

EPFL

Physics of Materials

Chapter 4: Defects of Crystals

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Masters Course PHYS-307

Fall 2024

Different Defects Categories

Different Dimensionalities

0D – Point Defects (interstitials, vacancies, antisite)

1D – Dislocations and Disclinations

2D – Grain Boundaries (symmetric and disordered)

3D

1. Amorphous

2. Glasses (paracrystalline materials)

3. Fractal microstructures

4. Quasicrystals

The Science of Dirt to Defects

Pauli opposed the publication of Peierls's manuscript and wrote, "The residual resistivity is caused by dirt and one should not dwell in the dirt."

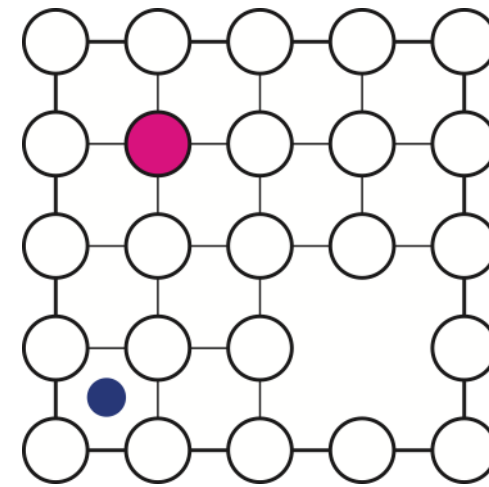
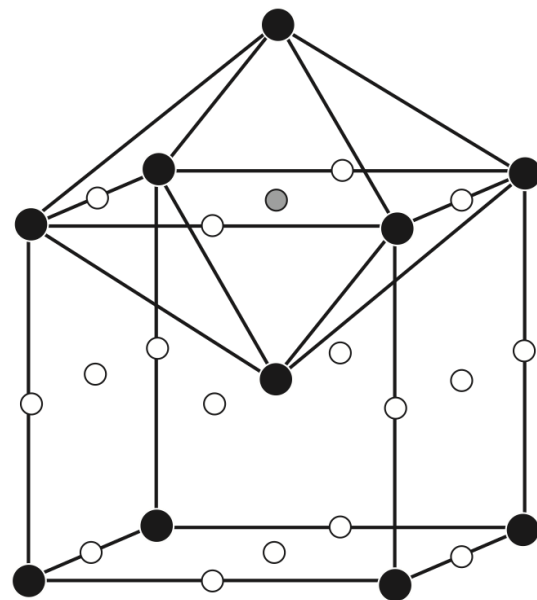
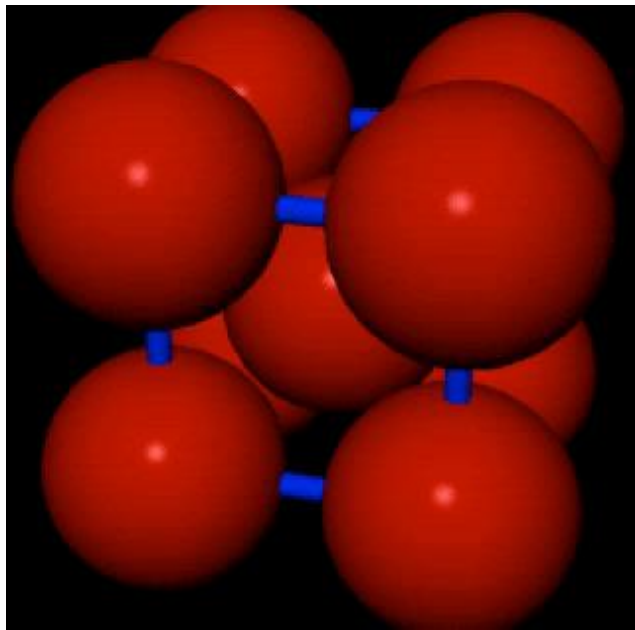
In his review commentary, Pauli added, "You should find more sensible questions to be answered; I find that you recently have concerned yourself too much with small issues."



Dirac Pauli Peierls

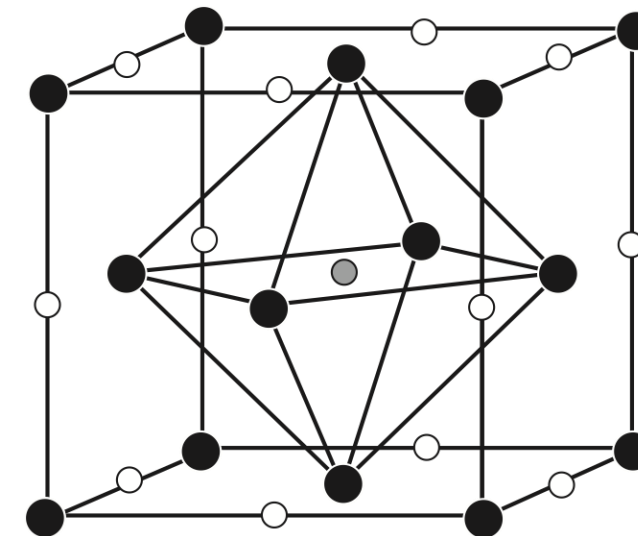
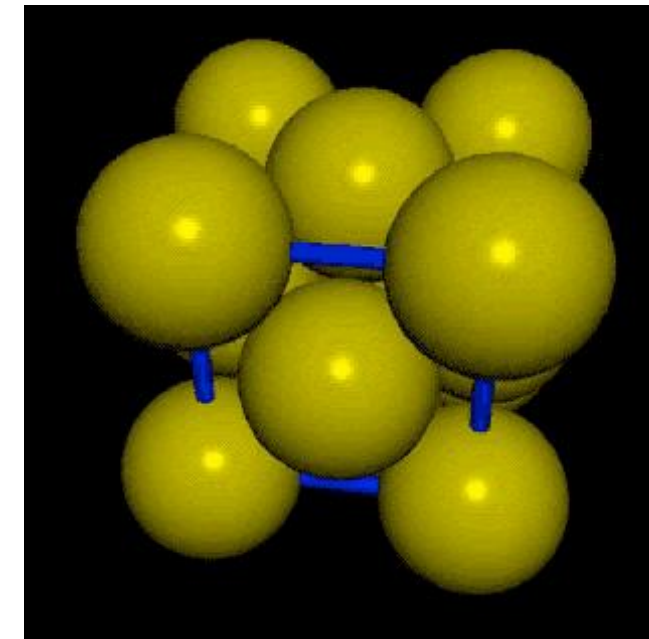
Point defects

Body-centered
cubic

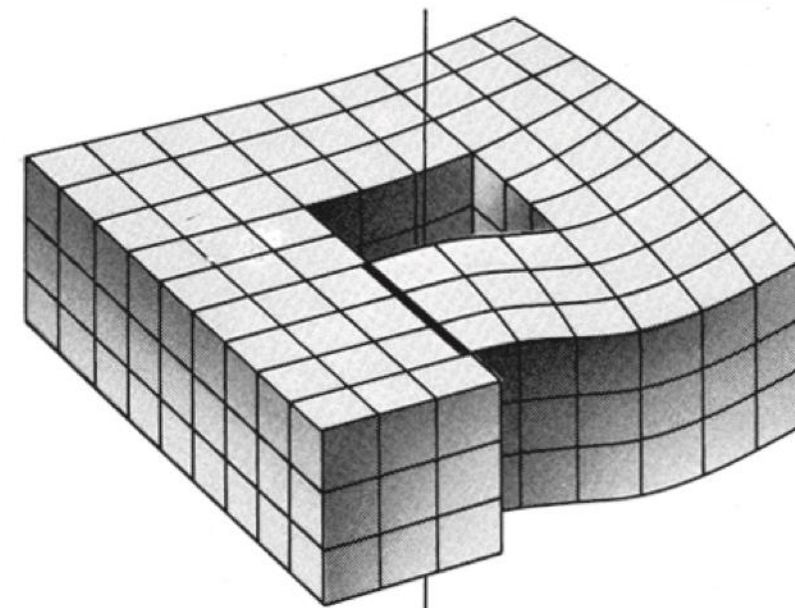


Interstitial
carbon
in Fe

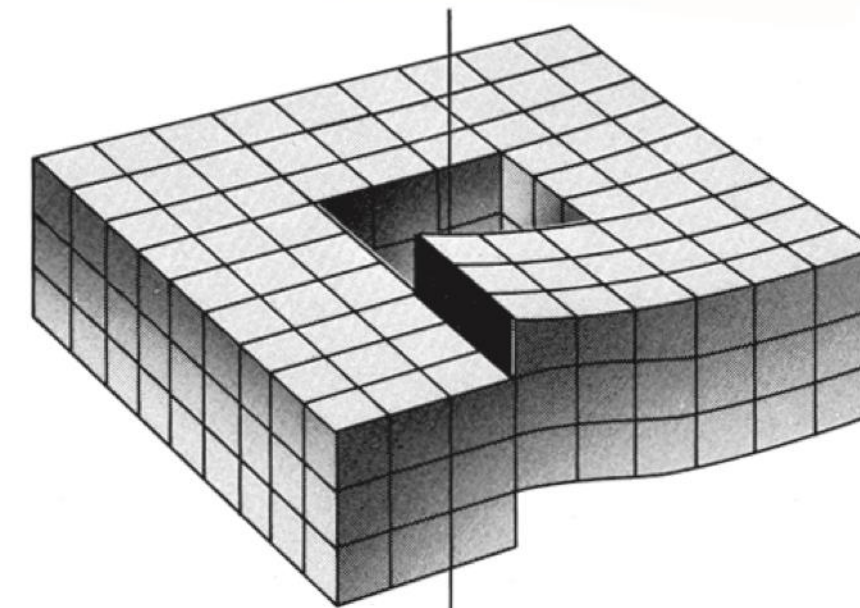
Face-centered
cubic



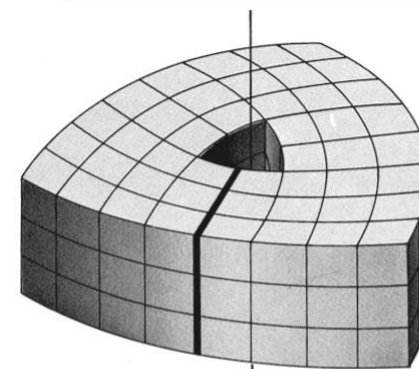
Dislocations and Disclinations



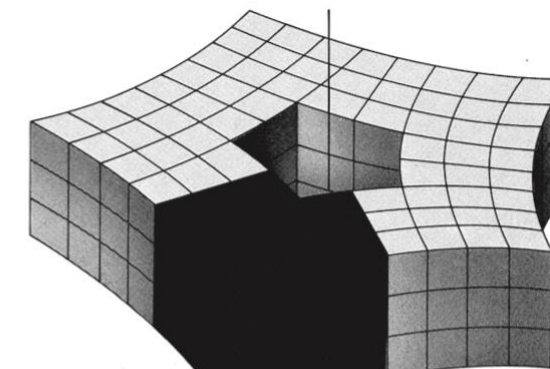
Edge dislocation



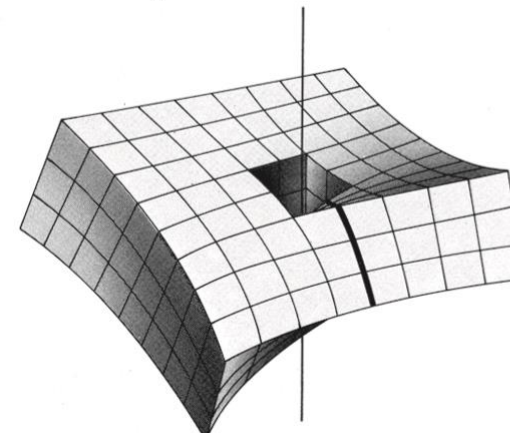
Screw dislocation



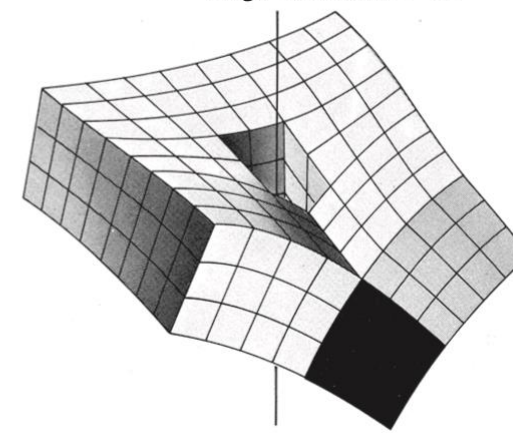
Edge disclination $+90^\circ$



Edge disclination -90°



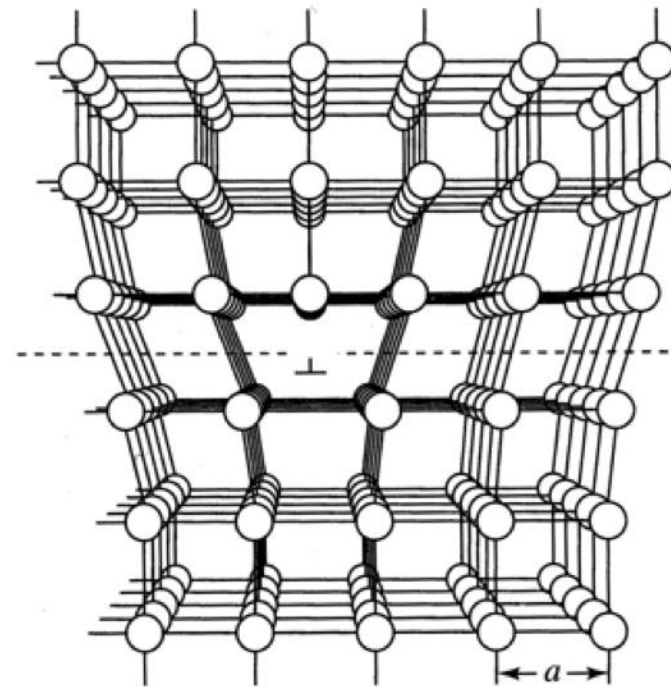
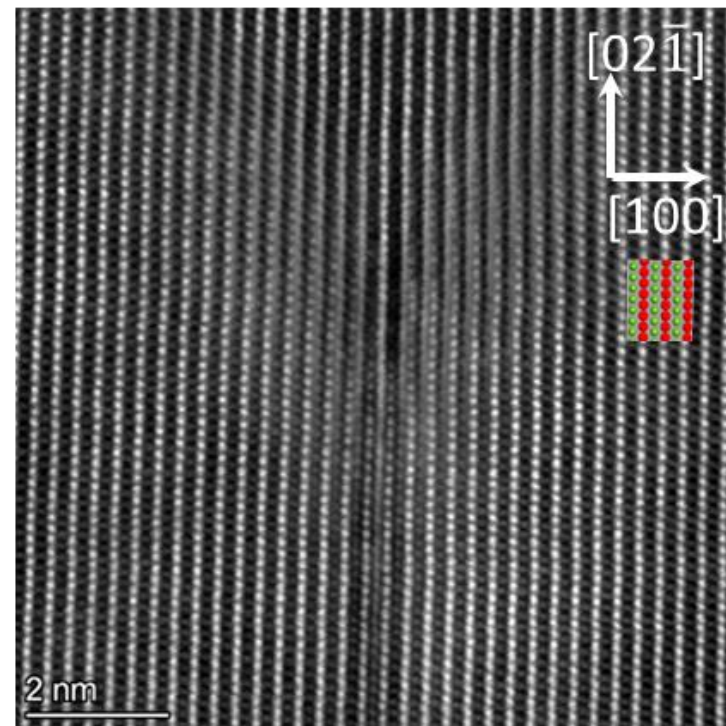
Twist disclination $+90^\circ$



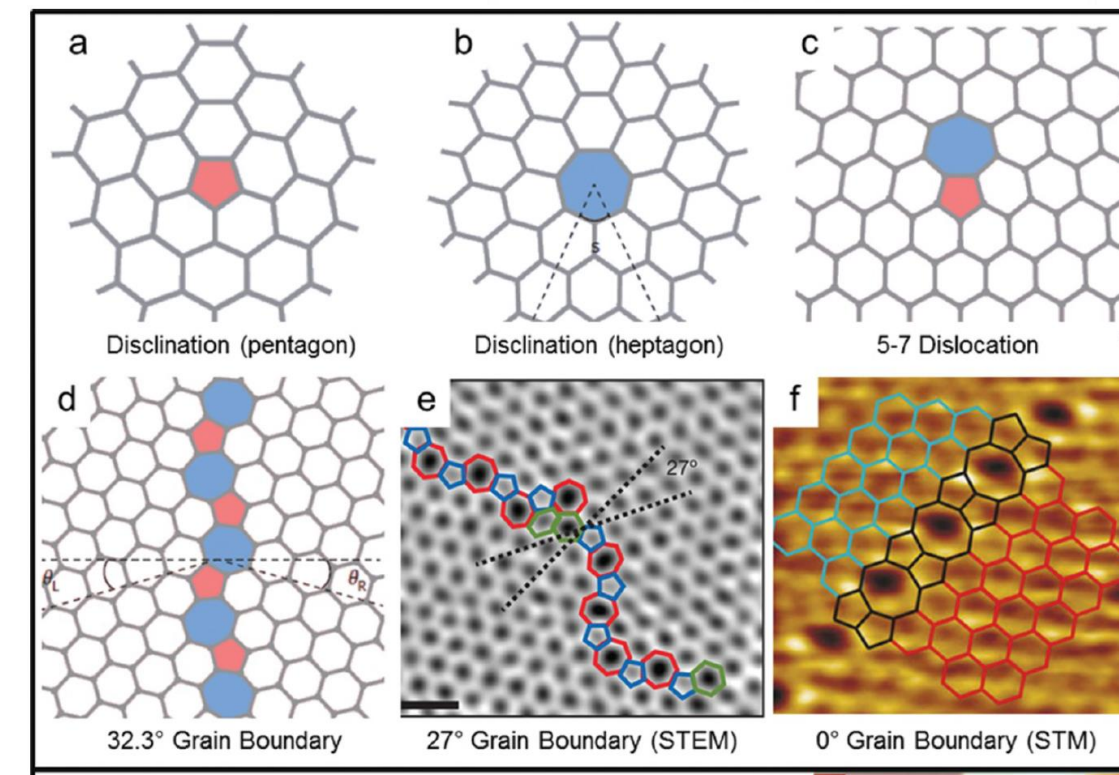
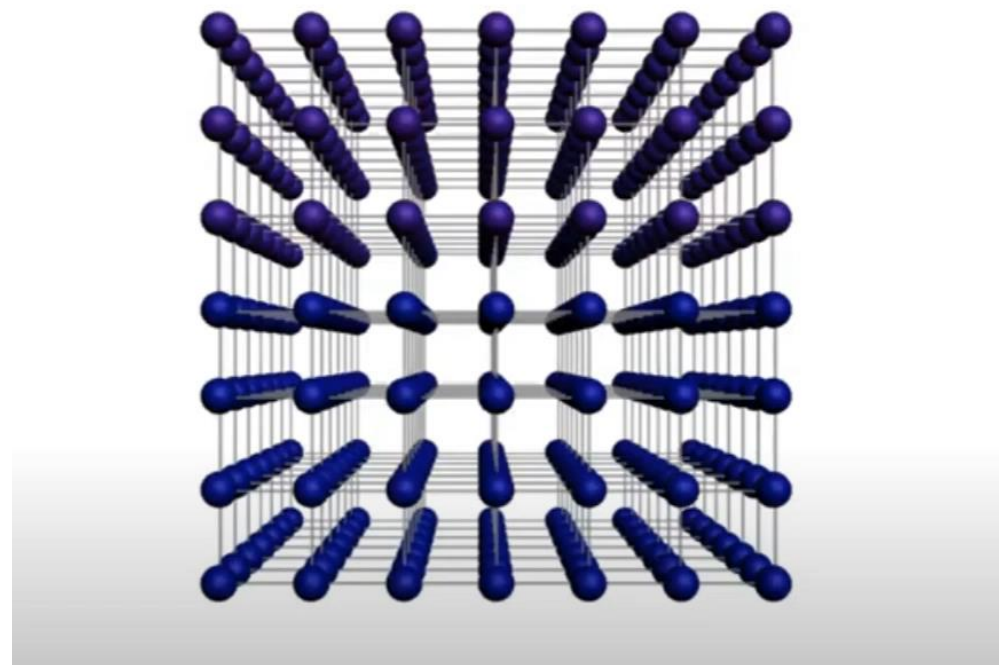
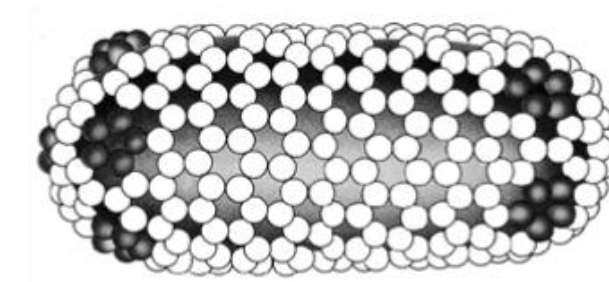
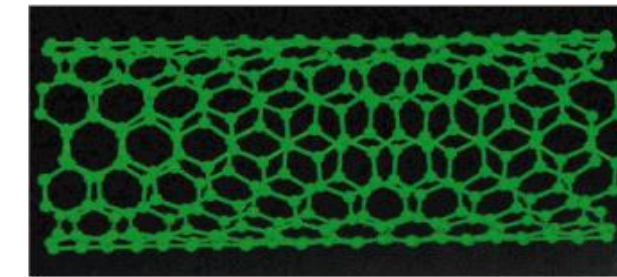
Twist disclination -90°

