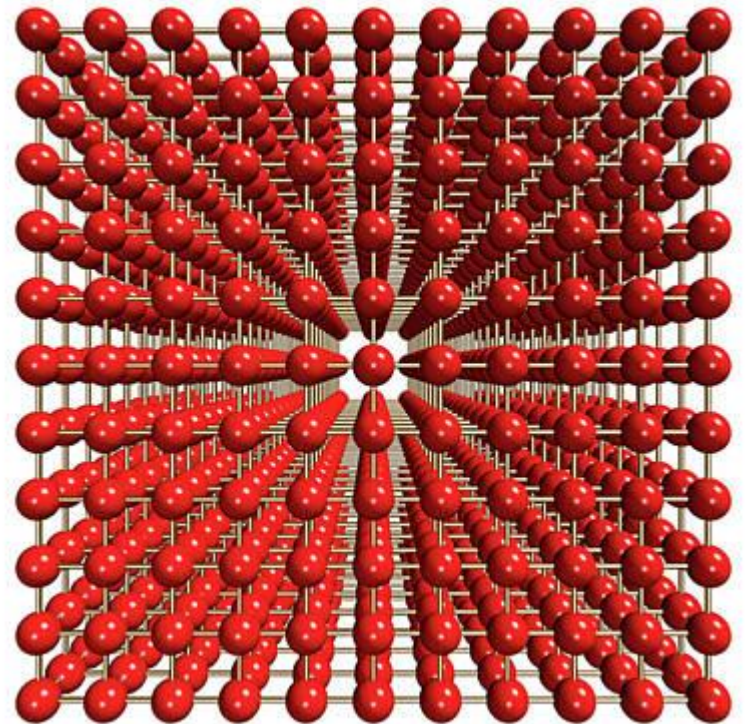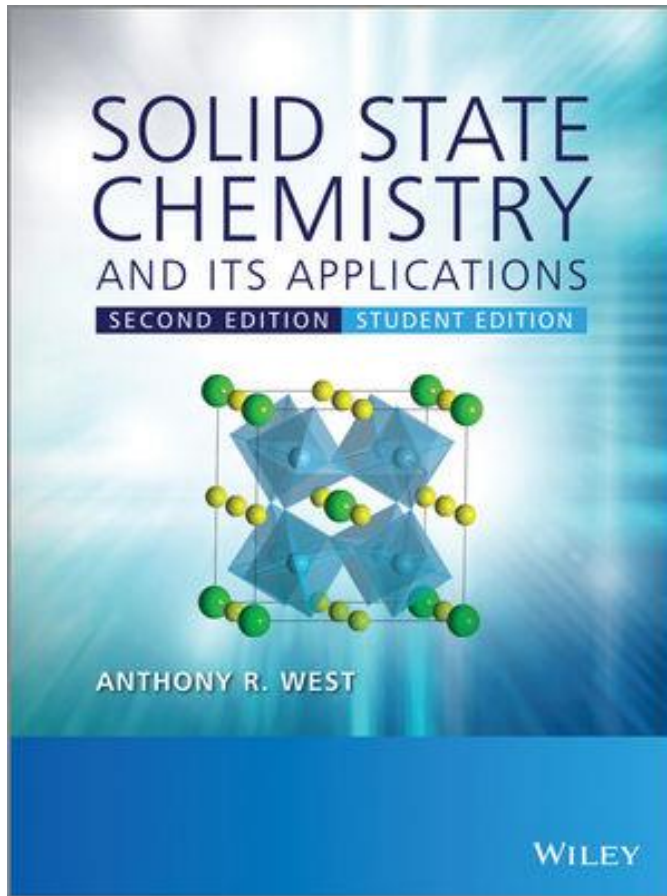# Lecture 1

Perfect and Imperfect Crystals

Objective of this course

✓ to have a broad understanding of structures of defect, how the defect structure looks like;

✓ their role in determining properties of materials.

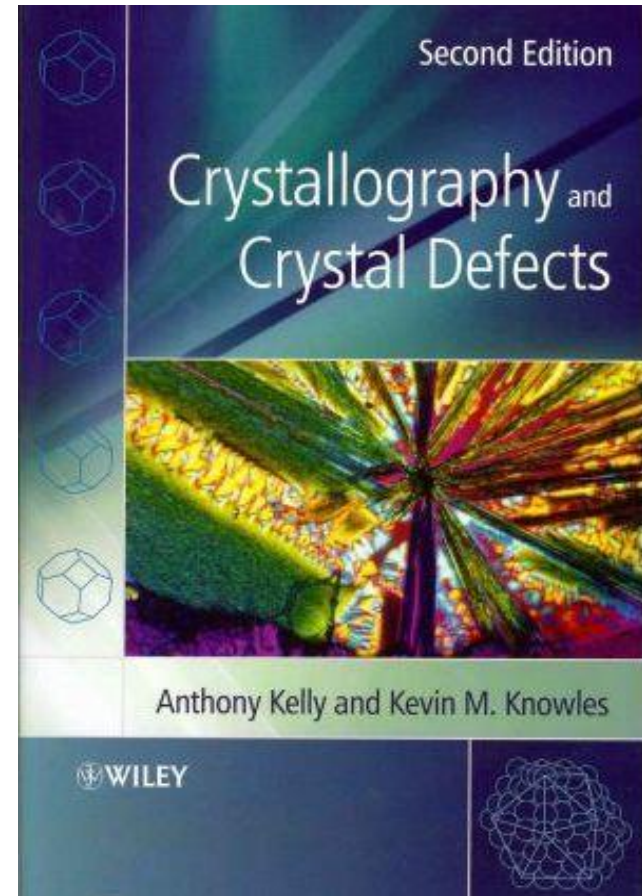✓ to be able to understand the structure of dislocation and their interaction

Solid State Chemistry and its Applications, 2nd Edition, Student Edition
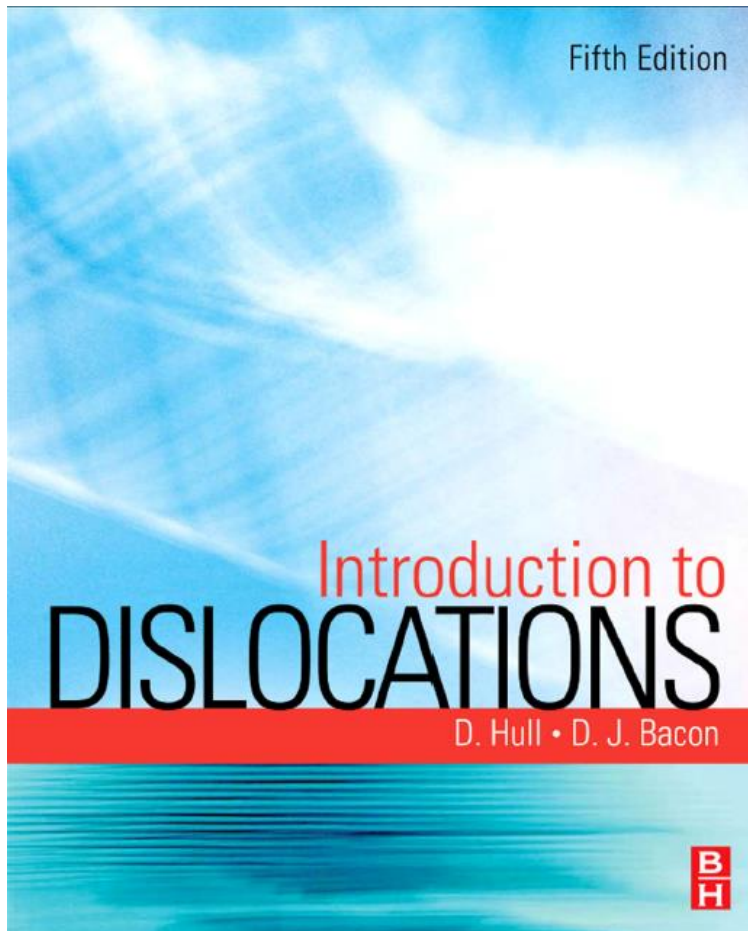Anthony R. West
2014
582 Pages
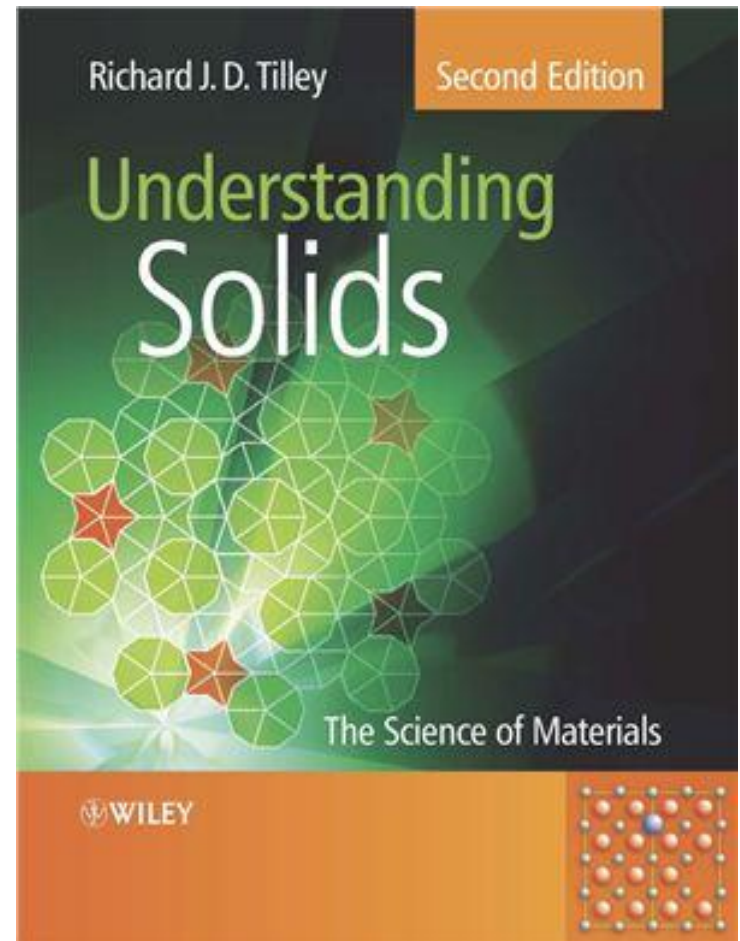
Crystallography and Crystal Defects, 2nd Edition
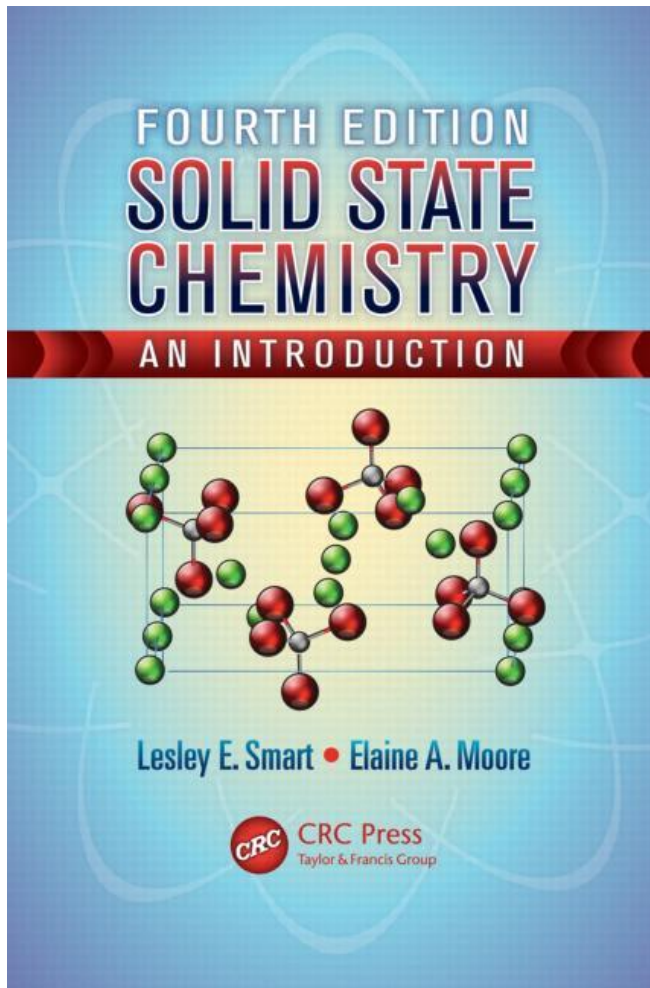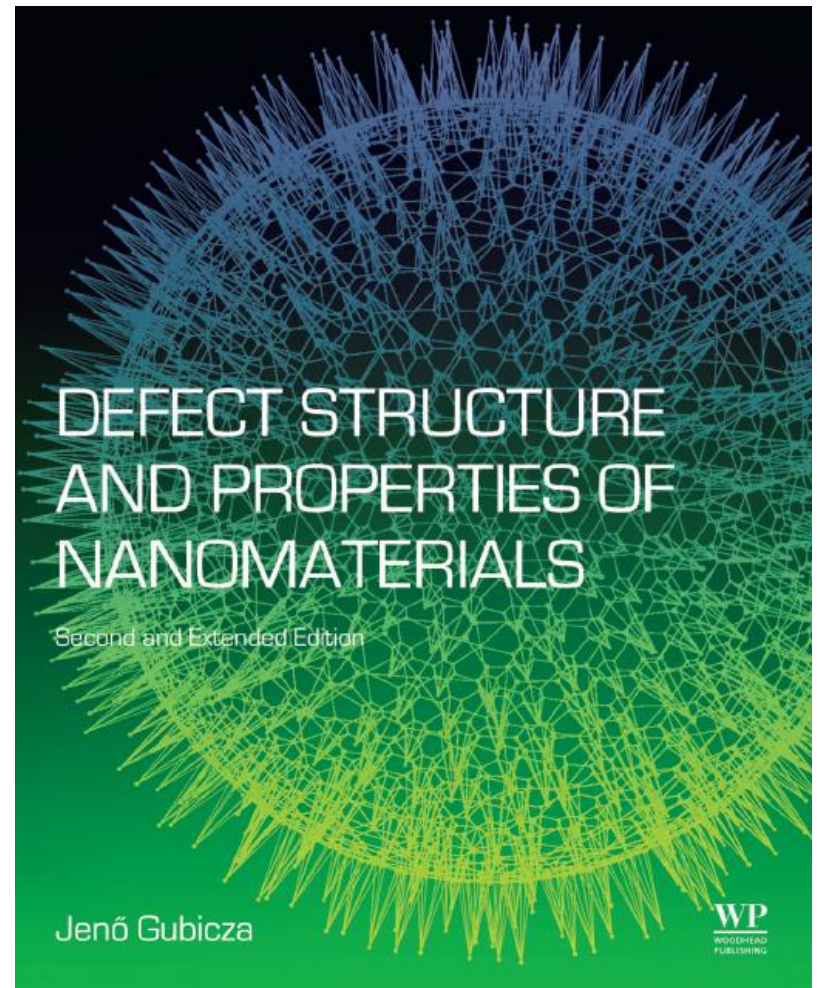Anthony Kelly, Kevin M. Knowles
2012
536 Pages

Introduction to Dislocations
Derek Hull
(2011, 260 pages)

Richard J. D. Tilley
Understanding Solids:
The Science of Materials
(2013, 584 Pages)

Elaine A. Moore, Lesley E. Smart
Solid State Chemistry: An Introduction
4th Edition
CRC Press, 2012, 494 Pages

**DEFECT STRUCTURE
AND PROPERTIES
OF NANOMATERIALS
JENO GUBICZA
2017, 412 pages**

Crystals are like people: it is the defects in them which tend to make them interesting!

