DISORDERED SYSTEMS AND MATERIALS SCIENCE

The Laboratoire Léon Brillouin is progressively putting in place a pole of research in the field of materials science, in strong relationship with external laboratories. Indeed, it is the role of a national research infrastructure such as LLB to train the scientists working in french applied research and industrial laboratories, and to give them access to its characterization facilities.

The research at LLB in materials science covers two main domains : soft matter and metallurgy (in the broad sense, i.e. including ceramics, metal matrix composites, etc...). The results concerning soft matter are included in the chapter "Chemical Physics and Biology" of this report.
In the domain of metallurgy and ceramics, the properties of technological interest depend on the defect properties and on the defect structure of the material at the atomic (vacancies, impurities,...) or at the mesoscopic (dislocations, porosities,...) level. This is why materials science requires a fundamental corpus of knowledge on defects and disorder. In particular, the fundamental study of atomically disordered systems allows to develop theoretical models, and to validate numerical simulations (Monte-Carlo, molecular dynamics, etc...) which are then applied to understand "real" materials. Particularly important is the extrapolation of their properties at long time in operating conditions, and the prediction of their behaviour under thermal or irradiation-induced ageing.
At the interface between the study of disordered systems and materials science is physical metallurgy, working on model systems (e.g. phase transformations in binary alloys, etc...).

1. DISORDERED SYSTEMS

1.1. Introduction

The scientific activity of LLB in the field of disordered systems is mainly concentrated on the study of local atomic arrangements in topologically or chemically disordered solids or liquids, by elastic diffuse neutron scattering. Two instruments are entirely devoted to these studies :

- the 7C2 diffractometer, installed on the "hot" source, with short wavelength (generally ˜ 0.7 Å) neutrons, and equipped with a 640 cell position sensitive linear multidetector, for liquid and amorphous systems;
- the G4.4 diffractometer, installed on a "cold" neutron guide, managed by ONERA and CEA/LSI, with time-of-flight analysis, devoted to the "in situ" high temperature study of local order in single crystals.

In the case of systems presenting a tendency towards phase separation, complementary studies by Small-Angle Neutron Scattering (SANS) are necessary.
Some studies of dynamics, mainly on glass transition, are also performed at LLB by external users, in particular with the time-of-flight inelastic spectrometer MIBEMOL.

1.2. Metallic alloys : local order, kinetics

This thematics is mainly developed at LLB by the team of LEM (ONERA-CNRS, R. Caudron et al).
A systematic "in situ" high temperature study of elastic diffuse neutron scattering in a series of f.c.c. binary transition metal alloys, performed on G4.4, has allowed a detailed understanding of their chemical order-disorder properties, and a fruitful dialogue with the statistical physics theory of alloys. This 10-years programme was concluded in 1997 by the PhD thesis of D. Le Bolloch on $Pt_{1-x}V_x$ alloys. In the frame of this work, it was in particular shown that, although $Pt_{0.75}V_{0.25}$ long-range orders below T_c = 500°C with superstructure diffraction peaks at (1 1/2 0), the maxima of the diffuse intensity above T_c are at the (100) positions. Moreover, the diffuse intensity for another concentration, x=1/9, displays a splitting around (100) with maxima at incommensurate positions. It was found that, despite this strong concentration dependence of the diffuse intensity shape, the Effective Pair Interactions deduced of the experimental data by a reverse Monte-Carlo method, are nearly concentration independent, in contradiction with *ab initio* theories. A high temperature expansion of the mean-field theory was developed, and explained successfully the origin of this splitting, and its dependence with concentration and temperature.

This work is now being extended to kinetic phenomena (PhD thesis of X. Flament). Mean-field theory suggests for Pd_3V two different spinodal (instability) temperatures for the two ordering wave-vectors, e.g. (100) and (1 1/2 0). Monte-Carlo simulations and preliminary synchrotron X-ray experiments are in agreement with these predictions.
Several studies of local order and concentration fluctuations in various crystalline (Ni_2Cr, Ni-based superalloys) or amorphous (Fe_2Zr, $Ti_{84}Si_{16}$, selenite glasses) systems have also been performed by other groups (LSI/Palaiseau, CEMES/Toulouse, LLB, MPI/Stuttgart, Bulgarian Academy of Sciences (Sofia)).

