Higher Dimensional Crystallography

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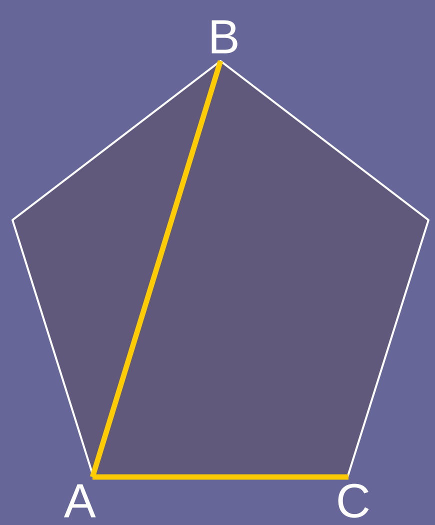
Talk Outline

- The ‘Golden Ratio’ in nature.
- Quasicrystals and incommensurate structures.
- Periodic functions vs. quasiperiodic functions.
- Aperiodic tiling.
- Embedding in higher dimensional space.
- Indexing in higher dimensional crystallography.

The 'Golden Ratio' in nature

- The Golden Ratio, τ or ϕ, can be found in many patterns in nature.
- Maximal packing.
- First defined by Euclid.
- Accurately describes the geometry of pentagons.[1]



$$\tau = \frac{AB}{AC}$$

$$\tau = 1.618034\ldots$$

1. Mario Livio, The Golden Ratio, Broadway Books, New York 2002.

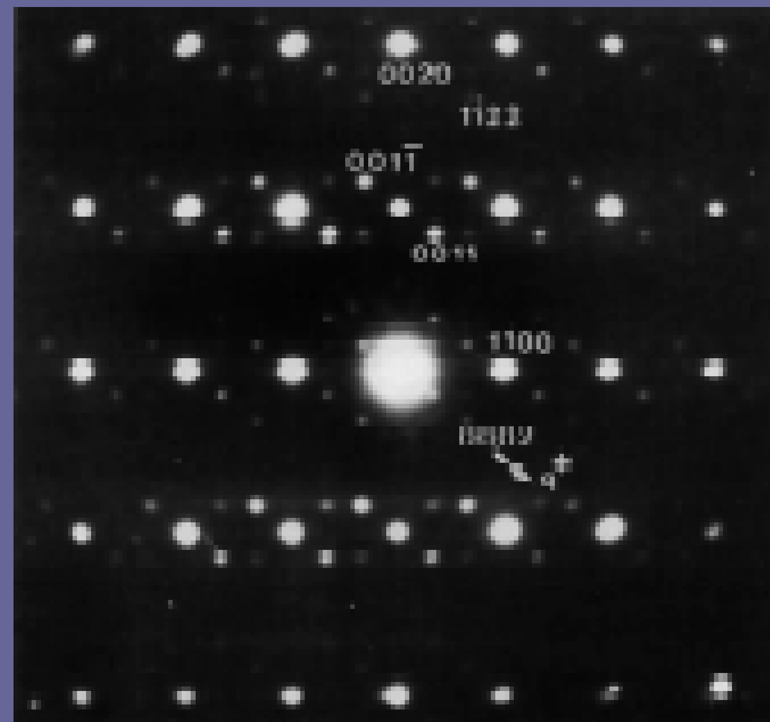
Incommensurately modulated structures (IMS)

- Periodic distortions incommensurable with the translation periods of the basic lattice.
- Satellite peaks around main peaks.
- Structure factor has an extra contribution from reflections.[3]

$$r_{u,j} = r_j^0 + r_u$$

$$r_{u,j} = r_j^0 + r_u + f_j\left(q \cdot \left(r_j^0 + r_u\right) - \phi\right)$$

