STRUCTURES AND PHASE TRANSITIONS

Both crystallographic and magnetic structural phase transitions are an important component of Laboratoire Léon Brillouin's scientific activity. Neutron studies, either diffraction and/or inelastic scattering, are performed as a function of external parameters, namely temperature and pressure. Many different physical problems, both fundamental and applied, are in connection with phase transitions and the present summary intends to show the main results of the research in the field in 1999 and 2000, from perovskites to molecular crystals, from superalloys to hydrides, from carbon nanotubes to ice surfaces, from incommensurate to quasicrystalline materials, with an important LLB contribution in solid state's theory. Let us note however that magnetic phase transitions are dealt with in a different chapter of this report.

PEROVSKITES : CHARGE/ORBITAL/SPIN ORDERING IN MANGANESE OXIDES

In manganese perovskites with giant magnetoresistance behaviour, correlations between Charge, Orbital and Spin orders is still a puzzling problem. In these compounds, insulating antiferromagnetism is usually understood within superexchange theory and an underlying ionic picture of charge and orbital ordering. This picture was recently "revisited" by a careful analysis of the crystal structure of a half-doped manganite (single crystal X-ray and neutron diffraction) [M. Daoud-Aladine, PhD, J. Rodriguez-Carvajal, LLB; in collaboration with L. Pinsard-Gaudart, A. Revcolevschi, Laboratoire de Physico-Chimie des Solides, Université Paris-Sud; M.T. Fernandez-Diaz, ILL]. A more complete description of the obtained results is given in the chapter "Magnetism and Superconductivity".

PEROVSKITES WITH ULTRA-HIGH ELECTRIC RESPONSES

Materials with ultra high piezoelectric, dielectric and electromechanical responses are widely used for technological applications such as capacitors, sensors, actuators… in the form of ceramics or thin films; they are mainly relaxor lead Pb(B,B')O3 oxides or belong to strontium titanate based compounds ($SrTiO_3$) in which a A-cation is substituted to strontium. They are extensively studied at LLB by the Laboratoire "Structures, Propriétés, Modélisation du Solide", UMR 8580, Ecole Centrale Paris (J.M. Kiat et al.; PhD: C. Ménoret). Physical properties are crucially dependent of the local polar order which drastically changes with the amount, size and charge of A, B, B' cations as well as the grain or film sizes, the electrical field and the thermal history. The combination of neutron scattering with high resolution X-ray diffraction is the only way to get information on the structural properties at nano- and meso-scales in order to understand and tailor the useful properties of these materials. In particular the structural evolutions within the phase diagrams of $PbMg_{1/3}Nb_{2/3}O_3/PbTiO_3$ (PMN/PT) and $SrTiO_3/BaTiO_3$ (SBT) have been determined and extensively studied using neutron diffraction (single crystal and high resolution powder studies, on 6T2 and 3T2 diffractometers respectively). In PMN/PT, a new monoclinic ferroelectric phase in the morphotropic concentrations was discovered, which allows the rotation of the polarisation between the rhombohedral and tetragonal adjacent ferroelectric phases: this new phase is clearly associated to the high piezoelectric response of these materials. In SBT, the $SrTiO_3$-like ferroelastic non ferroelectric distortion continuously decreases and vanishes with Ba concentration: above a critical concentration of 10% [Ba], $BaTiO_3$-like distortions appear and a long range ferroelectric order is recovered.

SUPERALLOYS

NiCr-based superalloys are of considerable interest because of their excellent mechanical behaviour up to high temperatures making them a key material in the construction of e.g. aircraft turbines. Their structure consists of an *fcc* γ–matrix containing cuboid-shaped precipitates of a $L1_2$-type ordered γ'-phase. While the contribution of the γ'-phase to the mechanical properties is quite well understood, much less is presently known about the influence of atomic ordering phenomena in the matrix. Aiming at an improved understanding of these ordering processes, which are important for the design of the next generation of NiCr-based high-performance materials, several modifications of the matrix of a presently used industrial superalloy were investigated with diffuse neutron scattering. The evolution of $D0_{22}$-type short-range order up to 1000°C was examined and interpreted in the context of complementary results obtained from electron

microscopy and mechanical testing. [Collaboration: M. Prem (LLB); G. Krexner, Institut für Experimentalphysik, Universität Wien, Austria; N. Clément and F. Pettinari, CEMES, Toulouse].
See F.Pettinari et al., Acta Mater. 49 (2001) 2549

