Aperiodic crystals: Phonon and phason

M. de Boissieu
SIMaP, Grenoble-INP, CNRS, UJF
St Martin d'Hères France.

Disclaimer and copyright notice

References on this lecture can be found in:

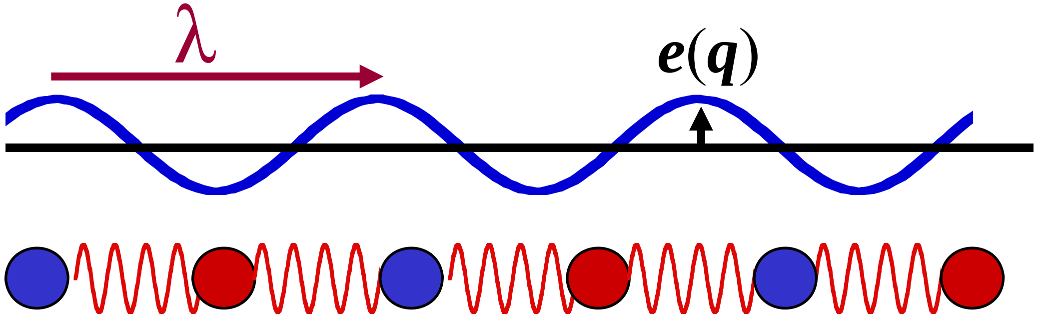
References in the book: Janssen T., Chapuis G. and de Boissieu M.: Aperiodic Crystals. From modulated phases to quasicrystals, *Oxford University Press, Oxford 2007*

And the review paper: de Boissieu M., Currat R. and Francoual S.: Phason modes in aperiodic crystals, in *Handbook of Metal Physics: Quasicrystals (Eds. T. Fujiwara and Y. Ishii), p. 107-169. Elsevier Science 2008*

Introduction to phonon

Phonon

- Equation of motion of atoms: ***plane wave***
- ***q*** wavevector = $2\pi/\lambda$, λ is the wavelength
- Frequency or energy $\hbar\omega$. Unit : THz or meV
  Phonon E is in the range 0-100 meV
- ***e***(***q***,s) *Polarisation* of the wave
- Displacement $u_n(x)= \boldsymbol{e}(\boldsymbol{q},s) \exp i(\mathbf{q}\mathbf{R}_n - \omega t)$



1D model

- 1D Chain 
- Interaction with first neighbors, spring constant K, 2 masses M et m.
- E=E0+1/2KΔu^2
- M=m. Long wavelength: Acoustic mode and linear dispersion relation.

$$\omega = a\sqrt{\frac{K}{m_{1(2)}}}\,q$$

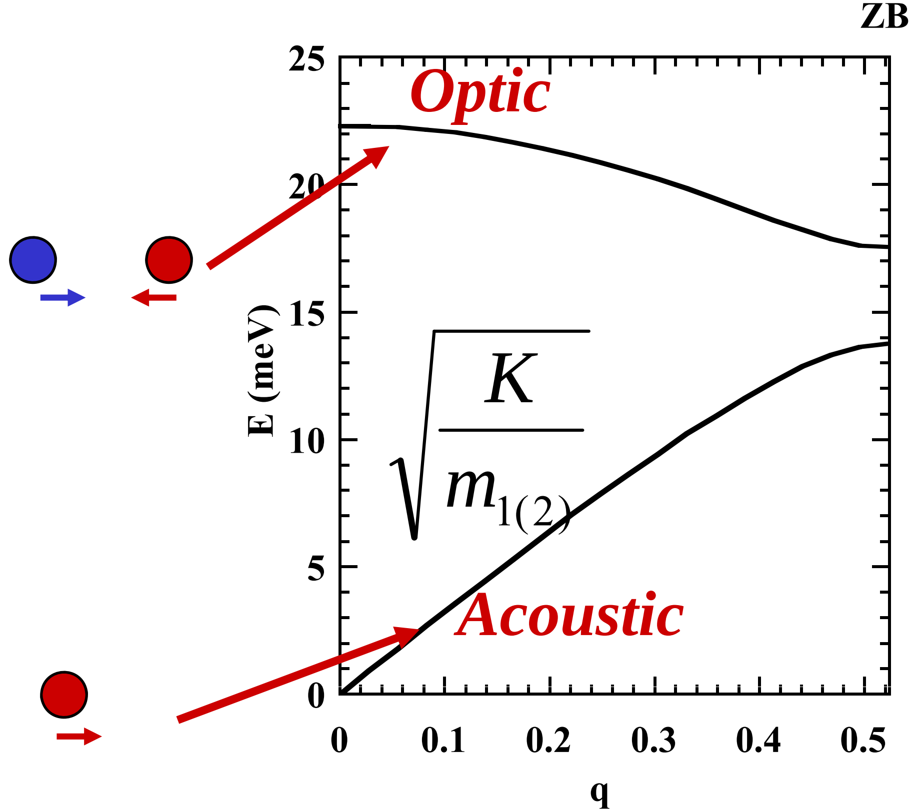
Phonons: a simple 1D model

2 atoms with masses M=τ m,

Interaction by a spring *K*. **LSLSLS….**

- Eigen mode: phase opposition

- Eigen mode: in phase

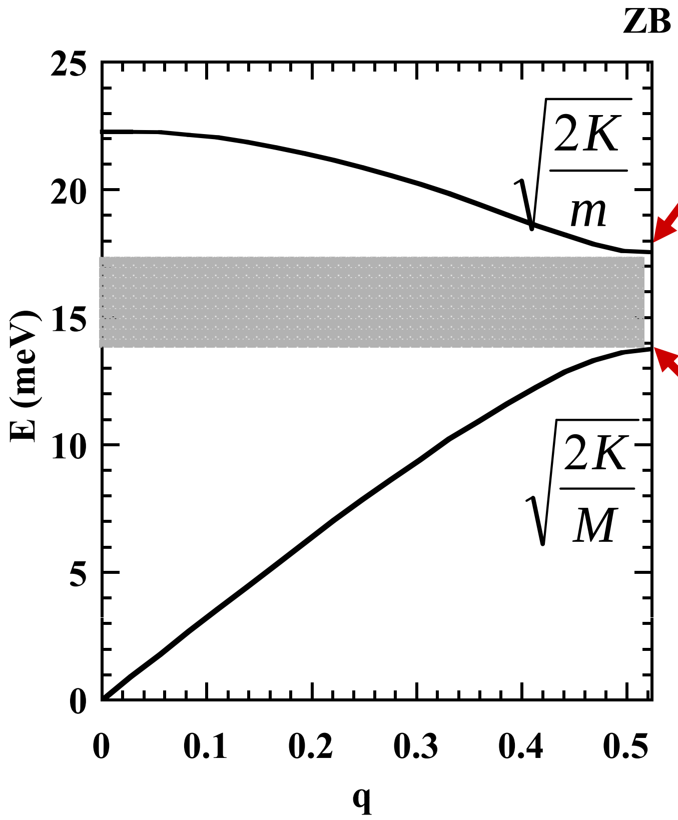


Phonon: wavevector q=2π/λ, energy E , eigenmode *e*

2 Atoms: gap opening

Brillouin zone boundary:

Gap opening



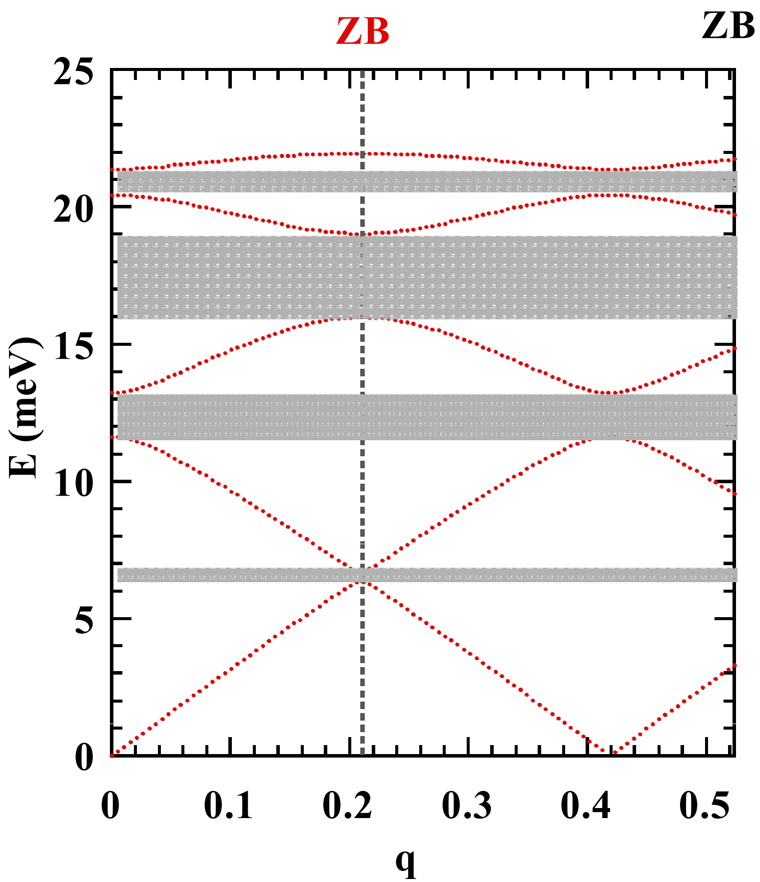
Light atom moves

Heavy atom moves

Stationary wave.

Phonon modes are Bragg reflected.

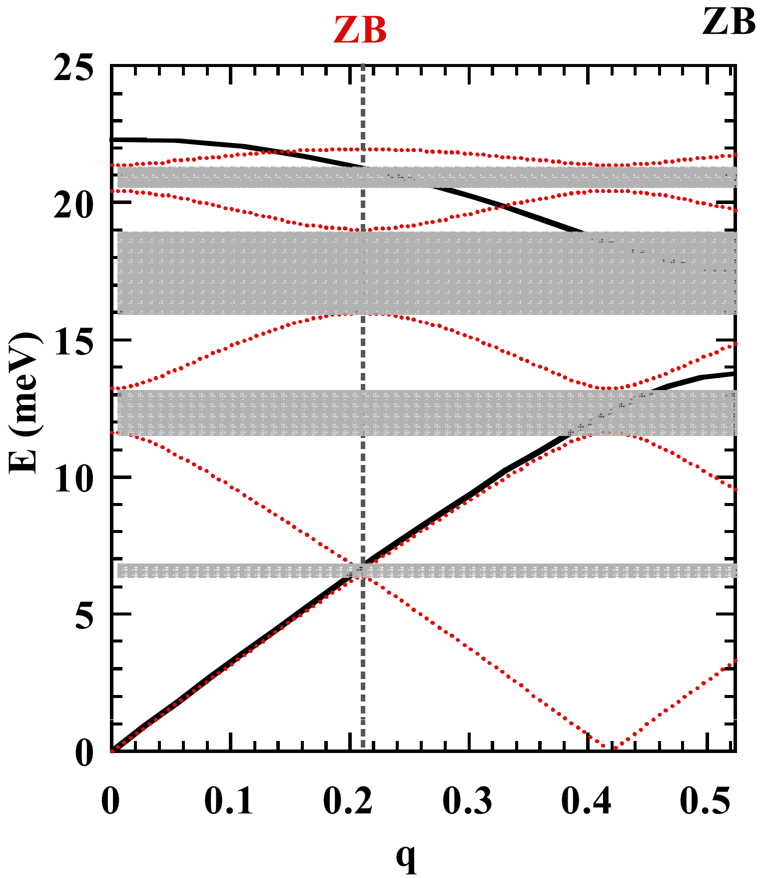
5 atoms in the unit cell



LSLLSLSLLS….

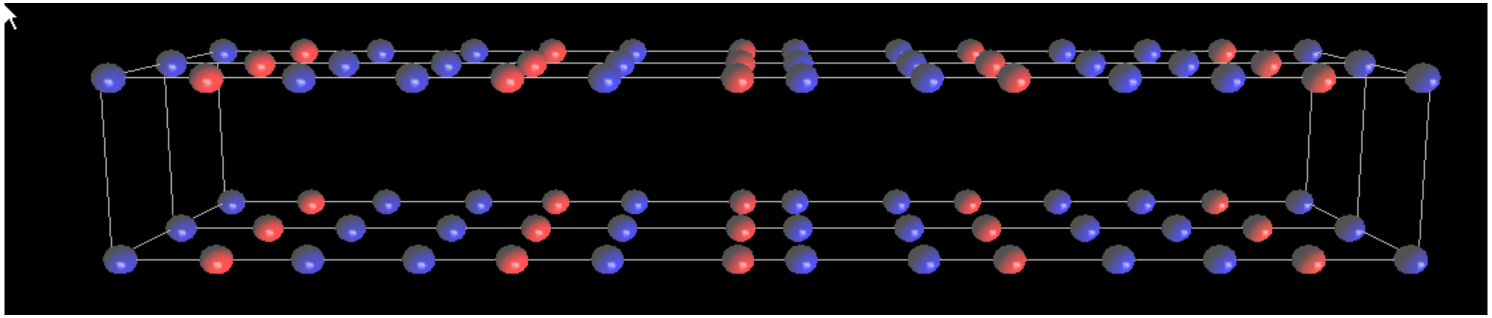
- ***5 branches***: 1 acoustic branch and 4 optic one
- 4 gaps
- Some similarity with the 2 atoms case

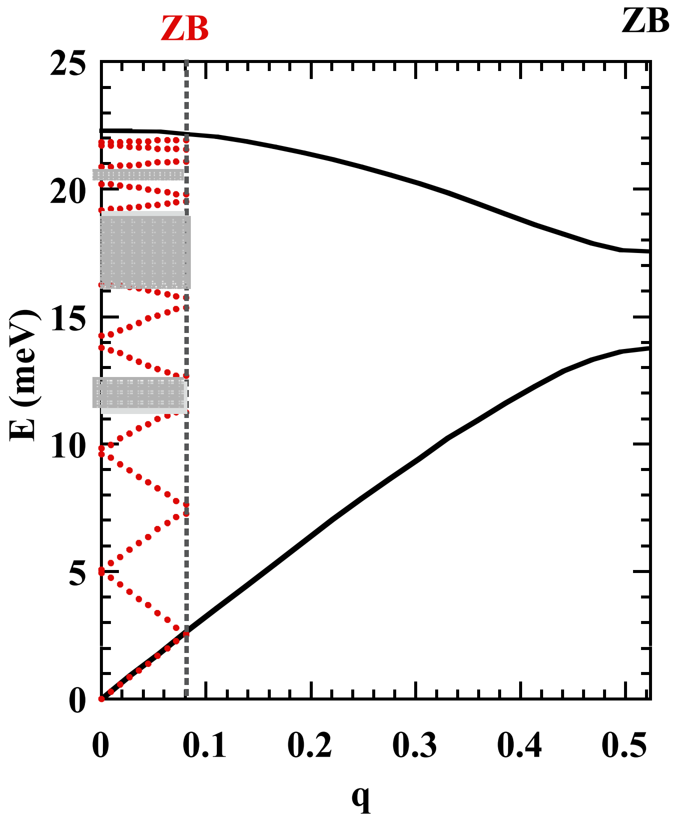
5 atoms in the unit cell



LSLLSLSLLS….

- ***5 branches***: 1 acoustic branch and 4 optic one
- 4 gaps
- Some similarity with the 2 atoms case

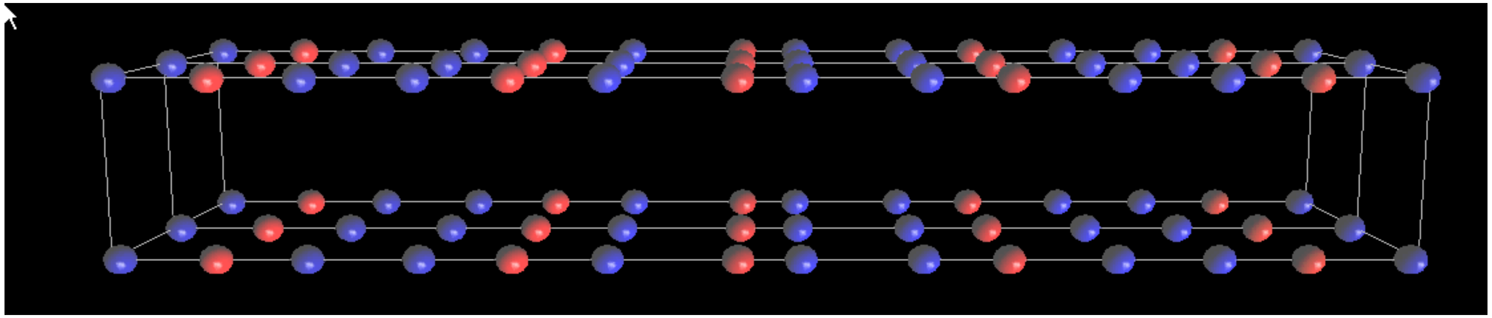


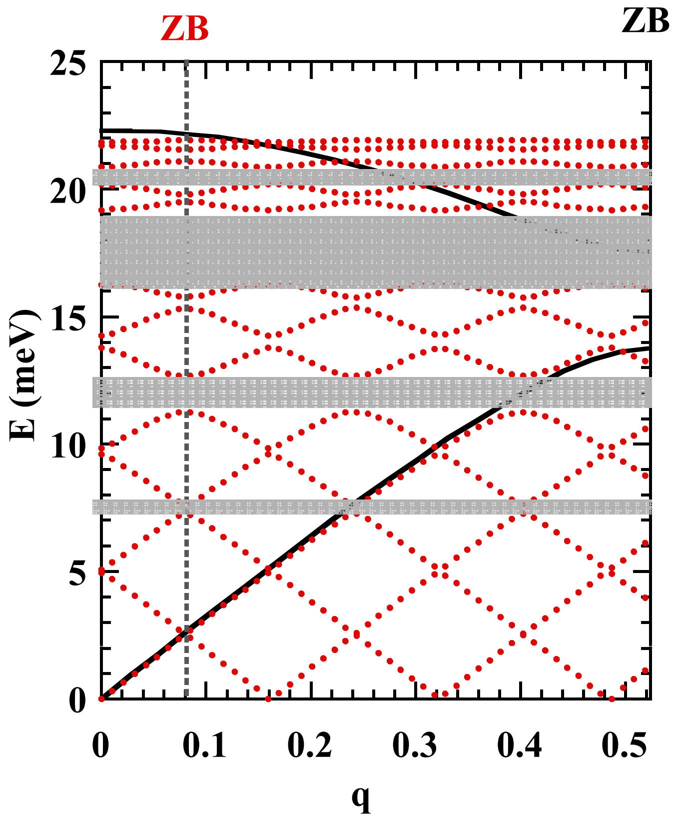


Phonons: 13 atoms

LSLLSLSLLSLLSL

- 13 'Branches'
- New gaps opening
- Large gap around 17 meV + optic 'bands'
- Smaller gap around 13
- E< 10 meV : acoustic character





Phonons: 13 atoms

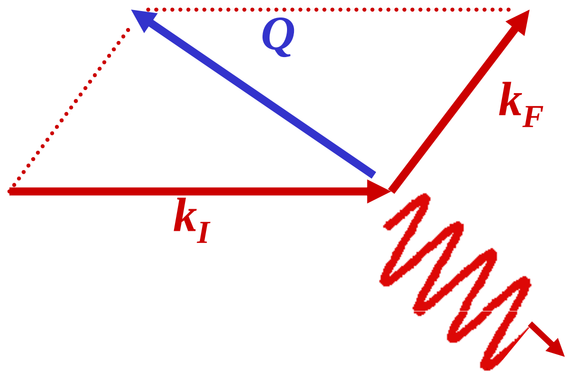
LSLLSLSLLSLLSL

- 13 'Branches'
- New gaps opening
- Large gap around 17 meV + optic 'bands'
- Smaller gap around 13
- E< 10 meV : acoustic character

Aperiodic crystals

- No periodicity: the Bloch theorem is no longer valid
- What is a phonon? Plane wave expansion?
- Phason degree of freedom and phason dynamics.

Measuring phonons
Coherent inelastic neutron (X-ray) scattering

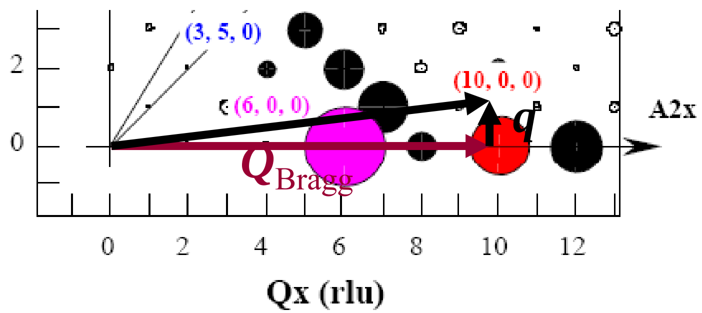


Neutron energy transfer to the crystal: *phonon creation or annihilation*

Energy analysis of scatt. neutron

$\Delta E = \hbar(k_F^2 - k_I^2)/2m$

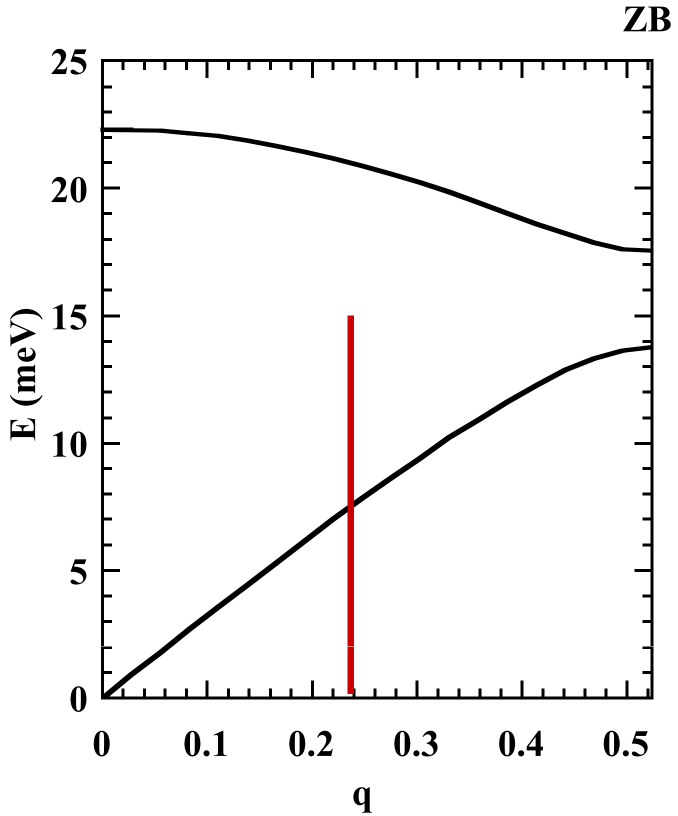
$\boldsymbol{Q} = \boldsymbol{k_F} - \boldsymbol{k_I}$

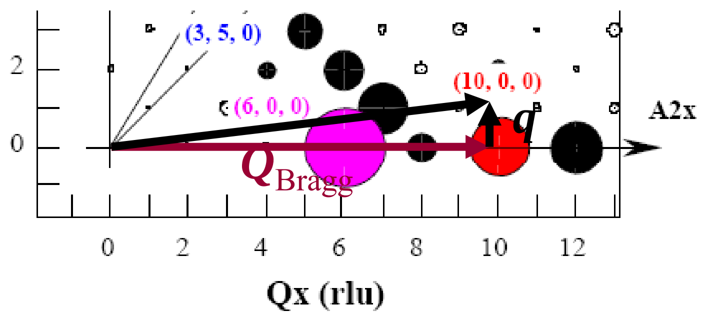


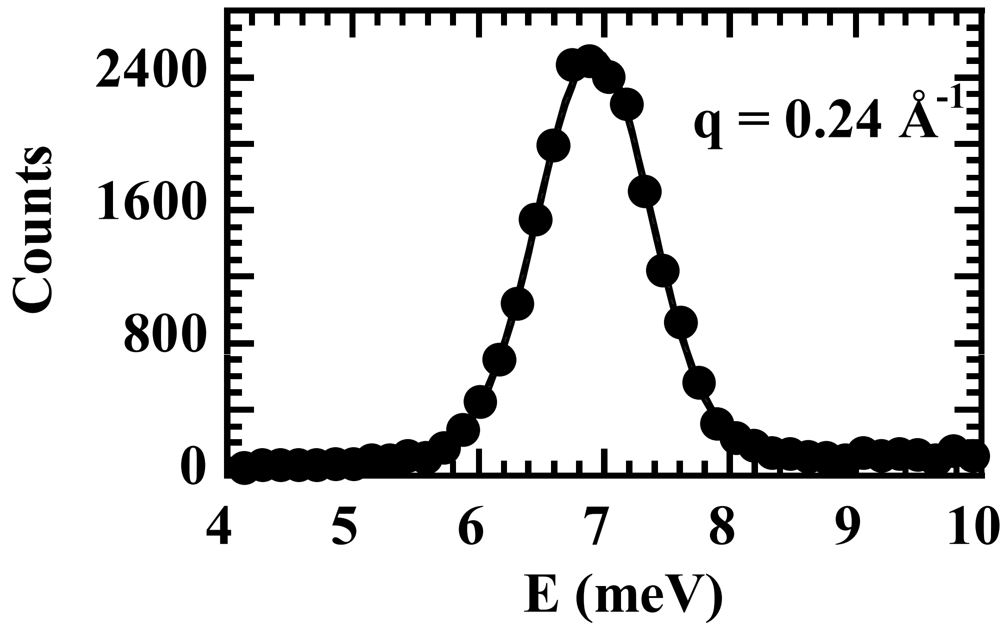
$\boldsymbol{Q} = \boldsymbol{Q}_{Bragg} + \boldsymbol{q}$

$\boldsymbol{q}$ is the phonon wave-vector

Mesure: Q-constant, scan en energie





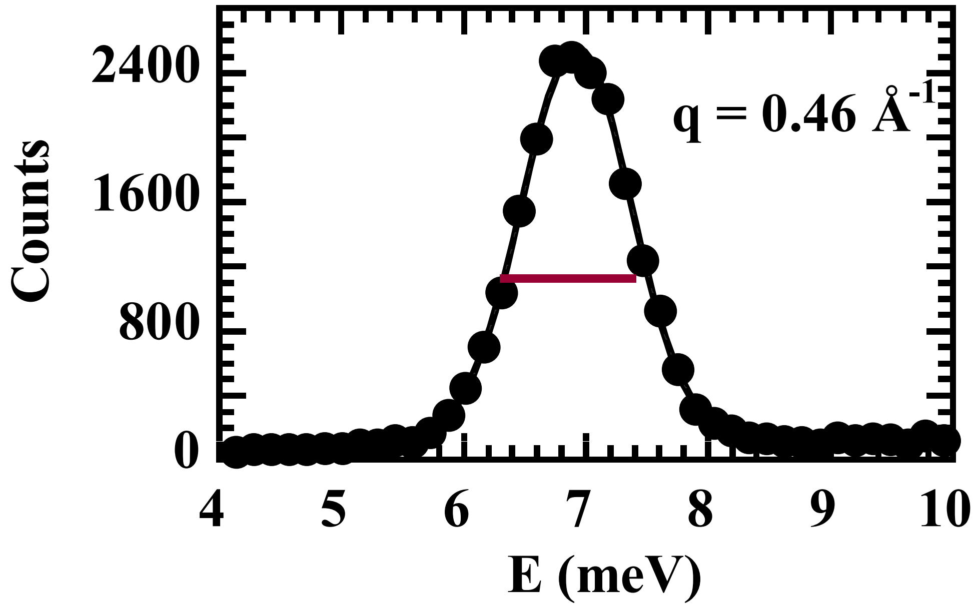


Coherent inelastic neutron scattering

Triple axis spectrometer

Constant Q, Energy scan

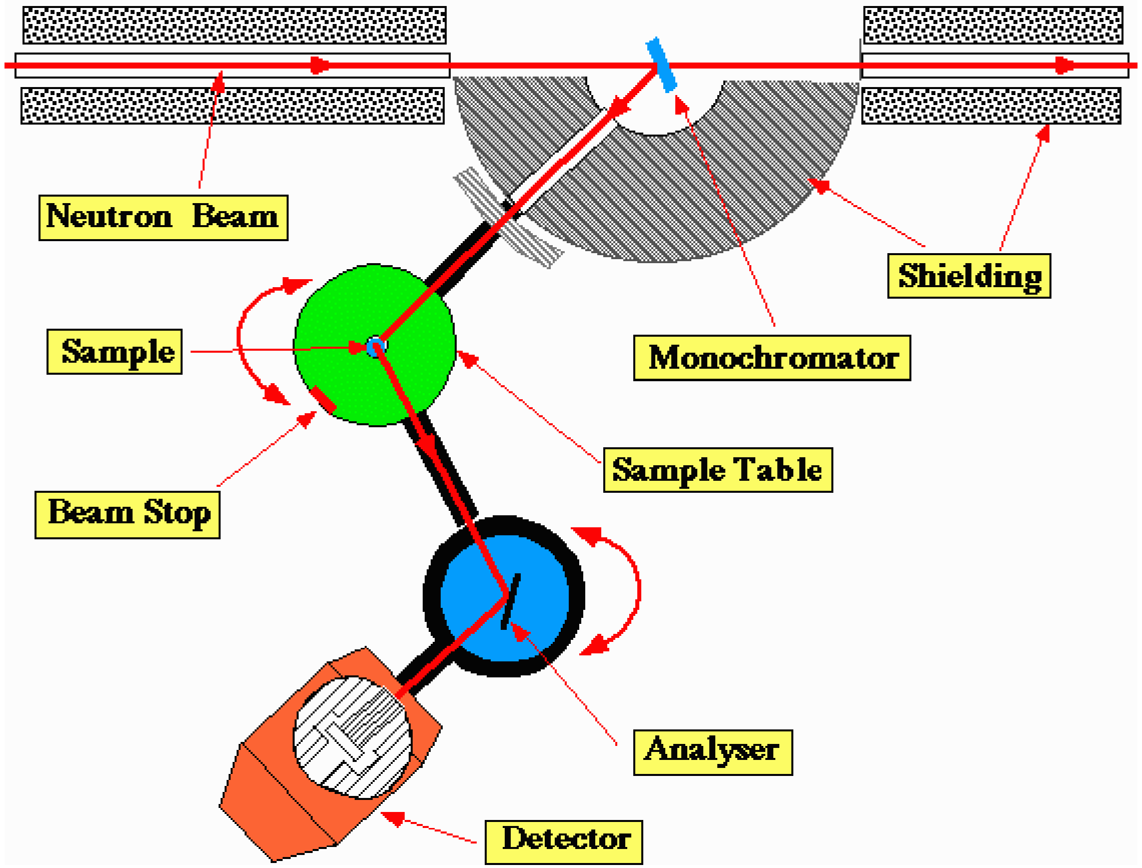
Measurement: ***$S(Q_B+q, E)$ Related to the space and time Fourier transform of the structure***



Damped Harmonic Oscillator

- ***E(q):*** Dispersion relation
- ***Γ (Width)*** : phonon lifetime
- ***Intensity***: related to the pattern of vibration (eigenvectors)

Triple axis: Inelastic neutron scattering



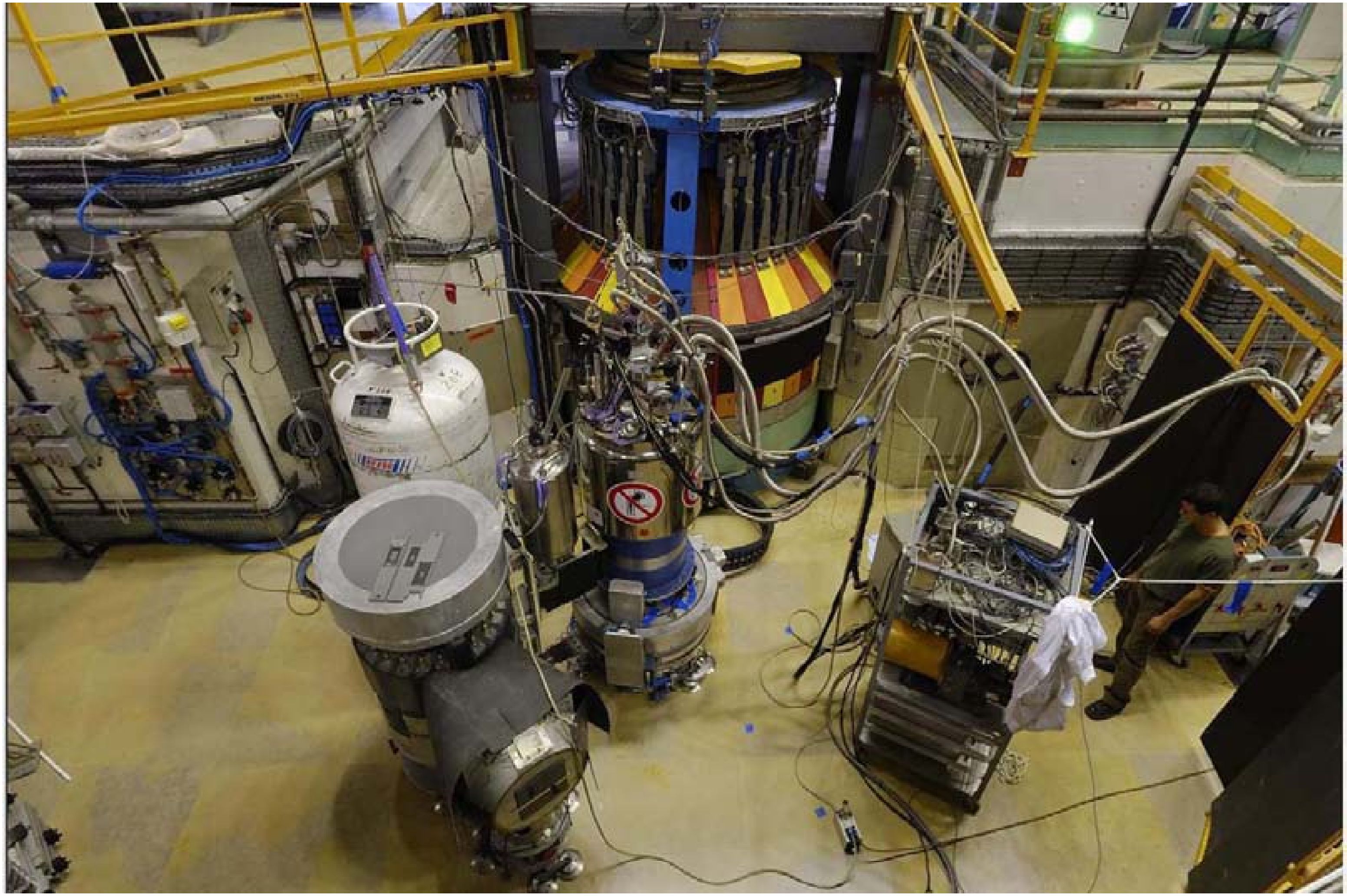
Incoming neutron energy: 20-100meV

Resolution of the order 1 meV

Graphite crystals analyser

Large single grain sample (1cm3)

Inelastic neutron scattering experiment



Inelastic x-ray scattering

- BL35XU, Spring8
- Ei=20 keV (Si 11 11 11)
- Energy resolution 2 meV ($\Delta E/E=10^{-7}$!! 1 mK monoc control!!)
- Spot size 0.1*0.1 mm2
- Flux 10^{10} photons/s

- Phason modes:

Hydrodynamic theory

Microscopical models

Experimental results

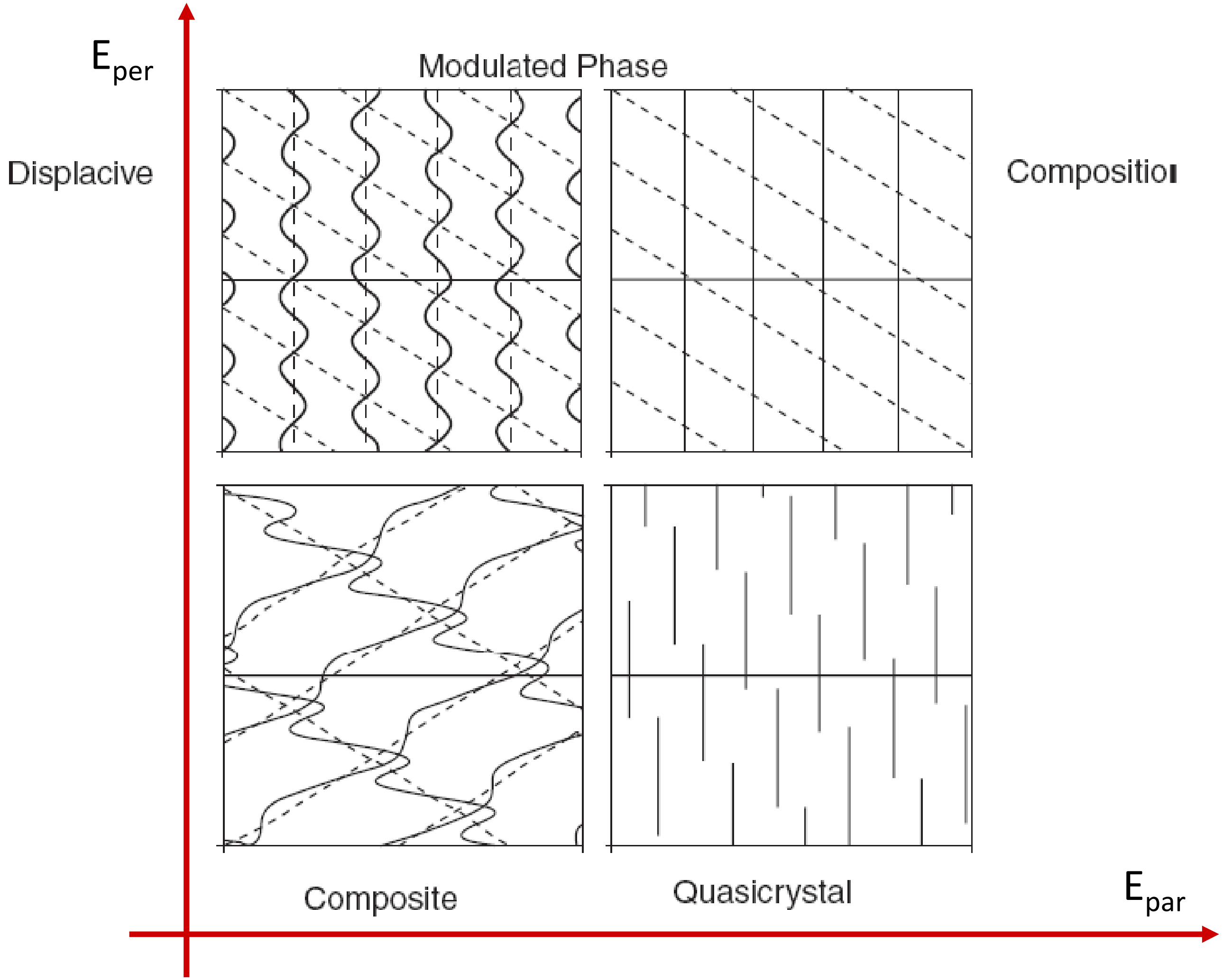
- Phonons

- Quasicrystal
- Composites

International School on Aperiodic Crystals

Introduction to phason modes

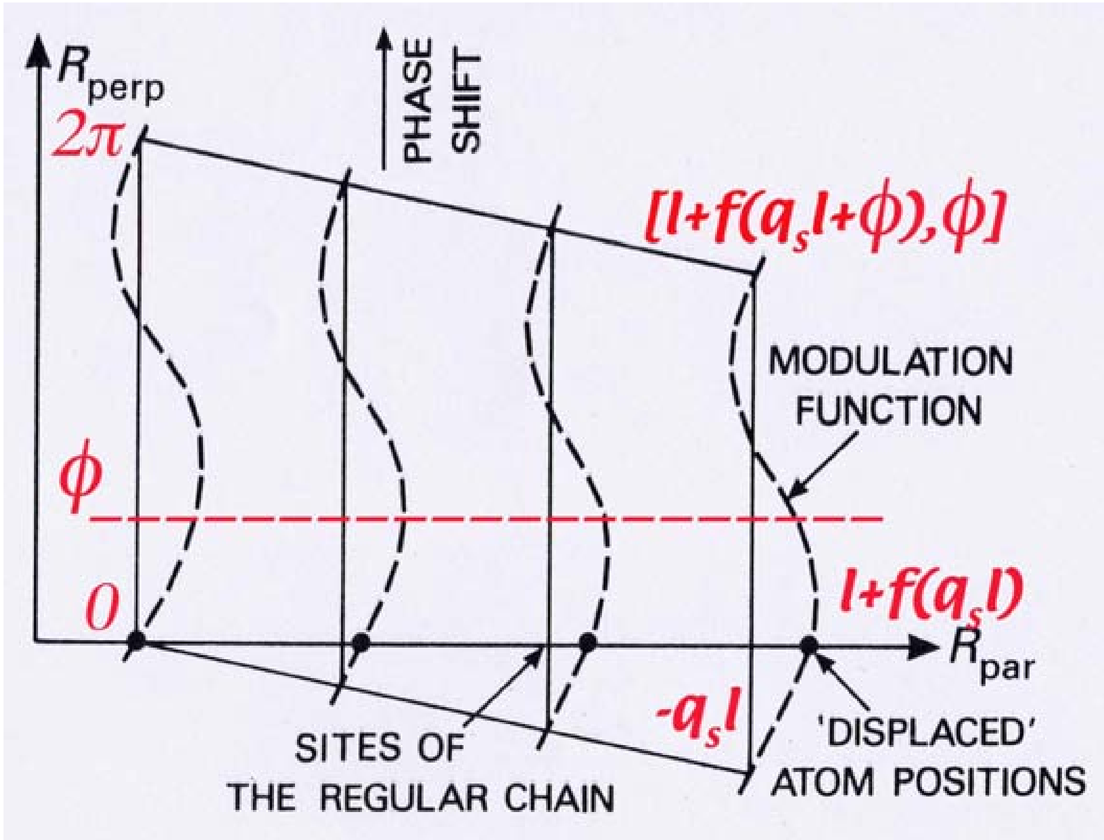
Phason modes in aperiodic crystals



The free energy of the system is invariant through a translation of the Epar space along the perpendicular direction

Phason mode

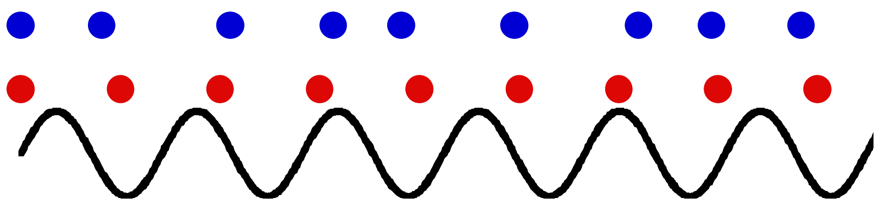
- Phase shift of the modulation function.
- Equivalent to a translation of the cut space.
- Leads to new excitations : phason.



