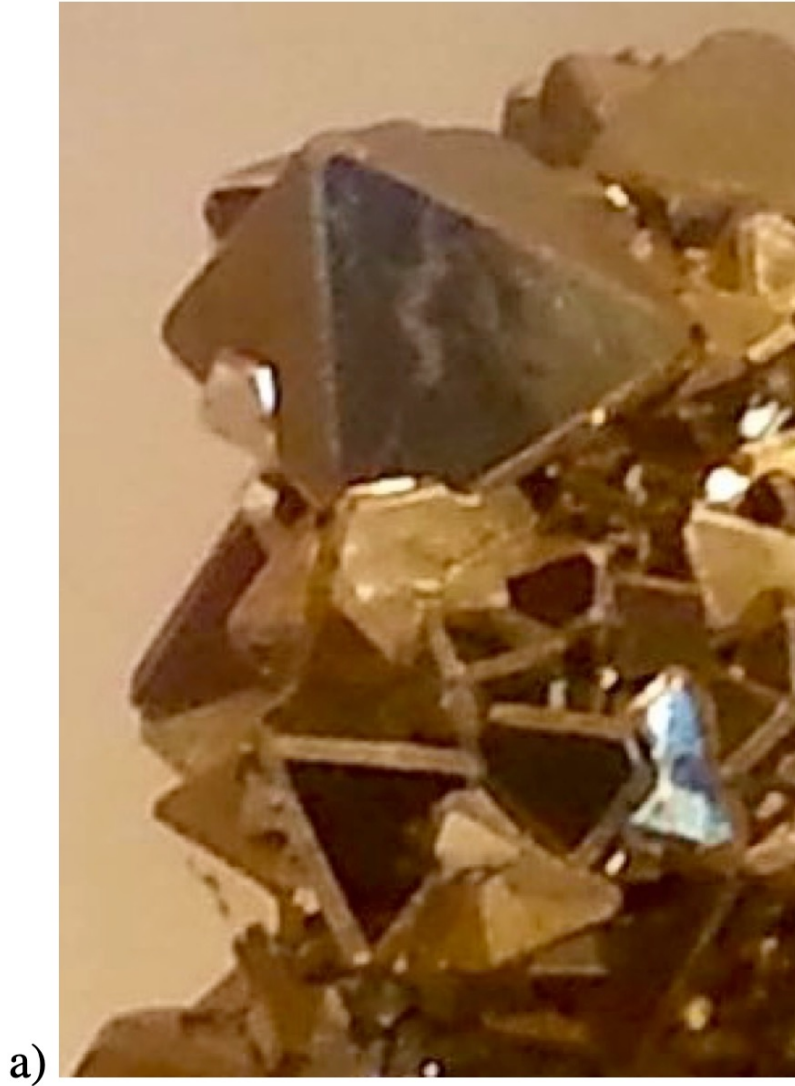


Substrates

Crystals

- Single crystals
 - (a) FeS₂
 - (b) Ni- alloy

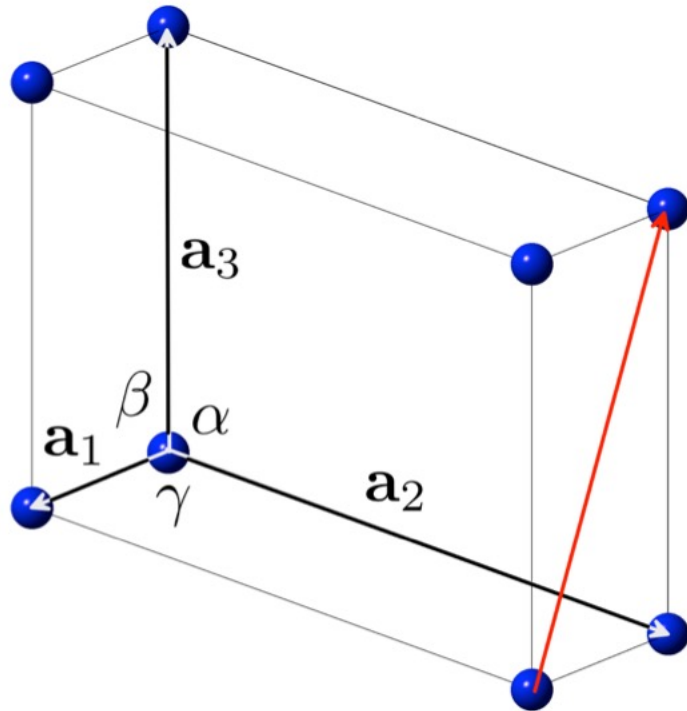


a)

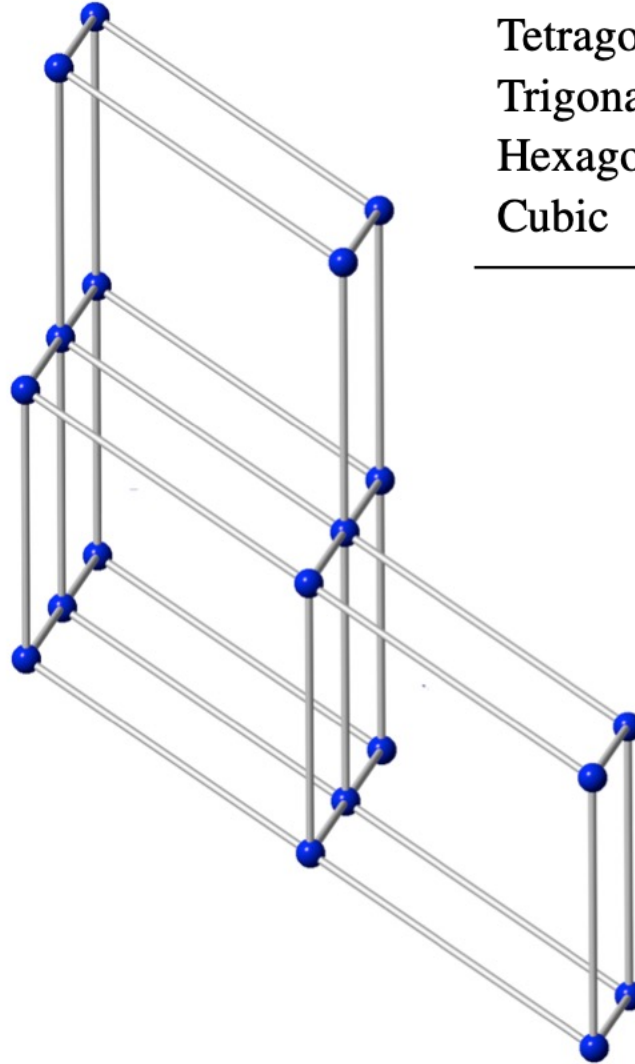


(b)

Crystals lattice



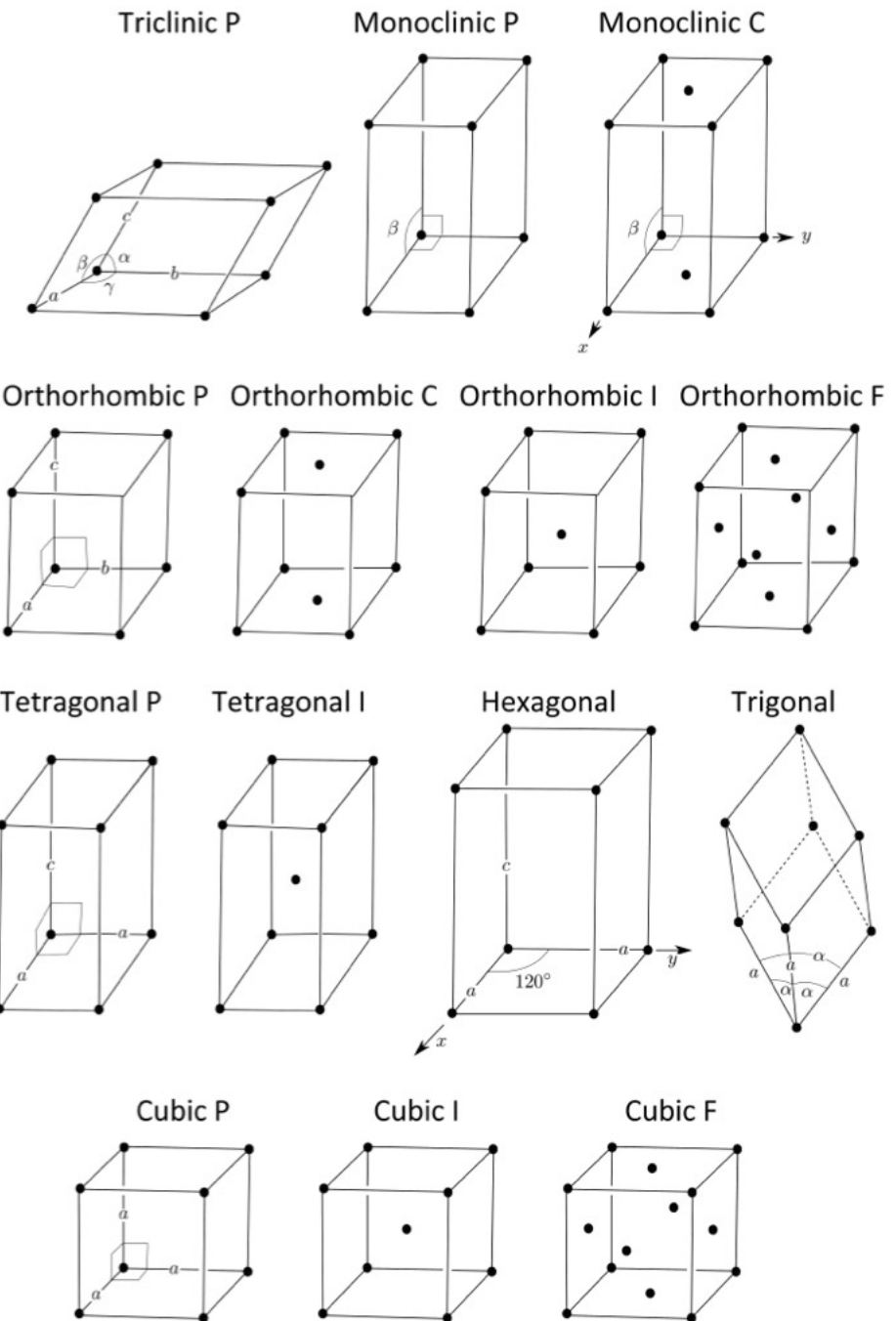
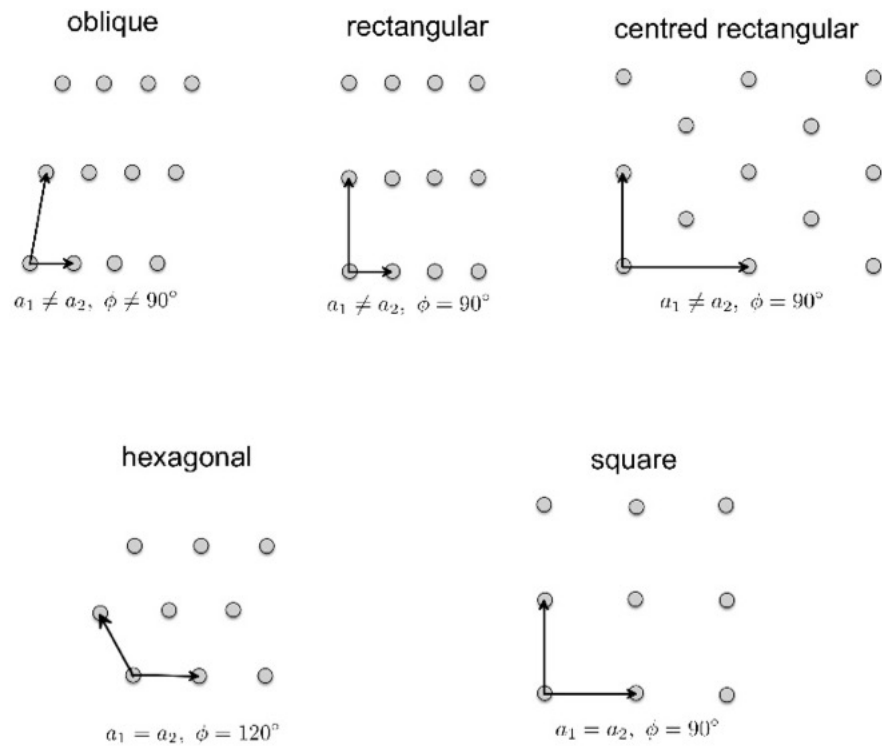
(a)



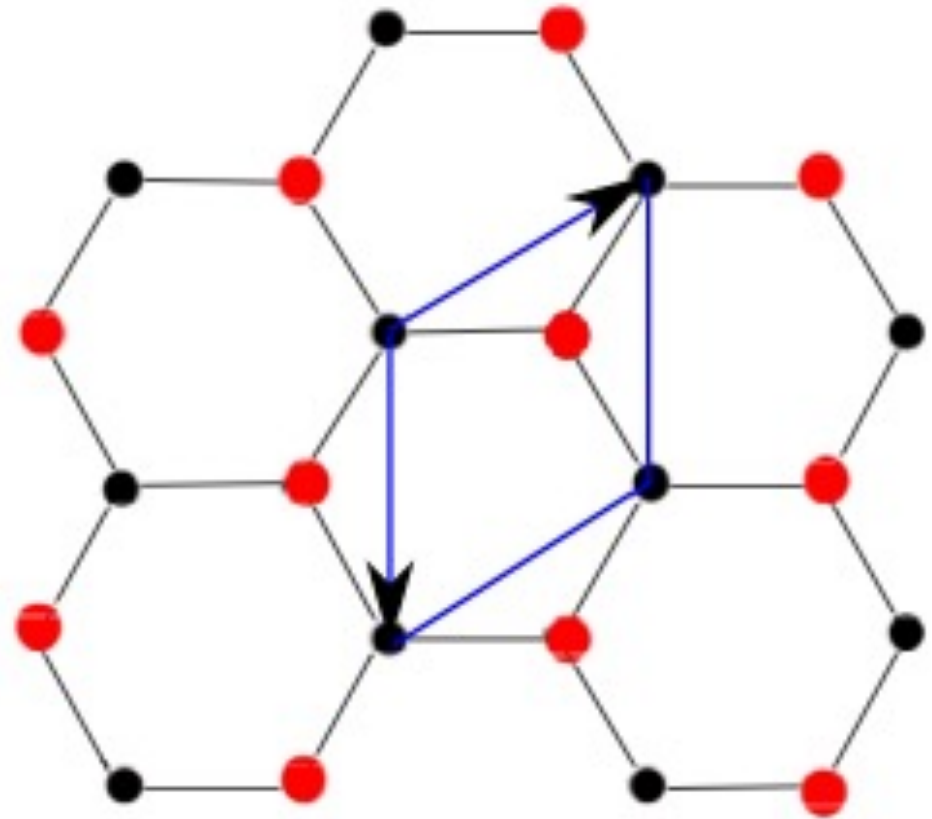
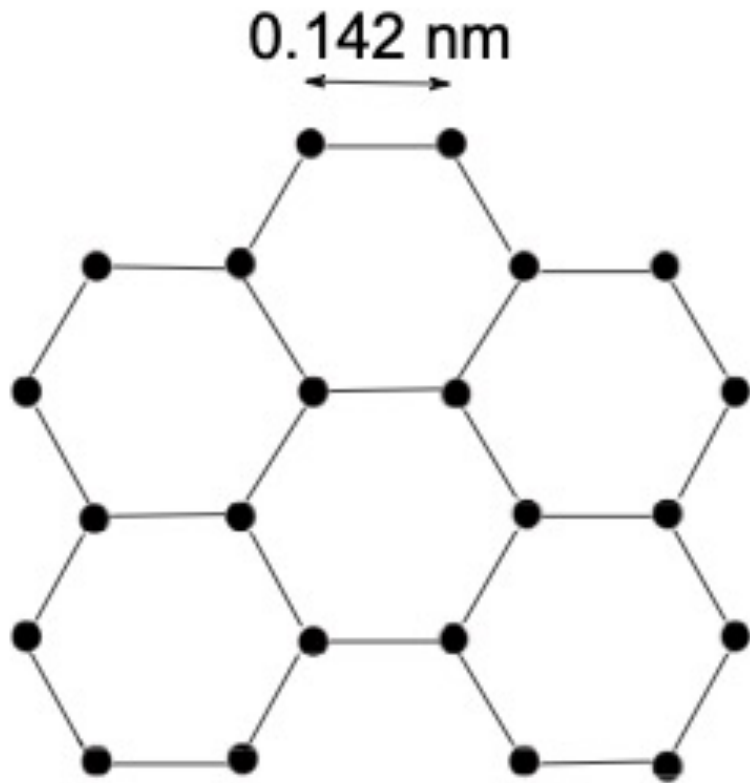
(b)