LITHIUM OXIDE

Owing to its highly unusual properties, lithium oxide (Li_2O) has increasingly stimulated both fundamental and applied research. On the one hand, Li_2O being a superionic conductor, potential applications are seen in the field of solid state batteries. On the other hand, it is discussed as a first-wall material in future fusion reactors due to the tritium breeding properties of the lithium nucleus. In this context structural changes coming about under various conditions of irradiation are of particular interest. Indirect evidence of earlier investigations (using ESR, NMR, DSC) has suggested the formation of two populations of large and small metallic colloids as well as bubbles of molecular oxygen during MeV-electron irradiation. Elastic diffuse and small-angle neutron experiments were performed to confirm the existence of lithium colloids and to determine their structure, size and shape as well as their orientation relations to the oxide matrix. In particular, a detailed investigation of the distortion scattering around Bragg peaks of the Li_2O matrix has permitted to characterize also the small colloids whose study is complicated by their low concentration [Collaboration: M. Prem (LLB); G. Krexner, Institut für Experimentalphysik, Universität Wien, Austria; P.Vajda and F. Beuneu, Laboratoire des solides irradiés, Ecole Polytechnique, Palaiseau] .
See P.Vajda et al., Characterisation of Li-colloids in electron-irradiated Li_2O-crystals by neutron scattering, Nucl. Instr. Meth. B 166/7 (2000) 275.

TRITIUM STORAGE: Pd AND Pd-ALLOYS

Helium damage during tritium storage, forming an indispensable part of future fusion reactor technology, is considered a major problem since it may entail leakage and mechanical failure. Due to continuous radioactive decay of tritium into helium ($T \rightarrow {}^3He + e^- + \nu_e^- + 18.6$ keV) with a half-life of $T_{1/2} = 12.3$ years, an increasing amount of helium atoms is created inside the storage material leading to the formation of helium clusters. Such bubbles give rise to the punching of dislocation loops finally resulting in a dense network of dislocations in the course of time. Agglomeration of helium atoms at grain boundaries induces macroscopic fracture and eventual decomposition of the material. Pd and Pd-alloys are candidate materials for long-term tritium storage. Alloys of various compositions (Pd, $Pd_{95}Pt_{05}$, $Pd_{90}Pt_{10}$, $Pd_{85}Pt_{15}$; $Pd_{95}Rh_{05}$, $Pd_{90}Rh_{10}$ and $Pd_{90}Pt_{05}Rh_{05}$) were loaded with tritium at the site of CEA-Valduc and aged for 15 days, 3 months and 1 year, respectively. Elastic neutron scattering experiments at the three-axis spectrometer VALSE (G4.3) show lattice parameter shifts due to lattice expansion induced by interstitial helium atoms and tritium as well as a decrease of Bragg intensities, up to several orders of magnitude in comparison with the unloaded samples. In addition, changes in the shapes of the Bragg peaks are observed depending on sample composition and aging time. The results of these experiments provide better insight into the specific defect structure induced by helium damage in different alloys and thus allow to assess their potential performance and storage capacities [Collaboration: M. Prem (LLB); G. Krexner, Institut für Experimentalphysik, Universität Wien, Austria; I. Moysan and S. Thiébaut, CEA Valduc ; V. Paul-Boncour, Laboratoire de Chimie Métallurgique des Terres Rares, CNRS, Thiais]

HYDROGEN/DEUTERIUM : STRUCTURAL STUDIES

The determination of crystal structure of compounds including hydrogen (either hydrides or molecular crystals) is an important problem that can "easily" be solved by neutron diffraction. Neutron diffraction is in fact particularly suitable as the neutron scattering amplitudes of the different constituents (light and heavy atoms) are of the same order of magnitude, in contrast with the situation of X-ray scattering. Moreover, in the particular case of hydrogen, the isotopes hydrogen and deuterium have very different coherent scattering lengths, one being positive and the other negative. Two such studies are described below.

