Physics of Materials

Chapter 4: Defects of Crystals

Dr. Thomas LaGrange

Masters Course PHYS-307

Fall 2025

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

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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

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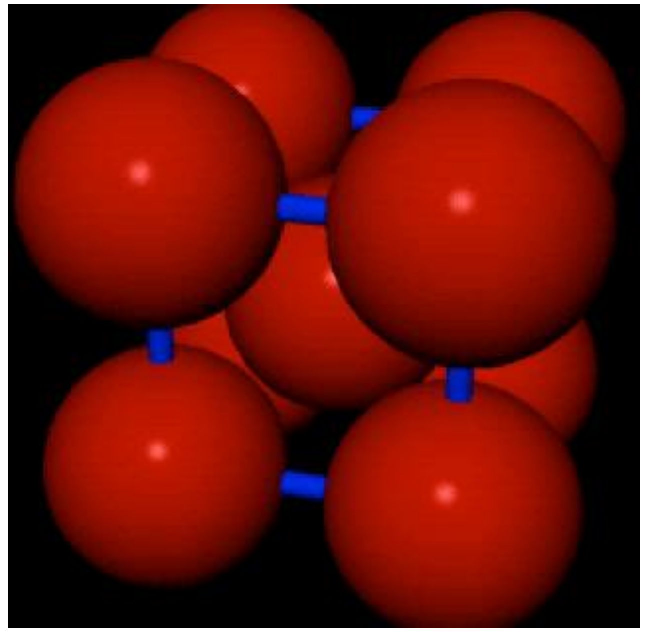
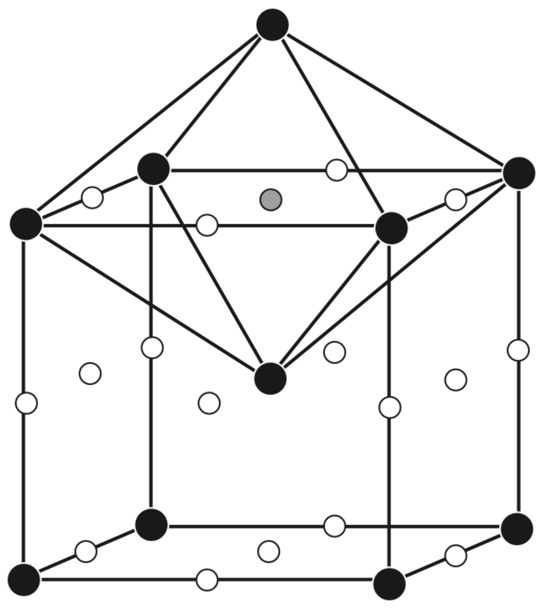
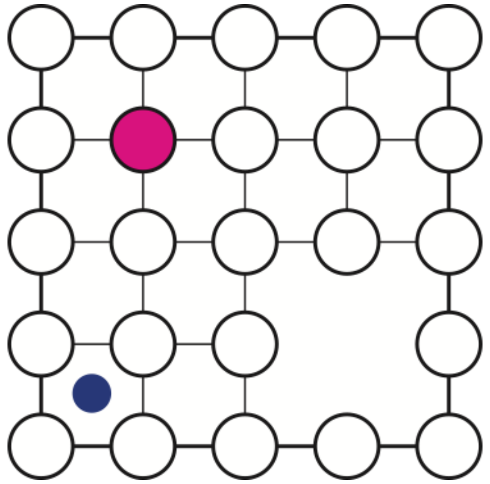
Point defects

