packages are to provide a beam between 6 and 40 keV with a flux increased by a factor 5 to 10, a beam sizereduced to about $100\mu m$ horizontally and $50\mu m$ vertically and to provide up-to-date instruments in the context of the opening of the new beam lines at SOLEIL and of the upgrade of ESRF source.

- DAFS spectrosopy applied to nanomaterials,
- GISAXS applied to structured surfaces,

will seen their potentialialities enhanced and new speciess of materials can be approached.

This project will strengthen the BM2-D2AM beam line capabilities for the characterisation of nano- and multi-scale materials, using its well established expertise in anomalous experiments. Attention will be paid to conserve its strengths : **beam stability, good signal to noise ratio, versatile instruments** on which laboratory sample environments can be installed.

5 Scientific production 2005-2009

5.1 Theses

Theses, PhD 2009

1. Collet Jean-Louis, *Les mécanismes de déformation d'un acier TWIP FeMnC : une étude par diffraction des rayons X*, 2009-03-09, Grenoble-INP

French DHDR ... 2009

1. Dooryhee Eric, *Etude par diffraction de super réseaux d'oxydes pérovskites*, 2009-03-25, UJF, Grenoble

Theses, PhD 2008

1. Osorio Anayancy, *Wiskers de chitosane pour bio nanocomposites*, 2008-09-30, Lyon
2. Marlaud T., *Microstructures de précipitation et mécanismes de corrosion feuilletante dans les alliages d'Aluminium de la série 7000 à très hautes caractéristiques mécaniques*, 2008-04-28, INPG, Grenoble

Theses, PhD 2007

1. Richard Marie-Ingrid, *The growth of Ge islands on nominal and pre-patterned Si(001) surfaces: in situ and ex situ X-ray studies*, 2007-12-14, UJF, Grenoble
2. Kosik Katalin, *Interactions de phenols avec des hydrogels fonctionnalisés* , 2007-10-11, Univ. Tech. and Eco., Budapest and Univ. J. Fourier, Grenoble
3. Pacheco Claire, *Etude de films d'or sur matière vitreuse : application à la céramique glaçurée Islamique médiévale Asie Centrale XIV-XVème s. Iran XII-XIIIème s.*, 2007-09-21, Université Michel de Montaigne, Bordeaux
4. Ladet Sebastien, *Nouveaux dispositifs multimembranaires, bioactif leures des milieux biologiques.*, 2007-01-16, Univ. C. Bernard, Lyon
5. Maiez Sarah, *Relation entre la structure chimique d'un copolymère à blocs et la nanostructuration d'un polymere réticulé*, 2007-01-16, INSA Lyon

Theses, PhD 2006

1. Reguer Solenn, *Phases chlorées sur les objets archéologiques ferreux corrodés dans les sols : caractérisation et mécanismes de formation.*, 2006-11-25, Universite Paris XI Orsay
2. Coraux Johann, *Etude par spectroscopie X en condition de diffraction de la croissance et de l'encapsulation de boites quantiques GaN/AlN.*, 2006-10-04, Univ. J Fourier, Grenoble
3. Francoual Sonia, *Phonons et phasons dans les quasicristaux de symetrie icosaédrique et dans leurs approximants 1/1 périodiques.*, 2006-04-25, INPG, Grenoble
4. Elazzouzi Samira, *Auto-organisation de wiskers de cellulose en suspension dans l'eau ou dans les solvants organiques apolaires.*, 2006-04-21, Lyon
5. Hakme Chady, *Microstructure et mobilité moléculaire du PEN étiré*, 2006-03-13, Univ. C. Bernard, Lyon
6. Wypych Alexandra, *Effect of structural changes on the relaxational and low-frequency vibrational dynamics of polymer glasses*, 2006-01-20, Univ. Lotz

Theses, PhD 2005

1. Celle Caroline, *Films mince et ultra-minces de polymères amorphe et semi-cristallins : Elaboration-Structure et Morphologie-Propriétés particulières (Tg, Tf, Tc)*, 2005-12-14, Univ. C. Bernard, Lyon
2. Mougin Bruno, *Elaboration de matériaux nanocomposites polyamide 6,6/ silice par génération de la charge inorganique in situ au cours de l'étape d'extrusion.*, 2005-06-16, Univ. C. Bernard, Lyon
3. Mendoza Rennan, *Morphologies induites dans les pièces en polyolefine moulées par injection.*, 2005-05-30, Ecole des Arts et Métiers, Lyon
4. Ramier J., *Comportement mécanique d'élastomères chargés, influence de l'adhésion charge - polymère, influence de la morphologie.*, 2005-03-30, INSA, Lyon

Other memories 2005

1. Martin Gregory, *Ingénieur ISTIL/DEA : Synthèse et caractérisation de nanocomposites polymère-oxyde de lanthane*, 2000-06-30, ISTIL/DEA

5.2 Articles

Articles 2009

1. Bloch E., Llewellyn P.L., Phan T., Bertin D., Hornebecq V., *On defining a simple empirical relationship to predict the pore size of mesoporous silicas prepared from PEO-b-PS diblock copolymers*, Chemistry of Materials (2009) **21**, 48-55
2. Boulle A., Conchon F., Guinebretiere R., *Strain profiles in thin films: influence of a coherently diffracting substrate and thickness fluctuations*, J. Appl. Cryst. (2009) **42**, 85-92
3. Cassol Bruner F., Clemens J.C., Hemmer C., Morel C., *Imaging performance of the hybrid pixel detectors XPAD3-S*, Phys. Med. and Biol. (2009) **54**, 1773-1789
4. Jousseaume V., Rolland G, Babonneau D., Simon J.P., *Influence of the polymeric porogen on porosity and on mechanical properties of spin coated Ultra Low K dielectrics*, Thin Solid Films (2009), accepted
5. Meneghini C., Boscherini , Pasquini L., Renevier H., *Diffraction anomalous fine structure study of iron/iron oxide nanoparticles.*, J. Appl. Cryst. (2009), à paraître
6. Palancher H., Wieschalla N., Martin G., Tucoulou R., sabatier C., Petry W., Berar J.F., Valot C., Dubois S., *Uranium-molybdenum nuclear fuel plates behaviour under heavy ion irradiation: An X-ray diffraction analysis*, J. Nucl. Mat. (2009) **385**, 449-455
7. Richard M.I., Favre-Nicolin V., Renaud G., Schulli T., Priester C., Zhong Z. , Metzger T.H., *Multiple scattering effects in strain and composition analysis of nanoislands by grazing incidence X-rays*, Appl. Phys. Lett. (2009) **94**, 013112-1-013112-3
8. Sarazin D., Rochas C., Kutsevol N., Guenet J.-M, *Anomalous behaviour of comb-like dextran–polyacrylamide* , Eur. Polym. J. (2009), in press
9. Simon J.P., Babonneau D., Drouet M., Lyon O., *Anomalous grazing incidence small-angle X-ray scattering of carbon-encapsulated Au and Cu clusters.*, J. Appl. Cryst. (2009) **42**, 312-322

Articles 2008

1. Amstatt B, Landre O., Favre-Nicolin V., Proietti M.G., Bellet-amalric E., Bougerol-Chaillout C., Renevier H., Daudin B., *Anisotropic strain state of the [1-100] GaN quantum dots and quantumwires*, J. Appl. Phys. (2008) **104**, 063521
2. Antion C., Donnadieu P., Blandin J.J., Bley F., Deschamps A., Tassin C., Pisch A., *Hardening precipitation and mechanical properties in new MgMnYGd alloys*, Int. J. of Mat. Research (2008) **99**, 168-177
3. Basolo S., Berar J.F., Boudet N., Breugnon P., Chantepie B., Clemens J.C., Delpierre P., Dinkespiler B., Hustache S., Medjoubi K., Menouni M., Morel C., Pangaud P., Vigeolas E., *A 20 kpixels CdTe photon-counting imager using XPAD chip*, Nucl. Instr. and Meth. A (2008) **589**, 268–274
4. Blasco J., Garcia J., Subias Peruga G., Renevier H., Stingaciau m., Herrero-martin J., *Resonant xray scattering study of the metalinsulator transition inthe layered perovskite TbBaCo2O5.5*, Phys. Rev. B (2008) **78**, 054123
5. Conchon F., Boulle A., Guinebretiere R., Dooryhee E., Hodeau J.-L., Girardot C., Pignard S., Kreisel J., Weiss F., *The role of strain-induced structural changes in the metal–insulator transition in epitaxial SmNiO3 films*, J. Phys. Cond. Mat. (2008) **20**, 145216
6. Conchon F., Boulle A., Guinebretiere R., Dooryhee E., Hodeau J.-L., Girardot C., Pignard S., Kreisel J., Weiss F., Libralesso L., Lee T.L., *Investigation of strain relaxation mechanisms and transport properties in epitaxial SmNiO3 films*, J. Appl. Phys. (2008) **103**, 123501-1-123501-8
7. Constantin D., Pansu B., Imperor-Clerc M., Davidson P., *Repulsion between inorganic particles inserted within surfactant bilayers* , Phys. Rev. Let. (2008) **101**, 098101
8. Czakkel O., Szilágyi I., Geissler E., Kanellopoulos N., Laszlo K., *Morphological Characterization of Oxidized and Metal Impregnated Spherical Carbons*, Progr. Coll. Pol. Sc. (2008), 135, 139-147
9. Dasgupta D., Manna S., Garai A., Dawn A., Rochas C., Guenet J.-M, Nandi A.K., *Morphology, structure, rheology, and thermodynamics of piezoelectric poly(vinylidene fluoride)-ethylene carbonate thermoreversible gel*, Macromolecules (2008) **41**, 779-787
10. Drogoz A., Munier S., Verrier B., David L., Domard A., Delair T., *Towards biocompatible vaccine delivery systems: Interactions of colloidal PECs based on polysaccharides with HIV-1 p24 antigen*, Biomacromolecules (2008) **9**, 583-591
11. Echard J.P., Cotte M., Dooryhee E., Bertrand L., *Insights into the varnishes of historical musical instruments using synchrotron micro-analytical methods*, Appl. Phys. A (2008) **92**, 77-81
12. Elazzouzi-Hafraoui S., Nishiyama Y., Putaux J.L., Heux L., Dubreuil F., Rochas C., *The shape and size distribution of crystalline nanoparticles prepared by acid hydrolysis of native cellulose*, Biomacromolecules (2008) **9**, 57-65

