2010 Spring

"Amorphous Materials"

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Contents for previous class

Glass: undercooled liquid with high viscosity

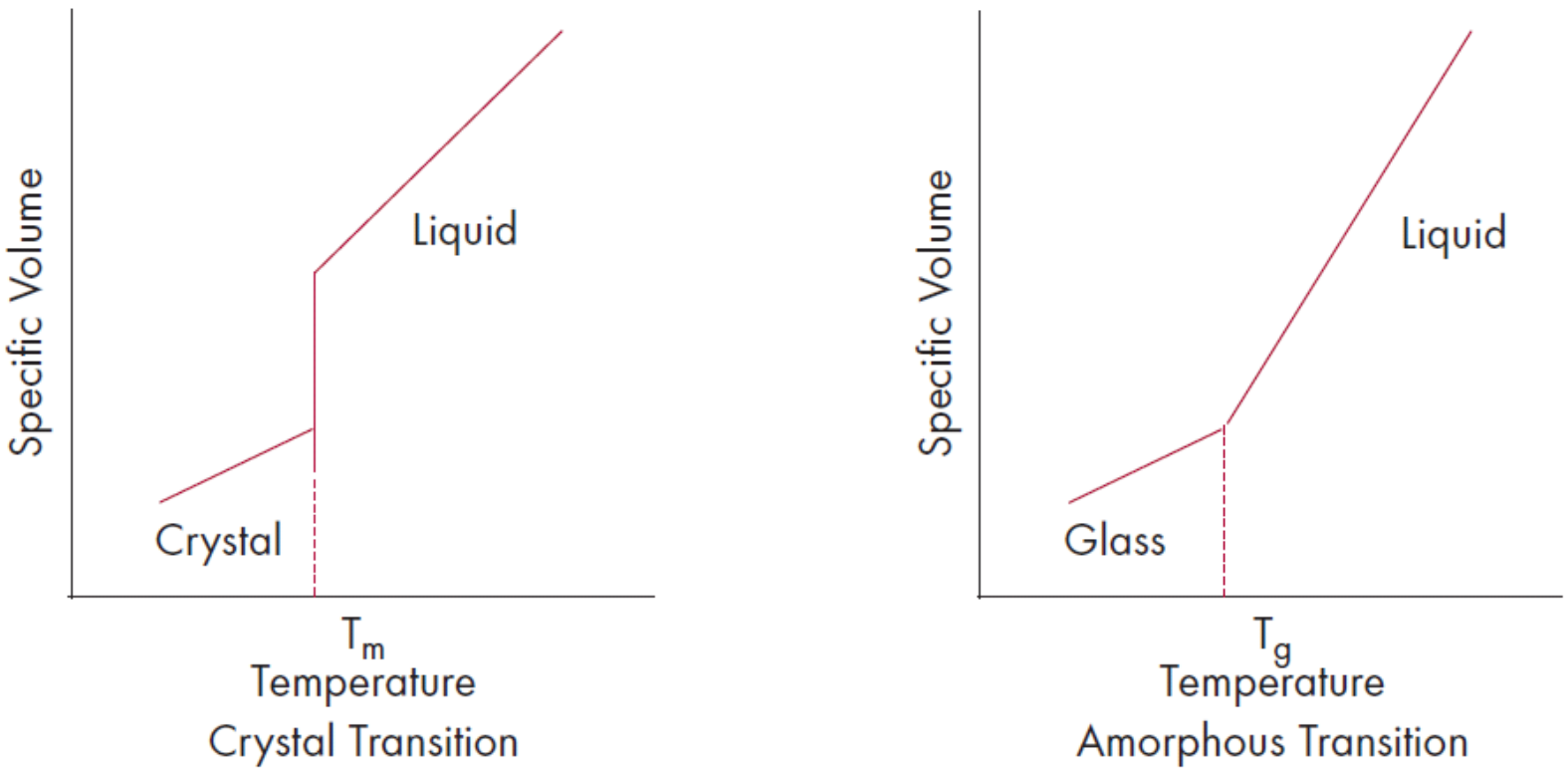


Figure 4. Liquid-Crystalline Solid Transition (Left) and Liquid-Glass Transition (Right).

Effect of cooling rate on glass transition temperature

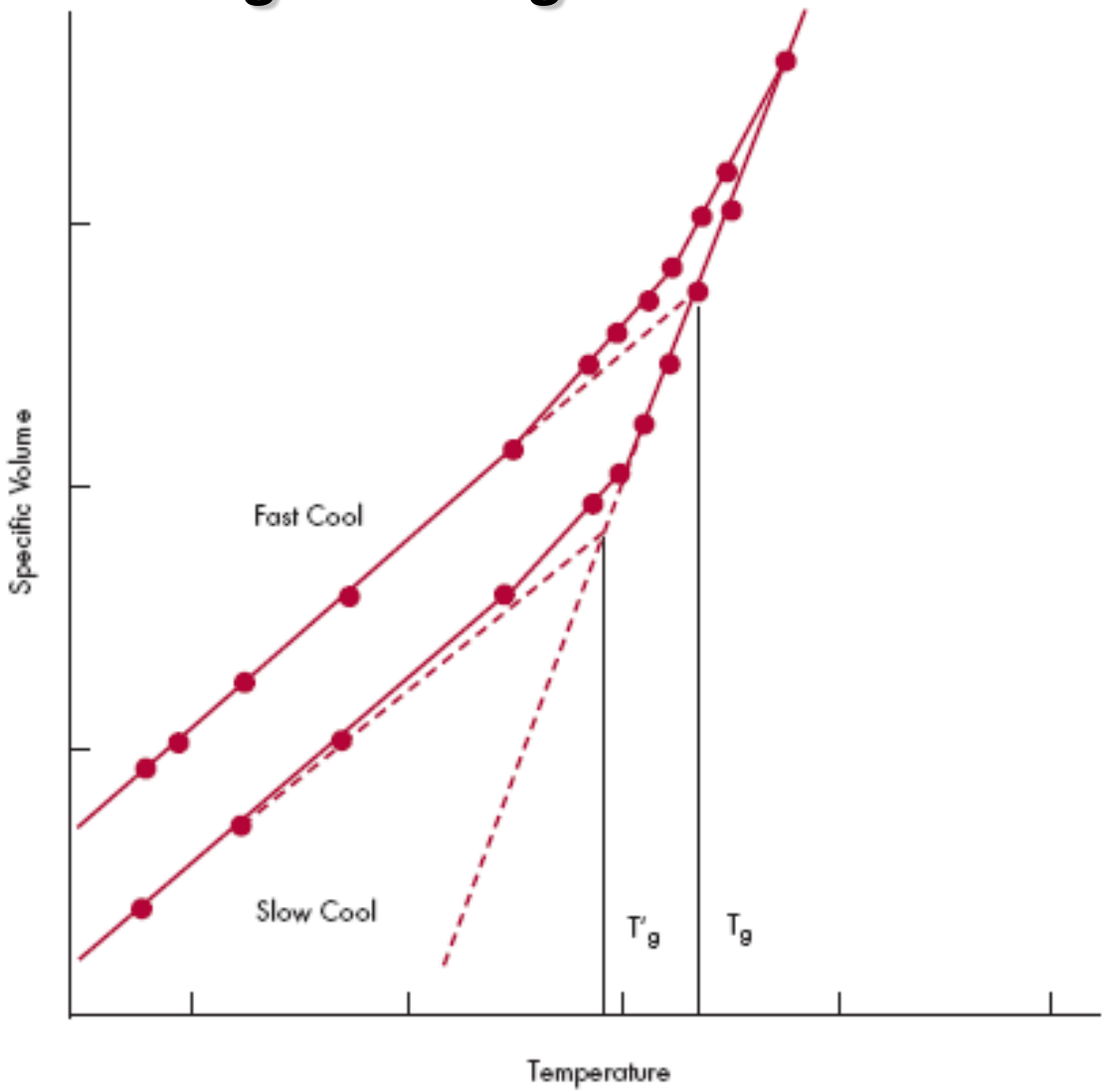


Figure 5. Schematic Representation of the Glass Transition. Note that the Glass-Transition Temperature (T_g) Shifts to a Lower Temperature with Slower Cooling (T'_g).

- ***Unique Properties for amorphous materials***

: not shared by crystalline solids at all

1) very hard, high strength ⟷ very brittle

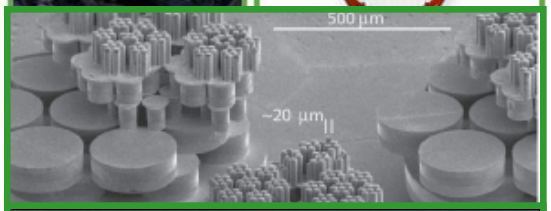
- Ex-situ or In-situ composite

2) large elastic strain limit

-Bouncing bearing … Application: sporting goods

3) processing metals as efficiently as plastics

- micro-forming … Application: MEMS



4) very soft magnetic material

- low magnetic loss ex) Iron-based amorphous m

5) high electrical resistivity

- 3~4 times higher than crystalline alloy

6) exceptionally high corrosion resistance

…Application: Industrial coating

Contents for today's class

- **Perfect Crystal**
- **Four Types of Disorder**
- **Quasicrystals**
- **Glass**

Perfect crystal → ***disorder*** → ***quasicrystal*** → ***amorphous***

: ***unit cell***

: ***underlying perfect crystalline lattice***

ex) ***icosahedral phase***

: ***no topological ordering***

Physics of amorphous materials (1990) - S.R. Elliott

- **Amorphous materials**

→ ***Material science aspect*** – ***wide variety of materials***

basically all materials can be amorphous

(limitation by kinetic condition)

→ ***Fundamental physics*** – **unique properties**

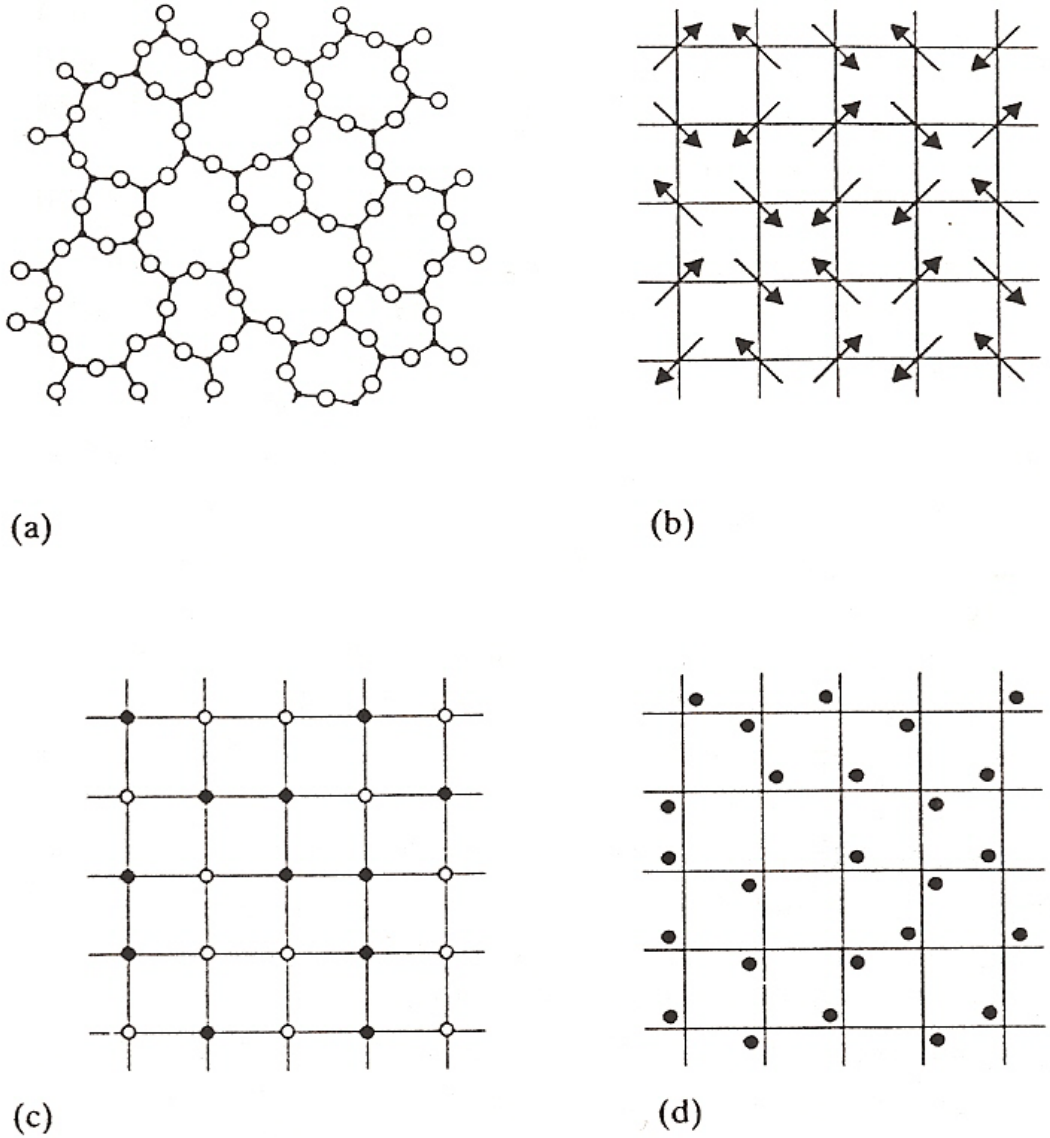
not shared by crystalline phase

→ ***Definition***: **non-crystalline materials with some degree of randomness**

What kind of randomness? Answer: Fig. 1.1 Types of disorder)

& How much? (randomness) Answer: chapter 3.