$$g = h a_1^* + k a_2^* + l a_3^* + m q$$



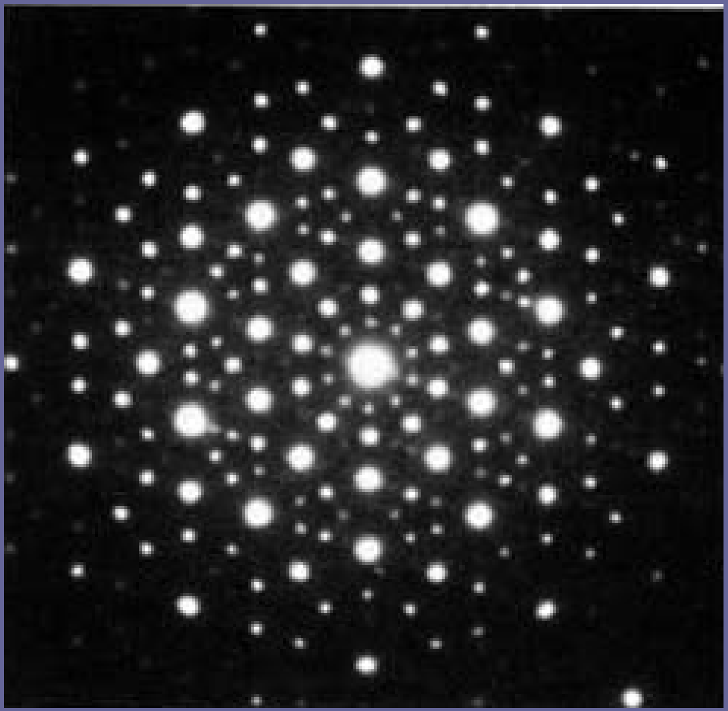
Electron diffraction pattern of $Ba_{0.85}Ca_{2.15}In_6O_{12}$ showing satellite peaks due to incommensurate modulation.[2]

2. G. Baldinozzi, F. Goutenoire, M. Hervieu, E. Suard and D. Grebille, *Acta Cryst.*, 780-789, **B52** (1996).

3. T. Janssen, *Physics Reports*, 55-113, **168** (1988).

Five-fold symmetry in quasicrystals

- Discovery in 1984 by Shechtman leads to the term **quasicrystals - any crystal that displays forbidden crystallographic symmetries.**
- In 3-D, cannot be tiled by a single parallelepiped.
- Exhibits long-range order but not periodicity.
- Special kind of incommensurate structures.



Diffraction pattern of Al-Mn alloy showing icosahedral point symmetry m-5-3.[4]

4. Shechtman, D., Blech, I., Gratias,D., and Cahn, J.W. (1984). *Phys. Rev. Lett.,* **53** 1951

The math of quasiperiodic functions

- Periodic function *f(x)* can be expanded in a Fourier series.

$$f(x) = f(x + np)$$

$$f(x) = \sum_{n_1=-\infty}^{\infty} f^*(n_1)\exp[2\pi i n_1 x]$$

$$f(x_1,\ldots,x_N) = \sum_{n_1,\ldots,n_N} f^*(n_1,\ldots,n_N)\exp[2\pi i(n_1x_1 + \cdots n_N x_N)]$$

$$g(x) = \sum_{n_1,\ldots,n_N} f^*(n_1,\ldots,n_N)\exp[2\pi i(n_1\nu_1 + \cdots n_N\nu_N)x]$$

- 2D to 1D example:

$$f(x,y) = A_1\sin(2\pi x) + A_2\sin(2\pi y)$$

$$y = \alpha x$$

$$f'(x) = A_1\sin(2\pi x) + A_2\sin(2\pi\alpha x)$$

- g(x) and f'(x) are quasiperiodic functions if υ and α are irrational numbers.

