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.

VERWEY-LIKE TRANSITION IN A LITHIUM BATTERY MATERIAL: THE SPINEL $LiMn_2O_4$

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An increasing interest has developed around Li-Mn-O spinels due to their potential use as positive electrode materials in lithium rechargeable batteries. A vast majority of the studies devoted to these compounds deals with their electrochemical characteristics in lithium cells[1]; only very recently, their structural and physical properties have also been studied[2-4]. The stoichiometric compound $LiMn_2O_4$ presents a first order structural transition close to room temperature (RT) that was attributed to a Jahn-Teller distortion[4]. In the case of Mn-perovskites close to the composition $(R_{1/2}D_{1/2})MnO_3$ (R: trivalent rare earth, D: divalent ion), structural phase transitions accompanied by sharp modifications of electronic and magnetic properties have been attributed to charge-ordering[5]. This phenomenon is supposed to be due to the Coulomb interaction that overcomes the kinetic energy of carriers below a certain temperature (Wigner crystallization) producing an alternating Mn^{3+}-Mn^{4+} NaCl-like lattice. This mechanism was first invoked by Verwey in 1941 to explain the low temperature transition in magnetite Fe_3O_4 as a Fe^{2+}-Fe^{3+} ordering within the B-sites of the spinel structure[6]. In spite of a different lattice organization of Mn ions in the spinel as compared to Mn-perovkites, it is reasonable to expect some kind of similar electronic behaviors in both families.

To date, the structural details of charge-ordered Mn-perovskites are quite limited, since the superstructure reflections in neutron powder diffraction patterns are barely visible and single crystals show complicated twinning effects. It is extremely important to know whether the ionic picture usually invoked to describe the charge ordering in these materials is supported by structural experimental evidence. For instance, the simple NaCl-like ordering picture of Mn^{3+} and Mn^{4+} ions in $La_{1/2}Ca_{1/2}MnO_3$ has not yet been confirmed definitively even if experimental data are not in contradiction with such a picture[7]. We have recently shown that the ionic picture is well supported in the case of $LiMn_2O_4$ spinel and we have demonstrated that the charge-ordered state is not complete at 230K[8, 9].

DSC (Differential Scanning Calorimetry) experiments confirmed the presence of a first order transition around RT. With a cooling rate of 5 K/mn, the cubic → orthorhombic transformation starts at 290K with a hysteresis of 10K (fig.1). An increase of resistivity is observed upon cooling to the low temperature phase (fig.1). The activation energy of the low temperature form is slightly higher but similar to that of the high temperature. The charge carriers are very probably Jahn-Teller small polarons.

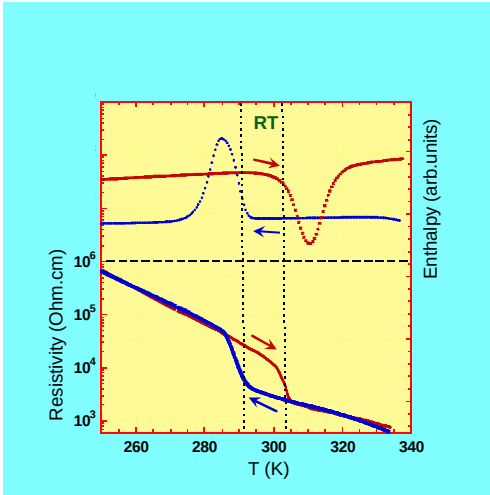

Figure 1: DSC and resistivity of $LiMn_2O_4$

Neutron diffraction experiments were performed using the high-resolution powder diffractometer 3T2. The high temperature form was carefully studied at 350K (a=8.2495(2)Å) to confirm the crystalline quality and the stoichiometry of the sample (fig.2). The refined value of the oxygen occupation was the nominal value within the experimental error. The unique Mn-O distance is 1.9609(3) Å, which is intermediate between what is expected for Mn^{3+}-O and Mn^{4+}-O bond lengths. Neutron powder diffraction at low temperature showed many small superstructure reflections (fig.2). The indexing of the pattern using solely the neutron data was ambiguous and gave several reasonable solutions due to the strong overlap between neighboring reflections. The information provided by electron diffraction at different temperatures was of capital importance for finding a "$3a \times 3a \times a$" supercell and extinction conditions compatible with the space group *Fddd*.

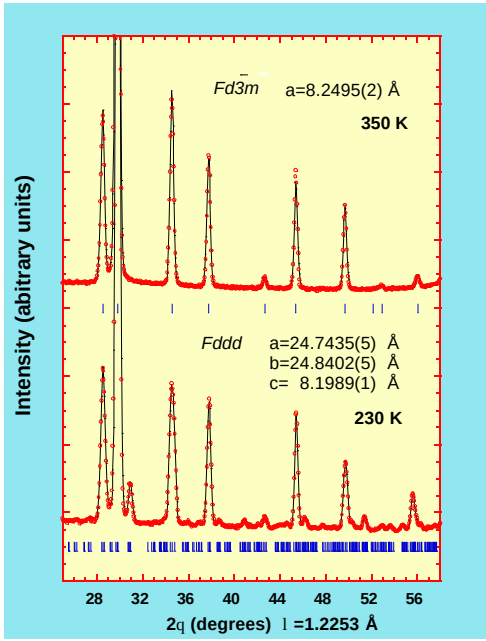

Figure 2: Details of the observed and calculated neutron diffraction patterns (l=1.2253 Å) of the high temperature charge-disordered phase (350K), and of the low temperature partially charge-ordered phase (230K) of $LiMn_2O_4$. Additional tick marks in the low temperature pattern correspond to the superstructure reflections.

The final atom positions can be found in reference [8]. The analysis of the structure obtained from the Rietveld refinement of our neutron data clearly shows the electron ordering nature of the phase transition and allows us to interpret the resistivity measurements. Two Mn-sites correspond to well-defined Mn^{4+} ions (the average Mn-O distance is 1.91Å). The other three sites are not pure Mn^{3+} ions. This is revealed by the average Mn-O distance for the three Mn-sites (2.00 Å) which is slightly smaller than what is expected for pure Mn^{3+} (2.02 Å). To simplify the visualization of the crystal structure we have represented in Fig. 3 an idealized projection along [001] of the Mn and Li sites within a unit cell. Neglecting the z-position of the atoms, it is apparent that octagonal cylinders surfaces (hole-rich regions), containing all the Mn^{4+}, wrap two types of Mn^{3+} columns (electron-rich regions) which are distinguished by the presence, or lack therein, of Li ions. The space between the octagonal cylinders is occupied by columns containing the Mn(1) site in the special position (16d).