Body-centered cubic

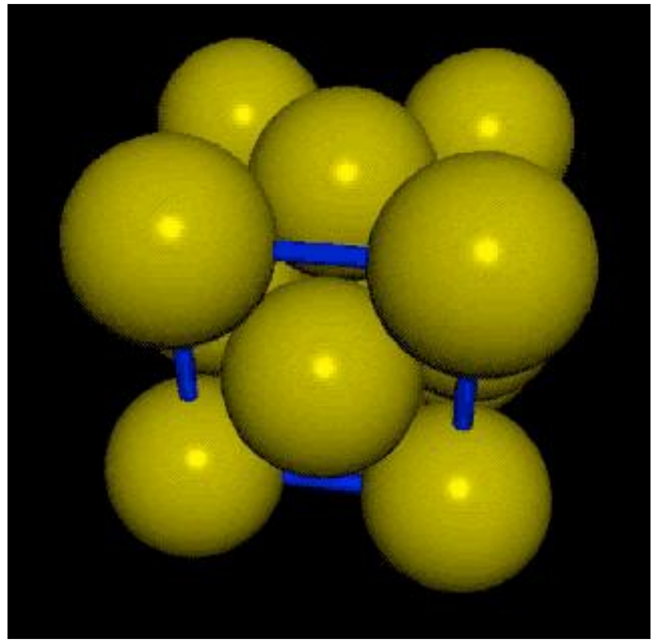


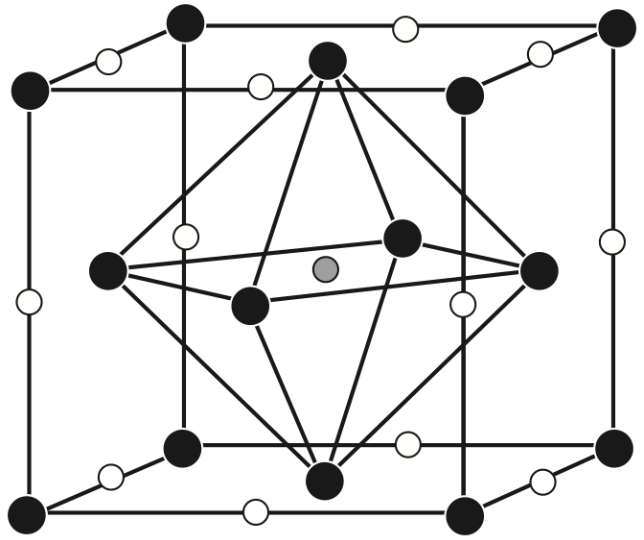




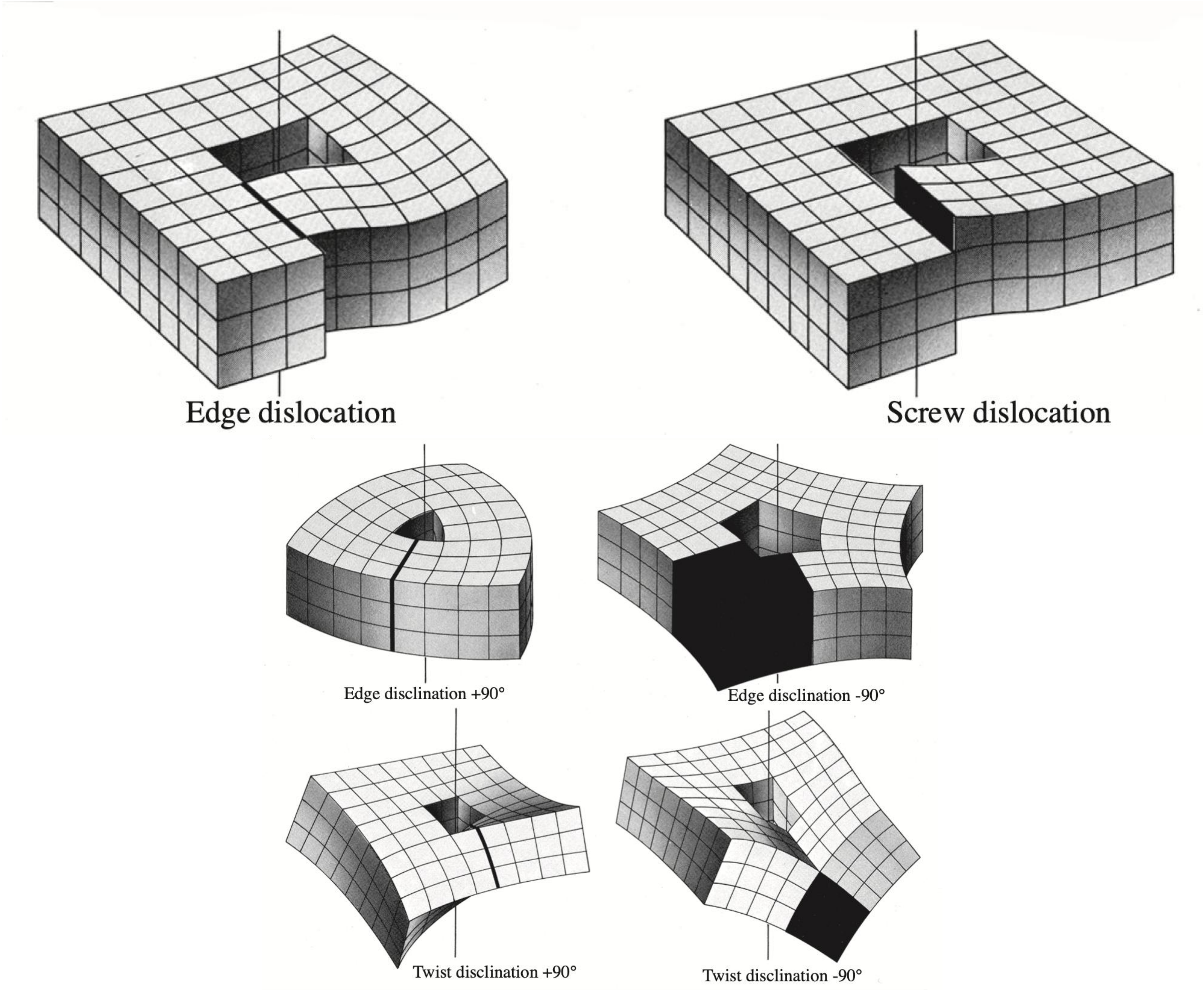
Interstitial carbon in Fe

Face-centered cubic



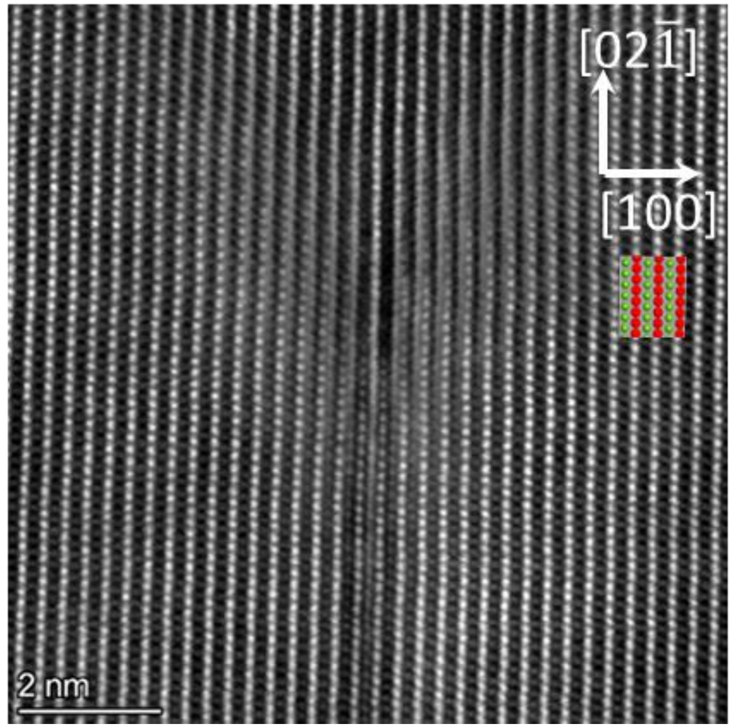


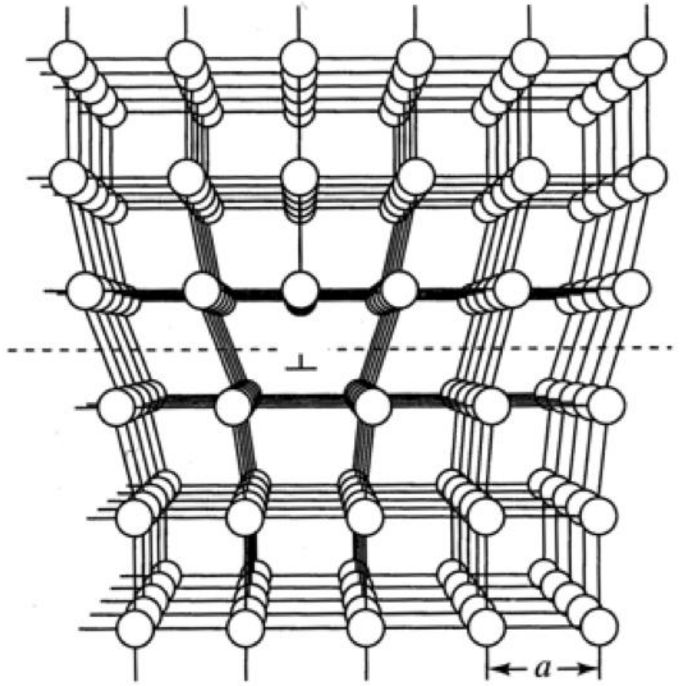
Dislocations and Disclinations

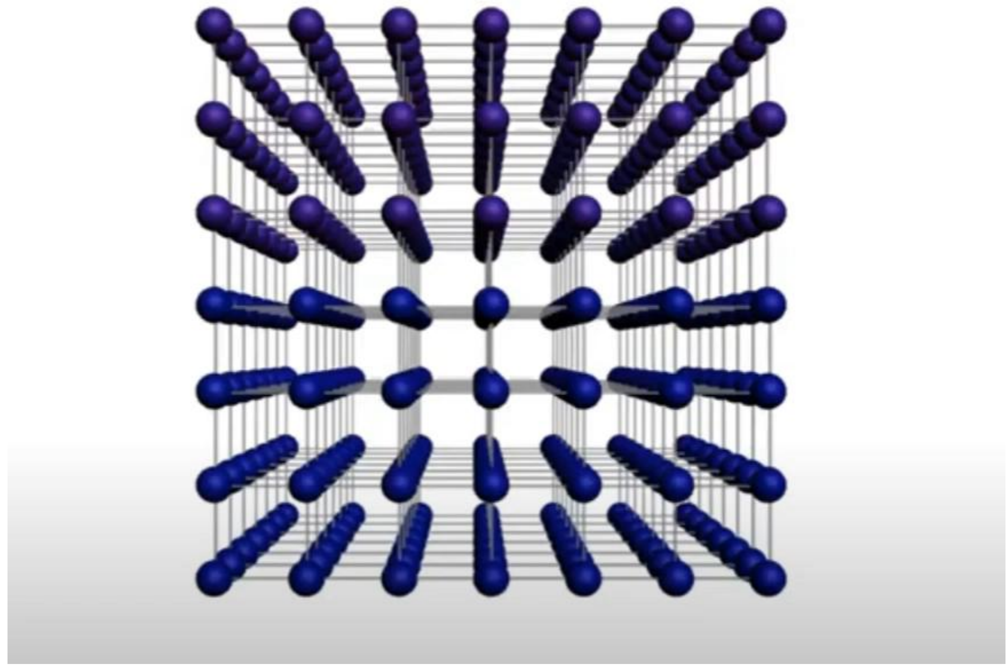


Dislocations and Disclinations

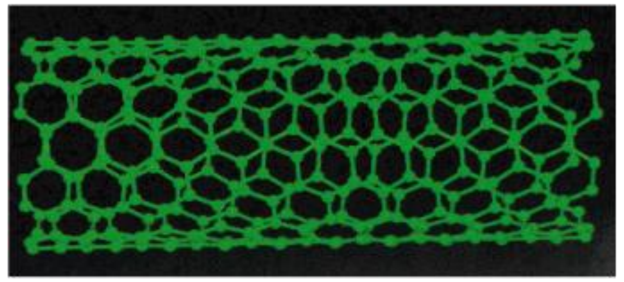
Edge dislocation

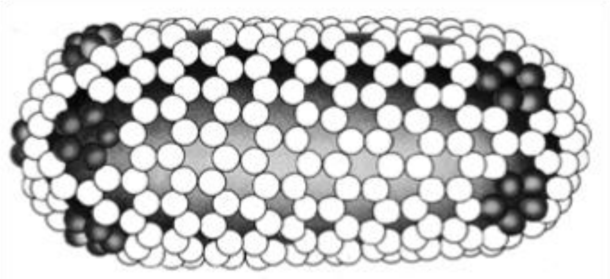


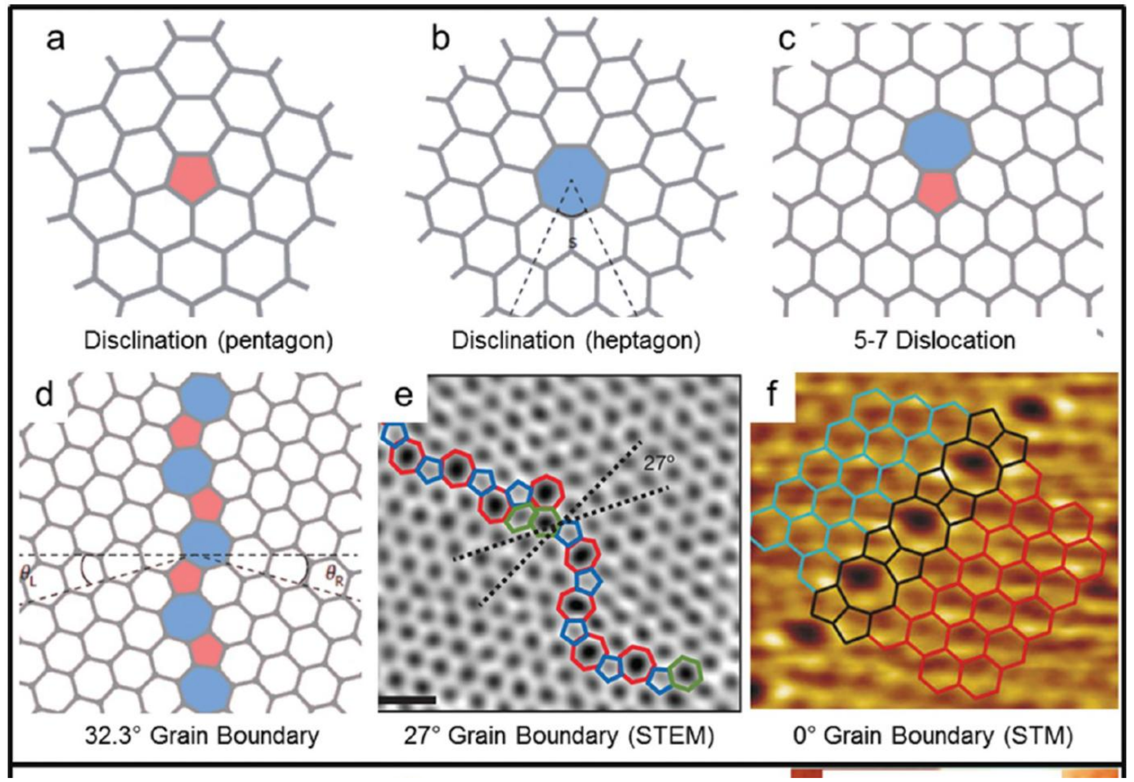




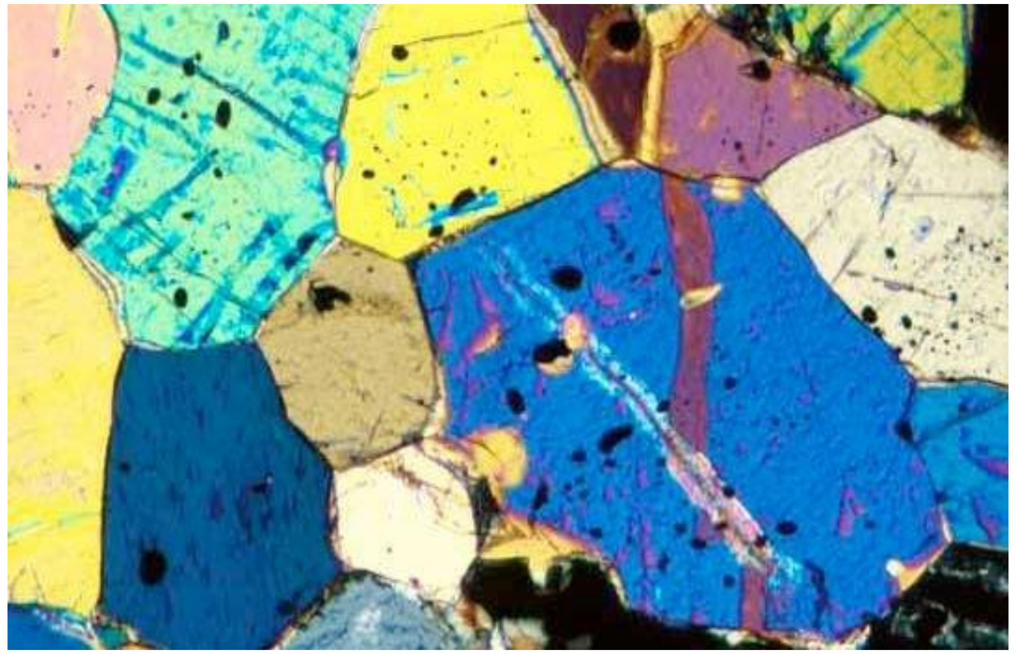
Disclinations close carbon nanotubes

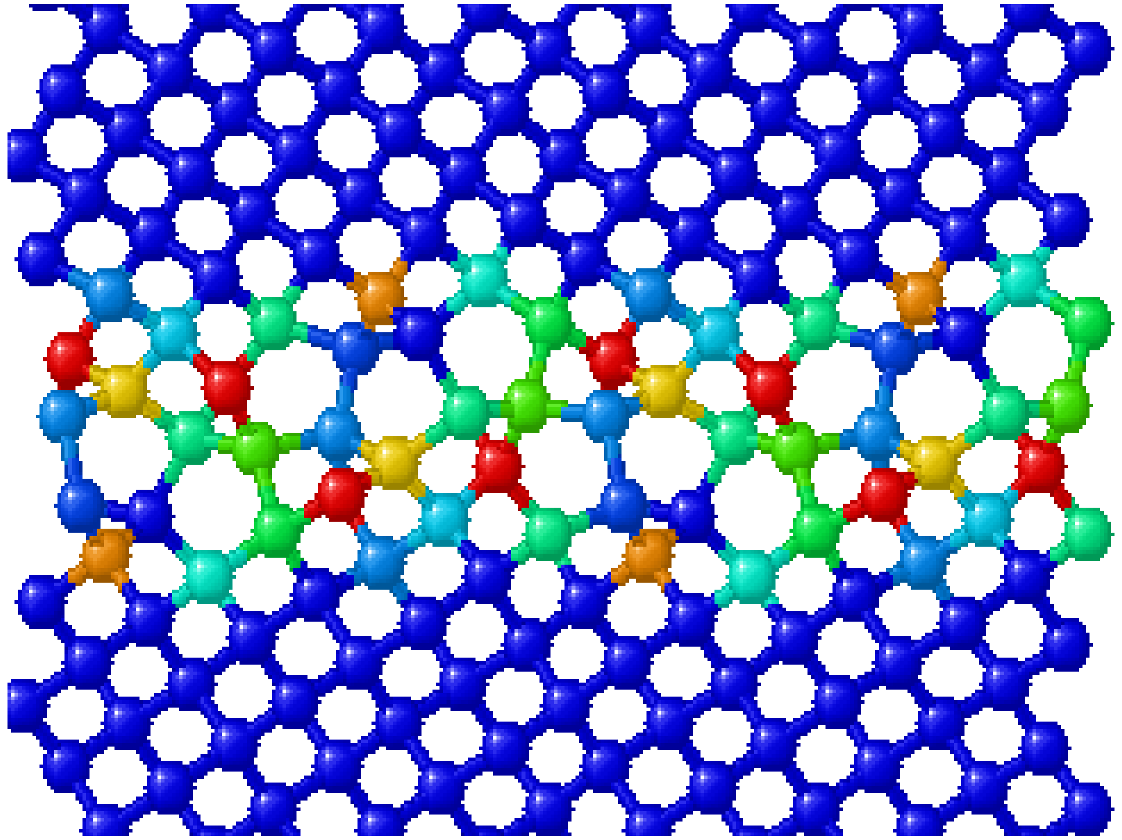


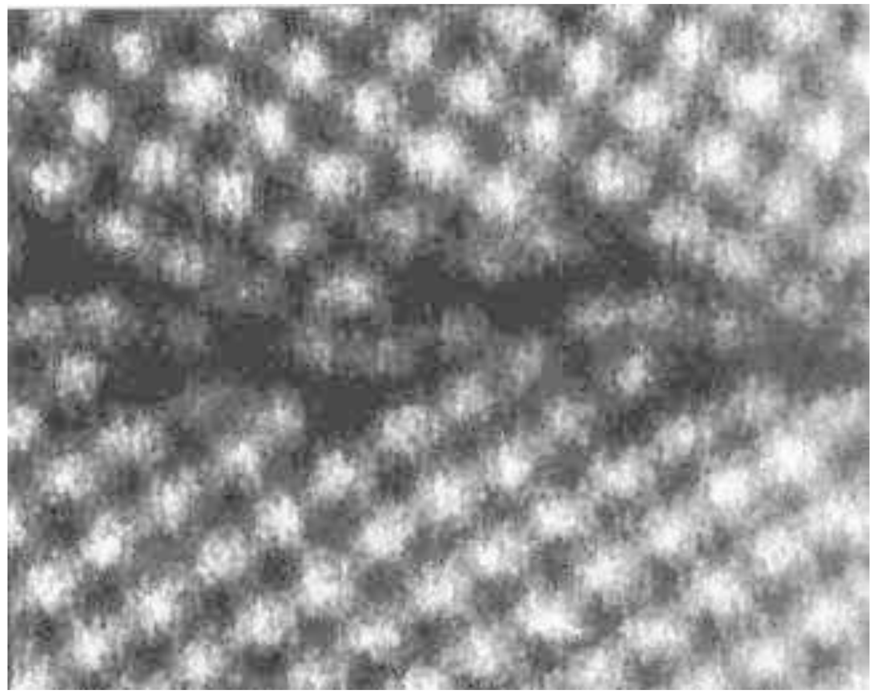


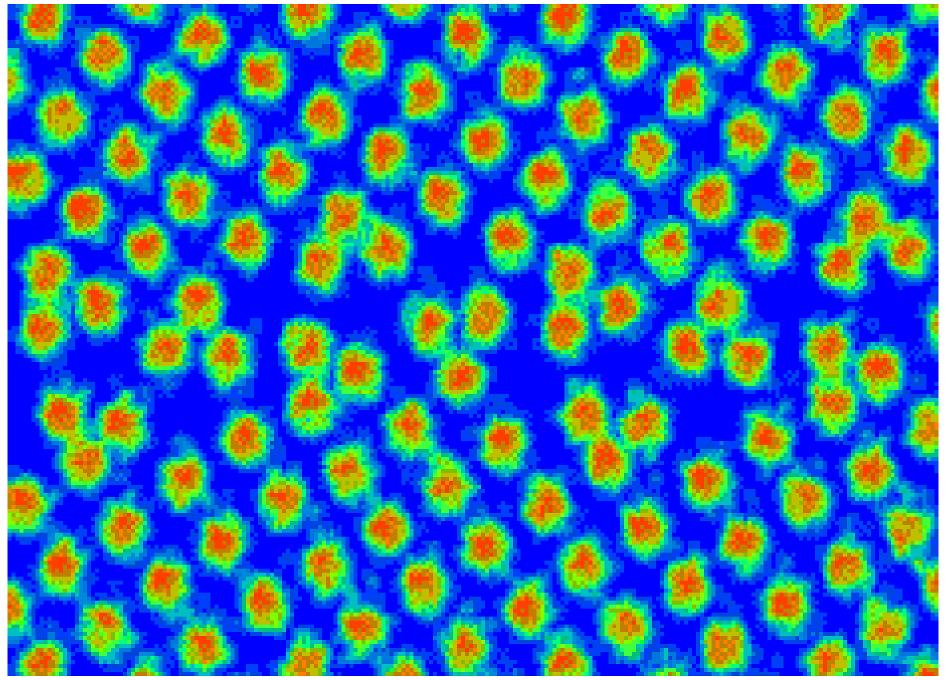


Grain Boundaries

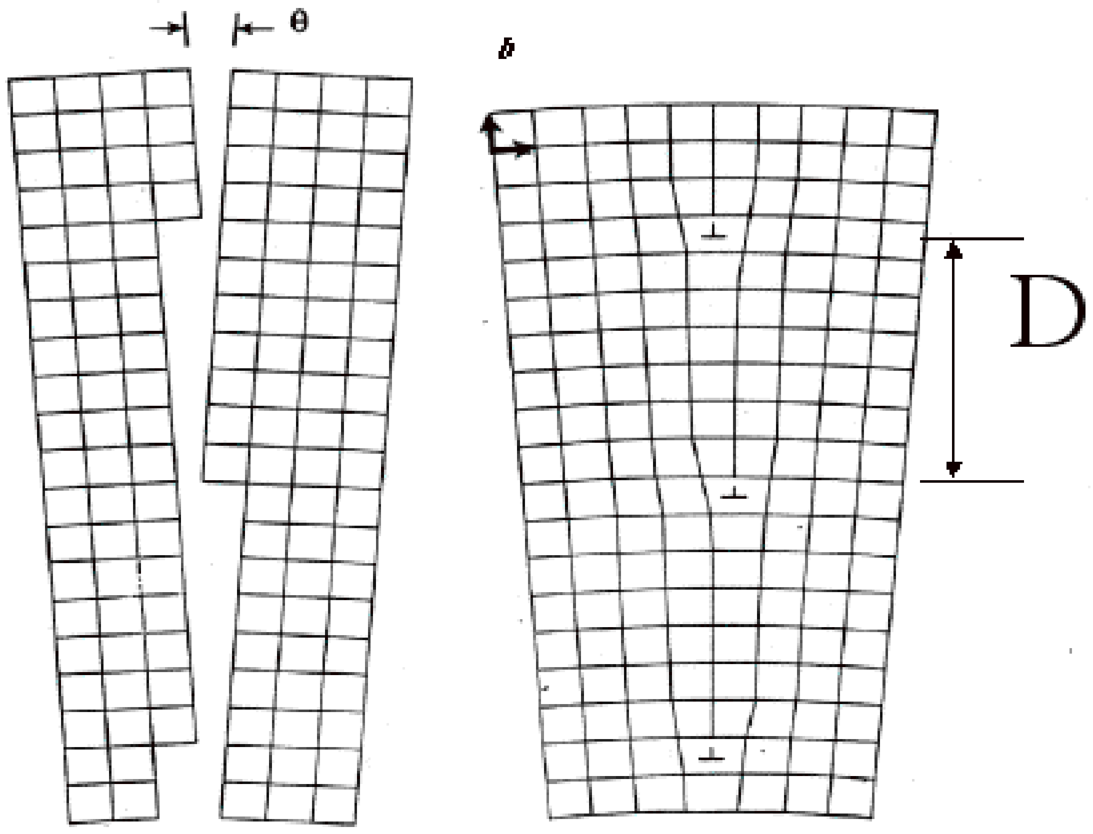


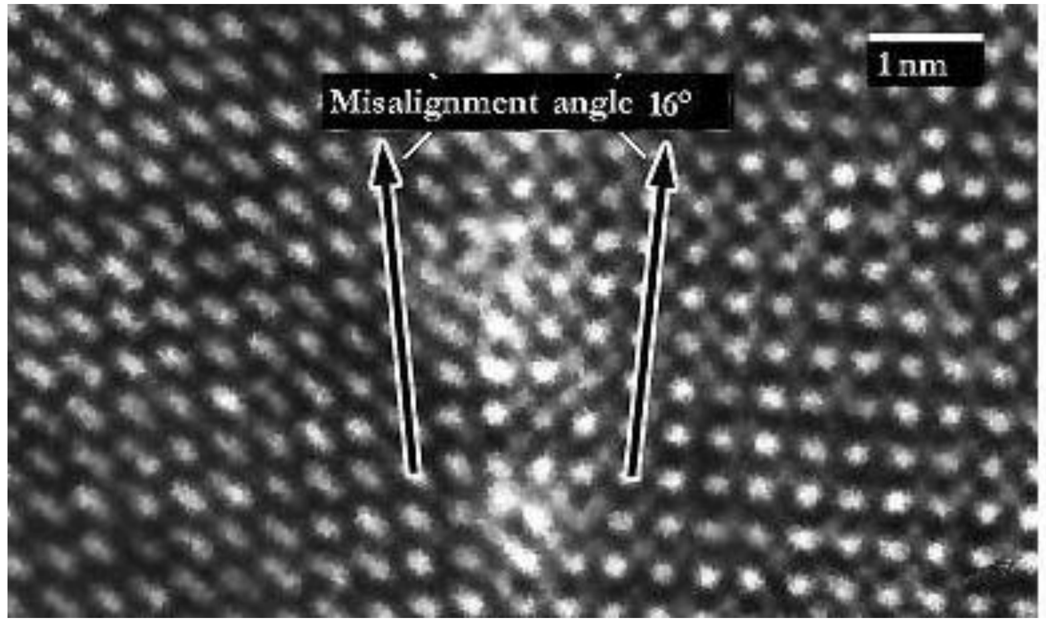


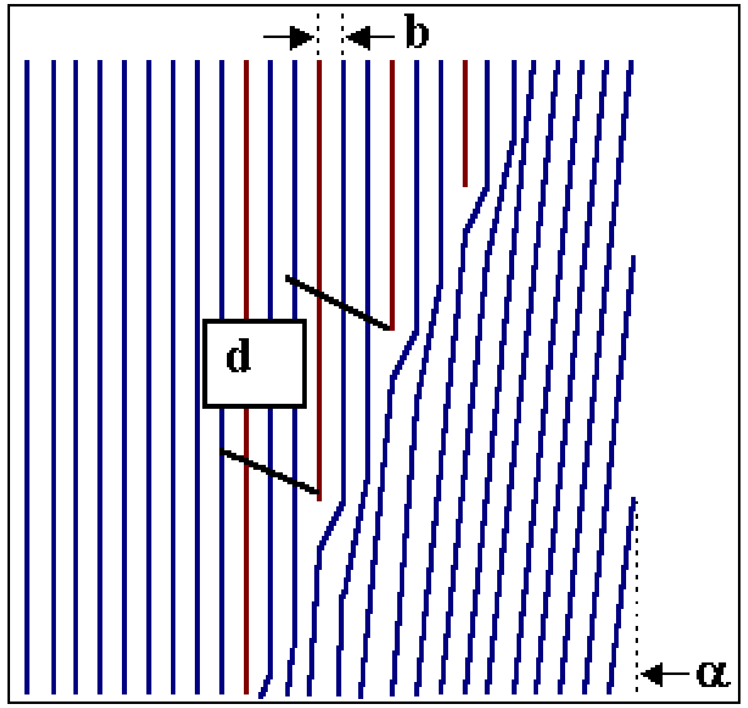


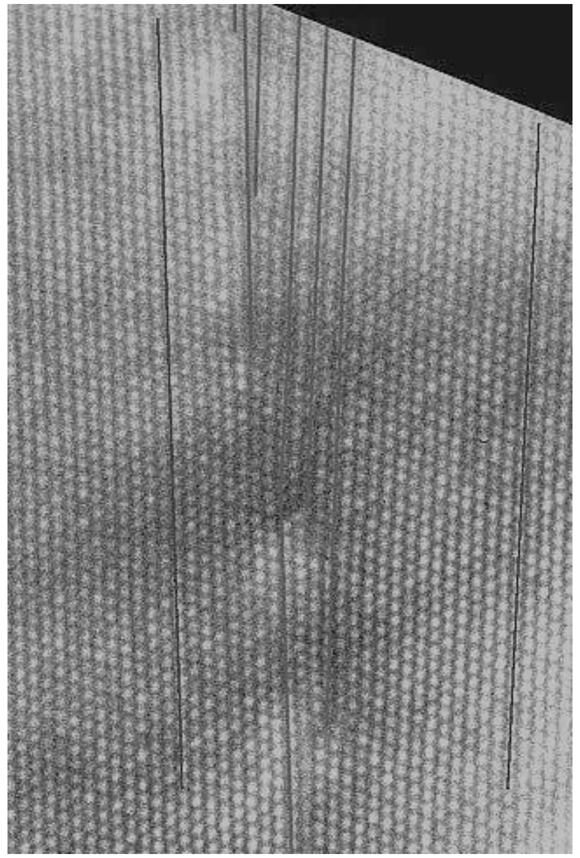


Small angle grain boudaries

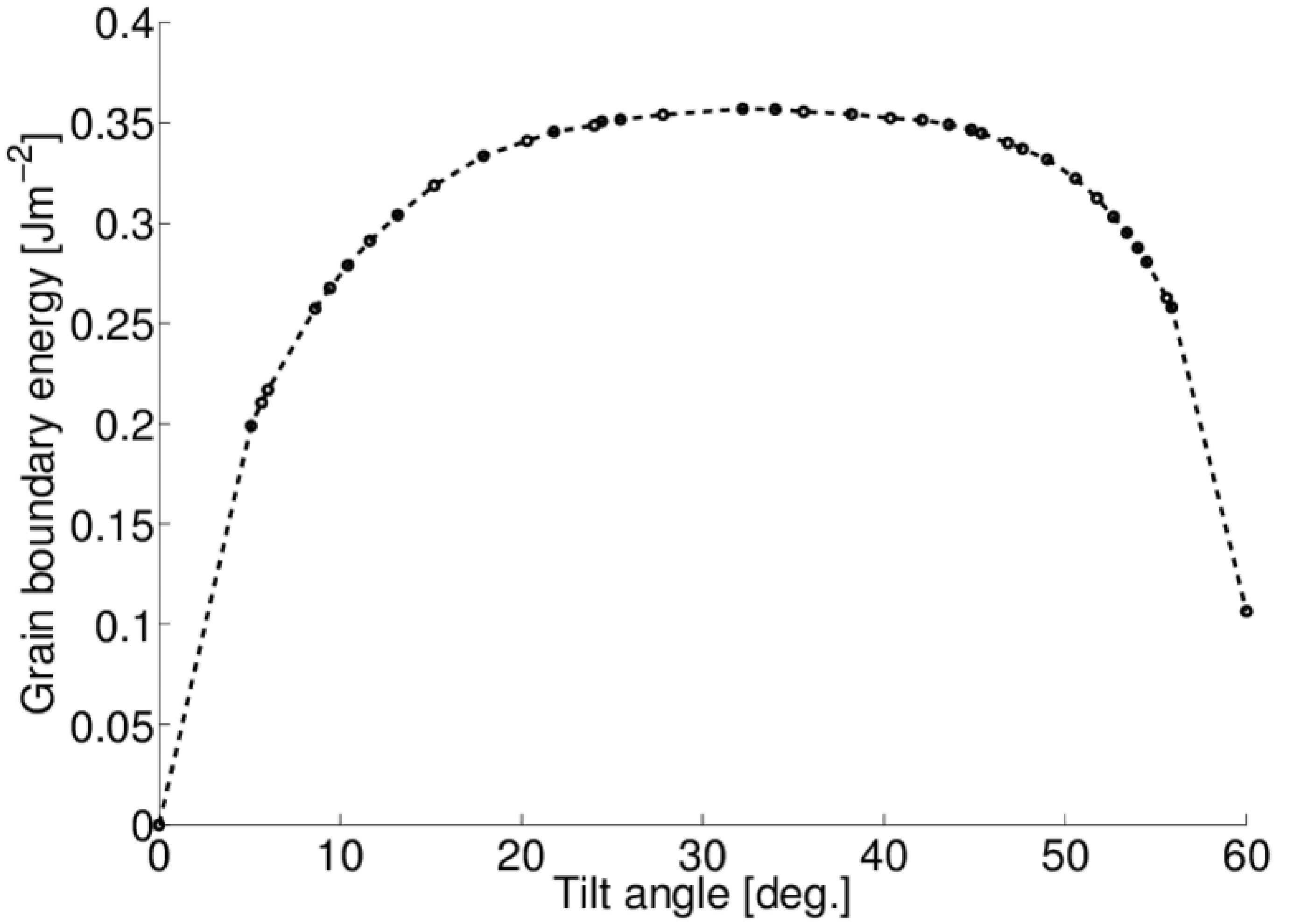


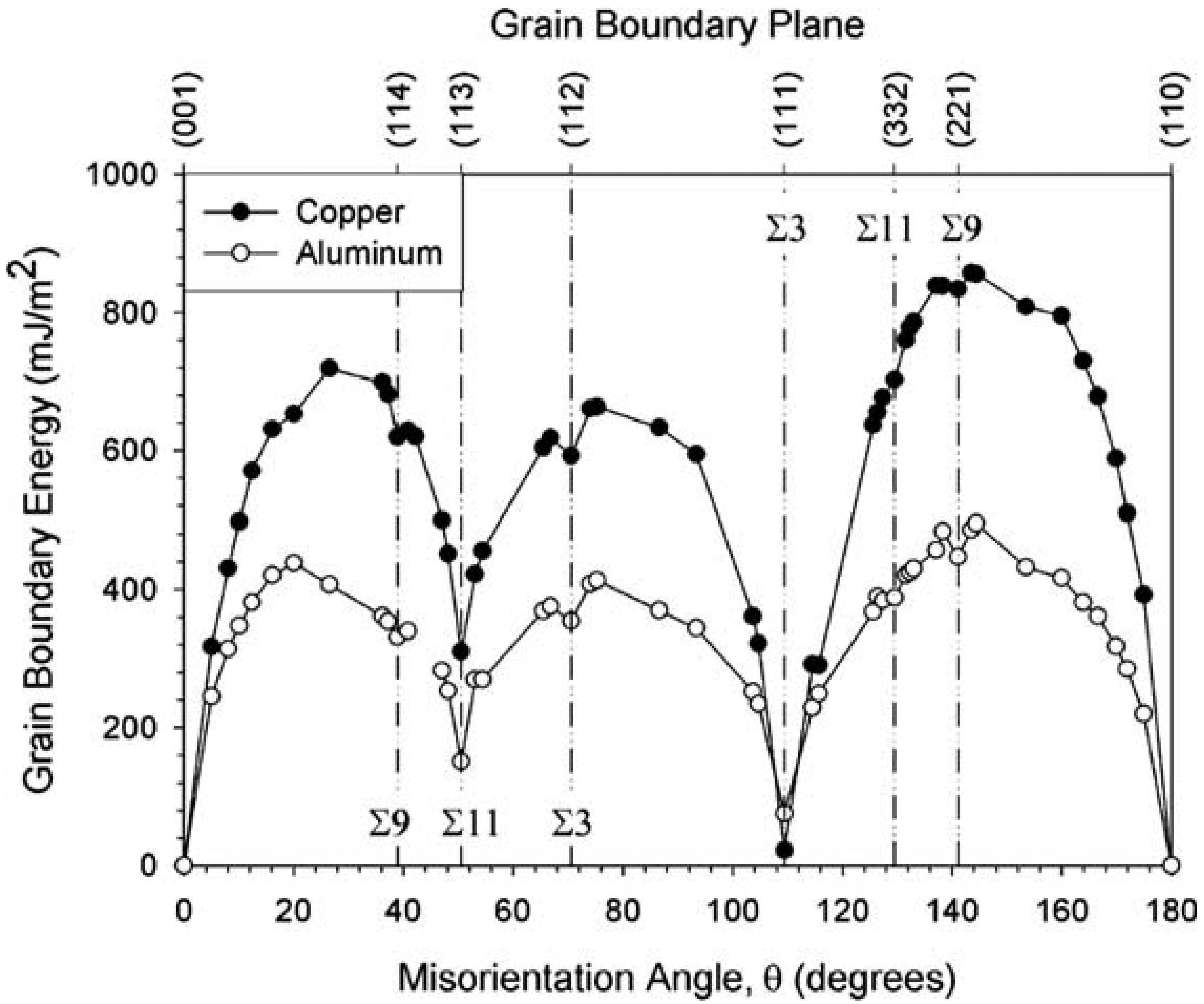






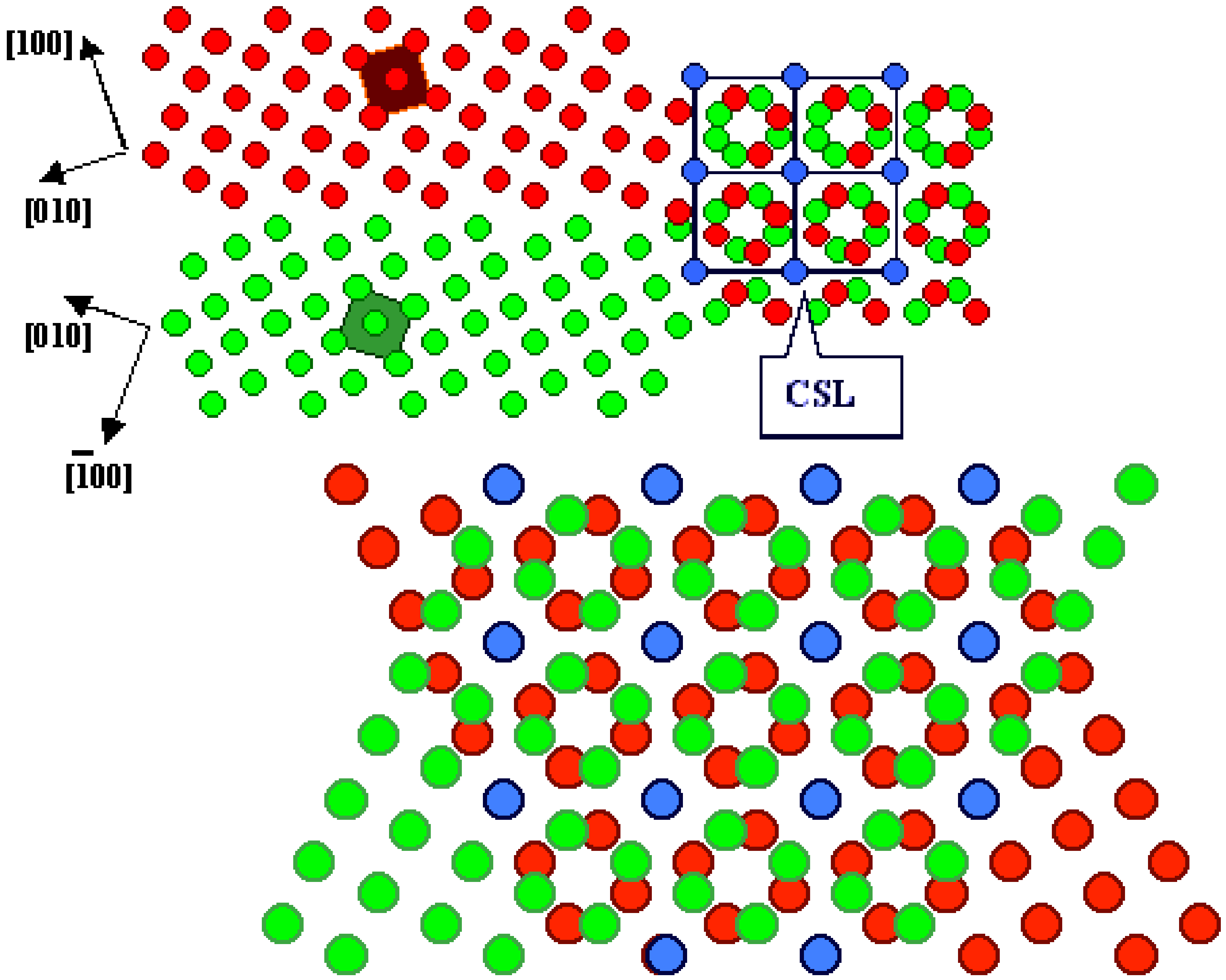
Coincidence Site Lattice (CSL) Boundaries





(111) type FCC twins are Σ3 type boundaries and are very stable.