Approximations with periodic functions

- Model with a series of delta functions (crosses and open circles).

$$\sum_n \delta(x - na)$$
$$\sum_m \delta(x - ma\,\tau/2)$$

$$\tau = 1 + \cfrac{1}{1 + \cfrac{1}{1 + \cfrac{1}{1 + \dots}}}$$

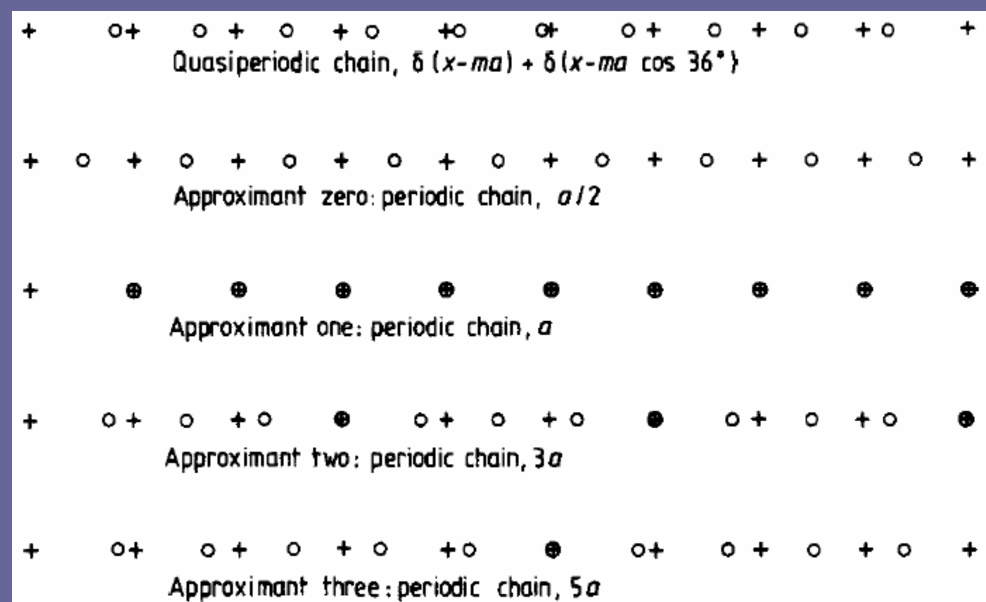
$\tau_N = \tau$

$\tau_0 = 1$

$\tau_1 = 1+1 = 2$

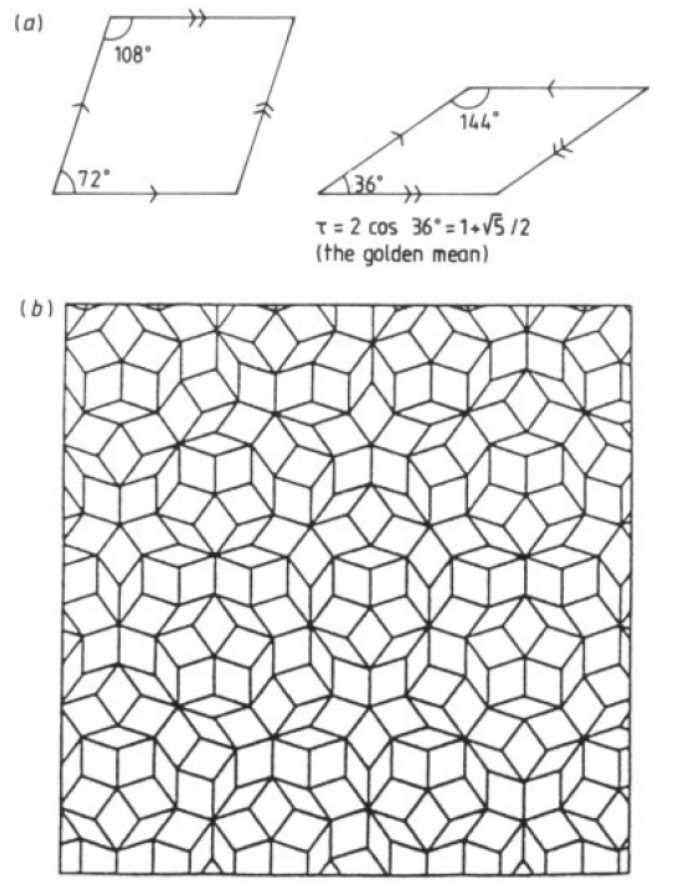
$\tau_2 = 1 + 1/(1+1) = 3/2$

$\tau_3 = 1 + 1/(1+1/(1+1)) = 5/3$



Penrose tiling

- Example of aperiodic tiling.
- Properties of Penrose quasicrystal.
  - Quasiperiodic translational order.
  - Minimal separation between atoms.
  - Orientational order.
- The two prototiles have matching rules.
- Matching rules correspond to physical forces in a material.
- Recently, Steinhardt and Jeong showed that you can tile with decagon and maximize density.[5]



