Survey of Materials. Lecture 4

Structural motifs

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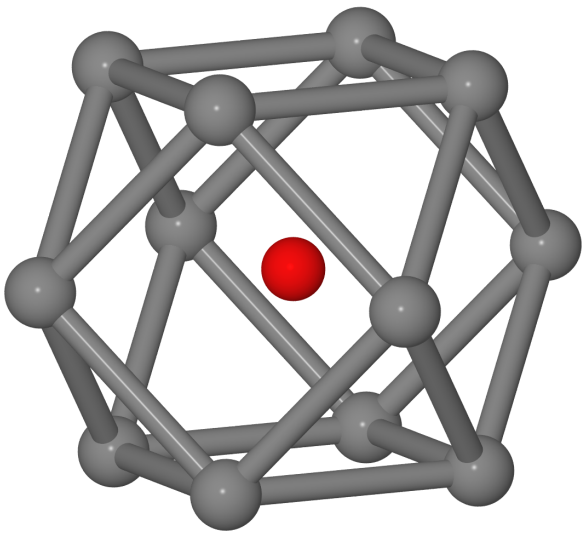
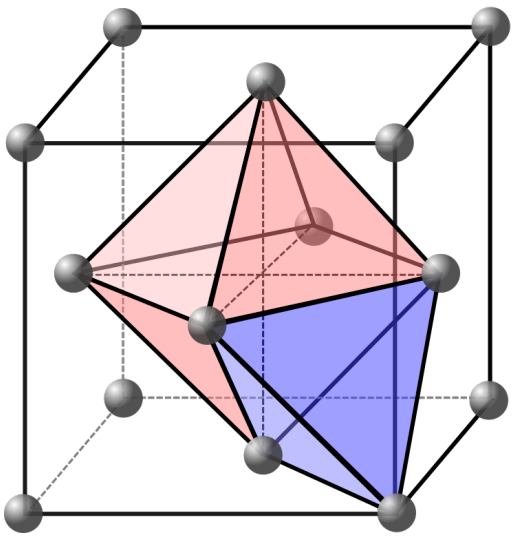
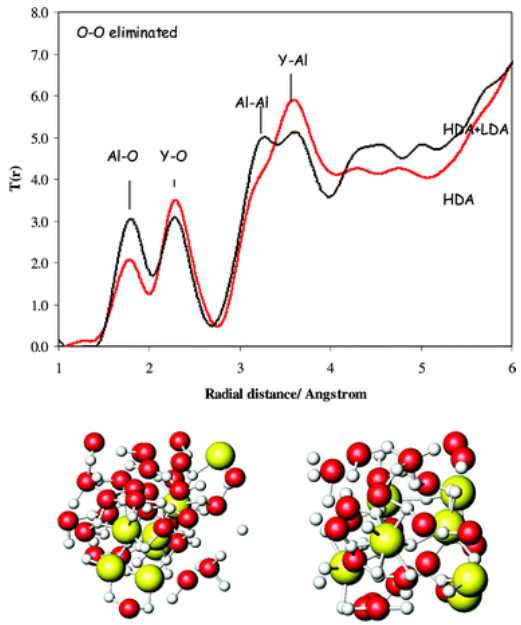
Outline

- Coordination, voids, packing
- Metallic lattices
- Ionic lattices
- Covalent crystals
- Molecular crystals
- Surfaces
- Structural transformations and polymorphism
- Exploring structure-property relationships

Coordination polyhedron/number and voids







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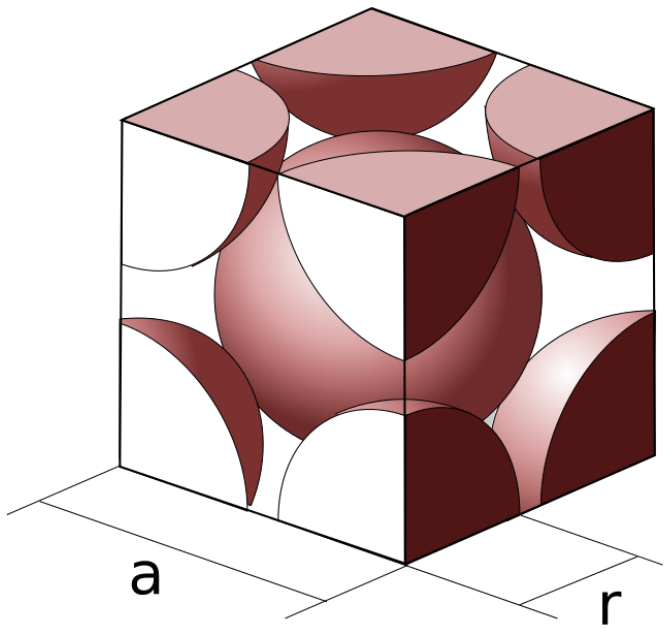
Atomic packing factor



