Structures of intermetallic phases

“Intermetallic phases have long been among the black sheep in the family of chemical compounds. Their chemical bonding has eluded description by the valence rules, which otherwise are extremely effective. As a result, understanding of the structure-bonding relationships in these phases to date has remained nebulous, even though they form the largest group of inorganic compounds.”

R. Nesper, Bonding patterns in intermetallic compounds, Angew. Chem. Intl. Edn. Engl. 30 (1991) 789.

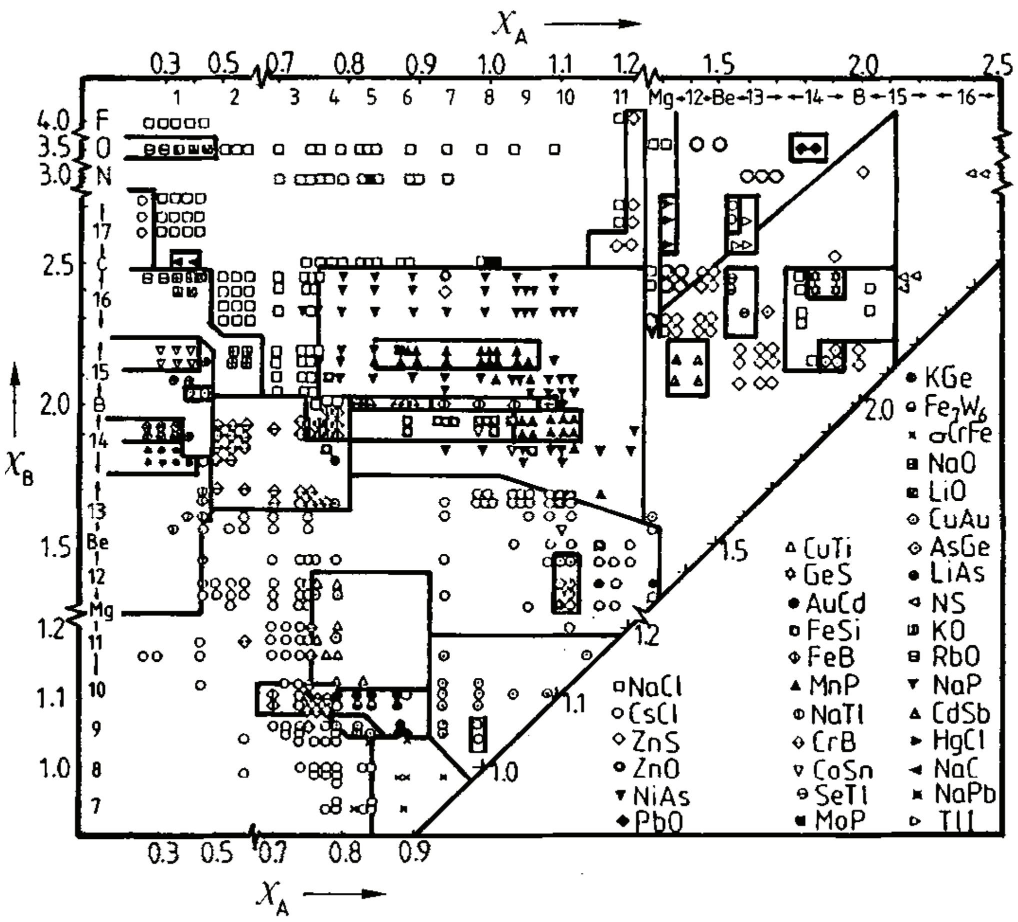
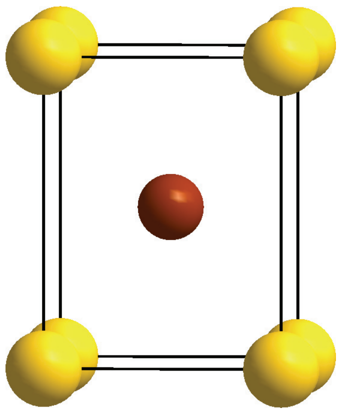


Fig. 2. Structural field after [45] with division of 574 AB compounds by means of a specially adjusted electronegativity.

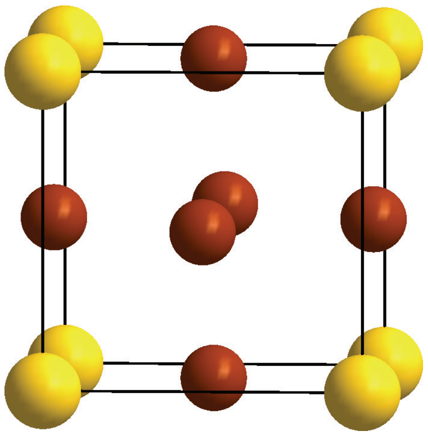
Structures of intermetallic phases

Au-Cu phase diagram: AuCu and $AuCu_3$



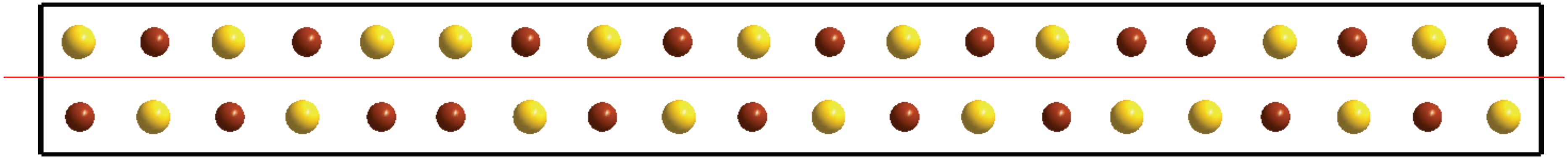
AuCu: *P4/mmm* *a* = 2.802 Å, *c* = 3.671 Å
Au at 0,0,0 and Cu at ½ ½ ½

Order-disorder phase transitions !



$AuCu_3$: *Pm-3m* *a* = 3.753 Å
Au at 0,0,0 and Cu at ½ ½ 0

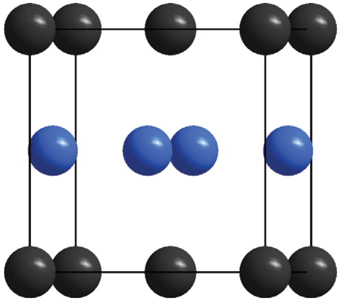
Structures of intermetallic phases



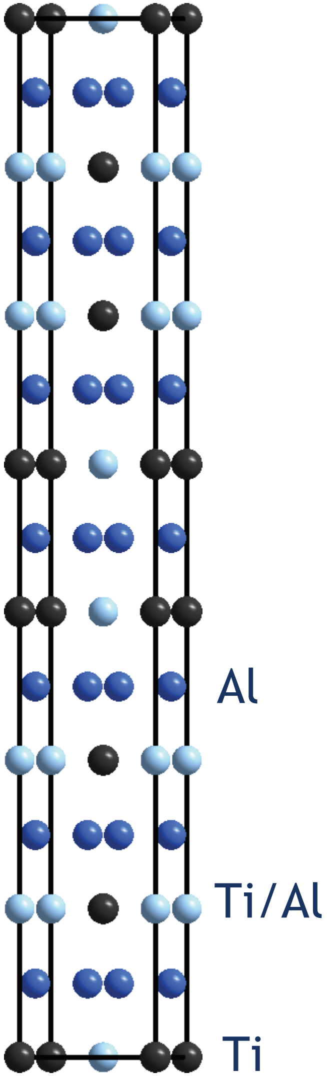
Modulated *Imma* structure of AuCu: 20 atoms per unit cell.
a = 3.676(2); b = 3.956(3); c = 39.72(2)

