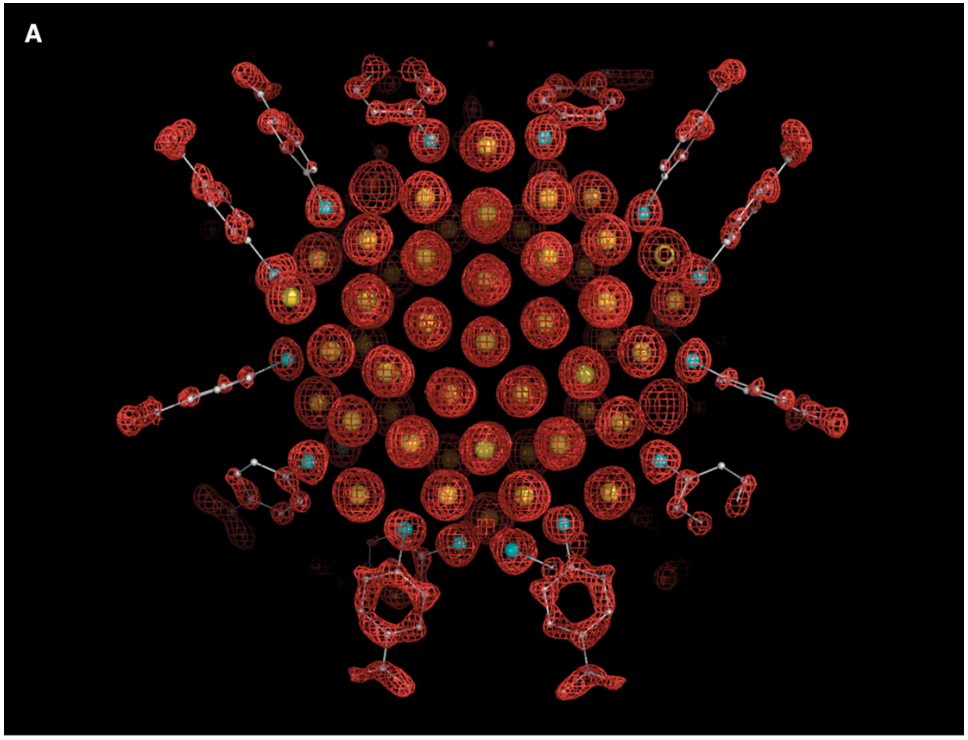
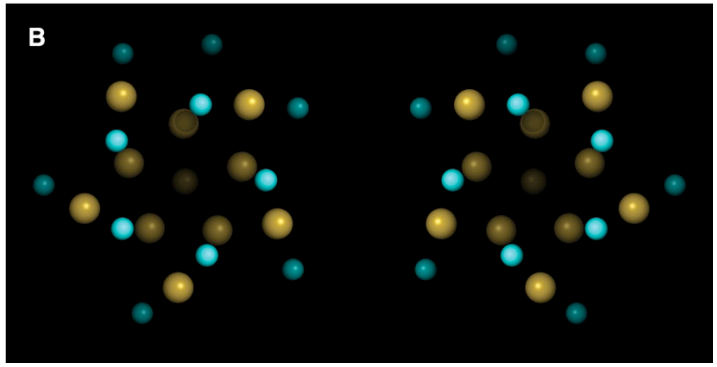
Noncrystalline Materials: Why crystalline materials ?





p-mercaptobenzoic (*p*-MBA) acid capped gold nanoparticles: 102 gold atoms, and 44 (*p*-MBA)

Jadzinsky *et al.*, Structure of a thiol monolayer-protected gold nanoparticle at 1.1 A resolution, *Science* **318** (2007) 430-433.

Noncrystalline Materials:

Disorder in crystalline materials (ice-I_h)

Metallic glasses

Quasicrystalline Materials

Liquid crystals

The pair distribution function

Ram Seshadri x6129 seshadri@mrl

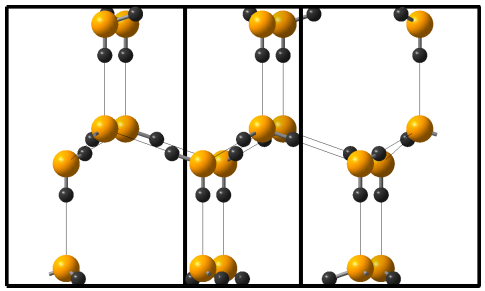
Ice

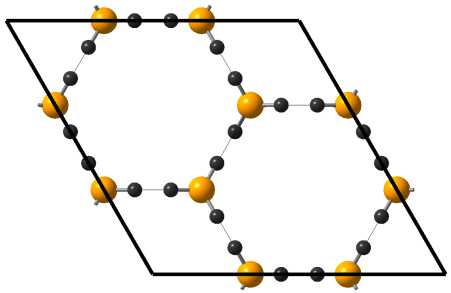
A Theory of Water and Ionic Solution, with Particular Reference to Hydrogen and Hydroxyl Ions, J. D. Bernal and R. H. Fowler, *J. Chem. Phys.* **1** (1933) 515-548.

Ice-I_h: a = 7.82 Å ; c = 7.36 Å $P6_3cm$ Proton ordering not proved

Atom	#	OX	SITE	x	y	z	SOF
O	1	-2	6 c	0.3333	0	0.0625	1.
O	2	-2	6 c	0.6667	0	0.9375	1.
H	1	+1	6 c	0.3333	0	0.174	1.
H	2	+1	6 c	0.438	0	0.026	1.
H	3	+1	12 d	0.772	0.105	0.975	1.

Views of the ordered Bernal-Fowler structure. Hydrogens positioned through guesswork.

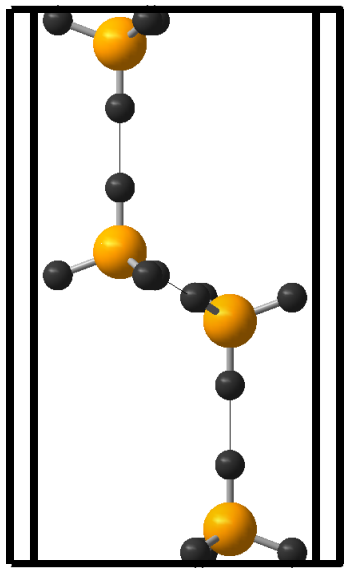




Ram Seshadri x6129 seshadri@mrl

Ice

Actual disordered structure of Ice-I_h: $P6_3/mmc$ hexagonal diamond lattice.



Ice-I_h: a = 4.511(3) Å ; c = 7.346(3) Å $P6_3/mmc$

O	1/3	2/3	0.06226(8)	
H1	1/3	2/3	0.178(3)	[Occ. = 0.5]
H2	0.439(3)	0.878(3)	0.020(3)	[Occ. = 0.5]

Goto *et al*. J. Chem. Phys. **93** (1990) 1412.

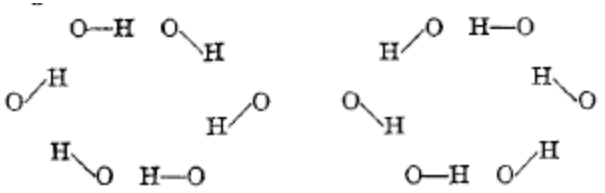
The Bernal-Fowler ice rules:

1) Each water molecule is oriented such that its two hydrogen atoms are directed approximately toward two of the four surrounding oxygen atoms (arranged almost in a tetrahedron).
2) Only one hydrogen atom is present on each O-O linkage.
3) Each oxygen atom has two nearest neighboring hydrogen atoms such that the water molecule structure is preserved.