CHAPTER 11

STEM IMAGING OF CRYSTALS AND DEFECTS

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*TEMPE, ARIZONA 85281 U.S.A.**

11.1 INTRODUCTION

Crystals are like people: it is the defects in them which tend to make them interesting! This chapter describes the use of STEM imaging for the structural characterization of crystalline materials, perfect and imperfect. The object of the chapter is to describe basic principles as clearly as possible, using a minimum of mathematics.

Sir Colin John Humphreys (born 24 May 1941) is a British physicist

Humphreys C.J. (1979) Stem Imaging of Crystals and Defects. In: Hren J.J., Goldstein J.I., Joy D.C. (eds) Introduction to Analytical Electron Microscopy. Springer, Boston, MA
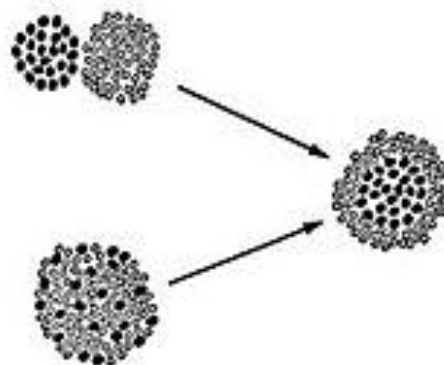
Atom
(Leucippus, 450BC)
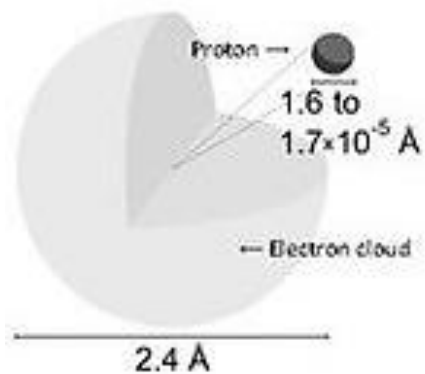
Molecule
(Gassendi, 1649)

Cell-as-molecule
(Harrison, 1993)

Human-as-molecule
(Sales, 1789)

Proton →

1.6 to
1.7×10^{-5} Å

← Electron cloud

2.4 Å

Oxygen

Hydrogen

Hydrogen

IUPAC Periodic Table of the Elements

The periodic table contains 118 elements. Only 90 of these elements occur naturally in the environment, and still fewer elements comprise the living world.
From bacteria to higher vertebrates and humans, nature has repeatedly selected for all life forms a basic group of only six elements.

Crystal Defects and Microstructure in Materials Science

The materials paradigm represented in the form of a tetrahedron:

Perfect Structure

Faulted layer

Adatom layer

Dimer layer

Material vapor

Surface of material

Vacancy
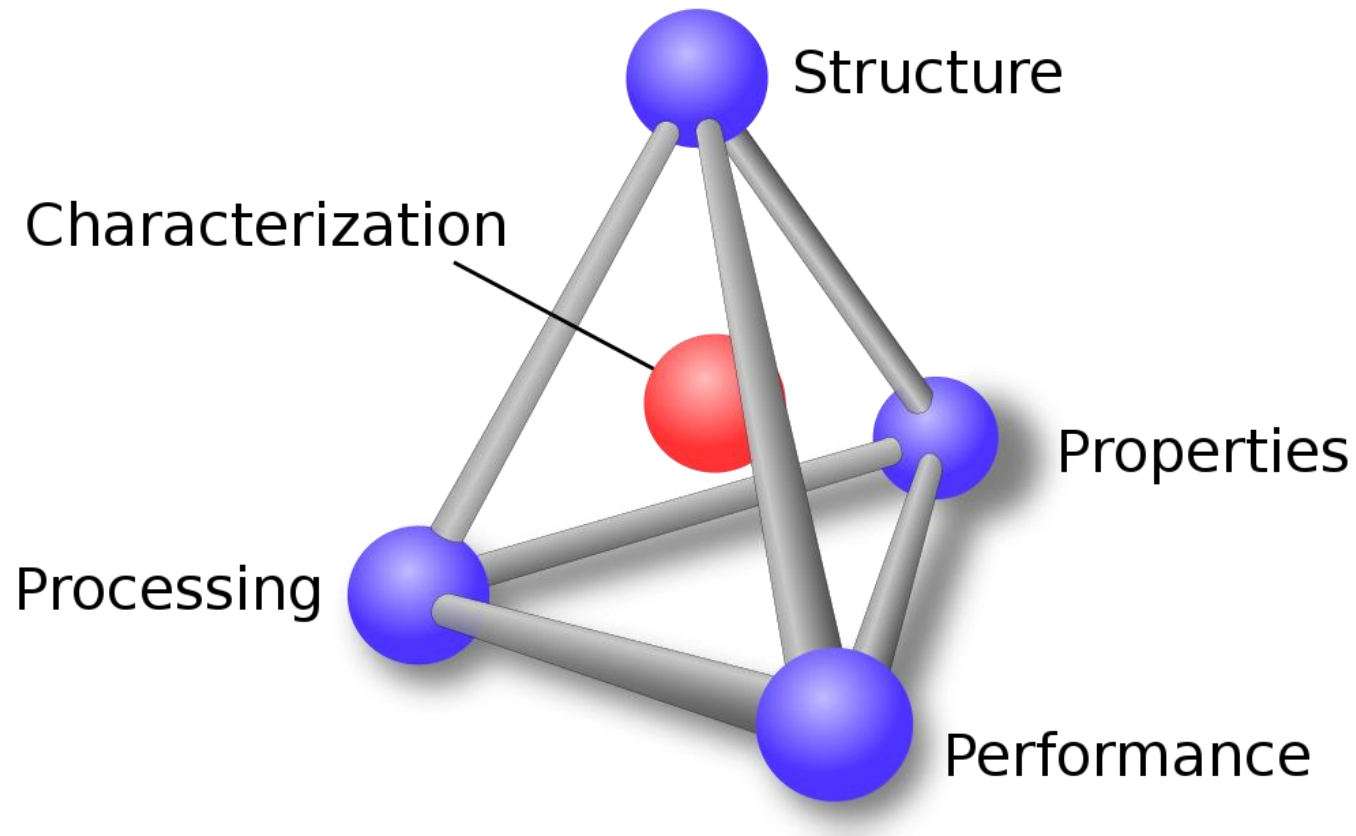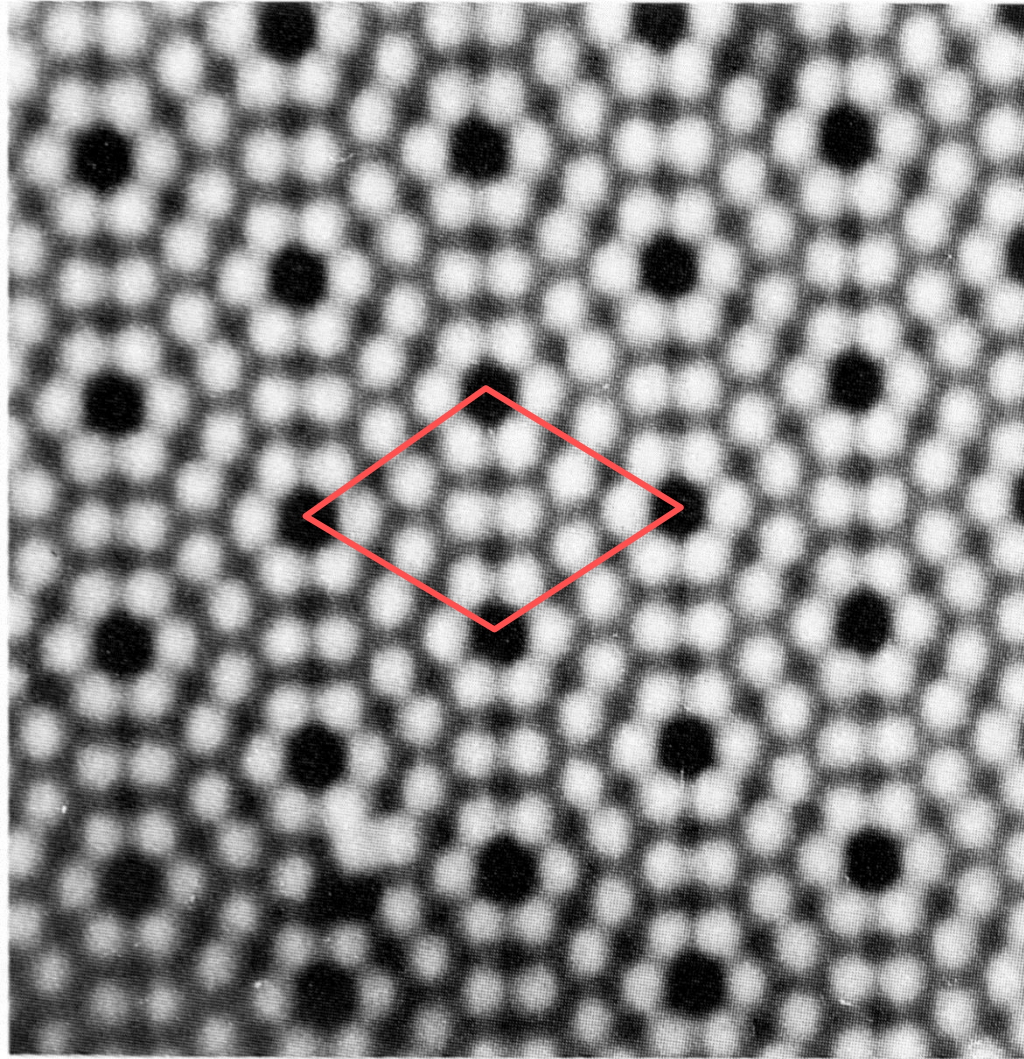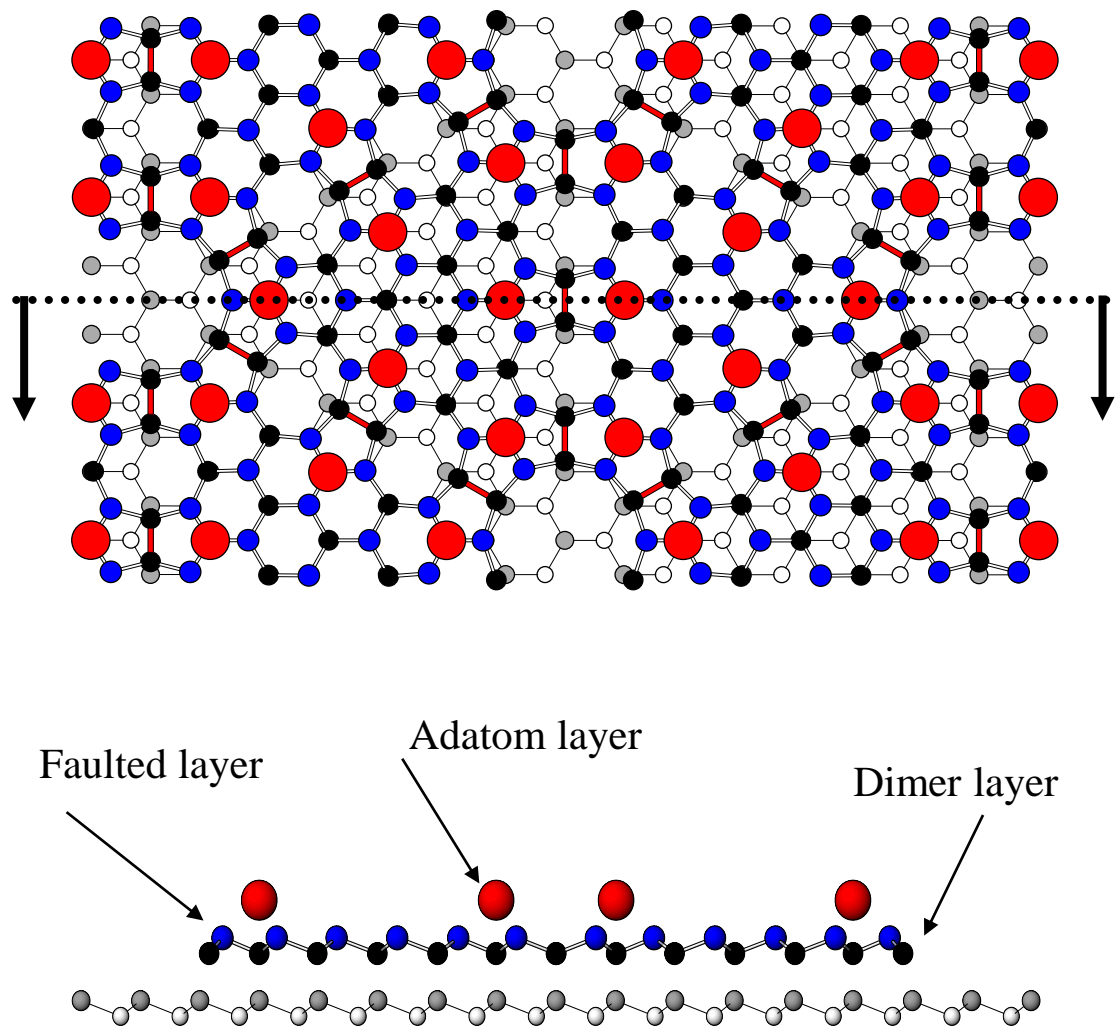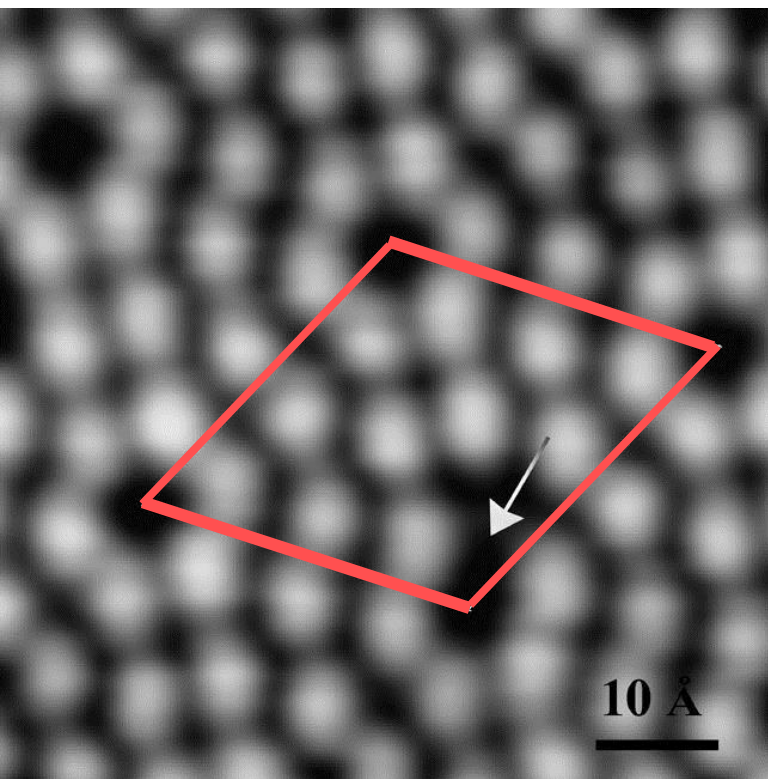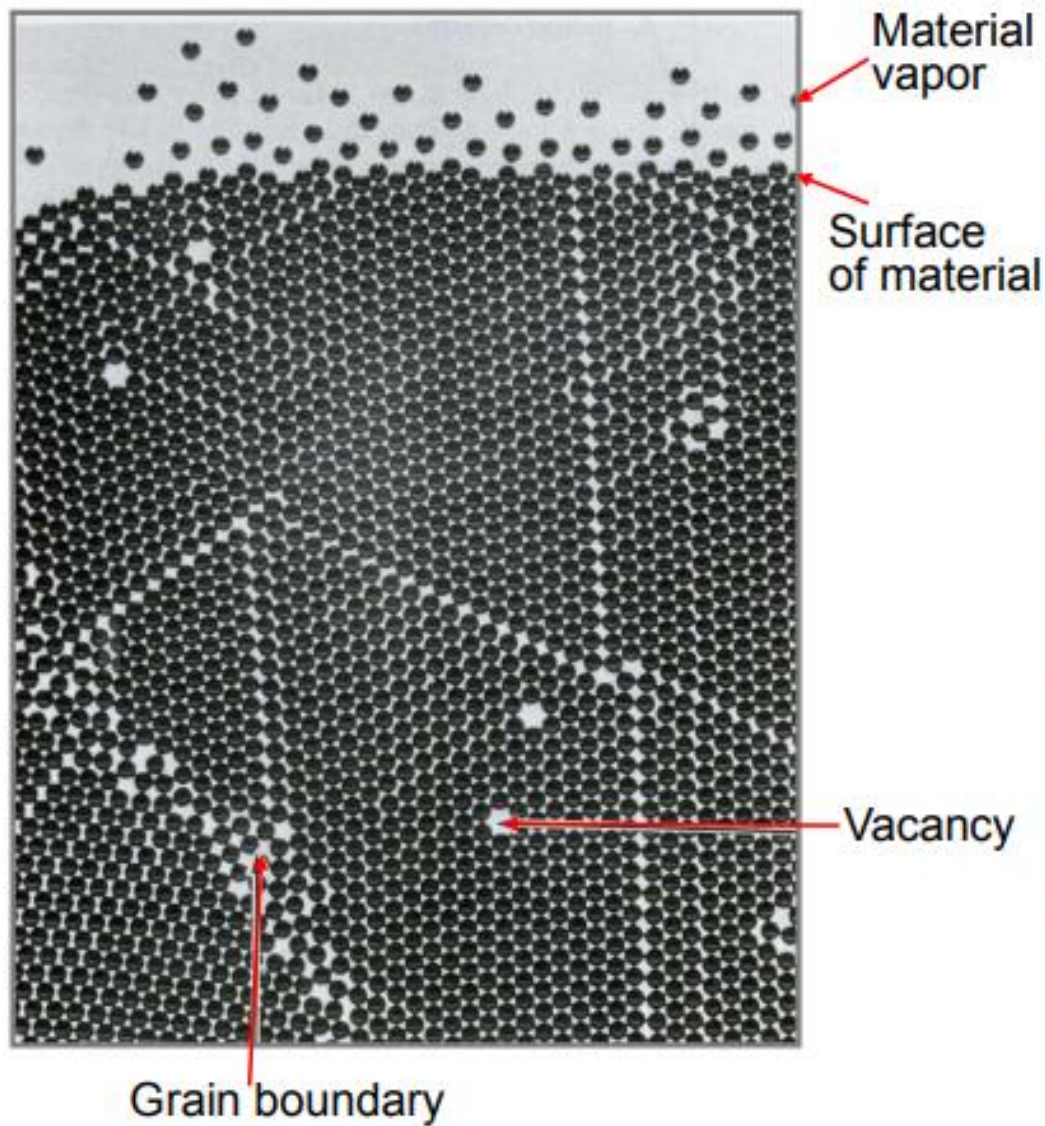
Grain boundary