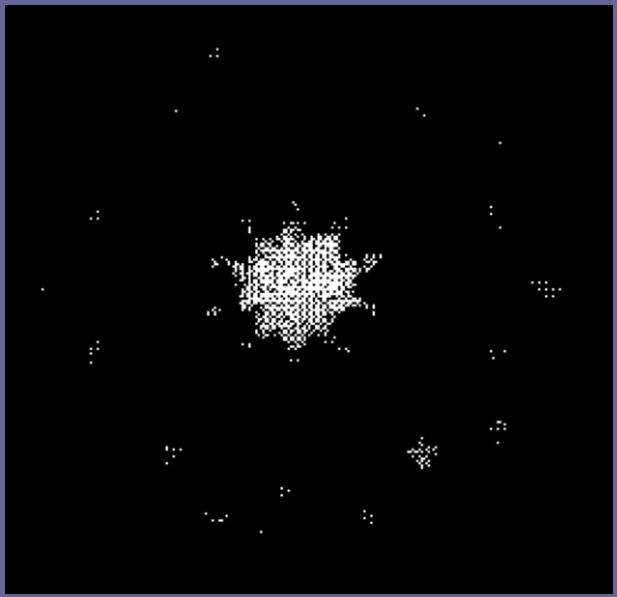
Penrose tiling from connecting two rhombi according to matching rules.[5]

5. Ch. Janot and J.M. Dubois, *J. Phys. F: Met. Phys.,* 2303-2343, **18** (1988).

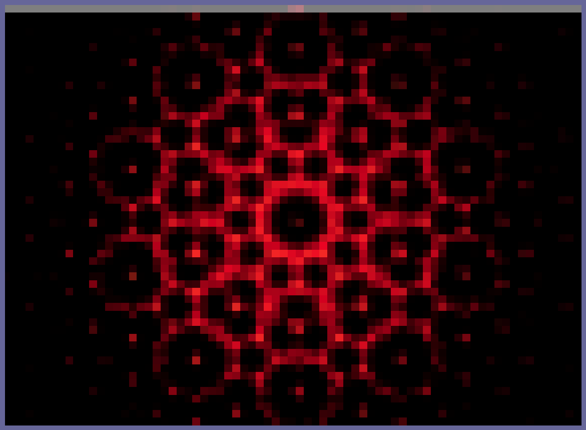
6. P.J. Steinhardt, and H.C. Jeong, *Nature*, 431-433, **382** (1996).

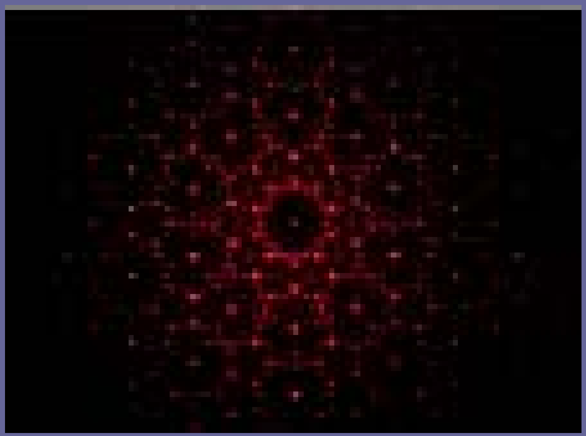
Fourier transforms of Penrose tiling and quasiperiodic functions

- In 1982 Mackay proves that aperiodic tilings can show sharp Bragg peaks.