Ram Seshadri x6129 seshadri@mrl

Ice

Linus Pauling and residual entropy:
The Structure and Entropy of Ice and of Other Crystals with Some Randomness of Atomic Arrangement, L. Pauling, *J. Am. Chem. Soc.* **57** (1935) 2680-2684. Also see hardcopy handout.



degenerate configurations of hydrogen in ice

There are N molecules in a mole of ice. A given molecule can orient itself in six ways satisfying condition 2. However, the chance that the adjacent molecules will permit a given orientation is $^1/_4$; inasmuch as each adjacent molecule has two hydrogen-occupied and two unoccupied tetrahedral directions, making the chance that a given direction is available for each hydrogen of the original molecule $^1/_2$, and the chance that both can be located in accordance with the given orientation $^1/_4$. The total number of configurations for N molecules is thus $W = (^6/_4)^N = (^3/_2)^N$.

The residual entropy of ice, extrapolated to 0 K is
$S = R\ln(3/2)$

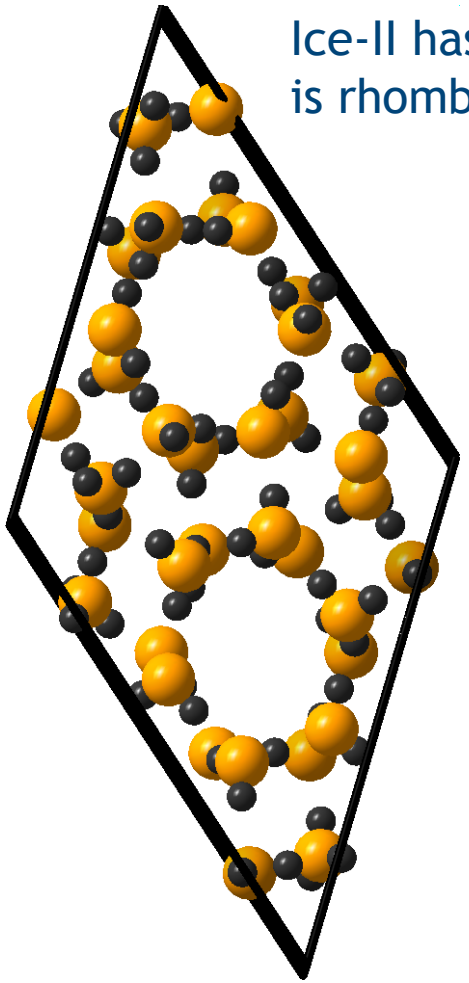
Proved by Giaque.

Also see: Residual entropy of square ice, E. H. Lieb, Phys. Rev. **162** (1967) 162.

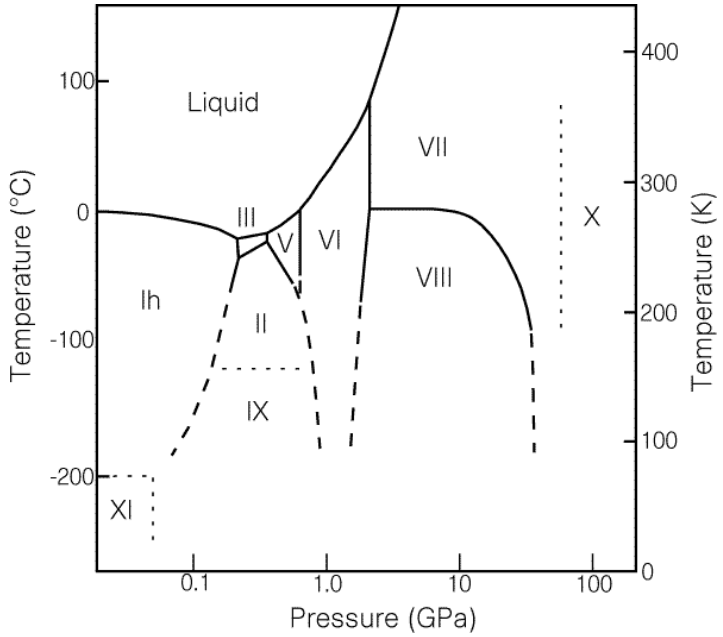
http://link.aps.org/abstract/PR/v162/p162

Ice

Ordering hydrogens though pressure: The many phases of ice.



Ice-II has all H(D) atoms located at 80 K. The structure is rhombohedral.

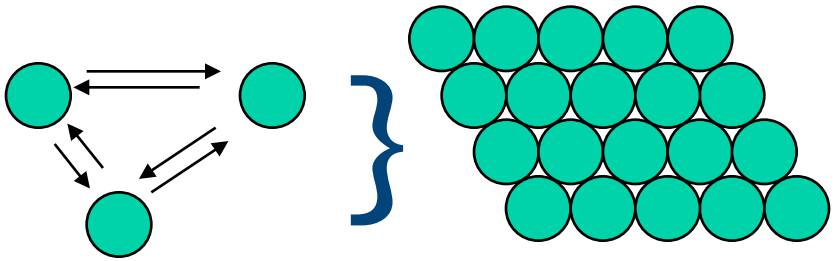


The structure of a new phase of ice, C. Lobban, J. L. Finney, and W. F. Kuhs, Nature 391 (1998) 268

Ram Seshadri x6129 seshadri@mrl

If the density of the hard spheres is increased, whether a crystal is formed depends on boundary conditions. Peas in a cylindrical glass jar do not crystallize easily [an experiment performed by Stephen Hales in 1727; See R. Zallen, *The Physics of Amorphous Solids*, John Wiley, 1983.] Instead they form a random-close packed (rcp) structure which Bernal determined to have a packing efficiency of 0.63 (*Cf.* fcc at 0.74) Metallic glasses have structures that can be described by such packings. See the handout. The *dual* of this packing is *continuous random network*, found in SiO_2 glasses.

It is important to consider that packings in 2D are quite distinct from 3D. One way of looking at this is to consider an attractive potential between disks (2D) and spheres (3D). In 2D, three disks will form a triangle, and these triangles can eventually (in the crystal) lead to *hcp*.



Ram Seshadri x6129 seshadri@mrl

In 3D, three spheres will form a triangle, and the fourth one will attach to the three to form a tetrahedron. Many tetrahedra should come together to form the crystal, but in fact, what is formed is an icosahedron which does not pack crystallographically. This is *topological frustration*. The local bonding rule is incompatible with crystalline packing. Liquid-solid transitions in 3D are never continuous.

One of the consequences in 2D of the *crystal nucleus* existing in the liquid (the triangles) is that the nature of 2D crystals is quite unusual and intermediate phases called *hexatic* phases are possible in 2D. These are phases with long range six-fold orientational order, but no long-range translational order. See P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics*, Cambridge 1998, and K. J. Strandburg, *Rev. Mod. Phys.* **60** (1988) 161.

Ram Seshadri x6129 seshadri@mrl

One way that 2D crystals lose their long-range translational periodicity is through the formation of *disclinations*:

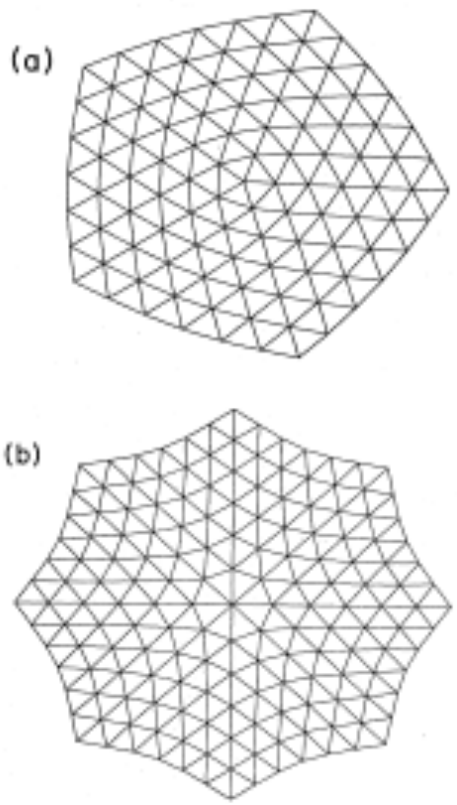


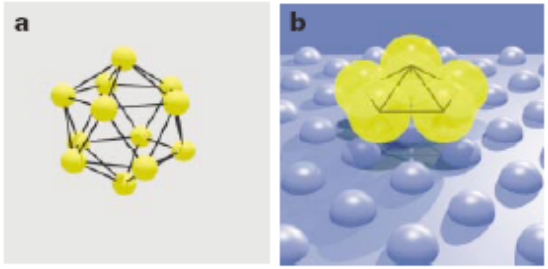
FIG. 4. Positive and negative disclinations in a triangular lattice. Note the rotation of the triangular cells by 60° (a) clockwise, and (b) counterclockwise, as a clockwise path around the disclination is traveled. Note that these disclinations may also be described as particles having (a) five, and (b) seven neighbors, respectively, rather than six.