Dislocations and Disclinations

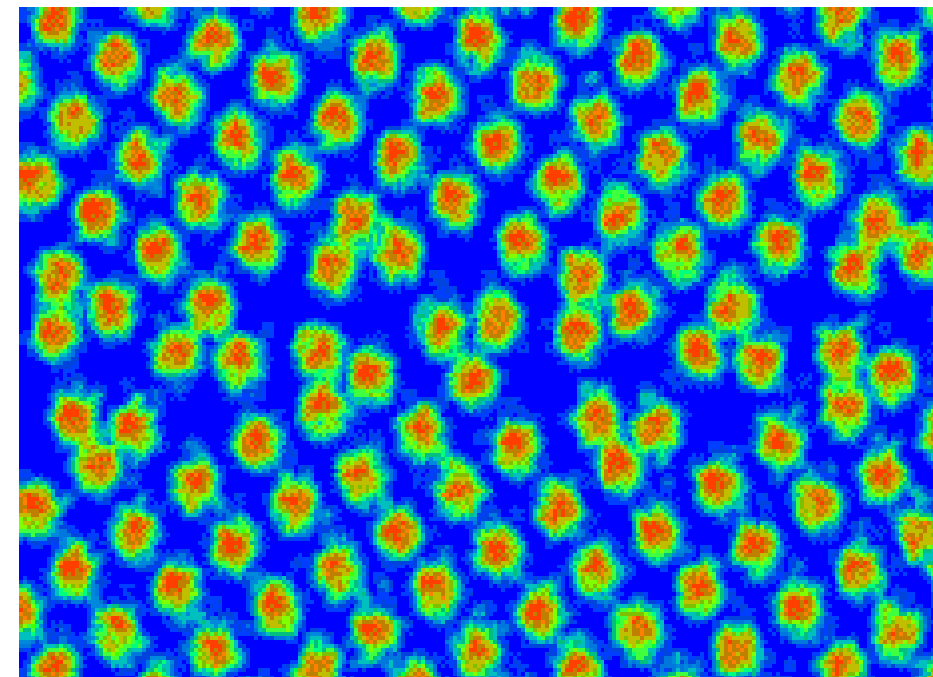
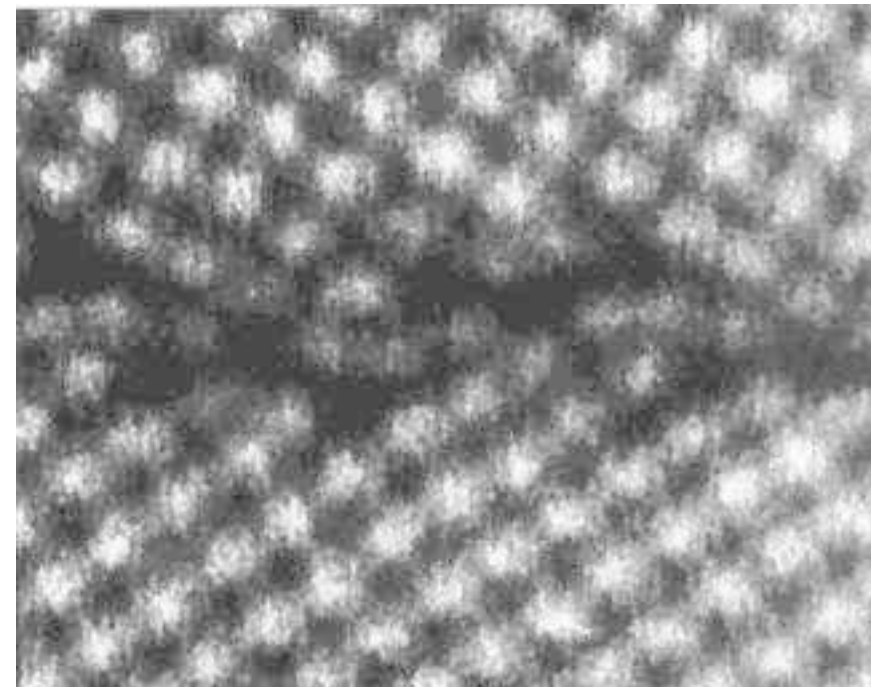
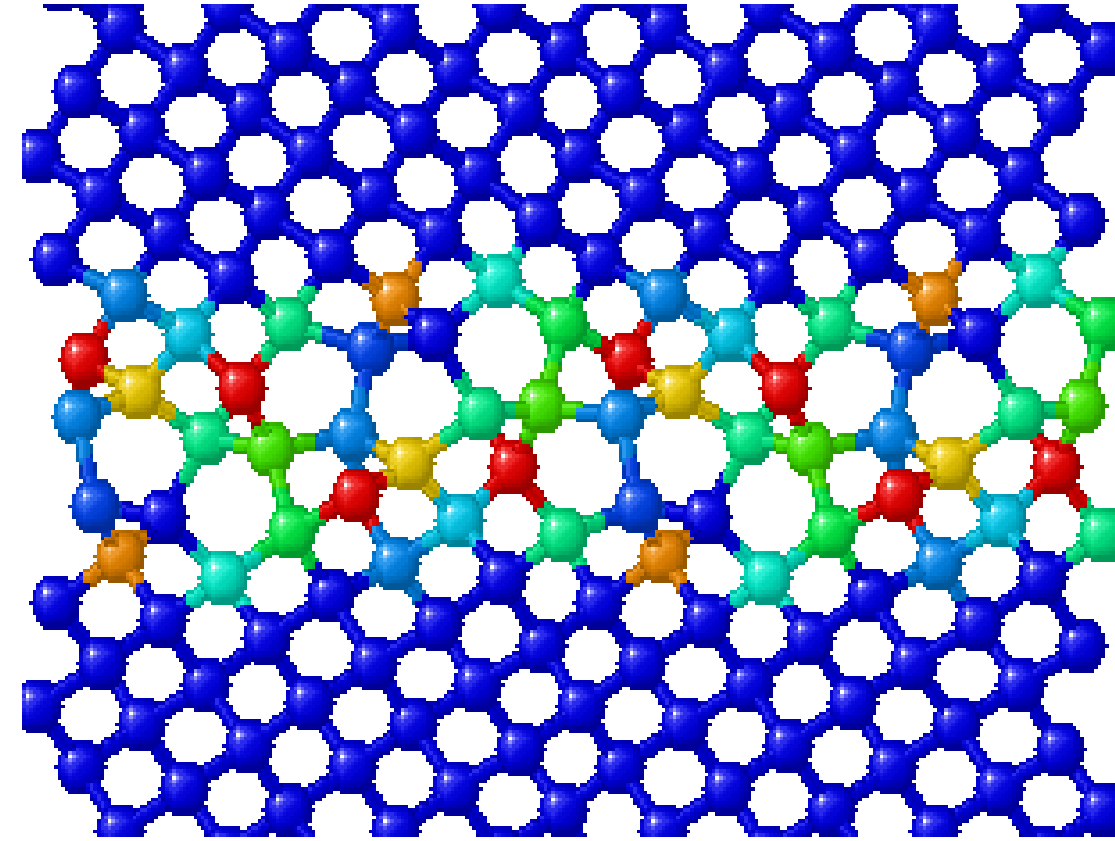
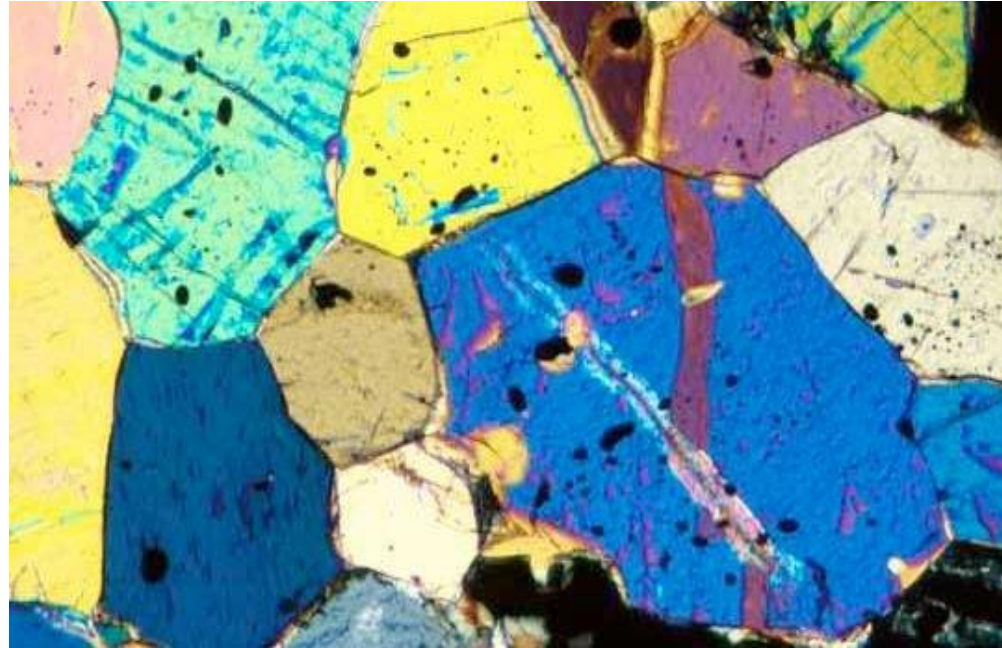
Edge dislocation



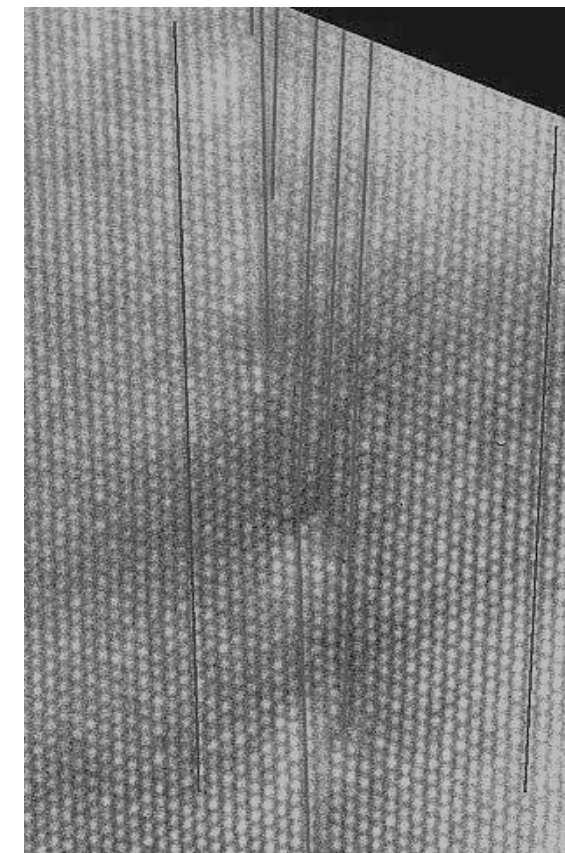
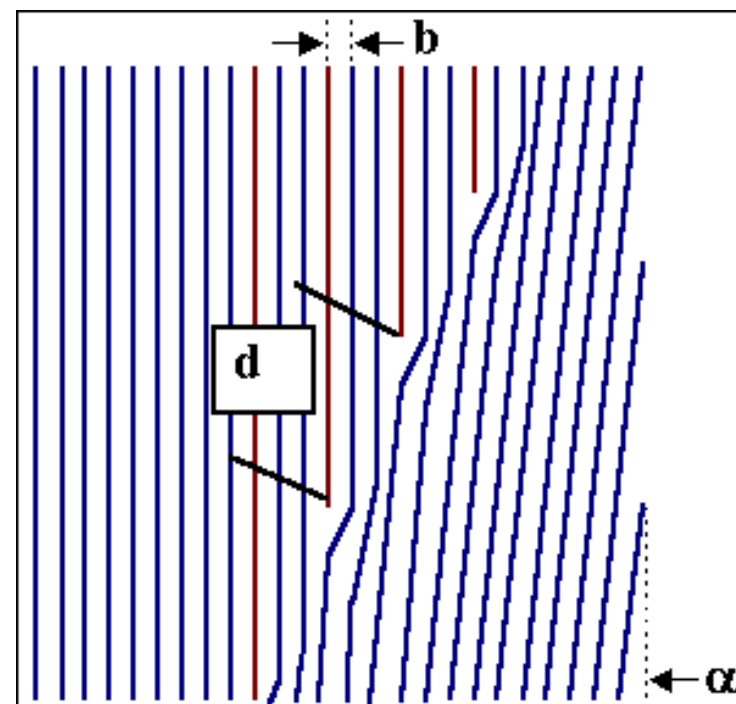
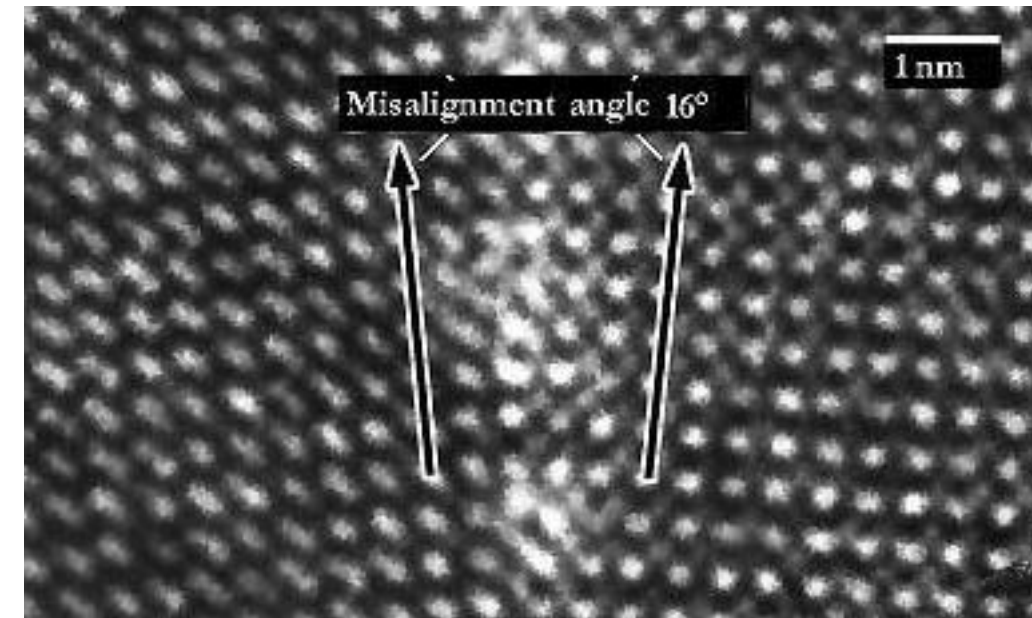
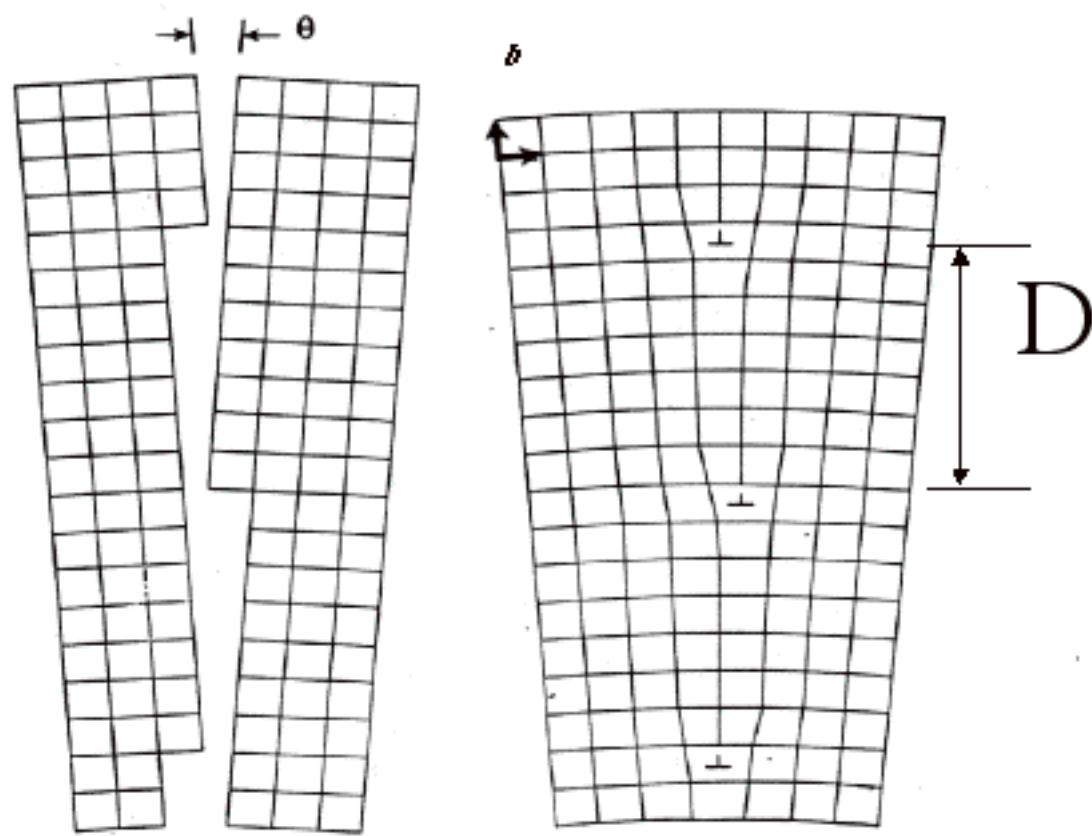
Disclinations close carbon nanotubes



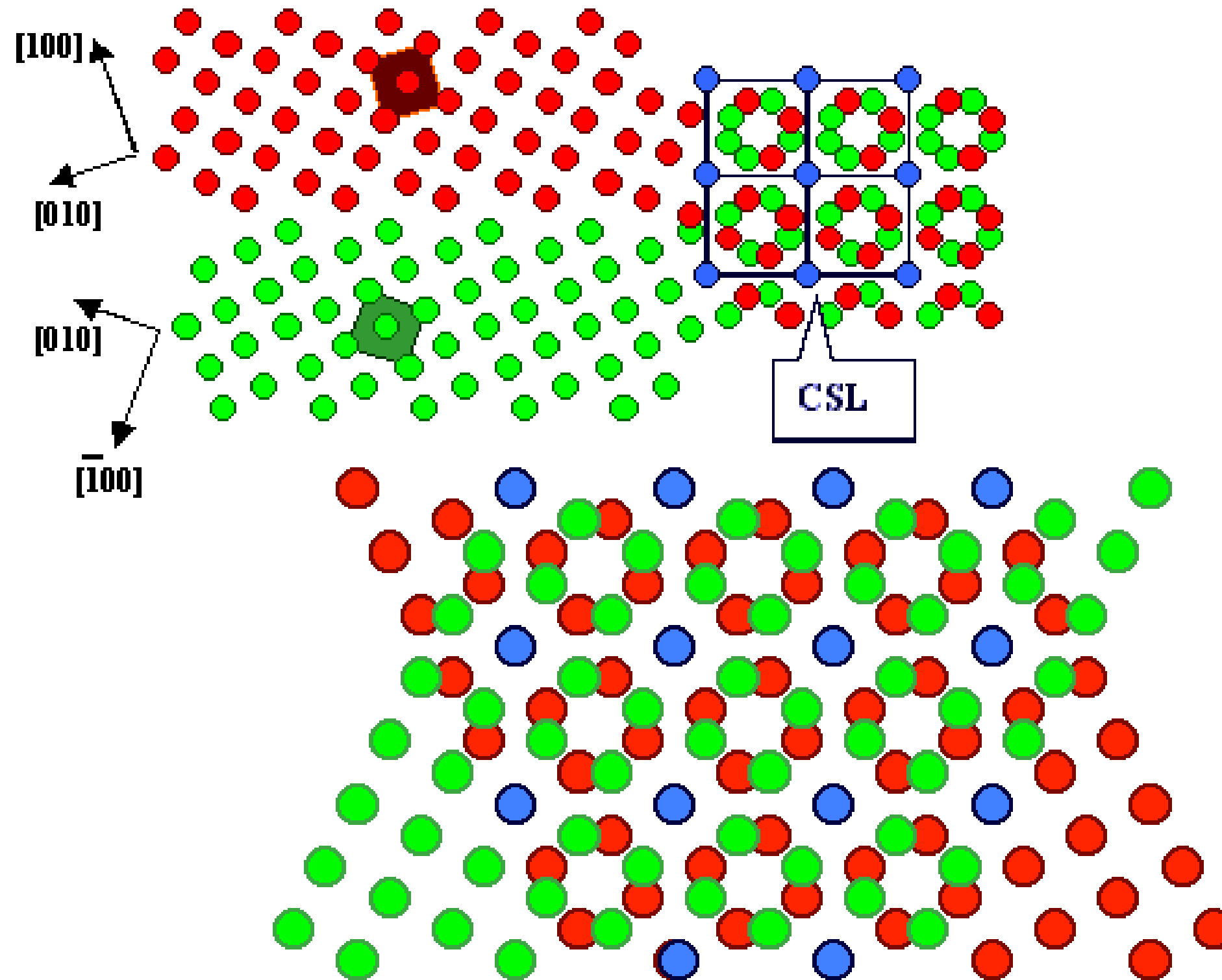
Grain Boundaries



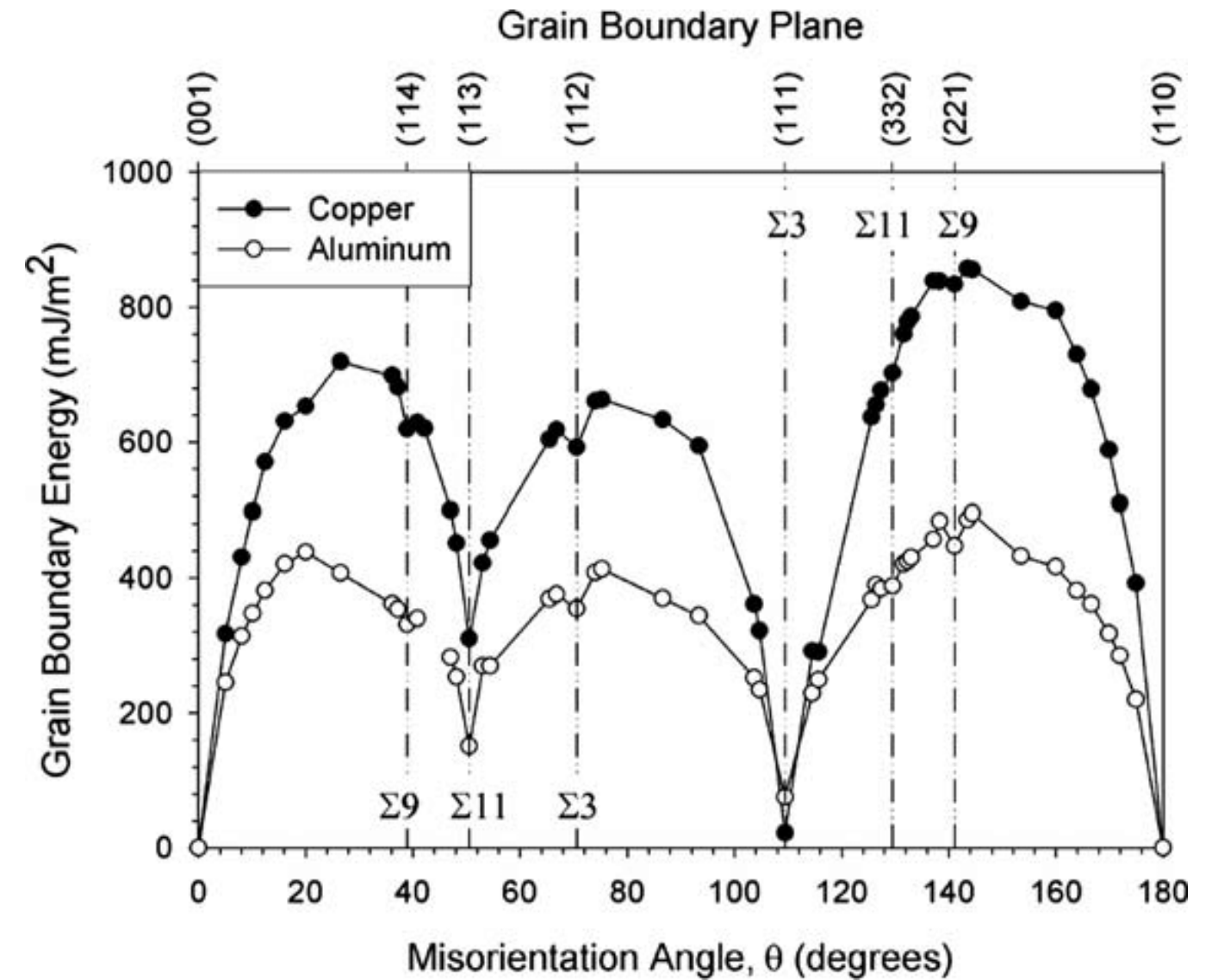
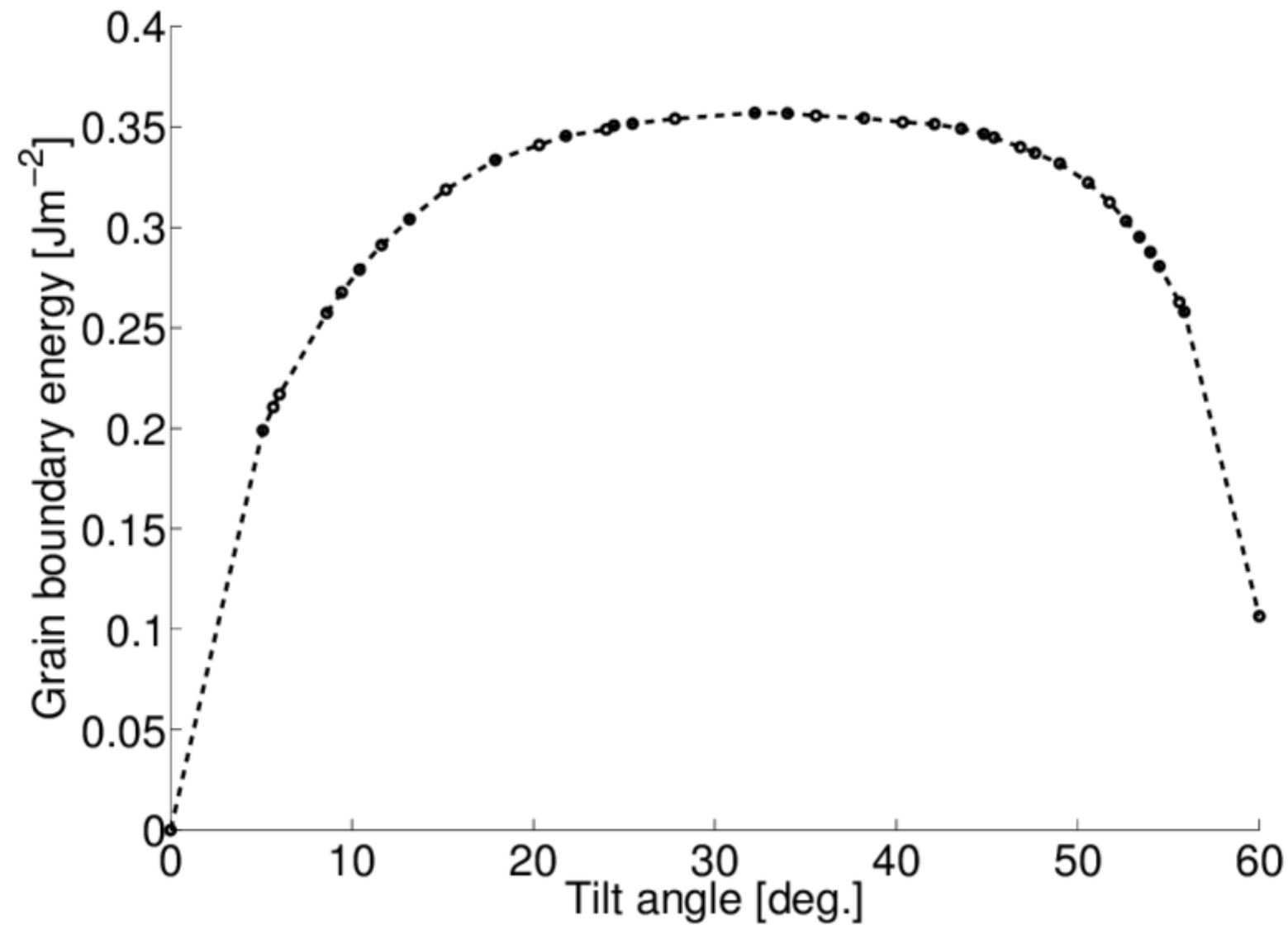
Small angle grain boundaries