Four types of disorder in Figure 1.1



Four types of disorder in Figure 1.1

a) Topological (or geometric) disorder

: ***no translational order at all***

: ***but some degree of short range ordering***

b) Spin disorder

: ***spin (or magnetic moment) exhibits random orientation.***

: ***underlying perfect crystalline lattice***

c) Substitutional disorder

: ***metallic alloy***

: ***solid solution***

: ***underling perfect crystalline lattice***

d) Vibrational disorder

at any finite temperature the random motion of atoms about their equilibrium position destroys the perfect periodicity

Four types of disorder in Figure 1.1

Standard – perfect crystal

Define, atoms (or group of atoms or 'motifs') are arranged in a pattern that repeat periodically in three dimensions to an infinite extent.

: *valid at the absolute zero of temperature*

(if zero-point motion is ignored)

Imperfect crystal

: *defect (vacancy, dislocation, stacking fault)*

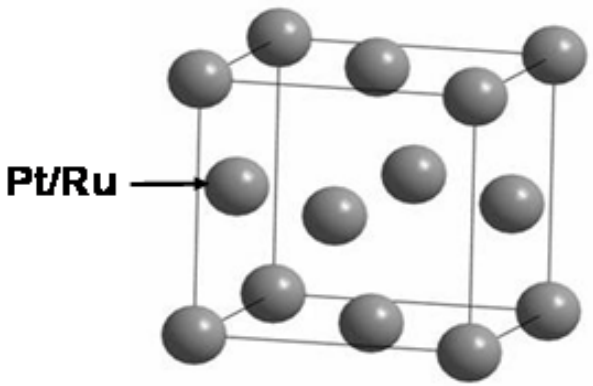
: *surface (interface)*

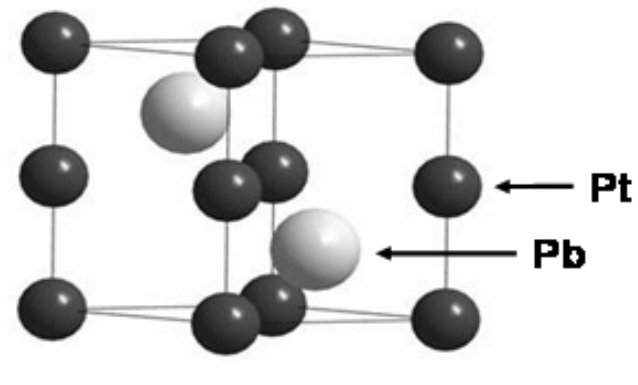
“ crystal- periodic structure ”

Alloying: atoms mixed on a lattice

➡ Solid Solution vs. Intermetallic Compounds

Crystal structure

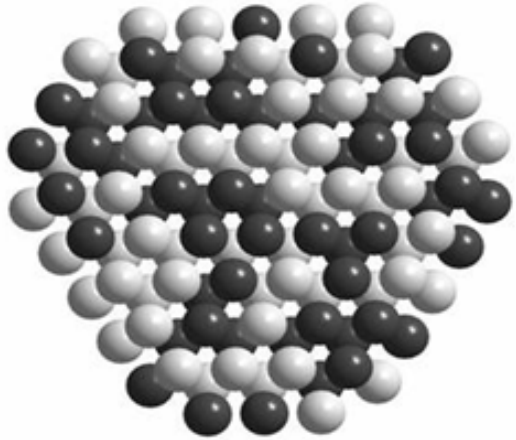


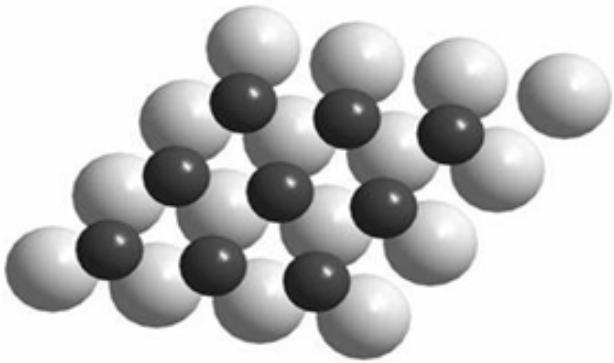


$Pt_{0.5}Ru_{0.5}$ – Pt structure (fcc)

PtPb – NiAS structure

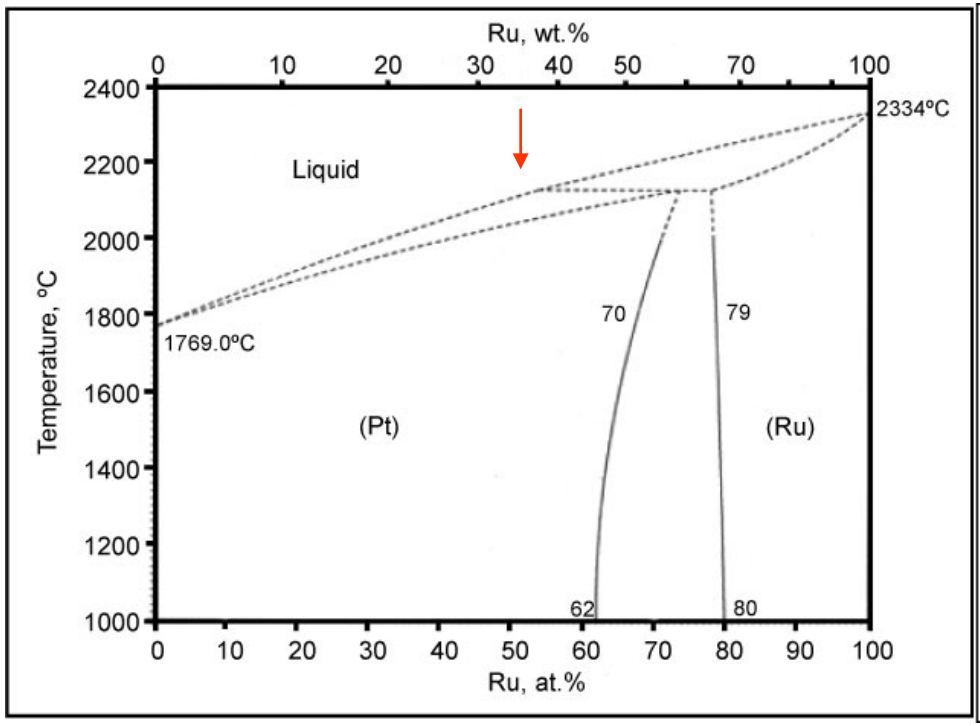
Surface

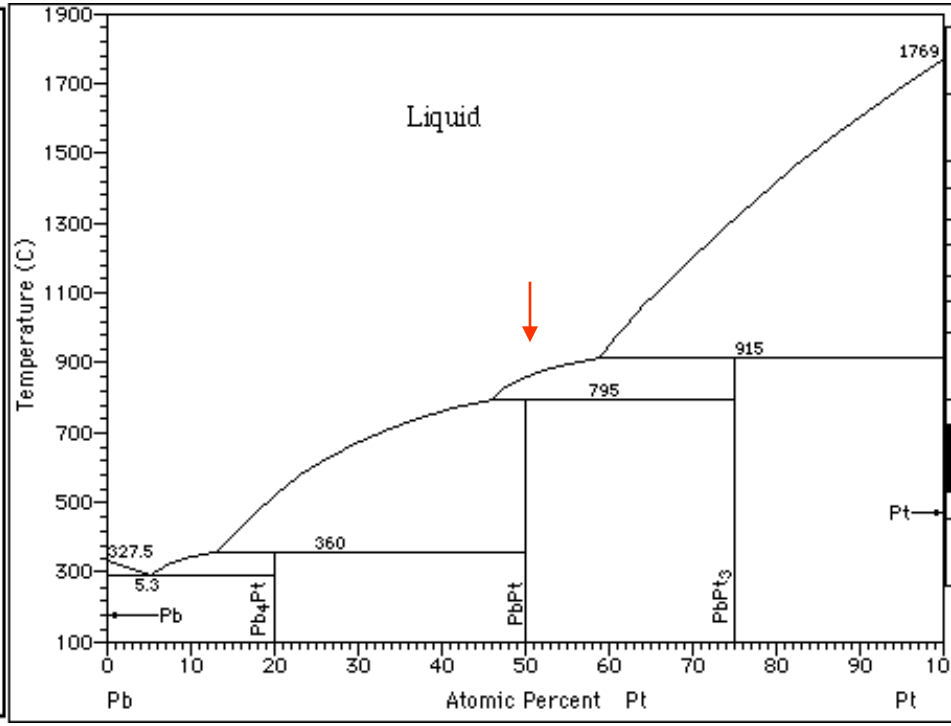




ruthenium 루테늄《백금류의 금속 원소;기호 Ru, 번호 44》

Solid Solution vs. Intermetallic Compounds



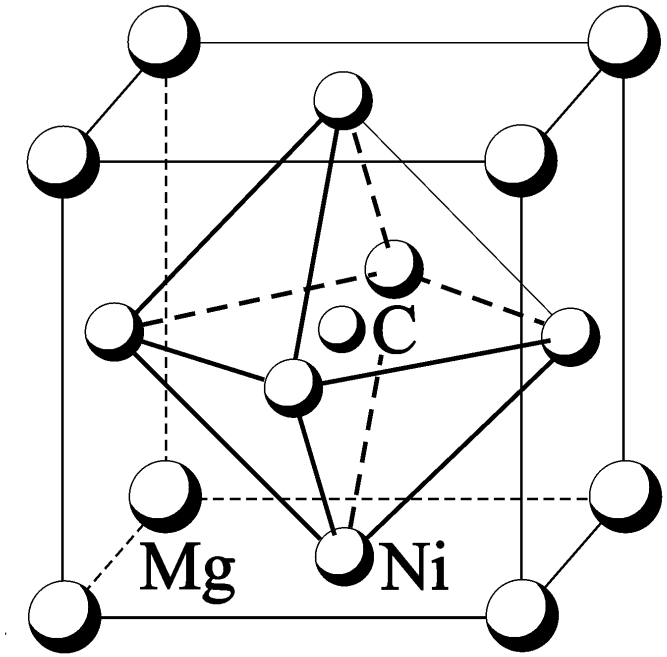


$Pt_{0.5}Ru_{0.5}$ – Pt structure (fcc)

PbPt – NiAS structure

- **Compound ; A – B – A – B ; → decided position of A, B, Ordered state**

B – A – B – A

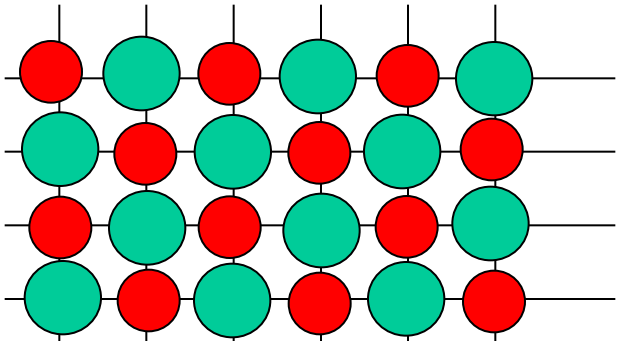


MgCNi3

Alloying: atoms mixed on a lattice
Solid Solutions and Ordered Compounds

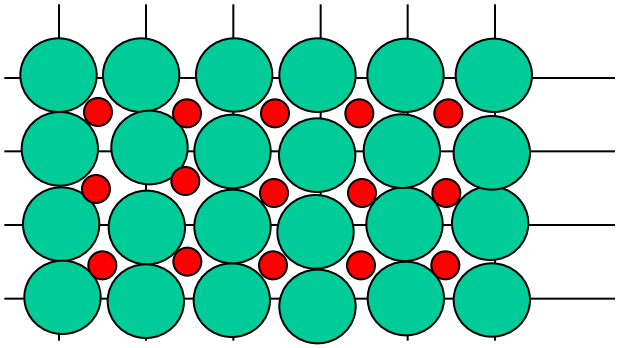
Ordered Substitutional and Interstititials Compounds

Substitutional
element replaces host atoms in an orderly arrangement



e.g., Ni_3Al (hi-T yield strength), $Al_3(Li,Zr)$ (strengthening)

Interstitial
element goes into holes in an orderly arrangement



e.g., small impurities, clays ionic crystals, ceramics.