Ball bearings can be used to simulate how atoms are packed together in solids.

The photo shows a ball-bearing model set up to show what the grain boundaries look like in a polycrystalline material.

The model also shows up another type of defect-the vacancy-which is caused by a missing atom.

Real crystals contain large numbers of **defects** (typically more than 10^4 per milligram), ranging from variable amounts of impurities to missing or misplaced atoms or ions.

These defects occur for three main reasons:

✓ It is impossible to obtain any substance in 100 % pure form. Some impurities are always present.

✓ Even if a substance were 100 % pure, forming a perfect crystal would require cooling the liquid phase infinitely slowly to allow all atoms, ions, or molecules to find their proper positions. Cooling at more realistic rates usually results in one or more components being trapped in the "wrong" place in a lattice or in areas where two lattices that grew separately intersect.

✓ Applying an external stress to a crystal, such as a hammer blow, can cause microscopic regions of the lattice to move with respect to the rest, thus resulting in imperfect alignment.

Crystal Defects and Microstructure in Materials Science

Defects have a profound impact on the various properties of materials:

✓ mechanical (plasticity, failure),

✓ optical (e.g., color centers),

✓ thermal and electrical transport (e.g., scattering of phonons and electrons),

✓ electronic (e.g., doping of semiconductors), etc.

Structural hierarchy, characteristic length- and time-scales

0.1 mm — Grain structure

10 μm — Single grain

0.2 μm — Dislocation cells

10 nm — Individual dislocations

5 Å — Atoms/crystal structure
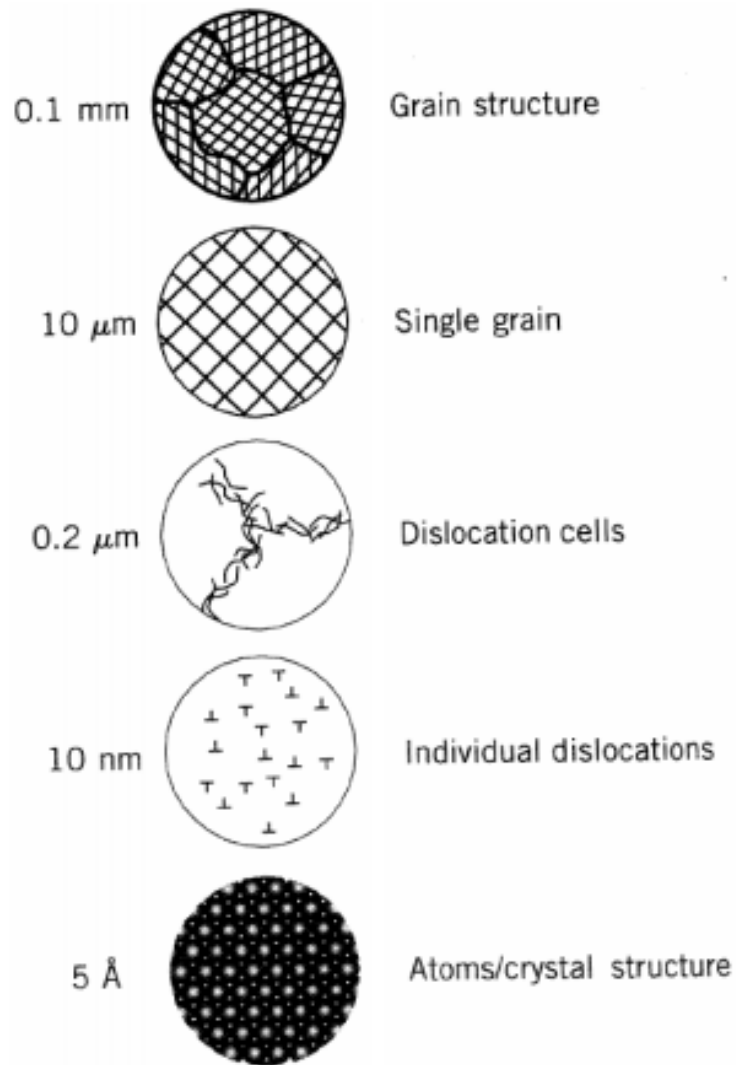
from Allen & Thomas, The Structure of Materials

dislocation micro-structures & patterning

μ-scale dislocation mobility

atomic mechanisms of dislocation mobility and intersections

electronic structure of dislocation core
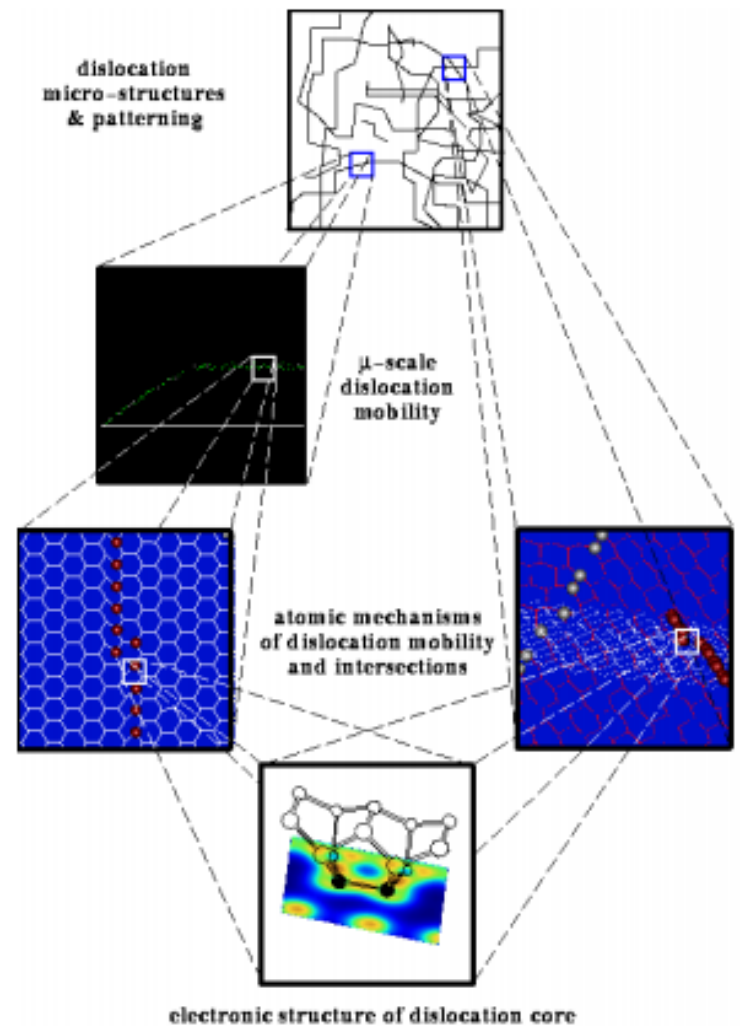
modeling of dislocations in semiconductors
V. Bulatov, LLNL

Crystal Defects → Material Properties

The effect of microstructure on material properties is defined by characteristics of individual defects:

- ✓ Structural - distortion of crystalline atomic arrangements
- ✓ Electronic - local modification of electronic structure
- ✓ Chemical - enhanced reactivity of defect sites
- ✓ Scattering - interaction with phonons, photons, electrons, positrons
- ✓ Thermodynamic - enthalpies and entropies of defects
- ✓ Kinetic - mobility of defects
- ✓ Elastic - defects can be softer or stiffer than perfect crystal … etc.

and the collective behavior of the totality of crystal defects (microstructure).