Atomic packing factor = "occupied volume" / "unit cell volume"
Relative packing factor $\delta = V_1^{\max} / V_1$

Structural type notations

- Common name (fcc, bcc)
- Prototype (rocksalt NaCl, rutile TiO2)
- Strukturbericht
- Incomplete specification: lattice type, space group, and Z

Metals

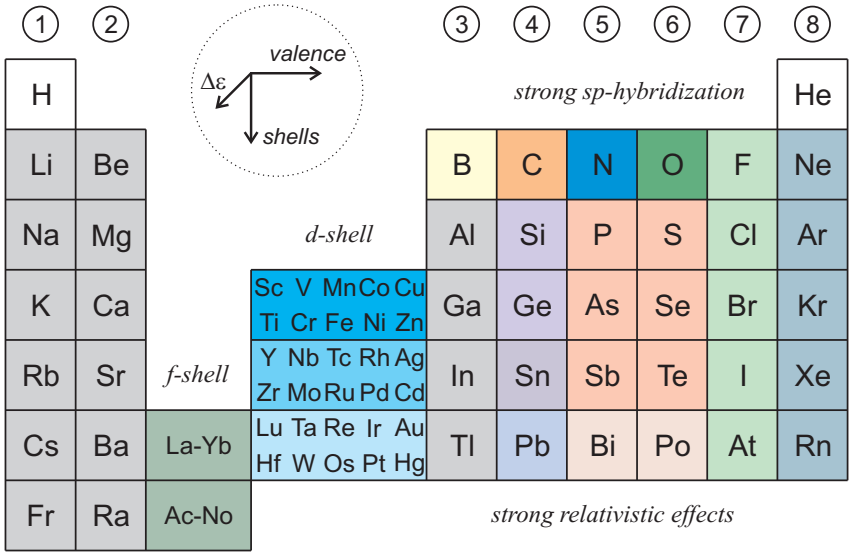
- Maximize density of "electron gas + ionic lattice" $\Longrightarrow$ close-packed lattices (CN $\gtrsim 12$, $\delta \gtrsim 3/4$)
- Details of band structure differentiate close-packed lattices
- At nonzero temperatures consider phonon dispersion

See here

Close-packed lattices: notations

See here

Metals: examples



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- most of metals — fcc, hcp, bcc
- α-Fe (bcc), γ-Fe (fcc), δ-Fe (bcc), melt $\Longrightarrow$ tempering
- Hg – close-packed hR lattice (A10) at $P > 12$ kbar
- In – fct (A6), α-Ga – A11, α-Pa – tcp, α-La – A', α-Mn
- β-Sn (A5) – not close-packed (best dia-deform.) $\Longrightarrow$ poor metal
- α-As (A7) – not close-packed, secondary bonding $\Longrightarrow$ semimetal
- B – semiconductor

Ionic crystals

Maximize eletrostatic energy, e.g. for binary compound $A_{n_A}X_{n_X}$:

$$M \frac{n_A + n_X}{2} \frac{Z_A Z_X e^2}{r_{AX}}$$

Here M is Madelung constant, which depends only on lattice geometry $\Longrightarrow$ closely copacked lattices, i.e. lattices with high Madelung constant