- **Solution** ; A – A – A ; → atomic scale mixing, **Random distribution**

```
        |       |
        A – B – A
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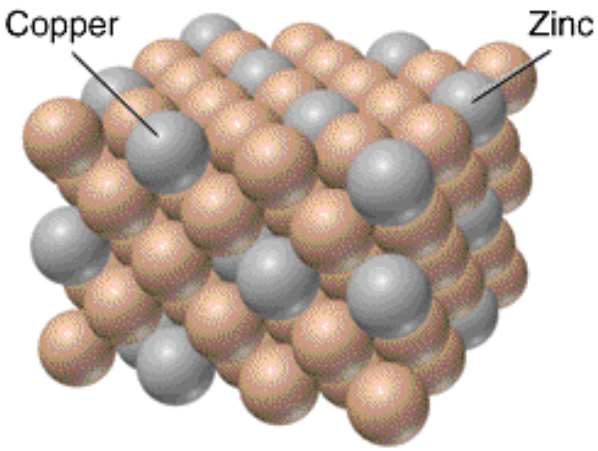
Two Possibilities for Solid Solutions: B atoms in A atoms

Substitutional

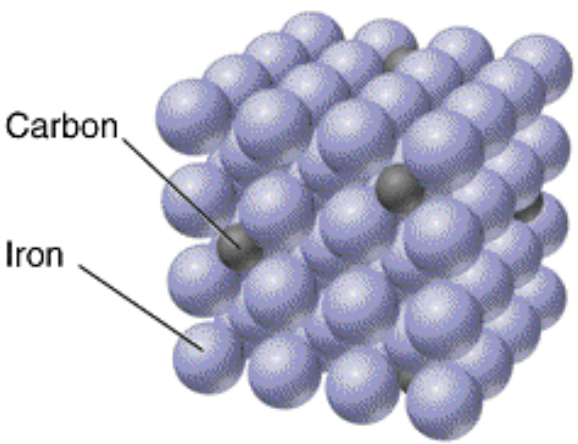
'new element replaces host atoms'

Interstitials

'new element goes in holes'



A Brass, a substitutional alloy

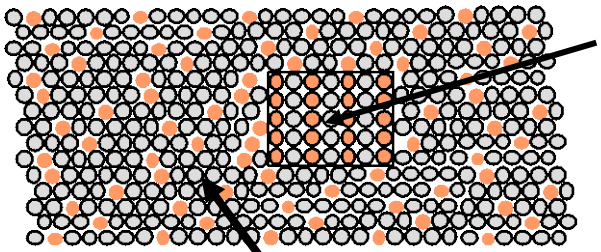


B Carbon steel, an interstitial alloy

Can we roughly estimate what atoms will form solid solutions?

Particles of New Phase in Solid-Solution Alloys

- Solid solution of B in A plus particles of a new phase (usually for a larger amount of B)

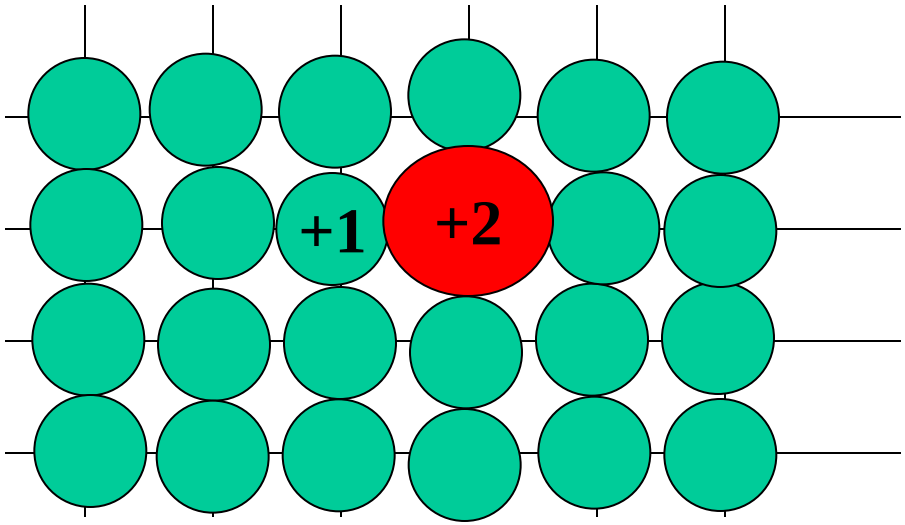


Second phase particle
--different composition
--often different structure.

Solid Solution phase B atoms in A

Hume-Rothery Rules for Alloys (atoms mixing on a lattice)

Will mixing 2 (or more) different types of atoms lead to a solid-solution phase?



Empirical observations have identified 4 major contributors through :

Atomic Size Factor , Crystal Structure, Electronegativity, Valences

Hume-Rothery Rules for Mixing

Empirical rules for substitutional solid-solution formation were identified from experiment that are not exact, but give an expectation of formation.
Briefly,

1) Atomic Size Factor **The 15% Rule**

If "size difference" of elements are greater than ±15%, the lattice distortions (i.e. local lattice strain) are too big and solid-solution will not be favored.