Optical diffraction of Penrose tiling displays 10-fold symmetry.[7]





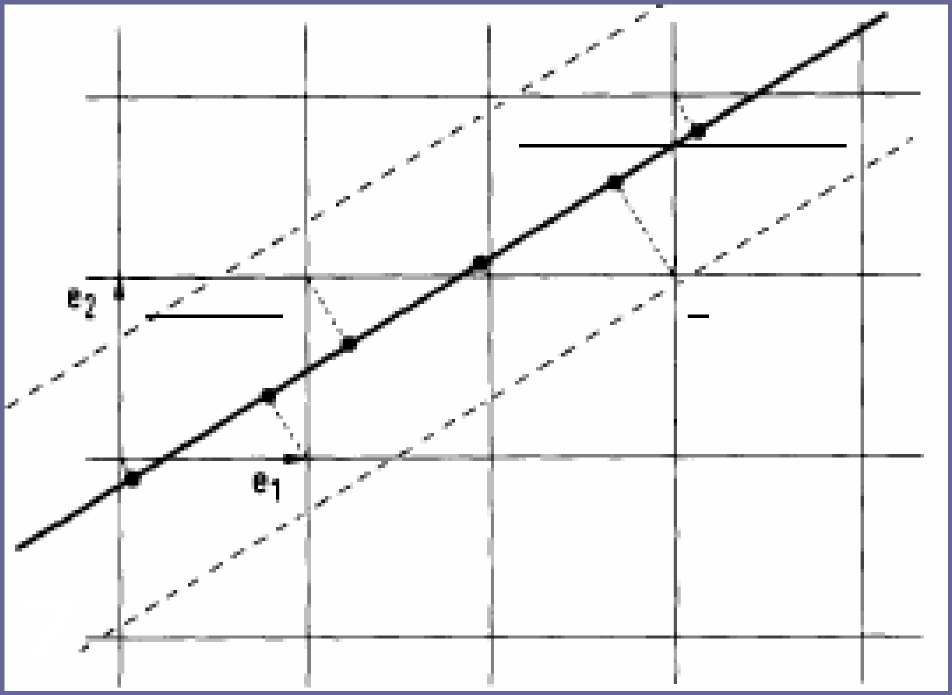
Optical diffraction of Penrose tiling with red laser.[8]

7. A.L. Mackay, *Physica*, 609-613, **114A** (1982).

8. T. R. Welberry website http://rsc.anu.edu/~welberry/Optical_transform/

Embedding in higher-dimensional crystallography

- Several methods
  - Multigrid method.
  - Cut-and-project method.
  - Projection method.
- Can extend the methods to higher dimensions.
- For icosahedral 3-D groups, can be thought of cut-and-project strips in 6-D.
- Would use h/h', k/k', l/l' to index an icosahedral superspace group.



Example of cut-and-project method in which a cut with an irrational slope through 2-D leads to Fibonacci sequence in 1-D.[5]

N-dimensional crystallography

- Deal with periodic functions and therefore the usual formalism of crystallographic space groups.
- For quasicrystals, new point groups can be achieved (e.g. pentagonal, octagonal, icosahedral).
- Crystallographic point groups have different ranks, or the number of dimensions to make the spacing periodic.

T. Janssen, *Physics Reports*, 55 -113, **168** (1988).

Table 4.3
Bravais classes of 2D quasicrystals of rank 4 with a 2D crystallographic point group

Tetragonal 4: $(1,0)$, (α,β) with $\beta \neq 0$; rank $= 4$

$$\begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{pmatrix}$$

Tetragonal 4m: $(1,0)$, $(\alpha,0)$; rank $= 4$

$$\begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{pmatrix}, \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \rightarrow D_5 + D_5$$

Tetragonal 4m: $(1,0)$, (α,α); rank $= 4$

$$\begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{pmatrix}, \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \rightarrow D_5 + D_5$$

Tetragonal 4m: (α,β); rank $= 4$

$$\begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \rightarrow D_5 + D_5$$

Hexagonal 6m: $(1,0)$, $(\alpha,0)$; rank $= 4$

$$\begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 1 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 1 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

