Defects in Crystals

“Crystals are like people, it is the defects that make them interesting!”

- Sir Colin Humphreys

"God made the bulk; the surface was invented by the devil."

- Wolfgang Pauli

“Often, it may be said that the interface is the device”

- Herbert Kroemer

Nobel Lecture 2000

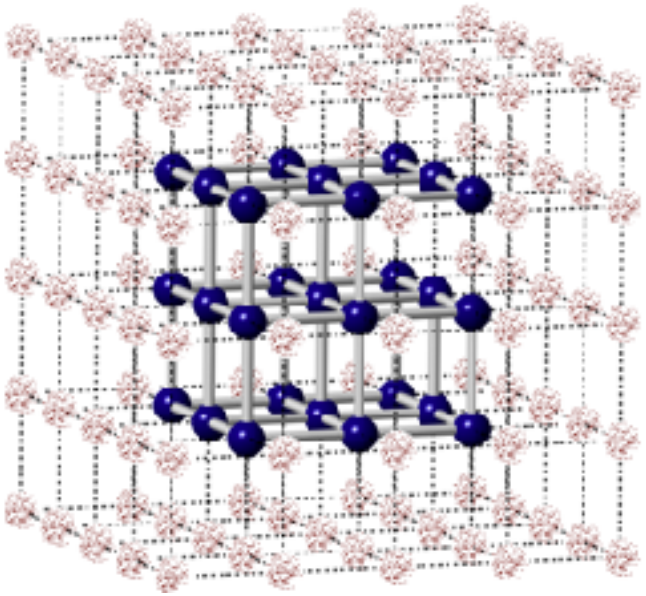
Higher Dimensional Defects

Materials Science and Engineering: A First Course, V. Raghavan
Sixth edition, Section 6.4

Higher dimensional defects - Interfaces

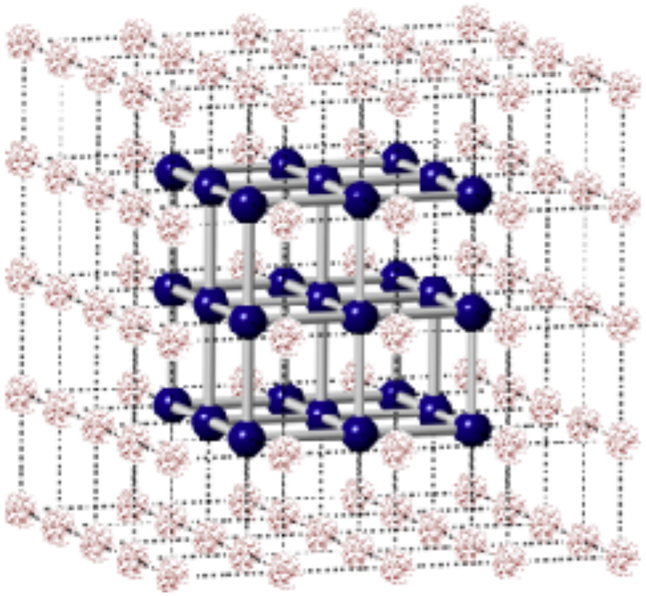
Higher dimensional defects - Interfaces

Surface



Higher dimensional defects - Interfaces

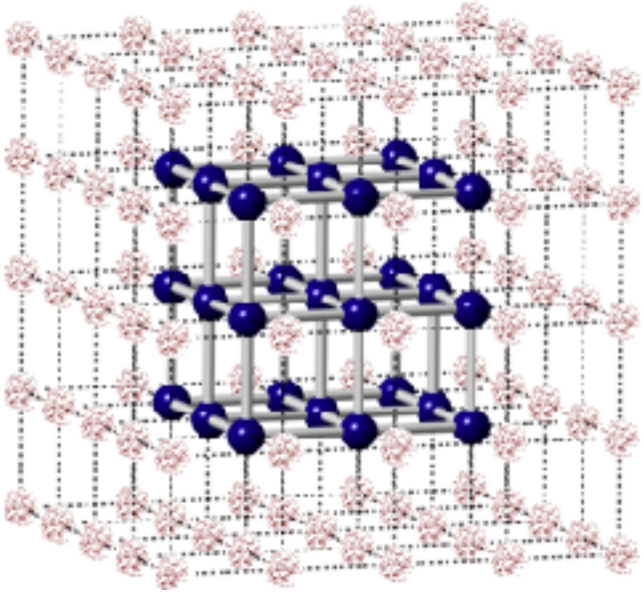
<u>Surface</u>



- between **material and ambient**

Higher dimensional defects - Interfaces

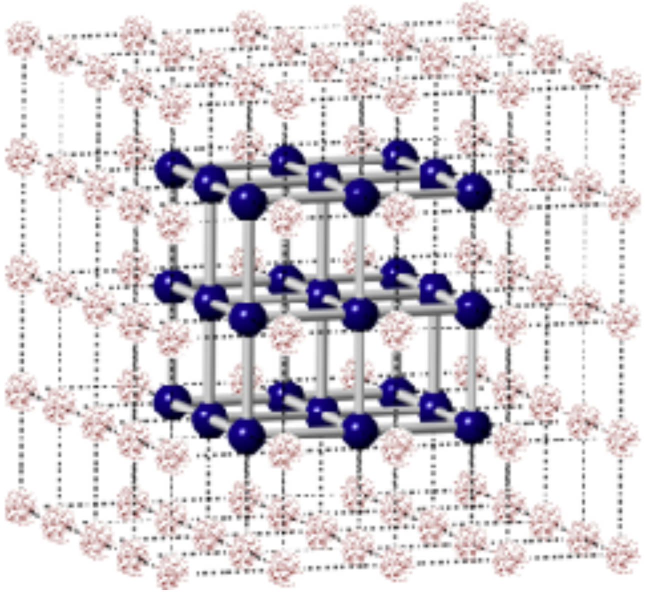
Surface



- between **material and ambient**
- **broken bonds**

Higher dimensional defects - Interfaces

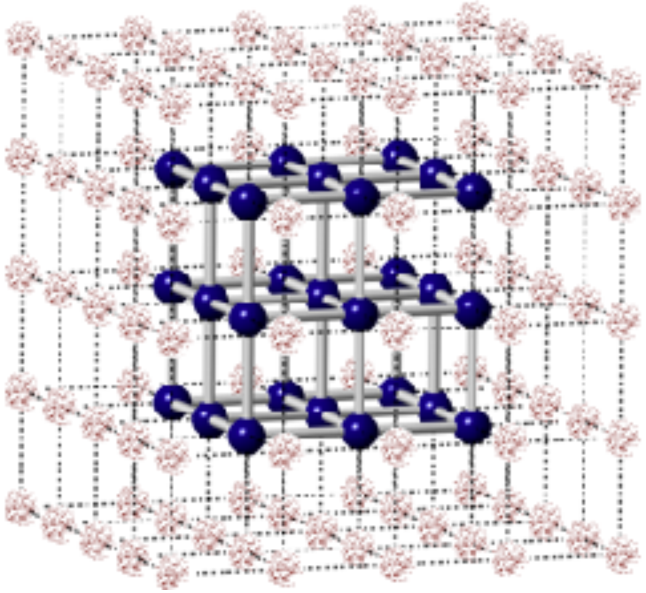
Surface



- between **material and ambient**
- **broken bonds**
- Different environment than bulk

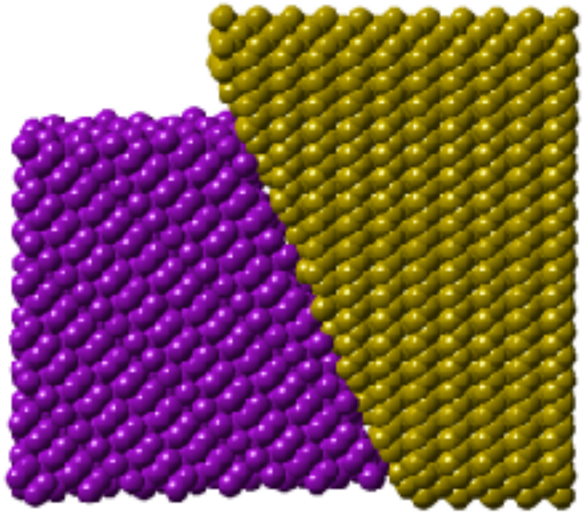
Higher dimensional defects - Interfaces

<u>Surface</u>



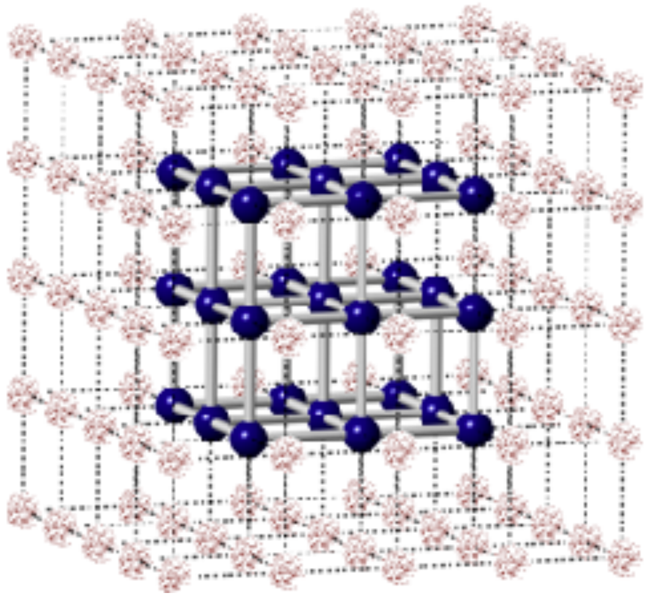
- between **material and ambient**
- **broken bonds**
- Different environment than bulk