1.3. Local order in quasi-crystals and their liquid precursors

If the indexation of diffraction peaks in quasi-crystals can be made with success, the problem of positions of specific types of atoms is far from being resolved. Is there or not chemical disorder ? This has an important impact on our understanding of the origin of the stability of these materials at room temperature : i.e. are they stabilized by defects when cooling from high temperature ? If such a disorder exists, it should manifest itself by an elastic diffuse scattering in the neutron or X-ray diffraction spectra. Scarce information existing up to now led to conflicting results. The advantage of neutrons over X-rays is the easiness to obtain absolute cross-sections and the possibility to separate experimentally the inelastic thermal diffuse scattering due to phonons. The difficulty with neutrons is their sensitivity to hydrogen contamination, and the lower q-resolution to well separate the Bragg peaks. We have therefore undertaken a study at LLB on this subject (PhD thesis of N. Schramchenko) in collaboration with LEM (ONERA-CNRS) and CECM-Vitry, where the samples are made.
First experiments performed on G4.4 at LLB on a single grain of Al-Pd-Mn, allowed to observe at room temperature a diffuse scattering far from the Bragg peaks. Normalized, it is in agreement with the theoretical disorder term from an approximant phase ξ' of similar composition. The data treatment is delicate, because one has to correct for a very large number of very small Bragg peaks.

The preliminary work presented in the previous LLB report (1995-96) on liquid precursors of Al-Pd-Mn, has been extended and completed in the frame of a multi-laboratory collaboration (LPS-Orsay, LTPCM-Grenoble, LLB-Saclay, PhD thesis of V. Simonet, Orsay, 1998, see highlight). The set of diffuse neutron scattering measurements performed at LLB on 7C2, and subsequently extended at ILL on D4B, confirmed the presence of a local order reminiscent from the solid, and could be fitted by a cluster-based ($Al_{12}Mn$ icosahedron) numerical simulation.
Polarized neutron scattering experiments performed at D7, ILL, have confirmed the appearance of a magnetic signal in the liquid state, deduced previously from coupled 7C2 neutron scattering and magnetic susceptibility measurements.

1.4. II-VI and IV-VI liquid compounds

The classical semi-conductors of group IV (Si, Ge) as well as the III-V compounds (GaAs, GaSb) undergo at the melting point a semi-conductor $\rightarrow$ metal transition, associated to a change of coordination number ($4 \rightarrow 6$). On the contrary, some II-VI compounds (CdTe, ZnTe) remain semi-conducting and tetrahedrically coordinated in the liquid state. To understand the origin of this behaviour, we have undertaken, in collaboration with the University of Liège, an experimental and theoretical study of Cd_xTe_{1-x} in all the concentration range (PhD thesis of G. Prigent).
Monte-Carlo simulations in the frame of a tight binding model, have shown that the local order in these systems is mainly governed by the competition between the $s \rightarrow p$ promotion and the gain in binding energy (resonance between sp^3 orbitals). The charge transfer plays only a small role. CdTe remains semi-conductor, because the s level of Cd and the p level of Te are close in energy.
A double metal $\leftrightarrow$ semi-conductor $\leftrightarrow$ metal transition versus composition in the liquid state was observed experimentally from electrical measurements performed at the University of Metz. A fine analysis of neutron scattering (obtained on 7C2) and EXAFS data suggests a coexistence of metal Cd-rich and semi-conducting CdTe-rich domains of nanometric size for $x > 0.5$.

On the same subject, the team of University de Liège observed on 7C2 an astonishing re-entrant Peierls distortion in several IV-VI compounds : SnS, SnSe, GeSe and GeTe (PhD thesis of D. Raty) : the Peierls distortion, observed at low temperature and which disappears when heating in the crystalline state, is recovered in the liquid state.

1.5. Fundamental structural studies of simple fluids

Very precise Small-Angle Neutron Scattering experiments, performed on noble gas (e.g. krypton) by an italian group of the University of Firenze (R. Magli et al.), succeeded to show, for the first time, the role of irreducible three-body forces in the interatomic potential. Density fluctuations in these fluids have been measured in function of temperature and pressure and near the critical point.