Phasons modes: modulated phases

- ***Displacive modulated structure***
- ***A change in the phase of the modulation induces a small change in atomic position.***

Modulated
Ideal
Modulation function

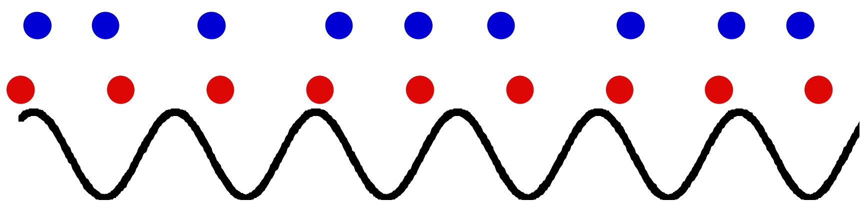


Relation with phonon

Phasons modes: modulated phases

- *Displacive modulated structure*
- *A change in the phase of the modulation induces a small change in atomic position.*

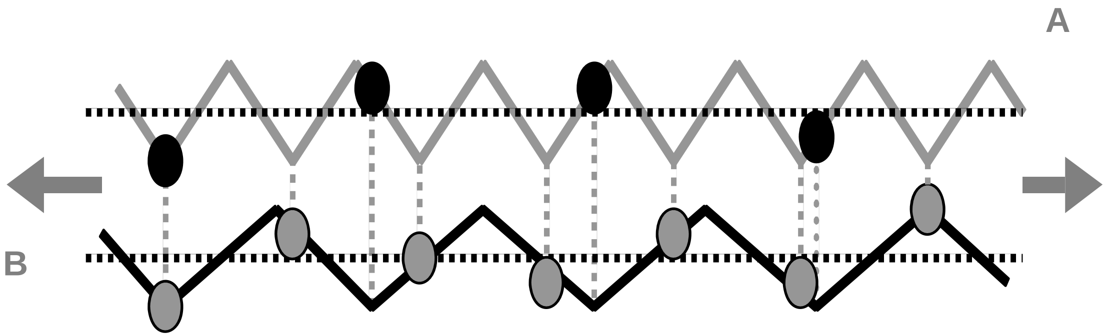
Modulated
Ideal
Modulation function



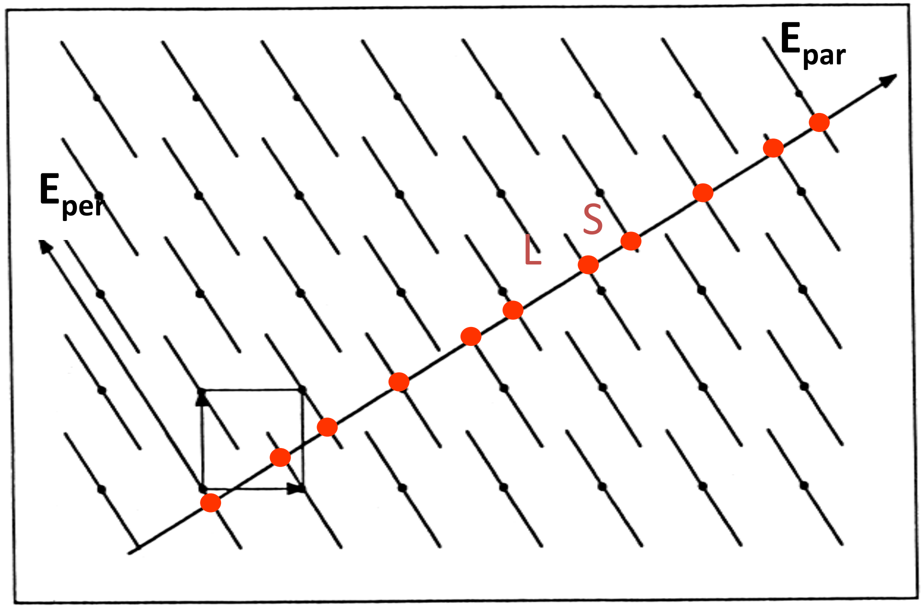
Relation with phonon

Composite

- Sliding modes: relative motion of the guest and host.



QC: Atom 'flip'

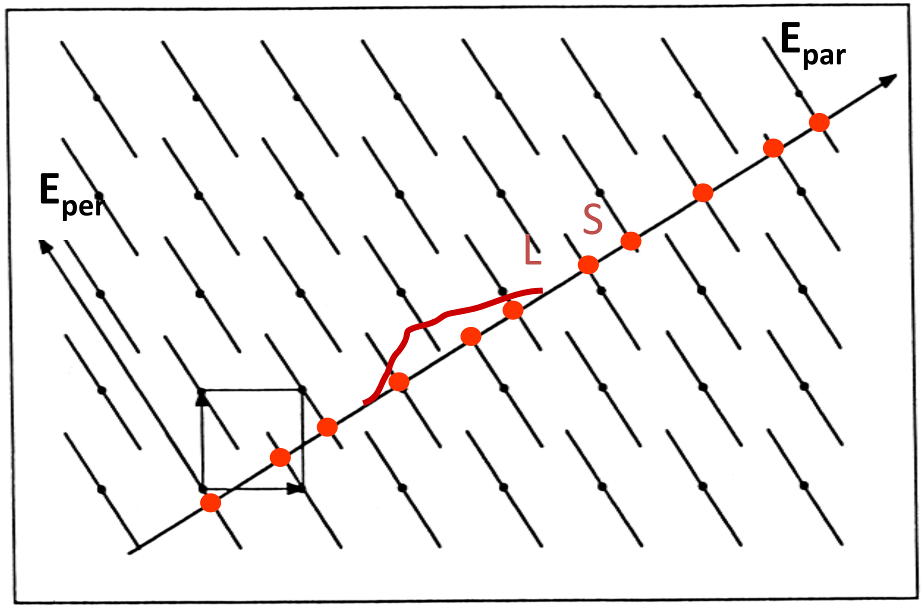


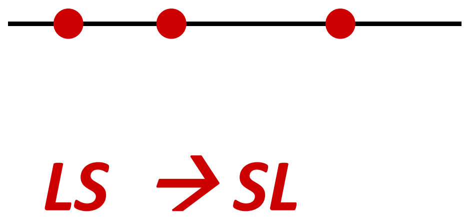
Local distortion of the cut space

Local rearrangement: Same local order

Phason mode: Clear diffusive process. $\tau^{-1}=Dq^2$

QC: Atom 'flip'





Local distortion of the cut space

Local rearrangement: Same local order

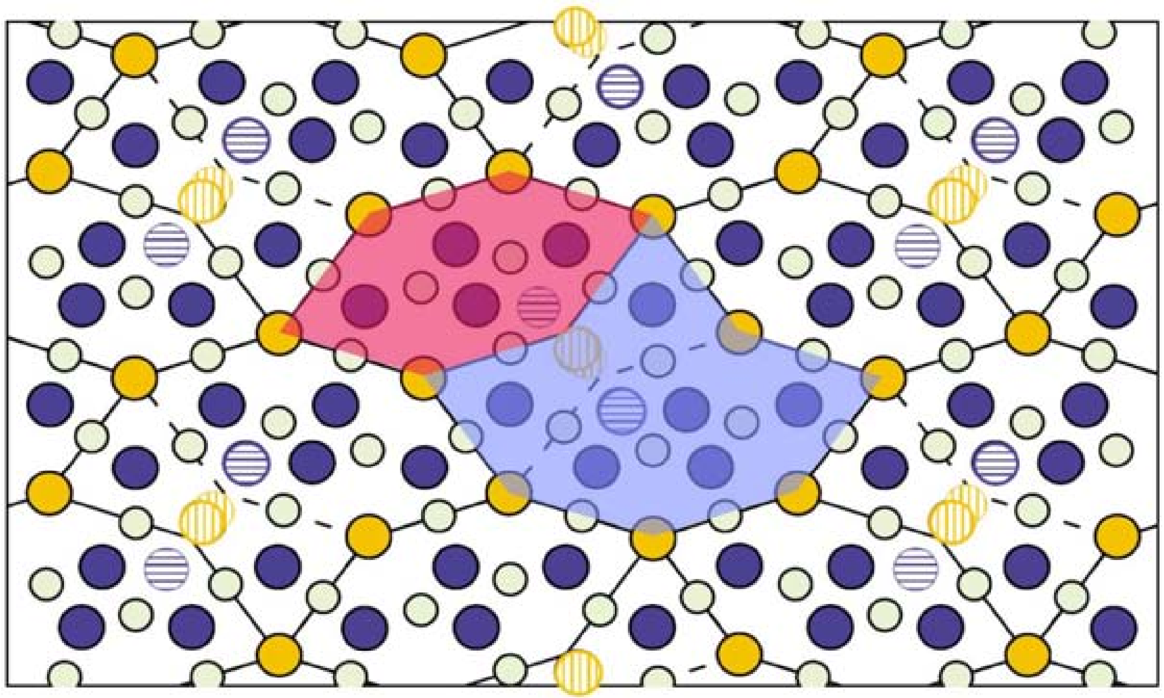
Phason mode: Clear diffusive process. $\tau^{-1}=Dq^2$

- ***What is a phason in quasicrystal?***

  Phason jump, phason strain, phason mode….

- ***Phasons appear everywhere in QC studies!!***

- Growth of QC: ‘phason’ entropy/local rules
- Stability of QC: phason entropy contribution



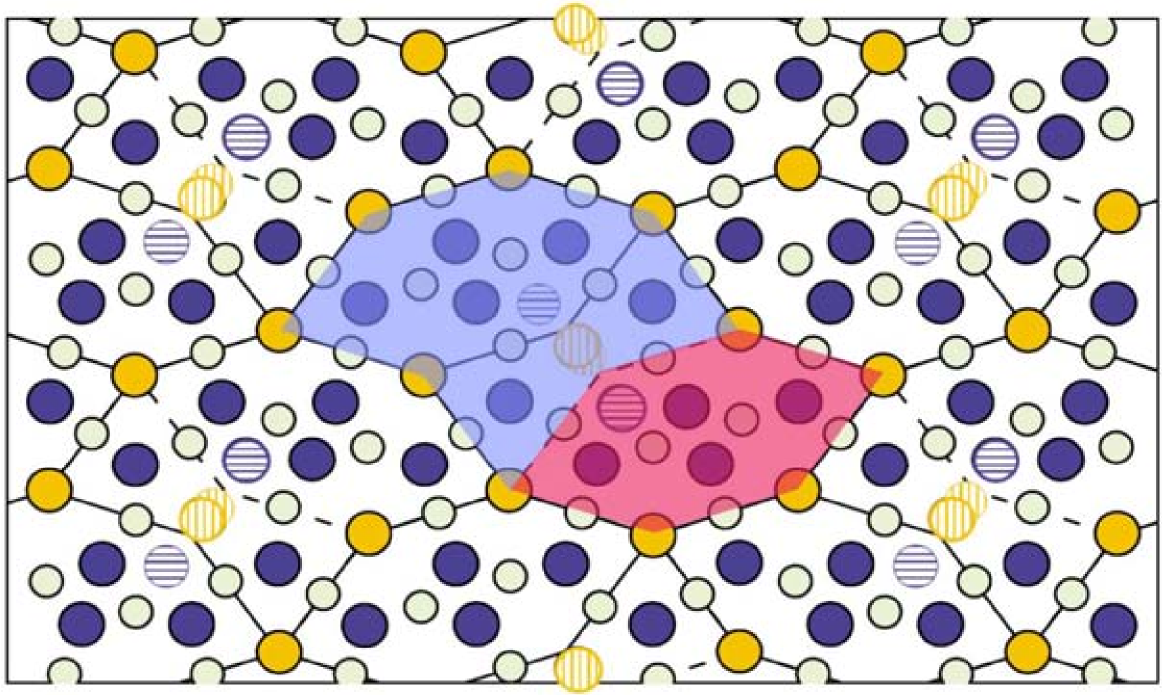
Decagonal B-Mg-Ru random tiling is stabilised by phason entropy

M. Mihalkovic and M. Widom, Phys. Rev. Lett. 93, 095507/1 (2004)

- ***What is a phason in quasicrystal?***

  Phason jump, phason strain, phason mode….
- ***Phasons appear everywhere in QC studies!!***

- Growth of QC: ‘phason’ entropy/local rules
- Stability of QC: phason entropy contribution



Decagonal B-Mg-Ru random tiling is stabilised by phason entropy

M. Mihalkovic and M. Widom, Phys. Rev. Lett. 93, 095507/1 (2004)

Hydrodynamic theory

- Symmetry breaking analysis
- Valid for all aperiodic crystals
- Introduction of symmetry and elastic constants.

Hydrodynamic modes

- Continuous symmetry is broken:

  Example: Fluid → Crystal

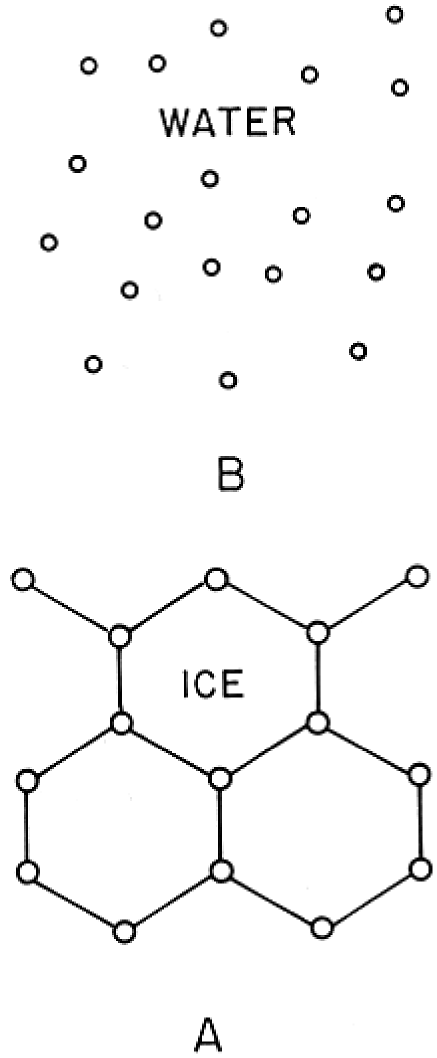
- Continuous translational symmetry is broken.

  Cristal(R) ≠ Cristal (R+r)

  But same free energy.

  Continuous degeneracy of the free energy with respect to translation.

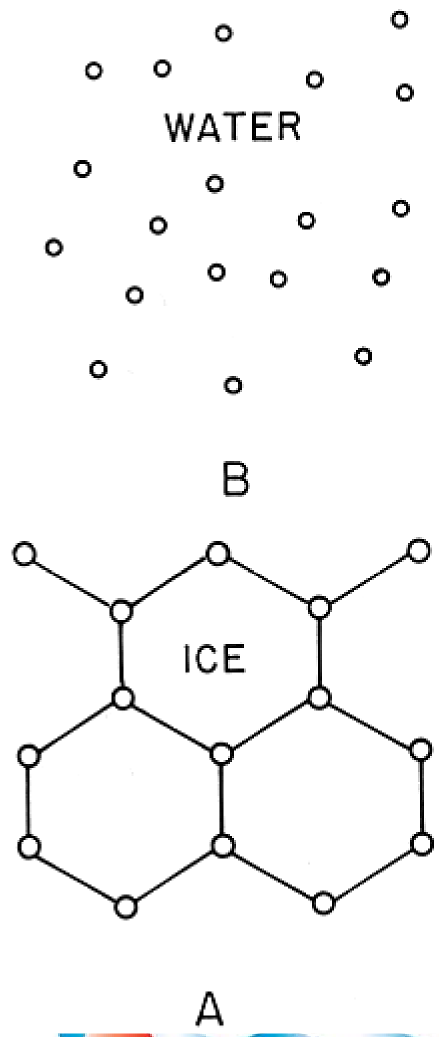
  Going continuously from R to R+dR has almost zero energy cost



From, James P. Sethna. See also Chaikin and Lubenski book.

Hydrodynamic modes

- Slow , long wavelength degree of freedom and modes for which the frequency vanishes as some power of the wavevector of the mode as q->0
- Identify the broken symmetry and define an order parameter (F(Q))
- Hydrodynamical variables related to conservation law: particle number, momentum and energy
- Symmetry and mode counting arguments



Hydrodynamic: phonons

- Fluid : 5 hydrodynamic variables: mass and energy conservation (2) + momentum (3)
- Fluid : 5 modes:

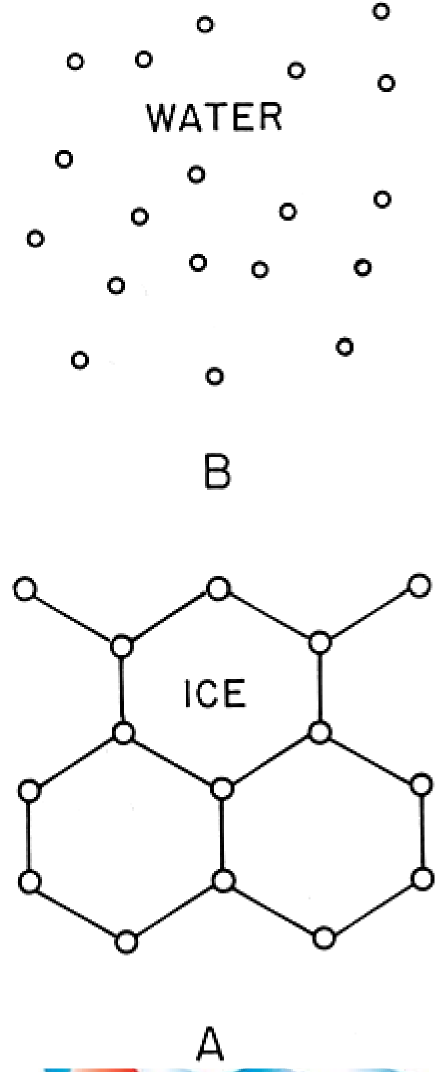
- Longitudinal propagative mode (2),

- 2 transverse ***diffusive*** shear waves

- heat diffusion

Note that the shear waves are not propagative, but diffusive.

A propagative mode counts for 2 (time reversal symmetry)



on Aperiodic Crystals

Hydrodynamic: phonons

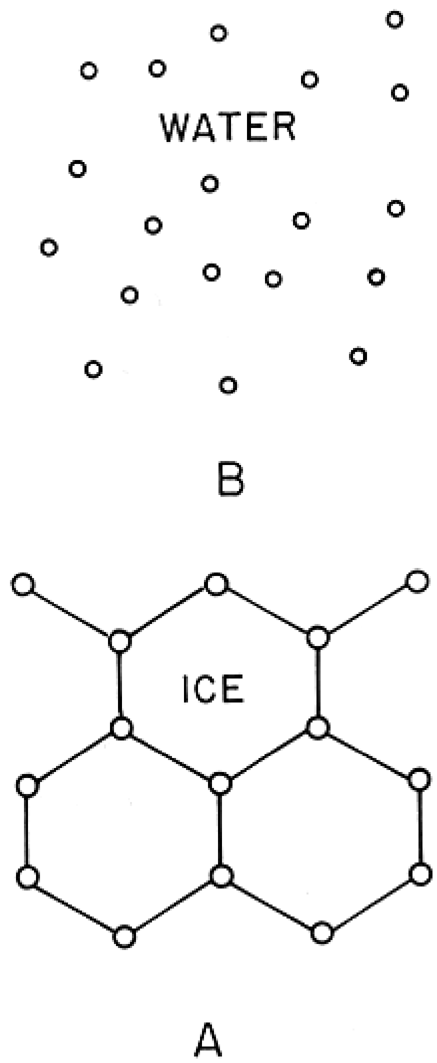
- Fluid : 5 modes: Longitudinal propagative mode (2), 2 transverse ***diffusive*** shear waves, heat diffusion
- Crystal: broken symmetry + Goldstone theorem. 8 modes instead of 5

- Two ‘new’ transverse ***propagating*** phonons: Goldstone modes (goes from diffusive to propagative: count for 2)

$$\omega = \pm vq$$

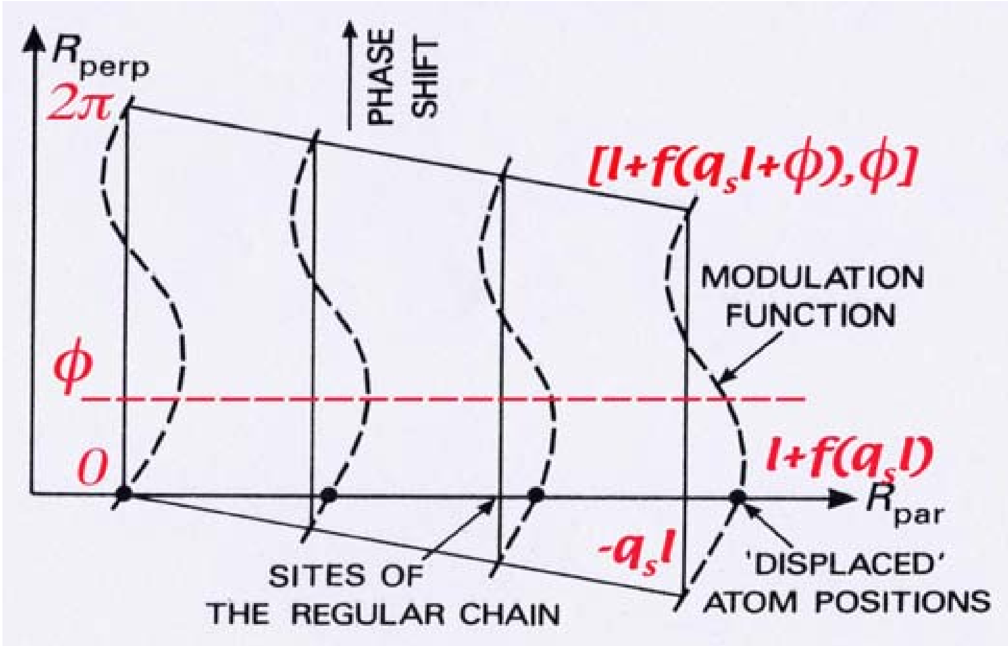
- Vacancy diffusion (diffusive, count for 1)

+ Longitudinal acoustic and heat diffusion



Aperiodic Crystals

Phason modes: Hydrodynamic theory



A translation of the cut space leads to a new structure **indistinguishable** from the previous one. Same Fourier spectrum.

Analogy with the treatment of phonon: small translation does not cost any energy. **1 new variable.**

Phason modes

- Hydrodynamic: in the case of a 1D displacive modulation, predict 1 supplementary mode.

New variable: Perp translation: 1D, counts for one

The new phason mode related to phase fluctuation of the modulation is a ***Diffusive*** phason mode.

The dispersion relation is : **$-i\omega = Dq^2$**

D is a phason diffusion constant, and one has an overdamped mode. This can be expressed in the time domain (FT of ω)

S(q, t) is decaying exponentially.

$$g(\mathbf{q}, t) = \exp(-2t/\tau_c(\mathbf{q})) \quad \tau_c^{-1} = Dq^2$$

CNRS

International School on Aperiodic Crystals

Phason mode and hydrodynamic theory

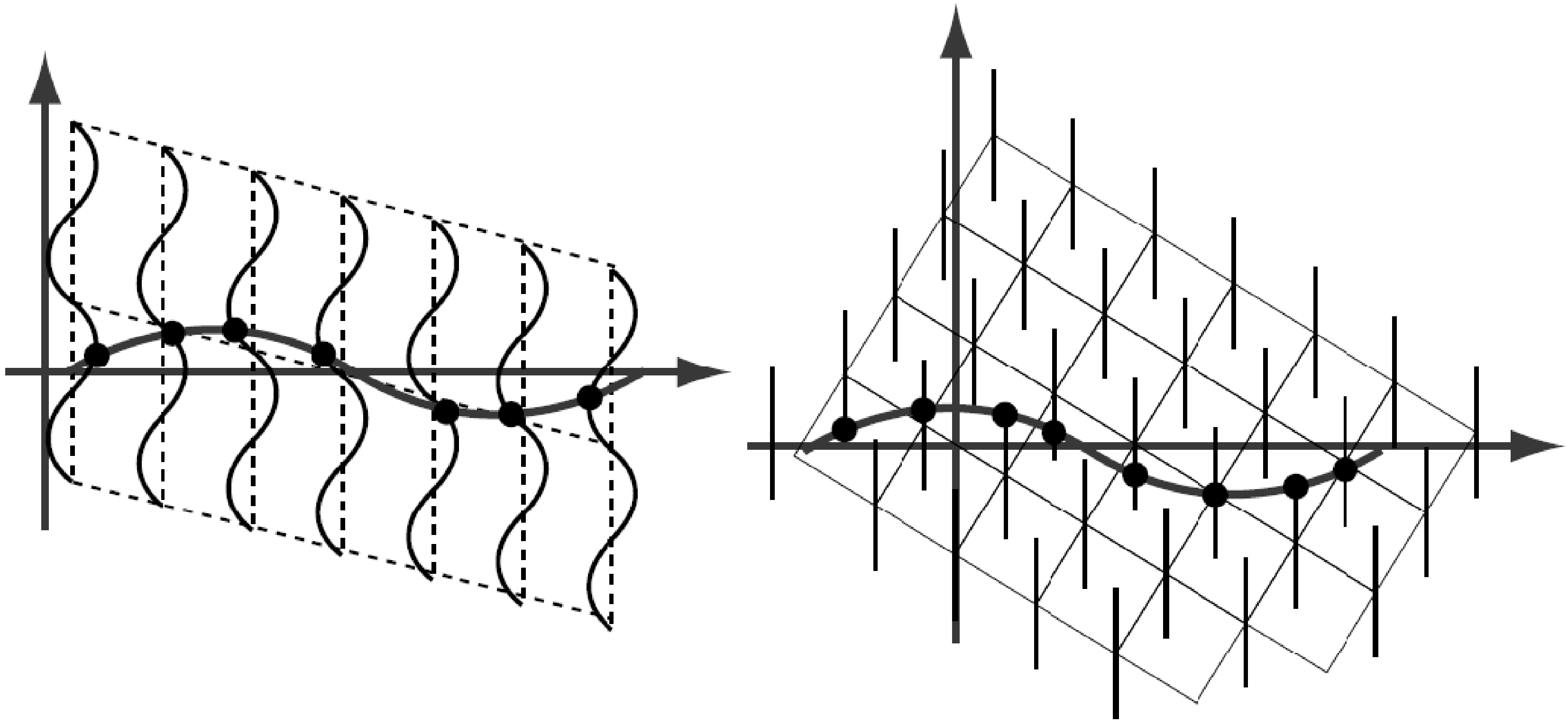
- The above arguments on diffusive modes hold for **all aperiodic crystals case.**

- For all aperiodic crystals the hydrodynamic theory predict a **phason diffusive mode**.
- Polarization of the mode in perp space
- Characterized by a phason diffusion constant
- Of course the value of this phason diffusion constant will depend on the nature of the aperiodic crystal.

Hydrodynamic theory of icosahedral QC

- It has been much developed for quasicrystal
- Importance of the symmetry
- Lead to a generalized elasticity theory for QC.

Phason modes in quasicrystals



Phason modes in QC right after the QC discovery:
P. A. Kalugin, A. Y. Kitaev, and L. S. Levitov, JETP Lett. 41, 145 (1985).
P. Bak, Phys. Rev. B 32(9), 5764 (1985).
T. C. Lubensky, S. Ramaswamy, and J. Torner, Phys. Rev. B 32(11), 7444 (1985).
J. E. S. Socolar, T. C. Lubensky, and P. J. Steinhardt, Phys. Rev. B 34, 3345 (1986)
V. Elser 1986

International School on Aperiodic Crystals

Hydrodynamics theory of aperiodic crystals

• *Hypothesis*:

Infinetesimal translation along E_{perp} does not cost energy.

Problem in some cases. For incommensurate modulated structure, breaking of the analyticity of the atomic surface shape (Aubry, Janssen) induces a q=0 phason gap.

• *Generalised elasticity*

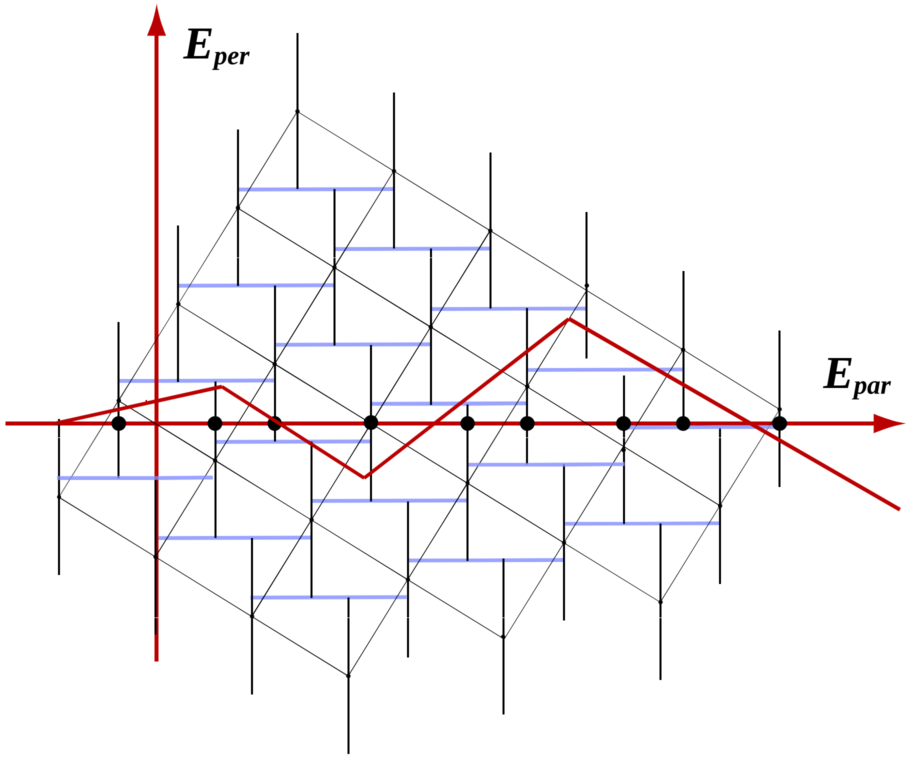
How does the system respond to a strain ?

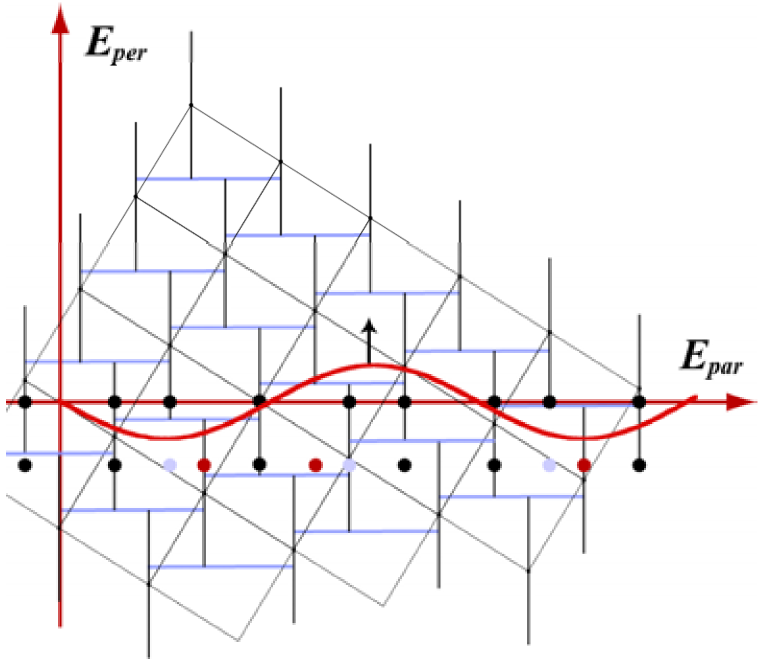
$$F = \alpha |\nabla \mathbf{u}_{\mathrm{par}}|^2 + \beta |\nabla \mathbf{u}_{\mathrm{per}}|^2$$

Phonon and phason strain.

Elastic constants, phonon, phason and phonon-phason coupling.

Phason strain and phason modes





Phason strain distribution
Diverging fluctuations
Bragg peak broadening

Long wavelength fluctuations
Phason modes. Non diverging.
Bragg peak + diffuse scattering

Elasticity of icosahedral phase

- From the hydrodynamic theory one can derive a generalized elasticity. (Kalugin et al. , Back, Lubenski):

- Continuum theory.

- Free energy density: squared gradient of phason strain.

- Ico phase: 5 elastic constants.

Phonon: isotropy of icosahedral symmetry: 2 phonons constant (1 longitudinal one transverse)

Phasons 2 constants: K1 and K2

Phonon/phason coupling term: K3

Elasticity of icosahedral phase

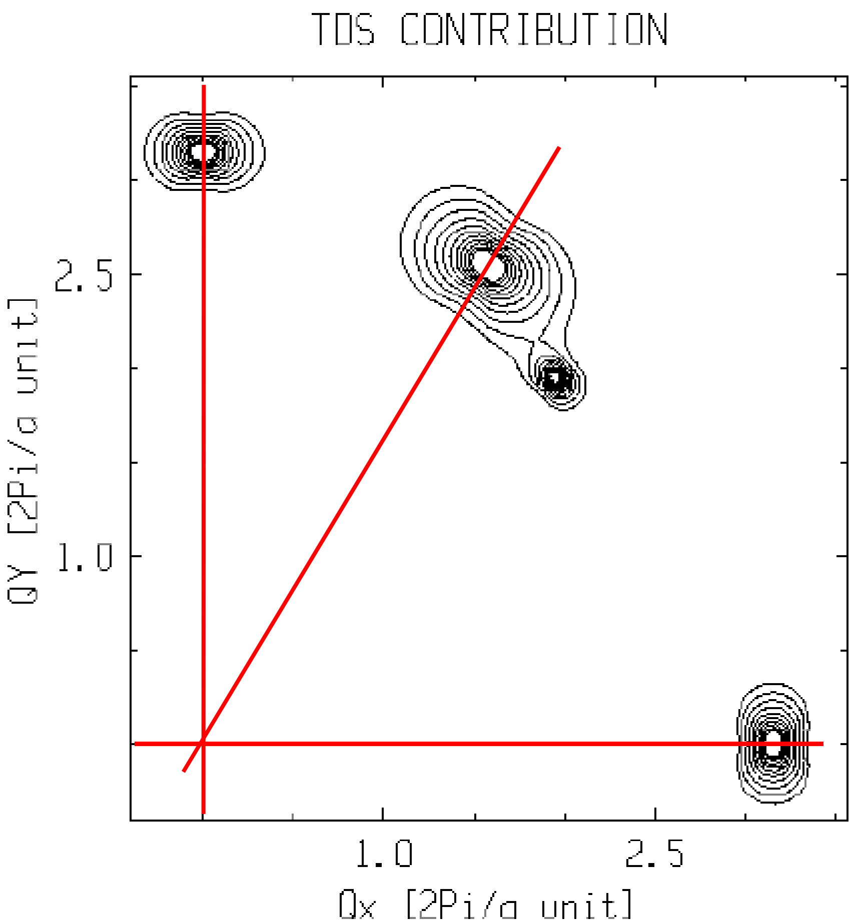
- Influence on diffraction spectrum:

Thermal equilibrium phonon and phason fluctuation (Jaric, Ishii, Widom):

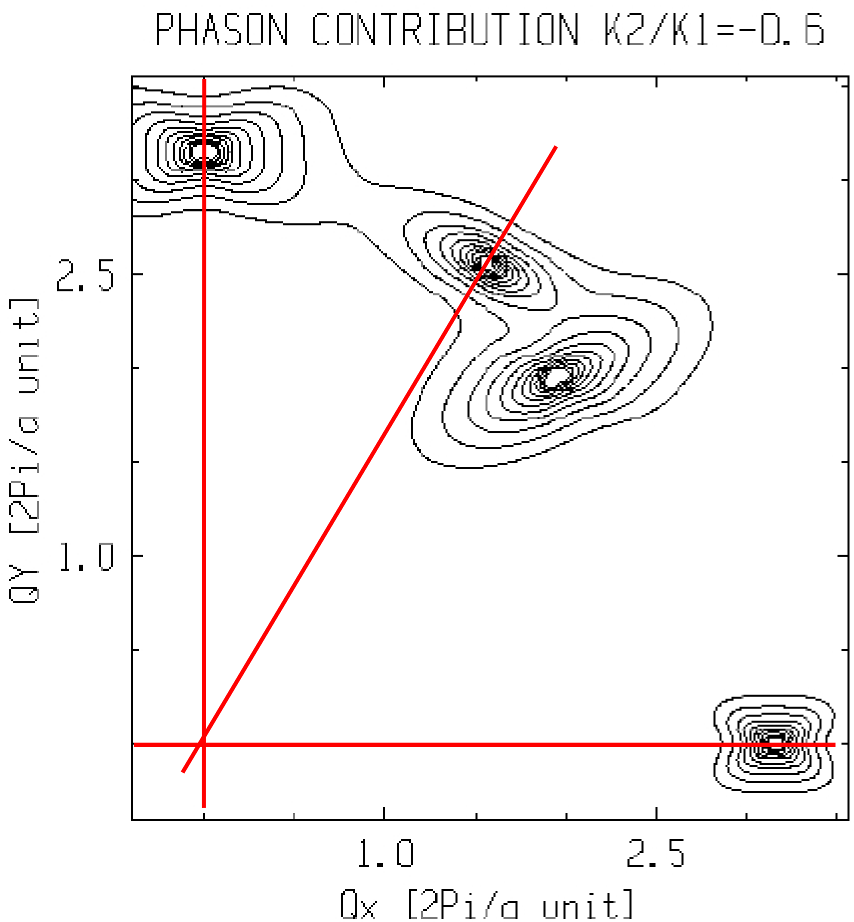
- In 3D, fluctuations are bounded: Bragg peak remain
- Phonon give rise to a Debye-Waller (Bragg peak decrease) and diffuse scattering
- In the same way phason fluctuation lead to diffuse scattering whose shape depends on K1 and K2 (see herafter).