Structures of intermetallic phases

Ti-Al phases

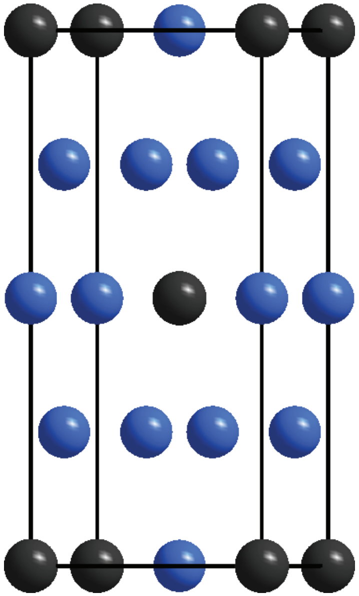


TiAl *P4/mmm*



Ti_2Al_5 *I4/mmm*

Al rich (Al is fcc)



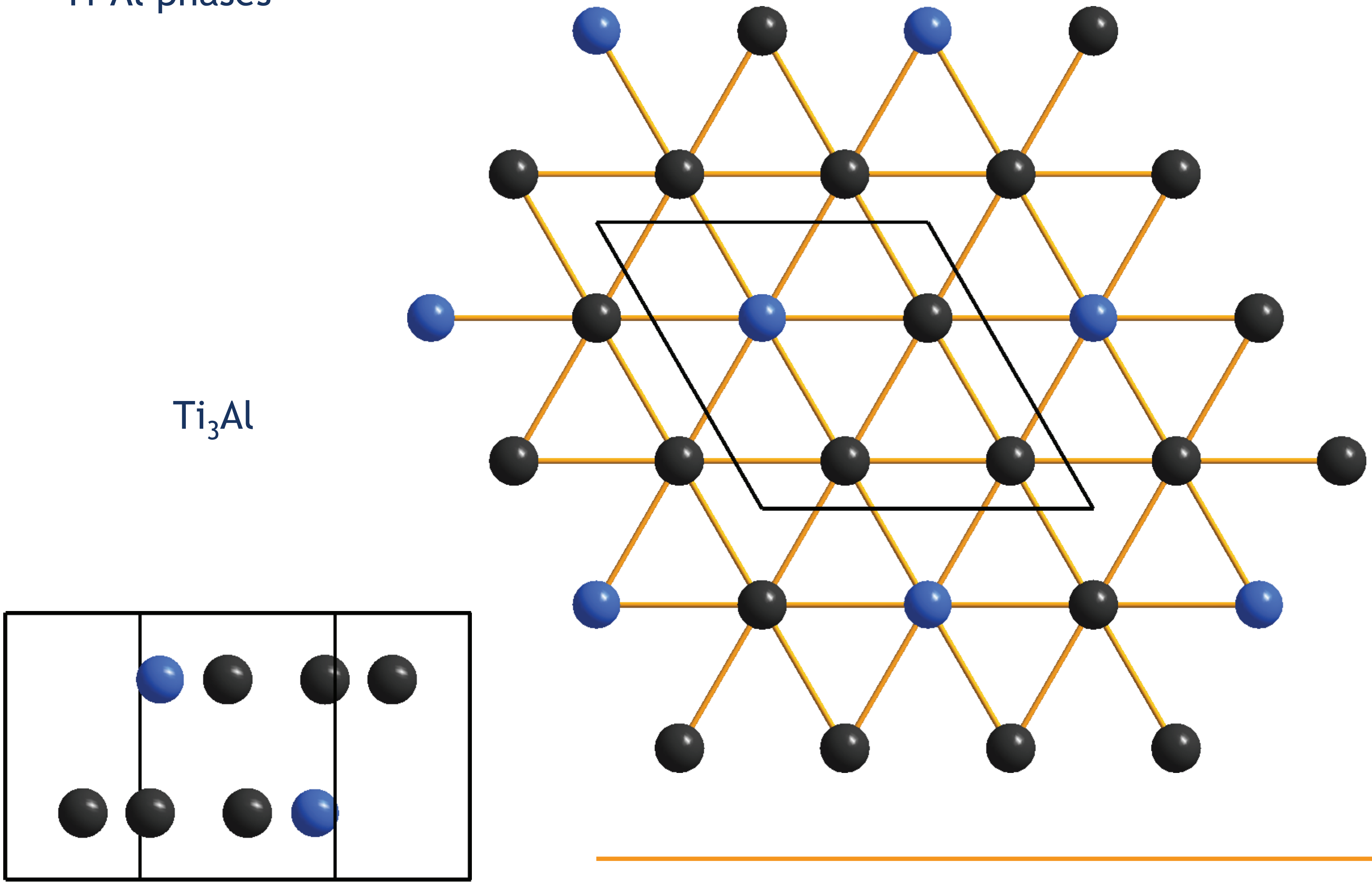
$TiAl_3$ *I4/mmm*

Structures of intermetallic phases

Ti-Al phases

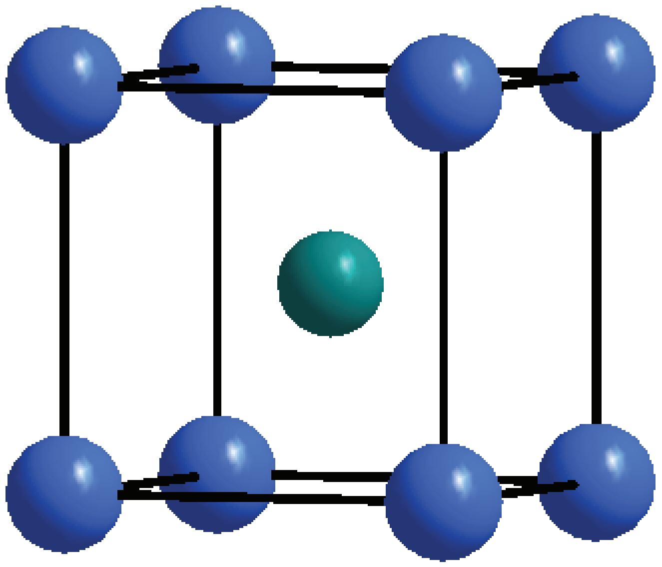
Ti rich (Ti is hcp)