System	Conventional unit cell	
Triclinic	$a_1 \neq a_2 \neq a_3$	$\alpha \neq \beta \neq \gamma$
Monoclinic	$a_1 \neq a_2 \neq a_3$	$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$
Orthorhombic	$a_1 \neq a_2 \neq a_3$	$\alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a_1 = a_2 \neq a_3$	$\alpha = \beta = \gamma = 90^\circ$
Trigonal	$a_1 = a_2 = a_3$	$\alpha = \beta = \gamma \neq 90^\circ$
Hexagonal	$a_1 = a_2 \neq a_3$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$
Cubic	$a_1 = a_2 = a_3$	$\alpha = \beta = \gamma = 90^\circ$

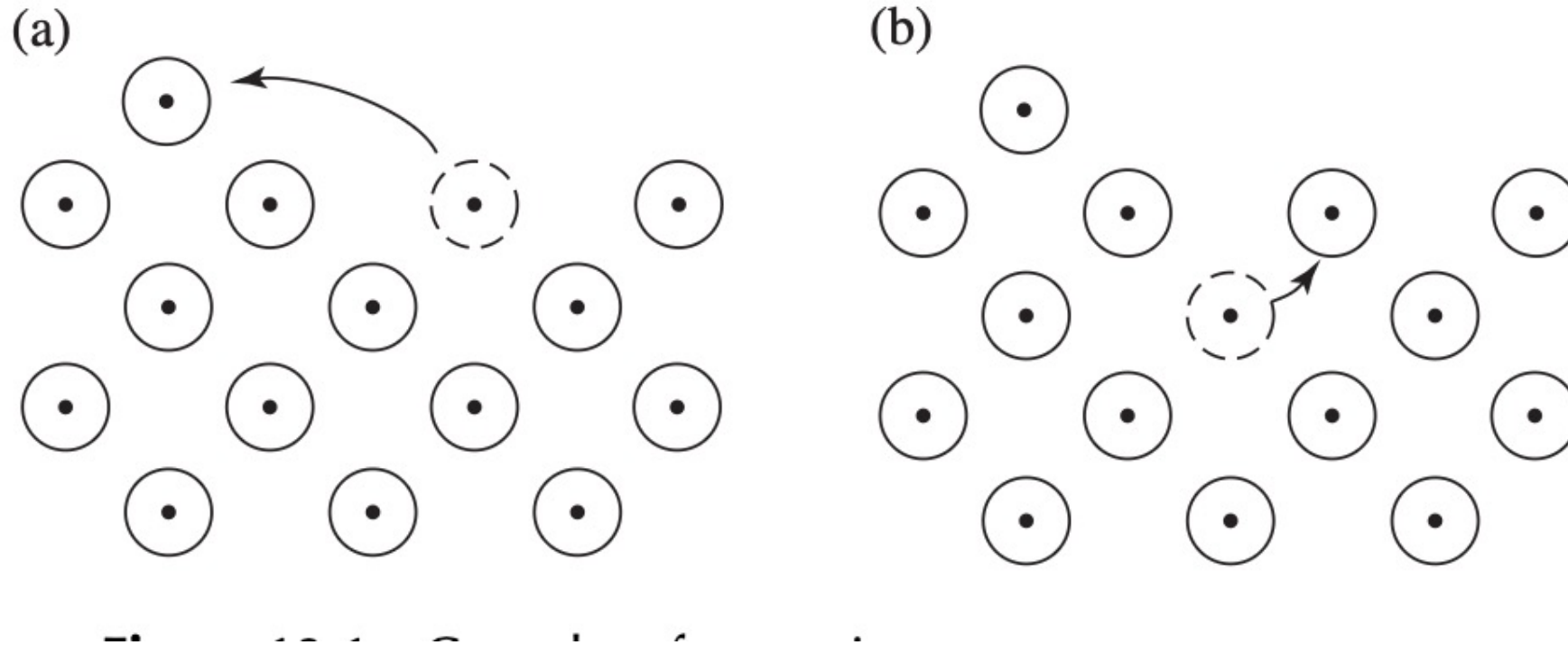
The lattice varieties



Crystal System

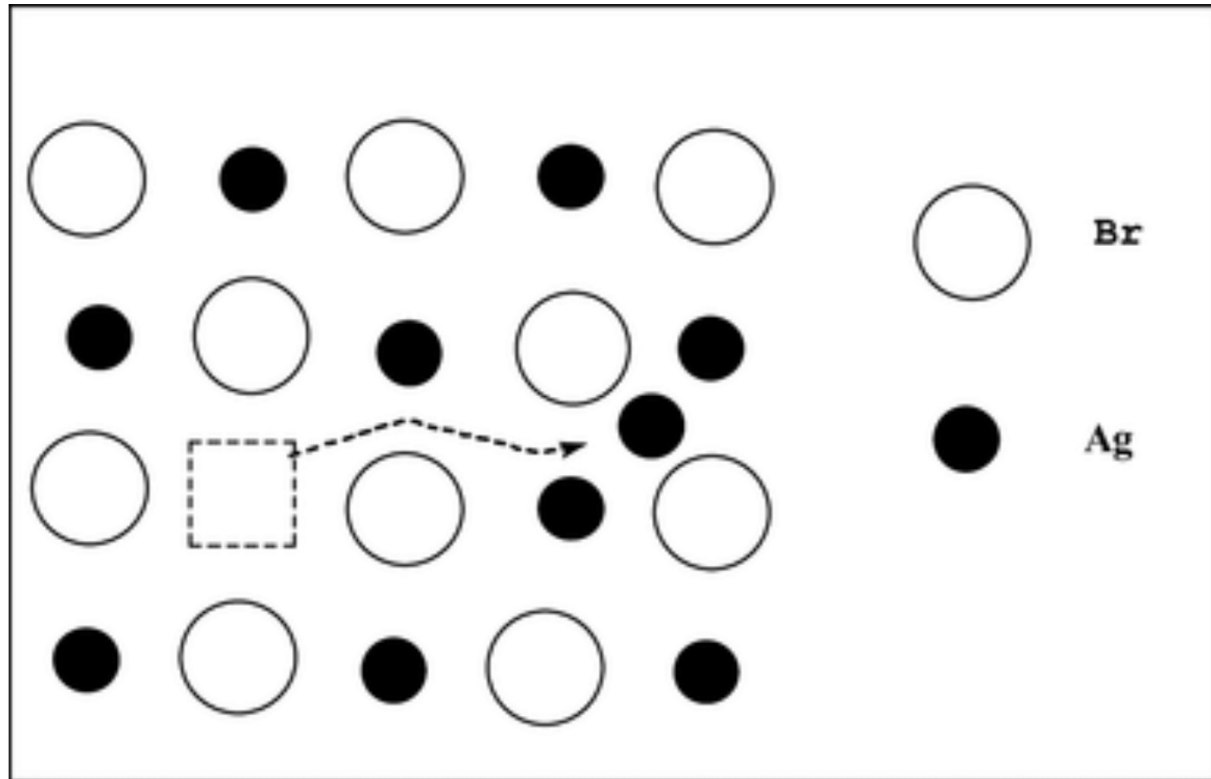


Imperfections in a crystal

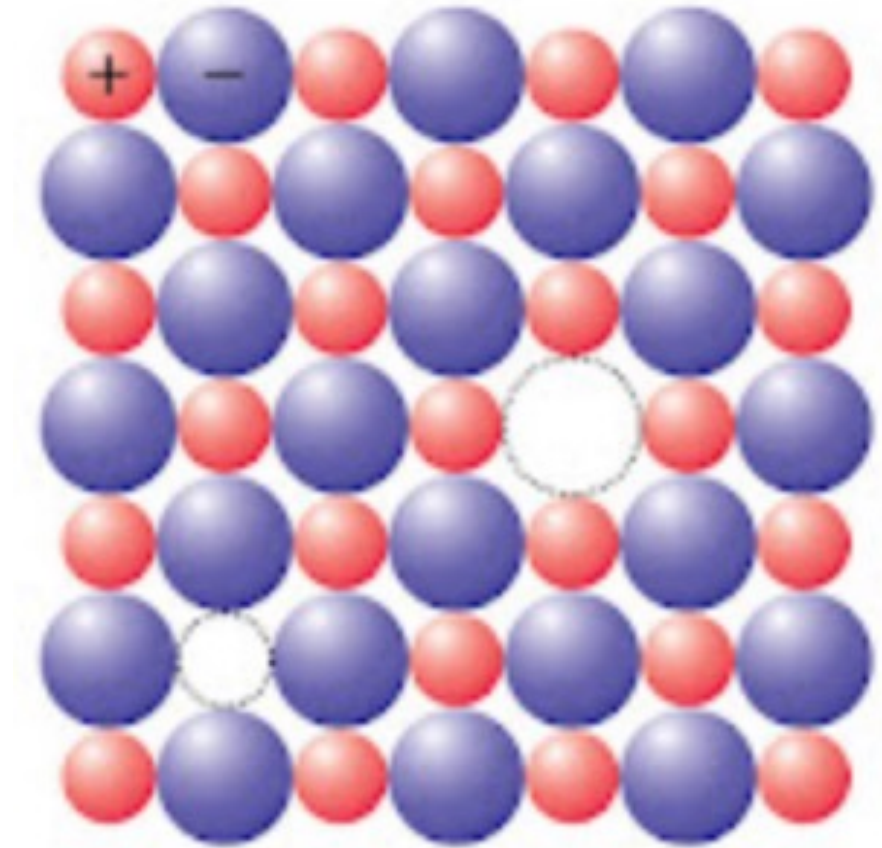


Surfaces, grain boundaries and dislocations are a source of vacancy.
The vacancies can later exchange atoms with the crystal internals.

Frankel Defect

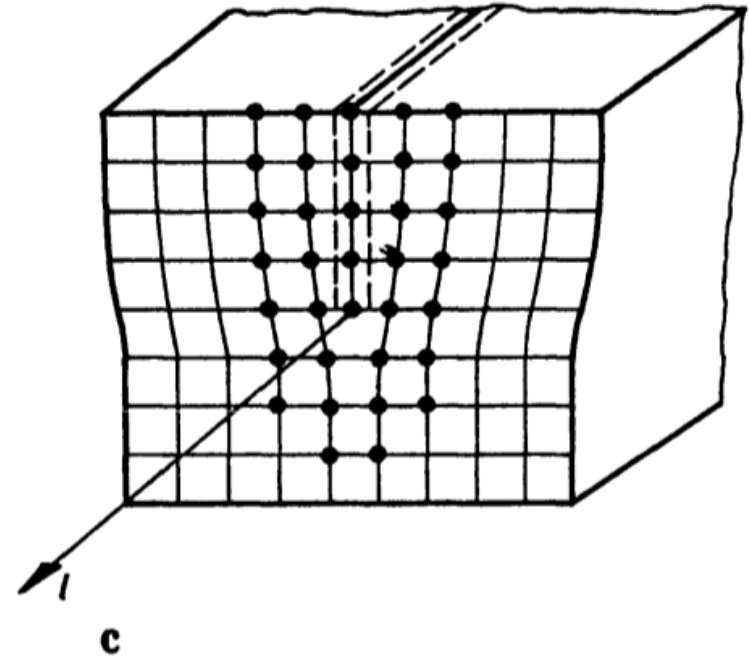
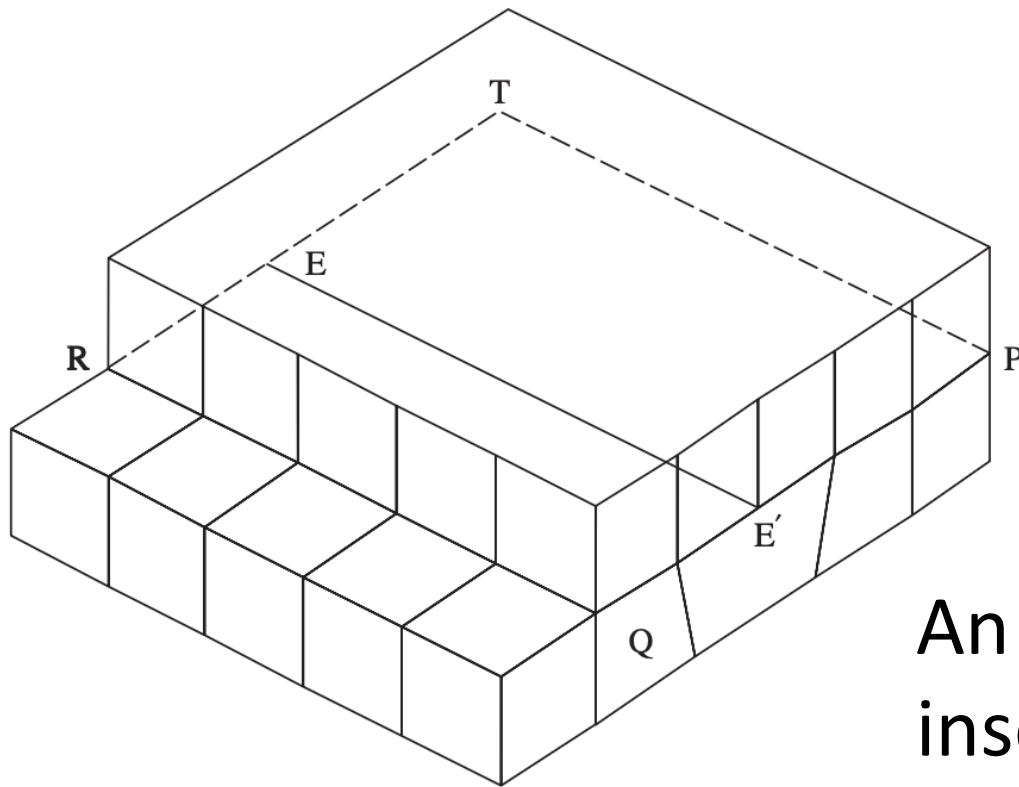


