Quasicrystals
Structure and dynamics

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Quasicrystals

Long range order with ‘Forbidden’ 5-fold symmetry
No periodicity

QUASICRYSTAL: A NEW KIND OF LONG RANGE ORDER
The notion of crystal is redefined

From A.P. Tsai and H Takakura
Stable Quasicrystals are observed in many different systems and can be grown as large single grains

Intermetallic alloys: AlLiCu, AlCuFe, AlPdMn, ZnMgY, CdYb (A.P. Tsai) ...
But also soft condensed matter.

Soft condensed matter
Metallic Phase with Long-Range Orientational Order and No Translational Symmetry

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and

D. Gratias
Centre d’Etudes de Chimie Metallurgique, Centre National de la Recherche Scientifique, F-94400 Vitry...

and

J. W. Cahn
Center for Materials Science, National Bureau of Standards, Gaithersburg, Maryland 20760
(Received 9 October 1984)

We have observed a metallic solid (Al–14-at.-%–Mn) with long-range orientational order, but with icosahedral point group symmetry, which is inconsistent with lattice translations. Its diffraction spots are as sharp as those of crystals but cannot be indexed to any Bravais lattice. The solid is metastable and forms from the melt by a first-order transition.
Symmetry of quasicrystals

Three dimensional Qc

Icosahedral symmetry

Two dimensional Qcs

Octagonal  Dodecagonal  Decagonal

8-fold  12-fold  10-fold

There is only one (icosahedral) 3-d Qc !!

Courtesy A.P. Tsai
Quasicrystalic diffraction pattern

i-AlCuFe
10-fold symmetry
Bragg peaks
No periodicity
$\tau = \frac{1+\sqrt{5}}{2} = 1.618$
Diffraction pattern of quasicrystals

- X-ray diffraction along 5-fold axis. i-AlPdMn. ESRF. (Log I scale)
- Only few very strong Bragg. $\tau$ scaling of position (Fm35).

6 integer indices
N/M short hand notation (Gratias et al.)

Self-similarity:
$\tau = (1 + \sqrt{5})/2 = 1.618$
Quasicrystal: Highly perfect Order
i-Al69.8Pd21Mn9.2 Single grain

- High resolution, coherent setup (ID20, ESRF): one speckle
  \( dQ = 10^{-4} \text{ Å}^{-1} \quad \xi \sim 10\mu m \)

- Rocking curve: 0.005° FWHM

- Dynamical diffraction is also observed

A. Létoublon et al.
Stable quasicrystals

i-AlPdMn, growth of centimeter size single grains by Bridgman and Czokralski methods.

M. Boudard et al.

W. Steurer, i-AlPdMn Laue
Quasicrystals

• Where are the atoms?

• Specific physical properties?
  Phason, modeling and stabilizing mechanisms.
Quasicrystals

• Where are the atoms?

• Specific physical properties?
  Phason, modeling QC and stabilizing mechanisms.
Where are the atoms?

Two main routes:

• **Decorated Penrose tiling**
  Trial and error method

• **High dimensional crystallography** (introduced by de Wolf, Janner and Janssen 1972-1979)

Only method to use the data
Modeling is necessary

• **Both method are using**
  - Periodic ‘approximant’
  - Cluster description.
The Penrose tiling (1974)

Diffraction: Alan Mackay (82)
Mosseri and Sadoc
3D: Amman tiling
Approximants, clusters and local icosahedral order

- Bergman-Pauling-Samson cluster description
  *Acta Cryst.* 10, 254 (1957). Example of the ZnAl-Mg alloy

- First QC models: Quasicrystal and approximant. Decoration with atomic clusters (V. Elser and Henley PRL 1985 - M. Audier and P. Guyot Phil Mag 1985)
Amman decorated tiling

- **Decoration of the Penrose tiling using clusters**
  (Levine and Steinhardt, PRL 84; Elser-Henley, PRL 1985; Guyot-audier, Phil Mag 1985)
superspace crystallography same structural tool for all aperiodic crystals

Invented by P.M. de Wolff, A. Janner and T. Janssen for incommensurate phases (2014 Ewald Prize)

For quasicrystals:
‘re-invented ‘ by
- Kalugin, Levitov, Kitaev (jetp, 85)
- Bak (PRL 85)
- Duneau and Katz (PRL 85)
- Elser (PRL 85)
Superspace crystallography

In this 2D reciprocal plane

All Bragg peaks positions are expressed as a linear combination of 4 vectors

\[ Q = n_1 a^* + n_2 b^* + n_3 c^* + n_4 d^* \]

4 integers:
4 dimensional space
Icosahedral phase: 6 indices
The three Icosahedral QC families

- Bergman cluster (Frank-Kasper type)
- Mackay cluster
- Tsai cluster (Yb-Cd type)