1.6. Critical and supercritical fluids

Water is always an important and "hot" topic and gave rise to many studies where the structure and H-bond dynamics have been explored in various states, including metastable states under pressure and water in confined geometries (see the chapter "Chemical Physics and Biology" of this report). In particular, recent modelisation of LLB neutron diffraction experiments suggest strongly that two forms of liquid water may coexist at very low temperatures, possibly shedding light on why water has such unusual properties compared to other liquids. These structural and dynamic studies have been extended to water in supercritical state.

Supercritical water presents physical and chemical properties, e.g. viscosity and dielectric constant, which differ greatly from those of the liquid water. In particular, it is possible to dissolve in supercritical water organic or mineral substances, which are hardly soluble in normal liquid water. This is of great interest, in particular for depollution applications.
In view of developing these techniques, a "Club of Supercritical Fluids applied to Nuclear Industry" has been created in 1994. M.C. Bellissent-Funel chairs this group since 1998. It was decided to study at LLB by neutron scattering the local structure and dynamics of critical and supercritical fluids (water, CO_2, aqueous solutions), in order to validate Molecular Dynamics simulations (LPTL, University of Paris VI).

The partial pair correlation functions $g_{OD}(r)$, $g_{DD}(r)$ and $g_{OO}(r)$ in supercritical heavy water (T=380°C, pressure : 600 bar, density : 0.73 g/cm^3) were determined by a reverse Monte-Carlo method from the 7C2 neutron data obtained on D_2O and two isotopic H_2O/D_2O mixtures, and from X-ray data (which gives the O-O partial structure factor). The structure of supercritical water is very different from that of water in ambient conditions. Nevertheless, modelisation of these data by Molecular Dynamics simulations show clearly that in dense supercritical water, although the tetrahedral arrangement of water molecules is lost, some hydrogen bonding is still present, contrary to previous statements of other authors.
SANS study of supercritical heavy water showed a large increase at small q (0.07 to 0.36 Å^{-1}) due to the divergence of density fluctuations at the critical point, and allowed the first measurement of the critical correlation length ξ_0 for water; the value, 1.36 ± 0.06 Å, is in fair agreement with theoretical predictions.
A first study of the (picosecond range) dynamics of supercritical H_2O by incoherent inelastic and quasielastic neutron scattering, performed by LLB researchers on IN6 at ILL, allowed to determine the evolution of D (translational diffusion coefficient of the water molecules), L (jump distance) and τ_0 (residence time) as a function of the density of the medium. D and L increase strongly as the density decreases. τ_0 is ten times shorter than that measured in liquid water at room temperature.

Simple fluids (CO_2, SO_2) or fluid mixtures (H_2O-benzene, CS_2-benzene, CS_2-C_6F_6, ...) are also the object of structural studies in the critical and supercritical states (LASIR, Lille, LPCM, Bordeaux, Universities of Lisboa and of Roma III).

1.7. Phase separation

Several studies performed by external laboratories approached the problem of phase separation in solids and liquids.

Isotope ordering of hydrogen and deuterium, predicted theoretically by Prigogine in 1954, was proved for the first time at LLB by an international team led by M. Bienfait (CRMC2, Marseille) (see highlight) : a clustering process of isotopic hydrogen mixtures H_2-D_2, adsorbed in order to form one monolayer on graphite (0001), was observed from 8 K downwards, at and above monolayer completion, by SANS and neutron diffraction measurements. This trend towards phase separation depends strongly on coverage and isotopic concentration.

A remarkable closed-loop miscibility gap has been found in the liquid tellurium-sulfur ($Te_{1-x}S_x$) binary diagram around x = 0.4, which is a unique observation in an inorganic system. Neutron diffraction measurements performed on 7C2, showed that this is directly related to a sudden change of the tellurium coordination at high temperature, from nearly 3 for $x < 0.4$ (as in pure Te), to around 2 for $x > 0.4$ (PhD thesis of M.V. Coulet, CTM Marseille).

A systematic study by neutron scattering of the local order of several liquid alloys (Mn-Sb, Mn-Ge, Ga-Pb), presenting a miscibility gap at lower temperature, has been undertaken on 7C2 by a team of the University of Metz (J.F. Gasser et al). It allowed to test interatomic potentials obtained by electronic structure calculations, and to explain the anomalous behaviour of electronic conductivity and thermal expansion in these alloys.

