



**HAL**  
open science

## Phason modes in quasicrystals

Marc de Boissieu

► **To cite this version:**

Marc de Boissieu. Phason modes in quasicrystals. Philosophical Magazine, 2008, 88 (13-15), pp.2295-2309. 10.1080/14786430701861486 . hal-00513856

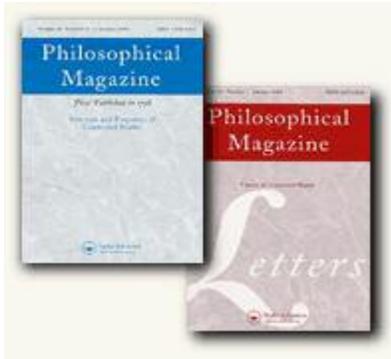
**HAL Id: hal-00513856**

**<https://hal.science/hal-00513856>**

Submitted on 1 Sep 2010

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



**Phason modes in quasicrystals**

Journal:	<i>Philosophical Magazine &amp; Philosophical Magazine Letters</i>
Manuscript ID:	TPHM-07-Dec-0354
Journal Selection:	Philosophical Magazine
Date Submitted by the Author:	03-Dec-2007
Complete List of Authors:	de Boissieu, Marc; SIMap, CNRS
Keywords:	diffraction methods, quasicrystals
Keywords (user supplied):	Phason, diffuse scattering



Only

Running heads (verso) *M. de Boissieu*  
(recto) *Phason modes in quasicrystals*

## Phason modes in quasicrystals

M. DE BOISSIEU\*§

§ Sciences de l'Ingénierie, des Matériaux et des Procédés (SIMaP), Grenoble INP, CNRS, UJF, BP 75 38402 St Martin d'Hères Cedex, France

\*Corresponding author. Email: Marc.de-Boissieu@ltpcm.inpg.fr

### Abstract

Studies on phason modes in quasicrystals, but more generally in aperiodic phases, which encompasses incommensurately modulated phases, composites and quasicrystals, are reviewed. After an introduction on phason modes in aperiodic phases, the hydrodynamic theory is presented. The case of incommensurately modulated phases is illustrated by results on the ThBr<sub>4</sub>. Atomic models used to simulate phason modes in quasicrystals are then presented followed by an overview of results obtained for icosahedral and decagonal phases.

*Keywords:* Quasicrystals, phason modes, diffuse scattering.

*AMS Subject Classification:*

### 1 Introduction

Right after the discovery of quasicrystals, the concept of phason has been introduced and became the subject of many investigations. Whereas the concept of phasons is well defined for incommensurately modulated phases, in the quasicrystal community the name phason is used to address quite different physics: there are phason modes, phason 'jump' or phason hopping, phason strain, phason disorder, random phason disorder... just to quote some of the wording which one can find in the literature. This being said, in the entire quasicrystals (QC's hereafter) research field phasons are believed to play a role, starting from the growth mechanism up to their physical properties. Studies on the QC growth have introduced phason as either an inherent part of the growth process and the resulting structure (random tiling), or have invoked phason annealing behind the growth front. Structural quality of quasicrystal is often referred to with the degree of 'phason strain' in the system. Atomic structure determination has been the subject of intensive investigations leading to a debate on random tiling versus perfect QC, or entropy versus energy stabilizing mechanisms, debate in which phason plays a crucial role. A generalized elasticity theory has been developed for QC's with

1  
2  
3  
4 the introduction of phason elastic constants: diffuse scattering and phason modes have been studied in this  
5 perspective. Some QC's structural phase transitions have been shown also to be driven by phason modes. Of  
6 course dynamics of QC's is intimately related to phason dynamics, especially long wavelength phason modes.  
7 Physical properties studies have also invoked phasons: the spiky electronic density of states might be  
8 smoothed out by phason disorder. Plastic deformation of QC's is intimately related to the introduction of  
9 generalized dislocations (in high dimension) which induce both a phonon and phason distortion field and the  
10 notion of phason walls. The concept of phason has even been used to analyze crystal approximant defects. In  
11 summary phasons are everywhere in QC's studies!

12  
13  
14 In this paper we review studies carried out on long wavelength phason modes. It is interesting to put these  
15 studies on phason modes in QC's in the broader perspective of phason modes in aperiodic crystals, where  
16 aperiodic crystals encompasses incommensurately modulated phases, intergrowth or composites structures  
17 and quasicrystals (A detailed introduction can be found in [1], and a detailed review in [2]). Indeed, although  
18 they might be very different systems, phason modes originate from the same description in the high  
19 dimensional picture of aperiodic crystals. We will first introduce in section 2 the hydrodynamic theory of  
20 aperiodic crystal, where a unified description of phason modes can be derived. Going from a continuous  
21 phenomenological description, as the one carried out in the hydrodynamic theory, to a detailed atomistic  
22 description is a difficult problem which is far from being achieved for QC's. We will thus first present what is  
23 understood in a few incommensurately modulated phases, where atomistic model are at hand. In particular  
24 results on phason dynamics of the ThBr<sub>4</sub> incommensurate phases will be presented section 3. In section 4, we  
25 give a rapid overview on theoretical models and simulations related to phason modes. Section 5 is dedicated  
26 to the review of experimental results, first in the i-AlPdMn phase for which there is the largest set of data,  
27 then for other quasicrystals and the relationship with crystal approximant and finally for decagonal phases.  
28 We end this review by some conclusion and perspectives in section 6.

## 36 2. Hydrodynamic theory of aperiodic crystals.

37  
38 The name phasons was coined in 1971 by Overhauser [3] in the context of charge density wave (CDW)  
39 systems. Studying the lattice excitation of an incommensurate CDW, he demonstrated that because the free  
40 energy of the system is invariant under a phase shift of the modulation there are new lattice excitations which  
41 he named phasons, showing up around the satellite reflections and whose dispersion is acoustic like. The  
42 nature and damping of those modes has been intensively studied from the microscopical view. We first  
43 present general results which can be derived from the hydrodynamic theory of aperiodic crystals.

44  
45 Hydrodynamics is based on symmetry breaking analysis and deal with long wavelength excitations for  
46 which the frequency  $\omega$  goes to zero as a function of some power of the excitation wavevector  $q$ . The basis for  
47 the analysis of all aperiodic phases is best understood in the high dimensional picture, where the high  
48 dimensional space decomposes into the parallel (or physical) and the perpendicular space. For all aperiodic  
49 phases the free energy of the system is invariant under a rigid translation of the parallel space in the  
50 perpendicular direction, as a direct consequence of the cut space having an irrational slope. From mode  
51 counting arguments it can be shown that for *all aperiodic crystals*, there are phason modes which are not  
52 propagative modes but collective diffusive modes for which one can write:  
53  
54  
55  
56  
57  
58  
59  
60

$$-i\omega = D_{\text{Phason}}q^2 \quad (1)$$

where  $D_{\text{Phason}}$  is the phason diffusion constant, which means that the phason mode decay exponentially with time with a characteristic time  $\tau$  inversely proportional to  $q^2$ . We stress here that the diffusive nature of phason modes also holds for incommensurately modulated phases and is not specific to quasicrystals. In fact, as illustrated in section 3, anharmonicity is crucial to reconcile the hydrodynamic and microscopic picture of phason modes [2, 4]. Indeed in the case of incommensurately modulated phases, phason modes have a finite lifetime independent of  $q$ , leading to two regimes: a long wavelength one for which the phason is diffusive and a shorter wavelength one for which the phason is a damped propagating mode.