Symmetric Grain Boundaries

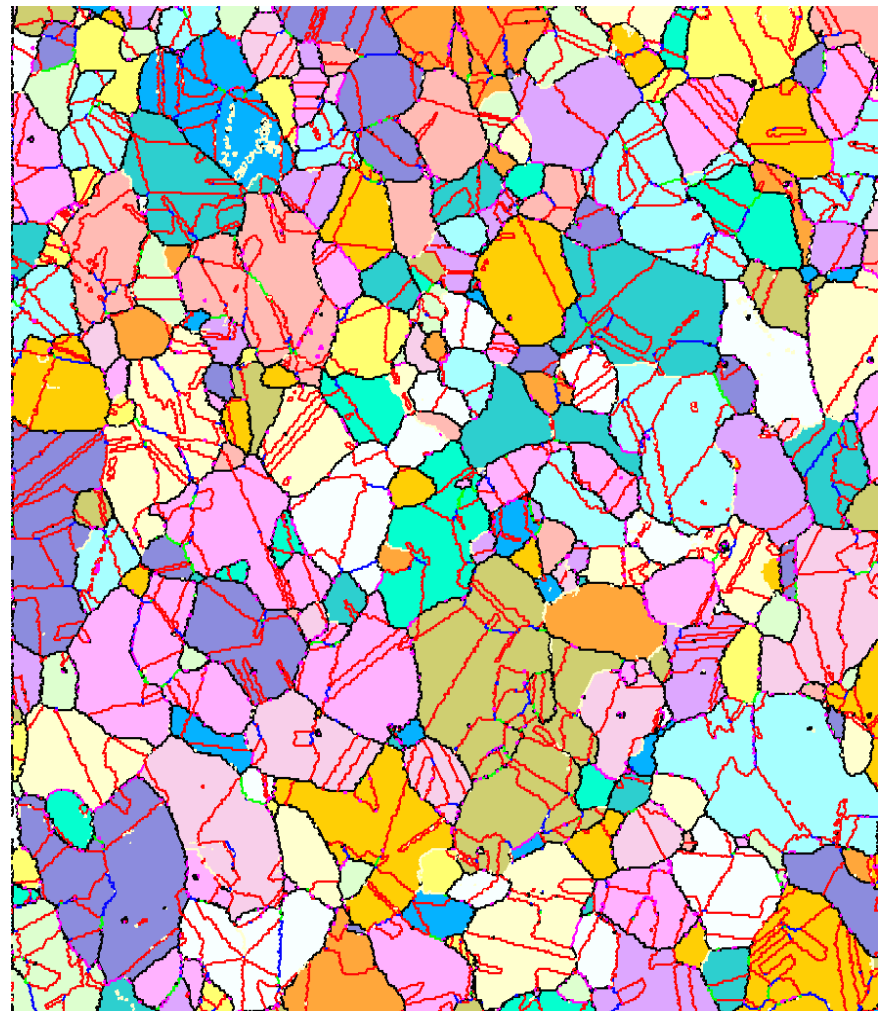


Coincidence Site Lattice (CSL) Boundaries

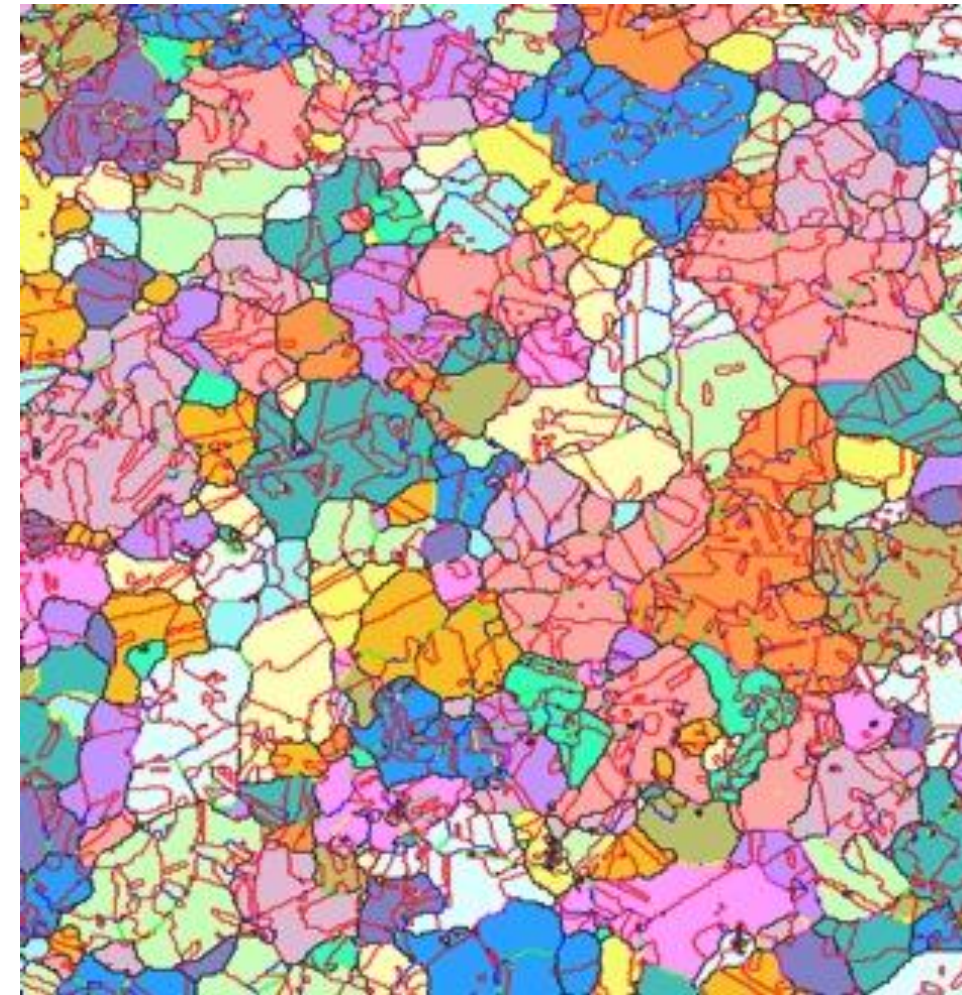


(111) type FCC twins are $\Sigma 3$ type boundaries and are very stable.

The networks are qualitatively and quantitatively different in normal and engineered materials (ones containing a high fraction of $\Sigma 3$'s)



300 μm Conventional Material, $f = 0.49$

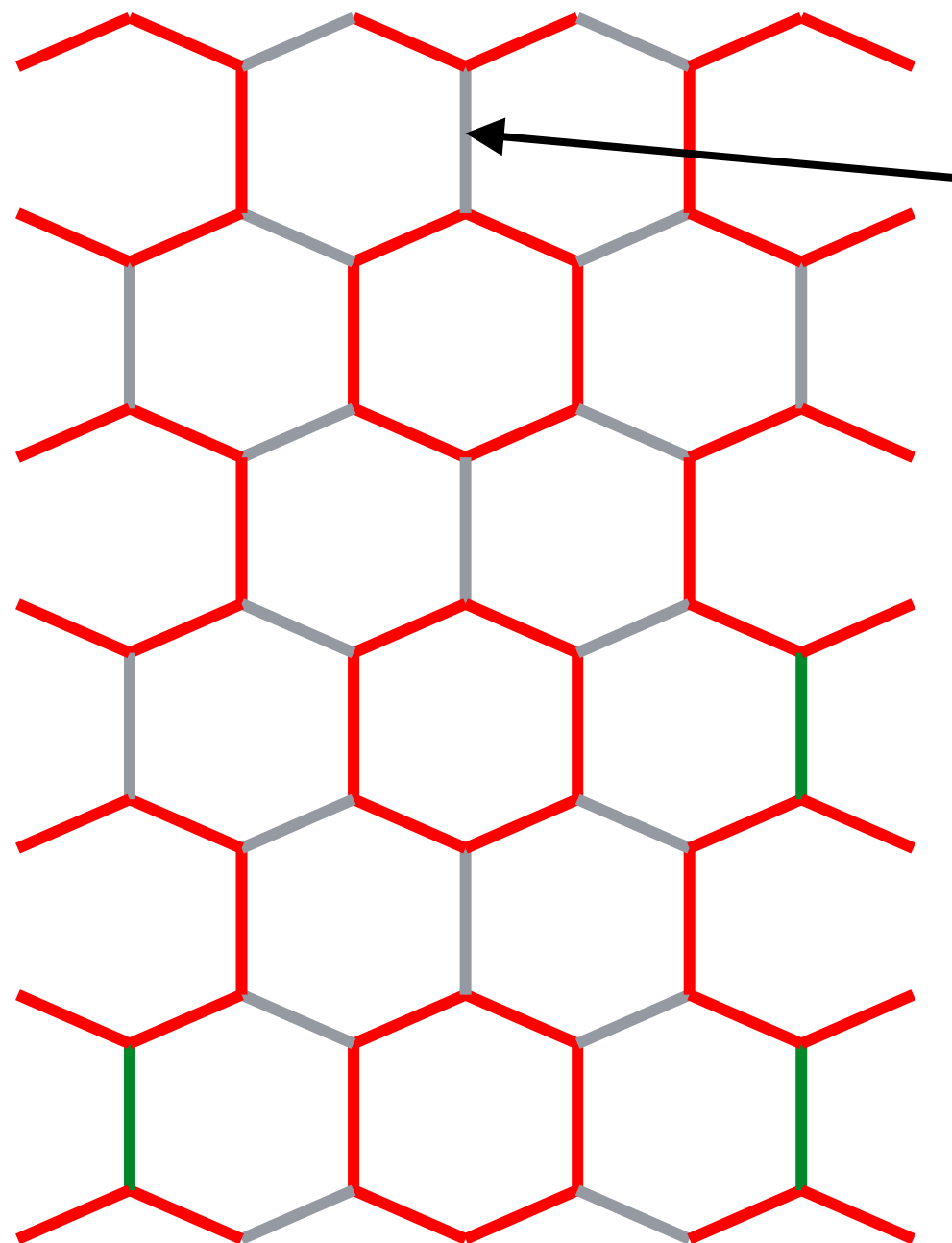


300 μm Engineered Material, $f = 0.60$

- Mostly flat S3's, twinning back-and-forth on the same {111} planes
 - Simple intra-domain networks
 - Few distinct orientations in each domain
- Highly complex intra-domain networks
 - More frequent inter-domain special boundaries
 - Many distinct orientations in each domain

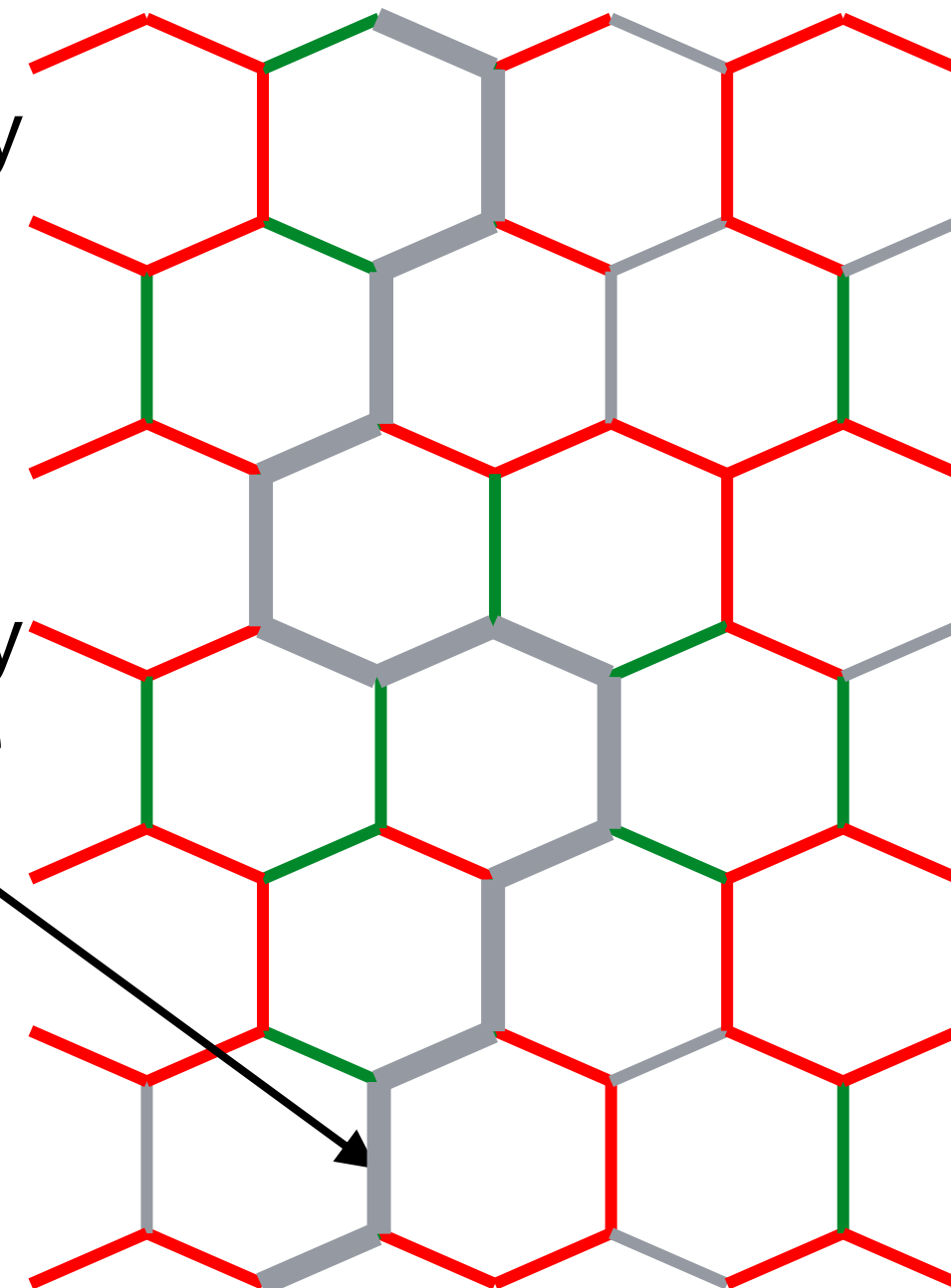
Key concept: The grain boundary *network* is essential component in a materials behavior

**Consider two grain boundary networks.
Suppose red boundaries are strong, blue boundaries are weak.**

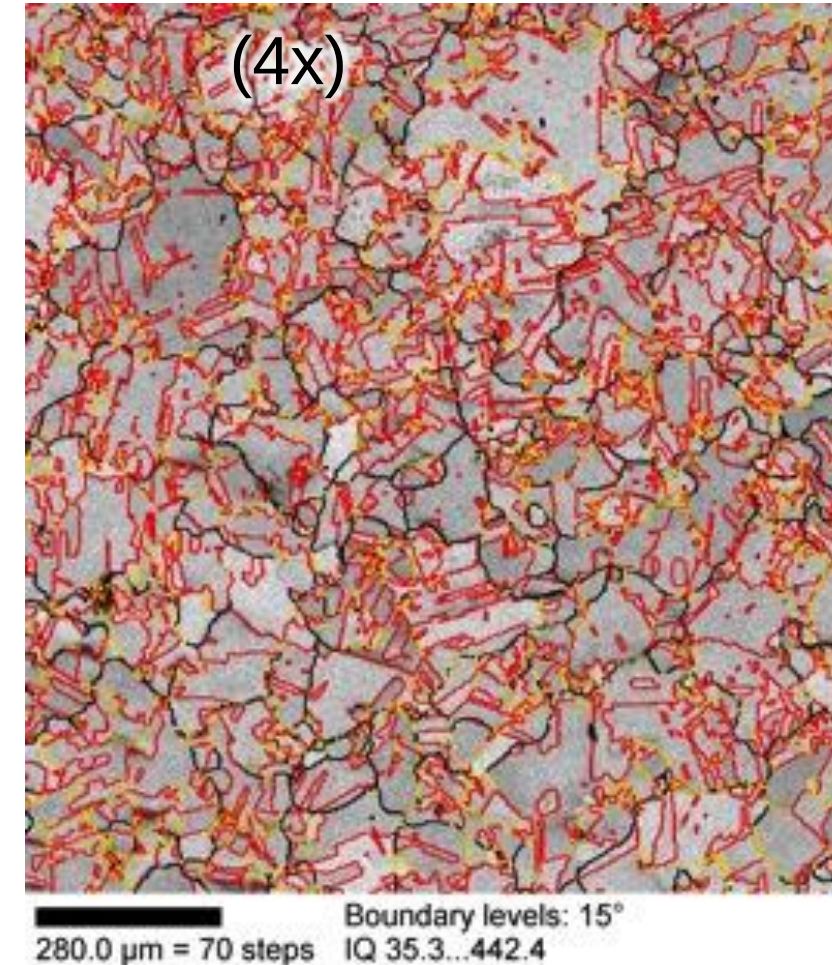
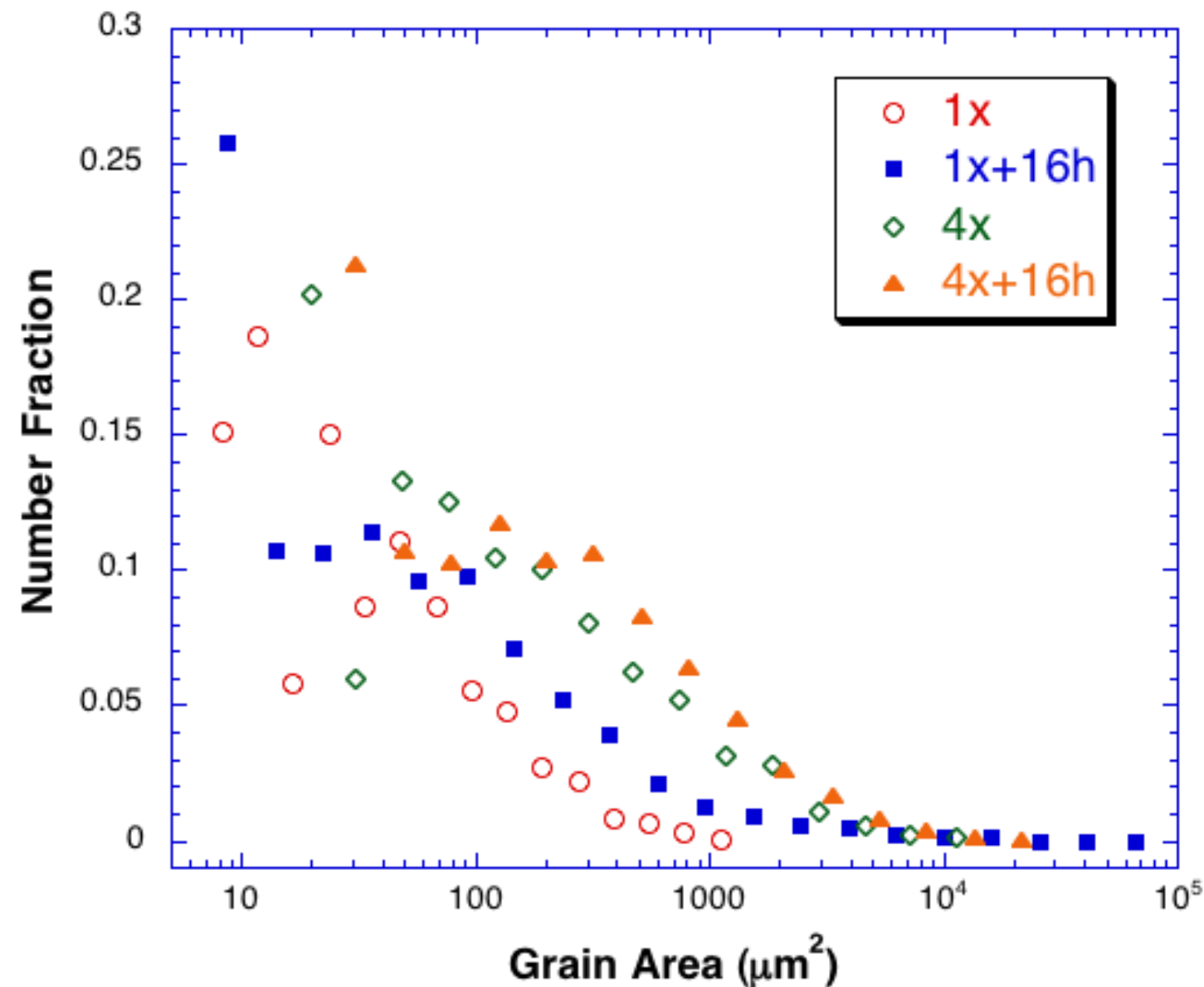


If this boundary fails, not much happens.

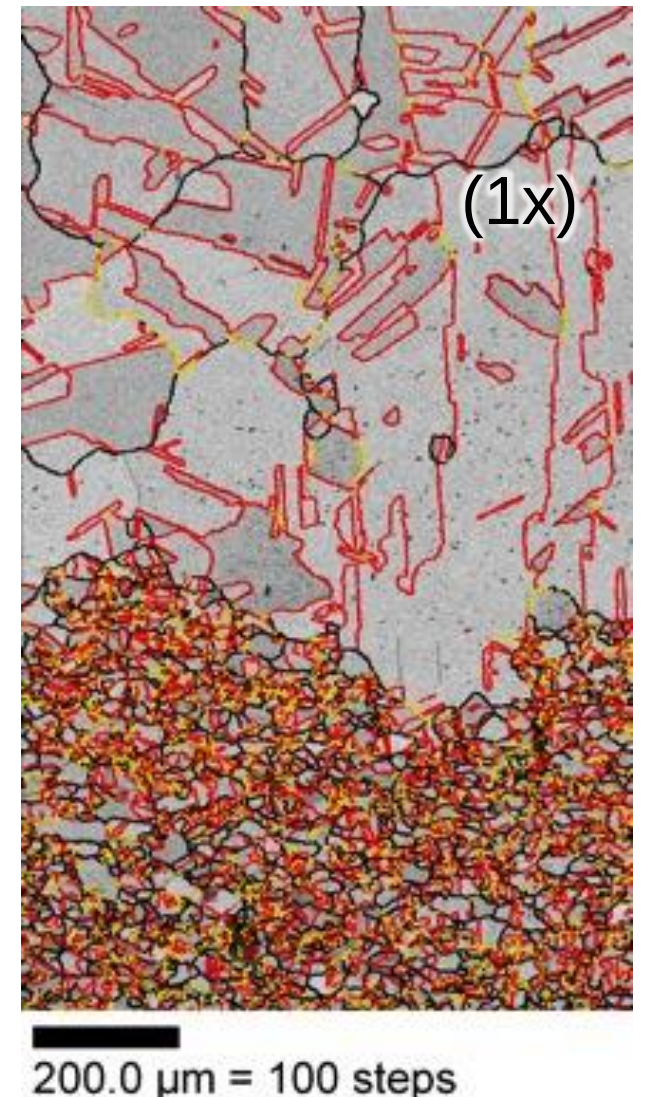
If this boundary fails, the whole material can come apart.



Grain coarsening kinetics are considerably slower in high special boundary content microstructures



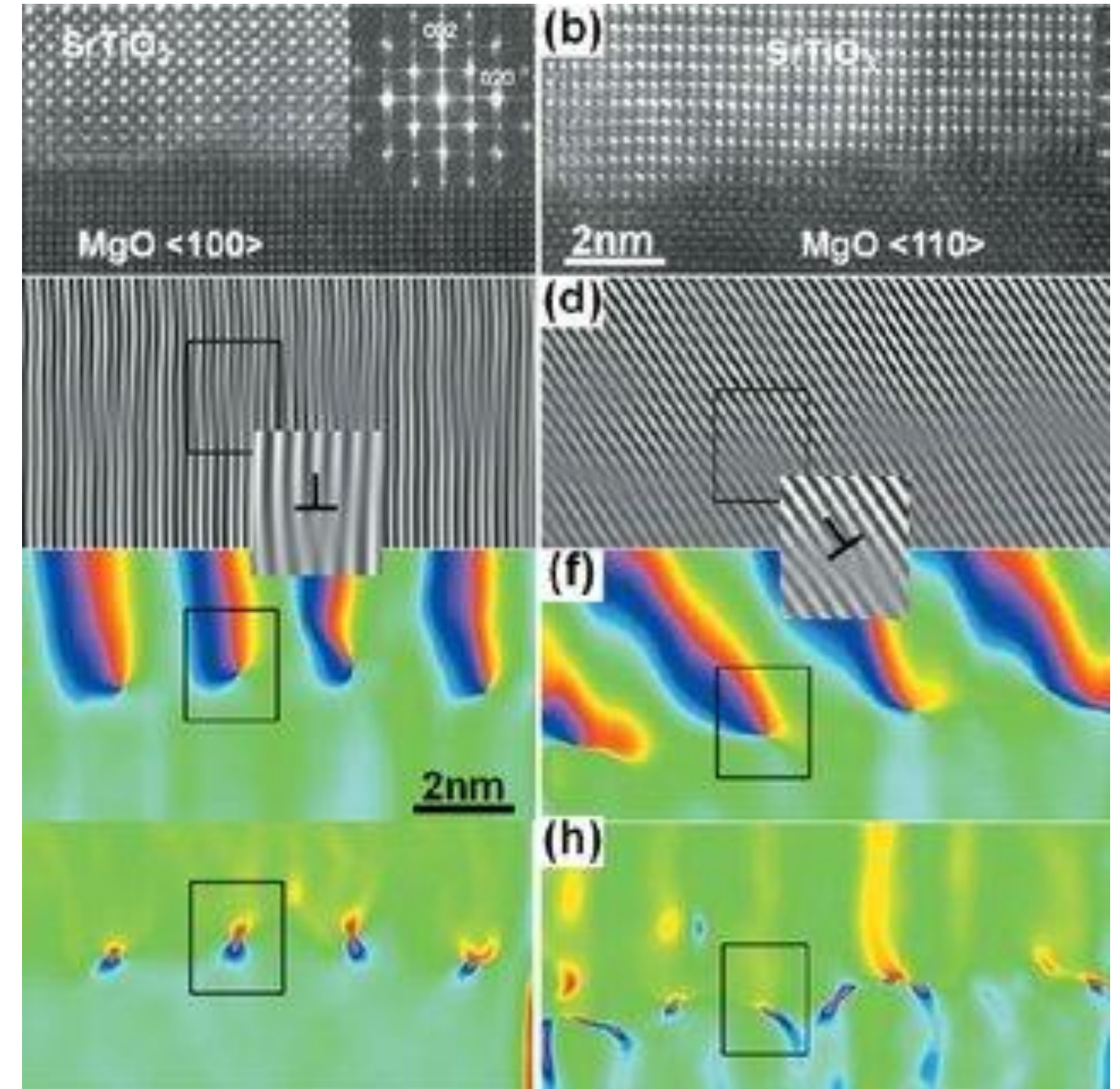
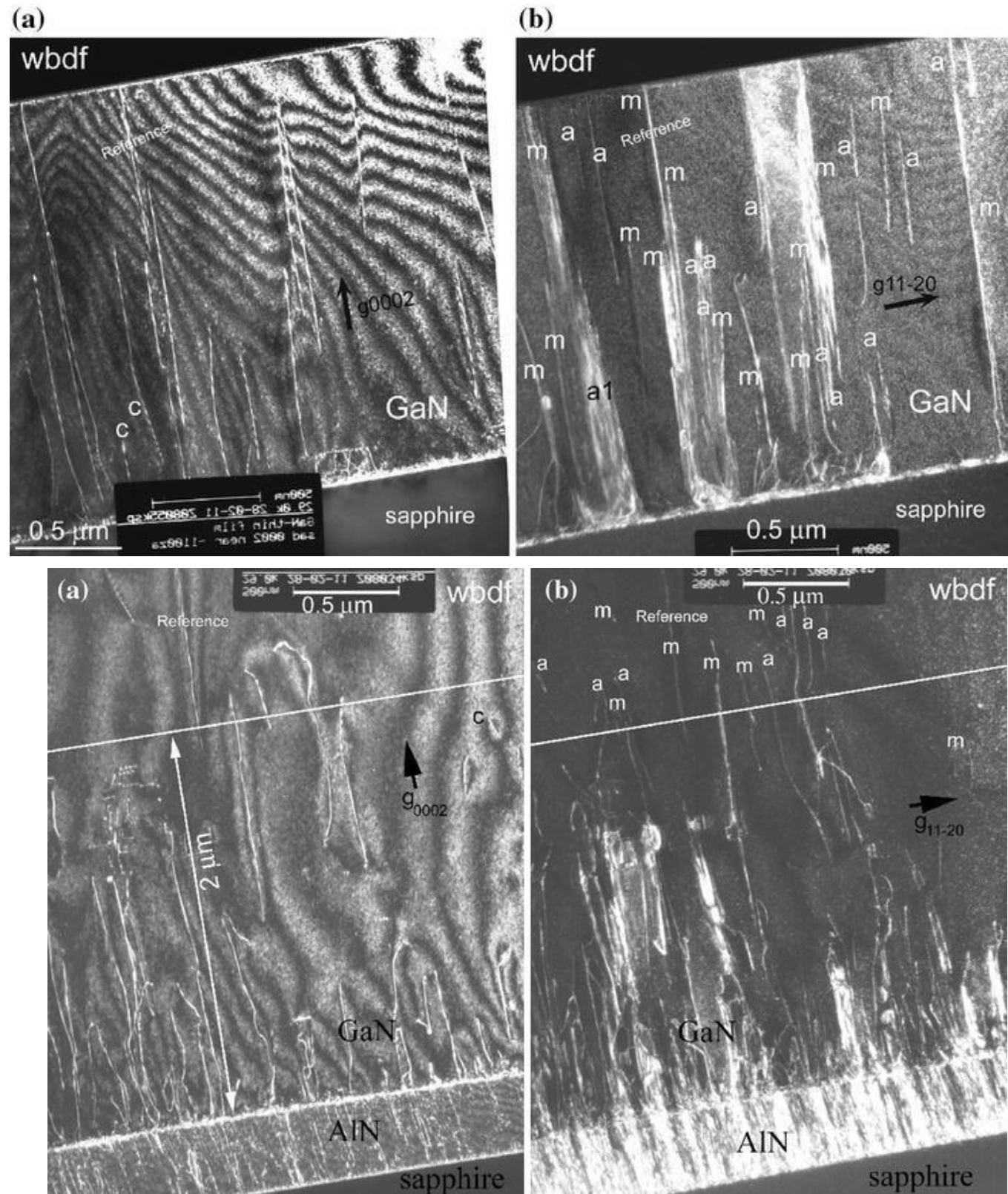
High-purity
Cu at 500°C