Schottky defect



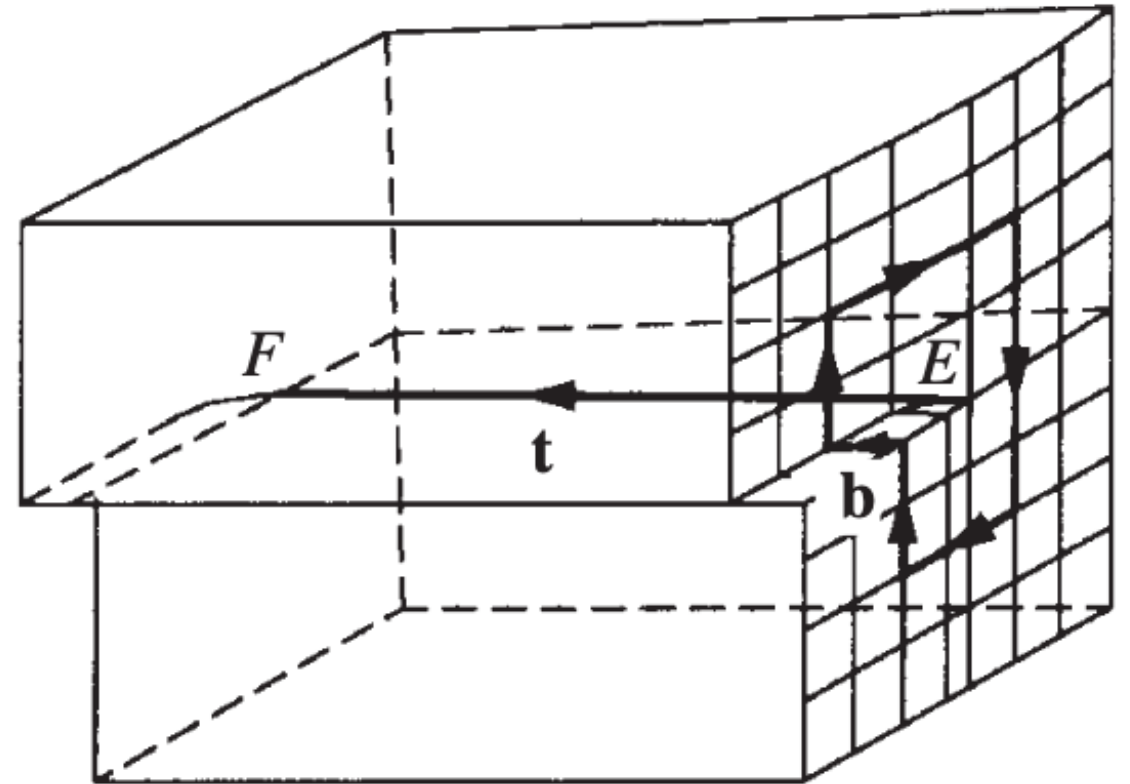
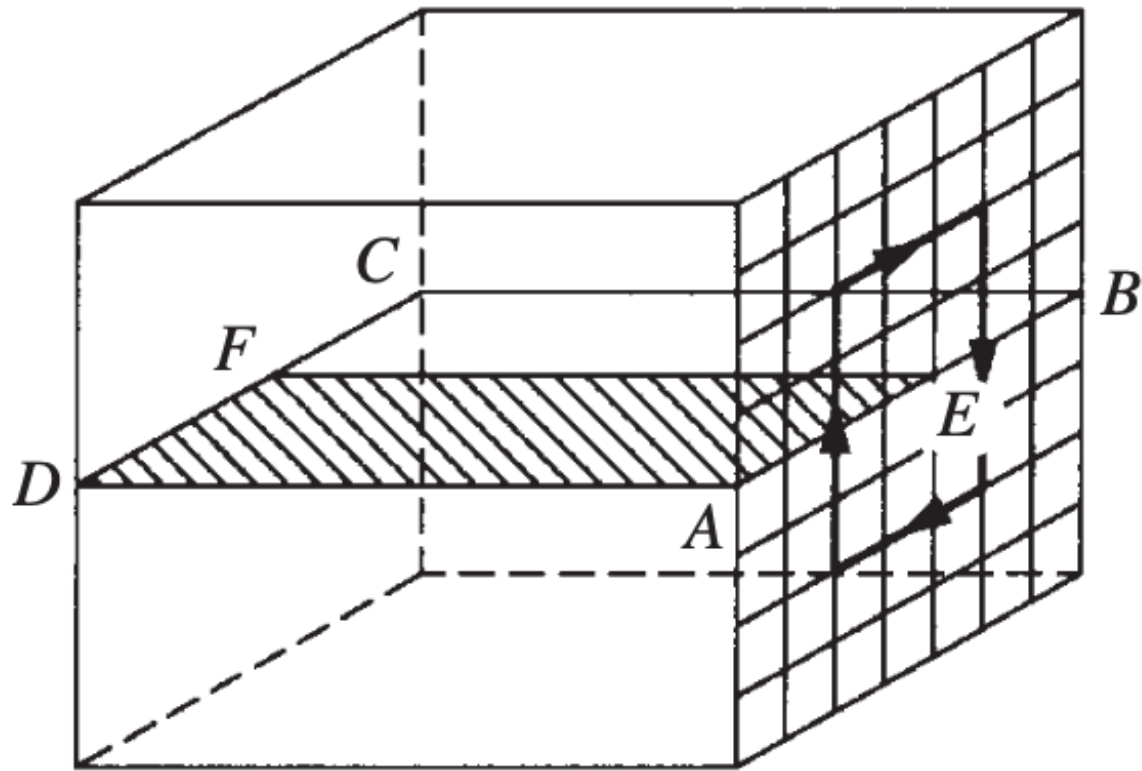
Line Defects

Disloc

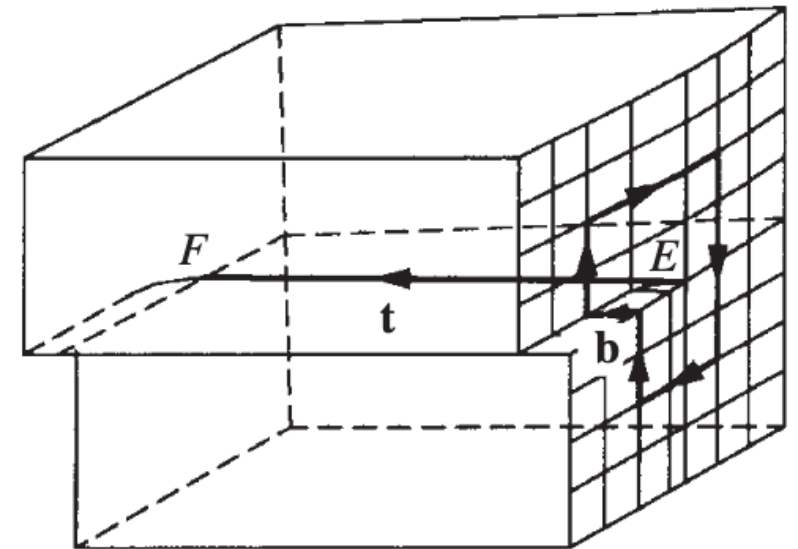
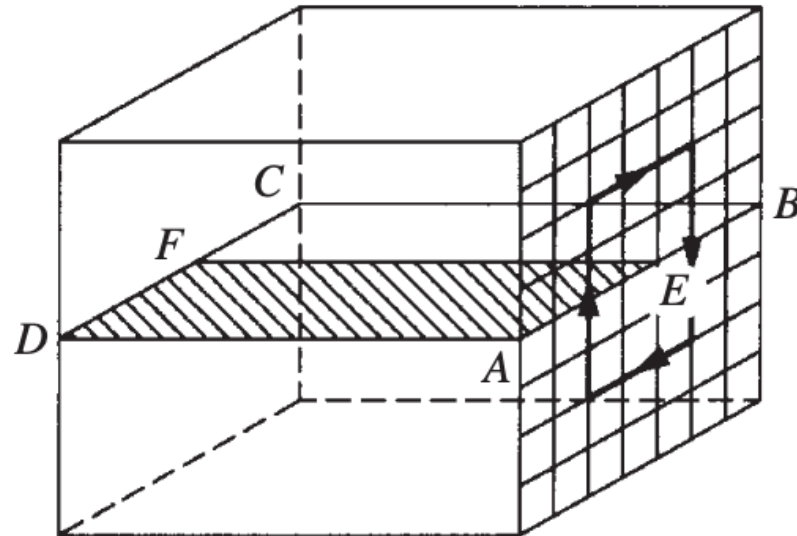
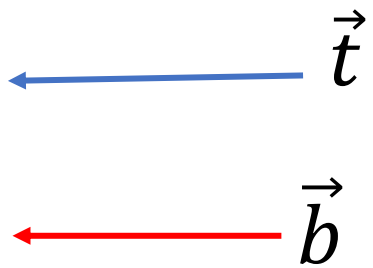
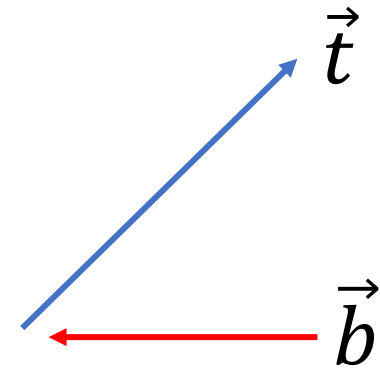
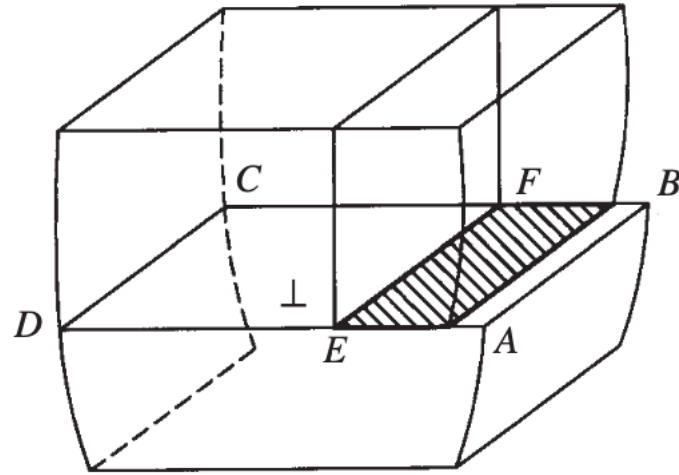
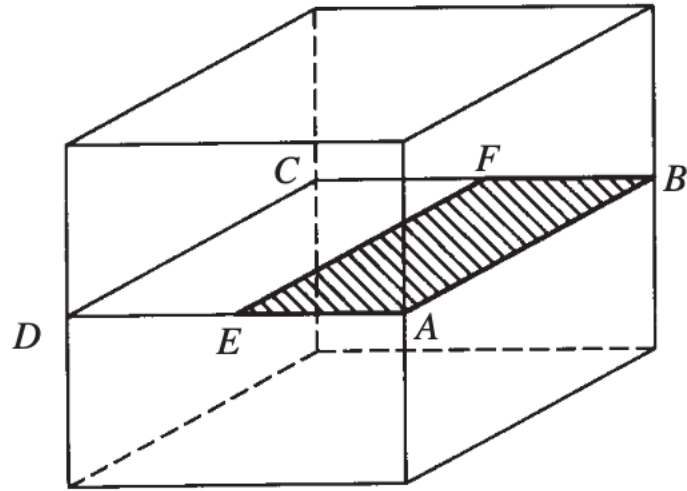


An extra-plane of atoms being inserted due to an external deformation

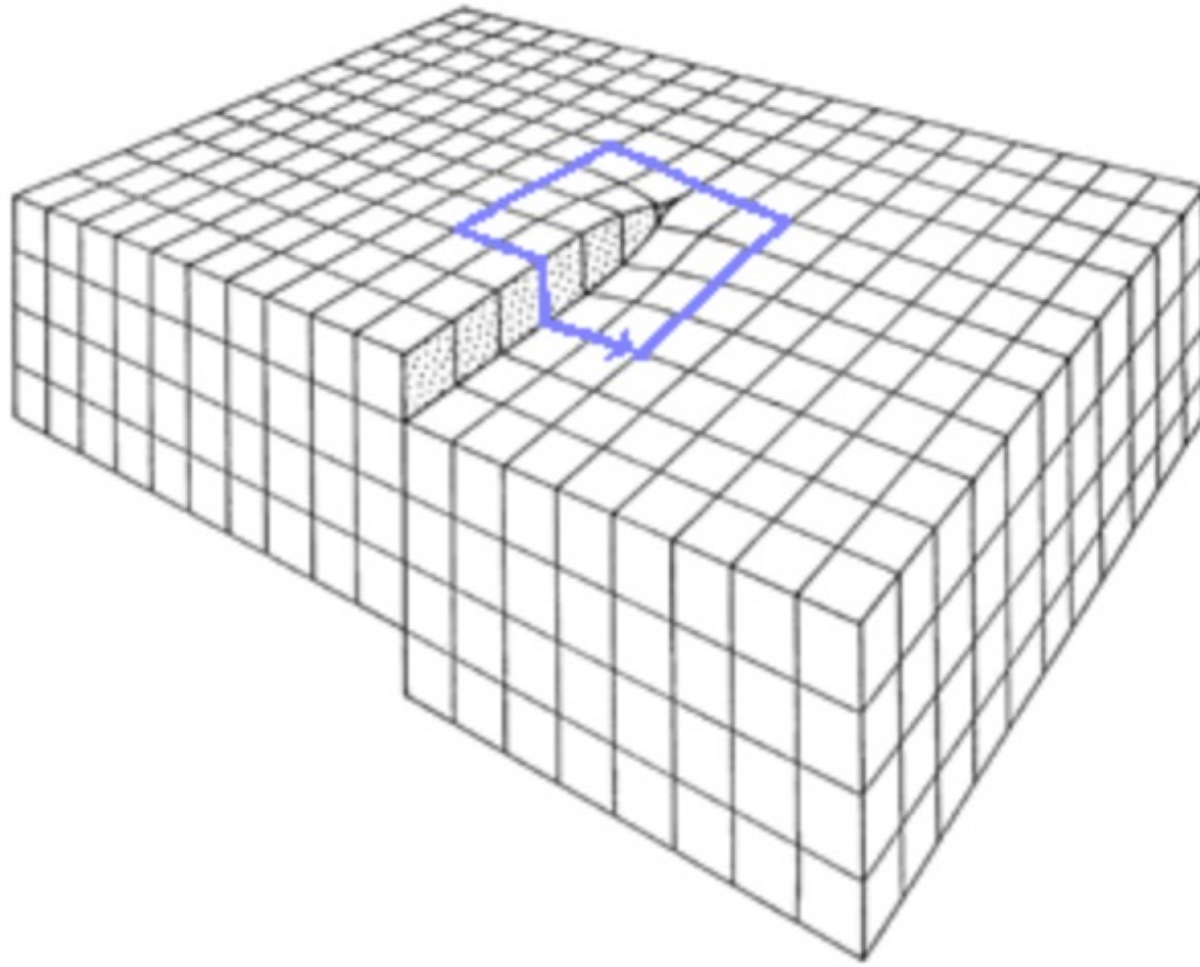
Screw Dislocations



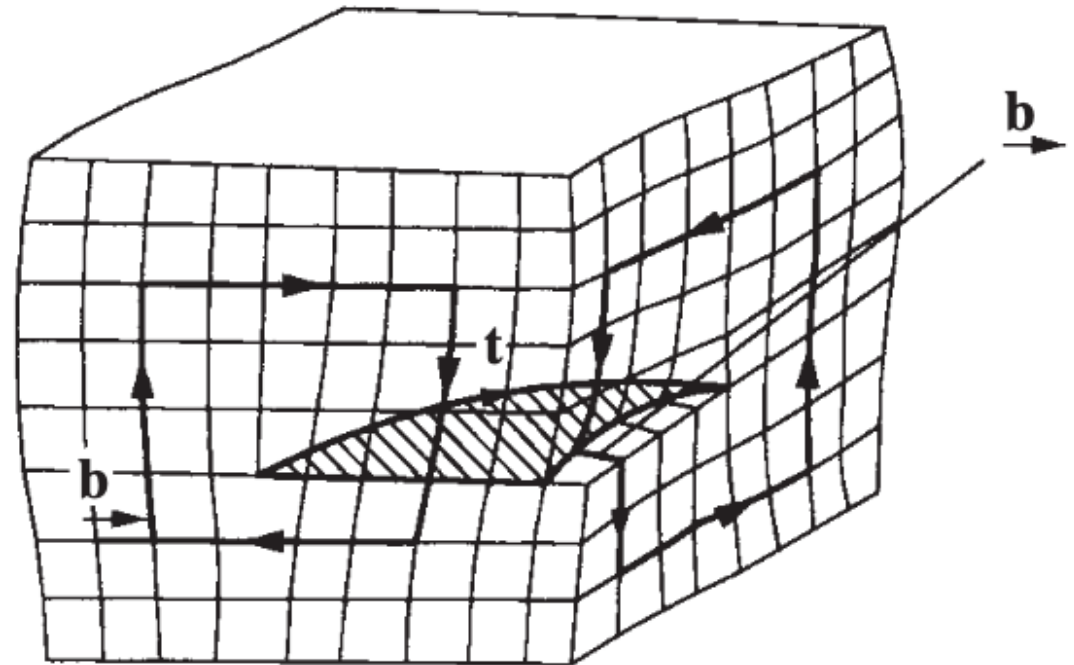
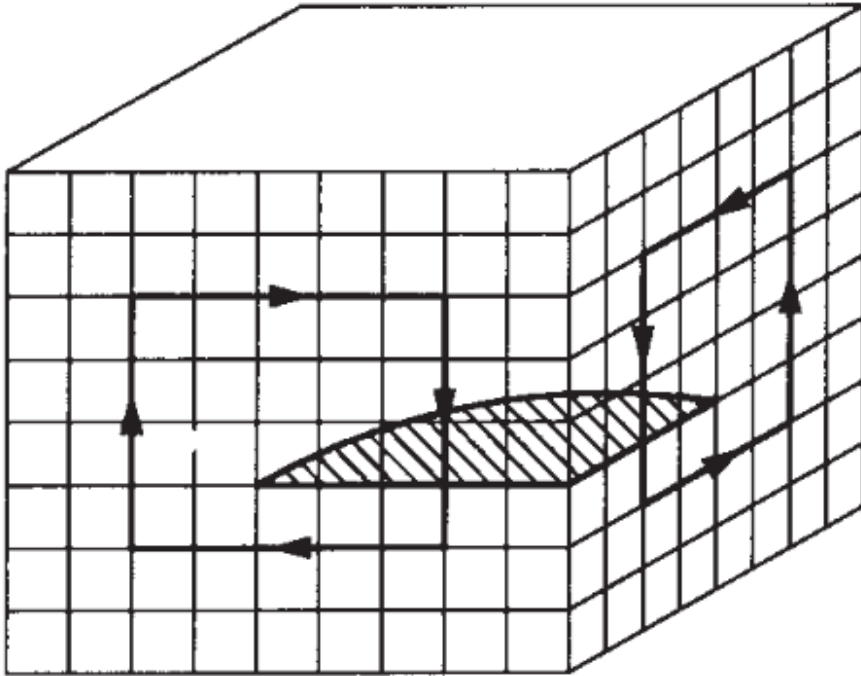
Edge and Screw Dislocation