This hydrodynamic theory relies on the hypothesis of a continuum approximation for which an infinitesimal displacement of the parallel space along the perpendicular direction does not cost energy. This has been studied in details in the Frankel-Kontorova type model and lead to the so-called analyticity breaking or to the existence of a phason gap.

Finally it is worth noting that phason modes can be viewed as modes with a wavevector in the parallel space and a polarization in the perpendicular space [5], as illustrated Figure 1. We stress again that modes are not propagative in this picture.

### 3. Phason modes in the incommensurately modulated ThBr<sub>4</sub> phase.

The ThBr<sub>4</sub> phase undergoes a phase transition at 95 K from a tetragonal phase to a 1D incommensurately modulated phase with a wavevector  $q=0.32c^*$ . The diffraction pattern shows weak satellite reflection, whose intensity is well reproduced by a simple sinusoidal modulation. The lattice excitation of this phase has been studied by inelastic scattering whose results has been analysed in the framework of the Landau soft mode theory [6, 7]. Above  $T_i$ , one of the optical mode shows a softening (Figure 2) with a minimum frequency at the incommensurate wavevector. In the incommensurate phase, the phason mode appears, with a linear dispersion around the satellite reflection (Figure 2). It is important to note that the slope of this dispersion is different from the sound velocity found in ThBr<sub>4</sub>, pointing to a new excitation which is specific to the incommensurately modulated state. The remaining optic like branch is a mode which induces variation of the amplitude of the modulation (named amplitudon). The phason mode can also be viewed in the high dimensional description as a mode having a wave-vector in the physical space and a polarisation in the perpendicular direction. In the frequency range shown Figure 2, this is a damped propagating mode. However, unlike the case of phonon, the phonon lifetime is constant and independent of  $q$ . This means that in the very long wavelength limit the phason mode is overdamped and become diffusive, in agreement with the hydrodynamics theory. Of course the found phason diffusion constant is rather rapid as expected from a process which is driven by small atomic displacements around an average position. There are very few systems for which such phasons modes have been evidenced. Another interesting system is the NaNO<sub>2</sub> crystal, in which the transition is of the order-disorder type and the elementary process is relaxational in nature, so that the phason mode only shows diffusive type behavior[8].

The origin of the incommensurability has been also the subject of many theoretical studies. One of the most elaborated model is the so called discrete frustrated  $\Phi^4$  model or DIFFOUR model. This is a model combining a discrete basis structure and continuous degrees of freedom. A key ingredient in this model is the

1  
2  
3  
4 first and second neighbors interactions with opposite direction leading to ‘frustration’ [1]. The phase diagram  
5 of this model can be computed. As a general rule, the low T phase is a locked phase in which the modulation  
6 wavevector takes a rational value, the incommensurately modulated phase being at intermediate temperature.  
7 In this picture the origin of the incommensurate phase contains two terms: the frustration term on one hand  
8 (which however can be ‘resolved’ on a rational wavevector) and the entropy term gained by phason  
9 fluctuation in the incommensurate phase.  
10

11 There are many open problems in this field, which are not discussed here: analyticity breaking, phason  
12 gap, sliding modes. The interested reader is referred to ref [2].  
13  
14

#### 15 **4. Phason modes: theory and simulation in quasicrystals**

16

17  
18 Soon after the discovery of quasicrystals, several groups pointed out the importance of phason modes [9-  
19 12]. This opened the way for a series of theoretical and modeling studies. A complete development of  
20 hydrodynamics and elasticity of quasicrystals can be found in the review by Lubensky [13]. The Landau  
21 theory of phase transitions driven by phason modes has also been developed [14, 15]. This gives the possible  
22 group sub-group relationship for a QC to crystal transformation. Relations between the phason elastic constant  
23 imposed by the QC thermodynamic stability have been derived [16, 17]. In a way completely analogous to  
24 phonons which give rise to the well known thermal diffuse scattering [18-20], phason modes lead to diffuse  
25 scattering in the diffraction pattern which is located beneath the Bragg peaks with three main characteristics  
26 [21]: (i) the diffuse scattering decays as  $1/q^2$ , its intensity is  $Q_{per}$  dependent, (iii) its shape anisotropy is given  
27 by the phason elastic constants (the ratio  $K_2/K_1$  of the two phason elastic constants for icosahedral phases).  
28 This anisotropy might also be temperature dependent close to phase transitions [16, 17]. As shown in section  
29 4, the study of diffuse scattering turned out to be a very efficient way of experimentally evidencing phason  
30 modes. One has thus a rather complete phenomenological description of phason modes.  
31  
32

33 One important question is however the relation between this continuous theoretical description and the  
34 microscopic description of quasicrystals. This is a difficult problem since for an atomistic modeling of phason  
35 modes one need (i) an atomic model, (ii) the corresponding Hamiltonian describing atomic interactions, and  
36 (iii) a plausible description of the elementary ‘phason move’. Moreover, any realistic simulation will be faced  
37 with the very long time scales needed for phason modes and difficult to achieve in simulations.  
38  
39

40 Most of the simulations have been carried out within the random tiling model proposed by Elser and  
41 Henley [22]. In this picture atoms or clusters of atoms are arranged in a tiling, whose tiles can be reshuffled.  
42 One difficulty is finding a tiling allowing this reshuffling in a simple way and allowing for the exploration of  
43 all the phase space. Most of the simulations have been done using either a Penrose type tiling for decagonal  
44 phases, and a Amman (or 3D Penrose) tiling for icosahedral phases. The first simulation has been carried out  
45 in a very simple model in which atoms are located only on the vertices of the 3D Amman icosahedral tiling  
46 which constitute a rigid framework (there are no atom interaction). Although this is a rather crude model, the  
47 important outcome of this study, is that the simulated diffuse scattering matches what is predicted by the  
48 hydrodynamics theory [23] showing that phason modes are related to the configurational entropy gained by  
49 the tile reshuffling (see also [24]). More sophisticated models have been since then designed, in particular for  
50 decagonal phases, where realistic models combined with ab-initio based calculation have been proposed (see  
51 M. Widom et al, this conference). Entropy stabilised structure have even been predicted [25] in the BMgRu  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3  
4 system. For icosahedral phases, up to now simulations have been restricted to model systems. Using an  
5 Hamiltonian favoring 3-fold connections, Mihalkovic and Henley designed a model whose phason elastic  
6 constants are changing with temperature, eventually leading to a crystal approximant [26]. In a simple model  
7 for which the ground state is a perfect QC, Dotera et al. have shown that free energy is quadratic as a function  
8 of the phason strain only above a critical temperature. Below this temperature, the hydrodynamic and  
9 elasticity theory no longer apply [27]. Finally, it is worth to note that phason modes are intimately related to  
10 chemical disorder, a point which has been studied in [28, 29]. In the debate on entropy versus energy  
11 stabilization of QC, the entropy contribution to the system free energy is of course crucial. This phason  
12 entropy has been determined in a few model systems[25, 30-32]. Along these lines, the recent work of  
13 Engel[33] and Trebin (see this proceeding) on molecular dynamics simulation of a 2D model system using  
14 double well pair potential interaction, is particularly interesting since it provides a phase diagram, illustrating  
15 the respective role of energy and entropy in the system stabilization.