Data suggests that special boundaries pin the (more mobile) random boundaries at triple junctions

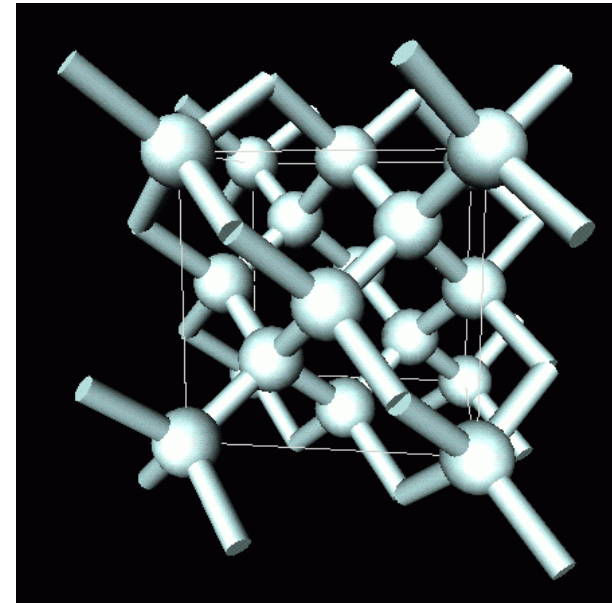
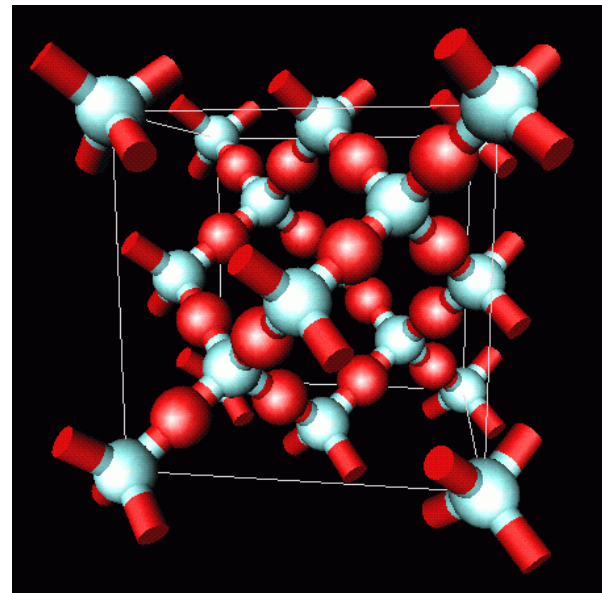
Schwartz, King, Kumar; *Scripta Materialia*, 54 (2006)

Misfit Dislocations



Amorphous

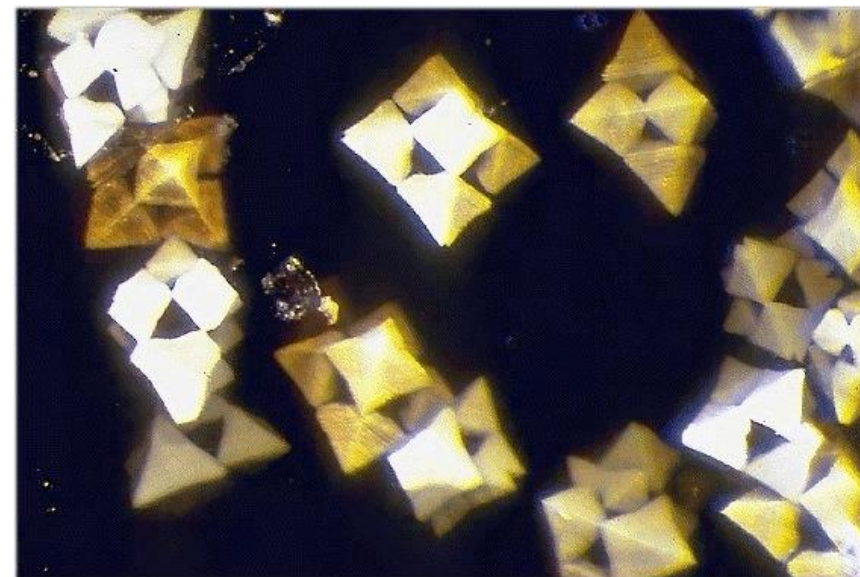
Crystalline silicon



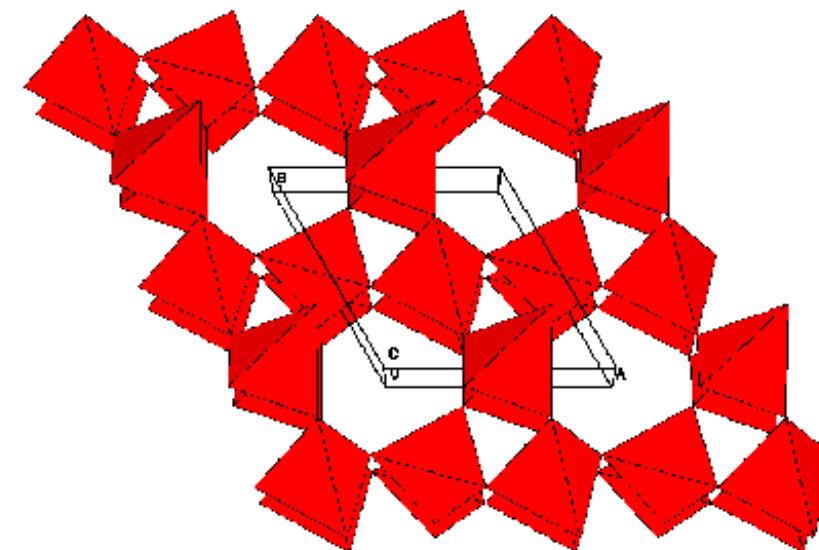
Quartz



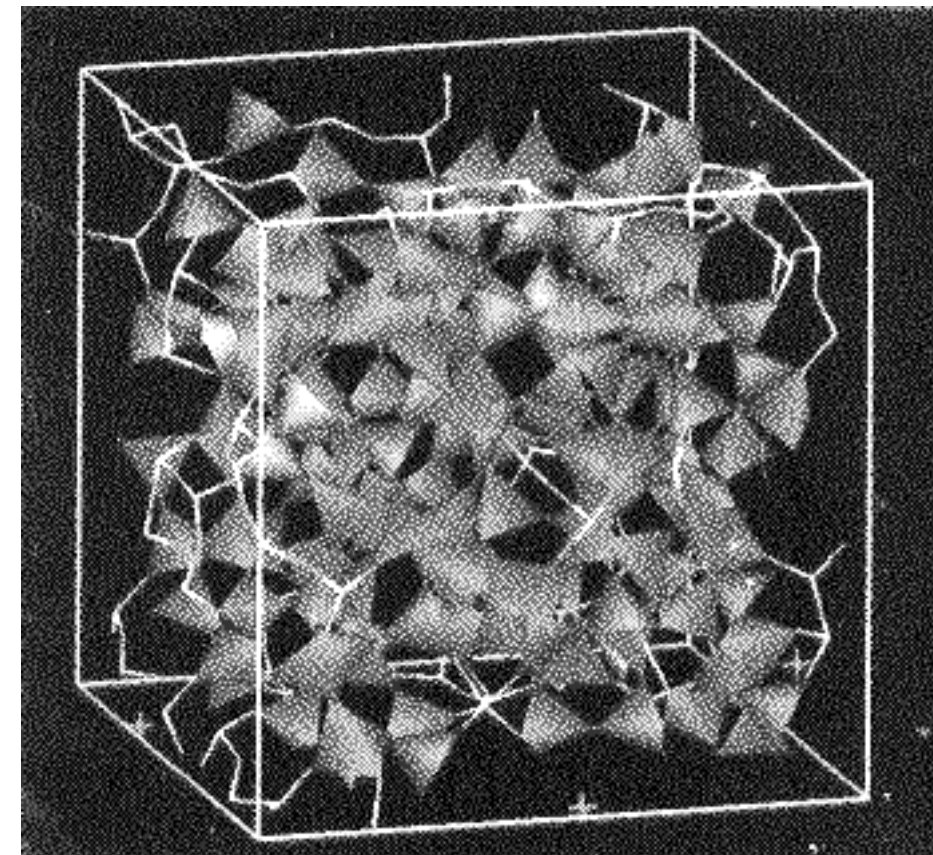
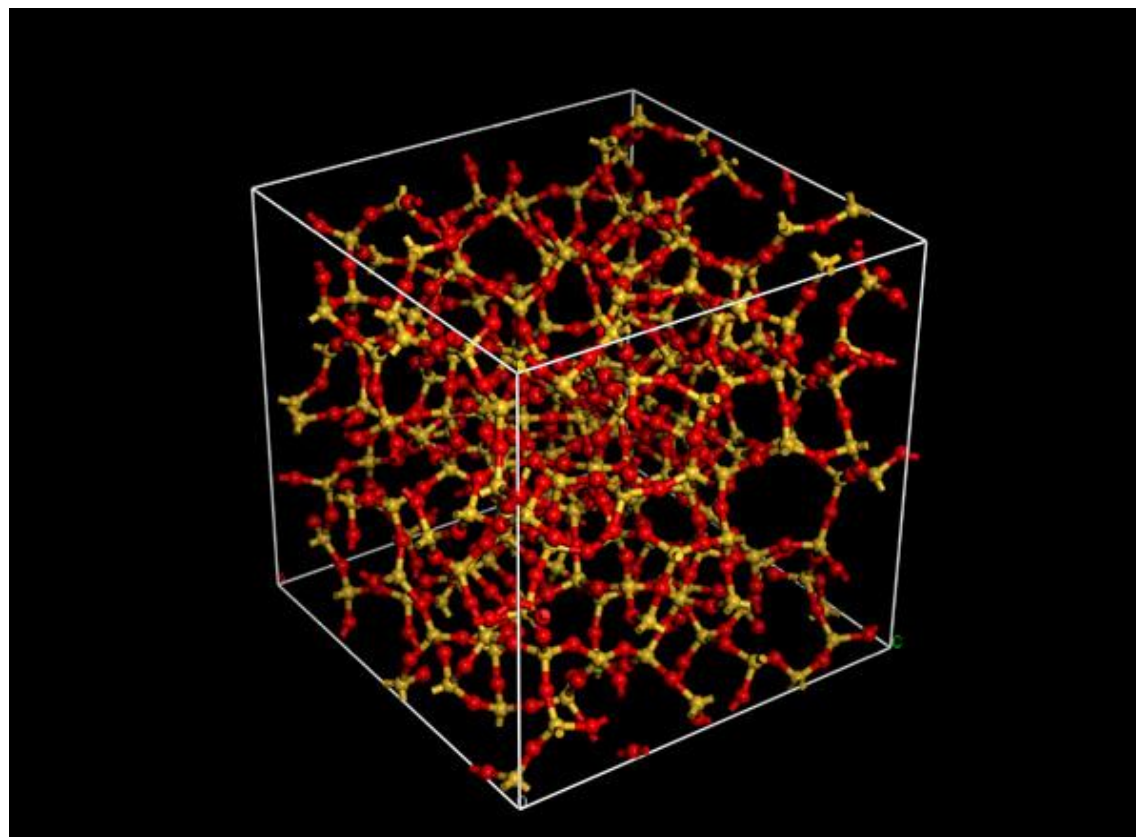
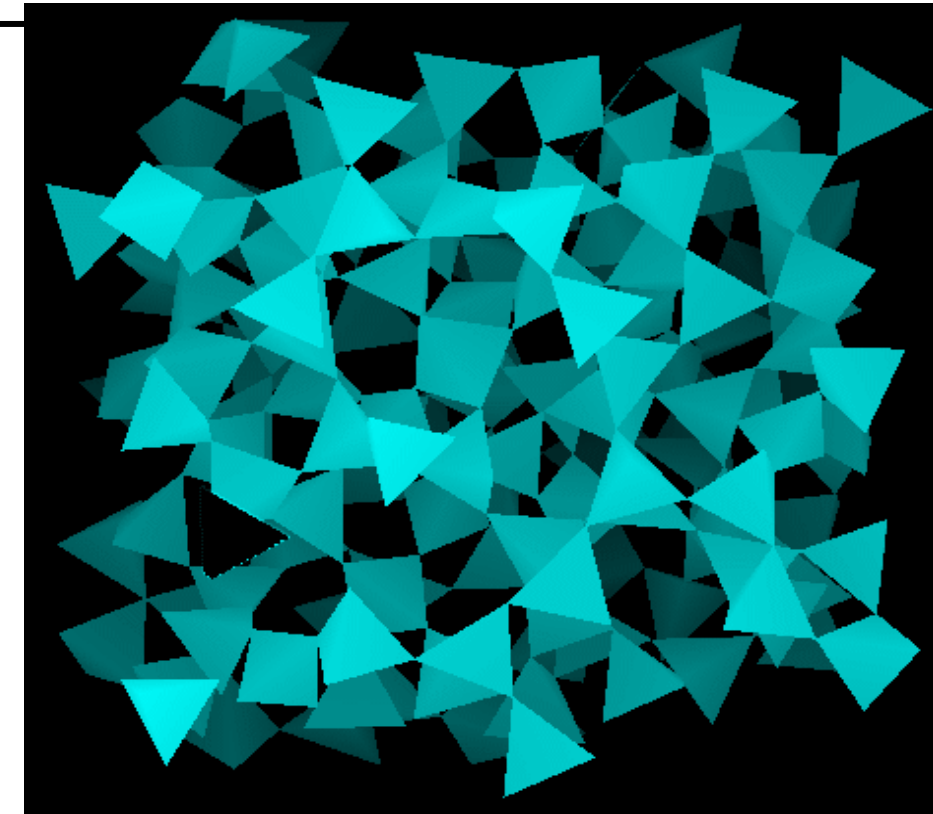
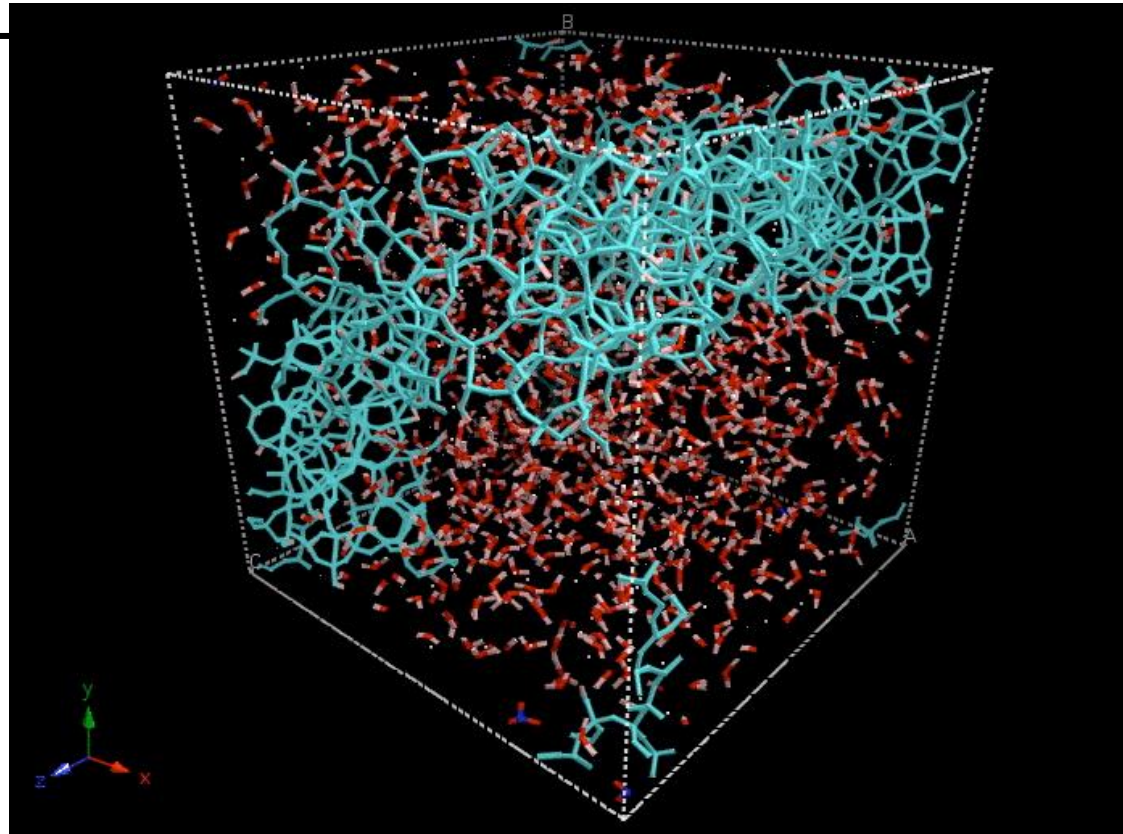
Cristobalite: SiO_4 tetrahedron
on a diamond lattice



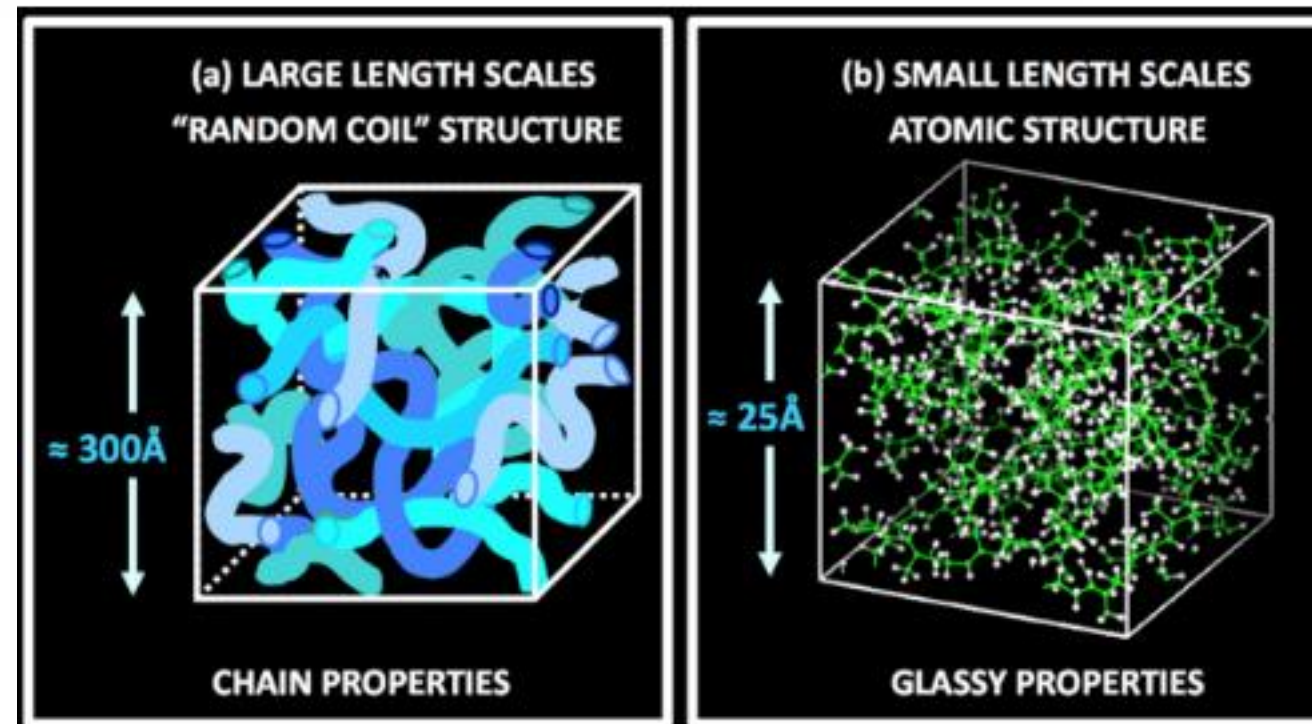
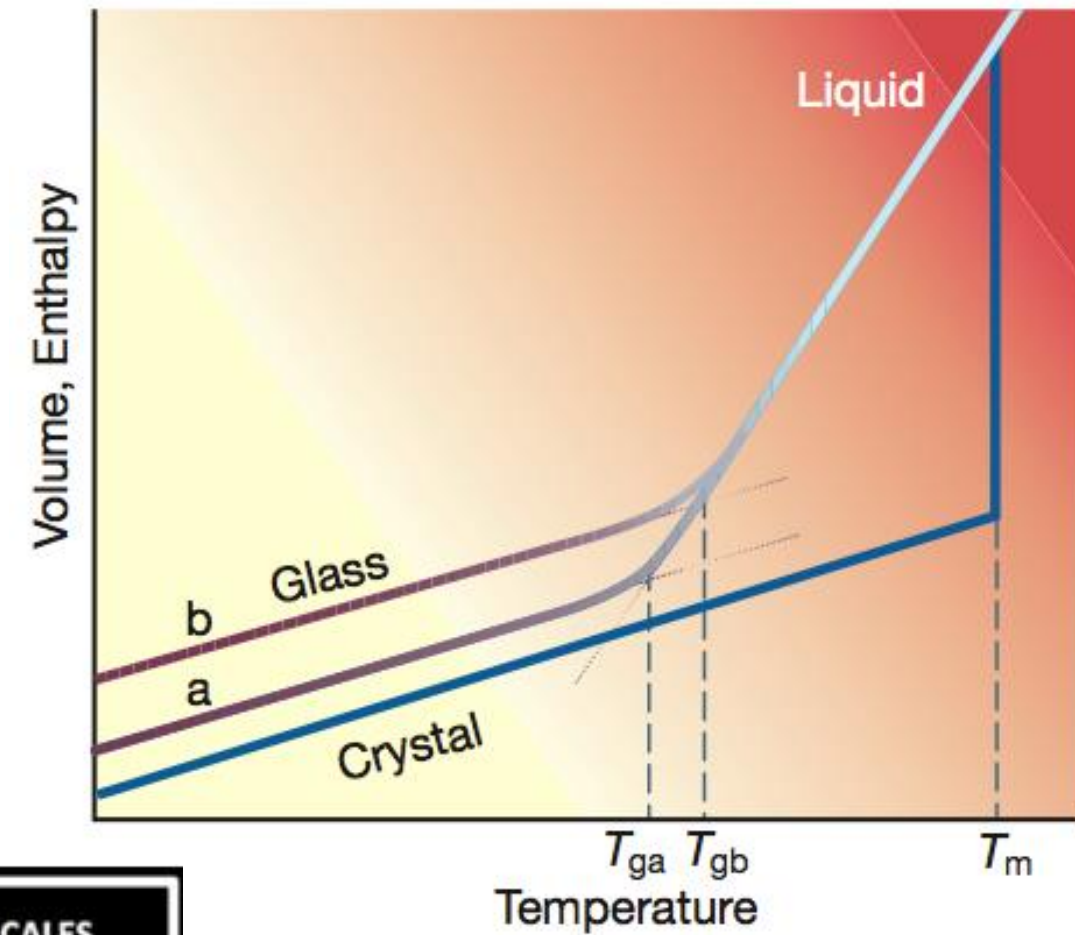
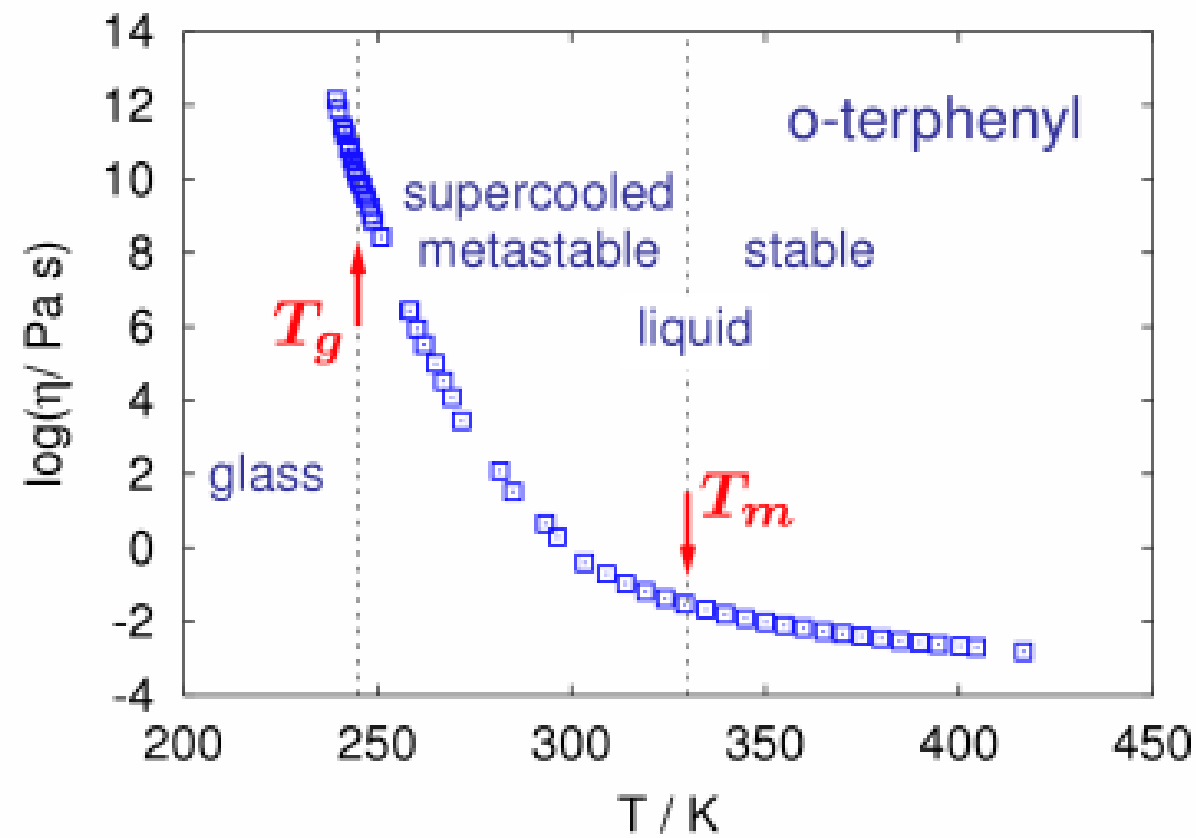
Rhombohedral cell