The understanding of the role of an uniaxial elastic strain on the phase separation in binary metallic alloys presenting a large size effect between the two atomic constituents, is object of a detailed small-angle neutron scattering work by the austrian team of University of Vienna associated to LLB (O. Blaschko†, M. Prem). In particular, they could show that such strain applied during thermal treatment induces an anisotropy in the shape of the precipitates formed in CuRh, which can be explained by a misfit compensation mechanism.

1.8. Dynamics. Glass Transition

The study of relaxation processes in liquids near the glass transition has been the object of several studies performed by C. Alba-Simionesco (CPMA, Orsay). Combination of quasi-elastic spectra obtained in a wide frequency range show the existence of two relaxation processes. Several studies were performed under pressure, in order to separate the respective roles of volume reduction due either to pressure increase or to temperature decrease in the structural arrest near the glass transition.
Several other studies of the dynamics of disordered systems were performed by external laboratories at the LLB, mostly on the time-of-flight inelastic instrument MIBEMOL. These include :
- the first study of the vibrational density of states of carbon nanotubes (University of Montpellier);
- measurement of the mobility of HD molecules adsorbed on incommensurate Kr plated graphite, which confirmed the existence of a reentrant fluid phase, squeezed in between the commensurate and incommensurate phases (collaboration between Universities of Mainz, Germany, and of Marseille, France);
- study of the vibrational dynamics in plastic crystals (where a periodic lattice coexists with translational disorder) (Universities of Augsburg and Munich, Germany);
- dynamical behaviour of molecules confined in the pores of SiO_2, which allowed to distinguish non-rotating molecules adsorbed on the pore walls, and rotating molecules within the pores (University of Kiel, Germany);
- influence of the cross-linking ratio on the dynamics of the glass transition (University of Montpellier).

1.9. Evolution and Perspectives

The specificity of neutron-matter interaction leads to develop its use on samples held in extreme conditions (e.g. high temperatures, high pressures,...), as exemplified by the LLB studies on supercritical fluids. In this aim, an important upgrade of the 7C2 diffractometer for liquids is planned, in collaboration with several external french laboratories. It consists in :

- developing high temperature devices, in particular contactless heating methods : gas levitation technique for insulating liquids, and electromagnetic levitation for conducting liquids;
- increasing the counting rate (new more efficient multidetectors, improved neutron optics), in particular to improve the signal-to-noise ratio in the case of the small samples required by the above techniques.

This instrument upgrade will allow new applications in several important fields :

- materials processing : local structure of the liquid formers of metallic or oxide materials prepared by solidification;
- geophysics : "in situ" study of the high density forms of silicate glasses.

2. MATERIALS SCIENCE

2.1. Introduction

Materials Science aims to understand the properties of solid systems in their full complexity, and to optimize these properties by acting on the composition, atomic structure, and microstructure. This is a different approach to that of condensed matter physics, which focuses on model systems to study a given property or phenomenon. Obviously, materials science has an immediate bearing on industry and applications.
Neutrons are an ideal probe for studying the structure of materials, particularly because of their low absorption, which makes it possible to work on centimetre-thick parts, and the relative ease with which experiments can be carried out under complex or extreme conditions, such as high temperatures or applied stress.

Research currently under way at LLB includes studies in :

- Residual stress evaluation in complex systems,
- Evolution of textures with thermal or mechanical processing,
- Structure heterogeneity, precipitation, ageing of materials,
- Properties of coated glasses and gratings.

Studies on industrial materials are usefully complemented by studies of model materials that are easier to interprete. Methods for analysing the reciprocal lattice (neutron and X-ray scattering) and the real lattice (electron microscopy, atomic probe, near-field microscopy) are complementary, and always used together, especially for complex industrial materials.