DIFFUSE SCATTERING

Phonon



Phason



Summary

- Hydrodynamic theory applies to all aperiodic crystal
- Phason mode, in the long wavelength limit, are diffusive mode or overdamped harmonic oscillator.
- Mode polarised in the perpendicular space
- 'Dispersion relation': $\tau_c^{-1} = D(q)q^2$
- In quasicrystal, phason elastic constant have been derived. Used for diffuse scattering.

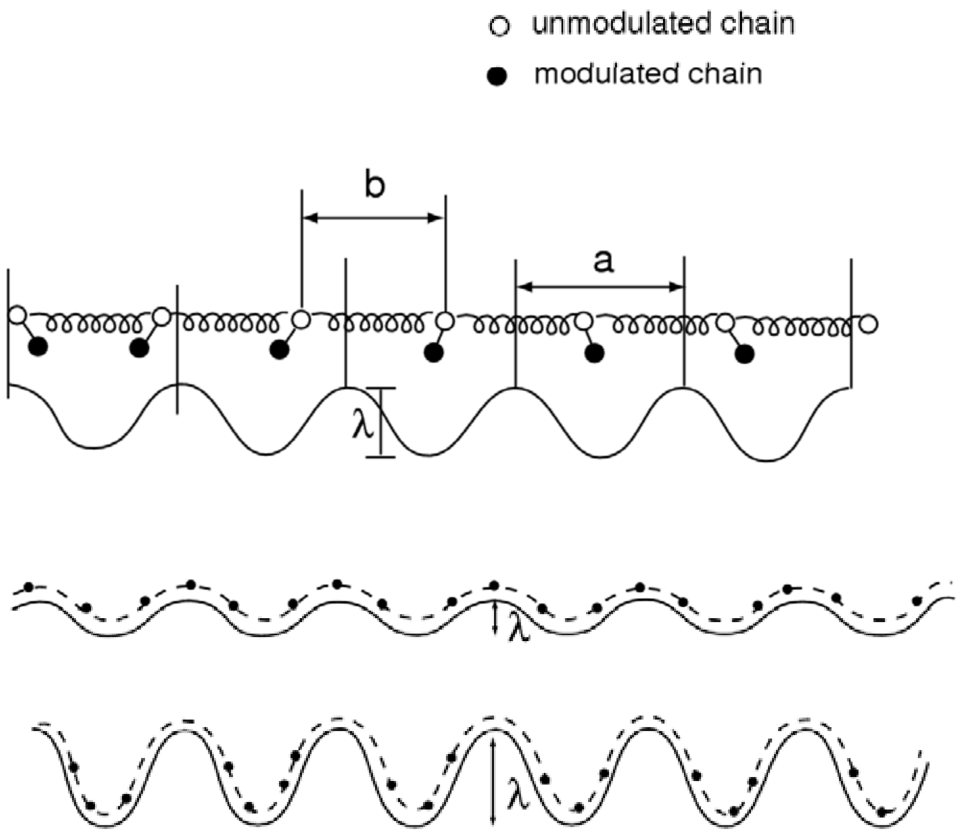
Microscopic models and phason modes

- Hydrodynamic theory is only a long wavelength, phenomenological theory
- Connection with microscopic models:

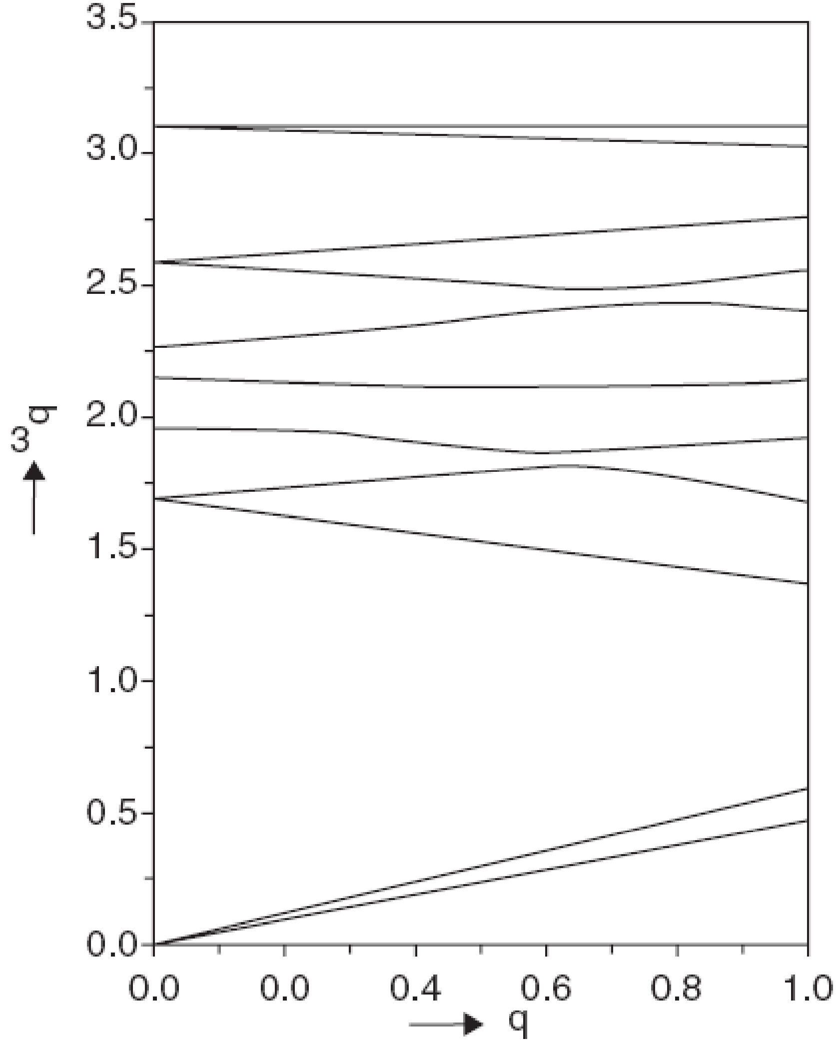
1. Frenkel-Kontorova model
2. DIFFOUR
3. Double chain
4. Amman 3D icosahedral tiling

Frenkel-Kontorova model

- a/b is an irrational number
- λ coupling param
- Weak and strong coupling
- Weak coupling: smooth modulation
- Strong coupling: the modulation function is discontinuous.



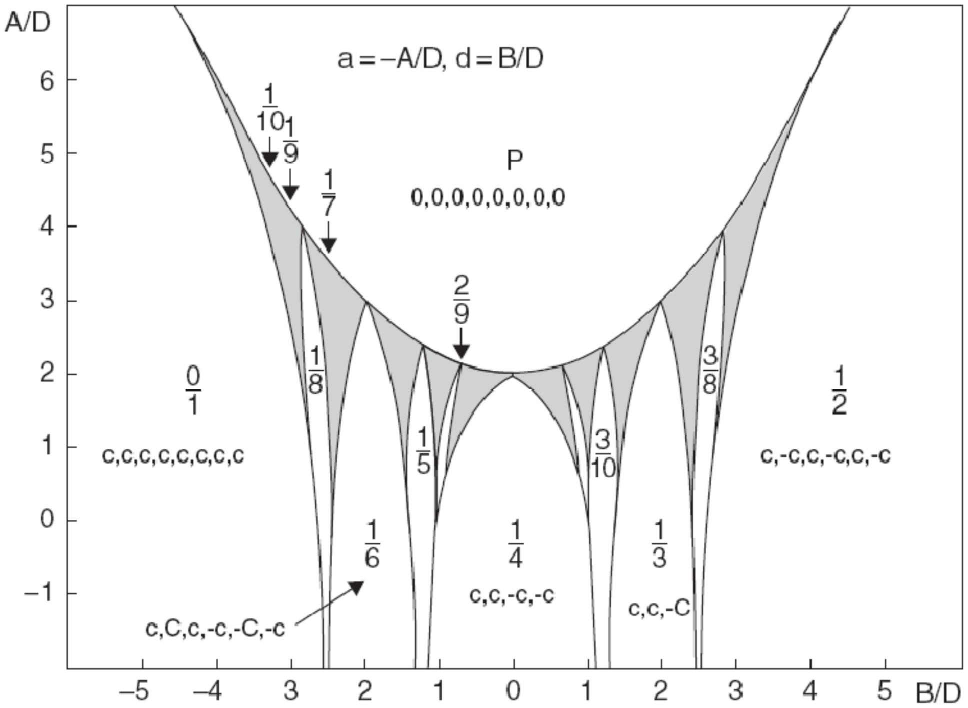
Analyticity breaking (Aubry)



- If the modulation function is smooth : phason branch is such that it goes to zero as q go to zero.
- Strong coupling: discontinuous atomic surfaces. There is a phason gap, i.e E of the phason branch is not zero as q goes to zero: Energy to overcome

Incommensurate modulation: the DIFFOUR model

T



Phase diagramm

First and second neighhbours interaction:

FRUSTRATION

(T. Janssen et al.)

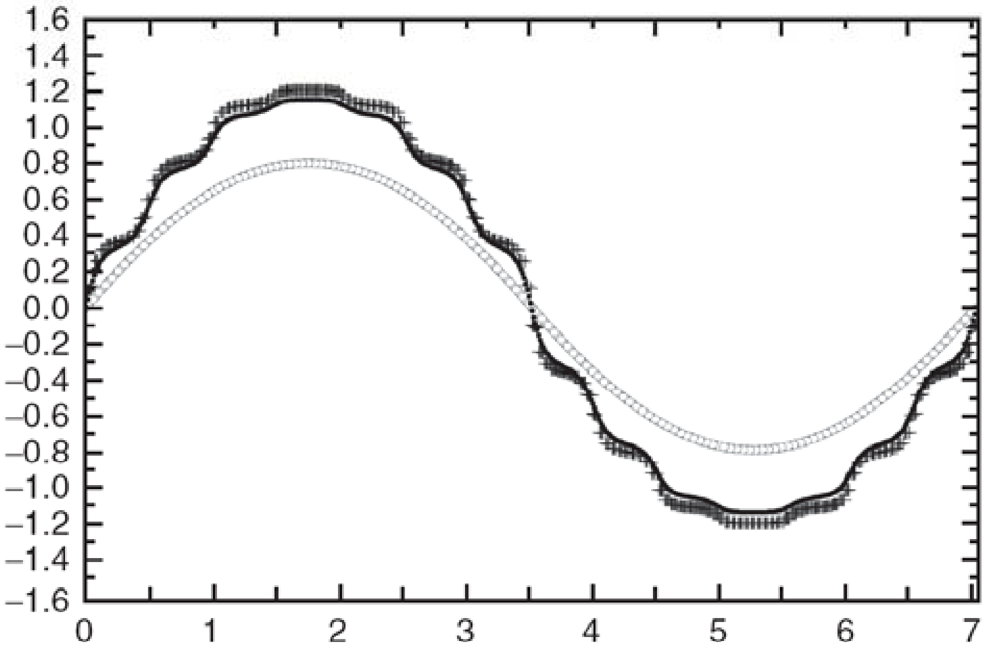
Gray color: incommensurate phase

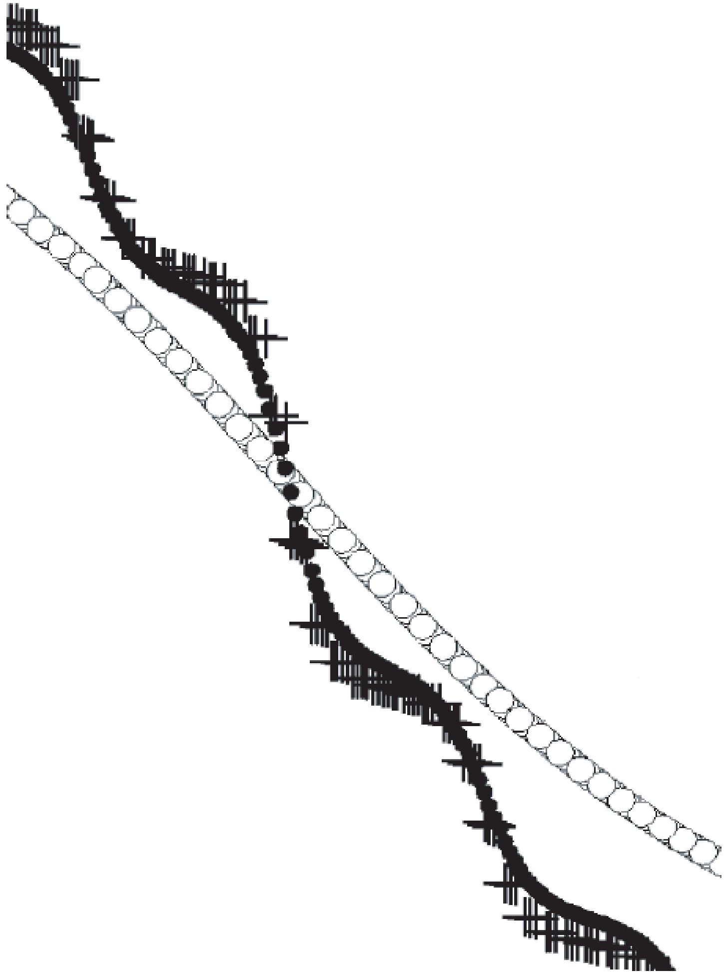
Succession of phase is reproduced, with the correct dynamics

The incommensurate phase is stabilized by phason entropy

Phason seen as a mode with a polarisation in perp space.

Analyticity breaking, DIFFOUR



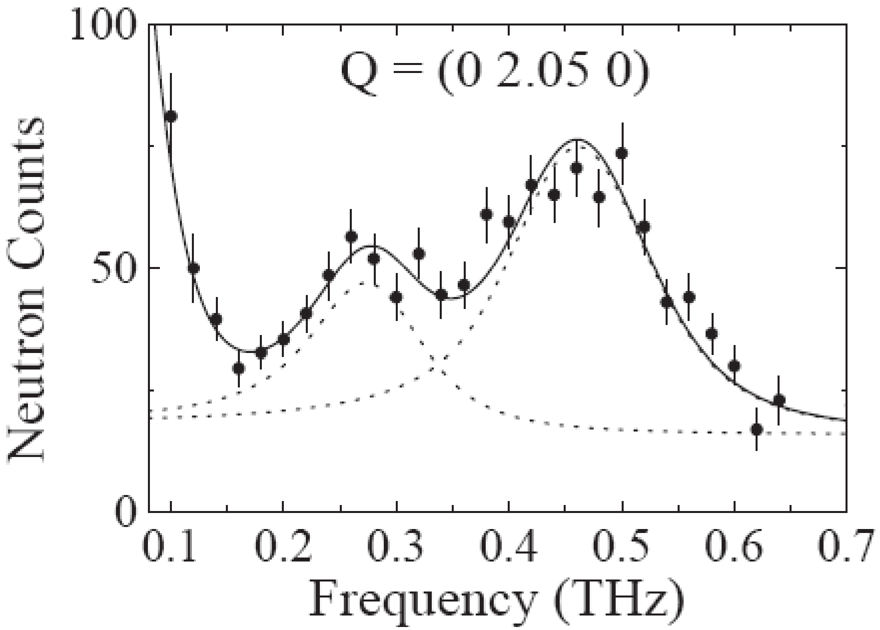


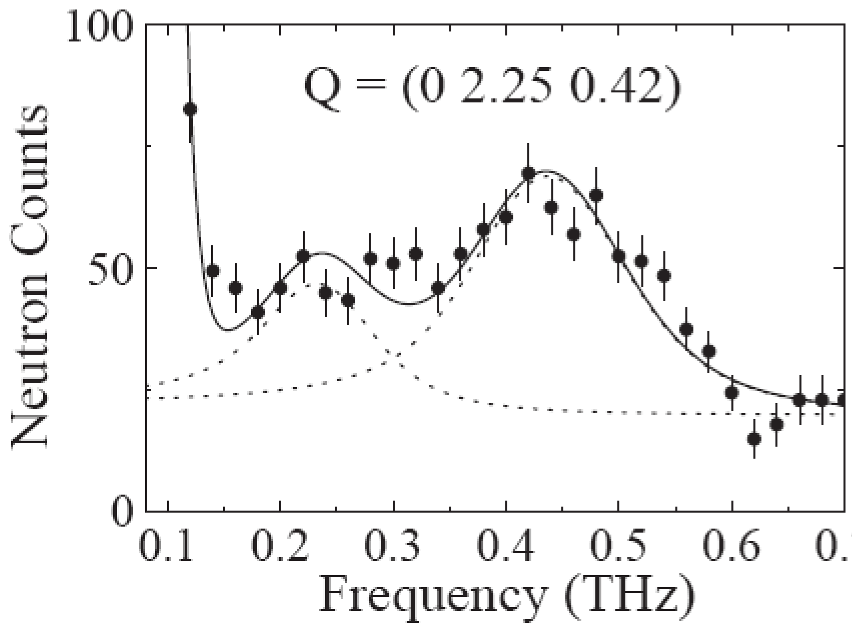
- A phason gap appears, when the discontinuity appears (T. Janssen): **E(q=0) is non zero.**

Composites

Low-frequency structural dynamics in the incommensurate composite crystal $Bi_2Sr_2CuO_{6+\delta}$

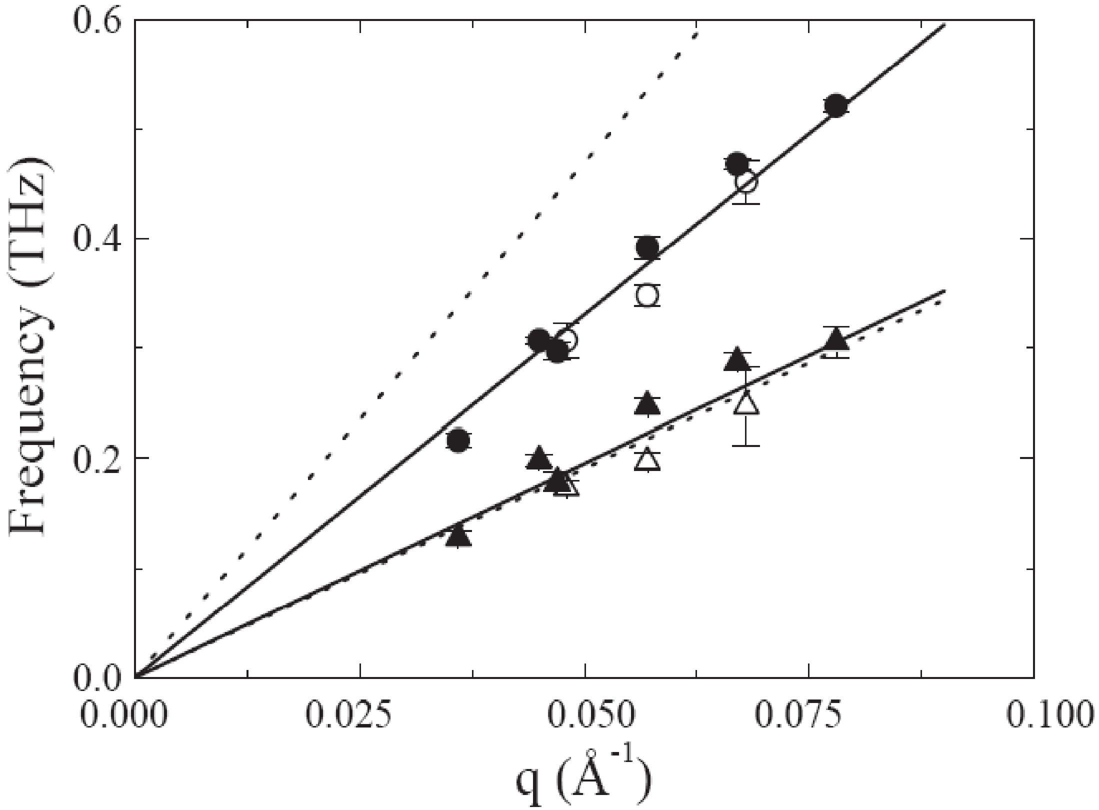
J. Etrillard[1,2], L. Bourgeois[1], P. Bourges[1], B. Liang[3], C. T. Lin[3] and B. Keimer[3]





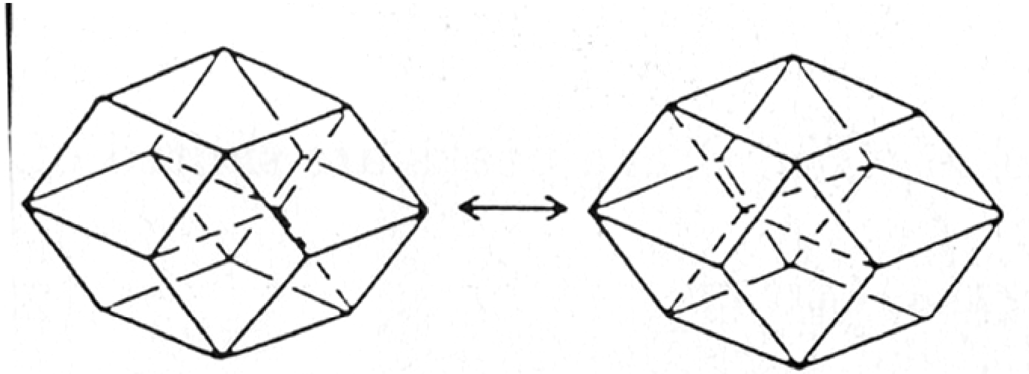
Composites

- The two sublattice react independently
- Two sound velocity
- Sliding modes?



Are phason hydrodynamic modes in QC ?

Simulation on a 3D 'Toy model': 3D Penrose tiling (or Ammann tiling) and the random tiling (Elser, Henley, Tang).



Phason flip in the 3D Amman tiling .

High T Monte-Carlo simulation (all configurations are equivalent).

Tang has shown that this maximally random tiling behaves as predicted by the hydrodynamic : **PHASON ELASTIC CONSTANT**

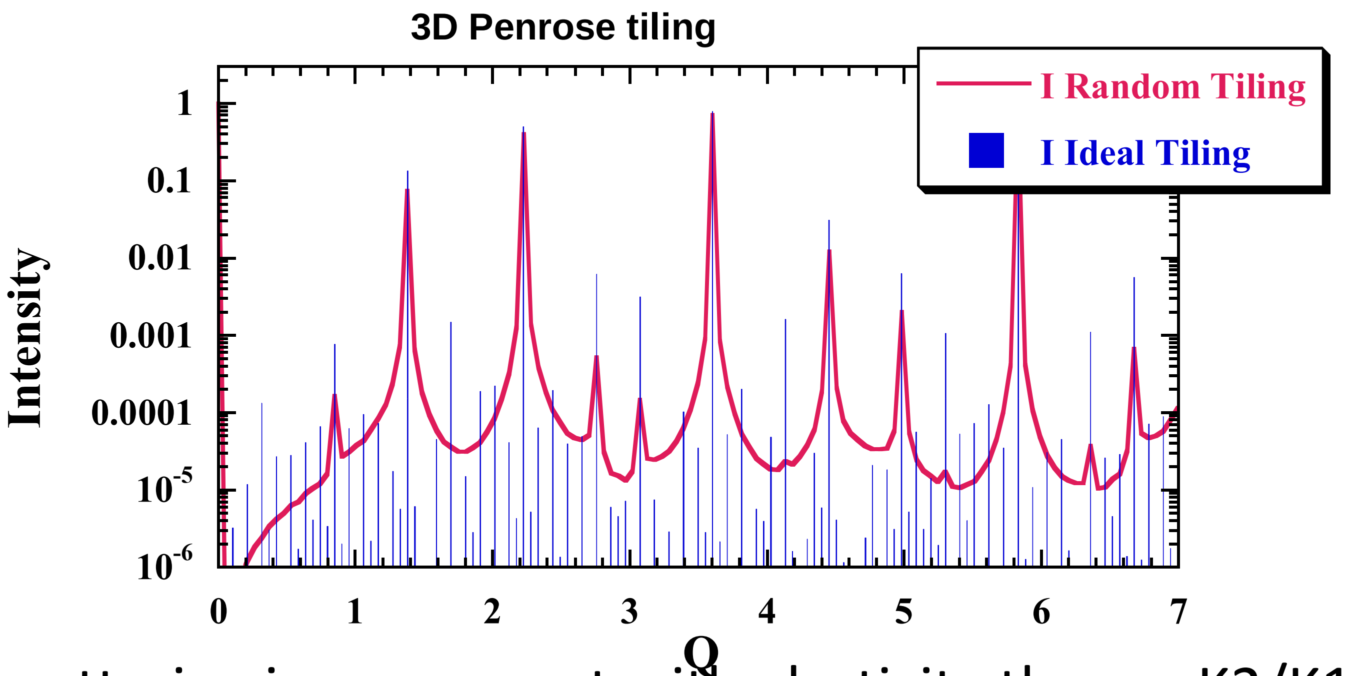
Restoring force: configurational entropy: Entropy is maximal for QP state and varies quadratically with phason strain.

See also chemical effect (Koschella et al.)

International School on Aperiodic Crystals

Diffuse scattering in the 3D random Penrose tiling.

(From M. Mihalkovic)



• Diffuse scattering in agreement with elasticity theory. K2/K1 is related to the tile and phason flip geometry

• Intensity decrease of the Bragg peak intensity proportional to Qper: perpendicular Debye-Waller factor.

Quasicrystal: analyticity?

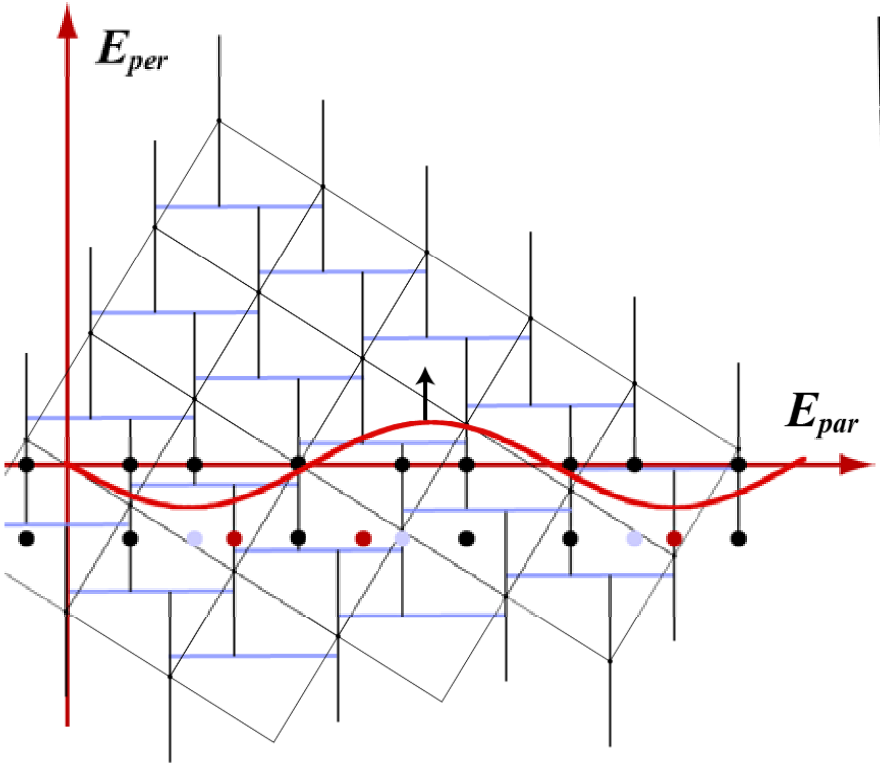
- In quasicrystal discontinuous atomic surfaces.
- Jeong and Steinhardt have shown that there is a breaking down of hydrodynamic in a model system with a T=0 QC as a ground state

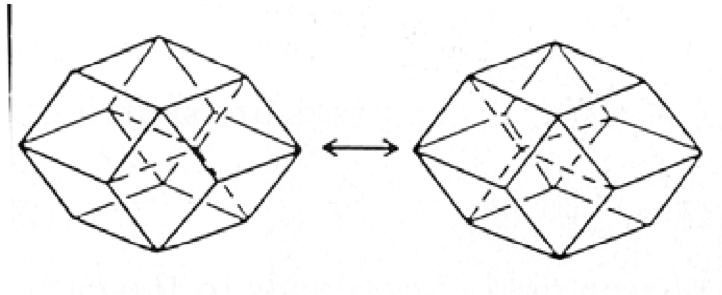
  - **Hydrodynamic behavior only above Tc**
- The ‘continuous’ parameter is not related to the shape of the atomic surface but to the fluctuations of the cut space (number of tile flip).

Quasicrystal: analyticity?

- **Hydrodynamic behavior only above Tc**

- The ‘continuous’ parameter is not related to the shape of the atomic surface but to the fluctuations of the cut space (number of tile flip).





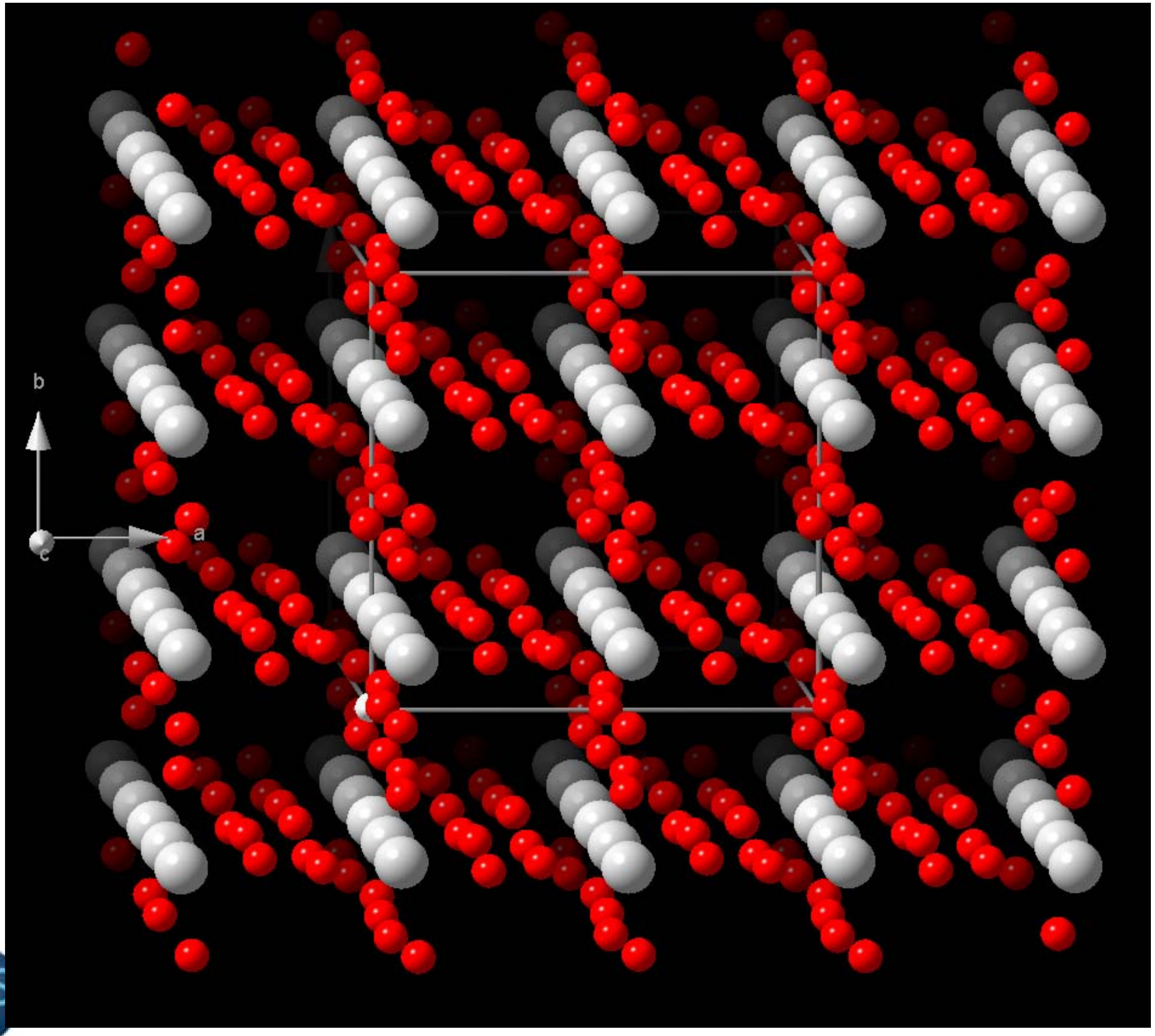
Entropic model.
‘Entropic’ elasticity.

Summary

- Atomistic models also predict phason modes
- Regime of wavevector were phason modes are damped propagative modes (incommensurately modulated phases)
- Longer wavevlength modes are diffusive
- Quasicrystals: always diffuse modes
- Phason modes in quasicrystal might be interpreted as an entropy term leading to a restoring force

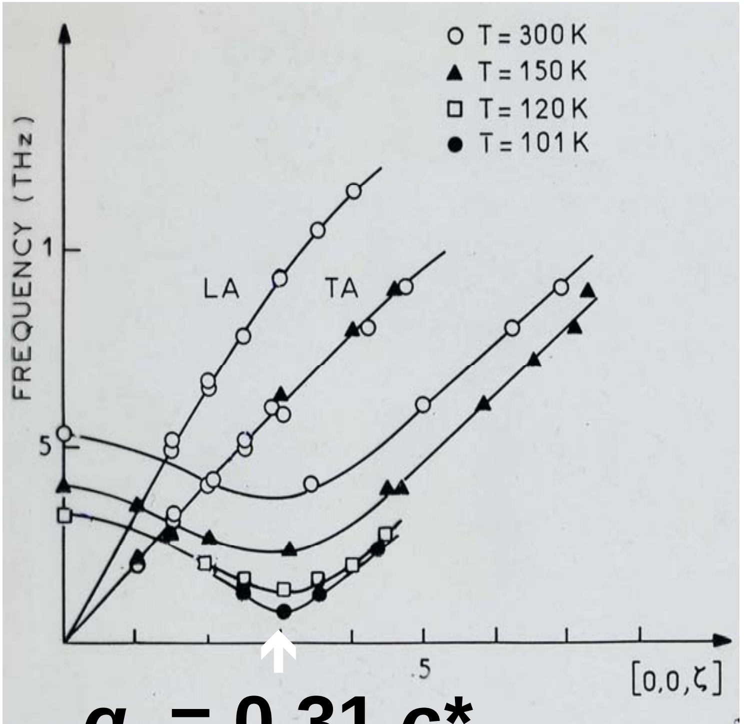
Phason modes: example

Displacive modulation: ThBr4



modulation along c.

Displacive modulation: $ThBr_4$



$q_s = 0.31\ c^*$

T<95K Incommensurate modulation along c.