13. Ersen O., Parmentier J., Drillon M., Pham-huu C., Solovyov L., Schultz P.J., Werckmann J., *Direct observation of stacking faults and pore connections in ordered cage-type mesoporous silica FDU-12 by electron tomography*, J. Amer. Chem. Soc. (2008) **130**, 16800-16806
14. Horkay F., Basser P.J., Hecht A.-M., Geissler E., *Gel-like behavior in aggrecan assemblies*, J. Chem. Phys. (2008) **128**, 135103-1-135103-7
15. Horkay F., Basser P.J., Hecht A.-M., Geissler E., *Insensitivity of Aggrecan Assembly to Salt*, Phys. Rev. Let. (2008) **101**, 068301
16. Kosik K., Wilk E., Geissler E., Laszlo K., *Interaction of phenols with thermo-responsive hydrogels*, Colloids and Surf. (2008) **A 319**, 159-164
17. Kosik K., Wilk E., Geissler E., Laszlo K., *Influence of a crown ether comonomer on the temperature-induced phase transition of poly(N-isopropylacrylamide) hydrogels*, J. Phys. Chem. B (2008) **112**, 1065-1070
18. Laszlo K., Czakkel O., Geissler E., *Wetting and non-wetting fluids in surface-functionalised activated carbons*, Colloid and Polymer Science (2008) **286**, 59-65
19. Laszlo K., Rochas C., Geissler E., *Water Vapour Adsorption and Contrast-Modified SAXS in Microporous Polymer-Based Carbons of Different Surface Chemistry*, Adsorption (2008) **14**, 447–455
20. Lemee N., Dooryhee E., Bouyanfif H., Le Marrec F., Nemoz M., Hodeau J.-L., Karkut M.G,, *Synchrotron x-ray scattering evidence for interlayer structural coupling in (PbMg1/3Nb2/3O3)(1-x)/(PbTiO3)x superlattices.*, Phys. Rev. B (2008) **78**, 140102
21. Marakov D., Liscio F., Brombacher C., Simon J.P., Schatz G., Maret M., Albrecht M., *CoPt alloy grown on the WSe2(0 0 0 1) van der Waals surface*, J. Mag. Mag. Mat. (2008) **320**, 1858-1866
22. Olivier L., Sabard D., Fulchiron R., Espuche E., David L., Guiu A., *Influence of alpha-ZrP fillers and process conditions on the morphology and the gas barrier properties of filled polyamide 6 films.*, J. Polymer Science B Pol Phys (2008), 46(16) p1734-1746
23. Pangaud P., Basolo S., Boudet N., Berar J.F., Chantepie B., Clemens J.C., Delpierre P., Dinkespiler B., Medjoubi K., Hustache S., Menouni M., Morel C., *XPAD3-s : A fast hybrid pixel readout chip for Xray Synchrotron facilities.*, Nucl. Instr. and Meth. A (2008) **591**, 159-162
24. Le Parc R., Champagnon B., Levelut C., Martinez V., David L., Faivre A., Flammer I., Hazemann J.-L., Simon J.P., *Density and concentration fluctuations in SiO2–GeO2 optical fiber glass investigated by small angle x-ray scattering*, J. Appl. Phys. (2008) **103**, 094917
25. Pascal C., Cabane B., Poncet-legrand Céline, Vernhet A., *Aggregation of a Proline-Rich Protein Induced by Epigallocatechin Gallate and Condensed Tannins: Effect of Protein Glycosylation*, J. Agric. Food. Chem. (2008) **56 (15)**, 6724-6732
26. Pereira F.V., Merlo A.A., Bley F., Morfin I., Ritter O.M.S., da Silveira N., Ehrburger-Dolle F., *Smectic ordering in side-chain liquid crystalline polymers (LCPs) and in CP-silica nanocomposites*, Liquid Cryst. (2008) **35(3)**, 299-313
27. Pereira F.V., Merlo A.A., Bley F., Morfin I., Pesce da Silveira N., Ritter O.M.S., Ehrburger-Dolle F., *Smectic ordering in side-chain liquid crystalline polymers (LCPs) and in LCP-silica nanocomposites*, Mol. Cryst. Liq. Cryst. (2008) **35**, 299-313
28. Perez P., Plieva F., Gallardo A., San Roman J., Aguilar M.R., Morfin I., Ehrburger-Dolle F., Bley F., Mikhalovsky S., Galaev I.Y., Mattiasson B., *Bioresorbable and nonresorbable macroporous thermosensitive hydrogels prepared by cryopolymerization. Role of the cross-linking agent*, Biomacromolecules (2008) **9**, 66-74
29. Robitzer M., David L., Rochas C., Di Renzo F., Quignard F., *Nanostructure of Calcium Alginate Aerogels Obtained from Multistep Solvent Exchange Route*, Langmuir (2008) **24**
30. Robitzer M., David L., Rochas C., Di Renzo F., Quignard F., *Nanostructure of Calcium Alginate Aerogels Obtained from Multistep Solvent Exchange Route*, Langmuir (2008), 24, 12547-12552
31. Robitzer M., David L., Quignard F., Rochas C., Di Renzo F., *Supercritically-Dried Alginate Aerogels Retain the Fibrillar Structure of the Hydrogels*, Macromolecular Symposia (2008) **273**, 80-84
32. Rohl A.L. , Moret M., Kaminsky W., Claborn K., Mckinnon J.J., Kahr B., *Hirshfeld surfaces identify inadequacies in computations of intermolecular interactions in crystals: Pentamorphic 1,8-dihydroxyanthraquinone*, Crystal Growth Design (2008) **8**, 4517-4525
33. Sigaev V.N., Golubev N.V., Stefanovich S.Yu., Komatsu T., Benino Y., Pernice P., Aronne A., Fanelli E., Champagnon B., Califano V., Vouagner D., *Second-order optical non-linearity initiated in Li2O-Nb2O5-SiO2 and Li2O-ZnO-Nb2O5-SiO2 glasses by formation of polar and centrosymmetric nanostructures*, J. Non-Crystal. Solids (2008) **354**, 873-881
34. Sinkó K. , Torma V., Kovács A, *SAXS investigation of porous nanostructures*, J. Non-Crystal. Solids (2008) **354**, 5466-5474
35. Vidal V., Thilly L., Girault B., Renault P.O., Le Bourhis E., Villain-valat P., Goudeau P., Tranchant

J., Landesman J.P., Tessier P.Y., Angleraud B., Besland M.P., Djouadi A., Geandier G., *Small scale mechanical properties of polycrystalline materials: In situ diffraction studies*, Int. J. Nanotechnology (2008) **5**, 609-630

Proceedings 2008 not cited in Conferences lists

1. Hazemann J.-L., Bruyere R., Prat A., Goujon C., *A new pressure regulation device using high pressure isolation valves*, J. Phys : Conf. Ser. (2008) **121**, 122003-1-122003-4

Articles 2007

1. Al Jebawi K., Sixou B., Seguela R., Vigier G., *Hot compaction of polyoxymethylene. II. Structural characterization*, J. Polymer Science B Pol Phys (2007) **106 (2)**, 757-764
2. Basolo S., Berar J.F., Boudet N., Breugnon P., Caillot B., Clemens J.C., Delpierre P., Dinkespiler B., Hustache S., Koudobine I., Meessen Ch., Menouni M., Mouget C., Palancher H., Pangaud P., Potheau R., Vigeolas E., *Application of hybrid pixel detector to powder diffraction.*, J. Sync. Rad. (2007) **14**, 151-157
3. Benoudia M.C., Roussel J.M., Labat S., Thomas O., Beke D.L., Langer G., Kis-Varga M., *Investigating interdiffusion in Mo/V multilayers from X-ray scattering and kinetic simulations*, Diffusion and Defect Data (2007) **264**, 13-18
4. Bershtein V.A., Egorov V.M., Yakushev P.N., David L., Fainleib A.M., Grigorieva O.P., Bei I., Kripotou S., Pissis P., *Structure and Dynamics/compositional Heterogeneity in polycyanurate-poly(Tetramethylene Glycol) hybrid networks*, J. Macromol. Sc. B Phys. (2007) **46**, 207-230
5. Bessada C., Rakhmatullin A., Rollet A.L., Zanghi D., *Lanthanide and actinide speciation in molten fluorides: A structural approach by NMR and EXAFS spectroscopies*, J. Nucl. Mat. (2007) **560**, 43-48
6. Boucart N., David L., Rochas C., Montembault A., Viton C., Domard A., *Polyelectrolyte microstructure in chitosan aqueous and alcoholic solutions*, Biomacromolecules (2007) **8**, 1209-1217
7. Bruning R., Levelut C., Le Parc R., Faivre A., Semple L., Vallee M., Simon J.P., Hazemann J.-L., *Temperature scanning small angle x-ray scattering measurements of structural relaxation in type-III vitreous silica*, J. Appl. Phys. (2007) **102**, 083535
8. Cabouro G., Chevalier S., Gaffet E., Vrel D., Boudet N., Bernard F., *In situ synchrotron investigation of MoSi2 formation mechanisms during current-activated SHS sintering*, Acta Materialia (2007) **55**, 6051-6063
9. Cabouro G., Chevalier S., Gaffet E., Rogachev A.S., Vrel D., Boudet N., Bernard F., *Reaction mechanism for SHS of MoSi2 from mechanically activated powder mixtures*, Int. J. Self-Propag. HT Synt. (2007) **16**, 79-86
10. Champagnon B., Martinez V., Martinet C., Le Parc R., Levelut C., *Density and density fluctuations anomalies of SiO2 glass: comparison and light-scattering study*, Phil. Mag. (2007) **87**, 691-695
11. Chenal J.M., Gauthier C., Chazeau L., Guy L., Bomal Y., *Molecular weight between physical entanglements in natural rubber: A critical parameter during strain-induced crystallization*, Polymer (2007) **48 (4)**, 1042-1046
12. Clemenson S., Espuche E., David L., *Structure and morphology of nanocomposite films prepared from polyvinyl alcohol and silver nitrate : influence of the thermal treatment*, J. Pol. Sc., Part A : Pol. Chem. (2007) **45(13)**, 2657-2672
13. Collet J.L., Bley F., Deschamps A., Scott C., *Study of the deformation mechanisms of TWIP steels (Fe-Mn-C) by X-Ray diffraction*, Adv. Mat. Res. (2007) **15-17**, 822-827
14. Compton J., Kranbuehl D. E., Martin G., Espuche E., David L., *In Situ Formation of a Uniform Distribution of Silver Nanoparticles in PVDF: Kinetics of Formation and Resulting Properties, Macromolecular Symposia*, Macromolecular Symposia (2007) **247(1)**, 182–189
15. Conchon F., Boulle A., Girardot C., Pignard S., Guinebretiere R., Dooryhee E., Hodeau J.-L., Weiss F., Kreisel J., Berar J.F., *Epitaxial stabilization of SmNiO3 films on (0 0 1) SrTiO3 substrates*, J. Phys. D. (2007) **40**, 4872-4876
16. Conchon F., Boulle A., Guinebretiere R., Girardot C., Pignard S., Kreisel J., Weiss F., Dooryhee E., Hodeau J.-L., *Effect of tensile and compressive strains on the transport properties of SmNiO3 layers epitaxially grown on (001) SrTiO3 and LaAlO3 substrates*, Appl. Phys. Lett. (2007) **91**, 192110
17. Conchon F., Boulle A., Girardot C., Pignard S., Guinebretiere R., Dooryhee E., Hodeau J.-L., Weiss F., Kreisel J., *Influence of strain relaxation on the structural stabilization of SmNiO3 films epitaxially grown on (0 0 1) SrTiO3 substrates*, Mat. Science and Engineering B (2007) **B 144**, 32-37
18. Connolly J., van Duijneveldt J.S., Klein S., Pizzey C., Richardson R.M., *Manipulation of modified clay particles in a nematic solvent by a magnetic field*, J. Phys. Cond. Mat. (2007) **19**, 156103