16  
17 In summarizing this section on phason theory in QC's, it can be said that whereas the phenomenological  
18 hydrodynamics and elasticity of QC's has been fully developed, a few realistic models are available for  
19 decagonal phases, but an atomistic understanding and modeling of phason modes is not yet achieved  
20 especially for icosahedral phases.

## 21 22 23 24 25 26 27 28 **5. Experiments and phason modes**

29  
30 A detailed presentation on experimental findings can be found in [2]. We give in the following an  
31 overview of the main experimental results, and its comparison with the hydrodynamic theory. As explained in  
32 section 4, the hydrodynamic theory of quasicrystal has been checked experimentally mainly using diffuse  
33 scattering measurements. Indeed diffuse scattering is related to the Fourier transform of the two body  
34 correlation function and carry the information on phason modes. A few experimental difficulties have to be  
35 pointed out. First there are several possible origins for the diffuse scattering in a metallic alloy, and one has to  
36 discriminate them. This is generally done by simulating their respective contribution in reciprocal space. In  
37 particular the very peculiar  $Q_{\text{per}}$  dependence and shape anisotropy of phason diffuse scattering is a key  
38 signature. Together with the phason diffuse scattering, there is also the thermal diffuse scattering (TDS) due  
39 to phonons. The TDS contribution can be suppressed using neutron scattering and an energy analysis with  
40 sufficient resolution. In the case of X-ray, this contribution can be evaluated, provided measurements are  
41 made on an absolute scale, i.e. the measured signal is converted in a differential cross section per atom.  
42 Moreover, if the diffuse scattering is on an absolute scale, it allows the determination of the phason elastic  
43 constant on an absolute scale. Finally, having diffuse scattering measurements on an absolute scale *is the only*  
44 *way* to compare the 'amount' of diffuse scattering for different samples.

45  
46 We first summarize results obtained in the i-AIPdMn phase for which a complete study has been carried  
47 out. We then continue by results in other icosahedral phases, and end up with a few results obtained in  
48 decagonal phases.

### 5.1 The *i*-AlPMn phase.

The *i*-AlPdMn phase is particularly interesting since it can be grown as centimeter size single grains [34-36]. Although the phase diagram is intricate, there is a narrow phase field for which the icosahedral phase is stable down to room temperature. Czochralski or Bridgman grown single grain quasicrystal, once annealed, have an exceptional structural quality, in term of mosaic spread and residual phason strain, leading to dynamical diffraction [37-39]. The large single grain size, allowed studies with neutron scattering and energy analysis, so that the TDS contribution was suppressed. A clear diffuse scattering signal shows up around the Bragg peaks, with all the characteristics of phason modes diffuse scattering:  $1/q^2$  decay,  $Q_{\text{perp}}$  dependence of the intensity and shape anisotropy. In fact the observed signal is perfectly reproduced using the hydrodynamic theory and two phason elastic constants whose ratio  $K_2/K_1 = -0.52$  [40]. These findings have also been confirmed by absolute scale measurements using synchrotron radiation X-ray scattering. Using the absolute scale measurement it has been shown that the TDS contribution is negligible, and that the amount of diffuse scattering is independent of the heat treatment, ruling out an interpretation in term of defects: the observed diffuse scattering is related to equilibrium long wavelength phason modes (Figure 3). The  $K_1/k_B T$  and  $K_2/k_B T$  elastic constants, extracted from this measurement were found equal to 0.1 and -0.052  $\text{atom}^{-1}$  respectively [41], values which are useful for any quantitative comparison with models. At room temperature, one does not expect the phason modes to be dynamics. This was shown by a T study of the diffuse scattering, which showed a rather unexpected result, i.e. that the diffuse scattering diminishes as the temperature is increased, while the shape anisotropy also decreases. The T dependence of the diffuse scattering is very well reproduced by a softening of the phason elastic constant towards a 3-fold type instability, as the temperature is decreased from 780°C down to 500°C [42]. Below 500°C, the diffuse scattering intensity does not change anymore, showing that phason fluctuations are most likely quenched in at RT. This phason softening is most likely a signature of pre-transitional fluctuations, as expected in the random tiling or entropy stabilized scenario, the transition being avoided because of kinetics reasons. Indeed, for a very nearby chemical composition, the icosahedral phase is only stable at high temperature, and transform around 700°C in a  $F2_M$  phase, which remains quasiperiodic but with a tetrahedral point group symmetry [43-45].

From these results, one expects thus phason dynamics to show up above 500°C. The dynamics has been studied using X-ray photon correlation spectroscopy (XPCS) at the ESRF [46], a third generation synchrotron. Indeed, the brilliance of the X-ray light is such that a coherent X-ray beam can be produced. The coherent X-ray beam acts as a laser light, and when measuring the phason diffuse scattering, instead of a smoothly decaying intensity one observes large intensity fluctuations named speckle pattern. The speckle pattern is related to the phason fluctuations, so that any time dependence of the phason fluctuations will lead to changes in the speckle pattern. This is best observed by computing the time intensity correlation function. At a temperature of 400°C, the correlation function is time independent, whereas at 650°C, the correlation function decays exponentially with time (Figure 4, left panel). From this decay one can extract a characteristic time  $\tau$ , which is found to depend on the phason wavevector  $q$ . As expected for a diffusive mode, the characteristic time increases as  $1/q^2$ , from which a phason diffusion constant equal to  $1.5 \cdot 10^{-16} \text{m}^2 \text{s}^{-1}$  has been determined [46, 47] (Figure 4, right panel). A few measurements carried out at 600°C indicate that the process is most likely thermally activated, with an activation energy of the order 3 eV. This diffusion constant is slower than the

Mn self diffusion ( $1.10^{-14} \text{m}^2 \text{s}^{-1}$ , 2 eV) [48], indicating that phason modes involve exchange of chemical species on neighboring sites, with thus a longer time scale. The measured time scale and activation energy are very close to what has been obtained by M. Feuerbacher et al. in the study of a phason wall relaxation left behind a moving dislocation [49] (see also these proceedings).

At much longer wavevector (i.e. short wavelength) Coddens et al. have evidenced a very fast process by measuring quasielectric neutron scattering, interpreted as an atomic jump. From data analysis they concluded that this is an assisted jump, an atom going from one site to an unoccupied one. A detailed study on a single grain, lead to the conclusion that there are 2 atoms, probably Pd, jumping simultaneously over a distance of about 0.3 nm [50]. This last process has not been related to the details of the atomic structure. Moreover, the time scale found in this study, is much too fast to be compatible with what has been observed at longer wavelength, so that most likely other process have to be invoked to explain the long wavelength phason dynamics.

Although the atomic structure of the i-AIPdMn phase is rather well understood, there is no model for phason modes in this phase. Some hint of what is the effect of a long wavelength phason mode might be nevertheless obtained looking at the 6D picture of the i-AIPdMn phase. The most detailed model, has been obtained by Yamamoto et al. [51], with the same rough features as those obtained in other models [52, 53]. The structure is built up with 3 atomic surfaces (AS), 2 large one's on the nodes and a smaller one (Pd) on one of the body center. The two large AS are decomposed (in a complex way) in smaller parts or sub-domains, each of which consist of Pd, Al, Mn or a disordered sites (Al/Mn ...), and have a small component in the parallel space. When looking at the effect of a translation of the cut space along the perpendicular direction, the effect on the 3D structure might be decomposed in two situations. In the first one, which corresponds to the case where atomic surfaces are connected and satisfy the closeness condition (see Katz and Gratias [54]), an atom 'jumps' from one position to another 'unoccupied' one having almost the same local environment. This situation corresponds to the LS to SL substitution in the Fibonacci sequence. For the i-AIPdMn QC, this concerns the external part of the AS and leads to short 'jump' distances of about 0.15 nm along 5-fold axis for Al atoms for instance. This is this situation which has been most of the time considered as a 'phason jump'. There is however a second case, corresponding to the inner part of the large atomic surfaces, which generally are not connected: as a result when the cut is moved along the perpendicular direction, there will be some chemical specie exchange (say Pd and Mn), between two sites which might be far apart. In other word a phason mode is coupled to chemical disorder, or more precisely, is chemical disorder which occurs on specific sites. This is most likely the limiting process in phason mode diffusivity, which makes them very slow.