2.2. Residual stresses

In the last decade, the use of neutron diffraction for stress analysis in components of technological interest has strongly developed. In fact, the unique properties of neutrons, in particular their high penetration depth, mean that neutron diffraction is the only non-destructive technique which enables the stress field evaluation within a defined volume in a bulk sample. Diffraction of hard X-rays, such as those available at the ESRF (Grenoble), open new possibilities, but also present technical difficulties and limitations (e.g. shape of the gauge volume).
In the last years, a new diffractometer entirely dedicated to stress analysis, DIANE (G5.2), was built up at the LLB in Saclay, in collaboration with the italian INFM (Istituto Nazionale di Fisica della Materia). It has been designed in order to meet engineering requirements : good spatial resolution (of the order of 1 mm^3), accurate positioning of the specimen in three orthogonal directions, an adequate space for manipulation of heavy and cumbersome samples on the diffractometer, good instrumental resolution (high monochromator take-off angle), and fast data collection (Position Sensitive Detector).
A widely spread activity has been developed in the last two years at the LLB in the field of residual stress analysis, partly in collaboration with the University of Reims-Champagne-Ardenne (Prof. A. Lodini).

The main fundamental studies performed at the LLB in the field of residual stress analysis are summarized below :

Microstrain evaluation. Measurements of the diffraction line profile on DIANE at LLB allowed for the first time to characterize non-destructively the plastic region (i.e. its size and the maximum strain) at the tip of a crack in a stainless steel fatigue test specimen (PhD thesis of K. Hirschi, see highlight).

Residual stresses in metal matrix composites (MMC). We have studied and modelized the effect of plasticity on the thermally induced residual stresses in an Al matrix MMC reinforced with SiC particles (PhD thesis of R. Levy-Tubiana, in collaboration with M. Fitzpatrick, The Open University, U.K., and A. Baczmanski, University of Krakow, Poland).

Strains in geological materials. Elastic residual strains, required by the natural continuity of solids, originate in the rocks during the fold of the upper crust. Neutron diffraction is the only technique which allows to determine the internal strain tensor in polycrystalline rocks. For the first time, residual elastic strains have been determined in polycrystalline samples of geological interest (quartzites). The components of the strain tensor, determined on DIANE at LLB, are weak in absolute value, but significant. These residual elastic strains were found to disappear in recristallized samples. An hydrostatic compressive state was also found in one sample, and is probably due to the presence of secondary phase inclusions (J.C. Guezou et al, University of Cergy-Pontoise).

Parallel to this fundamental activity, great effort is made to **open the neutron diffraction technique for stress analysis to industrial users**. To this end, we are involved in several international programs and industrial collaborations.

a) **VAMAS TWA 2O** is an international programme, the objective of which is to establish accurate and reliable procedures for making reproducible and standardized non-destructive neutron diffraction residual stress measurements. It includes representatives from industry, universities and 13 neutron sources, in Canada, Europe, Japan and the USA. Different types of samples, in which residual stresses have been introduced by various procedures, are examined by the participating neutron sources, according to a common protocol. In the last two years, an aluminium alloy shrink-fit and plug has been examined for "round robin" inter-laboratory comparison. The results obtained on DIANE allow to classify this instrument as one of the most performants.

b) **TRAINSS** is a 4-years (1998-2001) european network, of the Brite-Euram III programme, aimed to train european industrial laboratories to the use of neutron diffraction for determination of internal stresses. The TRAINSS network groups 4 neutron sources (among which LLB), 6 university laboratories (among which ENSAM, Paris), and 10 industrials which bring specific problems (among which SNCF and PSA-Peugeot-Citroen). Two weeks per year of neutron beam time are devoted to this programme on the DIANE diffractometer. SNCF is interested in the influence of residual stresses on the propagation of cracks in the wheel axles of railway engines and carriages. The PSA problem is the determination of residual stresses in the discs of motor-car brakes.

c) Two other contracts with french industry have been initiated recently : with SNECMA (residual stresses in a Ti matrix-SiC fiber MMC, for compressor discs and blades of airplane motors), and with Aerospatiale (residual stresses in a welding between aluminium alloy plates for Airbus).
EDF financed a PhD thesis, submitted in 1997 (E. Pluyette), which allowed to realize a numerical modelization of the DIANE diffractometer, aiming to improve the measurement of residual stresses across interfaces (e.g. a bimetallic welding).

d) Various studies of residual stresses in technological components were made by external laboratories, in particular :

- the stress profile was measured along the throat of automotive gears, which had undergone a surface treatment (R. Magli et al, University of Firenze and LLB);
- the stress gradient could be resolved in a ceramic (AlN) plate as thin as 0.6 mm, which is well below what is commonly achieved in neutron stress analysis, and proves the excellent performance of DIANE (L. Pintschovius, Kf Karlsruhe);
- residual strains and stresses in MMC's, weldings and brazings for nuclear fusion technology (NET / ITER programme), coated materials, etc... (University of Reims, University of Ancona, ENEA (Italy), The Open University (UK)).