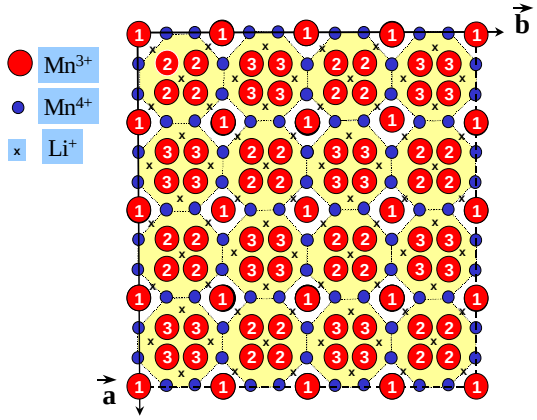

*Figure 3. Simplified projection of the charge-partially-ordered structure. Oxygen atoms have been removed from the drawing. Static holes (Mn^{4+}, blue circles) wrap columns of nearly pure Mn^{3+} ions along the **c**-axis. 8/72=1/9 of the total number of holes are mobile within the Mn^{3+} sublattices.*

The average valence of Mn ions, obtained from chemical analysis and structure refinement at high temperature, indicates that the number of holes (Mn^{4+}) in the e_g-band is equal to the number of electrons (Mn^{3+}) available for hopping. The crystal structure indicates that there are 64 localized holes per unit cell, so there are eight remaining holes per cell distributed within the remaining 80 Mn positions. Thus, a certain electron hopping should persist at low temperature as revealed by the previous analysis. This is consistent with the semiconducting characteristics of the compound below the transition temperature. The static distortion of the three $Mn^{3+}O_6$ octahedra is consistent with a slightly attenuated Jahn-Teller effect[9] due to the remaining electron hopping towards the 8 holes per cell. The charge ordering process is, consequently, accompanied by the presence of an orbital ordering which is the manifestation of the Jahn-Teller polaronic nature of the mobile charges above and below the transition temperature.

To our knowledge this is the first time that a partial charge ordering transition is clearly observed in a Mn oxide. The electronic crystallization observed in this compound must be due to a combination of Coulomb interaction and another mechanism implying electron-lattice coupling as is the Jahn-Teller effect. The analysis of the crystal structure shows that the ionic model seems to be adequate and the usual Mn^{3+}- Mn^{4+} picture is well justified in $LiMn_2O_4$.

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INELASTIC NEUTRON SCATTERING STUDY OF THE VIBRATIONAL PROPERTIES OF C_{60}

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Solid C_{60} is a prototypical example of a molecular solid with very strong *intra*molecular and very weak *inter*molecular bonds. The high symmetry of the C_{60} molecule is certainly a major reason that it has attracted considerable interest. Moreover, it also greatly facilitates theoretical computations of its properties, and so C_{60} has become the best studied member of the fullerene family. For this reason, C_{60} can be considered as an ideal testing ground of theories for strong (covalent) forces as well for weak (van der Waals-like) forces. The most detailed information for a check of the theoretical predictions can be obtained by inelastic neutron scattering, and so we have undertaken a series of experiments to explore the vibrational properties of C_{60}. In the beginning, only the external vibrations could be studied because of the small size of the available single crystals (V~5 mm^3)[1,2]. With the advent of fairly large single crystals (V~100 mm^3) we were able to investigate the internal vibrations, too, with energies up to E=70 meV. Moreover, we were able to study the pressure dependence of the external vibrations. In the following, we summarize the results of the most recent experiments.

An isolated C_{60} molecule has 46 distinct vibrational modes. When the molecules are packed into a lattice, the intermolecular interactions give rise to mode splittings and to some dispersion. However, these effects are rather small due to the weakness of the intermolecular forces and can therefore be neglected . So, the problem of verifying the results of a certain theory reduces to verify the predicted *frequencies and displacement patterns* of the eigenmodes of the C_{60} molecule. We emphasize that a good agreement between calculated and experimental frequencies is of little value unless it has been checked that the observed mode has the same character as the calculated one. A minimum requirement is that the symmetry of the displacement pattern of the observed mode is the same as predicted for this frequency. However, as most symmetry classes contain more than one member, their displacement pattern is not determined by symmetry alone, but by the force field as well. This is demonstrated in Fig. 1, where we plotted the displacement patterns of a number of C_{60} eigenmodes, including those of the three lowest modes of H_g symmetry. Inelastic neutron scattering has the particular advantage that it allows one not only to unambiguously assign an observed frequency to a mode of a certain symmetry but, moreover, to check in detail whether the predicted displacement pattern is correct or not. To this end, energy scans have to be made at many different points in reciprocal space. As can be seen from Fig. 2, the calculated scattering cross section versus momentum transfer differs widely for modes of the same symmetry but having different frequencies.

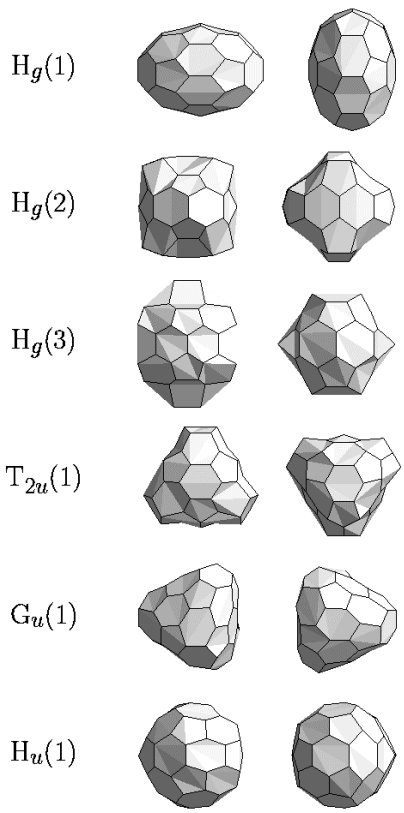

Figure 1: Displacement patterns for five different eigenmodes of the C_{60} molecule. The elongations are strongly exaggerated for the sake of clarity. The left-hand and the right-hand figures correspond to extremal distortions following each other at time intervals 1/2 n. Eigenvectors are taken from the ab initio calculations of Bohnen et al. (Ref. 4).