See two classes here

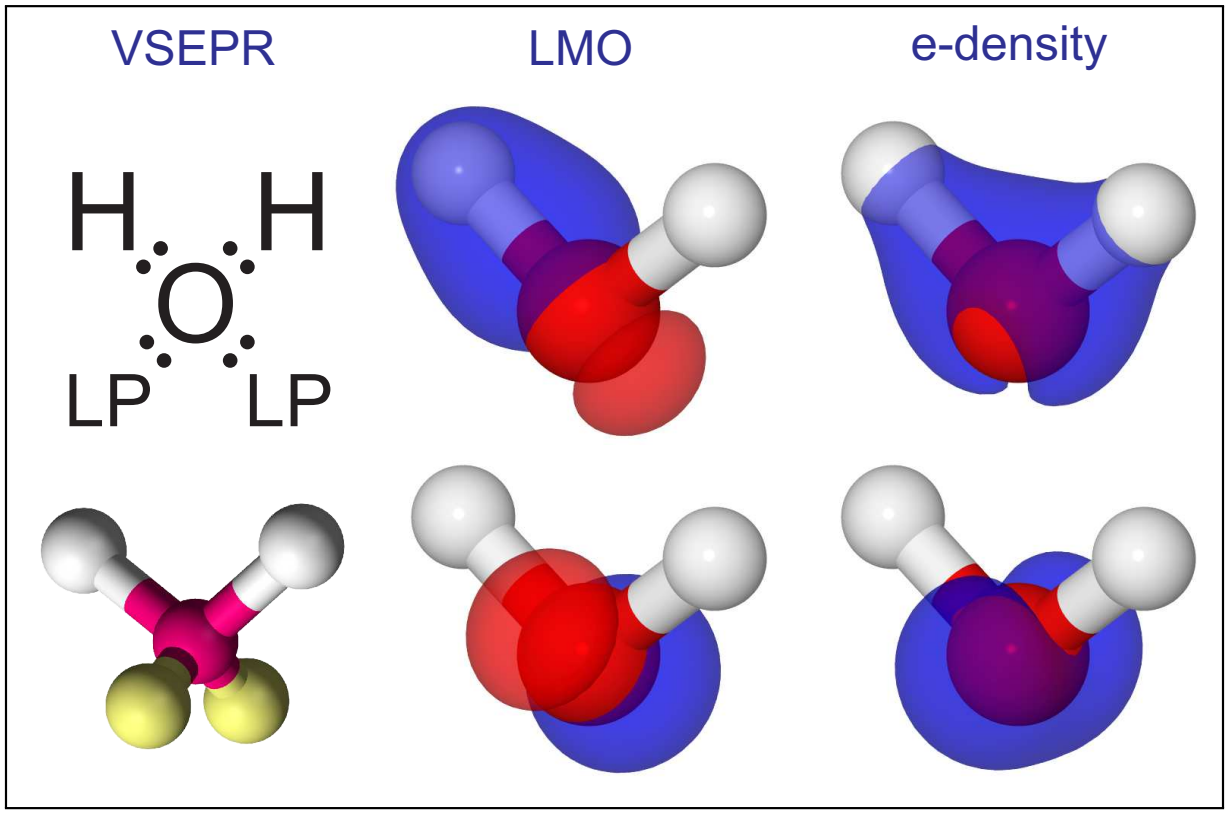
Covalent crystals

Satisfy coordination of atoms $\Longrightarrow$ locally coordinated lattices

Often disordered if there is a competition between local coordination and long range order (B, SiO_2, As_2Se_3)

See here

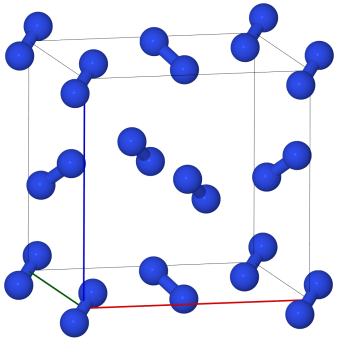
Molecules

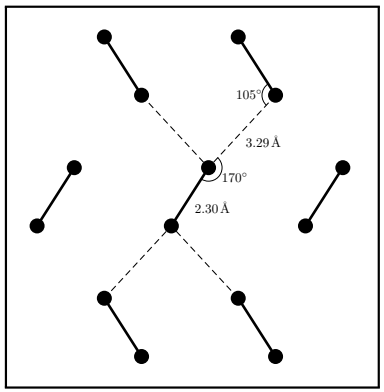


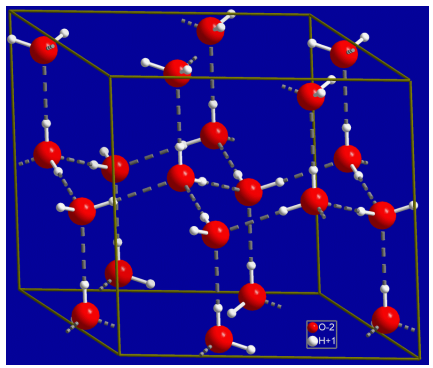
Valence shell electron pair repulsion (VSEPR) theory:

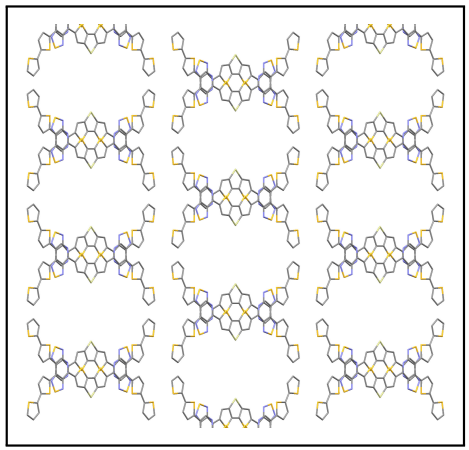
1. Distribute electrons between atoms according to octet rule
2. Pair them and minimize steric repulsion between pairs (including dihedrals as in CH_3–CH_3)