## 5.2 Other icosahedral phases.

Diffuse scattering studies have been carried out on several other quasicrystalline phases. The main result is that for all known quasicrystals, even the so called 'perfect' one's, phason diffuse scattering has been observed. The shape anisotropy (related to the ratio of the K1 and K2 phason elastic constants), and the amount of diffuse scattering (related to the magnitude of the phason elastic constants) is however strongly sample dependent. This is for instance the case of the isostructural quasicrystals, i-AIPdMn, i-AlCuFe [55] and i-AIPdRe [56]. Although they share a similar atomic structure the diffuse scattering shape anisotropy is

1  
2  
3  
4 quite different, with a 5-fold type diffuse scattering for instance in the i-AlCuFe phase, in agreement with a  
5 phason driven phase transition toward the rhombohedral phase with an intermediate 5-fold modulated phase  
6 [57-59].  
7

8 The recently discovered binary CdYb phase [60] and related family in the Zn-Mg-Sc system [61] has also  
9 been the subject of investigation. Phason diffuse scattering has been observed in the CdYb icosahedral phase  
10 [56]. Of particular interest is the comparison carried out between the i-ZnMgSc and the 1/1 cubic ZnSc  
11 approximant. Whereas the diffuse scattering observed in the ZnSc cubic approximant can be fully interpreted  
12 by a TDS contribution, in the i-ZnMgSc quasicrystal there is a supplementary contribution to the diffuse  
13 scattering arising from phason modes [62]. We stress here again the importance of having carried out  
14 absolute scale measurements, which allowed an exact computation of the TDS contribution. This result nicely  
15 demonstrates that the phason diffuse scattering is related to the long range quasiperiodic order, since both the  
16 QC and its approximant share the same local environment in term of atomic clusters. Moreover, in both cases,  
17 the inner tetrahedron corresponds to a site where the 'phason' jump occurs [63], experimentally illustrating  
18 the known result that one needs a quasiperiodic long range order for the long wavelength phason to take place.  
19 Finally it was found that the amount of diffuse scattering is much smaller in the i-ZnMgSc phase than in the i-  
20 AlPdMn one, as a consequence of larger phason elastic constants. This lead to a very large number of Bragg  
21 peaks, having a large  $Q_{\text{per}}$  component, which are observed in the diffraction pattern (Figure 5).  
22

23 In this review, we did not touch upon the phonon-phason coupling term. Although this term certainly  
24 exists, the observed diffuse scattering is in general dominated by the pure phason contribution. Note however,  
25 an interesting method to determine this constant proposed by Edagawa in comparing crystal approximant and  
26 quasicrystal lattice parameters [64-66]. Using this method, the phonon-phason constant could be evaluated in  
27 a few systems.  
28

### 29 **5.3 Decagonal phases**

30 Decagonal phases are described as a periodic packing of a few quasiperiodic layers. As such, TEM  
31 imaging technique can be used, especially when seen down the periodic axis. However, the 3D character of  
32 these phases should not be forgotten, especially when discussing phason modes.  
33

34 The first evidence for phason modes was obtained by Edagawa et al. in the d-AlCuCo [67, 68]. In an in-  
35 situ HRTEM experiment carried out at 1123 K, they observed time dependent contrast changes in the images,  
36 which could be mapped out onto a 2D Penrose tiling, with an edge length of about 2 nm. The contrast change  
37 corresponds to a 'phason tile flip' in the Penrose tiling. Images were obtained on rather thick part of the  
38 sample, so that what is observed corresponds to an atomic column 'flip', and thus correlated motion, and since  
39 the edge length of the tiling is 2 nm, the observed contrast is most likely a cluster column rather than an atom  
40 column. The flip occurs with an intermediate state, and long time scales of several tens of seconds between  
41 two flips. Whether the observed flip is related to the hydrodynamic theory of quasicrystal could not be proved  
42 in a further detailed analysis [68].  
43

44 Single atomic flips on a distance of the order 0.1 nm have been evidenced by Abe et al. using annular  
45 dark-field scanning transmission electron microscopy (ADF-STEM) at 1100K on a d-AlNiCo sample. They  
46 observed changes in the image contrast, which is interpreted as an anomalous Debye-Waller effect,  
47 anharmonic in nature. By comparing the experimental images with a model and its high dimensional picture,  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3  
4 they proved that the anomaly is caused by atoms ‘jumping’ from one site to another one with almost the same  
5 local environment, at a distance of about 0.1 nm and corresponding to the border of the atomic surfaces where  
6 the closeness condition apply. This is, up to now, the only experiment which has clearly revealed this small  
7 distance atomic jump. Of course the technique does not give any clue on the time scale of those jumps. This  
8 observation is consistent also with molecular dynamic simulation, where an anomaly on Al diffusion has been  
9 predicted [69].  
10

11 A large variety of diffuse scattering phenomena have been observed in decagonal phases. The diffuse  
12 scattering is strongly composition dependent and changes with temperature. Diffuse scattering has been  
13 observed both in between the quasiperiodic Bragg layers (as a result of a short range order along the periodic  
14 axis, doubling of the unit cell) and within the quasiperiodic Bragg layers. Various interpretation have been  
15 given in term of columnar cluster disorder, or Huang scattering... [70-74] . It is only recently that the phason  
16 diffuse scattering has been studied [75, 76]. Looking at the overall diffuse scattering distribution, the authors  
17 have extracted the phason and phonon/phason elastic constant, on a relative basis (measurements were not  
18 carried out on an absolute scale). Results have been also interpreted by mean of a random distribution of a  
19 cluster, which reproduces well the short range order extracted from a Patterson analysis of the diffuse  
20 scattering data. Although this model by its construction can not reproduce the long wavelength phason modes,  
21 it is a first step in understanding phason diffuse scattering in decagonal phases. Finally it is worth to note that  
22 in situ studies of the diffuse scattering showed that the diffuse scattering diminishes when the temperature is  
23 increased in a way similar to what was observed in i-AlPdMn (although the origin of the diffuse scattering is  
24 not attributed to phason modes in decagonal phases).  
25  
26  
27  
28  
29  
30  
31  
32

#### 33 ***5.4 Other quasicrystals.***

34  
35  
36 Recently, dodecagonal quasicrystals have been discovered in soft condensed matter [77] or polymer  
37 phases [78]. These are particularly interesting systems for several reasons. First, the length scale and  
38 interaction between the building blocks is fundamentally different from those in play in already known QC.  
39 Second, models used for the dodecagonal QC are known to have fractal surfaces. This is a challenging  
40 problem for simulation, since in this case it has been shown that the fractal shape of the atomic surfaces  
41 induces a very complex process called the zipper [79]. Whether this process is really playing a role in  
42 experimentally found systems is of great interest. Finally, the entropy gained by tile re-arrangement is known  
43 theoretically, so that some estimate of the configurational entropy might be carried out.  
44  
45  
46

47 To conclude this short section, it is worth noting the recent photonic quasicrystal, which allows to  
48 introduce dislocation like defects and phason in a completely new system, for which the Hamiltonian is again  
49 very different from other systems [80]. This offers the opportunity of studying phason modes in a controlled  
50 set up.  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

## 6. Conclusion

In conclusion we have seen that phason modes have been evidenced in a few aperiodic phases. Experimental results are consistent with the hydrodynamics theory, which is best derived in the high dimensional description of aperiodic crystals. Phason modes can be viewed as modes with a wavevector in physical space and a polarization in the perpendicular space, but as a result of the hydrodynamic theory, phason modes are always diffusive mode, provided the wavelength is large enough, i.e. phason modes are not propagative modes, but are decaying exponentially with time.