Ti_3Al



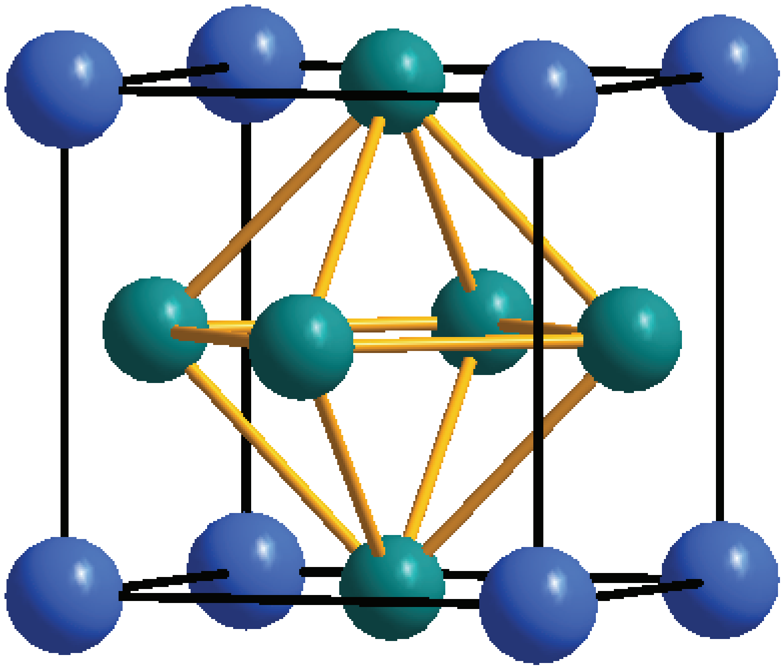
Structures of intermetallic phases

Ni-Al phases



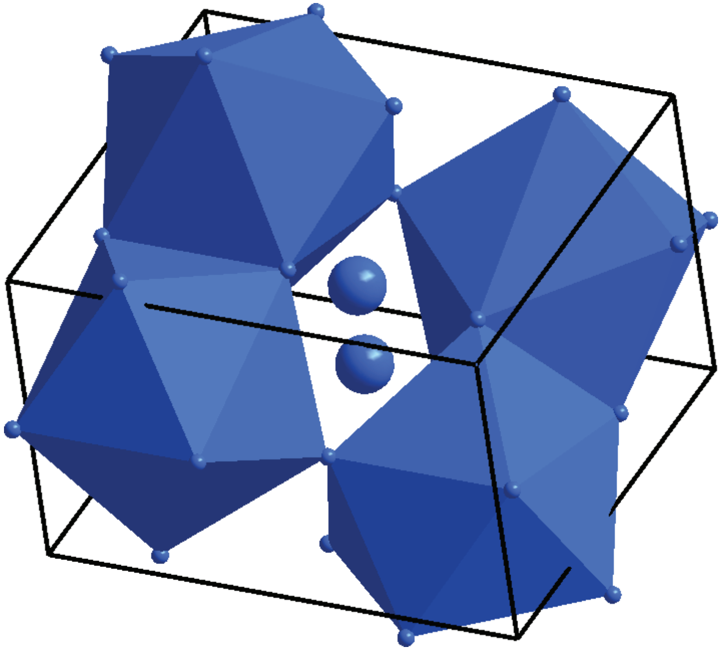
NiAl (CsCl)

Ni_3Al (Cu_3Au)

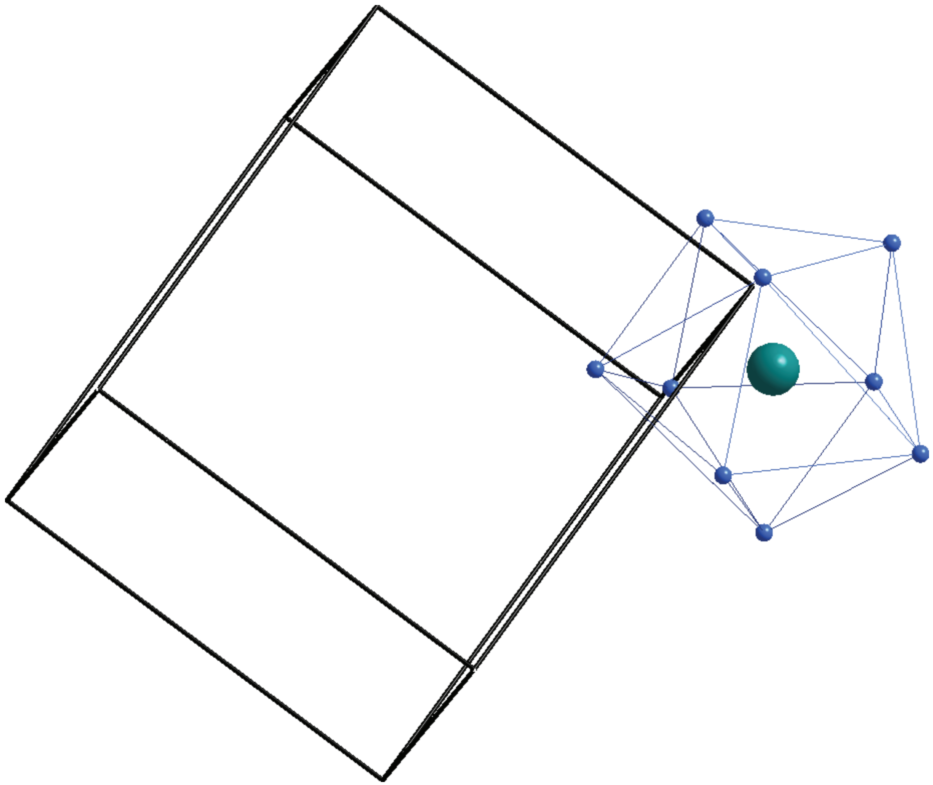


Structures of intermetallic phases

Ni-Al phases

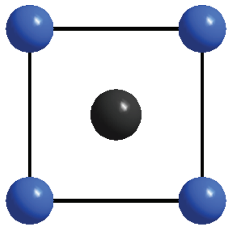


$NiAl_3$

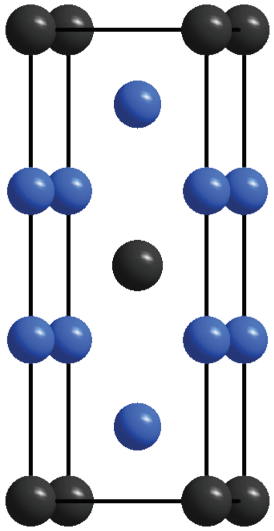


Structures of intermetallic phases

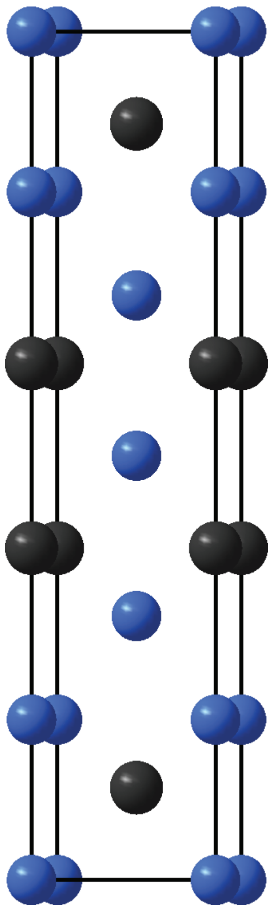
Os-Al phases



OsAl (CsCl)