<u>Grain boundary</u>



Higher dimensional defects - Interfaces

Surface



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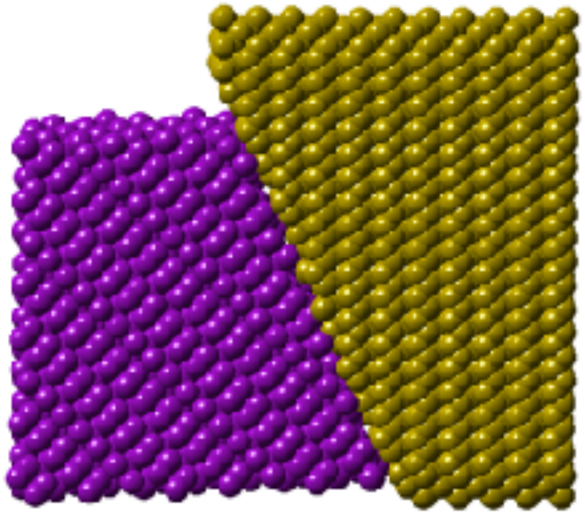
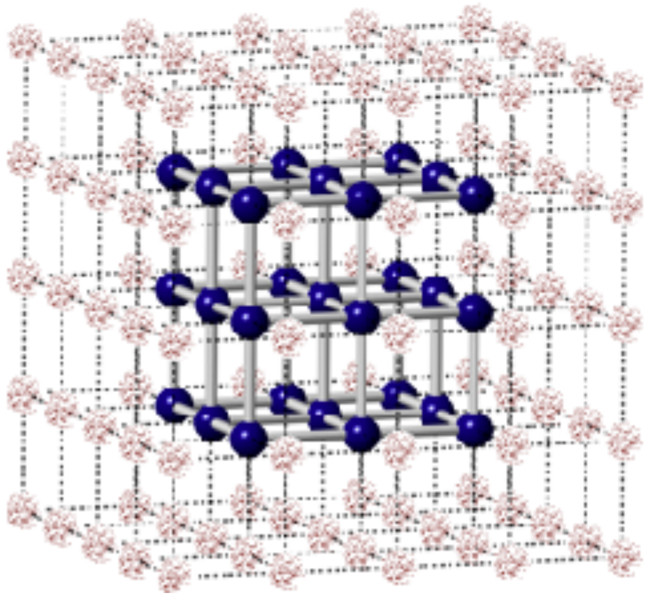
Grain boundary



- between **two grains**

Higher dimensional defects - Interfaces

<u>Surface</u>



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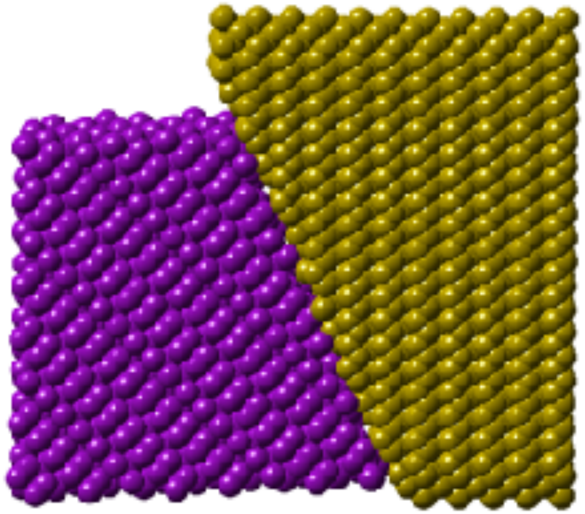
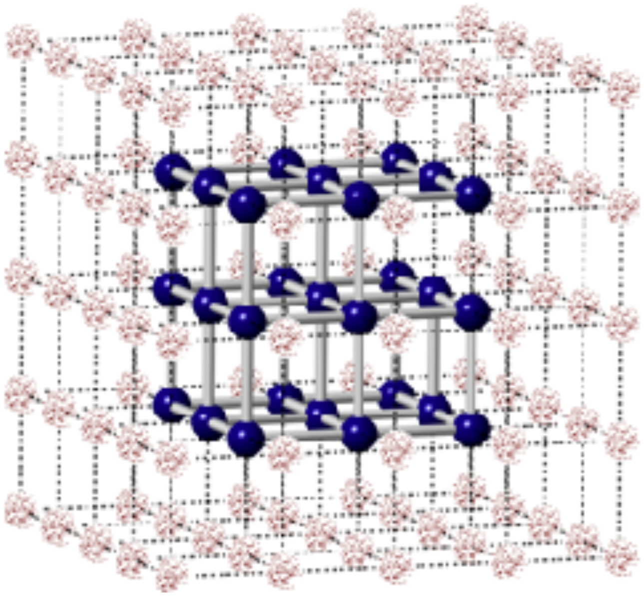


- between **two grains**
- **irregular bonding pattern**

Higher dimensional defects - Interfaces

<u>Surface</u>



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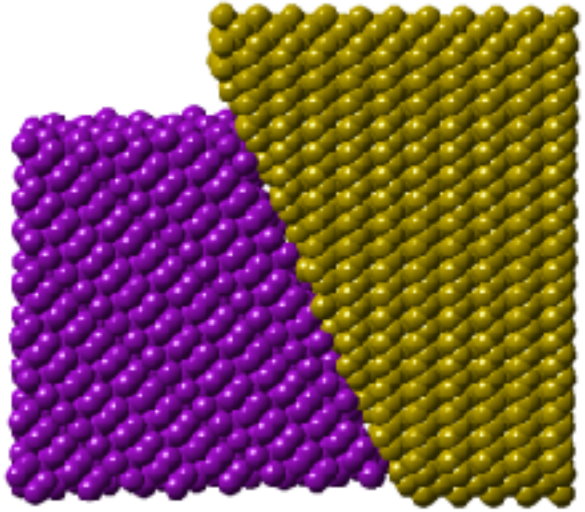
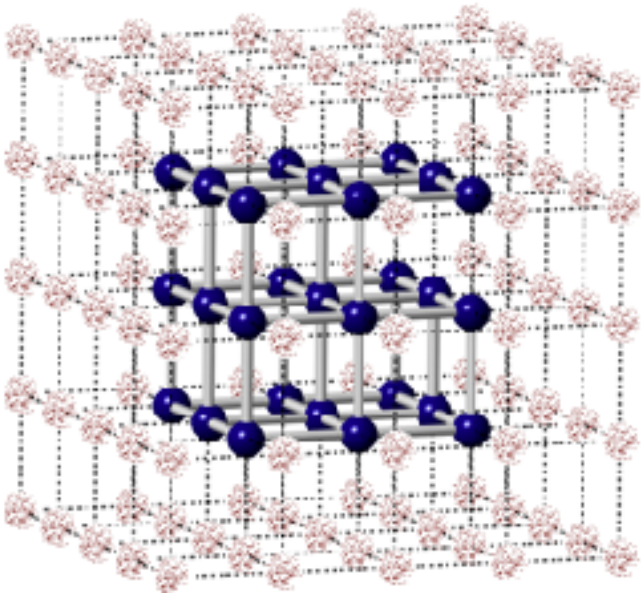
<u>Grain boundary</u>



- between **two grains**
- **irregular bonding pattern**
- Change in orientation/symmetry

Higher dimensional defects - Interfaces

Surface



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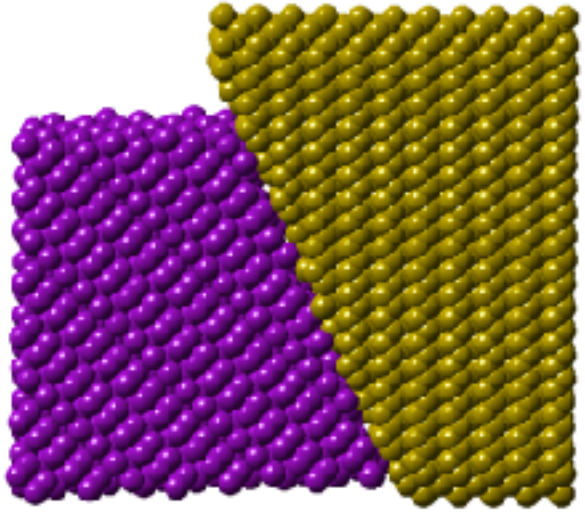
Grain boundary



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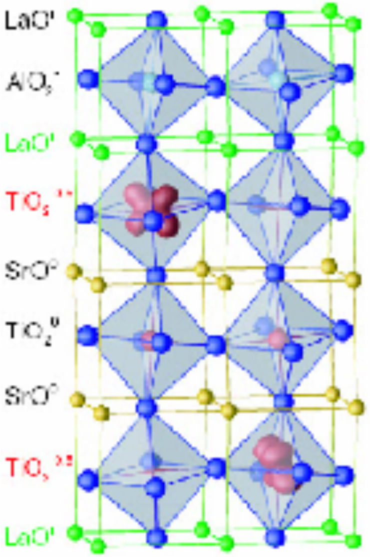
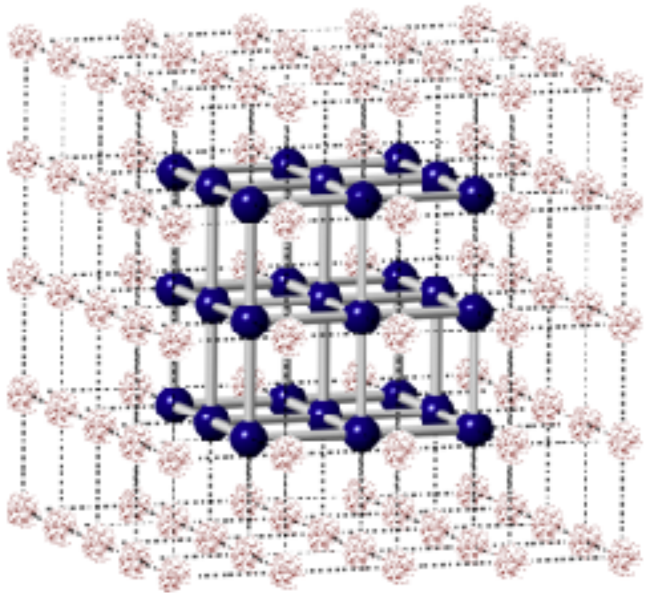
Hetero-interface



Higher dimensional defects - Interfaces

Surface



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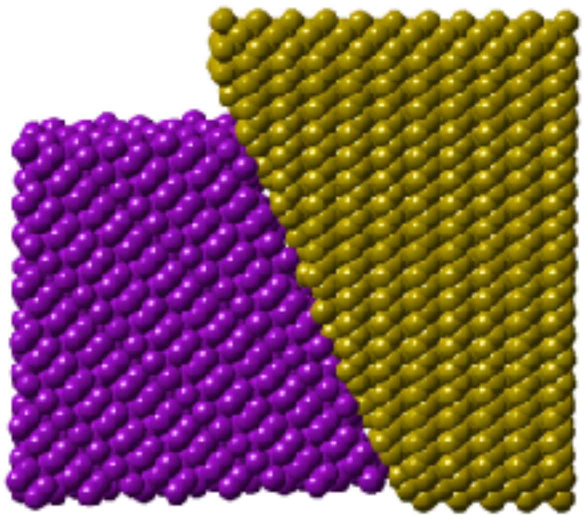
Grain boundary