Symmetric Grain Boundaries



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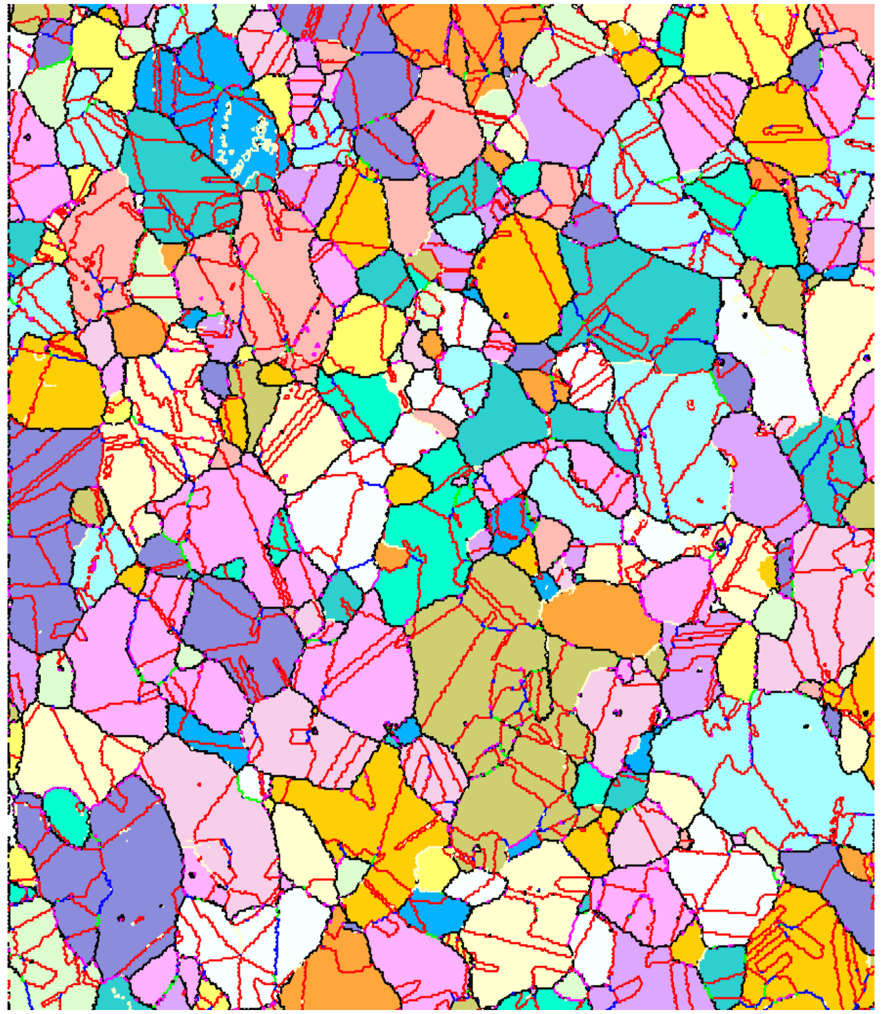
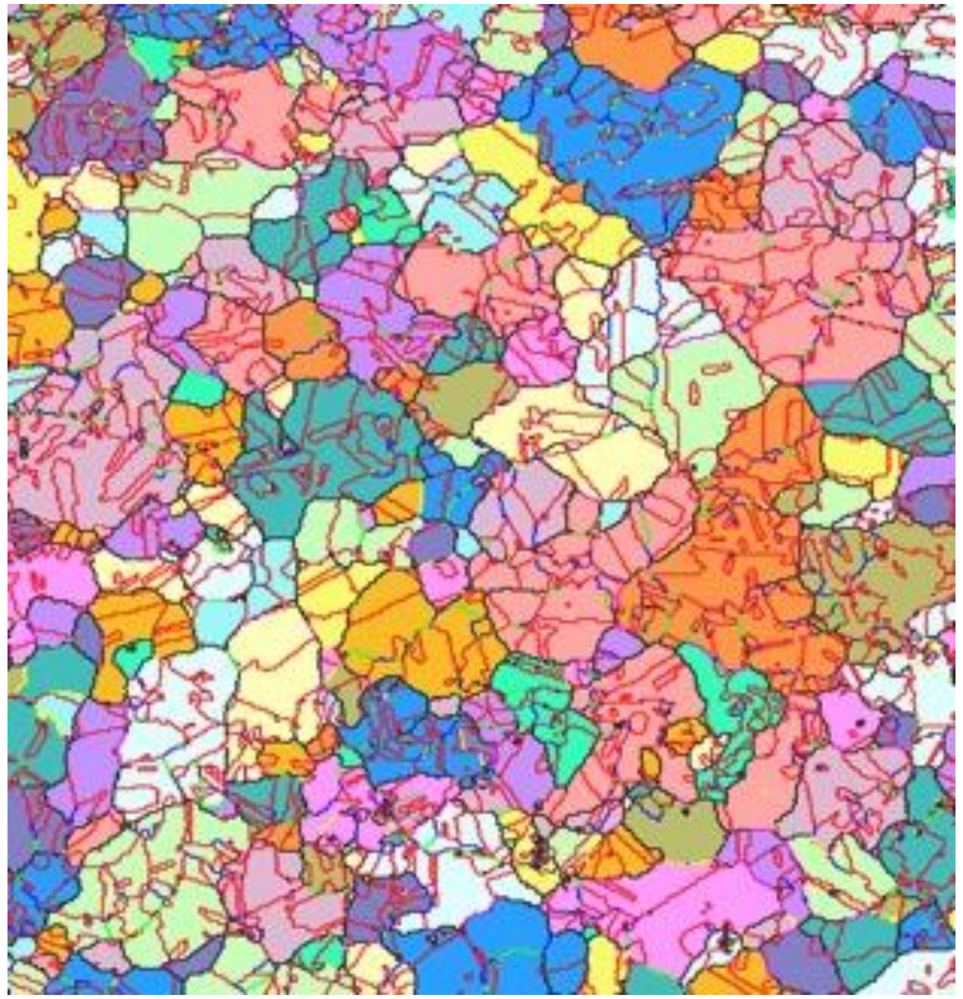
The networks are qualitatively and quantitatively different in normal and engineered materials (ones containing a high fraction of Σ3's)



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

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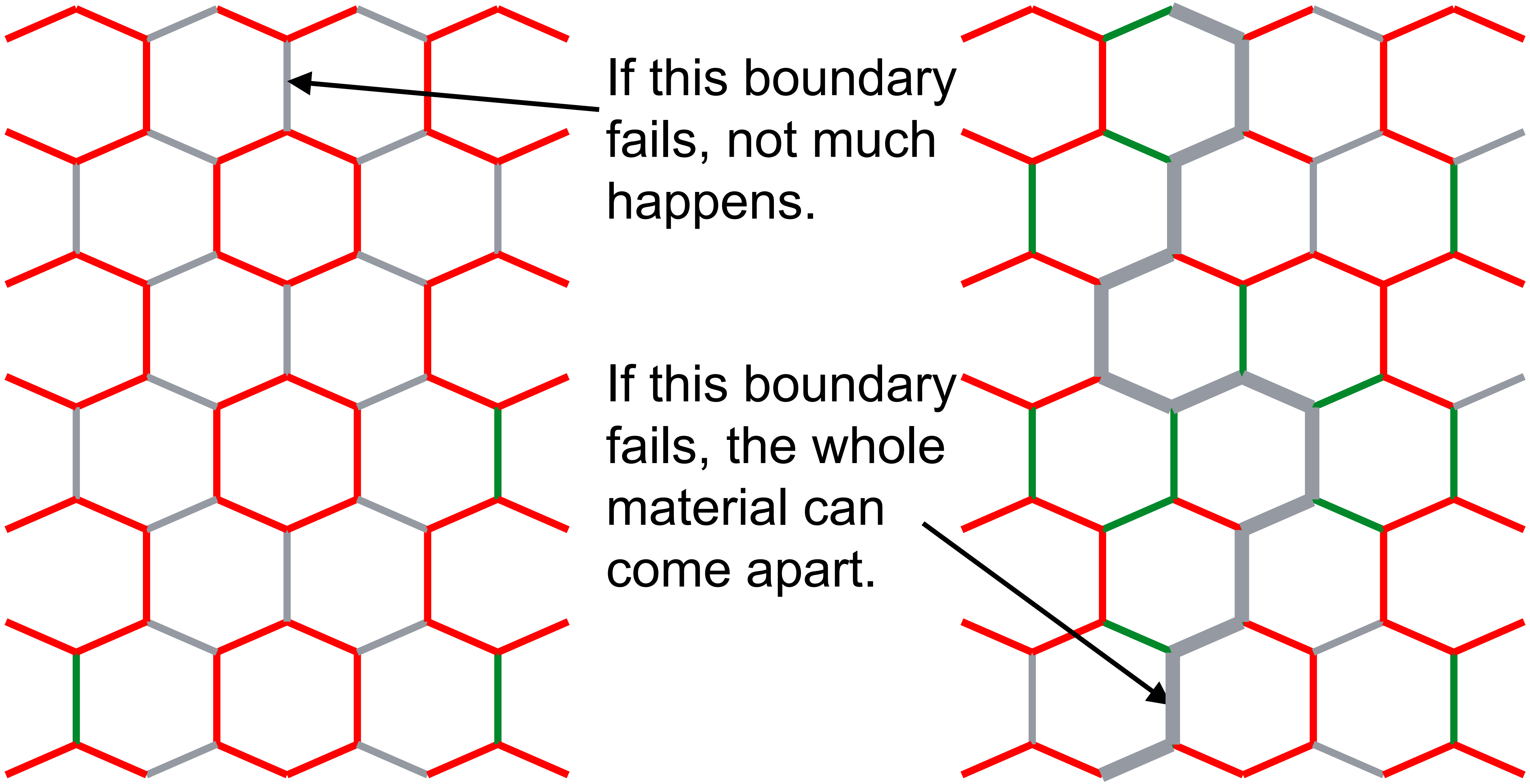
Key concept: The grain boundary *network* is essential component in a materials behavior

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



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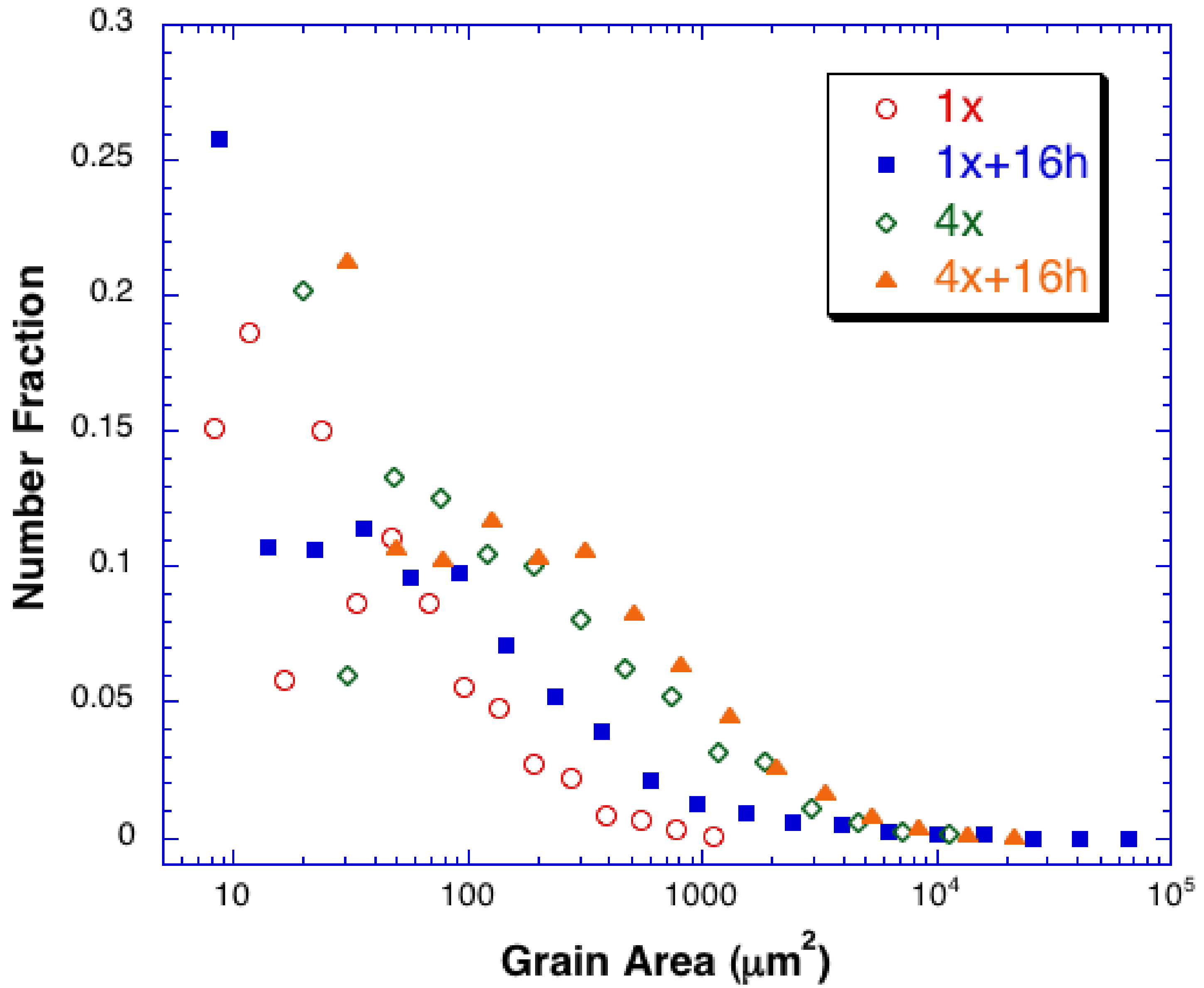
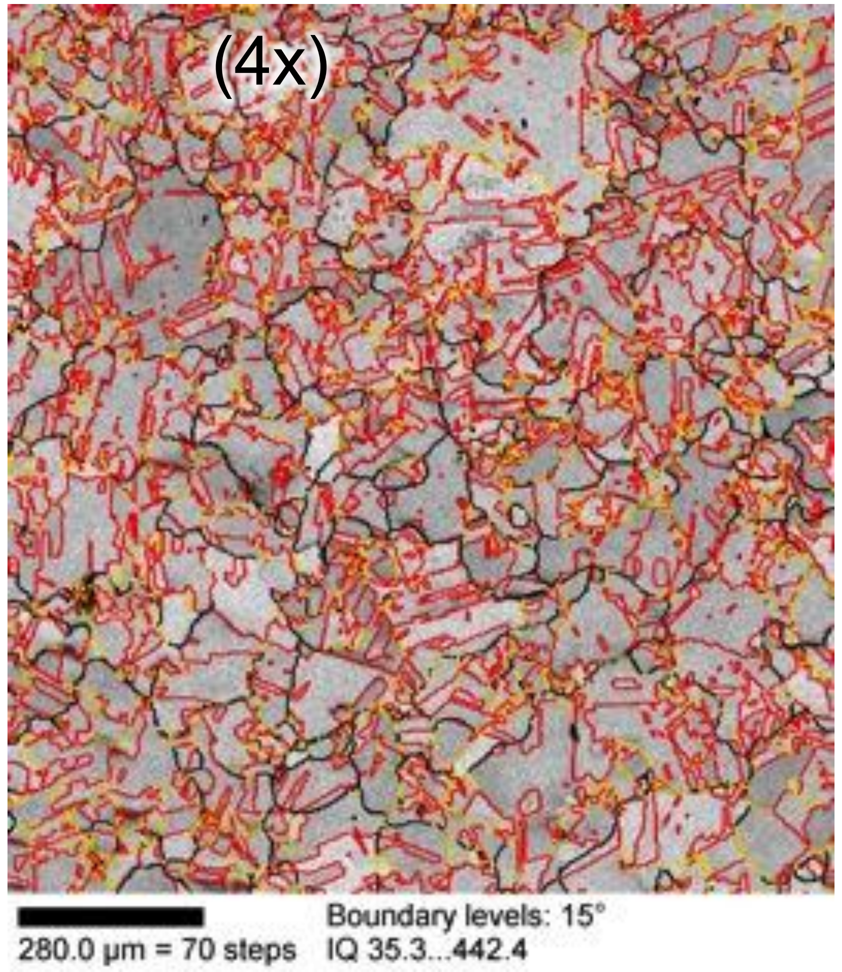
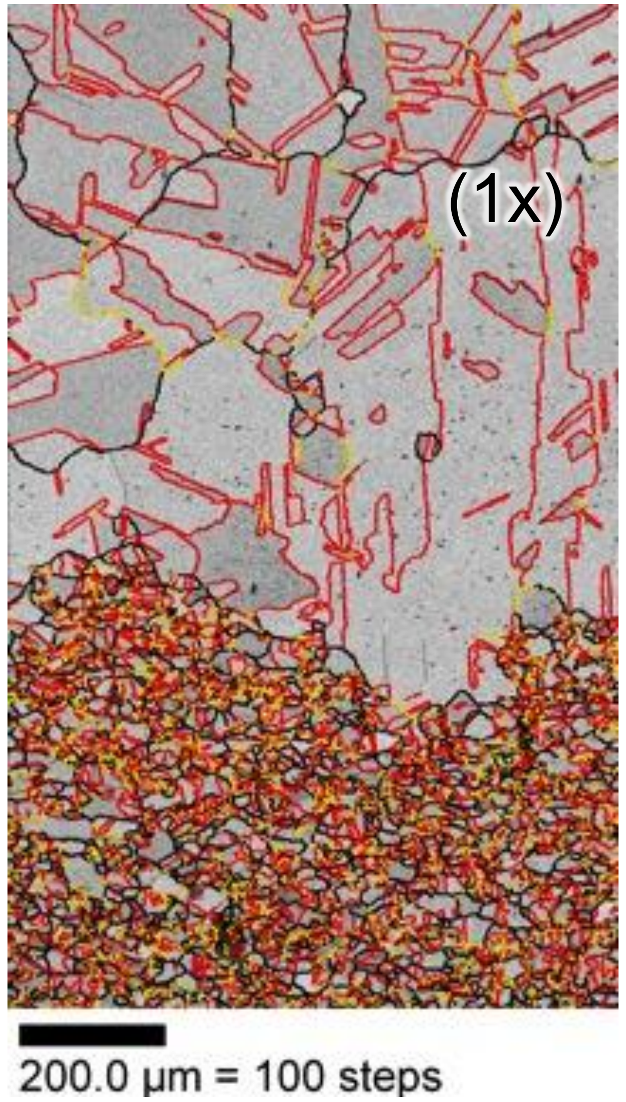
Grain coarsening kinetics are considerably slower in high special boundary content microstructures





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)

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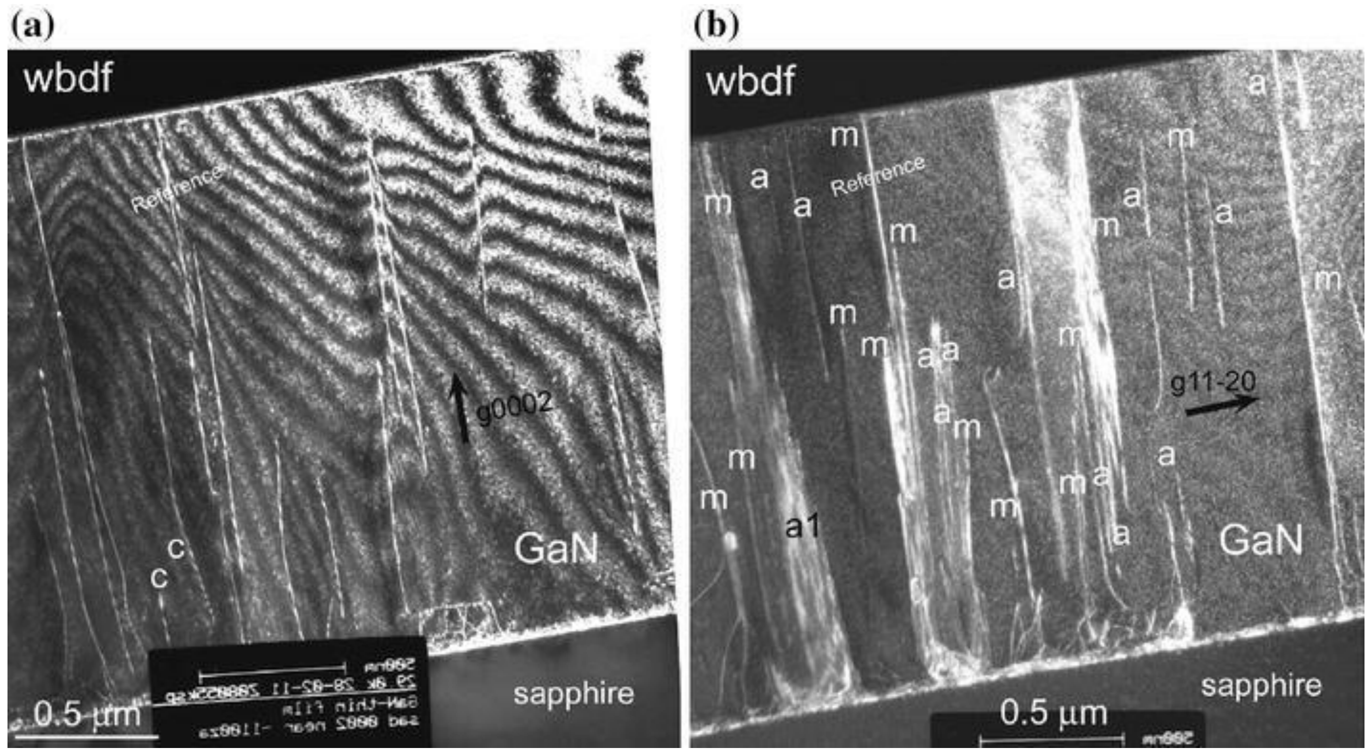
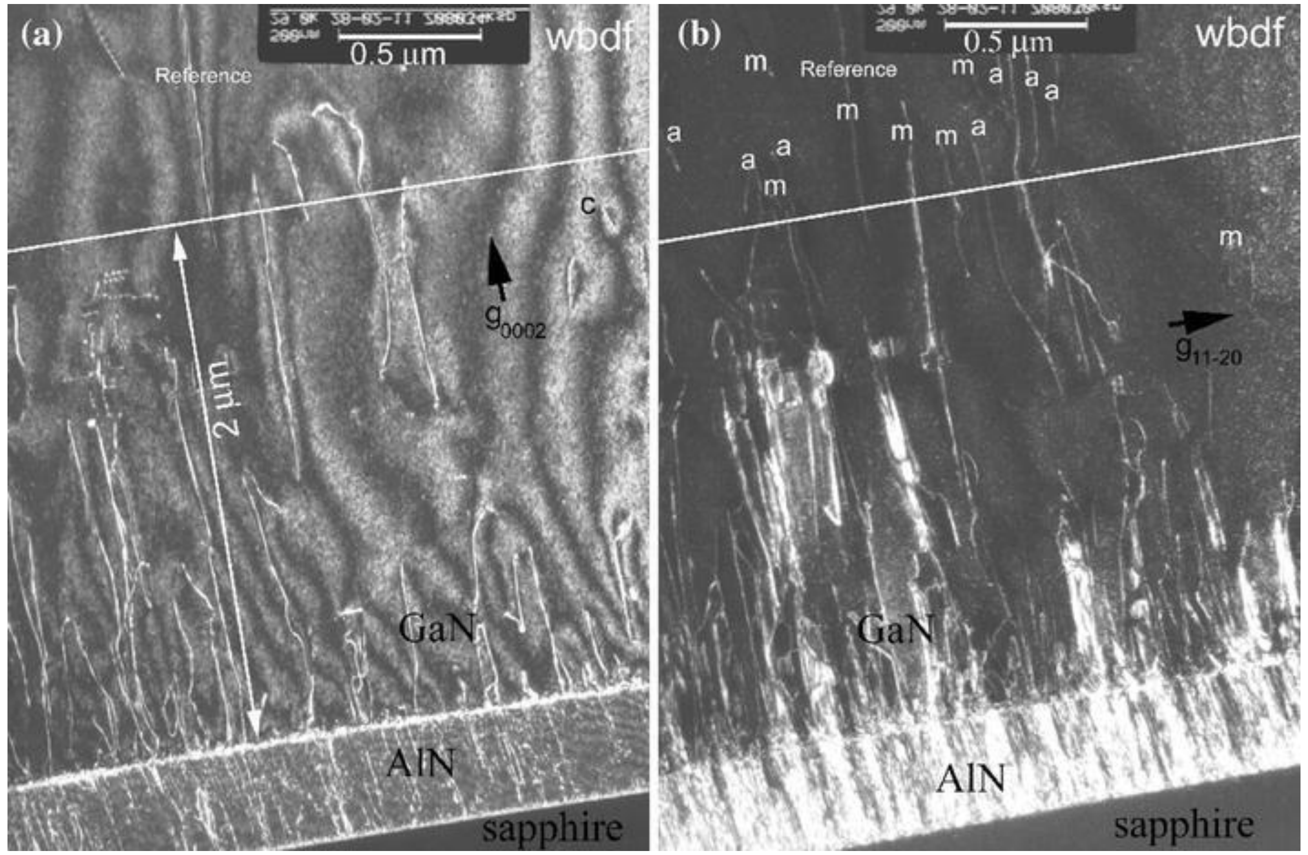
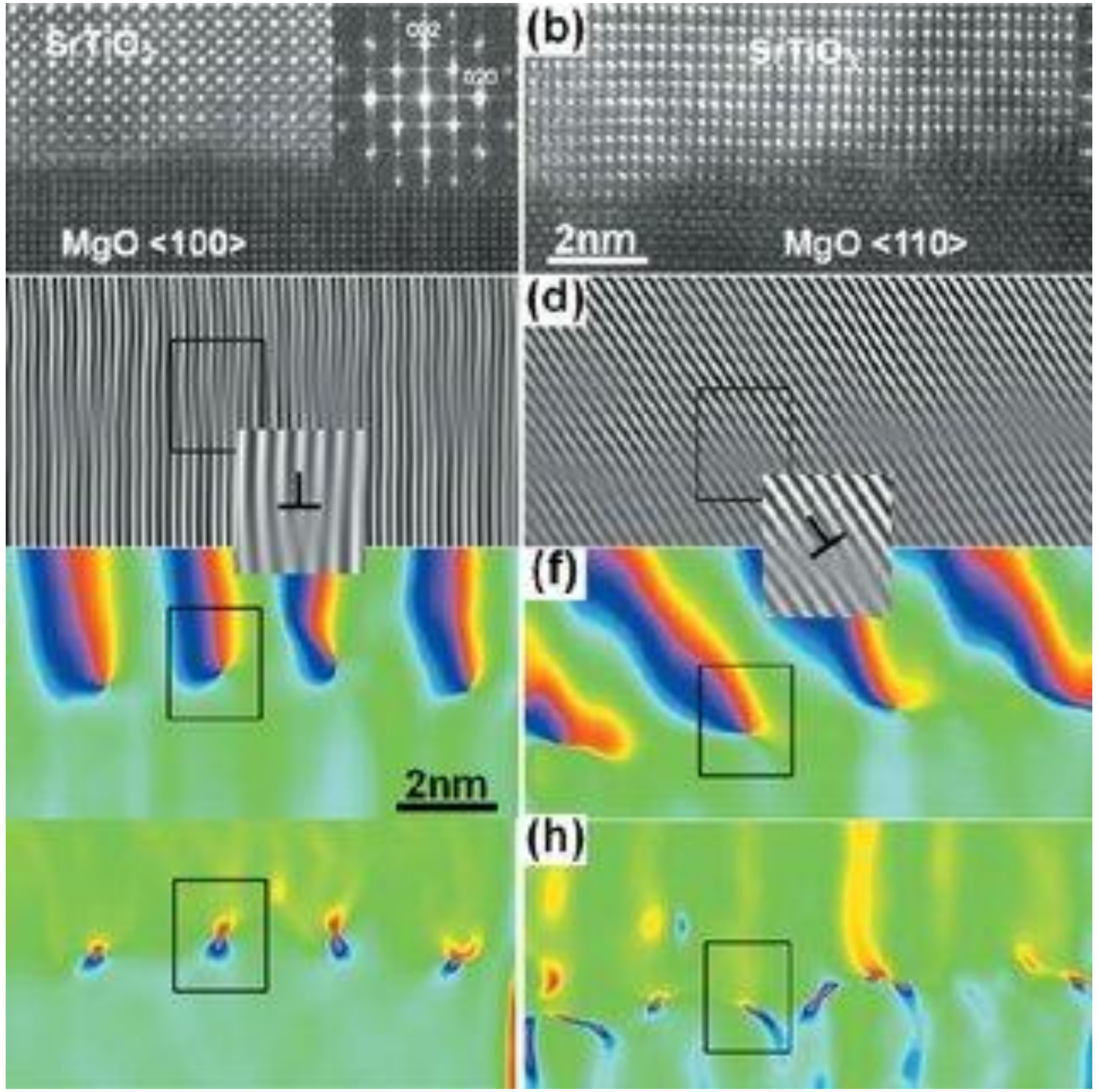
Misfit Dislocations