$OsAl_2$

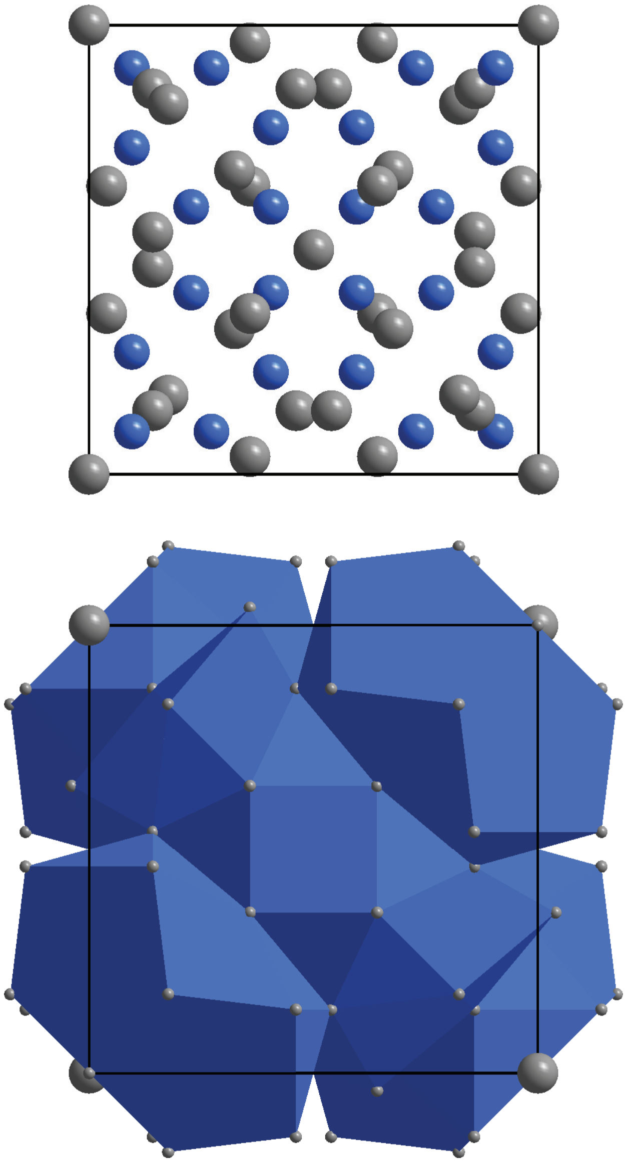


Os_2Al_3

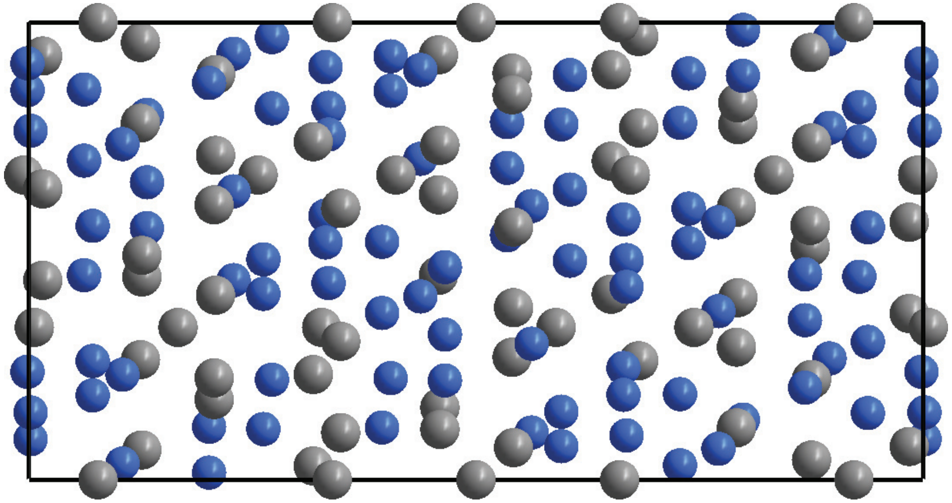
Structures of intermetallic phases

Mg-Al phases:

$Mg_{12}Al_{17}$



$Mg_{23}Al_{30}$



Topologically close packed phases

Structures of intermetallic phases

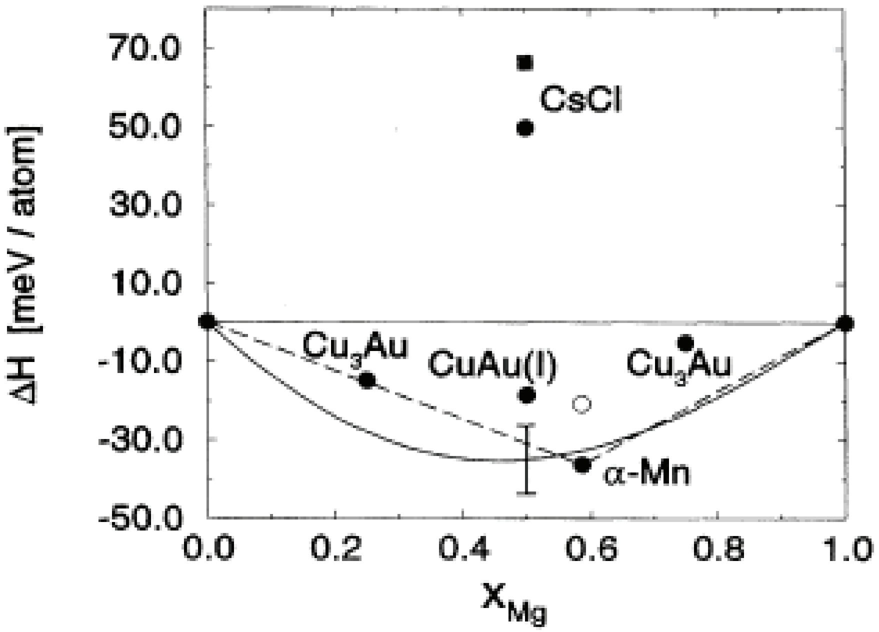


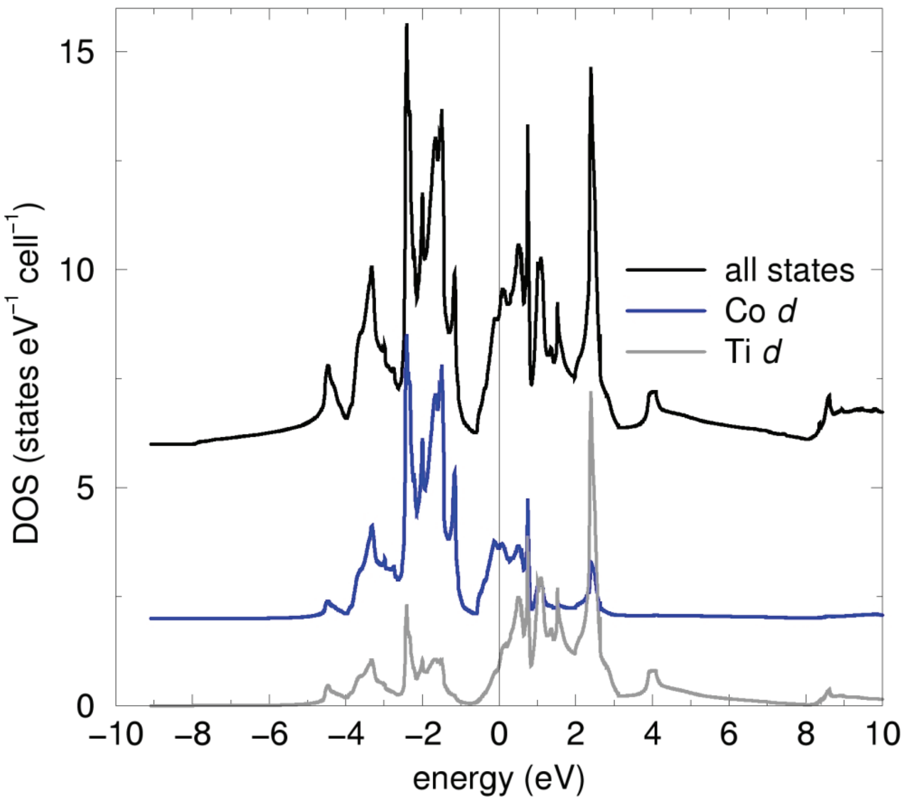
FIG. 1. Heats of formation for $Al_{1-x}Mg_x$ compounds, as a function of Mg concentration x. Labels indicate the structure considered. Filled circles are theoretical values from our calculations, the square is the result from the calculation of Pettifor and Gelatt (Ref. 16), and the solid line is the experimental data (with error bar) for the liquid state. The empty circle shows the theoretical value we obtain for $Al_{12}Mg_{17}$ when internal structural parameters are not relaxed but are set equal to the experimental values. The dashed lines are tie lines for $Al_{12}Mg_{17}$ (as a guide to the eye).