(from Strandburg)

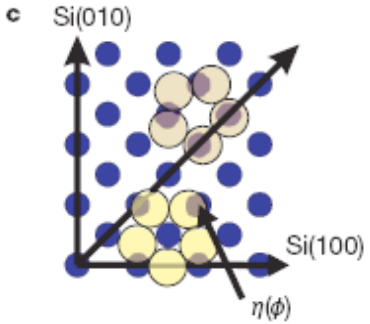
Disclinations become important for the structures of nanoparticles, liquid crystals, certain magnetic structures, block copolymer structures and liquid crystals.

Ram Seshadri x6129 seshadri@mrl

Liquid metals: Do they really have topological close packing ?



Evanescent x-ray scattering study of molten lead on Si. 5-fold local order is hard to directly observe in bulk liquids.

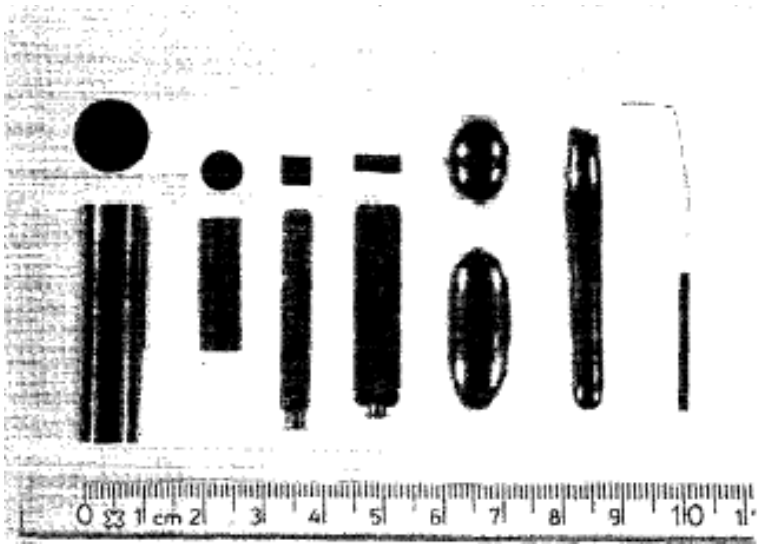


Observation of five-fold local symmetry in liquid lead, H. Reichert, O. Klein, H. Dosch, M. Denk, V. Honkimäki, T. Lippmann and G. Reiter, *Nature* **408** (2000) 839.

Figure 1 View of the dominant motif in the structure of bulk liquid lead and of interfacial liquid lead. **a**, Polytetrahedral arrangement predicted for close-packed monatomic liquids. **b**, Upper (pentagonal) half of the Pb icosahedron (**a**) captured by the potential landscape of the primitive Si(001) surface. **c**, Projection of the pentagonal structure onto four-fold coordinated sites of the Si(001) surface (lower pentagon, upper site position with minimum overlap of the projected electron density for rotation angle $\phi_n = 2\pi n/20$, where n is an integer; upper pentagon, hollow site with minimum overlap for $\phi_n = 2\pi(n+1/2)/20$; the overlap is denoted by η and shown in Fig. 3c as a function of the rotation ϕ of the pentagon).

Ram Seshadri x6129 seshadri@mrl

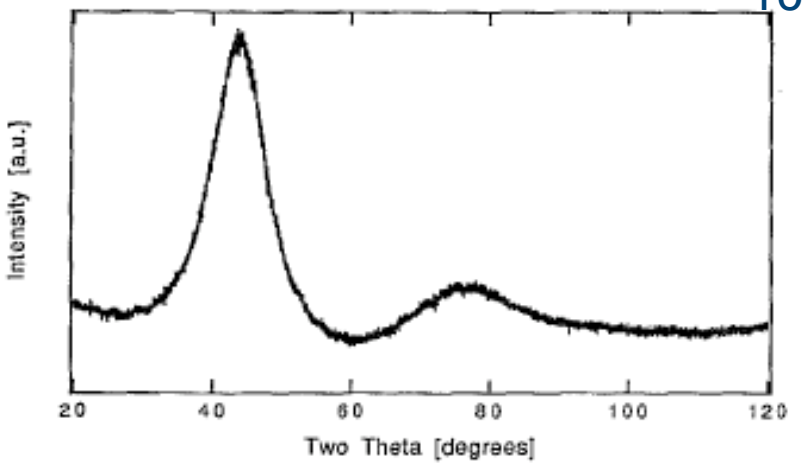
Liquid metals, intermetallics, metallic glasses and quasicrystals



A highly processable metallic glass: $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$, A. Peker and W. L. Johnson, *Appl. Phys. Lett.* **63** (1993) 2343.

Cooling rates are 10 K/s or less.

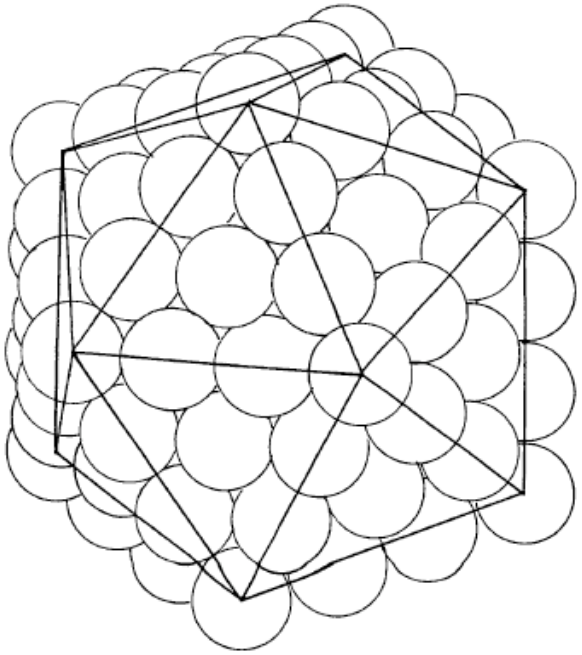
The very complex stoichiometry plays a role in trapping an amorphous state.



Liquidmetal Technologies
Cell phones, tennis racquets, golf clubs, terminator 2 …

Ram Seshadri x6129 seshadri@mrl

Mackay and Frank-Kasper polyhedra: Complex packings in intermetallics:



Third layer in an icosahedral packing of equal spheres.