Our results revealed that several modes had been assigned incorrectly in the literature. Furthermore, we were able to show that *ab-initio* theory based on the local density approximation[4] describes not only the mode frequencies with high accuracy (~ 2%), but also the eigenvectors in a very satisfactory way. We note that the agreement between calculated and observed eigenvectors was significantly worse for a sophisticated model fitted to the experimental frequencies[5], which shows that a good agreement between calculated and observed displacement patterns

is by no means granted even if the frequencies are reproduced correctly.

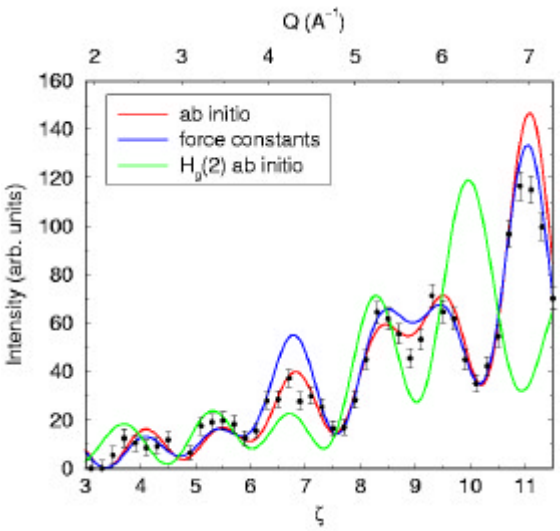

Figure 2: Intensity of the 33 meV peak versus momentum transfer (z,z,0) observed on a single-crystal sample at T=12 K. The red and blue lines denote the predictions of an ab initio theory (Ref. 4) and of a force-constant model (Ref. 5) for the $H_g(1)$ mode, respectively, and the green line shows the prediction of the ab initio theory for the $H_g(2)$ mode using the same scaling.

The good understanding of the covalent intramolecular forces contrasts with our rather poor understanding of the weak intermolecular forces. From the large distance between atoms on different molecules (≥ 3 Å) it was assumed that these forces are of van der Waals (vdW) type. However, it is known for long that the vdW potential taken from graphite gives a poor account of many properties depending on the intermolecular potential. In particular, the frequencies of the hindered rotations (librations) calculated from the vdW are too low by more than a factor of two [1,2].

In the absence of *ab-initio* calculations for the intermolecular forces, many empirical potentials have been proposed in the literature which were designed to improve the simple vdW ansatz by taking secondary interactions into account. For instance, several models have been developed which include Coulomb forces between charges placed on various locations on the C_{60} molecule. These models reproduce the dispersion of the external vibrations quite satisfactorily[2]. However, a recent experiment of us has shown that this is true only for the usual phase of C_{60}, where double bonds of one molecule face pentagonal faces of neighbouring molecules. By applying pressure, the C_{60} molecules can be switched to a different orientation, so that double bonds face hexagons. When the pressure is released at low temperatures, the 'hexagon' structure is frozen in. Measurements on this metastable phase have shown that there are surprisingly small differences between the frequencies of the external vibrations in the two phases (see Fig.3), whereas the empirical models predict very large frequency changes (≈50% for the librational modes, upwards or downwards, depending on the model) .

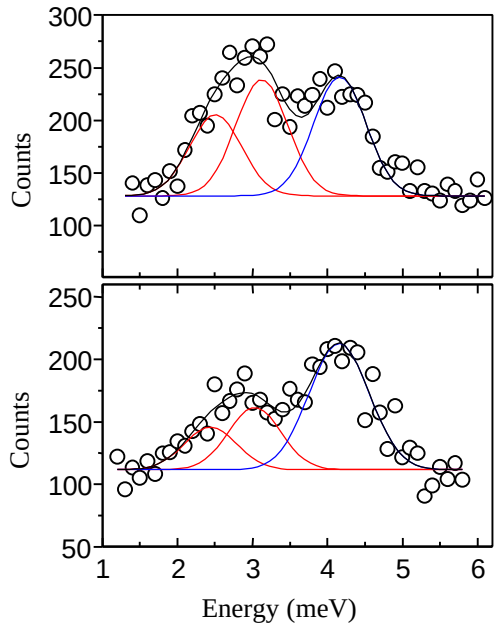

Figure 3: Energy scans taken at Q=(7.5,7.5,0) at T=70 K. The data were fitted with three Gaussians with a width corresponding to the experimental resolution. From model calculations we know that the two low energy peaks correspond to librational excitations and the high energy peak to a translational excitation, respectively. The upper and lower graph refer to measurements on the "pentagon" and the "hexagon" phase, respectively.

Measurements of the external vibrations at pressures up to 7 kbars are planned in the near future. The results are hoped to advance further our understanding of the intermolecular potential in C_{60}.

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CRYSTALLOGRAPHIC IMAGING OF A MOLECULAR CRYSTAL : Aspirin $C_8H_5O_4$-CH_2D

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The nuclear density distribution of partially deuterated aspirin at 300 K and at 15 K has been determined by single-crystal neutron diffraction coupled with Maximum Entropy image reconstruction (MEM). While fully protonated and deuterated methyl groups in aspirin (acetylsalicylic acid) have been shown to be delocalized at low temperature due to quantum mechanical tunnelling, we provide here direct experimental evidence that in partially deuterated aspirin-CH_2D the methyl groups are orientationally ordered at 15 K whilst randomly distributed over three sites at 300 K. This is the first observation of low temperature isotopic ordering in condensed matter by diffraction methods.

PHYSICAL BACKGROUND

The quantum mechanical behavior of ever larger and heavier molecules and molecular subunits in condensed matter is a subject of considerable interest . The onset of quantum behavior is usually observed at low temperature. Substitution of hydrogen with deuterium leads to large isotopic effects, in fact the largest ones known in chemical physics. Spectroscopic methods such as NMR and QENS are the prevalent tools to investigate these phenomena.

The rotational dynamics of molecules or side groups such as methyl groups is a very sensitive probe of the interatomic forces in crystals. Rotating a methyl group about the bond connecting it to the rest of the molecule makes it experience a rotational hindering potential which arises from the interactions of the methyl hydrogens with their surroundings.

This potential has at least three wells due to the molecular symmetry. At moderately high temperatures, the methyl groups undergo thermally activated reorientations between all three wells, whereas at low temperature, say below 30 K, the dynamics of the methyl groups is usually dominated by rotational quantum tunnelling [1].

While the dynamics of isotopically uniform methyl groups is by now well understood, little attention has been paid so far to the isotopically mixed CHD_2 and CH_2D groups. Due to the loss of the three fold permutation symmetry in the latter, dramatic differences in the dynamical behavior are expected.