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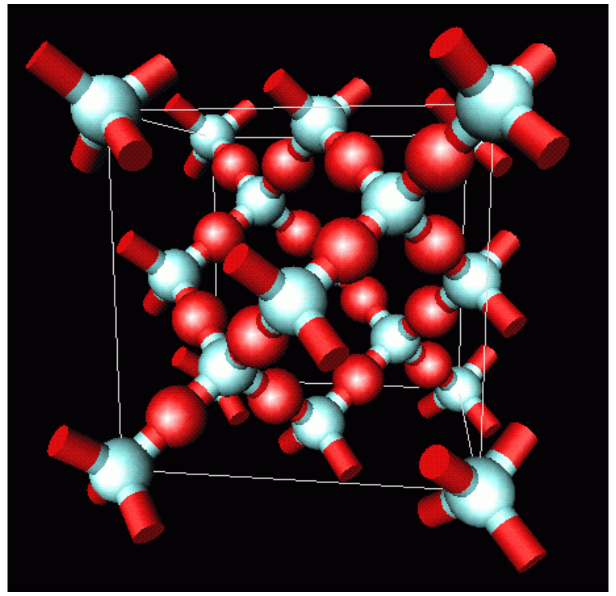
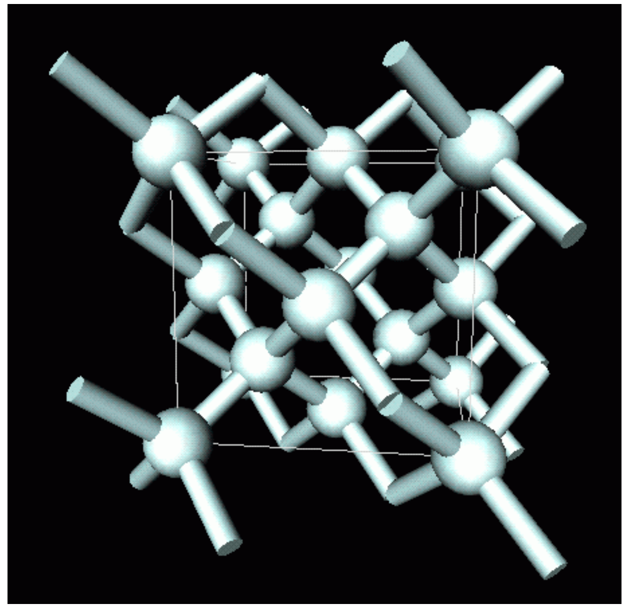
Amorphous

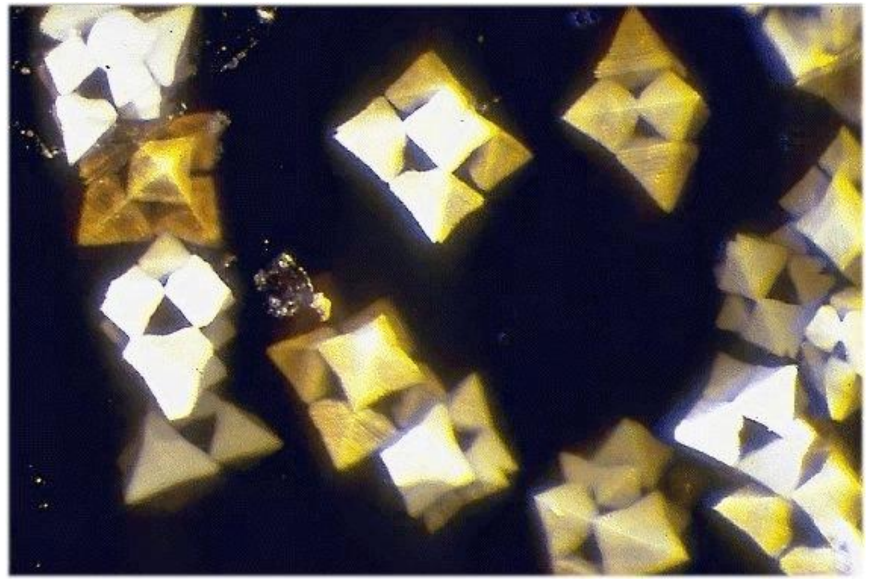
Crystalline silicon



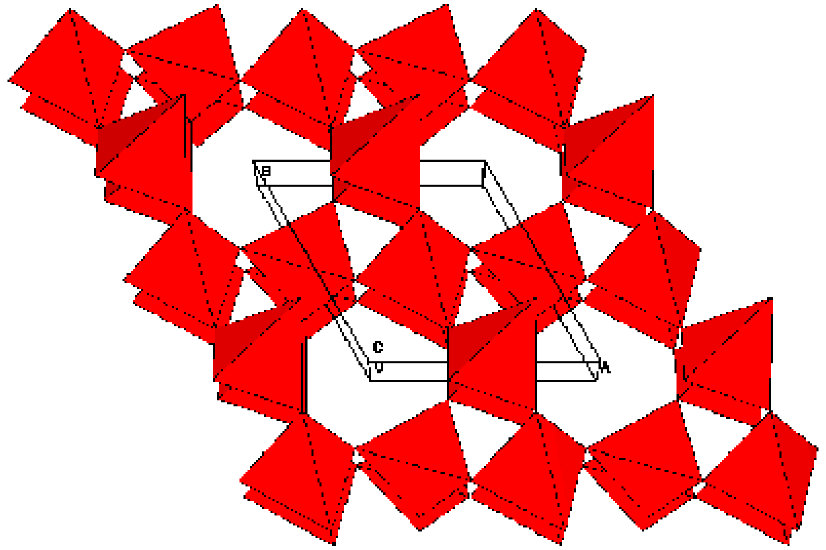


Quartz

Cristobalite:SiO_4 tetrahedron on a diamond lattice



Rhombohedral cell



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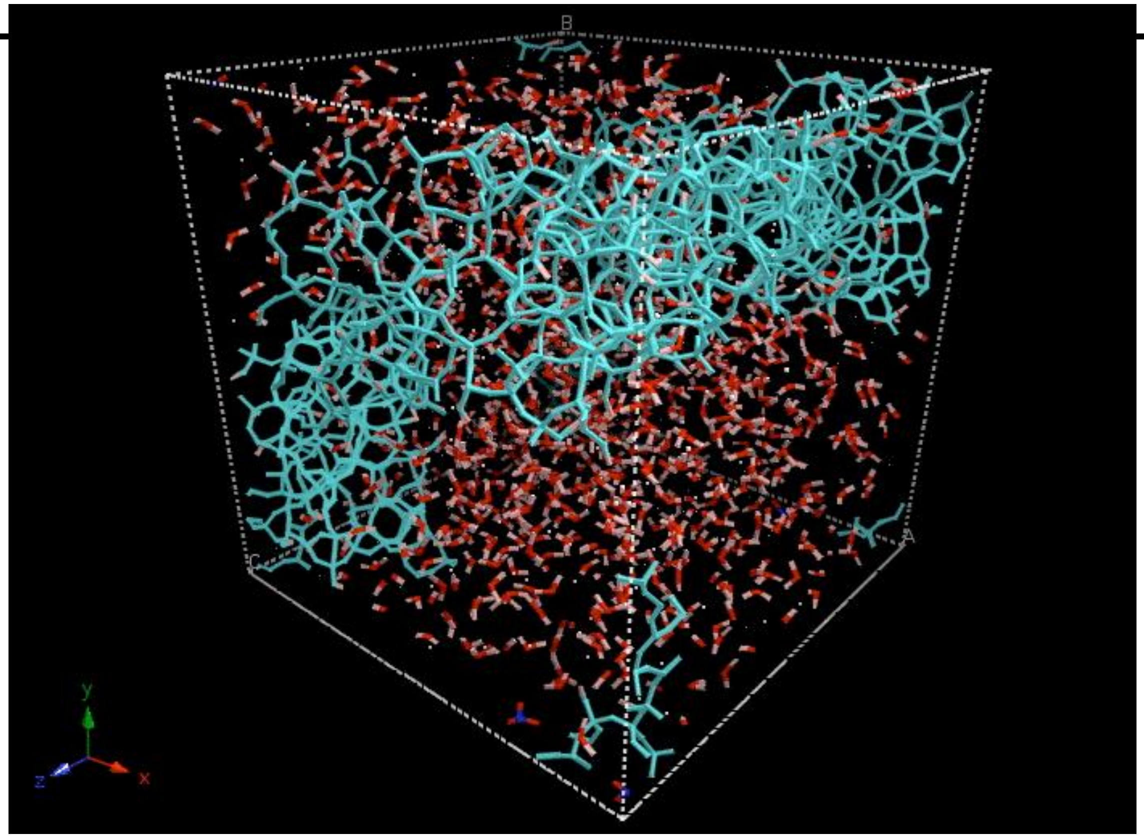
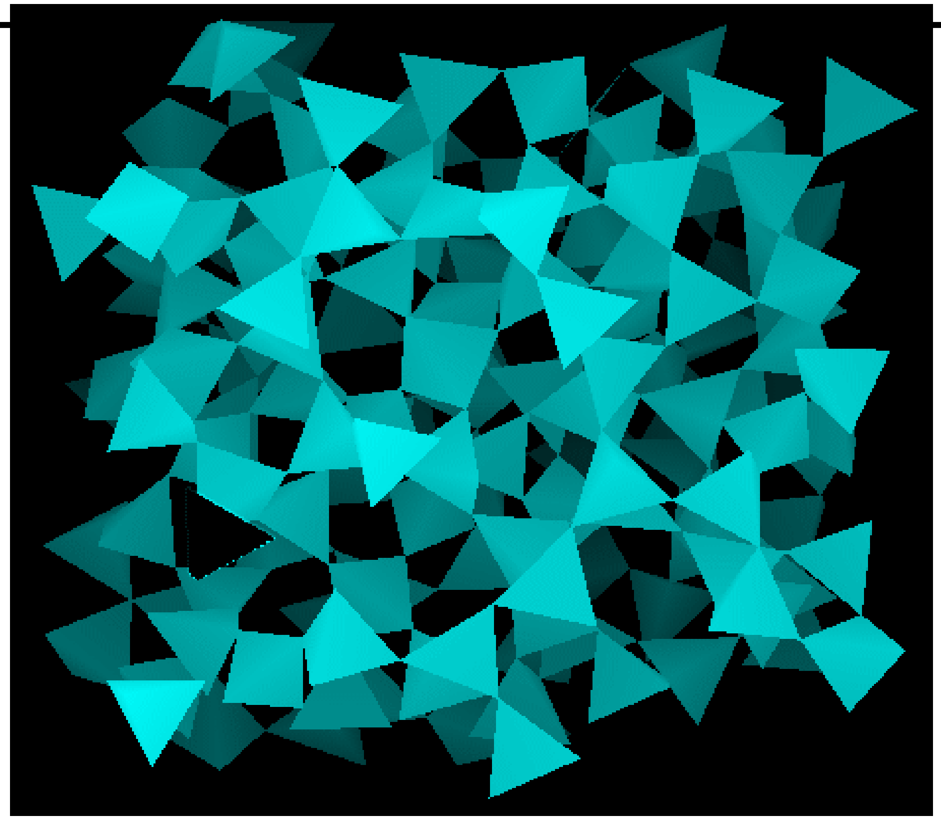
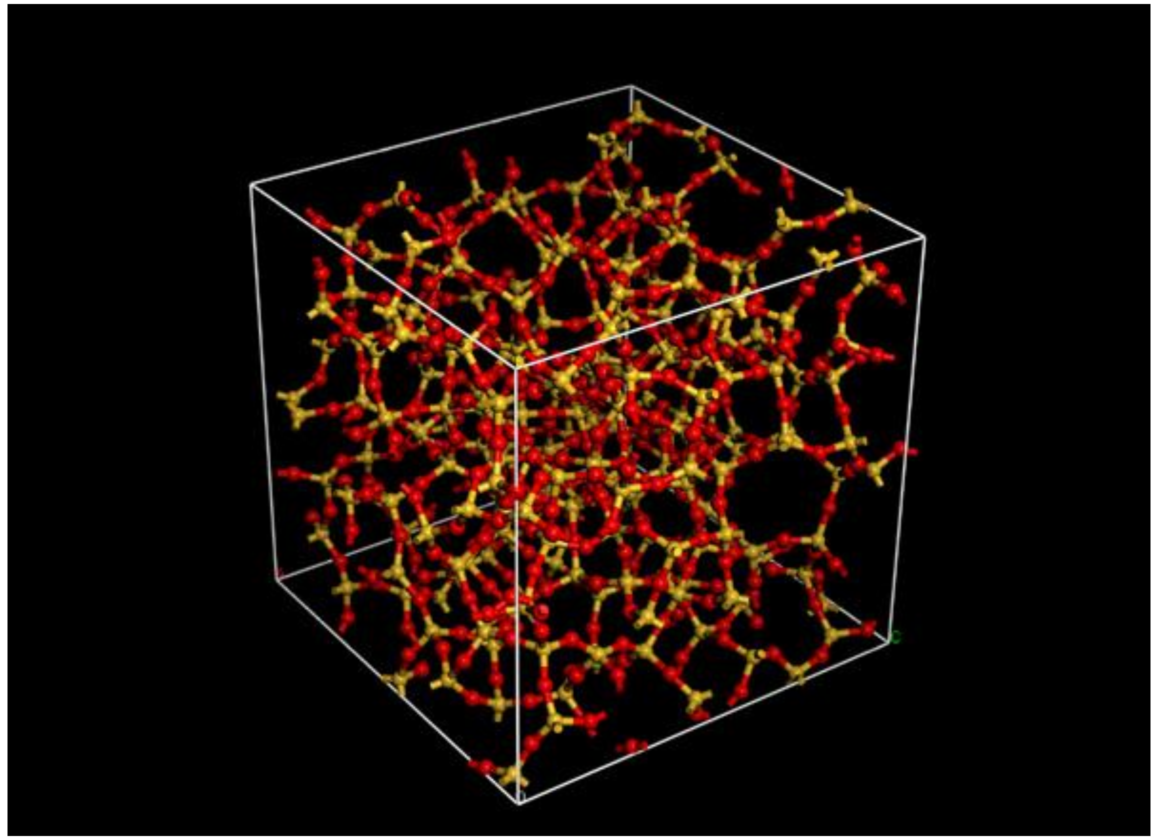
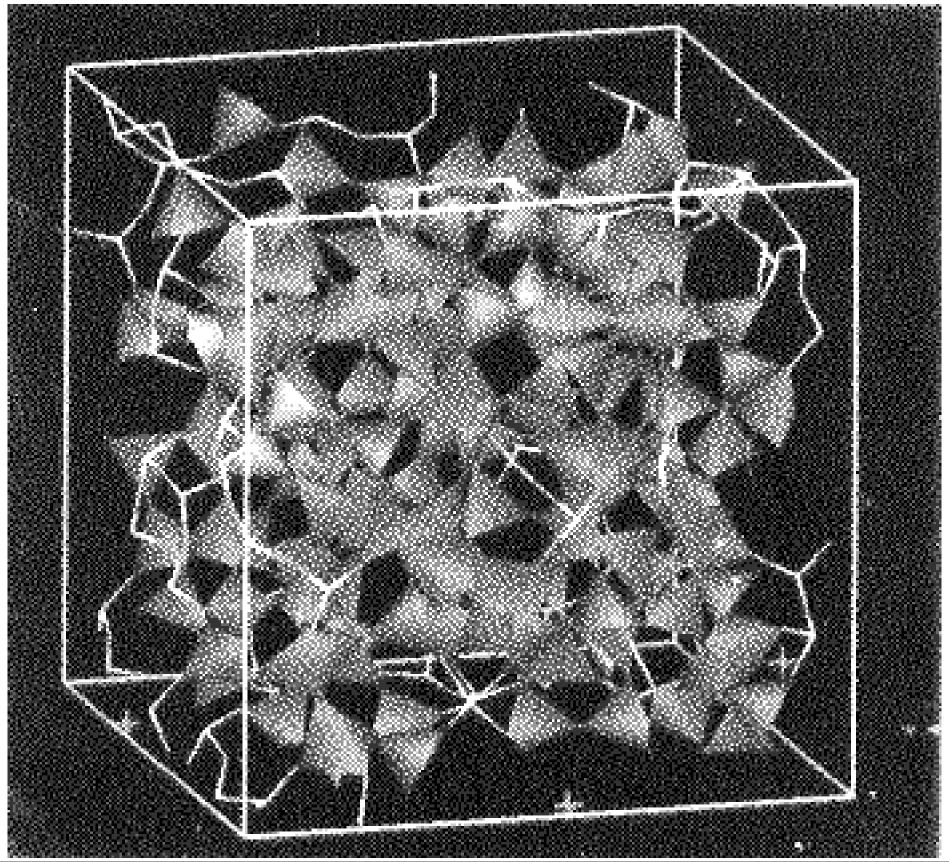
Amorphous: glass