RM_5-hydrides

Most of the intermetallic alloys of general formula RM_n (R : rare earth or transition metal ; M : transition metal ; n = 5, 2 or 1) are able to store large amounts of hydrogen to form metallic hydrides. The absorption/desorption reaction is reversible in a large domain of temperature and pressure. Therefore these compounds have been developed for energy storage applications. Among the hydride forming compounds,

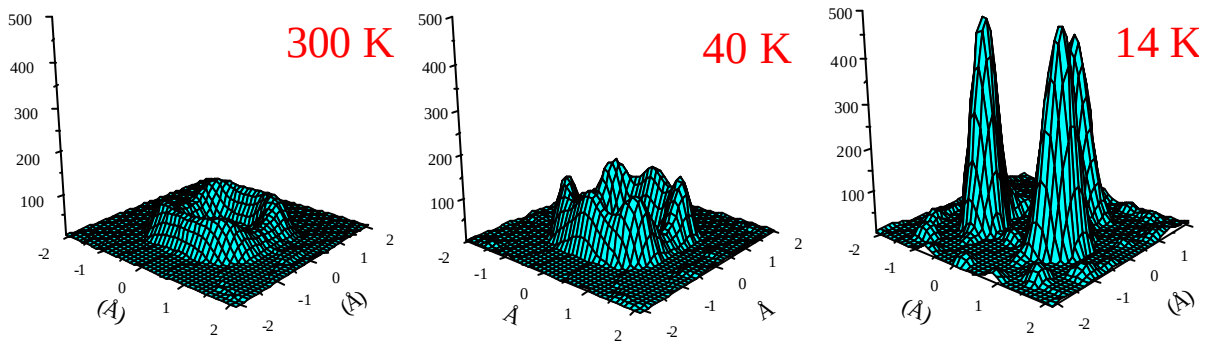
$LaNi_5$ is able to store more than 6H/formula unit at room temperature. Neutron diffraction is crucial for the determination of the structural properties of these phases: symmetry, nature of occupied insertion sites and occupation factor. Moreover, due to the neutron penetration depth, structural studies can be performed in closed cell under hydrogen pressure up to 100 bar allowing accurate control of the hydrogen composition. Different substitutions of nickel by other elements (Sn, Co, Al, Mn) have been studied. The crystal structures of three $LaNi_{5-x}Sn_x$ compounds (x=0.2, x=0.4 and x=0.5) and their deuterides have been investigated, for instance. The structural properties of $CeNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ and $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$, two potential materials for nickel-metal hydride batteries, as well as their hydrides have been studied and compared. Finally, the influence of superstoichiometry ($LaNi_{5+x}D_y$) on the structural properties has been considered [see Highlight: 'Influence of substitution and stoechiometry on the structural properties of RM_5-type hydride forming compounds", J.-M. Joubert & al, Laboratoire de Chimie Métallurgique des Terres Rares, CNRS, Thiais].

Molecular crystals

Determination of the crystal structure of molecular crystals is usually accessed via single crystal neutron diffraction. A first study, in connection with biology [Collaboration: Laboratoire de Chimie et Spectroscopie Biomoléculaire, Université Paris XIII, A. Navaza; LLB, G. Chevrier], allowed to localise all the deuterium atoms in $Y_2V_{10}O_{28}.24D_20$. The positions of the water molecules, and consequently the characteristics of hydrogen bonds, were analysed as a function of temperature (T = 60K, T = 300K). Let us note that such structural determinations are important for biology, but that they are rather rare due to the difficulty in obtaining crystals for "neutrons" (size…) of a sufficient quality.

The other studies in LLB are linked to the physics of methyl groups. A systematic study on methodology (comparison of neutron single crystal diffraction data, obtained either on a steady state reactor, or a pulsed reactor) was performed, via data obtained at ISIS on hexamine Nickel Chloride, Ni $(NH_3)_6Cl_2$ at T = 300K and T = 100K [Collaboration: LLB, R. Papoular; ISIS/RAL, C.C. Wilson; Tübingen University, W. Prandl].

