Chapter 4
IMPERFECTIONS IN SOLIDS

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Outline

- What are the solidification mechanisms?
- What types of defects arise in solids?
- Can the number and type of defects be varied and controlled?
- How do defects affect material properties?
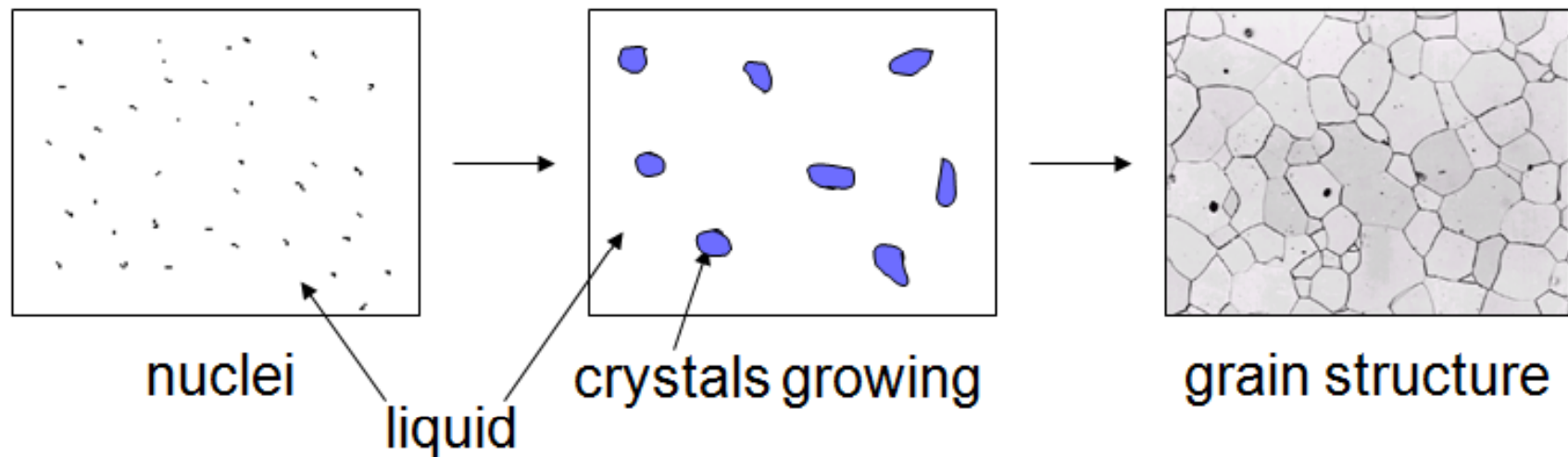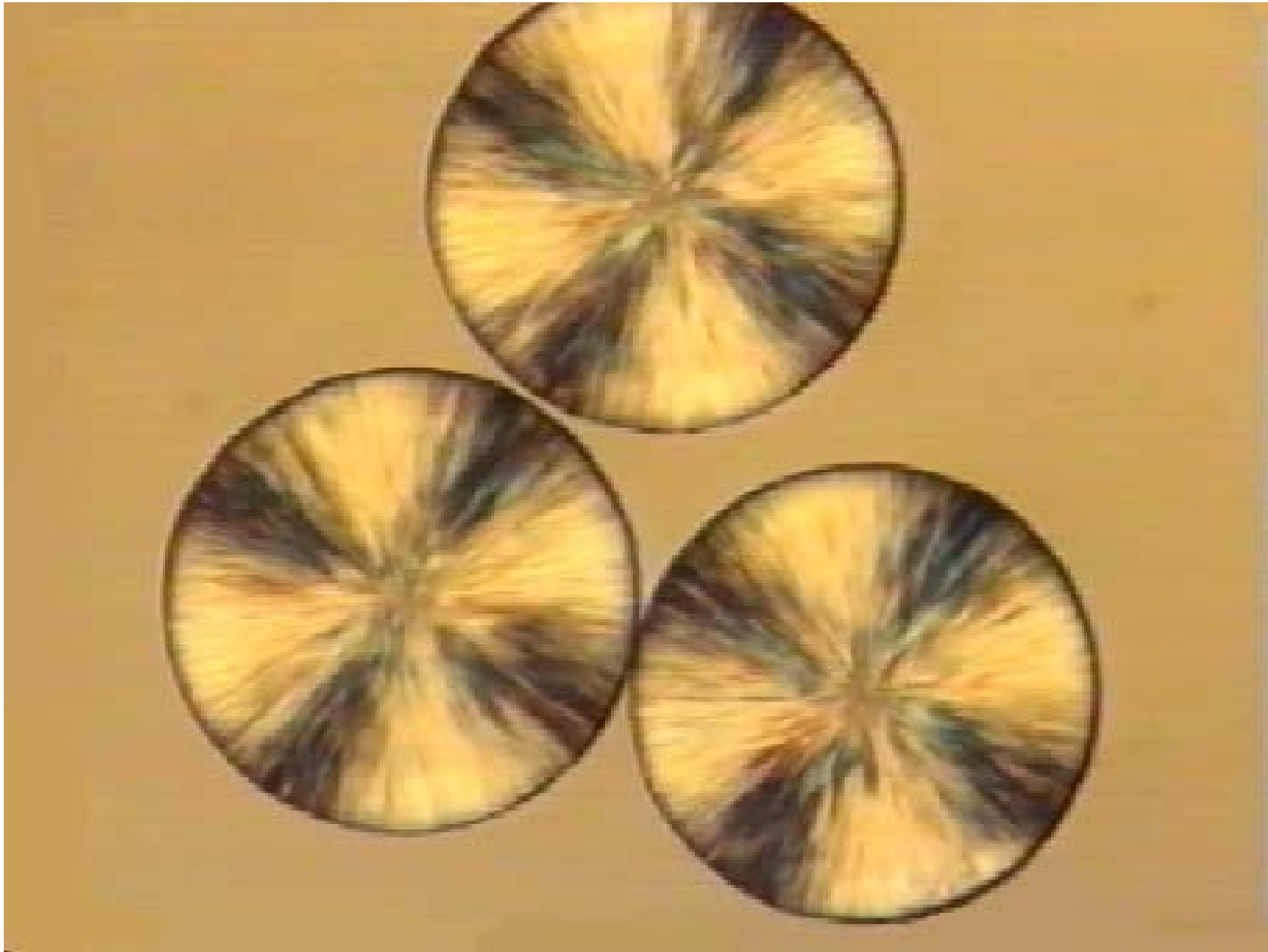- Are defects undesirable?

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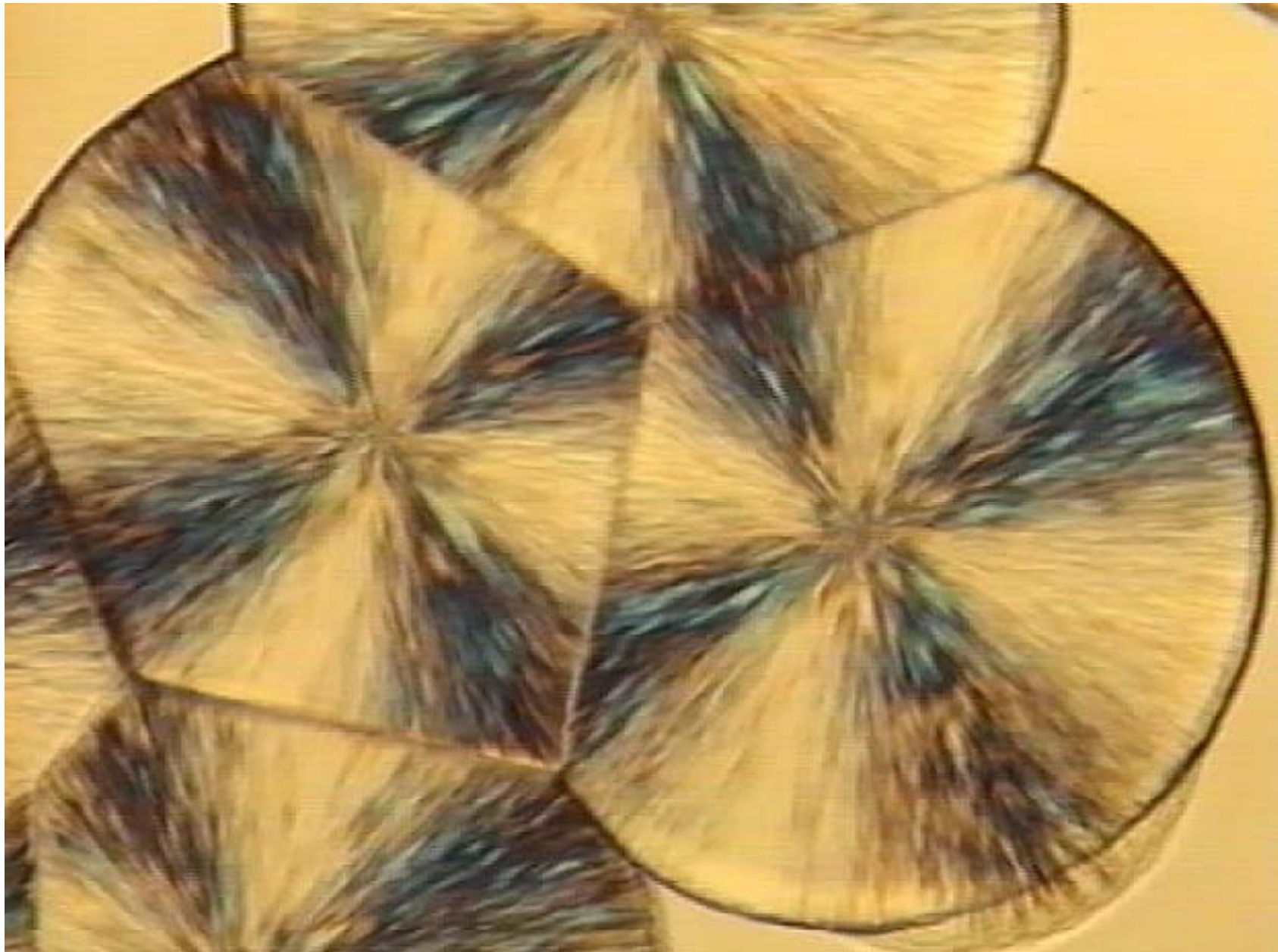# *Solidification*

Start with a molten material – all liquid

Result of casting of molten material:

