Lecture 3: Defects and Diffusion in Crystalline Solids

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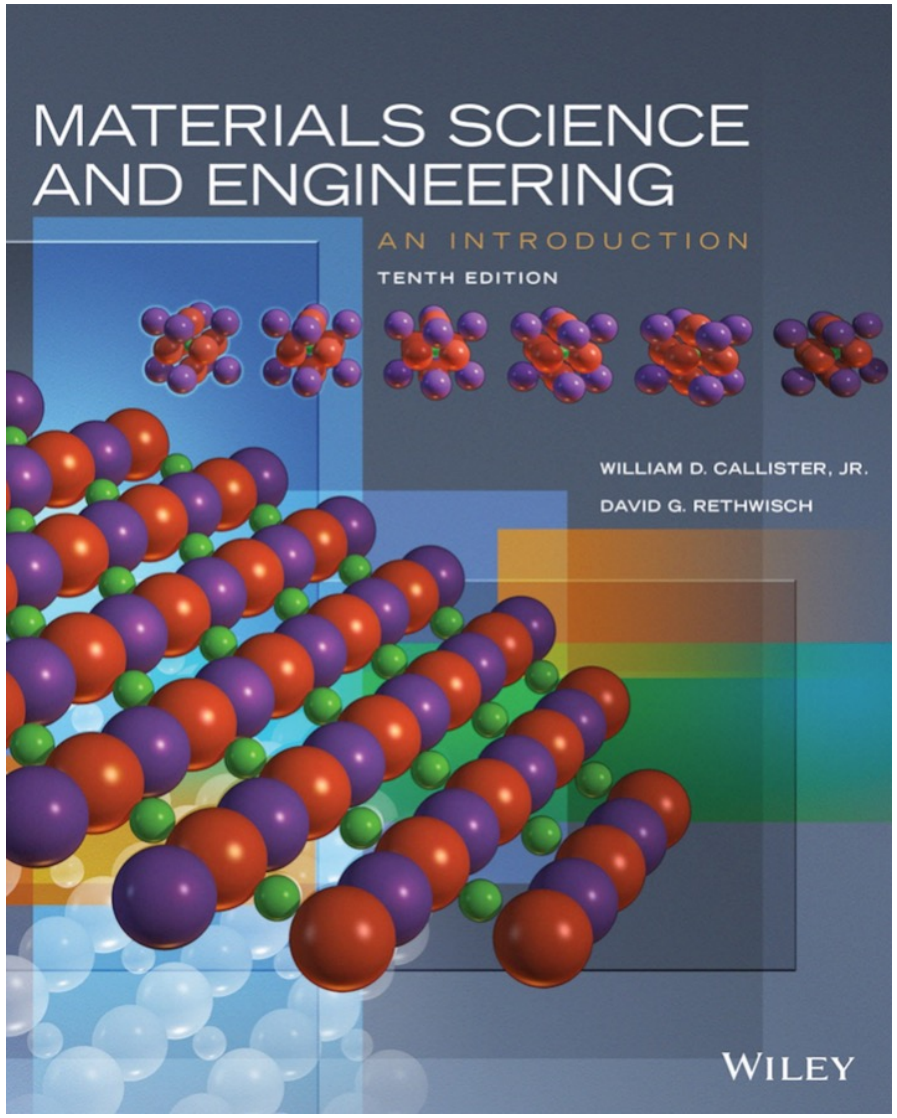
Reading for this subject



Chapter 4 Imperfections in Solids

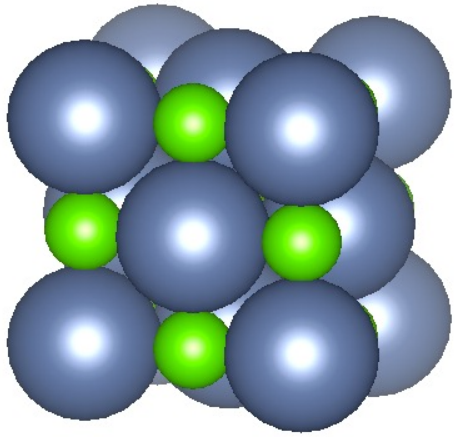
This discussion will closely follow **Chapter 4** of Callister, **pages 92-120** of the 10th edition.

Supplementary Texts:

- *Solid-State Materials Chemistry* by Woodward
- *Ceramic Materials* by Carter

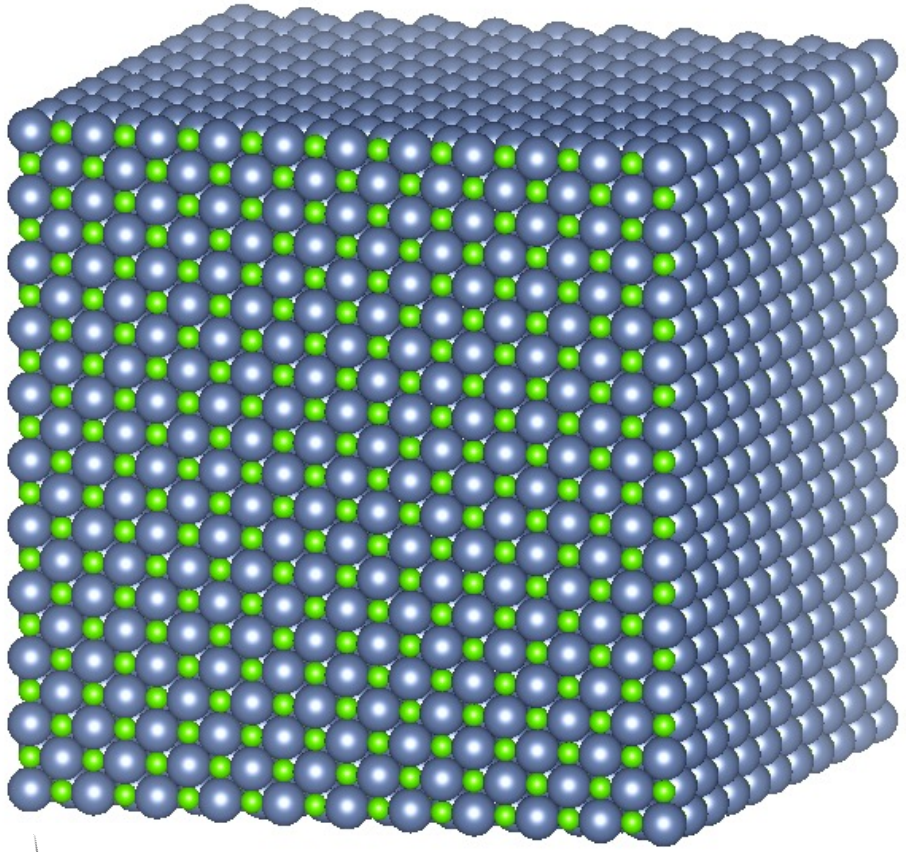
Single crystal versus polycrystalline materials

From last time:
We described a **unit cell…**



NaCl

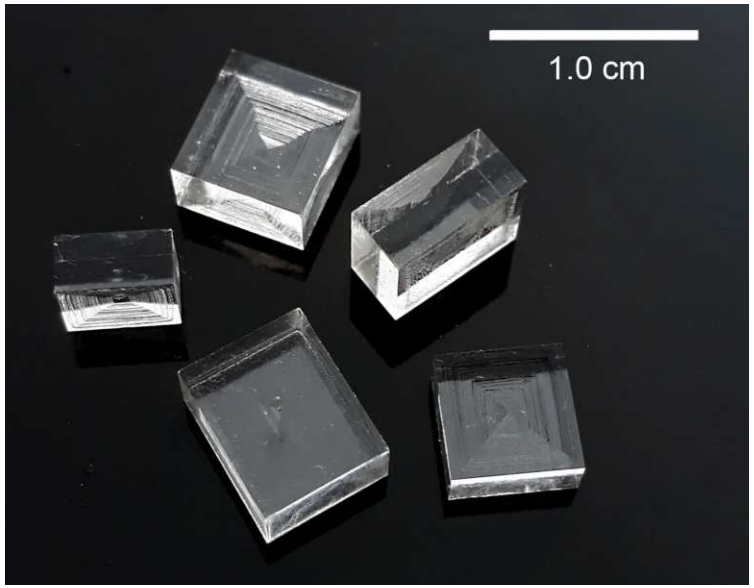
…That gets repeated many times in all three dimensions to form a **crystal**



$\times 10^{23}$

These are *single crystals*

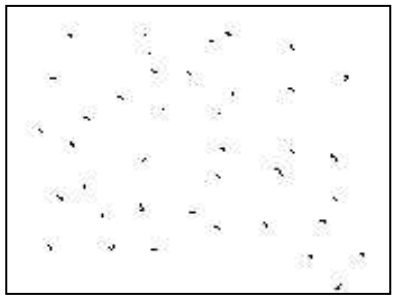
Most materials do *not* look like this



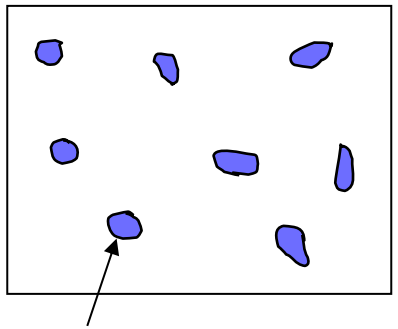
Single crystal versus polycrystalline materials