2.3. Textures

Crystallographic texture (preferred orientation of grains) is one of the parameters describing the microstructure of a polycrystalline material, which controls partly its mechanical properties. In metallic alloys, the texture appears during the solidification, then transforms during rolling or wiredrawing, and ultimately during recrystallization. The understanding and the mastering of its texture during thermomechanical and/or annealing treatments are necessary in order to optimize the mechanical behaviour of a material.

Neutron diffraction is the best technique for obtaining precise texture of bulk specimens (~ 1 cm^3), under the form of a distribution function of crystalline orientations. Its use is in particular necessary in the case of coarse-grained materials (= a few mm^3), where conventional X-rays are inapplicable.

LLB has a diffractometer specially devoted to the determination of crystallographic textures : 6T1, equipped with an Euler craddle. The study of textures at LLB is made in strong collaboration with the Laboratoire de Métallurgie Structurale (LMS) of the Orsay University (T. Baudin, R. Penelle), where are performed complementary studies by EBSD (Electron BackScattered Diffraction) and numerical simulations of the evolution of the microstructure.

An important number of experiments was made to determine the texture in two-phase materials of technological interest, and to study the relation between texture components of each phase. Let us mention two of them :

- In the two-phase Ti-based high strength alloy ßCEZ, developed for use in the compressor of jet engines, it was found that the sharpness of the crystallographic texture (but not its components which follow the usual orientation relationship) is strongly dependent on the morphology of the α-phase. This has important implications on the optimization of the thermomechanical treatments (LLB and University of Orsay).
- In a welded joint of 316L stainless steel containing coarse grains of f.c.c. austenite and a very small content (5%) of b.c.c. δ ferrite, the neutron diffraction analysis showed that on a macroscopic scale, both phases are in a cube-cube relationship, with a fiber texture [010] along the solidification direction. This unusual result shows that solidification has been duplex itself, with a solidification front and the growth of both ferrite and austenite primary phases; it is introduced in the numerical codes predicting the mechanical behaviour of the welding (J.L. Béchade et al, SRMA, Saclay, and Ecole des Mines de Paris).

Furthermore, the recrystallization process has been more specially investigated in different materials :

- The texture of Ti-Al based intermetallic alloys, considered for aerospace industry, influences their ductility and creep behaviour. A study of the dependence of texture on forging and (dynamic and static) recrystallization conditions has been undertaken, in order to suppress or reduce this texture and optimize the mechanical properties of the material (PhD thesis of Y. Hersart, University of Orsay).
- In a $Fe_{0.5}Ni_{0.5}$ alloy, neutron diffraction, associated to Transmission Electron Microscopy and EBSD experiments, allowed to follow the growth kinetics of the cube texture (which is interesting for magnetic applications) to the detriment of the deformation ones, after cold rolling and annealing. This study allows to improve the simulations of the recrystallization (LLB and LMS).

Since several years, a part of the texture activity at LLB is dedicated to the study of geological materials. In particular, neutron diffraction coupled to microstructural observations allowed, in quartzites coming from the betic zone of Spain, to identify two main components, {1-210} <10-10> and {1-101} <1-120>, which have been associated respectively to the deformation and the recrystallization (University of Cergy-Pontoise).

2.4. Phase analysis

A research programme has been undertaken since 1997 at LLB by the Direction of Nuclear Reactors in CEA, Saclay, to characterize and study hydrogen-containing zircaloy-4 alloys, used as fuel cladding in Pressurized Water Nuclear Reactors (PWR) (see highlight). Because of its low thermal neutron absorption and incoherent cross-sections, Zr is a very favorable material for such studies. In a single experiment, it was possible to obtain the total

hydrogen content with high sensitivity and precision (< 20 ppm weight), the hydrogen content in hydride form, the crystallographic characterization of precipitates (hydrides and Laves phases), and to follow "in situ" up to 500 °C the influence of H on the thermal expansion of zircaloy-4 and the thermal dissolution of hydrides. This last information allowed to determine the solubility of H in the material between room temperature and 500 °C.