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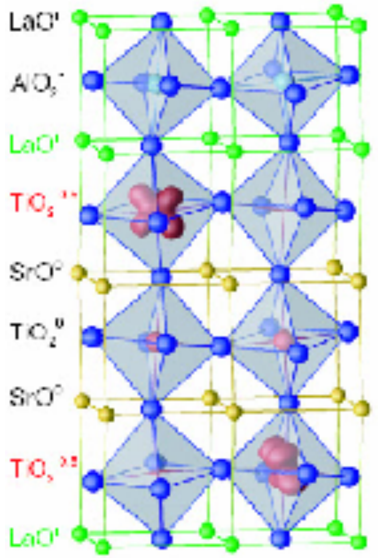
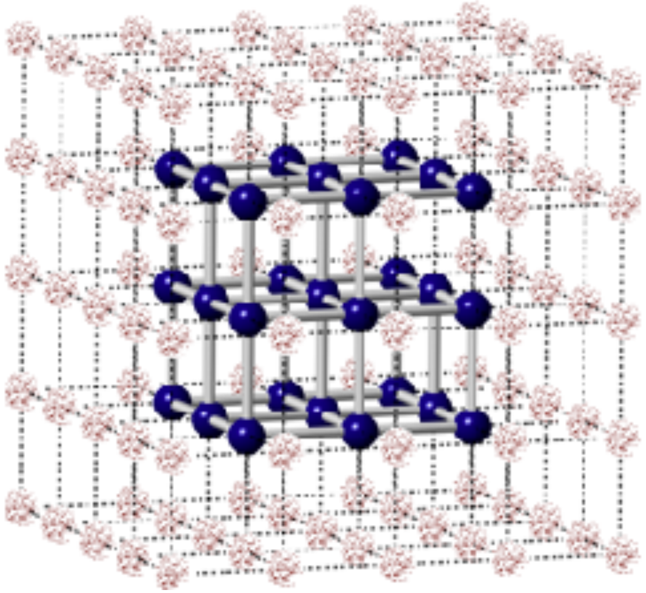


- between **two materials**

Higher dimensional defects - Interfaces

<u>Surface</u>



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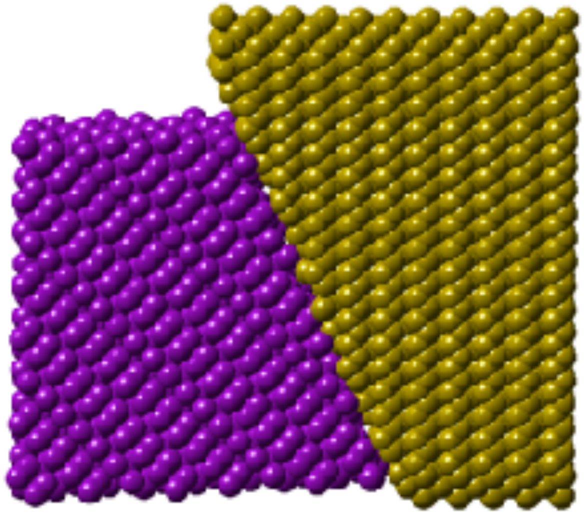

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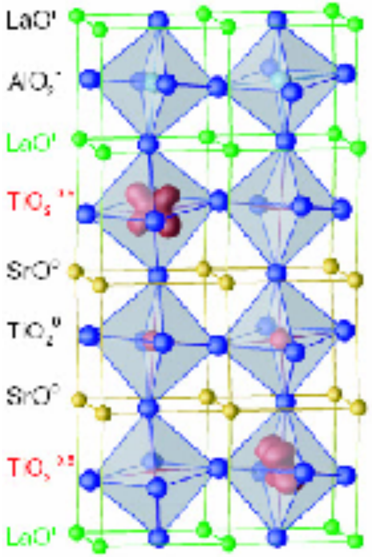

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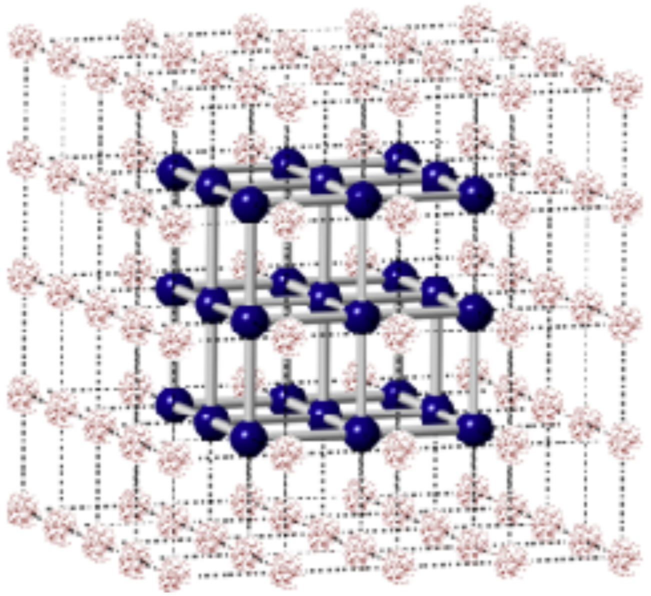
Higher dimensional defects - Interfaces

Surface



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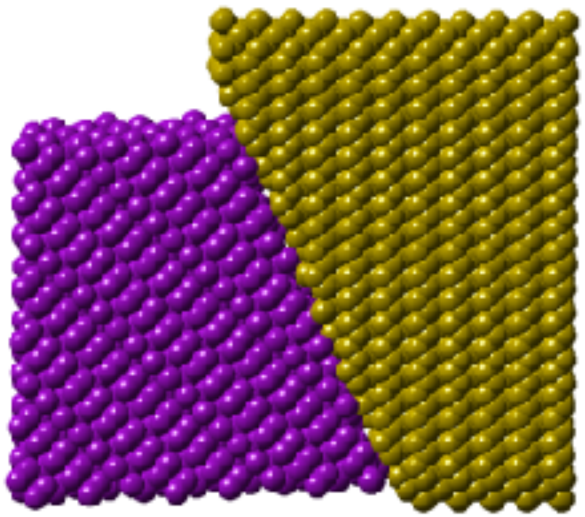

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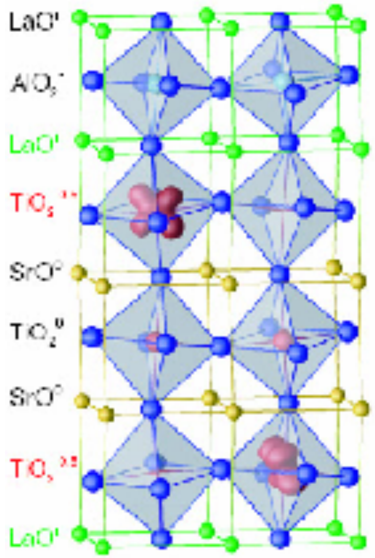
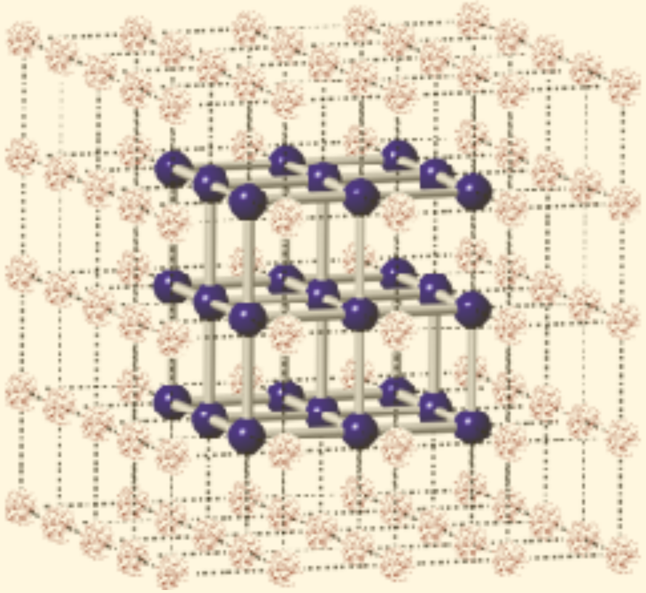
Hetero-interface



- between **two materials**
- **different bonding pattern**
- Different chemistry

Higher dimensional defects - Interfaces

Surface



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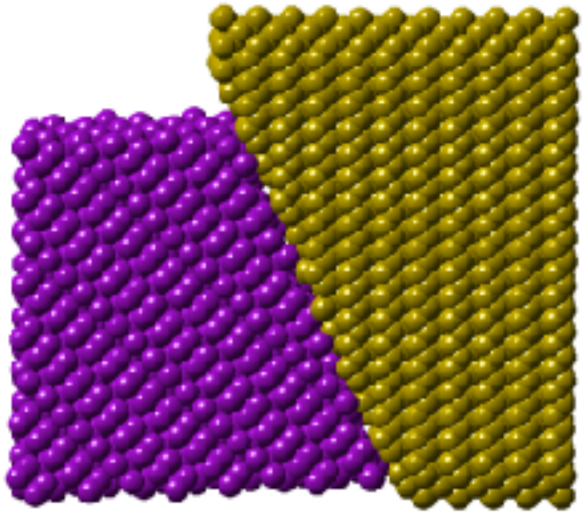

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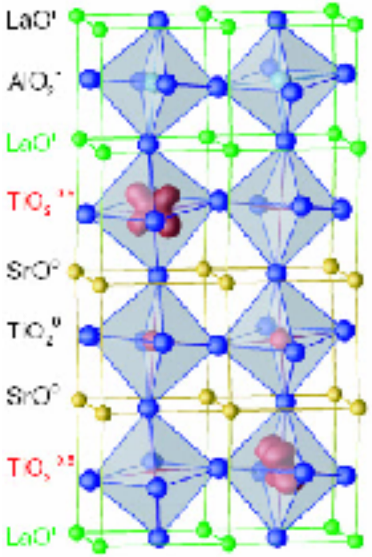