Think about a crystalline material that **solidifies from a melt**

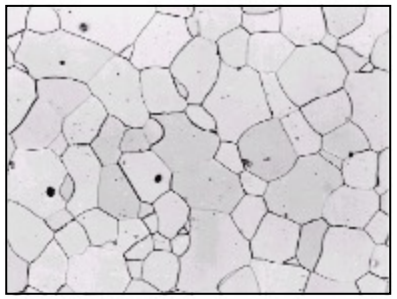




Nuclei form in liquid

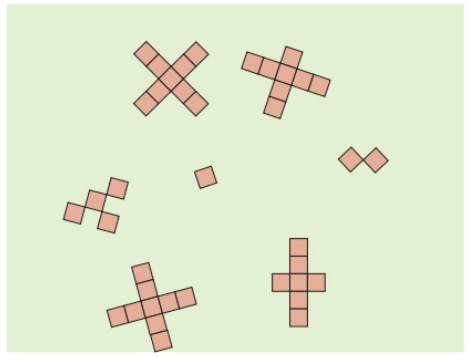


Crystals grow

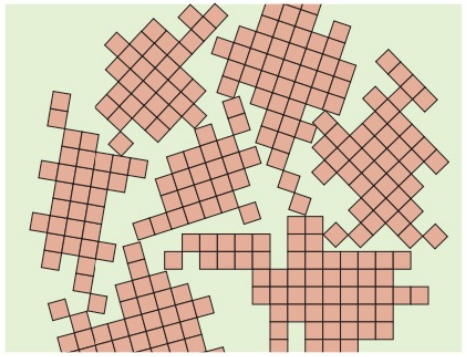


Grain structure

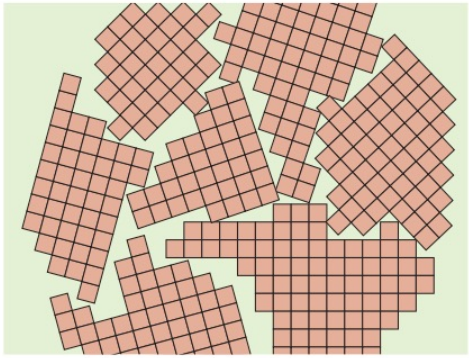
Polycrystalline material



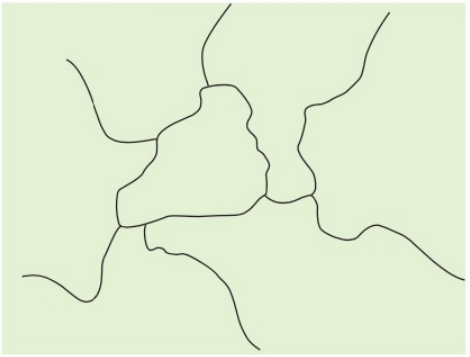
(a)



(b)

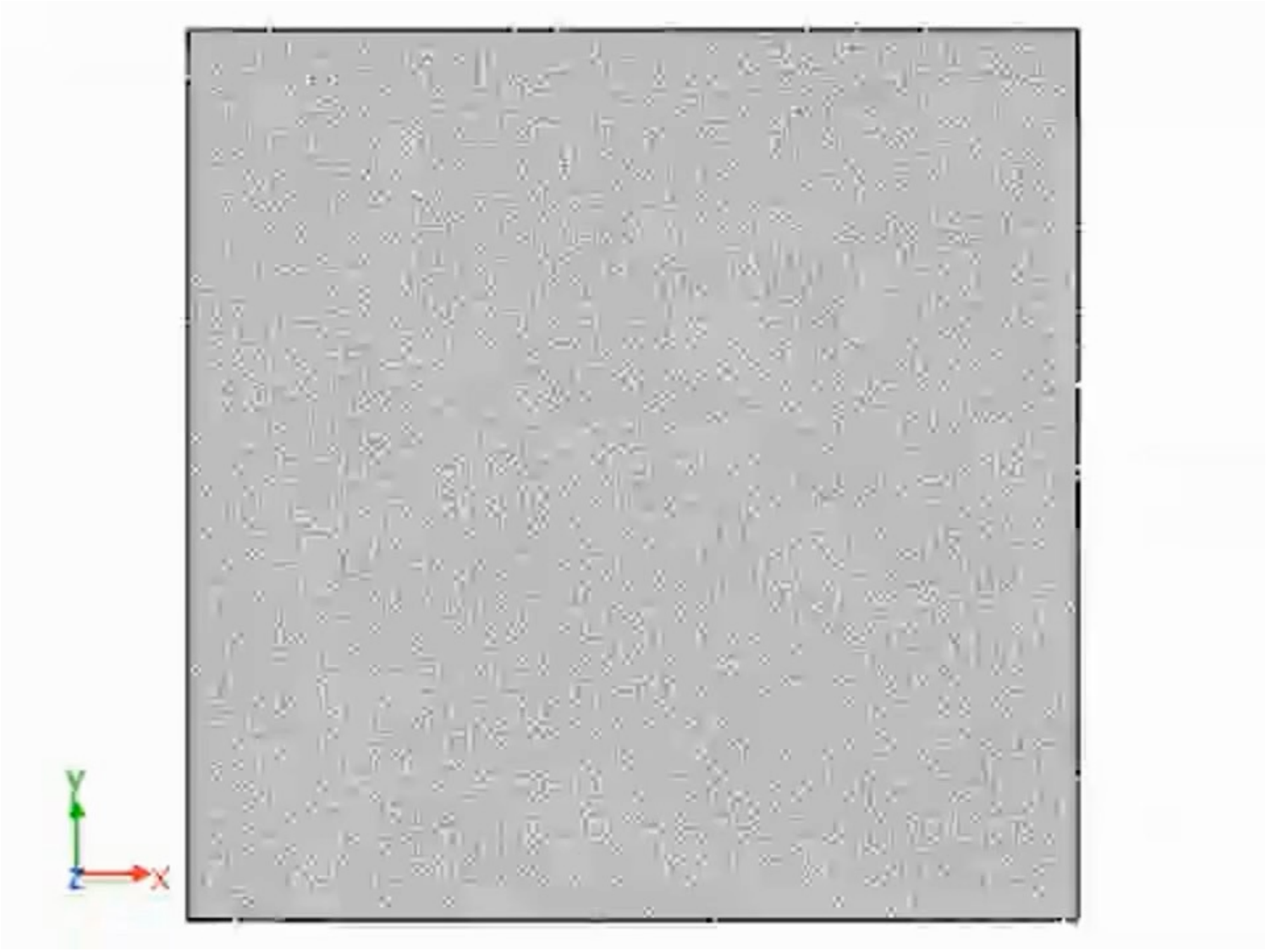


(c)



(d)

Simulation of polycrystalline Al formation



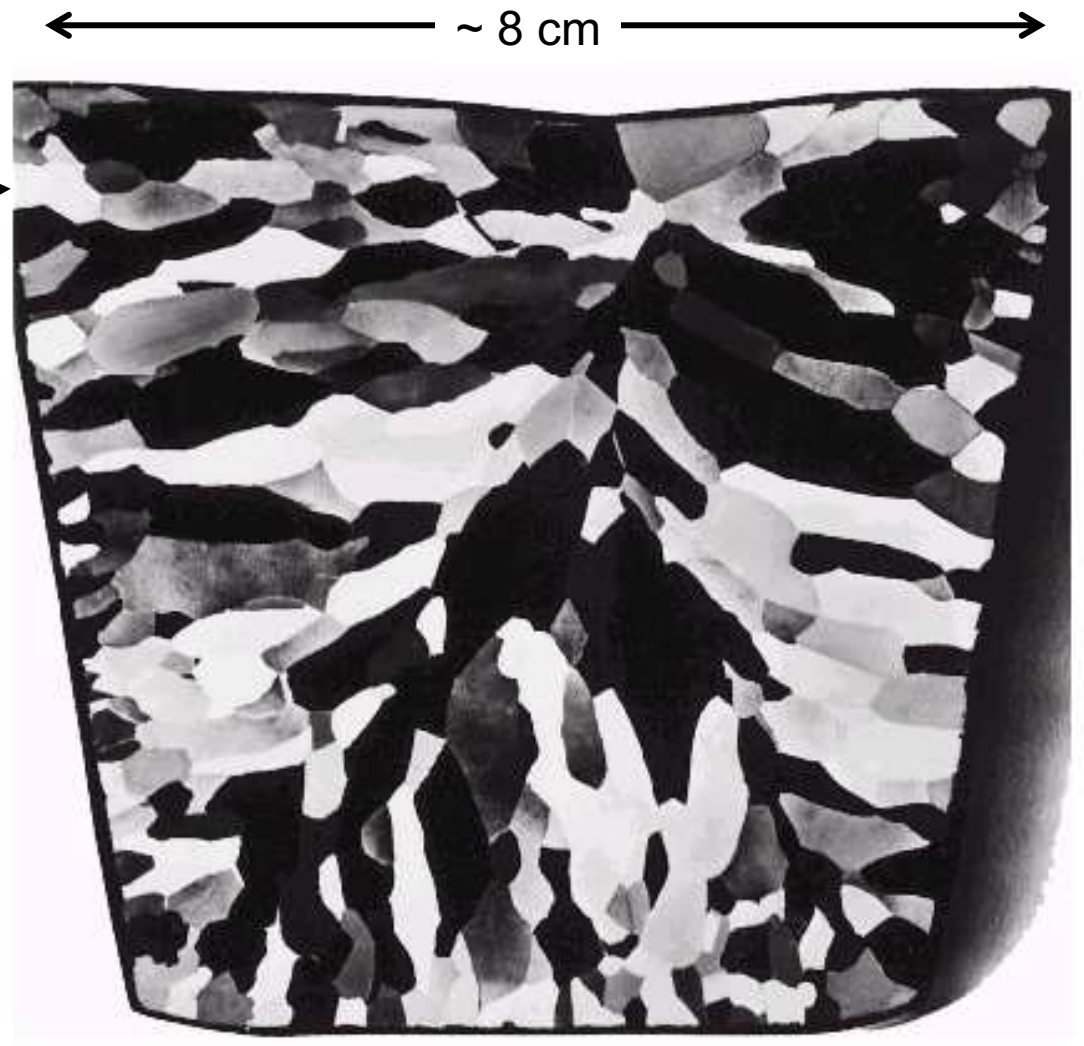
https://www.youtube.com/watch?v=Fhhfx036Zkc

Most of the materials we use are polycrystalline

Each of these crystals are referred to as **grains**

Sizes typically range from **microns (10^{-5} m) to cm (10^{-3} m)**

This is the first example of an imperfection, or ***defect***, in crystalline materials…
But not the only one