WHY ASPIRIN ?

A well-studied case of the dynamics of the CH_3 and CD_3 groups is that of aspirin $C_8H_5O_4$-CH_3 and $C_8H_5O_4$-CD_3. The observation of rotational tunnelling in this compound by NMR triggered a whole series of studies concerned with the potential and with the dynamics of these methyl groups. These studies show that from room temperature down to about 35 K the per-protonated, the per-deuterated as well as the isotopically mixed methyl groups perform thermally activated stochastic reorientations between the three potential wells. Upon cooling, the rate of the reorientations naturally slows down. What happens at low temperature depends crucially on the isotopic composition of the methyl group. For CH_3 and CD_3, coherent rotational tunnelling was inferred from NMR experiments. This implies that the wavefunction describing the methyl group is such that the three protons, respectively deuterons, are completely delocalized over three sites. By contrast, partial ordering, which implies localization as well as a rapid incoherent process between the almost degenerate upper two of the three wells were suggested for CH_2D, again on the basis of NMR results .

As shown below, Neutron Diffraction provides a direct check of the indirect NMR hints [2-4].

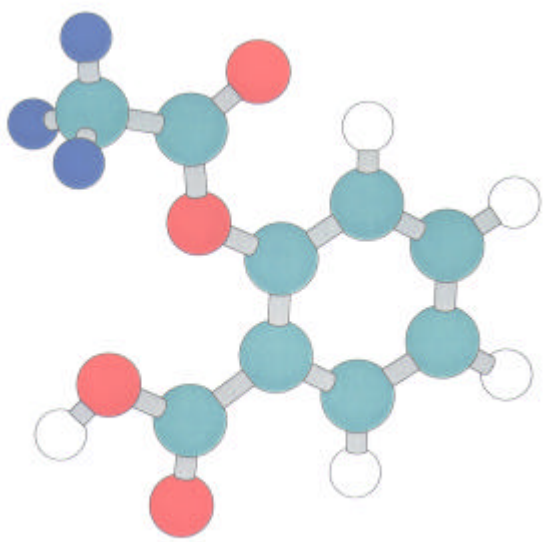

Figure 1. The aspirin molecule. Carbon and oxygen atoms are shown in blue-green and red. The hydrogen atoms from the methyl group are shown in blue and the

remaining protons attached to the backbone are shown in white .

SINGLE-CRYSTAL NEUTRON DIFFRACTION

This technique allows us to measure the nuclear density distribution within the crystallographic unit cell. This distribution is given by the probability density function of finding a nucleus at a given position, multiplied by the coherent neutron scattering length b of that nucleus. The probability density function relates to an average over space and time, *i.e.* over the volume of the sample and over the duration of the measurement. In case dynamic processes are involved, then neutron diffraction yields a direct long time exposure of those processes. Due to the opposite signs of the neutron scattering length of protons and deuterons (b_H=-3.74 fm, b_D=6.67 fm), the former yield a negative contribution to the nuclear scattering density, in contrast to the latter. Thus neutron diffraction is an excellent tool for distinguishing protons from deuterons, and hence for studying isotopic ordering processes such as those proposed for aspirin-CH_2D.

A ZERO AVERAGE CONTRAST SAMPLE

In order to improve the visibility of the alleged H/D orientational order of the methyl groups at low temperature, we aimed at an aspirin-CX_3 sample with an average scattering length $\langle b_X \rangle$ of zero. Consequently the single-site nuclear scattering length is expected to be close to zero for a random orientational distribution, for which there will hardly be any coherent scattering from the methyl hydrogens.

On the other hand, if ordering occurs, it will then be revealed by positive bumps and negative holes in the nuclear density distribution .

OUR EXPERIMENT

To test the above-mentioned ideas, we collected data sets from our crystal at 300 K and at 15 K on the four-circle 5C2 diffractometer (λ = 0.8302 Å) at LLB. At both temperatures the crystal was found to be isomorphous to normal protonated aspirin, which had been examined much earlier by X-ray diffraction [5]. The crystal is monoclinic, of space-group $P2_1/c$ with 4 molecular units per unit cell.

We used a crystal from a previous NMR study[3], and for which the requirement $\langle b_X \rangle$ =0 is nearly met. In fact, $\langle b_X \rangle \approx$ -0.6 fm, about 11 times smaller than $\langle b_D \rangle$. A further complication arises from the fact that our sample comprises approximately 70% CH_2D, 19% CH_3, 10% CHD_2 and 1% CD_3.

LEAST-SQUARES RESULTS

The program SHELXL97 was used for refinements. As expected, neither could methyl hydrogen positions be found, nor did the calculated difference Fourier map reveal any contribution from either the methyl protons or deuterons. Any information about these latter hydrogens (which is definitely present in our data) is swamped by the inherent residual noise due to series termination effects.

Taking this model which does not include methyl hydrogens as the starting point for the LT structure refinement, two proton positions and one deuterium position are easily located by their negative and positive contributions in the difference Fourier map calculated by SHELXL97. Including these in the structural model without any bond length or bond angle constraint yields a good final agreement factor R_1=0.0465.

MAXIMUM ENTROPY IMAGING

We are specifically interested in the nuclear density distribution arising from the methyl hydrogens. Since conventional Fourier syntheses would not reveal the latter when used on our room temperature data, we therefore applied the Maximum Entropy reconstruction method (MEM) to both our LT and RT data sets. We use our program GIFT (Generalized Inverse Fourier Transforms) which makes use of the Cambridge MemSys algorithm.

A projection of the 3D MEM-reconstructed nuclear density distribution along the monoclinic b-axis based on our 15 K data set is shown in Fig.2.

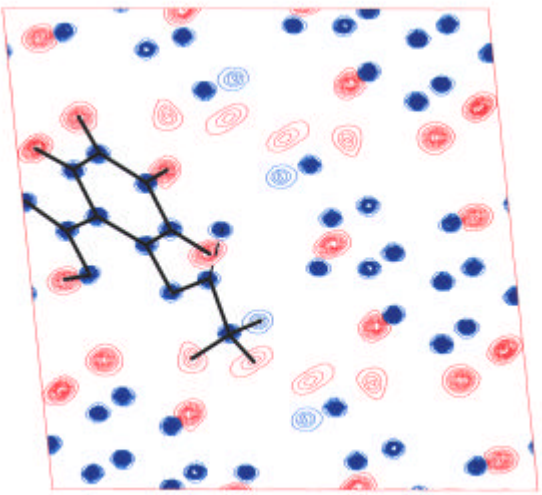

Figure 2. : Experimental nuclear density distribution of partially deuterated aspirin (acetylsalicylic acid) at 15 K projected along the monoclinic b-axis. Red contours pertain to protons, which have a negative scattering length, in contrast to deuterium, carbon and oxygen atoms shown here in blue. The solid line delineates a single aspirin molecule.