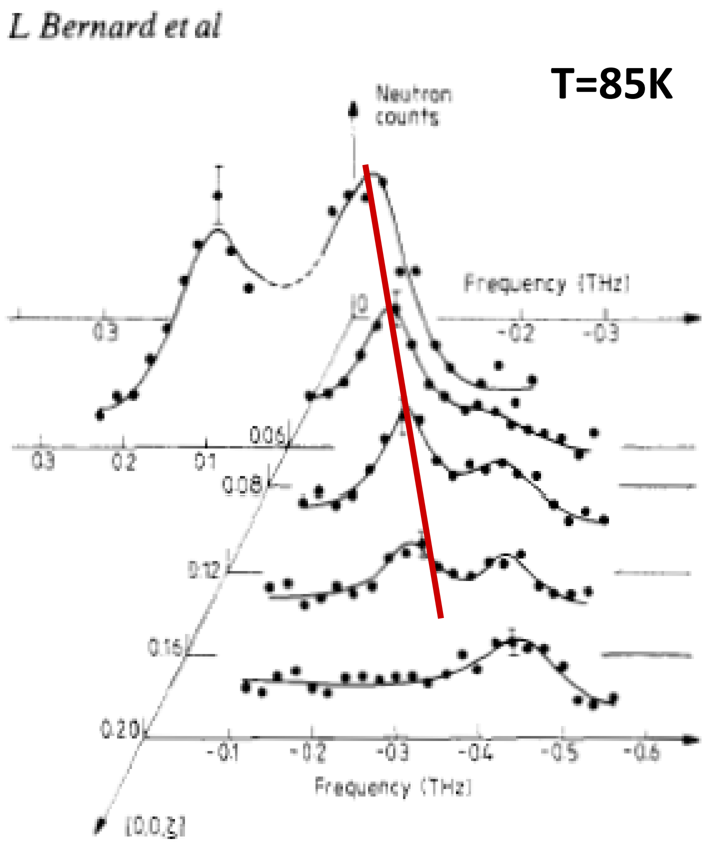
Above Tc: Soft mode transition

ThBr4: propagative phason mode

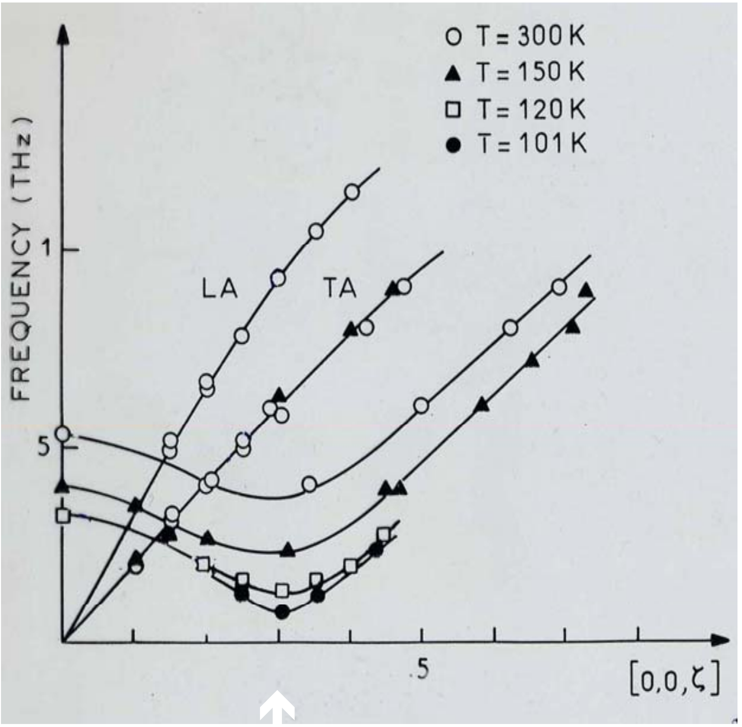
Inelastic neutron scattering: T<Tc

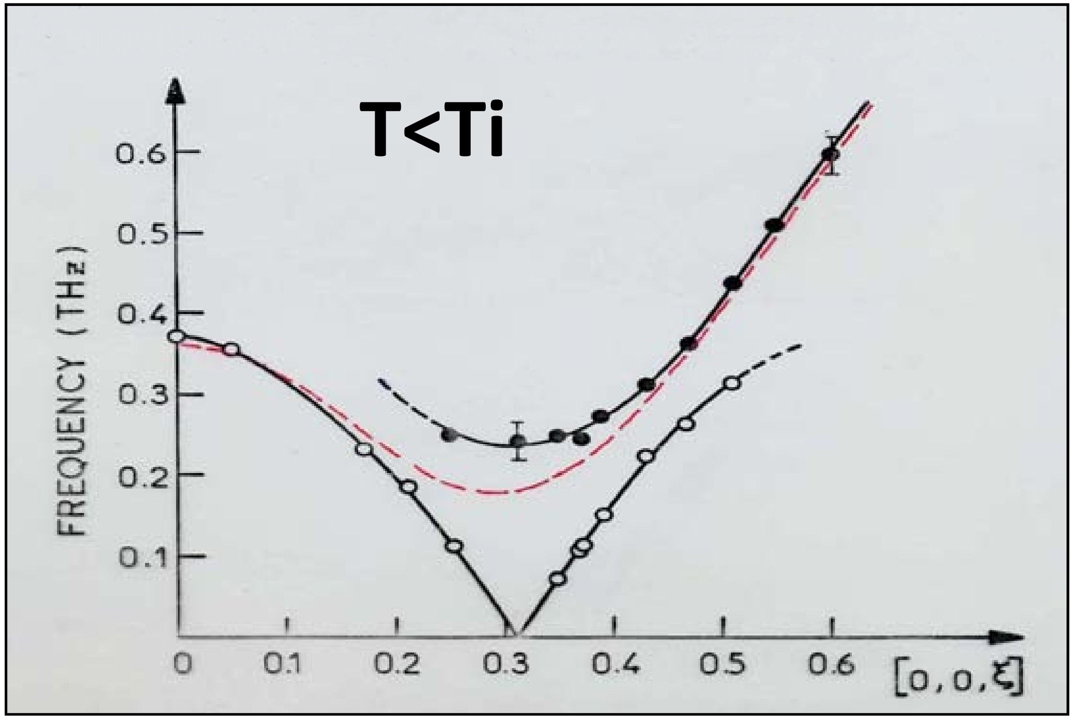
Near the satellite reflection: new zone center

The ‘acoustic’ like excitation *is not an acoustic phonon*: phason mode



Phason mode: $ThBr_4$
Dispersion slope is different from the acoustic one



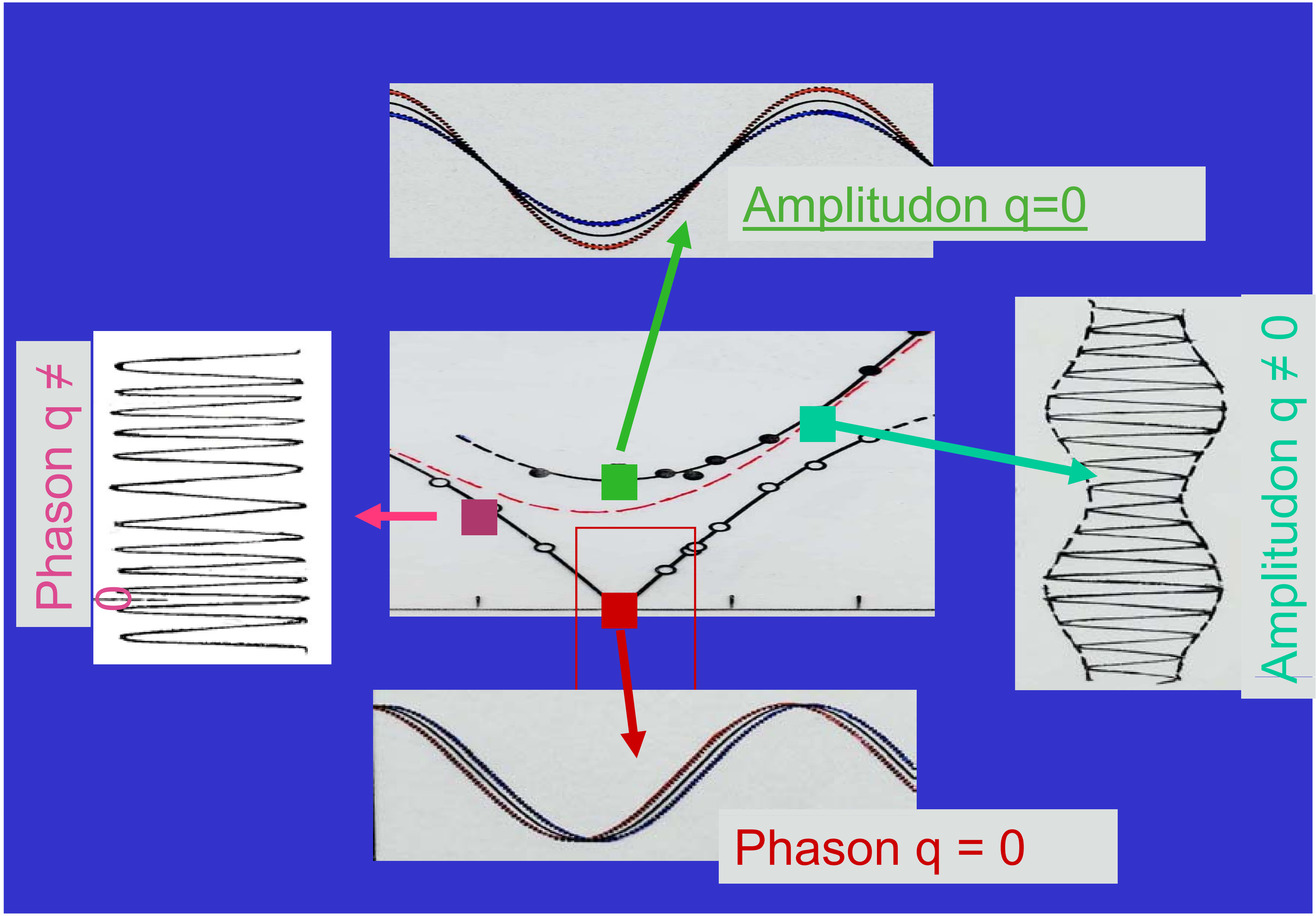


$q_s = 0.31\ c^*$

Phason and amplitudon mode

International School on Aperiodic Crystals

ThBr4: Phasons / Amplitudons eigenvectors



Phason modes: ThBr4

- In fact the hydrodynamic theory predicts only *one* mode: why two propagative phason and not a diffusive mode?
- Need to introduce lifetime: *Lifetime is finite* as q goes to zero. Phason has a finite width.
- Two 'half' hydrodynamic modes are equivalent to a diffusive mode.

Γ=0.3 meV for ThBr4

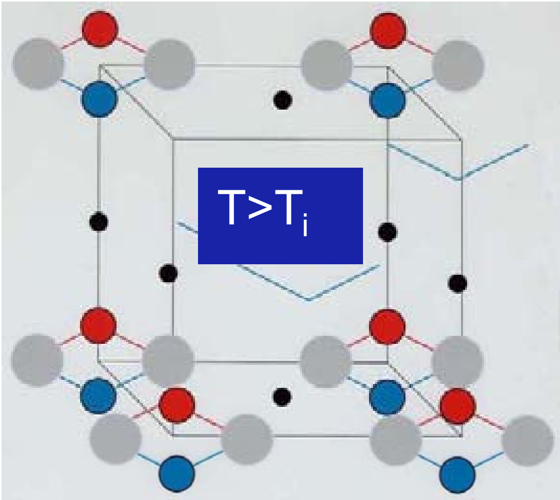
Mean free pass ~ a few 10 nm.

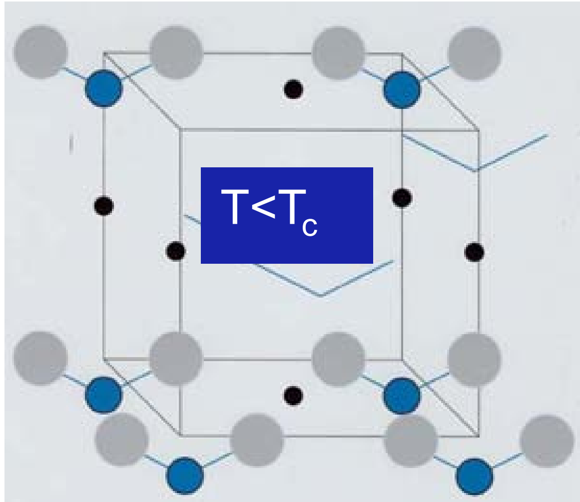
Mode with λ > mean free pass, do not propagate.

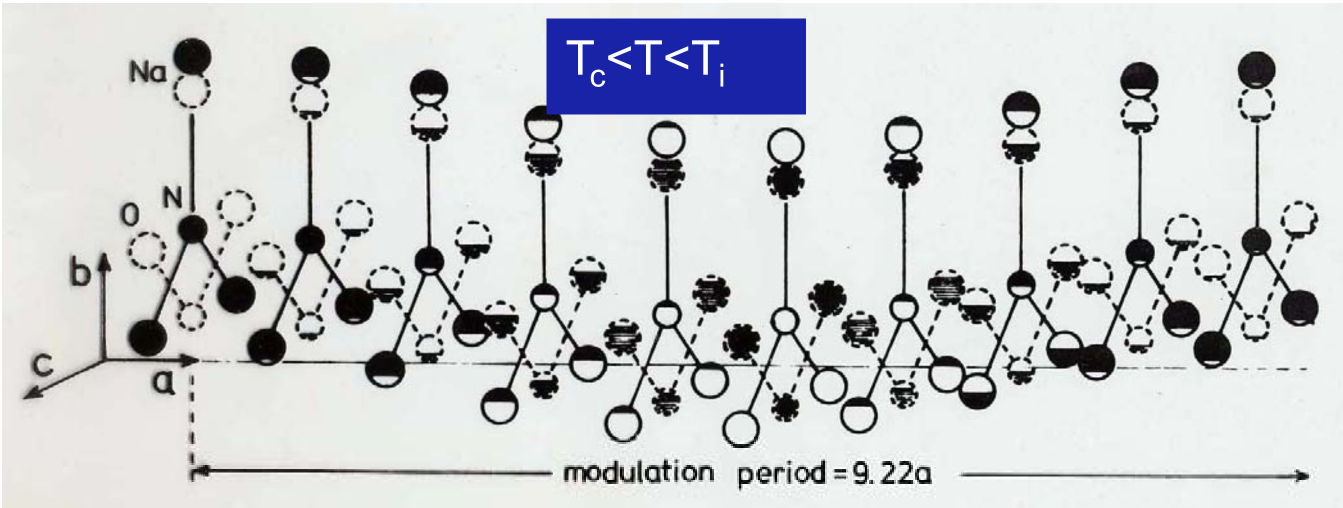
International School on Aperiodic Crystals

$NaNO_2$ orientational disorder

Order-disorder phase transition

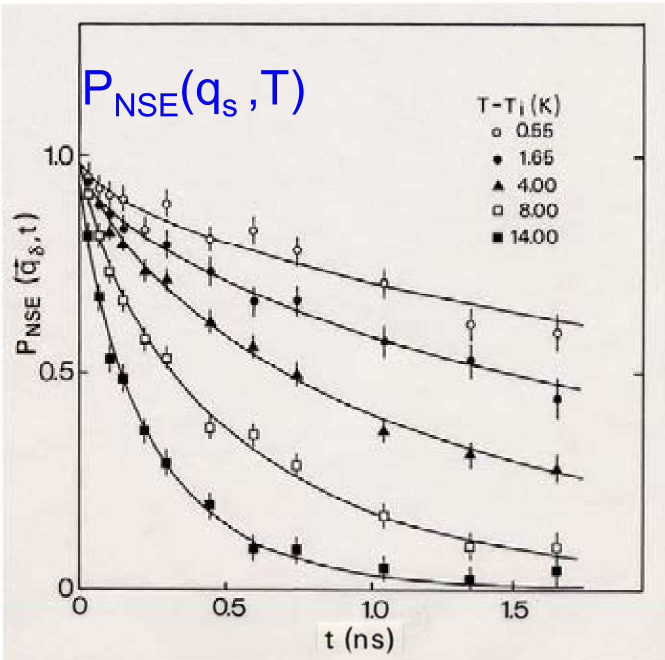


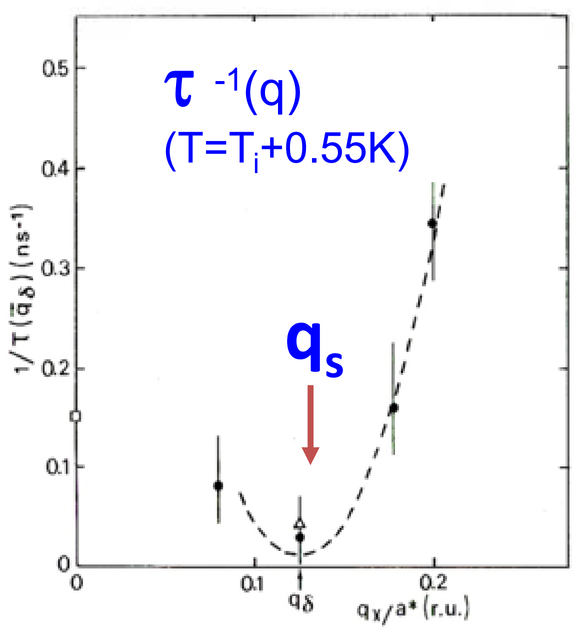




$NaNO_2$: diffusive phason mode

Modulation function is smooth but is an occupation probability: diffusive phason mode.



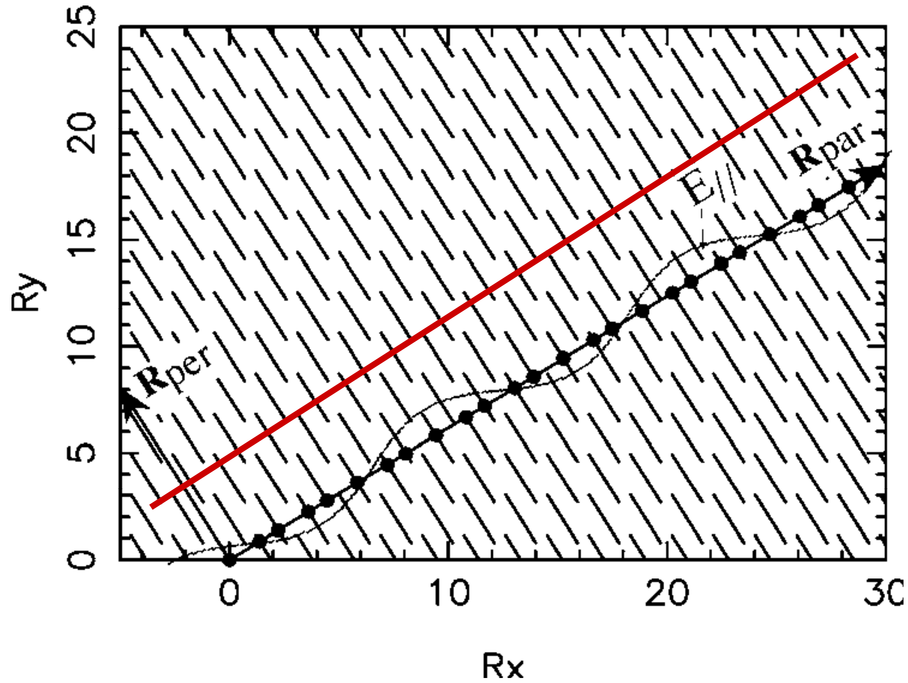


T<Ti $\tau^{-1}=Dq^2$? Hydrodynamic modes ?

D. Durand et al., Phys. Rev. B 43 (1991) 10690

International School on Aperiodic Crystals

Quasicrystals : Long-wavelength Phasons modes



- Long-wavelength phason modes: **collective diffusive modes**
- **Phason Mode: *q* and polarisation in perp space**
- **$-i\omega = D_{phason}\, q^2$ ('dispersion')**
- **$\exp(-t/\tau)$ $\tau = D_{phason}\, q^2$**
- Frozen at room T

Measuring long-wavelength phasons: **diffuse scattering**

Elasticity theory: calculation of diffuse scattering (similar to TDS) .

Two parameters: K2 and K1 the **phason elastic constants**.

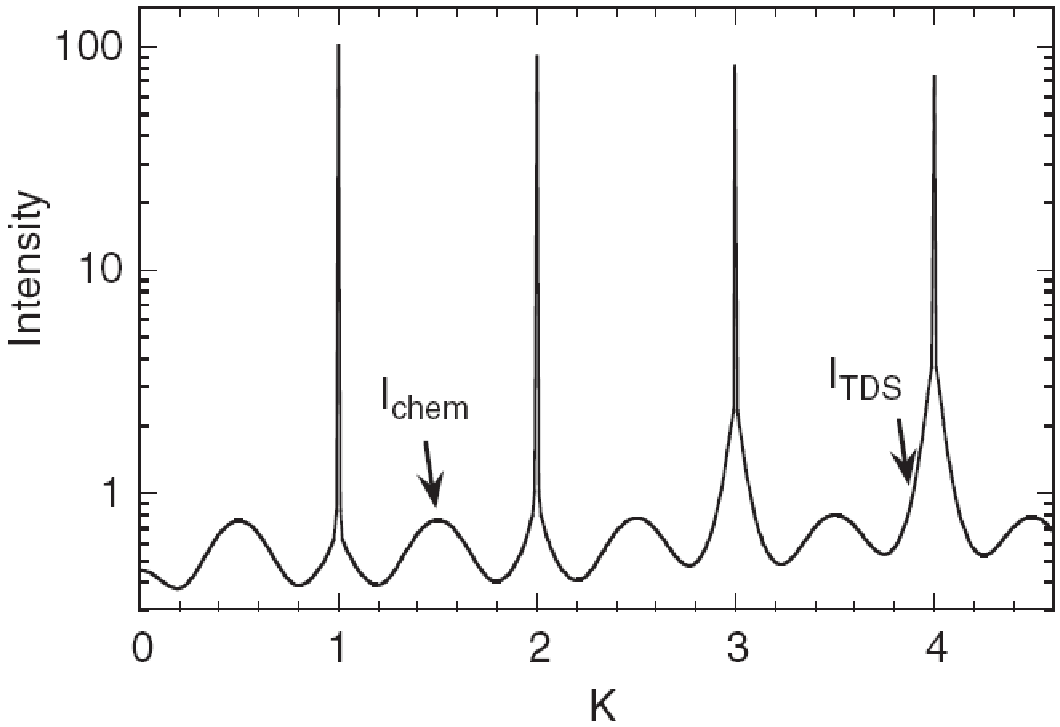
International School on Aperiodic Crystals

Diffuse scattering

- Structure= Ideal structure + fluctuations

  If fluctuations are bounded then

$$S(\mathbf{Q}) = S_{Bragg}(\mathbf{Q}) + S_{Diff}(\mathbf{Q})$$



Bragg FT $\langle \rho(R) \rangle$

Diffus FT

$$\langle \rho(\mathbf{r}_i)\rho(\mathbf{r}_j) \rangle - \langle \rho(\mathbf{r}) \rangle^2$$

International School on Aperiodic Crystals

Phason modes in quasicrystal

- Hydrodynamics theory and elasticity. For icosahedral phases, K1, K2 phason elastic constant K3 phonon-phason coupling (Jaric; Ishii; Widom)

Phason modes lead to diffuse scattering (similar to TDS) which can be computed using the hydrodynamic matrix C(K1,K2,K3,q)

- Thermal equilibrium phonon and phason fluctuations

- Scattered intensity in : $\mathbf{Q}=\mathbf{H}_{\text{Bragg}}+\mathbf{q}$

$\mathbf{Q}=\mathbf{H}_{\text{Bragg}}$ Bragg intensity + **Par and Perp Debye-Waller factor**

Fluctuations are limited in par and perp space

$$S_{Bragg}(\mathbf{H}_{par}) = S_{Ideal}(\mathbf{H}_{par})\exp(-\langle u_{par}^2\rangle H_{par}^2).\exp(-\langle u_{per}^2\rangle H_{per}^2)$$

Phason modes in quasicrystal

- **Diffuse scattering,** K3 negligeable: phonon and phason part

$$S_{Diffus}(\mathbf{H}_{par} + \mathbf{q}) = S_{Bragg}(\mathbf{H}_{par}) \left\langle \mathbf{H}_{par} \left| C^{-1}_{par,par}(\mathbf{q}) \right| \mathbf{Q}_{par} \right\rangle + S_{Bragg}(\mathbf{H}_{par}) \left\langle \mathbf{H}_{per} \left| C^{-1}_{per,per}(\mathbf{q}) \right| \mathbf{H}_{per} \right\rangle$$

Three main characteristics of phason diffuse scattering

- S(**Q**+**q**) decays as $1/q^2$
- Intensity is proportional to $I_{Bragg}\, Q_{per}{}^2$
- Shape anisotropy depends on K2/K1 and K3

- For Bragg peak along the same axis, and for weak K3

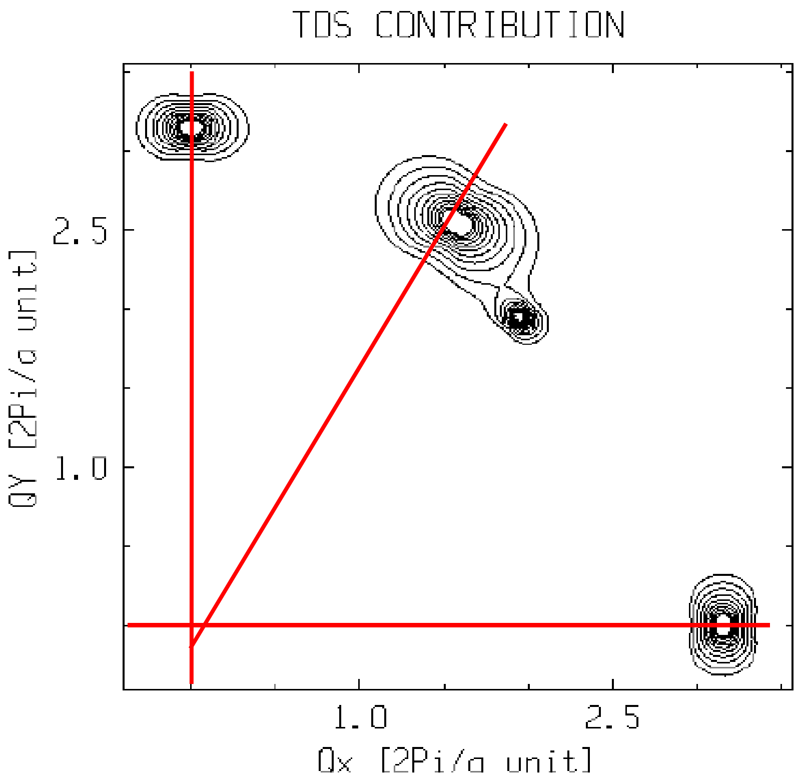
  $I(\mathbf{Q}+\mathbf{q}) = \alpha(\mathbf{q})\, I_{Bragg} Q_{per}{}^2 / q^2$

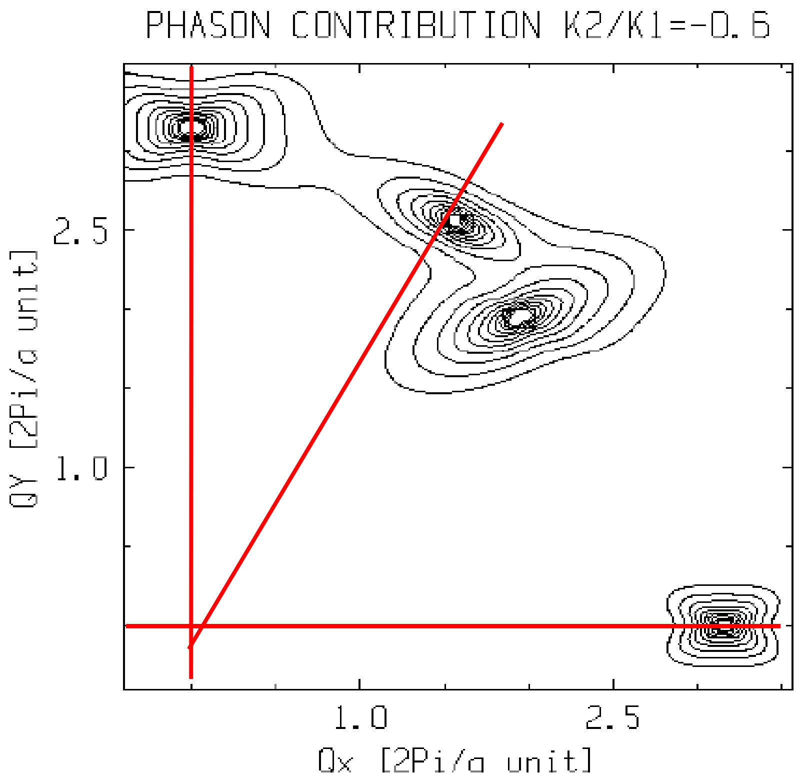
  $\alpha(\mathbf{q})$ depends only on the q direction

DIFFUSE SCATTERING

Phonon modes: 3 polarisation, longitudinal and transverse

Phason modes: 3 polarisation e_{per}. 'Selection rule' $e_{per}.H_{per}$

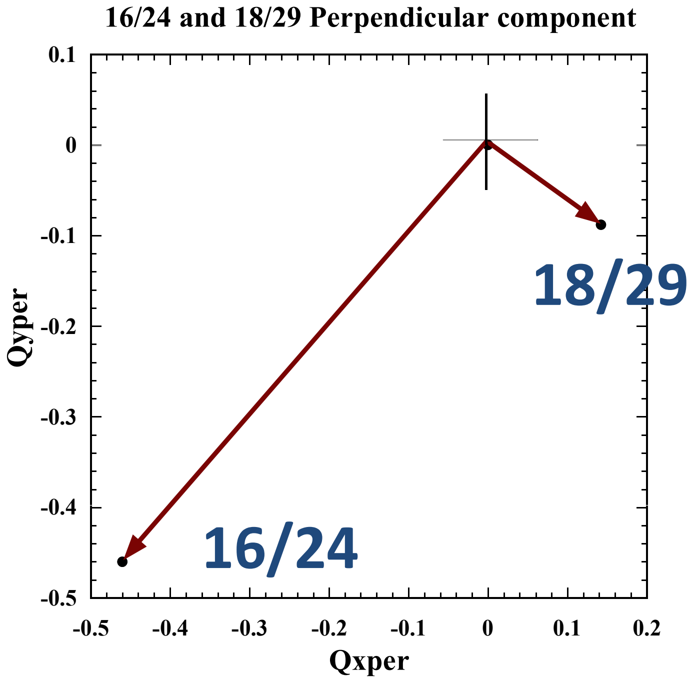




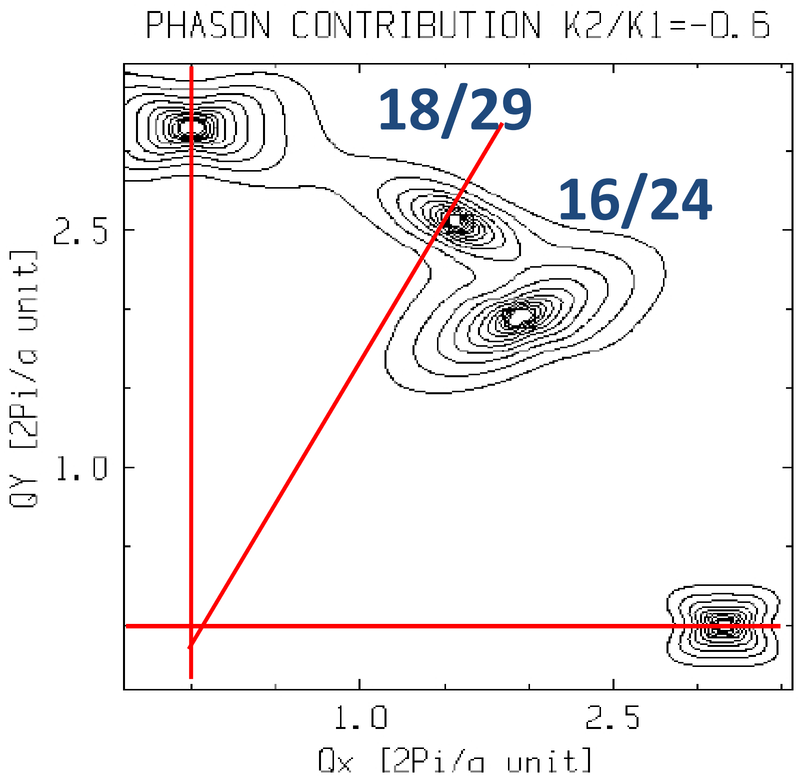
Aperiodic Crystals

DIFFUSE SCATTERING

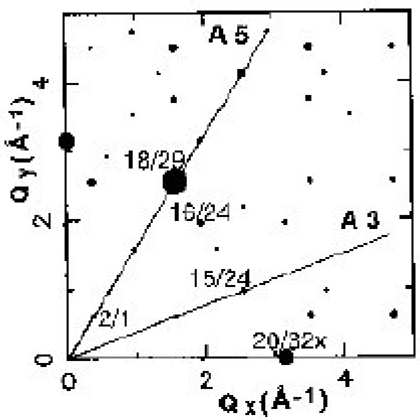
Selection rule: perpendicular Component are almost orthogonal



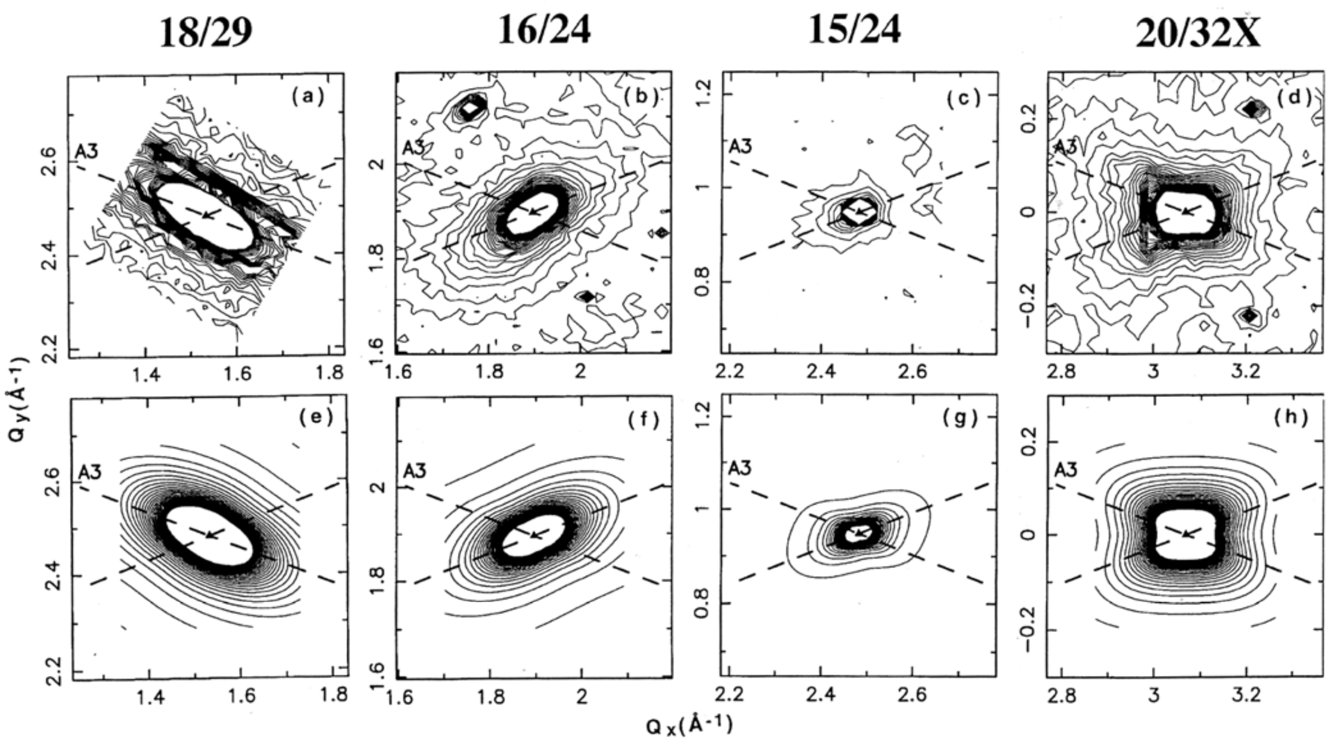
Phason modes: 3 polarisation e_{per}. 'Selection rule' $e_{per}.H_{per}$



i-AlPdMn: Neutron diffraction

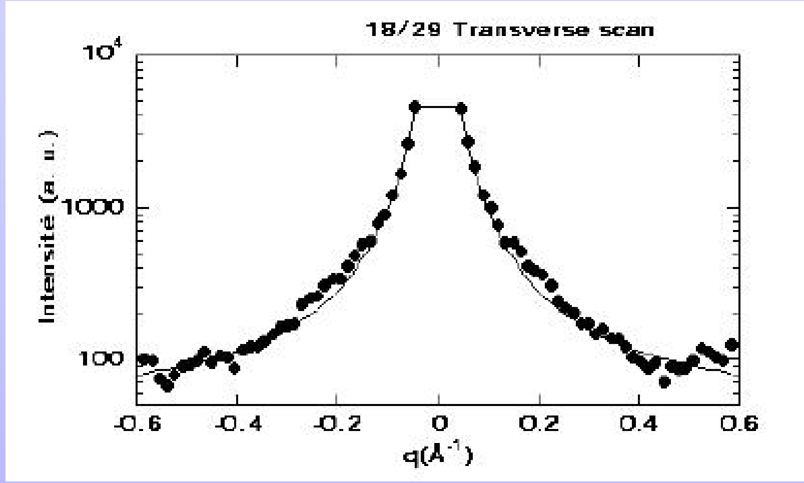


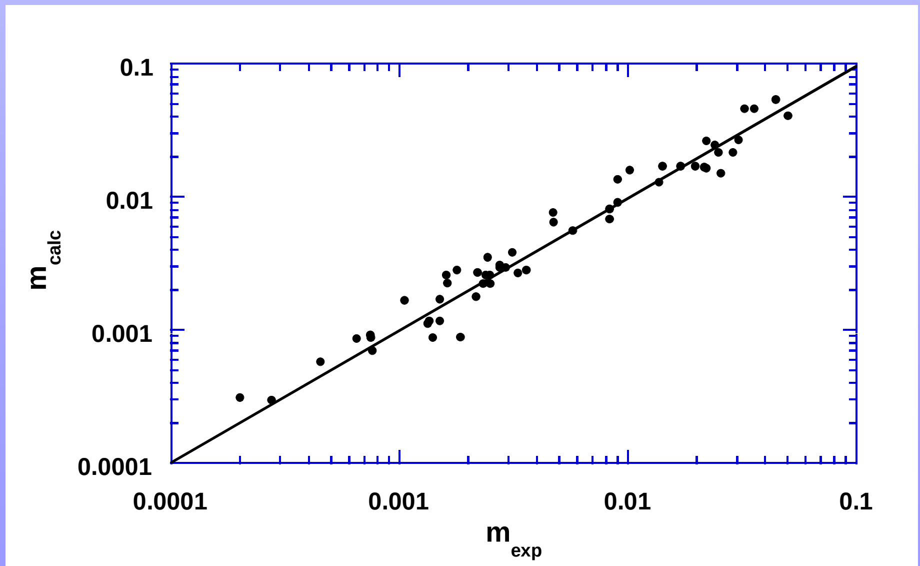
- Analyser: no TDS contribution
- The diffuse scattering around Bragg reflections is anisotropic
- Phason contribution to the diffuse scattering: 15/24 and 16/24 reflections



Simulation with a single parameter: K2/K1=-0.52

Neutron data



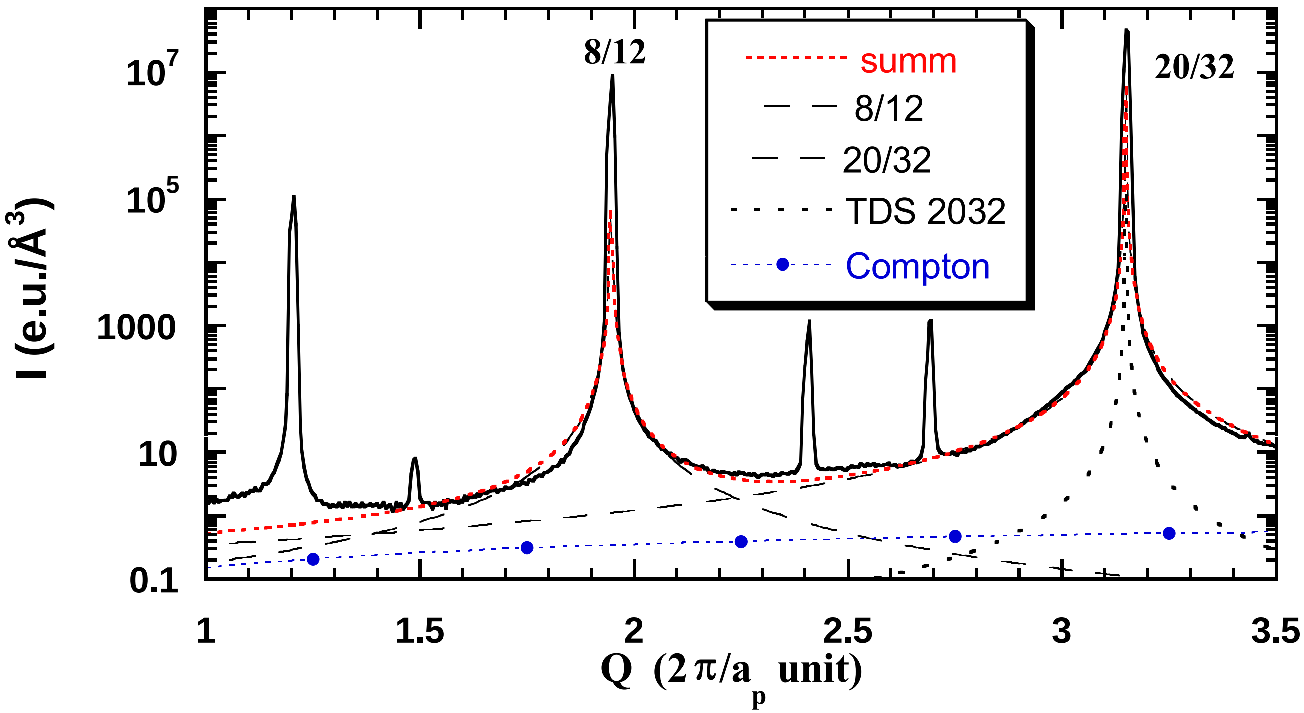


- Absolute scale measurement.
- 1/q2 fit along several directions.
- $K1/k_BT = 0.1$ atom^{-1}
- $K2/k_BT = -0.052$ atom^{-1}
- Good agreement with experimental data measured around 11 reflections and 4 directions. R=0.2

Absolute scale X-ray data (ESRF, D2AM)

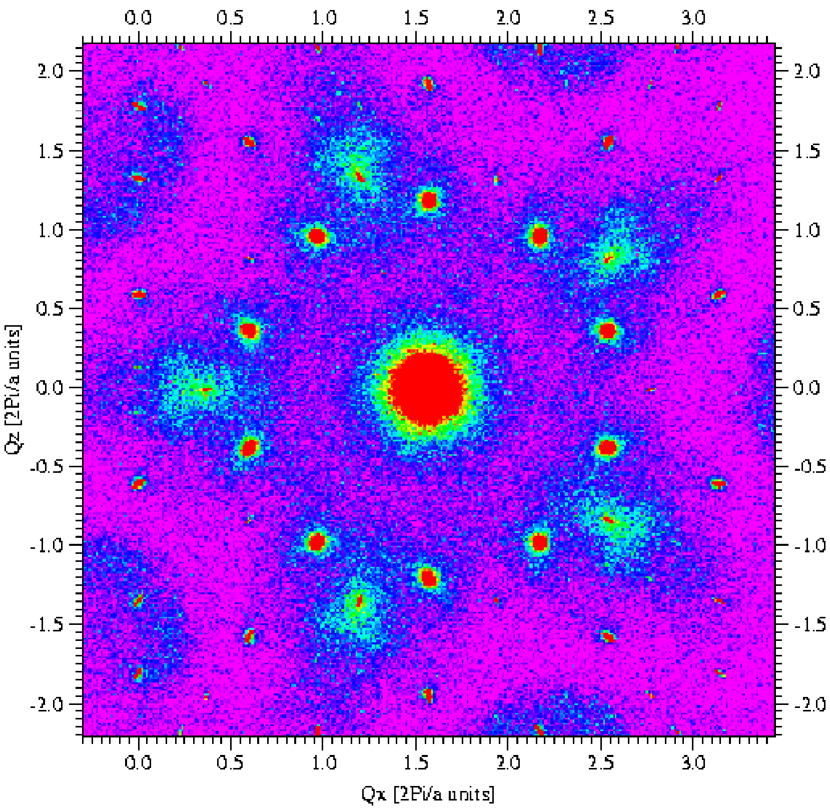
- $K1/k_BT = 0.06$ atom^{-1} $K2/k_BT = -0.03$ atom^{-1}

- Absolute scale measurement allows comparison between different sample and quasicrystals.