Hexagonal 6m: $(1,0)$, (α,α); rank $= 4$

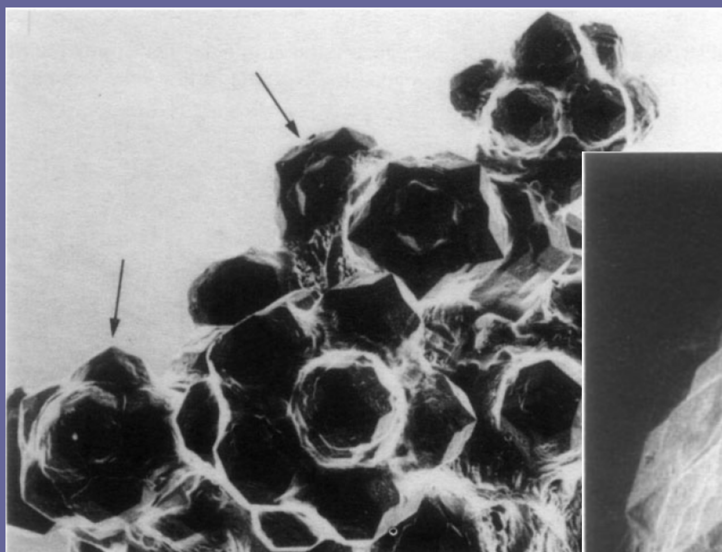
$$\begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 1 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