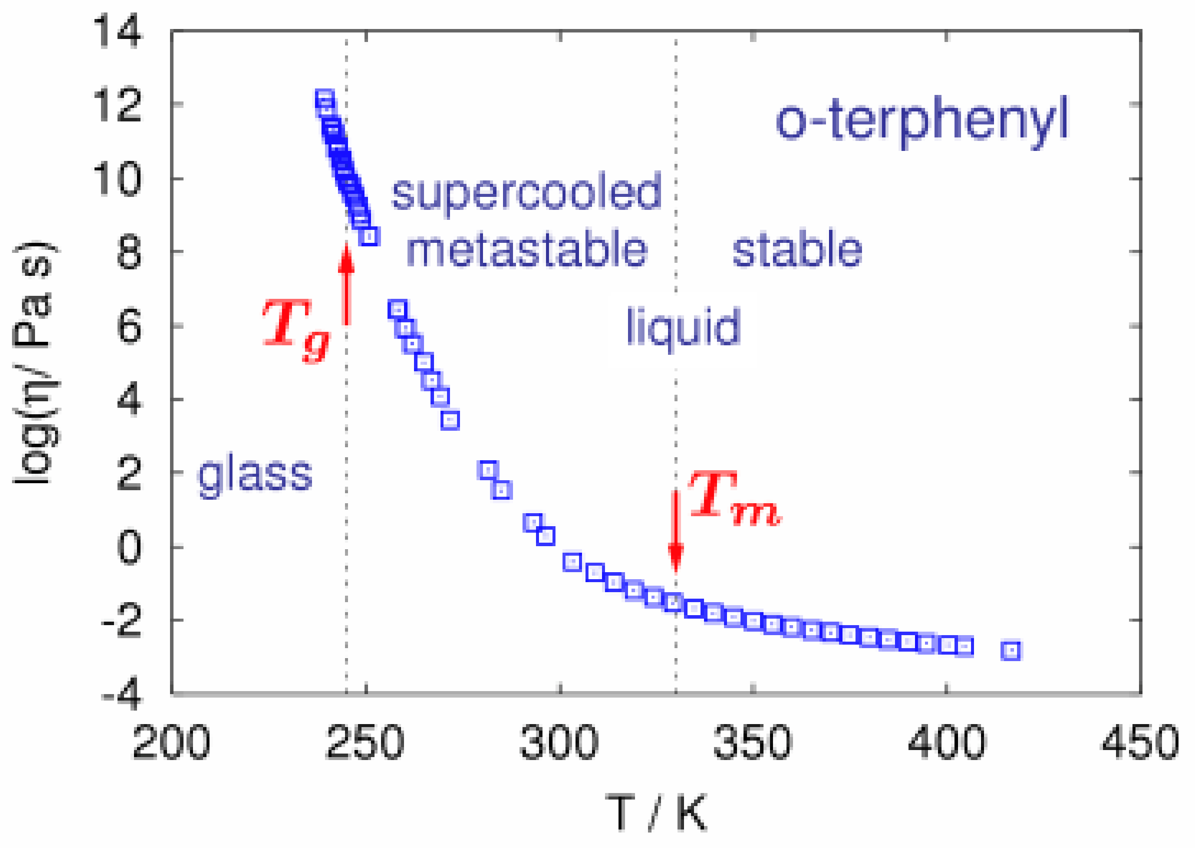


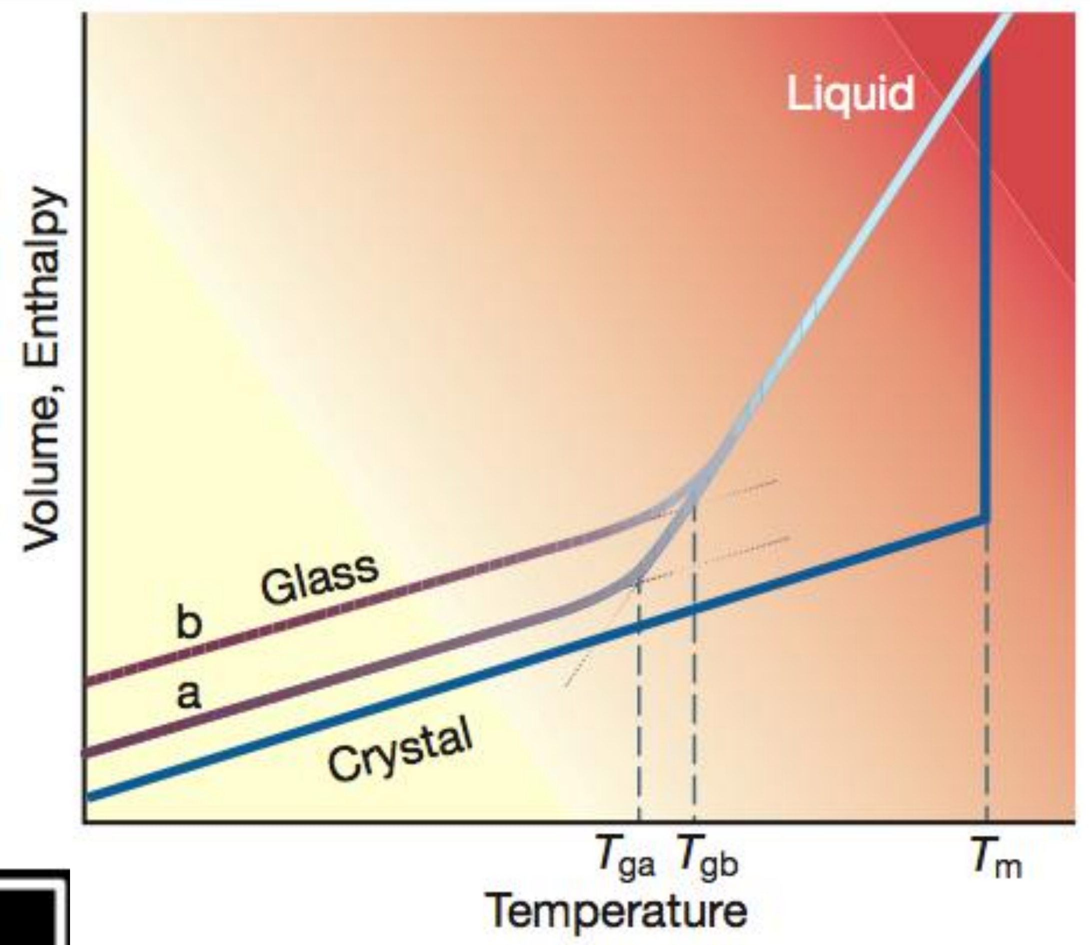


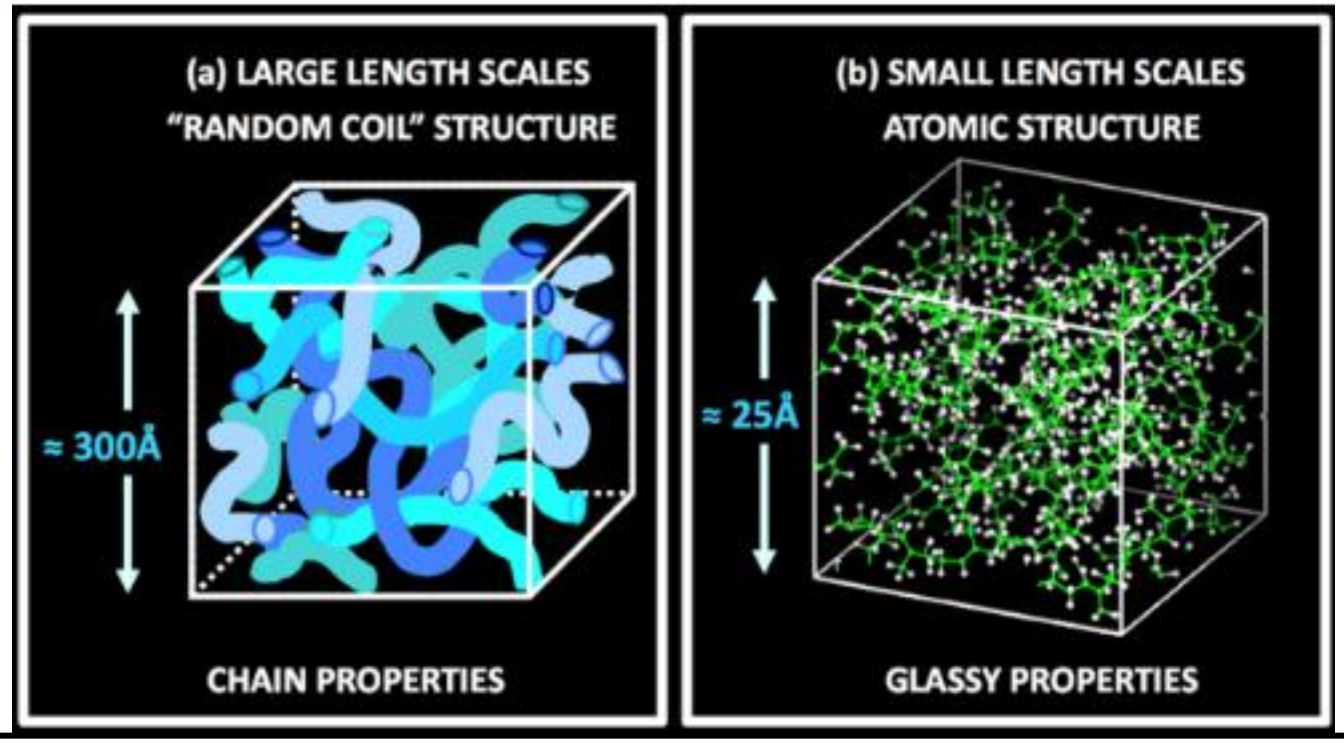




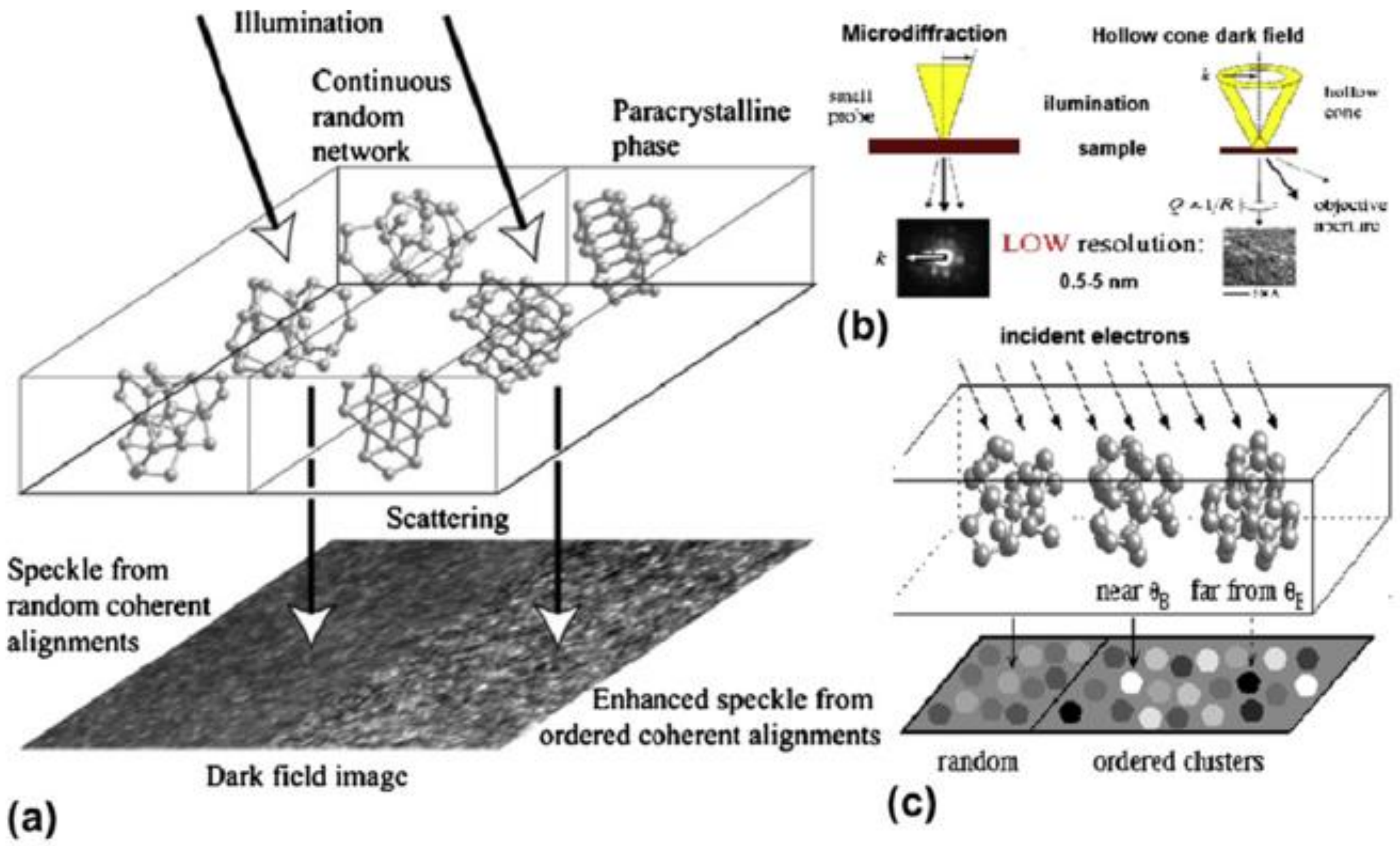
The Glass Transition T_g

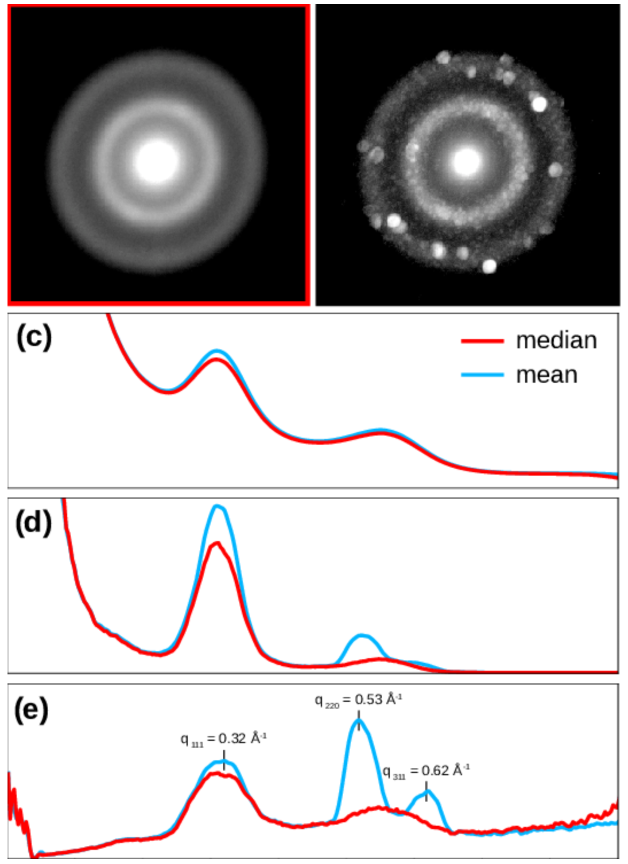




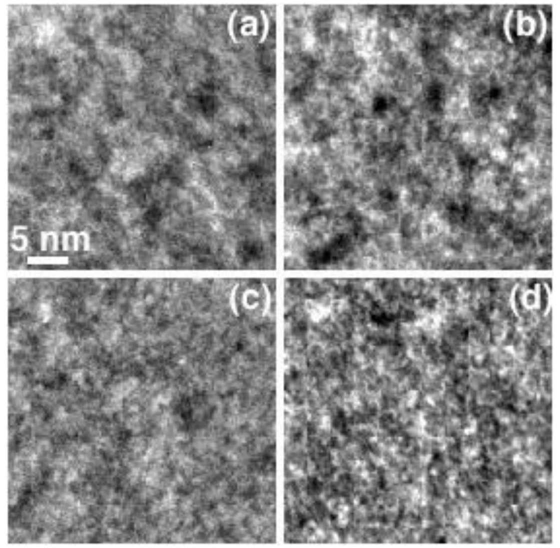


Amorphous Materials: Fluctuation Electron Microscopy

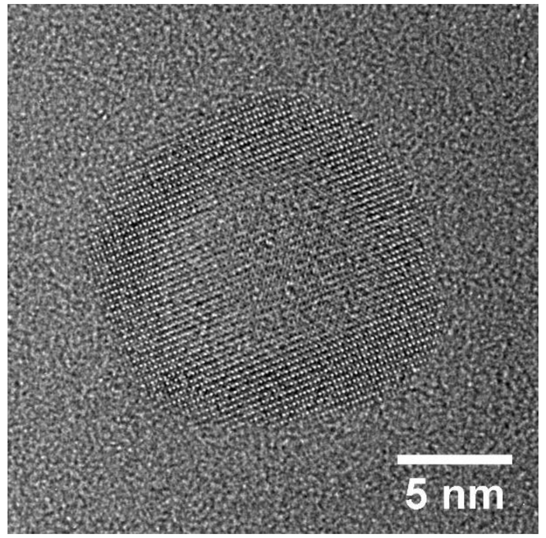




Darkfield TEM images

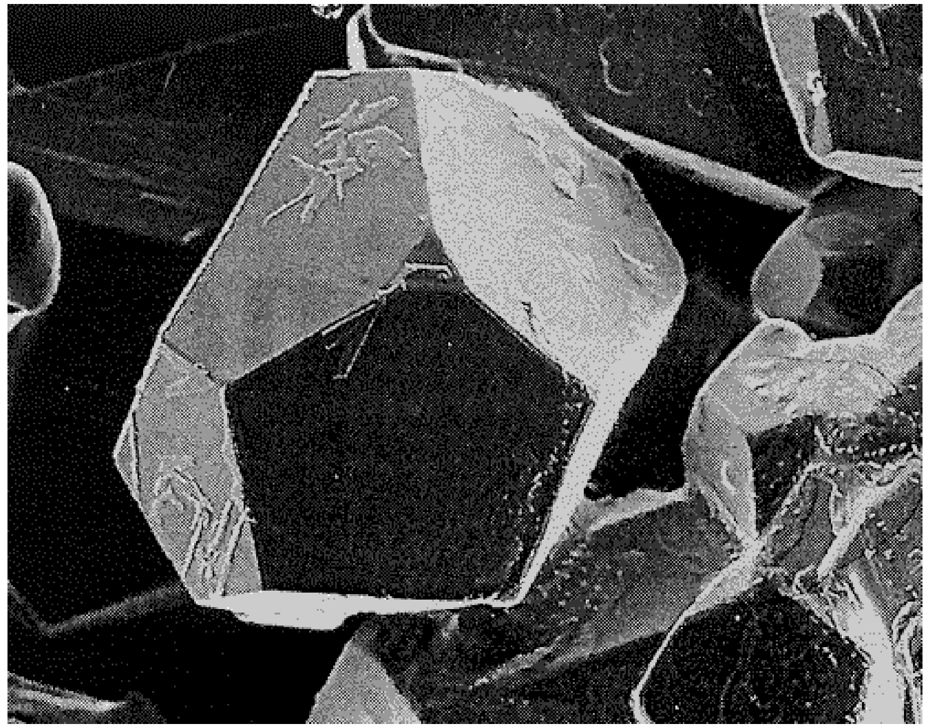


HRTEM image

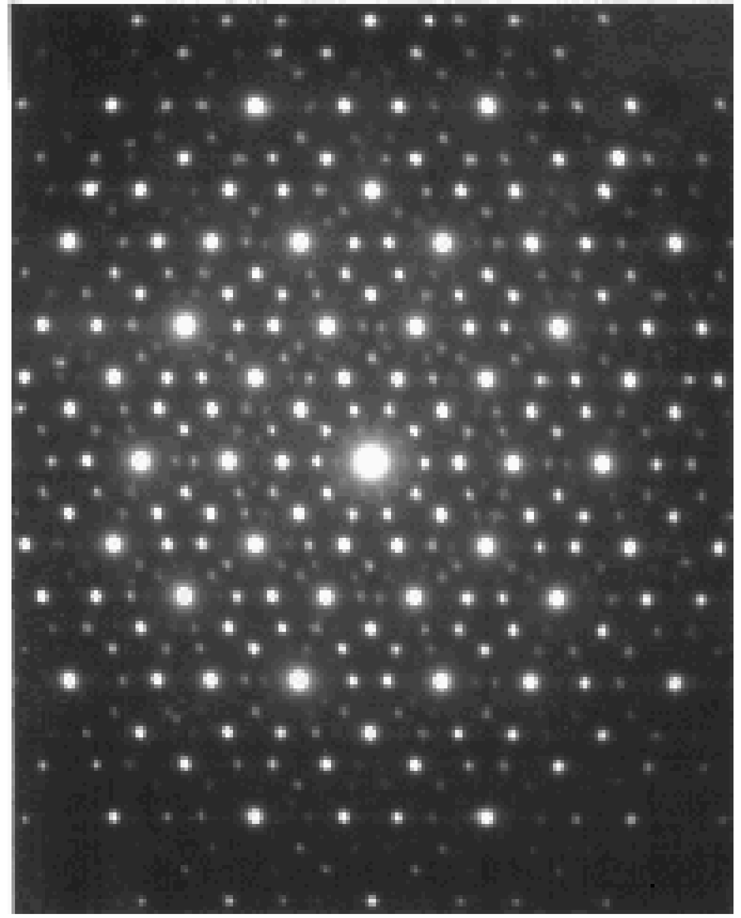


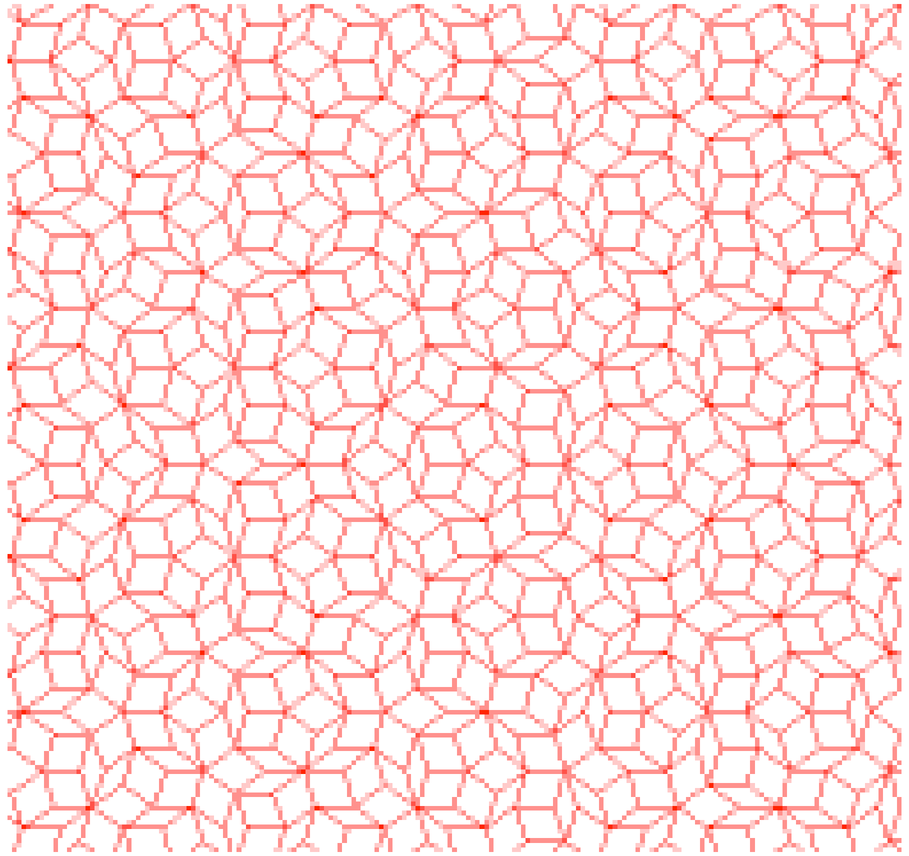
Fluctuation electron microscopy (FEM) is electron scattering technique for measuring nanometer scale order in amorphous materials. **Fluctuations** in the local scattering intensity reveal internal atomic arrangements on short range and medium range (nanometer-scale) order

Quasicrystals



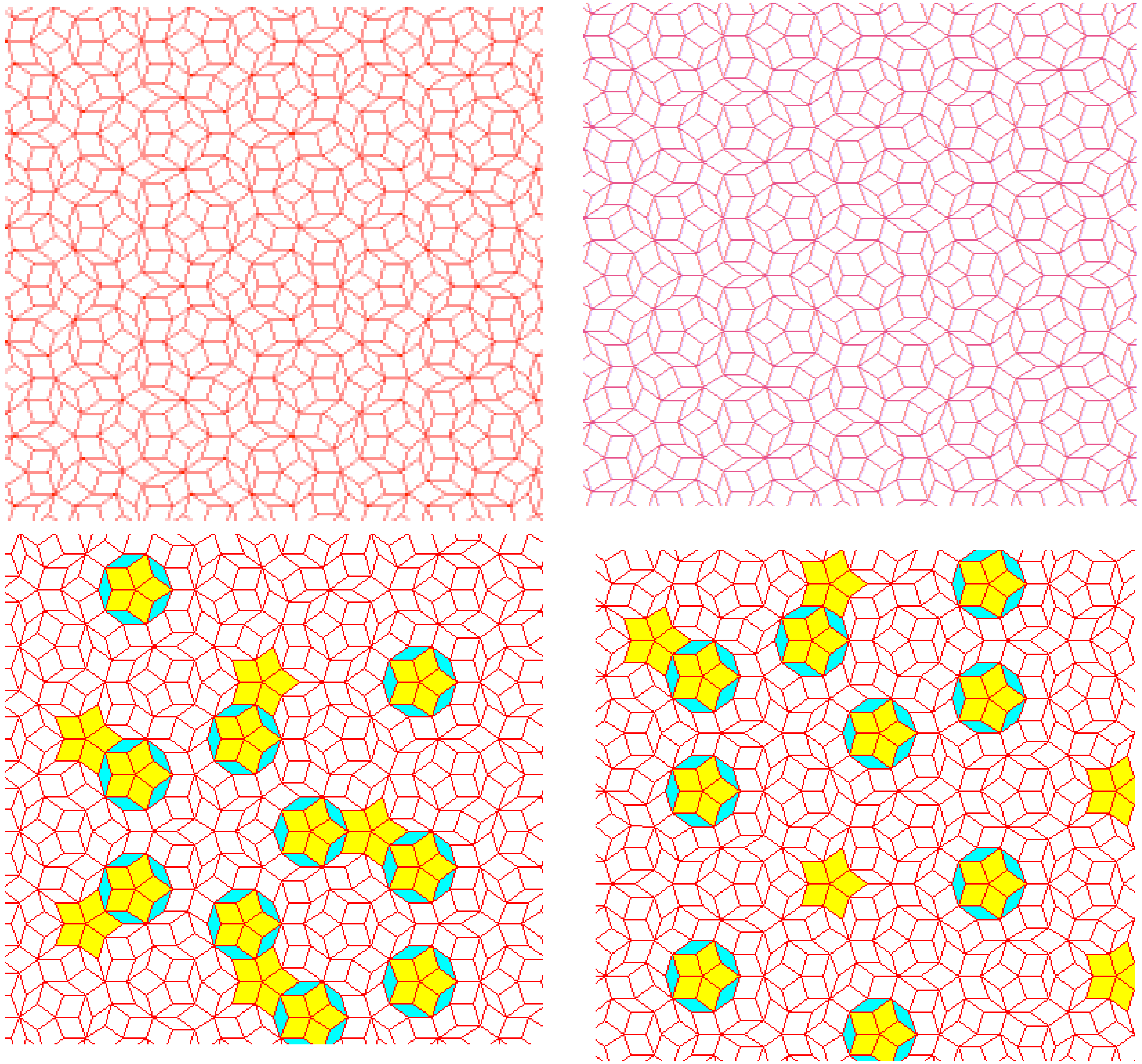
AlCuFe

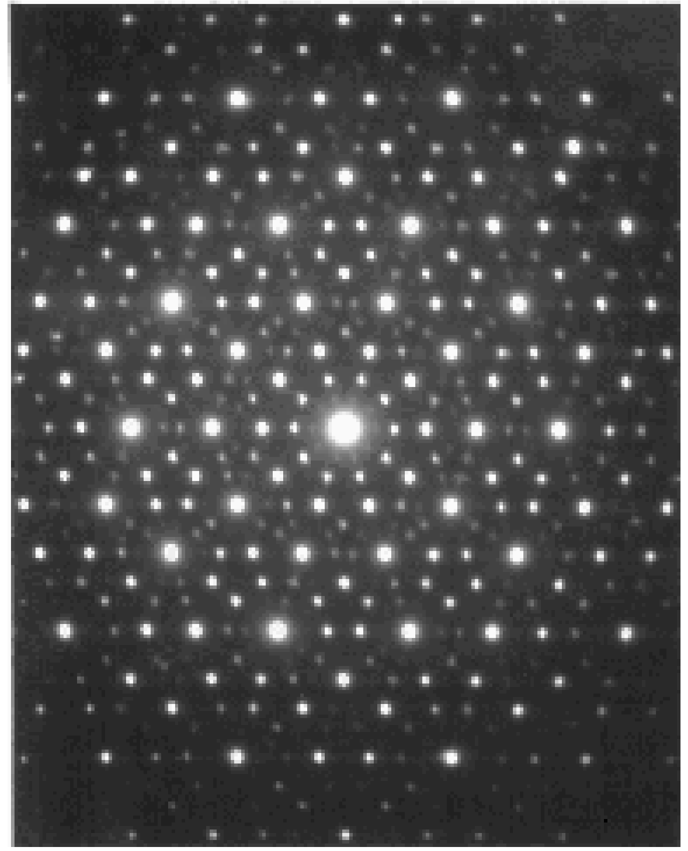




[Dan Shechtman](#)
[2011 Nobel Prize in chemistry](#)

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.

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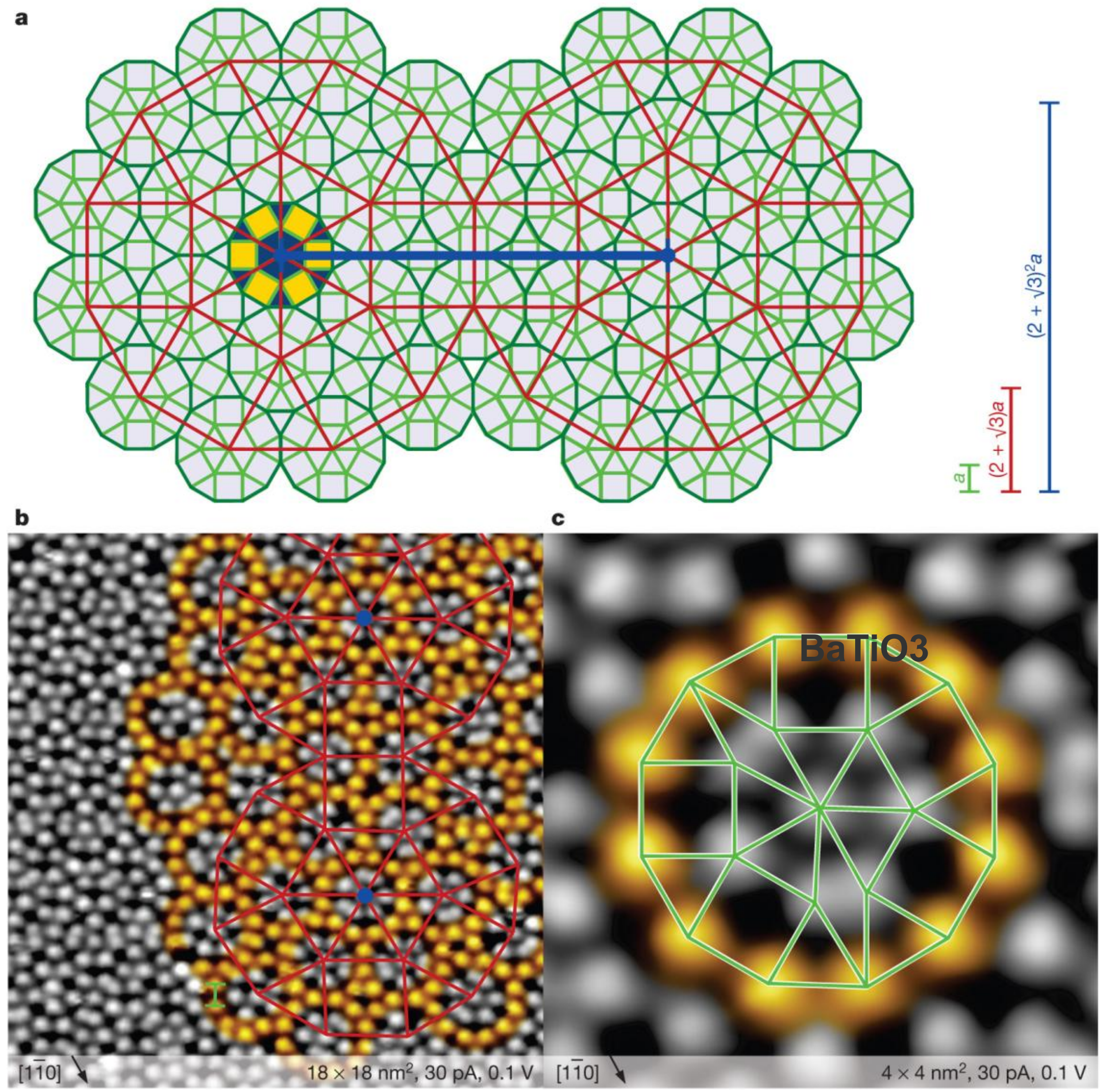
Quasicrystals

Dodecagonal tiling as measured by STM.