Drawing the Burger's circuit for a screw



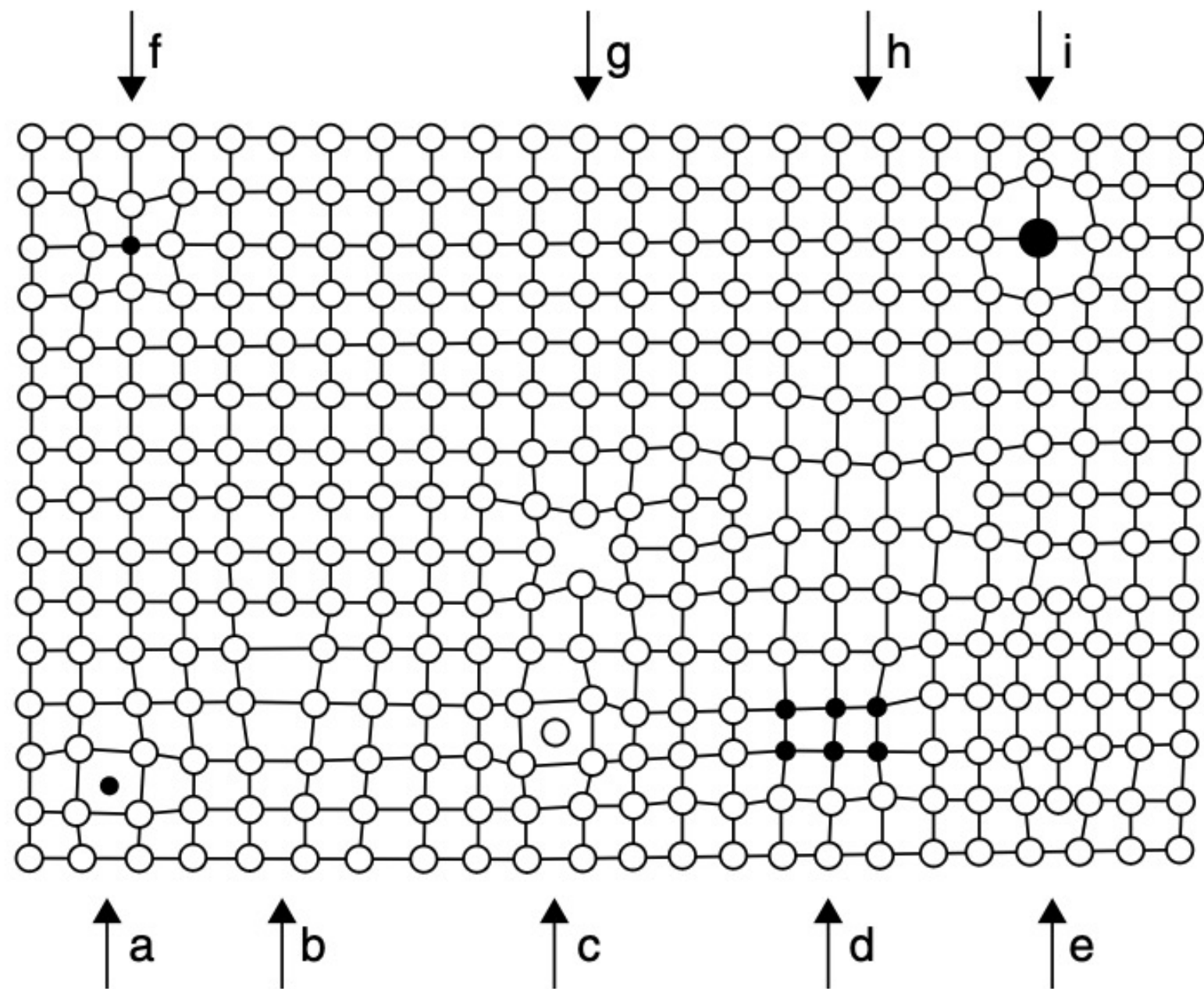
Mixed Dislocations



Relationship between $\vec{t}$ and $\vec{b}$ are neither parallel or perpendicular.

Pure screw on the right
Pure edge on the front

Everything in-between also observed.



Equilibrium Shape of Crystals

When a crystal is grown:

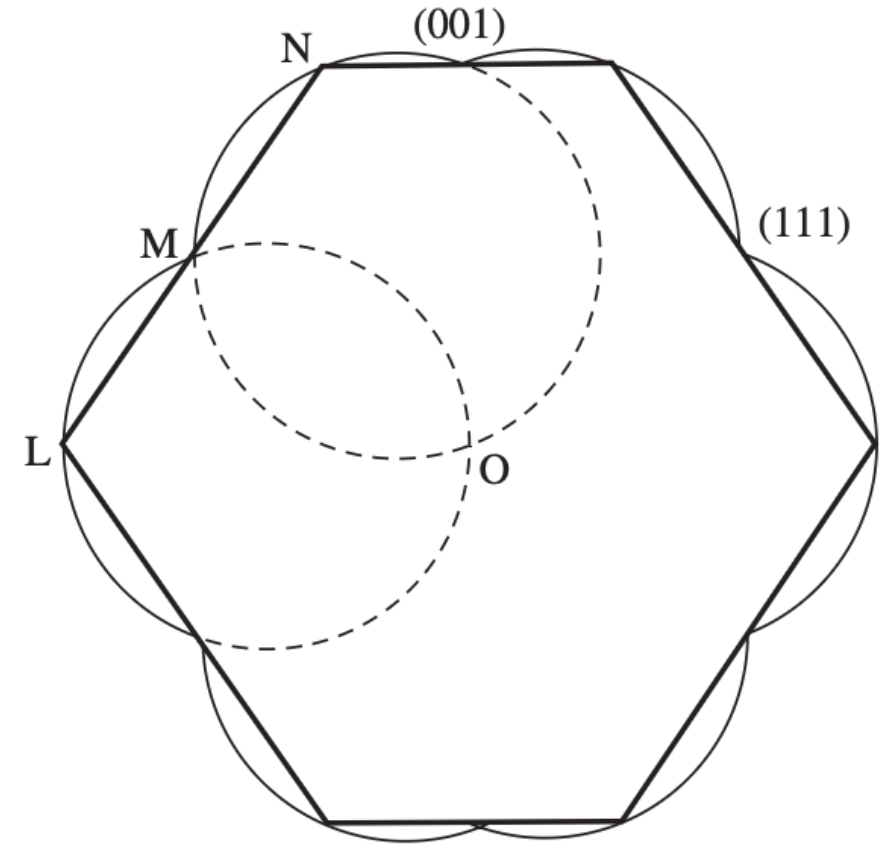
A stable surface is formed when

$$\int_A \gamma dA \text{ is minimum}$$

If system is isotropic:

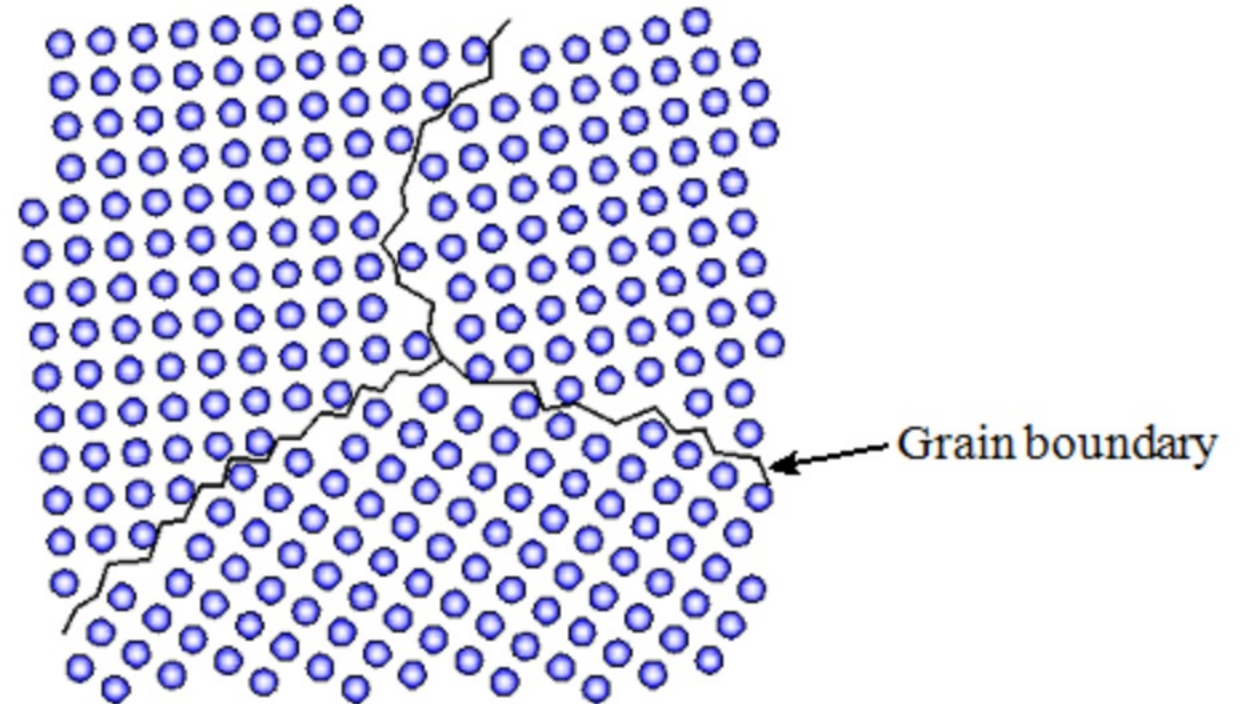
All crystal orientations have equal surface energy, a sphere is formed.

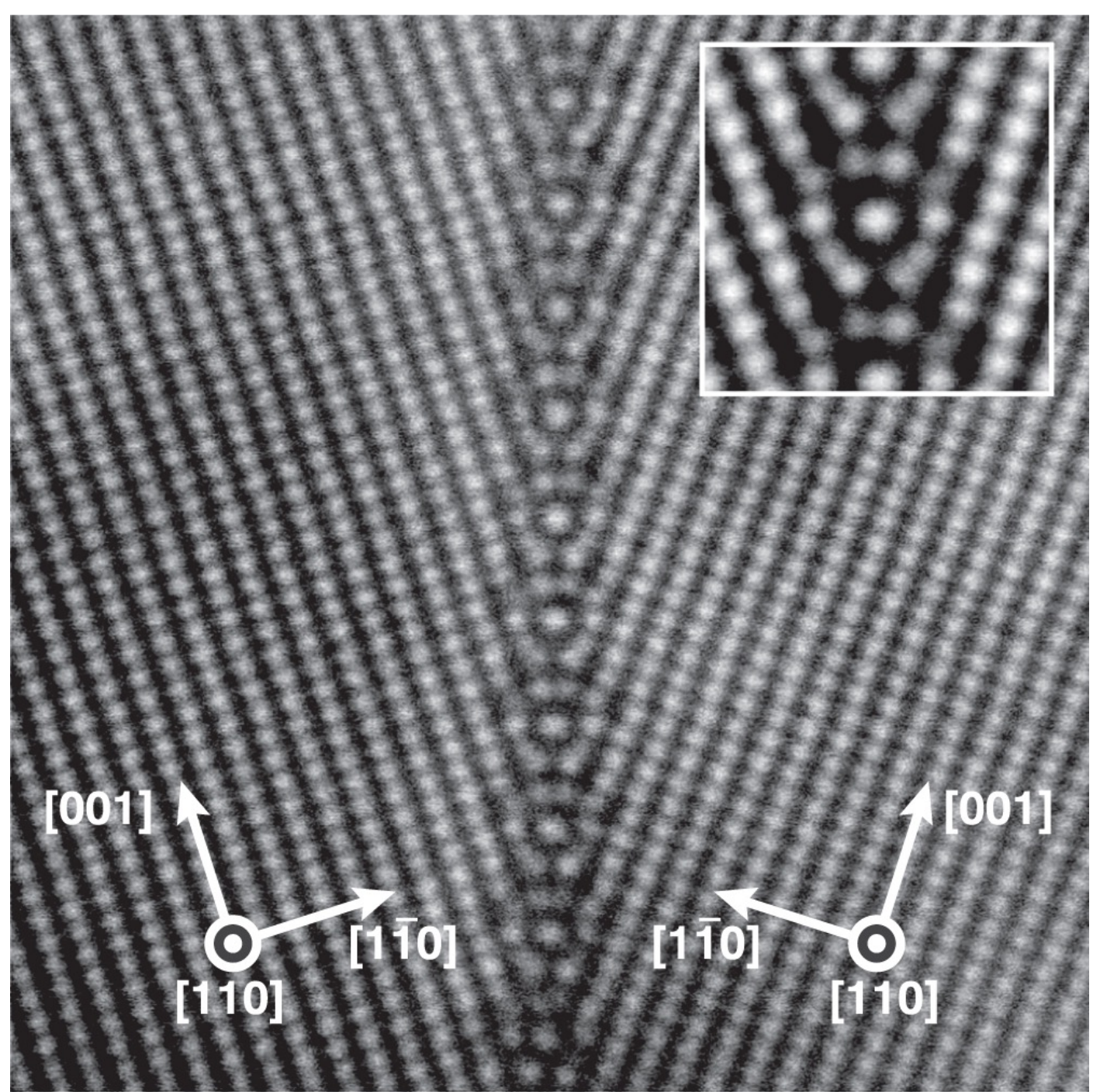
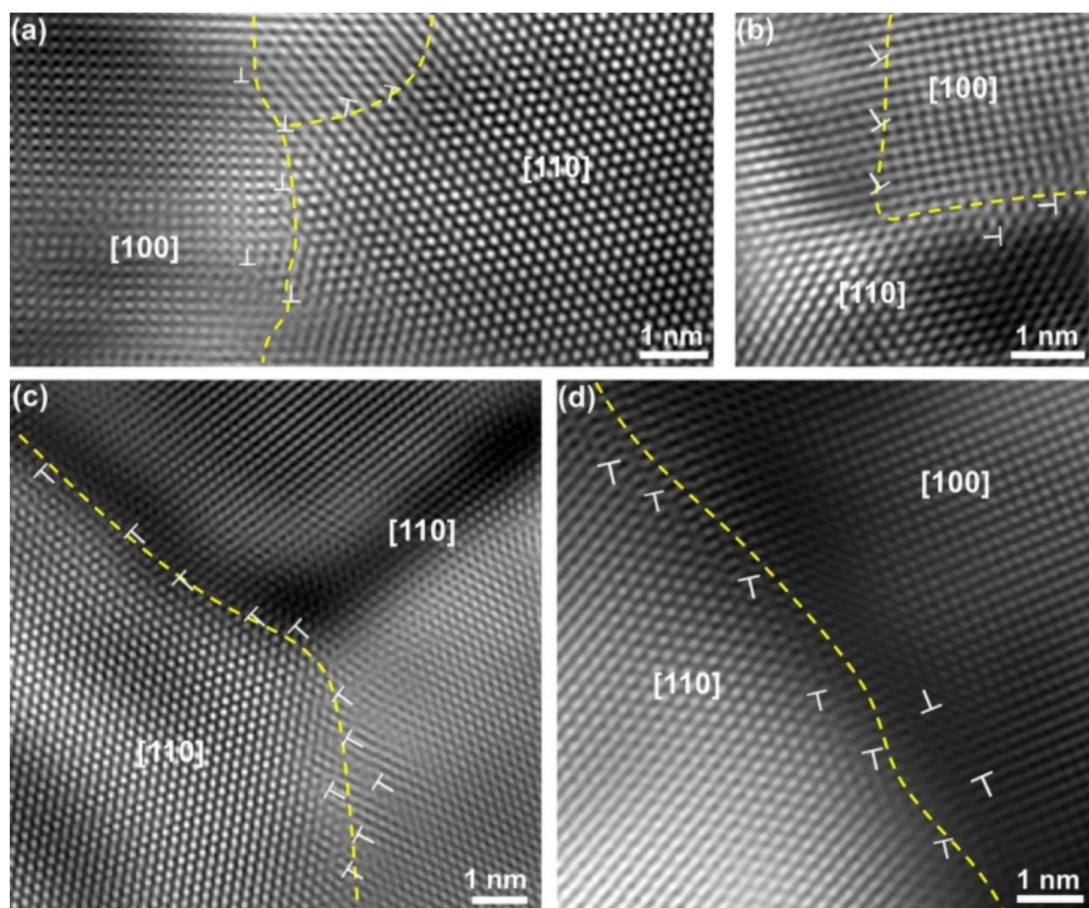
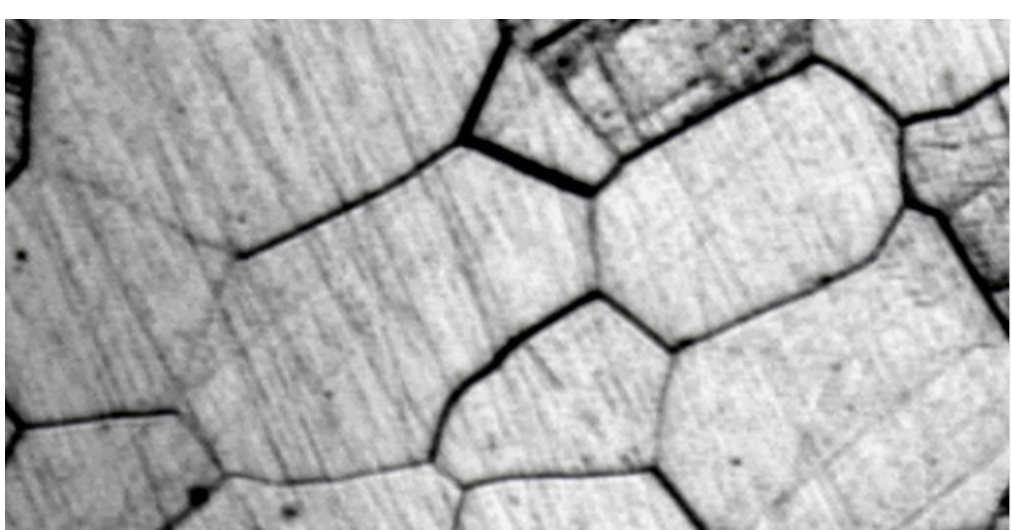
Distance of the plane from the central point 'O' is the surface energy of the plane!