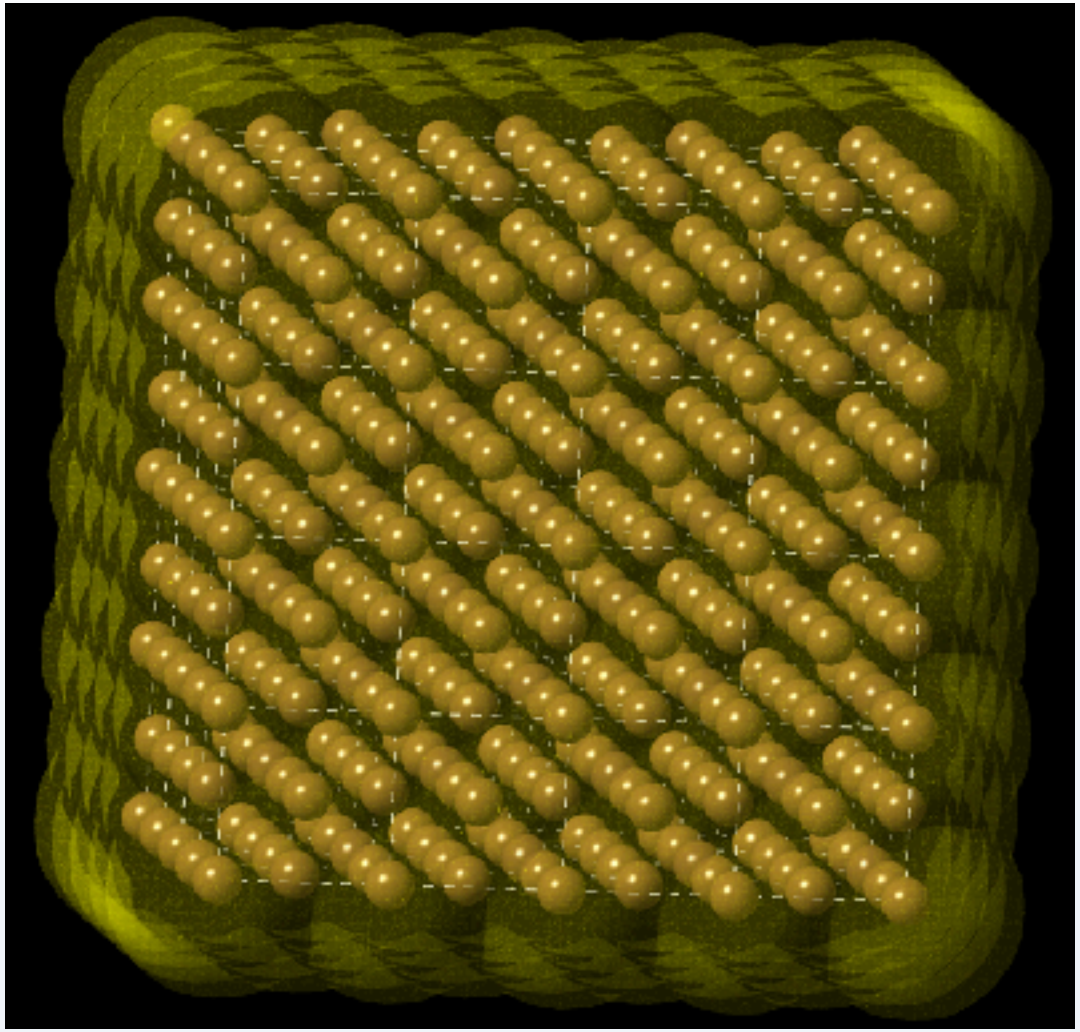
- between **two materials**
- **different bonding pattern**
- Different chemistry

Surface energy of Copper (Cu)

- Cu, cF lattice
  - Atomic radius of Cu is 127.8 pm
  - Cu at (0,0,0)
- Bond energy of Cu is 56.4 kJ mol^{-1} of bonds

Calculate surface energy of (111) plane of Cu.

Compare with (110) and (100) planes.

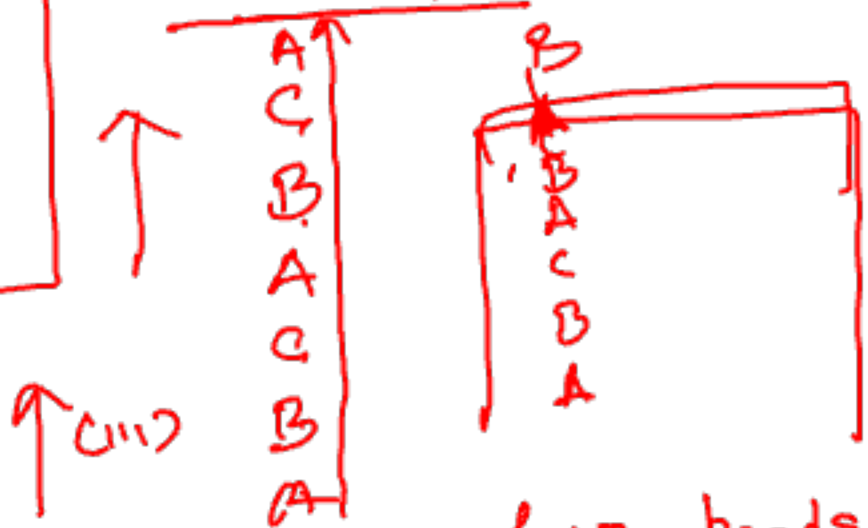


$r = 127.8$ pm.

$2a^2 = 4r^2$

$a = 2\sqrt{2}\, r$

(111) plane → close-packed plane



6 Cu atoms in the A-plane

3 Cu atoms in the B-plane

3 Cu atoms in the C-plane

→ 3 out of 12 bonds are broken.

touching the central atom in the A-plane.

bonded to.

every Cu atom is bonded to 12 other Cu atoms.

12 bonds to the central Cu atom.

Bond energy/mole of bonds, E_b

Bond energy/bond, $e_b = E_b/N_A$.

Each Cu atom has 12 bonds.

Bond energy/Cu atom $e_{b,Cu}$

$$e_{b,Cu} = \frac{E_b}{N_A} \times \frac{12}{2}.$$

Bonds between A-layer and B-layer are broken.

$$\left.\begin{array}{l}\text{Energy of broken} \\ \text{bonds / Cu atom}\end{array}\right\} \frac{3}{12} \times e_{b,Cu}$$

H.W: $\sigma_{(100)}$ and $\sigma_{(110)}$ of Cu.

$$\frac{E_b}{N_A} \times \frac{12}{2} \times \frac{3}{12}$$

Typically surface energy is given in units of $J\,m^{-2}$.

$$\text{P.D.}(111) = \frac{4}{\sqrt{3}\,a^2} = \frac{1}{2\sqrt{3}\,r^2}$$

$$\left.\begin{array}{l}\text{Surface} \\ \text{energy}\end{array}\right\} \frac{E_b}{N_A} \times \frac{3}{2} \times \frac{1}{2\sqrt{3}\,r^2}.$$

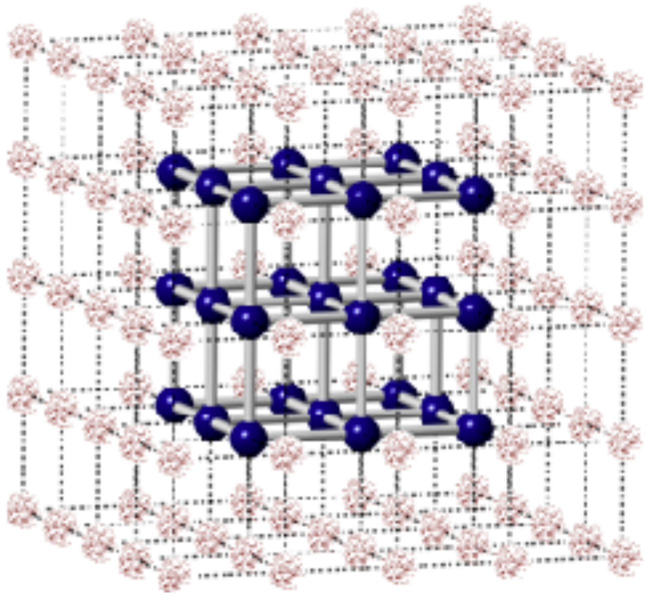
51.4 kJ mol^{-1}

127.8 pm

$$\sigma_{(111)}(Cu) = 2.48\ J\,m^{-2}.$$

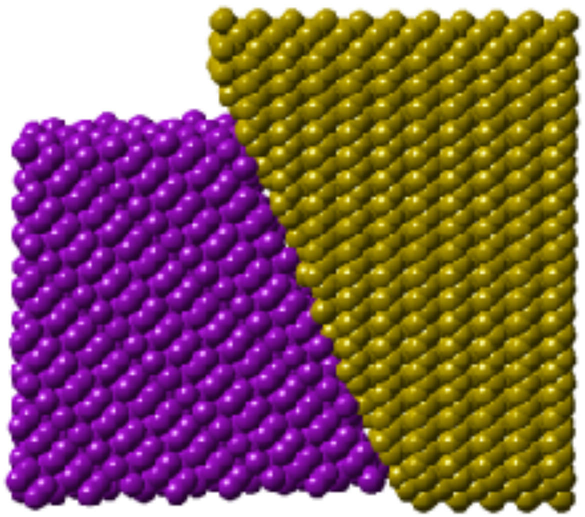
Higher dimensional defects - Interfaces

<u>Surface</u>



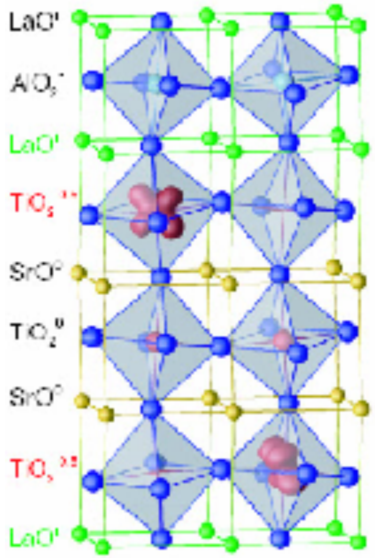
- between **material and ambient**
- **broken bonds**
- Different environment than bulk

<u>Grain boundary</u>



- between **two grains**
- **irregular bonding pattern**
- Change in orientation/symmetry

<u>Hetero-interface</u>



- between **two materials**
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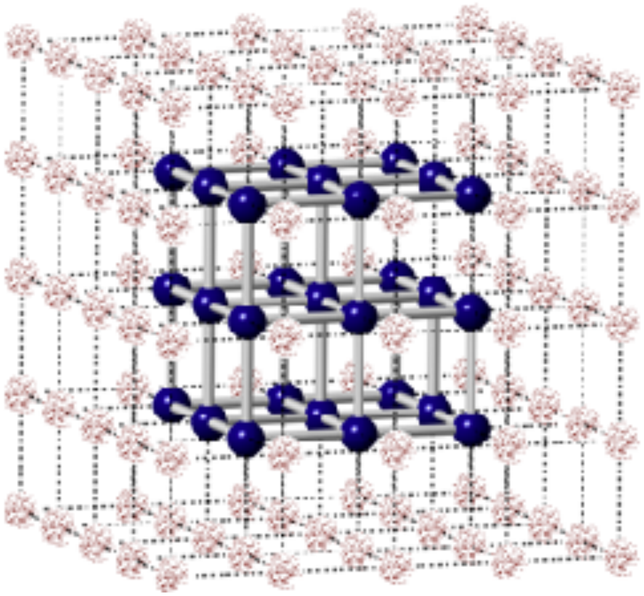
Higher dimensional defects - Interfaces