Ab initio study of polytetrahedral packing: The Al-Mg system, S. Narasimhan and J. W. Davenport, *Phys. Rev. B* **51** (1995) 659.

Unusual topologies are justified by the Fermi energies lying in pseudogaps and dips. This is associated with unusual stoichiometries and very large unit cells.

Structures of intermetallic phases

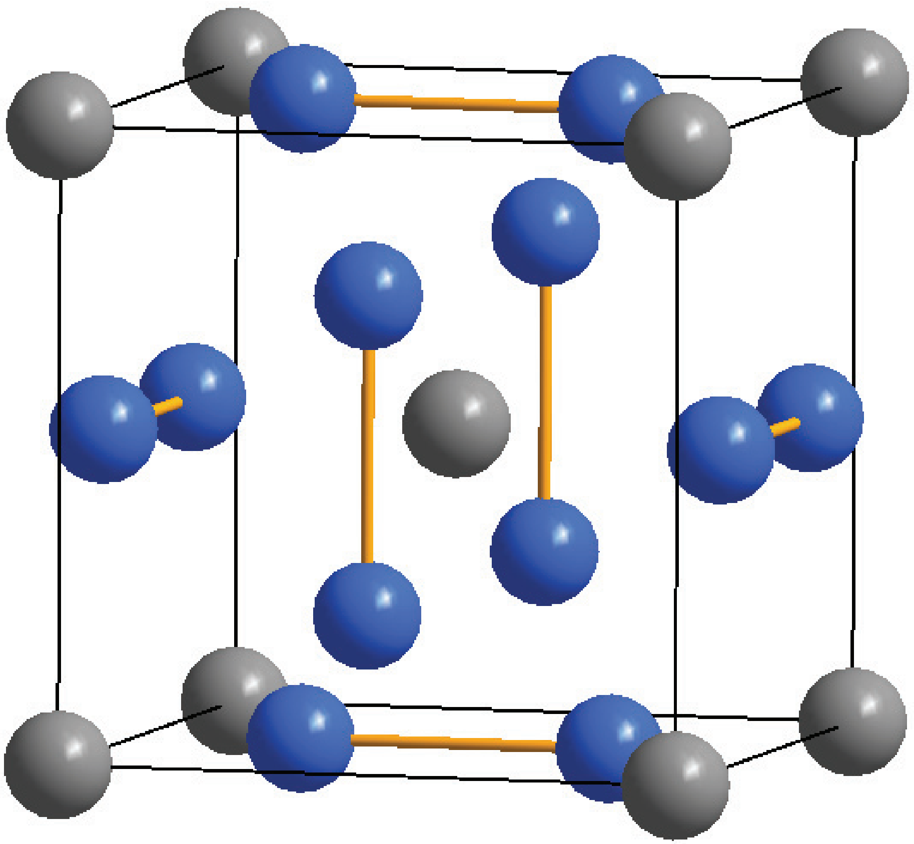
Polar intermetallic compounds: Compounds of early and late transition elements. *Transition metal alloys of extraordinary stability – example of generalized Lewsi-acid-base interactions in metallic systems*, L. Brewer and P. R. Wengert, *Metal. Trans.* **4** (1973) 83.



DOS of CoTi in the CsCl structure. Note that Co *d* is almost full and Ti *d* is almost empty.

Structures of intermetallic phases

A15 compounds (superconductors)



Nb_3Sn:
Pm-3n (223)
a = 5.290 Å
Sn at 0 0 0
Nb at ¼ 0 ½

Structures of intermetallic phases

Mathias' Rules:

(i) Superconductivity occurs only in metallic systems, and never if the system exhibits ferro- or antiferromagnetism.

(ii) Superconductivity occurs when the electron to atom ratio (e/a) lies between 2 and 8. T_c depends upon e/a for metals, and alloys between metals, in the same period of the periodic table. Nontransition metals show T_c increasing as e/a increases from 2 to 6 (beyond 6 the nontransition elements are nonmetallic). The transition metals show a much more complicated behaviour, with peaks at $e/a = 4{\cdot}7$ and 6·5, and a sharp minimum in between. A peak was originally thought also to exist at $e/a = 3$. This is due to the element lanthanum, whose behaviour is now regarded as atypical (Hamilton and Jensen 1963, Kondo 1963), and this peak is spurious.

(iii) Certain crystal structures are particularly favourable for superconductivity. The highest critical temperatures are found in the β Wolfram (A15) and sodium chloride (B1) structures, with $e/a \simeq 4{\cdot}7$. The σ phase ($D8_b$), α Mn (A12) and Laves phases are crystal classes which produce compounds with $e/a \simeq 6{\cdot}5$, and critical temperatures up to ~ 10 K. Superconducting compounds have been reviewed by Roberts (1968).

(iv) T_c is dependent upon atomic mass M and atomic volume v. For *elements* with the same e/a, the critical temperature depends upon M and v in the following way:

$$T_c \propto \frac{v^x}{M} \quad \text{where } 4 < x < 5.$$

D. Dew-Hughes,
Rep. Prog. Phys. **34** (1971) 821-873

Liquid metals, intermetallics, metallic glasses and quasicrystals

A great deal of insight into the structures of liquids, glasses and crystals, and phase transitions between them has been obtained by studies on colloidal (typical surface-modified polystyrene sphere) systems. For example, the critical density for crystallization of hard spheres is known to be 0.494 and between 0.494 and 0.545, liquid and crystal phases are stable. Additionally, hard spheres are known to crystallize because of *entropic* reasons. Crystals (*fcc*) have the best packing meaning that each hard sphere has the most room to rattle around in.