$$DR\% = \frac{r_{solute} - r_{solvent}}{r_{solvent}} x100\% < \pm 15\%$$ **will <u>not disallow</u> formation.**

2) Crystal Structure **Like elemental crystal structures are better**

For appreciable solubility, the crystal structure for metals must be the same.

3) Electronegativity **DE ~ 0 favors solid-solution.**

The more electropositive one element and the more electronegative the other, then "intermetallic compounds" (order alloys) are more likely.

4) Valences **Higher in lower alright. Lower in higher, it's a fight.**

A metal will dissolve another metal of higher valency more than one of lower valency.

Hume-Rothery Empirical Rules in Action

Is solid-solution favorable, or not?

- **Cu-Ni Alloys**

Rule 1: r_{Cu} = 0.128 nm and r_{Ni}= 0.125 nm.

DR%= $\frac{r_{solute} - r_{solvent}}{r_{solvent}} x100\%$ **= 2.3%** **favorable √**

Rule 2: Ni and Cu have the FCC crystal structure. **favorable √**

Rule 3: E_{Cu} = 1.90 and E_{Ni}= 1.80. Thus, DE%= -5.2%
favorable √

Rule 4: Valency of Ni and Cu are both +2. **favorable √**

Expect Ni and Cu forms S.S. over wide composition range.

At high T, it does (helpful processing info), but actually phase separates at low T due to energetics (quantum mechanics).

Hume-Rothery Empirical Rules in Action

Is solid-solution favorable, or not?

- **Cu-Ag Alloys**

Rule 1: r_{Cu} = 0.128 nm and r_{Ag}= 0.144 nm.

DR%= $\frac{r_{solute} - r_{solvent}}{r_{solvent}} x100\%$ **= 9.4%** **favorable √**

Rule 2: Ag and Cu have the FCC crystal structure. **favorable √**

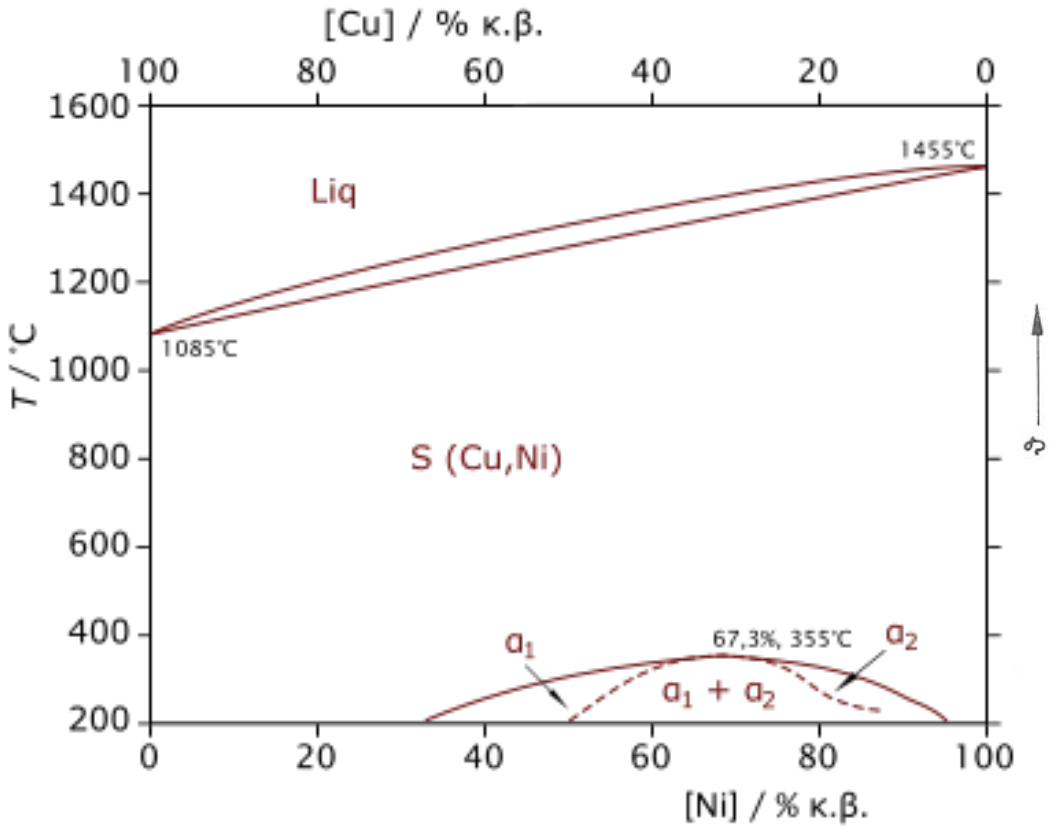
Rule 3: E_{Cu} = 1.90 and E_{Ni}= 1.80. Thus, DE%= -5.2%