1. Nuclei form

2. Nuclei grow to form crystals – grain structure
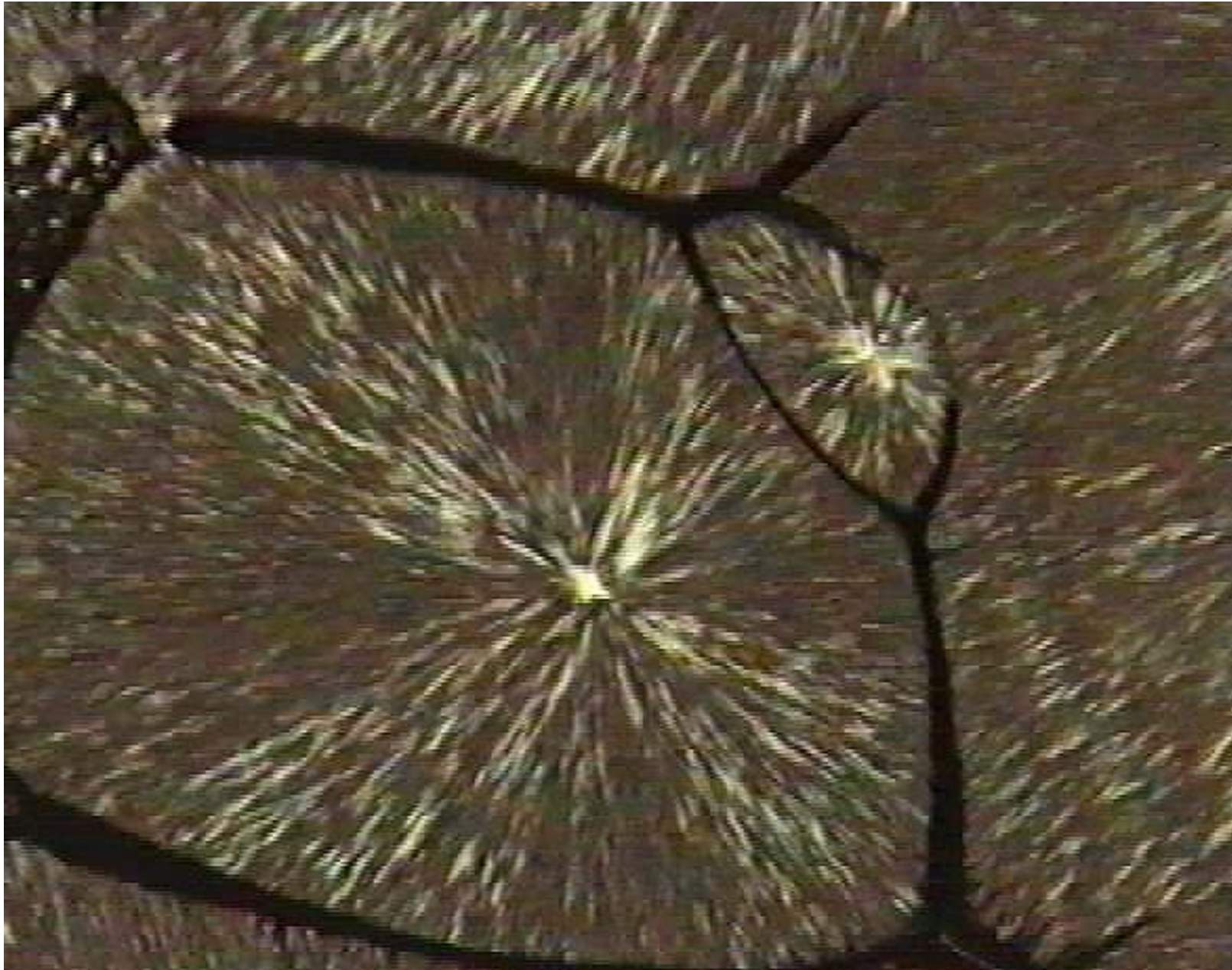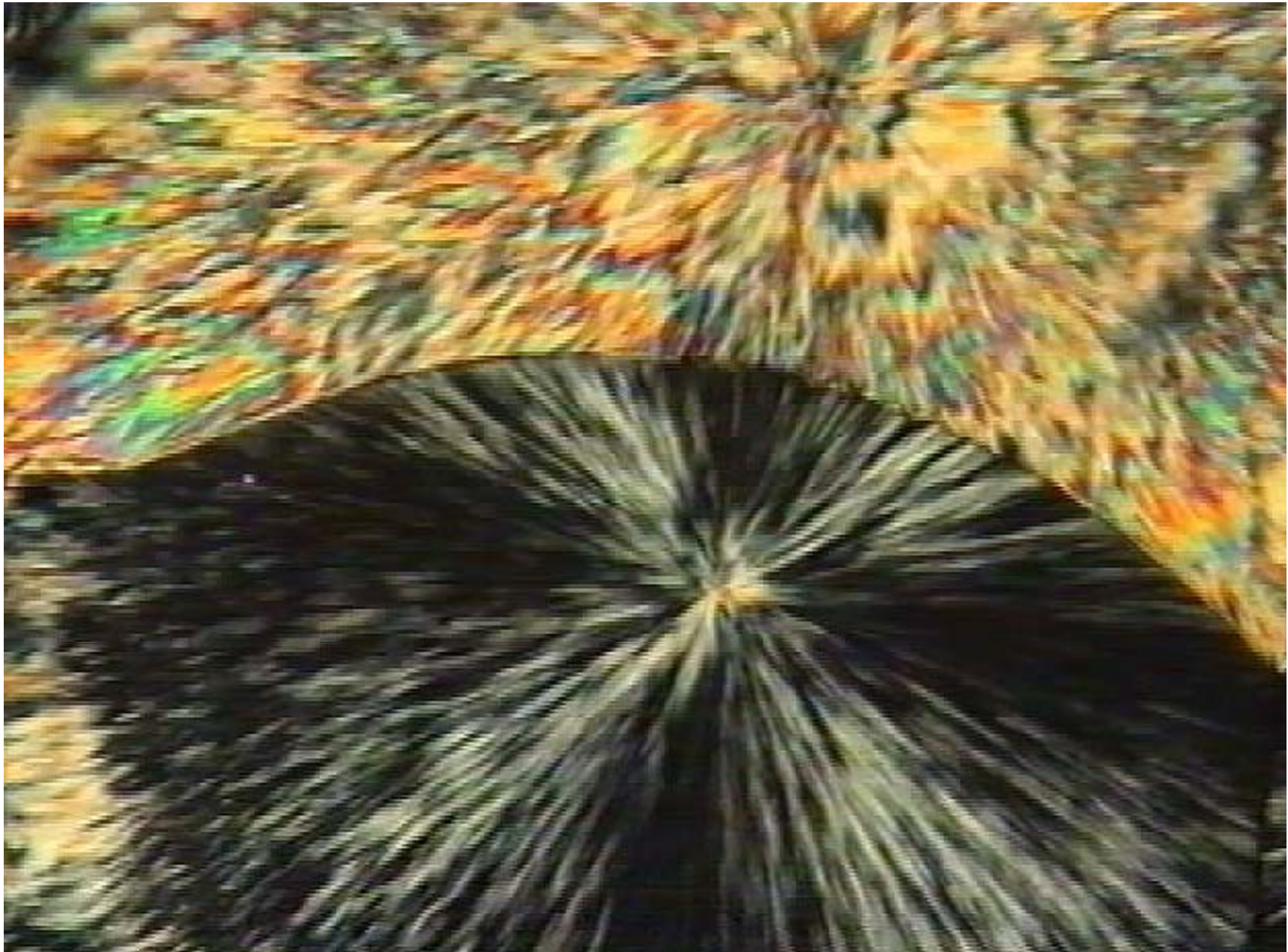
Crystals grow until they meet each other.

nuclei   crystals growing   grain structure
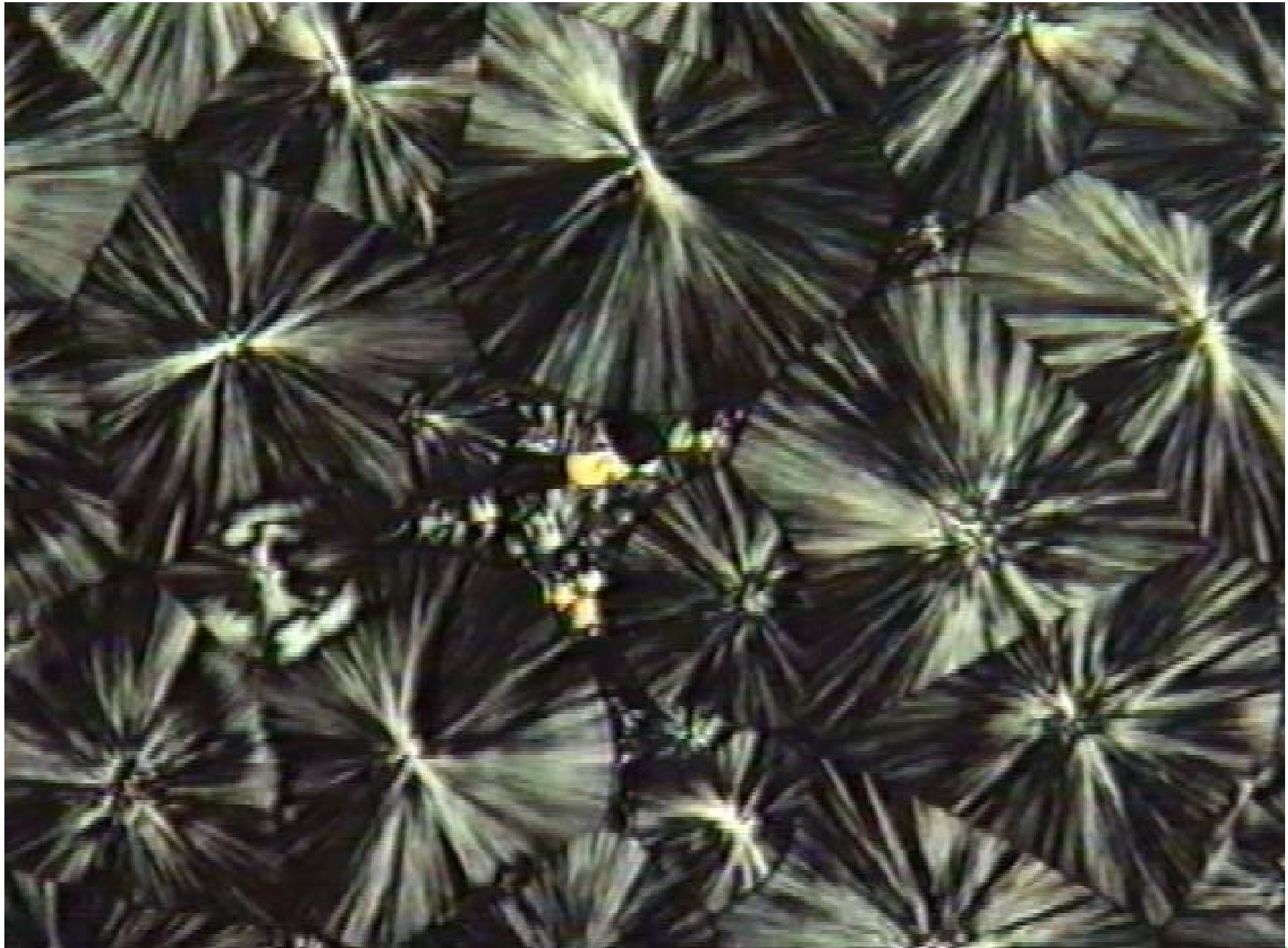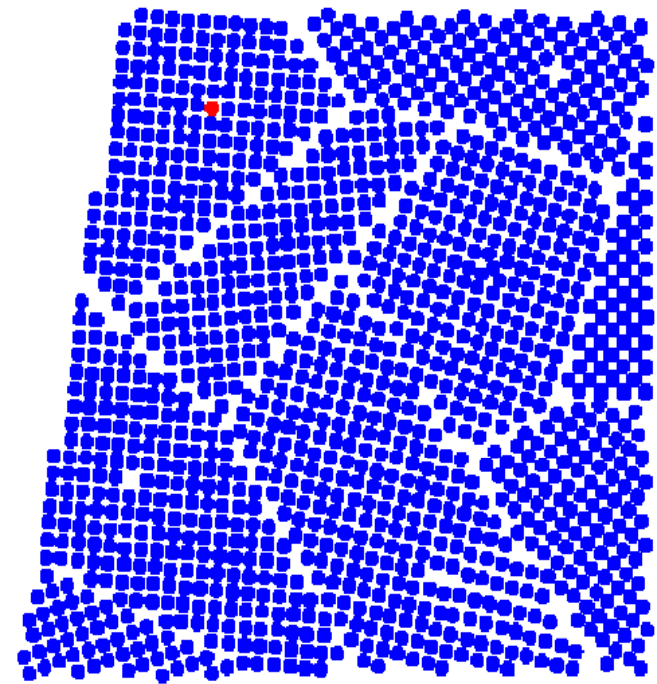liquid

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Imperfections in Solids

There is no such thing as a perfect crystal.