Imperfections in Solids

Atomic Composition

Bonding

Crystal Structure

Thermo-Mechanical Processing

Microstructure: Materials properties

Addition and manipulation of defects
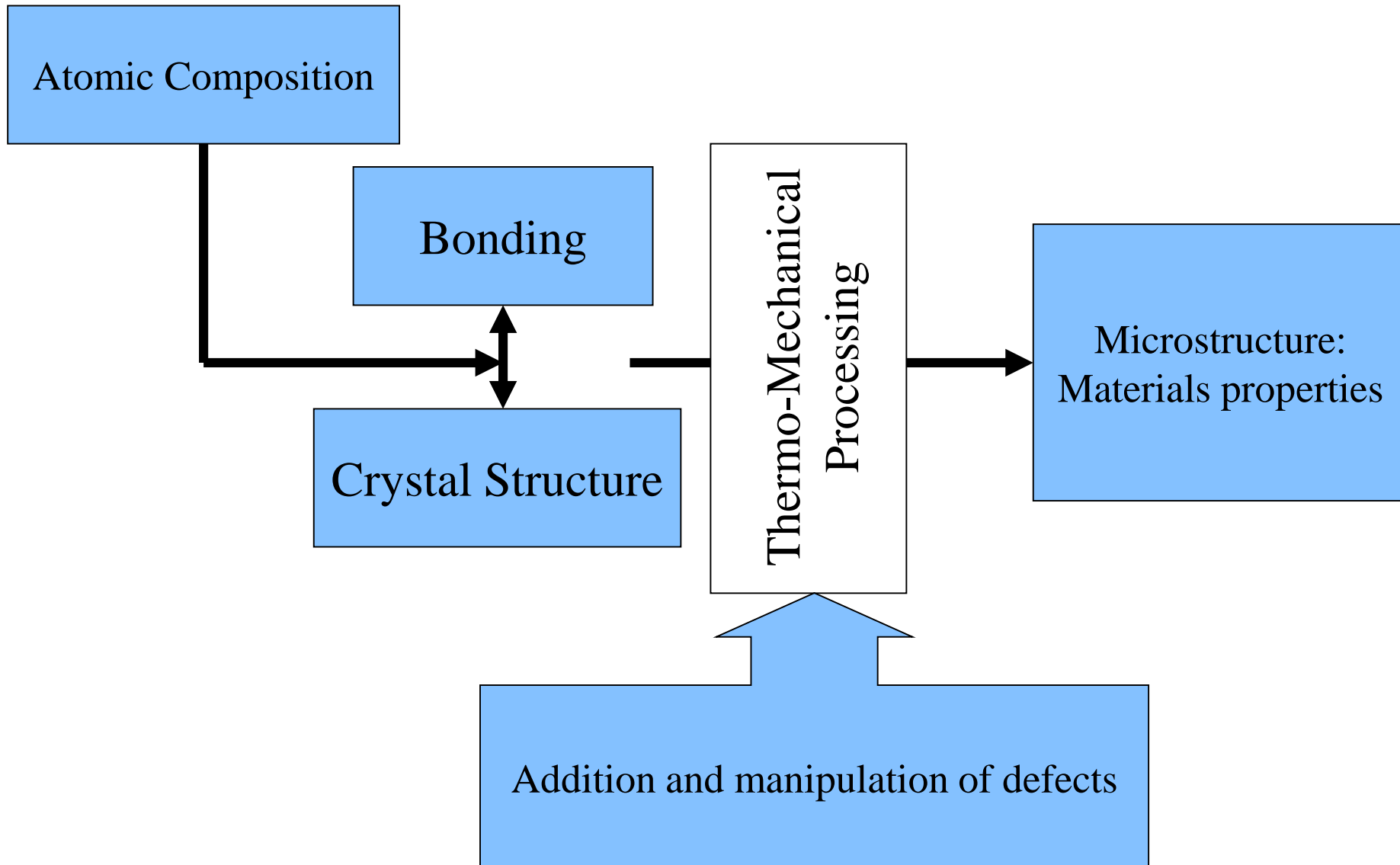
Why defect are important?

There are a lot of properties that are controlled or affected by defects, for example:

✓ **Electric and thermal conductivity in metals** (strongly reduced by point defects).

✓ **Electronic conductivity in semi-conductors** (controlled by substitution defects).

✓ **Diffusion** (controlled by vacancies).

✓ **Ionic conductivity** (controlled by vacancies).

✓ **Plastic deformation in crystalline materials** (controlled by dislocation).

✓ **Colors** (affected by defects).

✓ **Mechanical strength** (strongly depended on defects).

**Defects in crystalline solids are important because they modify properties.**

For example:

✓ just a trace of chromium impurity changes colourless aluminium oxide into ruby;

✓ metals are ductile when linear defects (dislocations) are free to move;

✓ crystals dissolve and react at increased rates at points where dislocations intersect external surfaces.
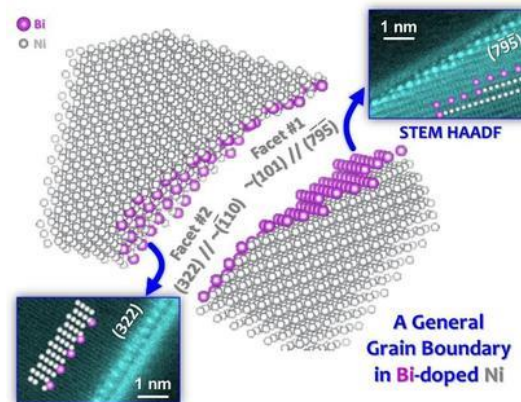
Al_2O_3

Ruby
$Al_2O_3+Cr^{3+}$
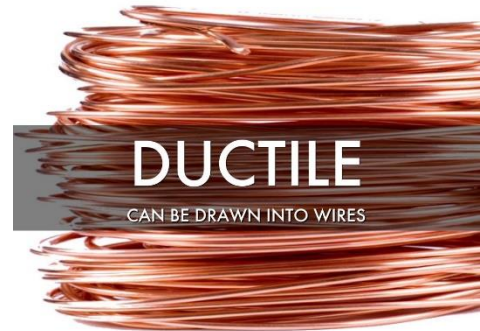
DUCTILE
CAN BE DRAWN INTO WIRES

A General
Grain Boundary
in Bi-doped Ni

Imperfections in Solids

BONDING
+
STRUCTURE
+
DEFECTS

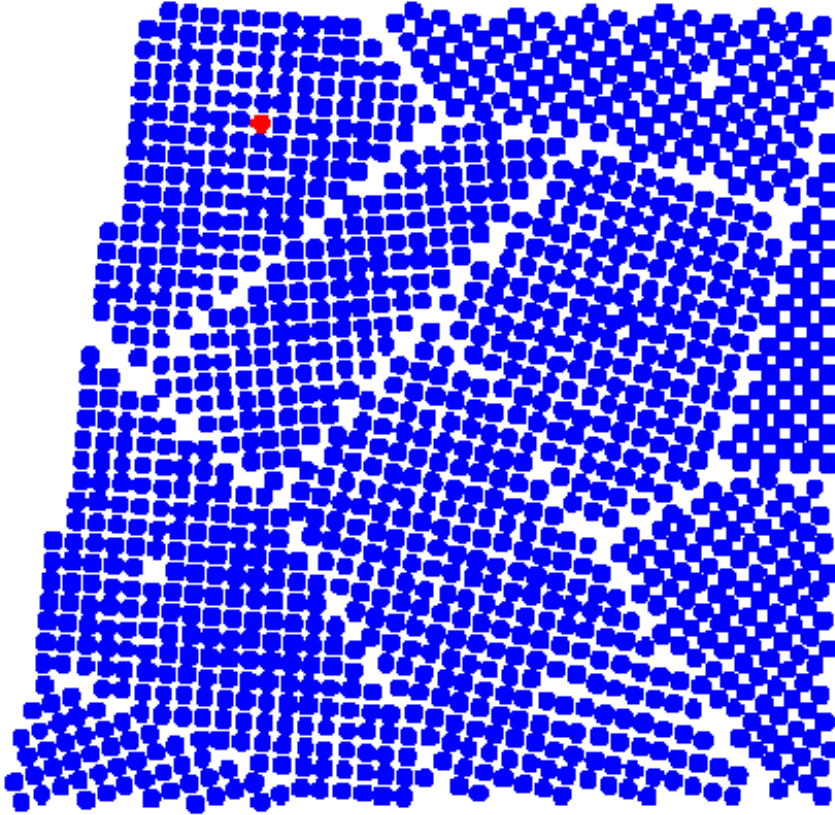Is it enough to know bonding and structure of materials to estimate their macro properties ?

PROPERTIES

Defects do have a significant impact on the properties of materials

Imperfections in Solids

Schematic drawing of a poly-crystal with many defects by Helmut Föll, University of Kiel, Germany.

Defects around us:
A- Color/Price of Precious Stones
B- Mechanical Properties of Metals
C- Properties of Semiconductors
D- Corrosion of Metals

Crystal structure

Crystal structure is a description of the ordered arrangement of atoms, ions or molecules in a crystalline material.

Ordered structures occur from the intrinsic nature of the constituent particles to form symmetric patterns that repeat along the principal directions of three-dimensional space in matter.

In a crystal, atoms are arranged in straight rows in a three-dimensional periodic pattern. A small part of the crystal that can be repeated to form the entire crystal is called a **unit cell**.

Asymmetric unit   Primitive unit cell   Conventional unit cell   Crystal
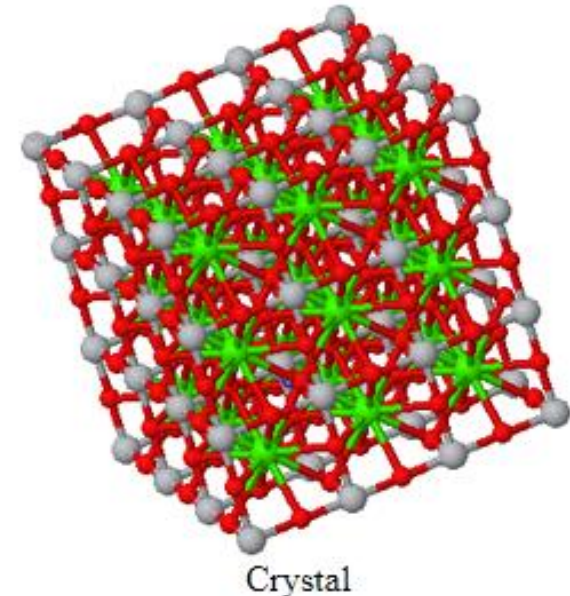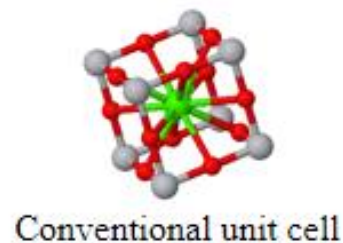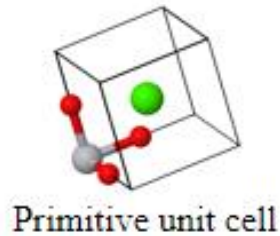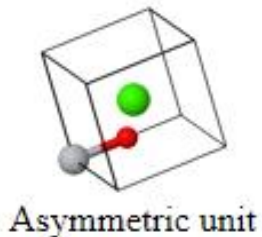
Devices such as **solid state transistors, lasers, solar cells, and light emitting diodes** are often made from **single crystals**.

Many materials, including most **metals and ceramics**, are **polycrystalline**. This means there are many little crystals packed together where the orientation between the crystals is random.

monocrystalline solar panel

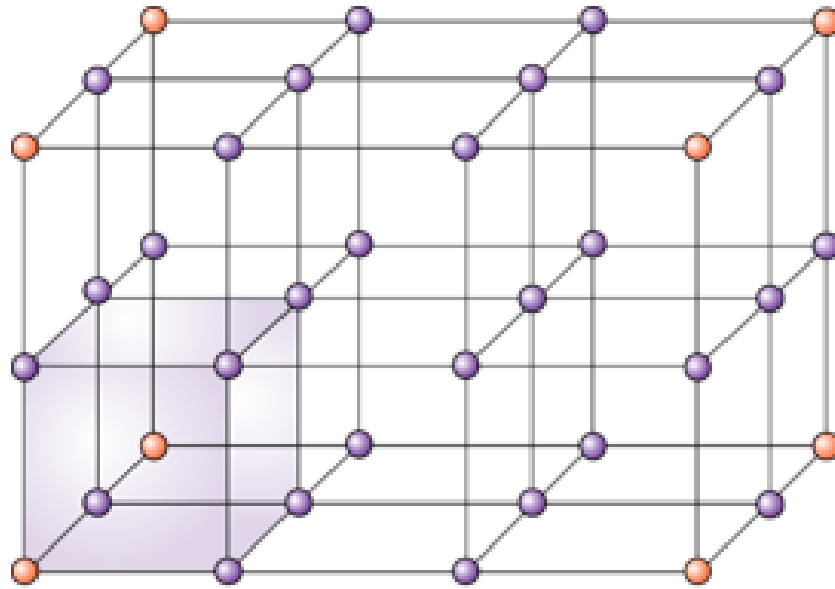**solid state transistors**

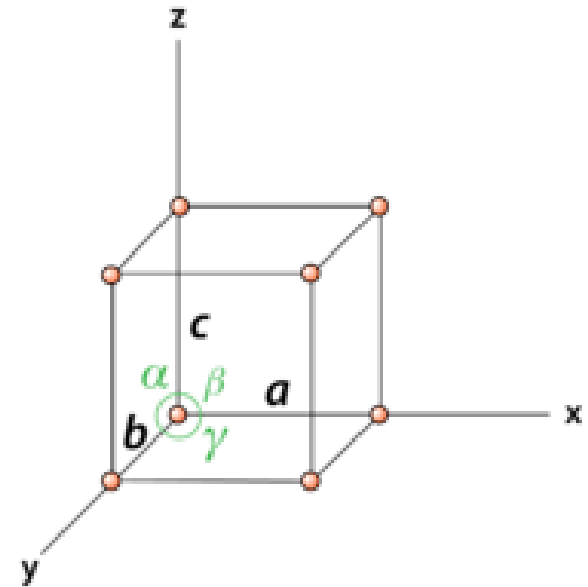**light emitting diodes (LED)**

laser

Unit cell

The **unit cell** is the smallest repeating unit having the full symmetry of the crystal structure.