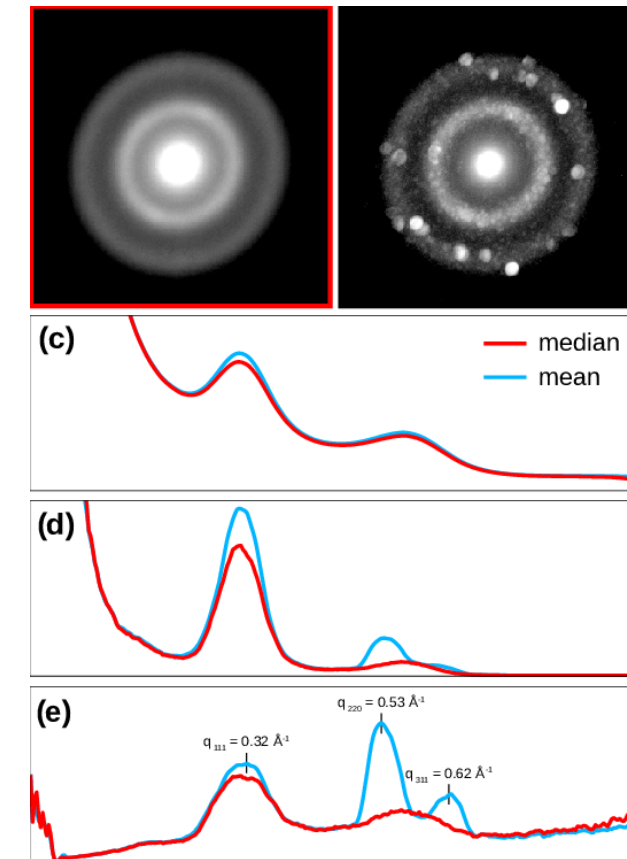
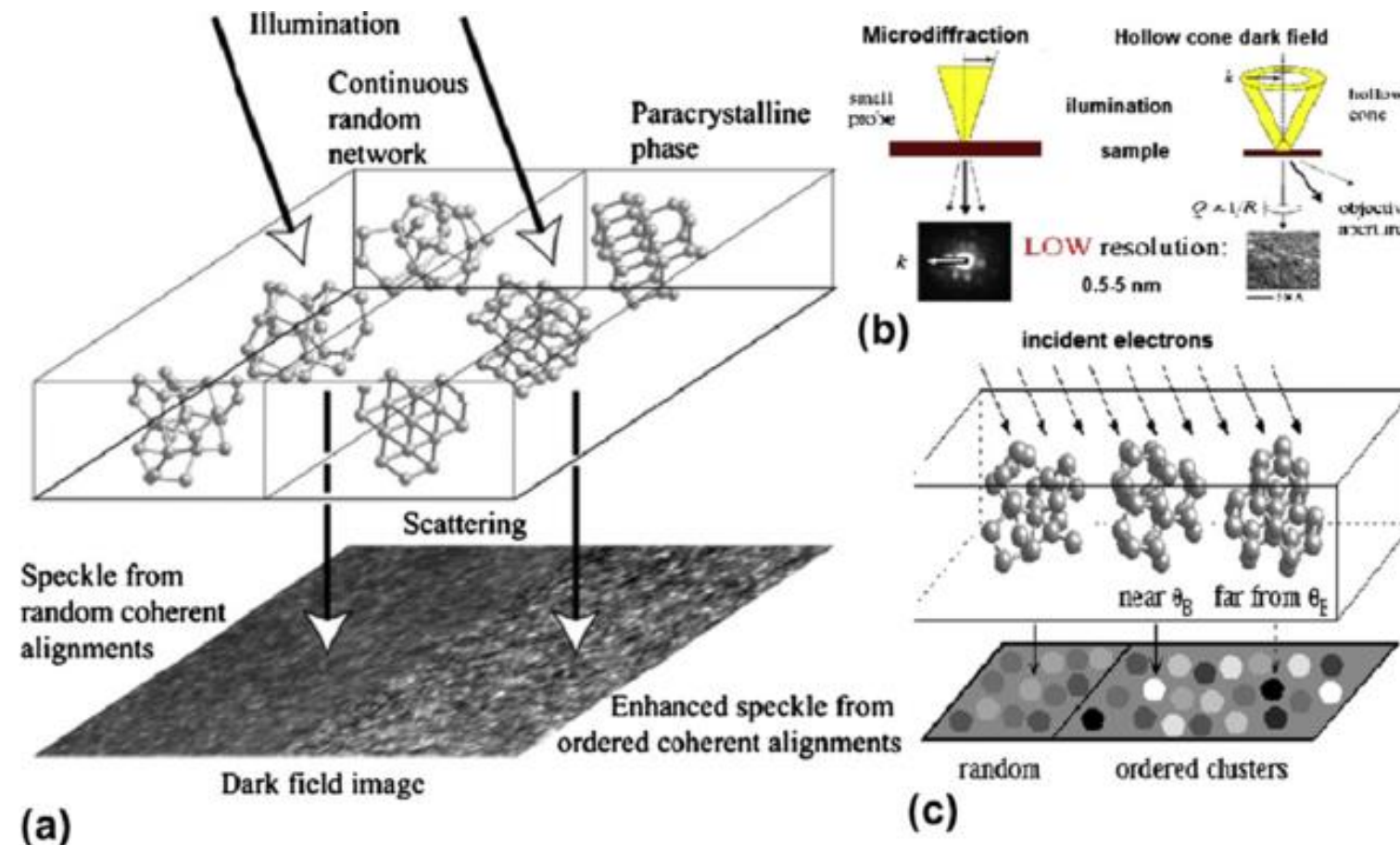
Amorphous: glass



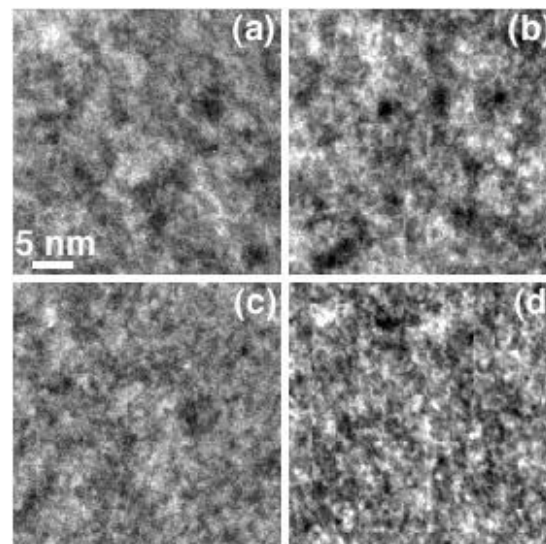
The Glass Transition T_g



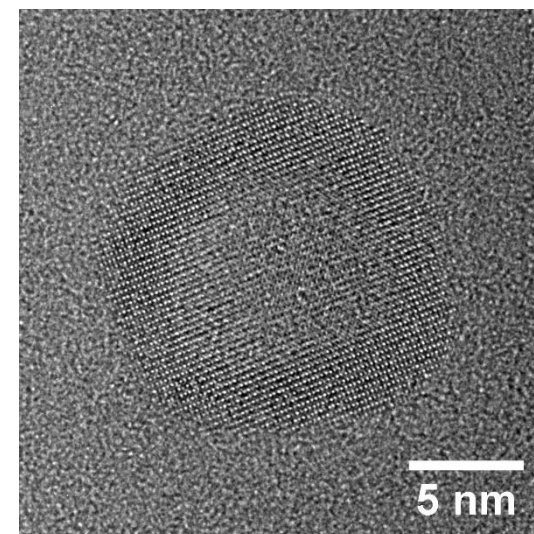
Amorphous Materials: Fluctuation Electron Microscopy



Darkfield TEM images

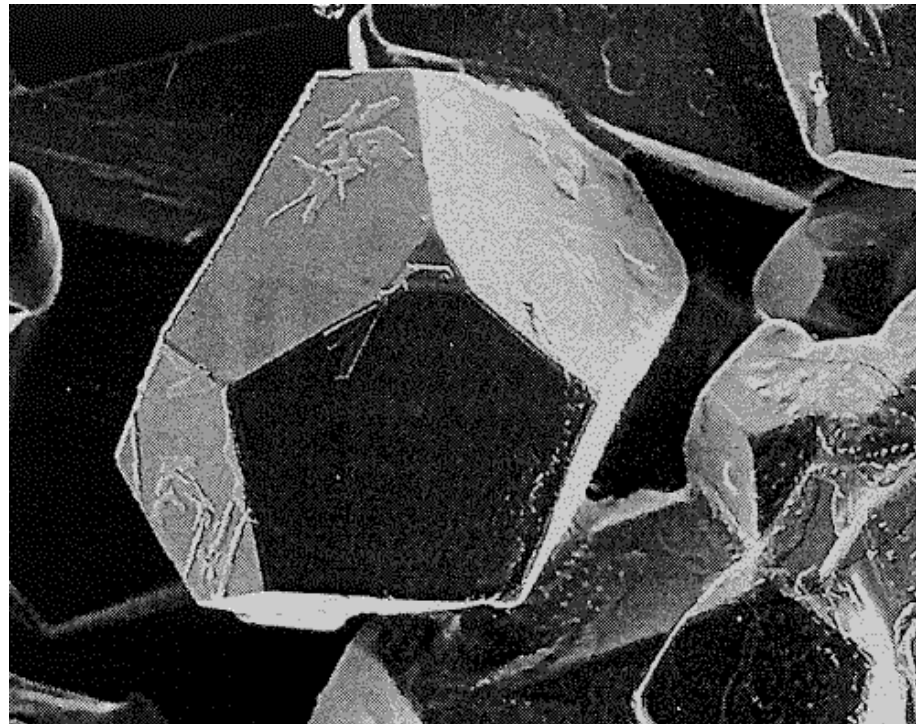


HRTEM image

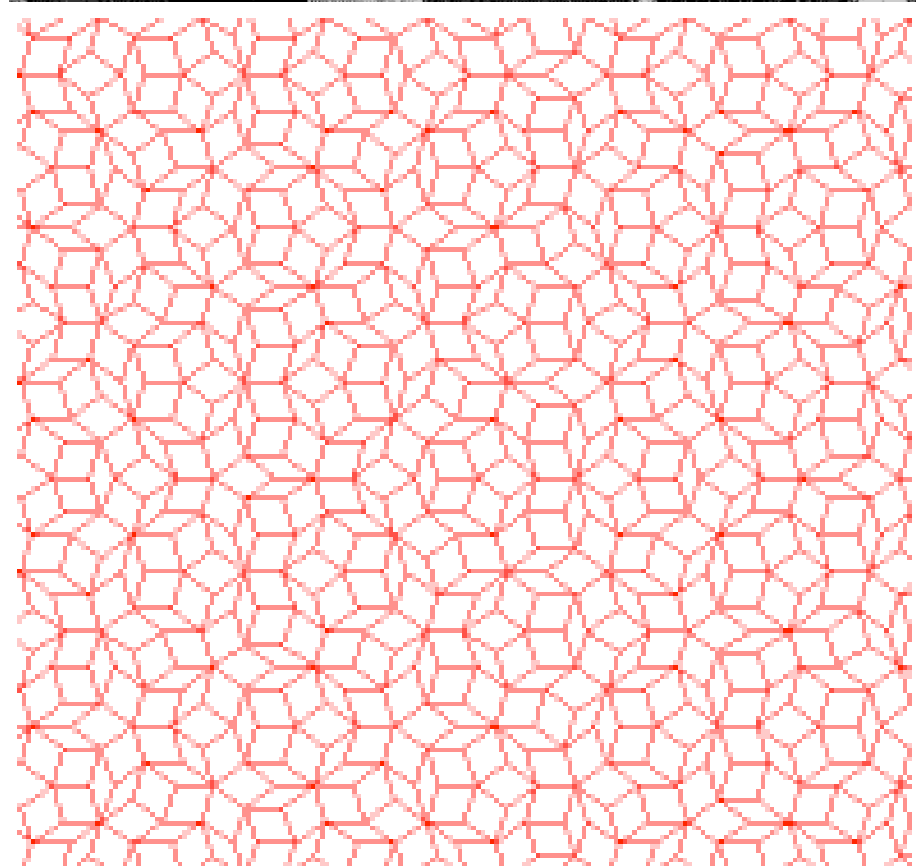
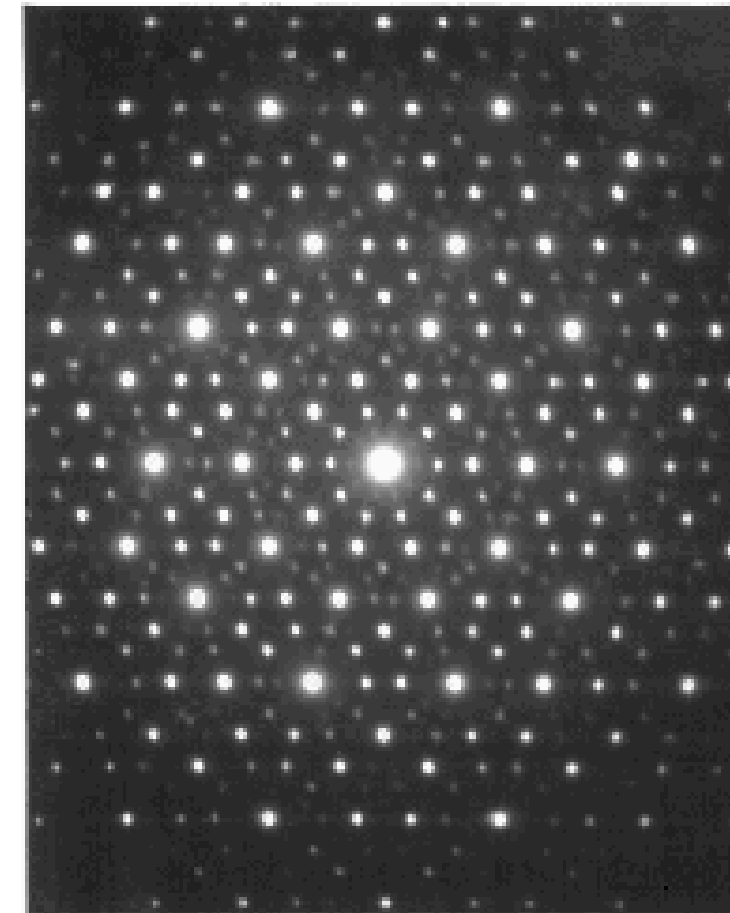


Fluctuation electron microscopy (FEM) is electron scattering technique for measuring nanometer scale order in amorphous materials. **Fluctuations** in the local scattering intensity reveal internal atomic arrangements on short range and medium range (nanometer-scale) order

Quasicrystals

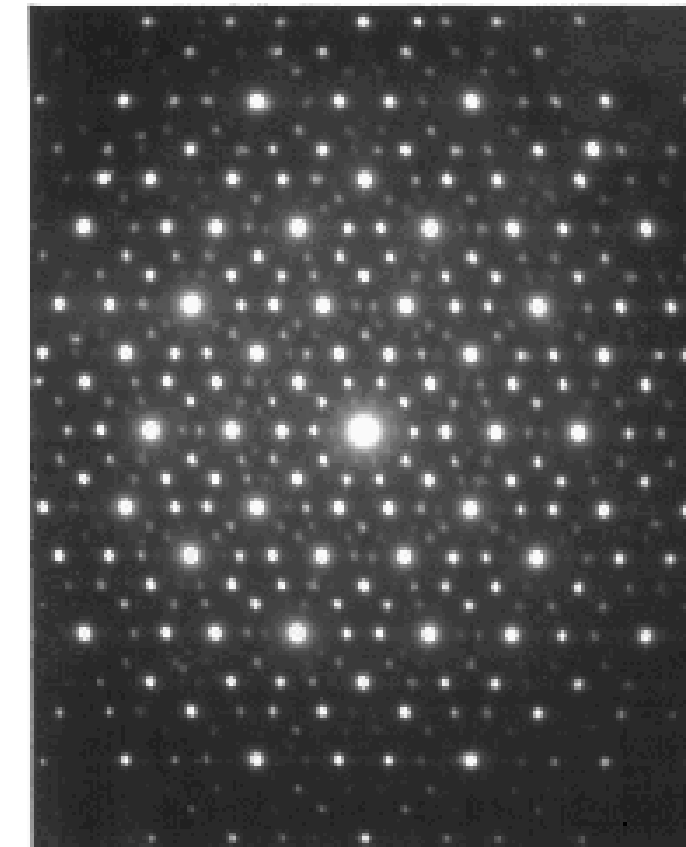
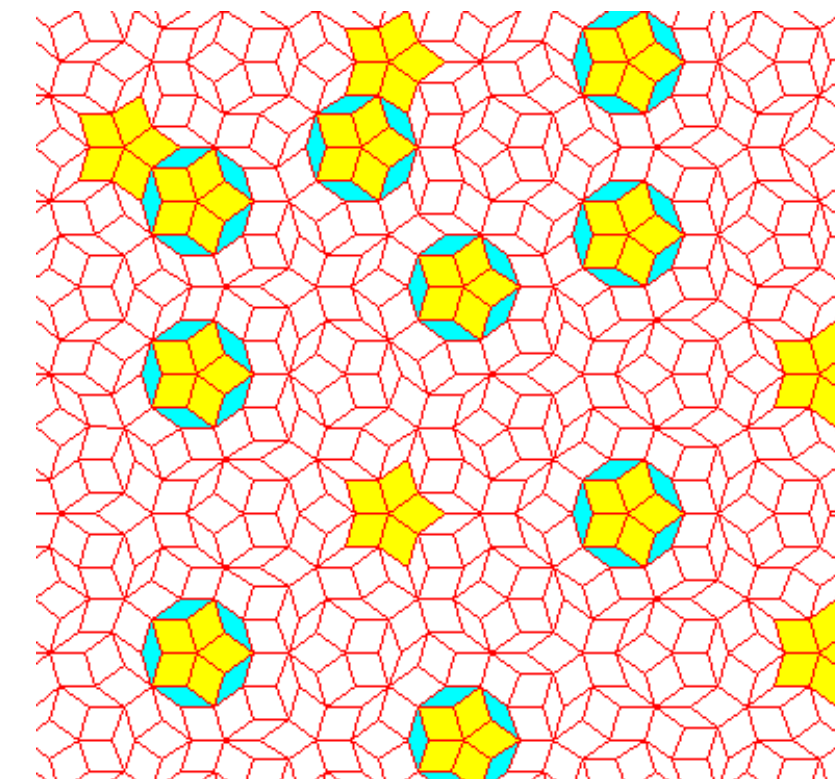
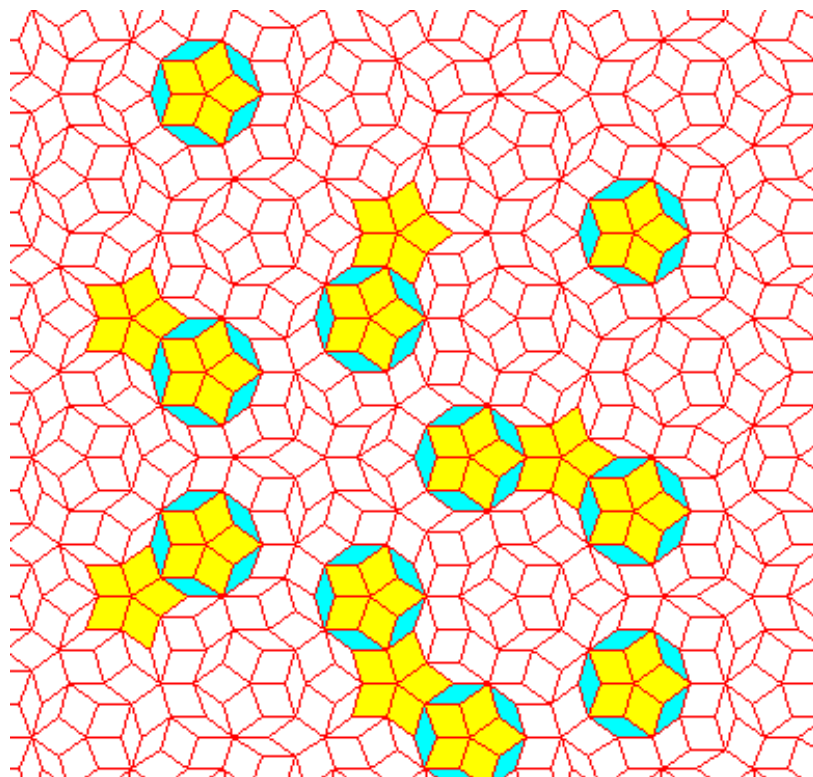
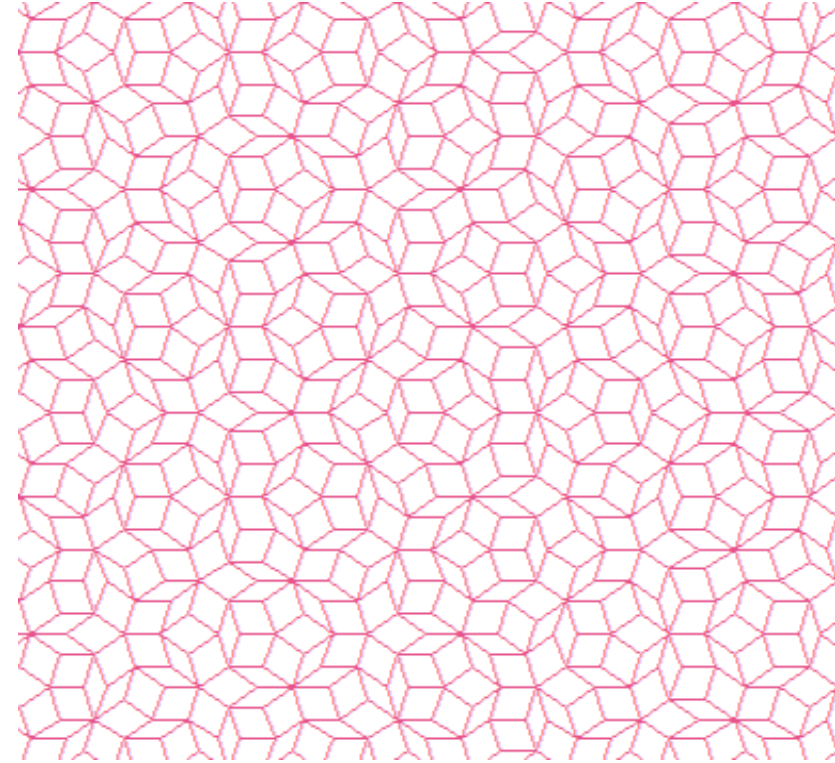
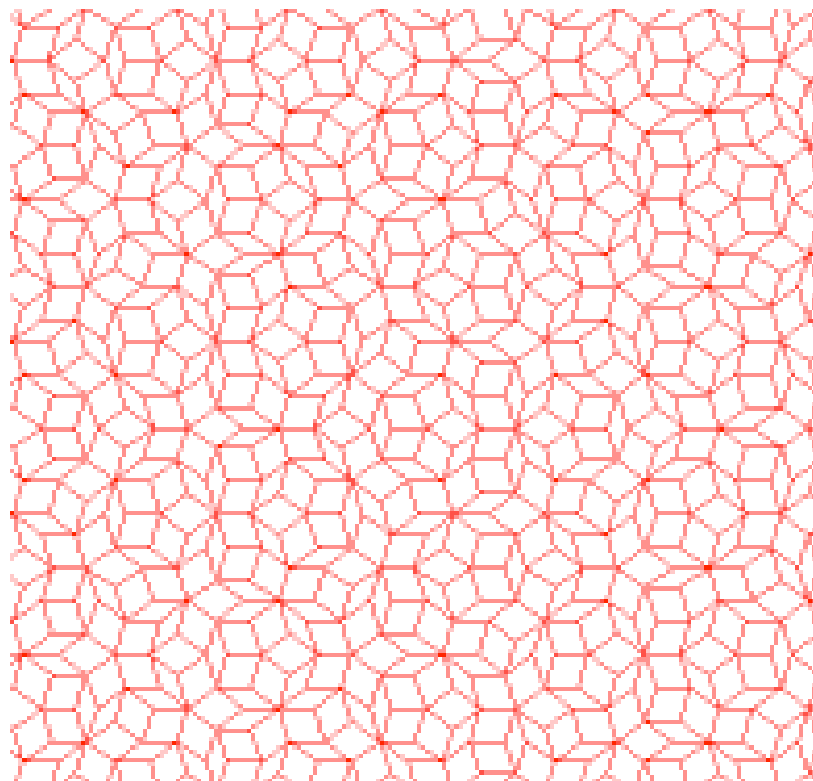