- What are these imperfections?

- Why are they important?

Many of the important properties of materials are due to the presence of imperfections.

- ❑ Semiconducting properties
- ❑ Yield stress
- ❑ Fracture strength
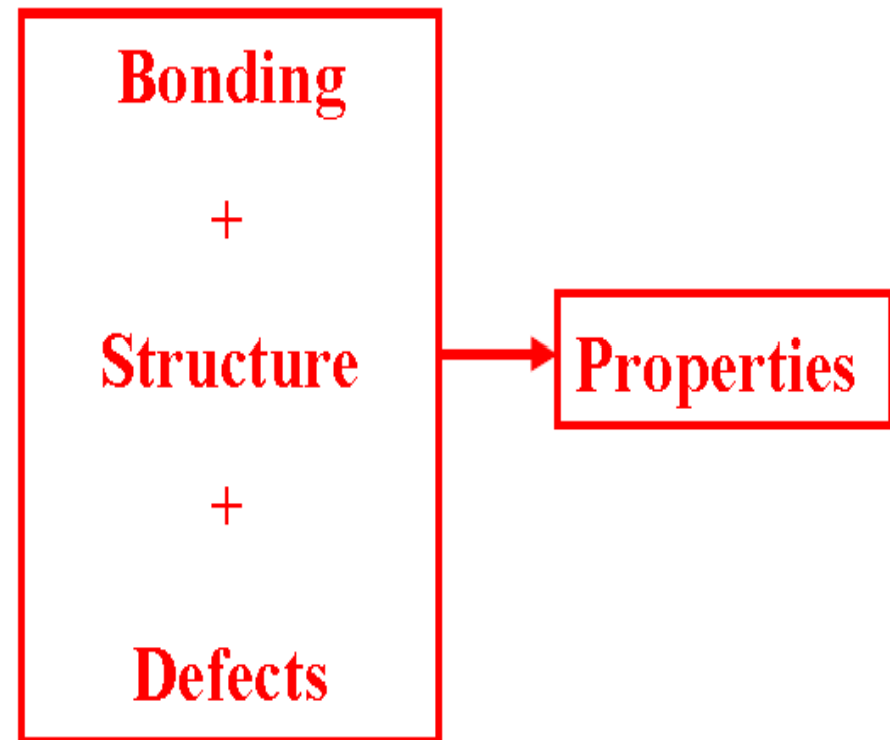- ❑ Electrical conductivity

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Imperfections in Solids

Many of the important properties of materials are due to the presence of imperfections.
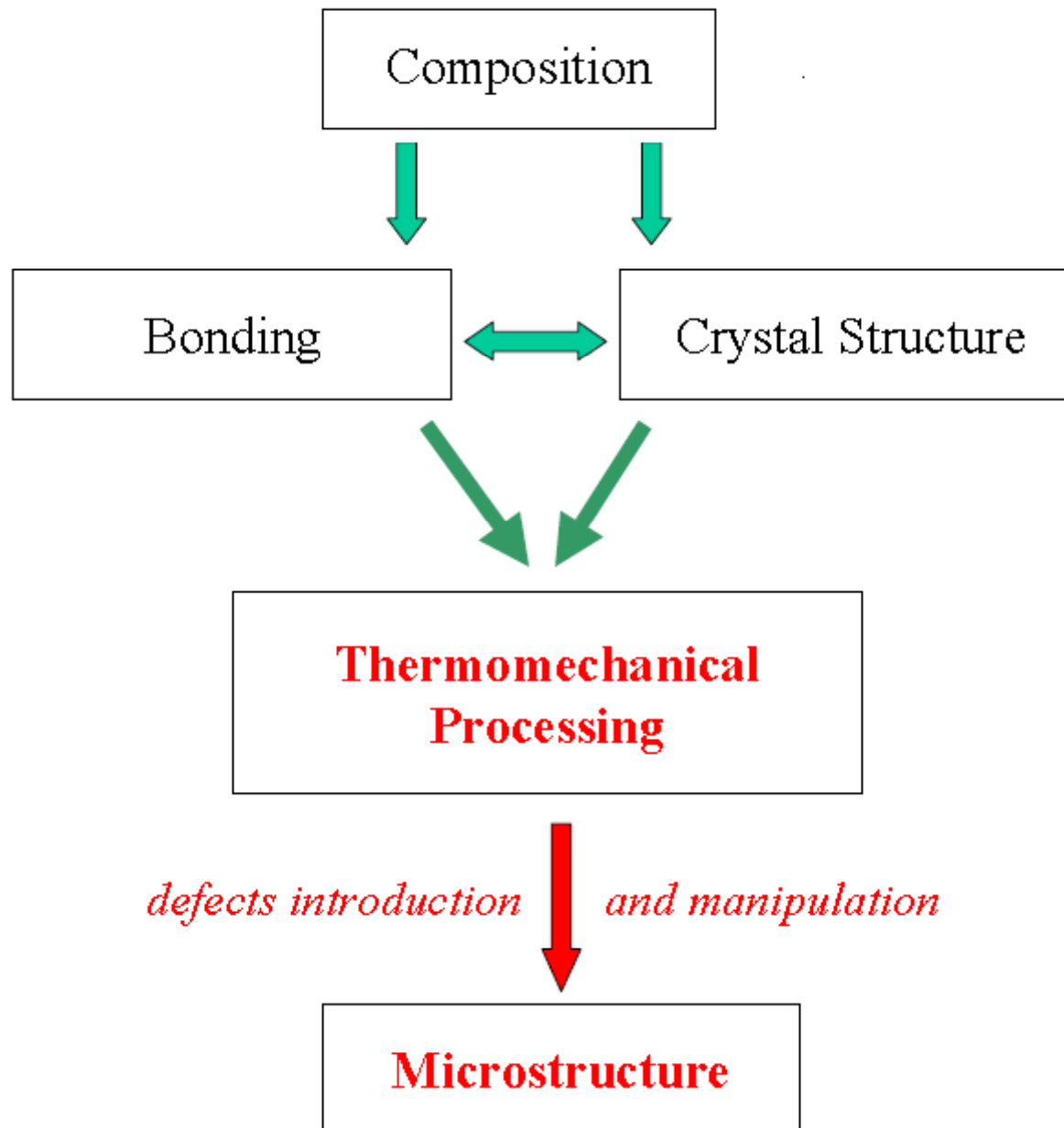
❑ Semiconducting properties

❑ Yield stress

❑ Fracture strength

❑ Electrical conductivity

Bonding

+

Structure

+

Defects

→ Properties

The processing determines the defects Imperfections

Types of Imperfections

1. Point defects: **atoms missing or in irregular places in the lattice**
   - vacancies
   - interstitials (space that intervenes between things).
   - impurities, weight and atomic composition
2. Line defects: **groups of atoms in irregular positions**
   - edge dislocations and screw dislocations
3. Area defects: **the interfaces between homogeneous regions of the material**
   - Grain boundaries
4. Bulk or Volume defects: **pores, cracks**
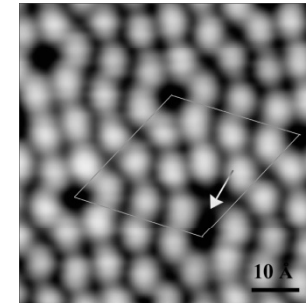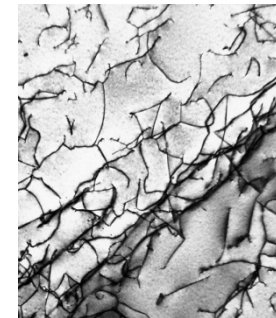
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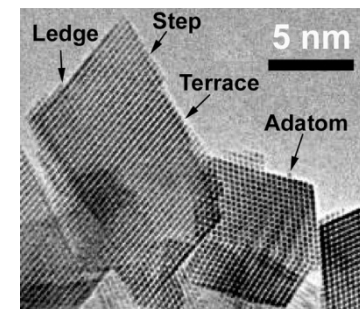
Point Defects

- Vacancies

  This figure shows a vacant atomic sites in a structure.

distortion of planes
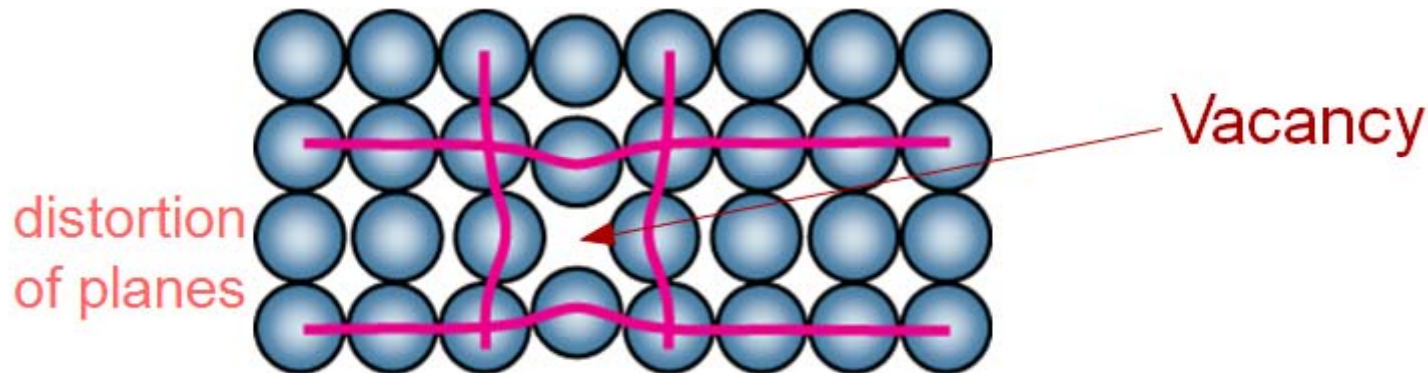
Vacancy

- Self-Interstitials

  -"extra" atoms positioned between atomic sites.

distortion of planes

self-interstitial

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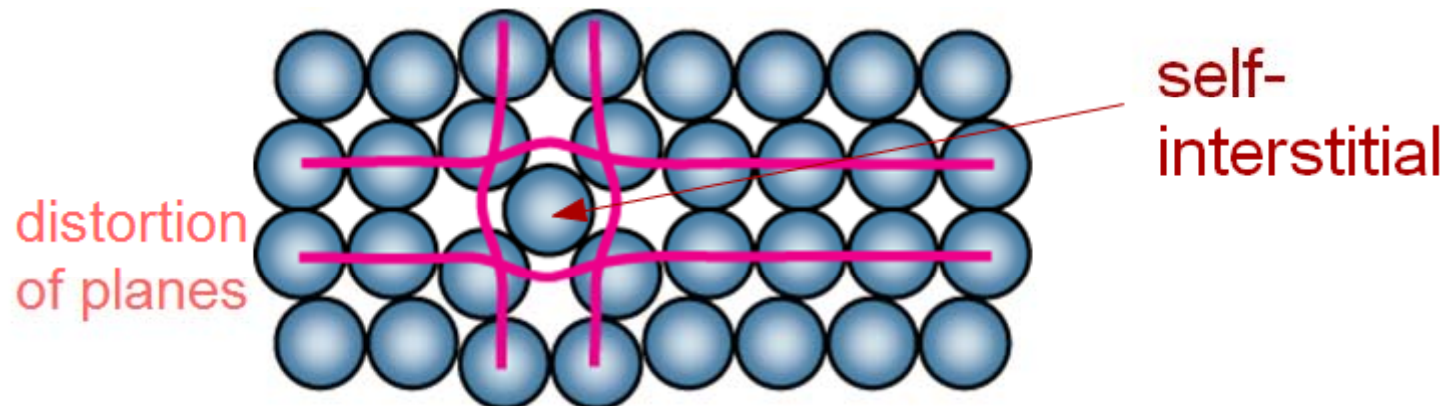
How many vacancies are there?