The roles of H and/or D on methyl rotation was evidenced in $LiCH_3COO,2H_2O$ comparing the neutron diffraction obtained with either fully hydrogenated, either fully deuterated, either "mixed" systems [Collaboration: LADIR, Thiais, F. Fillaux; LLB: B. Nicolaï (PostDoc), A Cousson]. Whatever the temperature, the crystal structure of $LiCH_3COO,2H_2O$ or Liac(H_7) is orthorhombic, with *Cmmm* symmetry, and free rotation observed for methyl groups at any temperature above ~ 1K. As a powder neutron diffraction study of the totally deuterated analogue, $LiCD_3COO,2D_2O$ or Liac(D_7) has evidenced a crystal phase transition from *Cmmm* to *Pman*, with CD_3 groups ordered at low temperature, the crystal structure of $LiCD_3COO$, $2H_2O$ or Liac(D_3H_4), was investigated on 5C2 at 300K, 40K and 14 K. In that "mixed" sytem, the *Cmmm* to *Pman* transition is observed at T = 17.5±0.5K. The Fourier maps below provide a graphic view of temperature effects on the localisation of the deuterium atoms of the methyl groups CD_3.



At 300 K free rotation occurs and the threefold symmetry of the methyl group is totally lost. At 14K the deuterium atoms are quite localised in a rather high potential barrier with threefold symmetry. At 40K, as compared to 300K, the methyl rotation is hindered and 6 maxima of density are distinguished, interpreted as a superposition of methyl groups in threefold potentials with two different and equally probable orientations rotated by 180°.

Structures and Phase Transitions

CARBON NANOTUBES

Since 1991, **carbon nanotubes** were extensively studied, due to their unique anisotropic structure and outstanding mechanical and electronic properties. Among all the techniques used for these studies, neutron and X-ray scattering were essential to obtain the structure over very large volumes: single-wall carbon nanotubes (SWNT) self assemblate into a two-dimensional hexagonal close packed lattice (SWNT bundles). The most common assumption as regards SWNT bundles' section is circular, but several theoretical models predict an elliptical deformation and/or a six-fold symmetry faceting of the tubes' section when the Van der Waals interaction between the tubes in the bundles is increased. Such an increase can be obtained via application of a pressure perpendicular to the tubes' surface. For the first time, this six-fold symmetry faceting of the tubes' section is clearly demonstrated when an external pressure is applied [see Highlight: "Structural changes in single-wall carbon nanotube bundles under pressure", S. Rols & al, Groupe de Dynamique des Phases Condensées, Université de Montpellier].

NEUTRAL-TO-IONIC PHASE TRANSITION

The "**neutral-to-ionic**" transition is an unusual type of transition associated to a change of electronic structure between two solid states. This transition is a consequence of the condensation and ordering (crystallisation) of charge transfer excitations. It has been observed in molecular materials of peculiar structures, when donor (D) and acceptor (A) molecules alternate in a linear chain. It is characterised by a cooperative modification of the electronic states of the molecules, accompanied by a significant increase of the level of charge transfer between the neutral and ionic states and by a dimerisation process taking place in the ionic state with formation of ionic pairs D^+A^- along the stacking axis. The prototype of such compounds is TTF-CA. Neutron scattering results, combined with complementary techniques like X-ray diffraction (conventional or synchrotron sources), dielectric response or nuclear quadrupolar measurements, have provided determinant insights necessary for the understanding of the cascade of cooperative phenomena, responsible for the peculiar electronic-structural instability of these one-dimensional materials. In that frame, the quality of the high pressure (up to 10kbar) experiments carried out at low temperature played a key role. This scientific axis is developed by the University of Rennes, Groupe Matière Condensée et Matériaux, in collaboration with LLB [see Highlight: "Neutral-ionic transitions as the condensation and ordering of charge-transfer exciton-strings", E. Collet & al].