The degree of understanding of phason modes at the atomic scale is however quite different in the systems investigated. For a few incommensurate displacive modulated phases, it has been found that two regimes exists: in a restricted wavelength range, phason modes are damped propagative mode, measurable by inelastic neutron scattering and resulting from a soft phonon mode transition toward an incommensurate phase. Models strongly suggest that the incommensurability arises because of frustration. At longer wavelength, phason modes become diffusive. In the study of an incommensurate density modulation (order disorder type) phason modes have been shown to have a relaxational character.

For quasicrystal, phason modes have been evidenced experimentally by X-ray or neutron diffuse scattering measurements. In all icosahedral phases studied so far, the phason diffuse scattering has been evidenced. However the magnitude and the sign of the phason elastic constant derived from such measurement is strongly sample dependent, even for isostructural phases. This suggests that phason modes in that case are strongly related with chemical disorder. The dynamic nature of phason modes has been studied only in the i-AlPdMn phase using XPCS, where results are in agreement with hydrodynamics and the phason diffusion constant has been extracted. The very slow phason diffusion constant is compatible with results obtained by dislocation relaxation studies. Finally, the temperature study of the diffuse scattering in the i-AlPdMn lead to result which are consistent with a softening of the phason elastic constant as a signature of 3-fold type pretransitional fluctuations.

The above results can be qualitatively explained by the shape and chemical distribution of the 6D models which have been derived in a few systems: indeed whereas the external shape of the atomic surfaces fulfils the so called closeness condition, this is generally not the case for the inner part of the atomic surfaces. This unavoidably induces chemical disorder on specific sites of the quasicrystalline structure: this is certainly the slow limiting process in phason mode relaxation. Of course, realistic atomic modeling is necessary for a better understanding of phason modes. Although some realistic simulations have been carried out in decagonal phases, the most promising system is the CdYb one, where both detailed atomic structure [63] and realistic pair potential are now available [81]. Moreover a detailed T study of the diffuse scattering in this system would be of great interest.

Phason modes remain one of the most fascinating subjects in the aperiodic crystal field. Understanding of phason modes would certainly benefit from an interdisciplinary approach encompasses all aperiodic phases, with an exchanges of the knowledge gained in the various field. Indeed there are only a few incommensurately modulated systems for which phason modes have been evidenced, the question of the sliding modes in composites (or intergrowth) being an open one. Diffuse scattering studies have been mainly used for QC but could certainly be used for modulated or composite structures. The hypothesis used in the

hydrodynamic theory, the possible analyticity breaking transition, the relation between approximant (or lock-in phase) and the aperiodic phase, all those problems would certainly benefit from a unified and broad approach. Finally, the still open and fascinating questions of why aperiodic order sets in, what is the driving force stabilizing the long range aperiodic order, can now be tackled using realistic models.

**Acknowledgements:** I would like to thanks S. Francoual, R. Currat and T. Janssen for fruitful discussions.

## References

- [1] T. Janssen, G. Chapuis and M. de Boissieu, *Aperiodic Crystals. From modulated phases to quasicrystals* (Oxford University Press, Oxford, 2007).
- [2] M. de Boissieu, R. Currat and S. Francoual, in *Physics of Quasicrystals*, edited by T. Fujiwara and Y. Ishii (Elsevier Science, 2007), p. 107.
- [3] A.W. Overhauser, *Phys. Rev. B* **3** 3173 (1971).
- [4] E. Zeyher and W. Finger, *Phys. Rev. Lett.* **49** 1833 (1982).
- [5] T. Janssen, O. Radulescu and A.N. Rubtsov, *Eur. Phys. J. B* **29** 85 (2002).
- [6] L. Bernard, R. Currat, P. Delamoye, C.M.E. Zeyen, S. Hubert and R. de Kouchkovsky, *J. Phys. C* **16** 433 (1983).
- [7] R. Currat and T. Janssen, *Sol. Stat. Phys.* **41** 201 (1988).
- [8] D. Durand, R. Papoular, R. Currat, M. Lambert, J.F. Legrand and F. Mezei, *Phys. Rev. B* **43** 10690 (1990).
- [9] P.A. Kalugin, A.Y. Kitaev and L.S. Levitov, *JETP Lett.* **41** 145 (1985).
- [10] P. Bak, *Phys. Rev. Lett.* **54** 1517 (1985).
- [11] T.C. Lubensky, S. Ramaswamy and J. Torner, *Phys. Rev. B* **32(11)** 7444 (1985).
- [12] V. Elser, *Phys. Rev. Lett.* **55** 1730 (1985).
- [13] T.C. Lubensky, in *Aperiodicity and order : Introduction to quasicrystals, Chap. 6*, edited by M. V. Jaric (Academic Press, 1988), Vol. 1, p. 199.
- [14] Y. Ishii, *Phys. Rev. B* **39(16)** 11862 (1989).
- [15] Y. Ishii, *Phil. Mag. Lett.* **62** 393 (1990).
- [16] M. Widom, *Phil. Mag. Lett.* **64(5)** 297 (1991).
- [17] Y. Ishii, *Phys. Rev. B* **45** 5228 (1992).
- [18] J. Laval, *C. R. Acad. Sci.*, **207** 169 (1938).
- [19] P. Olmer, *Acta Cryst.* **1** 57 (1948).
- [20] C.B. Walker, *Phys. Rev. B* **13** 547 (1976).
- [21] M.V. Jaric and D.R. Nelson, *Phys. Rev. B* **37** 4458 (1988).
- [22] C.L. Henley, in *Quasicrystals: the state of the art*, edited by D. P. DiVicenzo and P. Steinhardt (World Scientific, 1991), p. 429.
- [23] L.H. Tang, *Phys. Rev. Lett.* **64** 2390 (1990).
- [24] C.L. Henley, V. Elser and M. Mihalkovic, *Z. Krist.* **215** 553 (2000).
- [25] M. Mihalkovic and M. Widom, *Phys. Rev. Lett.* **93** 095507/1 (2004).
- [26] M. Mihalkovic and C.L. Henley, *Phys. Rev. B* **70** 09202\_1 (2004).
- [27] T. Dotera and P.J. Steinhard, *Phys. Rev. Lett.* **72(11)** 1670 (1994).
- [28] U. Koschella, F. Gahler, J. Roth and H.R. Trebin, *J. Alloys Compd.* **342** 287 (2002).
- [29] U. Koschella, F. Gahler, J. Roth and H.R. Trebin, *J. Non Cryst. Sol.* **334-335** 276 (2004).
- [30] M. Widom, *Phys. Rev. Lett.* **70** 2094 (1993).
- [31] N. Destainville, R. Mosseri and F. Bailly, *Journal of Statistical Physics* **87** 697 (1997).