19. Coraux J., Favre-Nicolin V., Proietti M.G., Daudin B., Renevier H., *Grazing-incidence diffraction anomalous fine structure: Application to the structural investigation of group-III nitride quantum dots*, Phys. Rev. B (2007) **75**, 235312
20. Coraux J., Favre-Nicolin V., Renevier H., Proietti M.G., Amstatt B, Bellet-amalric E., Daudin B., *Quantitative structural characterization of GaN quantum dot ripening using reflection high-energy electron diffraction*, J. Appl. Phys. (2007) **101**, 056106-1-056106-3
21. Cros A., Garro N., Canterero A., Coraux J., Renevier H., Proietti M.G., Daudin B., *Evolution of strain in GaN/AlN quantum dots with variable capping : a comparision of resonant Raman scattering and x-ray diffraction. A. Cros, N. Garro, A. Cantarero, J. Coraux, H. Renevier, M. G. Proietti, V. Favre-Nicolin et B. Daudin.*, Phys. Rev. B (2007) **76**, 165403.
22. David M.L., Pailloux F., Babonneau D., Drouet M., Barbot J.-F., *The effect of the substrate temperature on extended defects created by hydrogen implantation in germanium*, J. Appl. Phys. (2007) **102**, 096101
23. Deschamps A., Lae L., Guyot P., *In situ small-angle scattering study of the precipitation kinetics in an Al-Zr-Sc alloy*, Acta Materialia (2007) **55**, 2775-2783
24. Dhahri J., Boudard M., Zemni S., Roussel H., Oumezzine M., *Structure and Magnetic Properties of Bi1-xKxFeO3*, J. Solid State Chem. (2007)
25. Douillard A., Hackme C., David L., Stevenson I., Boiteux G., Seytre-kazmierczak T.G., Galeski A., *Morphology development of uniaxially stretched poly(ethylene naphtalate 26 dicarboxylate) (PEN) films*, J. Appl. Polymer Science (2007) **103**, 395-401
26. Drogoz A., David L., Rochas C., Domard A., Delair T., *Polyelectrolyte complexes from polysaccharides: Formation and stoichiometry monitoring*, Langmuir (2007) **23 (22)**, 10950-10958
27. Dumont M., Coulet M.V., Regula G., Bley F., *Characterization of nanocavities in silicon using small angle X-ray scattering*, Mat. Res. Soc. Symp. Proc. (2007) **994**, 119-124
28. Etienne S., Hazeg N., Duval E., Mermet A., Wypych A., David L., *Physical aging and molecular mobility of amorphous polymers*, J. Non-Crystal. Solids (2007) **353 (41-43)**, 3871-3878
29. Feuerbacher M., Thomas C., Makongo J.P.A., Hoffman S., Carrillo-cabrera W., Cardoso R., *The Samson phase, beta-Mg2Al3, revisited*, Z. Kristallogr. (2007) **222**, 259-288
30. Geissler E., Kosik K., Fluerasu A., Moussaid A., Laszlo K., *X-ray Photon Correlation Spectroscopy of Dynamics in Thermosensitive Gels.*, Macromolecular Symposia (2007) **256**, 73-79
31. Girardot C., Conchon F., Boulle A., Chaudouet P., Caillault N., Kreisel J., Guinebretiere R., Weiss F., Pignard S., *Influence of thickness on the epitaxial stabilisation of SmNiO3 thin films*, Surface and Coating technology (2007) **201**, 9021-9024
32. Hennet L., Pozdnyakova I., Bytchkov A., Price D.L., Greaves G.N., Wilding M., Fearn S., Martin C.M., Thiaudiere D., Berar J.F., Boudet N., Saboungi M.L., *Development of structural order during supercooling of a fragile oxide melt*, J. Chem. Phys. (2007) **126**, 074906
33. Hennet L., Pozdnyakova I., Cristiglio V., Cuello G.J., Jahn S., Krishnan S., Saboungi M.L., Price D.L., *Short- and intermediate-range order in levitated liquidaluminates*, J. Phys. Cond. Mat. (2007) **19**, 455210
34. Hennet L., Pozdnyakova I., Cristiglio V., Krishnan S., Bytchkov A., Albergamo F. , Cuello G.J., Brun J.F., Fischer H., Zanghi D., Brassamin S., Saboungi M.L., Price D.L., *Structure and dynamics of levitated liquid aluminates*, J. Non-Crystal. Solids (2007) **353**, 1705-1712
35. Jeol S., Fenouillot F., Rousseau A., Masenelli-Varlot K., Gauthier C., Briois J.F., *Drastic Modification of the Dispersion State of Submicron Silicaduring Biaxial Deformation of Poly(ethylene terephthalate)*, Macromolecules (2007) **40**, 3229-3237
36. Jousseaume V., Rolland G, Babonneau D., Simon J.P., *Structural study of nanoporous ultra low-k dielectrics using complementary techniques: ellipsometric porosimetry, X-ray reflectivity and grazing incidence small-angle X-ray scattering*, Appl. Surf. Sci. (2007) **24**, 15560
37. Jousseaume V., Zenasni A., Favennec L., Gerbaud G., Bardet M., Simon J.P., Humbert A., *Comparison Between E-beam and Ultraviolet Curing to Perform Porous a-SiOC:H*, J. Electrochem. Soc (2007) **154**, G103-G109
38. Kosik K., Wilk E., Geissler E., Laszlo K., *Distribution of Phenols in Thermoresponsive Hydrogels*, Macromolecules (2007) **40**, 2141-2147
39. Laszlo K., Dobos G., Onyestyák G., Geissler E., *Influence of silicon doping on the nanomorphology and surface chemistry of a wood-based carbon molecular sieve.*, Microporous and Mesoporous Materials (2007) **100**, 103-110
40. Livet F., *Diffraction with a coherent X-ray beam: dynamics and imaging*, Acta Cryst. A (2007) **63**, 87-107
41. Murayama H., Vitry D., Ueda W., Fuchs G., Anne M. , Dubois J.L., *Structure characterization of orthorhombic phase in MoVTeNbO catalyst by powder X-ray diffraction and XANES*, Appl. Catal. (2007) **A 318**, 137-142
42. Naudy S., David L., Rochas C., Fulchiron R., *Shear Induced Crystallization of Poly(m-Xylylene Adi-*

pamide) with and without Nucleating Additives., Polymer (2007) **48,**, 3273-3285
43. Niepce J.-C., Baras F., Bernard F., Bonnet J.P., Dubois S., Gachon J.C., Gaffet E., Gauthier V., *Main recent contributions to SHS from France*, Int. J. Self-Propag. HT Synt. (2007) **16**, 235-255
44. Ramier J., Chazeau L., Gauthier C., Stelandre L., Guy L., Peuvrel-Disdier E., *In situ SALS and volume variation measurements during deformation of treated silica filled SBR*, J. Mat. Sci. (2007) **42**, 8130-8138
45. Ramos-Fernandez M., Normand L., Sorbier L., *Structural and Morphological Characterization of Alumina Supported Pd nanoparticles by Colloidal Synthesis*, Oil Gas Sc. Tech. IFP (2007) **62**, 101-113
46. Remita S., Fontaine P., Lacaze E., Borensztein Y., Sellame H., Farha R., Rochas C., Goldmann M., *X-ray radiolysis induced formation of silver nano-particles: A SAXS and UV–visible absorption spectroscopy study.*, Nucl. Instr. and Meth. B (2007) **263**, 436–449
47. Remita S., Fontaine P., Rochas C., Muller C., Goldmann M., *radiation induced synthesis of silver nonaoshells formed onto organic micelles*, Eur. Phys. J. D (2007) **263**, 436–449
48. Saiani A., Novak A., Rodier L., Eeckhaut G., Leenslag J.-W., Higgins J.S., *Origin of Multiple Melting Endotherms in a High Hard Block ContentPolyurethane: Effect of Annealing Temperature.*, Macromolecules (2007) **40**, 7252-7262
49. Steuwer A., Dumont M., Peel M., Preuss M., Withers P.J., *The variation of the unstrained lattice parameter in an AA7010 friction stir weld*, Acta Materialia (2007) **55**, 4111-4120
50. Takakura H., Pay Gomez C., Yamamoto A., Boissieu M., Tsai P., *Atomic structure of the binary icosahedral Yb-Cd quasicrystal.*, Nature Mat. (2007) **6**, 58-63
51. Thevenot J., Troutier A.L., David L., Delair T., Ladaviere C., *Steric stabilization of Lipid/Polymer Particle Assemblies by PEG-Lipids*, Biomacromolecules (2007) **8 (11)**, 3651-3660
52. Toudert J., Babonneau D., Camelio S., Girardeau T., Yubero F., Espinos J.P., Gonzalez-Elipe A.R., *Using ion beams to tune the nanostructure and optical response of co-deposited Ag :BN thin films*, J. Phys. D. (2007) **40**, 4614-4620
53. Vallat P., Catala J.M., Rawiso M., Schosseler F., *Flexible conjugated polyelectrolyte solutions: A small angle scattering study*, Macromolecules (2007) **40**, 3779-3783
54. Vouagner D., Coussa C., Califano V., Martinet C., Champagnon B., Sigaev V.N., *UV nanosecond laser-induced birefringence in LBG glasses*, Phil. Mag. (2007) **87 (3)**, 535 - 542
55. Zhang H., Saiani A., Guenet J.-M, Curtis R., *Effect of Stereoregular Polyelectrolyte on Protein Thermal Stability*, Macromolecular Symposia (2007) **251**, 25-32

Proceedings 2007 not cited in Conferences lists

1. Pacheco C., Chapoulie R., Dooryhee E., Goudeau P., *Gold leaf decoration on medieval islamic glazed ceramics – in search of technological features with XRD*, Z. Krist. Suppl. (2007) **26**, 317-323

Other publications 2007

1. Takakura H., Pay Gomez C., Yamamoto A., Boissieu M., Tsai P., *Atomic structure of the binary icosehedral YbCd quasiCrystal.*, ESRF Highlights (2007) **Materials science**, p44-46

Articles 2006

1. Babonneau D., Toudert J., Camelio S., Pailloux F., Cabioc'H T., Girardeau T., *Encapsulation of metallic nanoclusters in carbon and boron nitride thin films prepared by ion-beam sputtering*, Surface and Coating technology (2006) **200**, 6251-6257
2. Babonneau D., Beaufort M.-F., Declemy A., Barbot J.-F., Simon J.P., *Grazing incidence small-angle x-ray scattering study of defects induced by helium implantation in silicon.*, J. Appl. Phys. (2006) **99**, 113507
3. Bica , Borsali R., Geissler E., Rochas C., *Dynamics of Cellulose wiskers trapped in agarose hydrogel.* , Macromolecules (2006) **39**, 3622-3627
4. Buron-Le Cointe M., Lemée-Cailleau M.H., Cailleau H., Ravy S., Berar J.F., Rouzière S., Elkaim E., Collet J.L., *One-Dimensional Fluctuating Nanodomains in the Charge-Transfer Molecular System TTF-CA and their First-Order Crystallization*, Phys. Rev. Let. (2006) **96**, 205503
5. Clouet E., Lae L., Epicier T., Lefebvre W., Nastar M., Deschamps A., *Complex precipitation pathways in multicomponent alloys.*, Nature Mat. (2006) **5**, 482-488
6. Compton J., Thompson D., Kranbuehl D. E., Ohl S., Gain O., David L., Espuche E., *Hybrid films of polyimide containing in situ generated silver or palladium nanoparticles: Effect of the particle precursor and of the processing conditions of the morphology and the gas permeability.*, Polymer (2006) **47**, 5303-5313