The equilibrium number of vacancies formed as a result of thermal vibrations may be calculated from thermodynamics:

No. of defects
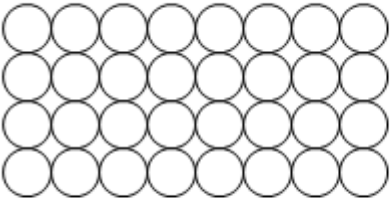
No. of potential defect sites.

$$\frac{N_v}{N_s} = \exp\left(\frac{-Q_v}{kT}\right)$$

Activation energy

Temperature

Boltzmann's constant

$(1.38 \times 10^{-23} \text{ J/atom-K})$

$(8.62 \times 10^{-5} \text{ eV/atom-K})$

Each lattice site is a potential vacancy site

Let's estimate the number of vacancies in Cu at room T

$$N_v = N_s \exp\left(-\frac{Q_v}{k_B T}\right)$$

The Boltzmann's constant $k_B = 1.38 \times 10^{-23}$ J/atom-K $= 8.62 \times 10^{-5}$ eV/atom-K

The temperature in Kelvin T = 27° C + 273 = 300 K.
$k_B T = 300$ K $\times 8.62 \times 10^{-5}$ eV/K = 0.026 eV

The energy for vacancy formation $Q_v = 0.9$ eV/atom

The number of regular lattice sites $N_s = N_A \rho / A_{cu}$
$N_A = 6.023 \times 10^{23}$ atoms/mol
$\rho = 8.4$ g/cm^3
$A_{cu} = 63.5$ g/mol

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$$N_s = \frac{\left(6.023 \times 10^{23} \text{ atoms}/\text{mol}\right) \times \left(8.4 \text{ g}/\text{cm}^3\right)}{63.5 \text{ g}/\text{mol}} = 8 \times 10^{22} \text{ atoms}/\text{cm}^3$$

$$N_v = 8 \times 10^{22} \frac{\text{atoms}}{\text{cm}^3} \exp\left(-\frac{0.9 \text{ eV}/\text{atom}}{0.026 \text{ eV}/\text{atom}}\right) =$$

$$= 7.4 \times 10^7 \text{ vacancies}/\text{cm}^3$$

T	Nv
27	61187298.81
40	259672879.5
100	55559422034
400	1.45791E+16

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Other point defects: self-interstitials, impurities
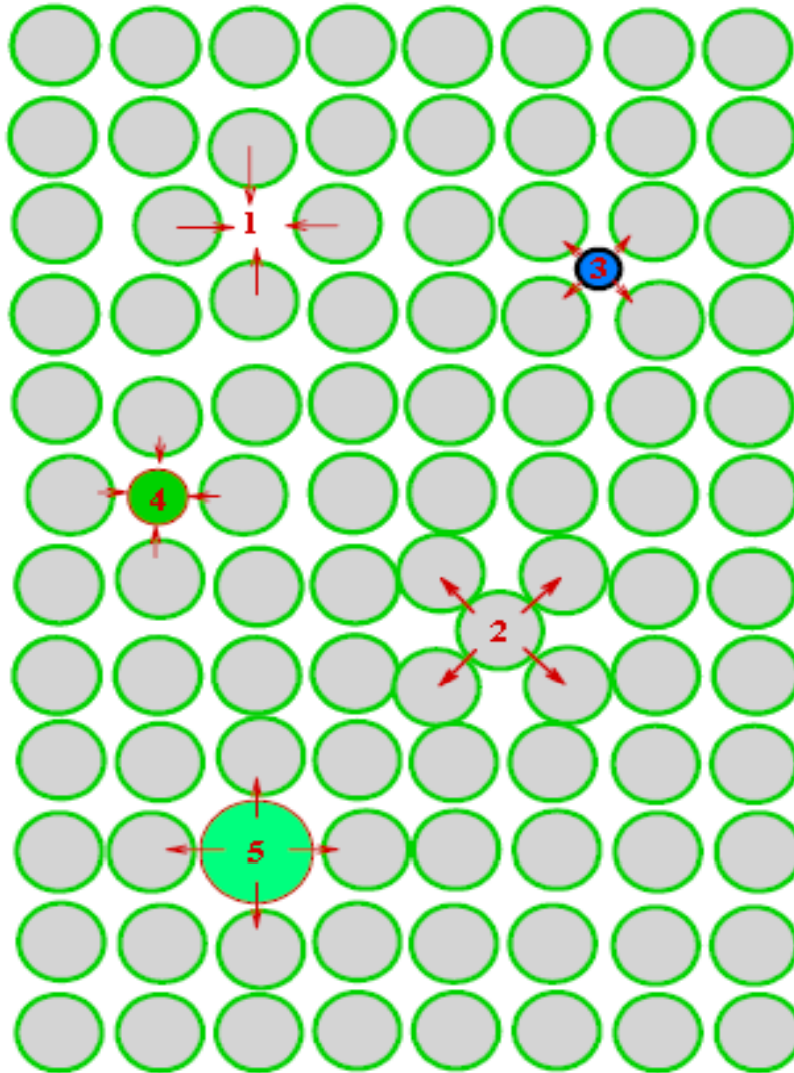
Schematic representation of different point defects:
(1) vacancy;
(2) self-interstitial;
(3) interstitial impurity;
(4,5) substitutional impurities

The arrows show the local stresses introduced by the point defects.

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Self-interstitials

❑ Self-interstitials in metals introduce large distortions in the surrounding lattice .

❑ The energy of self-interstitial formation is ~ 3 times larger as compared to vacancies (Q_i~ $3{\times}Q_v$).

❑ Equilibrium concentration of self-interstitials is very low (less than one self-interstitial per cm^3 at room T).

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Impurities

Impurities - atoms which are different from the host.

➤ All real solids are impure.

➤ Very pure metals 99.9999% - one impurity per 10^6 atoms.

➤ May be intentional or unintentional.

➤ Examples:

  • Carbon added in small amounts to iron makes steel, which is stronger than pure iron.

  • Boron added to silicon change its electrical properties.

➤ Alloys - deliberate mixtures of metals.

➤ Example: sterling silver is 92.5% silver – 7.5% copper alloy. Stronger than pure silver.

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Solid Solutions

❑ Solid solutions are made of a host (the solvent or matrix) which dissolves the minor component (solute).

❑ The ability to dissolve is called solubility.

❑ Solvent: in an alloy, the element or compound present in greater amount.

❑ Solute: in an alloy, the element or compound present in lesser amount.

1. **Solid Solution:**
   ➢ Homogeneous
   ➢ Maintain crystal structure
   ➢ Contain randomly dispersed impurities (substitutional or interstitial)

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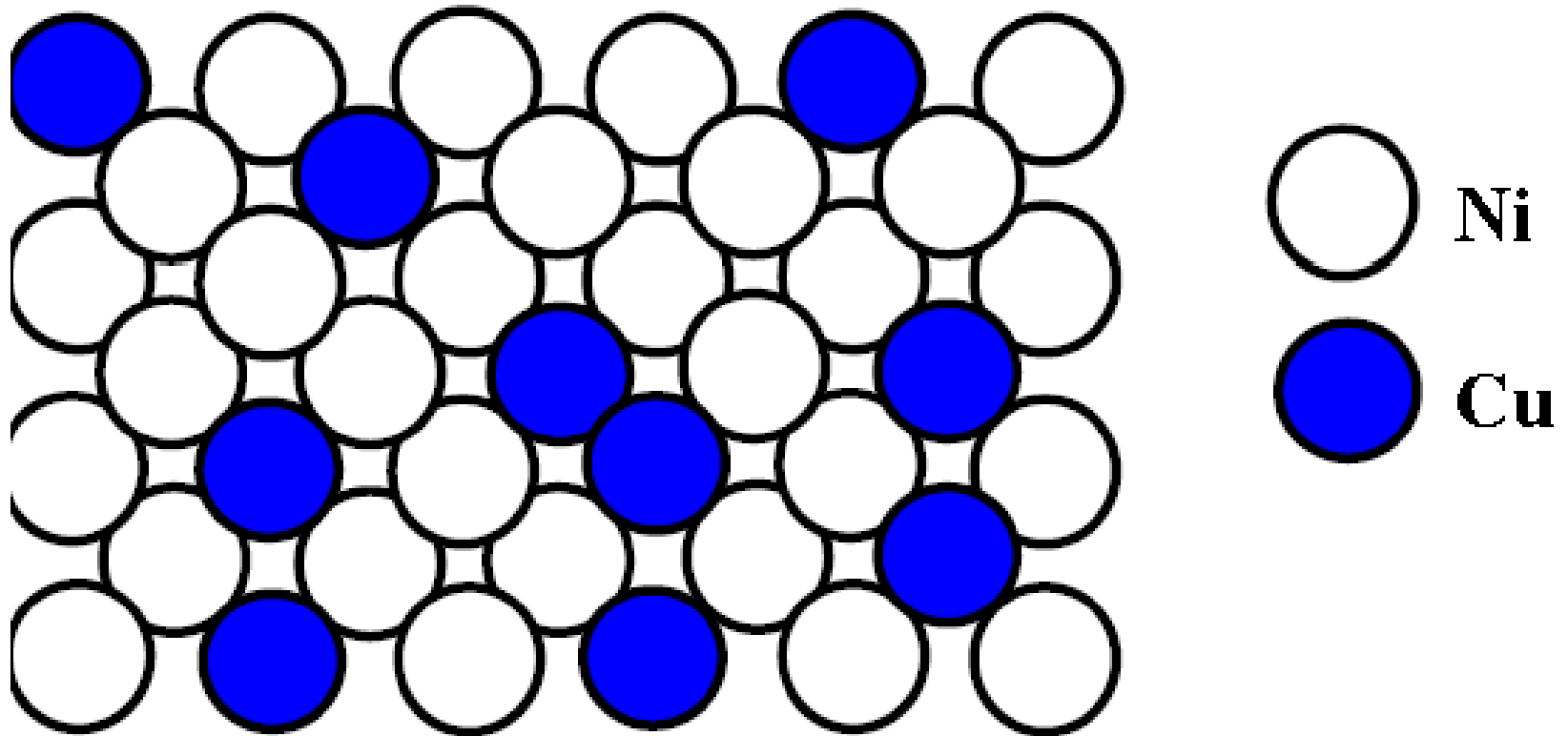
Solid Solutions

2. Second Phase:

As solute atoms are added, new compounds / structures are formed, or solute forms local precipitates.

❑ Whether the addition of impurities results in formation of solid solution or second phase depends the nature of the impurities, their concentration and temperature, pressure...

Substitutional Solid Solutions

Ni

Cu

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Substitutional Solid Solutions

Factors for high solubility: (**Hume – Rothery** rule)

❑ Atomic size factor - atoms need to "fit" ⇒ solute and solvent atomic radii should be within ~ 15%.

❑ Crystal structures of solute and solvent should be the same.