- [32] N. Destainville, Eur. Phys. J. B **52** 119 (2006).
- [33] M. Engel and H.R. Trebin, Phys. Rev. Lett. **98** 225505 (2007).
- [34] A.P. Tsai, A. Inoue, Y. Yokoyama and T. Masumoto, Mat. Trans., JIM **31** 98 (1990).
- [35] M. Boudard, E. Bourgeat-Lami, M. de Boissieu, C. Janot, M. Durand-Charre, H. Klein, M. Audier and B. Hennion, Phil. Mag. Lett. **71** 11 (1995).
- [36] Y. Yokoyama, T. Miura, A. Tsai, A. Inoue and T. Masumoto, Mater. Trans., JIM **33** 97 (1992).
- [37] S.W. Kycia, A.I. Goldman, T.A. Lograsso, D.W. Delaney, D. Black, M. Sutton, E. Dufresne, R. Bruning and B. Rodricks, Physical Review B - Condensed Matter **48** 3544 (1993).
- [38] A. Letoublon, F. Yakhou, F. Livet, F. Bley, M. de Boissieu, L. Mancini, R. Caudron, C. Vettier and J. Gastaldi, Europhys. Lett. **54** 753 (2001).
- [39] J. Gastaldi, S. Agliozzo, A. Letoublon, J. Wang, L. Mancini, H. Klein, J. Hartwig, J. Baruchel, I.R. Fisher, T. Sato, A.P. Tsai and M. de Boissieu, Phil. Mag. B **83** 1 (2003).
- [40] M. de Boissieu, M. Boudard, B. Hennion, R. Bellissent, S. Kycia, A.I. Goldman, C. Janot and M. Audier, Phys. Rev. Lett. **75** 89 (1995).
- [41] A. Létoublon, M. de Boissieu, M. Boudard, L. Mancini, J. Gastaldi, B. Hennion, R. Caudron and R. Bellissent, Phil. Mag. Lett. **81** 273 (2001).
- [42] M. Boudard, M. de Boissieu, A. Létoublon, B. Hennion, R. Bellissent and C. Janot, Europhys. Lett. **33(3)** 199 (1996).
- [43] M. de Boissieu, M. Boudard, T. Ishimasa, J.P. Lauriat, A. Létoublon, M. Audier, M. Duneau and A. Davroski, Phil. Mag. A **78** 305 (1998).
- [44] A. Létoublon, T. Ishimasa, M. de Boissieu, M. Boudard, B. Hennion and M. Mori, Phil. Mag. Lett. **80** 205 (2000).
- [45] M. Audier, M. Duneau, M. de Boissieu, M. Boudard and A. Létoublon, Phil. Mag. A. **79** 255 (1999).
- [46] S. Francoual, F. Livet, M. de Boissieu, F. Yakhou, F. Bley, A. Letoublon, R. Caudron and J. Gastaldi, Phys. Rev. Lett. **91** 225501/1 (2003).
- [47] S. Francoual, F. Livet, M. de Boissieu, F. Yakhou, F. Bley, A. Létoublon, R. Caudron, J. Gastaldi and R. Currat, Phil. Mag. **86(6-8)** 1029 (2006).
- [48] H. Mehrer, R. Galler, W. Frank, R. Blueher and A. Strohm, in *Quasicrystals - Structure and Physical Properties*, edited by H. R. Trebin (Wiley-VCH, Weinheim, 2003).
- [49] M. Feurbacher and D. Caillard, Acta Materialia **54** 3233 (2006).
- [50] G. Coddens, S. Lyonnard, B. Hennion and Y. Calvayrac, Phys. Rev. B **62(10)** 6268 (2000).
- [51] A. Yamamoto, H. Takakura and A.P. Tsai, Phys. Rev. B **68** 94201 (2003).
- [52] M. Boudard, M. de Boissieu, C. Janot, G. Heger, C. Beeli, H. Nissen, H. Vincent, R. Ibberson, M. Audier and J.M. Dubois, J. Phys: Cond. Matter **4** 10149 (1992).
- [53] M. Quiquandon and D. Gratias Phys. Rev. B **74** 214205 (2006).
- [54] A. Katz and D. Gratias, in *Lectures on Quasicrystals*, edited by F. Hippert and D. Gratias (Les Editions de Physique, 1994), p. 187.
- [55] M. Boudard, A. Létoublon, M. de Boissieu, T. Ishimasa, M. Mori, E. Elkaim and J.P. Lauriat, Mat. Sc. Eng. A **294-296** 217 (2000).
- [56] M. de Boissieu, H. Takakura, M. Bletry, J.Q. Guo and A.P. Tsai, J. Alloys Compd. **342** 265 (2002).
- [57] P.A. Bancel, Phys. Rev. Lett. **63** 2741 (1989).
- [58] P.A. Bancel, Phil Mag Lett **67** 43 (1993).
- [59] N. Menguy, M. de Boissieu, P. Guyot, M. Audier, E. Elkaim and J.P. Lauriat, J. Phys. I France **3** 1953 (1993).
- [60] A.P. Tsai, J.Q. Guo, E. Abe, H. Takakura and T.J. Sato, Nature **408** 537 (2000).
- [61] Y. Kaneko, Y. Arichika and T. Ishimasa, Phil. Mag. Lett. **81** 777 (2001).
- [62] M. de Boissieu, S. Francoual, Y. Kaneko and T. Ishimasa, Phys. Rev. Lett. **95** 105503\1 (2005).
- [63] H. Takakura, C.P. Gomez, A. Yamamoto, M. de Boissieu and A.P. Tsai, Nature Materials **6** 58 (2007).
- [64] K. Edagawa, Phil. Mag. Lett. **85** 455 (2005).
- [65] K. Edagawa and Y.G. So, Phil. Mag. **87** 77 (2007).
- [66] K. Edagawa, Phil. Mag. **87** 2789 (2007).
- [67] K. Edagawa, K. Suzuki and S. Takeuchi, Phys. Rev. Lett. **85(8)** 1674 (2000).
- [68] K. Edagawa, K. Suzuki and S. Takeuchi, J. Alloys Compd. **342** 271 (2002).
- [69] S. Hocker and F. Gahler, Phys. Rev. Lett. **93** 075901 (2004).