Point groups in higher dimensions

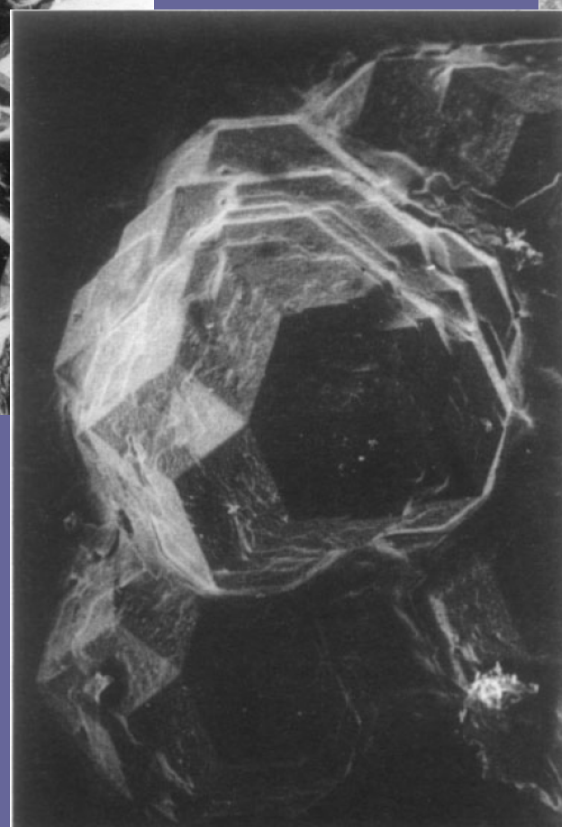
point group	k	rank	R_1	R_2	R_3
5	$(1,0,z)$	5	(y,z,u,v,x)		
5m		5	(y,z,u,v,x)	(x,v,u,z,y)	
			(y,z,u,v,x)	$(x+\frac{1}{2},v+\frac{1}{2},u+\frac{1}{2},z+\frac{1}{2},y+\frac{1}{2})$	
52		5	(y,z,u,v,x)	$(\bar{x},\bar{v},\bar{u},\bar{z},\bar{y})$	
$\bar{5}$		5	$(\bar{y},\bar{z},\bar{u},\bar{v},\bar{x})$		
$\bar{5}$m		5	$(\bar{y},\bar{z},\bar{u},\bar{v},\bar{x})$	(x,v,u,z,y)	
			$(\bar{y},\bar{z},\bar{u},\bar{v},\bar{x})$	$(x+\frac{1}{2},v+\frac{1}{2},u+\frac{1}{2},z+\frac{1}{2},y+\frac{1}{2})$	
5	(001), (100)	5	$(x+p/5,z,u,v,\bar{S})$ $p=0,1,2$		
5m1		5	$(x,z,u,v,\bar{S})$	(x,v,u,z,y)	
			$(x,z,u,v,\bar{S})$	$(x+\frac{1}{2},v,u,z,y)$	
51m		5	$(x,z,u,v,\bar{S})$	$(x,\bar{S},v,u,z)$	
			$(x,z,u,v,\bar{S})$	$(x+\frac{1}{2},\bar{S},v,u,z)$	
521		5	$(x+p/5,z,u,v,\bar{S})$ $p=0,1,2$	$(\bar{x},\bar{v},\bar{u},\bar{z},\bar{y})$	
512		5	$(x+p/5,z,u,v,\bar{S})$ $p=0,1,2$	$(\bar{x},S,\bar{v},\bar{u},\bar{z})$	
$\bar{5}$		5	$(\bar{x},\bar{z},\bar{u},\bar{v},S)$		
$\bar{5}$m1		5	$(\bar{x},\bar{z},\bar{u},\bar{v},S)$	(x,v,u,z,y)	
			$(\bar{x},\bar{z},\bar{u},\bar{v},S)$	$(x+\frac{1}{2},v,u,z,y)$	
$\bar{5}$1m		5	$(\bar{x},\bar{z},\bar{u},\bar{v},S)$	$(x,\bar{v},\bar{u},\bar{z},\bar{y})$	
			$(\bar{x},\bar{z},\bar{u},\bar{v},S)$	$(x+\frac{1}{2},\bar{v},\bar{u},\bar{z},\bar{y})$	
10		5	$(x+p/10,\bar{v},S,\bar{y},\bar{z})$ $p=0,\ldots,5$		
$\overline{10}$		5	$(\bar{x},v,\bar{S},y,z)$		
10/m		5	$(x,\bar{v},S,\bar{y},\bar{z})$	$(\bar{x},y,z,u,\bar{S})$	
			$(x+\frac{1}{2},\bar{v},S,\bar{y},\bar{z})$	$(\bar{x},y,z,u,\bar{S})$	
10mm		5	$(x,\bar{v},S,\bar{y},\bar{z})$	(x,v,u,z,y)	
			$(x+\frac{1}{2},\bar{v},S,\bar{y},\bar{z})$	(x,v,u,z,y)	
			$(x,\bar{v},S,\bar{y},\bar{z})$	$(x+\frac{1}{2},v,u,z,y)$	
			$(x+\frac{1}{2},\bar{v},S,\bar{y},\bar{z})$	$(x+\frac{1}{2},v,u,z,y)$	
10 22		5	$(x+p/10,\bar{v},S,\bar{y},\bar{z})$ $p=0,\ldots,5$	$(\bar{x},\bar{v},\bar{u},\bar{z},\bar{y})$	
$\overline{10}$ 2m		5	$(\bar{x},v,\bar{S},y,z)$	$(\bar{x},\bar{v},\bar{u},\bar{z},\bar{y})$	
			$(\bar{x}+\frac{1}{2},v,\bar{S},y,z)$	$(\bar{x},\bar{v},\bar{u},\bar{z},\bar{y})$	
$\overline{10}$ m2		5	$(\bar{x},v,\bar{S},y,z)$	$(\bar{x},y,\bar{S},v,u)$	
			$(\bar{x}+\frac{1}{2},v,\bar{S},y,z)$	$(\bar{x},y,\bar{S},v,u)$	
10/mmm		5	$(x,\bar{v},S,\bar{y},\bar{z})$	(x,v,u,z,y)	$(\bar{x},\bar{y},\bar{z},\bar{u},\bar{v})$
			$(x+\frac{1}{2},\bar{v},S,\bar{y},\bar{z})$	(x,u,v,z,y)	$(\bar{x},\bar{y},\bar{z},\bar{u},\bar{v})$
			$(x,\bar{v},S,\bar{y},\bar{z})$	$(x+\frac{1}{2},v,u,z,y)$	$(\bar{x},\bar{y},\bar{z},\bar{u},\bar{v})$
			$(x+\frac{1}{2},\bar{v},S,\bar{y},\bar{z})$	$(x+\frac{1}{2},v,u,z,y)$	$(\bar{x},\bar{y},\bar{z},\bar{u},\bar{v})$
8	(001), (100)	5	$(x+p/8,u,v,z,\bar{y})$ $p=0,\ldots,4$		
$\bar{8}$		5	$(\bar{x},\bar{u},\bar{v},\bar{z},y)$		
8/m		5	$(x,u,v,z,\bar{y})$	$(\bar{x},y,z,u,v)$	
			$(x+\frac{1}{2},u,v,z,\bar{y})$	$(\bar{x},y,z,u,v)$	
			$(x,u,v,z,\bar{y})$	$(\bar{x},y+\frac{1}{2},z+\frac{1}{2},u+\frac{1}{2},v+\frac{1}{2})$	
			$(x+\frac{1}{2},u,v,z,\bar{y})$	$(\bar{x},y+\frac{1}{2},z+\frac{1}{2},u+\frac{1}{2},v+\frac{1}{2})$	