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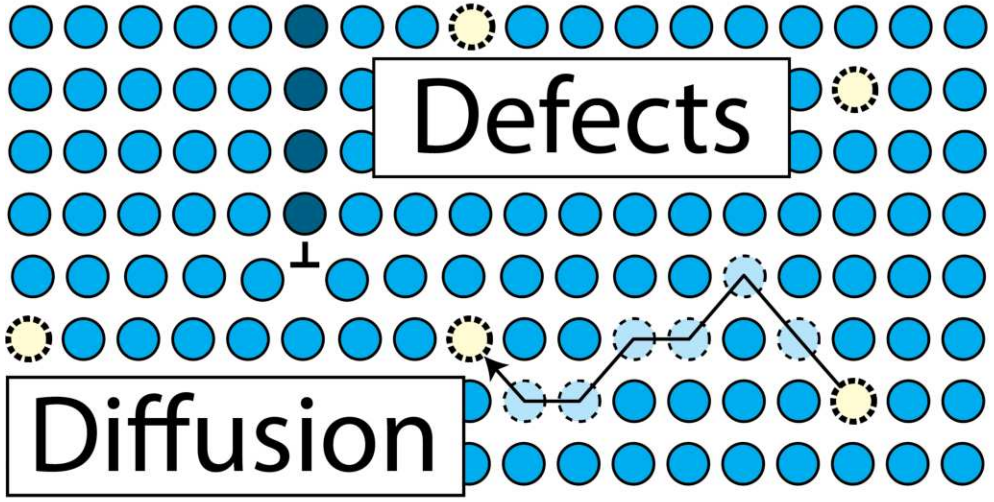
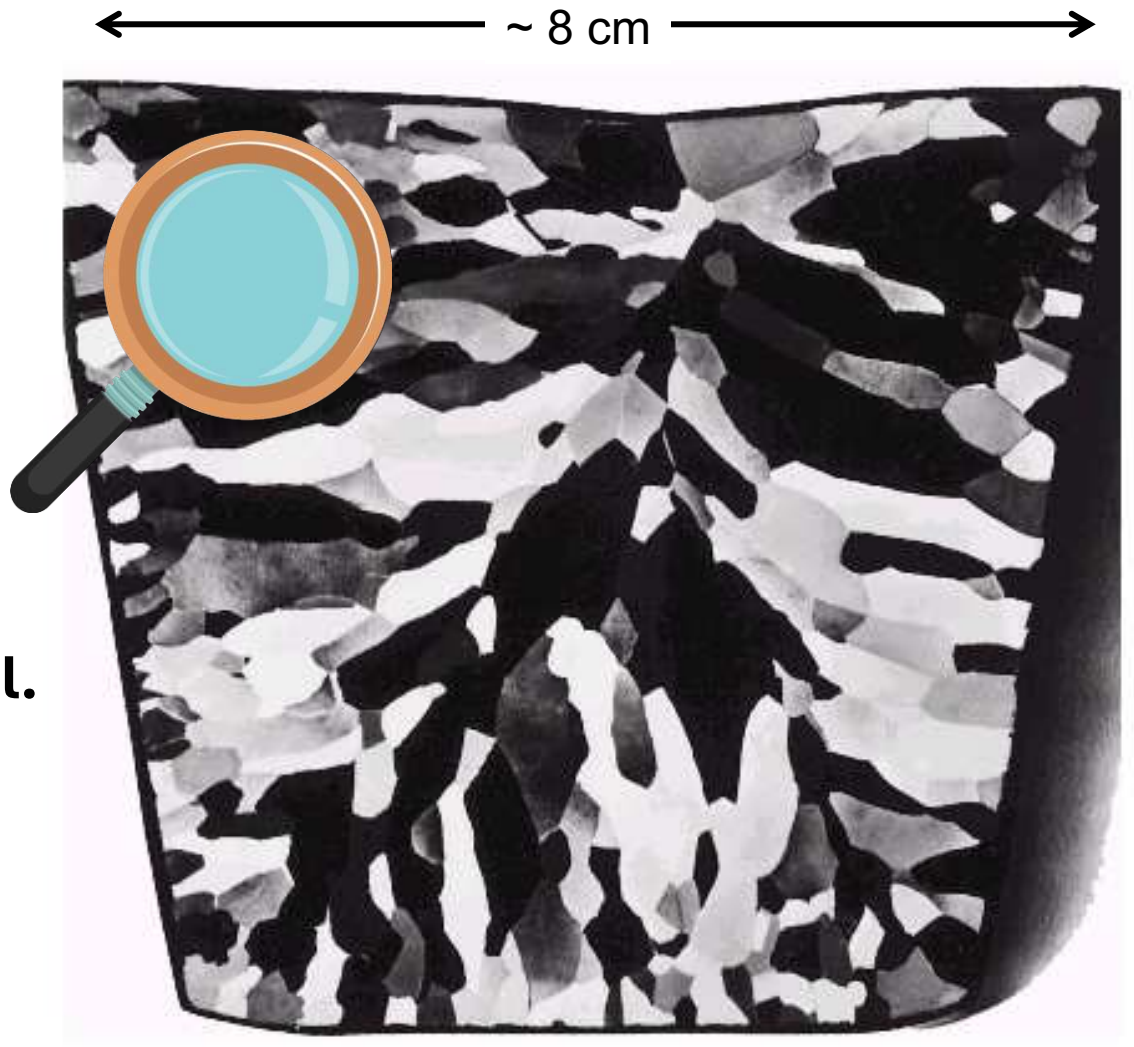
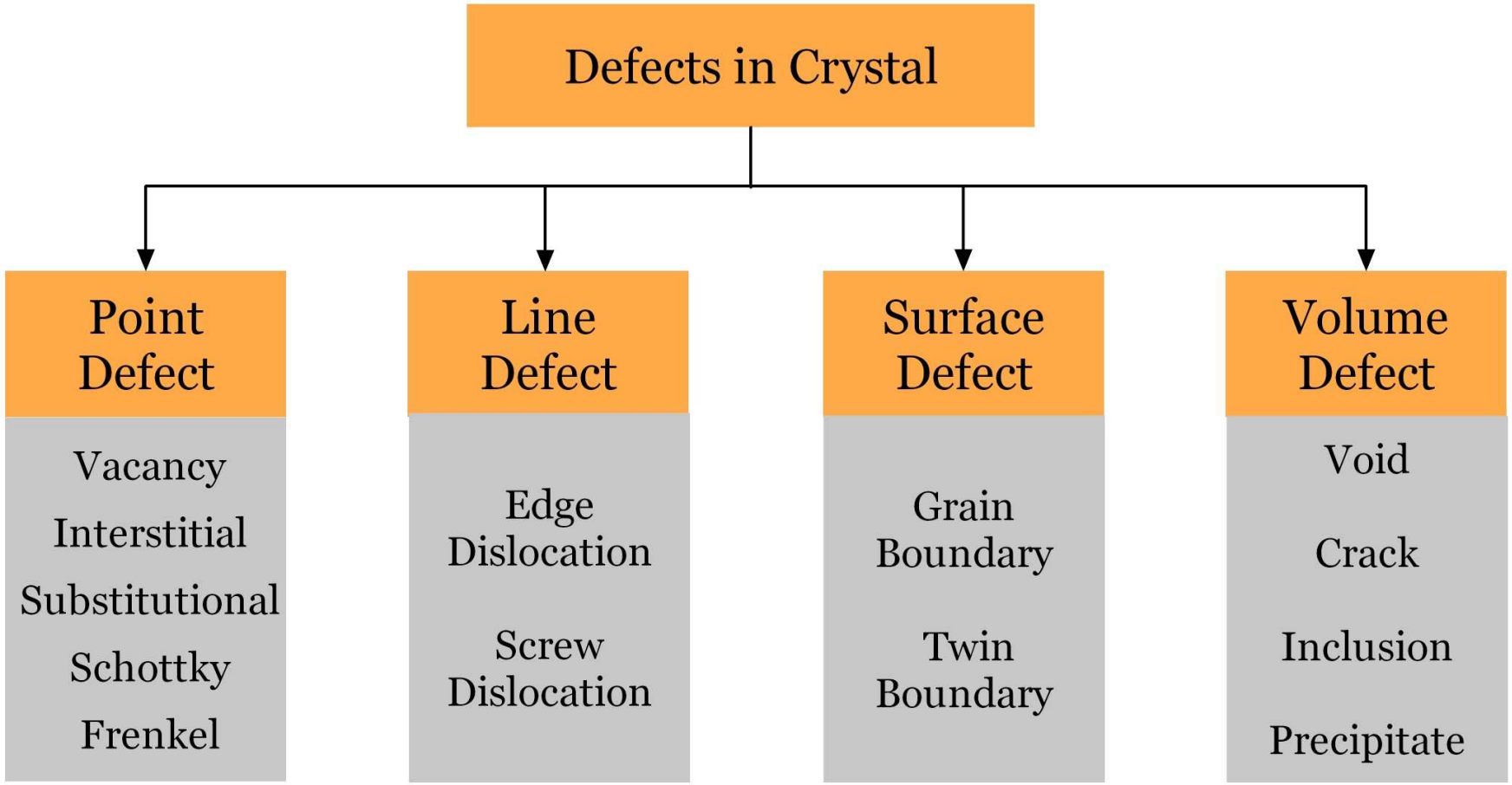




These is no such thing is a perfect crystal.
Defects are *always present*…useful?

"Crystals are like people. It is the defects in them which tend to make them interesting!"
– Sir Colin Humphreys (British Physicist)

Even within a grain: the crystal is not perfect



Single atom (0D)