Molecular crystals





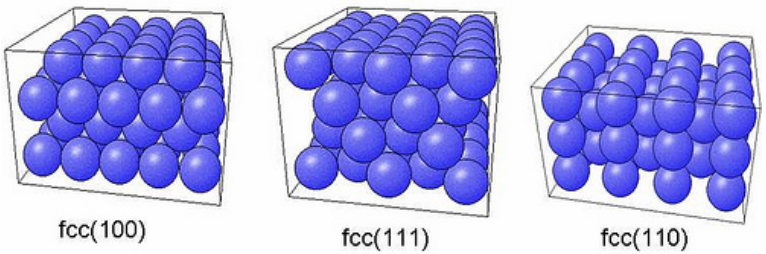


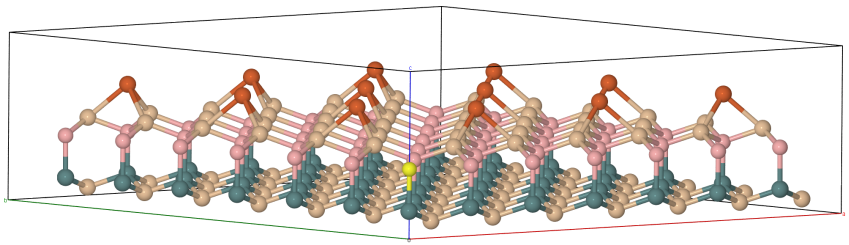


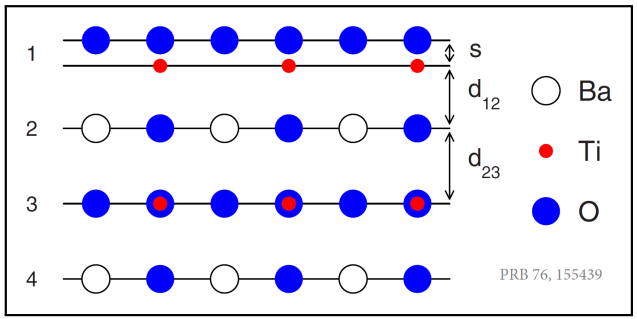
- Close packing under steric constraints
- Electrostatics
- Secondary bonding (Br_2), hydrogen bonding (H_2O)