Grain, and Boundaries

- As the crystal is grown
 - Several crystals compete
 - As they meet, perfect stitching is not often possible
 - Grain boundaries and junctions forms.





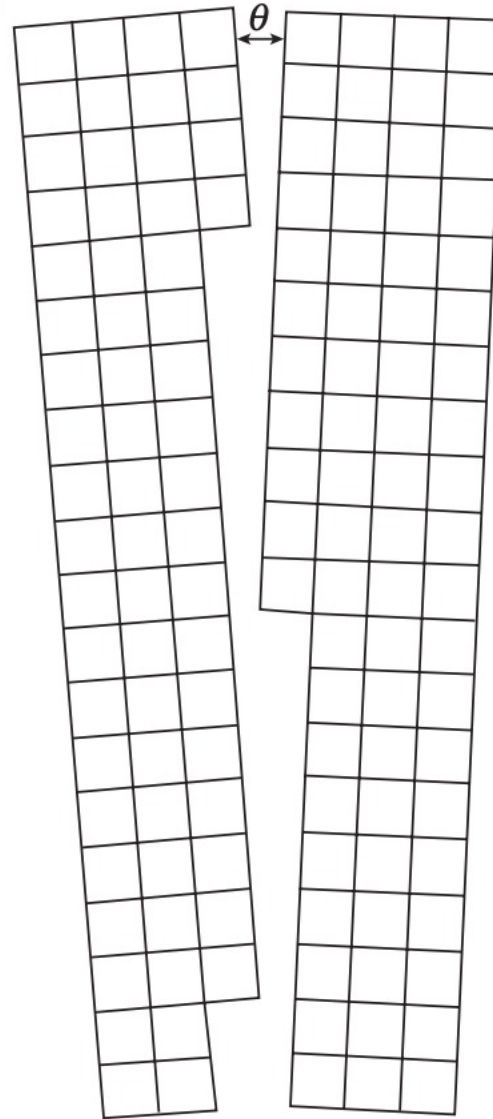
A simplest grain boundary

- Low angle tilt boundary
- Can be represented by string of edge dislocations
- Number of dislocations per unit length is

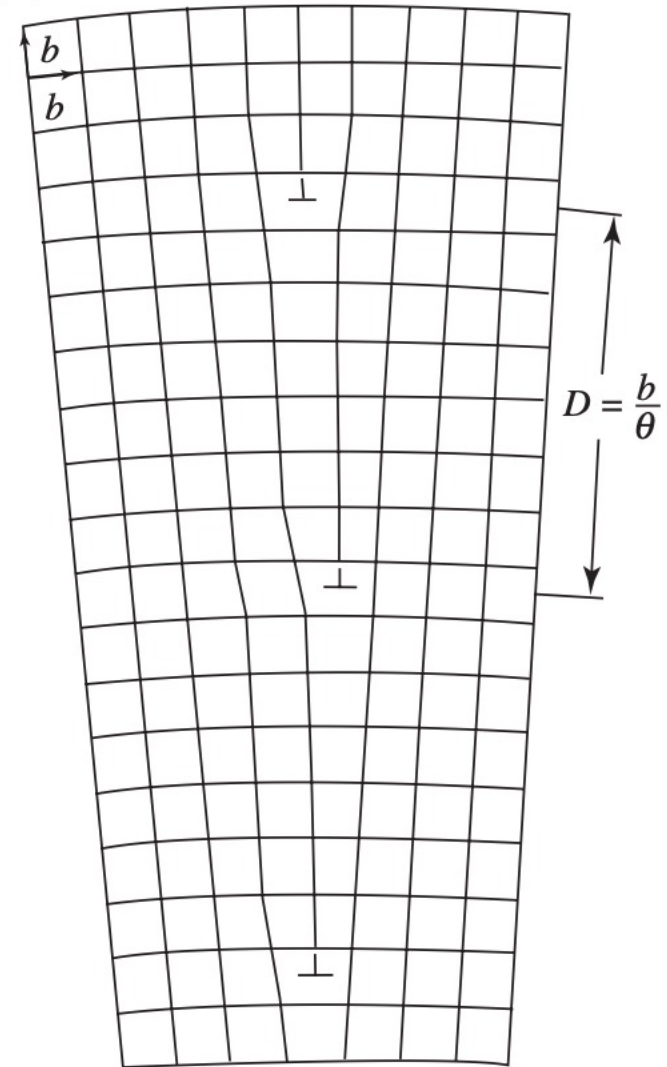
$$\frac{1}{D} = \frac{\theta}{b} \text{ (D is the separation)}$$

Self study: Various types of grain boundaries.

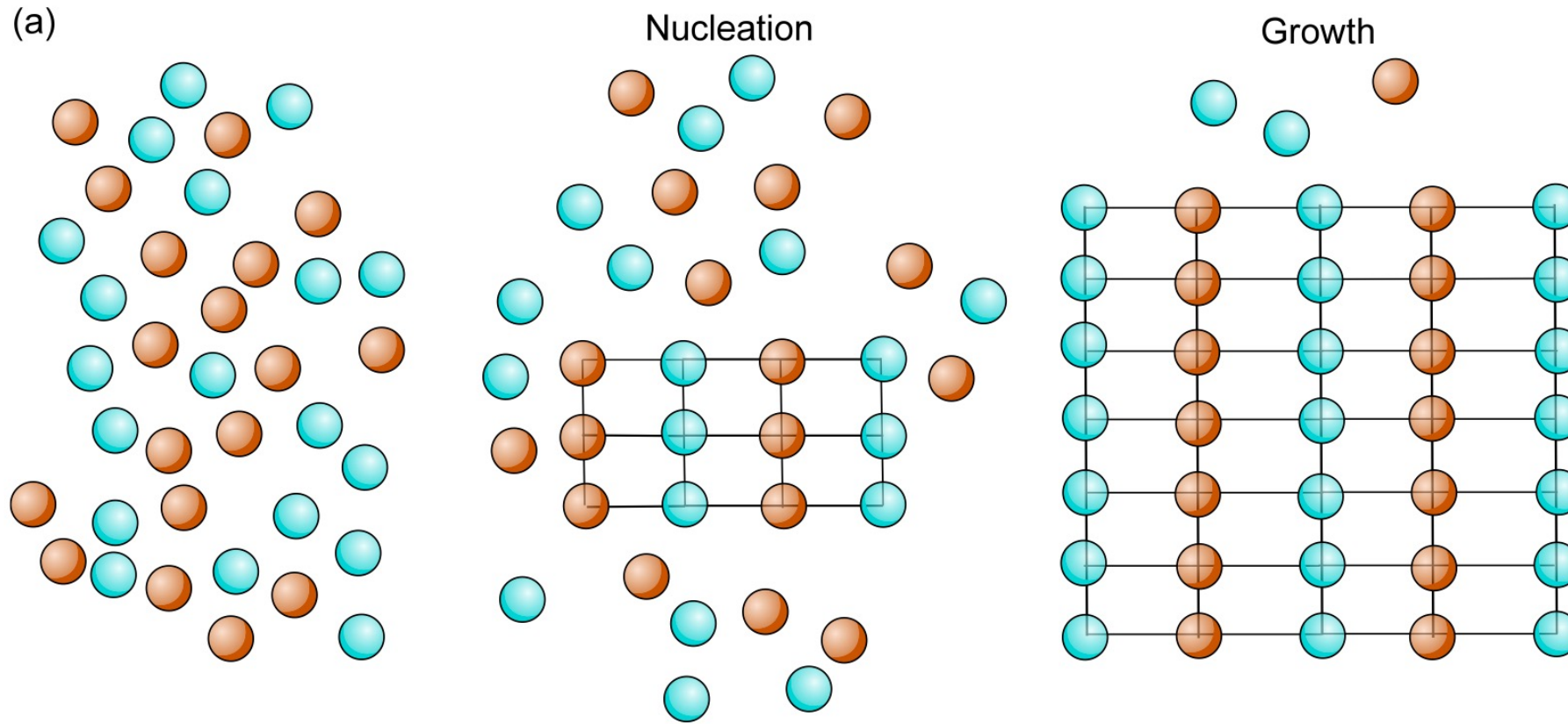
(a)



(b)



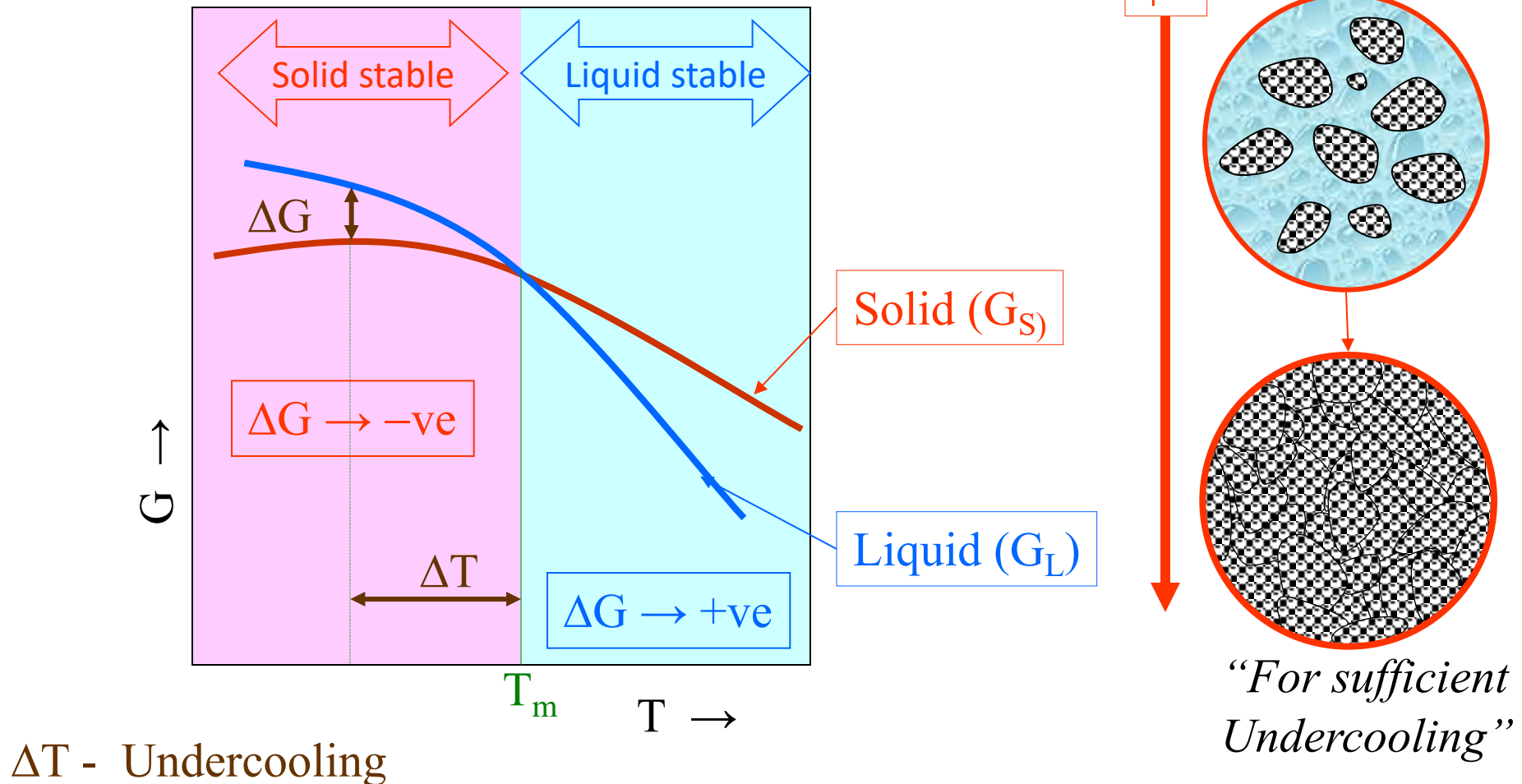
Crystal growth



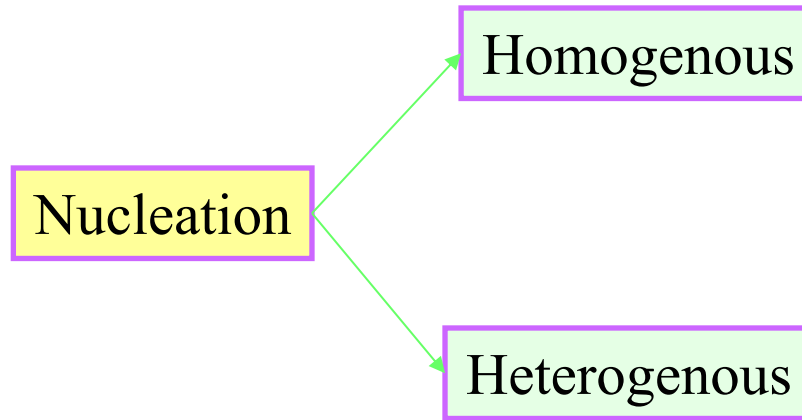
- Processes in growth
 - Classical nucleation of the new phase from parent phase
 - Growth of the new phase

Nucleation from Melts

- On cooling *just* below T_m solid becomes stable
- *But* solidification does not start
- E.g. liquid Ni can be undercooled 250 K below T_m