A. L. Mackay, *Acta Crystallogr.* **15** (1962) 916.

NB: Single tetrahedron packs 0.78

Table 1. *The packing densities of icosahedral packings with increasing numbers of shells*

P_n is the density with a central sphere and P_n' without such a sphere

$$P_n = C_n/n^3 \times 6 \times 2{\cdot}53615$$

$$P_n' = (C_n - 1)/(n - 0{\cdot}04894)^3 \times 6 \times 2{\cdot}53615.$$

Shell number	Number of spheres in shell	Contents C_n	P_n (density)	P_n'
0	1	—	—	—
1	12	3·5158	0·72585	0·60378
2	42	27·032	0·69760	0·72362
3	92	90·547	0·69237	0·71935
4	162	214·063	0·69053	0·71317
5	252	417·579	0·68969	0·70864
6	362	721·095	0·68923	0·70539
7	492	1144·611	0·68895	0·70299
8	642	1708·126	0·68877	0·70116
9	812	2431·642	0·68865	0·69971
10	1002	3335·158	0·68856	0·69856
∞	—	—	0·68818	0·68818

Ram Seshadri x6129 seshadri@mrl

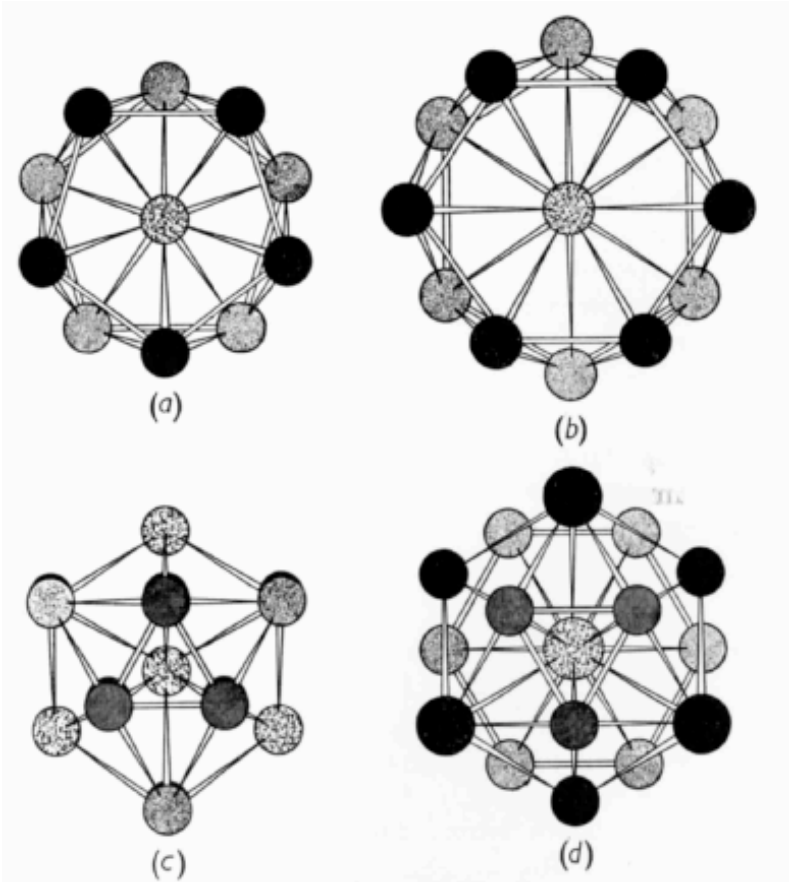


Fig. 1. The four 'normal coordination polyhedra' of complex alloy structures. For C.N. 12, two spheres above and below the central sphere, along the fivefold axis, are not shown. Similarly, two spheres above and below the central one of C.N. 14, along the sixfold axis are not shown. For C.N. 16 one sphere below the central one is not shown.
(*a*) Icosahedron, C.N. 12. (*b*) C.N. 14. (*c*) C.N. 15. (*d*) C.N. 16.

Frank-Kasper polyhedra with CN = 12, 14, 15 and 16. These are common in many alloy phases. CN = 12 is an icosahedron.

The addition of extra atoms (for example, to CN = 12) can be considered similar to the introduction of disclinations.

F. C. Frank and J. S. Kasper, *Acta Crystallogr.* **11** (1958) 184; **12** (1959) 483.

Ram Seshadri x6129 seshadri@mrl

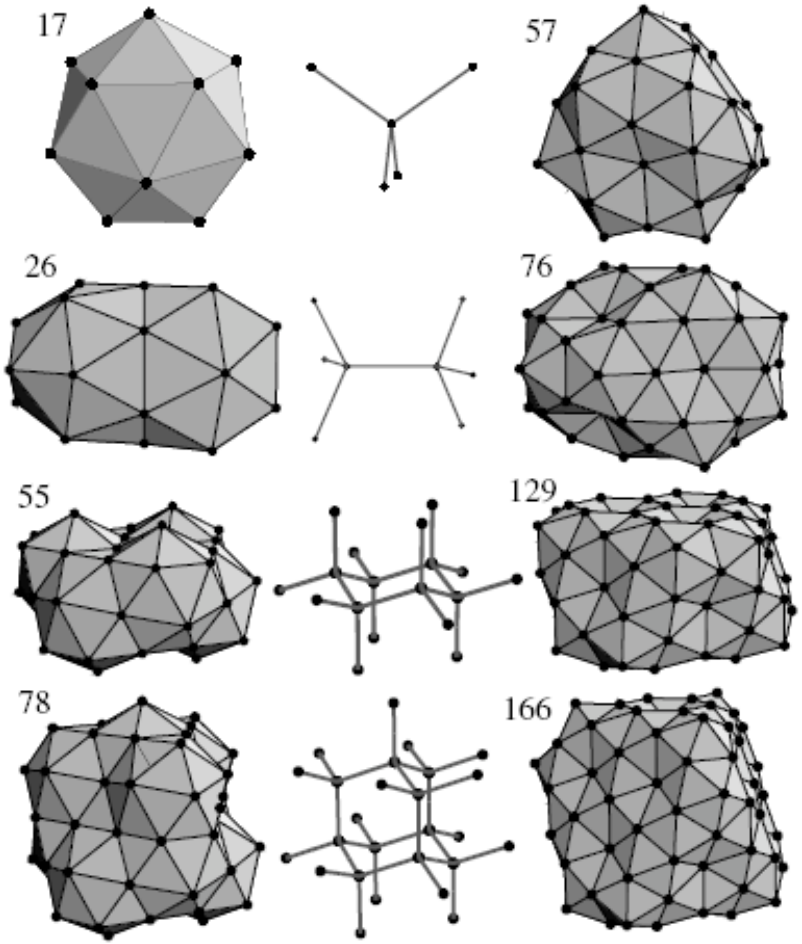


FIG. 3. Structures of some of the magic number clusters. On the right is the complete structure, in the middle the corresponding disclination network, and on the left the structure that is at the center of the cluster. All three have the same orientation.

Polytetrahedral clusters, J. P. K. Doye and D. J. Wales, *Phys. Rev. Lett.* 86 (2001) 5719.

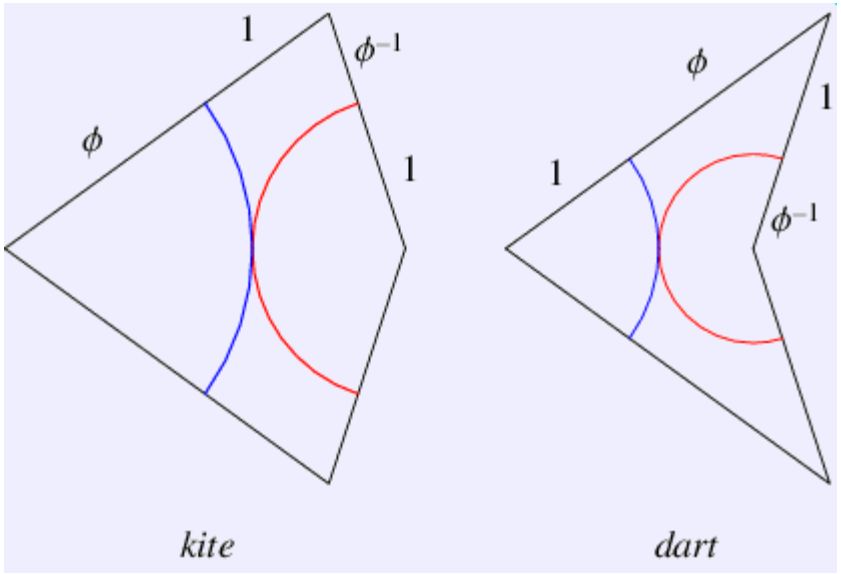
The authors used a potential that favors polytetrahedral packing and found that the disclination networks of stable clusters look like stable hydrocarbons.