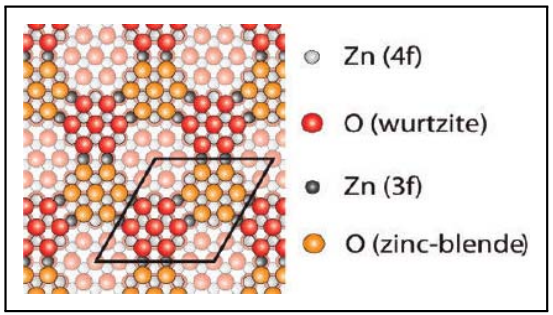
See also here

Surfaces





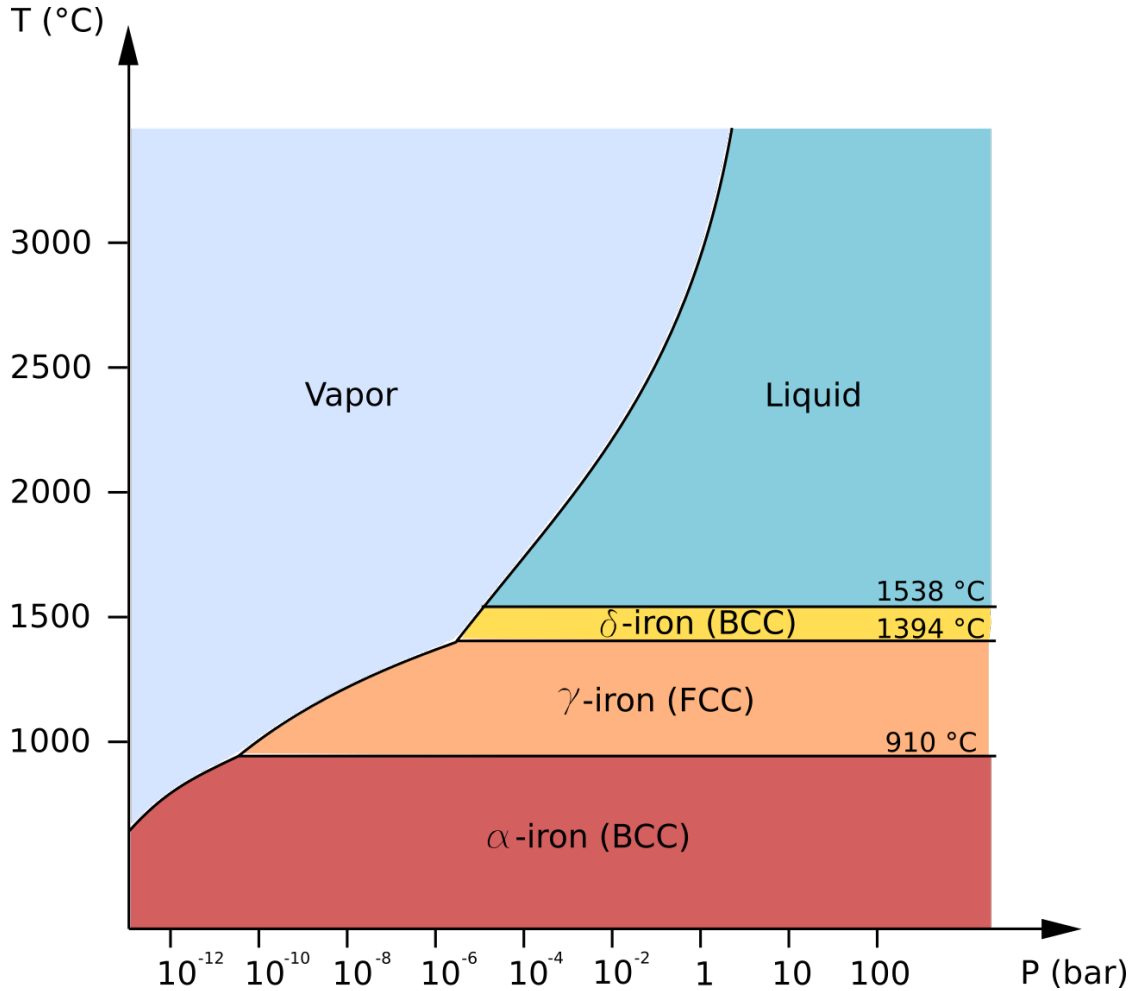




- Binding energy of surface atoms grows with number of ‘bonds’
- Covalent bonds prefer to be passivated
- Depends on environment

Structural transformations and polymorphism

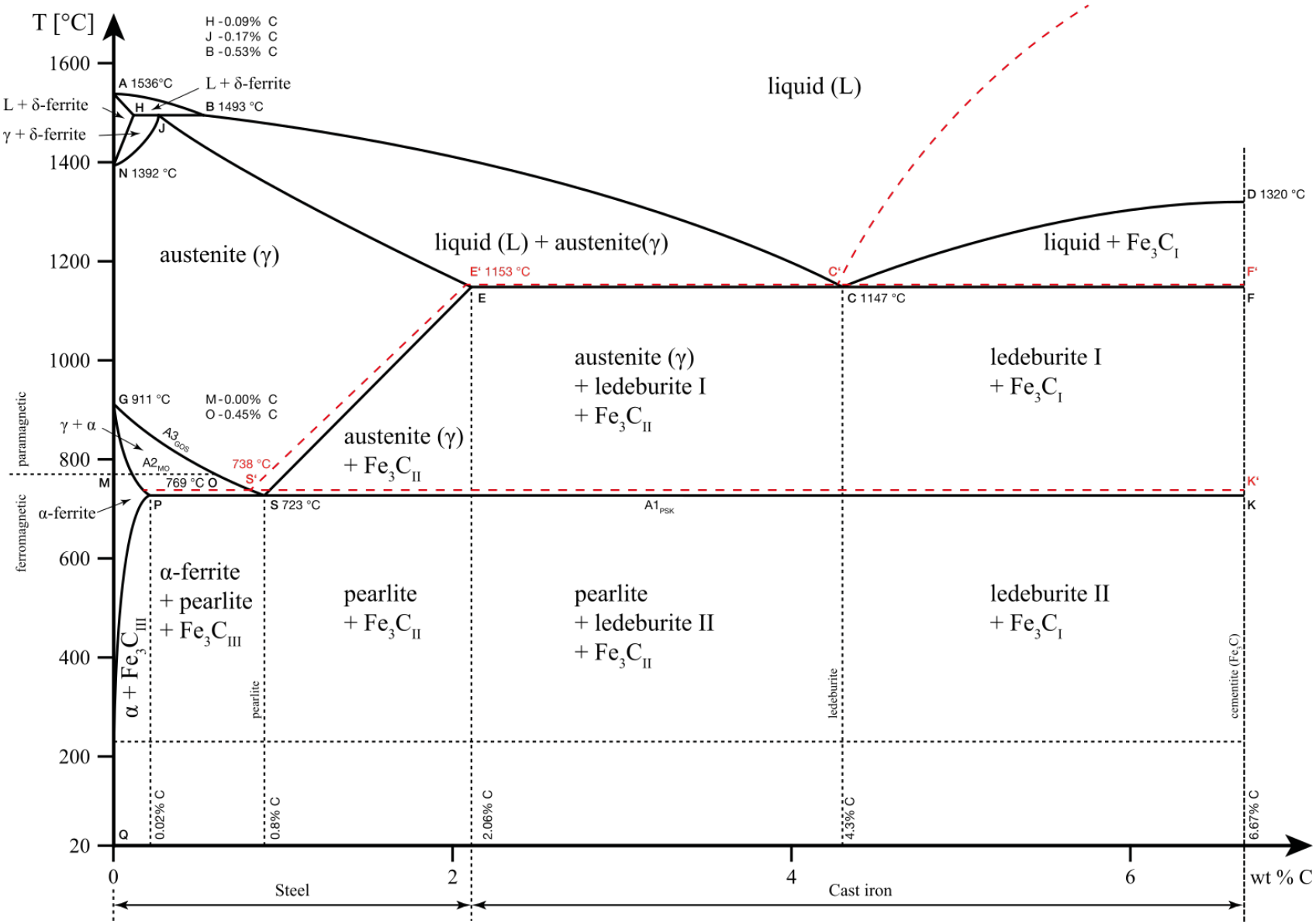
Iron – electronic & lattice properties are still far from understood [Sci Rep 4, 5585 (2014)]