The geometry of the unit cell is defined as a parallelepiped, providing six lattice parameters taken as the **lengths of the cell edges (a, b, c)** and the **angles between them (α, β, γ)**.
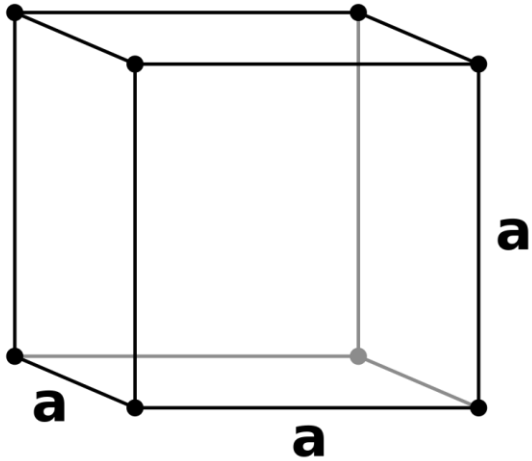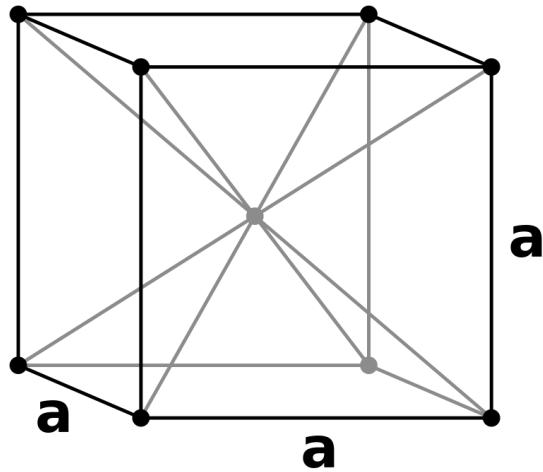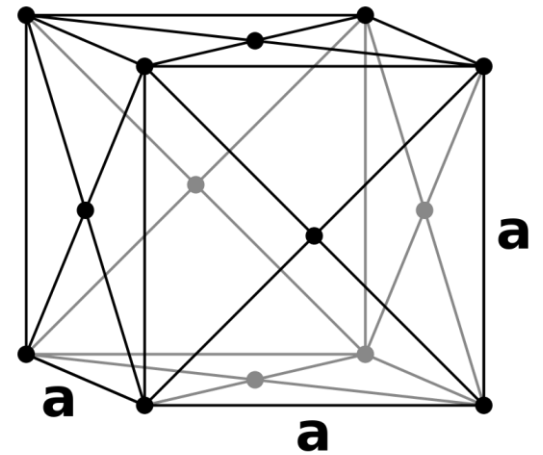
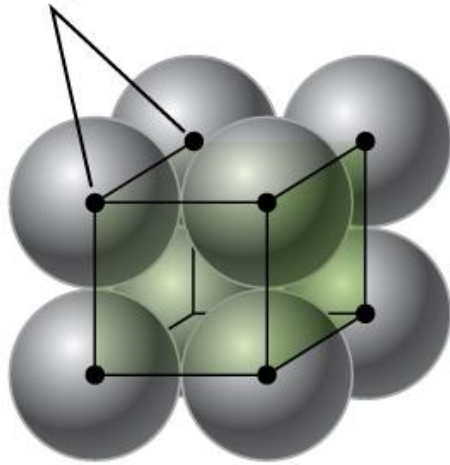

Crystal Lattice

Unit Cell

Unit cell

Simple cubic (P)

Body-centered cubic (I)

Face-centered cubic (F)

Lattice points

Lattice points

8 corners

Simple cubic lattice cell
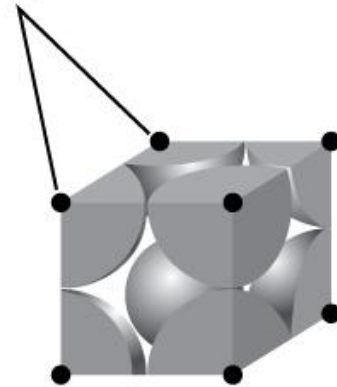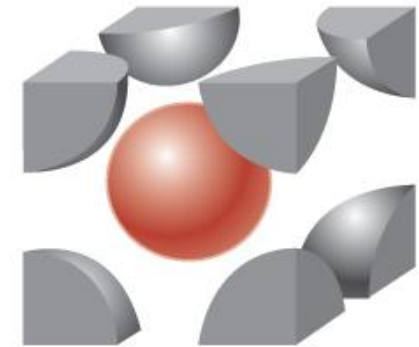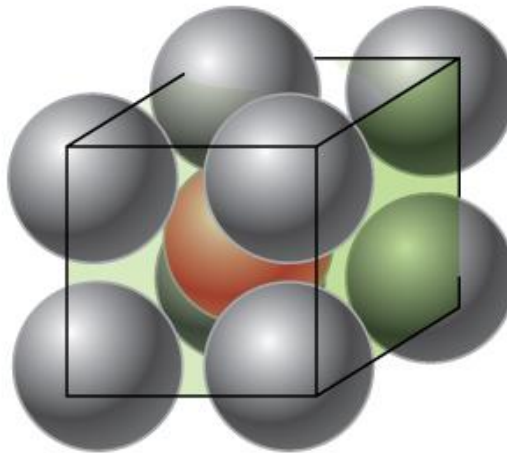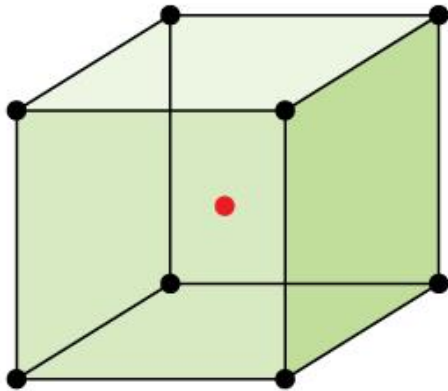
Body-centered cubic structure

In a body-centered cubic structure, atoms in a specific layer do not touch each other. Each atom touches four atoms in the layer above it and four atoms in the layer below it.
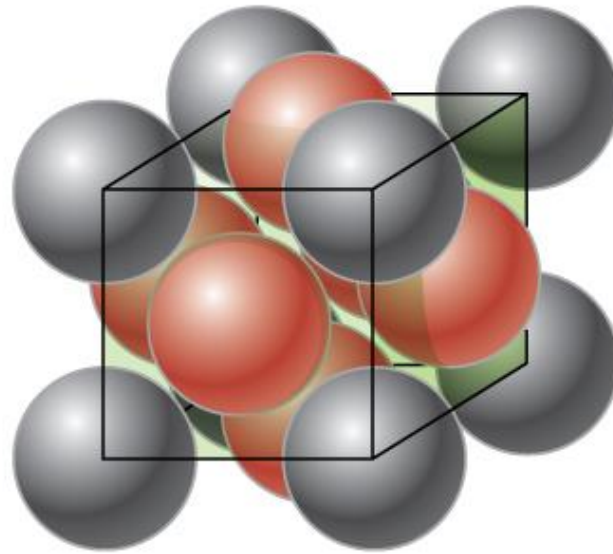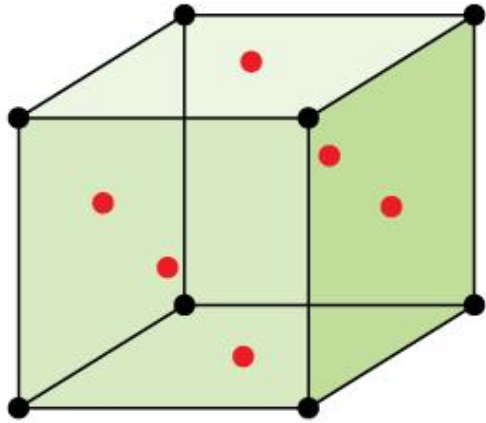
Face-centered cubic structure

A face-centered cubic (FCC) solid has atoms at the corners and, as the name implies, at the centers of the faces of its unit cells.

Lattice systems

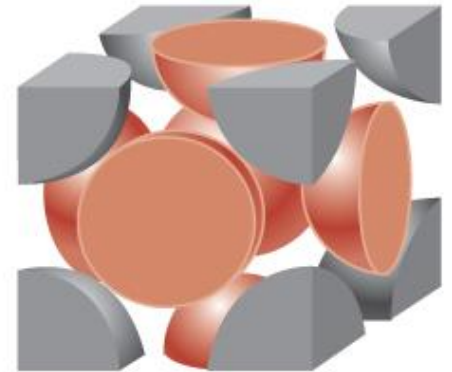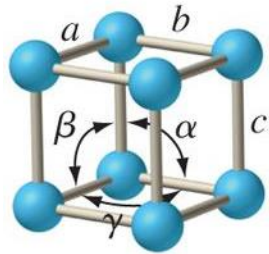**Simple cubic**
$a = b = c$
$\alpha = \beta = \gamma = 90°$
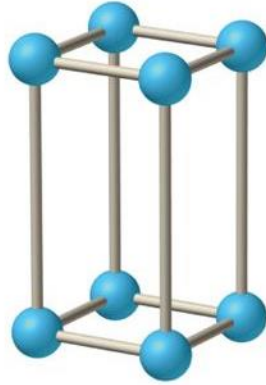
Tetragonal
$a = b \neq c$
$\alpha = \beta = \gamma = 90°$
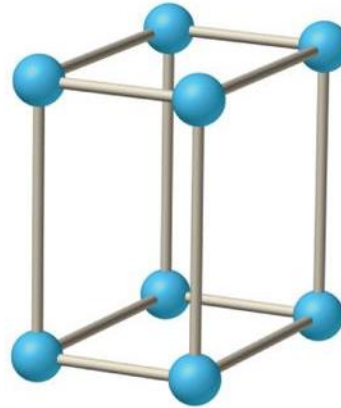
Orthorhombic
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$
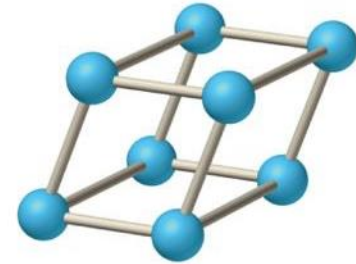
Rhombohedral
$a = b = c$
$\alpha = \beta = \gamma \neq 90°$
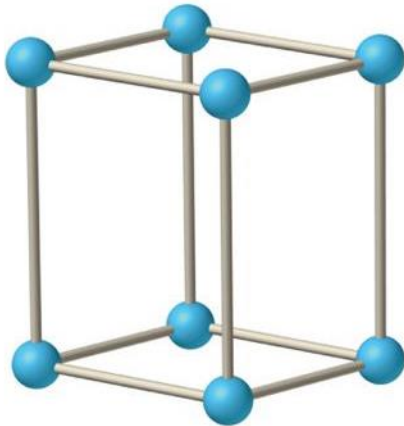
Monoclinic
$a \neq b \neq c$
$\gamma \neq \alpha = \beta = 90°$
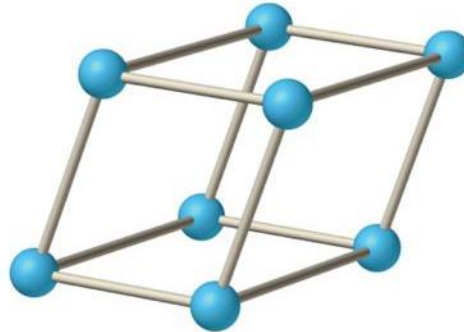
Triclinic
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90°$
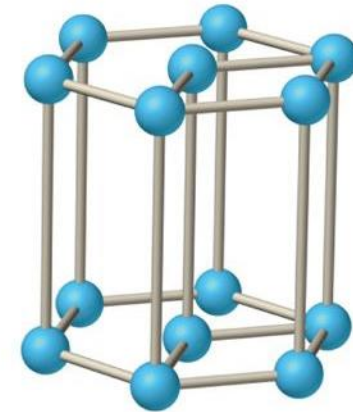
Hexagonal
$a = b \neq c$
$\alpha = \beta = 90°, \gamma = 120°$

14 Bravais lattices
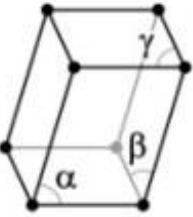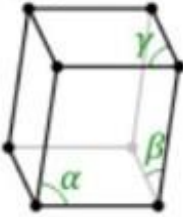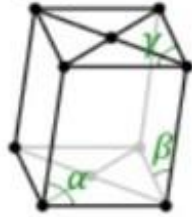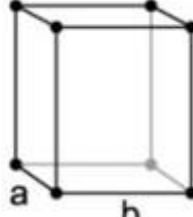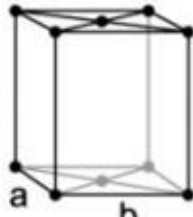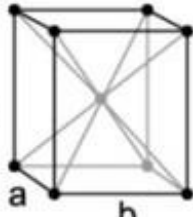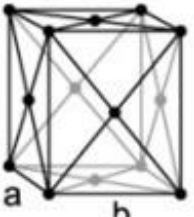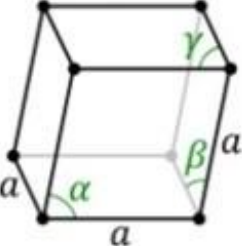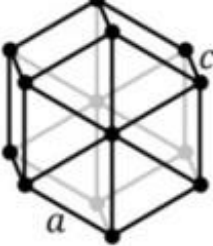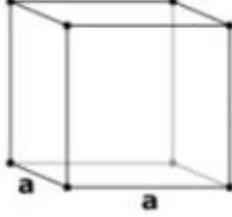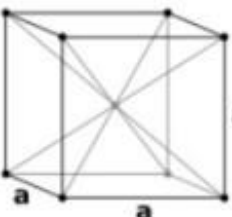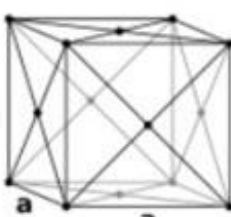
✓ There are 7 different kinds of crystal systems, and each kind of crystal system has 4 different kinds of centering (Primitive, Base-centered, Body-centered, Face-centered).