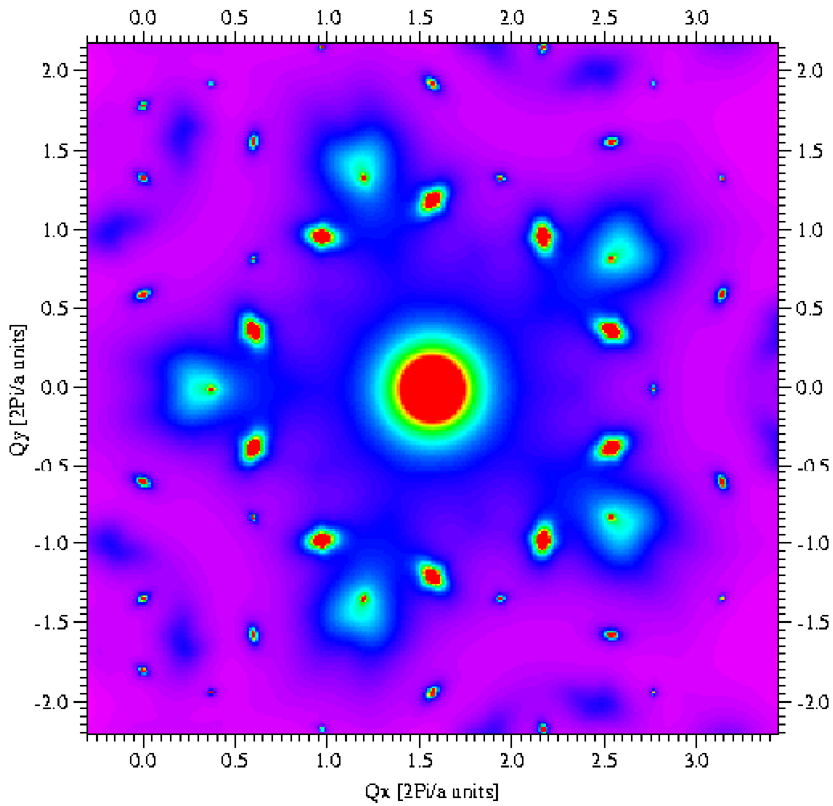


Phason fluctuations explains 90% of the observed diffuse scattering

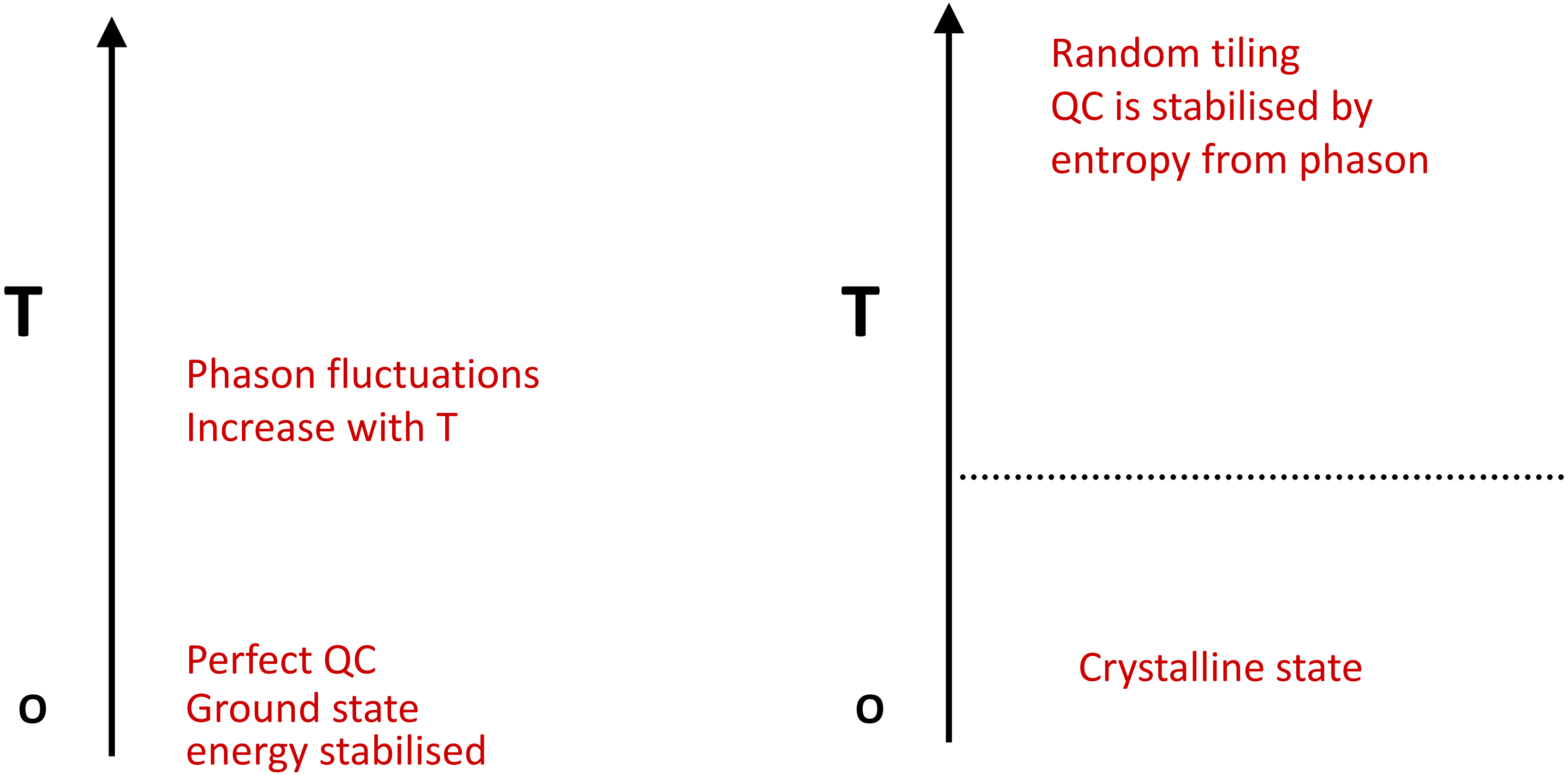
Measurement (rotating anode)



Simulation

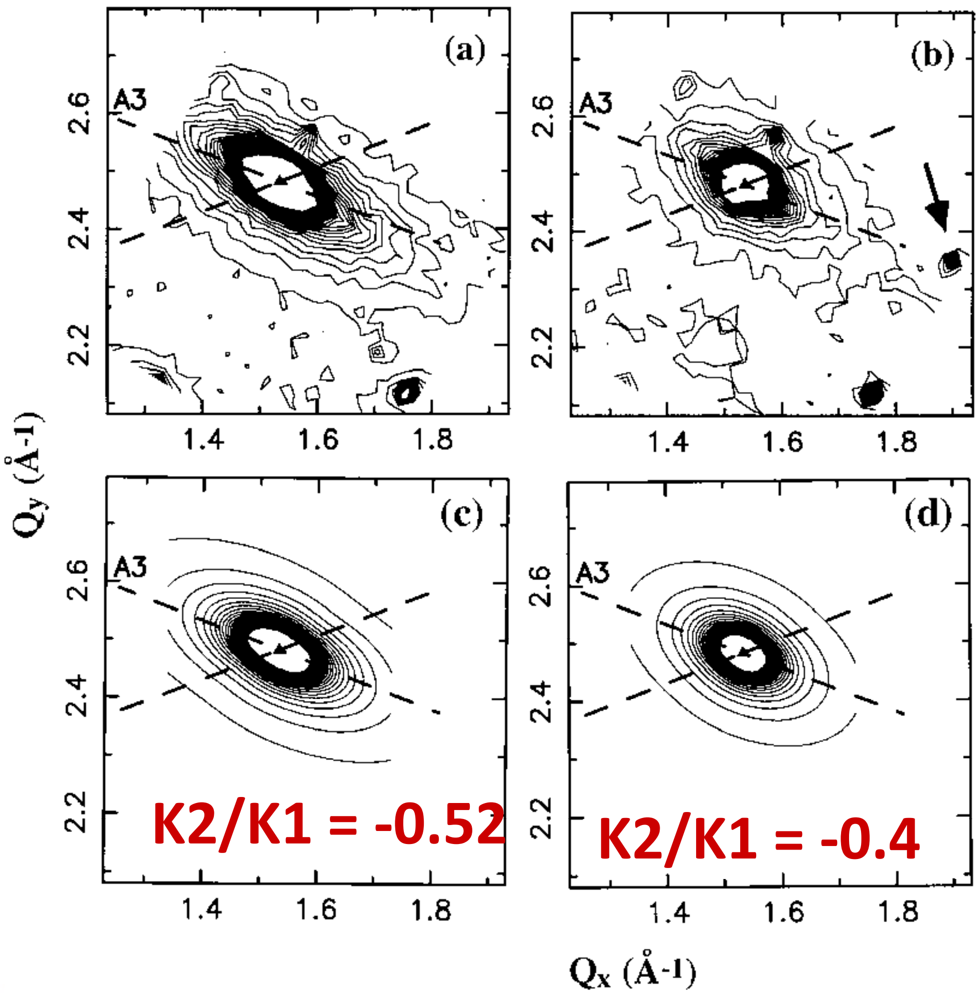


Stability: Two competing (simple) models



i-AlPdMn. Temperature neutron diff study

T= 200C T=750 C



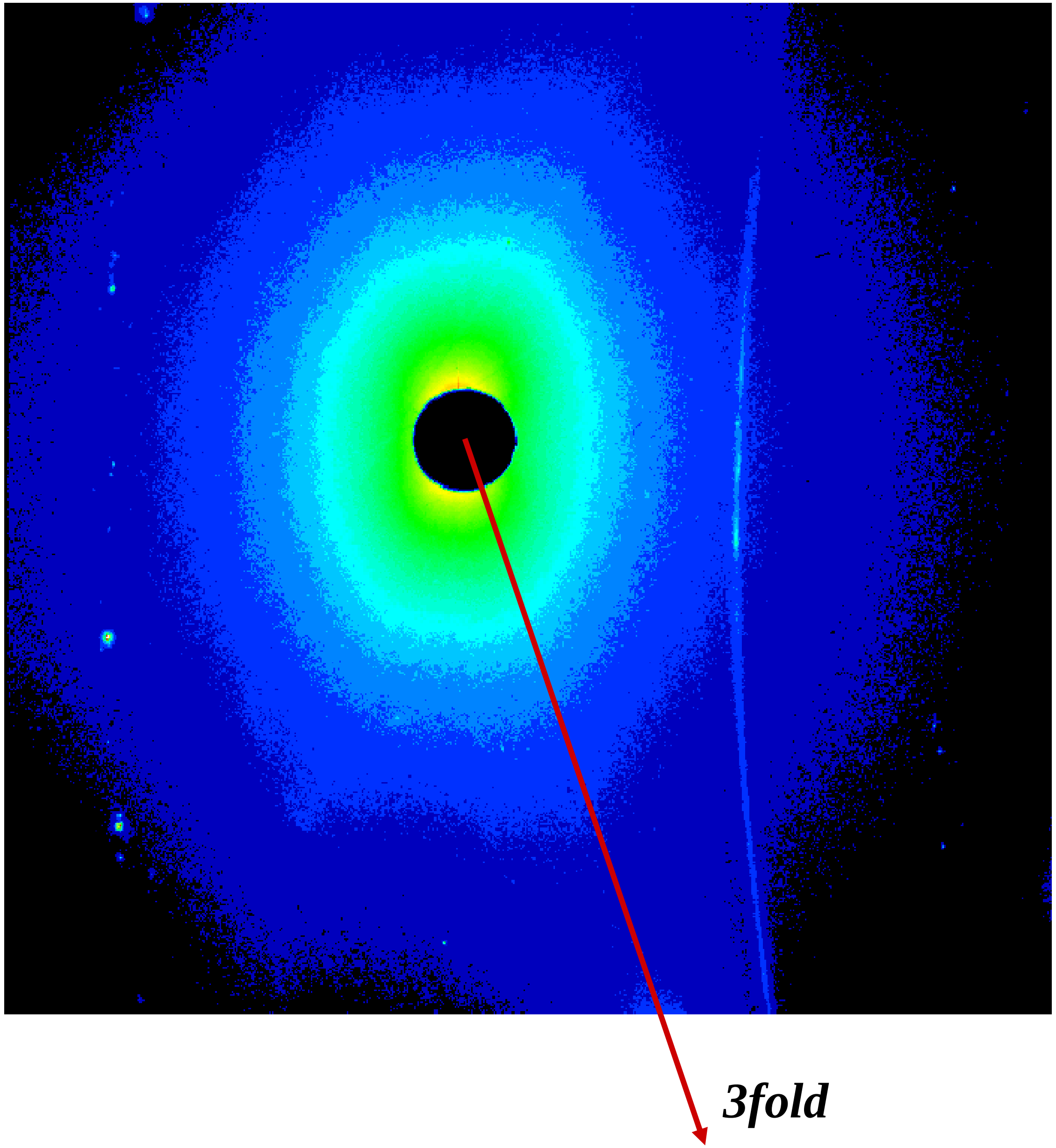
Diffuse scattering diminishes when T increases.

High Qper Bragg peaks intensity increases.

Phason softening when T decreases.

close to a *3-fold instability.*

i-AlPdMn quasicrystal. In situ T study



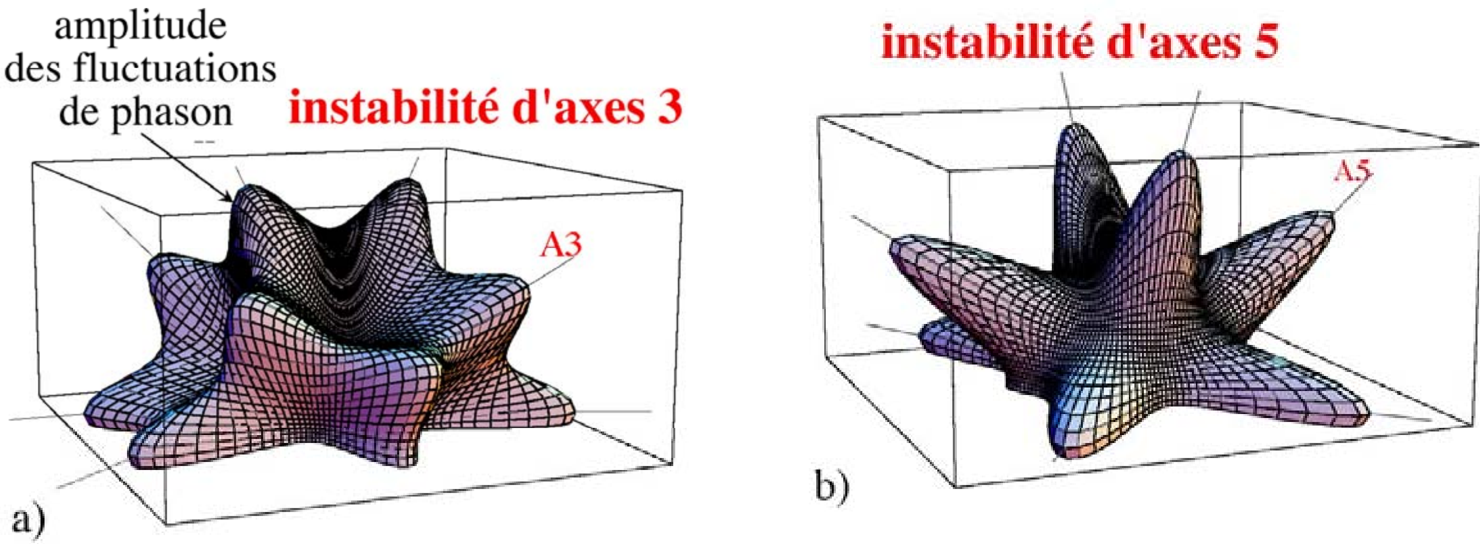
T evolution of the diffuse Scattering

FROM 750C to 500C

In situ X-ray.

The diffuse scattering is due to pre-transitional fluctuations *(3-fold)* **,** ***with a phason softnening***

Agreement with the random-tiling scenario



3-fold instability: K2/K1 = -0.75   **5-fold instability: K2/K1 = 0.75**

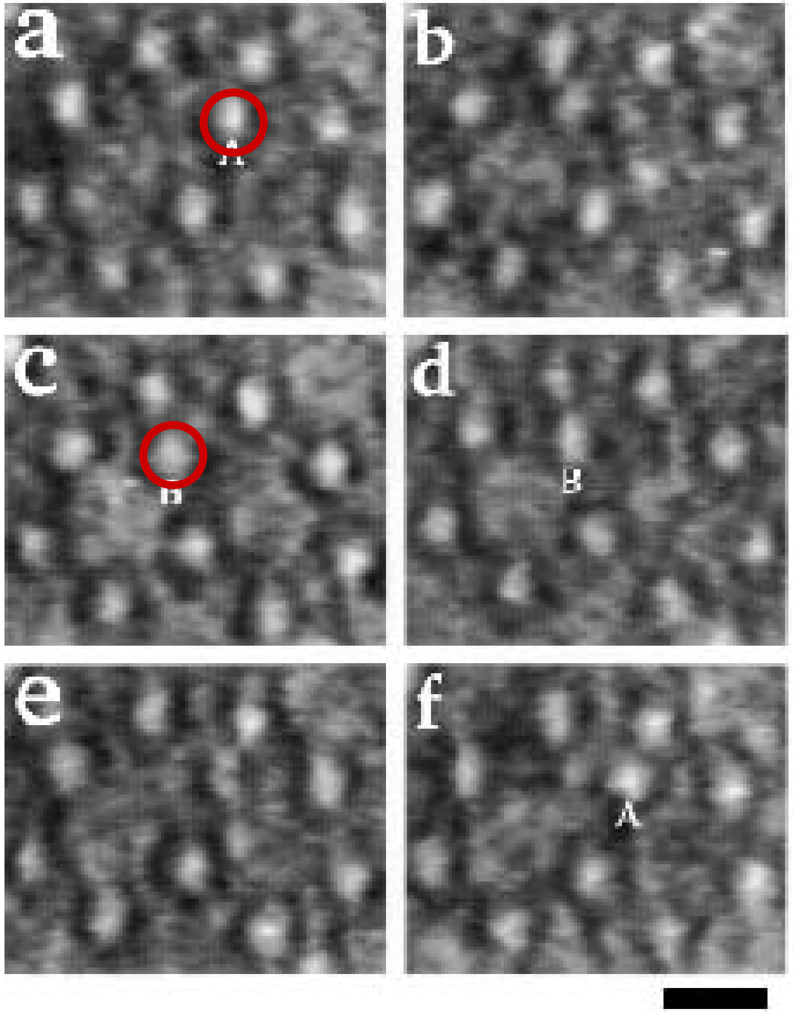
- ***Experimentally K2/K1 = -0.52 at RT and -0.4 at 700°C***
- ***Consistant with a softening of the phason mode:***

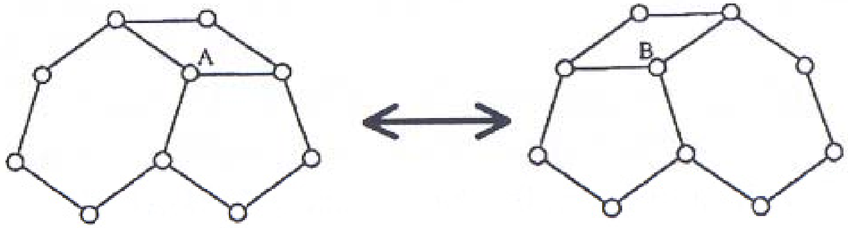
Phason diffuse scattering can then be interpreted as pre-transitional fluctuations.

Consistent with the random tiling scenario

International School on Aperiodic Crystals

Phason dynamics





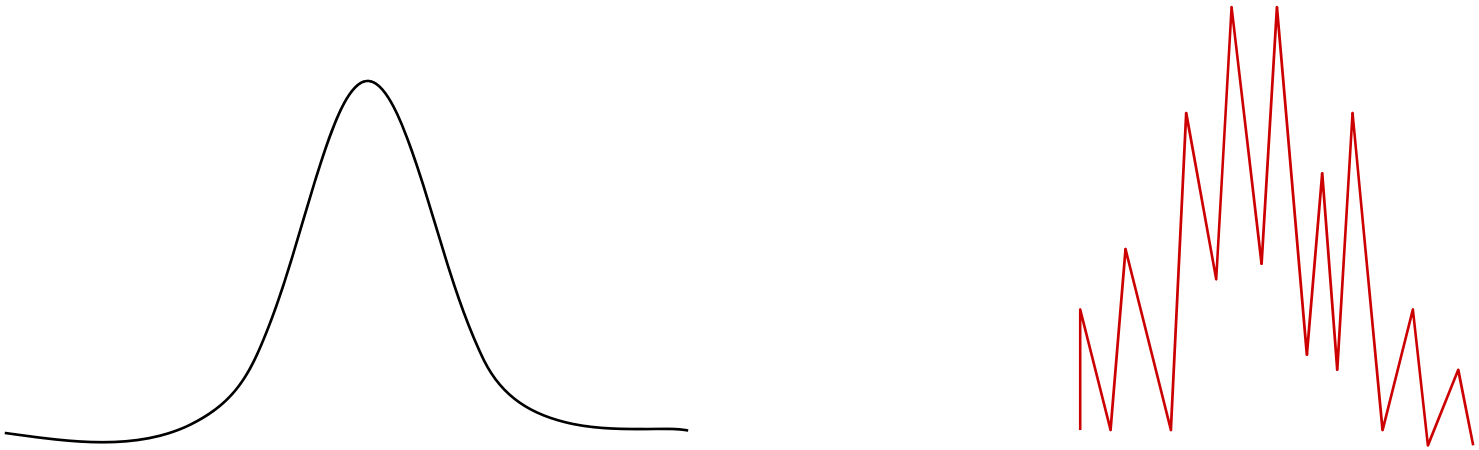
- HRTEM observed at 1123 K in d-AlCuCo (Edagawa et al., PRL, 8, 1676, 2000)
- Local ‘phason Jump’ , involving atoms columns.
- Time scale : 10 sec

International School on Aperiodic Crystals

Long-wavelength phason dynamics

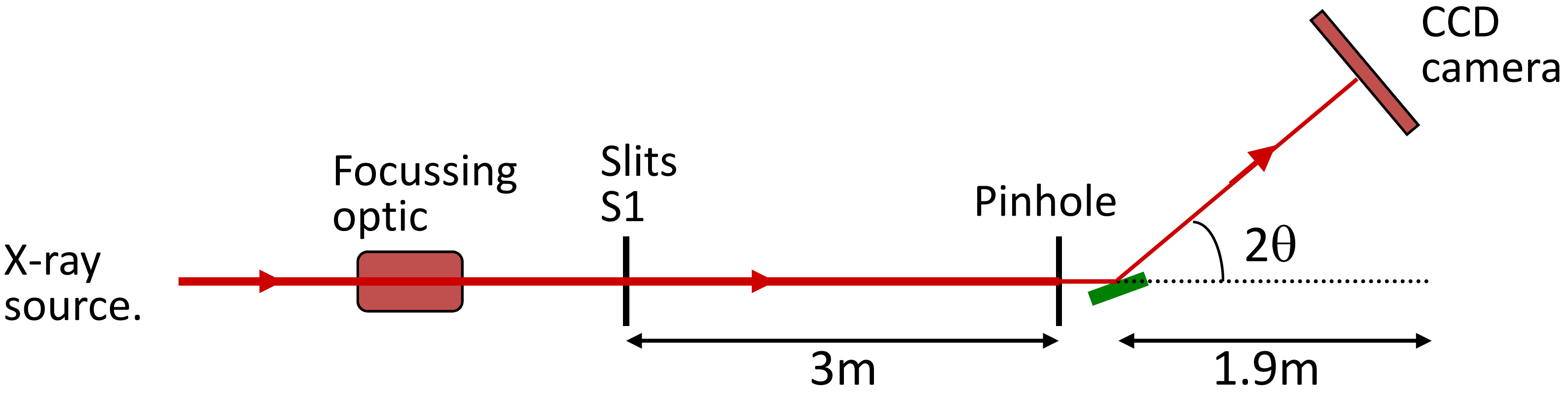
• **Collective diffusive mode**: exponential time decay of the correlations. Time scale? Too slow for inelastic neutron scatt.

• **Experimental study**: **coherent X-ray scattering** (ID20, ESRF)



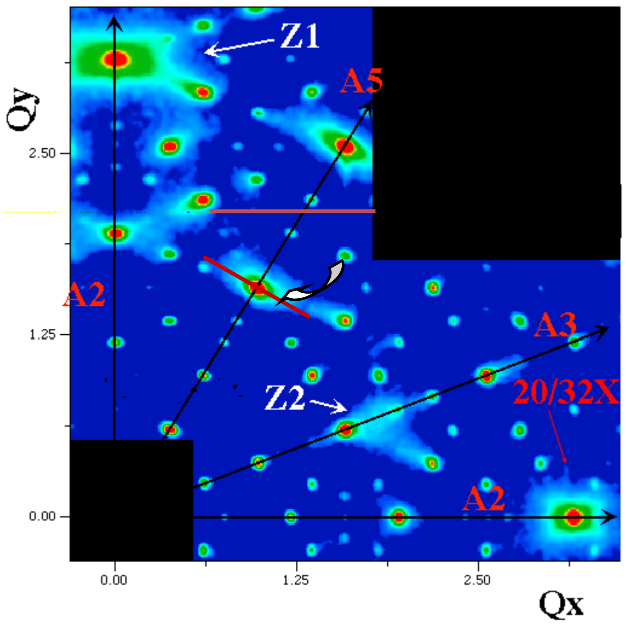
Incoherent scattering **Coherent scattering**

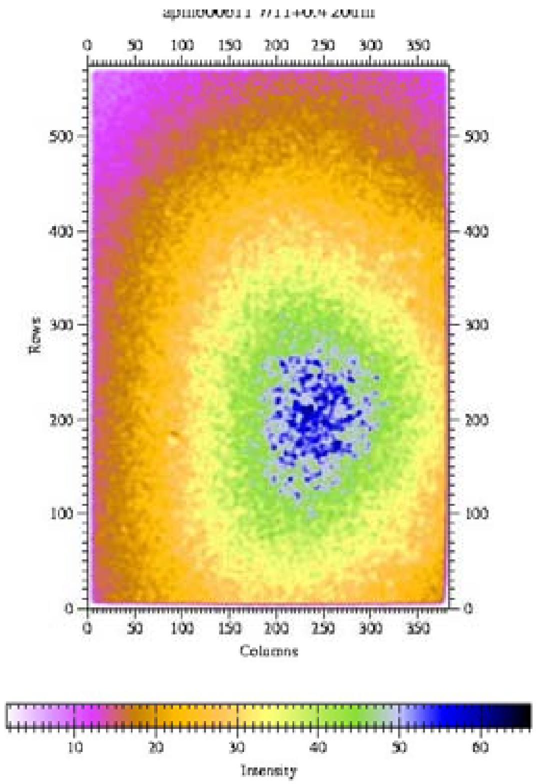
Experimental set up: ESRF ID20

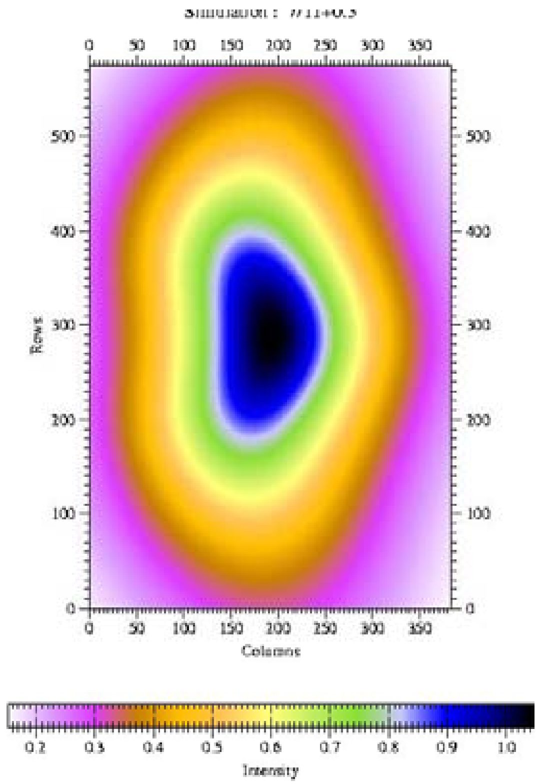


- Slits: S1 60x60 μm ; Circular pinhole D=10 μm
- CCD: Directly illuminated (photon counter); pixel 22x22 μm; $\Delta q = 5.10^{-5}$Å^{-1} ; Total area: 2.10^{-2}Å^{-1}
- Partial coherence 11% ; Flux 10^{9} photon/s

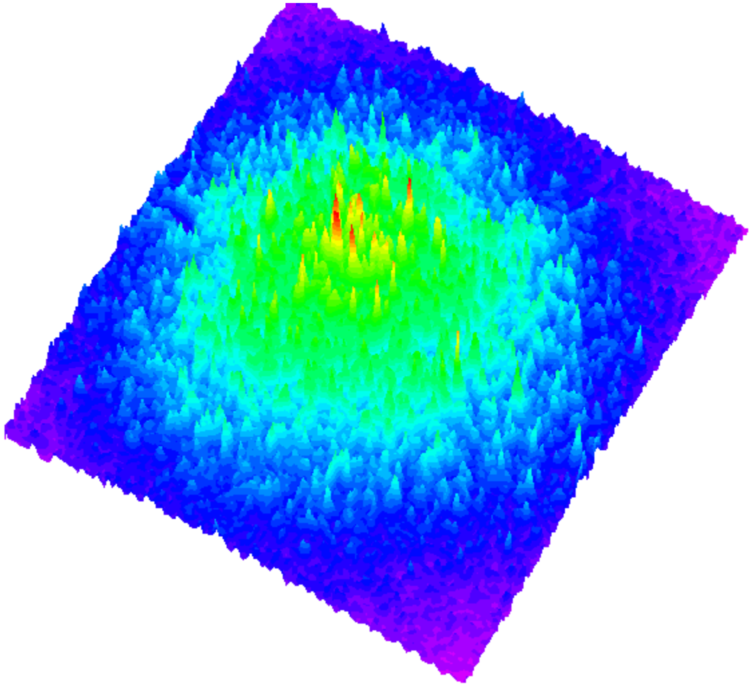
- **Measurement around the 7/11 5-fold reflection (1, t, 0)**
- **Along the direction of maximum intensity: (t,-1,0)**

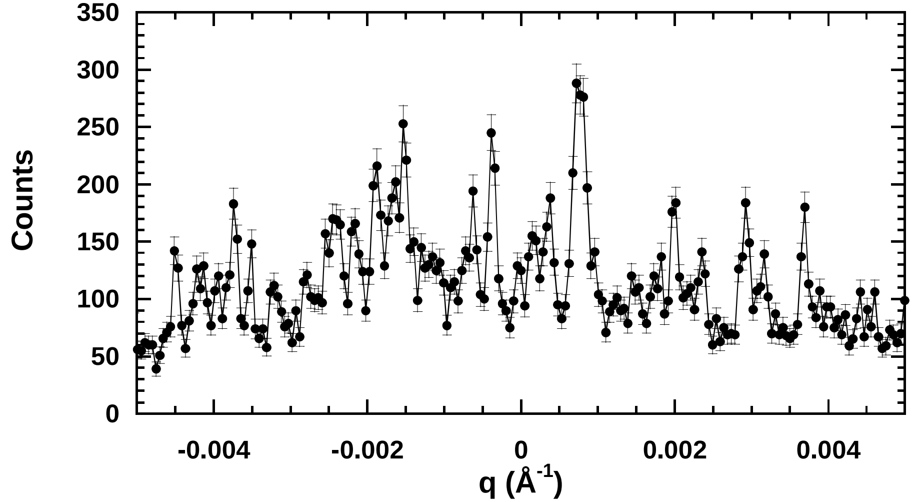






• The diffuse scattering intensity presents a **speckle pattern**

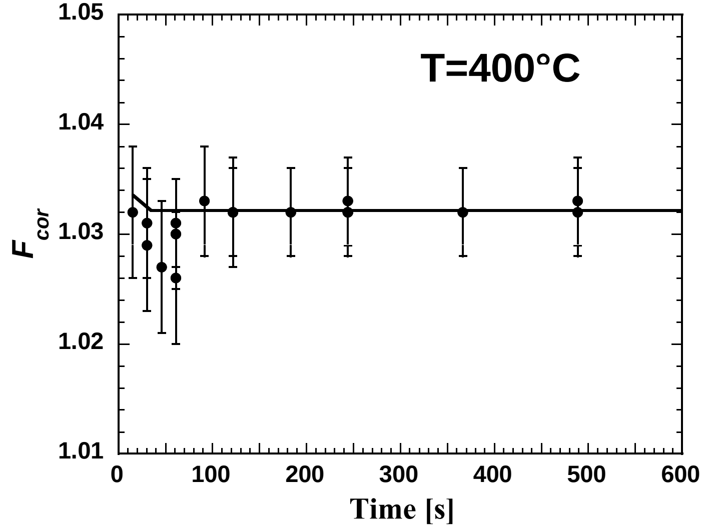




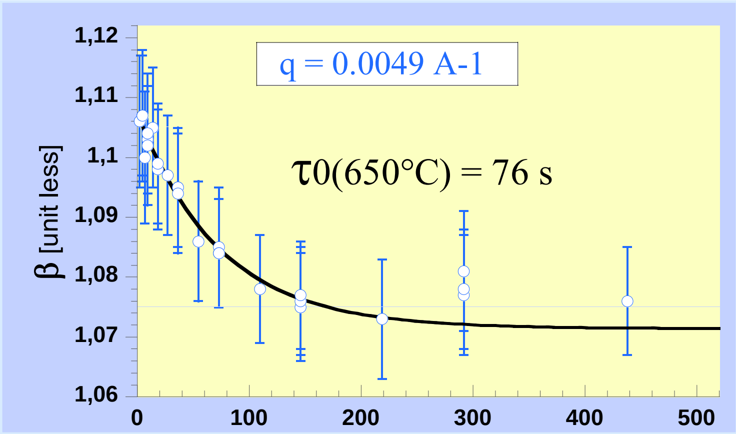
Time dependence of the speckle pattern in the diffuse scattering

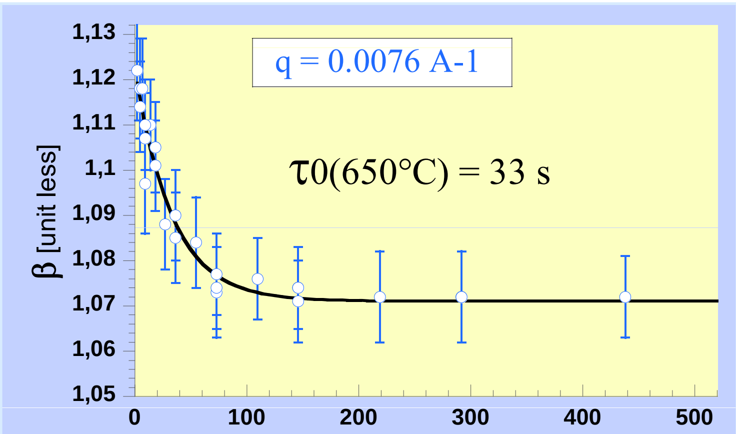
→Time dependence of phason fluctuations.