favorable √

Rule 4: Valency of Cu is +2 and Ag is +1. **NOT favorable**

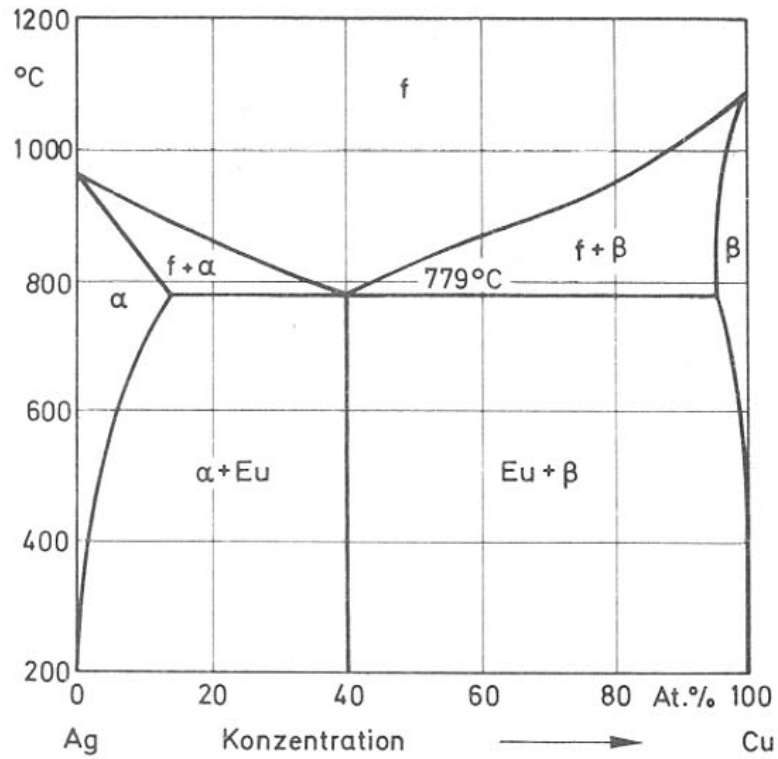
Expect Ag and Cu have <u>limited solubility</u>.

In fact, the Cu-Ag phase diagram (T vs. c) shows that a solubility of only 18% Ag can be achieved at high T in the Cu-rich alloys.

Cu-Ni Alloys



Cu-Ag Alloys



complete solid solution

limited solid solution

Quasicrystals

Crystal with 5 fold symmetry ***Mathematically impossible but exist***

1984 $Al_{86}Mn_{14}$ alloy **: rapidly solidified ribbon_*Shectman et al.***

: materials whose structure cannot be understood within classical crystallography rules.

"Quasiperiodic lattices", with long-range order but without periodic translations in three dimensions

- **long range order: quasiperiodic**
- **no 3-D translational symmetry**
- **sharp diffraction patterns**

http://www.youtube.com/watch?v=k_VSpBI5EGM

Icosahedral phase

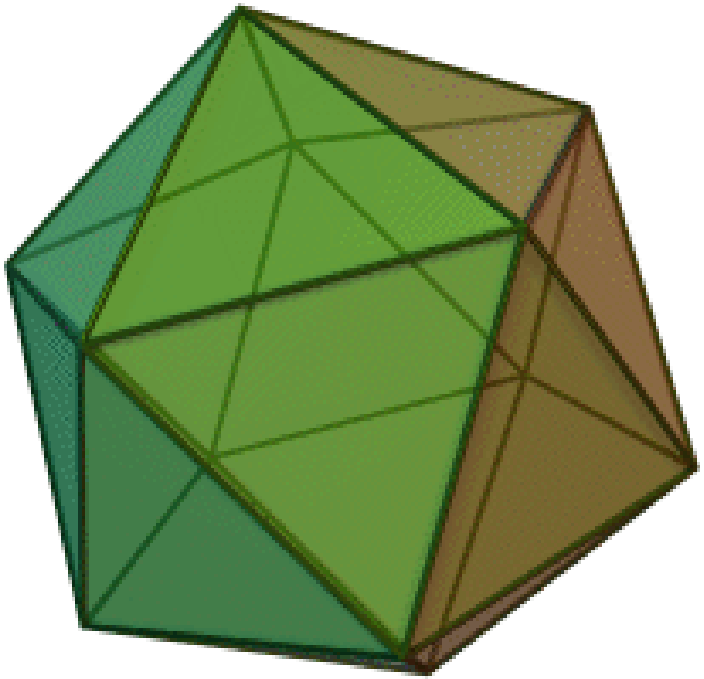
icosahedron has 12 corners

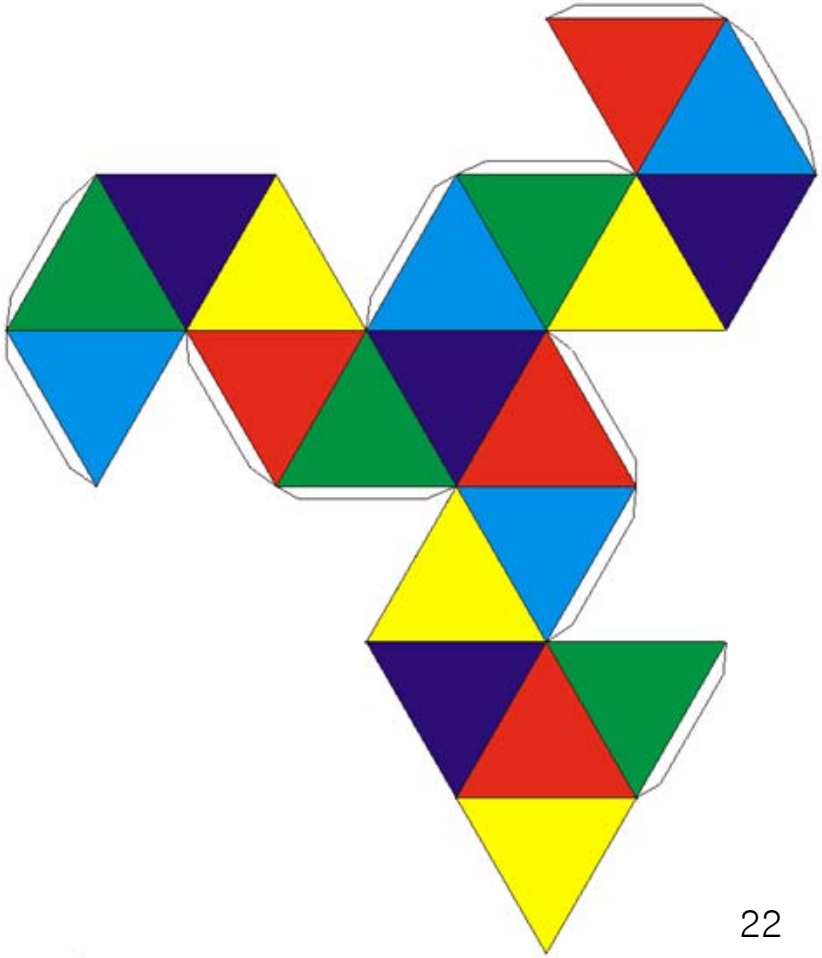
most definitions indicate 20 faces

Al-Pd-Mn

Al-Cu-Fe

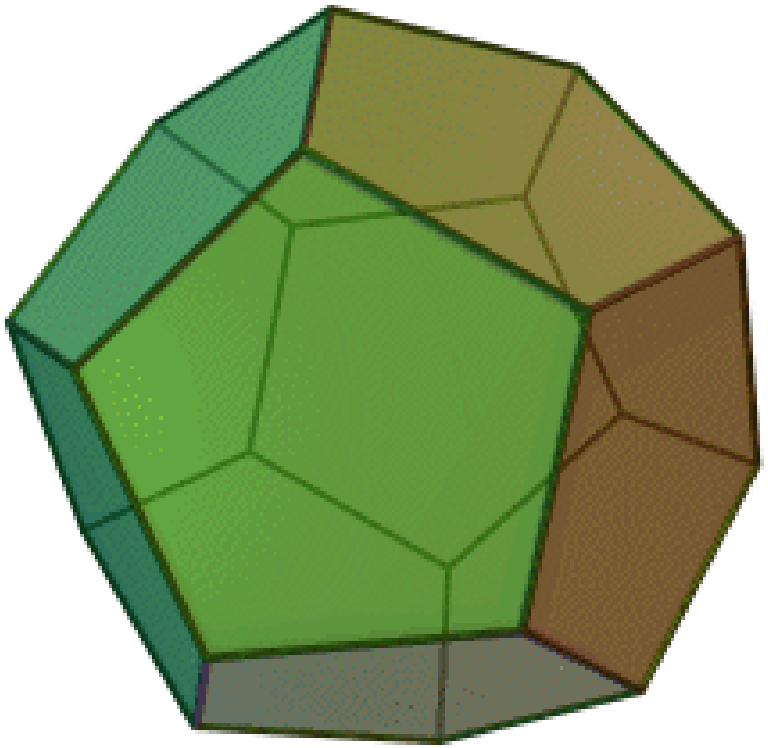
Ho-Mg-Zn

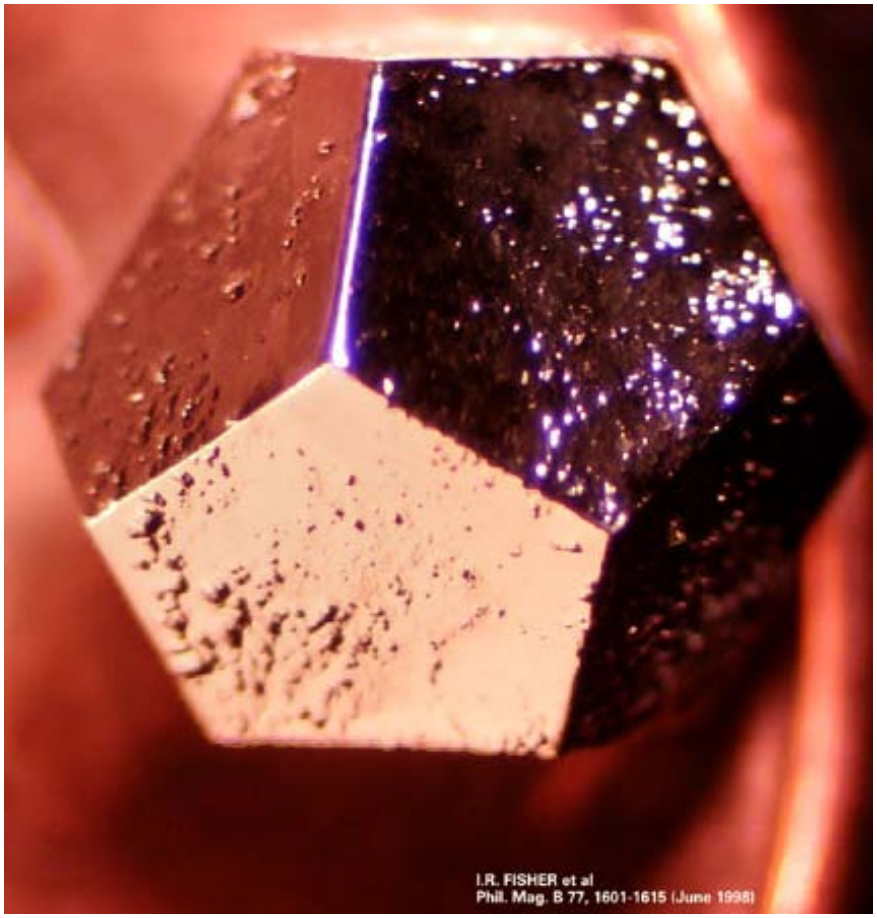




dodecahedron **has 20 corners**

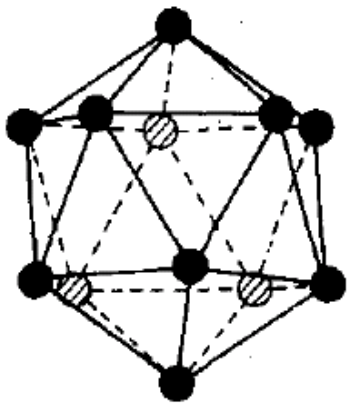
most definitions indicate 12 faces



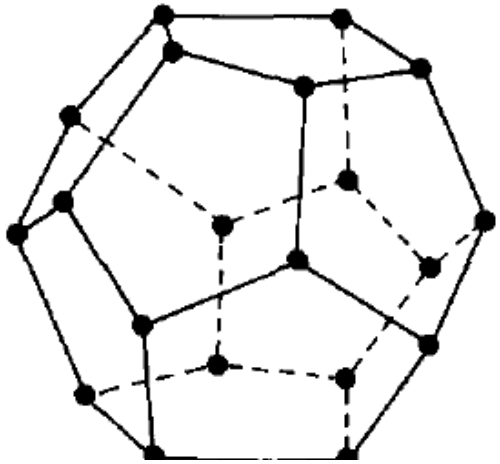


Polyhedra with the icosahedral symmetry

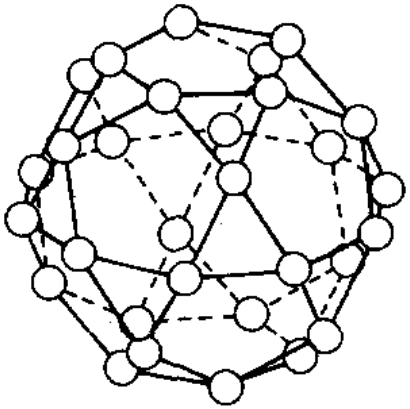
(a) icosahedron



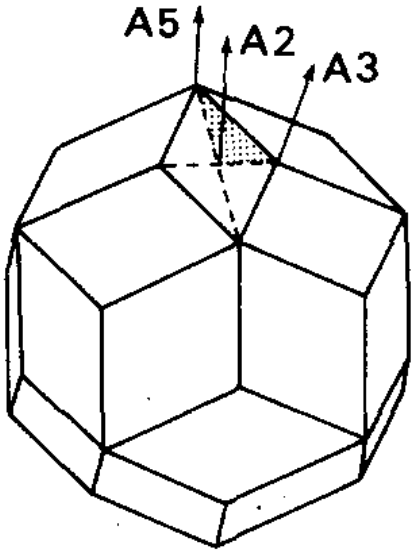
(b) dodecahedron



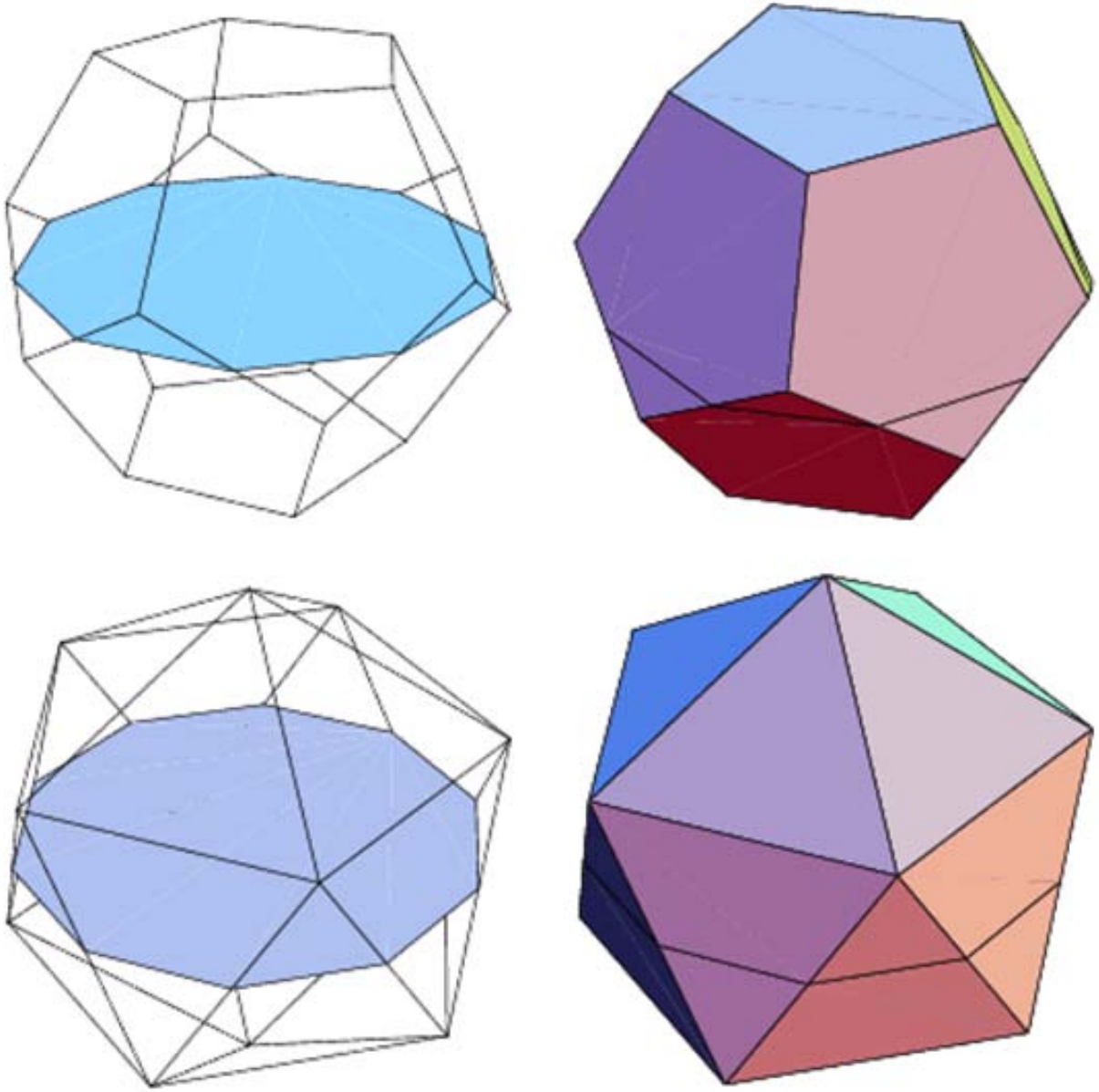
(c) icosidodecahedron



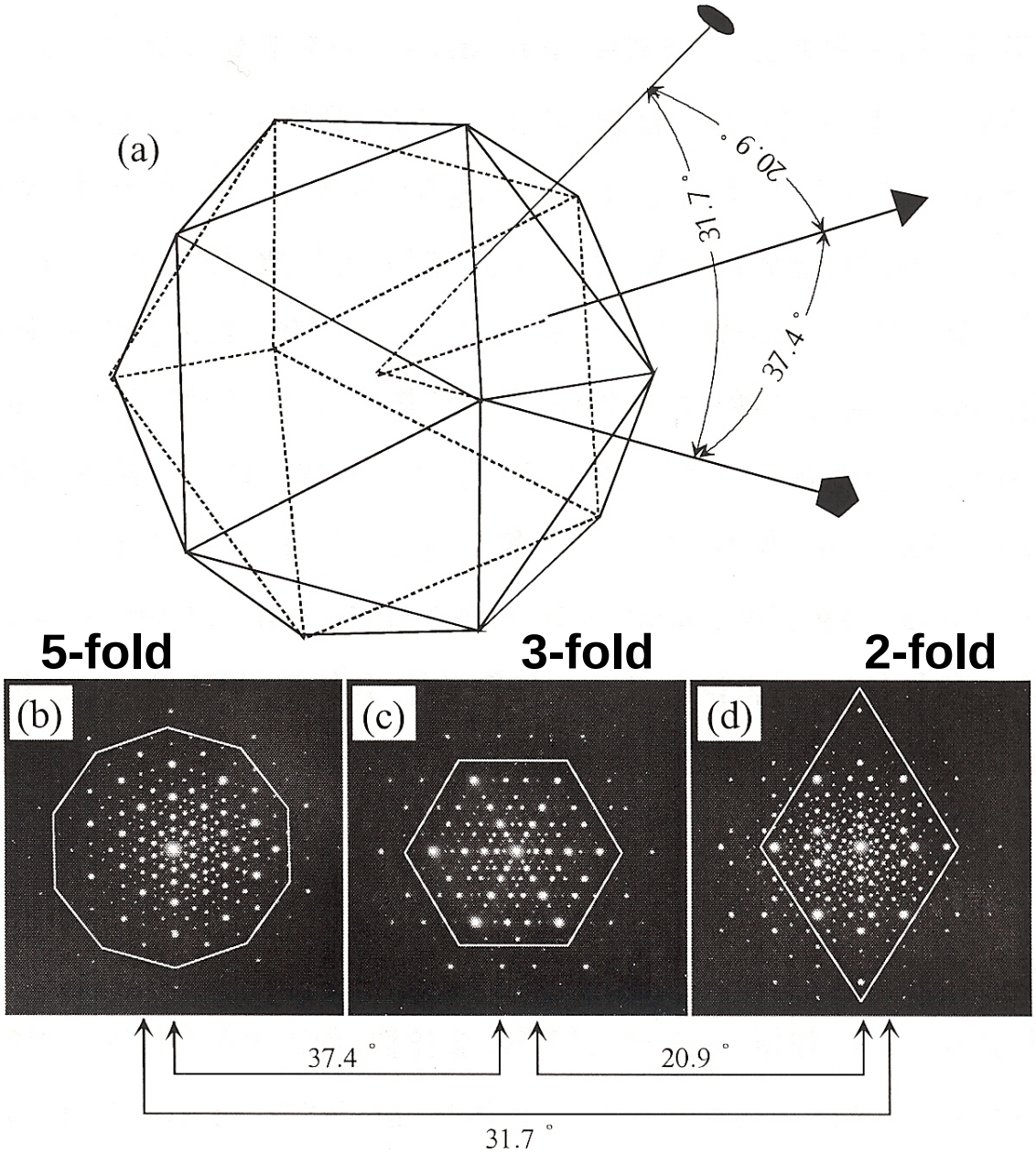