7. Connolly J., van Duijneveldt J.S., Klein S., Pizzey C., Richardson R.M., *Effect of surfactant and solvent properties on the stacking behavior of non-aqueous suspensions of organically modified clays*, Langmuir (2006) **22**, 6531-6538
8. Coraux J., Proietti M.G., Favre-Nicolin V., Renevier H., Daudin B., *Step-by-step capping and strain state of GaN/AlN quantum dots studied by grazinf-incidence diffraction anomalous fine structure.*, Phys. Rev. B (2006) **73**, 205343
9. Coraux J., Favre-Nicolin V., Proietti M.G., Renevier H., Daudin B., *Grazing incidence study of GaN/AlN quantum dots.*, Nucl. Instr. and Meth. B (2006) **246**, 58-63
10. Coraux J., Amstatt B, Budagoski J.A., Bellet-amalric E., Rouvière J.L., Favre-Nicolin V., Proietti M.G., Renevier H., Daudin B., *Mechanism of GaN quantum dots capped with AlN: An AFM, electron microscopy,and x-ray anomalous diffraction study*, Phys. Rev. B (2006) **74**, 195302
11. Dasgupta D., Malik S., Thierry A., Guenet J.-M, Nandi A.K., *Thermodynamics, morphology, and structure of the poly(vinylidene fluoride)-ethyl acetoacetate system*, Macromolecules (2006) **39**, 6110-6114
12. Dujardin R., Poydenot V., Devilliers T., Favre-Nicolin V., Gentile P., Barski A., *Growth mechanism of Si nanowhiskers and SiGe heterostructures in Si nanowhiskers.*, Appl. Phys. Lett. (2006) **89**, 153129-1-153129-3
13. Dumont M., Steuwer A., Deschamps A., Peel M., Withers P.J., *Microstructure mapping in friction stir welds of 7449 aluminium alloy using SAXS.*, Acta Materialia (2006) **39**, 4793-4801
14. Fagot S., Foury P., Ravy S., Pouget J.P., Lorenzo J. E., Joly Y., Greenblatt M., Lobanov M., Popov G., *X-ray anomalous scattering investigation of BaVS3.*, Phys. Rev. B (2006) **73**, 033102
15. Fairen-Jimenez D., Carrasco-Marin F., Djurado D., Bley F., Ehrburger-Dolle F., Moreno-Castilla C., *Surface Area and Microporosity of Carbon Aerogels from Gas Adsorption and Small- and Wide- Angle X-Ray Scattering Measurements*, J. Chem. Phys. (2006) **B 110**, 8681-8688
16. Favre L., Dupuis V., Bernstein E., Mélinon P., Perez J., Stanescu S., Epicier T., Simon J.P., Babonneau D., Tonnerre J.M., Hodeau J.-L., *Encapsulation of metallic nanoclusters in carbon and boron nitride thin films prepared by ion-beam sputtering.*, Phys. Rev. B (2006) **74**, 014439
17. Grelet E., Bock H., *Control of the orientation of thin open supported columnar liquid crystal films by the kinetics of growth*, Europhys. Let. (2006) **73**, 712-718
18. Horkay F., Hecht A.-M., Rochas C., Basser P.J., Geissler E., *Anomalous small angle X-ray scattering determination of ion distribution around a polyelectrolyte biopolymer in salt solution.*, J. Chem. Phys. (2006) **125**, 234904
19. Kutsevol N., Guenet J.-M, Melnik N., Sarazin D., Rochas C., *Solution properties of dextran?polyacrylamide graft copolymers.*, Polymer (2006) **47**, 2061-2068
20. Kuznetsov D., Baturin I., Shur V., Menou N., Muller C., Schneller T., Sternberg A., *Kinetics of polarization reversal in irradiated thin PZT films*, Phys. Sol. State (2006) **48**, 1174-1176
21. Kuznetsov D., Shur V., Baturin I., Menou N., Muller C., Schneller T., Sternberg A., *Effect of Penetrating Irradiation on Polarization Reversal in PZT Thin Films*, Ferroelectrics (2006) **340**, 161-167
22. Laszlo K., Geissler E., *Surface chemistry and contrast-modified SAXS in polymer-based activated carbons.*, Carbon (2006) **44**, 2437-2444
23. Levelut C., Le Parc R., Faivre A., Champagnon B., *Influence of thermal history on the structure and properties of silicate glasses.*, J. Non-Crystal. Solids (2006) **352**, 4495-4499
24. Malik S., Rochas C., Guenet J.-M, *Thermodynamic and structural investigations on the different forms of syndiotactic polystyrene intercalates.*, Macromolecules (2006) **39**, 1000-1007
25. Michel J.-M., Lacaze E., Goldmann M., Gailhanou M., Boissieu M., Alba M., *Structure of smectic defect cores : X-ray study of 8CB liquid crystal ultrathin films.*, Phys. Rev. Let. (2006) **96**, 027803
26. Morfin I., Ehrburger-Dolle F., Grillo I., Livet F., Bley F., *SAXS, SAXS and SANS investigations of vulcanized elastomers filled with carbon black.*, J. Sync. Rad. (2006) **13**, 445-452
27. Negrete-Herrera N.-L., Persoz S., Puteaux J.L., David L., Bourgeat-Lami E., *Synthethis of polymer latex particles decorated with organically modified laponite clay platelets via emulsion polymerization*, J. Nanoscience Nanotechn. (2006) **6**, 421-431
28. Negrete-Herrera N.-L., Puteaux J.L., David L., Bourgeat-Lami E., *Polymer/laponite composite colloids through emulsion polymerization : influence of the clay modification level on particle morphology*, Macromolecules (2006) **9177-9184**, 39
29. Nemoz M., Dooryhee E., Hodeau J.-L., Dubourdieu C., Roussel H., Bayle-Guillemaud P., *Sensitivity of synchrotron radiation x-ray diffraction to the chemical ordering in epitaxial perovskite multilayers*, J. Appl. Phys. (2006) **100**, 124110
30. Notin L., Viton C., Rochas C., David L., Alcouffe P., Domard A., *Morphology and mechanical properties of chitosan fibers obtained by pseudo dry-spinning: Influence of the dry-jet-stretching step and ageing.*, A. Biomaterialia (2006) **2**, 387-40206

31. Parmentier J., Solovyov L., Ehrburger-Dolle F., Werckmann J., Ersen O., Bley F., Patarin J., *Structural Peculiarities of Mesostructured Carbons Obtained by Nanocasting Ordered Mesoporous Templates via Carbon Chemical Vapor or Liquid Phase Infiltration Routes.*, Chemistry of Materials (2006) **18**, 6316-63236
32. Pereira F.V., Borsali R., Ritter O.M.S., Goncalves P.F., Merlo A.A., da Silveira N., *Structure-property relationships of smectic liquid crystalline polyacrylates as revealed by SAXS.*, J. Braz. Chem. Soc. (2006) **17**, 333-341
33. Ravy S., Rouzière S., Pouget J.P., Brazovskii S., Marcus J., Berar J.F., Elkaim E., *Disorder effects on the charge-density waves structure in V- and W-doped blue bronzes: Friedel oscillations and charge-density wave pinning.*, Phys. Rev. B (2006) **74**, 174102
34. Rousseau G., Desgranges L., Charlot F., Millot N., Niepce J.-C., Pijolat M., Valdiviesco F., Baldinozzi G., Berar J.F., *A detailled study of UO2 to U3O8 oxidation phases and the associated rate-limiting steps.*, J. Nucl. Mat. (2006) **355**, 10-20
35. Sciau Ph., Goudeau P., Tamura N., Dooryhee E., *Micro scanning X-ray diffraction study of Gallo-Roman Terra Sigillata ceramics*, Appl. Phys. A (2006) **83**, 219-224
36. da Silveira N., Ehrburger-Dolle F., Rochas C., Rigacci A., Pereira F.V., Merlo A.A., Westfahl Jr. H., *Structure-property relationships of smectic liquid crystalline polyacrylates as revealed by SAXS.*, J. Thermal Anal. Calorimetry (2006) **17**, 333-341
37. Sletmoen M., Stokke B.T., Geissler E., *Small angle X-ray scattering study of local structure and collapse transition of (1,3)- beta-D-glucan-chitosan gels.*, J. Chem. Phys. (2006) **125**, 054908
38. Stephan R., Zabrocki S., Wetzel P., Berling D., Mehdaoui A., Bubendorff J.L., Garreau G., Pirri C., Gewinner G., Boudet N., Berar J.F., *Strain state in bcc Fe films grown on Si(1 1 1).*, Surf. sci. (2006) **600**, 3003-3007
39. Usuki T., Hosokawa S., Berar J.F., *An anomalous X-ray scattering study on glassy superionic conductor (As2Se3)0.4(AgI)0.6 using a third-generation synchrotron radiation facility.*, J. Non-Crystal. Solids (2006) **352**, 1514-1516
40. Viviani D., Faivre A., Levelut C., Smaihi M., *Structural change in Li and Na aluminophosphate glasses*, J. Phys. Chem. B (2006) **B 110**, 7281-7288
41. Wypych A., Duval E., Boiteux G., Ulanski J., David L., Mermet A., Kozanecki M., Horie K., *Structural changes on nanometric level in copolymers of methyl methacrylate with benzyl methacrylate as investigated by low frequency Raman scattering and small angle X-ray scattering.*, J. Non-Crystal. Solids (2006) **352**, 1514-1516

Other publications 2006

1. Coraux J., Proietti M.G., Renevier H., Favre-Nicolin V., Daudin B., *Step-by-step capping of GaN/AlN quantum dots, studied by grazing-incidence anomalous diffraction.*, ESRF Highlights (2006) **Surface and Interface Science**, 67-68

Articles 2005

1. Bartholome C., Beyou E., Bourgeat-Lami E., Cassagnau P., Chaumont P., David L., Zydowicz N., *Characterization of PS-SiO2 nanocomposites synthesized by nitroxide-mediated polymerization.*, Polymer (2005) **46**, 9965-9973
2. Basolo S., Berar J.F., Boudet N., Breugnon P., Caillot B., Clemens J.C., Delpierre P., Dinkespiler B., Koudobine I., Meessen Ch., Menou N., Mouget C., Pangaud P., Potheau R., Vigeolas E., *XPAD Pixel detector for material Sciences*, IEEE TNS (2005) **52**, 1994-1998
3. Baturin I., Menou N., Shur V., Muller C., Hodeau J.-L., *Influence of irradiation on the switching behavior in PZT thin films*, Materials Science and Engineering (2005), B 120, 141-145
4. Bershtein V.A., David M.L., Egorov V.M., Grigorieva O.P., Yakushev P.N., Bey I., Fainleib A.M., *Structural compositional Nanoheterogeneity : glass transition plurality in amorphous polycyanurate-poly(tetramethylene glycol) hybrid networks*, J. Polymer Science B Pol Phys (2005) **B : Physics**, 43
5. Boissieu M., Francoual S., Kaneko Y., Ishimasa T., *Diffuse Scattering and Phason Fluctuations in the Zn-Mg-Sc Icosahedral Quasicrystal and Its Zn-Sc Periodic Approximant*, Phys. Rev. Let. (2005) **95**, 105503
6. Bruning R., Levelut C., Faivre A., Leparc R., Simon J.P., Bley F., Hazemann J.-L., *Characterization of the glass tranistion in vitreous silica by temperature scanning small-angle X-ray scattering*, Europhys. Let. (2005) **29**, 70
7. Ciatto G., Renevier H., Proietti M.G., Polimeni A., Capizzi M., Mobilio S., Boscherini , *Effects of hydrogenation on the local structure of 'In(x)Ga(1-x)N(y) quantum wells ', 'GaAs(1-y)N(y) epilayers.*, Phys. Rev. B (2005), 085322