<u>Surface</u>



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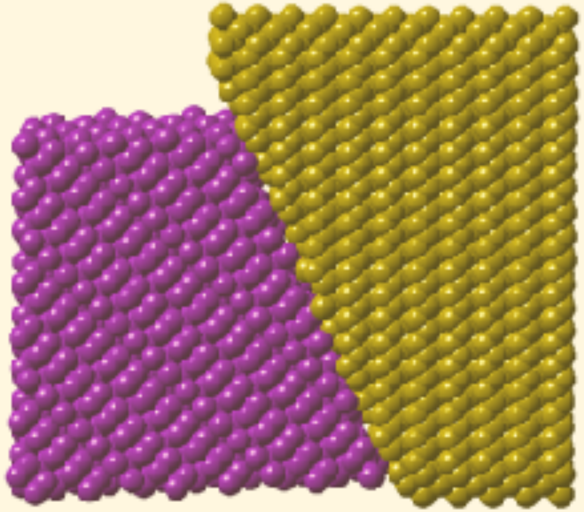

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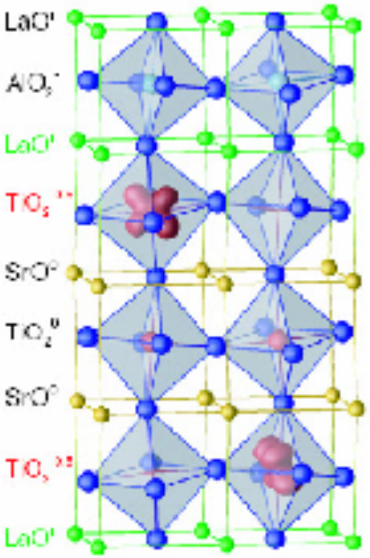

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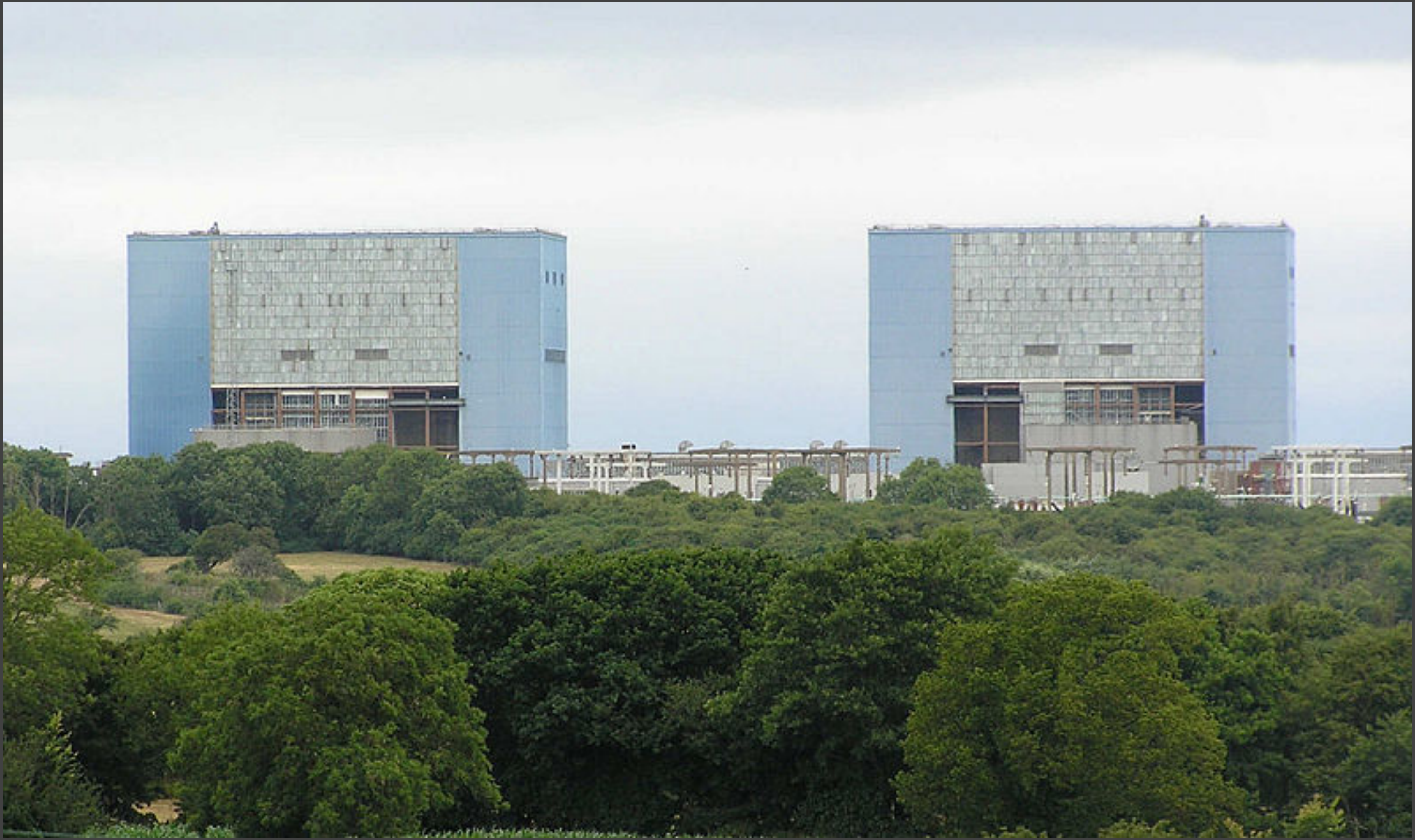
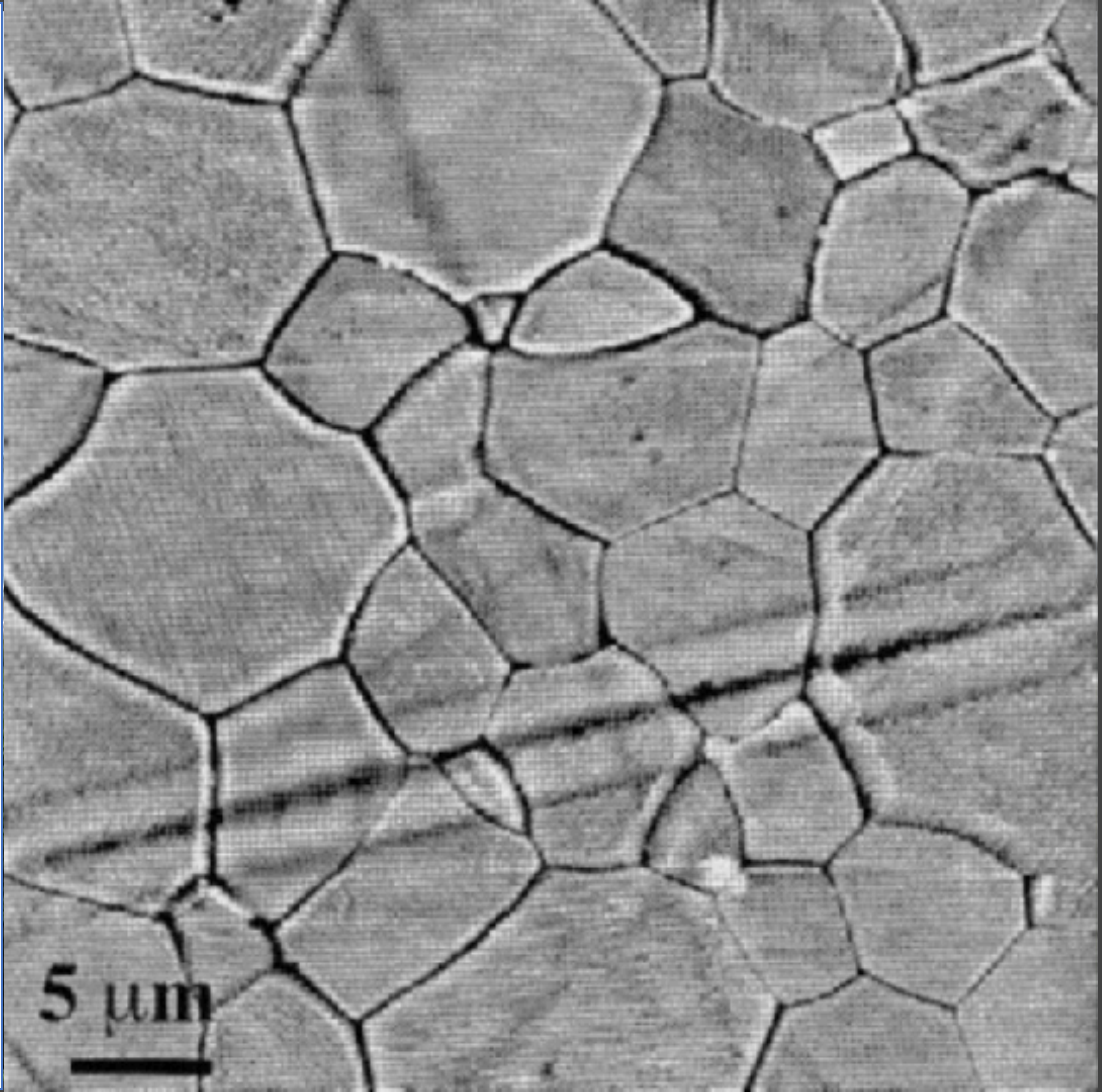
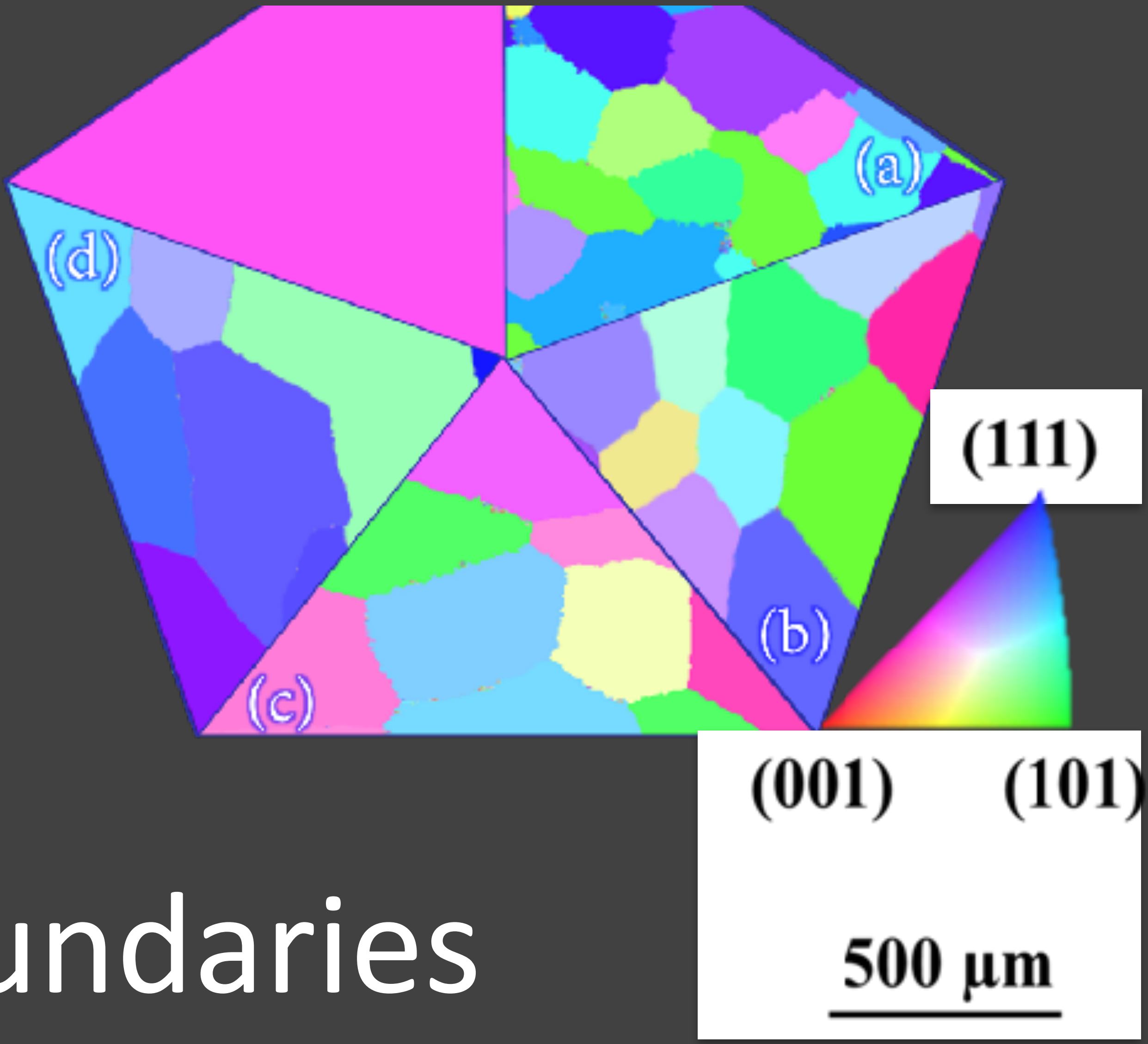