✓ However, not all of the combinations are unique; some of the combinations are equivalent while other combinations are not possible due to symmetry reasons.

✓ This reduces the number of unique lattices to the **14 Bravais lattices**.

Auguste Bravais (1811–1863) was a French physicist known for his work in crystallography, the conception of Bravais lattices.

14 Bravais lattices

✓ The distribution of the 14 Bravais lattices into lattice systems and crystal families is given in the following table:

space groups locate atoms within a cell:
help solve unknown structure

7 crystal
systems

add centres →

14 Bravais
lattices

→ 230
space
groups

macroscopic symmetry →

32 point
groups

microscopic symmetry →
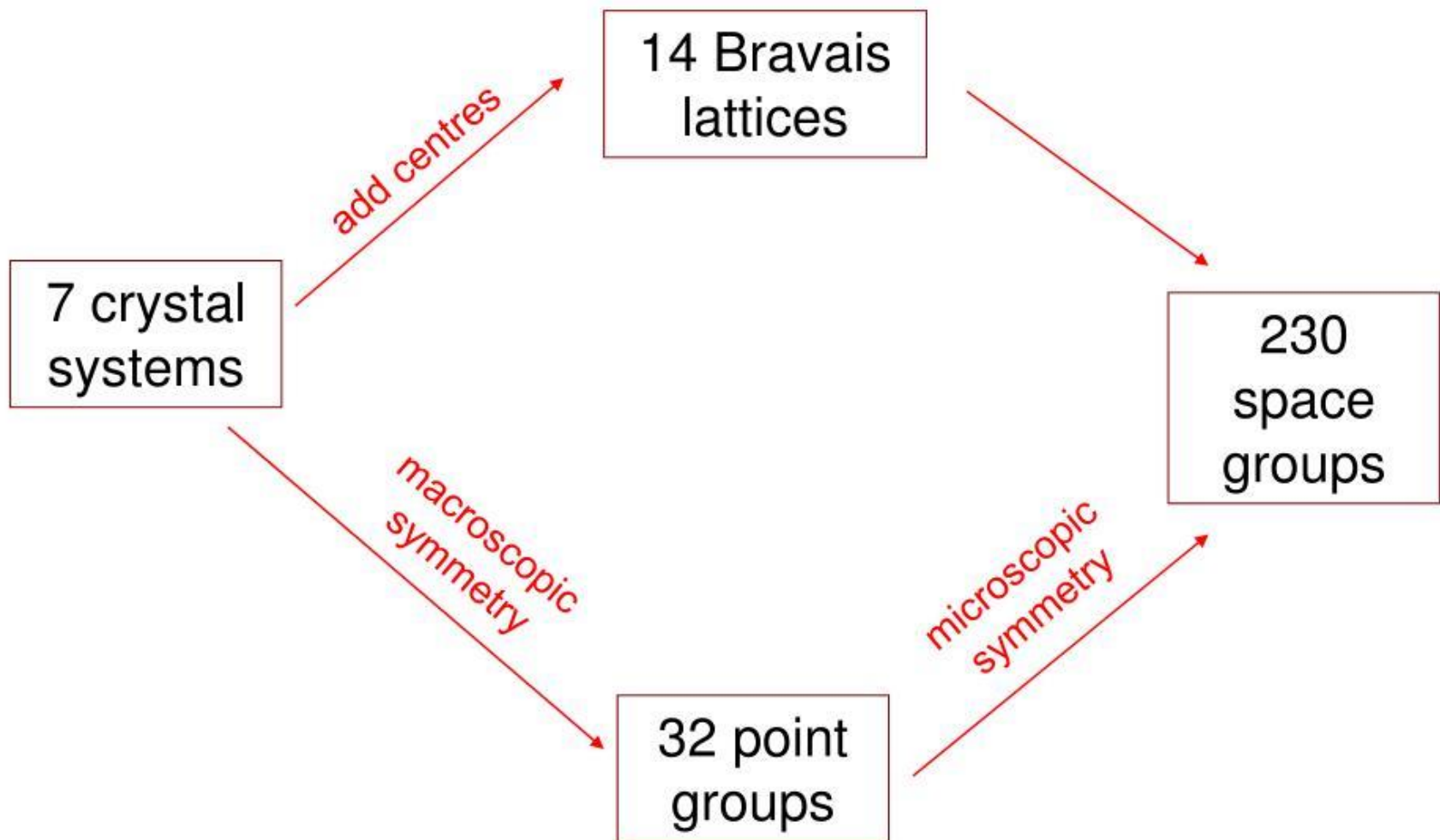
Perfect and Imperfect Crystals

Perfect crystal :

all the atoms are on their correct lattice positions (only true at 0 K)
- ✓ can be obtained, hypothetically, only at absolute zero
- ✓ S = 0

$$S = k \ln W$$

In some crystals, the number of defects may be very small,1%, as in, e.g., high-purity diamond or quartz.

Real Crystals = Imperfect Crystals

Imperfect crystal – at all real temperatures.

Real crystal: atoms vibrate
- ✓ There positions that are not occupied (vacancies)
- ✓ atoms displaced from ideal positions
- ✓ There are defects that modify the properties

Extended defects

- Dislocations
- Grain boundaries
- Stacking faults
- Twinning

Various classes of imperfections over the size range
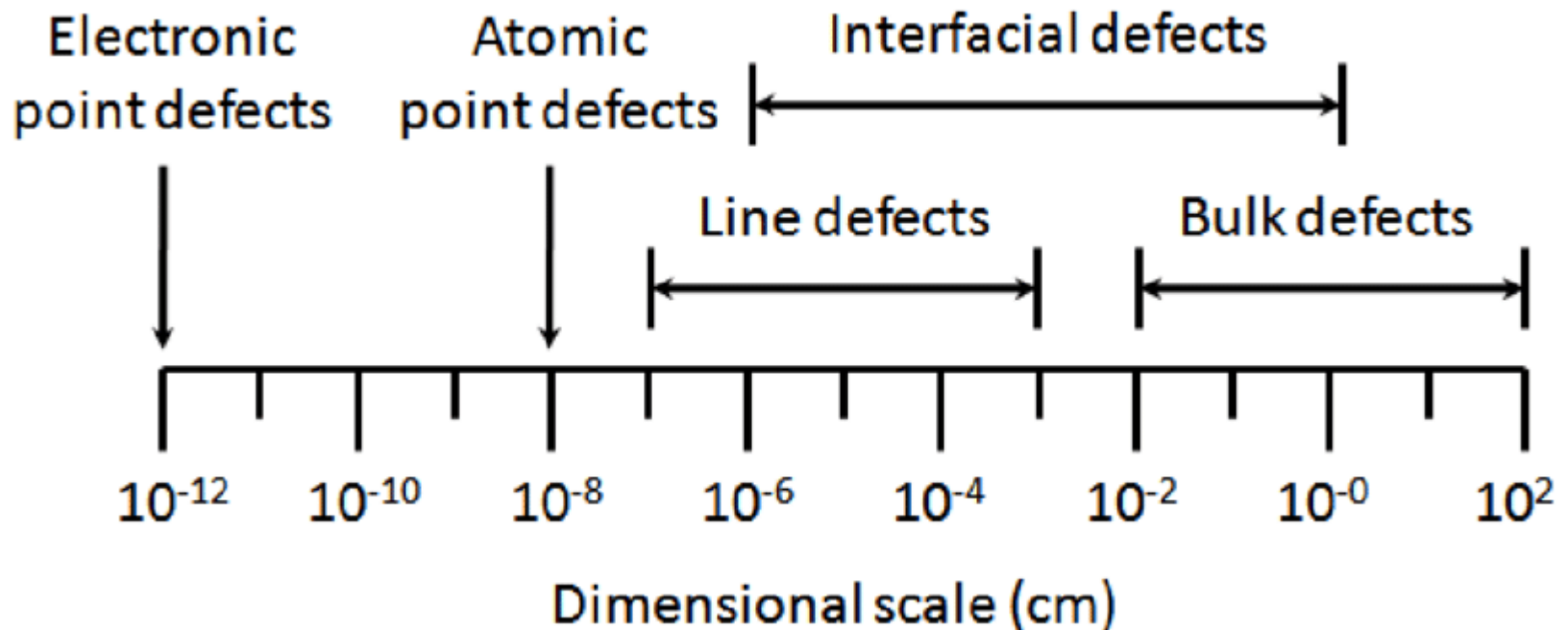
Defects in crystals of elements

(a)

(b)

Point defects in pure crystals such as silicon:

(a) a vacancy;
(b) an interstitial.

- ✓ Crystals of solid elements such as silicon contain only one atom type.
- ✓ The simplest localized defect that we can imagine in a crystal is a mistake at a single atom site. These defects are called point defects.
- ✓ Two types of point defect can occur in a pure crystal: an atom can be absent from a normally occupied position, to create a vacancy, or an atom can occupy a position normally empty to form an interstitial (Fig.).
- ✓ Such vacancies and interstitials, which occur in even the purest of materials, are called intrinsic defects.

silicon

- ✓ For these defects (vacancy and interstitial) to be stable, the Gibbs energy of a crystal containing defects must be less than the Gibbs energy of a crystal without defects.

- ✓ Initially, a population of defects lowers the Gibbs energy, but ultimately large numbers of point defects results in an increase in Gibbs energy.

- ✓ The minimum in the curve represents the equilibrium situation that will exist at a given temperature (Fig.).
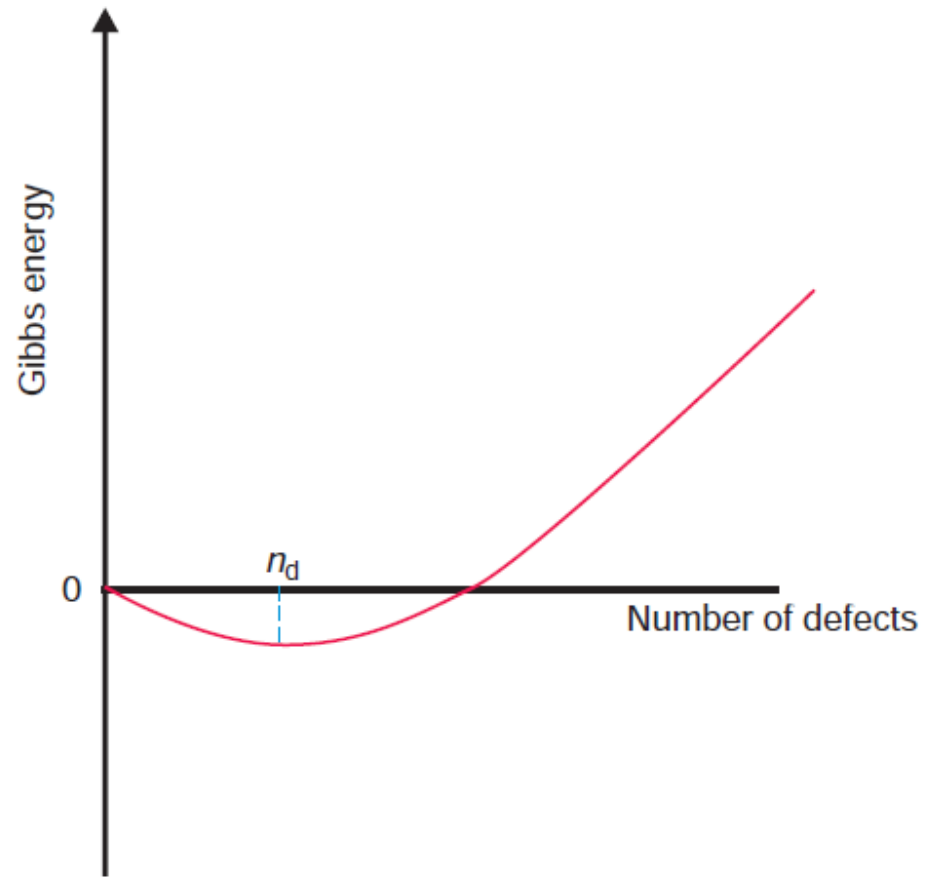
The Gibbs energy of a crystal as a function of the number of point defects present. At equilibrium, n_d defects are present in the crystal.

✓ The creating a single defect, say a vacant cation site, requires a certain amount of energy, *H*, but causes a considerable increase in entropy, *S*, because of the large number of positions which this defect can occupy.

✓ Thus, if the crystal contains 1 mol of cations, there are $\sim 10^{23}$ possible positions for the vacancy.

✓ The entropy gained is called *configurational entropy* and is given by the Boltzmann equation: $S = k \ln W$

where the probability, *W*, is proportional to 10^{23};
other, smaller, entropy changes are also present due to the disturbance of the crystal structure in the neighborhood of the defect.