8. Collet J.L., Bley F., de Monestrol H., Deschamps A., Scott C., *Study of the deformation mechanisms of TWIP steels Fe-Mn-C by X-ray diffraction*, Revue de Metallurgie (2005) **ATS-JSI**, 164-165
9. Czakkel O., Marthi K., Geissler E., Laszlo K., *Influence of drying on the morphology of resorcinol-formaldehyde-based carbon gels*, Microporous and Mesoporous Materials (2005) **86**, 124-133
10. Dasgupta D., Manna S., Malik S., Rochas C., Guenet J.-M, Nandi A.K., *Thermodynamic Structural and Morphological Investigation of Poly(Vinylidene Fluoride)-Camphor Systems, Preparing Porous Gels from a Solid Solvent.*, Macromolecules (2005) **38(13),**, 5602-5608
11. Dasgupta D., Malik S., Rochas C., Michel J.-M., Nandi A.K., Manna S., *Thermoreversible Gelation of Poly vinylidene fluoride - Camphor System*, Macromolecular Symposia (2005) **227**, 175-180
12. David L., Montembault A., Vizio N., Domard A., Viton C., Morfin I., Rochas C., *A. Crio et Ordering in Bio-Polyelectrolyte Chitosan Solutions*, Macromolecular Symposia (2005) **222**, 281-286
13. Deschamps A., Genevois C., Nicolas M., Perrard F., *Study of precipitation kinetics towards non-isothermal and coupled phenomena*, Phil. Mag. (2005) **85**, 3091-3112
14. van Duijneveldt J.S., Klein S., Leach E., Pizzey C., Richardson R.M., *Large scale structures in liquid crystal clay colloids*, J. Phys. Cond. Mat. (2005) **17**, 2255-2267
15. Dumont M., Lefebvre W., Doisneau-Cottignies B., Deschamps A., *Characterisation of the composition and volume fraction of eta' and eta precipitates in an Al Zn Mg alloy by a combination of atom probe, small-angle X-ray scattering and transmission electron microscopy*, Acta Materialia (2005), 53, 2881-2892
16. Ehrburger-Dolle F., Fairen-Jimenez D., Berthon S., Achard P., Bley F., Carrasco-Marin F., Djurado D., Moreno-Castilla C., Morfin I., *Nanoporous carbon materials Comparison between information obtained by SAXS, WAXS and by gas adsorption.*, Carbon (2005) **43**, 3009-3012
17. Espuche E., David L., Afeld J.L., Compton J., Kranbuehl D. E., *Characterization and properties of hybrid nanoparticles inactive and active metal films*, Polymeric Materials : Sc and Eng. (2005) **92**, 58-59
18. Espuche E., David L., Rochas C., Afeld J.L., Compton J., Thompson D., Scott C., Kranbuehl D. E., *In situ generation of nanoparticulate lanthanumIII-oxide -polyimide films characterization of nanoparticle formation and resulting polymer properties*, Polymer (2005) **46**, 6657-6665
19. Fine T., Lortie F., David L., Pascault J.P., *J.P. Pascault Structures and rheological properties of reactive solutions of block copolymers. Part I. Diblock copolymers in a liquid epoxy monomer.*, Polymer (2005) **46**, 6605-6613
20. Foulc M.P., Bergeret A., Ferry L., Ienny P., Crespy A., *Study of hygrothermal ageing of glass fibre reinforced PET composites*, Polymer Degradation and Stability (2005) **89**, 461-470
21. Genevois C., Deschamps A., Denquin A., Doisneau-Cottignies B., *Quantitative investigation of precipitation and mechanical behaviour for AA2024 friction stir welds*, Acta Materialia (2005) **53**, 2447-2458
22. Guhr I., Riedlinger B., Maret M., Mazur U., Barth A., Treubel F., Albrecht M., Schatz G., *'Structural and magnetic properties of CrPt3 111& films grown on WSe2(0001)*, J. Appl. Phys. (2005) **98**, 063520
23. Hlinka J., Currat R., Boissieu M., Livet F., Vysochanskii Yu. M., *Two-length scale behavior near the ferroelectric phase transition of Sn2P2S6.*, Phys. Rev. B (2005) **36**, 71
24. Laszlo K., Toth J., *Characteristic adsorption functions and the surface structure of solid adsorbents*, J. colloid interface sci. (2005) **286**, 425-432
25. Laszlo K., Czakkel O., Josepovits K., Rochas C., Geissler E., *Influence of surface chemistry on the SAXS response of polymer-based carbon gel.*, Langmuir (2005) **21**, 8443-8451
26. Laszlo K., Onyestyák G., Rochas C., Geissler E., *Honeycomb carbon monoliths from Pinus sylvestris.*, Carbon (2005) **43**, 2402-2405
27. Laszlo K., Czakkel O., Marthi K., Rochas C., Geissler E., *Influence of drying on the morphology of Resorcinol Formaldehyde-based Carbon gel.*, Microporous and Mesoporous Materials (2005) **86**, 124-133
28. Létoublon A., Favre-Nicolin V., Renevier H., Proietti M.G., Monat C., Gendry M., Marty O., Priester C., *Strain, size and composition of InAS quantum sticks, embedded in InP, determined via X-ray anomalous diffraction and diffraction anomalous fine structure in grazing incidence.*, Physica B (2005) **357**, 11-15
29. Maret M., Gilles B., Simon J.P., Verdier M., Guhr I., Riedlinger B., Albrecht M., Schatz G., *Self-assembling of alloy nanostructures on van der Waals surfaces*, J. cryst. growth (2005), 40, 275
30. Mayoral T., Martinez-Jalvez M., Perez-dorado I. , Sanz-aparicio J., Gomez-moreno C., Medina M., *Structural analysis of interactions for complex formation between ferredoxin-NADP+ reductase and its protein partners*, Proteins: Struct. Funct. Bioinfo. (2005) **59**, 592-602
31. Menou N., Castagnos A.-M., Muller C., Goguenheim D., Goux L., Wouters D.J., Hodeau J.-L., Doorhee E., Barrett R., *Degradation and recovery of polarization under synchrotron X-rays in SrBi2Ta2O9 ferroelectric capacitors*, J. Appl. Phys. (2005) **97**, 044106
32. Menou N., Muller C., Baturin I., Kuznetsov D., Shur V., Hodeau J.-L., Schneller T., *In situ synchrotron x-ray diffraction study of electrical field induced fatigue in Pt/PbZr0.45Ti0.55O3/Pt ferroelectric capacitors*, J. Phys. Cond. Mat. (2005) **17**, 7681-7688

33. Menou N., Castagnos A.-M., Muller C., Goguenheim D., Goux L., Wouters D.J., Dooryhee E., Hodeau J.-L., Barrett R., *In situ synchrotron x-ray diffraction study of electrical field induced fatigue in Pt/PbZr0.45Ti0.55O3/Pt ferroelectric capacitors*, J. Appl. Phys. (2005) **97**, 044106-1
34. Michel J.-M., Lacaze E., Goldmann M., Gailhanou M., Boissieu M., Alba M., *Revealing the structure of Focal Conics Cores and their influence on the evolution with temperature : an X-ray study of ultra-thin 8CB Films.*, Mol. Cryst. Liq. Cryst. (2005) **437**, 99-109
35. Nicolas M., Lefebvre W., Doisneau-Cottignies B., Deschamps A., *Characterisation of the composition and volume fraction of h and h precipitates in an Al-Zn-Mg alloy by the combination of Atom Probe, Small-Angle X-ray Scattering and Transmission Electron Microscopy.*, Acta Materialia (2005) **53**, 2881-2892
36. Notin L., Viton C., David L., Rochas C., Roger T., Domard A., *New method of Chitosan spinning : aoolication to reinforcing plate.*, Adv. Chitin Sc. (2005) **8**, 214-219
37. Palancher H., Hodeau J.-L., Pichon Ch., Berar J.F., Lynch J., Rebours B., Rodriguez-Carvajal J., *Direct Localization of Atoms in Mixed-Occupancy Powders by Resonant Contrast Diffraction*, Angew. Chem. Int. Ed. (2005) **44**, 1725-1729
38. Palancher H., Hodeau J.-L., Pichon Ch., Berar J.F., Lynch J., Rebours B., Rodriguez-Carvajal J., *A Cell for in situ dynamic X-ray diffraction studies : application to the dehydration of zeolite SrX*, J. Appl. Cryst. (2005) **38**, 370-373
39. Perez J., Perrard F., Massardier V., Kleber X, Deschamps A., de Monestrol H., Pareige P., Covarel G., *Low-temperature solubility of copper in iron: experimental study using thermoelectric power, small angle X-ray scattering and tomographic atom probe*, Phil. Mag. Letters (2005) **85**, 2197–2210
40. Pichon Ch., Palancher H., Hodeau J.-L., Berar J.F., *Towards operando Characterisation by Powder Diffraction Techniques of Molecular Sieves*, Oil Gas Sc. Tech. IFP (2005) **60**, 831-848
41. da Silveira N., Ehrburger-Dolle F., Rochas C., Rigacci A., Pereira F.V., Merlo A.A., Westfahl Jr. H., *Smetic ordering in polymer liquid crystal-silica aerogel nanocomposites. Studies by DCS and SAXS.*, J. Thermal Anal. Calorimetry (2005) **79**, 579-585
42. Sniechowski M., Luzny W., Djurado D., Dufour B., Rannou P., Pron A., Johnson M., Gonzales M., *Structure and dynamics of plast-doped conducting polyaniline compounds*, Fibres and Textiles in Eastern Europe (2005) **13**, 96-98
43. Subias Peruga G., Garcia J., Proietti M.G., Blasco J., Renevier H., Hodeau J.-L., Sanchez M.C., *MX-ray resonant scattering in Fe3O4, Mn3O4 and CoFe2O4 ferrites.*, Physica Scripta (2005) **T115**, 603-605
44. Testemale D., Coulet M.V., Hazemann J.-L., Simon J.P., Bley F., Geaymond O., Argoud R., *Small angle x-ray scattering of a supercritical electrolyte solution : the effect of density fluctuation on the hydrogenation of ions.*, J. Chem. Phys. (2005) **122**, 194505

Proceedings 2005 not cited in Conferences lists

1. Perez M., Perrard F., Massardier V., Kleber X, Schmitt V., Deschamps A., *Low-temperature solubility of copper in iron.*, Mater. Sci. Forum (2005) **500-501**, 631-638

Other publications 2005

1. Bruning R., Levelut C., Faivre A., Leparc R., Simon J.P., Bley F., Hazemann J.-L., *Characterization of the glass transition in vitreous silica by temperature-scanning SAXS.*, ESRF Highlights (2005) **High resolution and resonance scattering**, 24-25
2. Palancher H., Hodeau J.-L., Pichon Ch., Berar J.F., Lynch J., Rebours B., Rodriguez-Carvajal J., *Resonant Contrast Diffraction for Direct Localisation of Atoms in Mixed Occupancy Powders.*, ESRF Highlights (2005) **Materials science.**, 43-44
3. Testemale D., Coulet M.V., Hazemann J.-L., Simon J.P., Bley F., Geaymond O., Argoud R., *SAXS of a supercritical electrolyte solution: the effect of density fluctuations on ion hydration*, ESRF Newsletter (2005) **37**, 21

5.3 Conferences

Other Conferences 2009

1. Mourglia E., Long L., Odoni P., Sotta P., Rochas C., *Nanocomposites &* , ,

Invited Conferences 2008

1. Berar J.F., *XND dans la boite à outils.*, Software Workshop, European Powder Diffraction Conference (EPDIC 10) , 2008, Sept 18 Warsaw, Poland

2. Francoual S., Boissieu M., *Diffuse scattering and phason modes*, TMS 2008, Mar. 2008 New orleans, USA
3. Francoual S., Ishimasa T., Kashimoto S., Boissieu M., *Diffuse scattering and phason modes in ZnMgSc quasicrystals and its approximant*, IUCr 2008, Aug. 2008 Osaka, Japan
4. Fribourg G., Deschamps A., Brechet Y., Chemin J.L., *In-situ Small-Angle X-ray Scattering study of precipitation kinetics during thermomechanical treatments in a 7xxx Aluminium alloy (Keynote lecture)*, International Conference on Aluminium Alloys (ICAA 11) , 22-26 Sept 08 Aaren, Germany. *Proceedings:* p. 936-946 11th International Conference on Aluminium Alloys, vol 1 , Wiley-VCH , Weinheim, Germany, Aachen, Germany (2008)
5. Renevier H., Proietti M.G., Coraux J., Favre-Nicolin V., Richard M.I., Katcho N.A., Daudin B., *Structural properties of semiconductor nanostructures studied by Multiwavelength Anomalous Diffraction and Diffraction Anomalous Fine Structure spectroscopy.*, International Conference on Surface X-ray and Neutron Scattering SXNS-10 (SXNS-10) , 2-5 July 2008 Synchrotron SOLEIL, France.
6. Renevier H., Proietti M.G., Coraux J., Favre-Nicolin V., Richard M.I., Katcho N.A., Daudin B., *Structural properties of semiconductor nanostructures studied by Multiwavelength Anomalous Diffraction and Diffraction Anomalous Fine Structure spectroscopy.* , 6th International Conference on Synchrotron Radiation in Material Science , 20-23 Juillet 2008 Campinas, Brésil.