Similarly, the two sections shown below in Fig.3a,b are obtained from 3D scattering density reconstructions of the asymmetric unit of the aspirin

crystal by making use of MEM rather than conventional Fourier syntheses. Three dramatic improvements arise : (a) noise suppression, (b) flexibility to use non-uniform prior densities and (c) possibility to tackle partially phased data sets. In the present case, there is no phase problem : the phases of the structure factors are perfectly determined by the well-behaved atoms known from the X-ray study by Wheatley[5]. The decisive point is that MEM enables us to locate the methyl hydrogen even at room temperature. This is demonstrated in Fig.3a, in which a section of the nuclear density distribution function through the plane of the methyl hydrogens is displayed. Three holes, all negative as they should be since $\langle b_X \rangle < 0$, are clearly seen. Despite being very shallow, the three minima are robustly reconstructed by MEM. No matter how the reconstruction is carried out, with or without non-uniform prior scattering length densities , the three minima are consistently reproduced. No prior knowledge about the hydrogen positions, available in principle from the 15 K data, was used in reconstructing this density distribution. It demonstrates the superior power of MEM over both standard Fourier and least-square techniques and provides clear evidence of the random distribution of the methyl protons and deuterons at 300 K over three geometrically well-defined sites.

In Fig.3b, we finally show the nuclear density distribution at 15 K for the same section as in Fig.3a, again reconstructed by MEM. The clear message of this figure is that the methyl protons and deuteron in aspirin-CH_2D are well-ordered at 15 K. The deuteron obviously occupies with high preference the site associated with the large positive bump whereas the protons occupy almost exclusively the sites related to the negative holes. Truly, the localization of the methyl hydrogens at 15 K is also detectable in standard Fourier maps, albeit with a sizable background noise.

COPING WITH THE ISOTOPIC MIXTURE

Quantitatively, the density distribution displayed in Fig.3b corresponds to the [70%-19%-10%-1%] superposition of the four isotopic species mentioned earlier. This results in **effective** occupancies for both H and D different from unity when an assumed unique species CH_2D is refined using SHELXL97. We find 0.7, 0.7 and 0.53 for the two protons and the deuterium respectively. It can then be deduced that the probability of finding a deuteron from the CH_2D isotopic species at the position evidenced by the positive bump seen in Fig.3b is at least equal to 0.86.

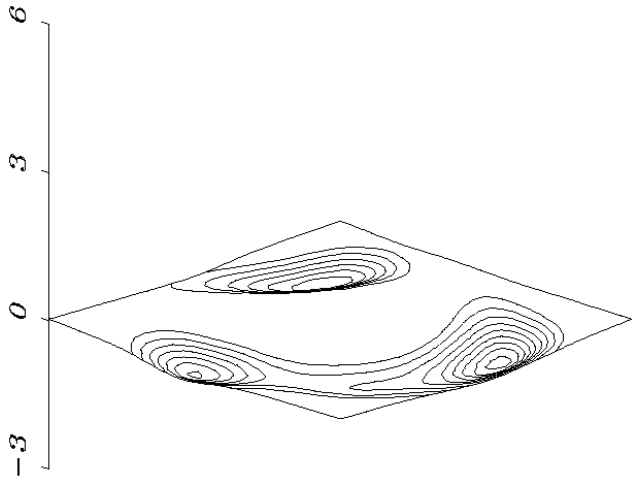

FIG.3a. MEM section of the nuclear density distribution through the methyl hydrogens of aspirin obtained from the 300 K data set. Note the three shallow minima of almost equal depth. They evidence the random occupation of the three methyl hydrogen sites by the protons and deuterons with weights corresponding to the isotopic composition of the crystal (see text). The residual (positive) contribution due to the thermal motion of the carbon atom of the CX_3 group has been removed numerically. (density unit : fm/A^3)

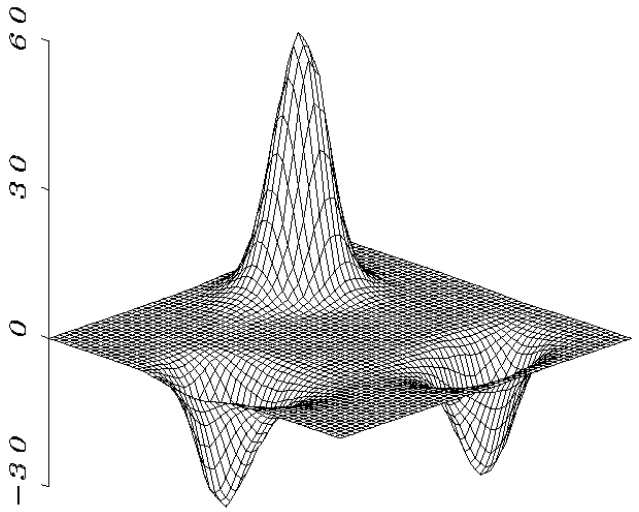

FIG.3b. MEM section of the nuclear density distribution through the methyl hydrogens of aspirin from the 15 K data set. Note that the vertical scale has been changed by a factor of 10 in comparison with that in Fig.3a. The graph demonstrates the orientational ordering at 15 K of the most abundant methyl isotopomer, CH_2D in our crystal sample. The deuteron occupies almost exclusively the site related to the (positive) bump while the protons preferentially occupy the two sites associated with (negative) holes. (density unit : fm/A^3)

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CORRELATED SIMULTANEOUS PHASON JUMPS IN AN ICOSAHEDRAL Al-Mn-Pd QUASICRYSTAL

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The relationships between quasicrystals and other incommensurately modulated crystals (IC) have many interesting theoretical aspects. An obvious link is that both can be derived from a common description based on an embedding in a higher-dimensional superspace that contains a periodic lattice of so-called atomic surfaces. The superspace cut-and-projection algorithm permits a group-theoretical classification of all possible structures. Hyperspace crystallography leads also to the possibility of an attractive analogy within the realm of lattice dynamics based on the introduction of the notion of " phasons " in addition to the usual phonons. Here we stumble onto a first real difficulty. Once we go beyond one-dimensional structures, there are very important differences in the topology of the atomic surfaces between QC and IC. This has been pointed out by many authors, and turns the subject into a really subtle issue. Generally spoken, the atomic surfaces in QC are not continuous[1].