2.5. Nanopowders and sintering

The last two years have seen an important development of studies in this domain by neutron scattering (SANS and diffraction). Among these, two correspond to a more systematic and fundamental approach.

- The austrian group at LLB was one of the first to undertake an understanding of the sintering mechanisms. Their recent results concern nanocrystalline Y_2O_3 powders : the behaviour, summarized as variation of the total surface of pores (deduced from the Porod law in SANS) versus the volume fraction of porosity, was found very different from that of conventional micrometre-sized powders. Two successive stages are distinguished; in the first one, the surface of irregularly-shaped pores is reduced by surface diffusion, at nearly constant porosity; the second one corresponds to a reduction of total pore volume by transport of vacancies towards the external surface.
- Since 1997, a research programme was undertaken at LLB by the Section de Recherches en Métallurgie Physique of CEA/Saclay, on reactive milling and sintering. The first study concerns the composite material Ag-SnO_2, which is developed for electrical connections applications (PhD thesis of N. Lorrain). Neutron scattering allowed to follow separately the thermal evolution of different types of porosities (using wetting techniques), and the size of Ag and SnO_2 particles during the sintering process. This evolution could be correlated with the formation of small cavities filled with gas, and their subsequent connection in channels at higher temperature.

2.6. Ageing of materials

Nanometer-sized precipitates dispersed in ductile metallic alloys, generally increase the hardness of the materials. A major drawback is the reduction of fracture toughness : this embrittlement, which may appear during ageing in operating conditions, raises safety problems in nuclear industry.

In this context, within the last decade, the thermal or irradiation-induced ageing of materials of nuclear interest has been the object of several studies at LLB by SANS : in many cases, this is the technique which displays the largest scattering contrast between matrix and precipitates; moreover, in the case of (ferromagnetic) steels, supplementary information is obtained from the magnetic interaction with the neutron. We shall mention here the main results obtained in the last two years by CEA and by the german team of Forschungzentrum Rossendorf.

The CEA programme in this field is the object of a collaboration between LLB, the Service de Recherches Métallurgiques Appliquées (SRMA, CEA / Saclay) and the Laboratoire des Solides Irradiés (LSI, CEA / Ecole Polytechnique, Palaiseau).

A new research programme started in 1996 on the ageing of low activation martensitic steels for the fusion reactors (ITER programme). SANS measurements performed at LLB under magnetic field on thermally-aged samples, allowed to characterize the precipitation of carbides (undetected by Transmission Electron Microscopy), and showed a direct correlation between the observed number density of precipitates and the hardening of the material. Furthermore, the stability under neutron irradiation was found to be strongly dependent of the chromium content in the alloy, some of the samples showing an accelerated coherent phase separation of the b.c.c. ferrite into an iron-rich (α phase) and a chromium-rich (α' phase) components (see highlight).

Two austeno-ferritic samples taken on valves situated on the primary circuit of the PWR nuclear reactor of CHOOZ-A, which operated 140 000 hours respectively at 301°C (hot pipe) and 266°C (cold pipe), were studied by SANS, and showed α-α' phase separation in the ferrite responsible of a strong embrittlement; surprisingly, the cold pipe showed a larger phase separation than extrapolated from laboratory ageing tests (= 30 000 hours).

Neutron-irradiated surveillance specimens of Russian VVER-440 type nuclear power plants were investigated and carefully analyzed by SANS at LLB by a German team (Forschungzentrum Rossendorf). The volume fraction of the nanoscaled defects was shown to increase with the neutron fluence, whereas their size distribution (1 to 4 nm) does not change. After post-irradiation annealing, one observes both coarsening and dissolution of the nanoscaled defects. By comparing the ratio of magnetic and nuclear scattering with ASAXS (Anomalous Small-Angle X-ray Scattering) and APFIM (Atomic Probe - Field Ion Microscopy) results, it could be shown that the irradiation-induced defects are clusters consisting of vacancies and different alloying atoms like Mn, Cu and Si in the case of commercial heats, but mainly vanadium carbide in the case of laboratory heats.