Published Conferences 2008

1. Berar J.F., Boudet N., Breugnon P., Caillot B., Chantepie B., Clemens J.C., Delpierre P., Godiot S, Hustache S., Medjoubi K., Meessen Ch., Menouni M., Pangaud P., Vigeolas E., *XPAD3 hybrid pixel detector applications.*, Iworid2008 , 30 Jun.- 4 Jul. 2008 Helsinski, Finland. *Proceedings:* Nucl. Instr. and Meth. A (2009)
2. Decreus B., Bley F., Deschamps A., Donnadieu P., *Quantitative characterization of the precipitation kinetics in an AA2198 Al-Li-Cu alloy*, International Conference on Aluminium Alloys (ICAA 11) , 22-26 Sept 08 Aaren, German. *Proceedings:* p1040-1046 11th International Conference on Aluminium Alloys, vol 1 , Wiley-VCH , Weinheim, Germany, Aachen, Germany (2008)
3. Hosokawa S., Berar J.F., Boudet N., Ichitsubo T., Matsubara E., Nishiyama Y., *Partial structure of Pd42.5Ni7.5Cu30P20 bulk metallic glass*, Rapidly Quenched and Metastable Materials Conference (RQ13) , 24-29 August 2008 Dresden, Germany. *Proceedings:* J. Phys : Conf. Ser. (2009) **144**, 012055-1-012055-4
4. Marlaud T., Deschamps A., Bley F., Baroux B., *In-situ study of precipitate composition in 7000 series aluminium alloys by Anomalous Small-Angle Scattering*, International Conference on Aluminium Alloys (ICAA 11) , 22-26 Sept 08 Aaren, Germany. *Proceedings:* p. 954-959 11th International Conference on Aluminium Alloys, vol 1 , Wiley-VCH , Weinheim, Germany, Aachen, Germany (2008)

Other Conferences 2008

1. Berar J.F., Boudet N., Breugnon P., Caillot B., Chantepie B., Clemens J.C., Delpierre P., Dinkespiler B., Godiot S, Medjoubi K., Meessen Ch., Menouni M., Pangaud P., Vigeolas E., *XPAD3 hybrid pixel detector applications.*, IEEE/NSS 2008 , Dresden, Germany
2. Berar J.F., Boudet N., Breugnon P., Caillot B., Chantepie B., Clemens J.C., Delpierre P., Dinkespiler B., Godiot S, Medjoubi K., Meessen Ch., Menouni M., Pangaud P., Vigeolas E., *XPAD3 hybrid pixel detector applications.*, IEEE/NSS 2008 , Dresden, Germany
3. Manet S., Grillo I., Durand D., undefined, *Mechanisms and kinetics of the synthesis of mesoporous materials investigated by small angle neutron and X-ray scatterin*, 4th International FEZA Conference , 2008-02-06 Paris
4. Hosokawa S., Usuki T., Boudet N., Berar J.F., *An Anomalous X-ray scattering study on superionic glassy (As2Se3)-(AgX) systems (X =halides)*, XTOP2008 , Sept, 2008 Linz, Austria
5. Imperor-Clerc M., Grillo I., Durand D., Manet S., *SANS study of the mechanisms and kinetics of the synthesis of mesoporous materials from micelles of tri-block copolymers*, , 2008-02-06 Paris
6. Imperor-Clerc M., Manet S., Grillo I., Durand D., Khodakov V., Zholobenko V., *Mechanisms and kinetics of the synthesis of mesoporous materials investigated by small*, , 2008-02-06 Paris
7. Liscio F., Marakov D., Brombacher C., Proux O., Meneghini C., Gauthier Y., Doisneau-Cottignies B., Mobilio S., Simon J.P., Albrecht M., Maret M., *Nanostructures de CoPt3 épitaxiées sur WSe2(0001) et NaCl(001)*, GDR nanoalliages, Oléron 9-11 Juin 2008 ,
8. Mourier E., Méchin F., Fulchiron R., *Nano-structuration of thermoplastic segmented polyurethanes under shear flow.*, XXIVth International Annual Meeting of the Polymer Processing Society , 2008-06-15 Salerno, Italie
9. Mourier E., Fulchiron R., Méchin F., *Nano-structuration sous contraintes de polyuréthanes segmentés thermoplastiques.*, 43eme colloque annuel du Groupe Français de Rhéologie , 2008-10-20 Palaiseau

10. Mourglia E., Long L., Odoni P., Sotta P., Rochas C., *Physical mechanisms in reinforced semi-cristalline* , GFP , 2008-11-27 Lyon
11. Simon J.P., Babonneau D., Maret M., Lyon O., *AGISAXS study of carbon-encapsulated Au and Cu clusters : a methodologu to separate different scattering contributions.*, SXNS08 , jul 2008 Soleil
12. Simon J.P., Jousseaume V., Zenasni A., Babonneau D., *GISAXS study of porous SiOCH dielectrics used in advanced microelectronic interconnections.*, SXNS 08, jul 2008 Soleil
13. Simon J.P., Jousseaume V., Zenasni A., Babonneau D., *GISAXS Study of Porous SiOCH Dielectrics used in Advanced Microelectronic Interconnections*, Grazing-Incidence Small-Angle X-Ray Scattering (MRS) , Boston

Invited Conferences 2007

1. Boissieu M., *Phason modes in Quasicrystals*, QC 2007, the Siver Jubilee (QC 2007) , Oct. 2007 Tel Aviv, Israel. *Proceedings:* Phil. Mag. (2008) **88**, 2295-2309
2. Coraux J., Favre-Nicolin V., Proietti M.G., Daudin B., Renevier H., *Multiwavelength Anomalous Diffraction (MAD) and Diffraction Anomalous Fine Structure (DAFS) in the study of structural properties of nanostructures.* , 24th European Crystallographic Meeting , 22-27 Août 2007 Marrakech
3. Simon J.P., *GISAXS studies of Dielectrics Thin Films*, 2nd Workshop: GISAXS – an advanced scattering method , Hambourg, 9-11 May 2007

Published Conferences 2007

1. Pacheco C., Pacheco C., Chapoulie R., Dooryhee E., *Gilded medieval Islamic glazed ceramics: non-destructive surface analyses in search of technological features*, International Conference on SurfaceModification Technologies (ICSMT 21) , 2007-00-00 Ecole des Mines, France. *Proceedings:* Surface Engineering (2008) **24**, 121-128
2. Hosokawa S., Berar J.F., Boudet N., Ichitsubo T., Pilgrim W.-C., Nishiyama Y., *Partial Stucture of Pd42.5Ni7.5Cu30P20 Bulk Metallic Glass: Comparisonto the Reference Pd40Ni40P20 Glass.*, liquid and amorphous metals Conference. (LAM 13) , Russia. *Proceedings:* J. Phys : Conf. Ser. (2008) **98**, 012013-1-012013-4
3. Hosokawa S., Berar J.F., Boudet N., Ichitsubo T., Pilgrim W.-C., Nishiyama Y., *Local structure around Pd atoms in Pd42.5Ni7.5Cu30P20 excellent glass-former studied by anomalous X-ray scattering.*, Japanese AXS meeting , 2007-03-01 Japan. *Proceedings:* Materials Transactions (2007) **48-9**, 2358-2361
4. Piskorska E., Holy V., Siebert M., Renevier H., Schmidt T., Falta J., Hommel D., *InGaN self assembled quantum dots investigated by X-ray diffraction-anomalous-fine structure technique*, 28th International Conference on the Physics of Semiconductors" , 2006-07-24 Vienna (Austria). *Proceedings:* AIP Conf. Proc. (2007) **893**, 79-80

Other Conferences 2007

1. Fribourg G., Deschamps A., Brechet Y., *In-situ Small Angle X-ray Scattering measurements of precipitation kinetics during thermomechanical treatments – Application to the study of the age-forming process of a precipitation hardening aluminium alloy*, EUROMAT 2007 , 10-13 Sept 2007 ,
2. Jousseaume V., Favennec L., Zenasni A., Gourhant O., Maury P., Simon J.P., *Nanoporous SiOCH Thin Films: from Sol Gel to PECVD*, 211th Meeting of the Electrochemical Society. May 6 - May 10, 2007.USA ,
3. Liscio F., Maret M., Simon J.P., Albrecht M., *GISAXS on alloy nanostructures grown by quasi van der Waals epitaxy*, 2nd Workshop: GISAXS – an advanced scattering method 9-11 May 2007 ,
4. Liscio F., Marakov D., Maret M., Simon J.P., Doisneau-Cottignies B., De Santis m., Tolentino H.C.N., Albrecht M., *Nanostructures magnétiques auto-assemblées sur des surfaces de faible énergie*, Journees Surfaces Interfaces, Paris, 29-31 Janv. 2007 ,
5. Saiani A., Higgins J.S., *High Hard Block Content Polyurethanes: Morphology and Phase Behavior J.S Higgins*, American Chemical Society 233rd National Meeting , 2007-03-00 Chicago
6. Saiani A., *Phase behavior and morphology of high hard block content polyurethanes*, American Physical Society Meeting , 2007-03-00 Denver, USA
7. Simon J.P., *Ultra low K dielectrics for microelectronics studied by GISAXS*, BCA workshop , ILL, July 07

Invited Conferences 2006

1. Berar J.F., Arnaud S., Basolo S., Boudet N., Breugnon P., Clemens J.C., Delpierre P., Dinkespiler B., Hustache S., Koudobine I., Menouni M., Palancher H., Pangaud P., Potheau R., Vigeolas E., *2D*

detectors and application of XPAD pixel detector in material sciences : powder and multilayers., Campinas Synchrotron Users Meeting , feb. 2006 Campinas (Brasil)
2. Berar J.F., Arnaud S., Basolo S., Boudet N., Breugnon P., Caillot B., Clemens J.C., Delpierre P., Dinkespiler B., Hustache S., Koudobine I., Menouni M., Palancher H., Pangaud P., Potheau R., Vigeolas E., *Detecteur 2D de nouvelle generation et application a la diffraction de poudres.*, Soleil-LLB : Rencontres scientifiques de Saint-Aubin , mar 2006 Saint-Aubin
3. Berar J.F., *XND : sous le capot.*, Powder Diffraction Software Workshop (EPDIC-10) , 1-4 Sept 2006 Geneve, Suisse
4. Boissieu M., *Structure determination of quasicrystals*, Aperiodic 2006, Nov. 2006 Zao, Japan. *Proceedings:* Phil. Mag. (2007) **87**, 2613-2633
5. Coraux J., Favre-Nicolin V., Proietti M.G., Daudin B., Renevier H., *Advances in anomalous diffraction and DAFS to study nanostructures.* , 8th Biennal Conference on High Resolution X-ray Diffraction and Imaging , 19-22 septembre 2006 Baden-Baden/Karlsruhe
6. Ehrburger-Dolle F., *Investigation of the structure and dynamics of carbon black and silica nanocomposites by means of static and dynamic X-ray scattering.*, Nanocomposites Workshop 2006 , 6-7 April 2006 Montpellier (France)
7. Ehrburger-Dolle F., Berthon-Fabry S., Bley F., *SAXS Characterization of Carbon Aerogels for Catalytic Supports.*, 11th International Conferences on Modern Materials and Technologies. (CIMTEC 2006) , 4-9 June 2006 Acireale, Italie. *Proceedings:* Adv. Sci. Technology (2006) **45**, 1847-1856
8. Simon J.P., Okuda H., *Contribution of Synchrotron Radiation in SAXS studies in Hard Condensed Matter.*, SAS 2006, 9-13 july 2006 Kyoto, Japan. *Proceedings:* J. Appl. Cryst. (2007) **40**, s1-s9