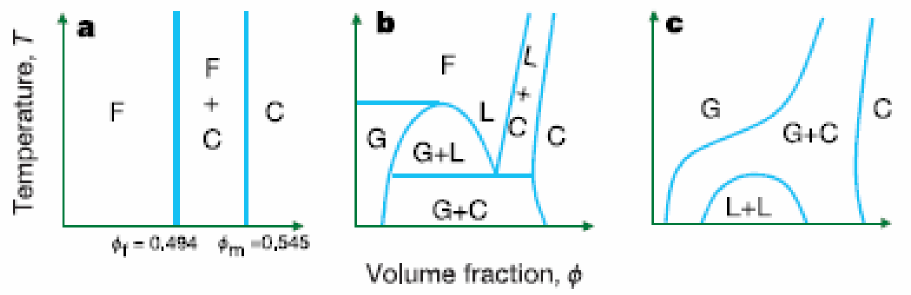


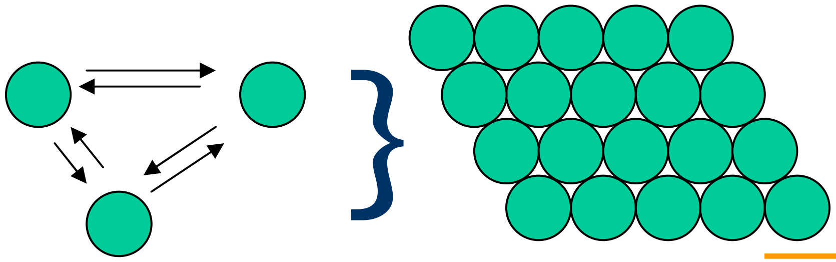
Figure 1 A wide range of phase diagrams occurs naturally. **a**, For a purely hard-sphere system the phase diagram shows only fluid (F) and crystal (C) phases. **b**, Atomic systems are often modelled by hard spheres with long-range attractions. This leads to equilibrium between gas (G), liquid (L) and crystal phases. **c**, In cases where the attraction is short-range, as in protein systems (important in physiology), equilibrium between gas and crystal is found, but the liquid–liquid transition becomes metastable.

From: Anderson and Lekkerkerker, *Nature* **416** (2002) 811 (see for a mini-review).

Liquid metals, intermetallics, metallic glasses and quasicrystals

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*.



Liquid metals, intermetallics, metallic glasses and quasicrystals

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.

Liquid metals, intermetallics, metallic glasses and quasicrystals

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

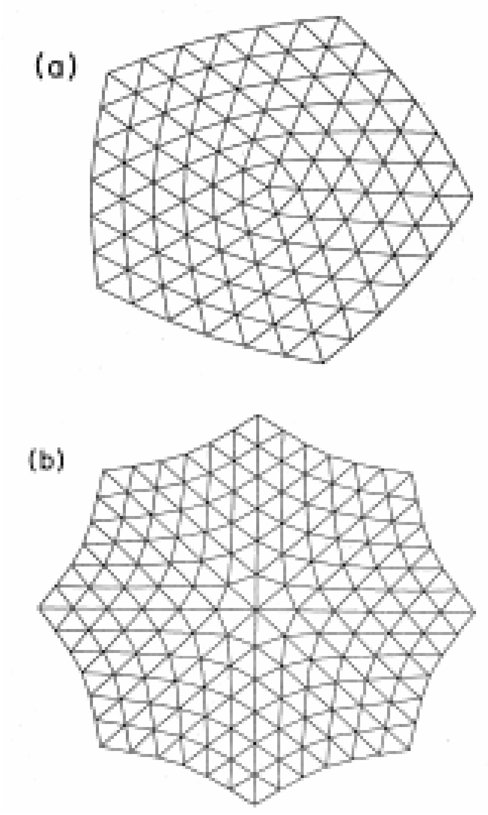


FIG. 4. Positive and negative disclinations in a triangular lattice. Note the rotation of the triangular cells by 60° (a) clockwise, and (b) counterclockwise, as a clockwise path around the disclination is traveled. Note that these disclinations may also be described as particles having (a) five, and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

Liquid metals, intermetallics, metallic glasses and quasicrystals

Liquid metals: Do they really have topological close packing ?

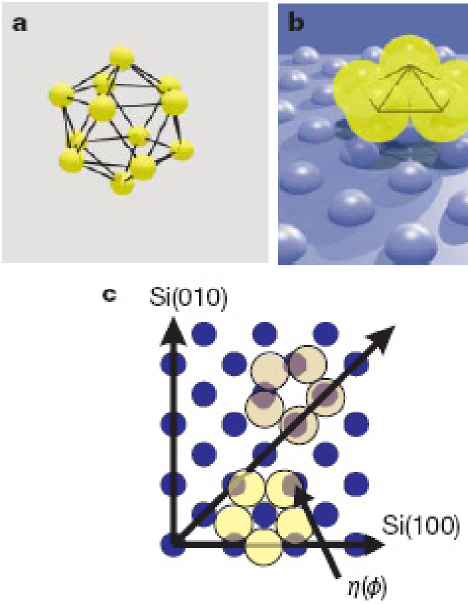


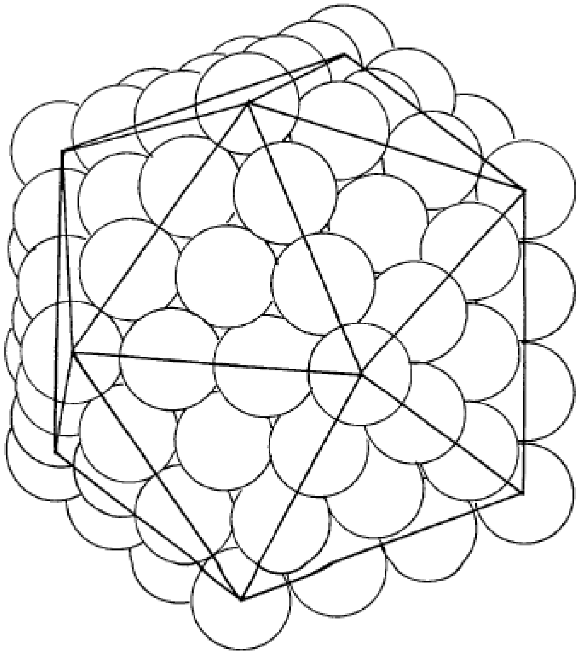
Figure 1 View of the dominant motif in the structure of bulk liquid lead and of interfacial liquid lead. **a**, Polytetrahedral arrangement predicted for close-packed monatomic liquids. **b**, Upper (pentagonal) half of the Pb icosahedron (**a**) captured by the potential landscape of the primitive Si(001) 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).

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.