Grain boundaries - Optical Micrographs



Optical Micrograph

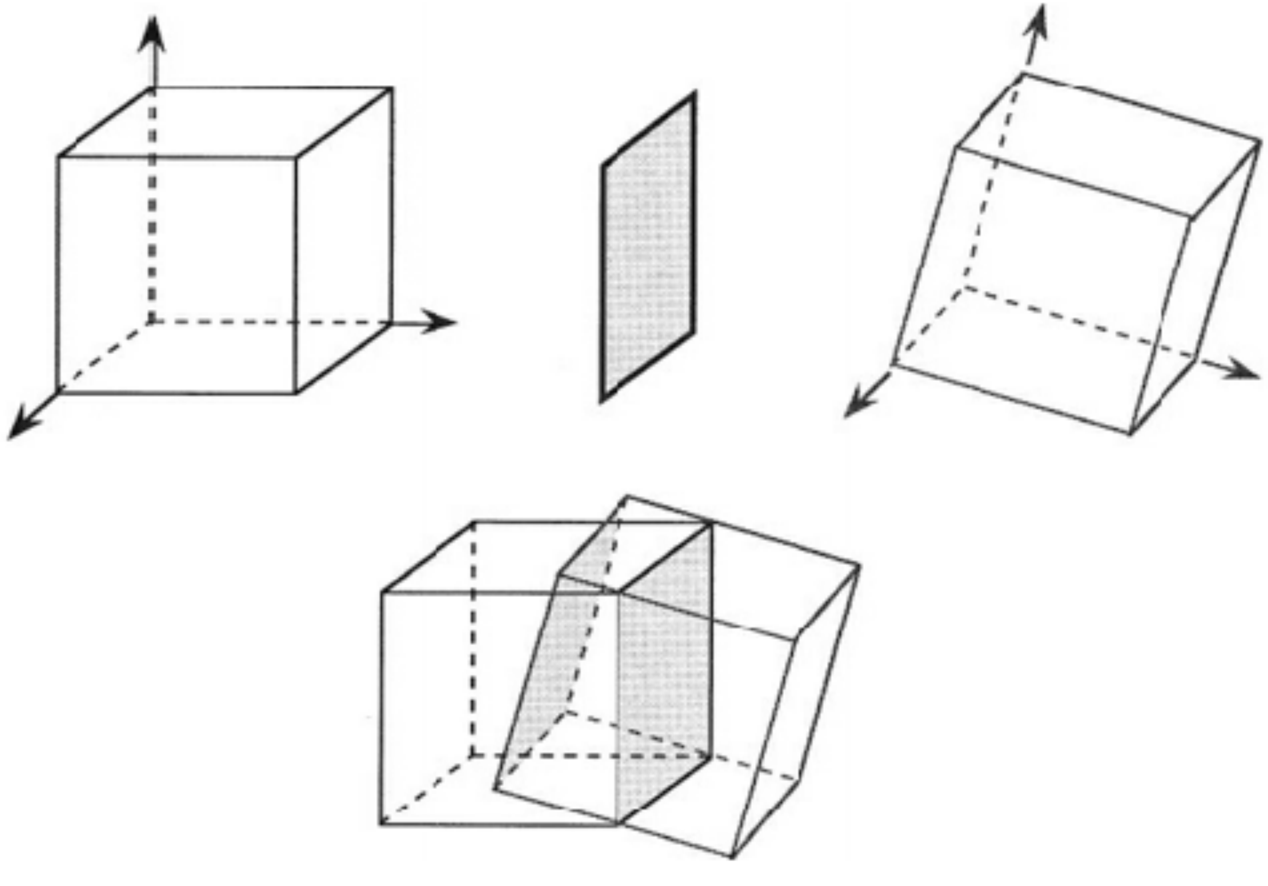
Orientation Imaging Micrograph



Grain boundaries

Garima et al., Journal of Physical Chemistry C, 123 26057–26064 (2019)

Grain boundaries - Tilt and twist



Grain boundaries - General characteristics

Additional Reading: Chapter 2, Section I of Structure and Bonding in Crystalline Materials, Gregory S. Rohrer

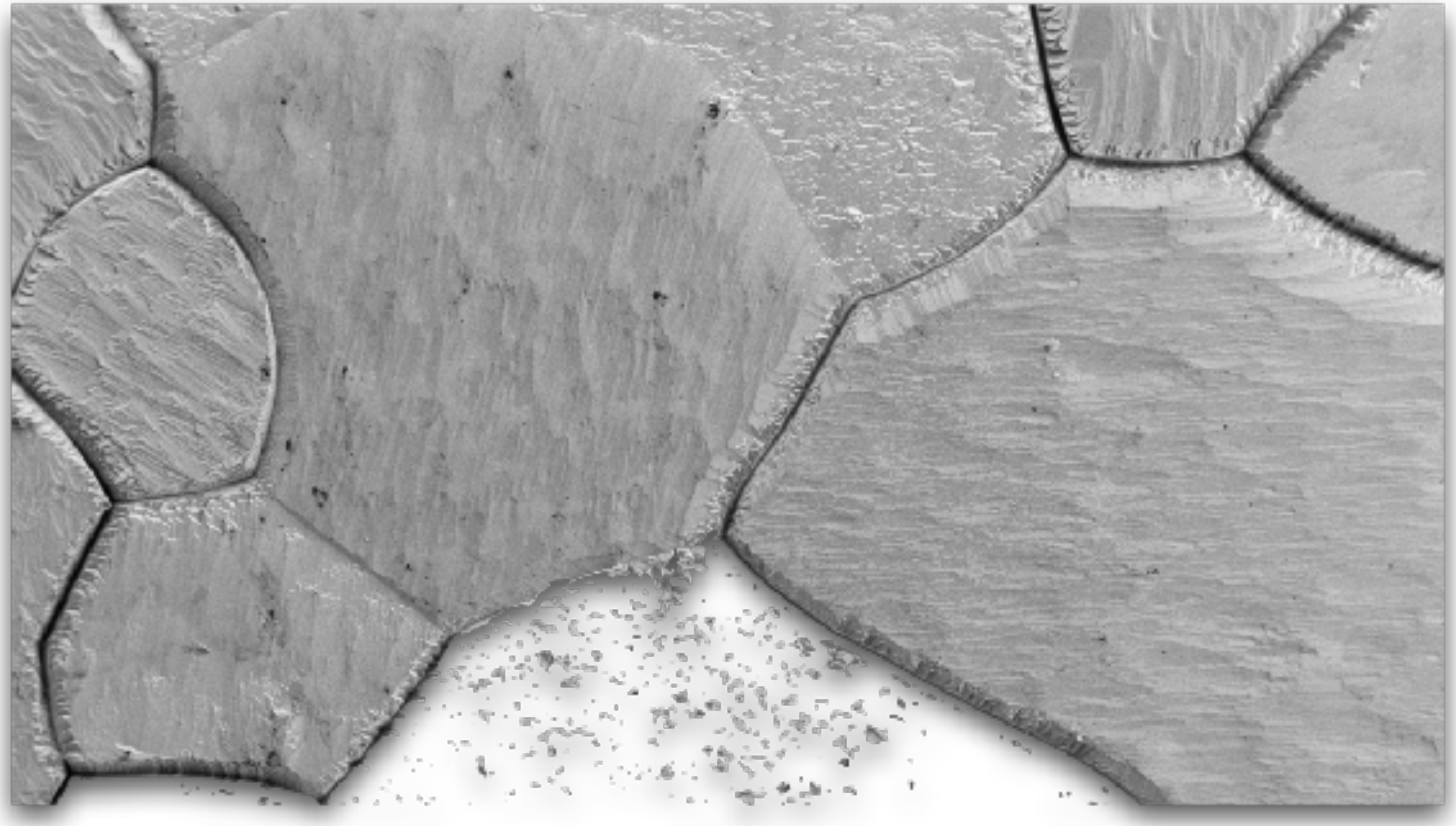
- angle of tilt/twist/tilt-twist
  - Small → low-angle GB
  - Large → high-angle GB