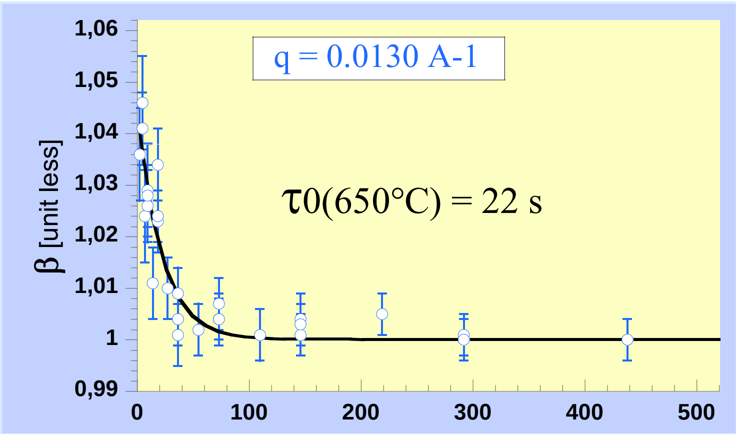
Intensity correlation=f(t)



Aperiodic Crystals







Time dependence of the speckle pattern
T=650°C

- Intensity correlation as a function of time
- Exponential decay fit:

$$F_{correl} = 1 + \beta . \exp(-t/\tau)$$

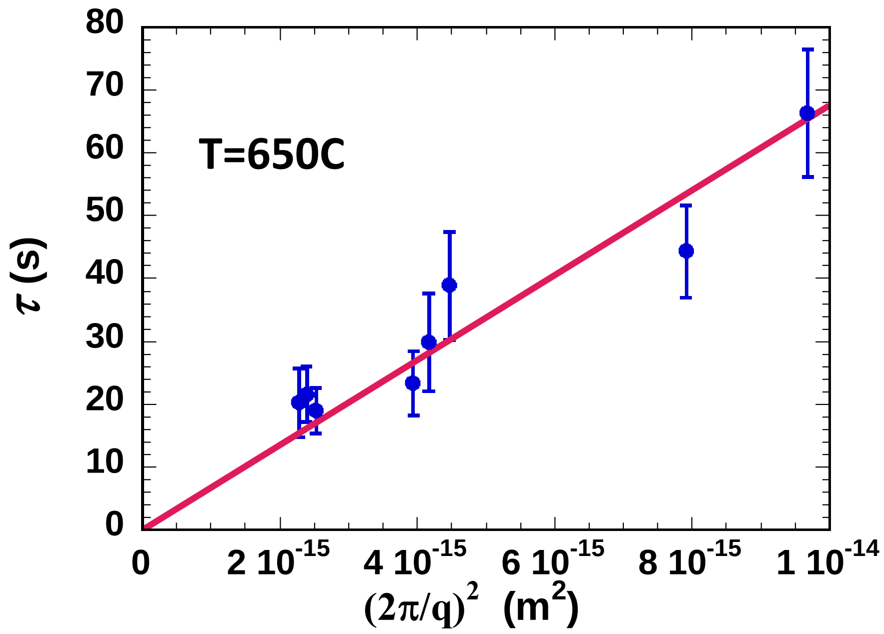
- Such a decay is expected for a diffusive process.

- τ should be proportional to q^{-2}

S. Francoual et al. Phys. Rev. Lett. , 22, 2003

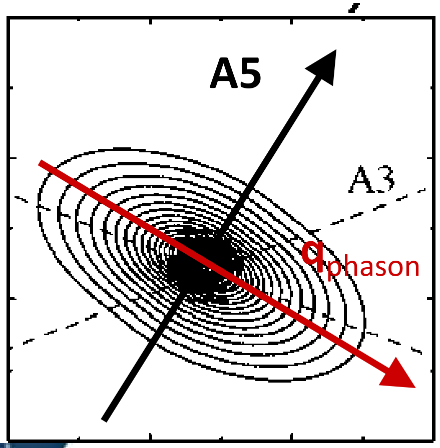
International School on Aperiodic Crystals

Phason fluctuations: a diffusive process



- $D_{phason} = 1/q^2\tau$
- $D_{phason} = 2.2\ 10^{-18}\ m^2s^{-1}$
- Phason 'dispersion curve'

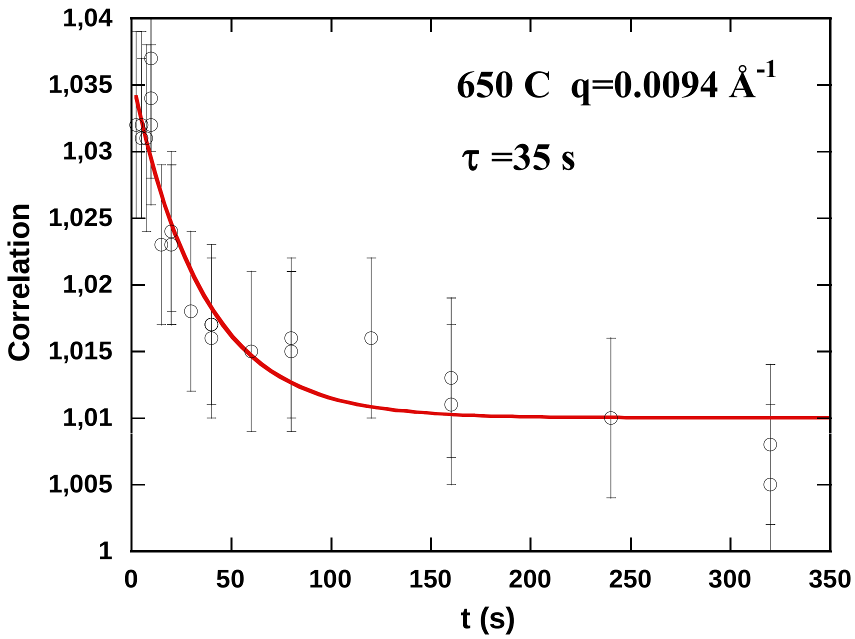
S. Francoual et al. Phys. Rev. Lett. , 22, 2003

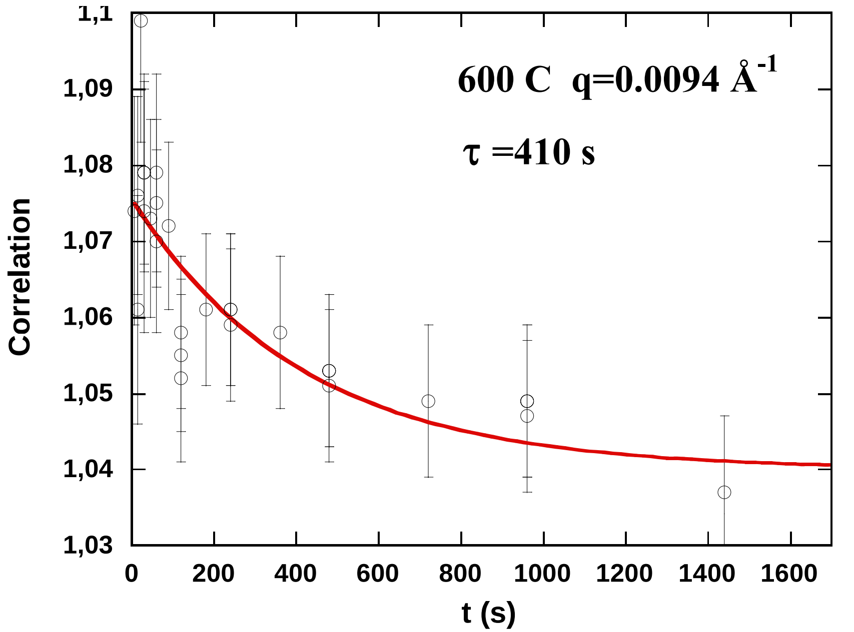


D_{phason} is anisotropic (3 values)

q_{phason}= (-τ,1,0), slow direction

Analogous to sound velocities





Phason fluctuation: Activated process

- Strong variation with temperature
- **Activation energy ~ 3 eV**

D_{phason} = 2.2 10^{-18} m^2s^{-1}

- **Comparison with atomic diffusion**:

Mn is a slow diffuser

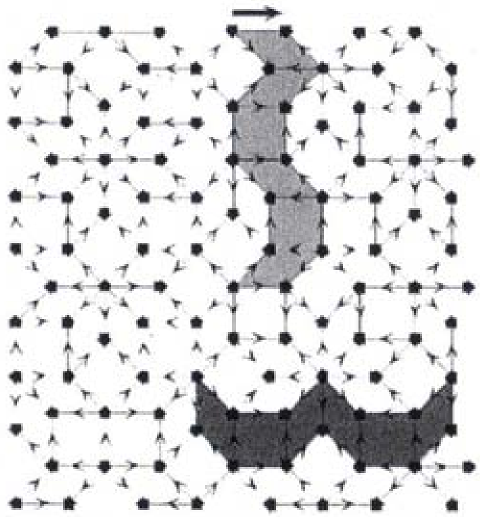
T=650°C D_{Mn}= 10^{-14} m^2s^{-1}

H ~ 2 eV.

(H Mehrer et al.)

International School on Aperiodic Crystals

Mechanical properties

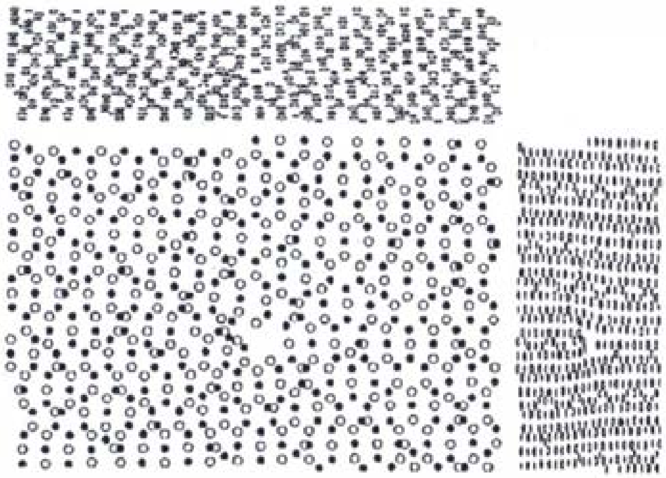


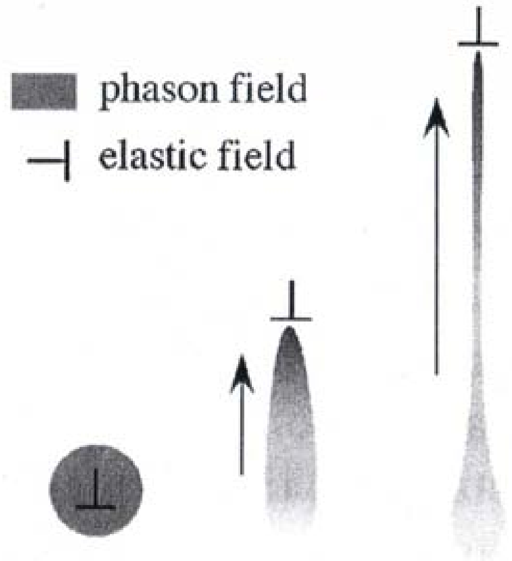
- **Dislocation in quasicrystal:**

Elastic field + Phason field

- **Plasticity: phason 'wall'**

(from Caillard et al.)

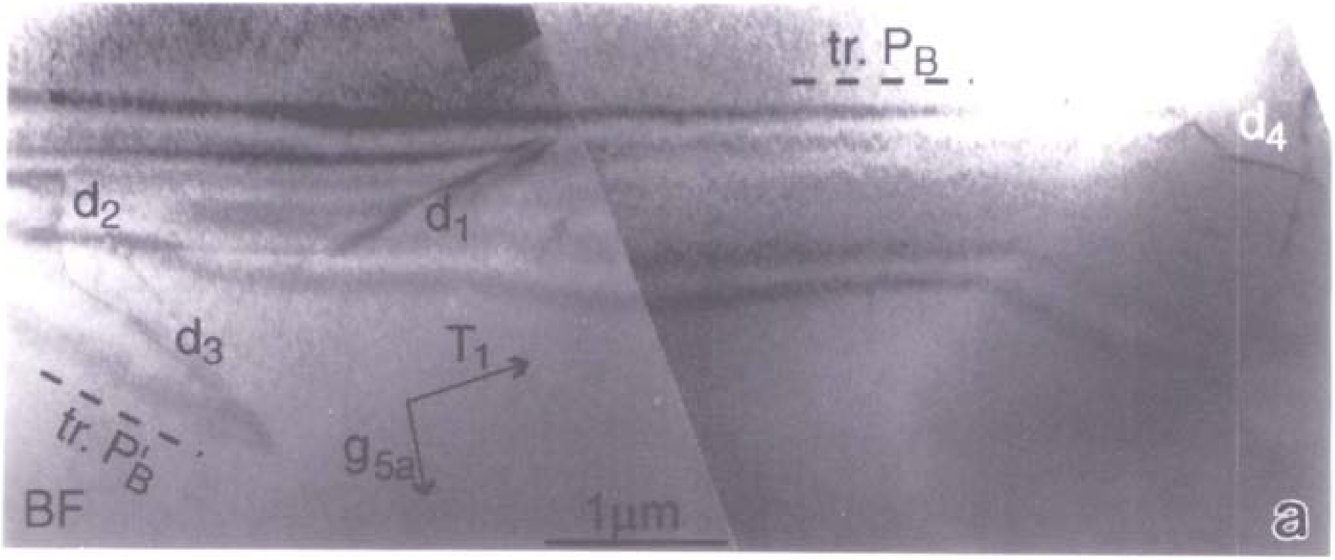


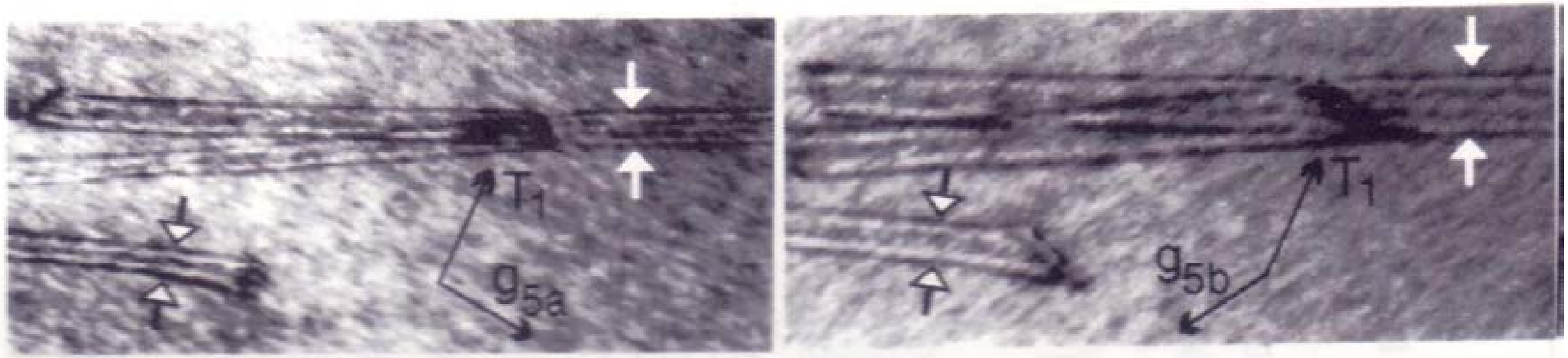


HREM Images: Phason walls

(Feuerbacher et al.; Wang et al.; Caillard et al.)

Relaxation at high T through phason fluctuations





Aperiodic Crystals

Dilaocation motion: Relaxation of phason walls (Caillard et al.)

Time scale compatible with phason diffusion.

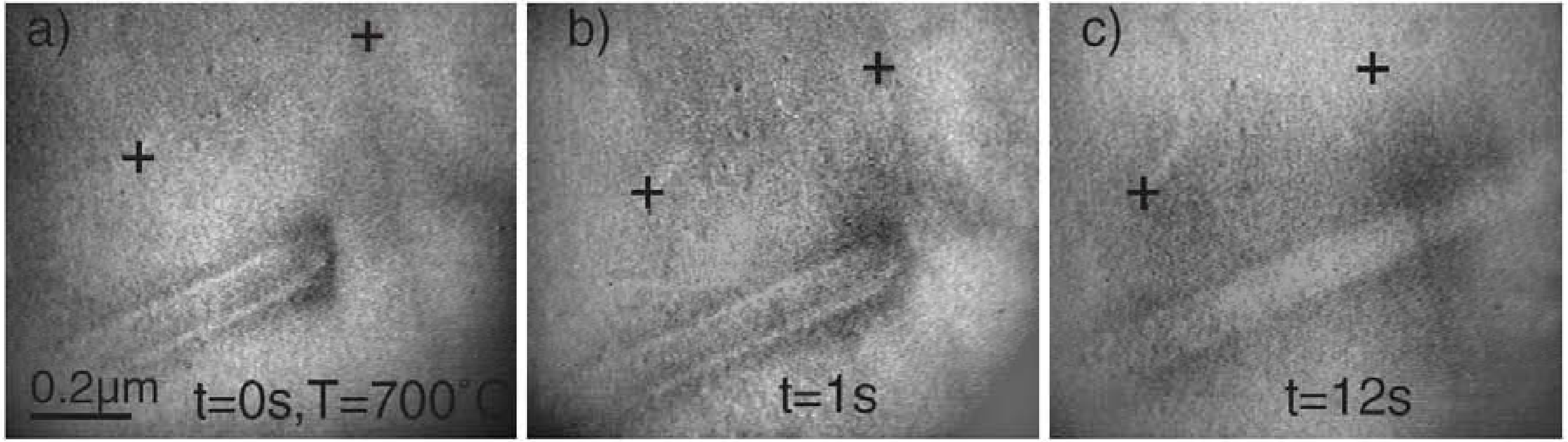


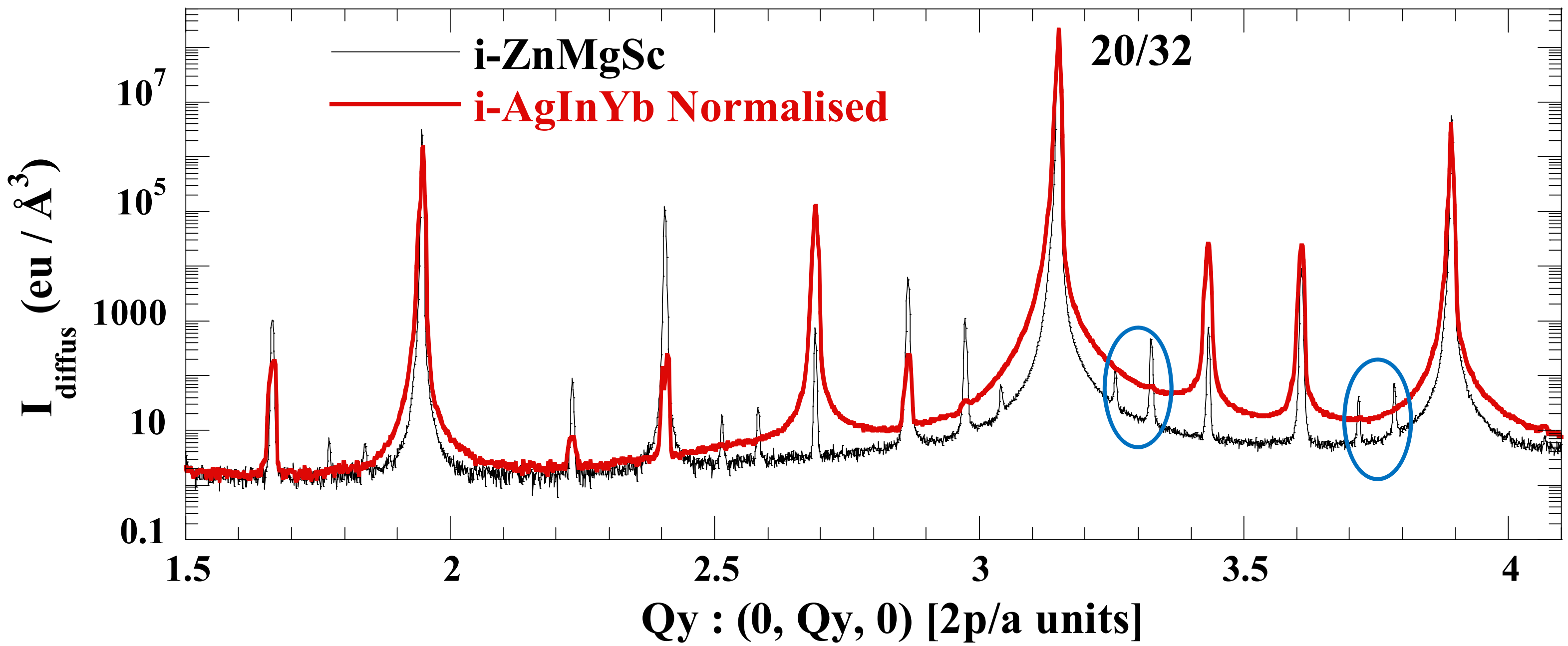
Figure 1. Dislocation motion in a twofold plane at 700°C. Note the fringe contrast behind the moving dislocation in (a) and (b), which has disappeared in (c). The crosses indicate fixed points in the sample.

International School on Aperiodic Crystals

i-AgInYb and i-ZnMgSc

- i-ZnMgSc (Ishimasa), very small diffuse scattering intensity (PRL,2005,95, 105503) . High Qperp Bragg: Qper=7

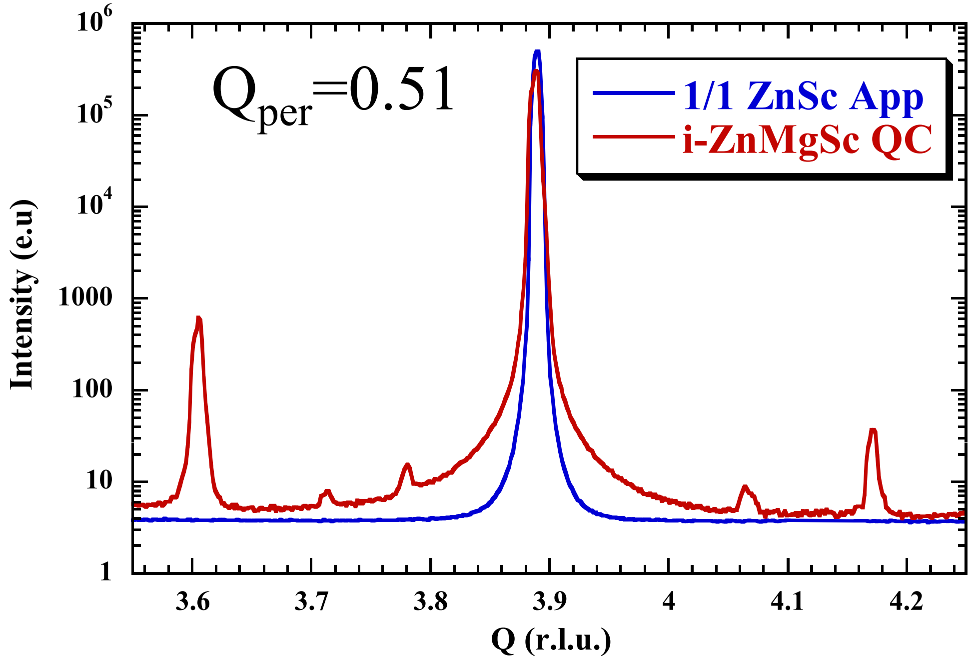
2-fold Q-scan



- i-AgInYb absolute scale and rescaled for Bragg peak power
- ***More diffuse scattering in i-AgInYb QC than in i-ZnMgSc***
- High Qper Bragg have disappeared. Qper max= 5

Diffuse scattering in QC and approximant

- Long wavelength phason fluctuations are a **consequence of the long range aperiodic order**
- A priori no phason diffuse scattering in periodic approximant
- Only one study: 1/1 Zn_6Sc as compared to i-ZnMgSc (S. Francoual, T. Ishimasa)



1/1 Zn6Sc approximant:

Only phonon diffuse scattering

No phason diffuse scattering

PRL,2005,95, 105503

Summary

- Phason modes are propagative modes in incommensuratly modulated phases, but with a finite width. Diffusive mode in the low q, long wavelength limit
- Composites. Sliding modes?
- Quasicrystal:

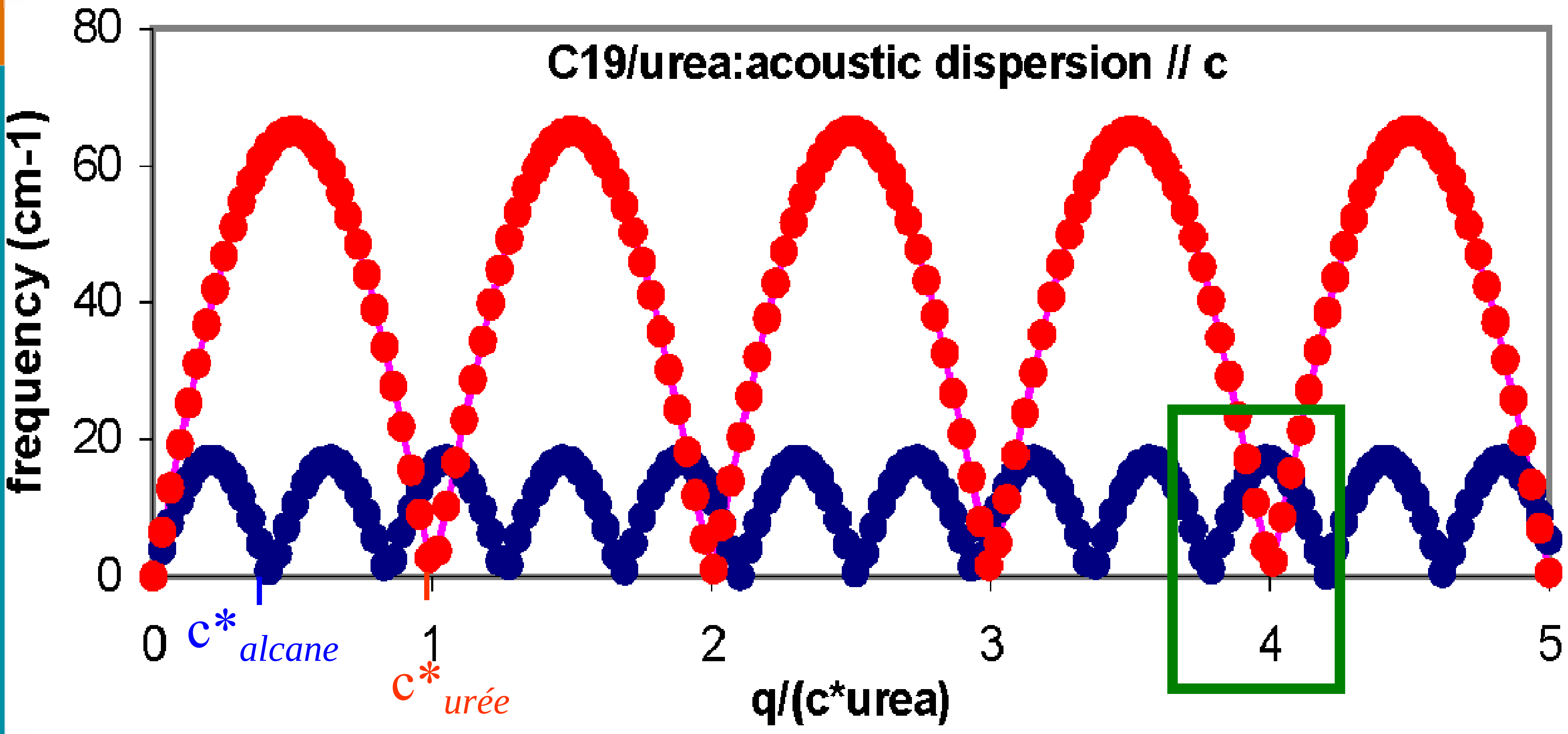
- Phason modes observed by diffuse scattering
- i-AlPdMn PDS due to pre-transitional fluctuations
- Phason dynamics is diffusive as measured by x-ray
- Different QC, present different PDS

PHONONS

- Incommensurately modulated phases

  new dynamic related to phason modes.
- Composites
- Quaiscrystals

Phonon in incommensurate composite

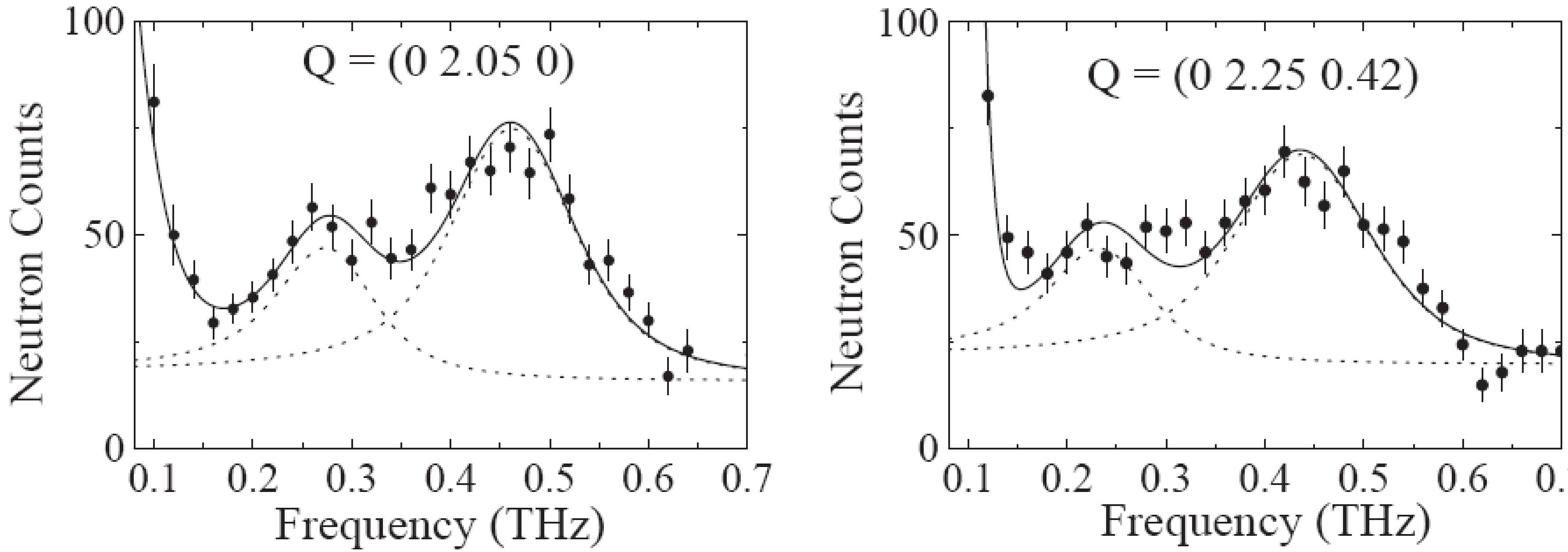


In aperiodic crystals, the Bragg peaks of the two sublattices never superimpose, but in zero.
The Bragg peaks do not define anymore a Center of Zone, since there are no more Brillouin Zone.

Composites

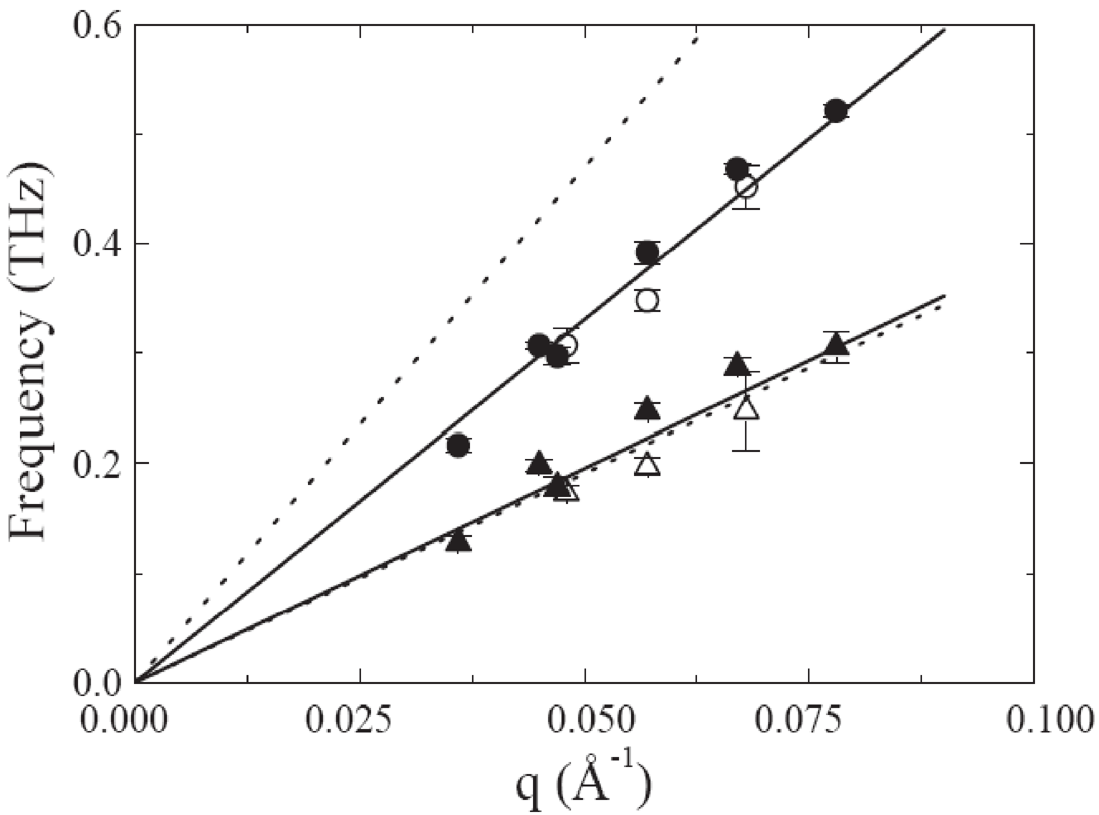
Low-frequency structural dynamics in the incommensurate composite crystal $Bi_2Sr_2CuO_{6+\delta}$

J. Etrillard[1,2], L. Bourgeois[1], P. Bourges[1], B. Liang[3], C. T. Lin[3] and B. Keimer[3]



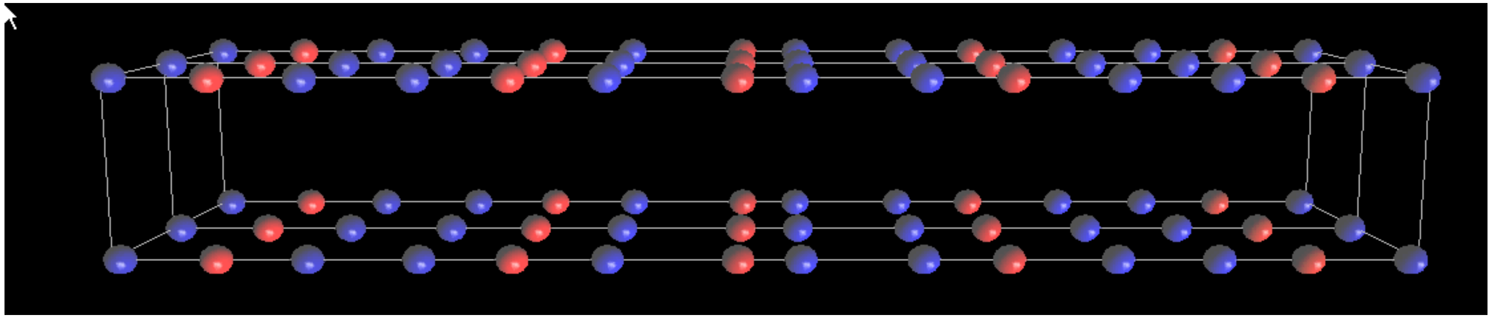
Composites

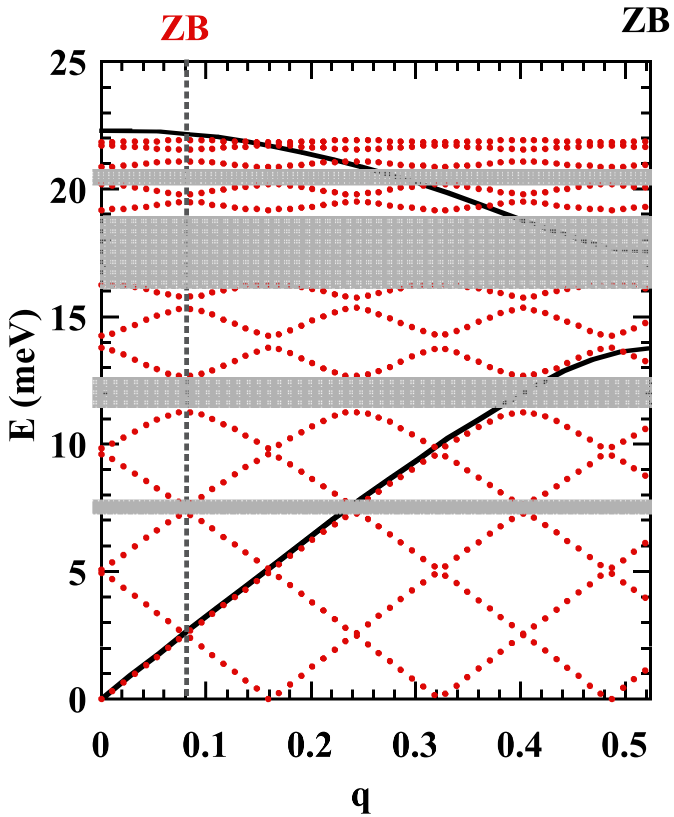
- The two sublattice react independently
- Two sound velocity
- Sliding modes?