A 1D line of atoms

2D planes of atoms

3D chunks of atoms

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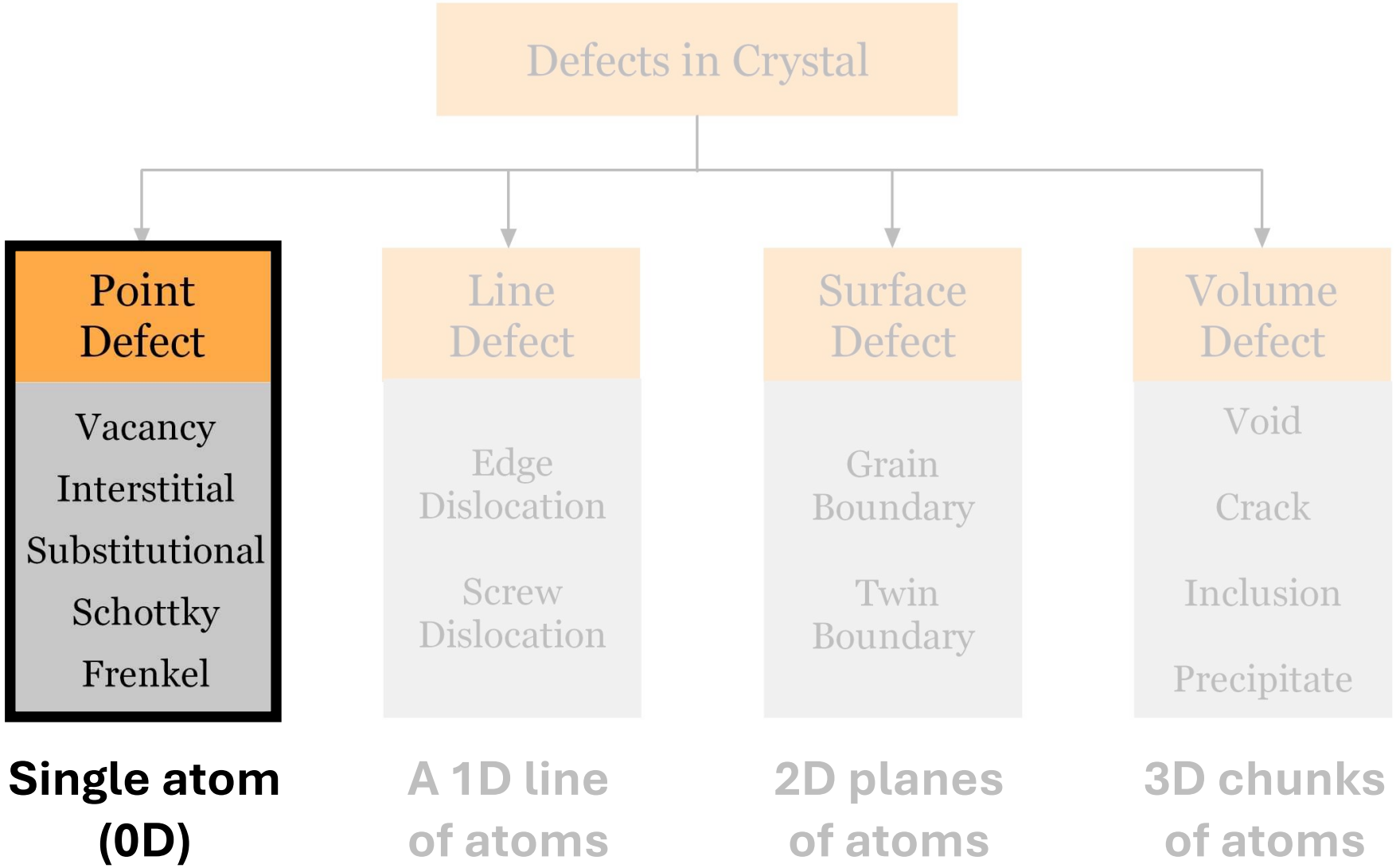
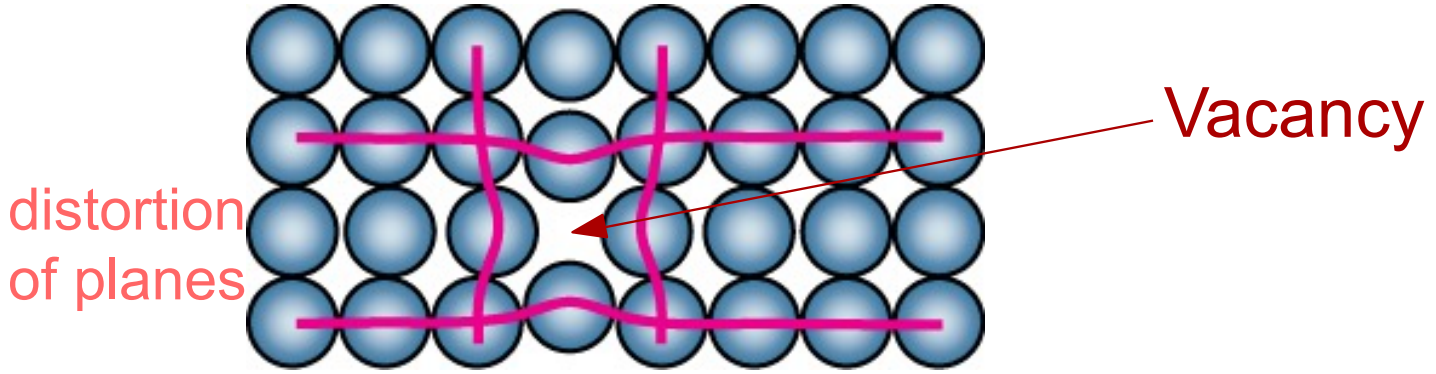
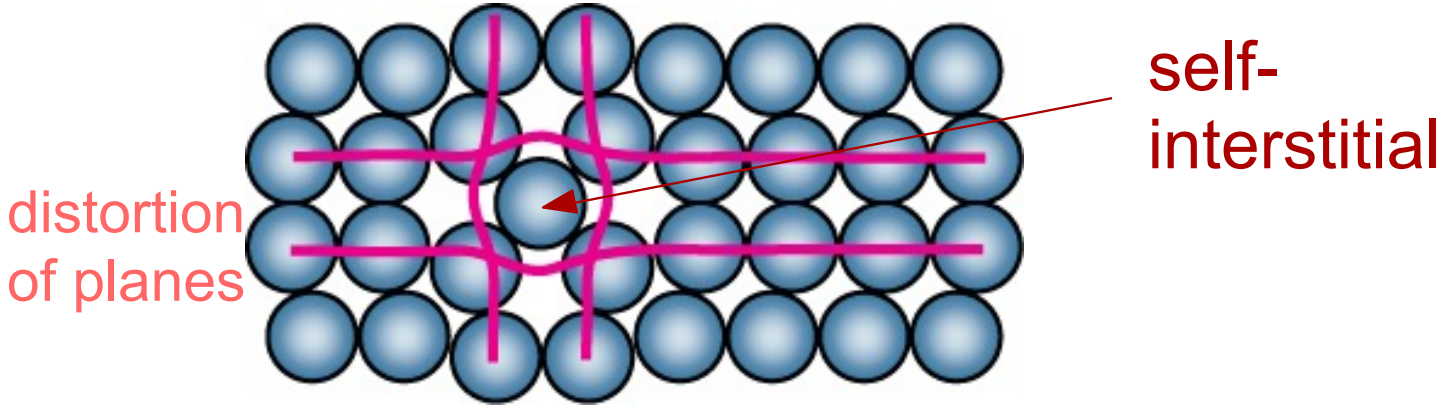


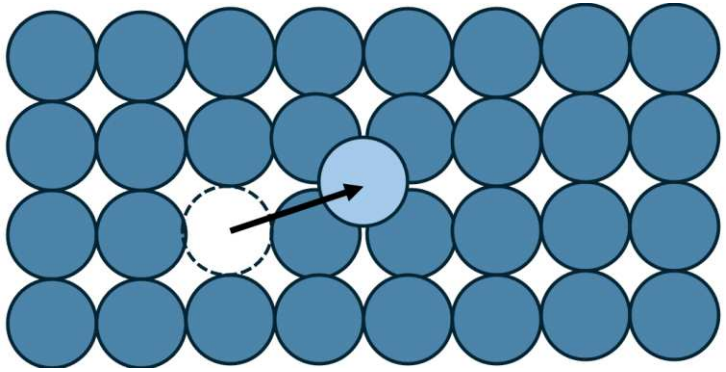
Point defects: vacancies and interstitials

A **vacancy** occurs when there is a **"missing atom"** from a lattice site



An **interstitial** occurs when there is an **"extra atom"** *between* the lattice sites





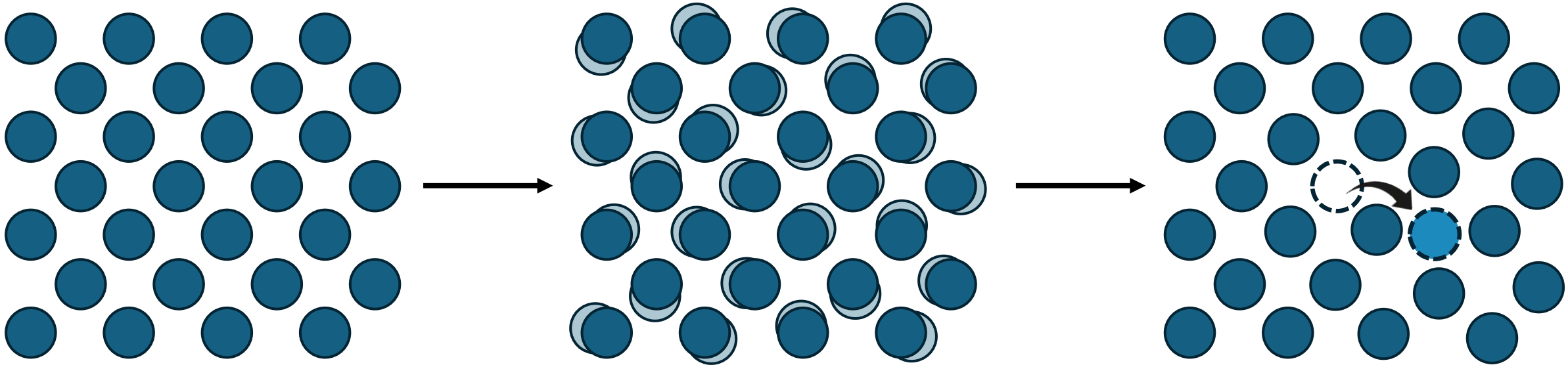
A **Frenkel defect** is a combination of the two: vacancy + interstitial

Why do point defects form?

Consider a perfect crystal at $T = 0$ K

As we heat it up, atoms vibrate

Vibrations "kick out" some atoms



There is an **energy cost** associated with defect (*e.g.*, vacancy) formation

→ The **activation energy (Q_v)**





But there is also an **entropy increase** when defects form



How many point defects form?

Let's focus on determining the **equilibrium concentration of vacancies:**

Number of vacancies

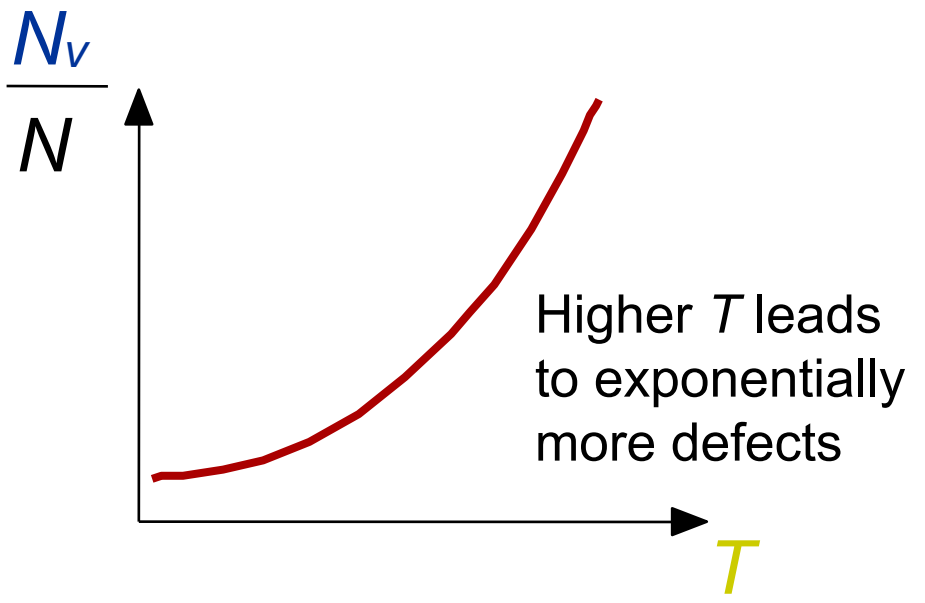
Total number of lattice sites

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

Activation energy: the energy cost of vacancy formation

Temperature

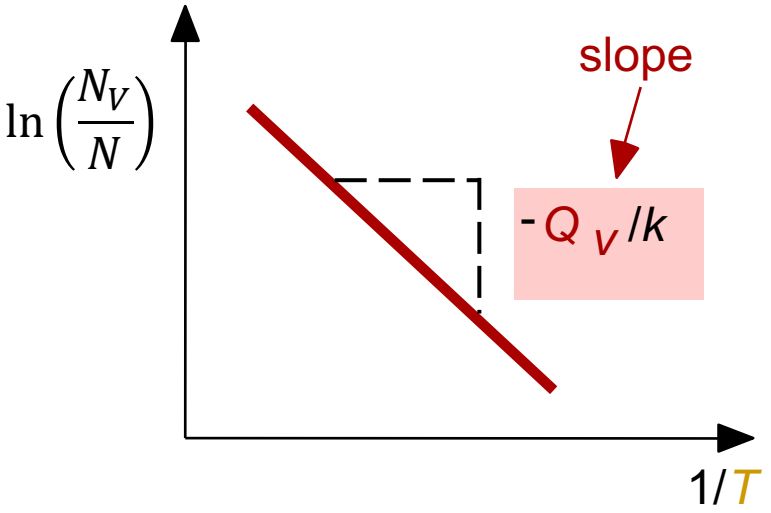
Boltzmann's constant (8.62×10^{-5} eV/atom·K)



Higher T leads to exponentially more defects

We can measure this curve and use it to determine the activation energy

Atomistic insight from bulk measurements!