❑ Electronegativities of solute and solvent should be comparable (otherwise new inter-metallic phases are encouraged).

❑ Generally more solute goes into solution when it has higher valency than solvent. All else being equal, a metal will have a greater tendency to dissolve a metal of higher valency than one of lower valency.

Solid Solutions

Application of Hume – Rothery rules – Solid Solutions

1. Would you predict more Al or Ag to dissolve in Zn?

2. More Zn or Al in Cu?

Element	Atomic Radius (nm)	Crystal Structure	Electro-nega-tivity	Valence
Cu	0.1278	FCC	1.9	+2
C	0.071			
H	0.046			
O	0.060			
Ag	0.1445	FCC	1.9	+1
Al	0.1431	FCC	1.5	+3
Co	0.1253	HCP	1.8	+2
Cr	0.1249	BCC	1.6	+3
Fe	0.1241	BCC	1.8	+2
Ni	0.1246	FCC	1.8	+2
Pd	0.1376	FCC	2.2	+2
Zn	0.1332	HCP	1.6	+2

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Interstitial Solid Solutions

Interstitial solid solution of C in α-Fe. The C atom is small enough to fit, after introducing some strain into the BCC lattice.

Carbon interstitial atom in BCC iron

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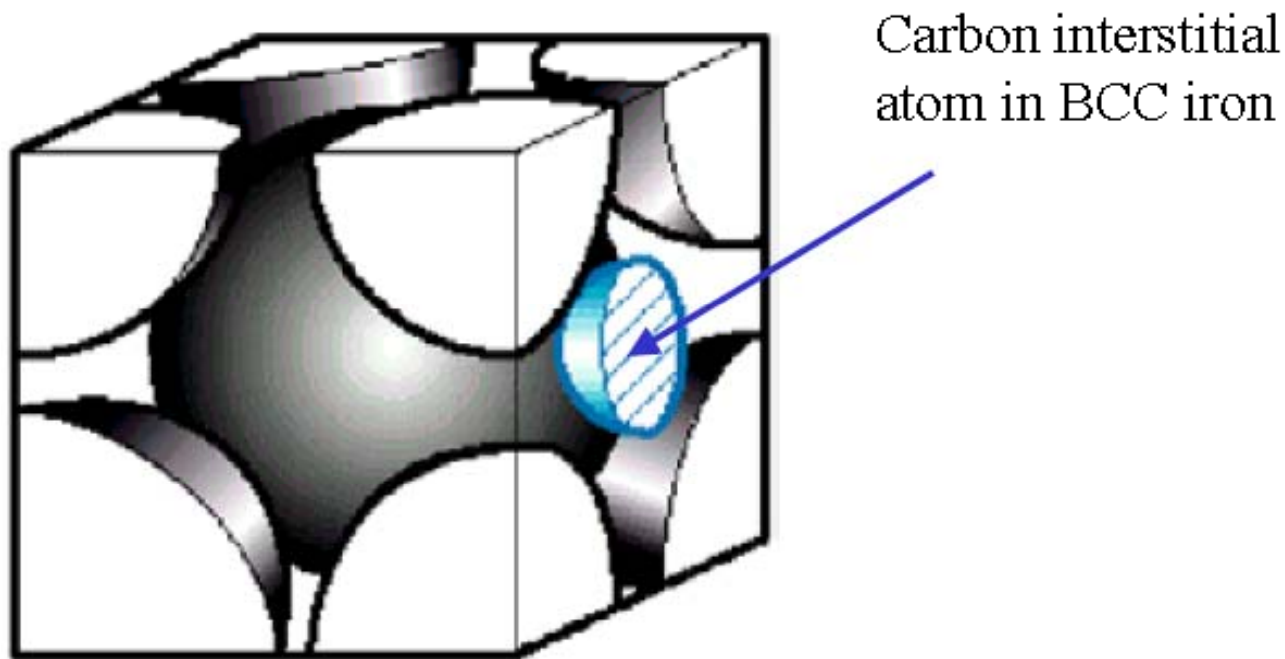
Interstitial Solid Solutions

Factors for high solubility:

❑   For FCC, BCC, HCP structures the voids (or interstices) between the host atoms are relatively small ⇒ atomic radius of solute should be significantly less than solvent.

❑   Normally, max. solute concentration ≤ 10%, (2% for C-Fe)

Composition / Concentration

Composition can be expressed in:

❑ **Weight percent**, useful when making the solution.

❑ **Atom percent**, useful when trying to understand the material at the atomic level.

❑ Weight percent (wt %): weight of a particular element relative to the total alloy weight.

❑ For two-component system, concentration of element 1 in wt. % is

$$C_1 = \frac{m_1}{m_1 + m_2} \times 100$$

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Composition / Concentration

❑ Atom percent (at %): number of moles (atoms) of a particular element relative to the total number of moles (atoms) in alloy.

❑ For two-component system, concentration of element 1 in at. % is:

$$C_1' = \frac{n_{m_1}}{n_{m_1} + n_{m_2}} \times 100$$

where $n_{m1} = m'_1/A_1$

m'_1 is weight in grams of element 1.

A_1 is atomic weight of element 1.

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Composition Conversions

Weight % to Atomic %:

$$C_1^{'} = \frac{C_1 A_2}{C_1 A_2 + C_2 A_1} \times 100$$

$$C_2^{'} = \frac{C_2 A_1}{C_1 A_2 + C_2 A_1} \times 100$$

Atomic % to Weight %:

$$C_1 = \frac{C_1^{'} A_1}{C_1^{'} A_1 + C_2^{'} A_2} \times 100$$

$$C_2 = \frac{C_2^{'} A_2}{C_1^{'} A_1 + C_2^{'} A_2} \times 100$$

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Dislocations — Linear Defects

Dislocations are very important in mechanical properties of material.
Introduction/discovery of dislocations in 1934 by Taylor, Orowan and Polyani marked the beginning of understanding of mechanical properties of materials.
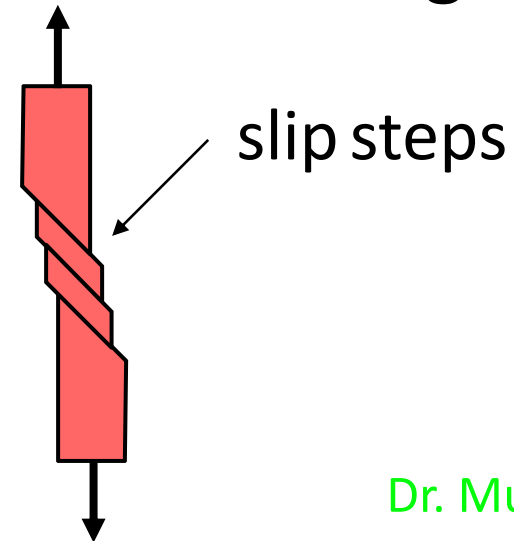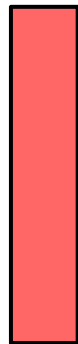
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Dislocations — Linear Defects

Dislocations:

• are line defects.

• slip between crystal planes result when dislocations move.

• produce permanent (plastic) deformation.

Schematic of Zinc (HCP):

• after tensile elongation

• before deformation

slip steps

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Dislocations — Linear Defects

- – Are one-dimensional defects around which atoms are misaligned

- **Edge dislocation**:

  - – extra half-plane of atoms inserted in a crystal structure

  - – **b** $\perp$ to dislocation line

- **Screw dislocation**:

  - – spiral planar ramp resulting from shear deformation

  - – **b** $\parallel$ to dislocation line

  Burger's vector, b: measure of lattice distortion

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Edge dislocation

❑ Dislocations are linear defects: the interatomic bonds are significantly distorted only in the immediate vicinity of the dislocation line.

❑ This area is called the dislocation core.

❑ Dislocations also create small elastic deformations of the lattice at large distances.

Burgers vector

b

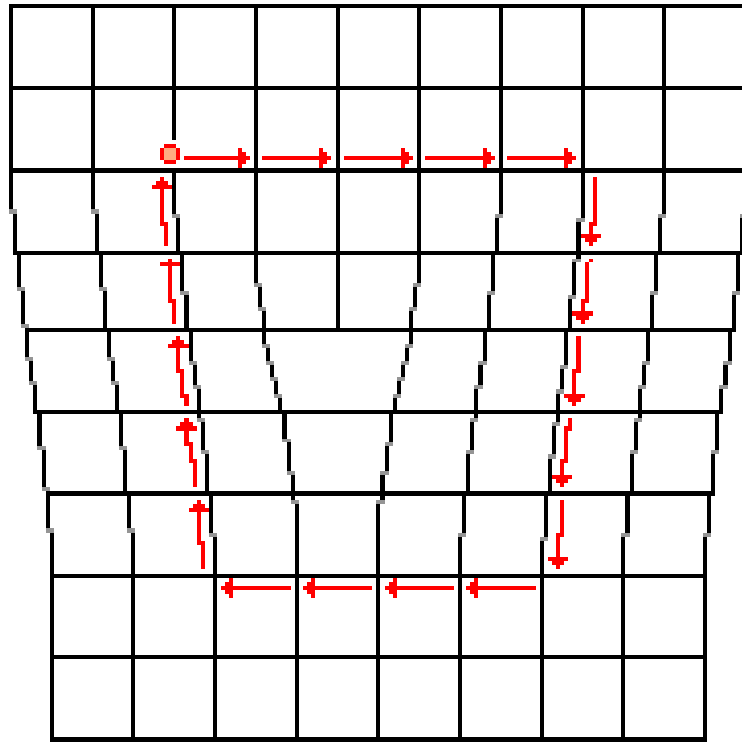Edge dislocation line

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Animation

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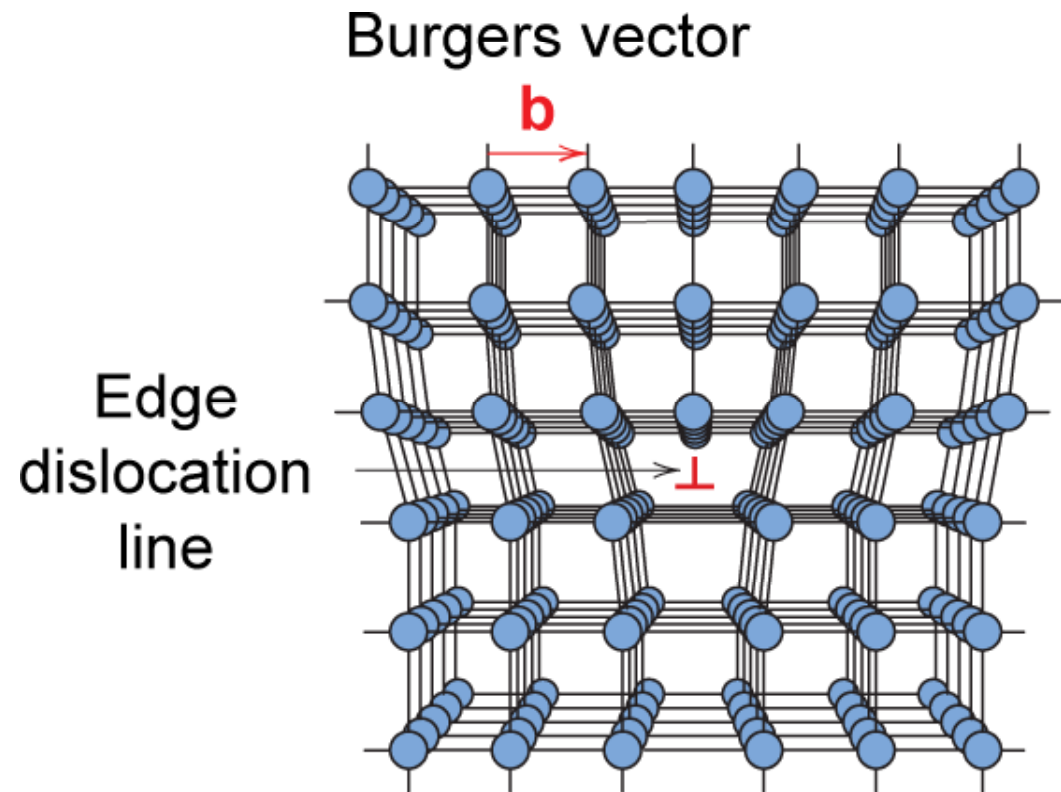
Motion of Edge Dislocation

❑ Dislocation motion requires the successive bumping of a half plane of atoms.