AlCuFe



Dan Shechtman
2011 Nobel Prize in chemistry

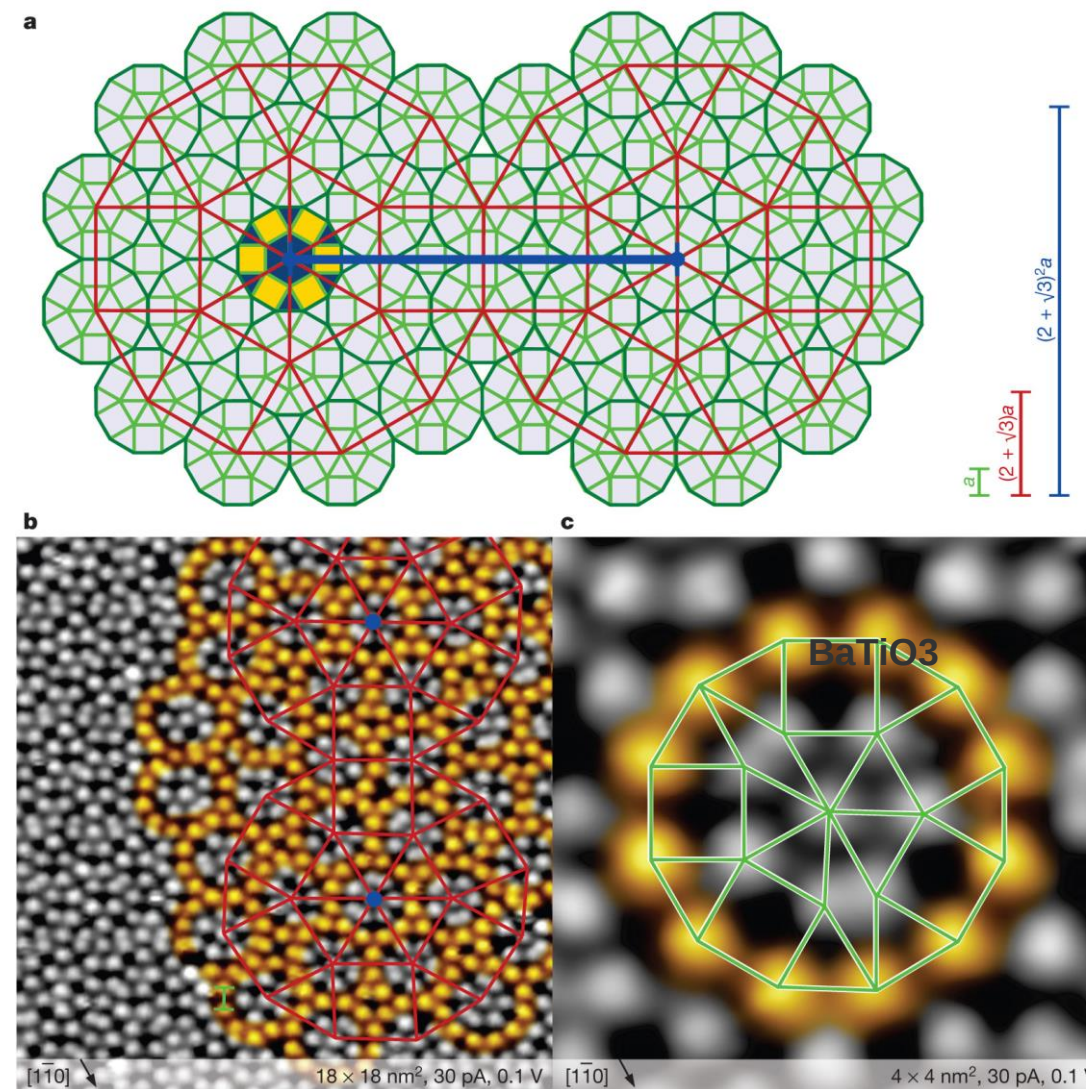
Quasicrystals



Whatever the region of the paving, we statistically find the same number of equivalent patterns. In diffraction, we can observe the symmetry of the patterns.

Quasicrystals

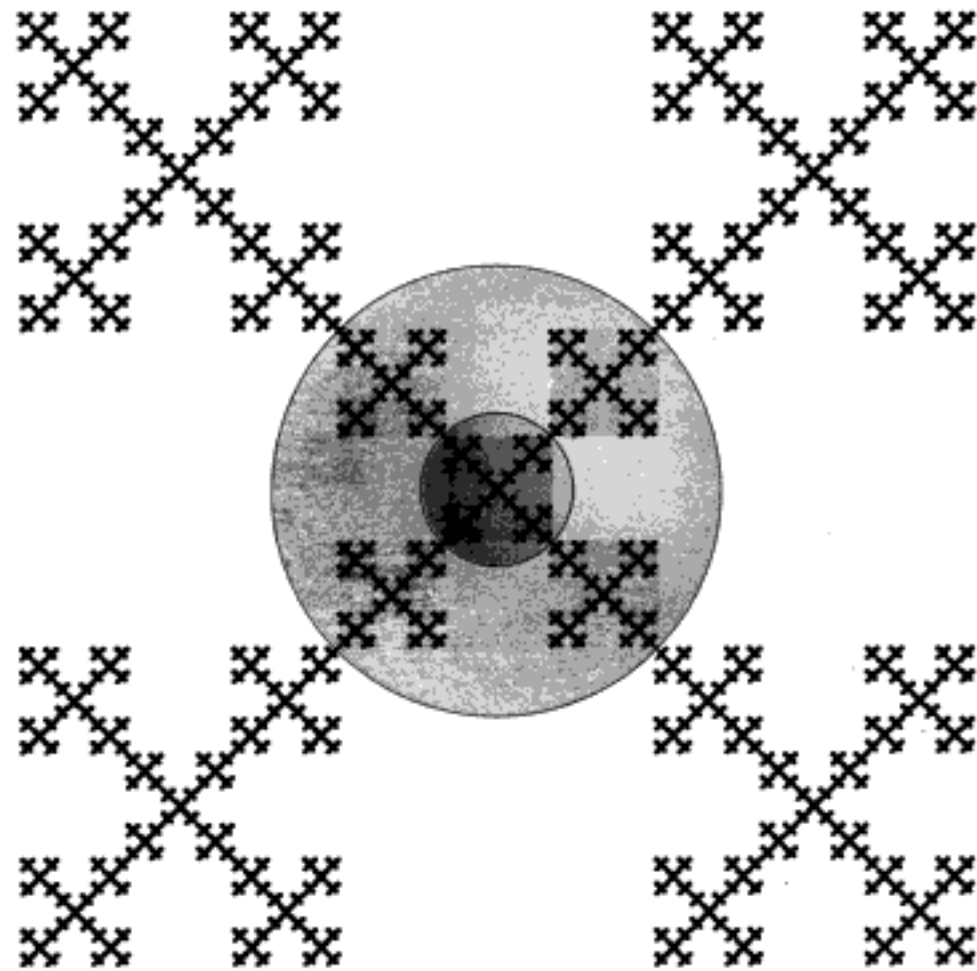
Dodecagonal tiling as measured by STM.



BaTiO₃ on Pt

S Förster *et al.* *Nature* **502**, 215-218 (2013)

Fractals



The mass of a fractal does not increase as r^3 but following a law

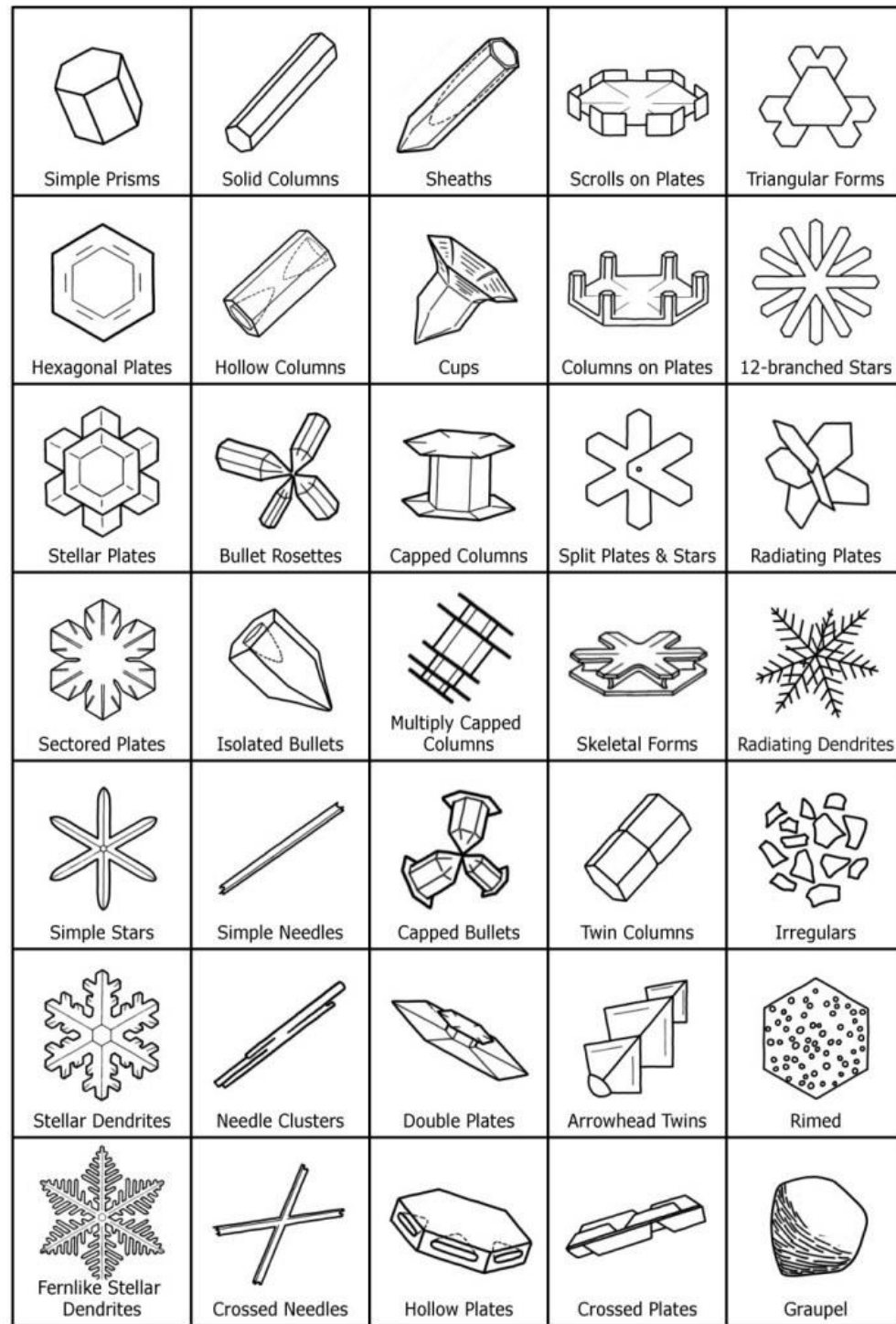
$$M(r) = Ar^d, \quad d < 3$$

Density

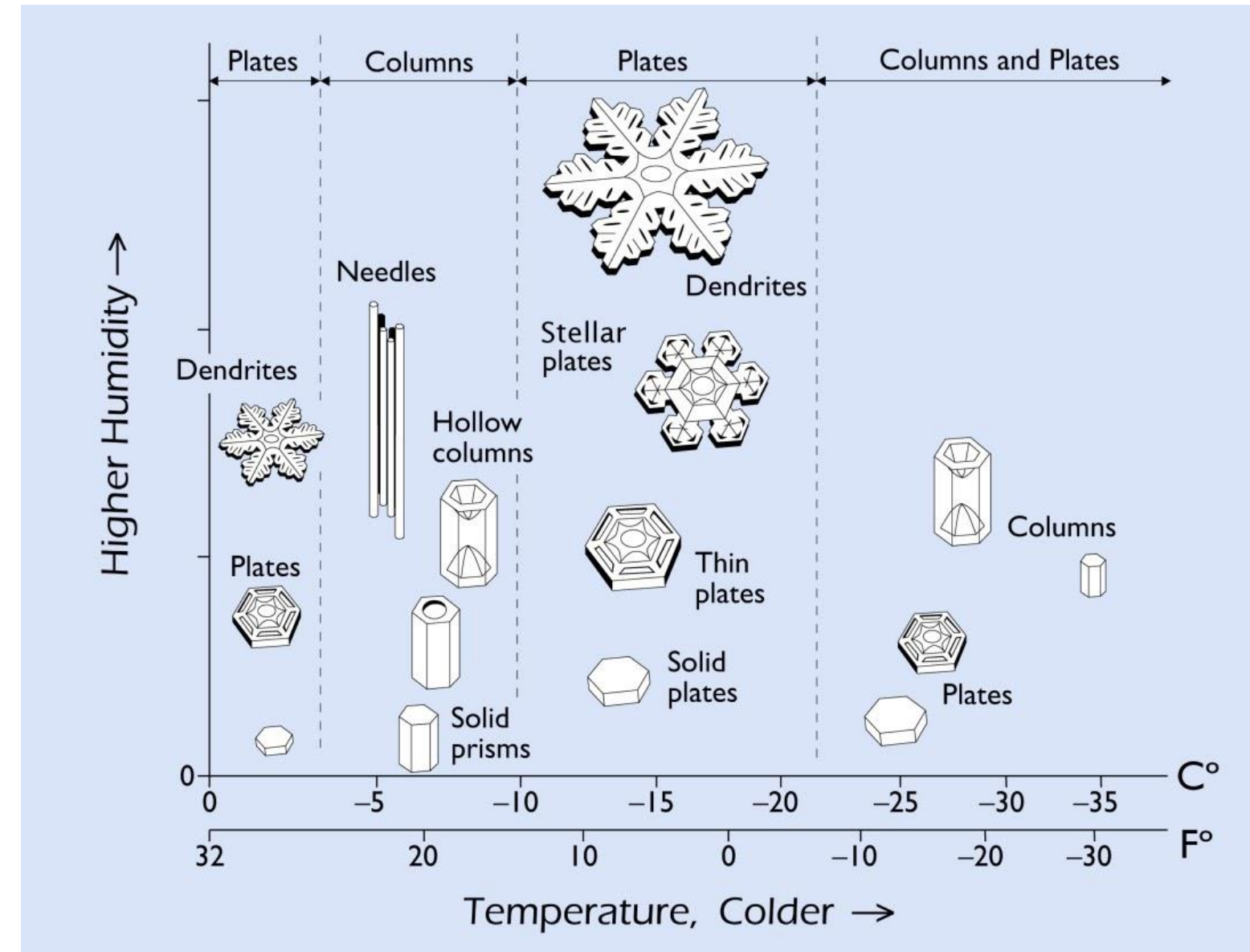
$$\frac{M(r)}{M(r_0)} = \frac{Cr^d}{Cr_0^d}$$

$$\rho(r) = \frac{M(r)}{V(r)} = Cr^{d-3}$$

Fractal Crystals

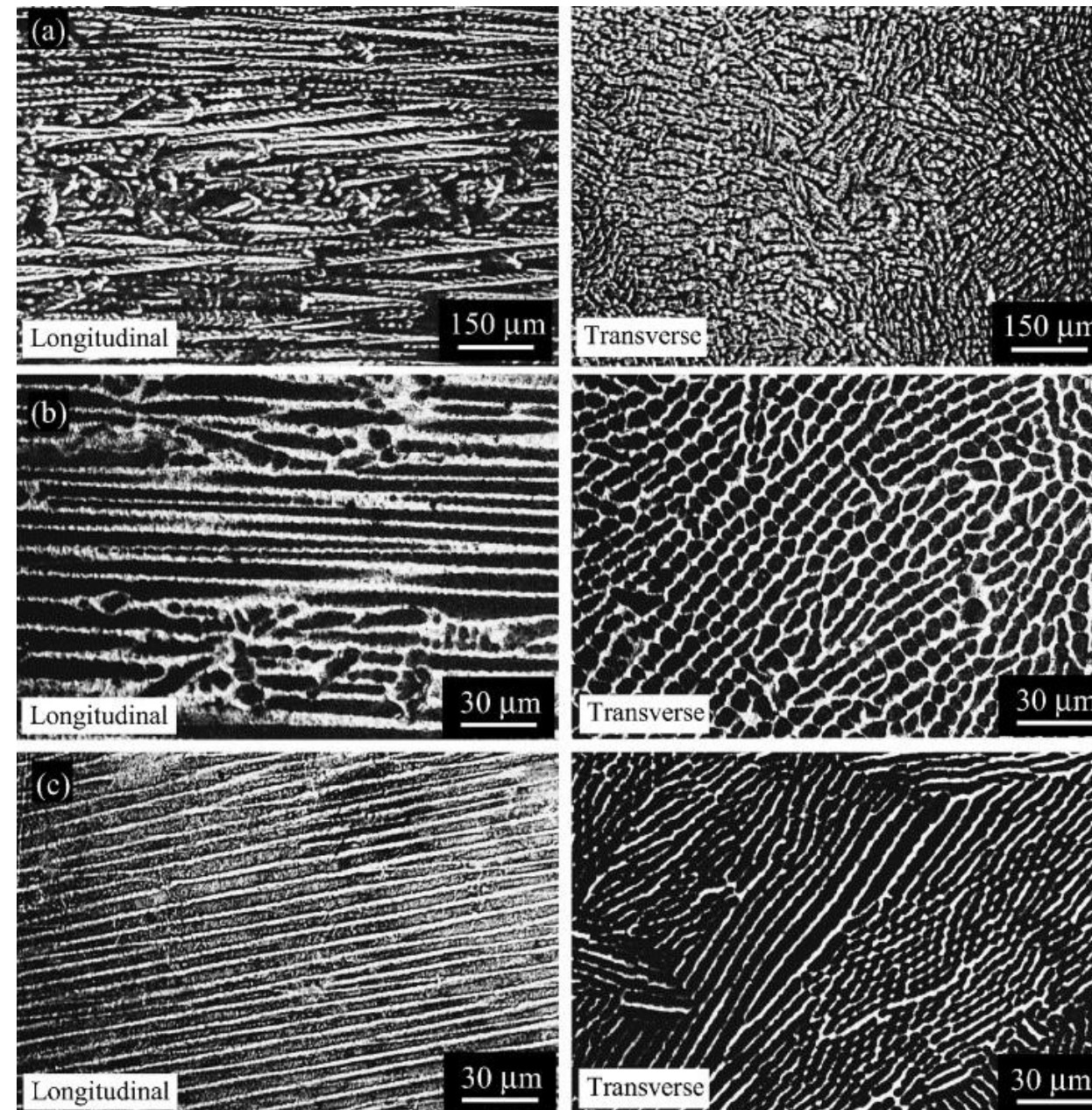
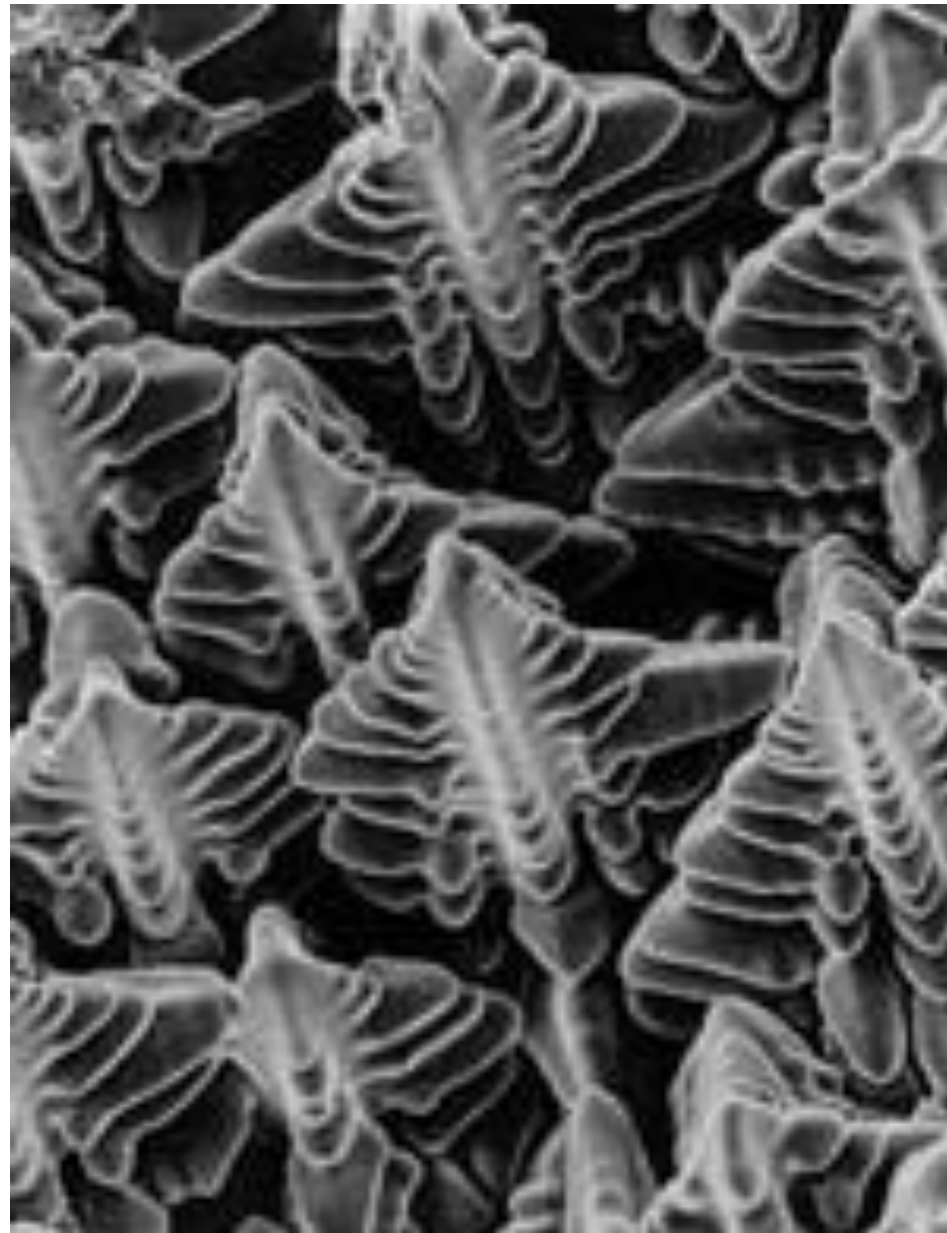