- Relative orientation of a grain w.r.t external axis
  - Euler angles: an ordered set of rotations, about specific axes, that can be used to rotate a crystal into coincidence with a frame of reference

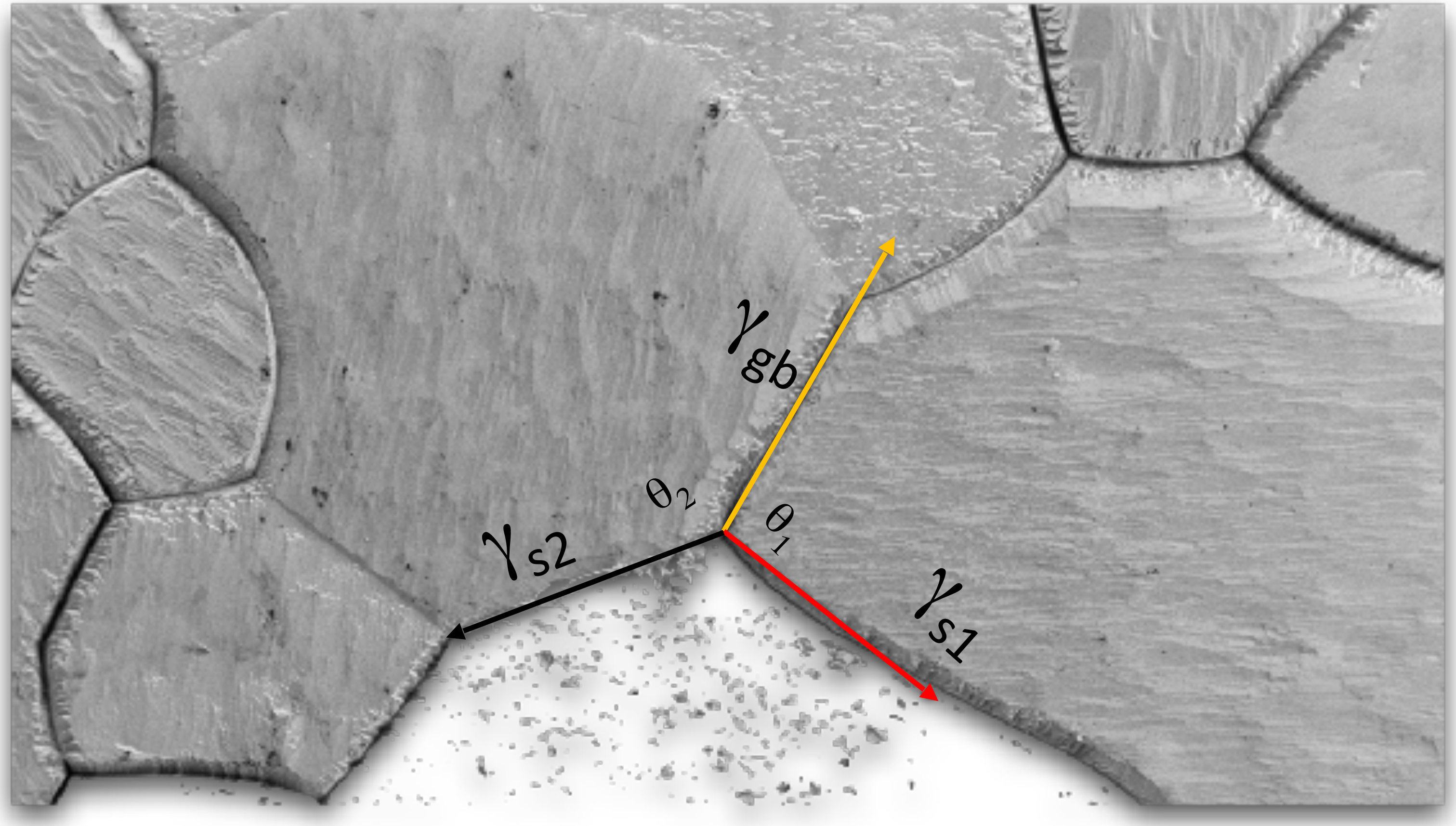
  - direction cosines of the angles between each of the crystal axes and each of the axes in the reference frame