❑ Bonds across the slipping planes are broken and remade in succession.

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Edge dislocation

To describe the size and the direction of the main lattice distortion caused by a dislocation we should introduce so-called **Burgers vector b**.
To find the Burgers vector, we should make a circuit from atom to atom counting the same number of atomic distances in all directions.
If the circuit encloses a dislocation it will not close.
The vector that closes the loop is the Burgers vector b.

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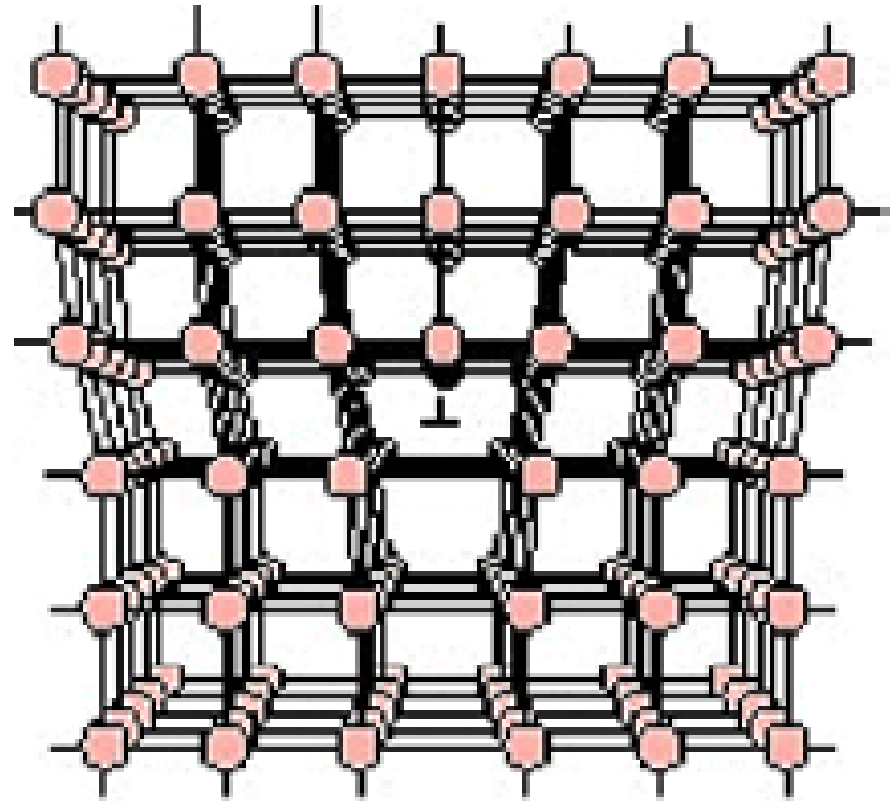
Dislocations shown above have Burgers vector directed perpendicular to the dislocation line. These dislocations are called edge dislocations.

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Glide Plane
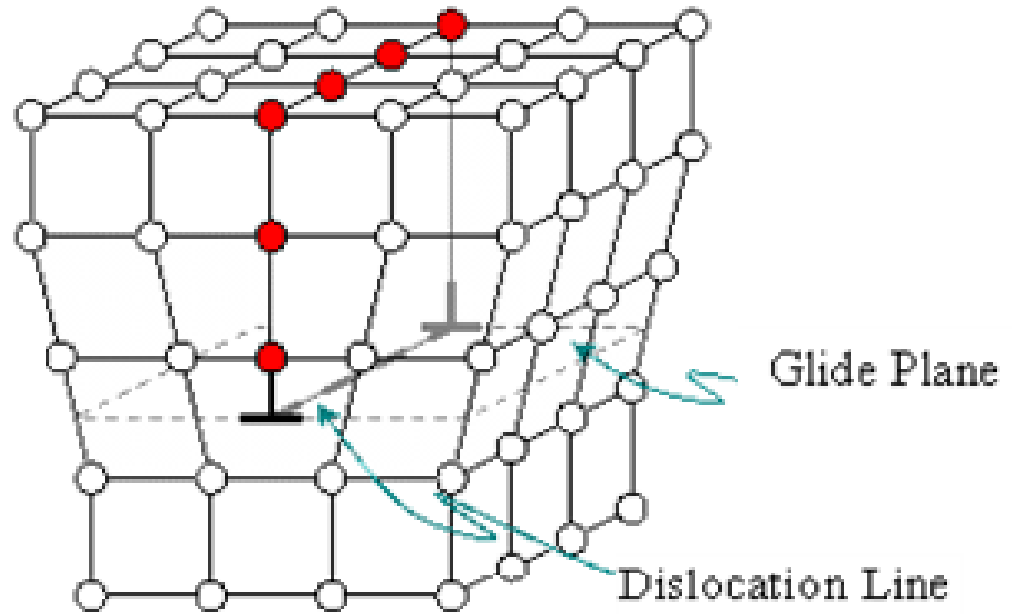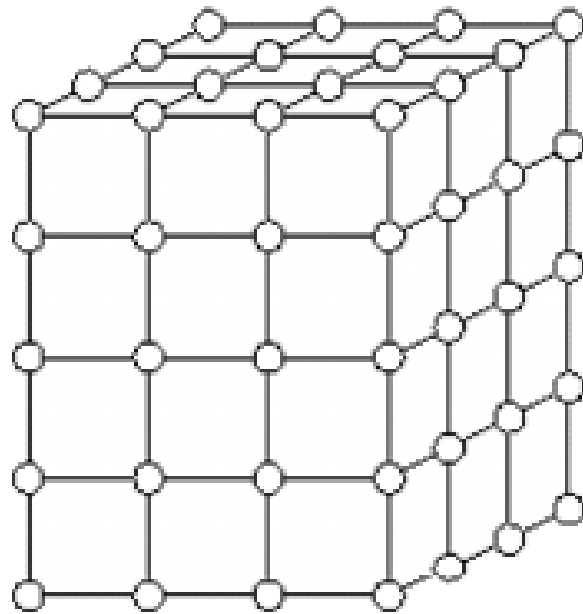
Dislocation Line

Introducing a dislocation into a crystal lattice by cramming in an extra half-plane. The dislocation line marks the edge of the half-plane. The inverted T symbol shows the location of the half-plane

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Burgers vector

Start at some point, going clockwise around the dislocation and counting our steps so that we take the same number right as we took left, the same number down as we took up and so on. Once we have circled the dislocation and our steps match up, the Burgers vector is the vector which points from Start to Finish.

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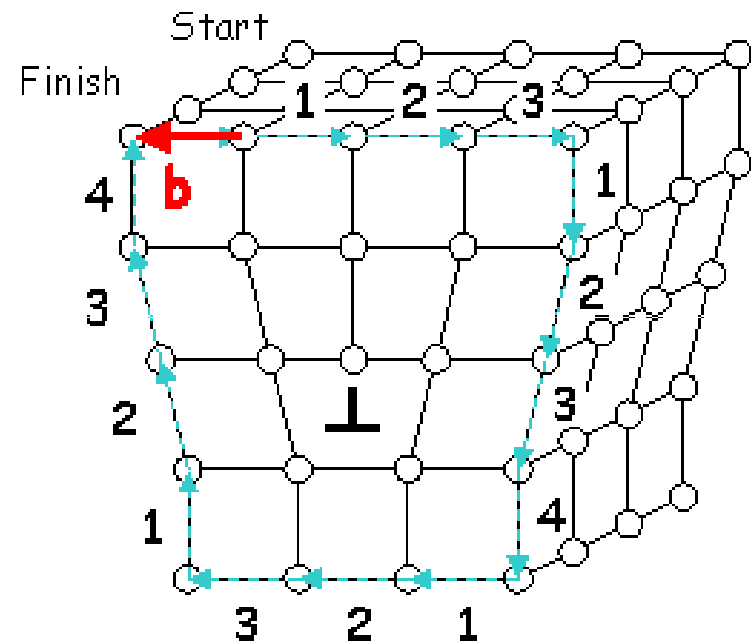
Screw dislocations

❑   Dislocations shown in previous slide are edge dislocations, have Burgers vector directed perpendicular to the dislocation line.

❑   There is a second basic type of dislocation, called screw dislocation.

Dislocation
line

Burgers vector b

(a)

b

A   B

D   C

(b)