Liquid metals, intermetallics, metallic glasses and quasicrystals

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

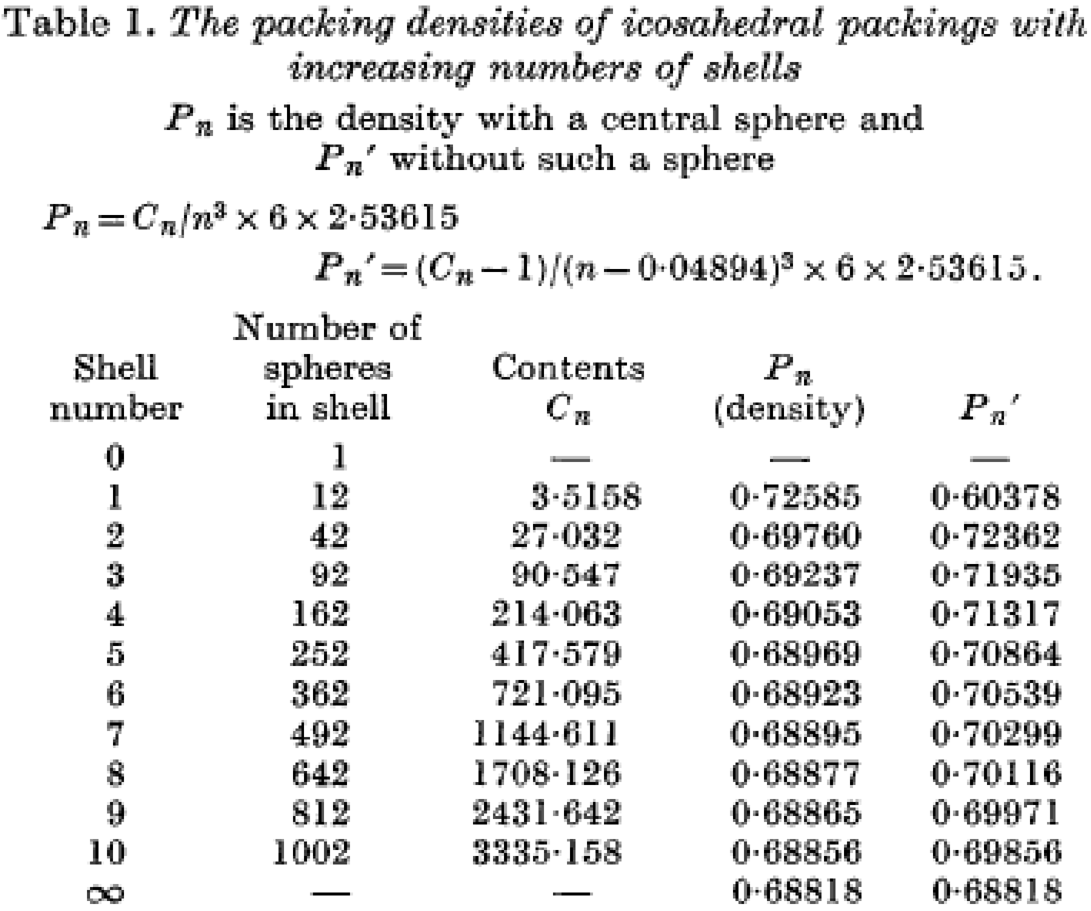


Table 1. *The packing densities of icosahedral packings with increasing numbers of shells*

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

Liquid metals, intermetallics, metallic glasses and quasicrystals

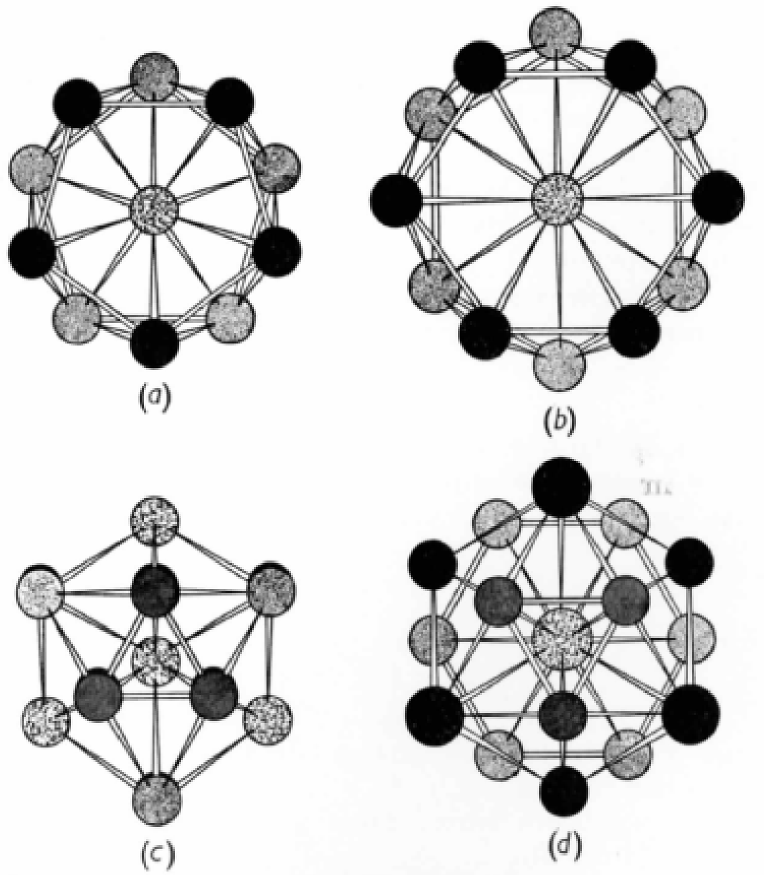


Fig. 1. The four 'normal coordination polyhedra' of complex alloy structures. For C.N. 12, two spheres above and below the central sphere, along the fivefold axis, are not shown. Similarly, two spheres above and below the central one of C.N. 14, along the sixfold axis are not shown. For C.N. 16 one sphere 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.

Liquid metals, intermetallics, metallic glasses and quasicrystals

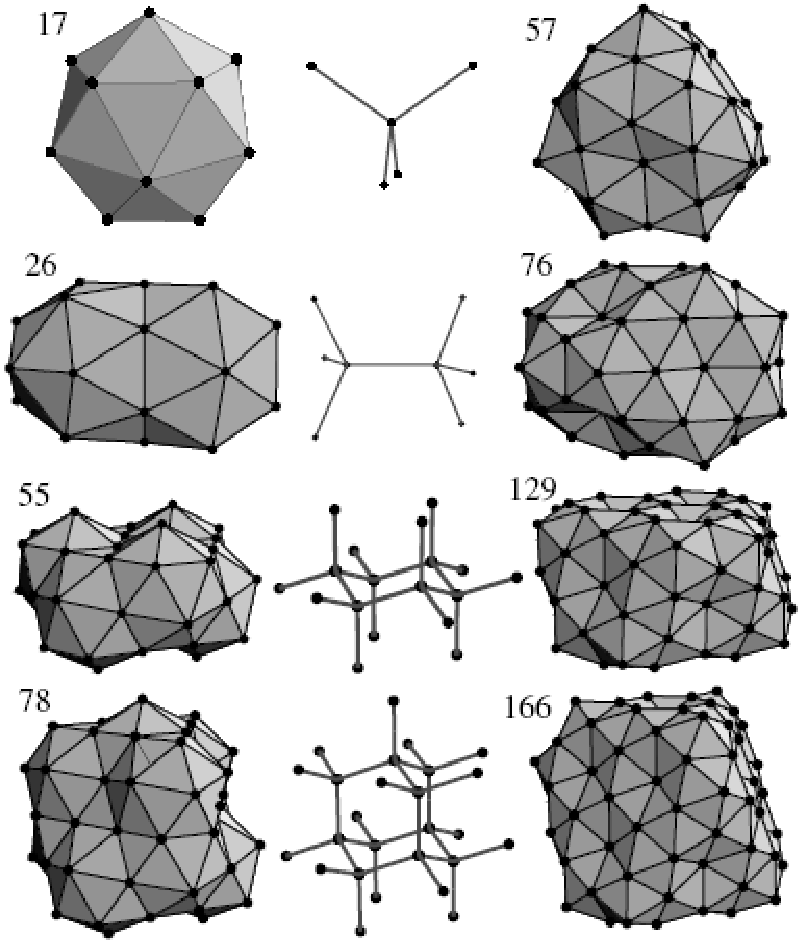


FIG. 3. Structures of some of the magic number clusters. On the right is the complete structure, in the middle the corresponding disclination network, and on the left the structure that is at the center of the cluster. All three have the same orientation.