PHASE TRANSITIONS : INFLUENCE OF HCl ON THE STRUCTURE AND DYNAMICS OF ICE SURFACE

The interaction of HCl with crystalline water ice has attracted much attention since the mid'80s owing to its importance in heterogeneous reactions occurring on the surface of polar stratospheric clouds involved in the annual depletion of both Antarctic and Arctic ozone. The LLB experiment on "HCl and ice", as described in [Highlight: "Influence of pollutant gases on the structure and dynamics of ice surface. Implications for the environment", B. Demirdjian & al, CRMC2-Université de Marseille, LPM-Université de Franche-Comté] is a two-step experiment: structural and dynamical studies on pure ice films as a first step, influence of HCl on the structure and dynamics of the ice films in the HCl monolayer coverage range as a second step, with ice films condensed on the (001) MgO surfaces. The obtained results are original, and clearly demonstrate the mechanism of HCl adsorption.

PHASE TRANSITIONS : LATTICE DYNAMICS

The study of phonons is one of the main domains accessible to inelastic neutron scattering. In this field, the results obtained at LLB by the Karlsruhe Research group (M. Braden & al) and their comparison with *ab initio* calculations are essential. Recently, in collaboration with S. Klotz (LPMC, Université Pierre et Marie Curie, Paris), a common programme to measure **phonon and magnon spectra under very high pressure**, has been developed. Phonon and magnon dispersion curves of bcc iron up to 10GPa (world's highest available pressure for inelastic scattering experiments on a triple-axis machine) have been determined (see Highlight). These measurements have established that, in bcc iron, a regular hardening of acoustic phonons occurs. But no softening is observed as precursor effect of the bcc-hcp phase transition which takes place at 11GPa. In the same way, no pressure effect on the spin wave stiffness constant has been detected.

INCOMMENSURATE MATERIALS AND QUASICRYSTALS

Another important domain of research at LLB concerns incommensurate materials both in their structural and dynamical aspects. Here, incommensurate must be understood both in its strict meaning and in relation to the physics of quasi-crystals and composites.

Incommensurate BCCD

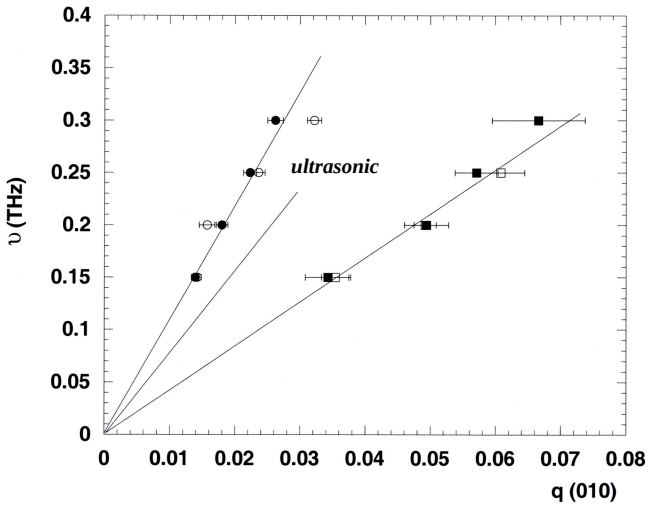
Betaine Calcium Chloride Dihydrate (**BCCD**) has been in recent years one of the most intensively studied dielectric compounds with an uniaxially modulated structure [Collaboration: M. Quilichini (LLB), O. Hernandez (Université de Rennes), J.M. Perez-Mato (Universidad del Pais Vasco, Bilbao), G. Schaak (Würzburg University) and L. Vieira (Minho University, Braga)]. Its rich phase diagram of incommensurate (*IC*) and commensurate (*C*) phases between T_I = 164 K and T_0 = 46 K is a textbook example of an incomplete devil's staircase behavior and neutron scattering has had a major contribution in establishing this fascinating phase diagram. Above T_I, BCCD is paraelectric and the neutron studies have allowed to show that the instability mechanism is of displacive type with a clear soft-phonon branch ($T \geq T_I$) and a phason branch ($T \leq T_I$). Below T_I, the modulation wavevector is $\mathbf{q} = \delta(T)\times\mathbf{c}^*$, $c^* = 2\pi/c_O$ with c_O lattice constant of the orthorhombic room temperature phase: up to fifteen phases have been observed at atmospheric pressure. For $T_I \geq T \geq T_C$ = 115 K, δ varies continuously, this *IC* region being interrupted by isolated narrow *C* phases (δ = 2/7, 3/11, 4/15…). Below T_C too, neutron scattering has been the unique technique allowing to show that the modulation was no more harmonic but square-waved: it has been clearly demonstrated that BCCD can then be considered to consist of microdomains of parallel Ising pseudospins separated by domain walls oriented normal to **c**: thus the phases with δ = 1/4 and δ = 1/5 have respective spin sequences (4 up, 4 down) (<4>) and (5 up, 5 down) (<5>), and phases $\delta = n/m$ with *n* even and *m* odd can be polar. Anomalies of the scattering intensity have been observed at *C*-*C* transitions and interpreted as due to critical scattering. To our knowledge, this phase diagram is unique and not encountered in any other 3-D system. Elastic neutron scattering experiments have also been performed at elevated hydrostatic pressure and high electric field respectively. The electric field experiments have shown a polarization spin-flip phase transition between phases with δ = 1/5, (<5>) and δ = 2/10 (<4,6>) ; the pressure experiments gave the pressure dependence of the critical scattering at T_0.