Phonons in quasicrystals

International School on Aperiodic Crystals



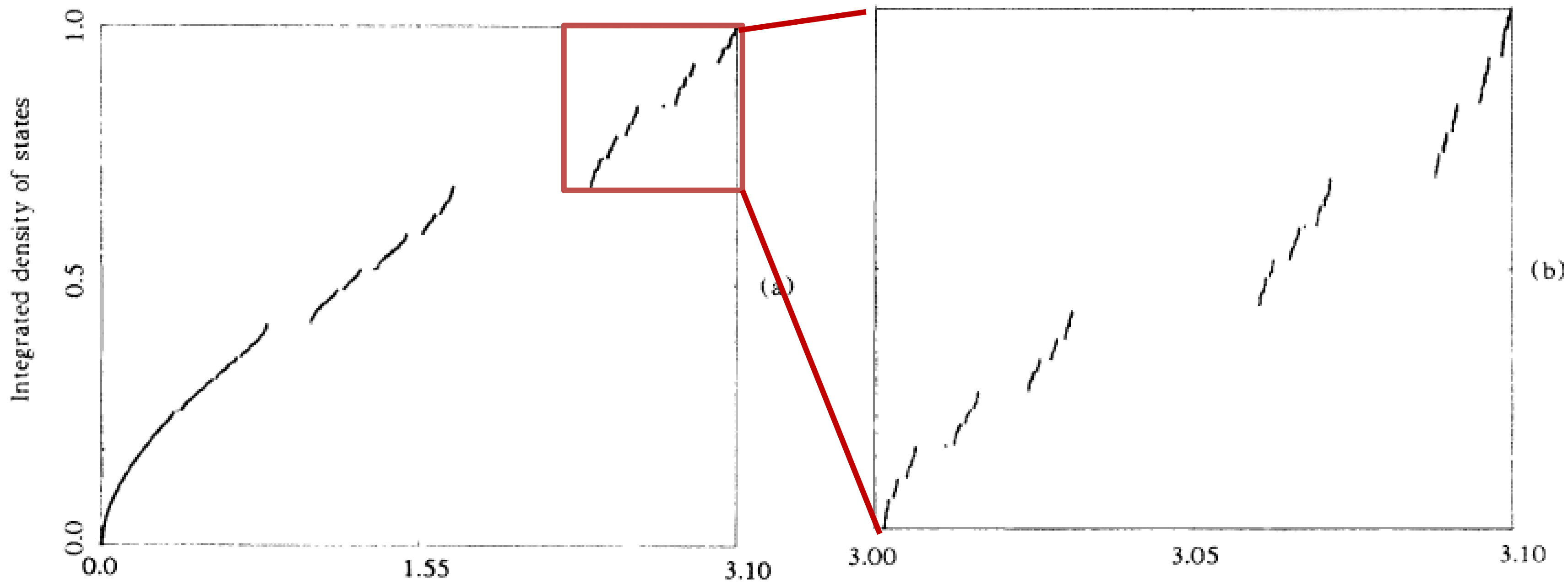


Phonons: 13 atoms

LSLLSLSLLSLLSL

- 13 ‘Branches’
- New gaps opening
- Large gap around 17 meV + optic ‘bands’
- Smaller gap around 13
- E< 10 meV : acoustic character

Phonon: 1D quasicrystal

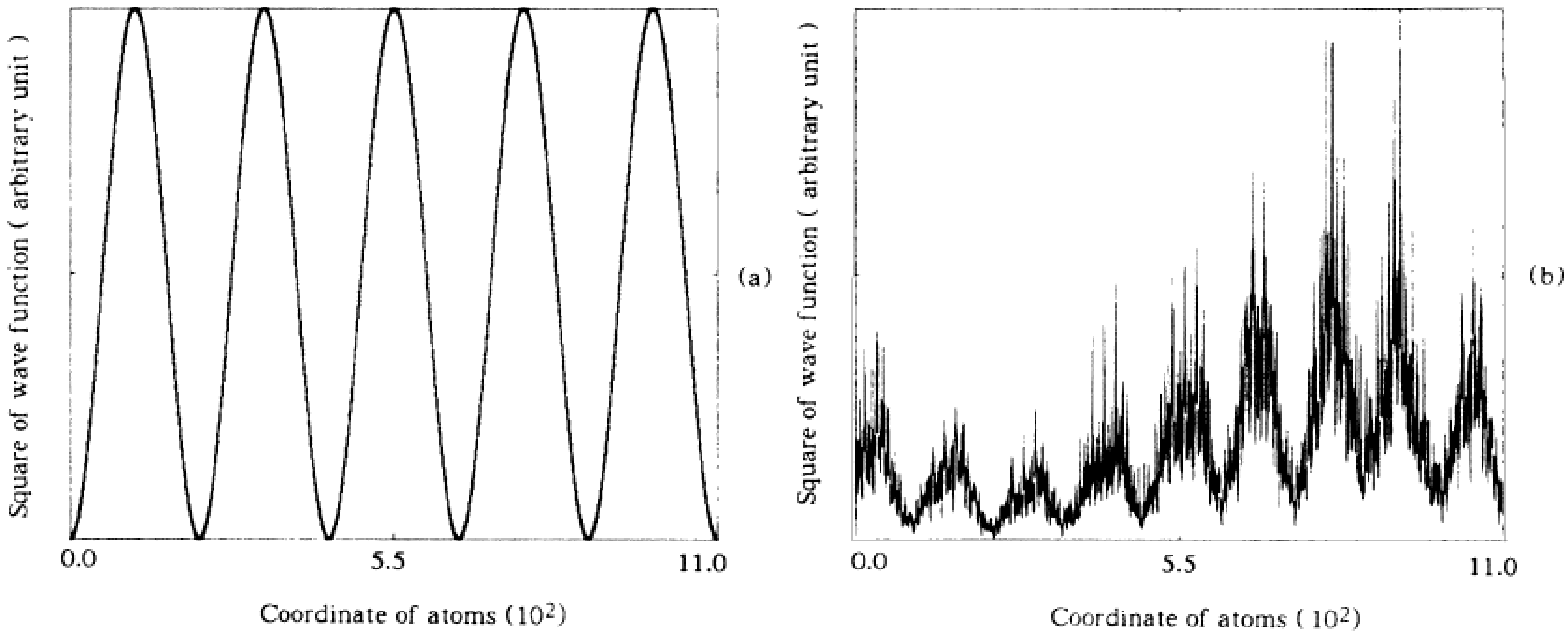


- Long wavelength: acoustic modes.
- Infinity of gap opening and self similarity

From Lu, Odaki and Birman, PRB, 1986, 33, 4809

Phonon: 1D quasicrystal

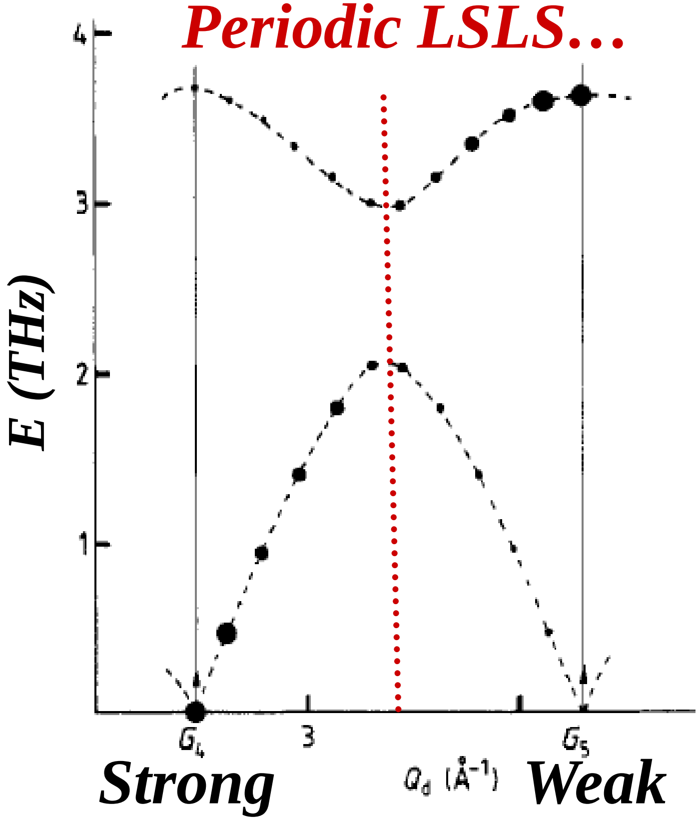
Higher energy: **modes are critical**: neither localised, nor extended. The eigenvector decays with a power law and recursion around similar environment.

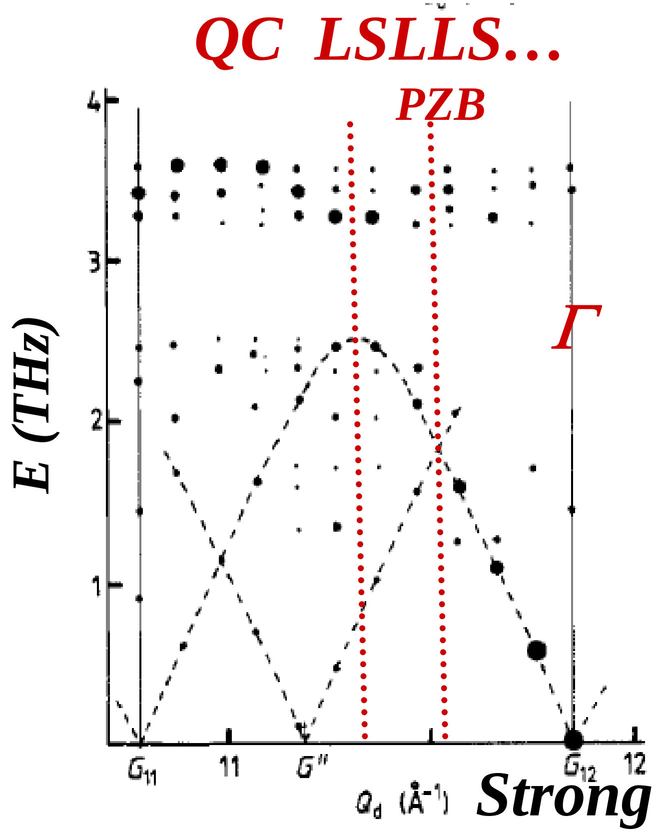


From Lu, Odaki and Birman, PRB, 1986, 33, 4809

Inelastic neutron scattering: Fibonacci chain

(From Benoit and Poussigue)

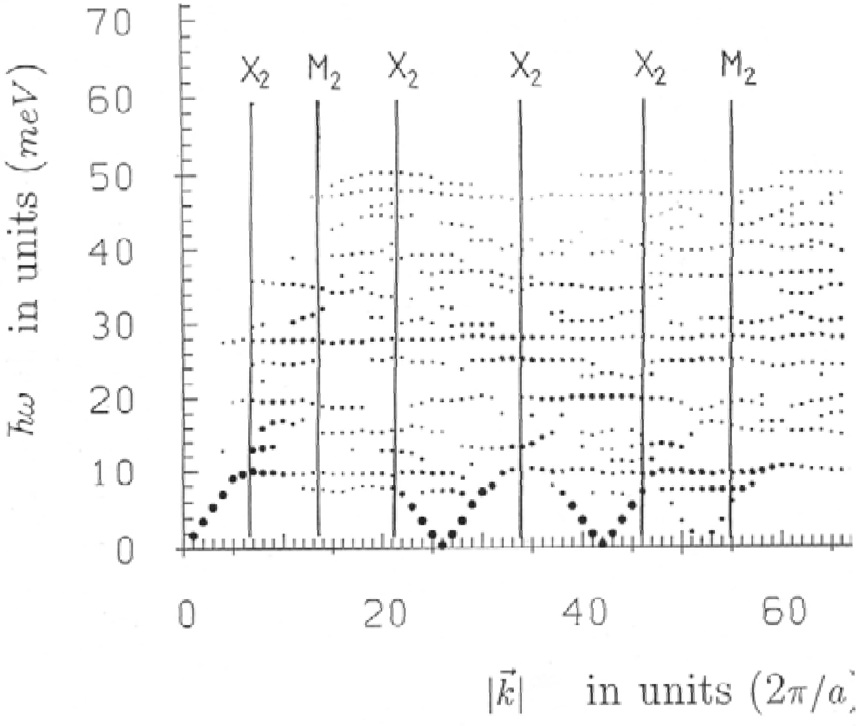




- ***Acoustic mode*** : S(**Q+q**) ~ $I_B Q^2/E^2$; Norme=S(**Q+q**)*E^2=cte
- Fibonacci chain: **Strong Bragg=Zone center** (Γ); Pseudo zone boundary (PZB)

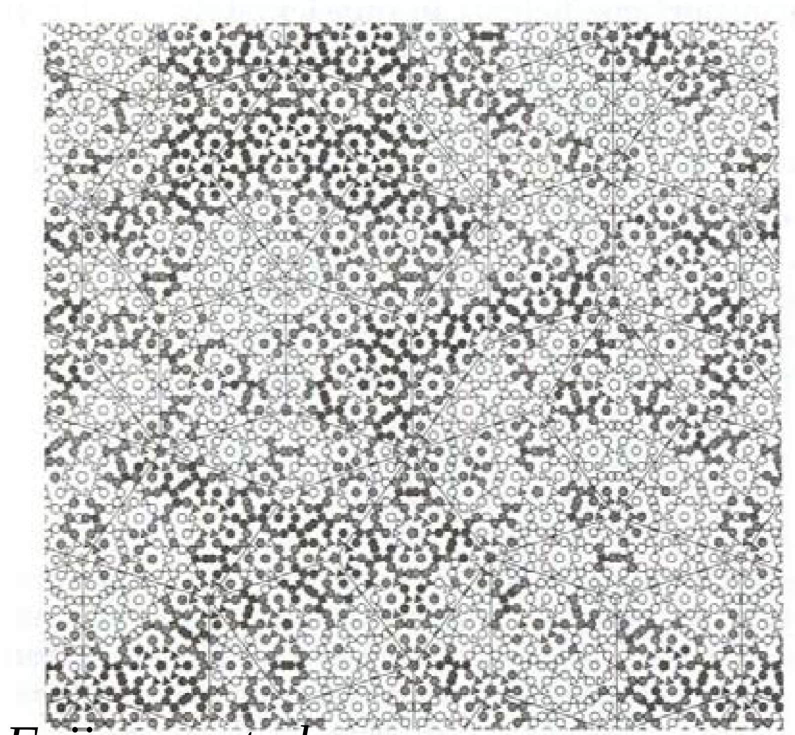
3D QC Systems

- **Acoustic mode**
- **Pseudo-zone boundary (Niizeki)**
- **Critical modes?**



AlLiCu 5/3 approximant simul.

(Krajci et al.)

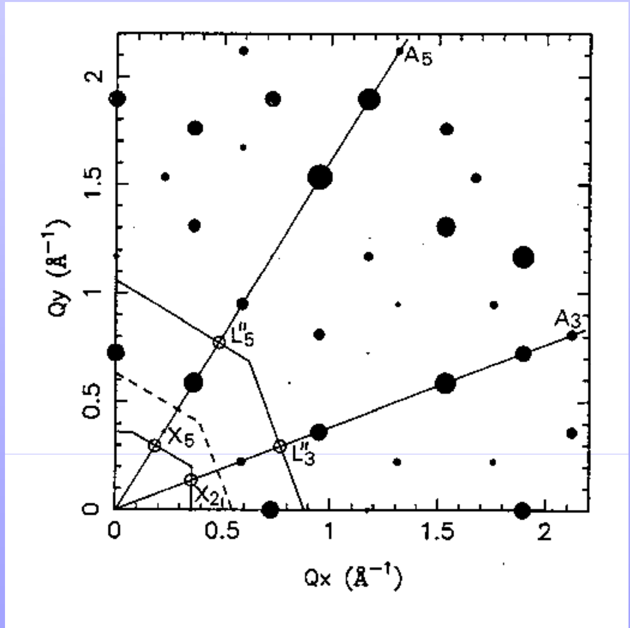


Fujiwara et al.

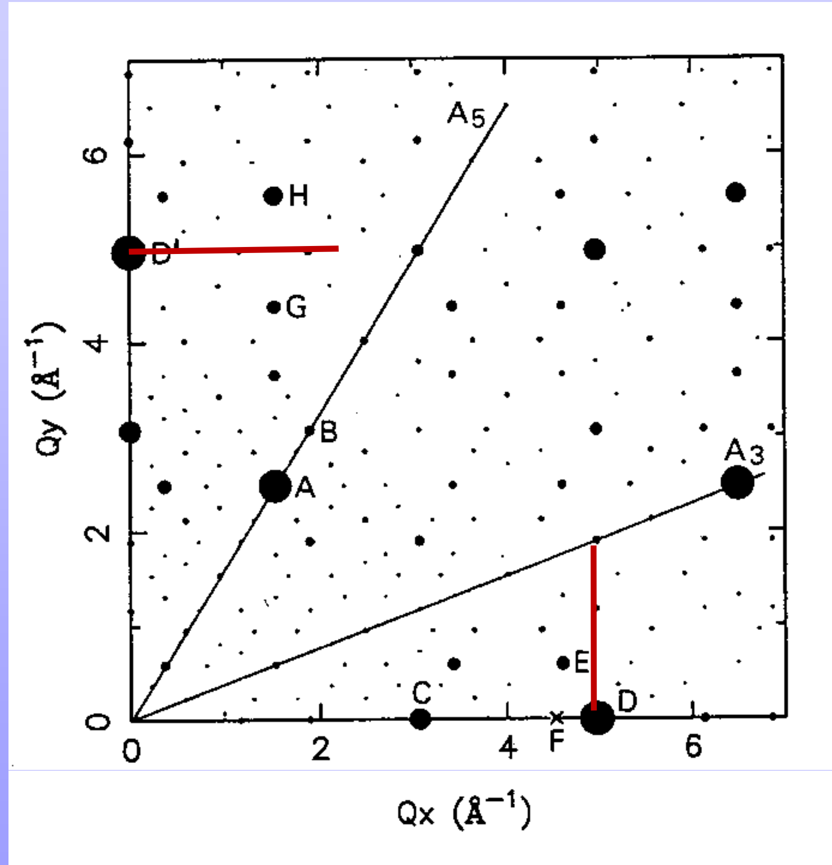
Critical modes: Neither localised nor delocalised.

i-AlPdMn phase

Pseudo Brillouin Zone Boundary Map (Niizeki)



2-fold diffraction pattern



Around each strong Bragg peak (zone center) : **stacking of PZB.** At the PZB: **stationnary mode** (Bragg reflected wave)

Acoustic mode

- In the long wavelength limit (continuum), there are acoustic phonons. Because of the icosahedral symmetry, there is an isotropy: 2 sound velocities, one transverse and one longitudinal.

Inelastic neutron scattering intensity. **Q=G+q**

$$I(\mathbf{G}+\mathbf{q}, \omega_q) \sim I_b(\mathbf{Q}.\mathbf{e}_{T(L)})^2/\omega_q^2$$

I_b : Bragg peak intensity; q phonon wavevector; ω_q Phonon energy, $\mathbf{e}_{T(L)}$ Phonon polarisation. **SELECTION RULE**

- *For an acoustic branch:* $I_{ph}\omega^2 = cte$ this define the acoustic regime

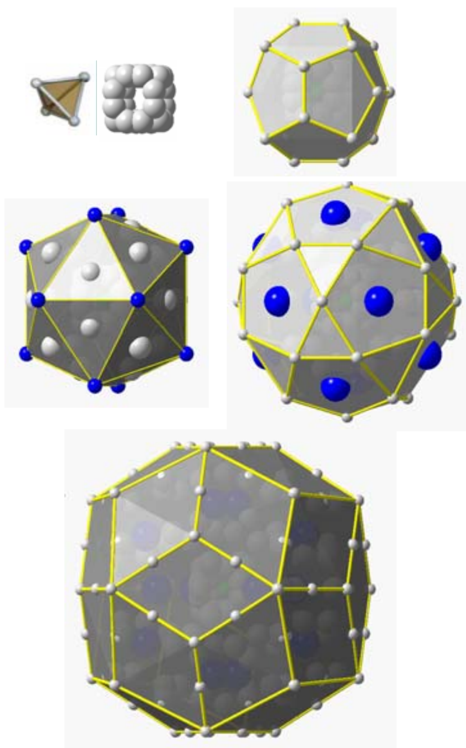
Phonons in i-ZnMgSc and c-ZnSc Quasicrystal specific?

- System isostructural to CdYb
- i-$Zn_{80.5}Mg_{4.2}Sc_{15.3}$ QC and $Zn_{86}Sc_{14}$ 1/1 approximant
- Respective influence of local order (clusters) and long range periodic or quasiperiodic
- Study by inelastic neutron and x-ray scattering on single grain samples.

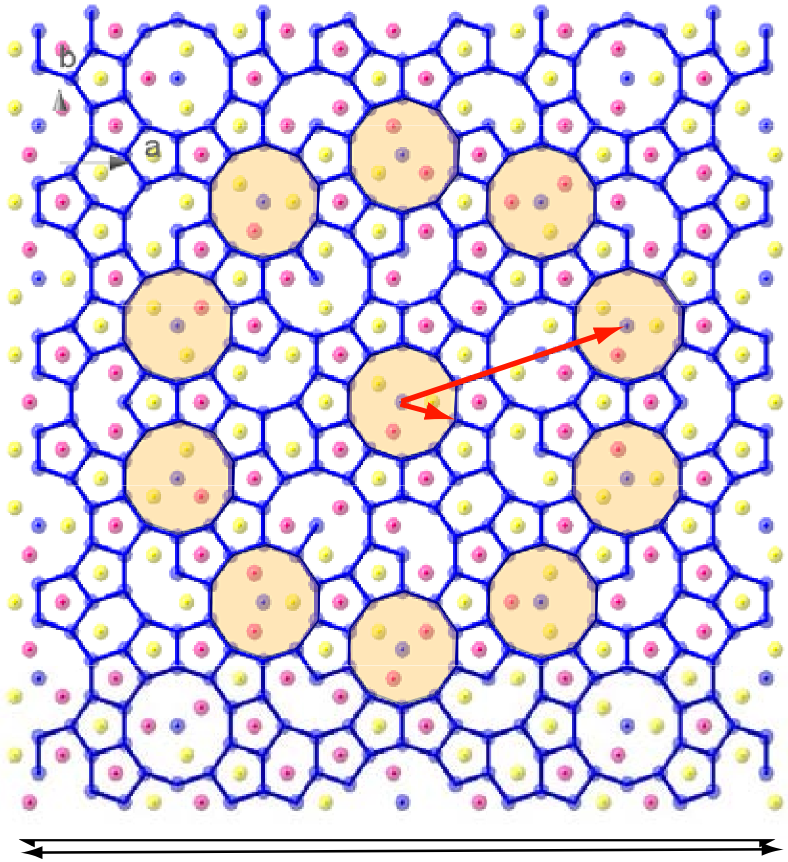
Quasicrystal structure

- ***Clusters*** packing with well defined chemical order: ***94% of atoms***
- Hierchical packing of the clusters in the QC

(Periodic packing in 1/1 approximant)

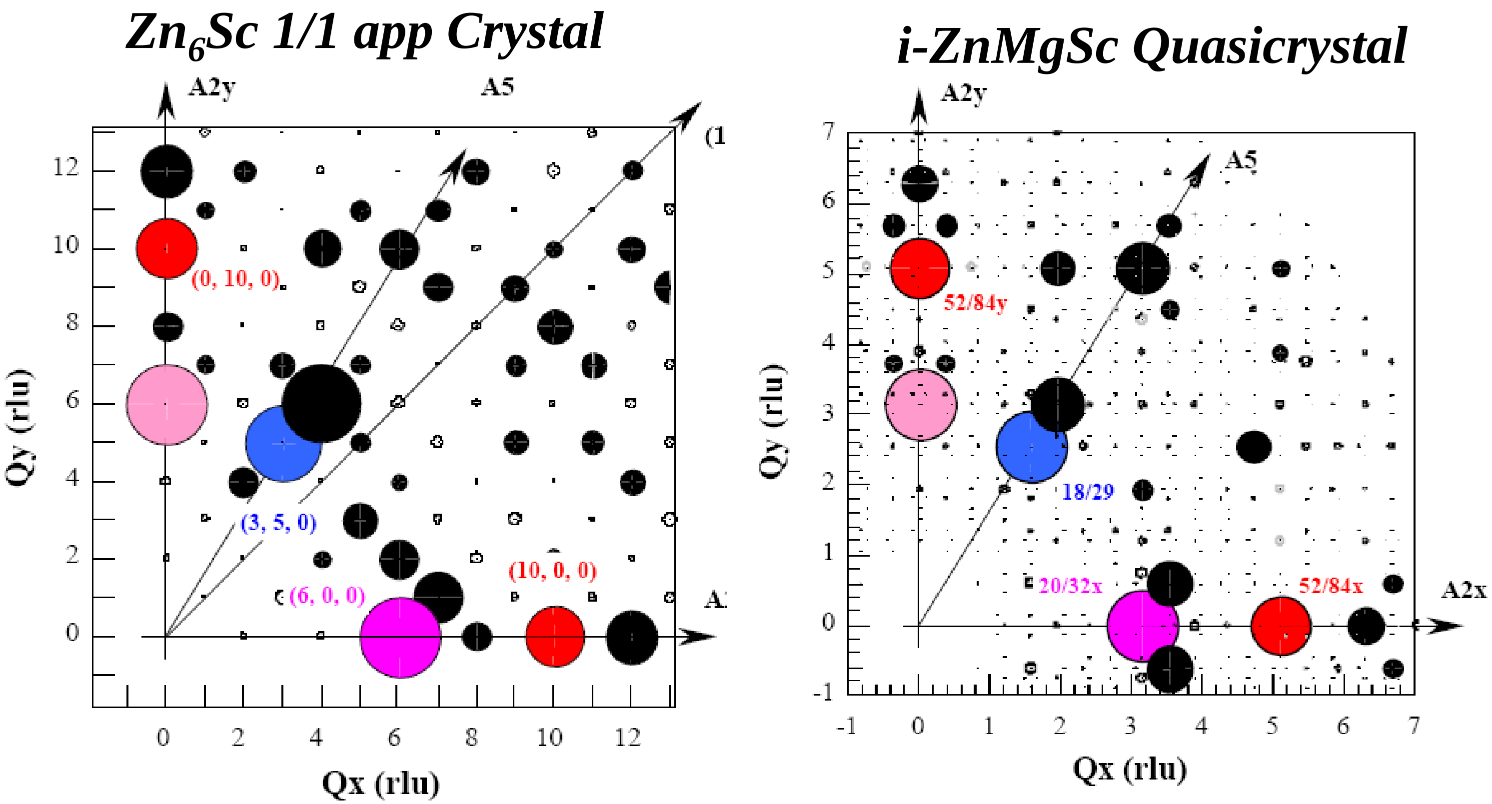


1.6 nm



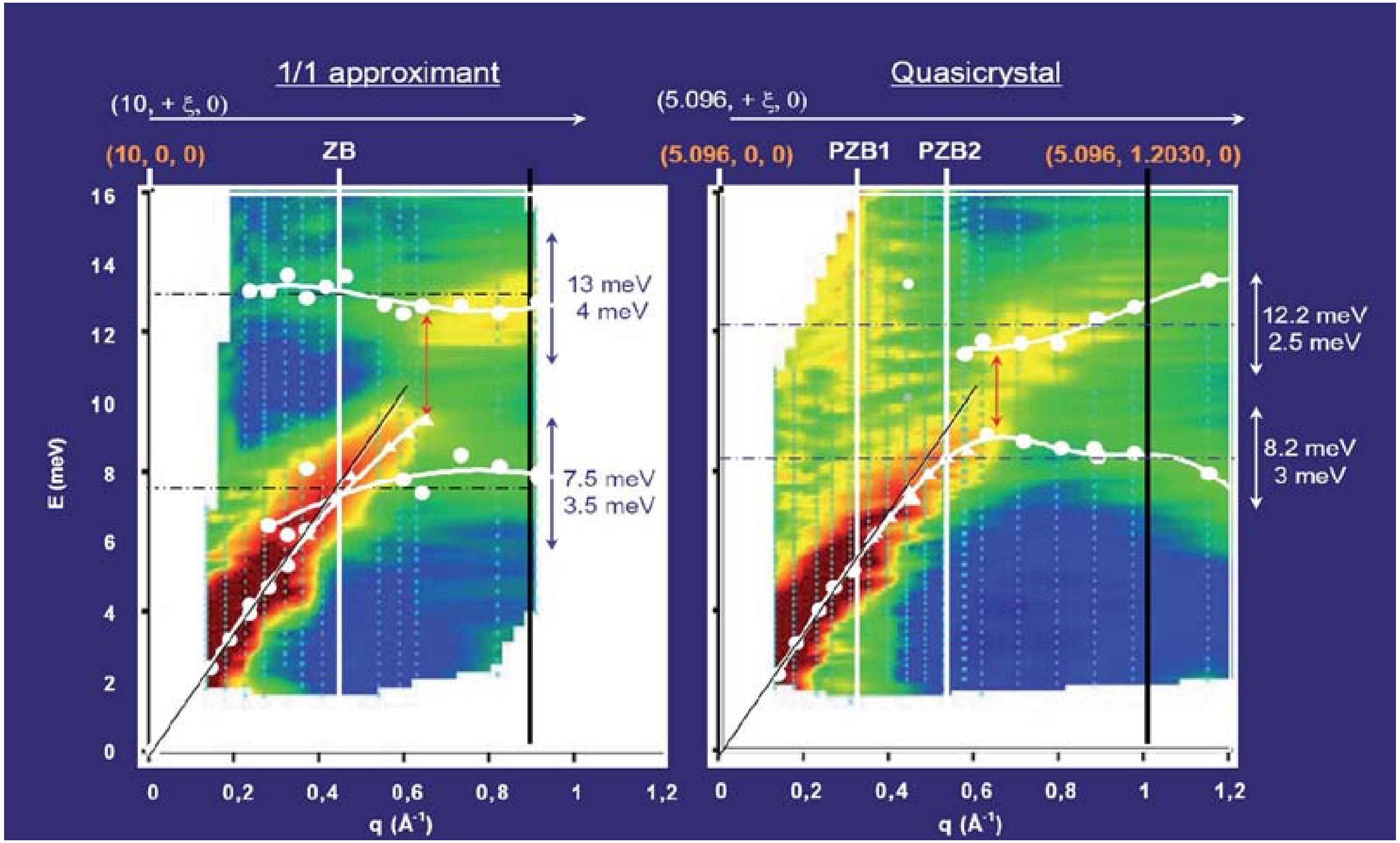
34 nm 34 nm

ZnSc: Comparison 1/1 approxt and QC



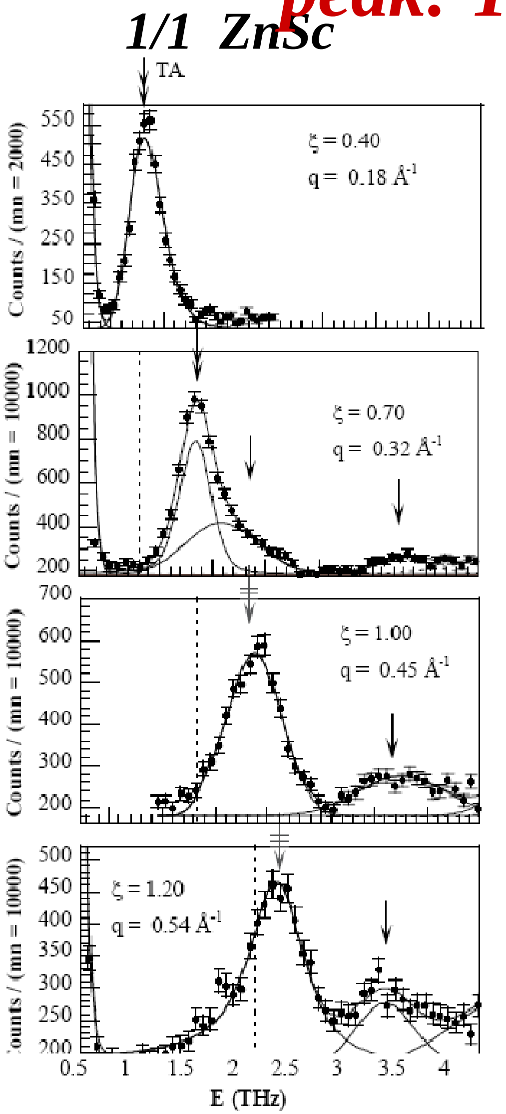
Same clusters: effect of local order and long range periodic or QP order.

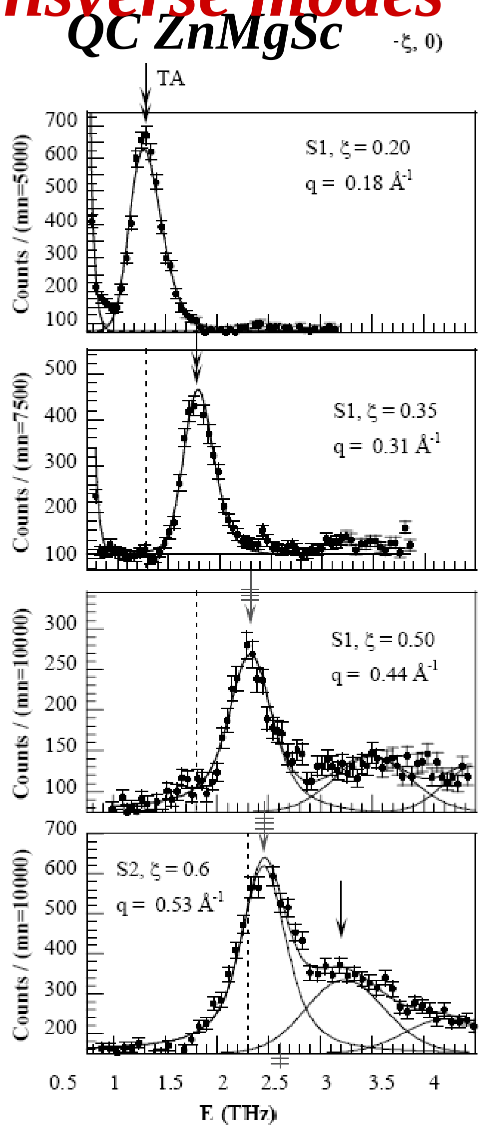
Experimental transverse phonon



- ***Pseudo gap observed in both QC and approximant***
- ***Pseudo gap is larger in the approximant***
- ***Related to the distribution of Brillouin zone and PBZ***

Inelastic neutron scattering close to a strong Bragg peak: Transverse modes





Well defined acoustic modes

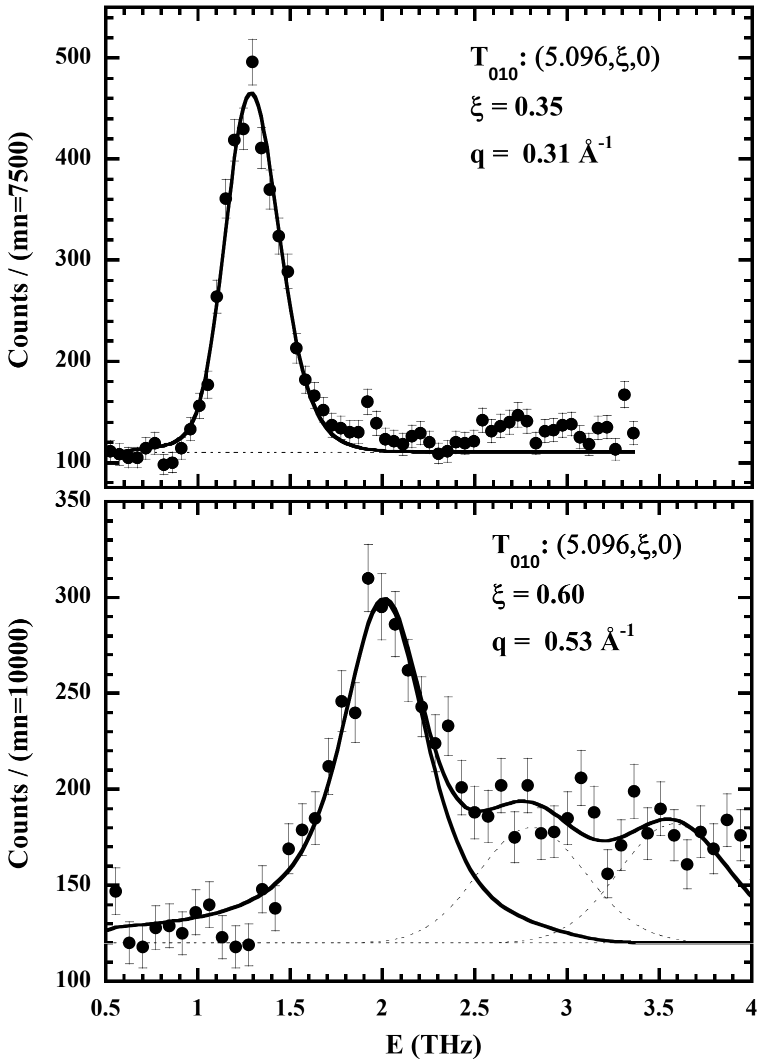
Abrupt broadening

Very similar in both cases

Optic modes are better defined in the 1/1 crystal

Acoustic mode broadening rate

i-ZnMgSc



i-ZnMgSc

- ***Abrupt broadening*** q>0.30 $Å^{-1}$
- q=0.31 $Å^{-1}$: ***λ=20 Å***; mean free path ***<l> ~ 160 Å***
- q=0.53 $Å^{-1}$: ***λ=12 Å***; mean free path ***<l> ~ 20 Å***
- ***Intensity: Norme increases : mode mixing.***

c-ZnSc

- Similar broadening, but larger mean free path.

- This abrupt broadening is observed in all other quasicrystals

- **i-ZnMgY**: **abrupt cross-over** between the acoustic regime and mixing of several states.

