STRUCTURES AND PHASE TRANSITIONS

The study of both crystallographic and magnetic structural phase transitions is an important activity of the Laboratoire Léon Brillouin. It makes use of several neutron scattering techniques, such as diffraction or inelastic scattering; the samples are either powders or single crystals. Most of the time, such studies are performed as a function of a unique parameter, namely the temperature, but pressure has recently become another important variable. Many different physical problems are related to these activities and the present summary intends to show the main goals of the research in the field. Magnetic phase transitions are treated in a different chapter.

FULLERENES AND CARBON NANOTUBES

Among the materials studied at LLB, fullerenes and carbon nanotubes are fashionable materials. The study of the former is older and the recent achievement of growing single crystals of $\mathbf{C_{60}}$ of sufficiently large size allowed the precise characterisation of the intramolecular dynamics of the molecule [L. Pintschovius et al, Kernforschungszentrum, Karlsruhe; see "*highlight*"]. Comparison with theory is particularly rich and yields the unambiguous identification of each of the internal modes of vibration. This comparison between experimental results and theory has been done, not only at the level of the frequencies, but also at the level of the intensities, in order to access the eigenvectors. The next step of this study will concern the intermolecular modes as a function of applied pressure. The problem of the nature of these interactions (which are weaker as compared with intramolecular interactions) is still not solved. It is currently assumed that they depend on the relative orientation of two neighbouring molecules and that the orientation is modified under pressure. Preliminary results show that pressure actually does not affect the vibrational frequencies as much as predicted by the theory.
More recently obtained (1991), **carbon nanotubes** are prepared by evaporation of graphite in the presence of metallic catalysts (Co, Ni, Fe...). The study of both the structure and vibrational dynamics of single wall carbon nanotubes (SWCN) has several interests. Firstly, SWCN are a model of one dimensional molecular systems that organise themselves as two dimensional crystalline bundles with a finite size. Also, their mechanical, optical and electronic properties are totally specific and dependent on the structure, which has been studied in real space by means of electronic and atomic force microscopies. However, even if they give useful information about the structure of the tubes and of the bundles, these techniques provide only a purely local picture. Studies in reciprocal space by neutron or X-ray scattering, are complementary and furnish the structure averaged over very large volumes. Comparison between experiment and theory yields the distribution of the diameters of the tubes and of the diameters of the bundles, and a relation to the processes of preparation of the SWCN is possible. The present activity in this domain concerns the pressure and temperature dependencies of the structural organisation of the tubes, by neutron scattering.
Concerning dynamic aspects, the low energy excitations (molecular and intermolecular) are very sensitive to the structure of the tubes. Raman scattering is widely used in studies of SWCN essentially because of the small amount of material requested by the technique and of the relatively high intensity of the signal. These experiments succeeded in obtaining the distribution of diameters from the analysis of the breathing modes of the tubes, in perfect agreement with former neutron scattering results. The first results obtained by inelastic neutron scattering showed clearly the breathing modes of the tubes in the domain 50-200 cm^{-1}, but also other low frequency excitations (< 50 cm^{-1}), such as librations, interactions between tubes and a peculiar vibrational density of states [S. Rols, E. Anglaret, J.L. Sauvajol, Groupe de Dynamique des Phases Condensées, Université de Monpellier].

CHARGE ORDERING IN MANGANESE OXIDES

Concerning the study of perovskites of manganese with a giant magnetoresistance, an important problem is at present the eventual existence of ordering of the charges Mn^{3+} and Mn^{4+} at low temperature, according to the nature of the cations and the stoichiometry of the structure. The crystallographic order of Mn^{3+} and Mn^{4+} is relatively difficult to observe for these perovskites, due to the presence on the powder diffraction diagram of only one superstructure peak, which is very weak and within the wing of a structural line. However, such order has been

clearly observed in the defined compound $LiMn_2O_4$ which has a spinel structure at high temperature. Previous measurements of the electrical resistivity and experiments performed by thermal differential analysis, showed the existence of a first order transition just above room temperature, which can be due to a cooperative Jahn-Teller effect. Combination of electronic and neutron scattering data on powders allowed the classification of the transition as an order/disorder of the charges Mn^{3+}, Mn^{4+} (octahedral site of the spinel structure). The analysis of the data at T = 230 K demonstrates that this ordering is only partial [Collaboration Laboratoire de Chimie des Solides, Université Paris-Sud - LLB; see "*highlight*"; current PhD: G. Rousse, LCS, Orsay].