- $\gamma \rightarrow \delta$ transition is due to vibrational entropy
- $\gamma \rightarrow \alpha$ transition is due to ee-correlations (magnetism)

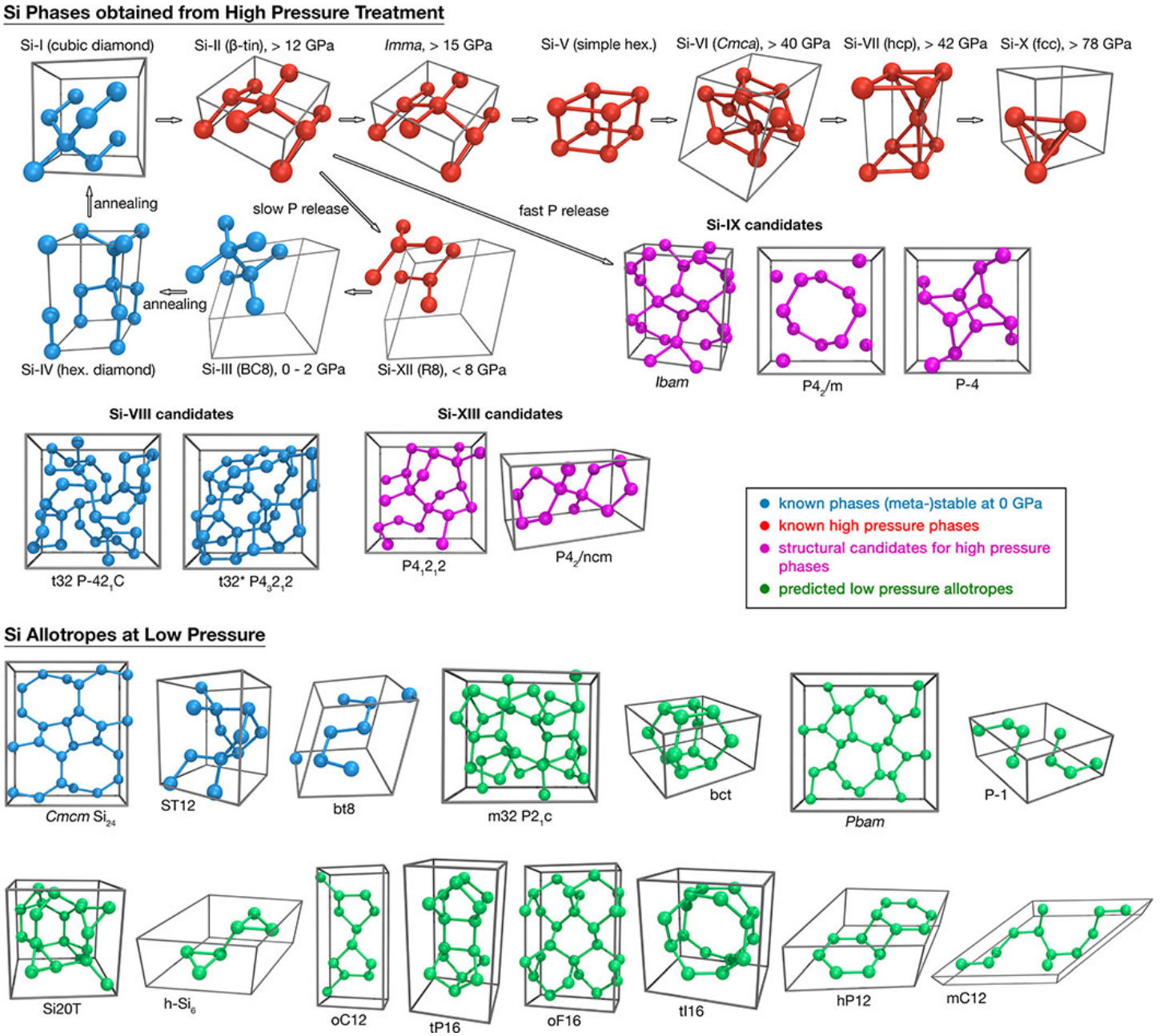
Structural transformations and polymorphism