- ***Acoustic limit*** : **MEAN FREE PATH ~24 Å**

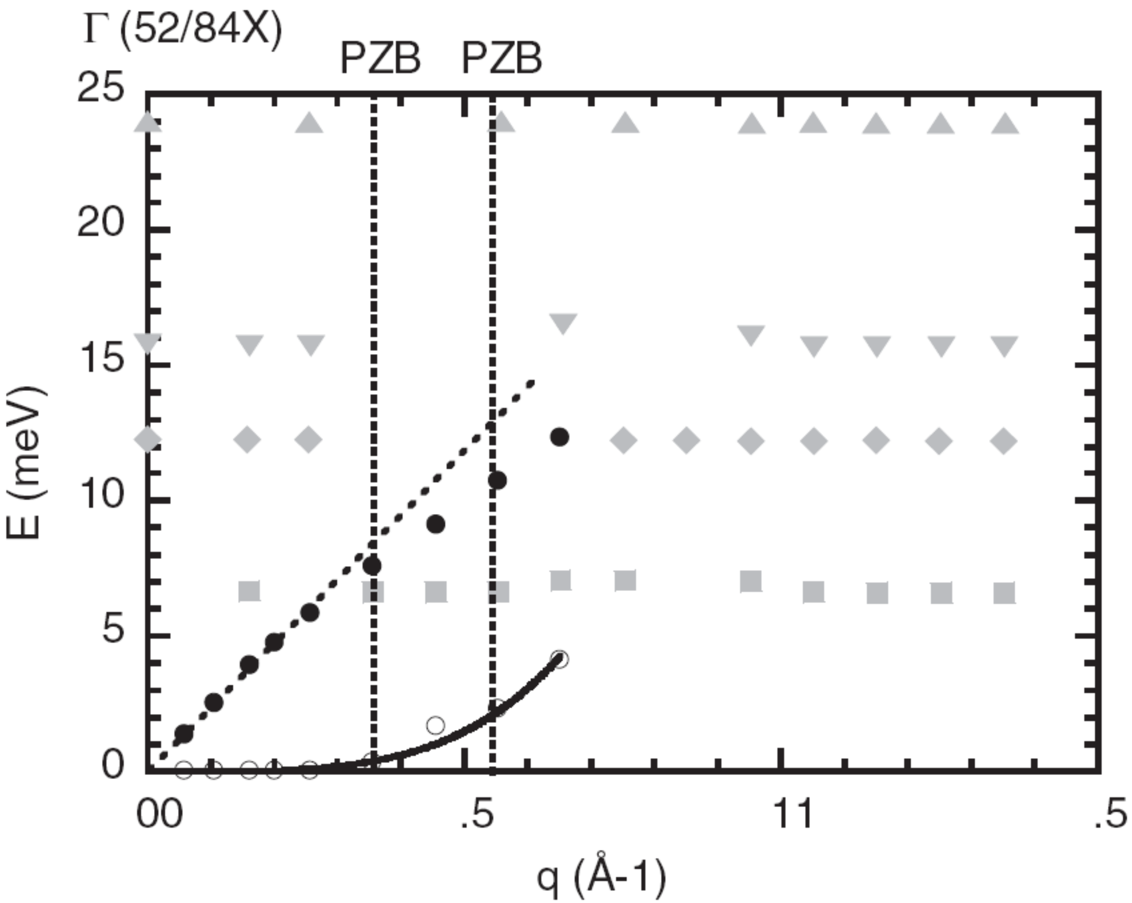
  Cluster diameter Dcl ~ 12 Å

  Wavelength Dcl; mean free path 2Dcl

- **i-AlpdMn: crossover for the same wavelength, but the mean free path is smaller ~ Dcl**

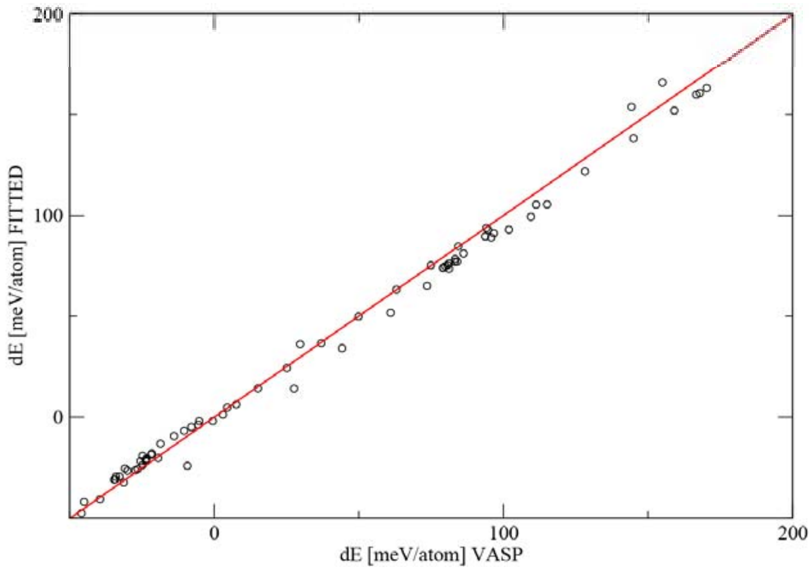
Phonons: i-AlPdMn

- Dispersion relation and Pseudo Brillouin Zones
- Abrupt broadening of acoustic excitations

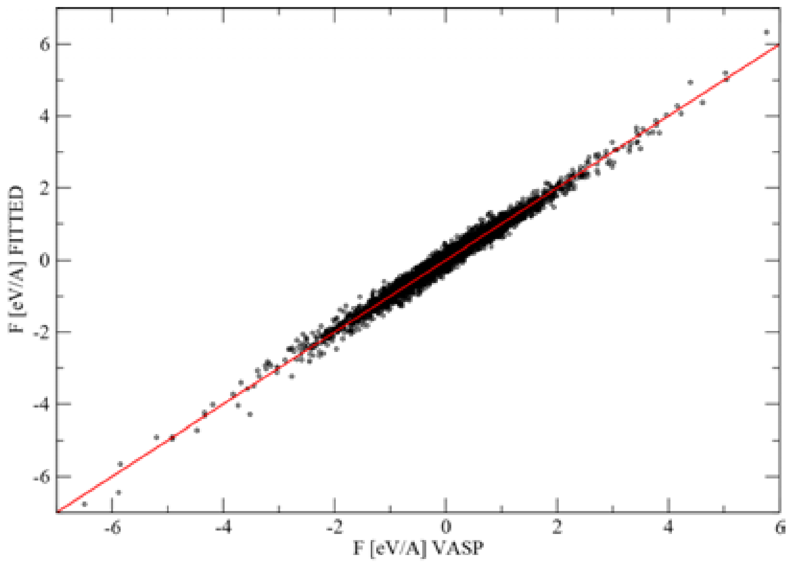


Simulations: ZnSc

- Ab initio limitations to ~ 100 atoms/cell.
- Adapted Hamiltonian is necessary : oscillating pair potentials.
- Allows to study large cells up to several 1000 atoms.
- Pair potentials fitted on a DFT data base (VASP) containing all simple phases in ZnSc. Fitting on E and Forces



Energy

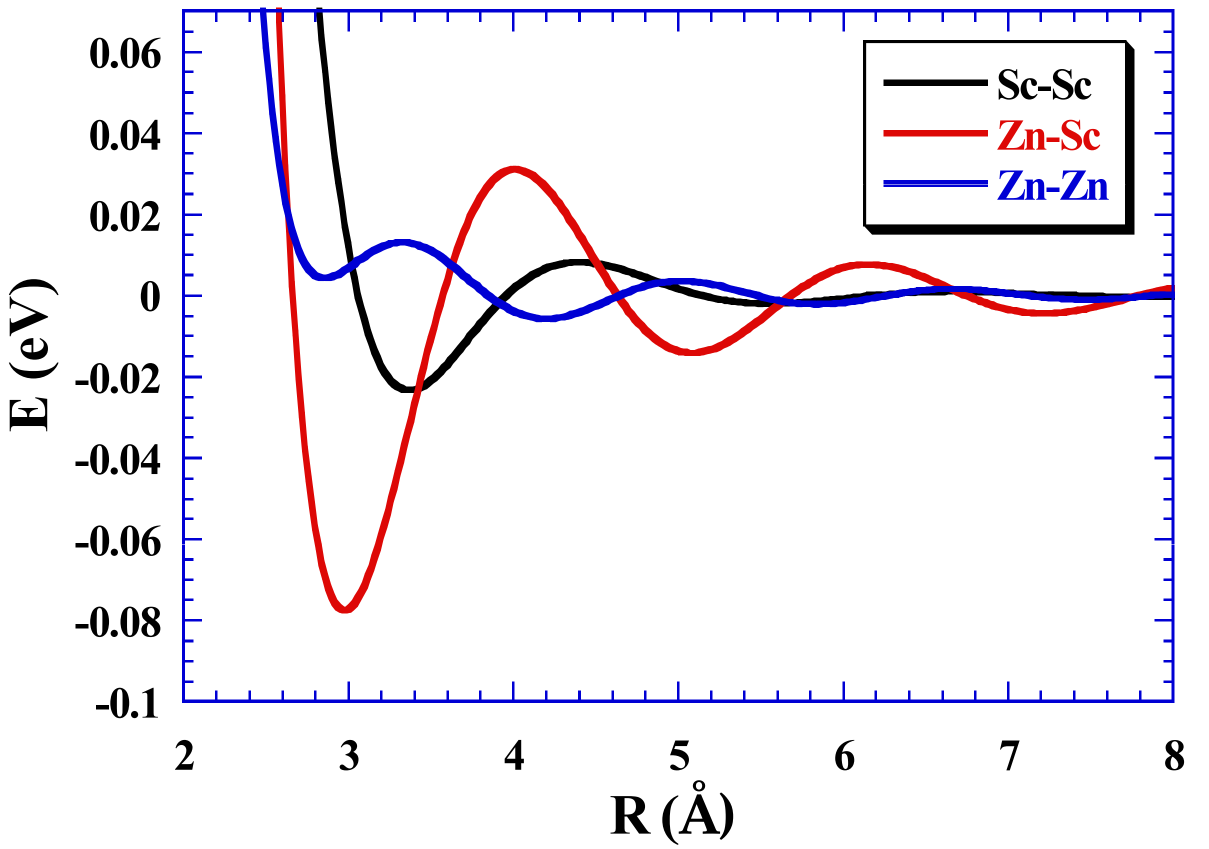


Forces

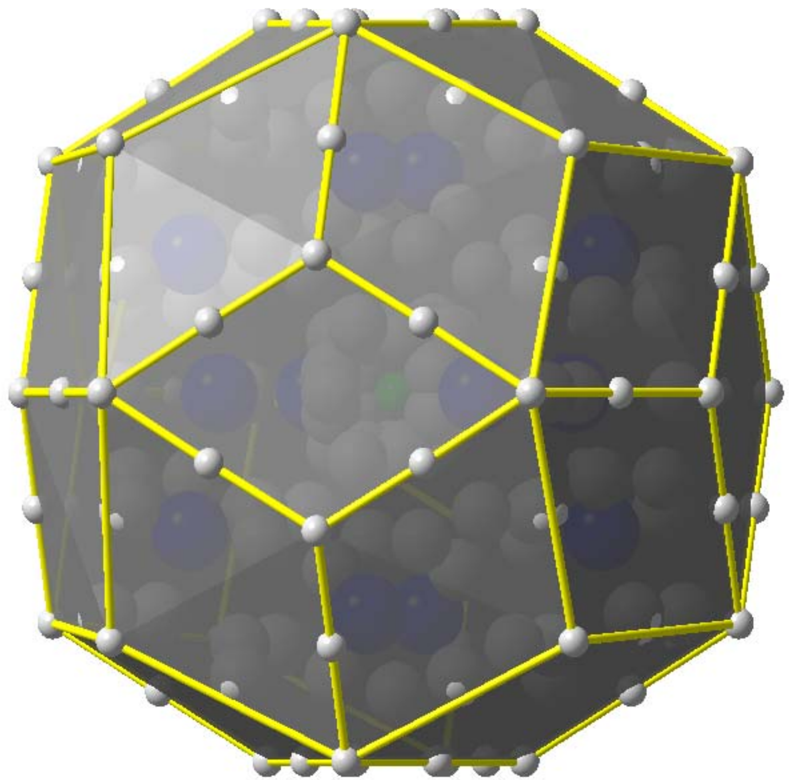
Oscillating pair potential

M. Mihalkovic, C. Henley et al.

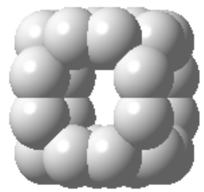
Phase diagram determination.



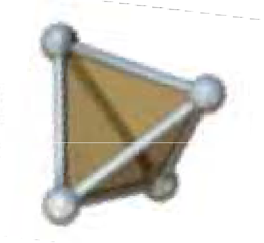
Simulations: atomic model



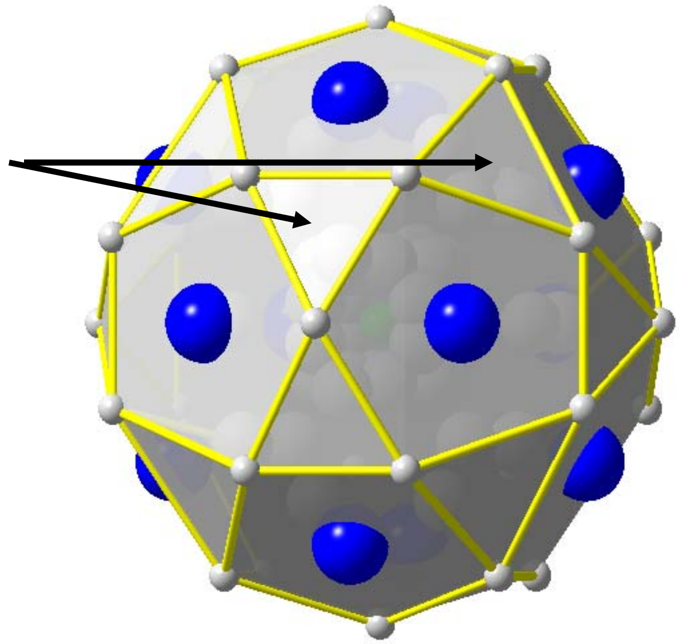
- 1/1 Approximant and 3/2 approximant for the QC
- Based on canonical cell model
- ***Problem: Cd orientation/correlation and disorder of the inner tetrahedron*.**



Simulations



Tetrahedron orientation induces ***cluster distortion***. ***Crucial in the simulation***



- 1/1 approximant: Super-cell containing 8 clusters. **Molecular dynamics at 300C to have a solution for relative orientation then quenched.**
- 3/2 approximant contains 32 clusters. Based on canonical cell model. a=3.6 nm. 2984 atoms per unit cell (2528 Zn, 456 Sc).

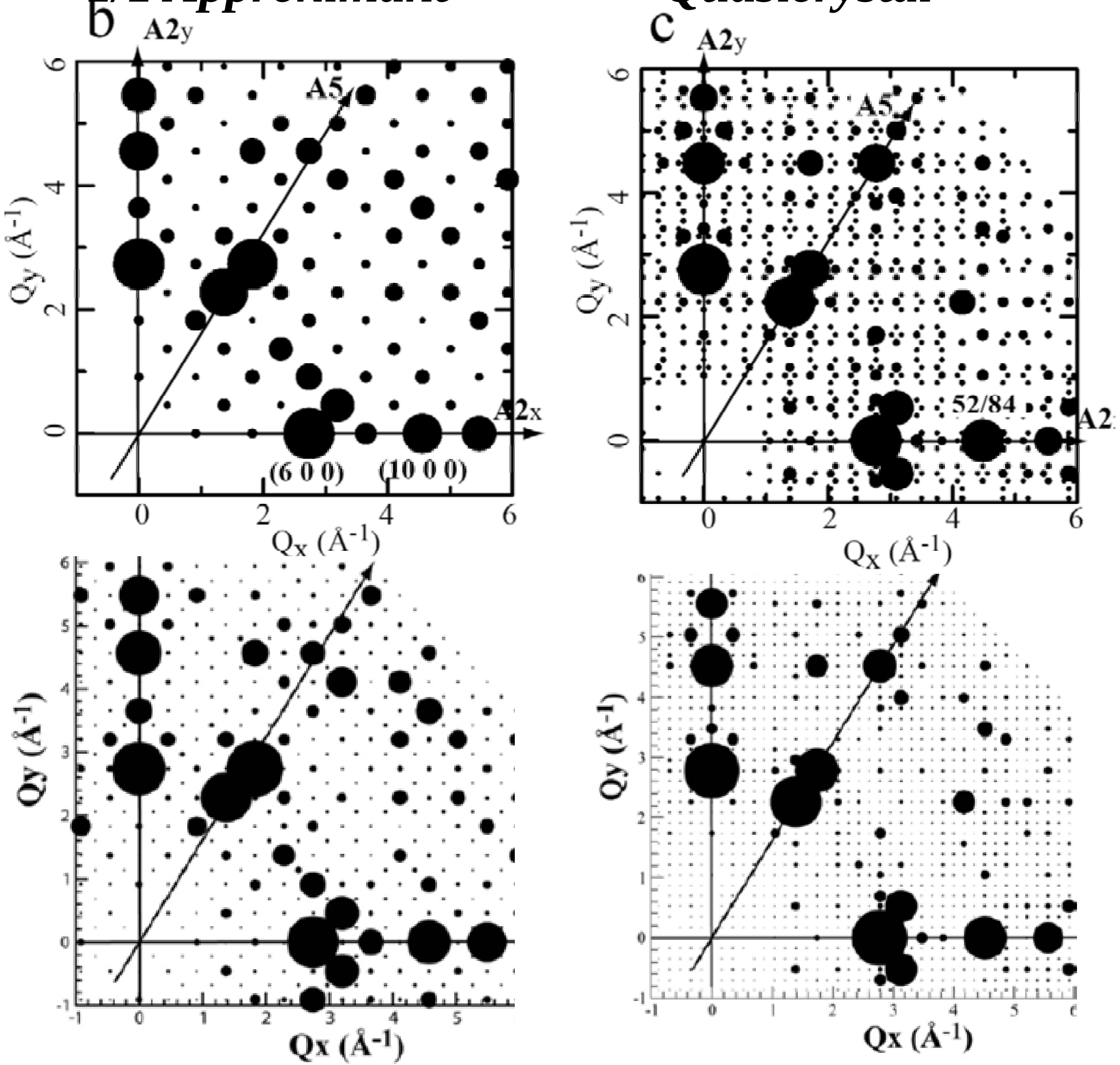
Molecular dynamics at 300C for the tetrahedra orientation followed by a quench.

- Lattice dynamic: Harmonic: inversion of the dynamical matrix.

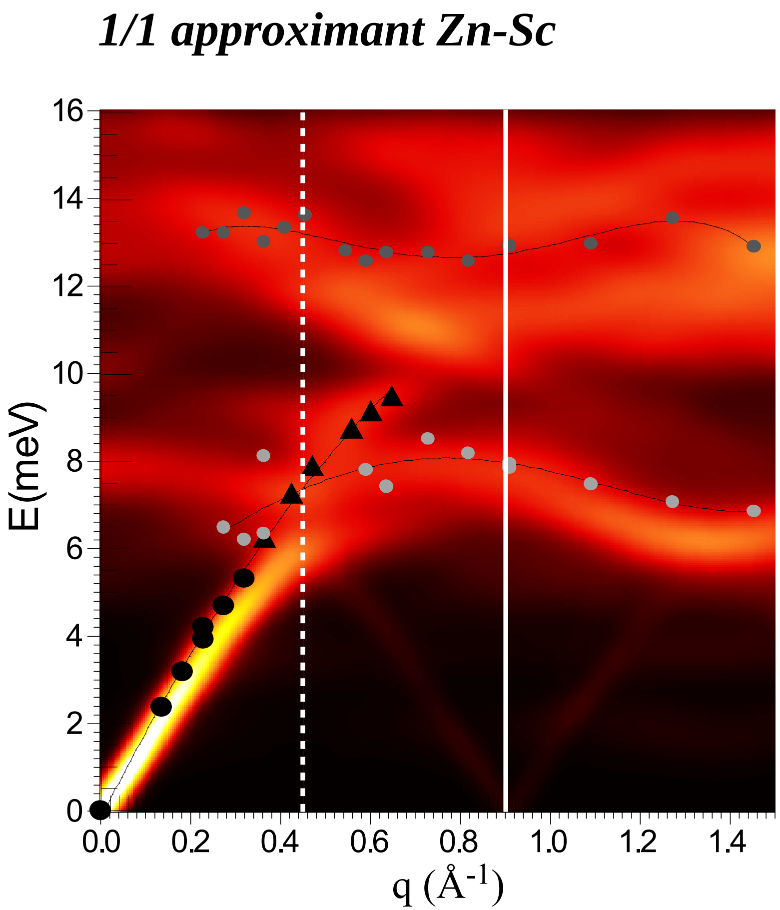
Simulated diffraction pattern in good agreement with experiment

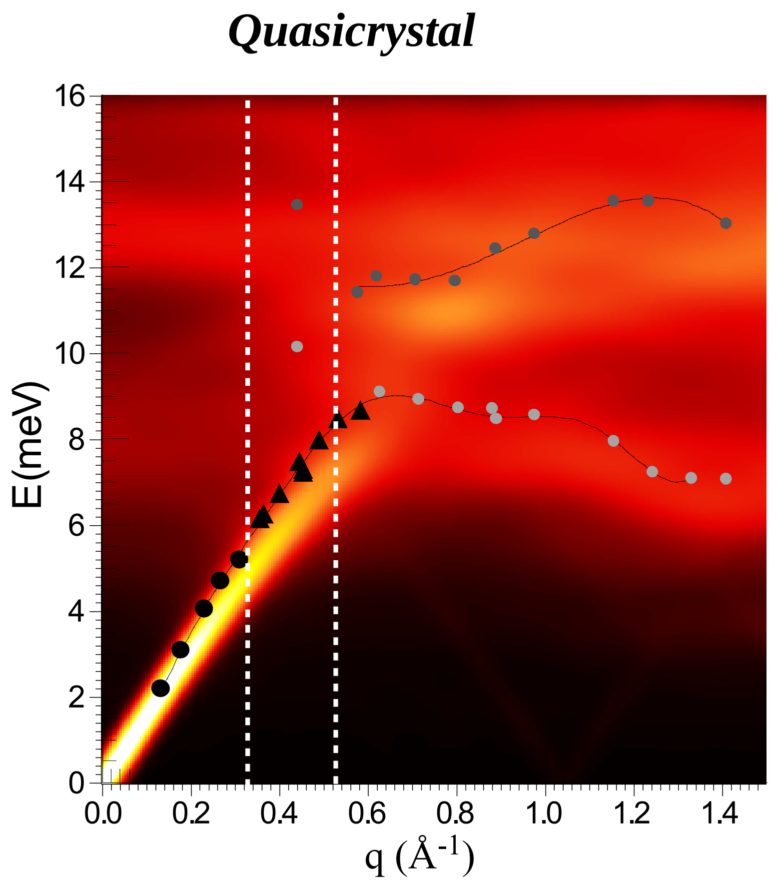
1/1 Approximant | ***Quasicrystal***

Data / ***Simulation***



Comparison simulation-measurement
Transverse modes

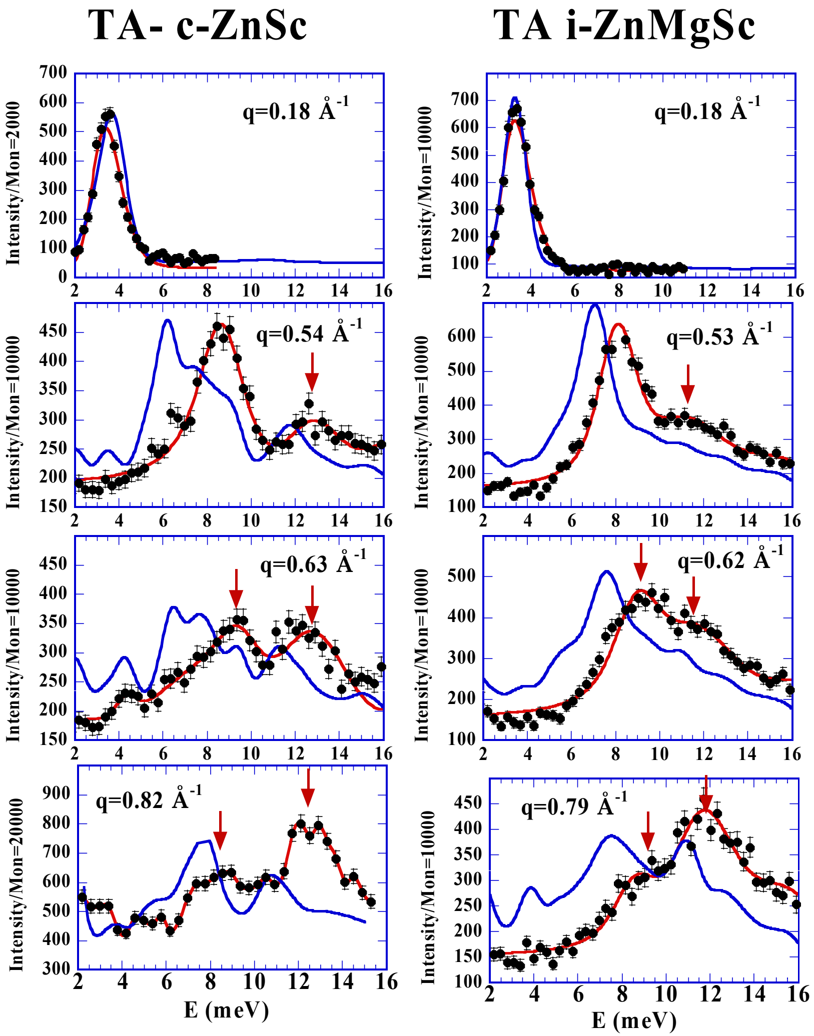




Good agreeement. Differences QC and 1/1 are well reproduced.

*Nature Materials **6** (2007) 977-984.*

Intensity distribution: comparison simulation-experiment.

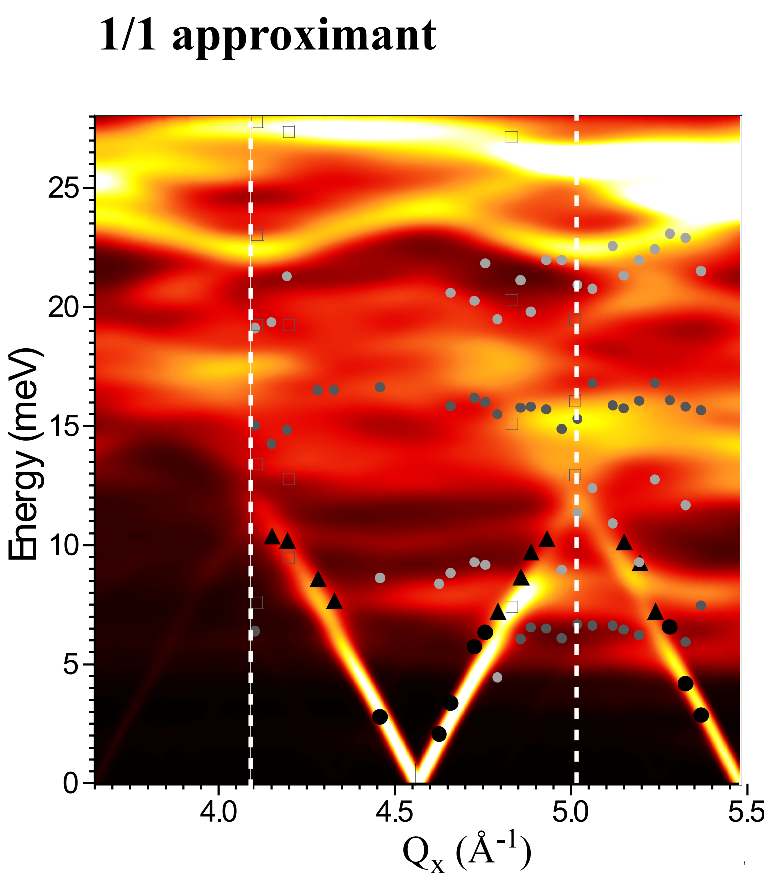


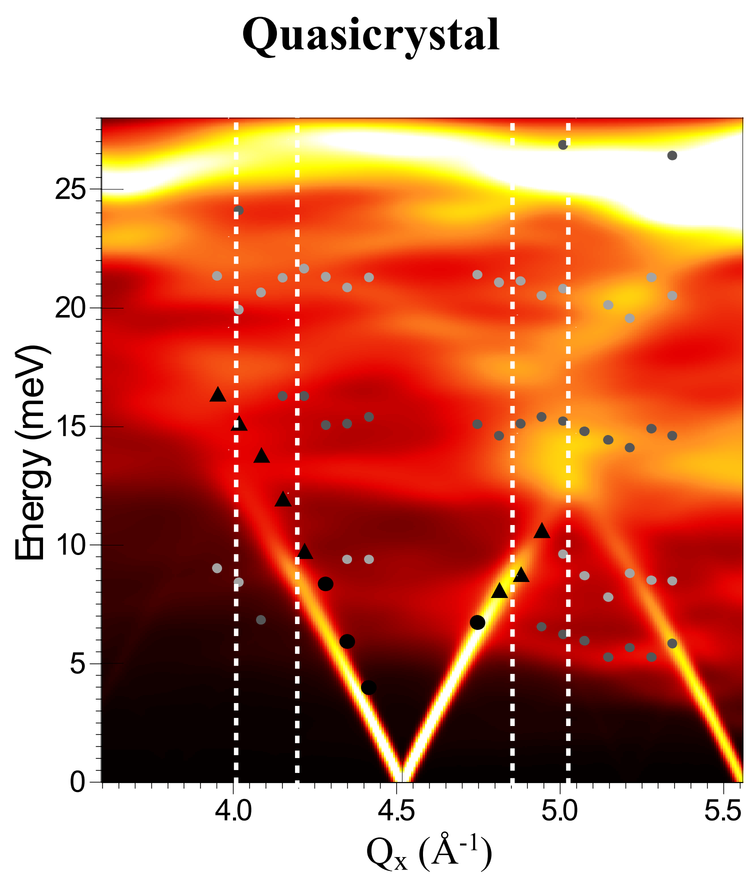
Blue curve: simulation

Nature Materials ***6*** *(2007) 977-984.*

- ***Energy is slightly too small in transverse geometry.***
- ***Good reproduction of the overall intensity distribution SENSITIVE TEST.***
- ***Broadening is due to mode mixing. Equivalent to finite lifetime.***

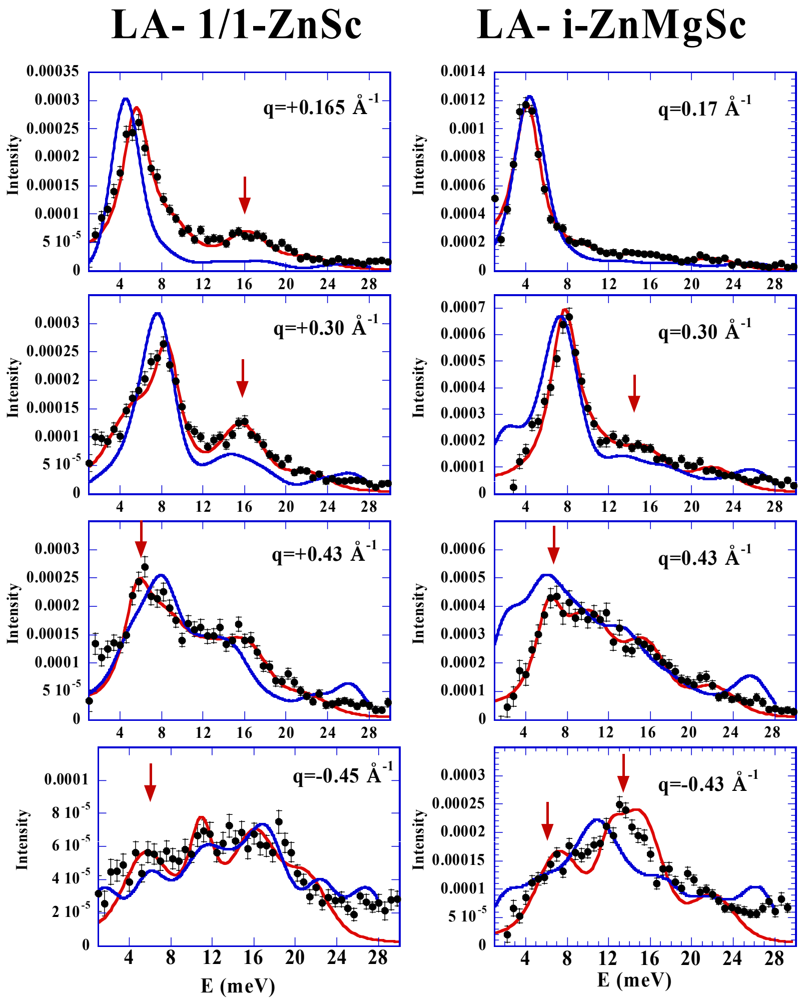
Longitudinal modes (Inelastic X-ray scattering)

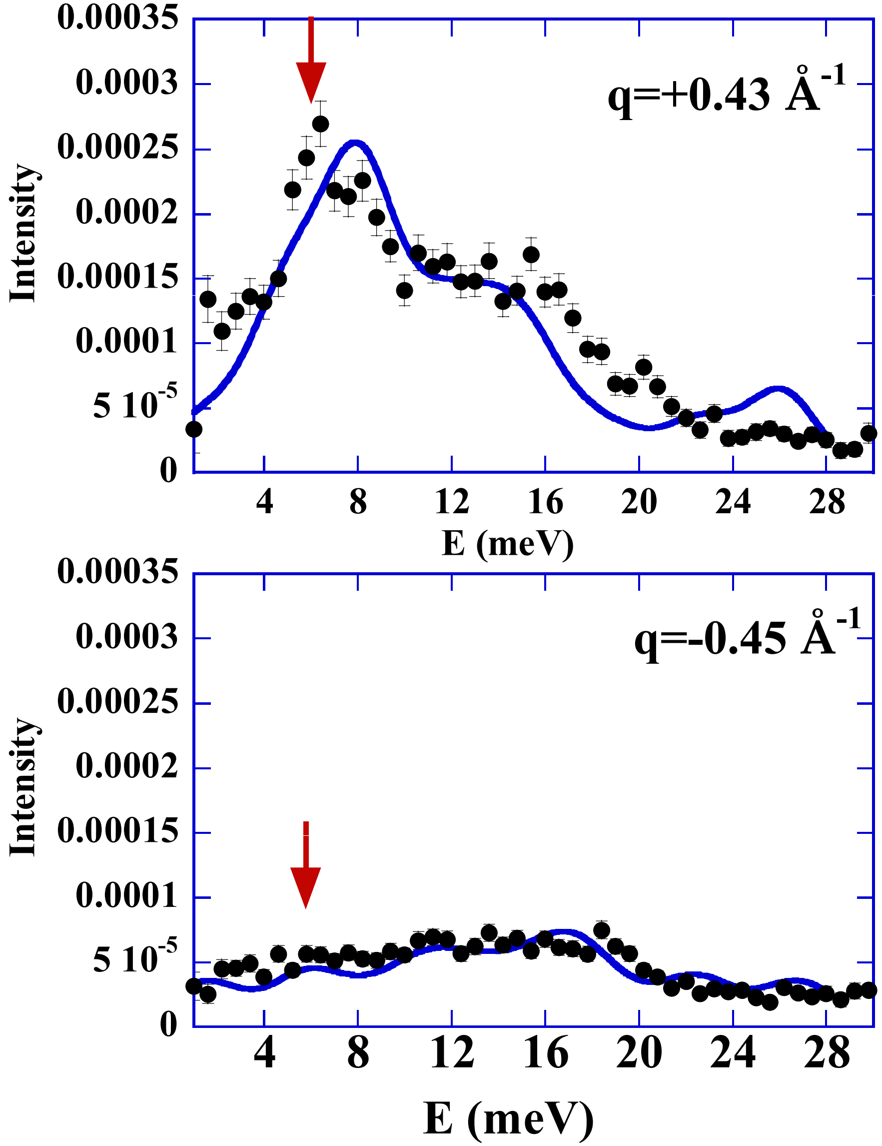




Very good agreement. The 6 meV low energy mode is well reproduced.
Differences are also reproduced. Link with BZB

Longitudinal modes : Intensity distribution.



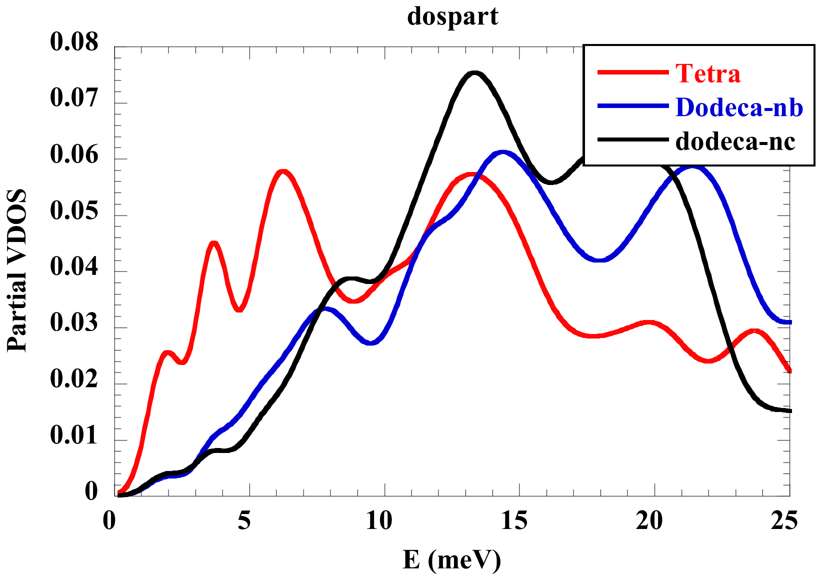


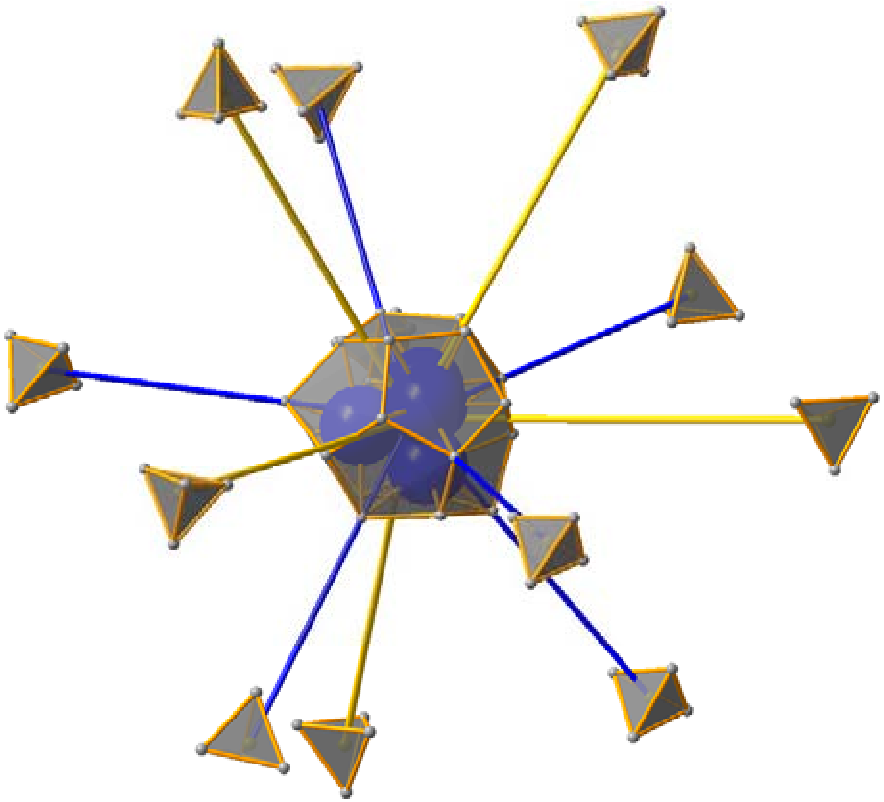
Blue curve: simulation

*Nature Materials **6** (2007) 977-984.*

- The simulation is thus in very good agreement with the experiment.
- The QC and 1/1 approximant differences are reproduced
- One can use this simulation with confidence to analyse the vibrational properties of he QC and 1/1 approximant.

- Cluster modes?
- Nature of the modes?





Partial density of vibrational sates

- Tetrahedra shows low energy mode, espacially in 1/1 approximant
- Related to the 1/1 ordering phase transition ? (Tamura et al.)

- Strong distortion of the dodecahedron both in 1/1 and 3/2 approximant.
- Consistant with Ishimasa structure at low T.

Conclusion

Phonon in QC:

Acoustic mode at low energy

Abrupt broadening, length scale ~ cluster size

Notion of quasi-Brillouin zone boundary

Modeling in good agreement

Are mode critical?

Cluster modes? Plane wave description?

CONCLUSION

- Dynamic of aperiodic crystals shows distinct features.
- Most prominent effect are the phason modes:

Phason mode are diffusive mode in the very long wavelength limit.

Damped propagating modes in a few incommensurately modulated systems.

- Lattice dynamics of quasicrystals: Notion of QZB, abrupt broadening and characteristic length scale.

  Critical modes?