PEROVSKITES RELAXORS

Another problem extensively studied at LLB by the Laboratoire "Structure, Propriétés et Modélisation du Solide" of Ecole Centrale de Paris [J.M. Kiat et al; PhD: C. Malibert, B. Dkhil, ECP], is that of relaxor materials such as the perovskites $Pb(B,B')O_3$, for which one observes a large dielectric constant, very soft in temperature and dependent upon the measuring frequency. Some of these materials have industrial applications, namely as capacitances. As far as structure is concerned, they are characterised by some disorder of the cations B and B' and one can actually observe ordered or disordered perovskites depending on the size and charge of the cations B and B'. The combination of X-ray and neutron diffraction allows the precise characterisation of the cationic order and its relation to the dielectric properties.

PHASE TRANSITIONS : STRUCTURAL STUDIES

Another example of structural determination using both X-rays and neutron diffraction concerns $ErFe_4Ge_2$. This compound is magnetically ordered at low temperature and characterised by the existence of a strong magnetoelastic coupling, which is at the origin of a crystalline phase transition. Below the temperature of magnetic ordering, two different crystalline structures are present in $ErFe_4Ge_2$ and the relative volume of each domain depends on temperature [Collaboration Laboratorium für Kristallographie, ETHZ, Zürich - LLB].

One can also mention the following structural determinations by neutron diffraction:

- localisation of hydrogen atoms in strontium nitroprussiate, $4H_2O$ [Collaboration Laboratoire de Physique, Centre Pharmaceutique, Chatenay-Malabry - LLB];
- study of phase transitions of Co-0.85%at Fe as a function of temperature or of time at fixed temperature (characteristic time of the order of hour, accessible to real time in situ neutron diffraction experiments) [Collaboration Institut für Experimental Physik, University of Vienna, Austria - LLB];
- study of tridimensional structures, such as iron phosphates or arseniates, of interest as possible anode materials in lithium batteries. The first members of the series were $Li_3Fe_2(PO_4)_3$ and $Li_3Fe_2(AsO_4)_3$, for which the order/disorder of alkaline cations in the structure has been followed as a function of temperature [Collaboration Laboratoire de Chimie des Solides, Université Paris-Sud - LLB; current PhD: C. Würm, LCS, Orsay].

MOLECULAR CRYSTALS

The determination of the structure of molecular crystals is an important problem for which neutron diffraction is particularly suitable because 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. This property has been used to study the structure of partially deuterated aspirin, $C_8H_6O_4$-CH_2D, a molecule where the methyl group is distinct from CH_3 or CD_3, i.e. non-symmetric. Earlier studies by NMR had shown that the protons of this group remain relatively mobile down to 15 K. Consequently, the diffraction experiment should give an averaged image of the position of the H/D atoms, in a "superposition" of three methyl groups shifted by 120°, D-H-H, H-D-H and H-H-D. The crystalline structure of $C_8H_6O_4$-CH_2D (monoclinic) has been determined first at room temperature (diffraction by a single crystal, data treatment using the maximum entropy method) and indeed, at this temperature, the nuclei H and D are not distinguishable, and an average scattering amplitude equal to $2/3\ b_H + 1/3\ b_D$ is obtained for each of the three sites H/D of the methyl group. However, at low temperature (T = 15 K), such analysis is no more adequate. Actually, one of the positions among D-H-H, H-D-H or H-H-D is more likely than the other two, i.e. the deuterium occupies preferentially one of the three possible H/D sites of the methyl group [Collaboration Institut für Kristallographie, Tübingen - LLB; see "*highlight*"].