Steel



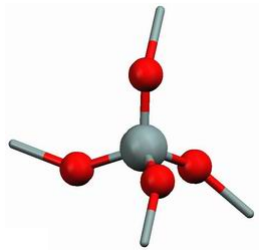
Structural transformations and polymorphism

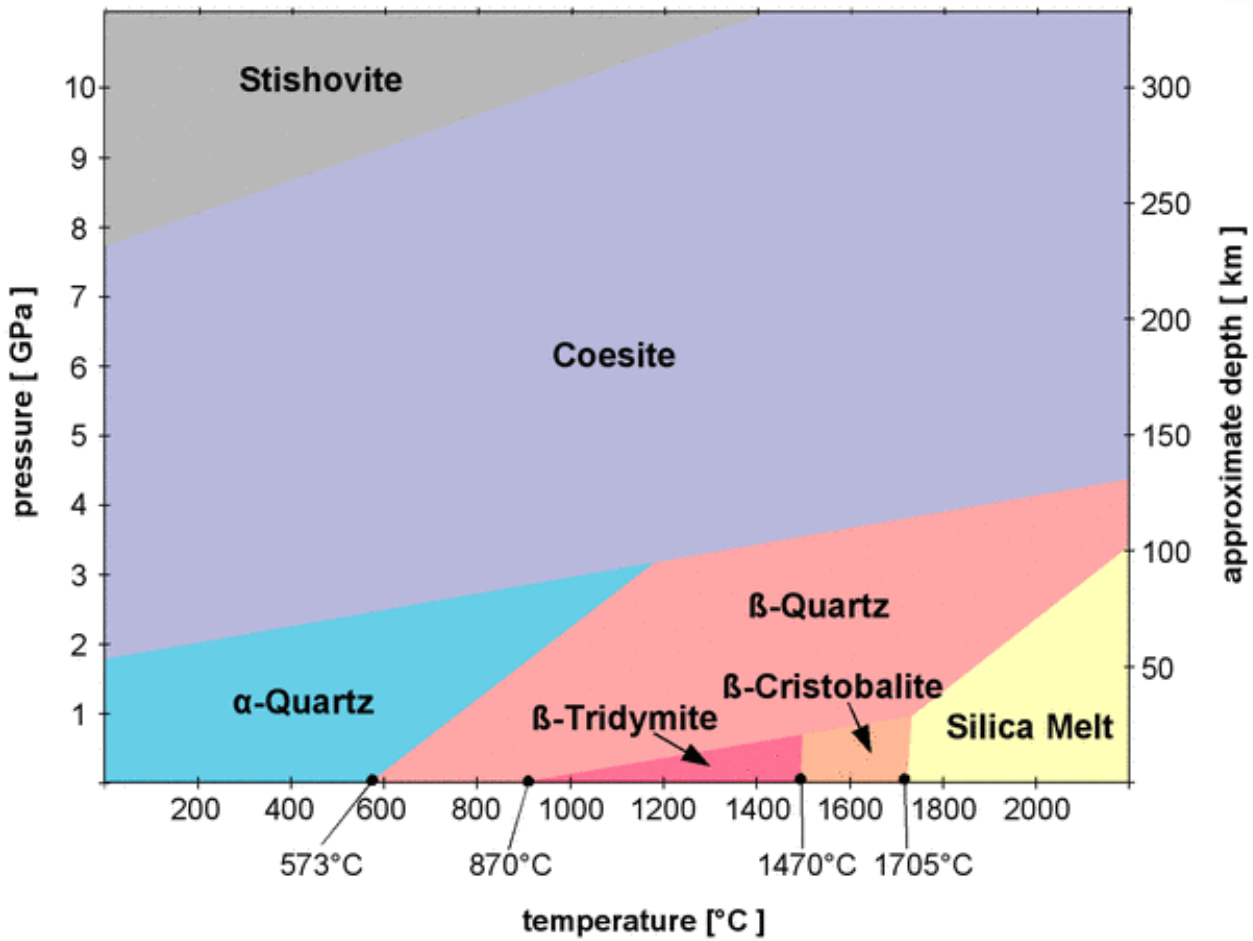
Silicon



Structural transformations and polymorphism

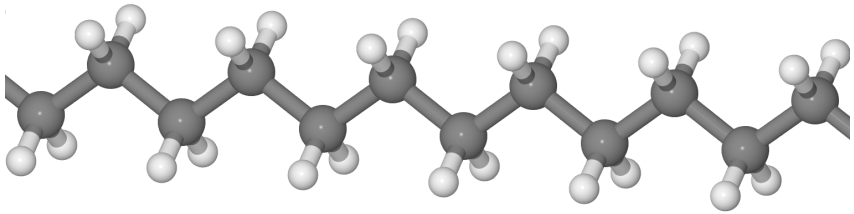
SiO2

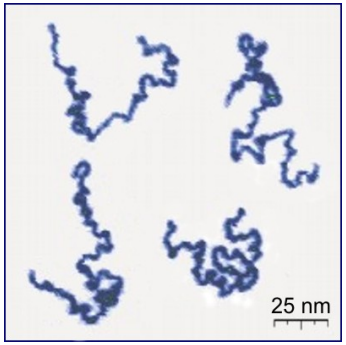


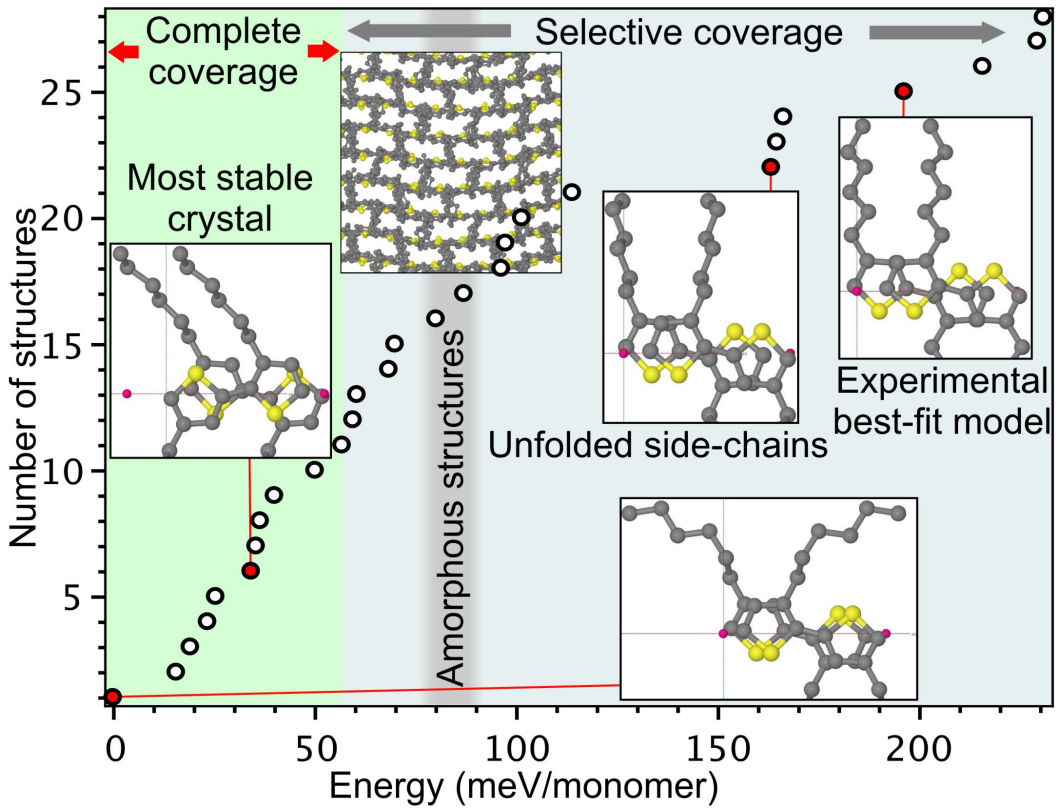


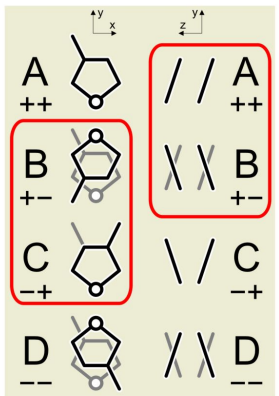
Structural transformations and polymorphism

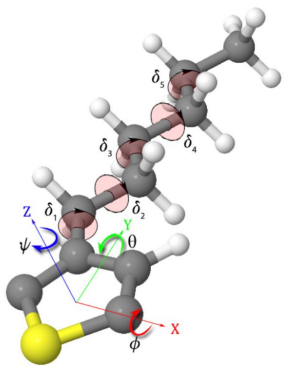
Polymers











Exploring structure-property relationships

(Functional materials)

- electronic conductors – metals
- ionic conductors – some ionic crystals
- high-T superconductors – layered t-metal pnictides/chalcogenides
- electrical insulators – wide-gap ionic-covalent solids
- field effect transistors – tetrahedral semiconductors
- flexible/printable electronics – conjugated polymers
- ferroelectrics and pyroelectrics – polar crystals
- optical rotation – chiral crystals
- phase change memory – some average valence 5 compounds
- photosensitive materials – pnictide/chalcogenide glass-formers
- lubricants – layered solids
- nanoporous materials – zeolites, clathrates
- anode/cathode materials for batteries

Summary and Resources

See summary here

- Wikipedia
- Crystal structures
- Crystallography Open Database
- R W G Wyckoff, Crystal structures (1963, 1964)
- References: structure, bonding, specific materials
- Textbooks