  - axis–angle pair

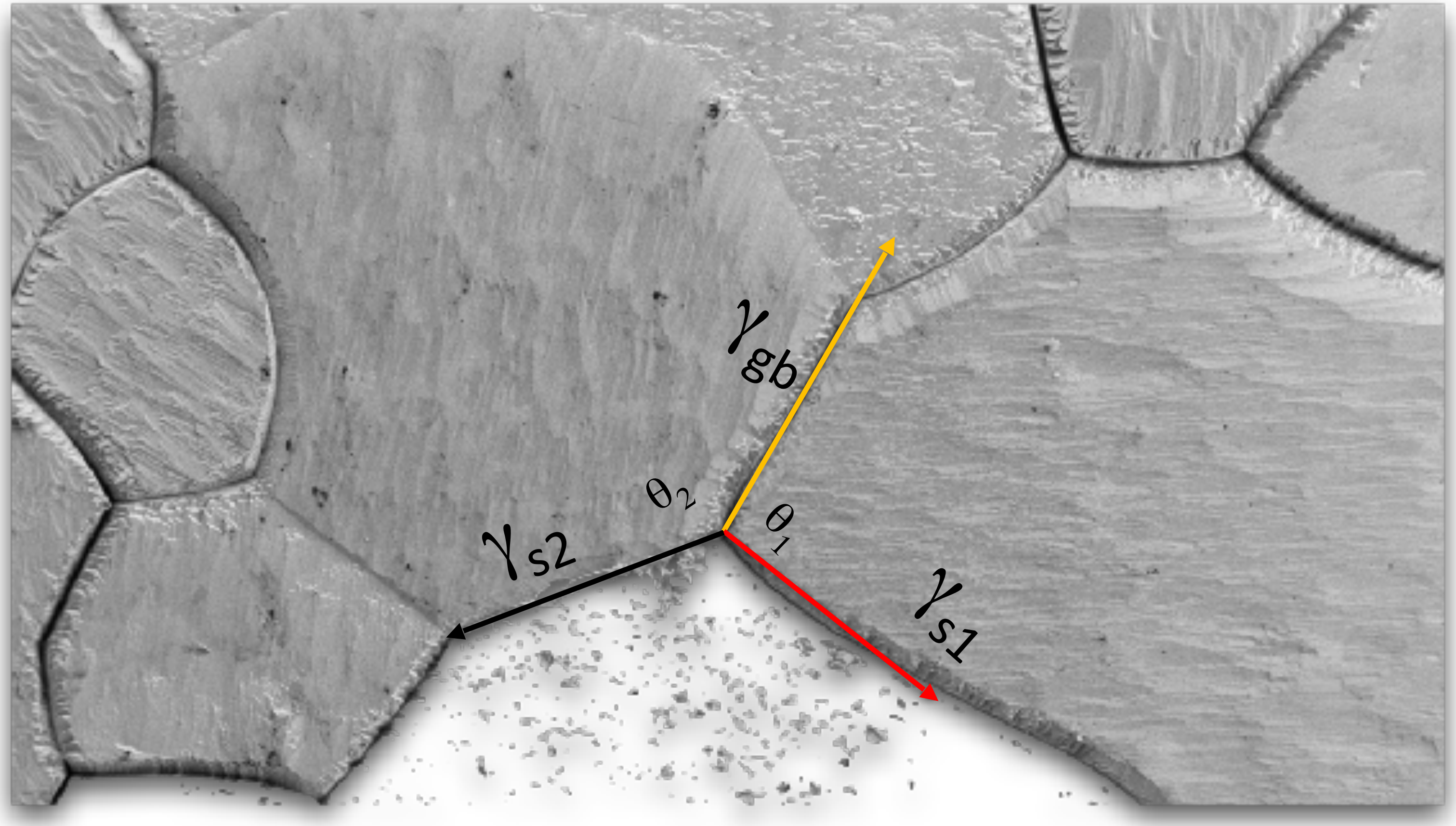
Grain boundary energy



Grain boundary energy

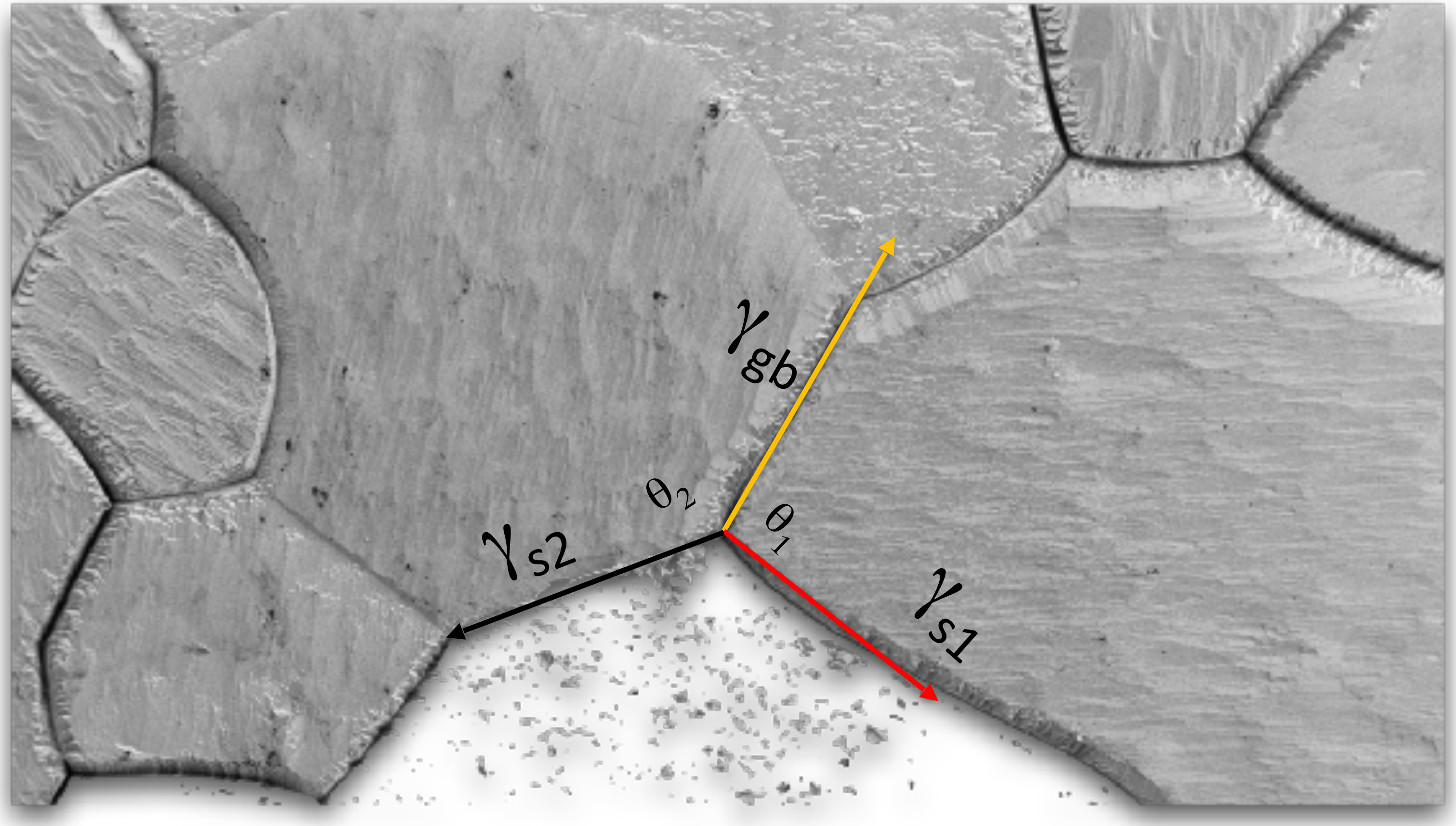


Grain boundary energy



- Knowing the surface planes at the triple junction
  - Calculate Surface energy
  - Measure θ_1 and θ_2

Grain boundary energy



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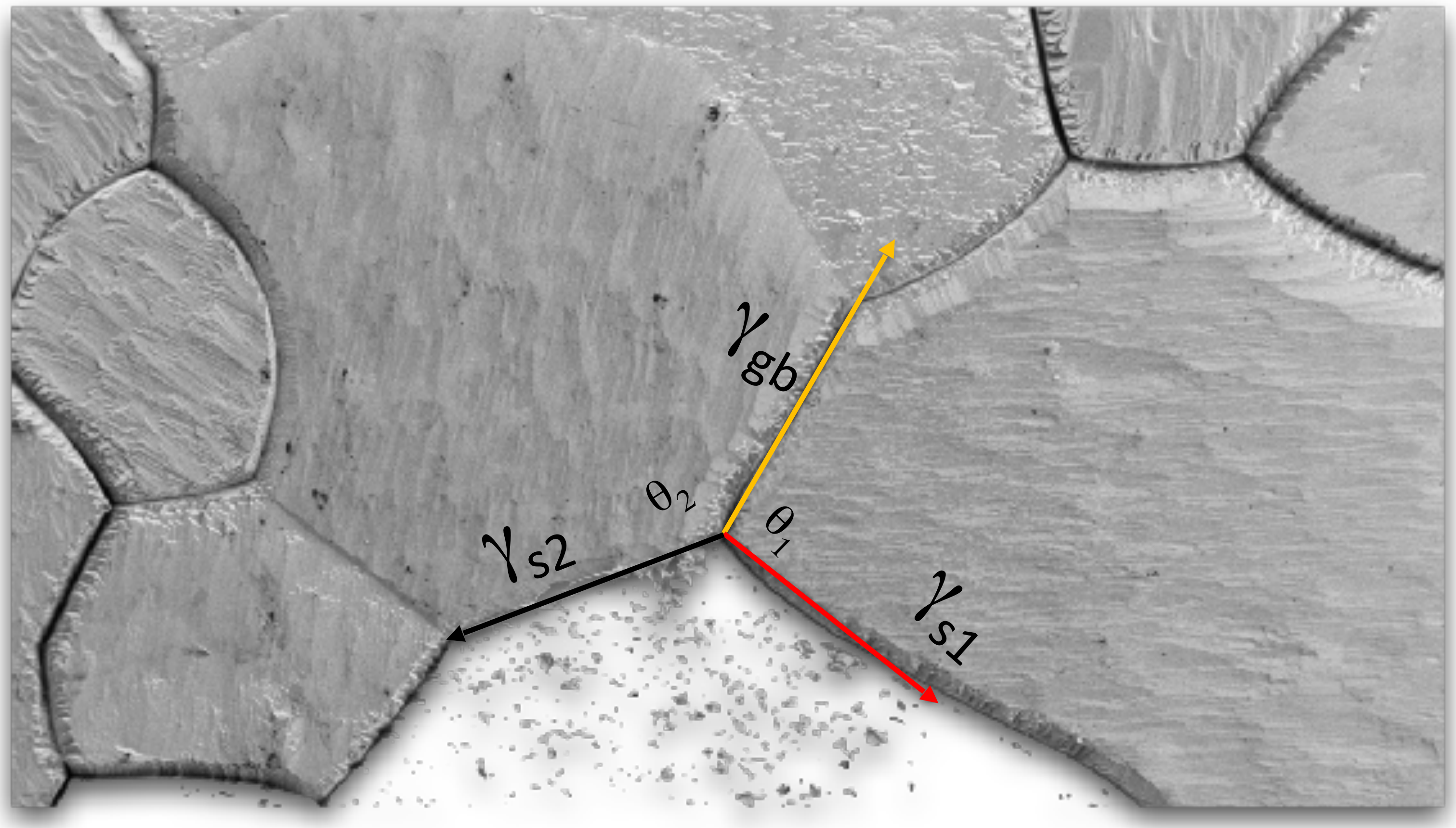
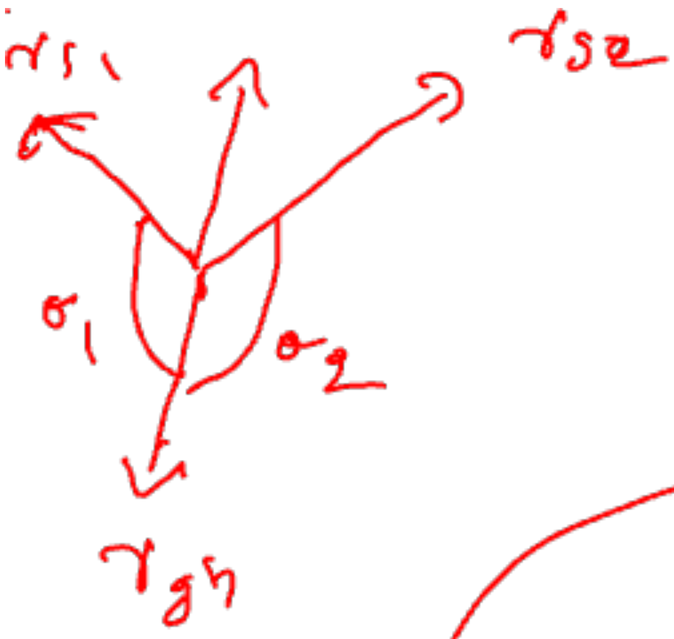
Grain boundary energy



- Knowing the surface planes at the triple junction
  - Calculate Surface energy
  - Measure θ_1 and θ_2

- Mechanical equilibrium determines surface energy of S2 and grain boundary energy



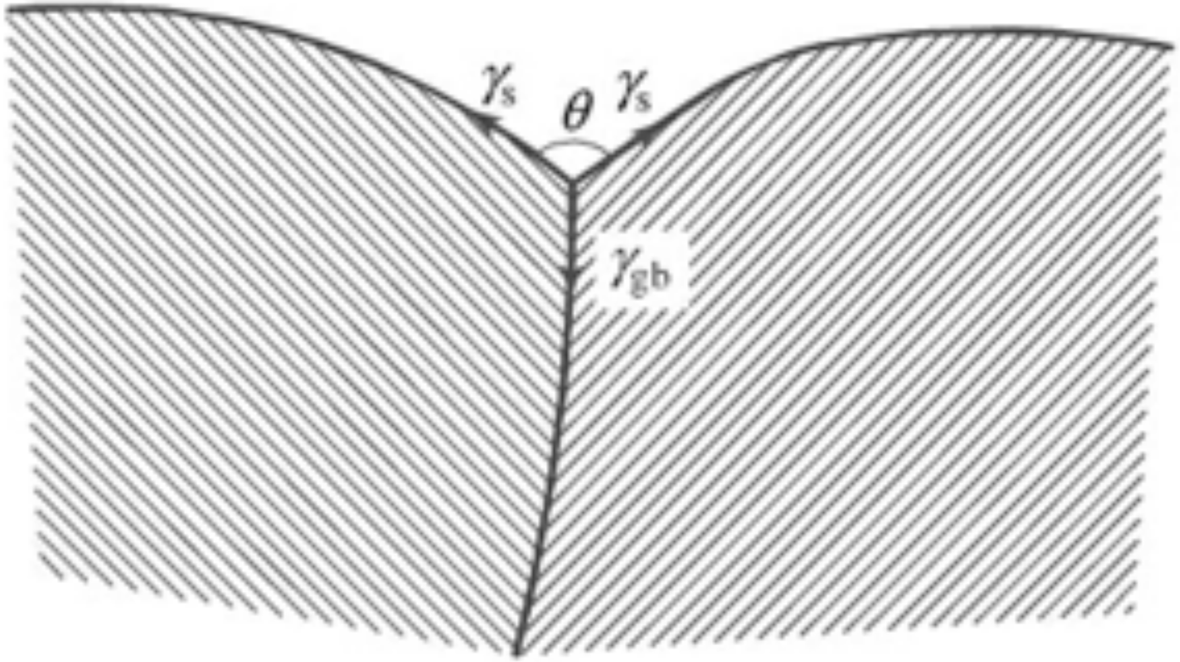
$$\gamma_{s_1} \sin\theta_1 = \gamma_{s_2} \sin\theta_2$$

$$\gamma_{s_1} \cos\theta_1 + \gamma_{s_2} \cos\theta_2 - \gamma_{gb} = 0$$

estimate this provided. I am given $(h_1 k_1 l_1)$ and $(h_2 k_2 l_2)$.

experiment.

γ_{gb} can be determined. for a particular set of grains.



- Given:
  - Given GB bisects the two surfaces
  - $\theta = 161°$
  - Surface is {111} Cu

- Estimate γ_{GB}