2.7. Thin films and multilayers

The major use of neutron reflectivity is in the field of magnetism (with polarized neutrons) and in soft matter. For non-magnetic and non-organic materials, X-ray reflectometry is the usual technique. Nevertheless, neutrons are

useful in the case of favorable contrast : e.g. multilayers or thin films containing titanium, which has a negative scattering length.

This is the case of SiO_y / TiO_x bilayers deposited on glass to optimize solar light transmission properties. A study performed with Stazione Sperimentale del Vitro (Murano, Italy) allowed to obtain much more information (i.e. thickness, roughness, composition) than spectrophotometry, and therefore to calculate the light transmission with improved precision.

The collaboration with Société CILAS on the behaviour of Ti-Ni supermirrors under neutron irradiation finished in 1997 (PhD thesis of K. Nguy). The neutron reflectivity data show that the supermirrors on boron glass cannot be guaranteed after a neutron dose of 3 10^{19} n.cm^{-2} (decrease of 30 % of the reflectivity), which corresponds to 8 years for the core side of the reactor beam holes of Orphée (which see a flux of ~ 10^{11} n.cm^{-2}.s^{-1}), and 80 years at the outlet of the beam holes (i.e. beginning of the guides, flux : ~ 10^{10} n.cm^{-2}.s^{-1}). For the HFR (ILL, Grenoble), because of the higher flux, these numbers are reduced respectively to 1 and 11 years.
Moreover, it was also shown that the boron glass substrate itself deteriorates, by formation of He bubbles.
In conclusion, for the installation of supermirrors at the entrance of the guides, a solution with a metallic substrate, which would offer also better thermal exchanges, should be tested.

In a more prospective direction, we could observe for the first time in non-specular reflectivity diffraction lines from micrometric periodic gratings realized on nickel films. This opens new perspectives for the study of magnetic nanostructures in the plane of thin films, through polarized neutron reflectometry.

2.8 Evolution and Perspectives

Applied research on materials using neutron scattering is expanding, driven by its non-destructive character and the technological needs of society. To meet these needs and promote the neutrons of Orphée by industry, LLB, with the help of its funding organisms (CEA and CNRS), is establishing a new strategy : marketing documents and web page, meetings and workshops, new internal organization. Two meetings have been recently organized in Saclay on the industrial applications of neutrons : a french-italian workshop (in january 1999), and an internal CEA workshop (in june 1999).
We intend also to put in place a new fast access procedure for testing and rapid characterization of samples (in particular in the field of powder diffraction); this is foreseen for the end of 1999.

It is of course important to upgrade the experimental facilities. With a financial participation of INFM (Italy), the stress spectrometer is being equipped with a testing machine that enables strain scanning under constant load (up to 25 kN), constant strain rate or fatigue cycles. The texture diffractometer will be improved with a furnace for in situ measurements and a multidetector to reduce the acquisition time.

From the fundamental point of view, we intend to develop the following subjects in the next years :

- in situ investigation by neutron diffraction (during thermal treatment and/or applied load) of the structure, microstructure and internal stresses in composite materials, with emphasis on line profile analysis *(University of Wien, LLB, University of Reims-Champagne Ardenne, and INFM)*;
- fundamental understanding of the microstructure and texture evolutions of a model two-phase material (50-50 austeno-ferritic steel) during deformation and recrystallization *(International Programme involving LMS/Orsay, LLB, and the Institute of Metallurgy and Materials Science of Krakow)*;
- correlation between milling conditions and microstructure of Giant MagnetoResistive nanocomposite materials (such as (Co, Fe) Cu) *(PhD thesis of S. Galdeano, LLB and CEA / SRMP, Saclay)*;
- SANS study of the influence of irradiation on spinodal decomposition (i.e. α-α' phase separation in b.c.c. Fe-Cr solid solution) *(LSI / Palaiseau and LLB)*.

Future trends in the field are the following :

- enlarged realization of "in situ" experiments;
- coupling with numerical simulations of the behaviour of materials, one major objective of the neutron experiments being the validation of models or codes;
- study of non-metallic materials : e.g. microstructure and ageing of cements;
- development of the study of materials of geological interest : the problems here are very similar to those encountered in metallurgy, with a predominant role of thermomechanical history on the microstructure.