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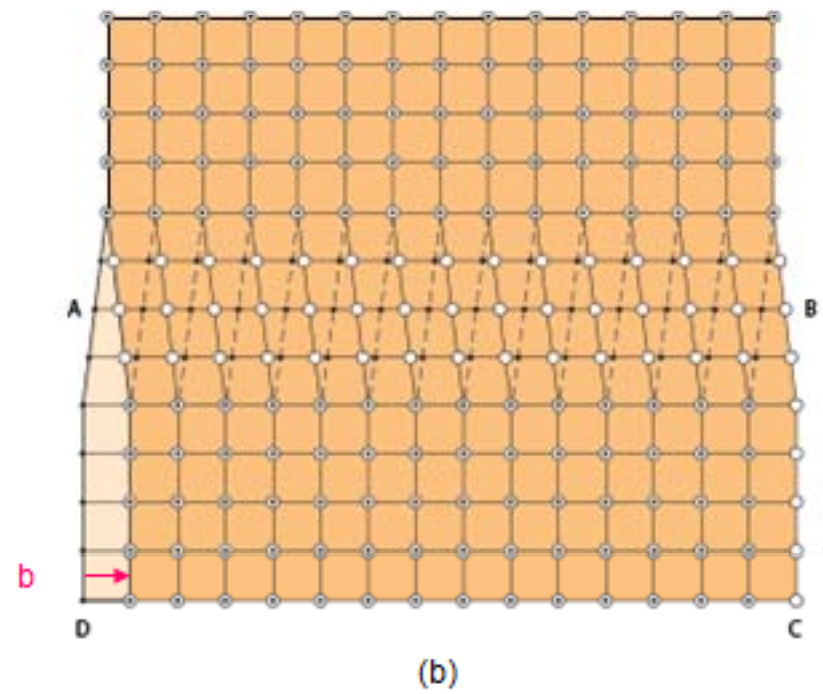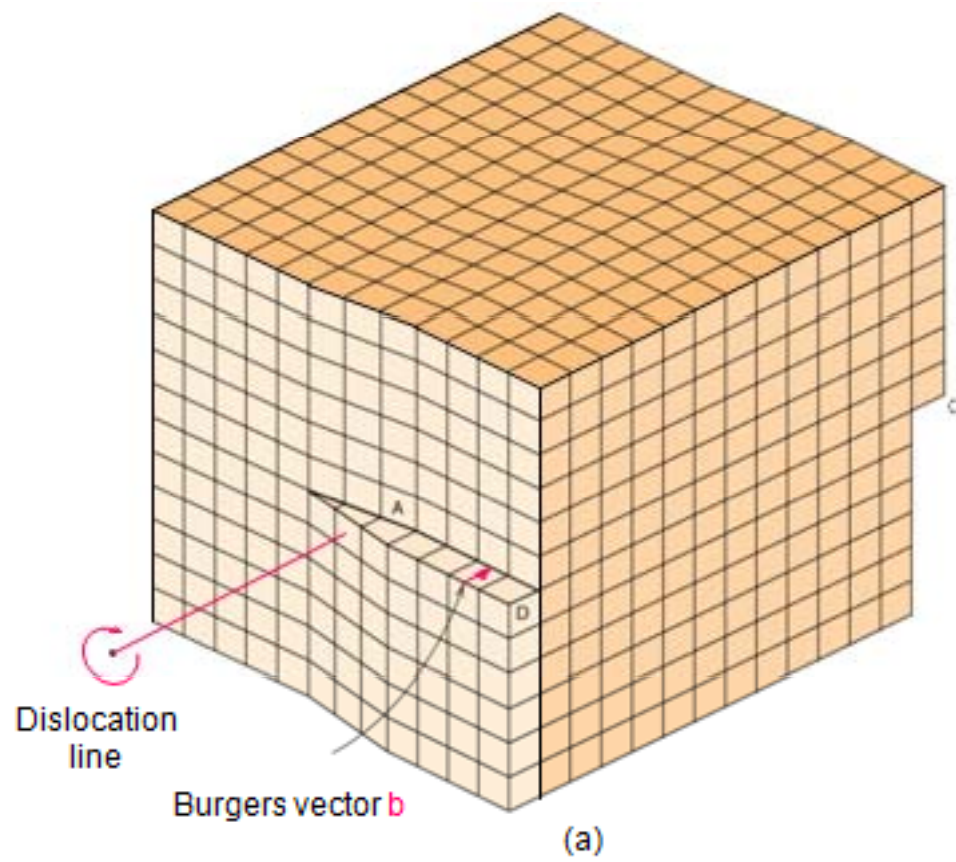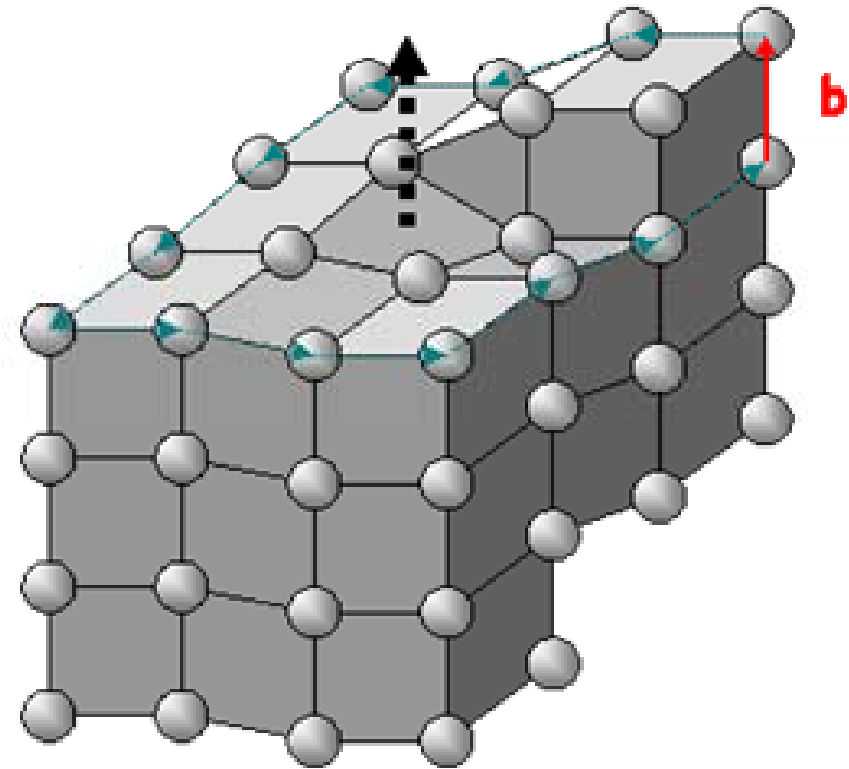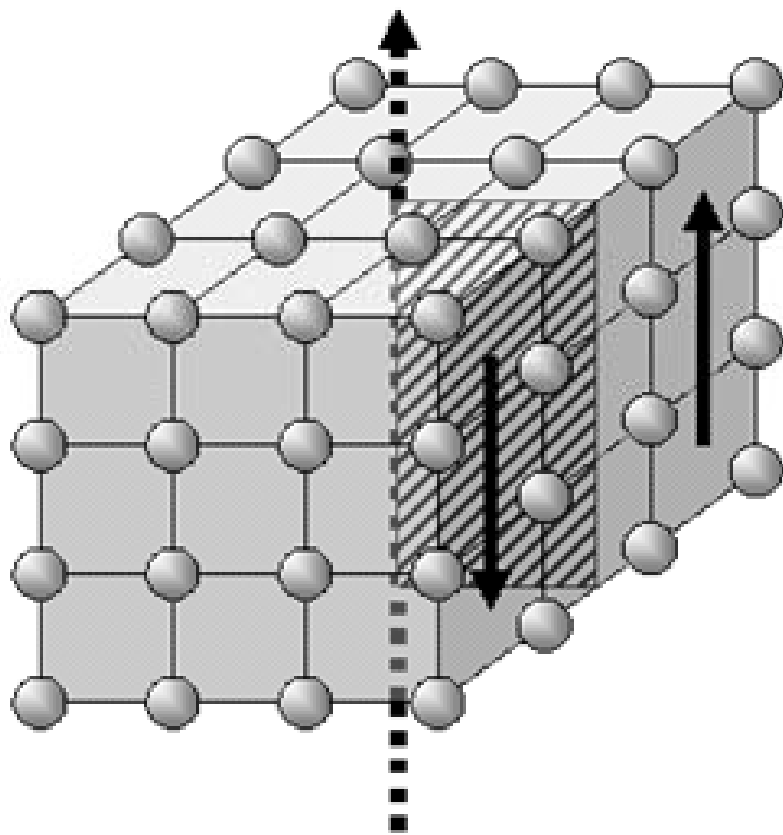
A screw dislocation is like a spiral staircase or a parking garage. The dislocation line is the axis of the helix.

Screw dislocations

❑ The screw dislocation is parallel to the direction in which the crystal is being displaced (Burgers vector is parallel to the dislocation line).

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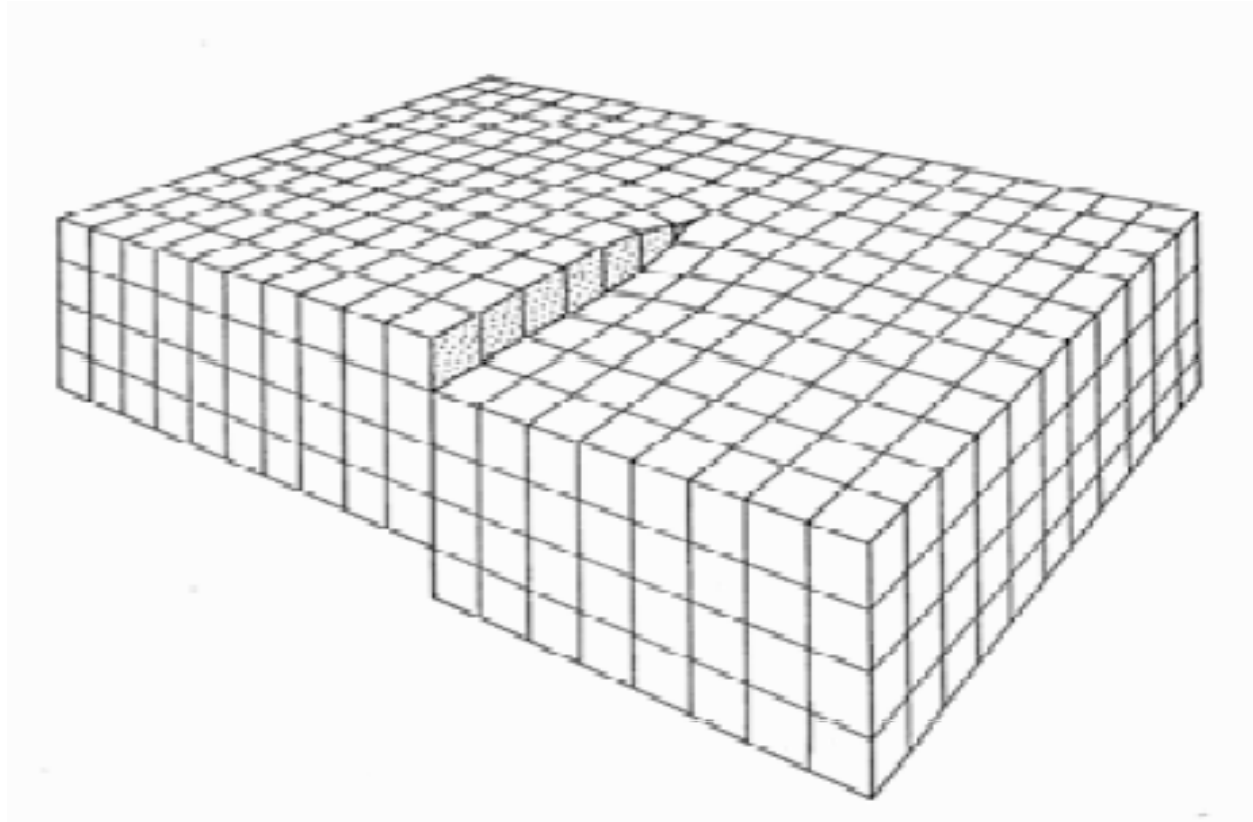
Mixed/partial dislocations (not tested)

❑ The exact structure of dislocations in real crystals is usually more complicated than the ones shown in the edge and screw dislocations.

❑ Edge and screw dislocations are just extreme forms of the possible dislocation structures.

❑ Most dislocations have mixed edge/screw character.