- 1  
2  
3 [70] H. Abe, H. Saitoh, T. Ueno, H. Nakao, Y. Matsuo, K. Ohshima and H. Matsumoto, *J. Phys. Cond. Matt.*  
4 **15** 1665 (2003).  
5 [71] E. Weidner, F. Frey, J.L. Lei, B. Pedersen, C. Paulmann and W. Morgenroth, *J. Appl. Cryst.* **37** 802  
6 (2004).  
7 [72] S. Katrych and W. Steurer, *Z. Krist.* **219** 606 (2004).  
8 [73] F. Frey, E. Weidner, K. Hradil, M. de Boissieu, R. Currat, K. Shibata, A.P. Tsai and T.J. Sato, *Phil. Mag.*  
9 *A* **80** 2375 (2000).  
10 [74] F. Frey, E. Weidner, K. Hradil, M. de-Boissieu, A. Letoublon, G. McIntyre, R. Currat and A.P. Tsai, *J.*  
11 *Alloys Compd.* **342** 57 (2002).  
12 [75] M. Kobas, T. Weber and W. Steurer, *Phys. Rev. B* **71** 224206 (2005).  
13 [76] M. Kobas, T. Weber and W. Steurer, *Phys. Rev. B* **71** 224205 (2005).  
14 [77] X. Zeng and e. al., *Nature* 157 (2004).  
15 [78] K. Hayashida, T. Dotera, A. Takano and Y. Matsushita, *Phys. Rev. Lett.* **98** 195502 (2007).  
16 [79] M. Oxborrow and C.L. Henley, *Physical Review B - Condensed Matter* **48** 6966 (1993).  
17 [80] B. Freedman, R. Lifshitz, J.W. Fleischer and M. Segev, *Nature Materials* **6** 776 (2007).  
18 [81] M. de Boissieu, S. Francoual, M. Mihalkovic, K. Shibata, A.Q.R. Baron, Y. Sidis, T. Ishimasa, D. Wu, T.  
19 Lograsso, L.P. Regnault, F. Gähler, S. Tsutsui, B. Hennion, P. Bastie, T.J. Sato, H. Takakura, R.  
20 Currat and A.P. Tsai, *Nature Materials* **6** 977 (2007).  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

## FIGURE CAPTIONS

Figure 1: Illustration of a phason mode in the high dimensional picture of aperiodic crystals. The left and right panel illustrates the incommensurately modulated displacive phase and QC phase respectively. The resulting atomic positions are indicated by full dots. Note that the phason mode is not propagative but diffusive, i.e. it will decay exponentially with time.

Figure 2: Experimental dispersion relation as obtained in the ThBr<sub>4</sub> by inelastic neutron scattering above the transition (left) and in the incommensurate regime (right) (from [6]). The soft mode condenses towards the position of the satellite reflection, left panel. The right panel displays only the phason and amplitudon modes as measured close to the satellite reflection. Note that the slope of the phason mode is significantly different from the slope of the acoustic branch.

Figure 3: Left panel: diffuse scattering measured in the i-AlPdMn phase in a 5-fold plane. Right panel, simulated map, using phason diffuse scattering and the 2 phason elastic constants (see text).

Figure 4: Measurement of the phason dynamics in the i-AlPdMn phase using XPCS, at 650°C. Left panel: exponential time decay of the phason mode. The wavevector and characteristic time are indicated in the inset. Right panel: Evolution of the inverse characteristic time as a function of the square of the phason wavevector. The dependence is linear, from which a phason diffusion constant is extracted (see text). From [46] and [47].

Figure 5: Comparison of the diffuse scattering in the i-ZnMgSc and i-AlPdMn as measured along a 2-fold axis. In both cases the diffuse scattering intensity is expressed in absolute scale unit. The amount of diffuse scattering is larger in the i-AlPdMn phase than in the i-ZnMgSc one. The number of large  $Q_{\text{per}}$ , weak reflections is much larger in the i-ZnMgSc phase. The vertical bars stand for the position of theoretically calculated reflection with a maximum  $Q_{\text{per}}$  value of 7 and 2.5 in the i-ZnMgSc and i-AlPdMn phases respectively (from [62]).

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

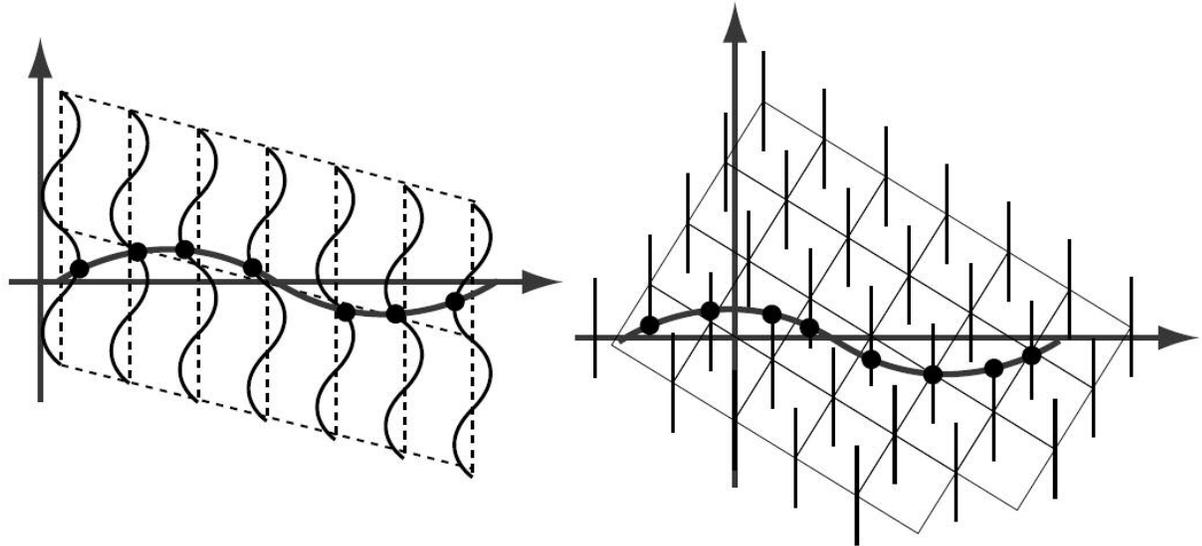
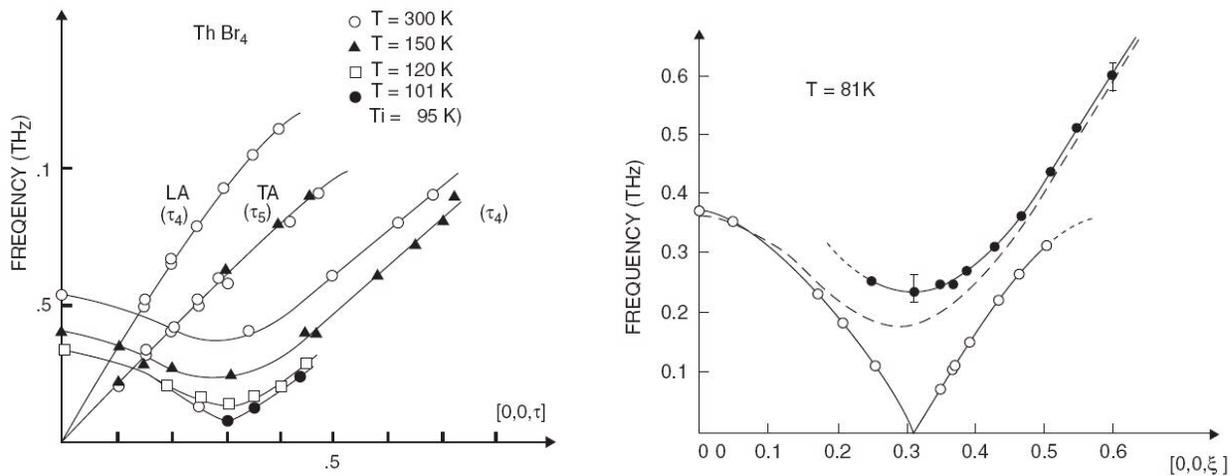