Incommensurate composite crystals

Aperiodic crystals can be subdivided into three classes: modulated incommensurate phases, incommensurate composite systems and quasicrystals. Composite crystals, which are usually classified between incommensurate systems and quasicrystals, consist of two ore more interpenetrating modulated sublattices. The sublattices are generally incommensurate in at least one direction, which implies that they are nonstoichiometric. The main difference from the modulated structure case is that one cannot define an average structure for the full crystal. Due to the lack of a single Brillouin zone, the elementary vibrational excitations should be qualitatively different. Experimental studies about the lattice dynamics in composite crystals are actually very scarce: intergrowth (inclusion) compounds [alkane/urea, Groupe Matière Condensée et Matériaux, Université de Rennes] and layer structures [BISCO and spin ladder systems, J. Etrillard & al , LLB and GMCM].

Interest in the dynamics of composite structures has been recently revived with the discovery of new materials for which large single crystals of good quality can now be synthetized. The high-temperature superconductors $\mathbf{Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+d}}$ are generally known to have incommensurate modulated structures. Numerous refinements using the superspace formalism have given some discrepancies in the description of the BiO layers. According to recent neutron diffraction investigations of a member of the series, Bi-2212 (n=2), J. Etrillard, P. Bourges, LLB, in collaboration with B. Keimer, C.T. Lin, H.F. He and B. Liang, MPI, Stuttgart, suggested the composite approach. The assumed sublattices, BiO layer (rocksalt-type) and CuO_2 blocks (perovskite-type), seem to play equally important roles and such a description is introduced in new structural refinements, using a complete neutron data collection [J.M. Kiat]. In contrast, each (modulated/composite) model has distinct lattice dynamics properties. Recent inelastic neutron scattering experiments revealed the existence of two acoustic-like longitudinal branches along the incommensurate direction (Figure). This observed collective dynamics is more likely interpreted within the composite model .

$Bi_2Sr_2CaCu_2O_{8+d}$; room temperature



Bi-2212: dispersion curves of the two longitudinal acoustic phonons originating from Q= (0 2 0) (full symbols) and Q = (0 2.21 1) (open symbols) reflections. Q = (0 2 0) and Q = (0 2.21 1) are the main reflections originating from each subsystem. Straight lines correspond to linear fits: the slopes v_1 and v_2, $v_1<v_2$, are respectively associated to each of the subsystems (respective masses m_1 and m_2). The intermediate slope comes from ultrasonic measurements and obeys the law: $v = \mathrm{Sqrt}\ \{(m_1v_1^2+m_2v_2^2)/(m_1+m_2)\}$.