Solidification = Nucleation + Growth



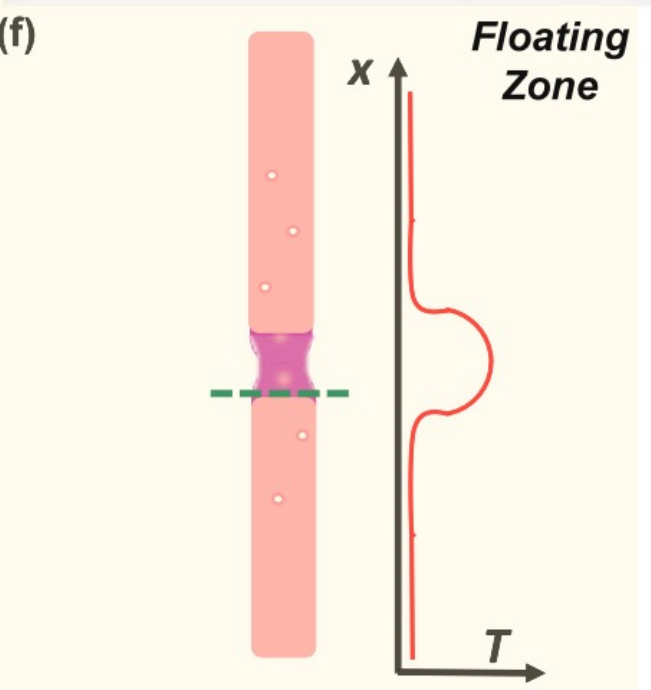
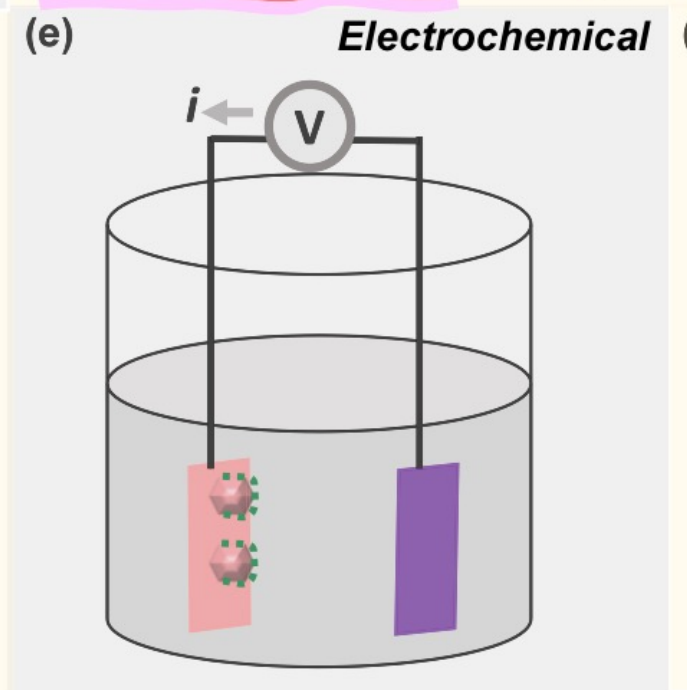
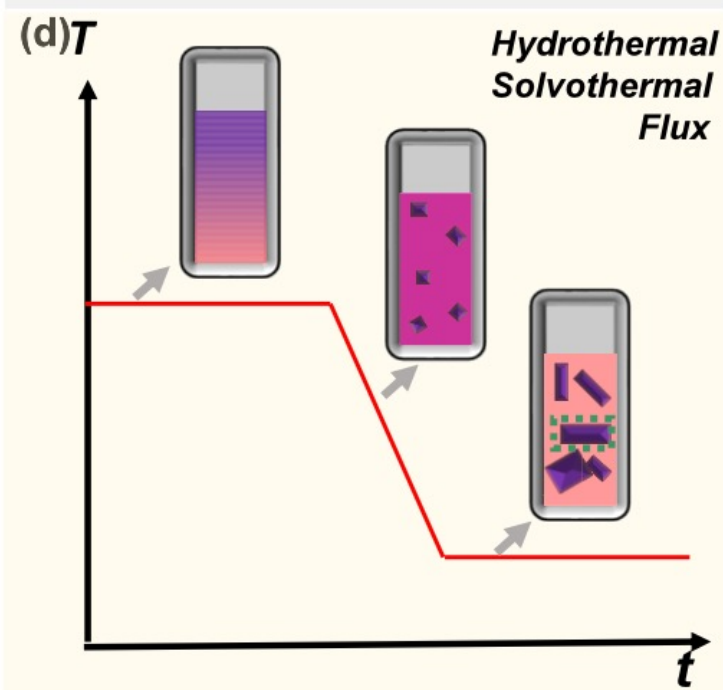
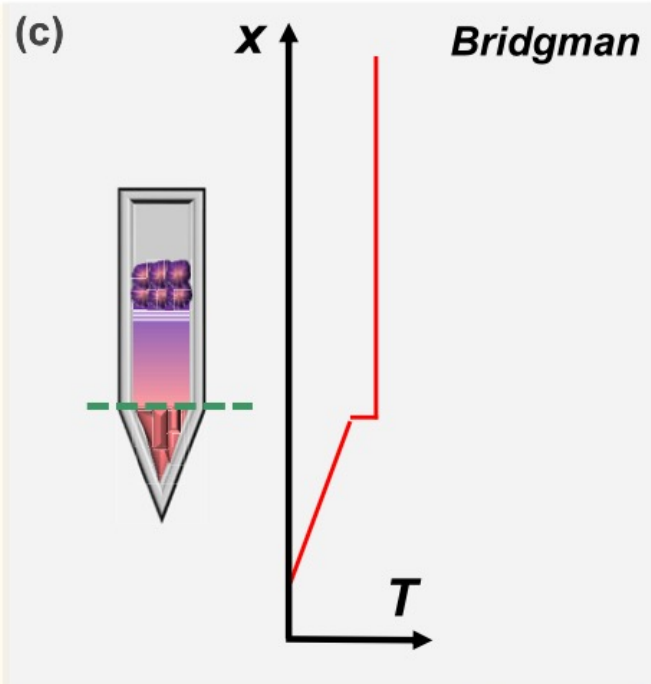
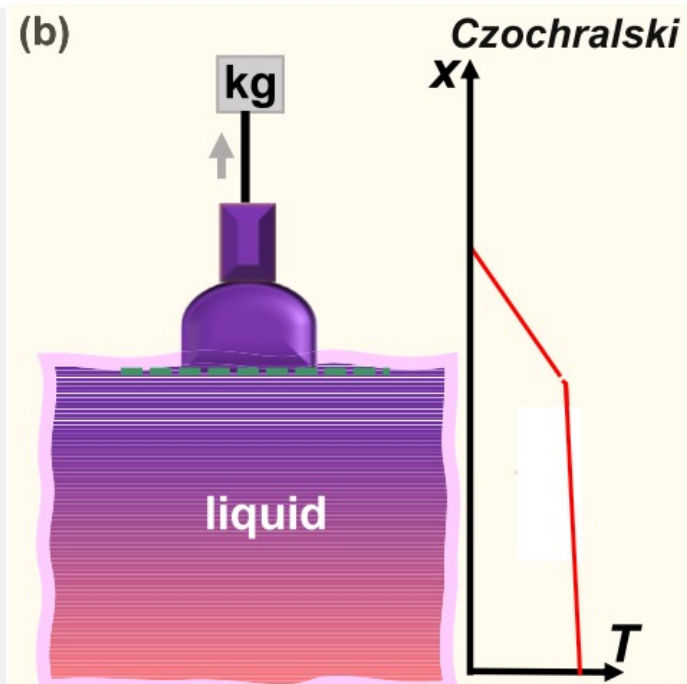
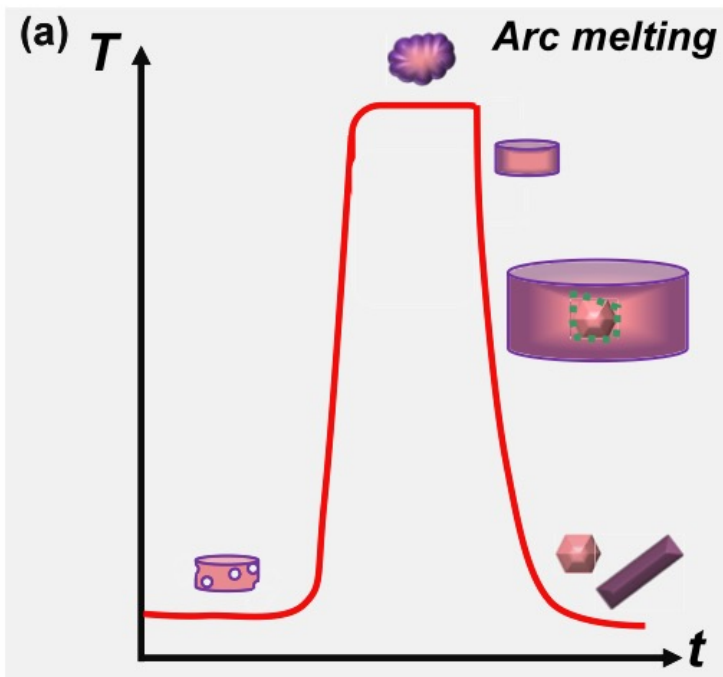
- Liquid → solid
walls of container, inclusions
- Solid → solid
inclusions, grain boundaries, dislocations, stacking faults

- ❑ The probability of nucleation occurring at point in the parent phase is same throughout the parent phase
- ❑ In heterogeneous nucleation there are some preferred sites in the parent phase where nucleation can occur

Various methods of single crystal growth

- Arc melting
- Czochralski
- Bridgman
- Hydro-thermal Solvo-thermal
- Electrochemical
- Floating Zone

One commonality – All methods require growth from melts.



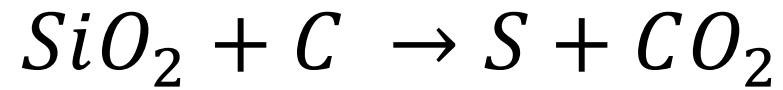
	Flux Growth	Arc Melting	Hydrothermal	Bridgman Growth	Czochralski Growth	Electrochemical Solvothermal	Optical Floating Zone
Crystal Size	0.1 mm–5 cm	1 mm–10 cm	1 μ m–1 mm	5 mm–20 cm	5 mm–20 cm	1 μ m–1 mm	5 mm–10 cm
Material Compatibility	Determined by flux	Nonvolatile metals, oxides	Determined by water solubility	Most	Most	Soluble in chosen solvent	Absorbs directed light
Temperature	300–1250 °C	1500–3500 °C	100–800 °C	1000–2000 °C	300–3000 °C	100–500 °C	1000–2500 °C
Pressure	10 ^{−6} –100 bar	10 ^{−6} –3 bar	1–2500 bar	10 ^{−6} –100 bar	10 ^{−6} –100 bar	1–2500 bar	10 ^{−6} –8000 bar
Preparation Time	Minutes–Hours	Seconds–Minutes	Minutes–Hours	Minutes–Hours	Hours–Days	Minutes–Hours	Hours–Days
Growth Speed	Days–Months	Seconds–Minutes	Days–Months	Hours–Months	Hours–Months	Days–Months	Hours–Months
Sample Recovery	Centrifugation, Flux Dissolution	Direct	Filtration	Direct	Direct	Filtration	Direct
Likely Defects	Grain boundaries, Inclusions, Substitution	Vacancies, Internal strain	Vacancies, Solvent inclusion	Grain boundaries, vacancies	Grain boundaries, vacancies	Vacancies	Grain boundaries, vacancies
Chemical Control	Choice of flux	Limited by volatilization	Water solubility	Molten phase composition	Gas presence, Molten phase purity	Electrical conductivity, solubility	Gas flow, optical absorptivity

Czochralski's method for single crystals

- 1918 – First demonstrated (accidentally) by Czochralski for metals
- 1950 – Teal first demonstrated this method for Si
- Requirements: Need Si that is very pure (99.999999999%)
- 9N (99.9999999) has 1 impurity in 1 parts per billion.
- Such a Silicon is called Electronic grade Si

Type equation here.

Step: 1 Get EGS



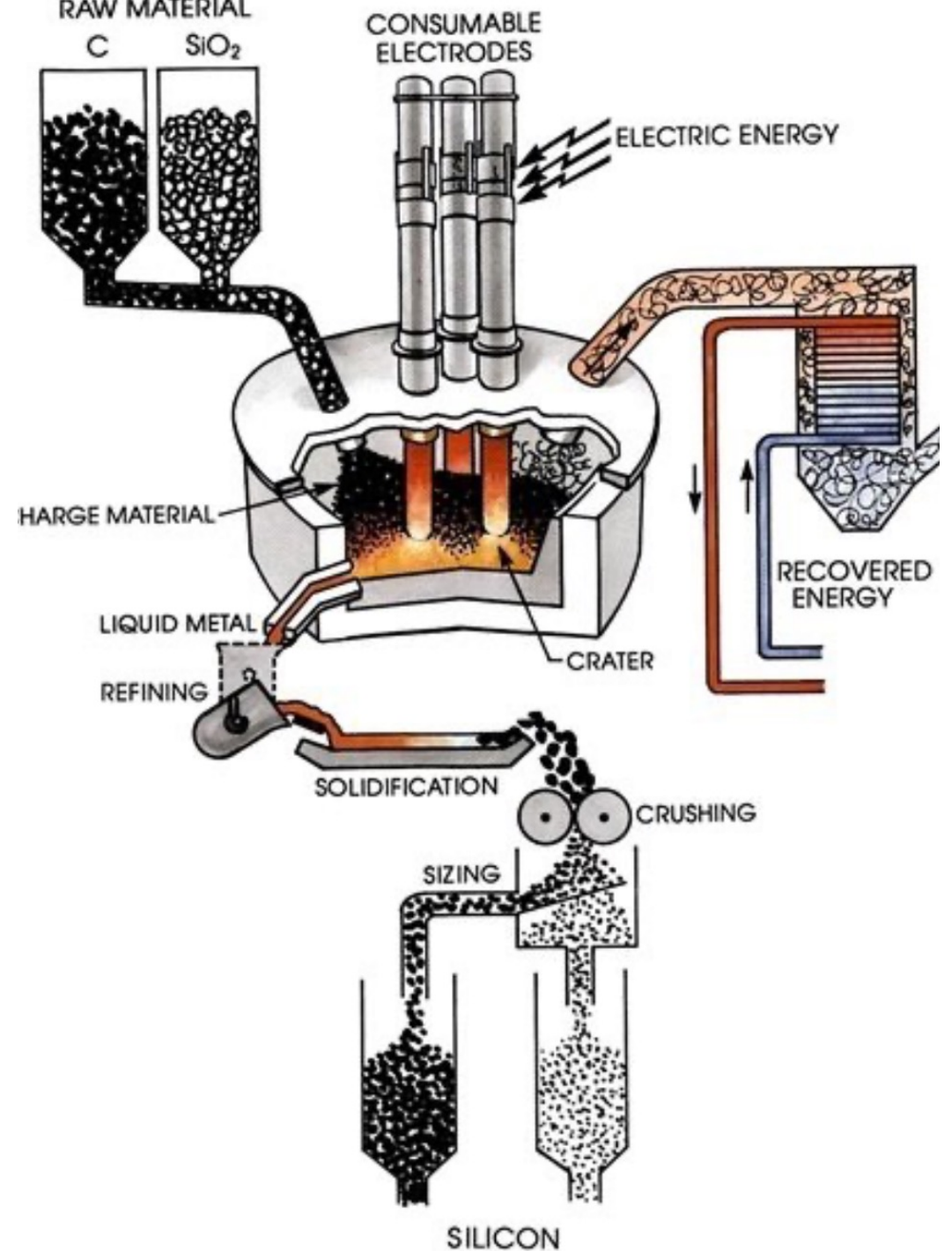
Heating Sand and coke gives you 98% pure Silicon!