(Courtesy C. Pay Gomez)
Clusters, tilings, connectivity and superspace

Crystal and Quasicrystal Structures in Al-Mn-Si Alloys

Veit Elser and Christopher L. Henley
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

Sphere packings and local environments in Penrose tilings

C. L. Henley

IV. TWELVEFOLD VERTICES OF 3D PENROSE TILINGS
A. Distribution of twelvefold sites

2-fold and 3-fold cluster connexion

FIG. 5. The 54-atom Mackay icosahedron which appears as a structural unit in $\alpha$-(AlMnSi) and $\alpha$-(AlFeSi). The dark atoms are Mn or Fe.
The 12-fold Penrose vertices distribution
Not a tiling. Cluster center position

Where are the atoms: CdYb quasicrystal and approximant

- **Binary stable quasicrystal**: i-Cd$_{5.7}$Yb (Tsai A P, Guo J Q, et al. 2000 Nature **408** 537.)
- Very good chemical order: large and small atoms.
- Same atomic clusters
- **QC: Synchrotron data** (5000 Bragg peaks, weak ones)
- **QC: Phasing** and 6D modeling plus **Fitting tools**
- **Structure of the quasicrystal is well understood** (Takakura et al. Nat Mat, 2007)
Cluster in approximant and QC

Disordered Cd tetrahedron
Cluster in approximant and QC

Cd dodecahedron

$R = 4.6 \, \text{Å}$
Cluster in approximant and QC

Yb Icosahedron

$R=5.6 \text{ Å}$

CHEMICAL ORDER
Cluster in approximant and QC

Cd icosidodecahedron
Small distortions
R=6.5 Å

CHEMICAL ORDER
Cluster in approximant and QC

Cd Triacontahedron and middle edges

$R=7.8 \text{ Å}$

Total 158 atoms

Closed packed structure, small (Cd) and large (Yb) atom.

Same cluster in quasicrystal and approximant

158 atoms. Chemical order Closed packed structure with a large and a small atom.

Same cluster connectivity in the QC and approximant: 2-fold and 3-fold bonds
Cluster connexion 1/1 approximant

- BCC Packing. 2-fold and 3-fold connected

2-fold connection  
$b=15.7 \, \text{Å}$

3-fold connection  
$c=13.6 \, \text{Å}$
Cd$_6$Yb 1/1 and Cd$_{5.8}$Yb 2/1 approximant

1/1: 15.7 Å
2/1: 25.3 Å

2-fold connection
b = 15.7 Å

3-fold connection
c = 13.6 Å

3 building blocks

i-CdYb Modeling

6D Modeling related to cluster description

Network of interpenetrating Triacontahedra 2- and 3-fold connected

Remaining space is filled with the prolate and oblate (same decoration as in the 2/1 approximant)

H. Takakura, C. Gomez, A. Yamamoto et al.
i-CdYb Atomic clusters
New environments

H. Takakura, C. Gomez, A. Yamamoto et al.,
Nature Materials, 2007, 6, 58
Quasicrystal: Hierarchical packing of clusters  Position of the cluster centers

Clusters are distorted in the quasicrystal

- Inner tetrahedron plays a crucial role
- It breaks the cluster shell icosahedral symmetry.
- Overall icosahedral symmetry with different cluster orientation
Quasicrystals

• Where are the atoms?

• Specific physical properties?
  Phason, QC modeling and stabilizing mechanisms.
Can quasiperiodic long range order propagate with local rules?

Matching rules are not local growing rules
Oxford Math building

Texas A M University
Matching rules are not growing rules
Can quasiperiodic long range order propagate with local rules?

- Matching rules are not growing rules, but possible to grow with a few defects.
- Which atomic surfaces for matching rules?? Icosahedral bounded by 2-fold planes (Katz and Gratias). Set of polyhedra to be used.
Phason modes and random tilings

- **Phason modes** are a specific excitation for all aperiodic crystals:
  - incommensurately modulated phases
  - Incommensurate composites (sliding mode)
  - Quasicrystals

- Hydrodynamic theory of aperiodic crystal. (P. Bak, Kalugin et al., Lubenski et al.)

- Diffusive excitations
Invariance of the system free energy with respect to perp space translation: phason modes
Phason modes in QC

Invariance of the system free energy with respect to perp space translation: phason modes
Phason mode and hydrodynamic theory

Phason mode: Collective diffusive process (non propagative)
$S(Q+q, t)$ is decaying exponentially
Ico phase: K2 and K1 elastic constants
Phason modes in all aperiodic phases

Local atom ‘flip’

LS → SL
Phason mode: Collective diffusive process (non propagative)

S(Q+q, t) is decaying exponentially

Ico phase: K2 and K1 elastic constants

Phason modes in all aperiodic phases
Phason dynamics: hydrodynamic (Engel and Trebin
PRL 2012)
**Quasicrystal Stabilizing mechanisms?**

- Quasicrystal versus approximant

  1/1-Cd$_6$Yb : cubic 1.57 nm  
  2/1-Cd$_{5.8}$Yb: cubic: 2.53 nm  
  i-Cd$_{5.7}$Yb : quasicrystal ico  

- ‘Frustration’ might be resolved in 1/1 but not in the QC

- Cd-Yb hybridization (Ishii)

- **Phason modes?**

  1/1 local environment (Ishimasa)  
  Two sites  CN16-CN17
What mechanisms stabilize quasicrystals?