Example: calculating equilibrium vacancy concentration

Find the equilibrium number of vacancies in 1 m^3 of Cu at 1000°C.

Given: $\rho = 8.4\ \mathrm{g/cm^3}$ $A_{\mathrm{Cu}} = 63.5\ \mathrm{g/mol}$

$Q_{\mathrm{V}} = 0.9\ \mathrm{eV}$ $N_{\mathrm{A}} = 6.02 \times 10^{23}\ \mathrm{atoms/mol}$

First, let's determine **how many lattice sites are in 1 m^3 Cu:**

$$N = \frac{(6.022\times10^{23}\ \text{sites/mol})(8.4\ \text{g/cm}^3)}{63.5\ \text{g/mol}}\left(\frac{10^6\text{cm}^3}{\text{m}^3}\right) = 8.0 \times 10^{28}\ \text{sites/m}^3$$

Example: calculating equilibrium vacancy concentration

$$\frac{N_v}{N} = \exp\left(\frac{-Q_v}{kT}\right) \qquad N_v = N \exp\left(\frac{-0.9\ \text{eV/atom}}{(8.62 \times 10^{-5}\ \text{eV/atom-K})(1273\ \text{K})}\right)$$

$$N_V = (8.0 \times 10^{28}\ \text{sites/m}^3)(2.7 \times 10^{-4}) = 2.2 \times 10^{25}\ \text{vacancies/m}^3$$

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$$N_V = (8.0 \times 10^{28}\ \text{sites/m}^3)(2.7 \times 10^{-4}) = \mathbf{2.2 \times 10^{25}\ vacancies/m^3}$$

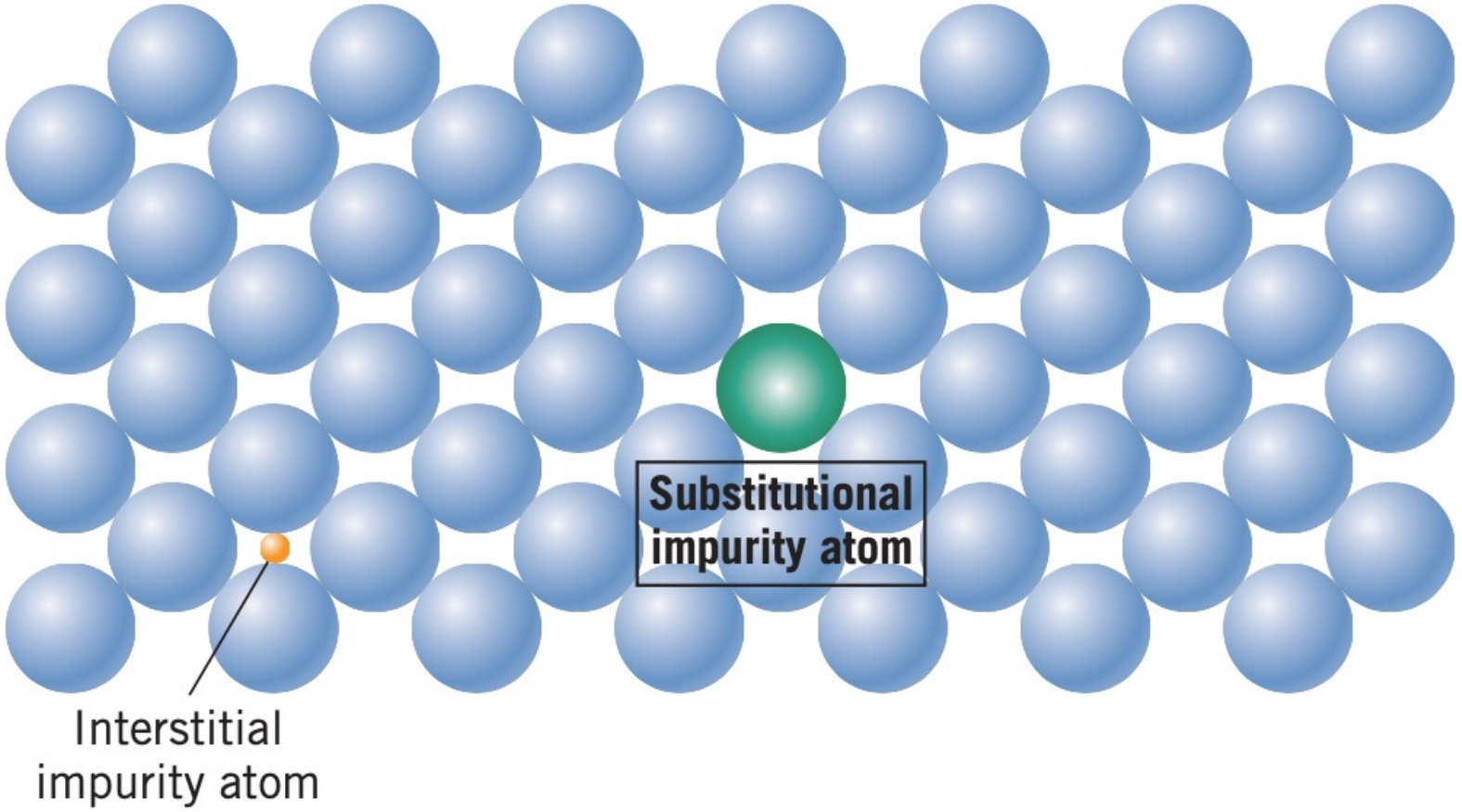
An activation energy of 1 or 2 eV is pretty typical

→ there are ***many*** **vacancies in real materials!**

(and *always* a non-zero amount at $T > 0$ K)

Point defects may also come from *impurities*

So far, we have only covered **intrinsic defects** (within an isolated material). But in reality, materials are always interacting with their environment and may form **extrinsic defects** by taking in "other" elements.

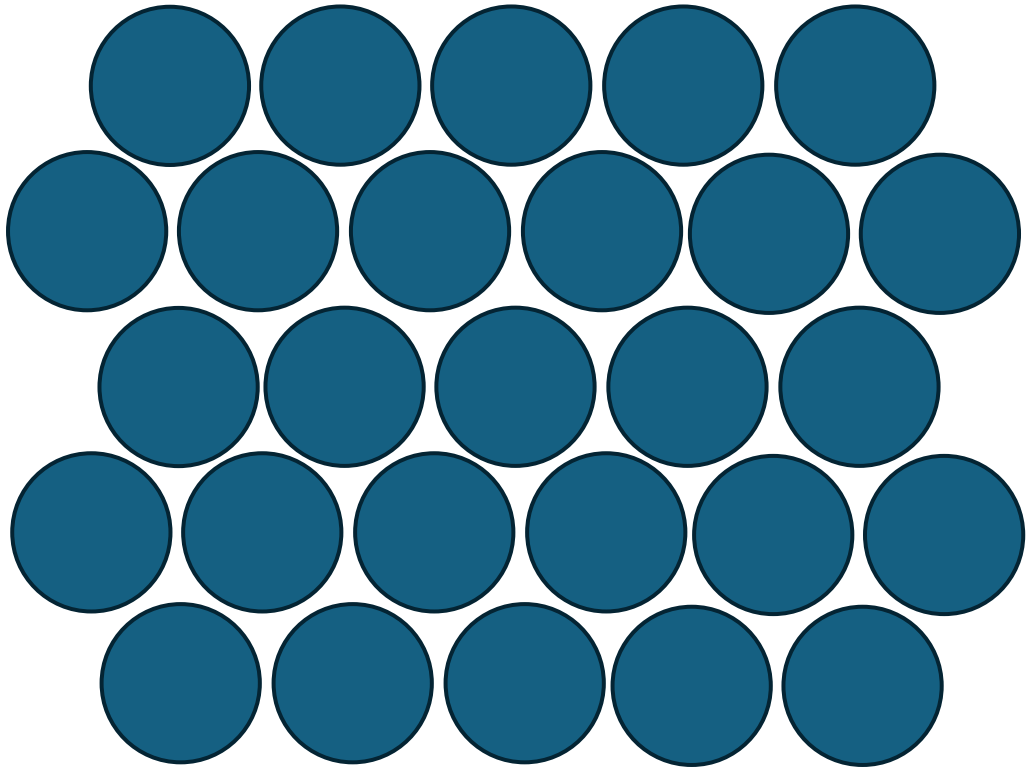


Two classes:

1) **Substitutional impurities**
2) **Interstitial impurities**

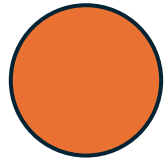
Point defects may also come from *impurities*