The composite character of the **spin ladder** compound, $Sr_{14-x}Ca_xCu_{24}O_{41}$ [M. Braden, in collaboration with U. Ammerahl and A. Revcolevschi, Laboratoire de Chimie des Solides, Orsay] has been already established. One sublattice [$(Sr,Ca)_2Cu_2O_3$] contains two-leg ladders with (Sr,Ca) atoms on both sides, while the other sublattice consists of one-dimensional [CuO_2] chains. New inelastic neutron scattering studies have given two acoustic (transverse and longitudinal) dispersion curves with different velocities arising from each sublattice. At low frequencies, an additional optic-like branch has been detected and is explained by a relative displacement of both subsystems. Special attention is given to characterise this branch which may be attributed to the sliding mode.

Quasicrystals

The structure of **quasi-crystals** and the nature of their dynamic phasons are two main problems which have been solved.

The structural model of icosahedral Al-Pd-Mn quasicrystal has been studied by N. Shramchenko (LLB, PhD) in collaboration with D. Gratias and M. Quiquandon (LEM-CNRS/ONERA). The atomic structure of icosahedral Al-Pd-Mn quasicrystal, which can be obtained as large "single quasicrystal", has been the subject of intensive research during these last ten years. So far, two basic structural models have emerged, both based on the « cut and projection method » from 6D to 3D: (i) M. Boudard & al [*Philos. Mag. Lett. 64, 197 (1991)*] proposed atoms obtained by the 3D cut of 6D lattice with three family of spheres (called atomic surfaces) perpendicular to the physical space; (ii) Yamamoto & al [*Mater. Sci. Forum 150/151, 211 (1994)*] proposed a refined model where the previous spheres are replaced by complex polyhedra. Although these two models are satisfactory from a diffraction point of view, they both generate a non-negligible fraction of short interatomic distances that burdens their physical plausibility. The present contribution to that field had a double goal: first, to collect a fresh new set of neutron diffraction data measured on a well-characterized icosahedral Al-Pd-Mn sample (Y. Calvayrac, CECM, Vitry); secondly, to build out of this data set a physically acceptable atomic structure model with no small interatomic distances and simple chemical order. The neutron diffraction measurements were made using a 4-circle diffractometer (5C2, λ = 0.830Å): a total of 1025 reflections were measured, out of which only 217 independent reflections with $I>3\sigma$ were chosen for the modeling. The chemistry ordering of the model was done using the clusters description (M. Boudard & al [*Philos. Mag. Lett. 64, 197 (1991)*], C. Janot & al [*Phys. Rev. Lett. 72, 1674 (1994)*]) for which recent studies (see for instance: D. Gratias & al [*Phys. Rev. B, Vol 63, 1-16 (2000)*] have shown that using two types of

clusters, similar to Bergman and Mackay clusters, allows to describe 95% of the structure. The final model has the composition $Al_{69.92}Pd_{21.72}Mn_{8.36}$ and density 4.98 g/cm^3. In conclusion, this neutron diffraction study has shown that it is possible to construct an atomic model of Al-Pd-Mn structure presenting a relatively simple chemical order with physically acceptable composition, density and atomic distribution. This model agrees well with STM high resolution images of surface perpendicular to the 5-fold axis of i-Al-Pd-Mn, recently done by L. Barbier (DRECAM).

In contrast with the case of crystalline incommensurate materials, phasons in quasicrystals are not propagative modes but atomic jumps. An extensive triple-axis neutron scattering study of phason hopping in a single-domain of a perfect icosahedral $Al_{70.4}Mn_{8.6}Pd_{21.0}$ quasicrystal has been performed at LLB by G. Coddens (LSI, Ecole Polytechnique), S. Lyonnard (SCM, DRECAM) and B. Hennion (LLB). The quasielastic intensities exhibit important anisotropies. They are compared with theoretical models at various level of sophistication. This comparison strongly suggests the occurrence of **simultaneous correlated jumps**. They behave like a wave of collective jumps, as an elastic response of the quasiperiodic medium to a periodic external source of deformation. This elastic response is governed by the **phason** elastic constants. These surprising results represent an important contribution to the understanding of atomic mobility in quasi-crystals.