✓ As a result of this increase in entropy, the enthalpy required to form the defect initially is more than offset by the gain in entropy.

✓ Consequently, the free energy, given by $\Delta G = \Delta H - T \Delta S$ decreases.

$$\Delta G = \Delta H - T\Delta S$$

Energy changes on introducing defects into a perfect crystal
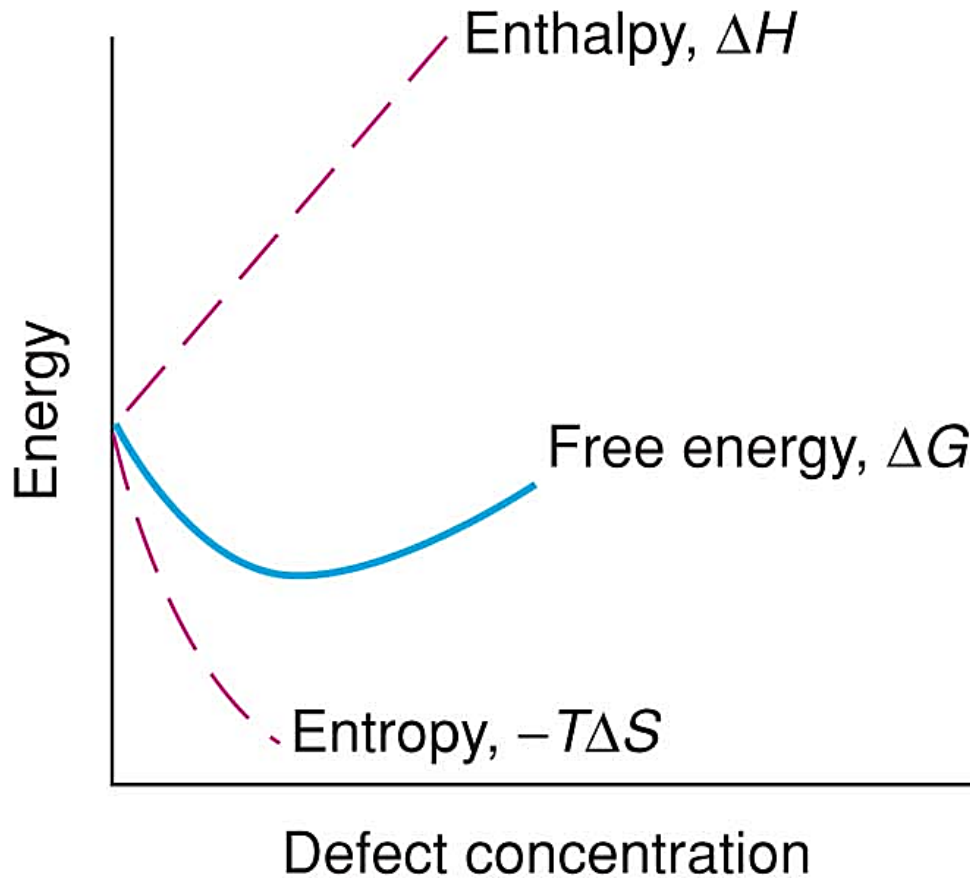
- ✓ Energy is required to form a defect (endothermic process)
- ✓ Although there is a cost in energy, there is a gain in entropy in the formation of a defect.

Predominant point defects in various ionic crystals

Crystal	Crystal structure	Predominant intrinsic defect
Alkali halides (not Cs)	Rock salt, NaCl	Schottky
Alkaline earth oxides	Rock salt	Schottky
AgCl, AgBr	Rock salt	Cation Frenkel
Cs halides, TlCl	CsCl	Schottky
BeO	Wurtzite, ZnS	Schottky
Alkaline earth fluorides, CeO_2, ThO_2	Fluorite, CaF_2	Anion Frenkel
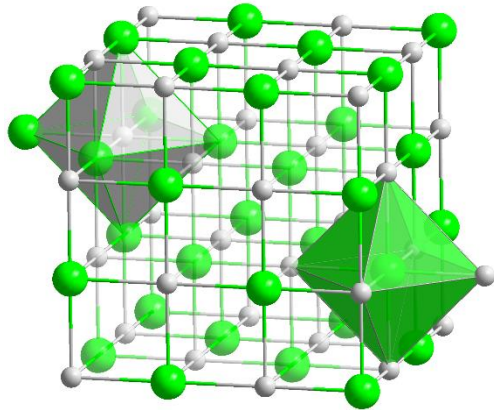
NaCl
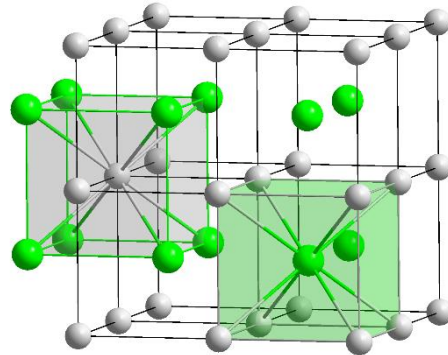
CsCl
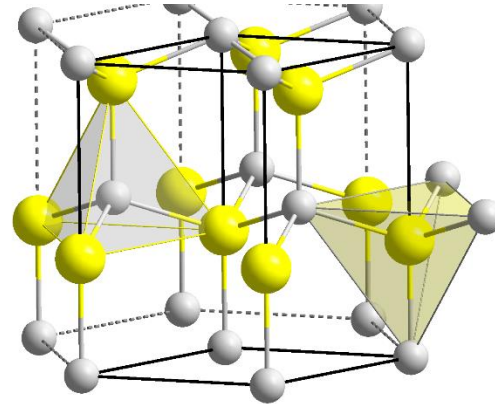
ZnS
wurtzite
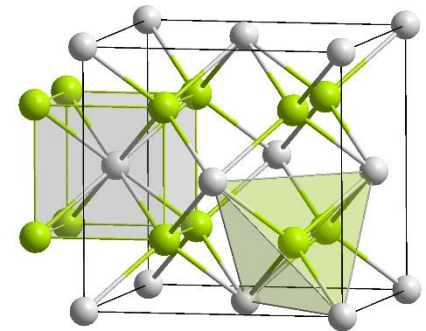
CaF_2

ESTIMATING VACANCY CONC.

- Find the equil. # of vacancies in $1m^3$ of Cu at 1000^oC.
- Given:

$$\rho = 8.4 \text{ g /cm}^3 \qquad A_{Cu} = 63.5 \text{g/mol}$$

$$Q_V = 0.9 \text{eV/atom} \qquad N_A = 6.02 \times 10^{23} \text{ atoms/mole}$$

$$\frac{N_D}{N} = \exp\left(\frac{-Q_D}{kT}\right) = 2.7 \cdot 10^{-4}$$

0.9eV/atom

1273K

8.62×10^{-5} eV/atom-K

For $1m^3$, $N = \rho \times \dfrac{N_A}{A_{Cu}} \times 1m^3 = 8.0 \times 10^{28}$ sites

- Answer:

$$N_D = 2.7 \cdot 10^{-4} \cdot 8.0 \times 10^{28} \text{ sites} = 2.2 \times 10^{25} \text{ vacancies}$$

LOWER END ESTIMATION !

- ✓ No material is completely pure, and foreign atoms will be present.

- ✓ If these are undesirable or accidental, they are known as **impurities**, but if they have been added deliberately, to change the properties of the material on purpose, they are called **dopants**.

- ✓ Foreign atoms can rest in sites normally occupied by the parent atom type to form **substitutional defects**.

- ✓ Foreign atoms may also occupy normally empty positions to create **interstitial impurities** or **interstitial dopants** (Fig.).

- ✓ There is no simple thermodynamic formula for the number of impurities present in a crystal.

(a)

(b)
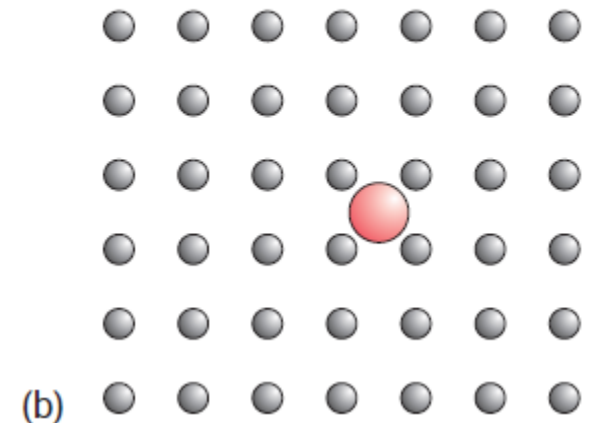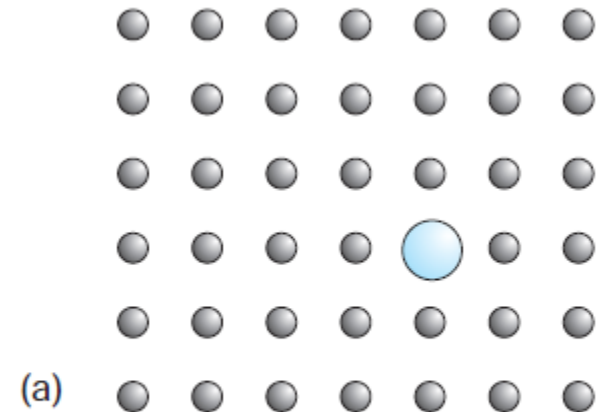
Impurity or dopant point defects in a crystal:
(a) substitutional;
(b) interstitial.

Thermodynamics of defect formation

Perfect → imperfect

n vacancies created

$$\Delta G = G_{def} - G_{per} = \Delta H - T \Delta S$$

$$\Delta H = n\, \Delta H_i$$

ΔH_i: **enthalpy of formation of one vacant site**

$$\Delta S = \Delta S_{osc} + \Delta S_c$$

ΔS_{osc}: **change of oscillation entropy of atoms surrounding the vacancy**

ΔS_c: **change in cofigurational entropy of system on vacancies formation**

Concentration of defects

The idea that the second law of thermodynamics or "entropy law" is a law of disorder (or that dynamically ordered states are "infinitely improbable") is due to Boltzmann's view of the second law of thermodynamics.

The **Boltzmann formula** tells us that the entropy of such a system is:

$$S = k\ln W$$

where:

W is the number of ways of distributing ns defects over N possible sites at random,

k is the Boltzmann constant (1.38×10^{-23} J/K)

Probability theory shows that W is given by:

$$W = \frac{N!}{(N-n)!\,n!}$$

N! is 'factorial N'. $N \times (N-1) \times (N-2)\ldots \times 1$

Boltzmann's grave in the Zentralfriedhof (Vienna) with bust and entropy formula.

Schottky Defects

Compound	ΔH (10^{-19} J)	ΔH (eV)
MgO	10.57	6.60
CaO	9.77	6.10
LiF	3.75	2.34
LiCl	3.40	2.12
LiBr	2.88	1.80
LiI	2.08	1.30
NaCl	3.69	2.30
KCl	3.62	2.26

Frenkel Defects

Compound	ΔH (10^{-19} J)	ΔH (eV)
UO_2	5.45	3.40
ZrO_2	6.57	4.10
CaF_2	4.49	2.80
SrF_2	1.12	0.70
AgCl	2.56	1.60
AgBr	1.92	1.20
β-AgI	1.12	0.70

NaCl (T_f=801 ºC) ΔH_s= 3.69x10^{-19} J
T=300K n_s= 2.64x10^4 vacancies/mol
T=1000K n_s= 9.38x10^{17} vacancies/mol

MgO ΔH_s= 10.57x10^{-19} J
T=300K n_s= 2.12x10^{-32} vacancies/mol
T=1000K n_s= 1.39x10^7 vacancies/mol

$$\Delta H_s(MgO) > \Delta H_s(NaCl)$$
$\Rightarrow n_s$ low, more difficult to create vacancies.