Alternative framing: what happens if we **add some element *B* to compound *A***



Compound *A*

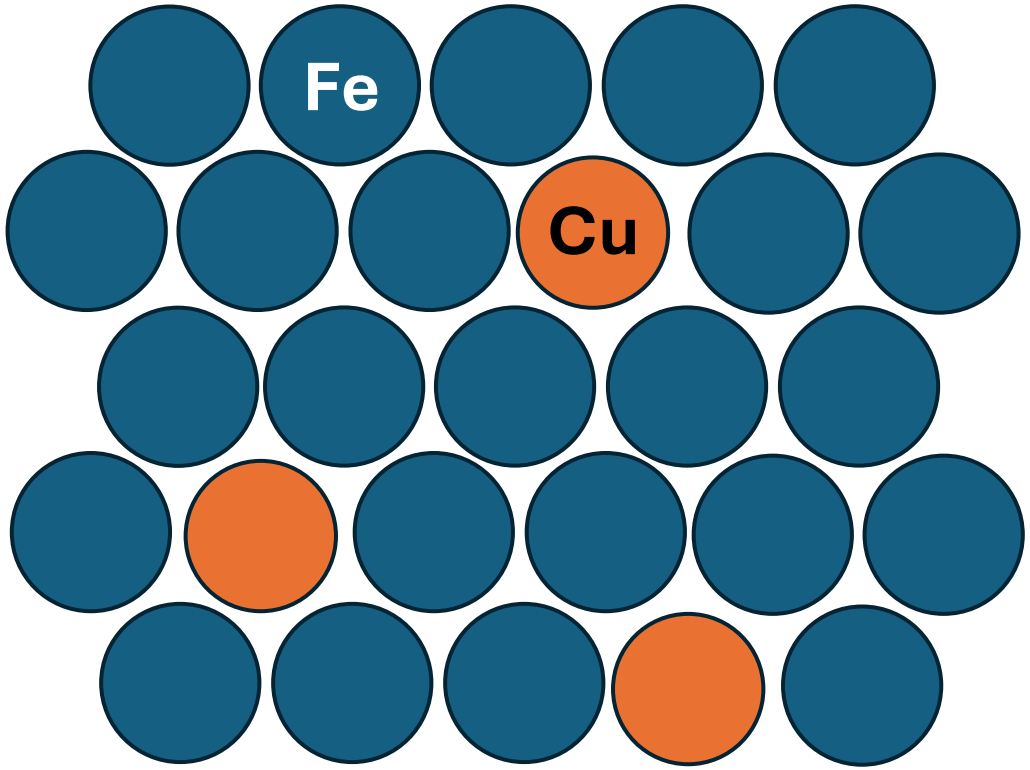
+



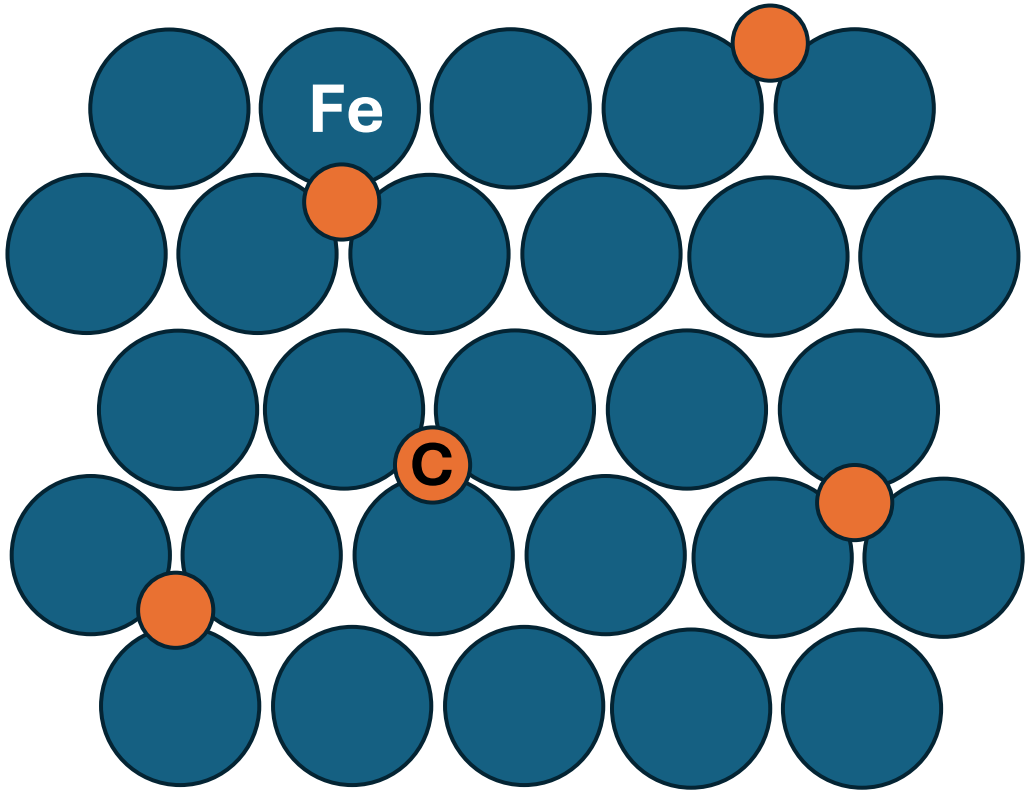
Element *B*

Point defects may also come from *impurities*

Option 1: Substitution
(if A and B are comparable in size)



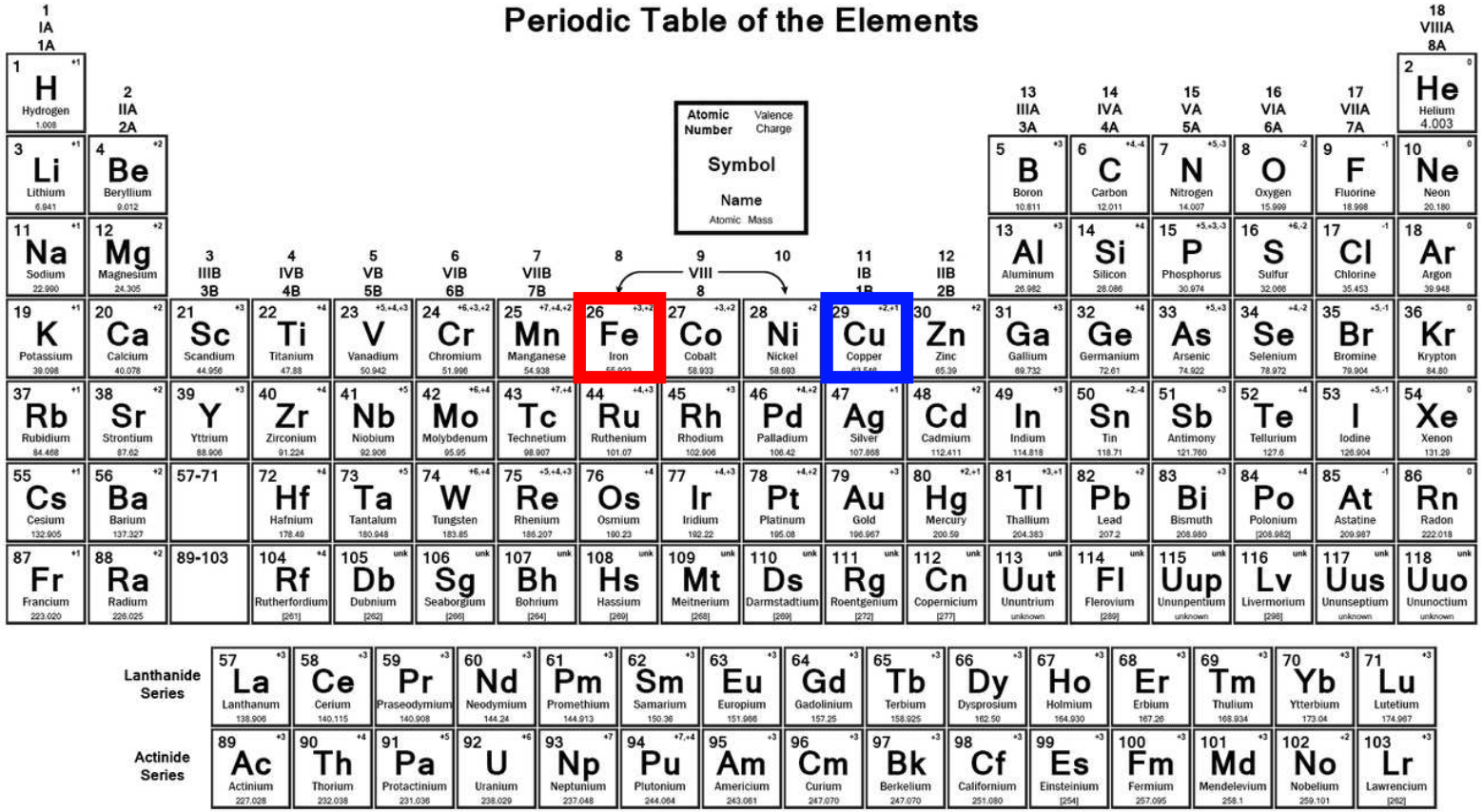
Option 2: Interstitial formation
(if they are not comparable in size)



These are often referred to as **solid solutions** of *A* and *B*

Conditions for *substitutional* solid solutions

Hume-Rothery rules tell us (roughly) when substitution can be expected:



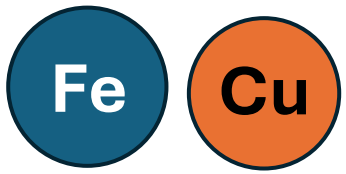
Will these two elements form a substitutional solid solution?

Conditions for *substitutional* solid solutions

Hume-Rothery rules tell us (roughly) when substitution can be expected:

A substitutional solid solution between *A* and *B* is likely when:

1) Their **atomic radius differs by < 15%**



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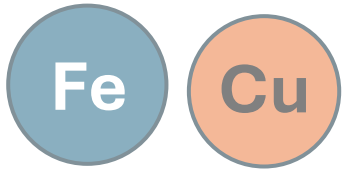

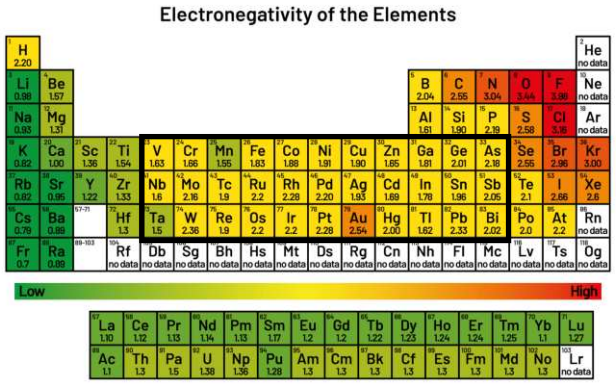

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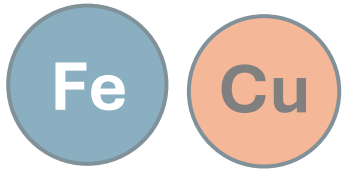
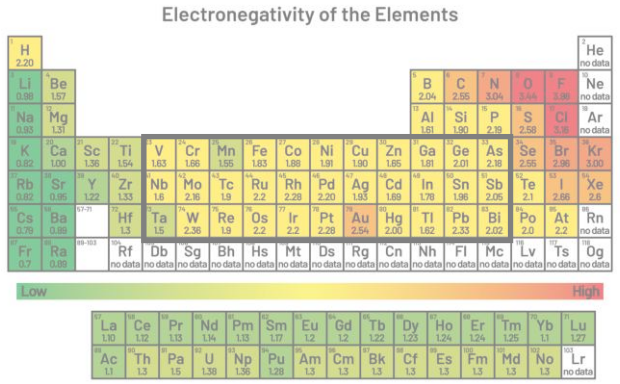
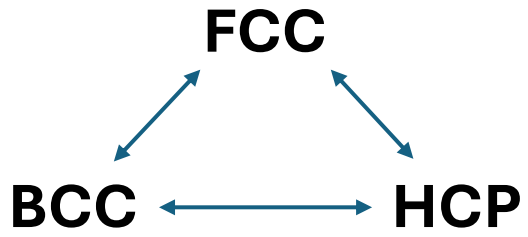