*Free Energy* = *E* - TS

**Energy term**
- Close Packing of large (Sc) and small (Zn) atom
- Electronic stabilization (Hume-Rothery, ...)
- sp-d hybridization in Zn-Sc

**Entropy term**
- Vibrational entropy
- Chemical Disorder

*Phason modes: only in the QC*

*Random Tiling* (Henley and Elser)
Mechanisms stabilizing quasicrystals

Random tiling and atomic scale modeling.

Modeling quasicrystals

Tilings or 6D models and oscillating pair potentials

PHYSICAL REVIEW B 85, 092102 (2012)

Empirical oscillating potentials for alloys from *ab initio* fits and the prediction of quasicrystal-related structures in the Al-Cu-Sc system

Marek Mihalkovič¹,² and C. L. Henley¹

Applied to the i-CdYb type quasicrystal
The CdYb type QC and approximant

158 atoms. Chemical order

Periodic Approximant


Quasicrystal 5-fold plane

~ 340 Å

15.6 Å

~ 15.6 Å
Simulations

• Two ingredients: *atomic structure and Hamiltonian*.

• *QC Structure*: large periodic approximant: 3/2 (to 8/5) approximant with about 3000 atoms.

• Adapted Hamiltonian: *oscillating pair potential* fitted on ab-initio data (VASP). Fitting of energies and forces.
Oscillating pair potential

M. Mihalkovic, C. Henley PRB 85, 092102, 2012

Fitted on energy and forces from structures relaxed with VASP

Comparison simulation-measurement
Transverse modes

1/1 approximant Zn-Sc

Quasicrystal

Good agreement. Differences QC and 1/1 are well reproduced.
Intensity distribution: comparison simulation-experiment.

Excellent quantitative agreement

The atomistic simulation is validated

Blue curve: simulation

Mode analysis: Partial density of vibrational states

- Tetrahedra shows low energy mode, especially in 1/1 approximant: cluster modes??

- Strong distortion of the dodecahedron both in 1/1 and 3/2 approximant.
ZnSc cubic approximant. Quasielastic Neutron and simulation: Tetrahedron ‘jump’
A unique dynamical flexibility: displact 0.5 Å
Jump time scale: 1 ps at RT, 0.3 ps at 170K

H. Euchner, T. Yamada et al., JPCM 2012, 24, 415403
T. Yamada, H. Euchner et al, JPCM 2013, 25, 205405
i-ZnMgSc and i-ZnAgSc quasicrystals

Jump of the tetrahedron also in the quasicrystal.

Gradual freezing as in a glassy system: at RT only about 30% jumps

Related to the large number of local environment

At RT in QC an exceptional dynamical flexibility
i-ZnMgSc and i-ZnAgSc quasicrystals

At RT in QC an exceptional dynamical flexibility

Phason modes in quasicrystals

Hydrodynamic theory and elasticity: Phenomenological theory

Long wavelength phason modes: diffuse scattering

\[ I(Q_{\text{Bragg}} + q) = I_{\text{Bragg}} + I_{\text{Diffus (Phonons)}} + I_{\text{Diffus (Phasons)}} \]

Phasons diffuse scattering:

- Near Bragg peaks (similar to TDS)
- Anisotropy of diffuse scattering: \textbf{two parameters: phason elastic constants K1 and K2}

Phason modes are diffusive modes, unlike phonons
i-AlPdMn: Phason mode and diffuse scattering

- Diffuse scattering is reproduced by the hydrodynamic theory: 2 parameters!
  - $K_1/k_B T = 0.1$ and $K_2/k_B T = -0.03$ atom$^{-1}$

M. de boissieu et al. PRL 1995
Létoublon et al. Phil Mag Lett 2001
Phason Diffuse scattering is observed in all icosahedral QC. Quenched in.

2 parameters for the diffuse scattering simulation!
i-AlPdMn quasicrystal. In situ T study

T evolution of the diffuse scattering

*FROM 750°C to 500°C*

In situ X-ray.

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

Agreement with the random-tiling scenario

Conclusion

• **Good understanding of the atomic structure** in the Tsai type QC; exceptional dynamical flexibility

• **Phason modes** are characteristic of the QC state.

• **Realistic atomic simulation** are at work for QC.

• **Need for new theoretical tools for simulation analysis**

• **Stabilizing mechanism of aperiodic crystals** remains one of the main challenging question.
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