$BaTiO_3$ on Pt

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

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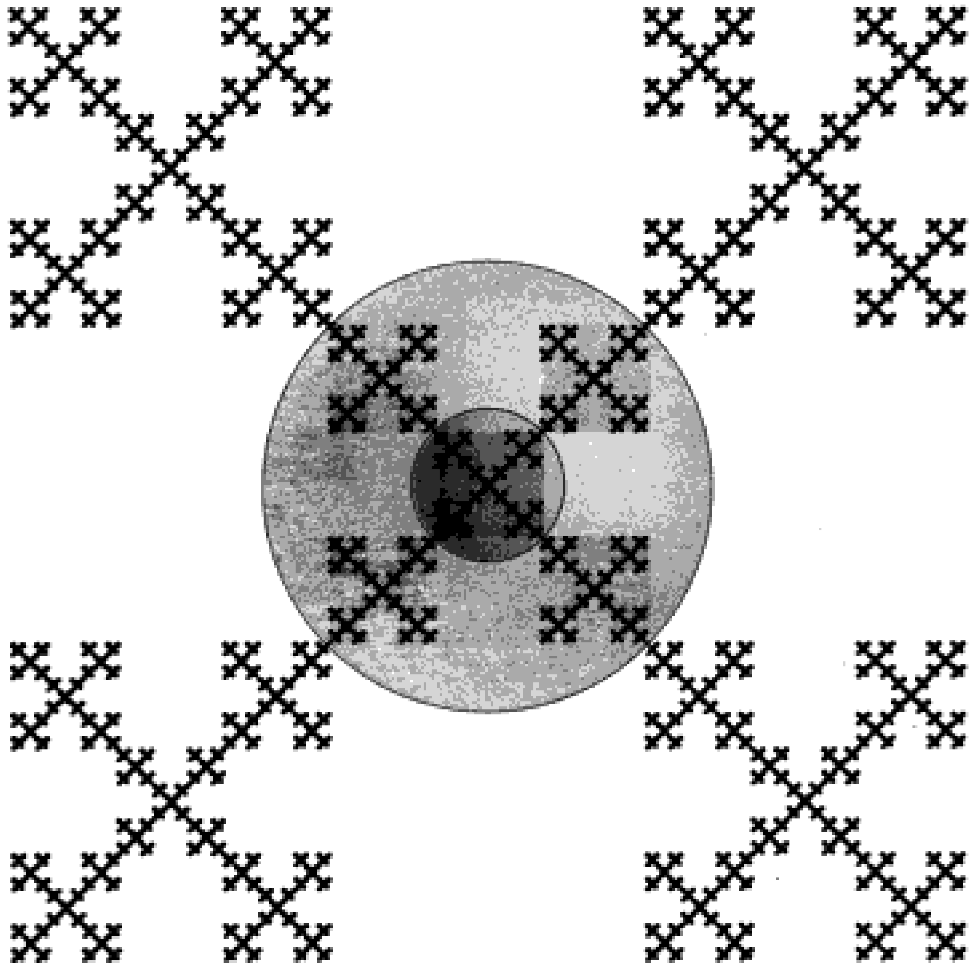
Fractals



$$\frac{M(r)}{M(r_0)} = \frac{Cr^d}{Cr_0^2}$$

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

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

Density

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

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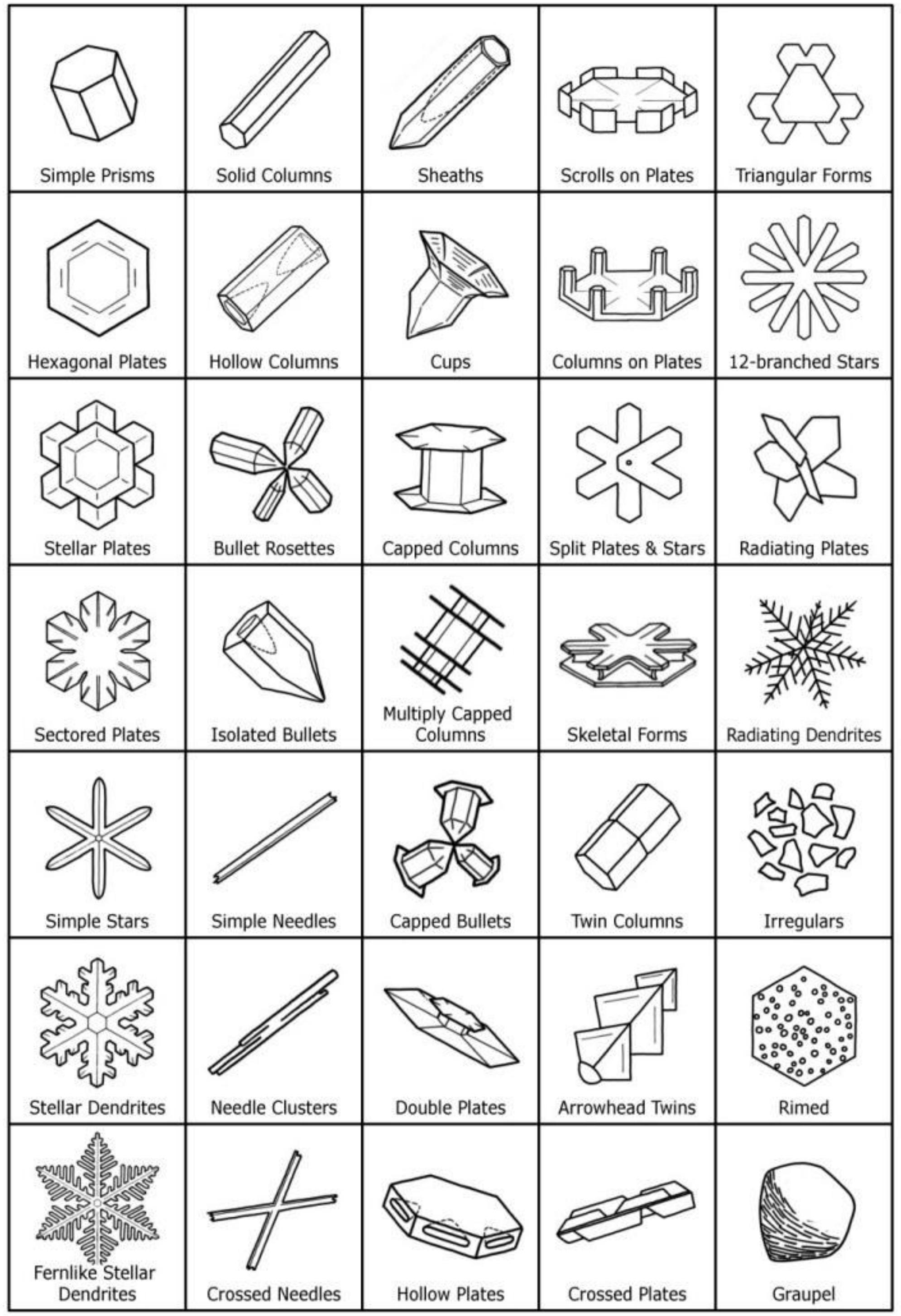
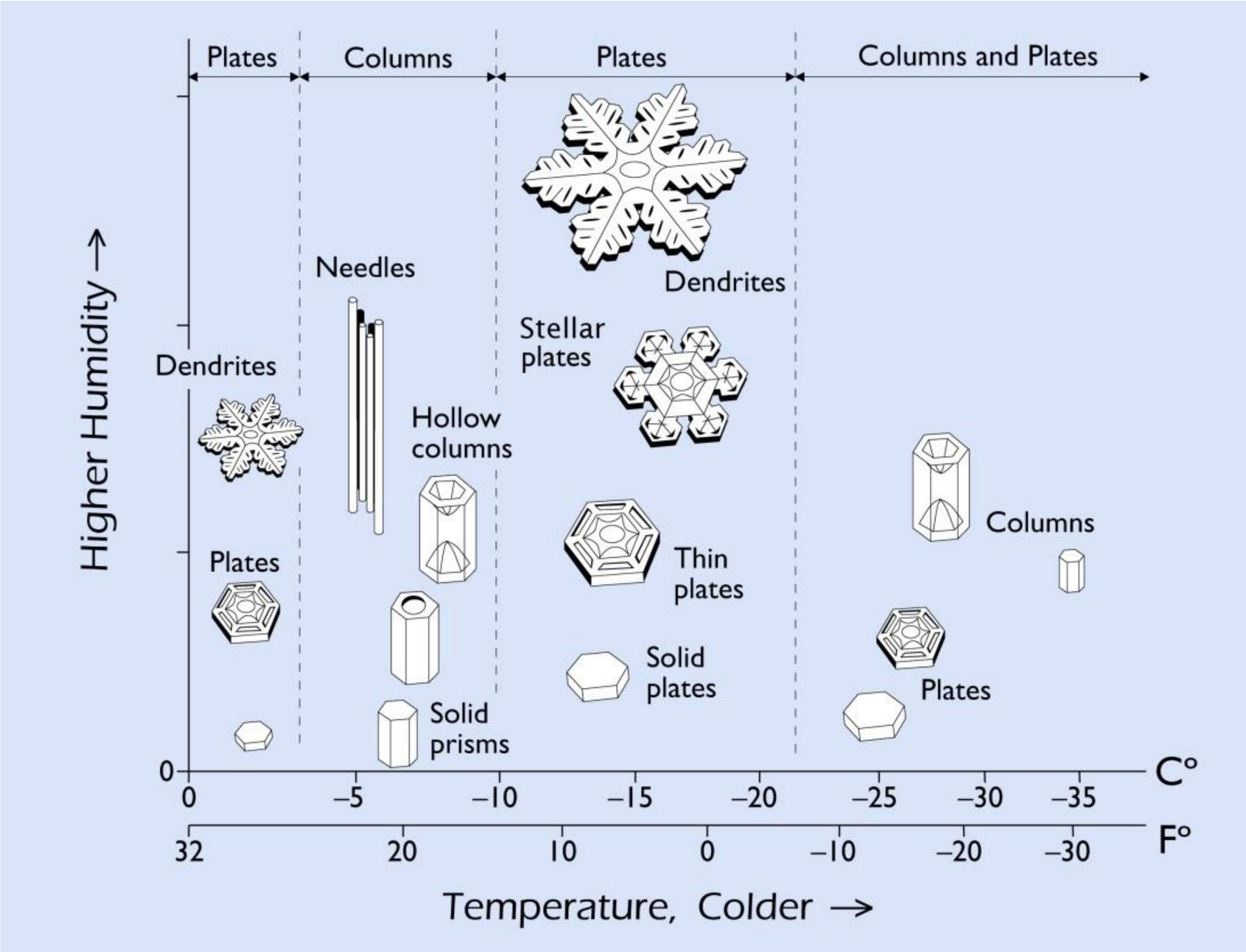
Fractal Crystals



Types of Snowflakes ... SnowCrystals.com



Oscillation of structures between dendritic plates and columns/plates

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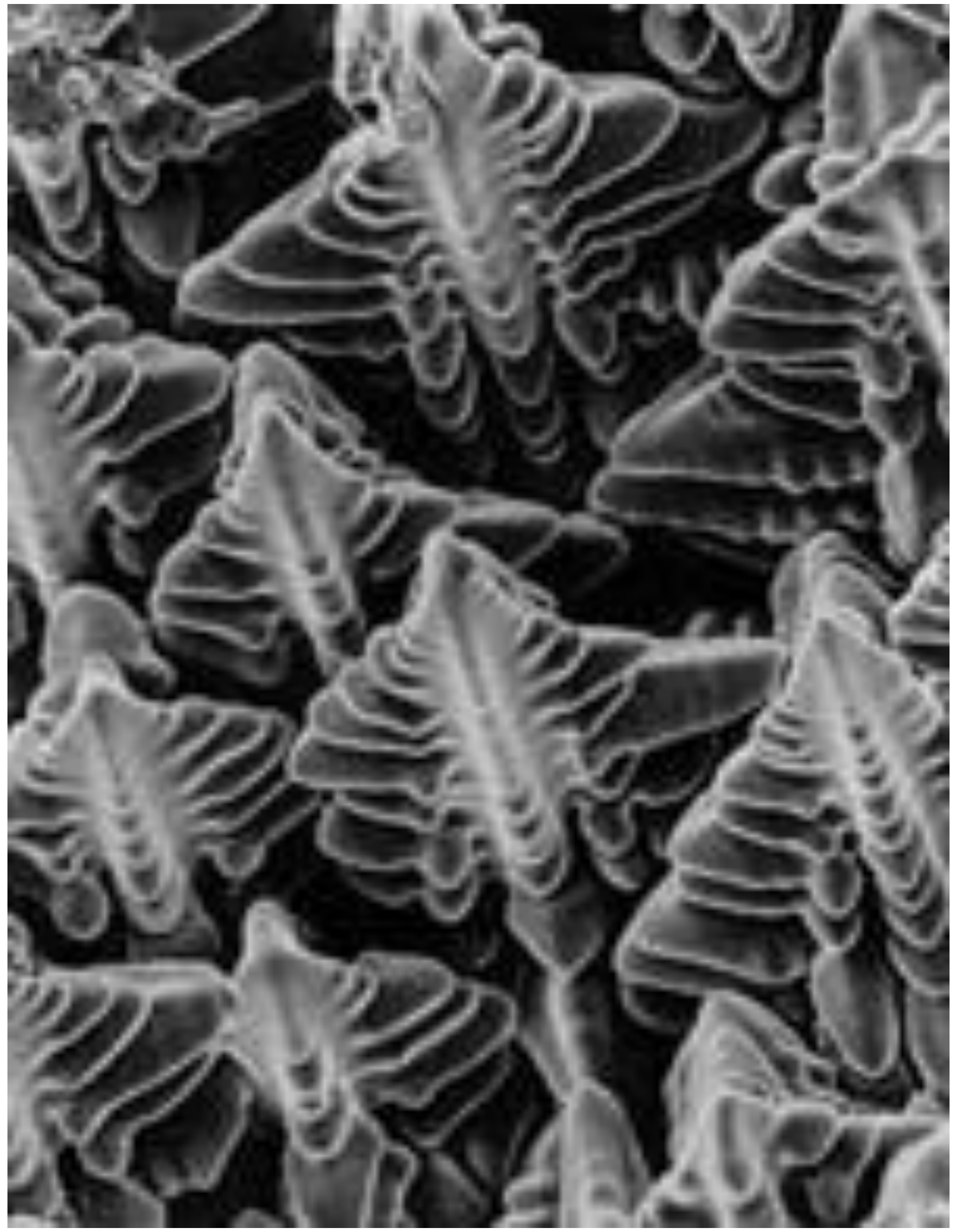
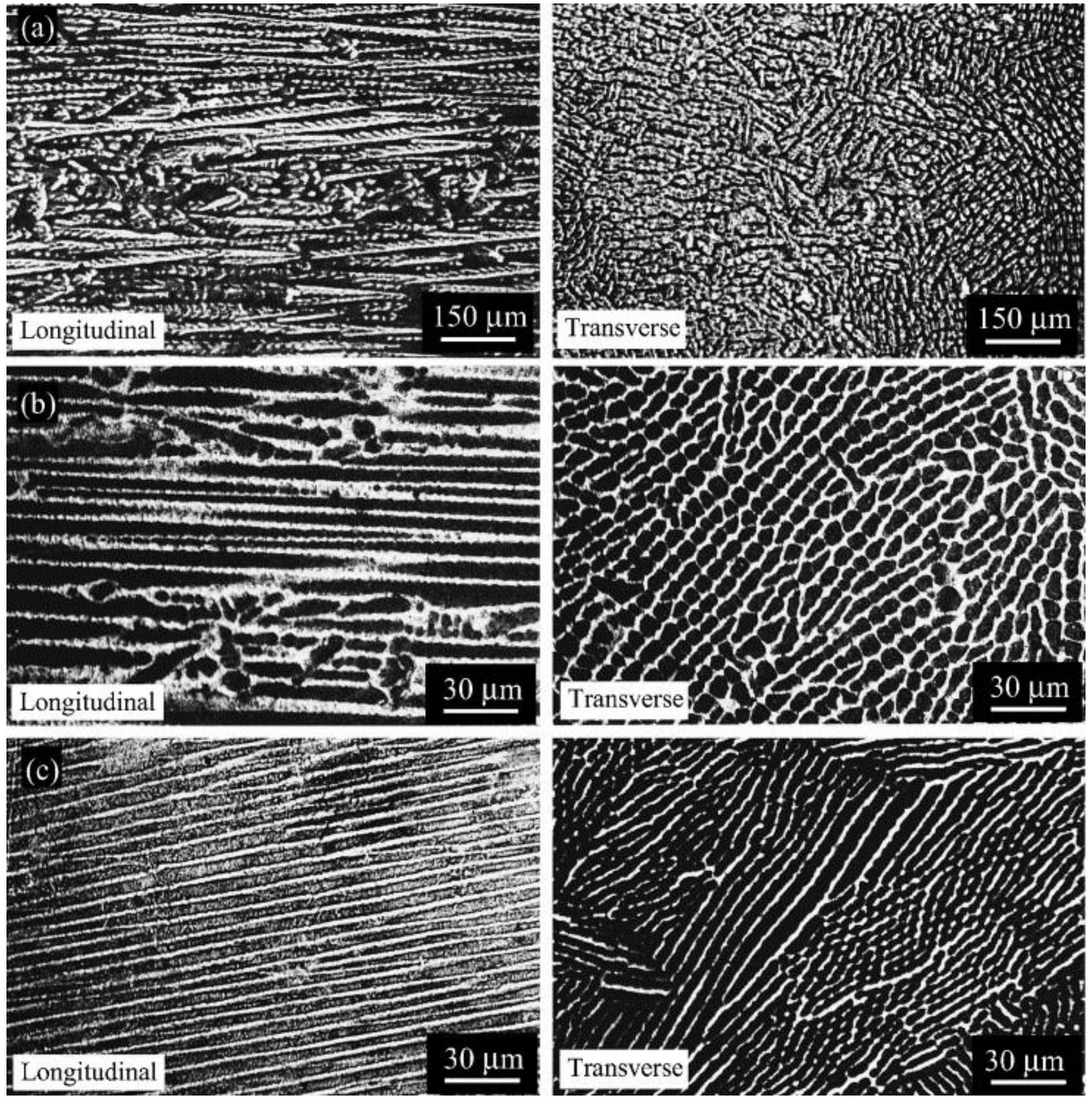
Fractal Microstructures





Dendritic growth during solidification
Mullens-Sekerka instability

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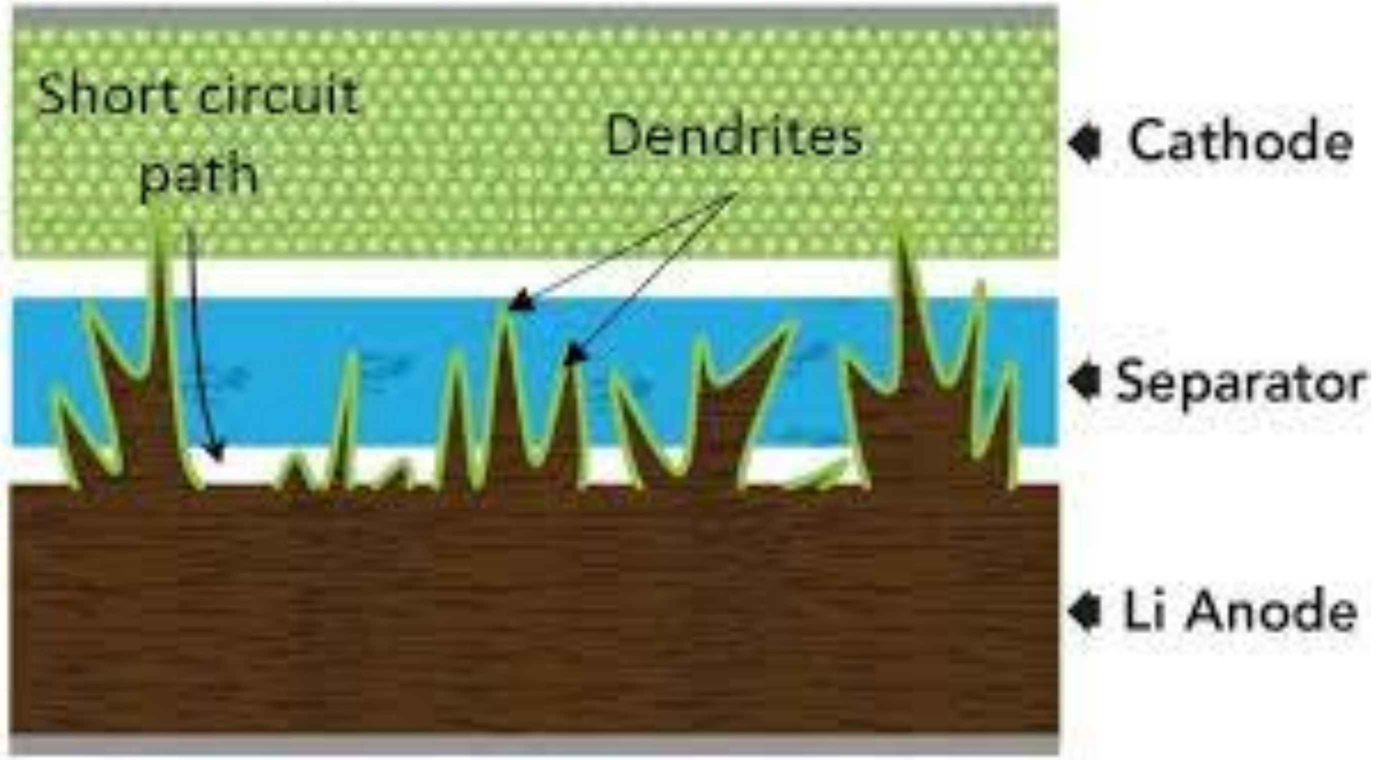
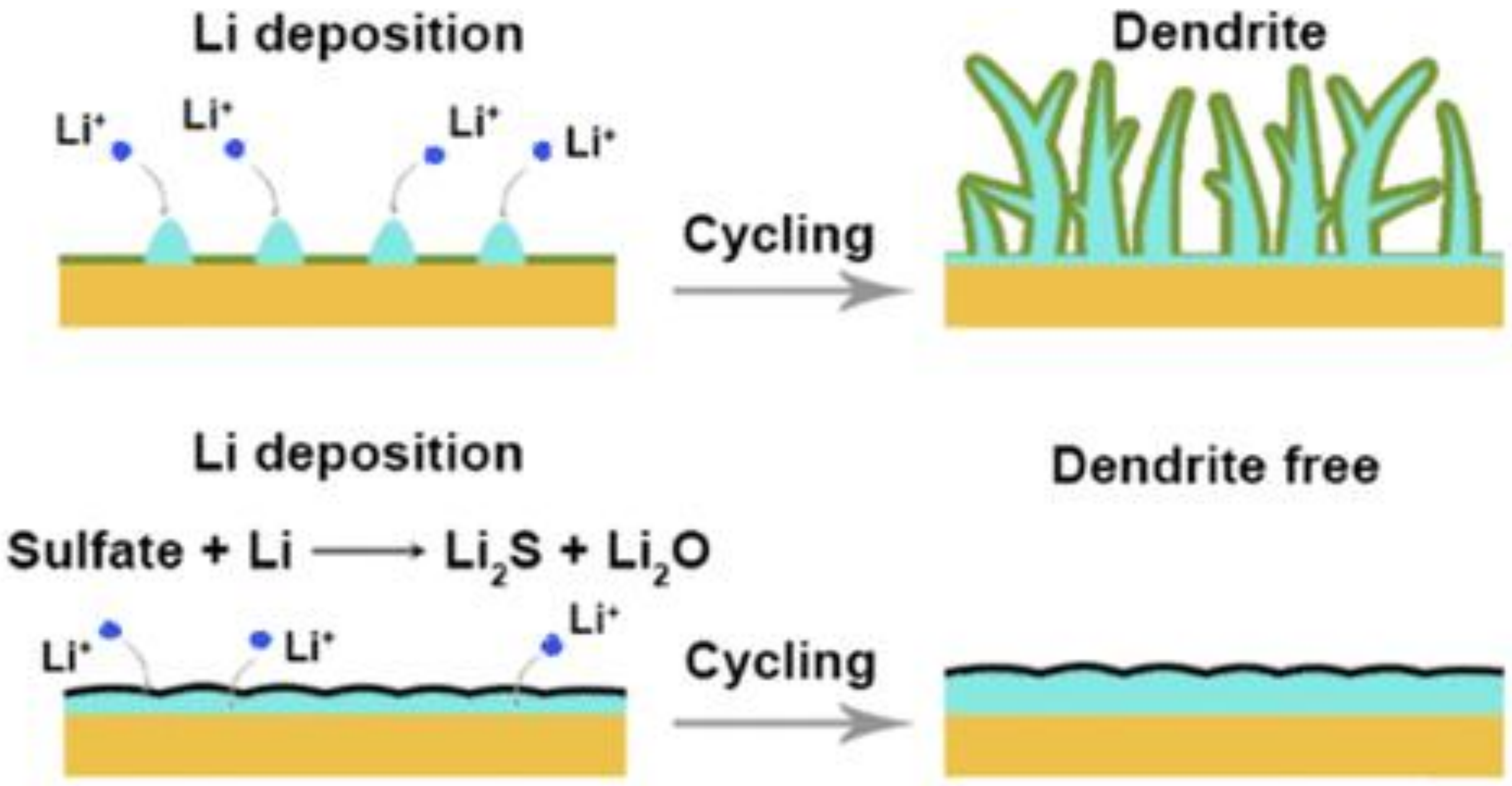
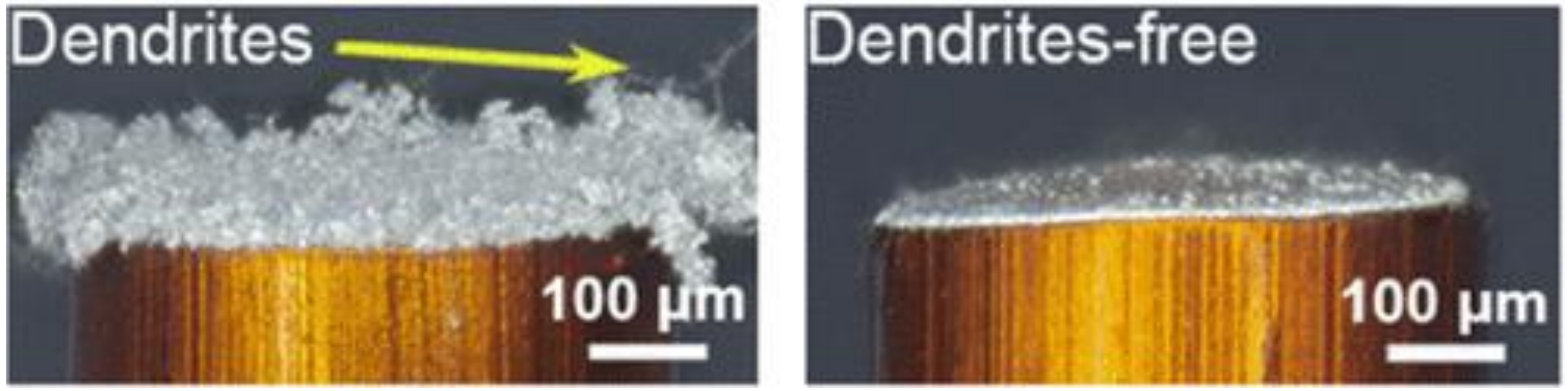
Fractal Microstructures