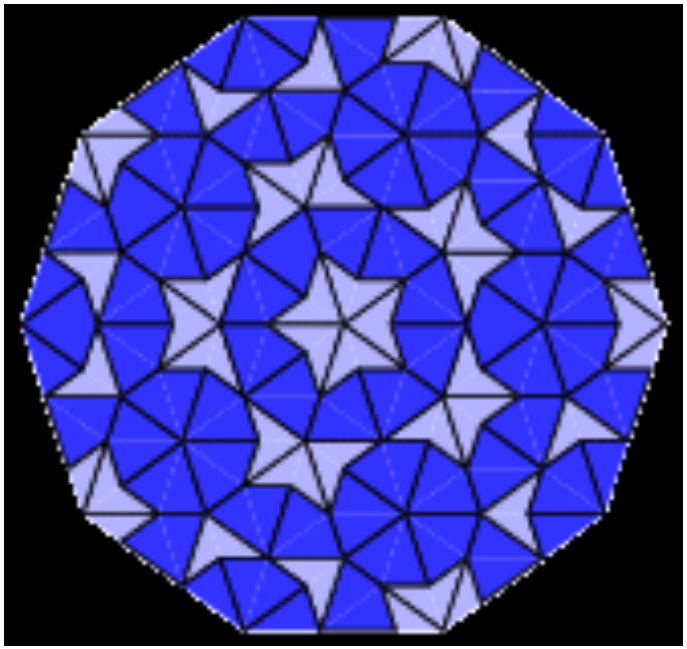
The cluster on the top left (17 atoms) has one atom in the center of a CN=16 F-K polyhedron. The CN=16 F-K polyhedron is generated from an icosahedron by introducing 4 disclinations and so on …

Ram Seshadri x6129 seshadri@mrl

Quasicrystals:

The Penrose tiling of darts and kites:





No translational periodicity (no unit cell) but sharp Bragg diffraction peaks (Alan Mackay, Birkbeck College, London).

Ram Seshadri x6129 seshadri@mrl

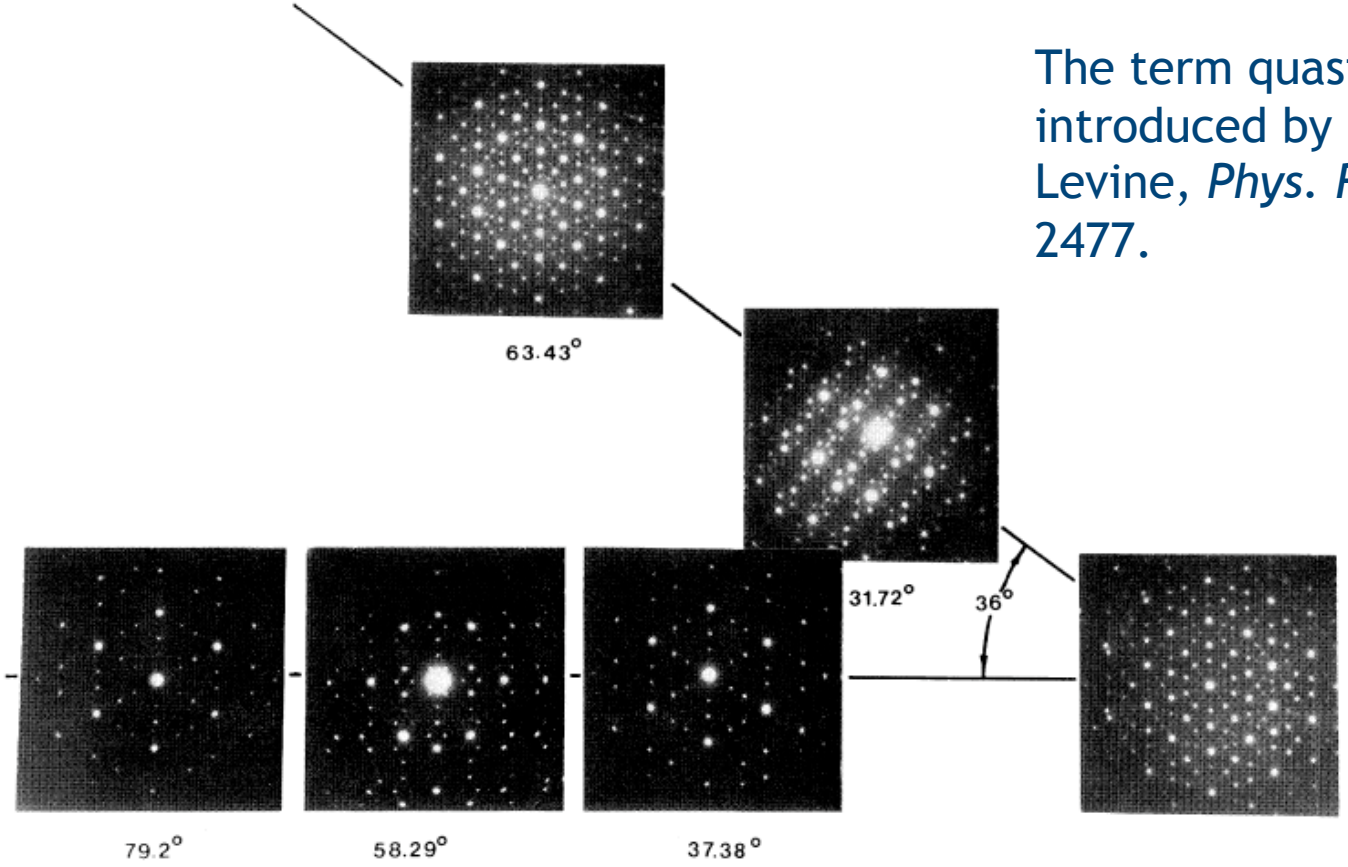


FIG. 2. Selected-area electron diffraction patterns taken from a single grain of the icosahedral phase. Rotations match those in Fig. 1.

The term quasicrystal was introduced by Steinhardt and Levine, *Phys. Rev. Lett.* **53** (1984) 2477.