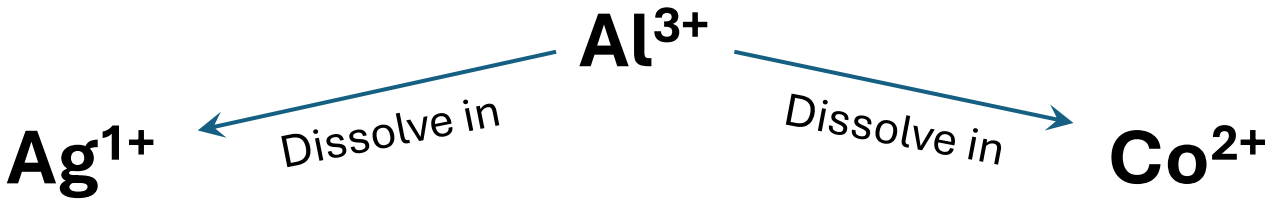


Conditions for *substitutional* solid solutions

Hume-Rothery rules tell us (roughly) when substitution can be expected:

A substitutional solid solution between *A* and *B* is likely when:

1) Their **atomic radius differs by < 15%**
2) They have **similar electronegativity** (are close on periodic table)
3) They have **the same crystal structures** as pure elements
4) All other factors being equal: **metals with higher valency** (oxidation state) **will dissolve in those with lower valency**



Conditions for *substitutional* solid solutions

Would you predict **Al or Ag** to be **more soluble** (that is, form more substitutional defects) **in Zn metal?**

1) Al, Ag, and Zn are all comparable in size
2) Al and Zn have similar electronegativity
3) Structures (FCC/HCP) differ but only slightly
4) Al^{3+} has a higher valence than Zn^{2+}

Element	*Atomic Radius (nm)*	*Crystal Structure*	*Electro-negat.*	*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

→ **Al is more soluble in Zn**

Common metal alloys are solid solutions



For example, **stainless steel** has a composition around:

70% Fe, 20% Cr, 9% Ni, 1% C

All metal alloys contain solid solutions



For example, **stainless steel** has a composition around:

70% Fe, 20% Cr, 9% Ni, 1% C

Host metal

Substitutional

Interstitial

Each serves a unique purpose and has a big effect on properties!

These numbers are written in terms of **% mass**, but we can also describe **atomic %**

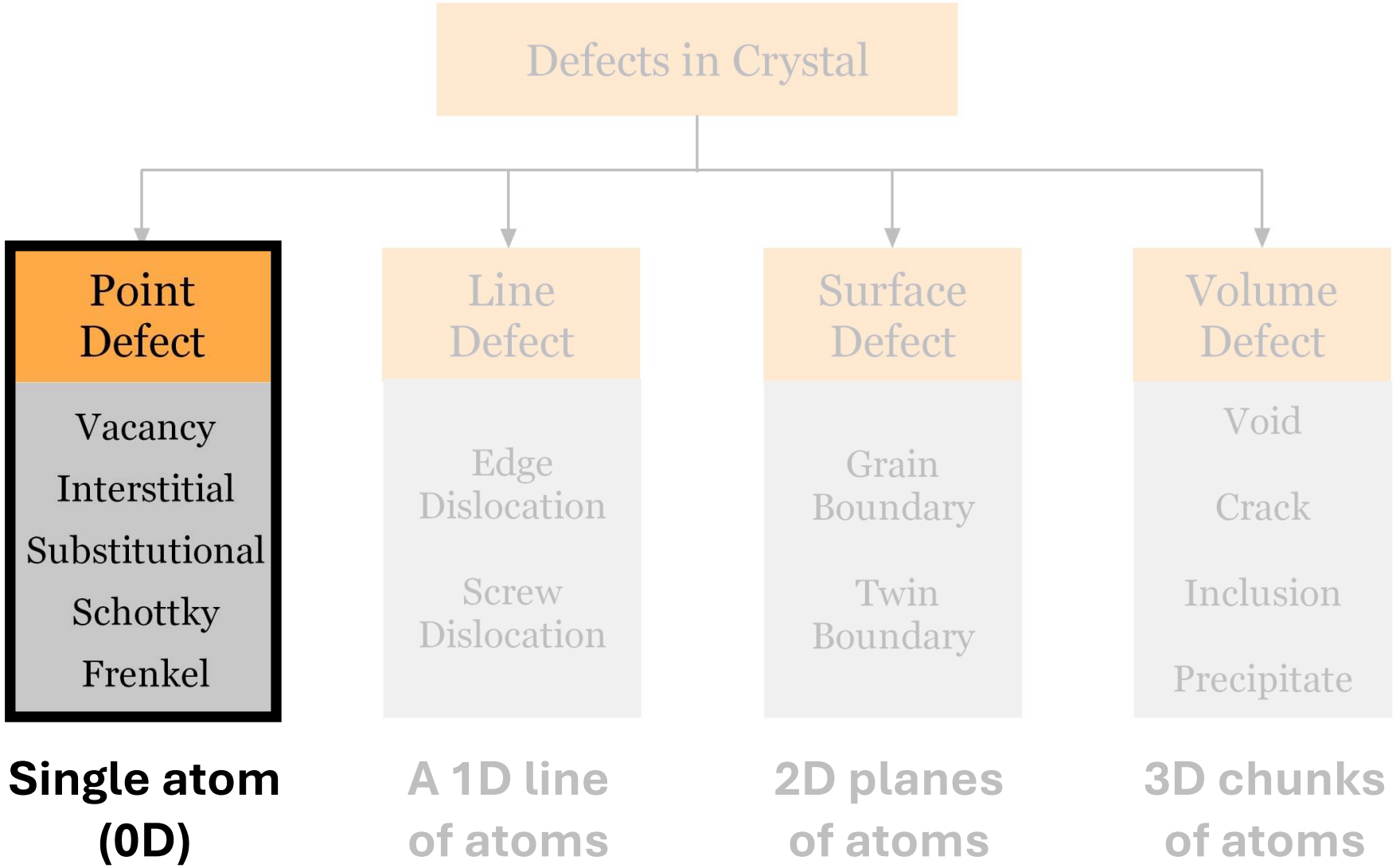
These are for binary alloys (2 components)