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

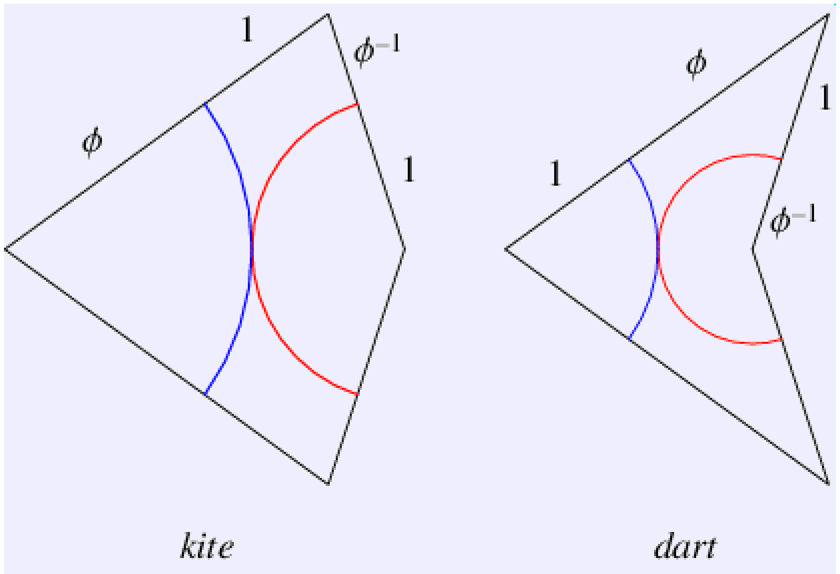
The authors used a potential that favors polytetrahedral packing and found that the disclination networks of stable clusters look like stable hydrocarbons.

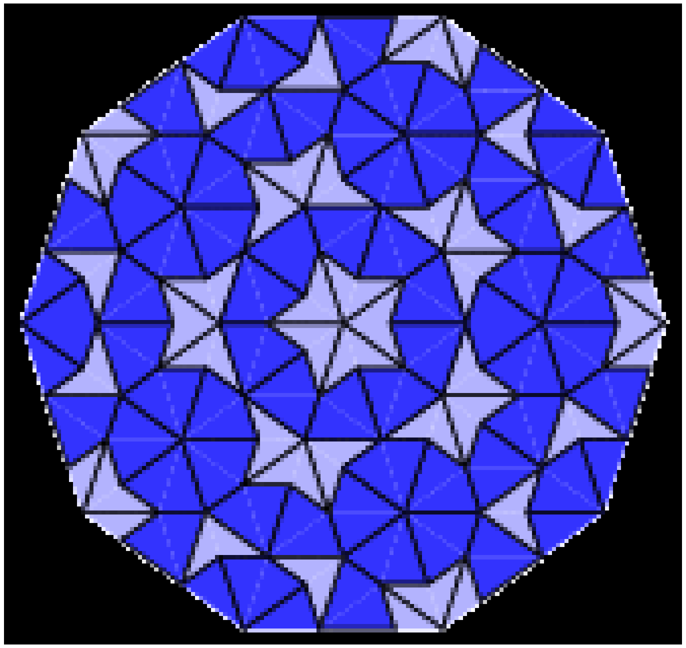
The cluster on the top left (17 atoms) has one atom in the center of a CN=16 F-K polyhedron. The CN=16 F-K polyhedron is generated from an icosahedron by introducing 4 disclinations and so on …

Liquid metals, intermetallics, metallic glasses and quasicrystals

Quasicrystals:

The Penrose tiling of darts and kites:





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

Liquid metals, intermetallics, metallic glasses and quasicrystals

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

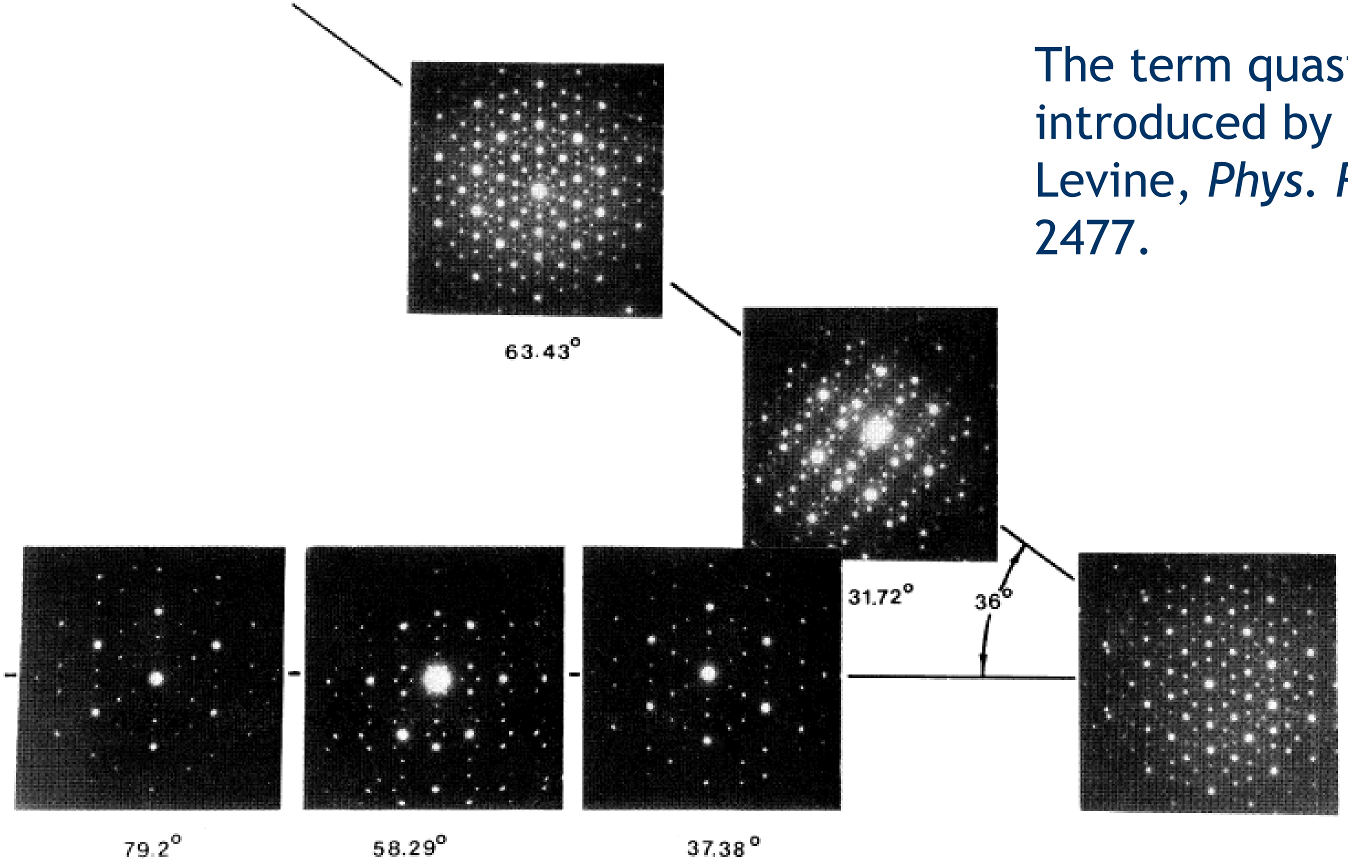


FIG. 2. Selected-area electron diffraction patterns taken from a single grain of the icosahedral phase. Rotations match those in Fig. 1.

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.

Class 12: Liquid metals, intermetallics, metallic glasses and quasicrystals

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.