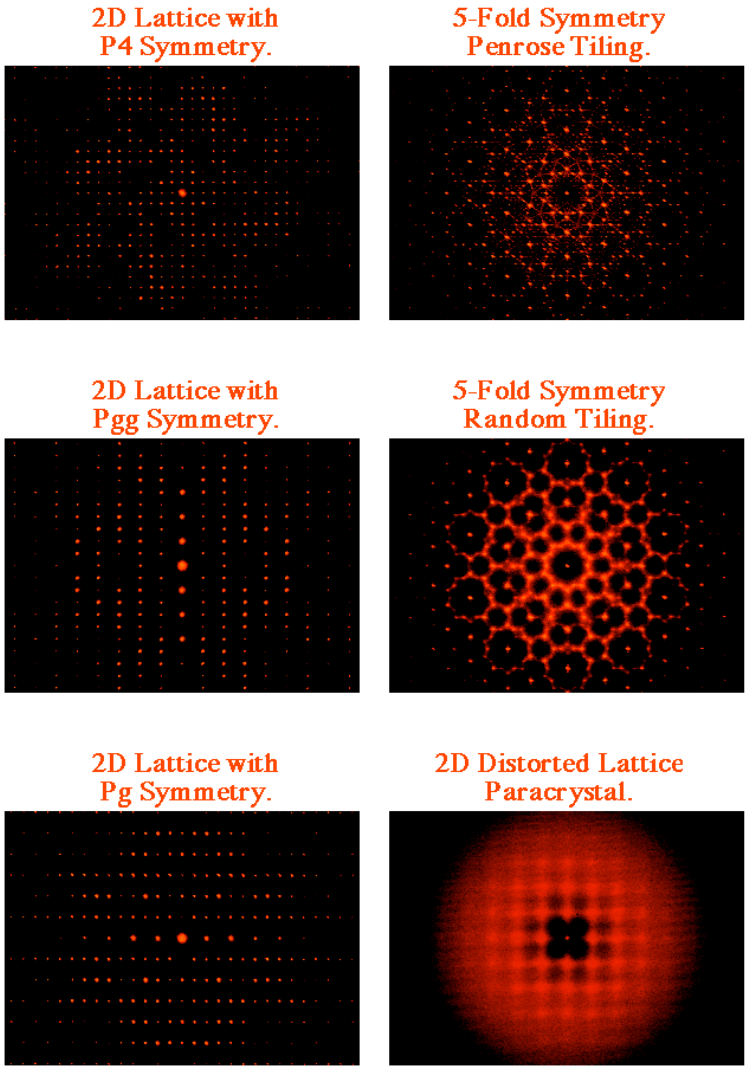
Al-14% Mn. Metallic phase with long range orientational order and no translational symmetry, D. Schectman, I. Blech, D. Gratias and J. W. Cahn, *Phys. Rev. Lett.* **53** (1984) 1951.

Ram Seshadri x6129 seshadri@mrl

The connection: D. R. Nelson and F. Spaepen, *Polytetrahedral order in condensed matter*, Solid State Physics (San Diego, CA: Academic Press) **42** (1989) 1-90. The question is how does one accommodate tetrahedral motifs in condensed phases: In liquids, the disclination network is dynamic and disordered; in metallic glasses, it is static and disordered; in quasicrystals, it looks like a Penrose tiling; in intermetallics such as the F-K phases, the disclination network is crystalline. Also D. R. Nelson, *Phys. Rev. Lett.* **50** (1983) 982.

Ram Seshadri x6129 seshadri@mrl

Liquid metals, intermetallics, metallic glasses and quasicrystals

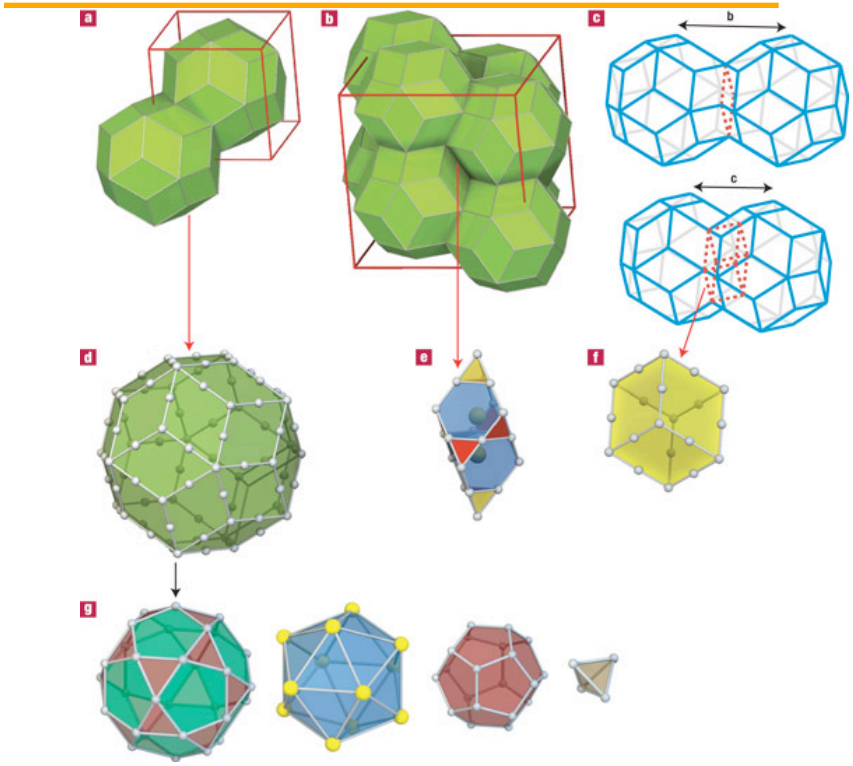


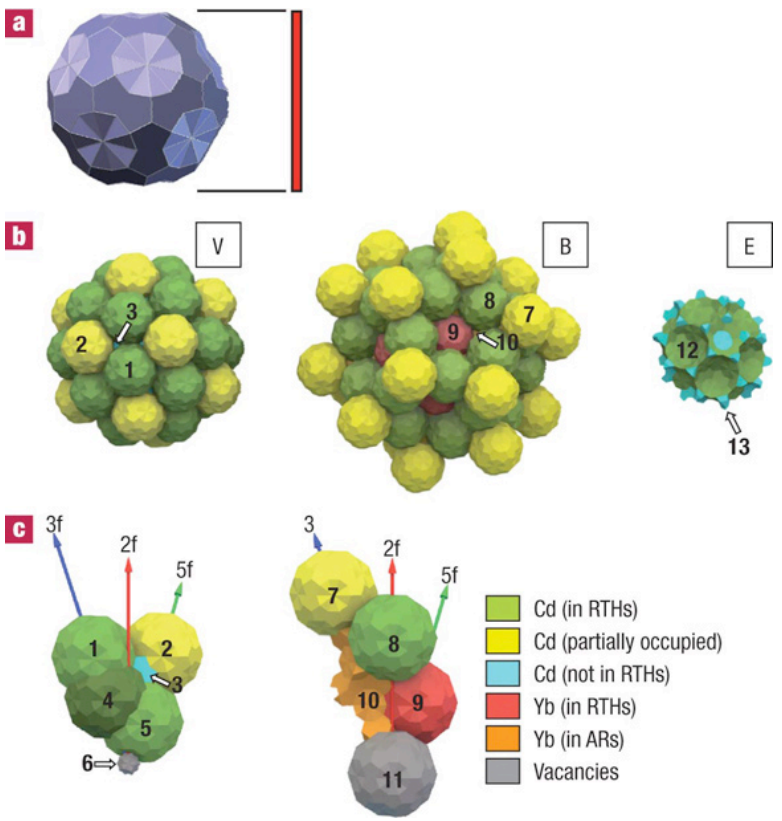
Optical diffraction patterns of two-dimensional tilings. This is from the website of T. R. Wellberry in ANU. http://rsc.anu.edu.au/~welberry/Optical_transform/

Mackay in 1981 showed that a Penrose tiling showed sharp Bragg peaks in its optical transform (laser diffraction pattern).