Potassium hydrogenomaleate [KH(OOC-CH=CH-COO)] is a typical example of an intramolecular hydrogen bond, very strong and symmetric. The nature of the potential that explains the dynamics of the hydrogen bond has been the object of several discussions, because of the absence of a well defined crystalline structure at different

temperatures, of the complexity of the vibrational spectra and of the natural limitations of the quantum chemistry calculations. The structure determined by neutron diffraction shows that the hydrogen bond is rigorously centred at all temperatures. Following this experimental result, a new form of interaction potential has been proposed in order to take into account the inelastic neutron scattering spectra. This function is symmetric about the centre of the bond and has three wells. As far as we know, this is the first example of such form of potential. This study illustrates the complementarity of structural and dynamic studies. It is also a contribution toward a better knowledge of the mechanisms of proton transfer and of the elementary steps of chemical reactivity in solutions [Laboratoire de Dynamique, Interactions et Réactivité, CNRS, Thiais].

PHASE TRANSITIONS : LATTICE DYNAMICS

The study of phonons is one of the main domains accessible to inelastic neutron scattering. In this domain, the main results obtained at LLB, by the Karlsruhe research group, concern fullerenes (see above) and iridium. In both cases, comparisons between experiment and ab initio theory have been carefully established.
In the case of solid solutions $(BaF_2)_{1-x}(RF_3)_x$, where R represents a rare earth, the modifications of the phonon spectrum have been followed as a function of the temperature (from room temperature to 1000°C) and of the thermal history of the sample. These compounds are ionic conductors. Two main results have been obtained: first, the lattice vibrations are hardly observed at room temperature and appear more clearly at higher temperatures (R=Nd, T ≥ 400°C), as a consequence of the coupling between phonons and the mobility of the fluorine ions. One also observes low frequency components that correspond to localised vibrations of clusters formed by the ions R^{3+} and the ions F^- at neighbouring interstitial sites (compensation of charge). Such modes depend strongly on the geometry of the clusters, thus on the thermal history of the sample [PhD: P. Kadlec, Institute of Physics, Praha and CRMHT, Orléans].
The University Pierre et Marie Curie in Paris [S. Klotz et al, Laboratoire de Physique des Milieux Condensés], in collaboration with the LLB, has developed a common programme with the objective of measuring **phonon spectra under pressure** (cell "Paris-Edinburgh", see the chapter on Technical and Instrumental Developments). Measurements on iron oxide, $Fe_{1-x}O$, one of the most studied compounds in Geophysics, have been performed intending to study more in detail the origin of the cubic-rhomboedric phase transition, observed around 15 GPa. Other authors, using different techniques (ultrasound, P < 5 GPa) have shown that the frequency of acoustical modes was reduced under pressure, suggesting that a soft mode could be at the origin of the observed phase transition. The results obtained by inelastic neutron scattering contradict this hypothesis: even if the frequency does decrease linearly as pressure increases, no soft mode is observed up to 12 GPa. It is worth noting that this pressure is the highest one at which a phonon has been observed so far.
The "**neutral-to-ionic**" transition is an unusual type of transition because it is 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 (TetraThiaFulvalene-ChlorAnile), which has been studied at LLB by the Groupe Matière Condensée et Matériaux of the University of Rennes [Current PhD: E. Collet, GMCM, Rennes]. Complementary measurements of Quadrupole Nuclear Resonance of ^{35}Cl and of inelastic neutron scattering under pressure, allowed the establishment of a phase diagram containing the neutral-to-ionic transition on TTF-CA. Actually this phase diagram "pressure, temperature" (for P ≤ 1.2 GPa) is similar to a 3-phase (solid-liquid-gas) diagram, but concerns only the solid.