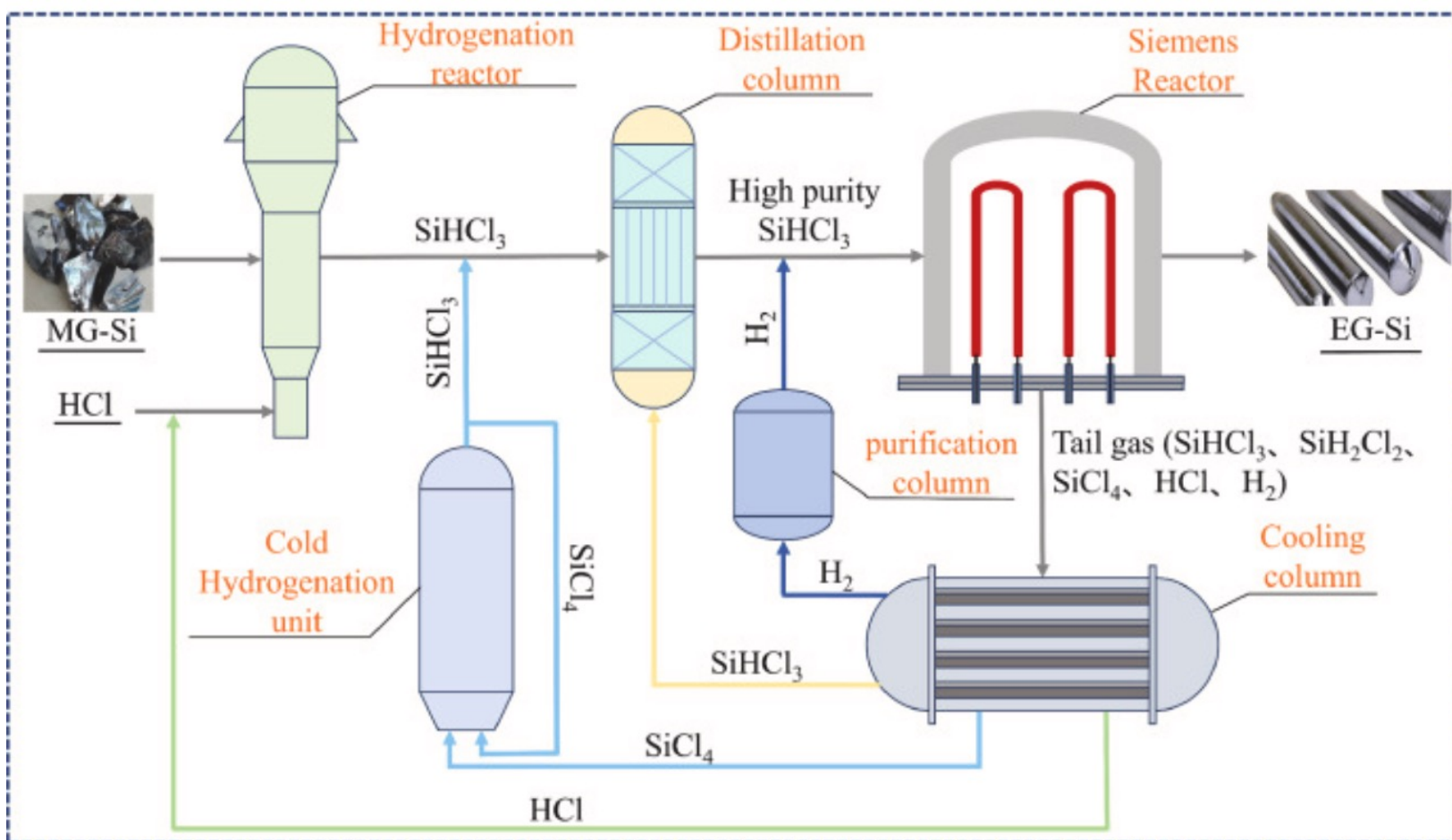
This Si is called metallurgical grade Si

This Silicon is now purified further by fractional distillation

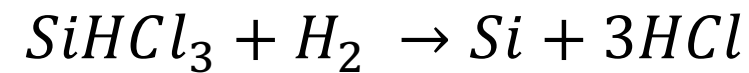


Trichloro silane has a boiling point of 32C.





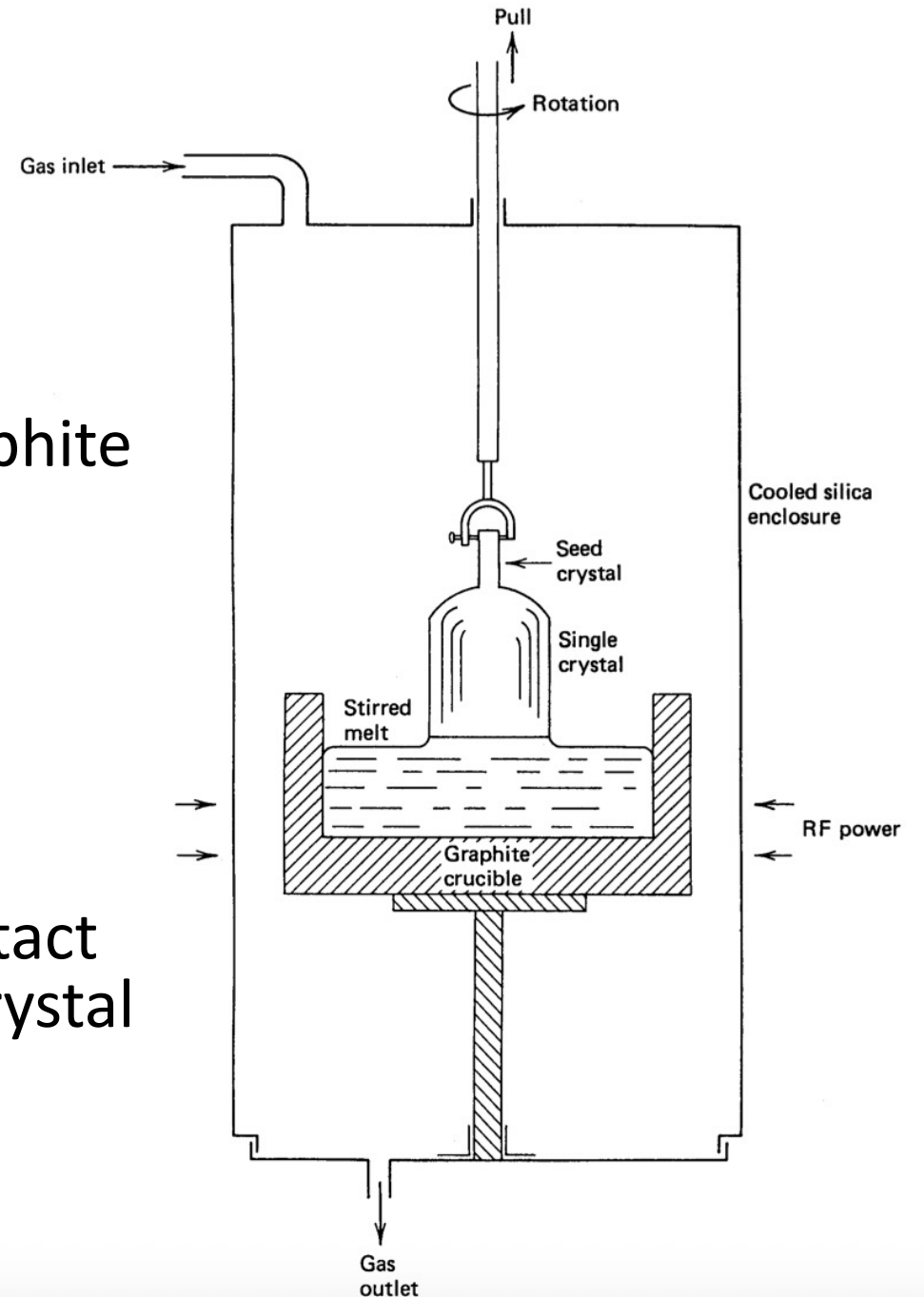
Siemen's Process



Gives you Si that is 99.999999999% pure. Electronic grade Silicon.

General Process

- The EGS is taken in melt at about 1450C
- The melt is taken in a crucible that is graphite with fused Silica lining.
- The melt now contains impurities
 - Intentional (doping)
 - Un-intentional
- The chamber is filled with inert gas
- A single crystal seed (boule) is made contact and slowly pulled with rotation for the crystal growth.

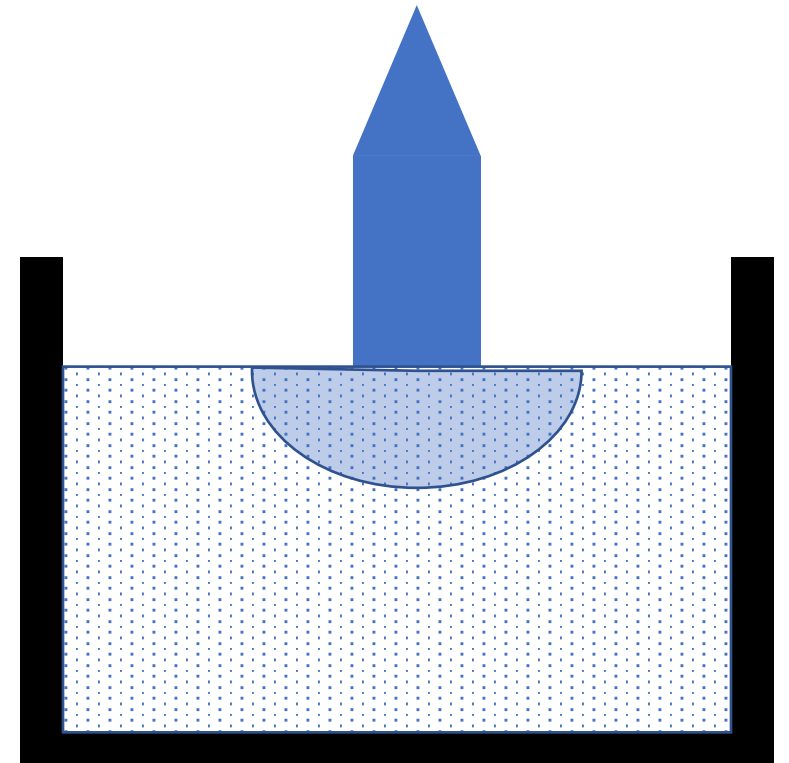


Growth thermodynamics

- As the solid is made in contact with the melt
- A temperature gradient is set.
- The boule loses heat by radiation and natural convection.
- This leads to under-cooled liquid near the interface.

Solidification from melt is an exo-thermic process.

There is Heat released upon crystallization (The latent heat of fusion)



This leads to increased temperature in crystallization region

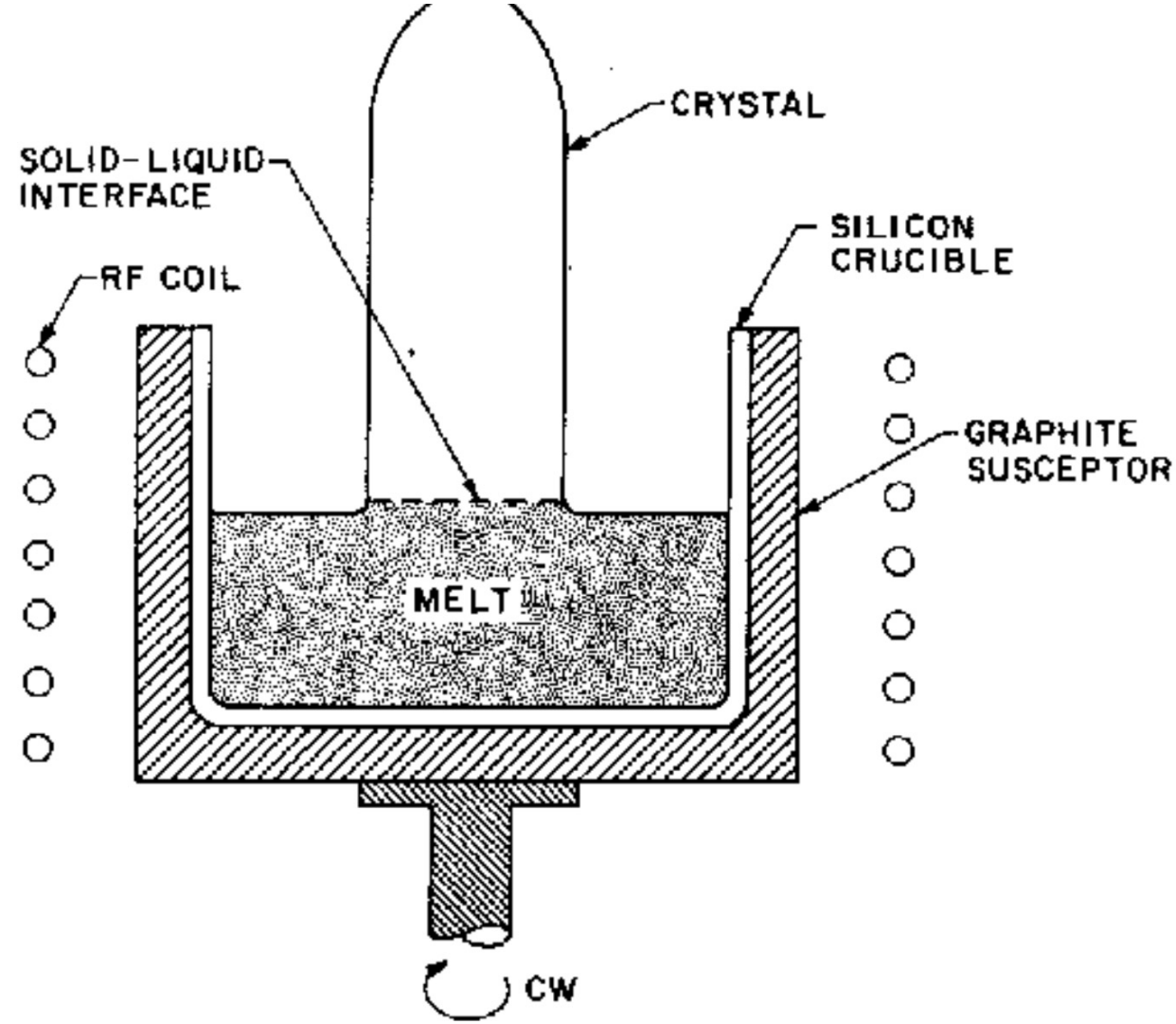
Detailed balance:

- The latent heat of fusion is $L \frac{dm}{dt}$. For silicon $L = 340 \text{ cal/g}$
- This lost energy is balanced by thermal flux difference between liquid to solid.

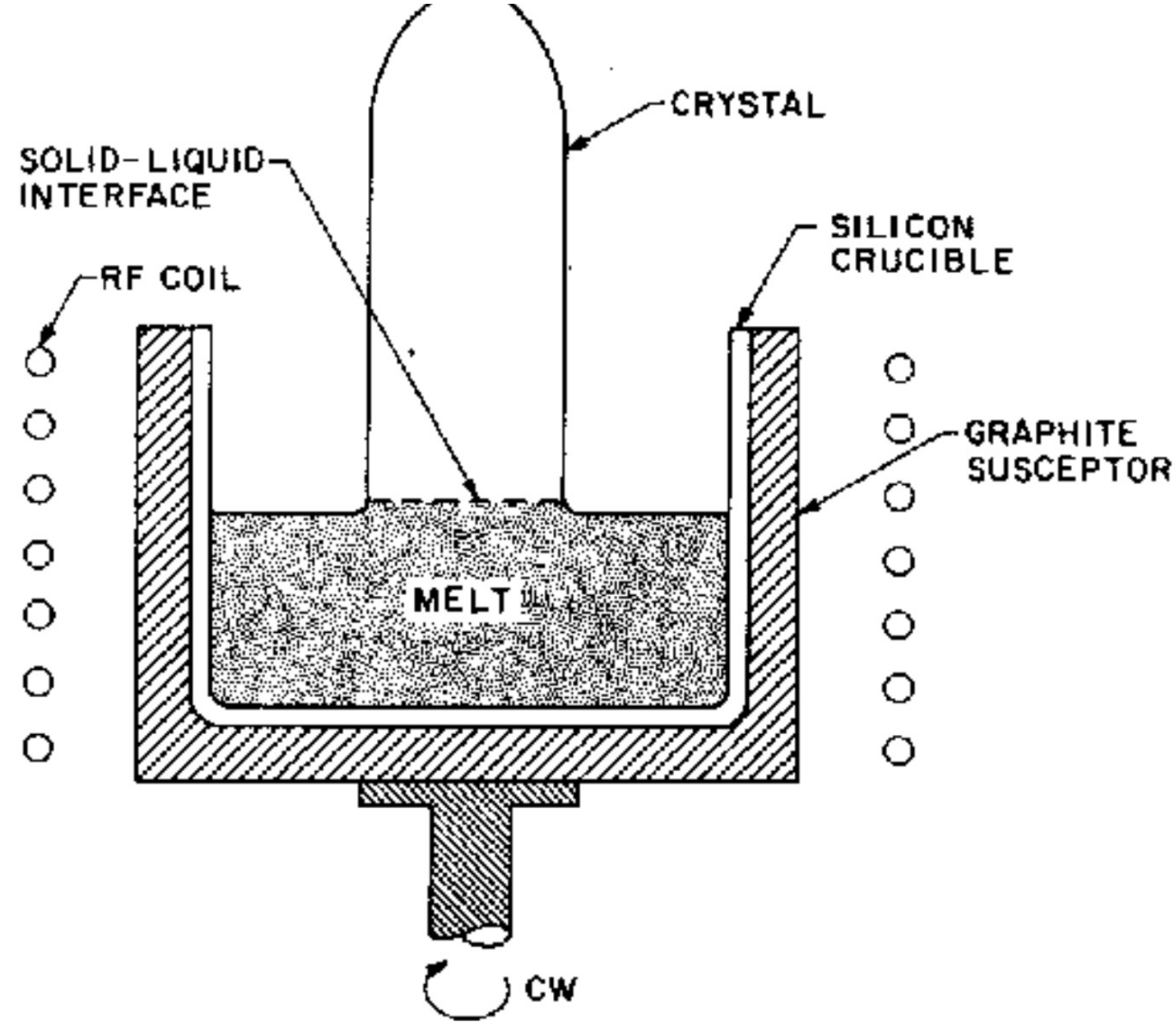
$$-k_l A \frac{dT}{dx} \Big|_l - \left(-k_s A \frac{dT}{dx} \Big|_s \right) = L \frac{dm}{dt}$$

The speed of the boule pull is the most critical parameter

- When the crystal pull rate is slow:
 - There is significant thermal gradients
 - This leads to higher growth rate
 - Increase in the crystal diameter.
 - Increase in number of defects (particularly point defects)
 - The defects also tend to agglomerate given larger time (slower pull rate).
- To reduce the thermal gradients at the interface, the melt and the crystal are rotated in opposite directions.