Published Conferences 2006

1. Collet J.L., Bley F., Deschamps A., Scott C., *Study of the deformation mechanisms of TWIP steels (Fe-Mn-C) by X-Ray diffraction*, THERMEC 2006 , Vancouver. *Proceedings:* Adv. Mat. Res. (2007) **15-17**, 822-827
2. Collet J.L., Bley F., Deschamps A., de Monestrol H., Berar J.F., Scott C., *The deformation mechanisms of TWIP steels (Fe-Mn-C) viewed by X-ray diffraction.*, XX International Conference on Applied Crystallography , Wisla, Poland. *Proceedings:* Solid State Phenomena (2007) **130**, 53-56
3. Delpierre P., Debarbieux F., Basolo S., Berar J.F., Bonissent A., Boudet N., Breugnon P., Caillot B., Cassol Bruner F., Chantepie B., Clemens J.C., Dinkespiler B., Khouri R., Koudobine I., Mararazzo V., Meessen Ch., Menouni M., Morel C., Mouget C., Pangaud P., Peyrin F., Rougon G., Sappey-Marinier D., Valton S., Vigeolas E., *PIXSCAN : Pixel Detector CT-Scanner for Small Animal Imaging.*, EUROMEDIM 2006, 9-12 May 2006 Marseille. *Proceedings:* Nucl. Instr. and Meth. A (2007) **571**, 425-428
4. Delpierre P., Basolo S., Berar J.F., Bordesoule M., Boudet N., Breugnon P., Caillot B., Chantepie B., Clemens J.C., Dinkespiler B., Hustache S., Meessen Ch., Menouni M., Morel C., Mouget C., Pangaud P., Potheau R., Vigeolas E., *XPAD : a photons counting pixel detector for material sciences and small-animal imaging.*, X Pisa Meeting on Advanced Detectors : Frontier Detectors for Frontier Physics (X Pisa Meeting on Advanced Detectors) , May 21th-27th 2006 Elba island (Italie). *Proceedings:* Nucl. Instr. and Meth. A (2007) **572**, 250-253
5. Deschamps A., Dumont M., Lae L., Bley F., *Use of Small-Angle X-ray Scattering for the characterisation of precipitates in Aluminium alloys*, Aluminium Alloys 2006 (ICAA10) , Vancouver. *Proceedings:* Materials Science Forum Vols. 519-521 (2006) pp. 1349-1354
6. Hosokawa S., Berar J.F., *Anomalous X-ray scattering using third-generation synchrotron Radiation.*, Synchrotron Radiation Instrumentation : 9th International Conference. (SRI 2006) , 28 May - 2 June 2006 Daegu, Korea. *Proceedings:* AIP Conf. Proc. 879 (2007) 1743
7. Pangaud P., Basolo S., Berar J.F., Boudet N., Chantepie B., Delpierre P., Dinkespiler B., Hustache S., Menouni M., Morel C., *XPAD3 : a new photon counting chip for X-ray CT-scanner.*, EUROMEDIM 2006, 9-12 May 2006 Marseille. *Proceedings:* Nucl. Instr. and Meth. A (2007) **571**, 321-324
8. Simon J.P., Jousseaume V., Rolland G, *Grazing incidence small-angle X-ray scattering study of porous dielectrics used in advanced microelectronic interconnections.*, SAS 2006, 9-13 july 2006 Kyoto, Japan. *Proceedings:* J. Appl. Cryst. (2007) **40**, s363-s366
9. Villain P., Girault B., Renault P.O., Le Bourhis E., Goudeau P., Bawadi K.F., *Experimental study of size-effects on the mechanical properties of nanometric W/Cu multilayers*, MRS fall meeting, Boston, Nov 06 , . *Proceedings:* Mater. Res. Soc. Symp. Proc. 977 (FF7.1) (2007) 1-6.

Other Conferences 2006

1. Berar J.F., Arnaud S., Basolo S., Boudet N., Breugnon P., Clemens J.C., Delpierre P., Dinkespiler B., Hustache S., Koudobine I., Menouni M., Palancher H., Pangaud P., Potheau R., Vigeolas E., *XPAD*

: an hybrid pixel detector for material sciences studies using X-ray synchrotron radiation, Campinas Synchrotron Users Meeting , feb. 2006 Campinas (Brasil)

2. Chenal J.M., Chazeau L., Guy L., Bomal Y., Gauthier C., *In situ WAXD measurements of strain induced crystallization of natural rubberÂ : Effects of fillers.*, IRCO 2006 , 16-18/05/06 Lyon (France)
3. Chenal J.M., Chazeau L., Guy L., Bomal Y., *Influence de nanocharges sur la microsctructure crystalline du caoutchouc naturel induite par dÃ©formation uniaxiale*, Materiaux 2006 , 13-17/11/06 Dijon (France)
4. Clemenson S., Alcouffe P., David L., Espuche E., *Structure and morphology of membranes prepared from polyvinyl alcohol and silver beheneta: influence of the anealing treatment and of the film thickness.Desalination, vol 200 (1-3) 437-439*, Euromembrane 2006 , 24-28 Sept. 2006 Giardini Naxos, Italy
5. Ehrburger-Dolle F., Fairen-Jimenez D., Berthon-Fabry S., Bley F., Morfin I., Achard P., Carrasco-Marin F., Djurado D., Moreno-Castilla C., *Investigation of the microporous texture of carbon materials by SAXS-WAXS using contrast variation.*, The International Carbon Conference , 16-21 July 2006 Aberdeen (UK)
6. Ehrburger-Dolle F., Morfin I., Bley F., Parmentier J., Patarin J., Vix-Guterl C., *Investigation of the structure of templated carbon materials by low-angle X-ray diffraction using synchrotron radiation.*, The International Carbon Conference , 16-21 July 2006 Aberdeen (UK)
7. Ehrburger-Dolle F., Fairen-Jimenez D., Berthon-Fabry S., Bley F., Morfin I., Achard P., Carrasco-Marin F., Djurado D., Moreno-Castilla C., *Gas Adsorption and X-Ray Scattering Measurements in Carbon Aerogels Prepared with Different Polymerisation Catalysts.*, The International Carbon Conference , 16-21 July 2006 Aberdeen (UK)
8. Hosokawa S., Berar J.F., *by anomalous X-ray scattering.*, 21st Int. Conf. on Amorphous and Nanocrystalline Semiconductors. , 2006-07-01 Lisbon, Portugal
9. Hustache S., Bordesoule M., Medjoubi K., Berar J.F., Boudet N., Caillot B., Basolo S., Breugnon P., Clemens J.C., Delpierre P., Dinkespiler B., Koudobine I., Meessen Ch., Menouni M., Morel C., Pangaud P., Vigeolas E., *The hybrid pixel single photon counting detector XPAD.*, International Symposium On Detector Development For Particle, Astroparticle And Synchrotron Radiation Experiments. (SNIC 2006) , 3-6 apr 2006 Stanford - California (USA)
10. Pichon Ch., Palancher H., Lynch J., Hodeau J.-L., Berar J.F., *Cationic distribution of Ca2+ and Sr2+ cation s in hydrated and dehydrated zeolite SrX, CaX and CaSrX. An in situ anomalous X ray diffraction study*, RTNO,

Invited Conferences 2005

1. Berar J.F., *Application of XPAD detector in material science : powders and multilayers*, PSI Detector Workshop , 18-19 Oct. 2005 PSI - Suisse
2. Berar J.F., *Pixel Detectors and Material Science: an Opportunity or the Future for Synchrotron Experiments ?*, New Science with new detectors, ESRF Workshop , 9-10 Feb. 2005 ESRF - Grenoble - France

Published Conferences 2005

1. Boissieu M., *Stability of quasicrystals : energy, entropy and phason modes.*, ICQ9, Mai. 2005 Ames, USA. *Proceedings:* Phil. Mag. (2006) **86**, 1115-1122
2. Henley C. L., Boissieu M., Steurer W., *Discussion on clusters, phasons and quasicrystal stabilisation*, ICQ9, Mai. 2005 Ames, USA. *Proceedings:* Phil. Mag. (2006) **86**, 1131-51
3. Hosokawa S., Wang J., Pilgrim W.-C., Berar J.F., Mamedov S., Boolchand P., *Partial structural analysis of glassy As2Se3 using anomalous X-ray scattering*, ICANS21, . *Proceedings:* J. Non-Crystal. Solids (2006) **352**, 1517-1519

Other Conferences 2005

1. Régnier , Mendoza R., David L., Fulchiron R., Rochas C., *Determination of the spatial molecular orientation in injection molded iPP, ,* , 8th ESAFORM conference on material forming , 2005-04-28 Cluj Napoca, Roumania
2. Saiani A., *Phase Behaviour and Structure of Model High Hard Block Content Polyurethanes,*, European Polymer Congress , 2005-06-00 Moskow, Russia

5.4 Books and chapters

in Books (conferences excluded) 2008

1. Boissieu M., Currat R., Francoual S., *Phason modes in aperiodic crystals*, Handbook of Metal Physics: Quasicrystals , editors: T. Fujiwara and Y. Ishii , Elsever Science (2008)

2. Metzger T.H., Favre-Nicolin V., Renaud G., Renevier H., Schulli T., *Nanostructures in the light of synchrotron radiation : Surface sensitive x-ray techniques and anomalous scattering. T. Metzger, V. Favre-Nicolin, G. Renaud, H. Renevier, T. Schülli,*, Characterization of Semiconductor Heterostructures and Nanostructures , editors: Lamberti , Elsevier Science , Amsterdam (2008)
3. Proietti M.G., Coraux J., Renevier H., *Grazing Incidence Diffraction Anomalous Fine Structure in the study of structural properties of nanostructures*, Characterization of Semiconductor Heterostructures and Nanostructures , editors: Lamberti , Elsevier Science , Amsterdam (2008)

Books 2007

1. Janssen T., Chapuis G., Boissieu M., , Aperiodic Crystals. From modulated phases to quasicrystals , Oxford University Press , Oxford (2007)

in Books (conferences excluded) 2007

1. Laszlo K., Geissler E., *SAXS Characterization of Solid/Vapor Interfaces in Polymer Based Microporous Carbons with Different Surface Chemistry*, Recent Advances in Adsorption Processes for Environmental Protection andSecurity , editors: J.P. Mota, S. Lyubchik , Springer (2007)

in Books (conferences excluded) 2005

1. Bershtein V.A., David M.L., Egorov V.M., Pissis P., Yakushev P.N., Bos S., *Peculiarities of segmental dynamics in complex polyimide materials for advanced technologies*, Polyimides and other high temperature polymers - Vol. 3 , editors: Mittal, K , VSP , Utrecht-Boston (2005)

5.5 Softwares

bm2hkl from image to reciprocal space (*language IDL*)
available on beamline or contact boudet@esrf.fr

bm2img an image preprocessing tool with grid corrections allowing to extract radial distribution (*language c, Linux, MSWindows*)
ftp://ftp.grenoble.cnrs.fr/pub/xnd/BM2 or http://perso.neel.cnrs.fr/jean-francois.berar/bm2img (bm2img_1.25 release)

bm2py From images to high resolution powder pattern, (*language Python*)
http://perso.neel.cnrs.fr/jean-francois.berar/bm2py (preliminary release)

guifit multilayer fit program (*language IDL*)
available on beamline or contact eric.dooryhee@grenoble.cnrs.fr

spec2grace tool for converting spec files (*language c, Linux*)
ftp://ftp.grenoble.cnrs.fr/pub/xnd/BM2 (spec2grace_2.21 release)

xnd a rietveld program (*language c, Linux, MSWindows*)
ftp://ftp.grenoble.cnrs.fr/pub/xnd or http://perso.neel.cnrs.fr/jean-francois.berar/xnd (xnd_1.41 release)

6 Selected publications

The following 5 papers do not cover all scientific fields but are representative of the beamline activity. The choice focusses on results rather than on methods (DAFS, GISAXS, ...), which are described in the text.