Based on these studies it was anticipated that "phasons" in QC would not be *collective propagating modes* as in IC but rather atomic jumps[2], that can be visualized by configuration flips within Penrose-like tiling models. Ensuing experimental studies confirmed this picture. In our current understanding an atomic jump is a stochastic single-particle process. The phonon heat bath produces a fluctuating environment that from time to time will open a low-energy gateway that is prosperous for a jump. Starting from this conceptual image that thrives on disorder, it is hard to imagine an orderly concerted choreography of simultaneous jumps of two or more atoms. This only stresses the fact that, although they are both materialized by a sliding of the cut in superspace, phasons in QC and IC should correspond to very different, antipodal types of dynamics. Nevertheless, this poses a number of small problems in QC. First of all, the (anomalous) temperature dependence of the (quasielastic) neutron-scattering signal that reveals the existence of the hopping does not tally with the description we gave above of the jump process in terms of a phonon bath[3]. Secondly, tile flips in real, *i.e. not mono-atomic* structural models entail in general several simultaneous atomic jumps. It was therefore inferred that the elementary phason building brick would rather be the atomic jump than the tile flip.

In triple-axis neutron-scattering experiments on a large single-grain sample of the icosahedral phase Al-Mn-Pd, we came across some evidence that seems to challenge this common-sense based paradigm. In fact, we found a **Q**-dependence of the quasielastic signal that we are only able to explain by assuming that two (or more) atoms jump simultaneously keeping their separation vector fixed.

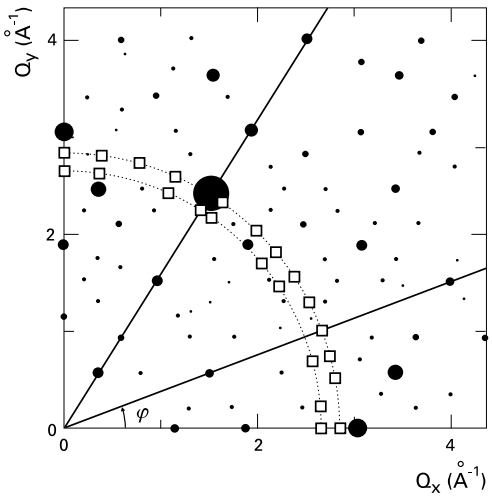

Figure 1. Binary scattering plane. The sizes of the full circles represent the intensity of the Bragg peaks. The locations of the various constant-Q scans have been drawn: they were all made in the k_f = 1.64 Å^{-1} configuration. The angle φ is defined with respect to Q_x

These experiments were performed with the cold-neutron double-monochromator triple-axis spectrometer 4F2 of the LLB in the fixed k_f = 1.64 Å^{-1} and k_f = 1.96 Å^{-1} configurations. The loci of some of the constant-*Q* energy scans in the binary scattering plane of the QC are indicated in Fig. 1, which also shows the intensities of the most prominent Bragg peaks. The choice of the binary plane allows to explore all types of symmetry axes (2-, 3-, and 5-fold) of the QC in one set-up. The 3 cm^3-sized single-grain sample has been grown by the Czochralsky method.

A typical data set is featured in Fig. 2 together with a fit based on a Lorentzian quasielastic signal convoluted with the Gaussian resolution function. Also included in this fit are the elastic peak and a linear incoherent phonon background. The **Q**-dependence of the quasielastic intensity for Q = 2.85 Å^{-1} is displayed in Fig. 3. It is strongly anisotropic. In a simple single-particle model in the white-noise approximation for atomic jumps between two sites separated by jump vectors $\mathbf{d}_j$ along a m-fold axis of the QC, the quasielastic intensity should follow an (incoherent) structure factor:

$$S_{q.el}(\mathbf{Q}) = \sum_{j=1}^{30/m} \frac{1}{2}\left[1 - \cos(\mathbf{Q}.\mathbf{d}_j)\right] \qquad (1)$$

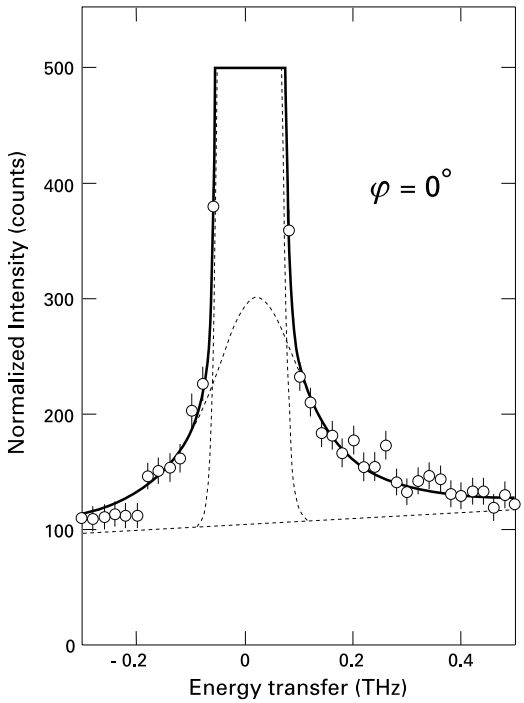

Figure 2. Typical constant-Q scan with fit. The data shown here correspond to |Q| = 2.85 Å^{-1} and φ = 0°.