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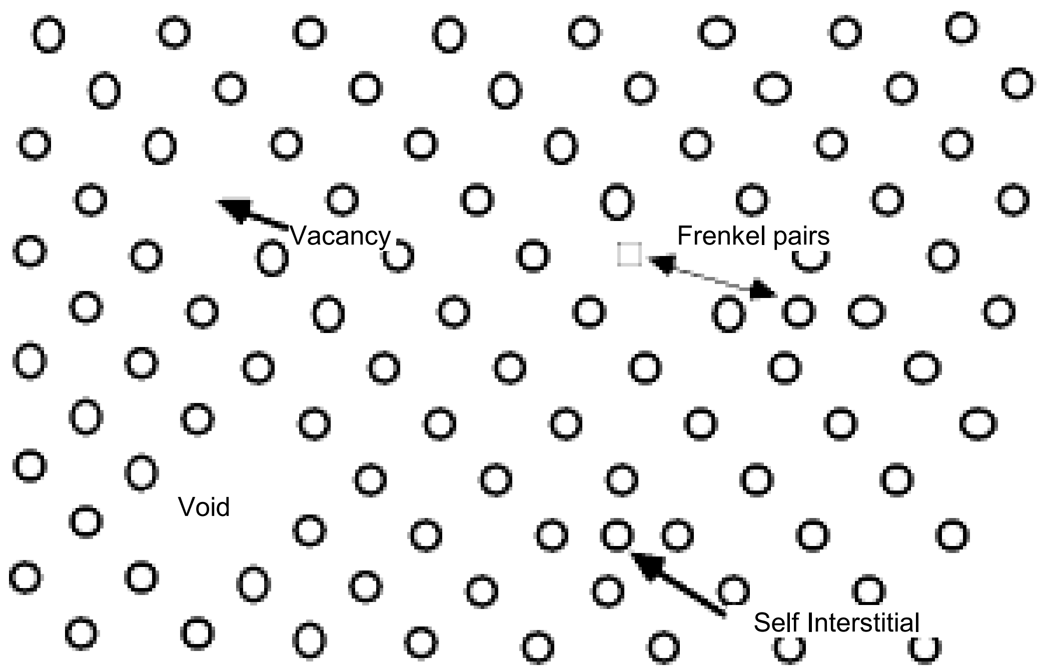
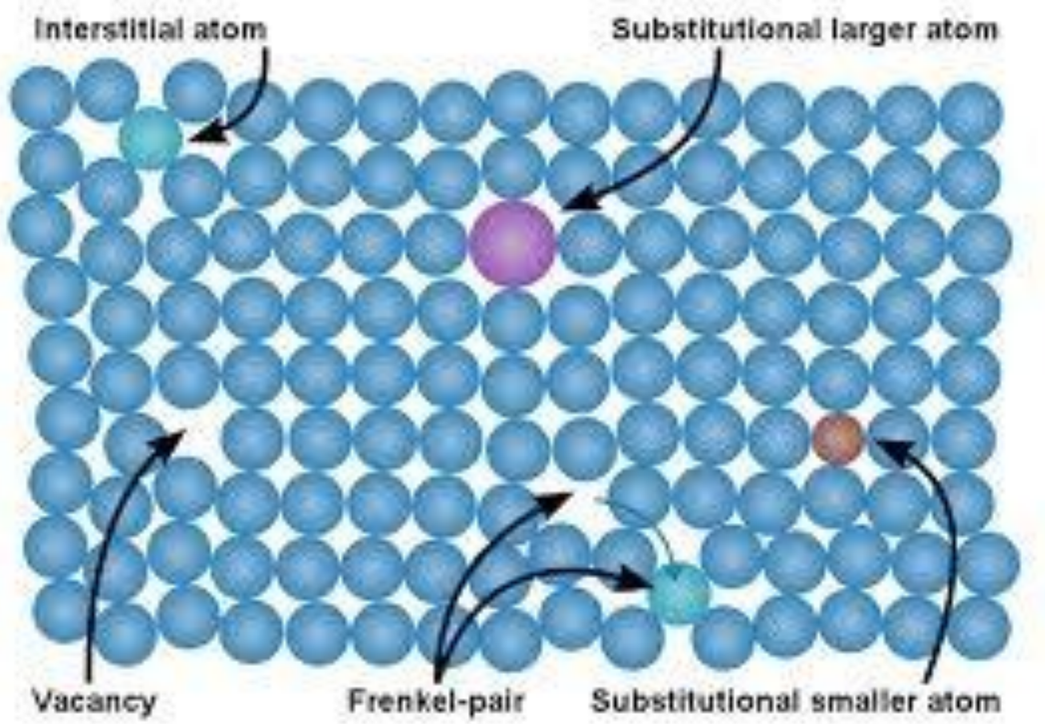
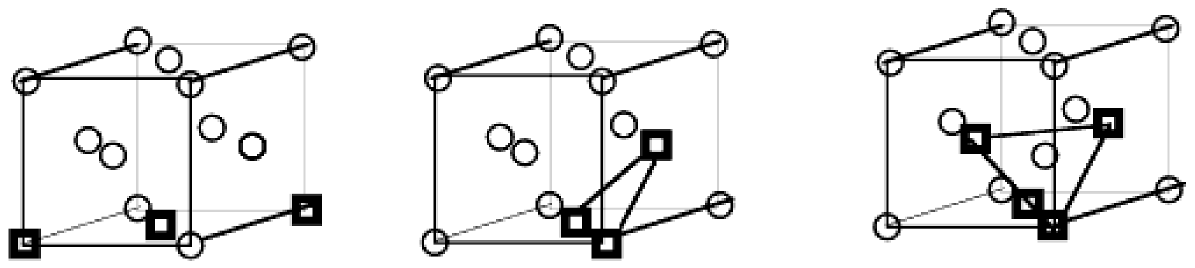
Point defects





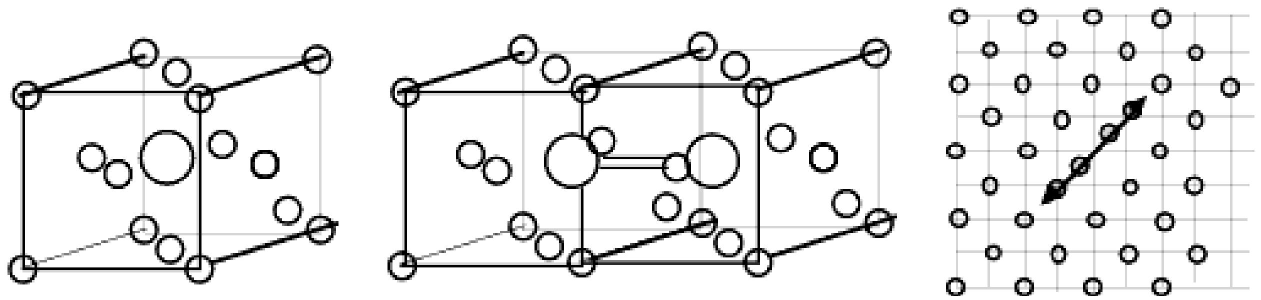
Intrinsic

Extrinsic



linear plane tetrahedral (most stable)

tri-vacancy



centered dumbell crowdion

Interstitials in fcc

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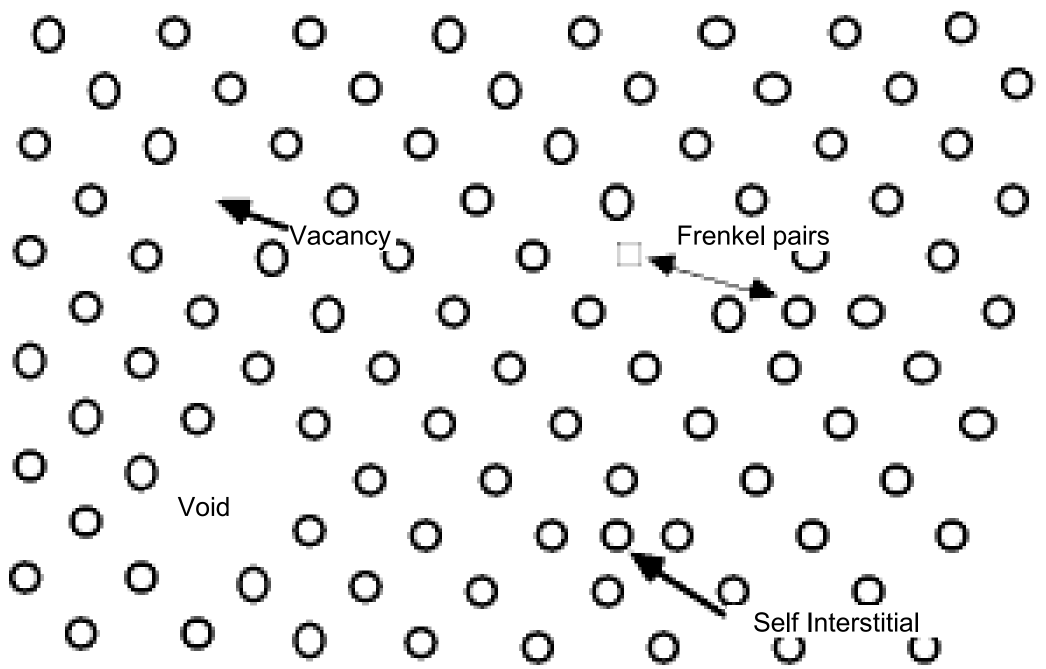
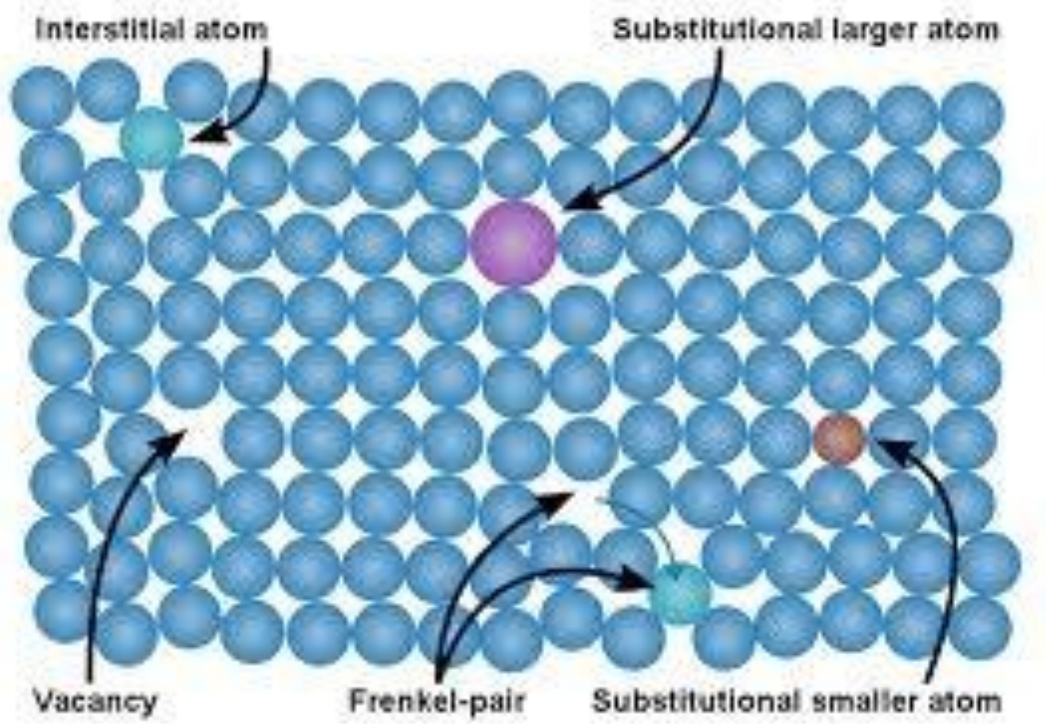
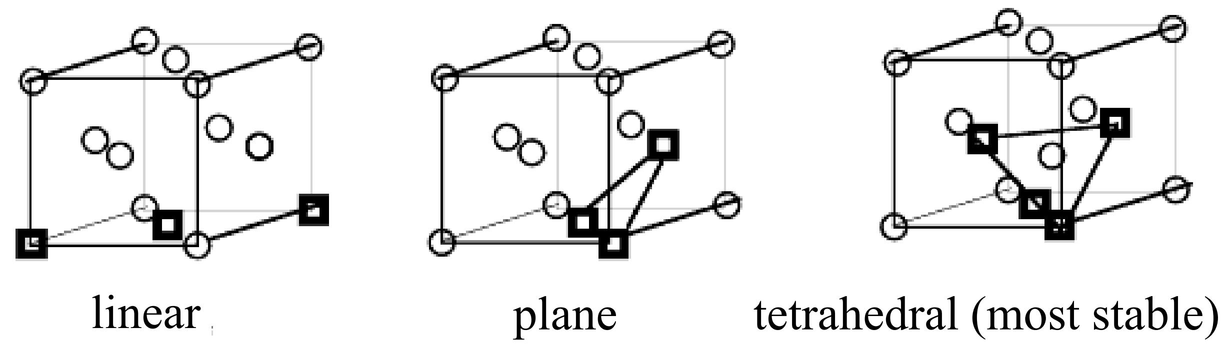
Point defects



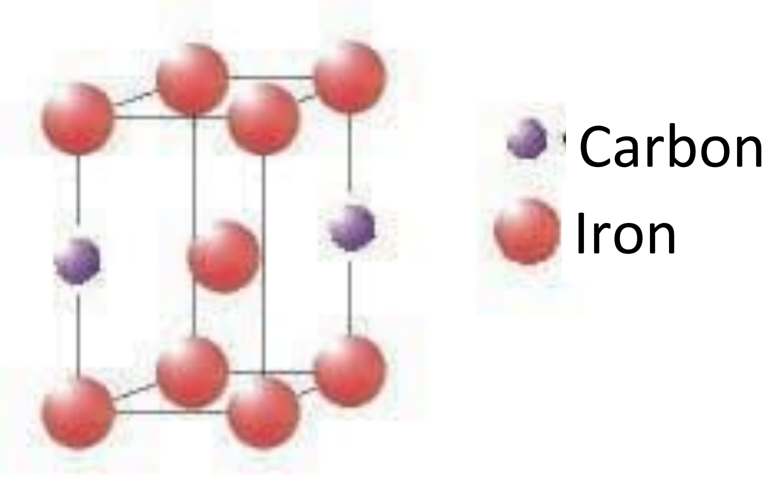


Intrinsic

Extrinsic



tri-vacancy



Interstitials in bcc

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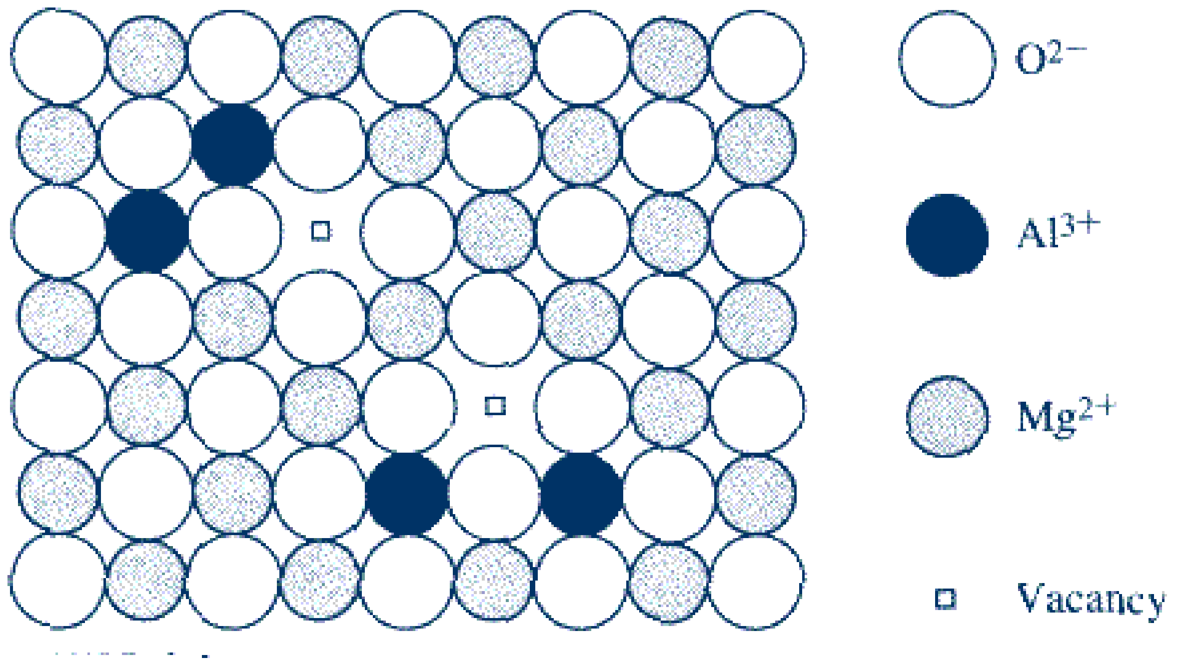
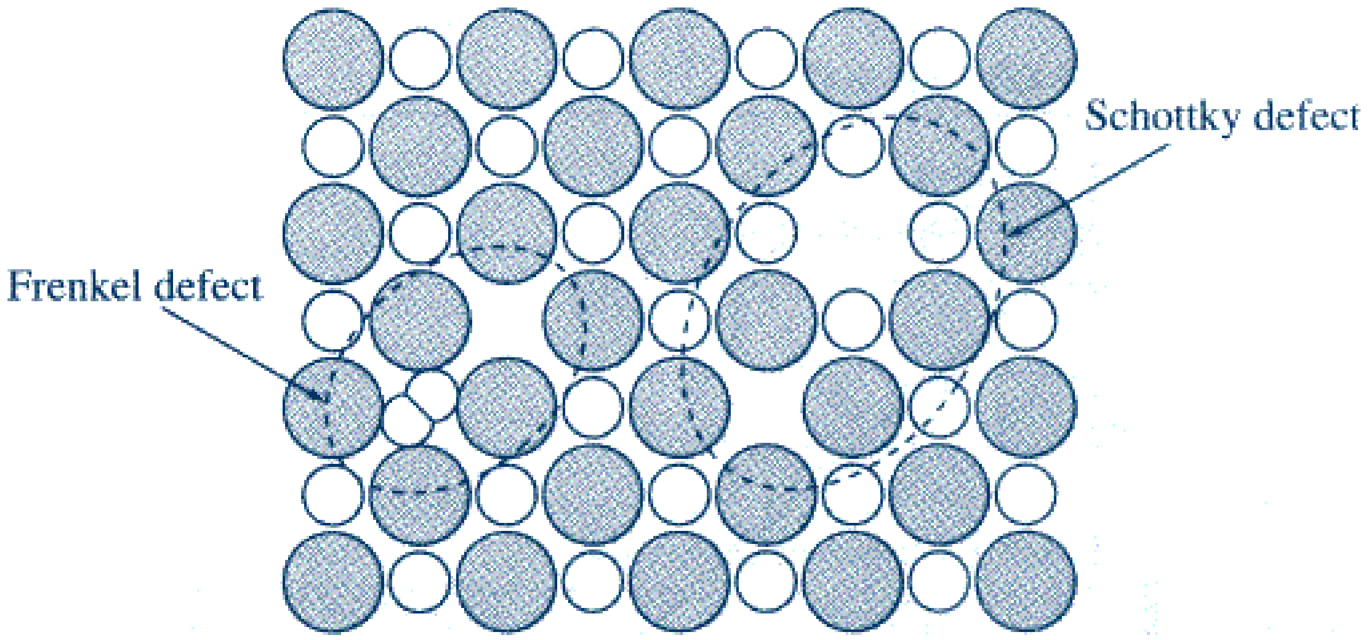
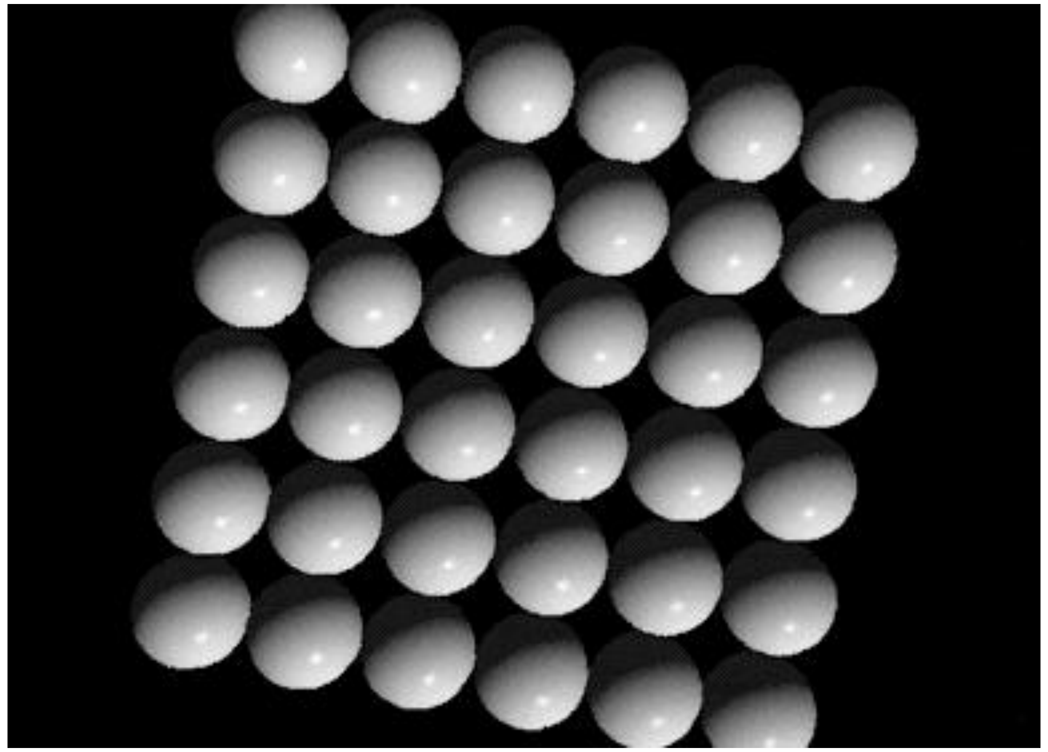
Point defects in ionic crystals





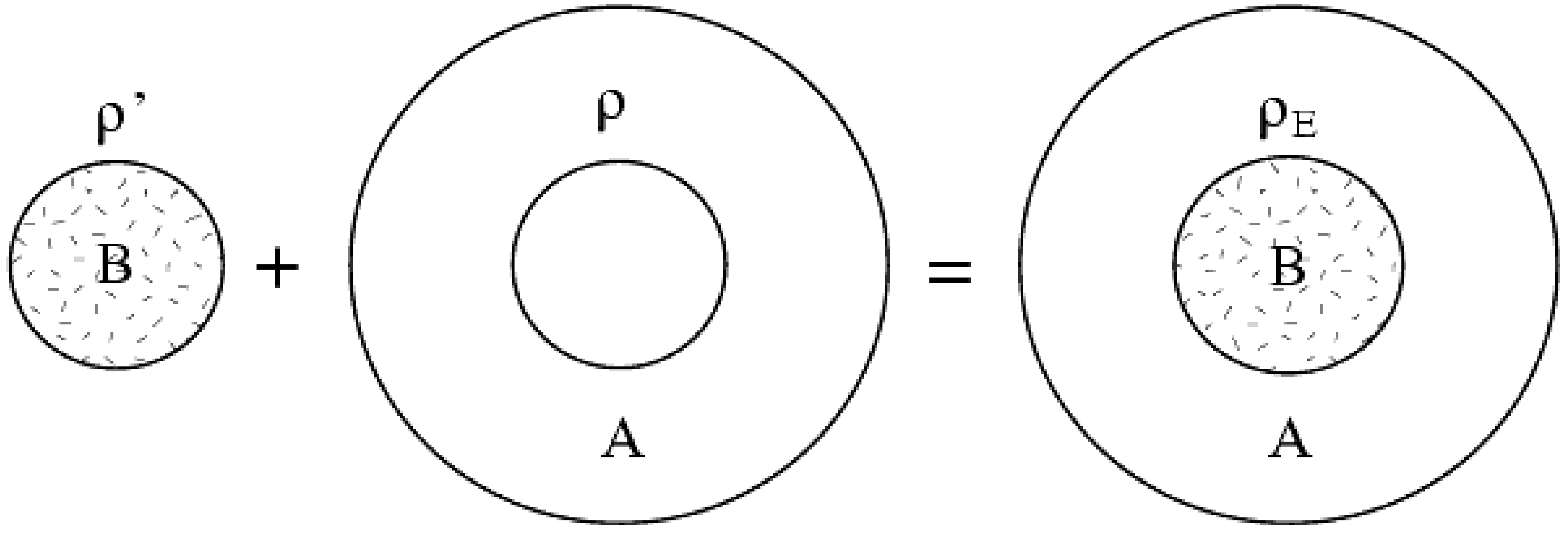


Two types of Vacancy defects in ionic crystals that must be charge neutral

1) <u>Schottky defects</u>
   - V cation+ and V anion-

2) <u>Frenkel defects</u>
   - V cation+ and I anion-
   - V anion- and I cation+

Elastic energy of a substitutional defect



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

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

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

Equilibrium energy

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

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

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

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

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

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

η = relative variation of the radius

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Concentration of vacancies at thermodynamic equilibrium

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

Mixing entropy

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

$N+n$ sites

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

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

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

ΔE_V^F is the formation energy of a vacancy ~ 0.5-1 eV = 0.5-1 10^{-5} Joules/mole

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

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

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

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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.