- ✓ Real crystals do not have a perfect lattice structure but show so-called *crystallographic defects*.
- ✓ At these defects, the real lattice deviates from the idealized perfect structure.
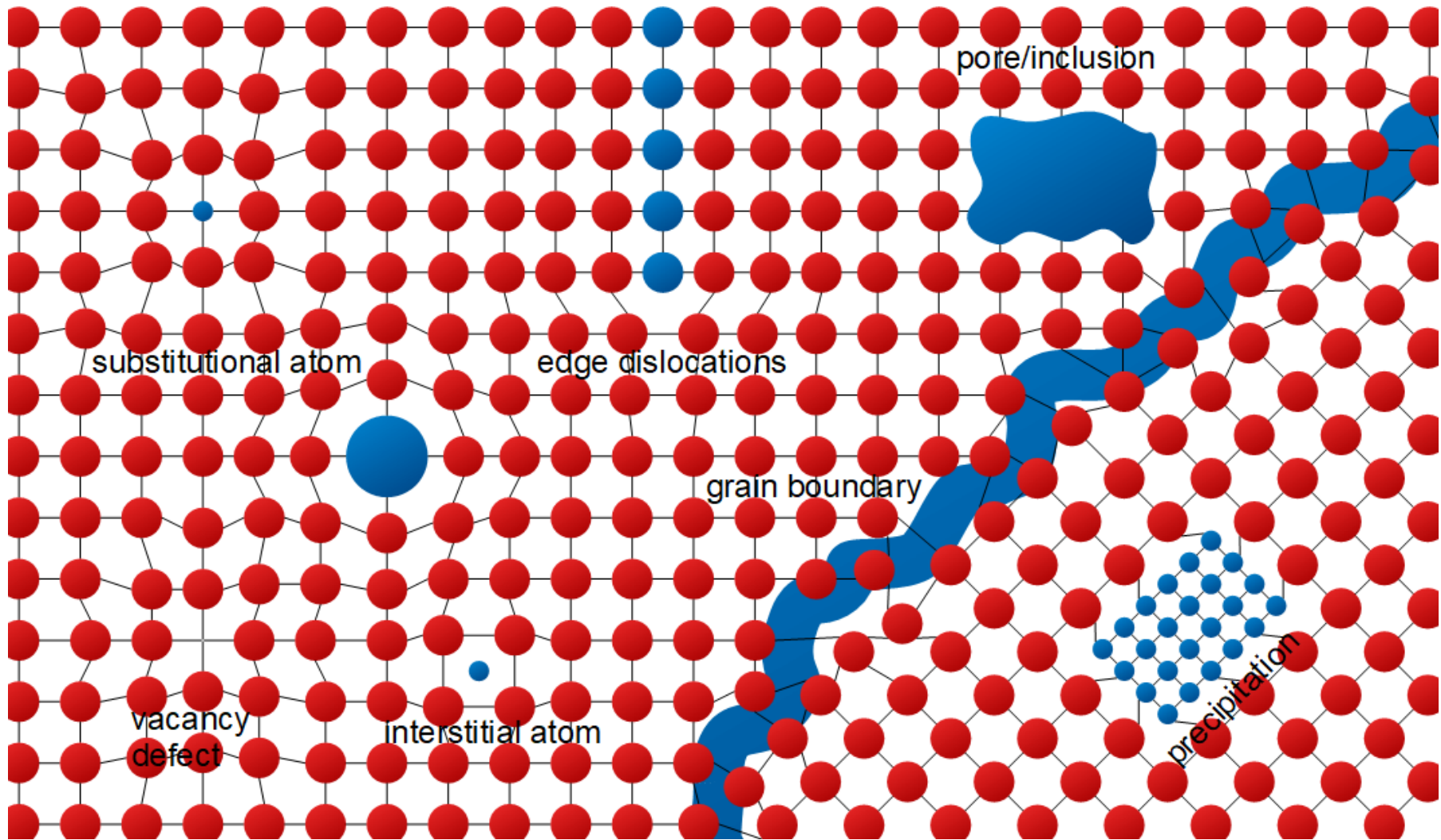
Defects may be classified into four categories based on their dimension:
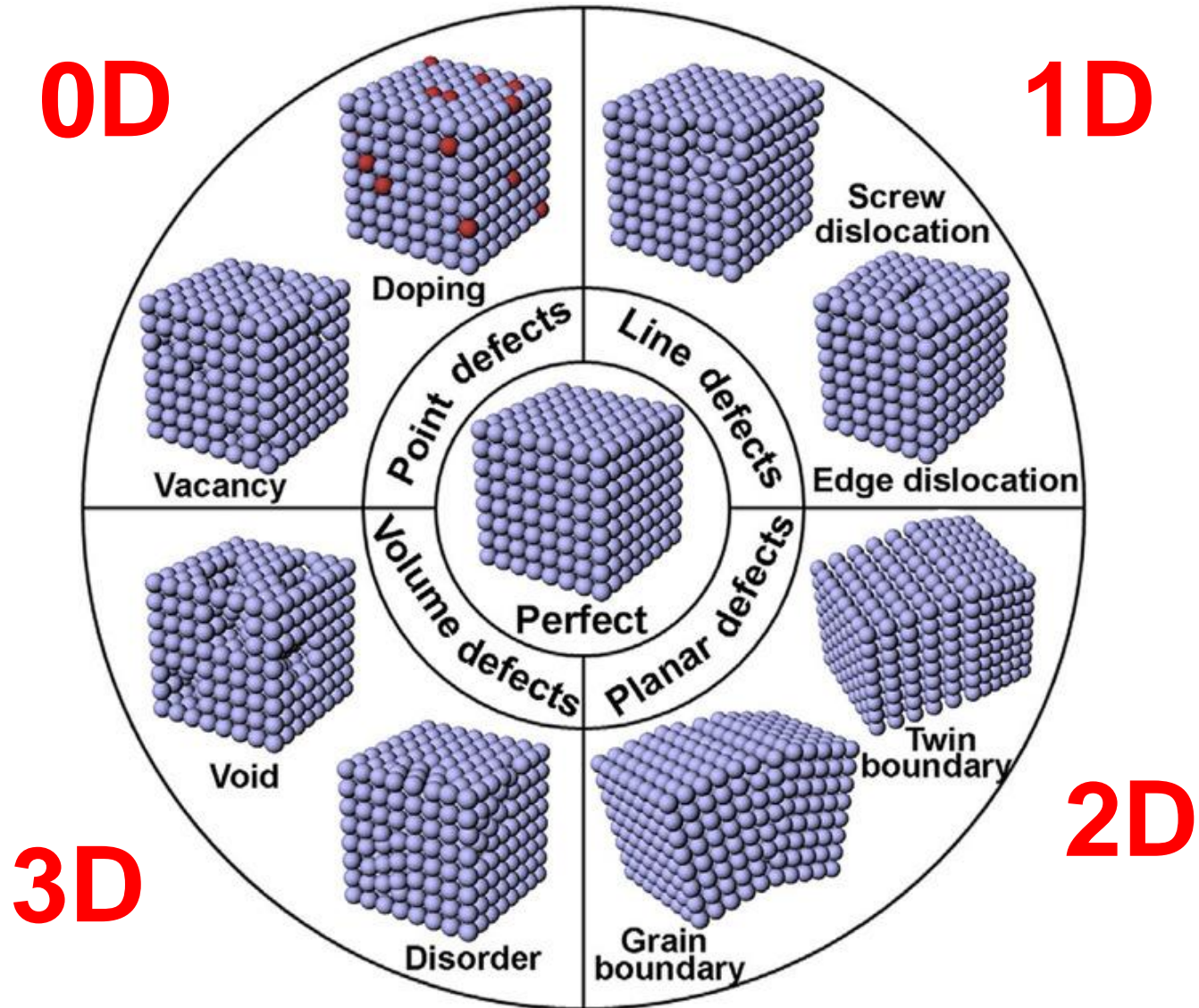
Imperfections in Solids

Crystals in nature are never perfect, they have *defects !*

Defects in Solids

0-D, Point defects

- Vacancy
- Interstitial
- Substitutional

  Atoms in irregular positions

1-D, Line Defects / Dislocations

- Edge
- Screw

  Planes or groups of atoms in irregular positions

2-D, Area Defects / Grain boundaries

- Tilt
- Twist

  Interfaces between homogeneous regions of atoms

3-D, Bulk or Volume defects

- Crack, pore
- Secondary Phase

MATERIALS PROPERTIES
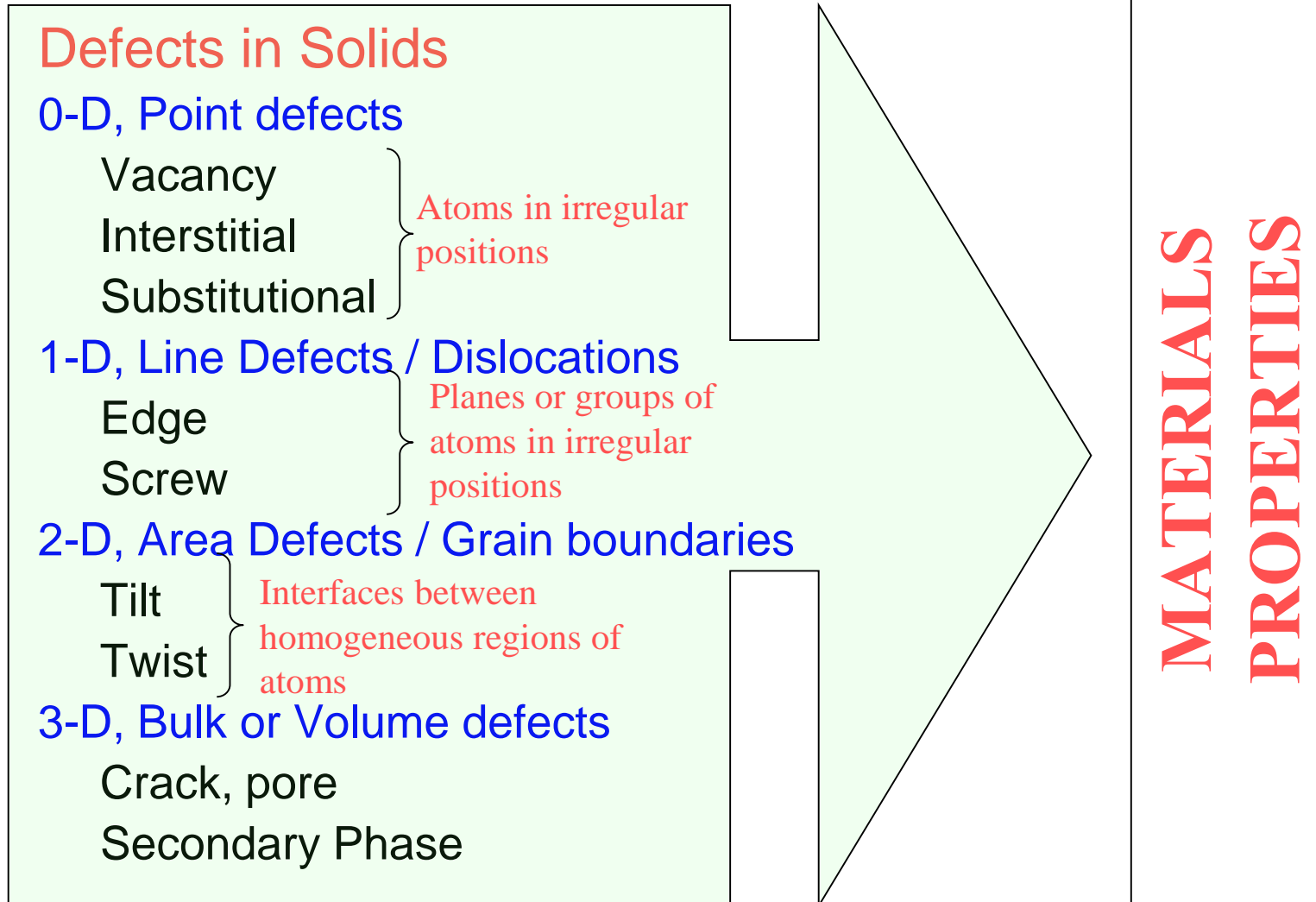
Crystal Defects → Material Properties

Even properties that are normally not affected by defects can become sensitive to microstructure at very high defect densities.

Example: melting of nanocrystalline materials

atomistic simulation of laser melting of nanocrystalline Au
20 nm Au film irradiated by a 200 fs laser pulse

laser pulse   20 ps   50 ps   100 ps
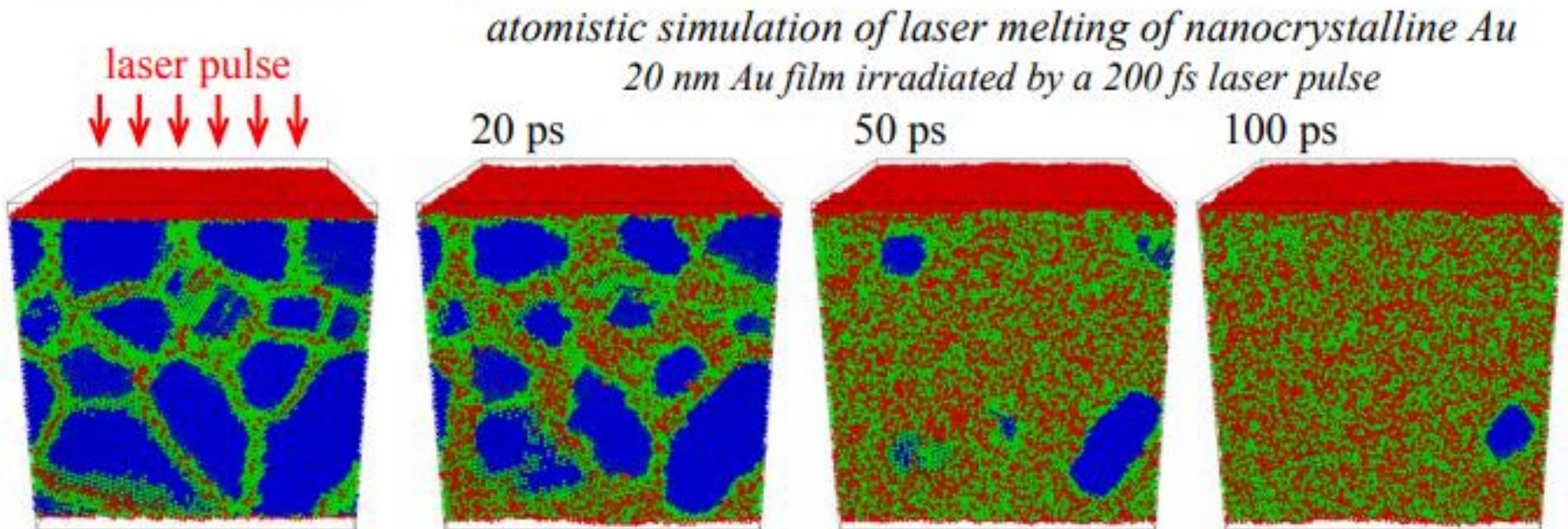
Melting starts at grain boundaries, temperature drops (energy goes into $\Delta H_m \times V_l$). Melting continues even after T drops below the equilibrium melting temperature T_m at ~30 ps and the last crystalline region disappears at ~250 ps.

Lin, Leveugle, Bringa, Zhigilei, *J. Phys. Chem. C* **114**, 5686, 2010

Impurities / Solid Solutions

- **Impurities** are atoms which are different from the host/matrix
- All solids in nature contain some level of impurity
  - Very pure metals 99.9999%
  - For Cu how much does that make ? ~ 1 impurity per 100 atoms
- Impurities may be introduced intentionally or unintentionally.
  - Examples: carbon added in small amounts to iron makes steel, which is stronger than pure iron. Boron is added to silicon change its electrical properties. Pt and Cu are added to Gold to make it stronger, also!
- Alloys - deliberate mixtures of metals
  - Example: sterling silver is 92.5% silver – 7.5% copper alloy. Stronger than pure silver.