The sum allows for the fact that for jumps along m-fold directions there are 30/m symmetry-related jump vectors. If the direction of the jump is not along a symmetry axis, then the sums will have to extend over the whole icosahedral group. (This corresponds to the case m=1). The quasielastic and elastic intensities obey a sum rule such that the incoherent elastic structure factor is obtained from Eq.(1) by changing the sign in front of the cosine term:

$$S_{el}(\mathbf{Q}) = \sum_{j=1}^{30/m} \frac{1}{2}\left[1 + \cos(\mathbf{Q}.\mathbf{d}_j)\right] \qquad (2)$$

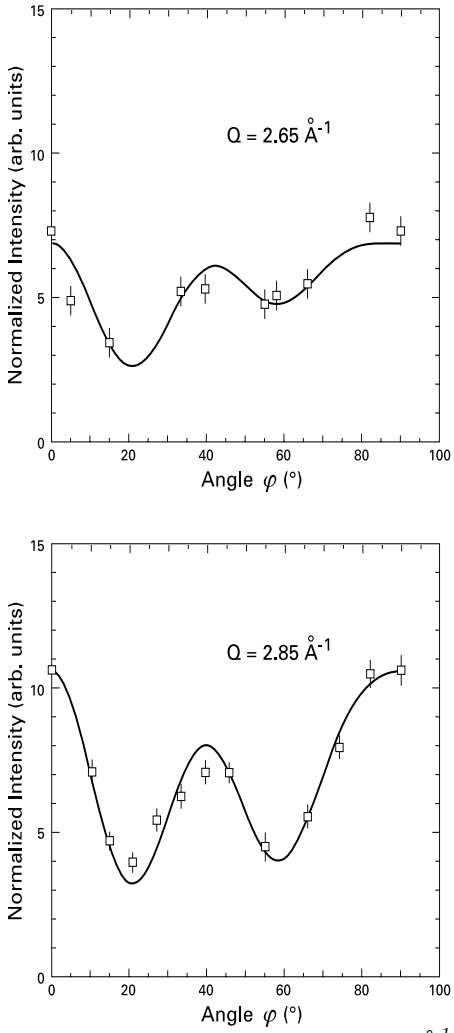

Figure 3. Quasielastic intensities for |Q| = 2.65 Å^{-1} and |Q| = 2.85 Å^{-1} . A fit with model function (2) is also shown. (Data collected with a second sample, both in k_f = 1.64 Å^{-1} and k_f = 1.97 Å^{-1} set-ups, bear out the reproducibility of these results).

The quasielastic structure factors embodied by equation (1) all exhibit an isotropic first local maximum in Q, as can be appreciated from Fig.4 for two-fold jumps. This remains true if the direction of the jump is not a symmetry axis. This is quite at variance with the experimentally observed data which do not display such a spherical shell of maximum intensity and on the contrary exhibit their strongest anisotropy at low Q. We should point out that none of the three models (m=2; m=3; m=5) expressed by equation (1) can reproduce the peak/valley-ratios that occur in Figure 3. This means that one needs another type of model. By some serendipity we found out that the data shown in Fig. 3 are perfectly described by equation (2) for $m=3$ and d= 3.85 Å. Among the (idle) lines of thought we followed in our attempts to come to grasps with this alienating finding, we can mention models as proposed

by Katz and Gratias[4] and down-sized versions of Elser's escapement model[4]. The failure to represent our data by such models helped us to realize where the minus signs in front of the cosines in equation (1) come from. Each time an atom jumps from A to an empty site B, the neutron-scattering contrast between A and B is inverted, which amounts to a π-flip of its phase. Therefore, the only way to obtain a plus sign is by designing a model that preserves the contrast despite the occurrence of the jump. This can only be achieved by admitting that two atoms in A and B are jumping simultaneously to A' and B' respectively, whereby the vectors AB and A'B' are equipollent. This leads to expressions of the type

$$S_{q,el}(\mathbf{Q}) = \sum_{j=1}^{30/m} \frac{1}{m}\left[1-\cos(\mathbf{Q}.\mathbf{d}_j)\right]\left[1+\cos(\mathbf{Q}.\mathbf{s}_j)\right],$$ where

the correlation vector $\mathbf{s}_j$ is analogous to the separation vector AB. The $[1 - \cos(\mathbf{Q}.\mathbf{d}_j)]$ parts are responsible for the first radial maximum, while $[1 - \cos(\mathbf{Q}.\mathbf{s}_j)]$ terms entail a modulation of this local maximum that otherwise would have been an isotropic spherical shell. In our data we thus have s_j = 3.85 Å, while d_j cannot be determined. At once, this means that phasons in QC could nevertheless share some collective character with propagating phason modes that are typical of IC. We must admit that such collective motion clashes with our *Weltanschauung*, as we were strong believers of the heat-bath-driven scenario outlined above. We must signal that the description of the data by Equation (2) breaks down at higher *Q*-values, where we are unable to explain the observed intensities. At 2.65 and at 2.85 $Å^{-1}$ we are so lucky to find ourselves in the small-*Q* limit, where the largest characteristic distance within the dynamics can be discerned in an isolated fashion, free from the obfuscating presence of signals corresponding to shorter length scales. We think that this novel result constitutes an important step towards the elucidation of the physical nature of phasons in QC.

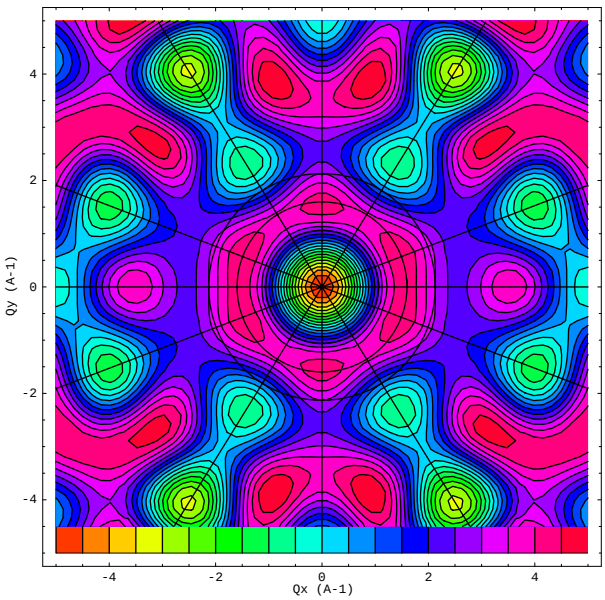

Figure 4. Contour plots for the quasielastic intensity, calculated in a model with two-fold jumps according to Equation (1), m=2. Note the almost isotropic first maximum of the intensity around Q = 1. 5 $Å^{-1}$. The color code is shown at the bottom of the Figure, going from left to right, e.g. the first color on the left codes numerical values between 0 and 1.