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.
Experimental studies on **BCCD** (Betaine and Calcium Chloride di-hydrated) are numerous and performed as a function of several external parameters: temperature, pressure, electrical field. The preceding activity report of LLB described most of this activity [PhD: O. Hernandez, LLB]. In a more recent experiment, chlorine has been partly replaced by bromine, introducing a "negative" pressure of chemical origin. The subsequent modification of the phase diagram has been followed as a function of temperature.
$(ClC_6D_4)_2SO_2$ (**BCPS**) is a molecular compound for which a displacive phase transition is observed, from a high temperature phase to an incommensurate phase at low temperature. Inelastic neutron scattering allowed the

evolution of collective excitations below the transition temperature (phasons) to be followed. It is worth noting that the observation of phasons is not usual because of their overdamped character at the neighbourhood of other satellite reflections: BCPS is one of the rare cases where phasons have been observed [Groupe Matière Condensée et Matériaux, Université de Rennes; PhD: J. Ollivier, GMCM, Rennes].

Incommensurate composite crystals are built with at least two interpenetrating lattices with periodicities that are mutually incommensurate at least in one direction. Such aperiodic systems are intermediate between incommensurate modulated systems (e.g. BCCD and BCPS) and quasi-crystals. The aim of the study performed by the Groupe Matière Condensée et Matériaux (Université de Rennes) was to use neutron scattering as a tool for the characterisation of structural and dynamic aspects of these little known materials. The study has been done on urea inclusion compounds. The determination of the structure is complementary to that performed by X-rays and has been done with a single crystal: the structure can be described in a 4-dimension space. The first observations of phonons associated with the host lattice have been done and show the presence of an anomalous high damping of the longitudinal acoustical mode propagating along the direction of incommensurability [PhD: R. Lefort, GMCM, Rennes].

A fundamental problem of the physics of **quasi-crystals** is the nature of the dynamic phasons. In contrast with the case of crystalline incommensurate materials, phasons in quasi-crystals are not propagative modes but, instead, atomic jumps. Experiments of inelastic neutron scattering on a large single domain sample of icosahedral Al-Mn-Pd demonstrated that indeed a correlation between simultaneous jumps is present. This surprising result represents an important contribution to the understanding of dynamic phasons in quasi-crystals [G. Coddens et al; see "*highlight*"; PhD: S. Lyonnard, LLB]. Atomic jumps have been studied also in the decagonal system Al-Co-Ni as a function of temperature, wave-vector and isotopic composition.

Many other aspects of the physics of quasi-crystals will be the objects of further studies. One can mention the study of the dynamics of hydrogen and deuterium atoms in Ni-Ti-Zr, the structural study of Al-Cu-Fe which will be approached by different techniques, namely quasielastic neutron scattering (isotopic substitution), inelastic neutron scattering, anomalous X-ray scattering and Mössbauer spectroscopy (for the correlations iron-iron).

THEORY : « DISCRETE BREATHERS »

Finally, one of the important activities of LLB is the theoretical studies of S. Aubry and co-workers [Current PhD: A.M. Morgante, LLB; PhD: J.L. Marin, Zaragoza, Spain; T. Cretigny, ENS-Lyon] about "discrete breathers", periodic excitations in time that are localised in space. Their existence has been proved in non-linear systems whatever their dimensionality. One knows that spatial localisation can also be obtained by linear modes in a random medium. Consequently, the theoretical study of excitations in non linear systems has been extended to random media. Several one dimensional physical systems have been studied, such as the case of a periodic chain of atoms [see "*highlight*"] using an hamiltonian with harmonic frequencies randomly distributed at each site and a quadratic coupling of neighbouring sites. One of the interests of these models relates to new possible interpretations of relaxation in glasses and amorphous materials.

CONCLUSION

It is clear that neutron scattering is quite often a complementary technique of X-ray scattering, particularly in the case of molecular compounds. The isotopic substitution H/D, for example, is one of the major tools in structural determinations. We have seen that, for the first time, the positions of H and D in a crystalline structure have been clearly separated. In dynamic studies, the access to the whole Brillouin zone and the absence of selection rules complement the information obtained by optical spectroscopic techniques.

The very large variety of problems treated at LLB, such as Mn^{3+}/Mn^{4+} charge ordering, incommensurate systems, quasi-crystals (observation of phasons), fullerenes and carbon nanotubes, studies under pressure (up to 12 GPa) and neutral-to-ionic transition, exemplifies the amplitude of the domain of research performed by neutron scattering and the role played by LLB in collaboration with several French and European groups.