- When the crystals are pulled fast:
 - The thermal gradients are moderate
 - The crystal growth rate is slow.
 - Lesser defects
- However, the pull cannot also be too fast.
 - The solid cannot conduct the heat away.
 - No growth will happen!

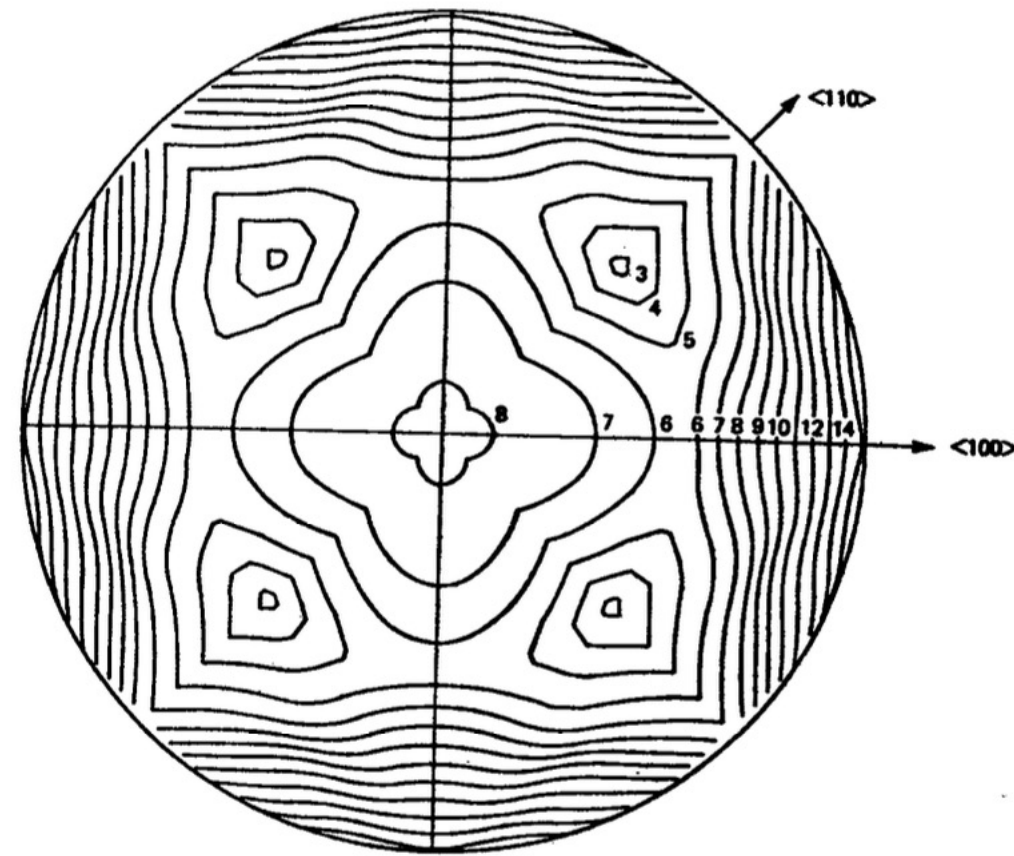


Considerations for good single crystal

- Equilibrium concentration of defects $N = N e^{-\frac{E_f}{skT}}$
 - $s = 1$ for Schottky and $s = 2$ for Frankel (Vacancy – interstitial pair)
- As the crystal cools, the point defects have supersaturation
 - This leads to agglomeration to form dislocations.
- Oxygen solubility at temperature T
$$O_i = 5.5 \times 10^{20} e^{-\frac{0.89}{kT}} \text{ atoms/cm}^3$$
 - As crystal cools, clumps and platelets of SiO_2 forms that leads to strain
- C from the graphite crucible also gets incorporated upto 10^{17} cm^{-3}

- Thermal gradients:
 - The crystal cools by radiative heat flow largely.
 - Outer cools faster (smaller lattice constant)
 - Radial compressive stress that is highest at the center (σ_r)
 - This leads to tangential stress (σ_θ) that is largest at the circumference reduces to center
 - This is a hoop stress – happens when the outer jacket is too small for the inner contained. The inner region tries to break-open the outer jacket!
 - In FCC, the dominant slip planes are $\{111\}$
 - Most densely packed!
 - The maximum resolved shear stress then becomes

$$\sigma_s = 0.5 [\sigma_r - \sigma_\theta]$$



Elaborate heat shielding is often used to control the cooling

Other aspects

- Turbulence in the melt:
 - Thermal fluctuations leads to buoyancy.
 - This leads to un-even growth
 - Often corrected by applied magnetic fields
- Influence of growth orientation
 - For FCC, $\{111\}$ growth planes are the fastest, most stable.
 - Any twin that forms, will immediately re-twin $\{-1,-1,-1\}$ to self correct
 - However, we many times need $\{100\}$ silicon. Which requires care.
- Solution hardening helps reduce dislocation density

Doping in melts

- Doped semiconductors are obtained by doping melts.
- If C_l is the concentration of the dopant in the liquid,

The solid single crystal has $C_s = kC_l$

k – distribution coefficient

TABLE 3.3 Distribution Coefficients of Impurities in Silicon [40, 41]

Dopant	Type ^a	Atomic Weight	Distribution Coefficient
As	<i>n</i>	74.92	0.3
P	<i>n</i>	30.97	0.35
Sb	<i>n</i>	121.75	0.02
Al	<i>p</i>	26.98	2×10^{-3}
B	<i>p</i>	10.81	0.72
Ga	<i>p</i>	69.72	7.2×10^{-3}
In	<i>d</i>	114.82	3.6×10^{-4}
Ag	<i>d</i>	107.87	1.7×10^{-5}

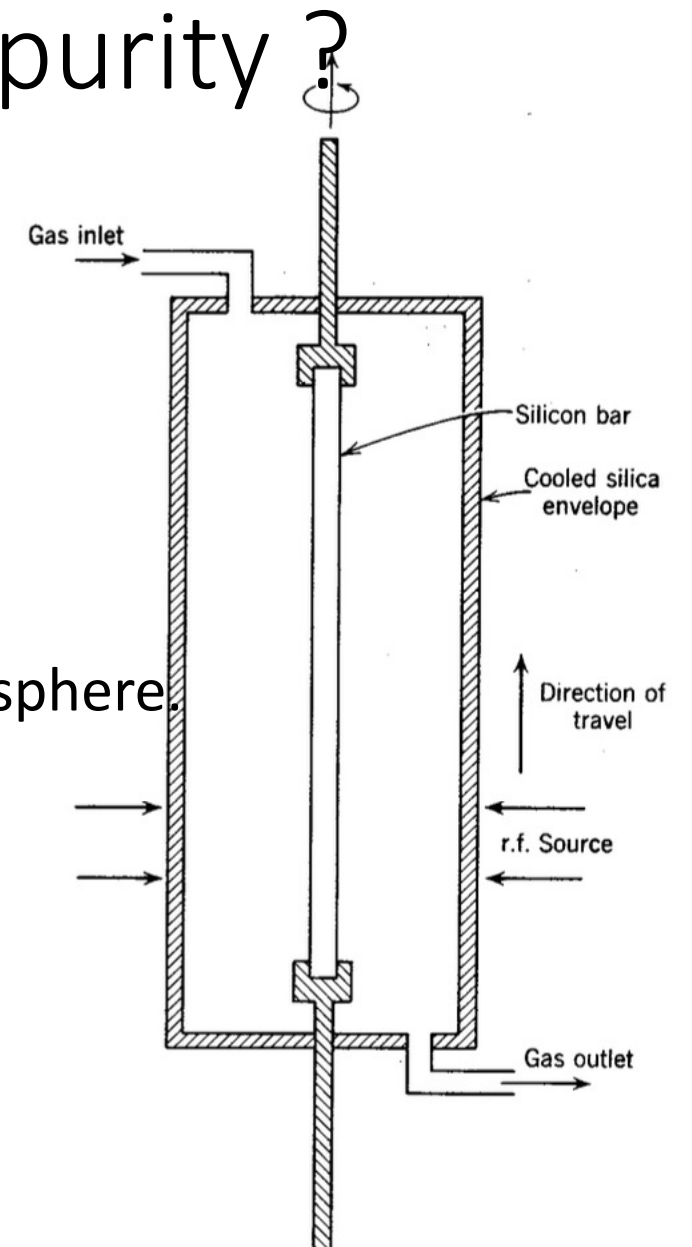
How to get materials with higher purity ?

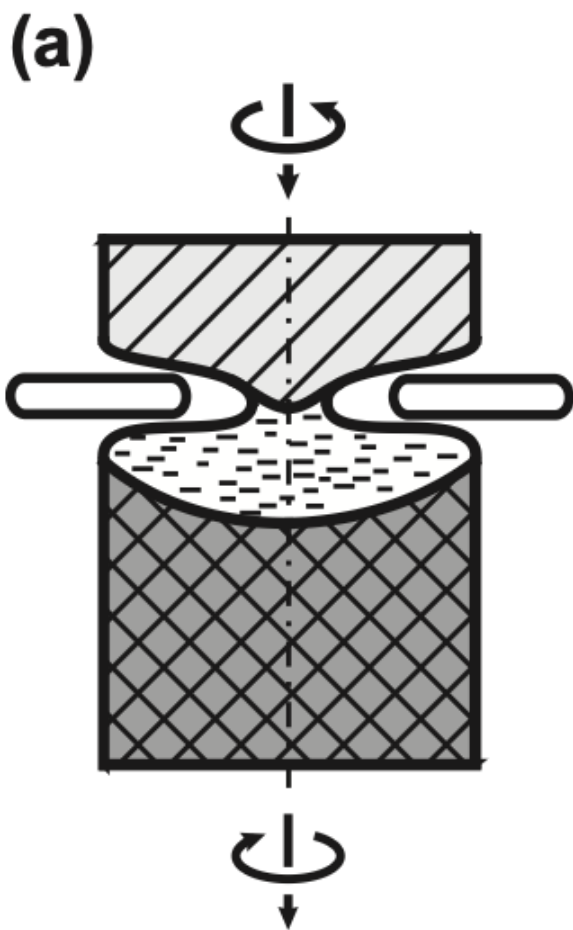
- Float Zone Technique

- A bar of the semiconductor is taken and rotated.
- A non-contact heating element melts “zones”
- A seed layer is made in contact at one end.
- As the zone moves, the material crystallizes.
- The entire thing is in a sealed chamber with inert atmosphere.

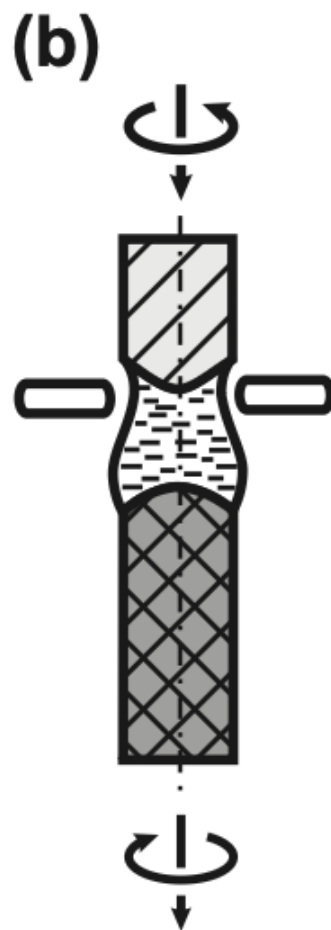
- Advantages:

- Reduced dislocation density due to smaller crystal size
- Reduced contamination, oxygen concentrations.

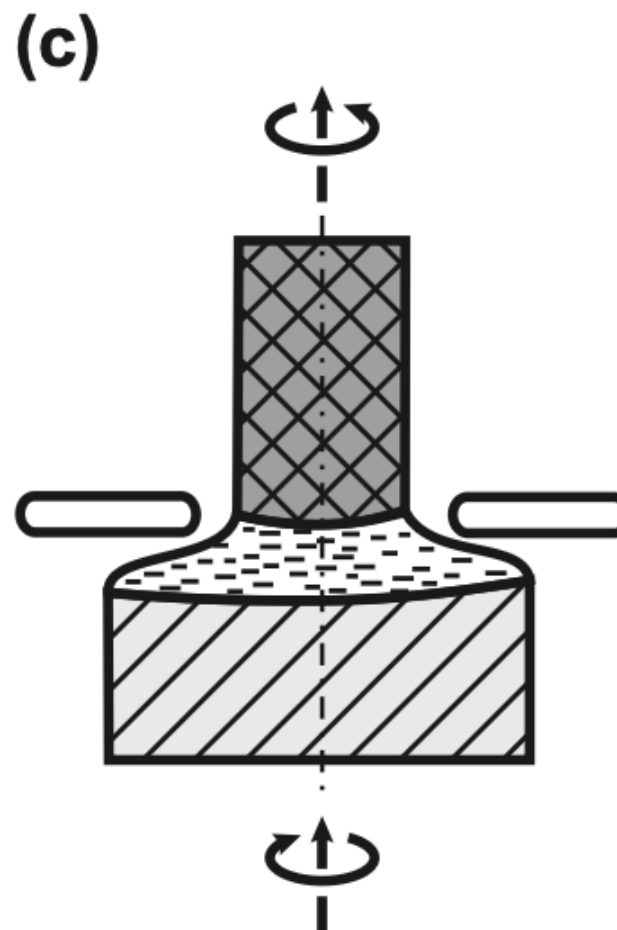




Needle-eye float zone



Traditional float zone



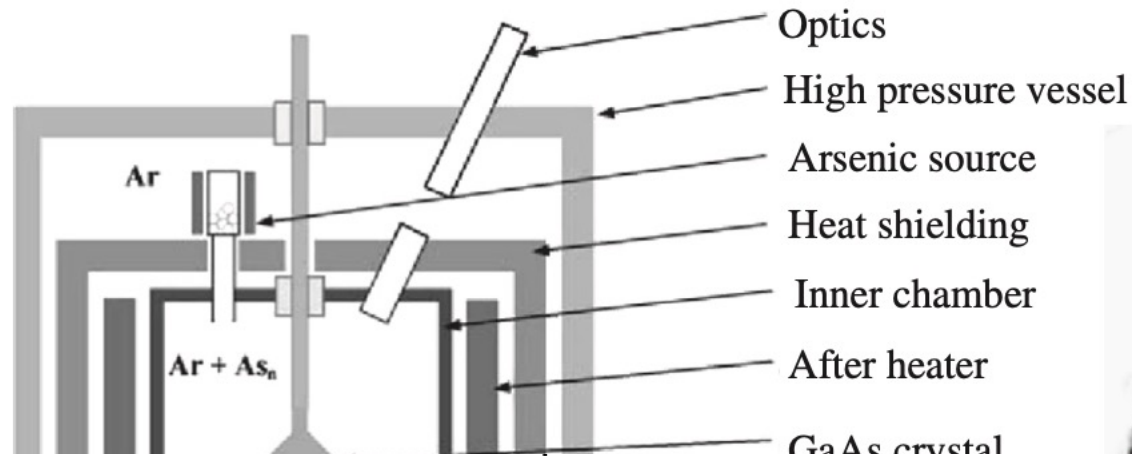
pedestal float zone

High Purity –Electronic grade SC

- Tight control of heater power and the movement rate
- The diameter of the crystal is slowly varied
- Slow changes to reduce dislocation density



Other single crystal materials



Semiconductor	Melting Point (°C)	Dissociation Pressure at m.pt. (bar)	CRSS (Mpa) Near m.pt.	Thermal Conductivity κ (W/cm k) Near m.pt.
Si	1420		6–9	0.21
InSb	525	4×10^{-8}		0.04
GaSb	712	1×10^{-6}		0.09
InAs	943	0.33		0.08
GaAs	1238	2.2	0.3–0.5	0.07
InP	1062	27.5	0.6	0.09
GaP	1465	32		0.8
CdTe	1092	0.07	0.2	0.009

- Vapor pressure controlled Czochralski
- Materials with high vapor pressure at the melting temperatures leads to rapid vaporization and surface stress
- There is need for surface passivation efforts