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Edge, Screw, and Mixed Dislocations
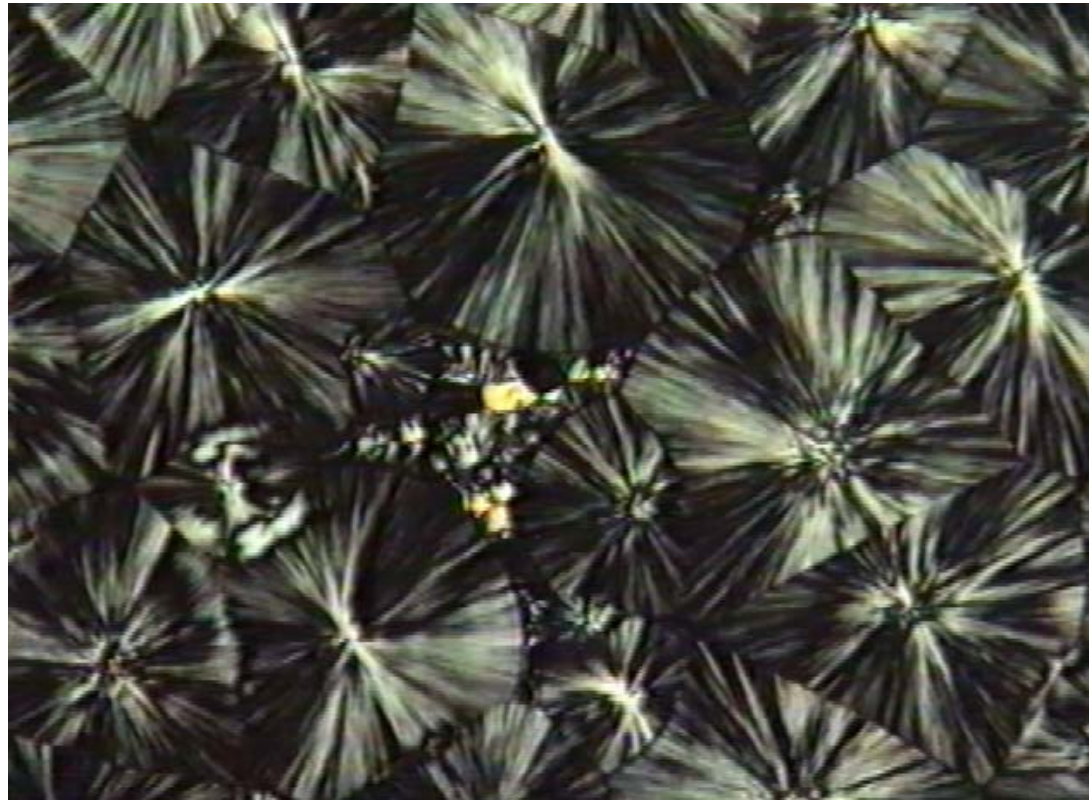

Mixed

Edge

Screw

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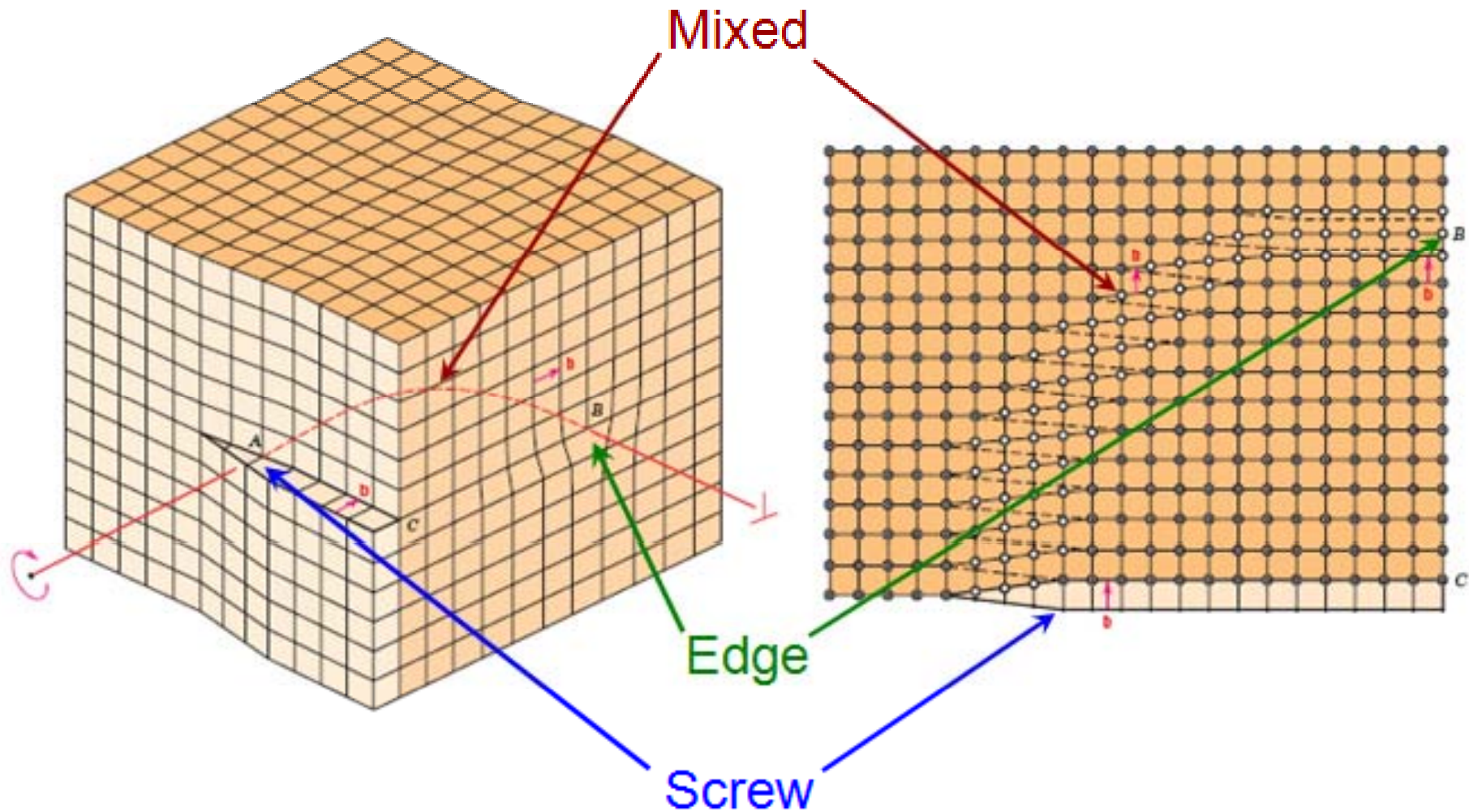
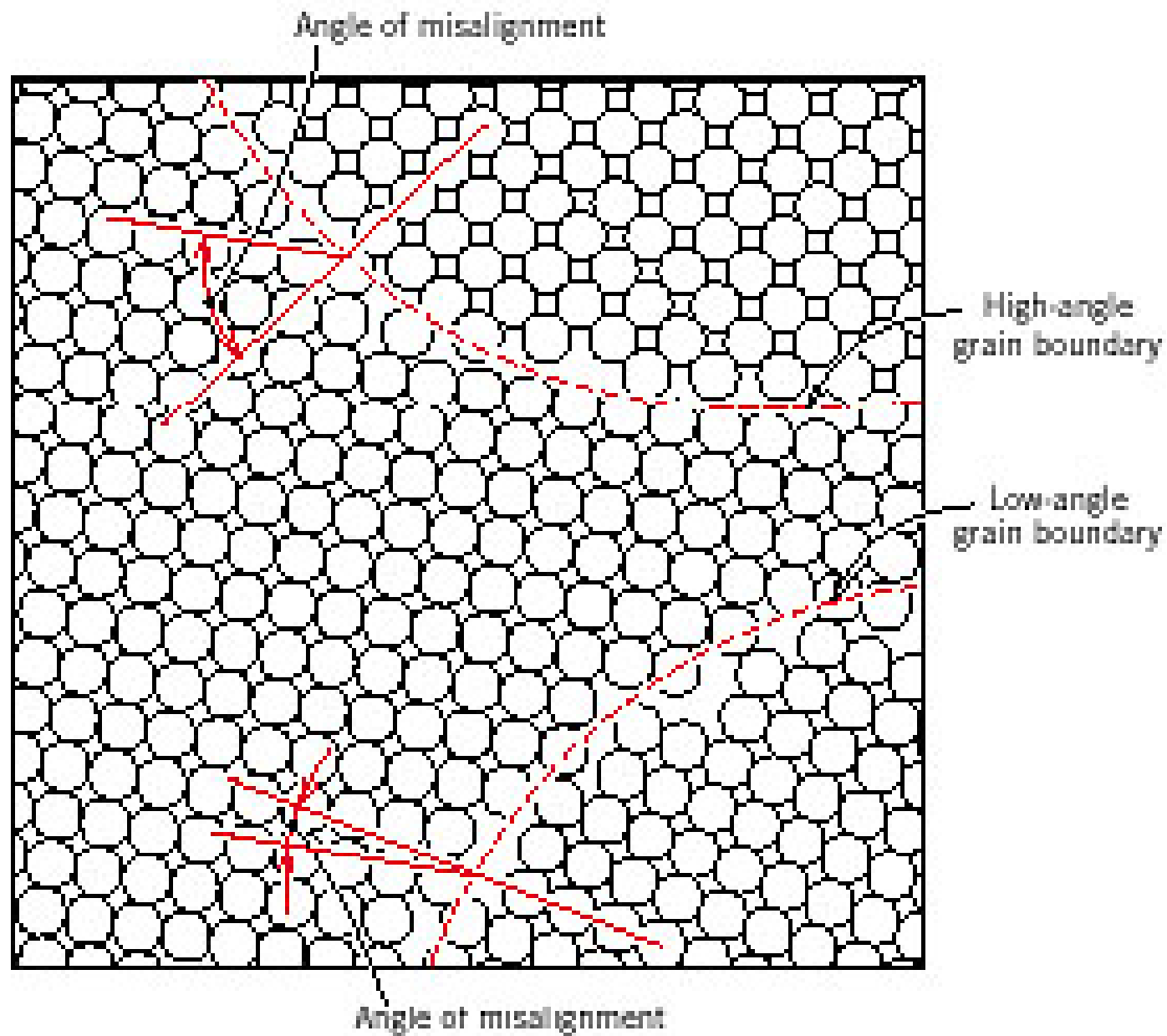# *Interfacial Defects*

❑ **Grain Boundaries**

   ❑ Polycrystalline material comprised of many small crystals or grains.

   ❑ The grains have different crystallographic orientation.


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❑ **Grain Boundaries**

❑ There exist atomic mismatch within the regions where grains meet. These regions are called grain boundaries.

❑ Surfaces and interfaces are reactive and impurities tend to segregate there. Since energy is associated with interfaces, grains tend to grow in size at the expense of smaller grains to minimize energy.

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Angle of misalignment

High-angle grain boundary

Low-angle grain boundary

Angle of misalignment

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Bulk or Volume Defects

❑ Pores - can greatly affect optical, thermal, mechanical properties.

❑ Cracks - can greatly affect mechanical properties.

❑ Foreign inclusions - can greatly affect electrical, mechanical, optical properties
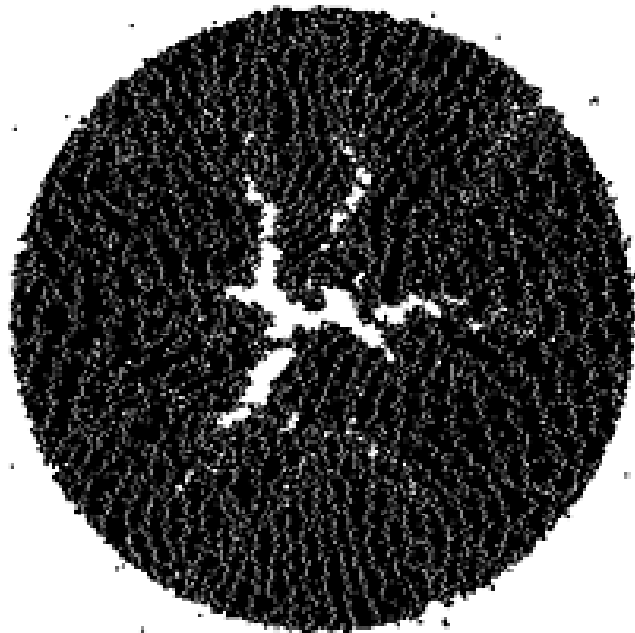
❑A cluster of microcracks in a melamin granule irradiated by a short laser pulse.

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Atomic Vibrations

- ❑   Heat causes atoms to vibrate.
- ❑   Vibration amplitude increases with temperature.
- ❑   Melting occurs when vibrations are sufficient to rupture bonds.
- ❑   Vibrational frequency ~ 10^{13} Hz.
- ❑   Average atomic energy due to thermal excitation is of order kT.

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