- **Soft condensed matter**
  - Michel J.-M., Lacaze E., Goldmann M., Gailhanou M., Boissieu M., Alba M., *Structure of smectic defect cores : X-ray study of 8CB liquid crystal ultrathin films*, Phys. Rev. Let. **96**(2006) 027803. 44
  - Elazzouzi-Hafraoui S., Nishiyama Y., Putaux J.L., Heux L., Dubreuil F., Rochas C. , *The shape and size distribution of crystalline nanoparticles prepared by acid hydrolysis of native cellulose*, Biomacromolecules **9** (2008) 57-65. 44
- **Nano structured layers**
  - Coraux, *J. Coraux, V. Favre-Nicolin, M. G. Proietti, B. Daudin, H. Renevier* , Grazing incidence diffraction anomalous fine structure investigation of III-nitride quantum dots. Phys. Rev. B **75**, (2007), 235312. 44
  - Lemee , *Lemee N., Dooryhee E., Bouyanfif H., Le Marrec F., Nemoz M., Hodeau J.-L., Karkut M.G* , Synchrotron x-ray scattering evidence for interlayer structural coupling in $(PbMg_{1/3}Nb_{2/3}O_3)$(1-x)/$(PbTiO_3)$x superlattices. Phys. Rev. B **78**, (2008) 140102. 46
- **Metal engineering**
  - Deschamps A., Lae L., Guyot P. , *In situ small-angle scattering study of the precipitation kinetics in an Al-Zr-Sc alloy*, Acta Materialia **55**,(2007) 2775. 46

This short booklet version does not include in extenso the articles but only their abstract.

PRL **96,** 027803 (2006) PHYSICAL REVIEW LETTERS week ending 20 JANUARY 2006

Structure of Smectic Defect Cores: X-Ray Study of 8CB Liquid Crystal Ultrathin Films

Jean-Philippe Michel, Emmanuelle Lacaze,* and Michel Goldmann
INSP, Universités Paris 6 et 7, UMR-CNRS 7588, Campus Boucicaut, 140 rue de Lourmel, F-75015 Paris, France

Marc Gailhanou
LURE, Batiment 209D, Universit Paris Sud, F-91405 Orsay CEDEX, France

Marc de Boissieu
LTPCM, INPG, BP 75, 38402 Saint Martin d'Hères, France

Michel Alba
LLB, UMR12 CEA-CNRS, CEA-Saclay, F-91191 Gif-sur-Yvette CEDEX, France
(Received 19 April 2005; published 19 January 2006)

We study the structure of very thin liquid crystal films frustrated by antagonistic anchorings in the smectic phase. In a cylindrical geometry, the structure is dominated by the defects for film thicknesses smaller than 150 nm and the detailed topology of the defects' cores can be revealed by x-ray diffraction. They appear to be split in half tube-shaped rotating grain boundaries (RGB). We determine the RGB spatial extension and evaluate its energy per unit length. Both are significantly larger than the ones usually proposed in the literature.

DOI: 10.1103/PhysRevLett.96.027803 PACS numbers: 61.10.−i, 61.30.−v, 68.35.Bs, 68.35.Md

Biomacromolecules **2008,** *9,* 57–65 **57**

The Shape and Size Distribution of Crystalline Nanoparticles Prepared by Acid Hydrolysis of Native Cellulose

Samira Elazzouzi-Hafraoui,[†] Yoshiharu Nishiyama,[*,†] Jean-Luc Putaux,[†] Laurent Heux,[†] Frédéric Dubreuil,[†] and Cyrille Rochas[‡]

Centre de Recherches sur les Macromolécules Végétales (CERMAV-CNRS), BP 53, F-38041 Grenoble cedex 9, France - affiliated with Université Joseph Fourier and member of the Institut de Chimie Moléculaire de Grenoble, and Laboratoire de Spectrométrie Physique, UMR 5588, BP 87, F-38402 Saint Martin d'Hères, France

Received July 11, 2007; Revised Manuscript Received September 25, 2007

The shape and size distribution of crystalline nanoparticles resulting from the sulfuric acid hydrolysis of cellulose from cotton, Avicel, and tunicate were investigated using transmission electron microscopy (TEM) and atomic force microscopy (AFM) as well as small- and wide-angle X-ray scattering (SAXS and WAXS). Images of negatively stained and cryo-TEM specimens showed that the majority of cellulose particles were flat objects constituted by elementary crystallites whose lateral adhesion was resistant against hydrolysis and sonication treatments. Moreover, tunicin whiskers were described as twisted ribbons with an estimated pitch of 2.4–3.2 μm. Length and width distributions of all samples were generally well described by log-normal functions, with the exception of tunicin, which had less lateral aggregation. AFM observation confirmed that the thickness of the nanocrystals was almost constant for a given origin and corresponded to the crystallite size measured from peak broadening in WAXS spectra. Experimental SAXS profiles were numerically simulated, combining the dimensions and size distribution functions determined by the various techniques.

PHYSICAL REVIEW B **75**, 235312 (2007)

Grazing-incidence diffraction anomalous fine structure: Application to the structural investigation of group-III nitride quantum dots

J. Coraux,[1,2] V. Favre-Nicolin,[1,2] M. G. Proietti,[3] B. Daudin,[1] and H. Renevier[1,2,*]

[1]*Département de Recherche Fondamentale sur la Matière Condensée, Commissariat à l'Energie Atomique, SP2M/NRS, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France*

[2]*Université Joseph Fourier, BP 53, 38041, Grenoble Cedex 9, France*

[3]*Departamento de Física de la Materia Condensada, Instituto de Ciencia de Materiales de Aragón, CSIC-Universidad de Zaragoza, c. Pedro Cerbuna 12, 50009 Zaragoza, Spain*

(Received 27 October 2006; revised manuscript received 12 February 2007; published 11 June 2007)

The relevance of grazing-incidence anomalous diffraction as a tool to investigate the strain and structure of small-size embedded nano-objects is examined. Multiple scattering effects, originating from the grazing-incidence setup, are analyzed with a special emphasis on the cusp of the diffraction anomalous spectrum and the extended diffraction anomalous fine-structure oscillations. It is shown that even for grazing-incidence angle, a Born approximation treatment is justified for quantum dots (QDs) on top of a thin wetting layer. The discussion focuses on the overgrowth of AlN on top of GaN QDs. Both the in-plane and out-of-plane strains in the dots can be specifically determined, by extracting the Ga partial scattering amplitude from measurements of the scattered intensity along both the in- and out-of-plane directions, close to the $(30\bar{3}0)$ and $(30\bar{3}2)$ reflections, at several energies across the Ga *K* edge. The study is complemented by the analysis of the local environment of Ga atoms in the dots through the measurement of the fine-structure oscillations in diffraction condition. The oscillations are found almost insensitive to the grazing-incidence multiple-scattering effects. Accordingly, the out-of-plane strain and possible intermixing specifically in the dots can be deduced. The QDs are shown to remain pure GaN all along the capping process. The QDs strain state exhibits a larger strain relaxation than expected from an elastic model, suggesting the presence of a plastic strain relaxation, possibly through dislocations at the vicinity of the QDs. Finally, the influence of the substrate as regards strain relaxation in the QDs is discussed by comparing our results to those we previously obtained for a series of samples grown on AlN/sapphire.

DOI: 10.1103/PhysRevB.75.235312 PACS number(s): 61.12.Bt, 61.10.Ht, 61.10.Nz, 61.46.−w

RAPID COMMUNICATIONS

PHYSICAL REVIEW B **78**, 140102(R) (2008)

Synchrotron x-ray scattering evidence for interlayer structural coupling in $(PbMg_{1/3}Nb_{2/3}O_3)_{(1-x)\Lambda}/(PbTiO_3)_{x\Lambda}$ superlattices

N. Lemée,[1,*] E. Dooryhée,[2] H. Bouyanfif,[1] F. Le Marrec,[1] M. Nemoz,[2,†] J. L. Hodeau,[2] and M. G. Karkut[1]

[1]*LPMC, Université de Picardie Jules Verne, 33 rue St. Leu, 80039 Amiens, France*

[2]*Institut Néel, CNRS-UJF, UPR 2940, 25 avenue des Martyrs, BP 166, 38042 Grenoble, France*

(Received 7 July 2008; revised manuscript received 19 September 2008; published 10 October 2008)

We present evidence for in-plane coupling in relaxor $PbMg_{1/3}Nb_{2/3}O_3$ / ferroelectric $PbTiO_3$ superlattices $[PMN_{(1-x)\Lambda}/PT_{x\Lambda}]_{10}$. For constant superlattice wavelength $\Lambda = d_{PMN} + d_{PT}$, we find that by varying the constituents thicknesses d_{PMN} and d_{PT} a significant effect is observed on the internal a_1/a_2 domain structure of the PT layers as well as on the appearance of domains in PMN. Since the strain effects on the structural patterns can be modulated by adjusting x, this is one way to control the polarization axis on a nanoscale level.

DOI: 10.1103/PhysRevB.78.140102 PACS number(s): 77.84.−s, 61.05.cp, 68.65.Cd, 77.80.Dj

ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

Acta Materialia 55 (2007) 2775–2783

Acta MATERIALIA

www.actamat-journals.com

In situ small-angle scattering study of the precipitation kinetics in an Al–Zr–Sc alloy

A. Deschamps *, L. Lae, P. Guyot

SIMAP, INPGrenoble-CNRS-UJF BP 75, 38402 St Martin d'Hères, France

Received 18 July 2006; received in revised form 12 December 2006; accepted 15 December 2006
Available online 12 February 2007

Abstract

A time-resolved small-angle X-ray scattering (SAXS) study was carried out to investigate the precipitation kinetics of $L1_2$ $Al_3(Zr,Sc)$ precipitates in aluminium at temperatures ranging between 400 and 475 °C. It is shown that the chemical heterogeneity of the precipitates, which consist of a Sc-rich core and a Zr-rich shell, results in a characteristic SAXS signal, which can be fitted by a three-phase model to extract the chemical and morphological features of the precipitate size distribution. The experimental results show a strong effect of the heating rate on the precipitation kinetics, and a precipitate density strikingly constant with time in the investigated range. These results are discussed in view of the mechanisms proposed in the existing literature for the formation of the core–shell structure of these precipitates.

Keywords: Small angle X-ray scattering; Aluminium alloys; Al–Zr–Sc; Precipitation; Chemical heterogeneity