T. Janssen, *Physics Reports*, 55 -113, **168** (1988).

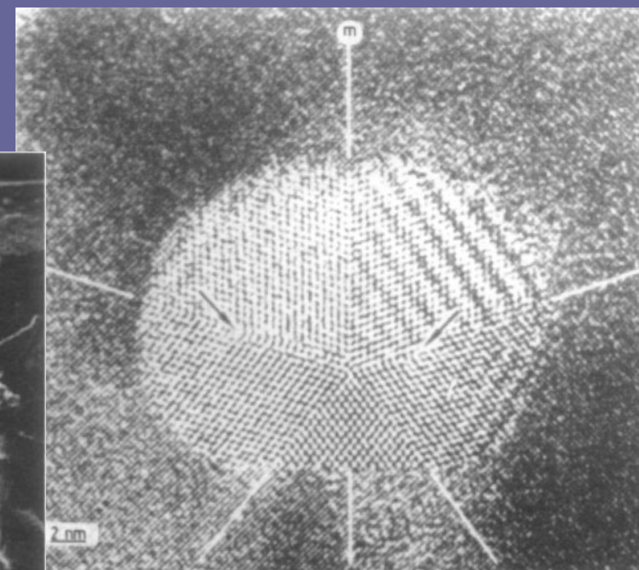
Materials systems solved with higher dimensions



Dendritic aggregate of Al-Li-Cu alloy.



Single grain of the Al-Li-Cu alloy.



Pentagonally twinned Ge precipitate in Al matrix.

Ch. Janot and J.M. Dubois, *J. Phys. F: Met. Phys.*, 2303-2343, **18** (1988).

Programs for solving in higher dimensions

- **DIMS Direct Methods for Incommensurate Modulated/Composite Structures - Fan, Hai-fu & colleagues**
  http://cryst.iphy.ac.cn/VEC/Tutorials/DIMS/DIMS.html

- **Fullprof Rietveld** - Juan Rodriguez-Carvajal and **WinPlotr Interface** - T. Roisnel Jana2000
  http://www-llb.cea.fr/fullweb/powder.htm

- **JANA2000 Single Crystal and Powder Diffraction Software** - Vaclav Petricek
  http://www-xray.fzu.cz/jana/jana.html

- **XND Rietveld** - Jean-Francois Berar
  http://www-cristallo.grenoble.cnrs.fr/xnd/xnd.html

In Summary

- Special structural properties IMS and quasicrystals show the need for a more detailed crystallography.
- Quasiperiodic functions and aperiodic tilings help prove that long-range order does not require periodicity, just non-random packing.
- Embedding quasicrystals and IMS in higher dimensions leads to periodic structures that follow the rules of ordinary crystallography.