Types of Snowflakes ... SnowCrystals.com



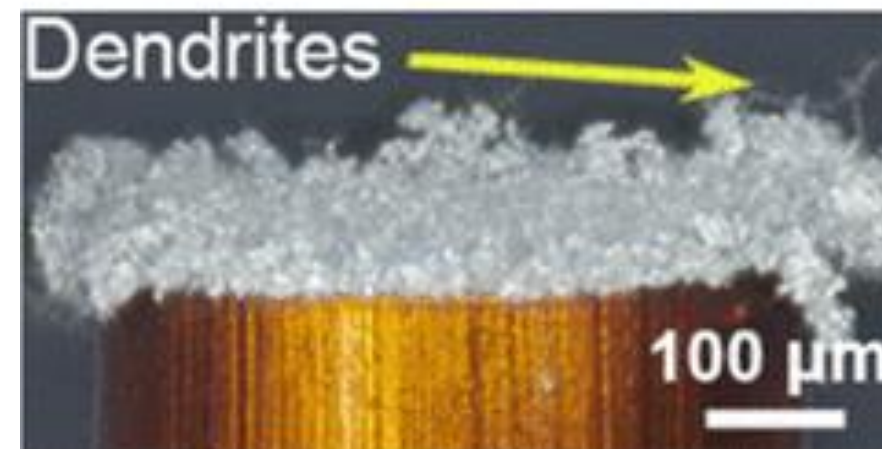
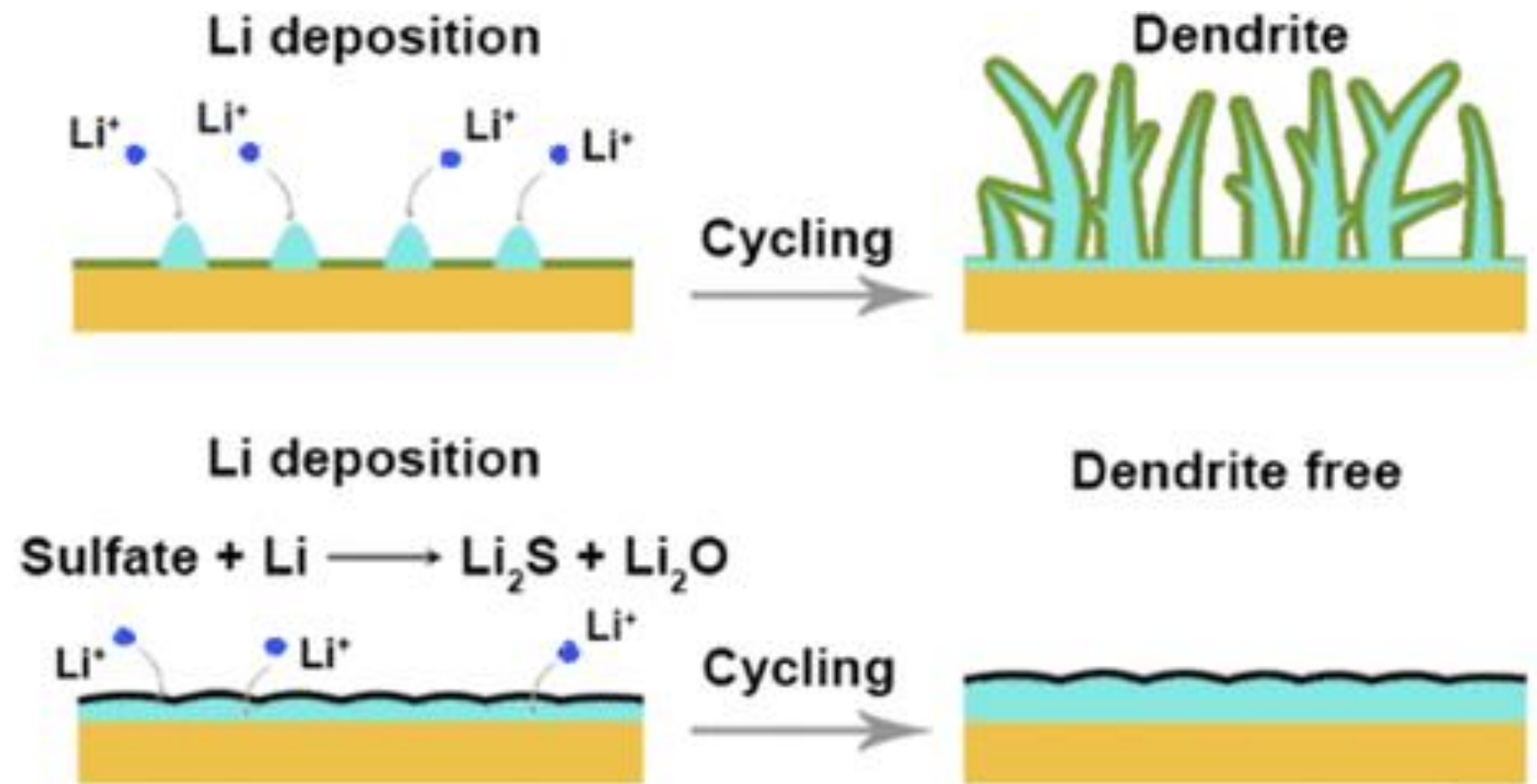
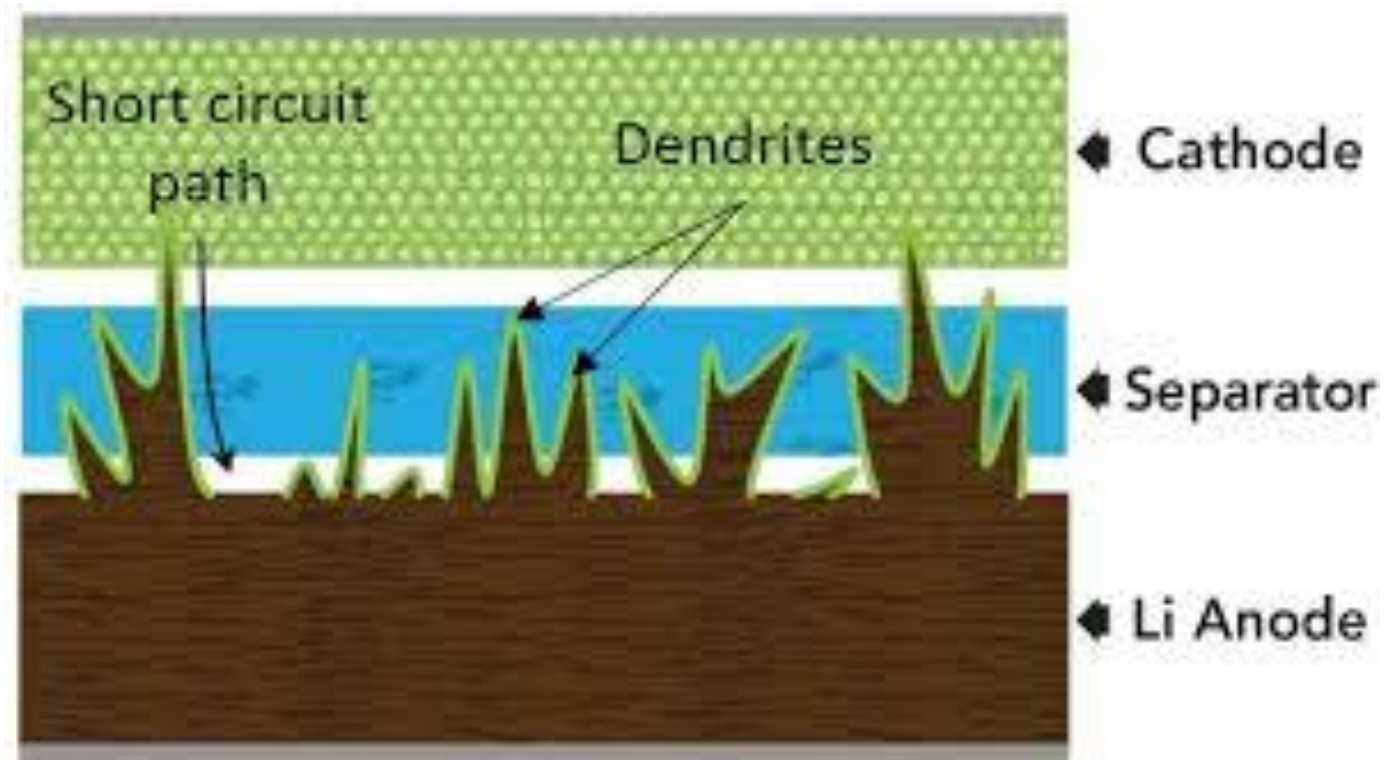
Oscillation of structures between dendritic plates and columns/plates

Fractal Microstructures

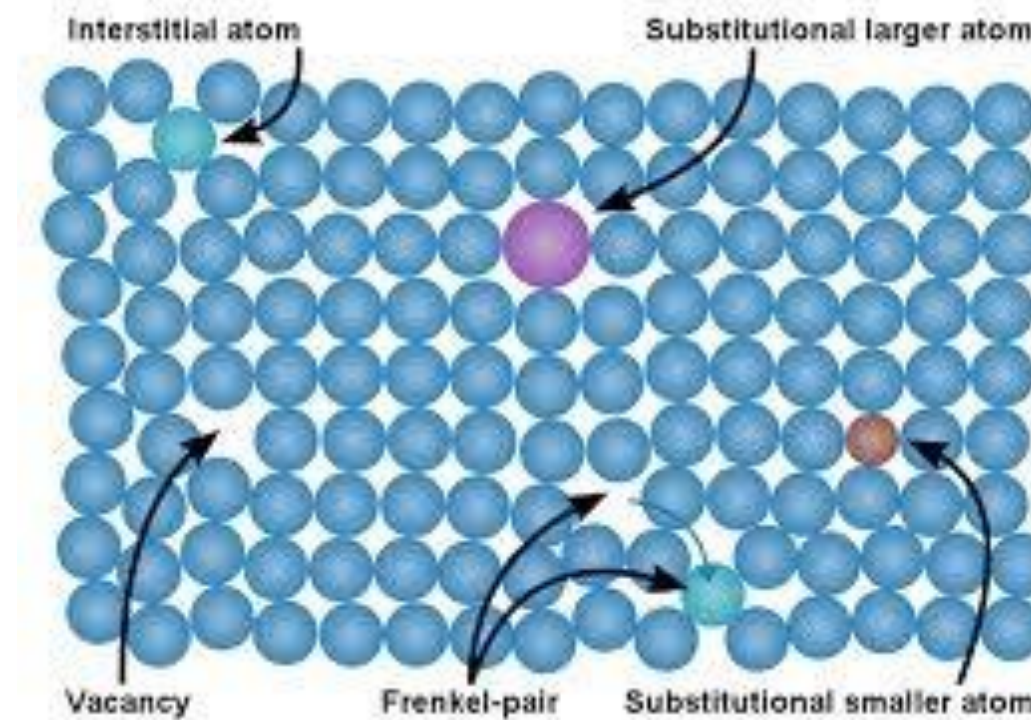
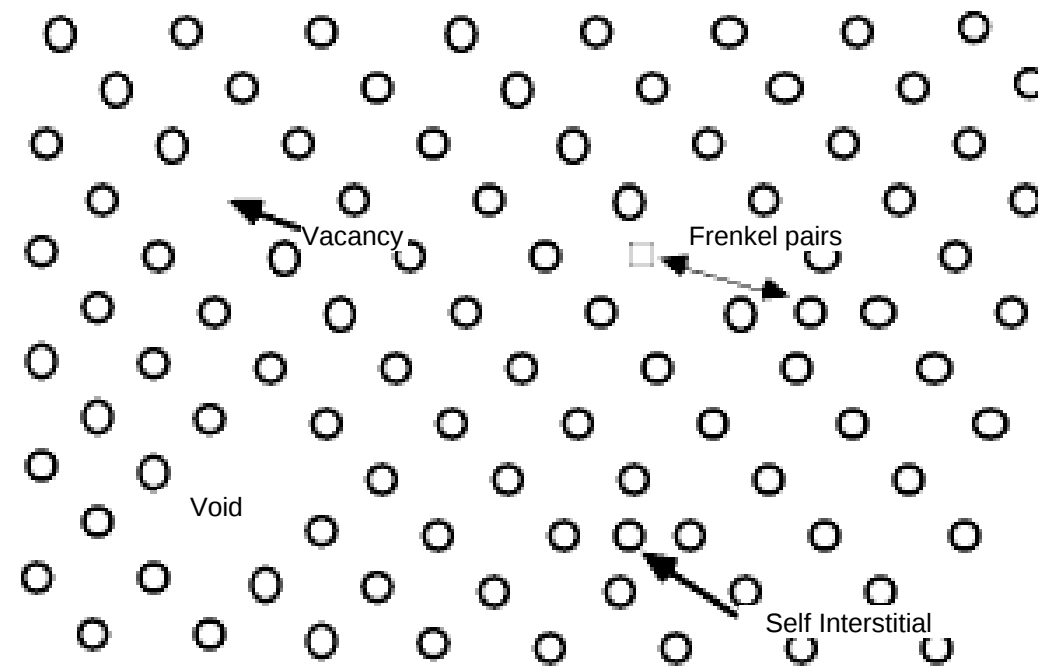


Dendritic growth during solidification
Mullens-Sekerka instability

Fractal Microstructures

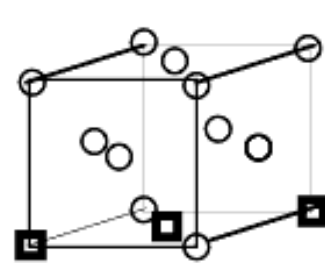


Point defects

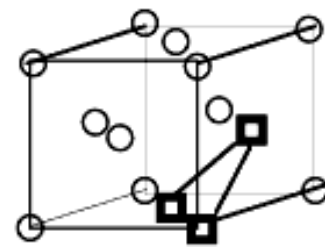


Intrinsic

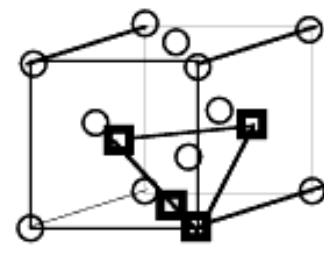
Extrinsic



linear

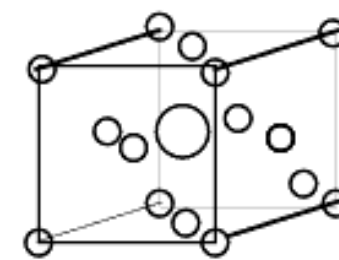


plane

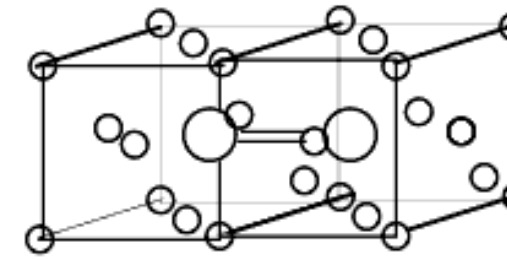


tetrahedral (most stable)

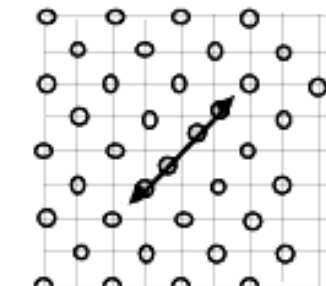
tri-vacancy



centered



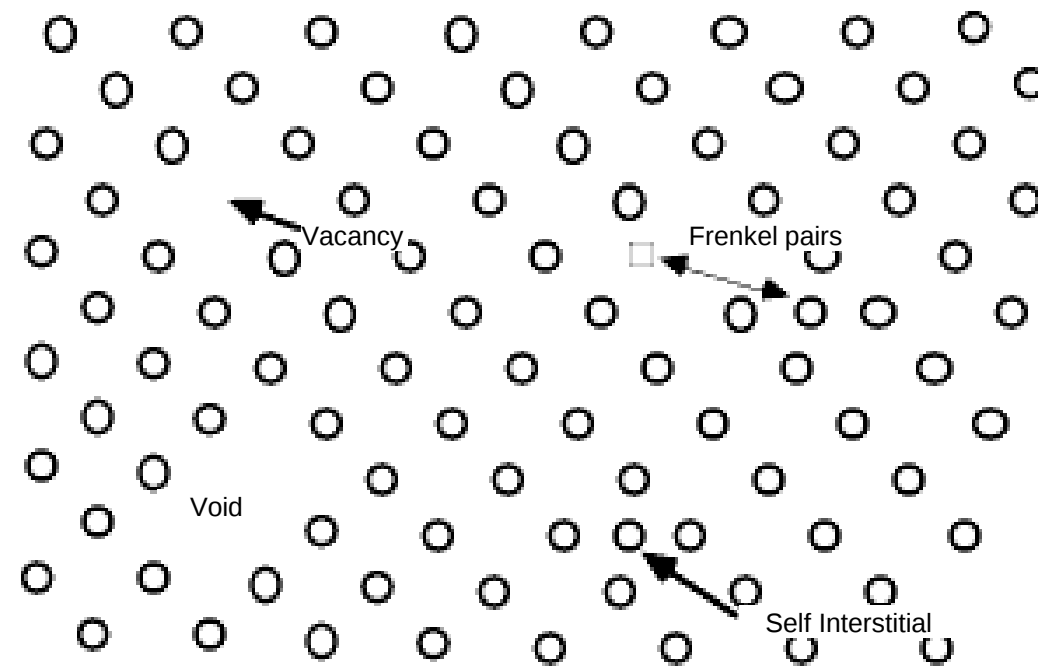
dumbbell



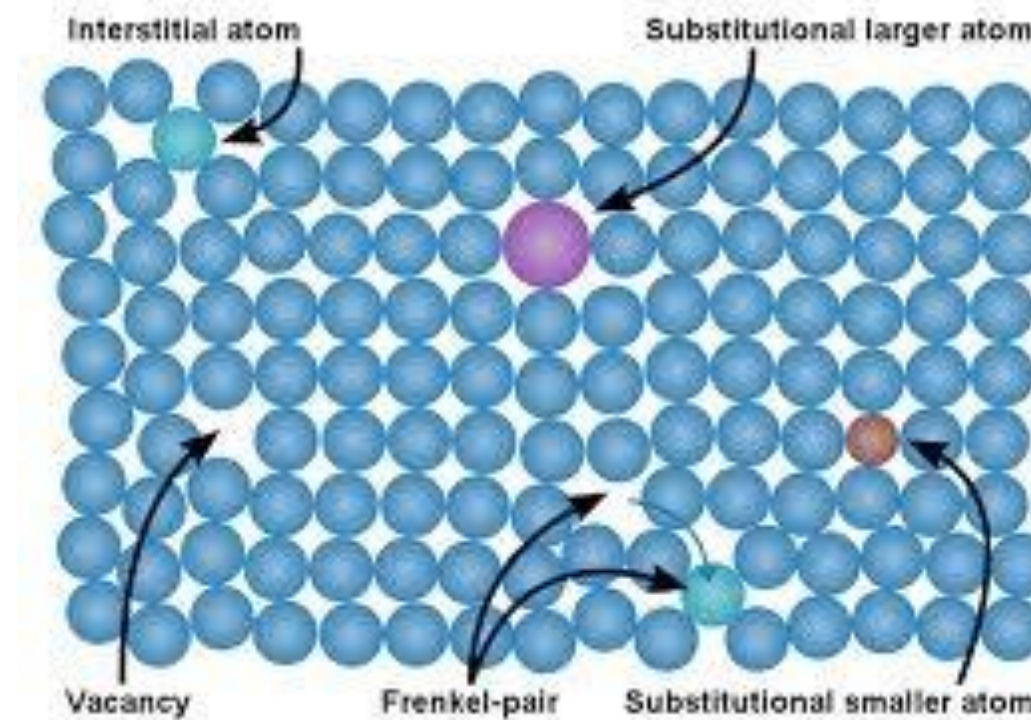
crowdion

Interstitials in fcc

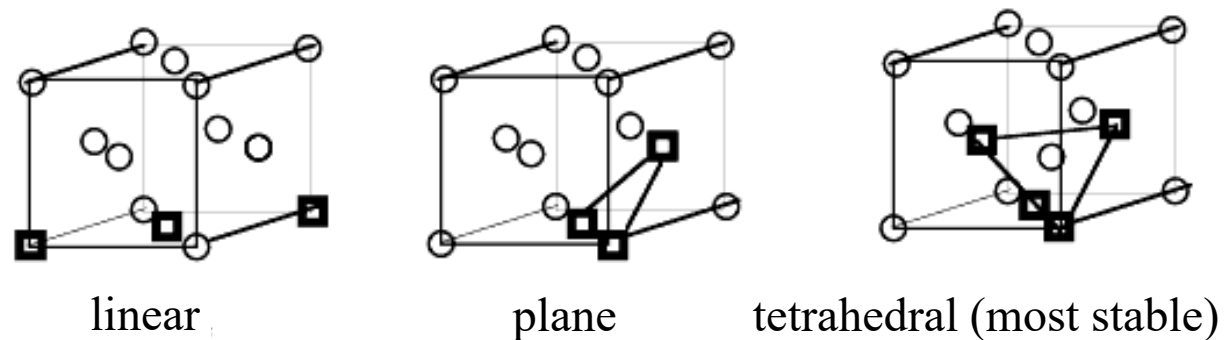
Point defects



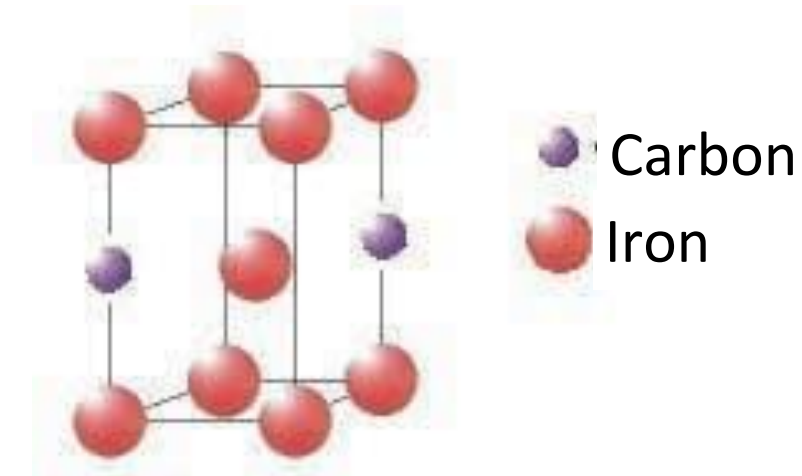
Intrinsic



Extrinsic

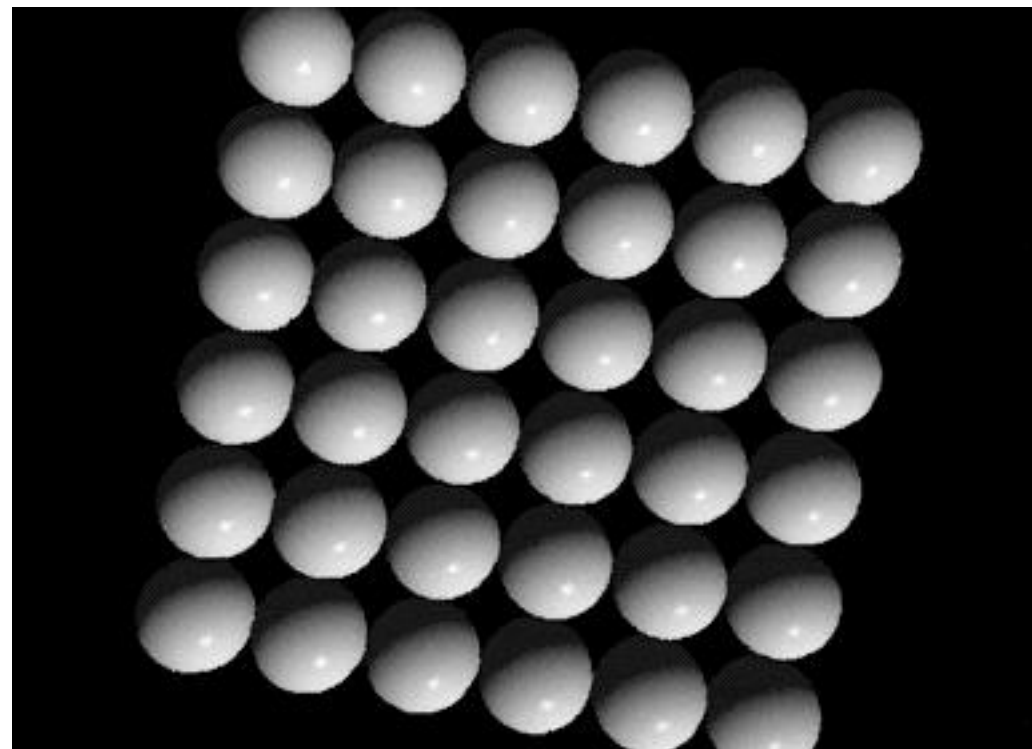
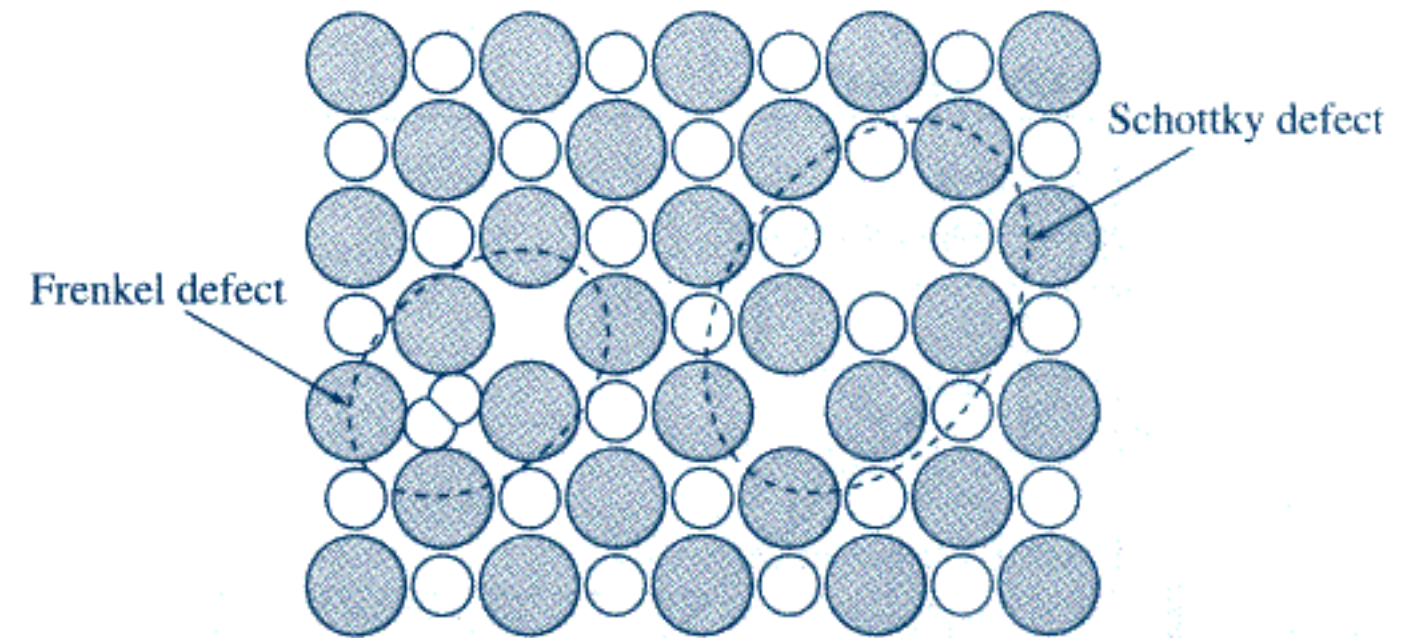
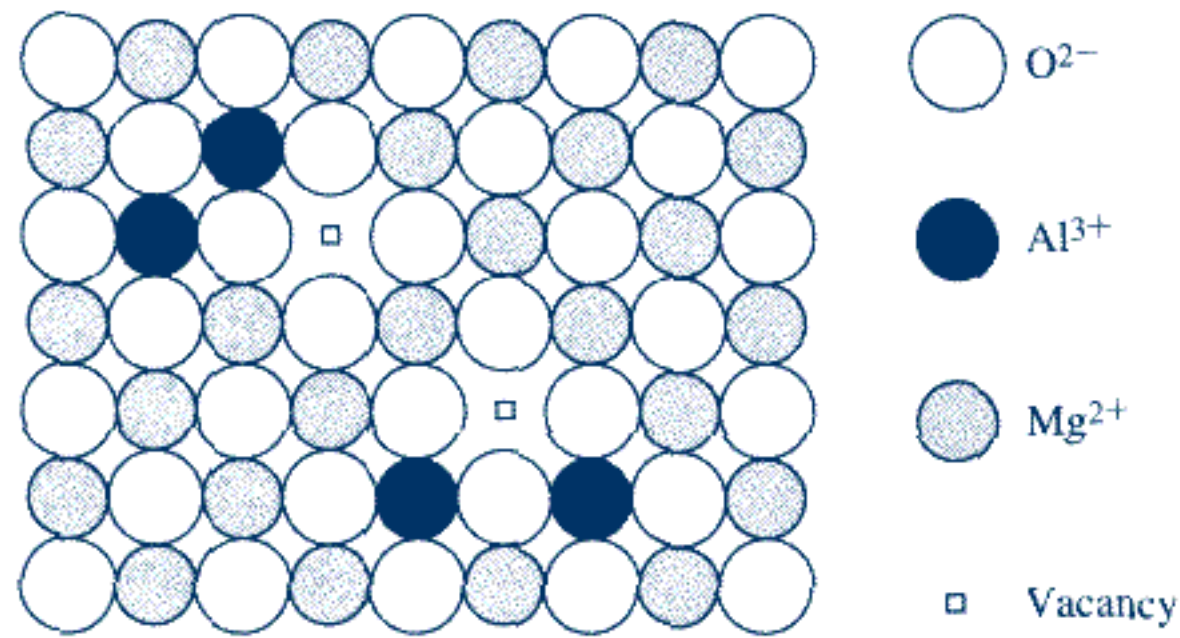