(d) triacontahedron



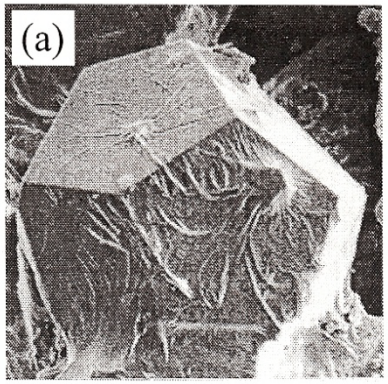
A plane perpendicular to the c axis of a *dodecahedron* or *icosahedron* cuts the solid in a regular decagonal cross section

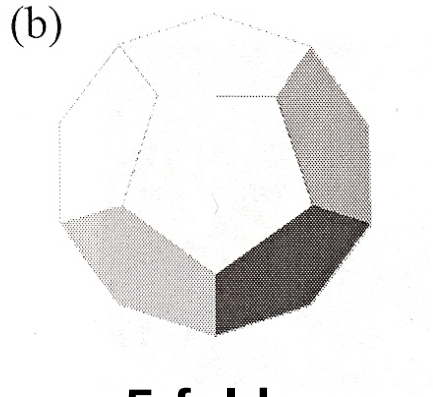


Geometry and typical diffraction patterns of icosahedral phase

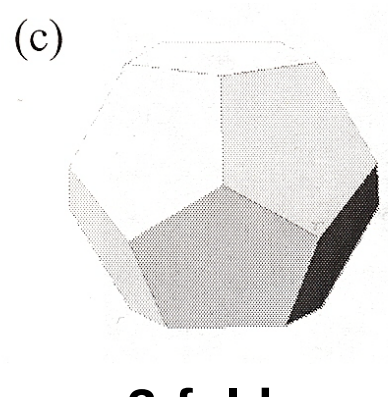


Pentagonal dodecahedron shape

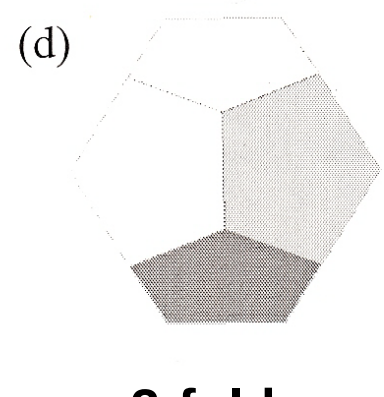




5-fold

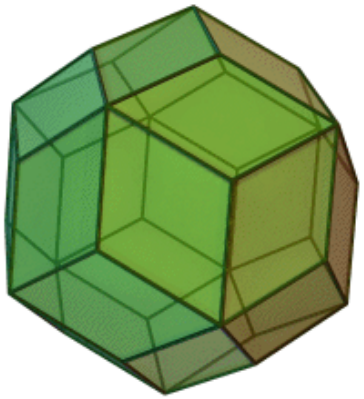


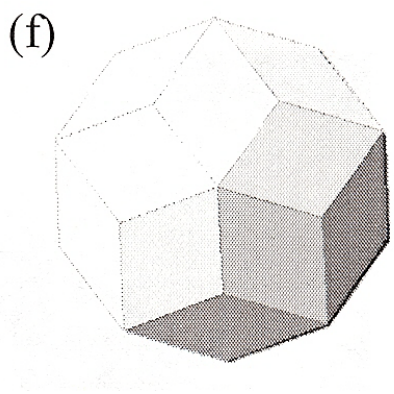
3-fold



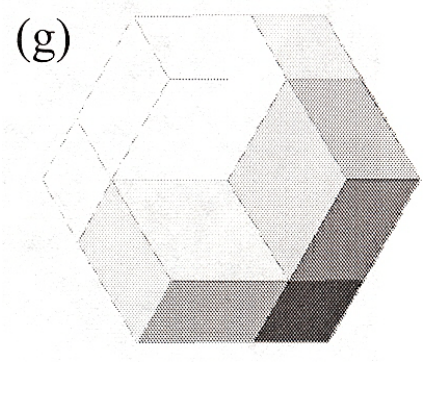
2-fold

Rhombic triacontahedron shape

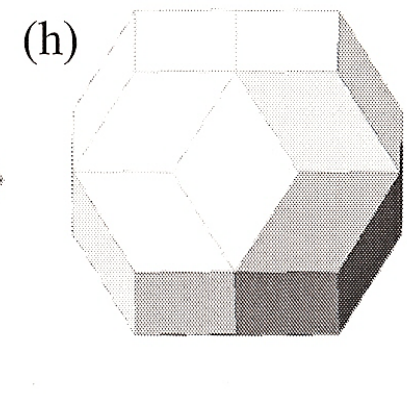




5-fold



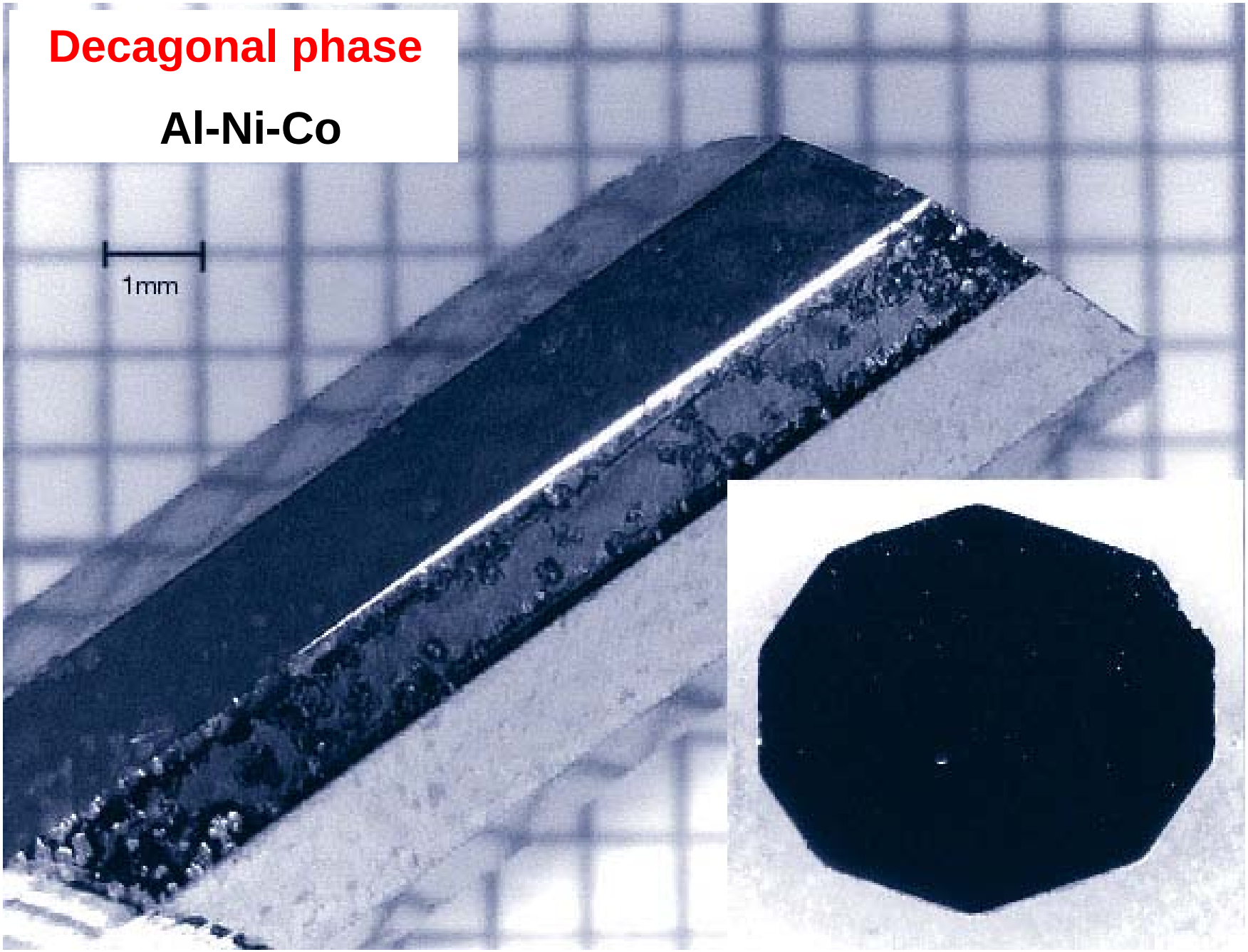
3-fold



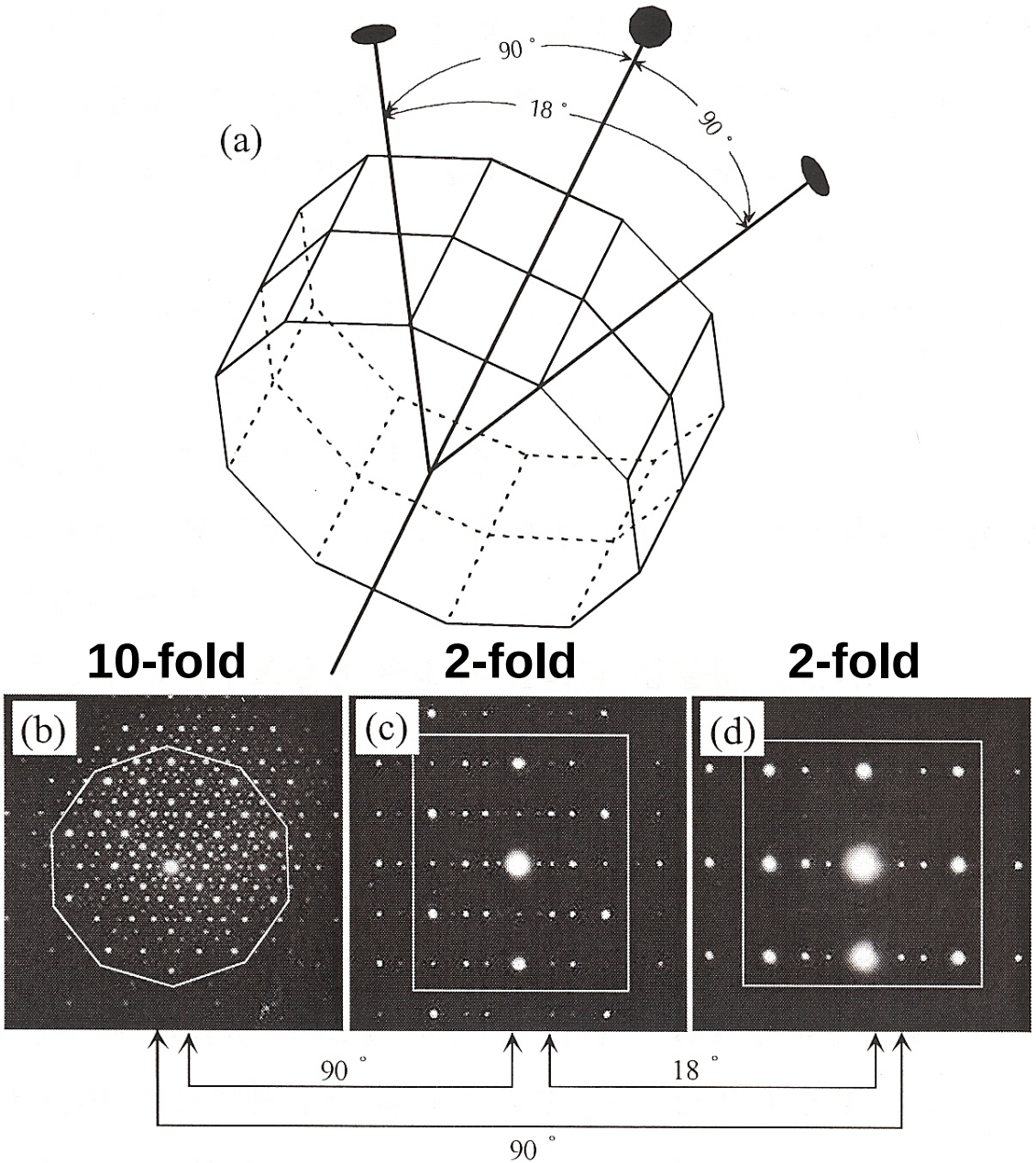
2-fold

Decagonal phase

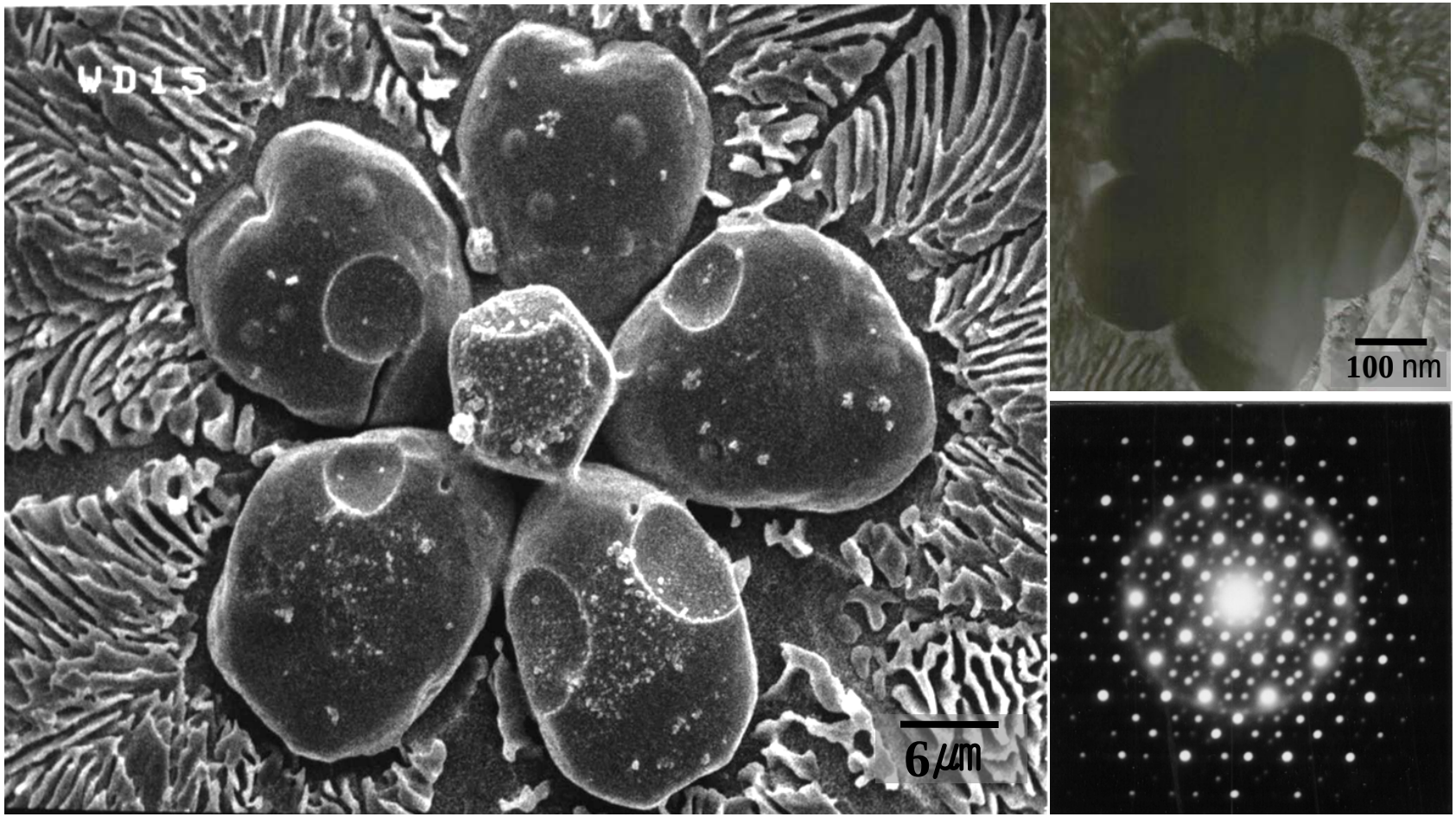
Al-Ni-Co



Geometry and typical diffraction patterns of decagonal phase



*S*EM image obtain from primary icosahedral phase in $Mg_{68.4}Zn_{28.1}Y_{3.5}$ alloy

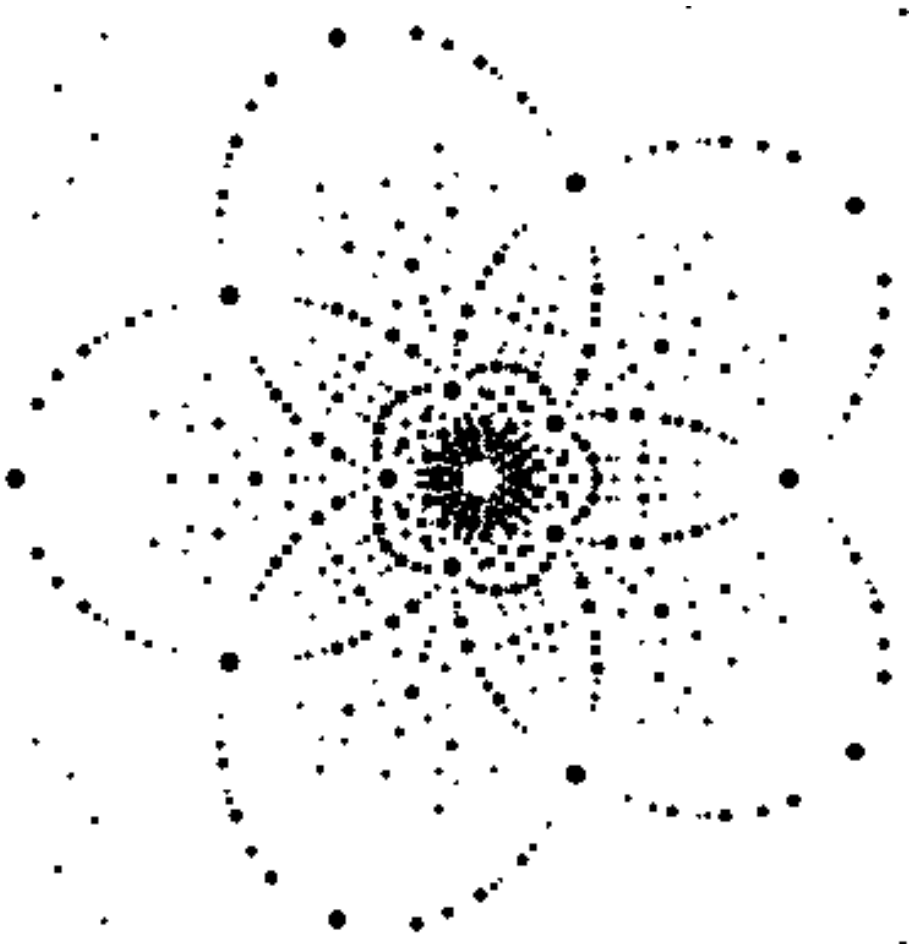


***D*uring solidification, the primary I-phase grows into a dendrite and remaining liquid solidifies into a eutectic structure with α-Mg and I-phase.**

Laue Simulation

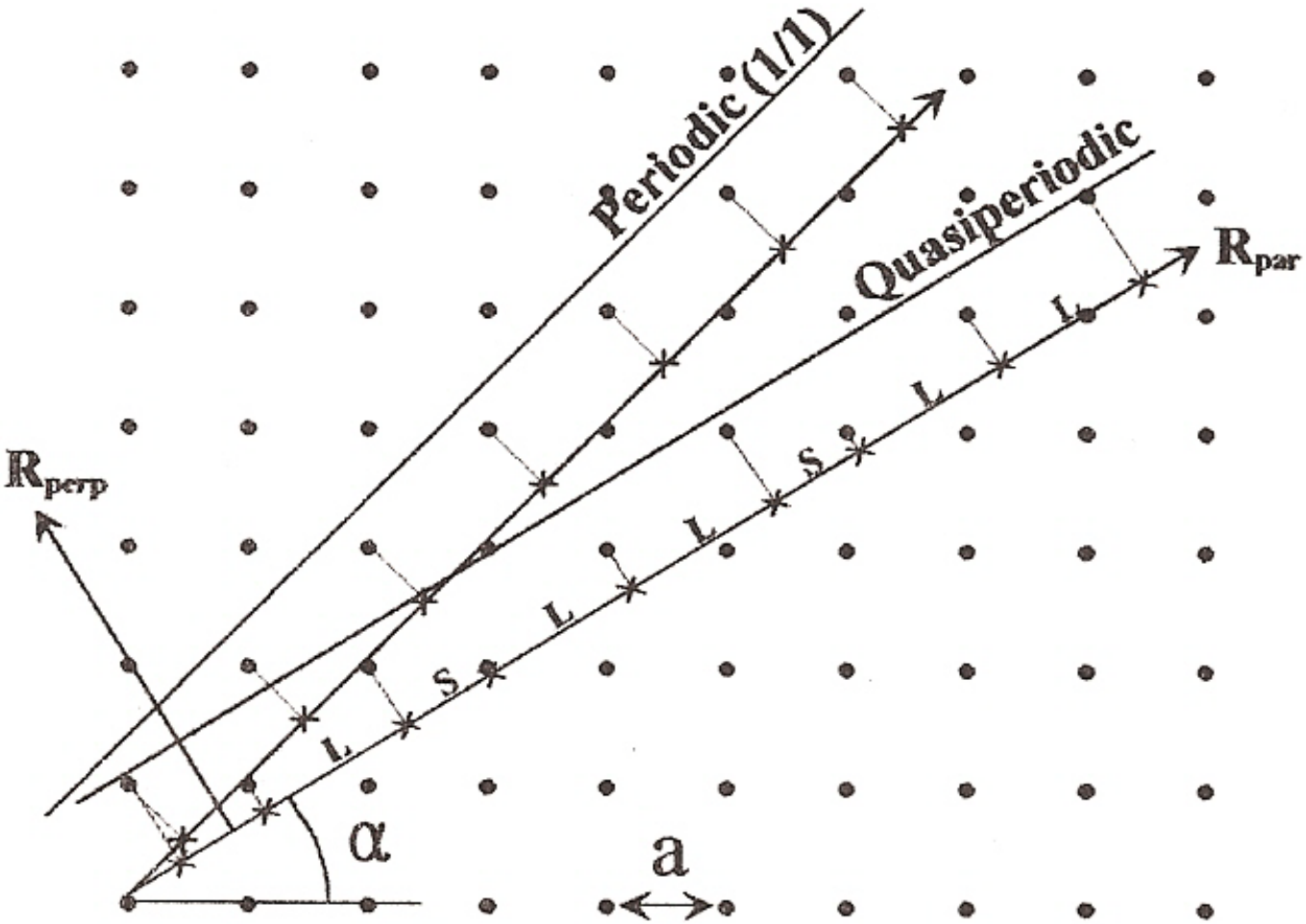
face-centered icosahedral quasicrystal along five-fold axis

maximum internal component of wavevectors qint=4



Simulation of Electron Beam Channeling patterns (from SEM)

One dimensional illustration of the cutting and projection method to generate quasi-periodic and approximant periodic structure.



$1/\tan\alpha = p/q =$

1. Irrational (quasiperiodic) ; τ