Ram Seshadri x6129 seshadri@mrl

Liquid metals, intermetallics, metallic glasses and quasicrystals



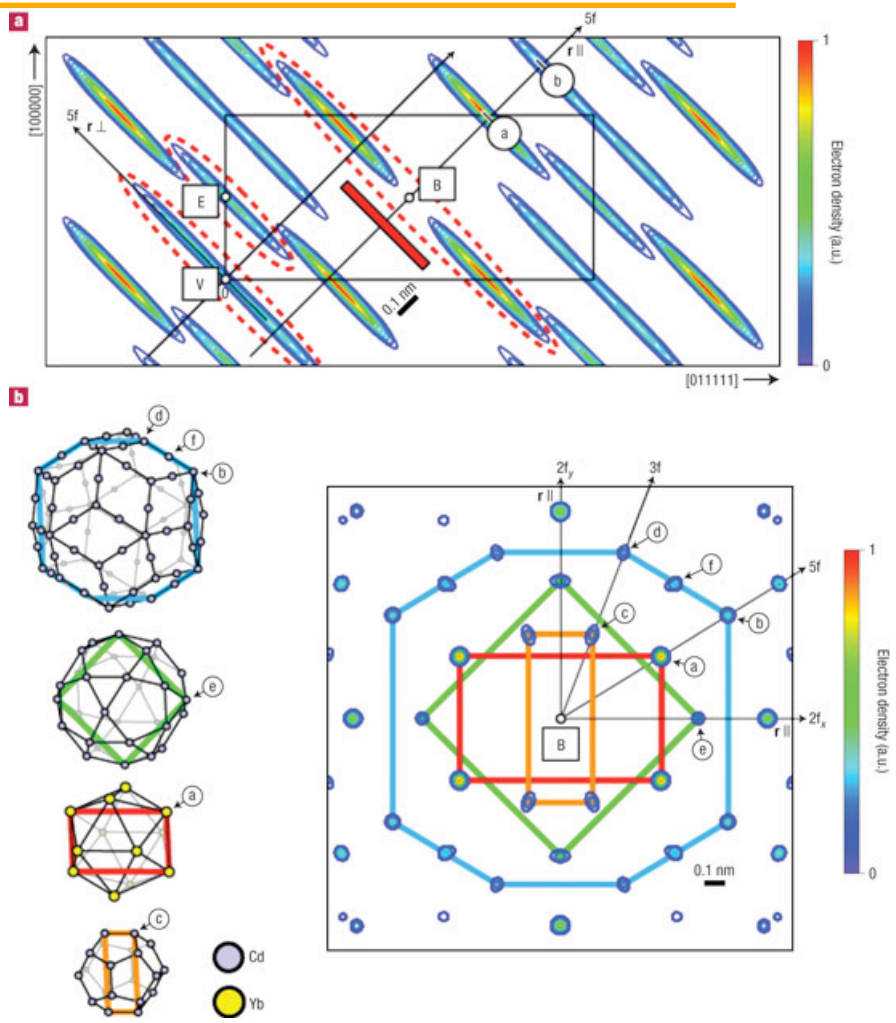


"first detailed structure solution of *i*-$YbCd_{5.7}$, one of the very few stable binary *i*-QCs, by means of X-ray structure determination. Three building units with unique atomic decorations arrange quasiperiodically and fill the space. These also serve as building units in the periodic approximant crystals."

H.Takakura, C. Pay Gómez, A. Yamamoto, M. De Boissieu, A. P. Tsai, Atomic structure of the binary icosahedral Yb–Cd quasicrystal, *Nature Mater.* **6** (2007) 58-63.

Ram Seshadri x6129 seshadri@mrl

Liquid metals, intermetallics, metallic glasses and quasicrystals

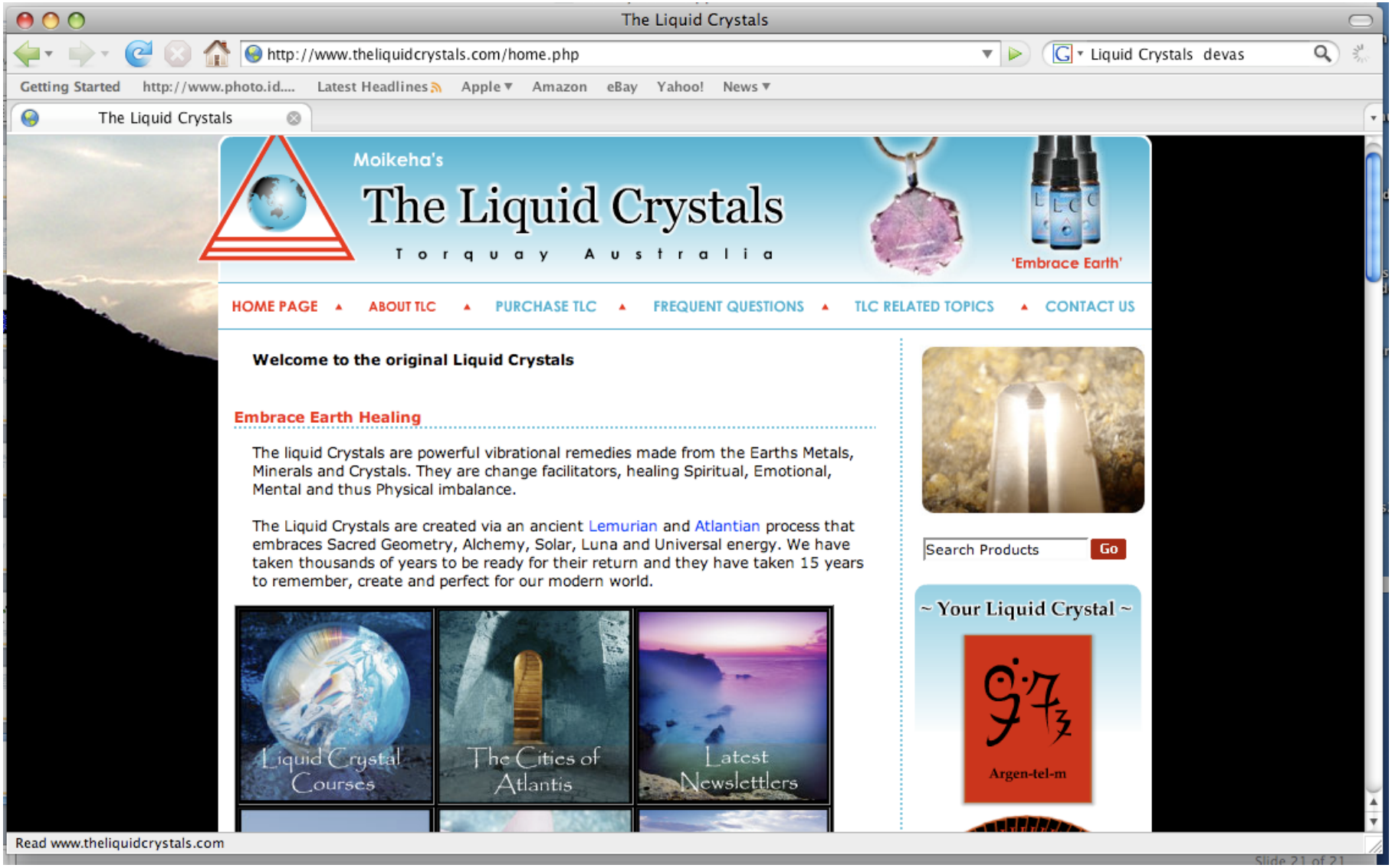


Quasicrystallography is facilitated by the existence of crystalline lattices in higher dimensional space (here in 6D) that project to the quasicrystal in lower-dimensional (3D) space. Note the 6 numbers used to index the electron density projections in the image on the left.

H.Takakura, C. Pay Gómez, A. Yamamoto, M. De Boissieu, A. P. Tsai, Atomic structure of the binary icosahedral Yb–Cd quasicrystal, *Nature Mater.* **6** (2007) 58-63.