tri-vacancy



Interstitials in bcc

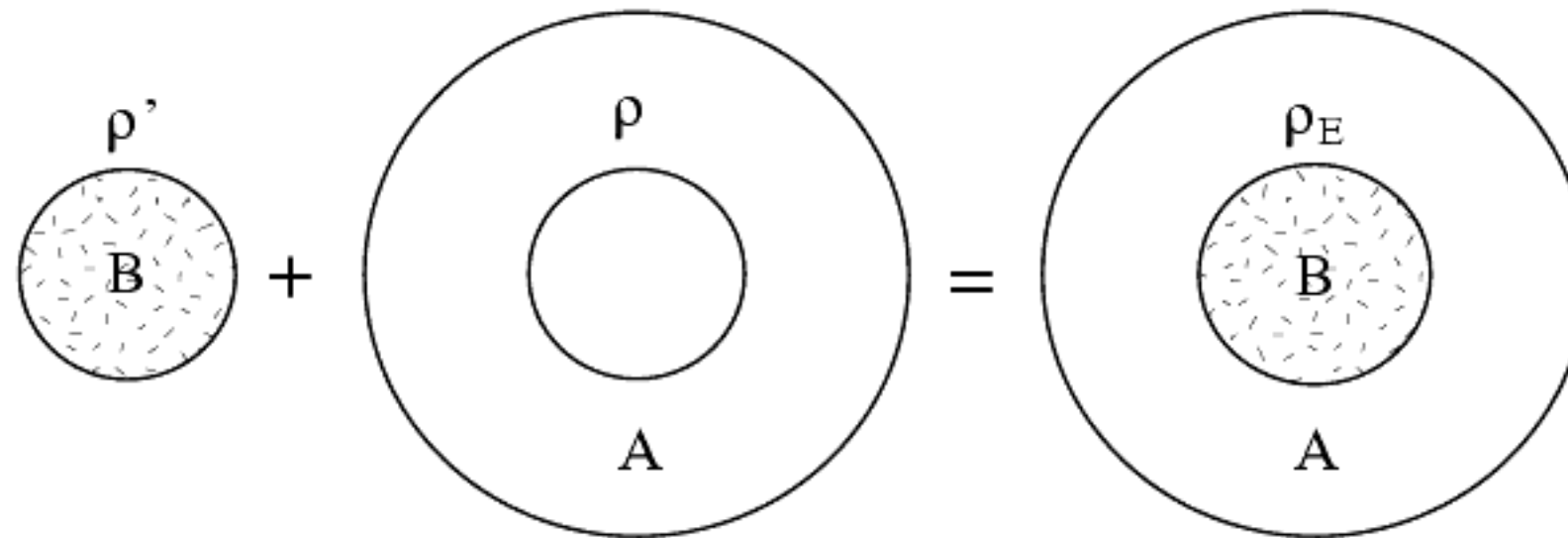
Point defects in ionic crystals



Two types of Vacancy defects in ionic crystals that must be charge neutral

- 1) Schottky defects
 - V cation+ and V anion-
- 2) Frenkel defects
 - V cation+ and I anion-
 - V anion- and I cation+

Elastic energy of a substitutional



Equilibrium energy

$$a' = -\frac{4\mu\eta}{3K' + 4\mu}$$

$$a = \frac{4\mu b}{3KR^3}$$

$$b = \eta \frac{\rho_E^3}{1 + \frac{4\mu}{3K'}}$$

$$\rho_E = \rho' + \frac{4\mu}{3K' + 4\mu}(\rho - \rho')$$

$$(1 - 2\nu)\Delta\vec{u} + \overrightarrow{\text{grad}}(\text{div}(\vec{u})) = 0 \quad \sigma_{rr}' = \sigma_{\phi\phi}' = \sigma_{\theta\theta}' = 3K'a'$$

$$2(1 - \nu)\overrightarrow{\text{grad}}(\text{div}\vec{u}) - (1 - 2\nu)\overrightarrow{\text{rot}}(\overrightarrow{\text{rot}}\vec{u}) = 0 \quad \sigma_{rr}'(\rho_E) = \sigma_{rr}(\rho_E) \rightarrow 3K'a' = 3Ka - \frac{4\mu b}{\rho_E^3}$$

$$W = W_{inclusion} + W_{matrix} = \frac{1}{2}\sigma_{incl.}\epsilon_{incl.} + \frac{1}{2}\sigma_{matr.}\epsilon_{matr.} \quad W = \pi\mu\rho_E^3\eta^2 \frac{8}{1 + \frac{4\mu}{3K'}}$$

$$W \approx 16\eta^2 [eV]$$

$$\eta = \frac{\rho' - \rho}{\rho_E}$$

η = relative variation of the radius

Concentration of vacancies at thermodynamic equilibrium

$$\Delta G = n\Delta G_F^V - TS_m$$

Mixing entropy

$$S_m = k \ln \frac{(N+n)!}{N!n!} \quad N+n \text{ sites}$$

Equilibrium $\frac{\partial \Delta G}{\partial n} = 0$

Result $C_V = \frac{n}{N+n} = e^{-\frac{\Delta G_V^F}{kT}}$

$$C_V = e^{\frac{\Delta S_V^F}{k}} e^{-\frac{\Delta E_V^F + P\Delta V_V^F}{kT}} = C_0 e^{-\frac{\Delta E_V^F + P\Delta V_V^F}{kT}} = C_0 e^{-\frac{\Delta H_V^F}{kT}}$$

ΔE_V^F is the formation energy of a vacancy $\sim 0.5\text{-}1 \text{ eV} = 0.5\text{-}1 \cdot 10^{-5} \text{ Joules/mole}$

$$\Delta E_V^F = E_{\text{sublimation}} = \frac{p}{2} E_{\text{bond}}$$

ΔV_V^F is the formation volume of a vacancy $\sim$ atomic volume $\sim 10^{-29} \text{ m}^3$

$$P\Delta V_V^F \sim 10^{-25} \text{ J} = 6.0 \cdot 10^{-2} \text{ eV negligible}$$

Concentration of vacancies at thermodynamic equilibrium

ΔS_V^F is the formation entropy of a vacancy.

Due to the change in the vibration entropy of the crystal, when the vacancy is introduced.

$$\Delta S_V^F \sim 3k \Rightarrow C_0 = e^{\frac{\Delta S_V^F}{k}} \sim 20 \rightarrow C_V \approx 3 \cdot 10^{-16} \text{ vacancies per atoms}$$

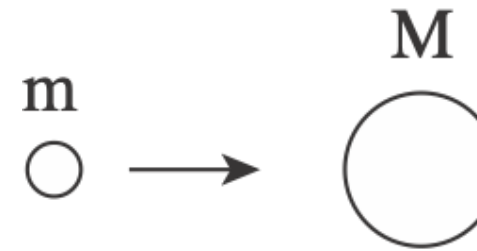
The complete derivation of the ΔS_V^F is in the lecture notes, which involves the solutions of vibrational entropy using Einstein's approximation and approximations using Grüneisen parameters associated with the material's constants and crystal structure.

Exercise 4, problem 2 asks to derive C_V

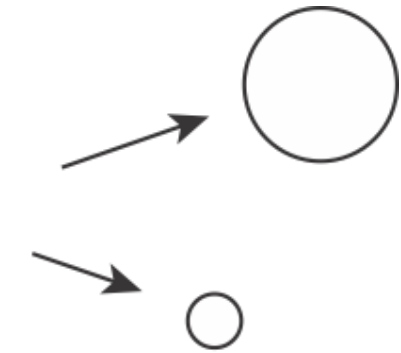
Creation of vacancies

- Quenching
- Strain hardening
- Irradiation

Elastic shock



Before

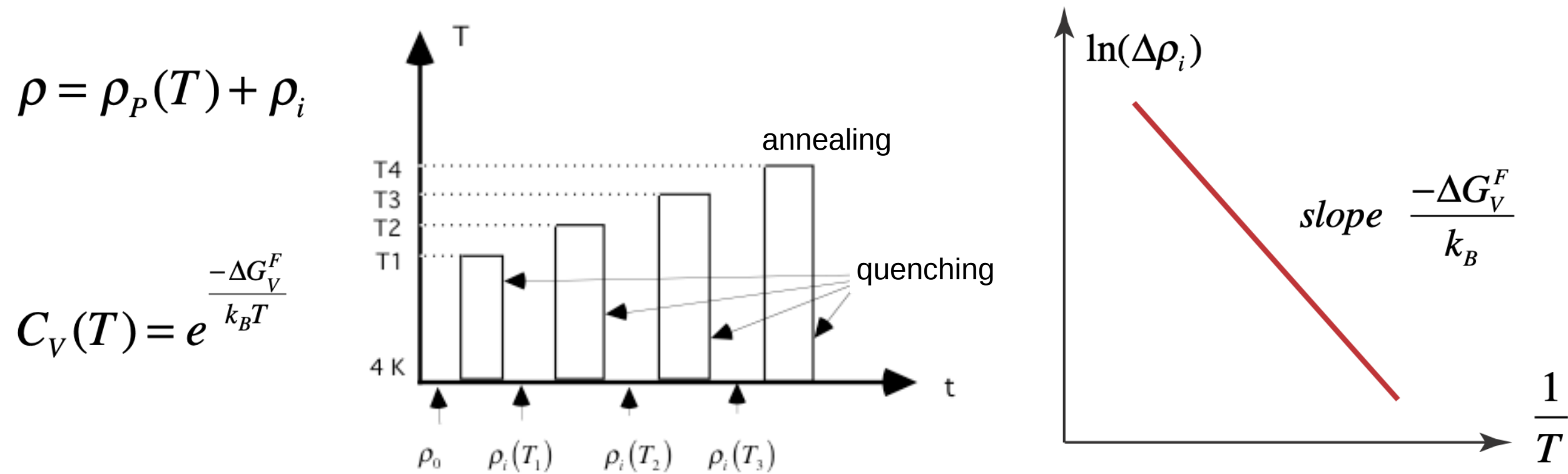


After

$$T_{\max} = \frac{4mM}{(m+M)^2} E \quad \text{Kinetic energy } E = \text{energy of a particle with mass } m$$

$$T_{\max} \sim 10 - 40 \text{ eV} \gg E_{\text{cohesion}}$$

Measurement of the density of vacancies



$$T = T_0 \rightarrow C_V = C_V^0 \rightarrow \rho = \rho(T_0) = \rho_0 + \rho_V(T_0) \text{ with } \rho_V(T_0) = \alpha e^{\frac{-\Delta G_V^F}{k_B T_0}}$$

$$T = T_1 \rightarrow C_V = C_V^1 \rightarrow \rho = \rho(T_1) = \rho_0 + \rho_V(T_1) \quad \Delta\rho_1 = \rho_V(T_1) - \rho_V(T_0)$$

$$T = T_2 \rightarrow C_V = C_V^2 \rightarrow \rho = \rho(T_2) = \rho_0 + \rho_V(T_2) \quad \Delta\rho_2 = \rho_V(T_2) - \rho_V(T_0)$$

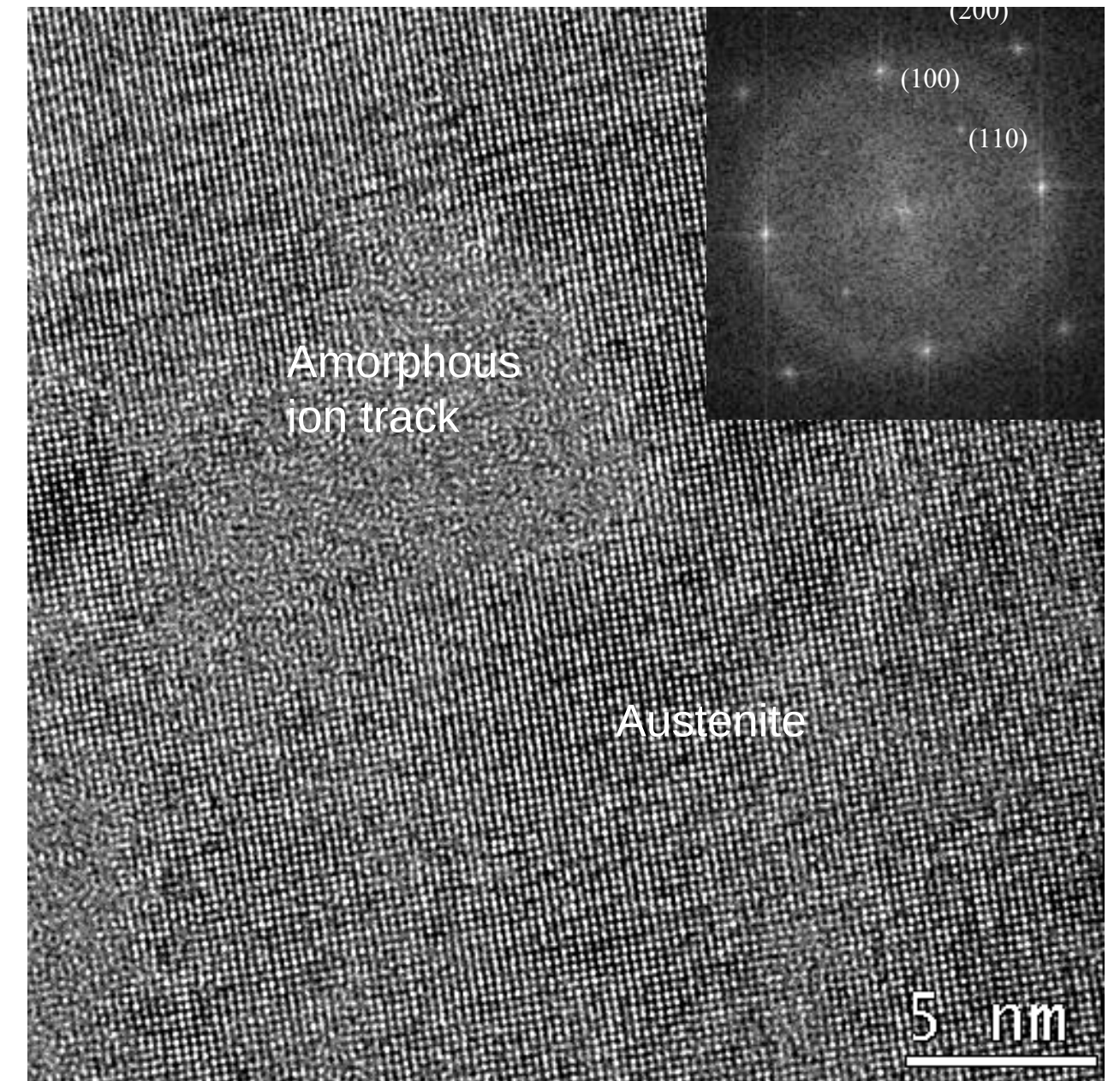
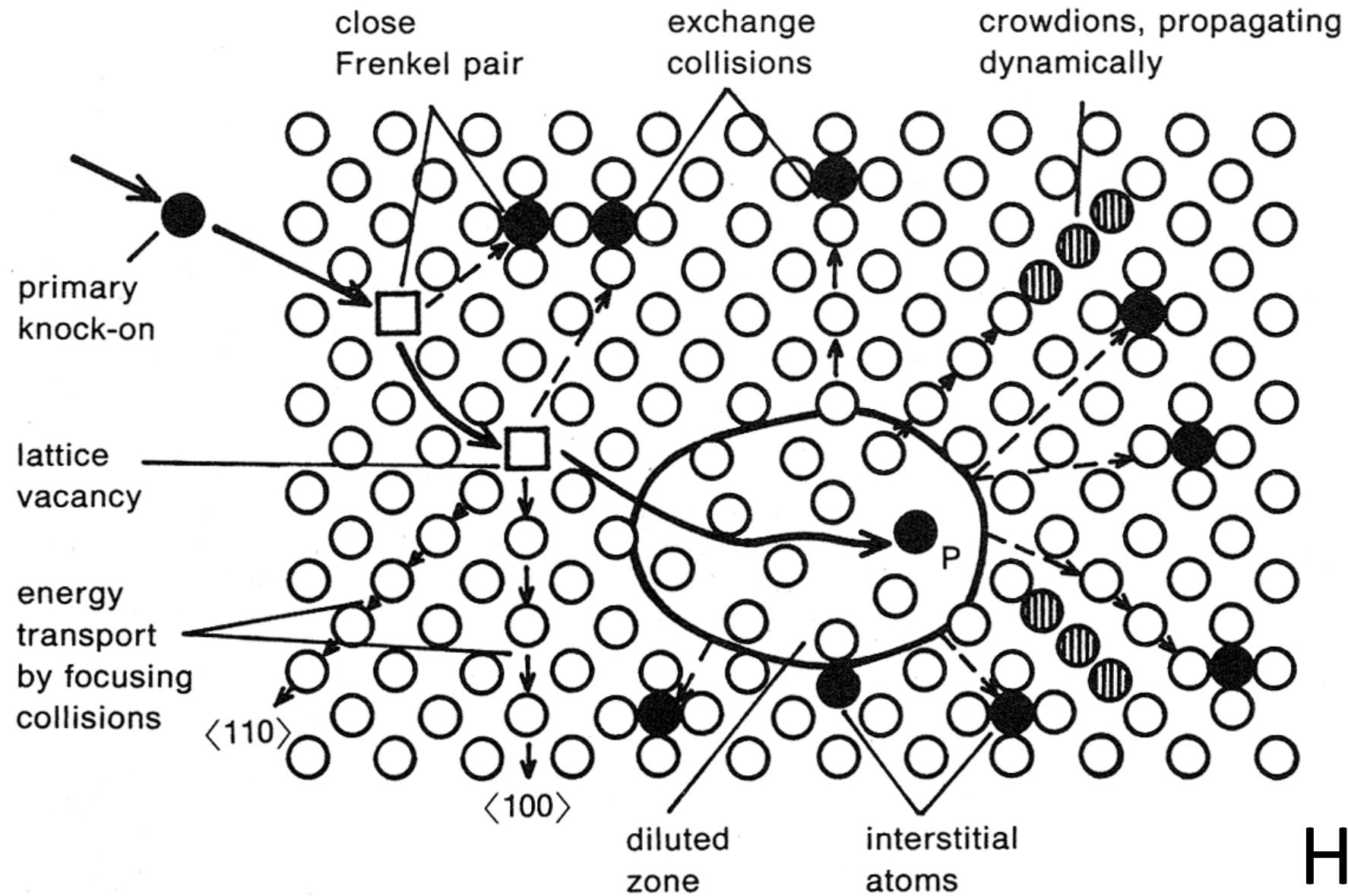
$$\Delta\rho_1 = \alpha(C_V^1 - C_V^0) = \alpha \left(e^{\frac{-\Delta G_V^F}{k_B T_1}} - e^{\frac{-\Delta G_V^F}{k_B T_0}} \right) \approx \alpha e^{\frac{-\Delta G_V^F}{k_B T_1}}$$

Formation Energy for Vacancies

Al=0.76 eV and Cu=1.1 eV

Creation of vacancies

Ion Displacement Cascade



HRTEM image of an amorphous metal track created by a 350 MeV Au ion

Creation of vacancies

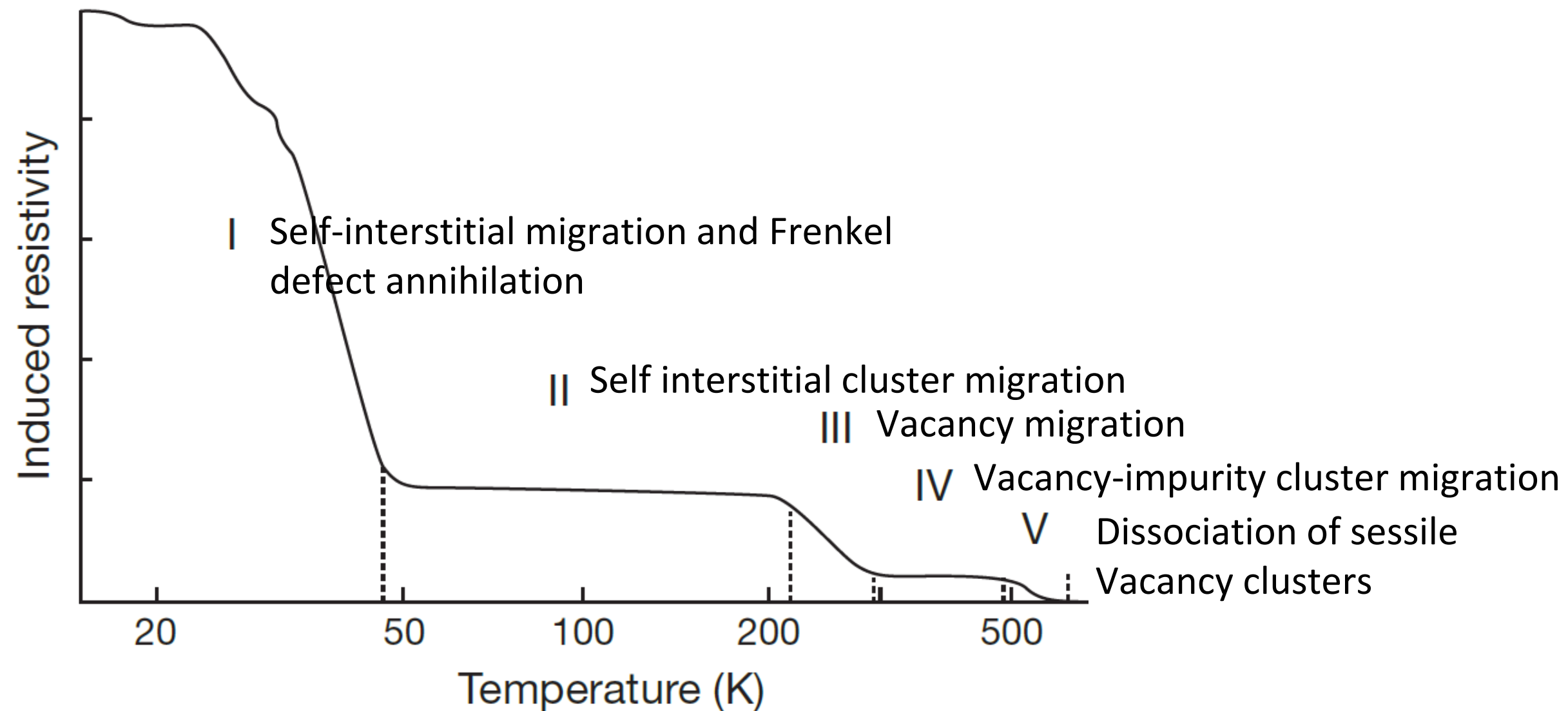


Figure 6 Electrical resistivity defect recovery stages for copper following electron irradiation at 4 K. Reproduced from Agullo-Lopez, F.; Catlow, C. R. A.; Townsend, P. D., *Point Defects in Materials*. Academic Press: San Diego, CA, 1988; p 445.

Void Formation during MeV Electron Irradiation of Nanotwinned Cu

In-situ observations

- High-angle boundary GBs absorb Frenkel defects, causing them to move
- Special GBs (CSL- Σ) do not move
- HAGBs and LAGBs connected with TJs containing two special boundaries did not change.
- Voids tend to form in high density around the latter-like $\Sigma 3$ twins within the columns