2. Rational (periodic) ; 1/1, 2/1, 3/2, 5/3, 8/5, ...

Two dimensional Penrose tiling,

illustrating how the arrowed rombuses fit together.

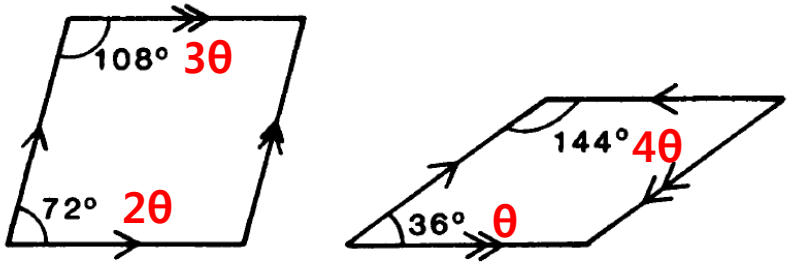
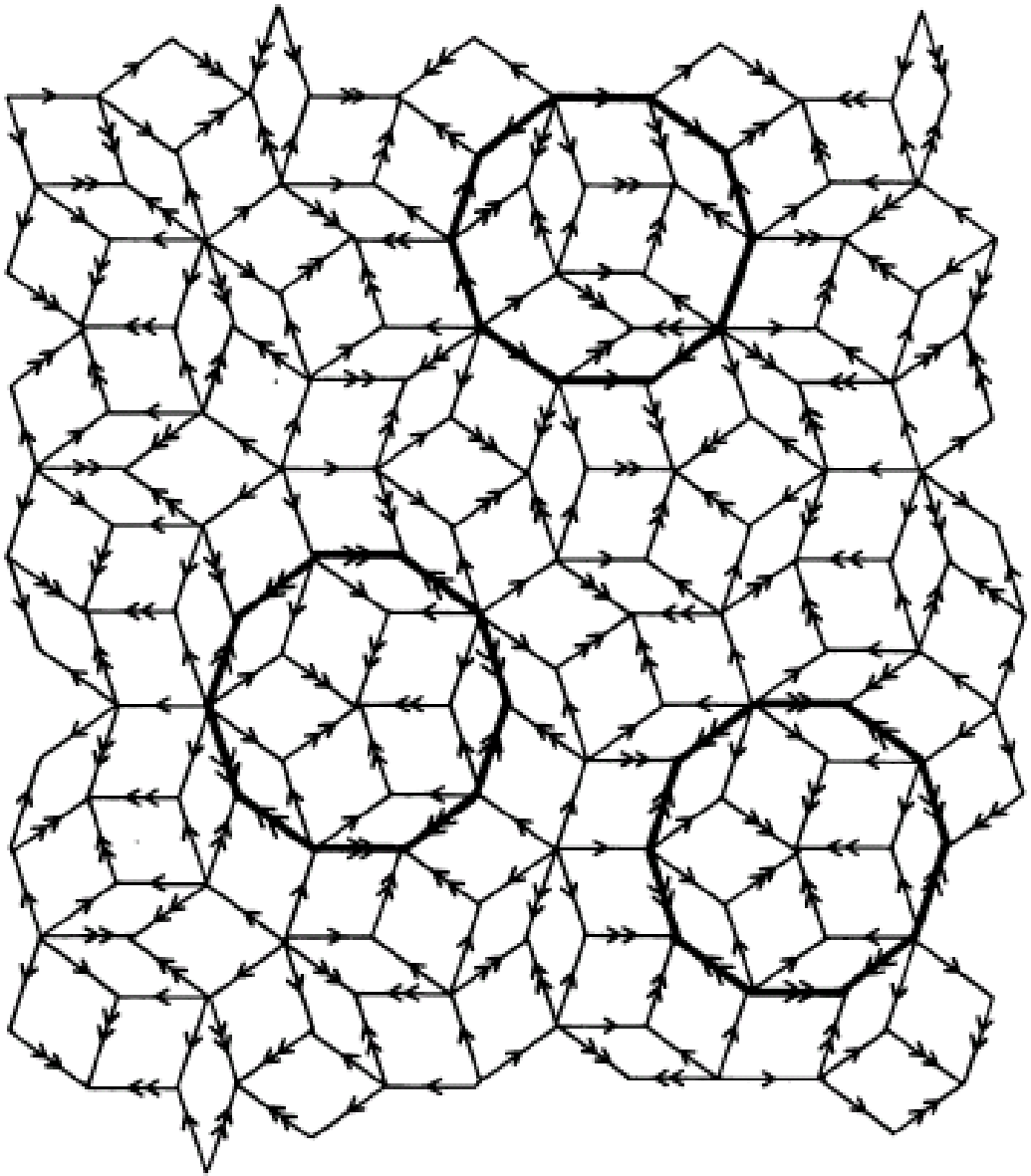


Fig. 3. Arrowed rhombuses, which are the building blocks of the two-dimensional Penrose patterns.

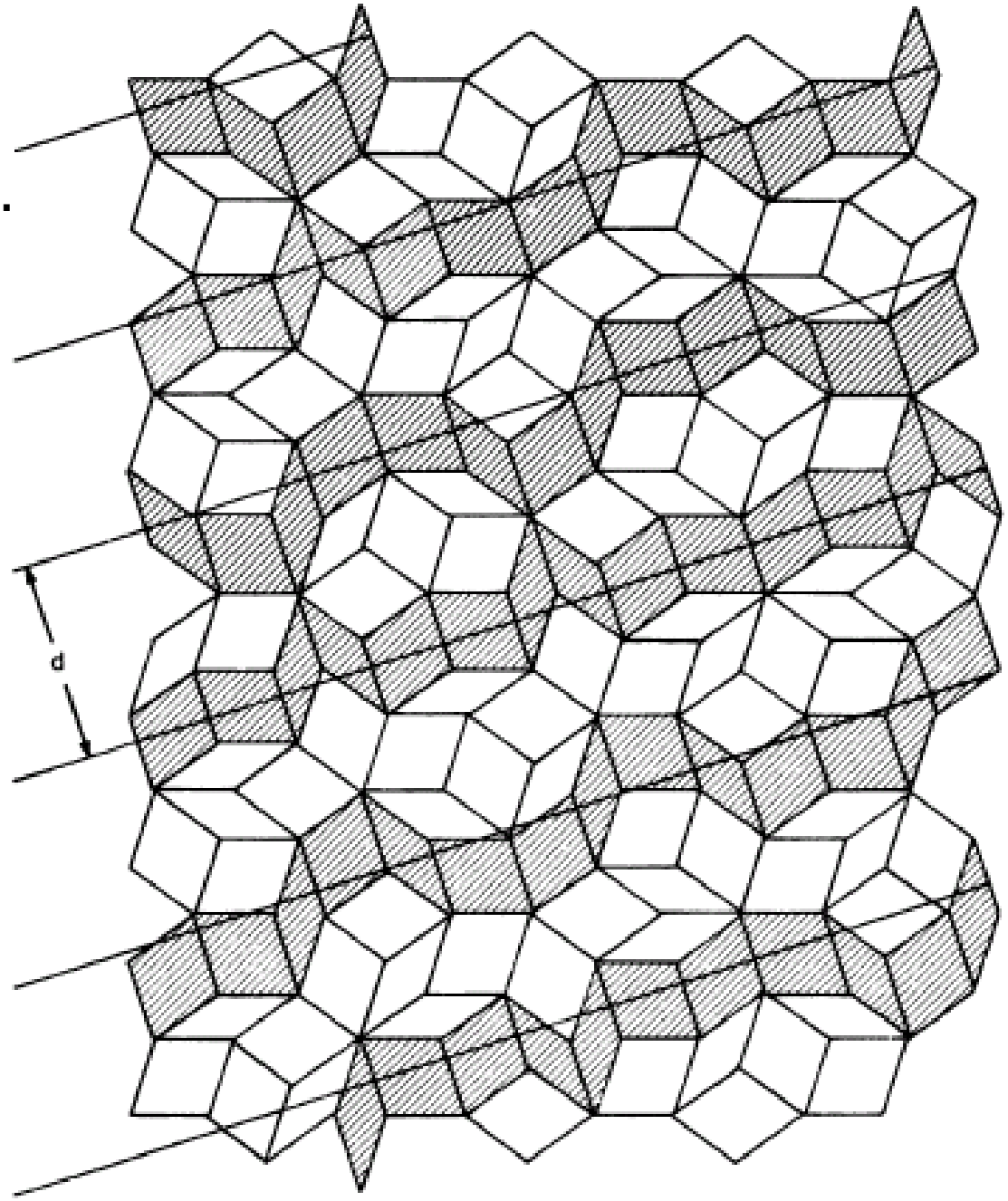


Three decagons, all with the same orientation, are shown in boldface. All decagons contain five thick and five thin rhombuses.

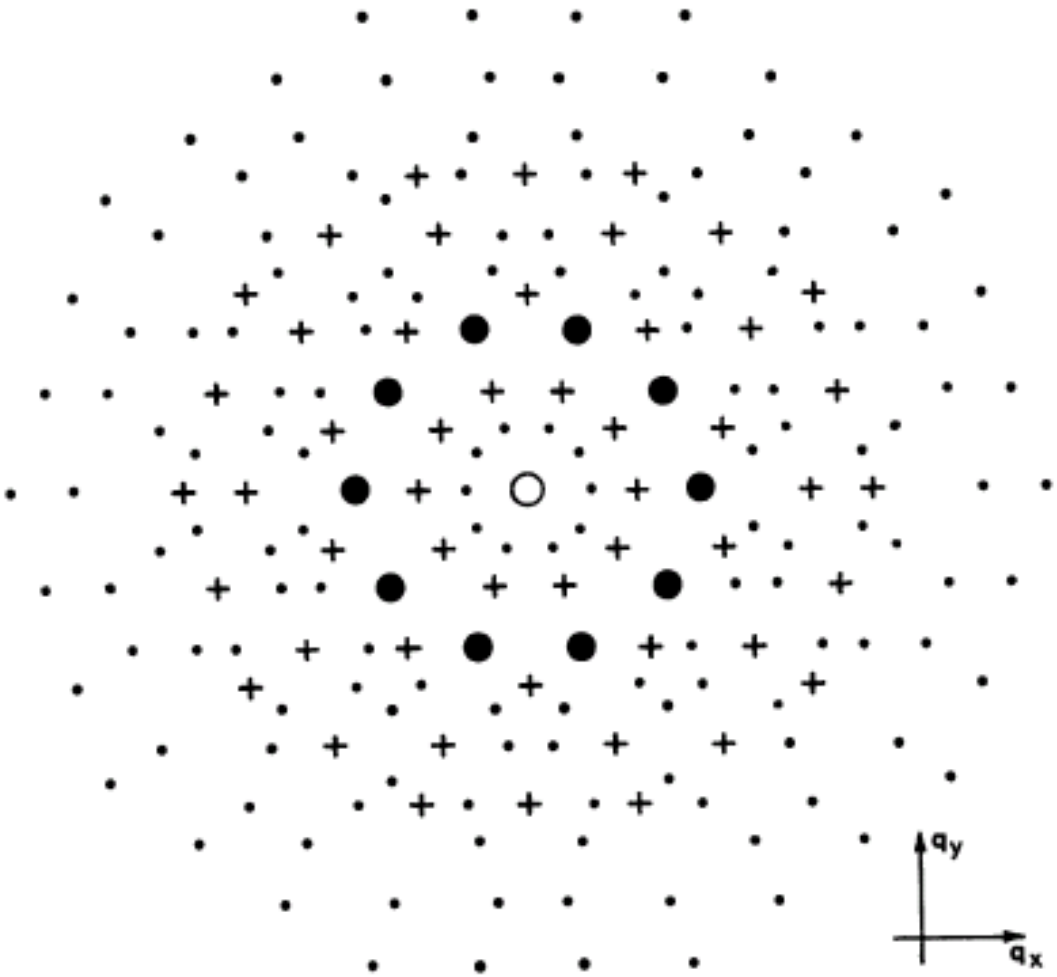
A regularly spaced diffraction grid is superimposed on the Penrose pattern of previous Fig.

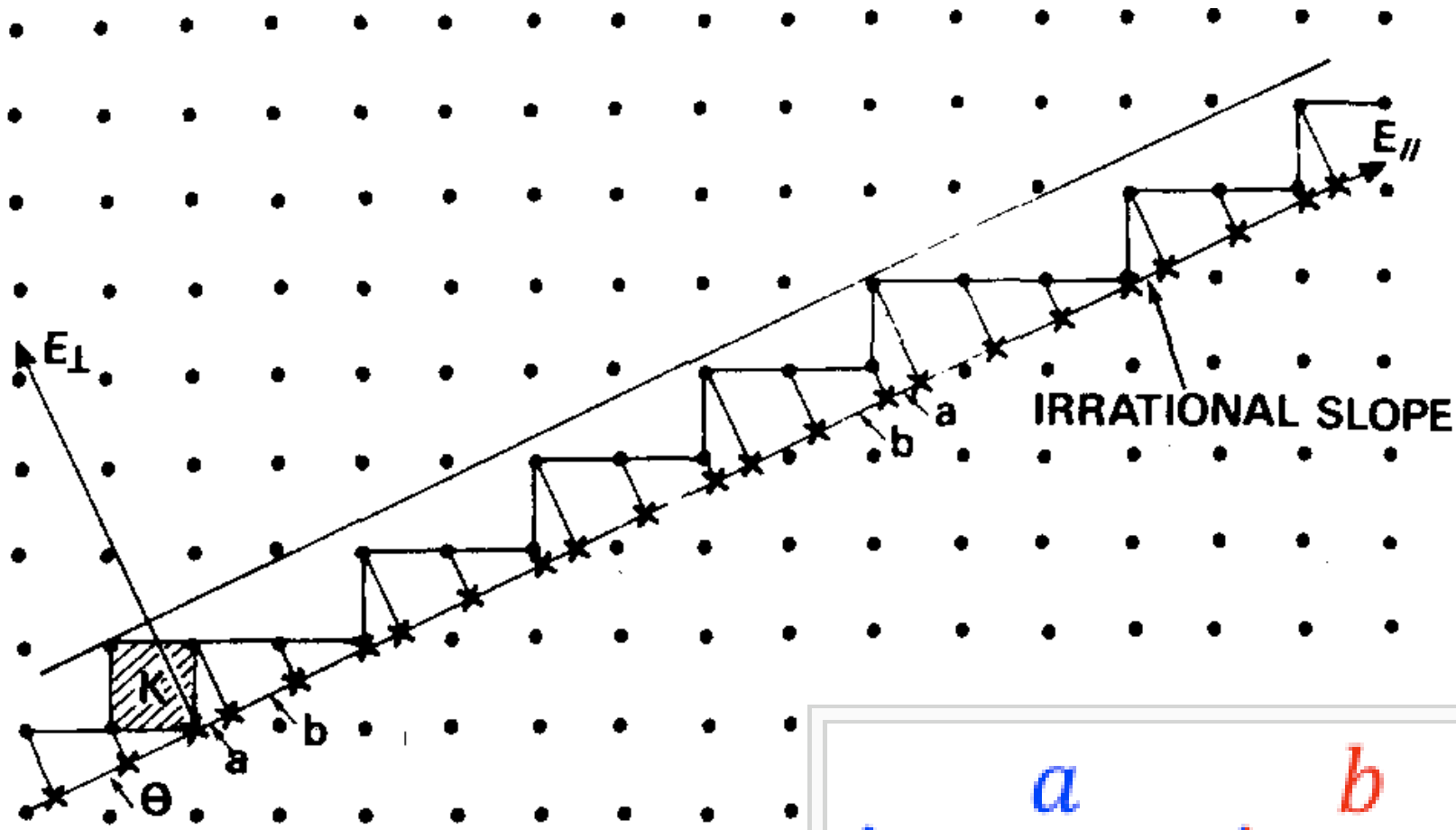
Each shaded row of tiles may be associated with a particular grid line.

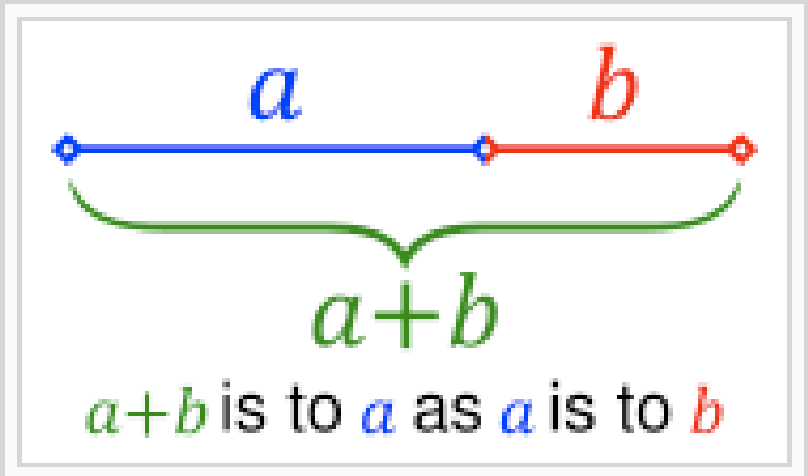
Four similar sets of grid lines with the same spacing d may be constructed at angles of 36° and 72° to the set shown.



First three generations of intensity maxima in reciprocal space for a two-dimmensional Penrose tiling. Symbol: (●) first generation; (+) second generation; (•) third generation.





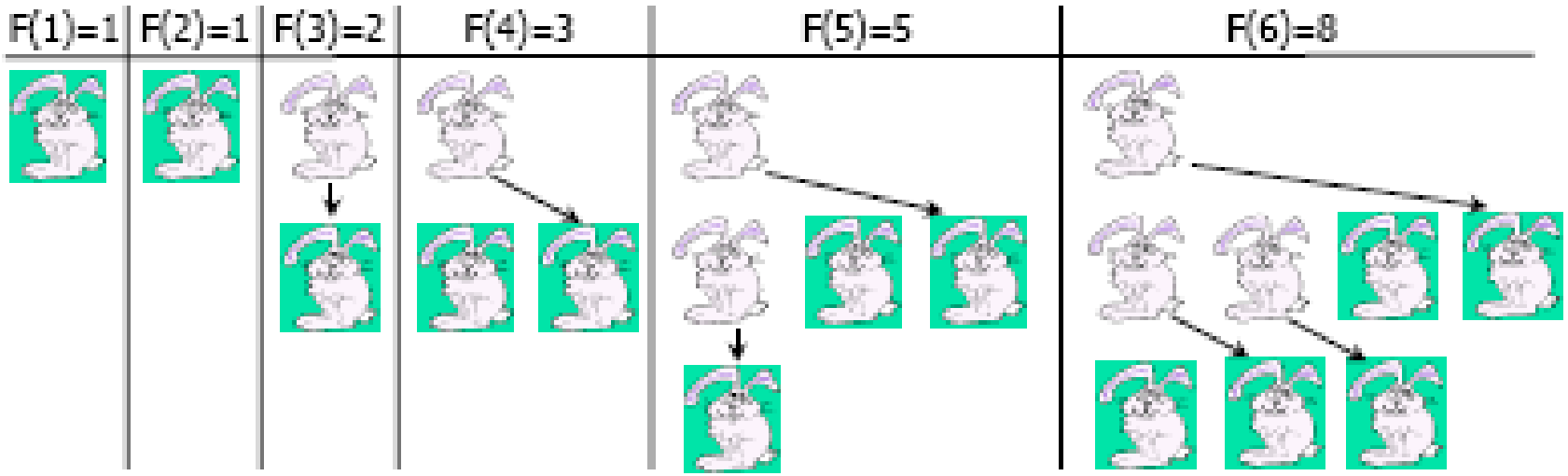


Nodes of the square lattice inside the strip projection E// in a perfectly ordered nonperiodic structure made of two tiles a and b of incommensurate sizes that are arranged according to a Fibonnacci (or musical) sequence.

fibonccci chain

Fibonacci Numbers

- Leonardo Fibonacci (1202):
  - A rabbit starts producing offspring on the second generation after its birth and produces one child each generation
  - How many rabbits will there be after n generations?