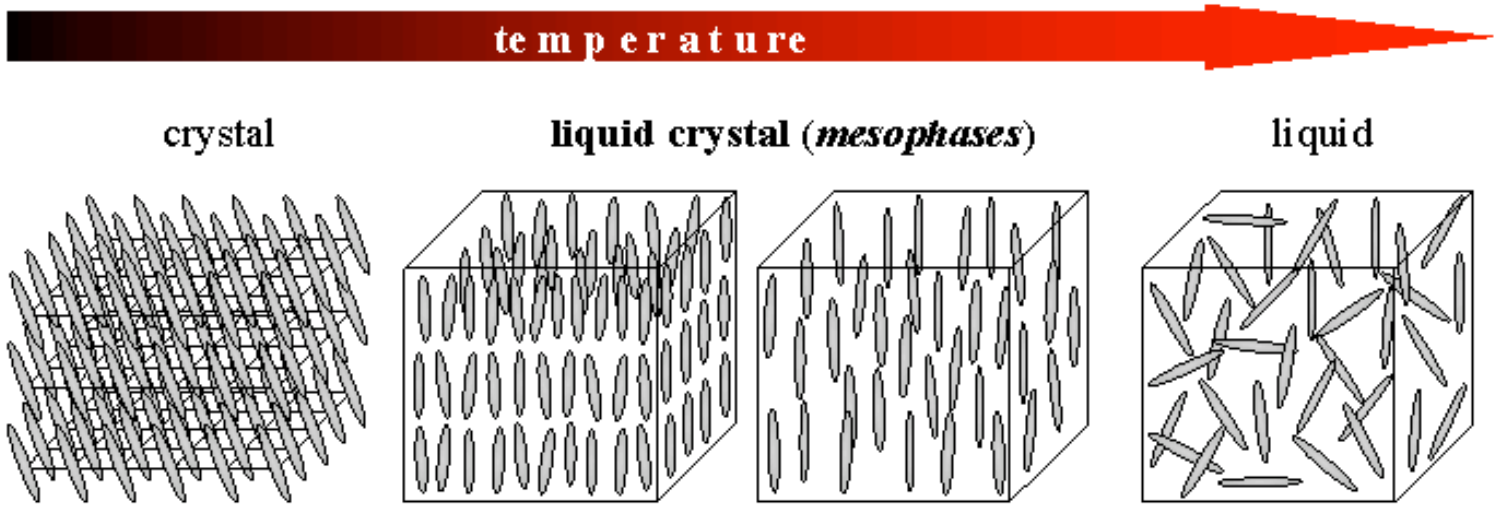
Ram Seshadri x6129 seshadri@mrl

Liquid Crystals



Ram Seshadri x6129 seshadri@mrl

thermotropic liquid crystals



crystal	liquid crystal (*mesophases*)		liquid
• 3-D lattice	• 1- (2-)D lattice	• no lattice	• no lattice
• orientation	• orientation	• orientation	• no orientation
• solid	• fluid	• fluid	• fluid
↳ *anisotropic*	↳ *anisotropic*	↳ *anisotropic*	↳ *isotropic*

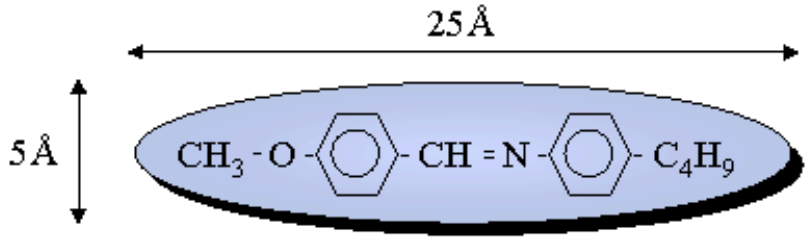
http://moebius.physik.tu-berlin.de/lc/lcs.html

Ram Seshadri x6129 seshadri@mrl

building blocks

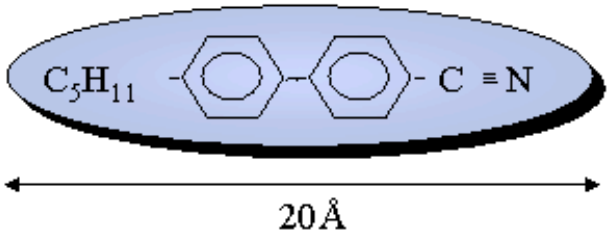
☞ *sterical organic molecules*

↳ i.e. **rod like (calamitic):**



MBBA
(4-methoxybenzyliden-4´-butylanilin)

C 22° N 47° I



5CB
(4-pentyl-4´-cyanobiphenyl)

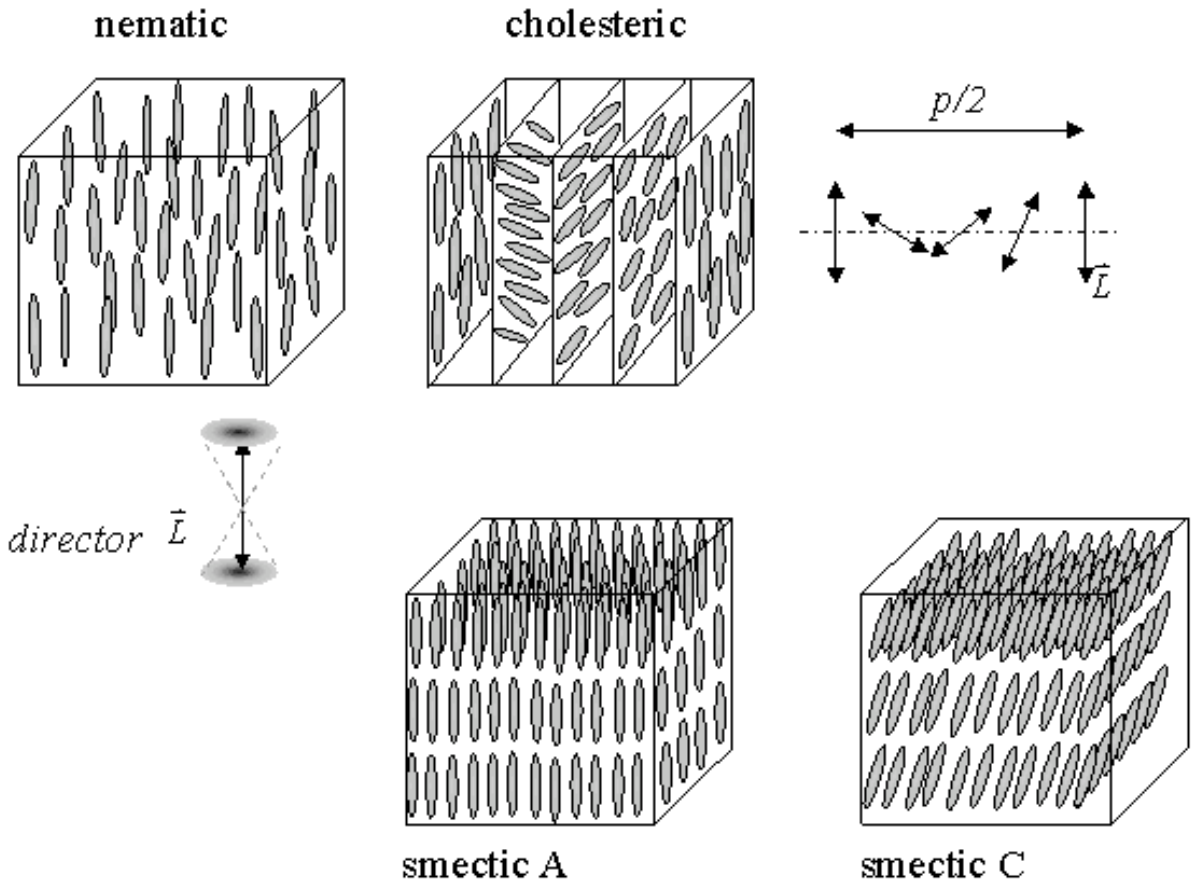
C 18° N 36° I

↳ others: **disk like (discotic)**

http://moebius.physik.tu-berlin.de/lc/lcs.html

Ram Seshadri x6129 seshadri@mrl

liquid crystalline phases



http://moebius.physik.tu-berlin.de/lc/lcs.html

Ram Seshadri x6129 seshadri@mrl