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DELOCALIZATION INDUCED BY NONLINEARITIES OF ANDERSON LOCALIZED LINEAR MODES IN A RANDOM MEDIUM

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It is known for many decades that in some very particular models, there are exact solutions which correspond to spatially localized time periodic vibrations ("breathers"). About a decade ago, it has been realized that in classical systems which are both *nonlinear* and *discrete*, such solutions generically exist, that is no special potential forms are required[1].
In principle, *discrete breathers* may exist in any periodic nonlinear model at any dimension taking into account the whole complexity of real systems, and moreover they are robust against model perturbations.
The existence of these *discrete breathers* is a consequence of the facts that on one hand the vibration frequency of an oscillation in a nonlinear system depends on its amplitude and on the other hand, the linear phonon spectrum is bounded in frequency because the system is discrete. Then, when the frequency and the harmonics of the *discrete breathers* are in the phonon gaps, no energy radiation is possible so that this localized vibration persists forever as an exact solution[2].
These discrete breather solutions are often linearly stable, that is the small fluctuations do not grow exponentially[3]. This result implies physically that in the presence of moderate fluctuations, for example the thermal fluctuations at low temperature, their life time will be much longer that those predicted by standard models of relaxation. Thus, it is not by chance that these classical excitations were first found numerically by molecular dynamics in a series of model with increasing complexity. It has been found that they appear spontaneously in some conditions out of thermodynamical equilibrium, for example under the effect of a thermal shock.
Otherwise, it is well-known since the pioneering works of Anderson[4] in the fifties that the linear modes of a random medium may be spatially localized. In that case, disorder detunes in some sense, all the resonances which would exist between the vibrations which are localized at different spots of the system, which forbids any propagation of vibrational energy over long distance. This theory was also very successful for explaining the insulating properties of some random metallic alloys (e.g. $Nb_x V_{1-x}$) or of semiconductors.
Thus, it seems natural to expect that when both nonlinearity and disorder are involved in the same system, the localization effect of vibrational excitations will be enhanced. Indeed, since the localized phonons of the linearized system cannot propagate any energy, the energy of a localized excitation cannot be dissipated through the system even if its frequency belongs to the phonon spectrum, and then it should persist indefinetely.
Actually, the phenomenon is more complex than one could believe, because nonlinearities play a "*double-game* ". On one hand, disorder and nonlinearity may cooperate for generating discrete breathers which then are exact well localized solutions. On the other hand, for other time periodic solutions, disorder and nonlinearity conflict. Nonlinearity may restore resonances between sites which are far apart, and then generate unexpectedly spatially extended modes which can propagate some flux of energy.
We analysed in detail this effect on a very simple model which consists into a one dimensional chain of quartic oscillators coupled by harmonic springs. For that purpose, we improved and developed several original and reliable techniques for calculating very accurately both localized and the extended modes in large systems (which could become possibly very complex such as macromolecules)[5].

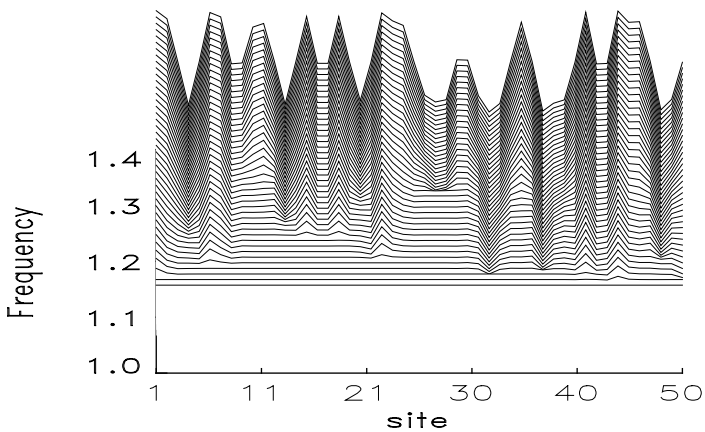

Figure: Profile of the initial positions for an exact time periodic and time reversible solution at different amplitudes which is initially a localized linear mode (on site 44) at zero amplitude for the hamiltonian

$$H = \sum_i \left(\frac{1}{2}u_i^2 + \frac{1}{2}\omega_{i,0}^2 u_i^2 + \frac{1}{4}u_i^4 + \frac{C}{2}(u_{i+1} - u_i)^2\right)$$

ω_{0i}^2 *is uniformly random in the interval* [0.5,1.5] *in a finite system with 50 sites. Each line corresponds to a given frequency and amplitude of the initial localized mode, increasing from lower to upper line.*

With these methods, we can follow continuously the evolution of a time periodic solution as a function of its frequency (or amplitude of the initially localized linear mode) when model nonlinearities are present. The figure shows an example of such an evolution, for a solution which is initially a localized linear mode (on site 44) at amplitude zero. It is first observed as expected that the frequency of this solution increases as a function of its amplitude because of nonlinearities. However, it is clear that extra oscillations grow at spots which are possibly very far from the initial excited spot. These new oscillations start to develop precisely at the location of linear localized modes the frequency of which becomes resonant with those of the solution. Thus for an infinite system with a dense phonon spectrum, an infinite number of resonant frequencies are crossed for any small variation of the amplitude (or equivalently the frequency). As a result, the initial solution immediately delocalizes with small peaks at the corresponding resonant spots. However, while the solution is still small, the distribution of these spots is sparse which only allows a tiny transport of energy which nevertheless is not zero. When the amplitude becomes larger, the amount of energy which can be propagated by such a solution increases and becomes comparable to those of a nonlinear phonon in a similar but non random system.

We are also able to calculate accurately localized discrete breathers in the same systems, but with other methods[6]. Our numerical results agree with a theorem of Albanèse and Fröhlich[7] proven on a similar model, which states that there is a "quasicontinuum" of solutions with frequency in a fat Cantor set (that is with a finite measure). The gaps in this Cantor set are the consequences of the resonances with the linear modes which destroy the localized character of the solution and must be avoided. Since there are infinitely many possible resonances, there are infinitely many gaps but however the widths of these gaps, decay as an exponential function of the distance between the breather to the resonant localized linear mode. Because of that, the frequency Cantor set is not void and keeps a finite measure.

These original results open new perspectives for a better understanding of glasses and other amorphous materials, which is non phenomenologic. On one hand, we predict that nonlinearities even very small imply that a nonvanishing residual thermal conductivity persists at low temperature but drops very fast to zero at zero K. On the other hand, a substantial part of the vibrational energy of the system may be spontaneously trapped as localized discrete breathers for very long times, which become macroscopic at very low temperature. This effect, which can be easily checked by molecular dynamics test, provides an alternative interpretation for the slow relaxation processes in glasses usually described by the old phenomenological two-level model of Anderson. Our interpretation only requires some nonlinearity in the model, which may be very weak and thus which should always exist. On contrary, the Anderson model requires the existence of double wells which actually has never been confirmed by direct structural observations (at least in most materials).

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