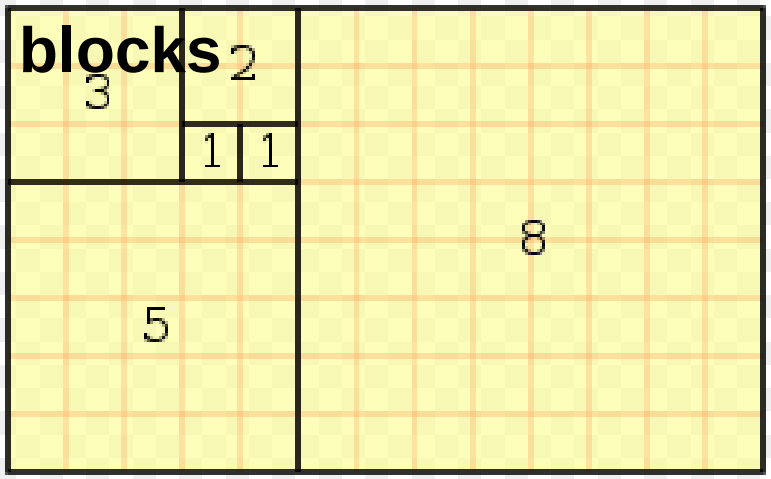


Fibonacci Numbers (2)

- F(n)= F(n-1)+ F(n-2)
- F(0) =0, F(1) =1
  - 0, 1, 1, 2, 3, 5, 8, 13, 21, 34 ...

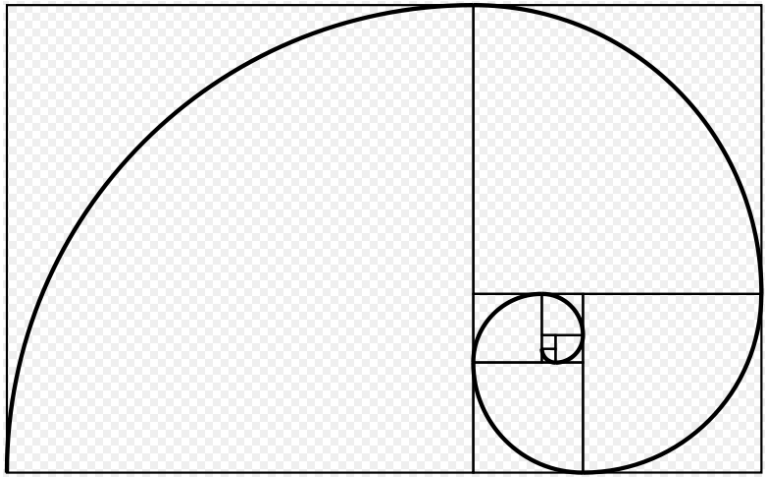
```
FibonacciR(n)
01 if n ≤1 then return n
02 else return FibonacciR(n-1) + FibonacciR(n-2)
```

fibonacci blocks



A tiling with squares whose sides are successive Fibonacci numbers in length.

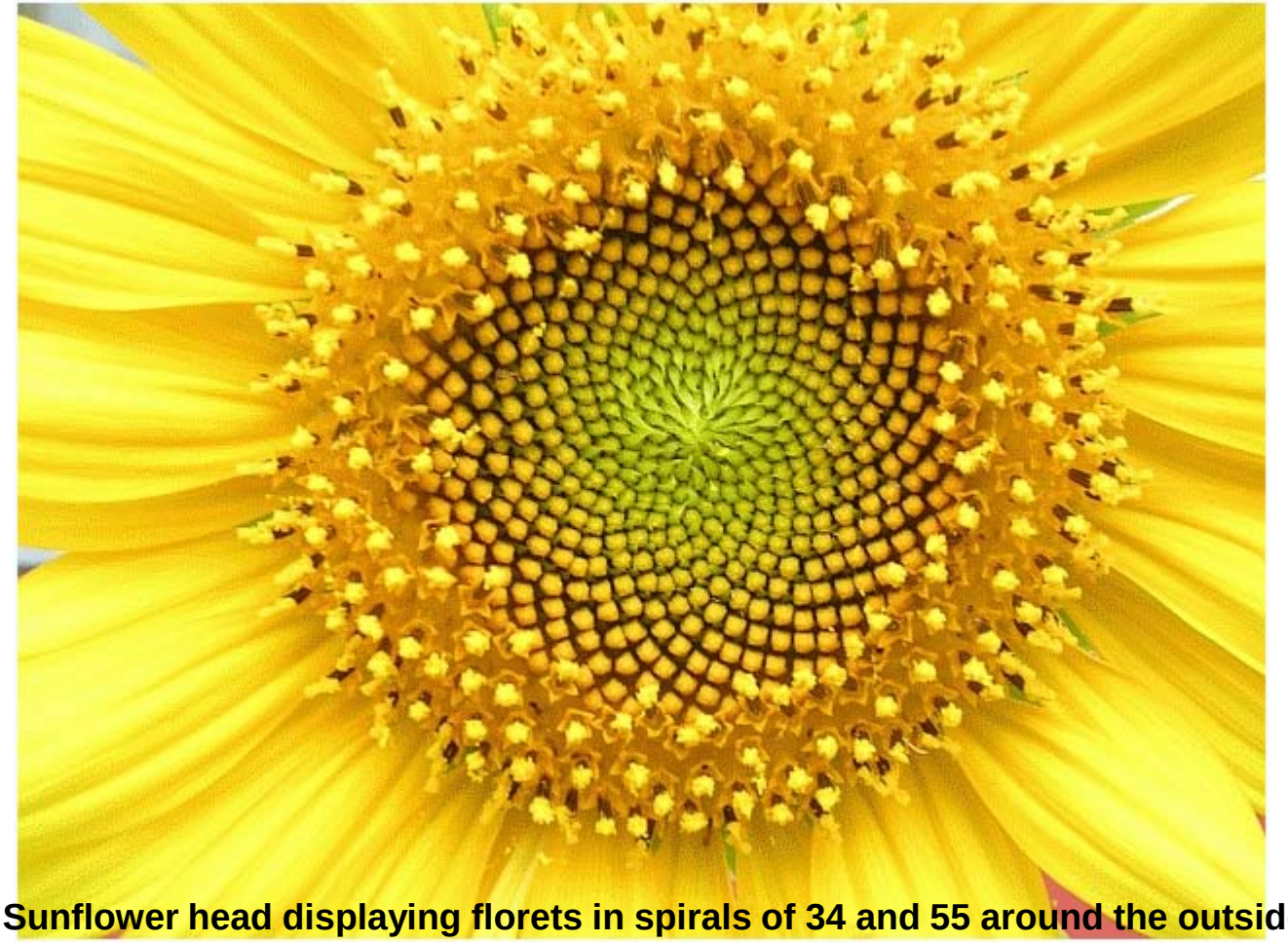
fiboncci spiral



A Fibonacci spiral created by drawing arcs connecting the opposite corners of squares in the Fibonacci tiling; this one uses squares of sizes 1, 1, 2, 3, 5, 8, 13, 21, and 34.

Fibonacci numbers in nature

Fibonacci sequences appear in biological settings, in two consecutive Fibonacci numbers, such as branching in trees, arrangement of leaves on a stem, the fruitlets of a pineapple, the flowering of artichoke, an uncurling fern and the arrangement of a pine cone. In addition, numerous poorly substantiated claims of Fibonacci numbers or golden sections in nature are found in popular sources, e.g. relating to the breeding of rabbits, the spirals of shells, and the curve of waves[citation needed]. The Fibonacci numbers are also found in the family tree of honeybee.



Sunflower head displaying florets in spirals of 34 and 55 around the outside

Classification of materials with structure

Perfect crystal → ***disorder*** → ***quasicrystal*** → ***amorphous***

: ***unit cell***

: ***underlying perfect crystalline lattice***

(b, c, d)

ex) ***icosahedral phase***

: ***no topological ordering*** **(a)**

ex) ***icosahedral glass***