« DISCRETE BREATHERS » , FROM THEORY TO APPLICATIONS

Finally, one important activity of LLB is theory, with S. Aubry and co-workers: A.M. Morgante, LLB, PhD; M. Latkovic, Zagreb University, PhD; M. Johansson, LLB, PostDoc; G. Kopidakis (University of Crete). The main topic of these studies is "Discrete Breathers" (DB), or intrinsic localised modes, that are time-periodic spatially localised solutions of discrete classical non-linear hamiltonian systems. This self-localisation is the consequence of non-linearity and discreteness, independent of possible disorder. Discrete Breathers are non-linear modes, which are rather universal and can be found in many finite and infinite systems, of arbitrary dimension, which can be spatially periodic, random, and highly complex. Different problems have been studied by the LLB theoretical group. One of the most recent is the study of existence and stability properties of non-linear spatially periodic or quasiperiodic standing waves in one-dimensional lattices of coupled anharmonic oscillators [A.M. Morgante, M. Johansson, G. Kopidakis, S. Aubry, Physica D, 2001]. Another example is DB in hydrocarbon structures. The authors focus on carbon-hydrogen stretch vibrations, the frequencies of which are well separated from the rest of the vibrational modes. In the anharmonic region of the interaction potential, these spatially localized solutions persist for time scales which are orders of magnitude longer than the period of the atomic vibrations and with frequencies that are different from the normal mode frequencies. The conditions under which these DB solutions are created, the implications on energy relaxation fairly compare with experiments [G. Kopidakis, S. Aubry, Physica B].
Another recent work concerns the formulation of a new existence proof of DB (S. Aubry, G. Kopidakis). This new approach is purely variational. The method holds for systems either with optical phonons or with acoustic phonons (non-vanishing sound velocity), and does not use the concept of anticontinuous limit. Discrete breathers are obtained as loops in the phase space which maximize a certain energy function for a fixed pseudoaction appropriately defined. As a straightforward application of the method, DB are proven to exist at any energy in the quartic one-dimensional model, which up to now was lacking a rigorous existence proof. The method can also work for piezoactive DBs in one or more dimensions and in many more complex models.
The interest of the group is also focused on the problem of targeted energy transfer by DB. As a matter of fact, an interesting property of DBs is that in some cases they can transport energy beetween two anharmonic oscillators, in a highly selective way. Models for energy transfer, and recently for catalysis mechanism, have been formulated.

CONCLUSION

If we had to have a short summary of the above results, the first characteristics to be pointed out would be the wide diversity of the subjects needing neutron scattering. These span both above fundamental and applied research. Some are more or less classical goals for neutron scattering, but some new domains of investigations are emerging, such as environment physics. As for experimental conditions, non "ambient" temperatures, with electric or magnetic fields, and samples under controlled atmospheres are easily available

with neutron scattering. A "new" parameter is also more and more used in neutron experiments: "high pressure". And, in the recent years, neutron diffraction experiments under very high hydrostatic or quasi-hydrostatic pressures became available at the LLB. At the present moment, the LLB disposes of higher pressures (up to 500 kbar) than any other neutron source in the world. The development is based on a combination of a high-intensity neutron diffraction and compact pressure cells with sapphire (pressures up to 100 kbar) or diamond (pressures up to 500 kbar) anvils. New high pressure version of the G6.1 diffractometer ("MICRO"), equipped by a special focusing system, allows to study samples as small as 0.1-0.001 mm^3 in the wide range of pressures and temperatures. The technique is especially adopted to study magnetic orders and structural transformations in "mesoscopic" systems like, for example, nanomaterials. The advantages of neutron diffraction in measurements of structural properties of the "mesoscopic" systems have been recently demonstrated in the study of single-wall carbon nanotubes under applied pressures. The long-wavelength neutron diffraction provided a detailed information about the low-Q part of the diffraction spectra, hardly accessible for the conventional high pressure X-ray diffraction. Possibility to use different orientations of the pressure cell regarding to the incident and scattering beams allowed to study effects of pressure and unaxial stress on facetisation of the nanotubes.