Figure 1

er Review Only

Figure 2



1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

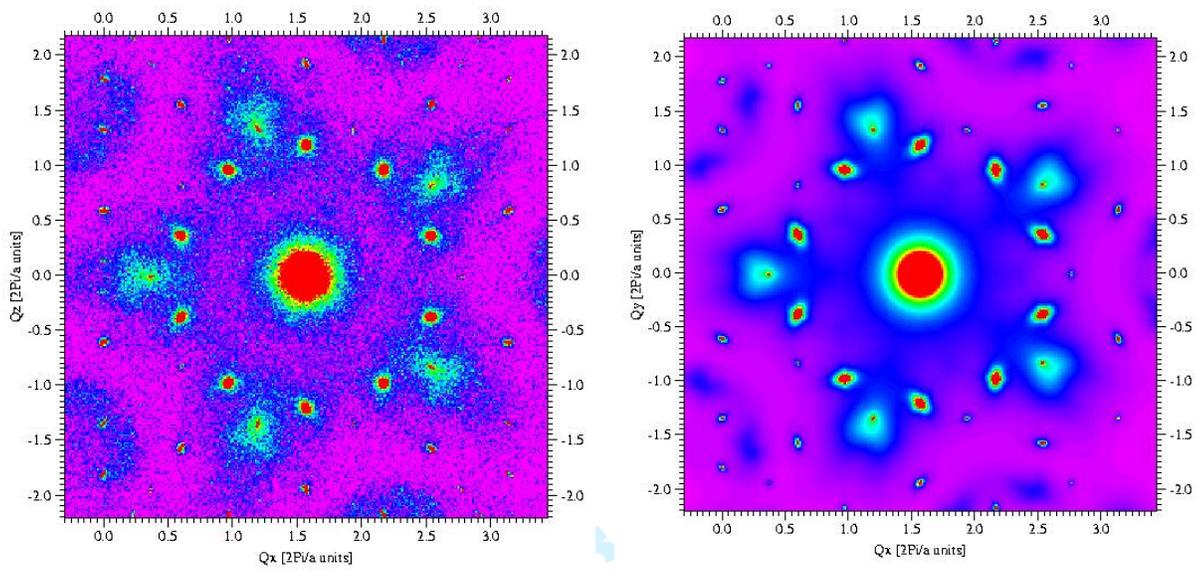


Figure 3

Review Only

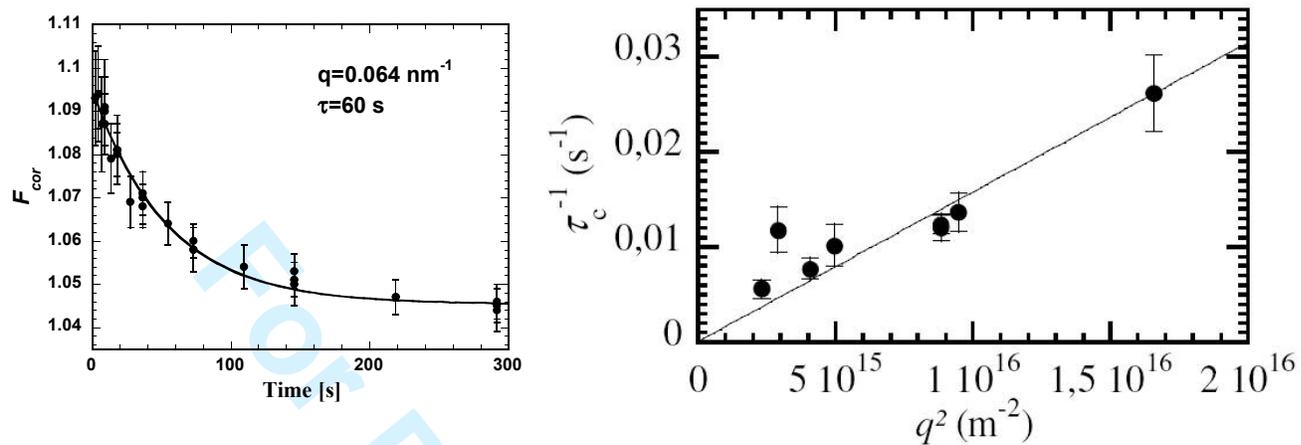


Figure 4

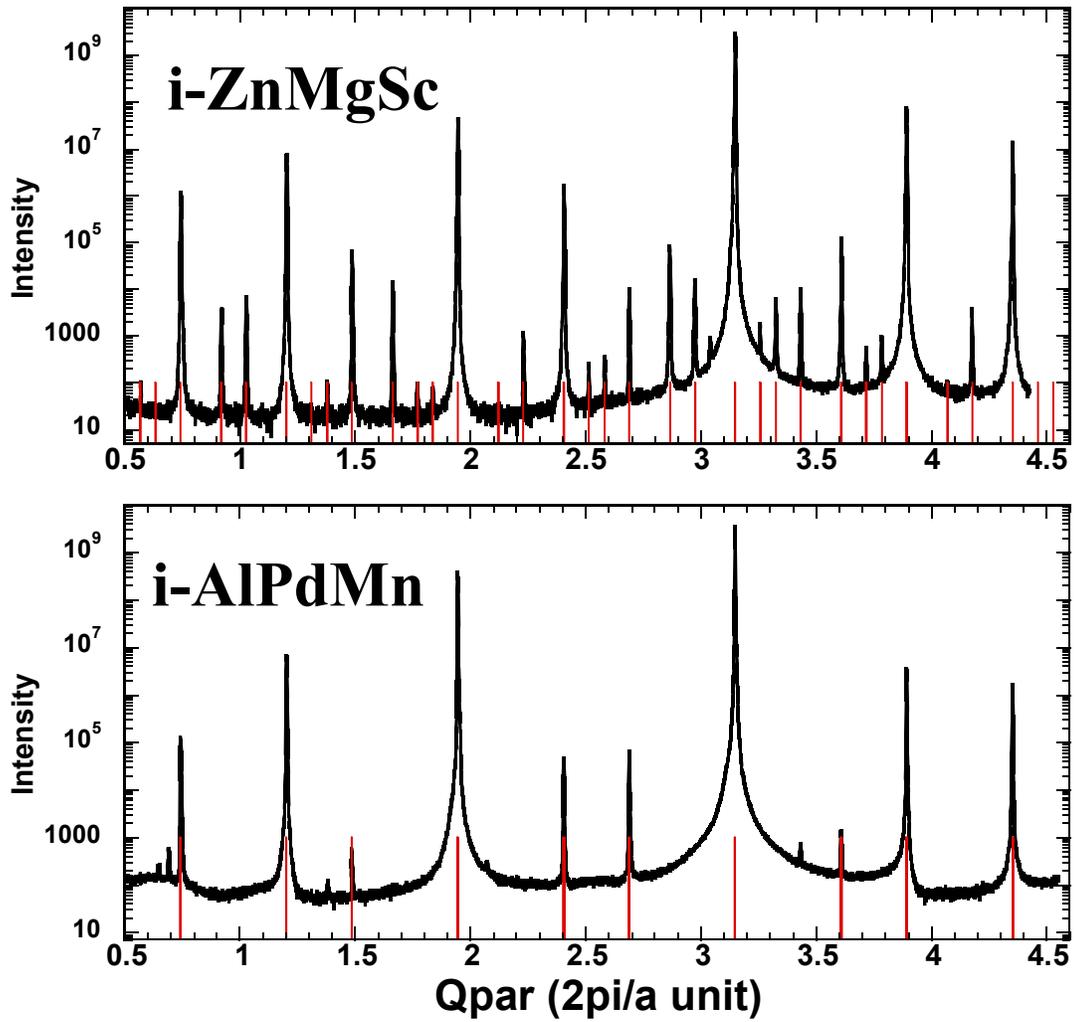


Figure 5.