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

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

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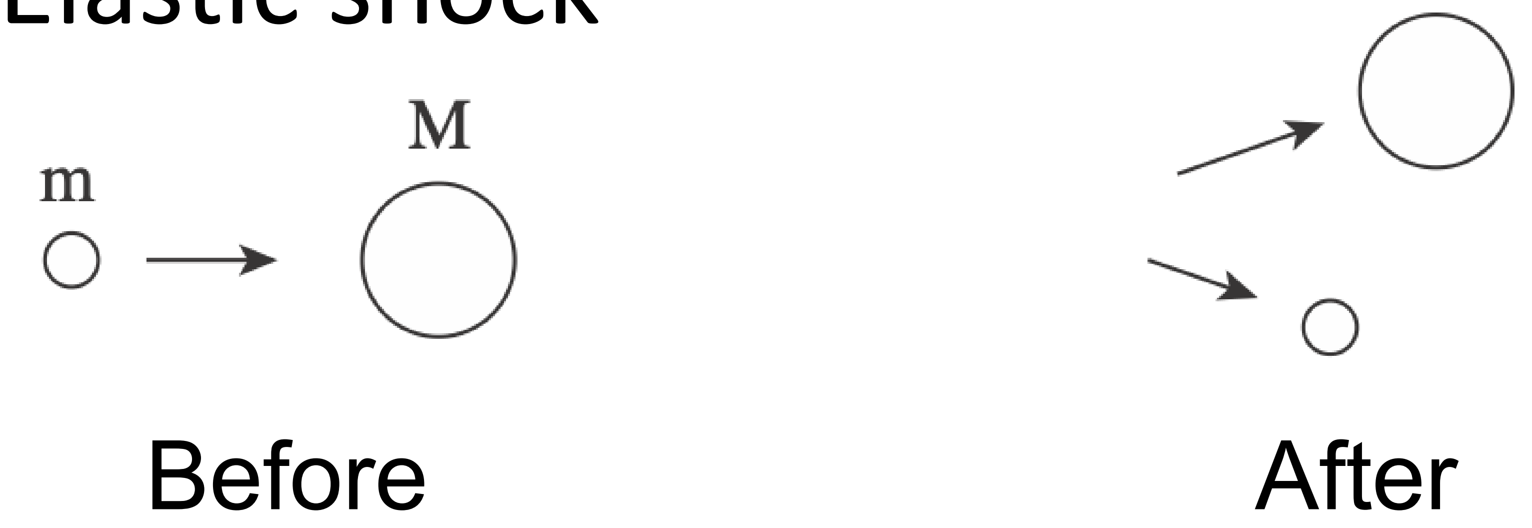
Creation of vacancies

- Quenching
- Strain hardening
- Irradiation

Elastic shock



$$T_{\max} = \frac{4mM}{(m+M)^2} E$$

Kinetic energy E = energy of a particle with mass m

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

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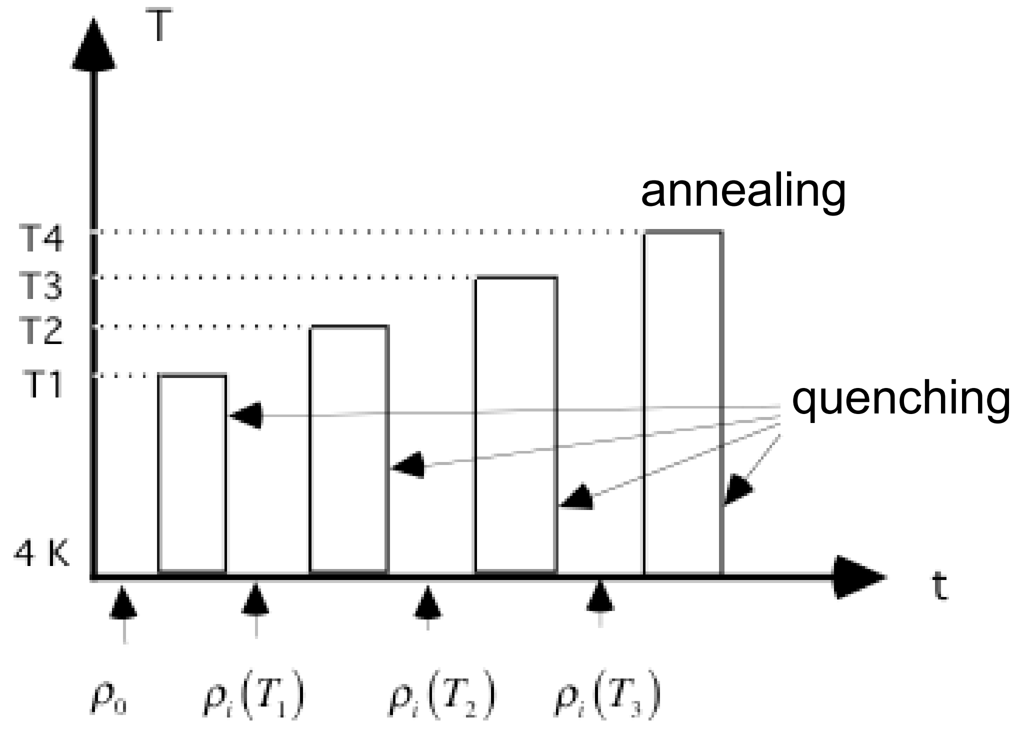
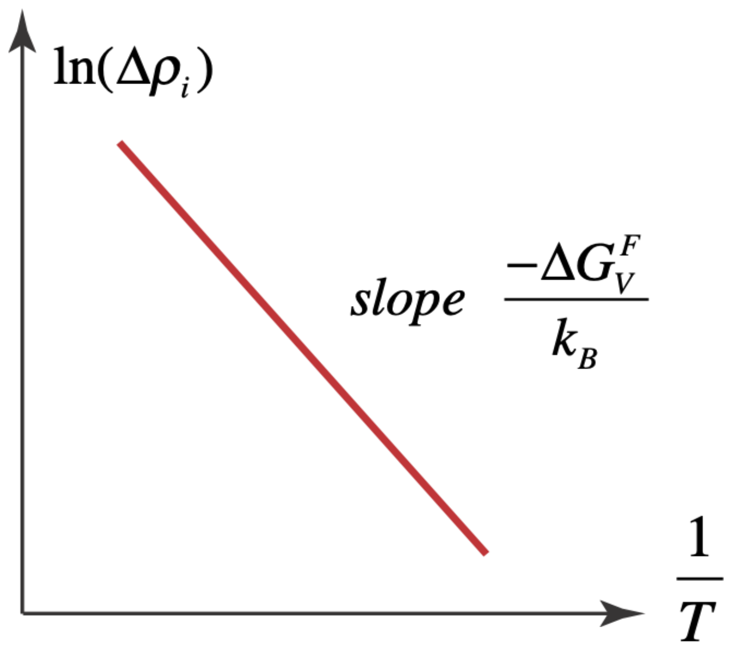
Measurement of the density of vacancies

$$\rho = \rho_P(T) + \rho_i$$

$$C_V(T) = e^{\frac{-\Delta G_V^F}{k_B T}}$$





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

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

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

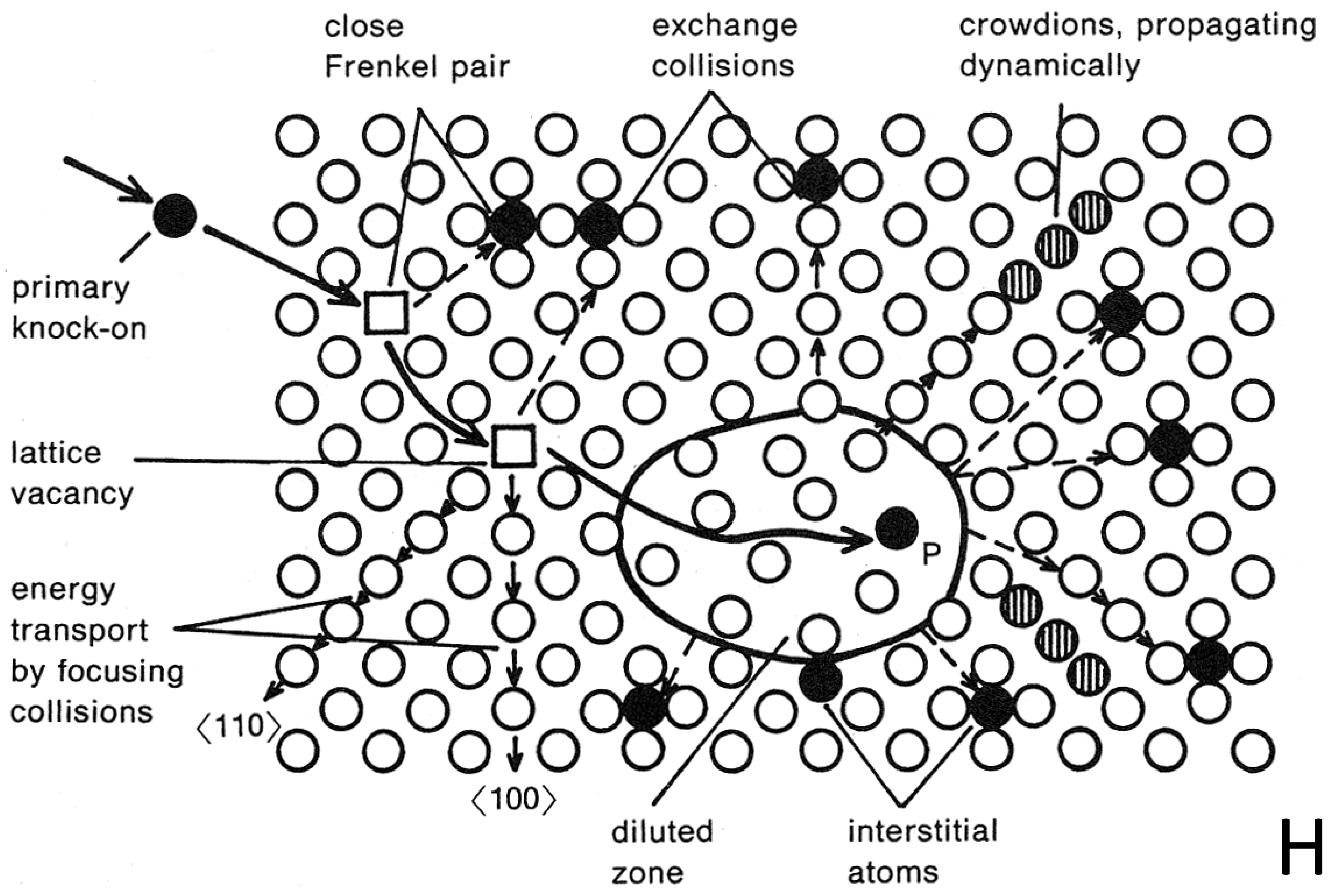
$$\Delta\rho_1 = \alpha\left(C_V^1 - C_V^0\right) = \alpha\left(e^{\frac{-\Delta G_V^F}{k_B T_1}} - e^{\frac{-\Delta G_V^F}{k_B T_0}}\right) \approx \alpha e^{\frac{-\Delta G_V^F}{k_B T_1}}$$

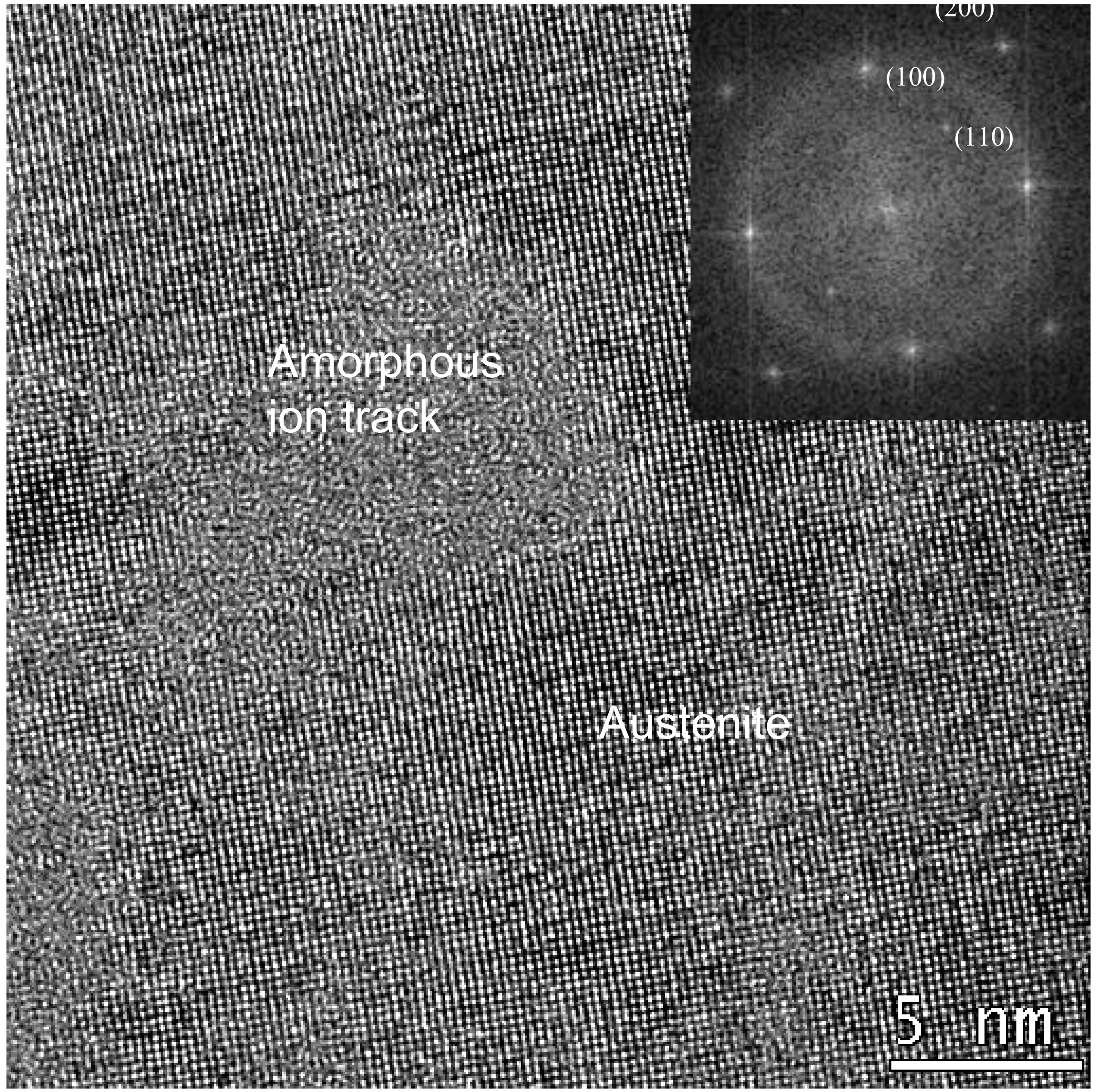
Formation Energy for Vacancies

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

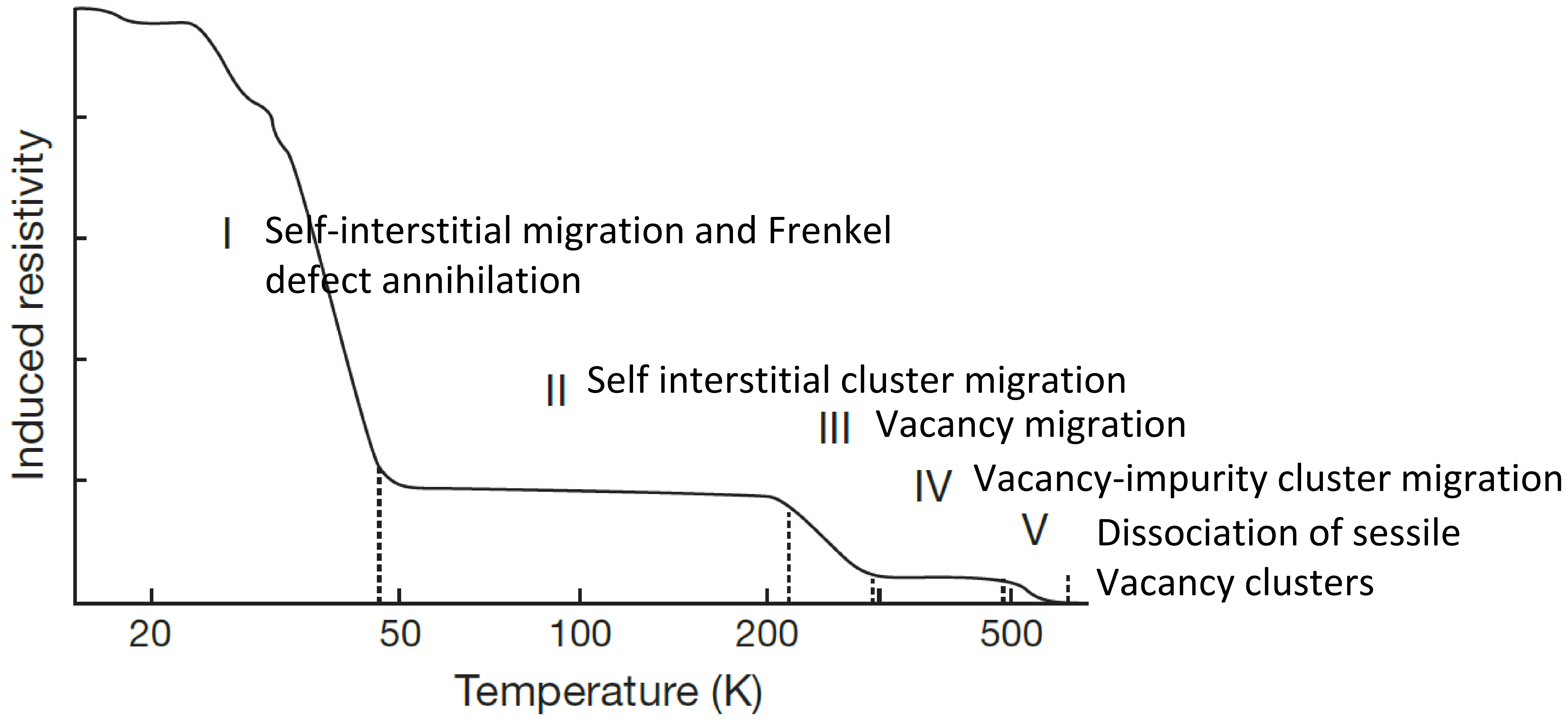
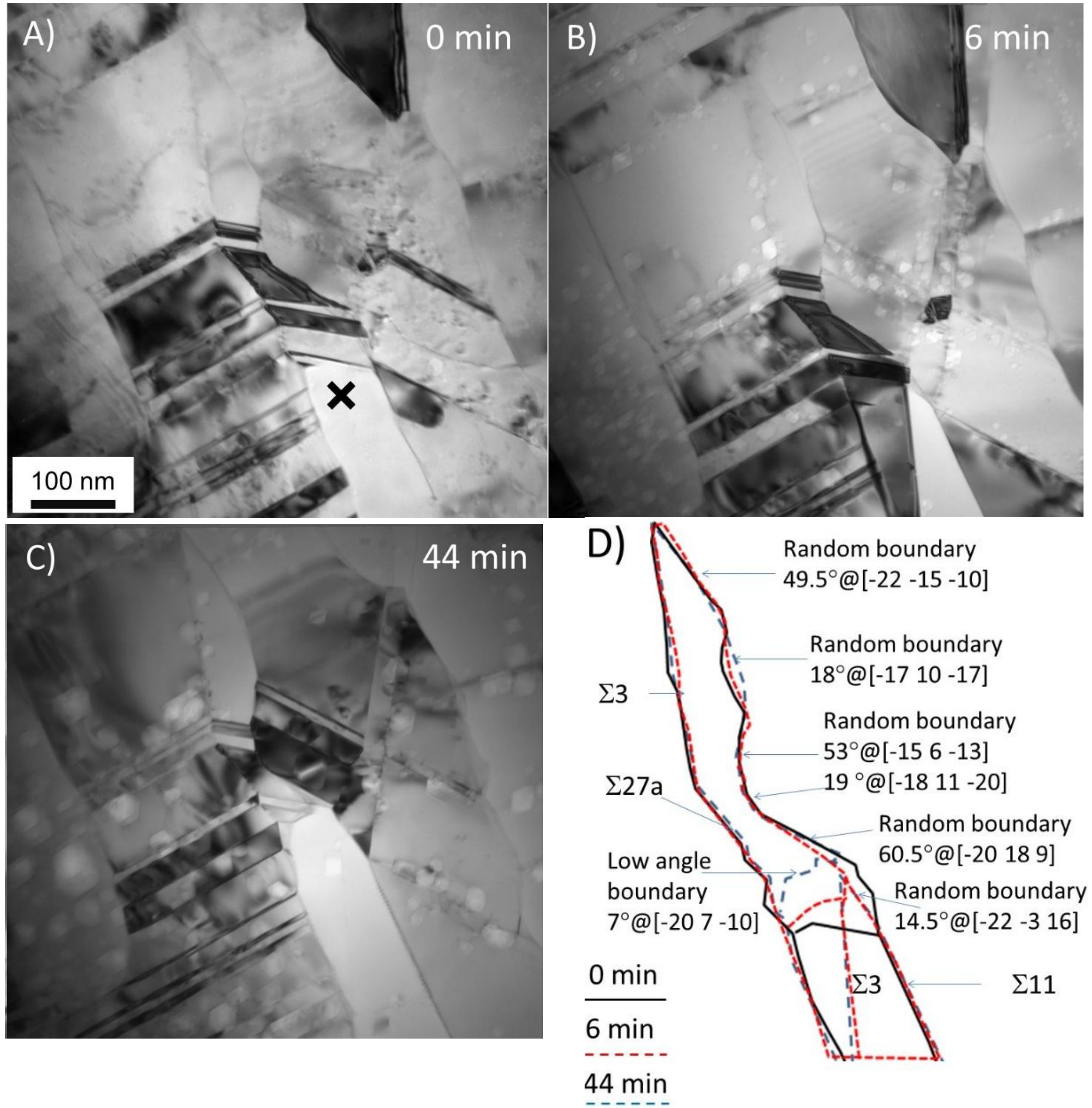


Figure 6 Electrical resistivity defect recovery stages for copper following electron irradiation at 4 K. Reproduced from Agullo-Lopez, F.; Catlow, C. R. A.; Townsend, P. D., *Point Defects in Materials*. Academic Press: San Diego, CA, 1988; p 445.

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 Σ3 twins within the columns



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