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

$$C_1' = \frac{n_{m1}}{n_{m1} + n_{m2}} \times 100$$

Convert between these using atomic masses of elements 1 and 2

From 0D (point) to 1D (linear) defects



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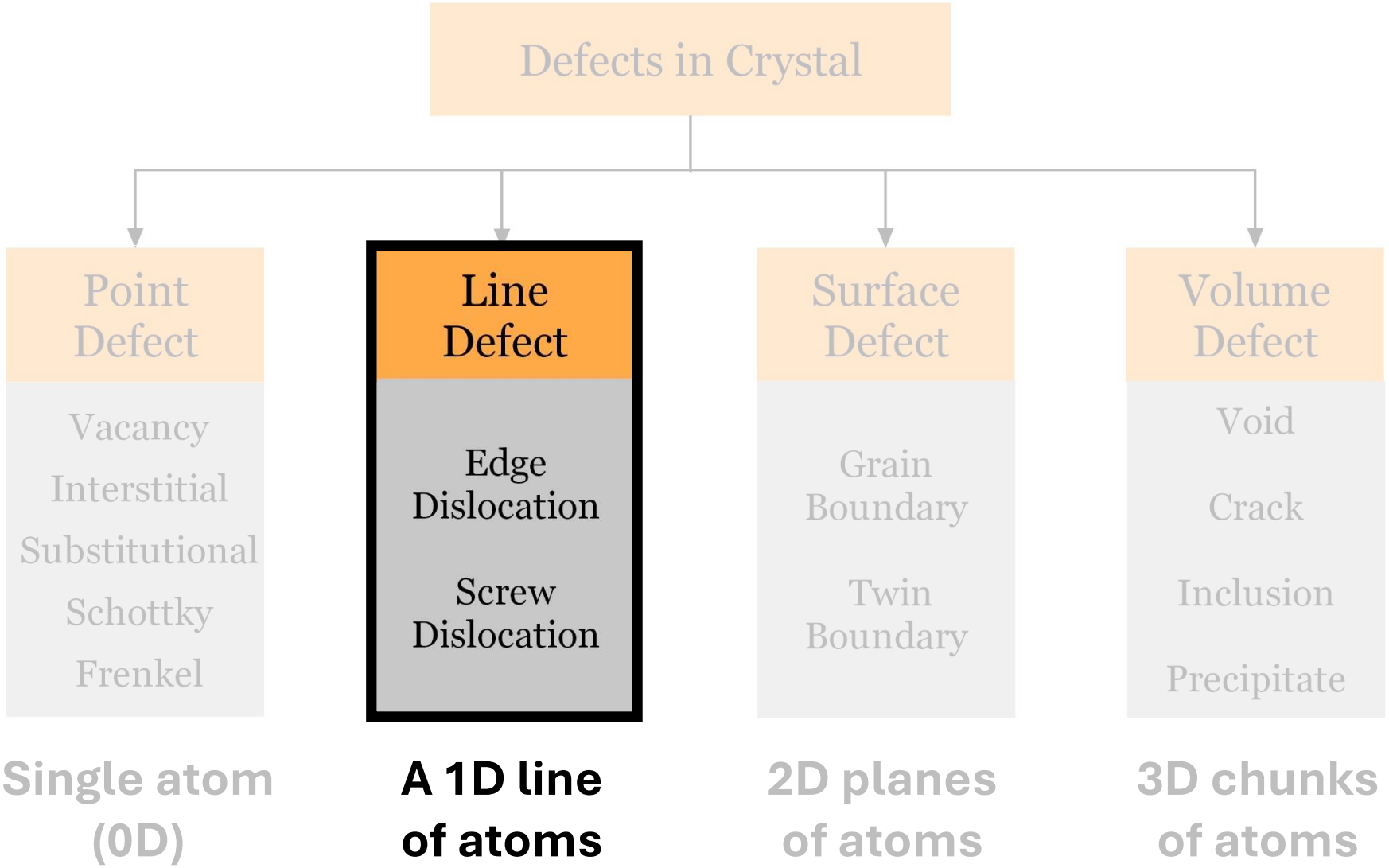
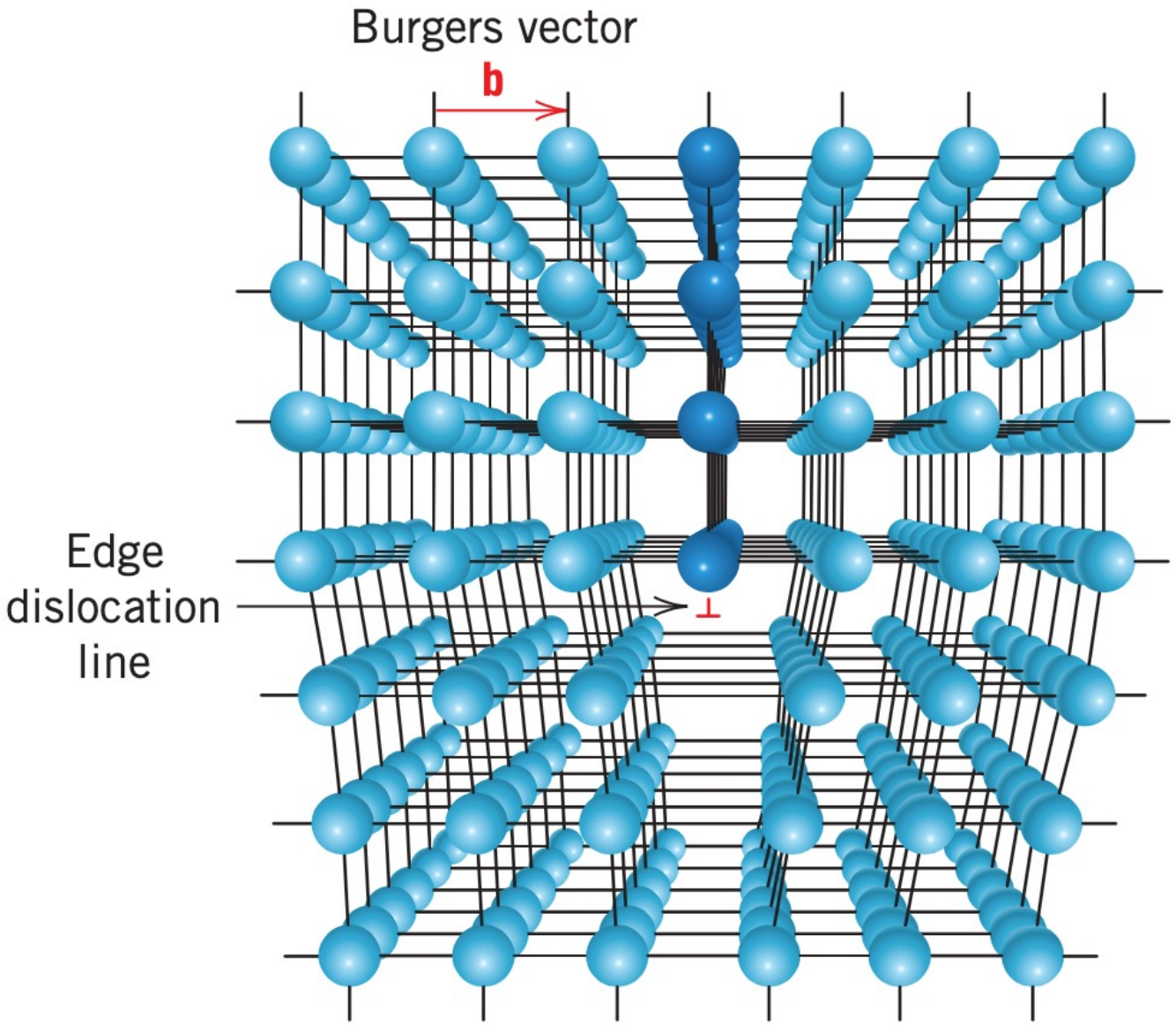


Line defect type 1: *Edge* dislocations

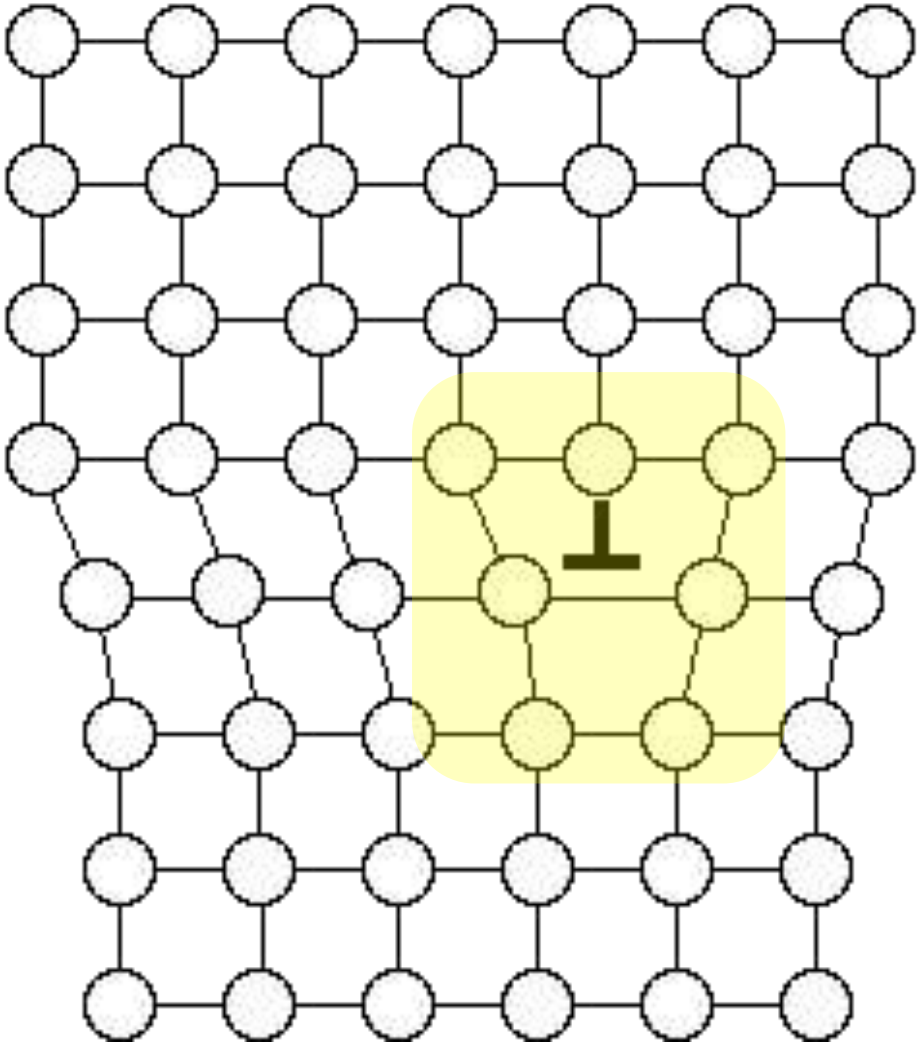


An **edge dislocation is an extra half-plane of atoms** wedged between the usual lattice sites

Some terminology:

- **Dislocation line** (⊥) describes where the extra half-plane exists
- The **Burgers vector ($\vec{b}$)** describes the magnitude and direction of lattice distortion. For edge dislocations, this is perpendicular to ⊥

Line defect type 1: *Edge* dislocations

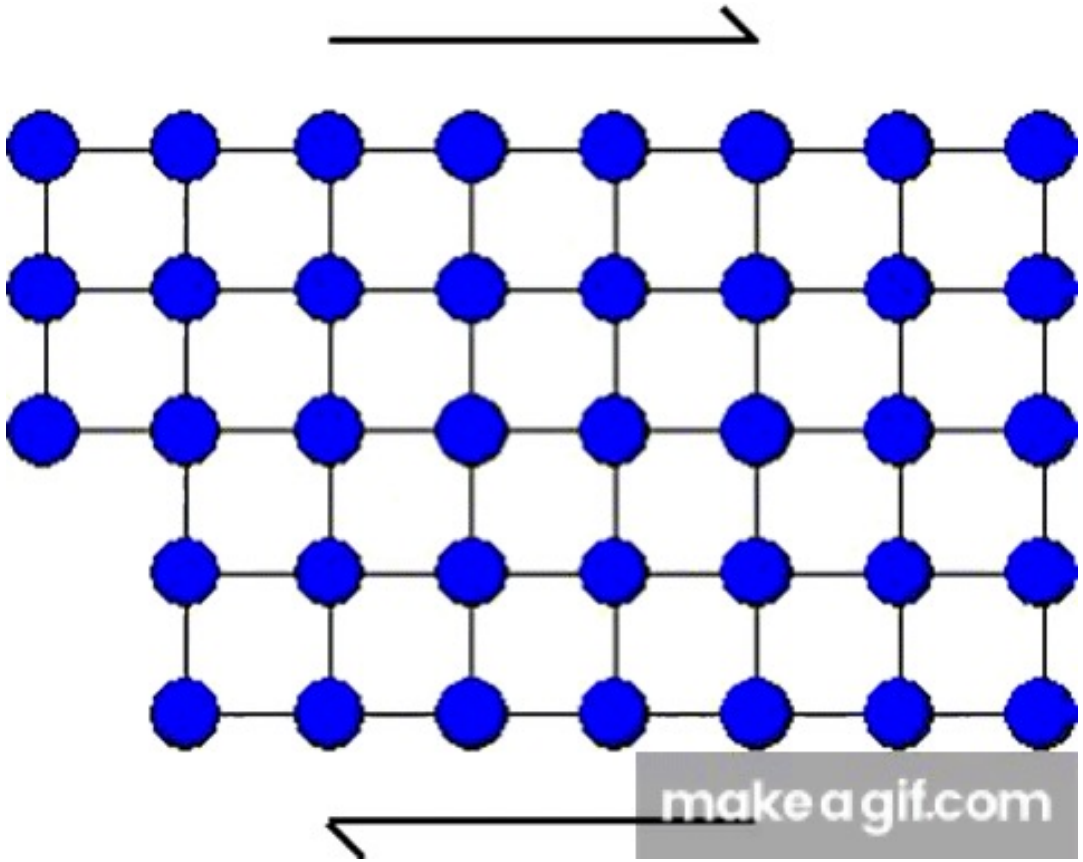


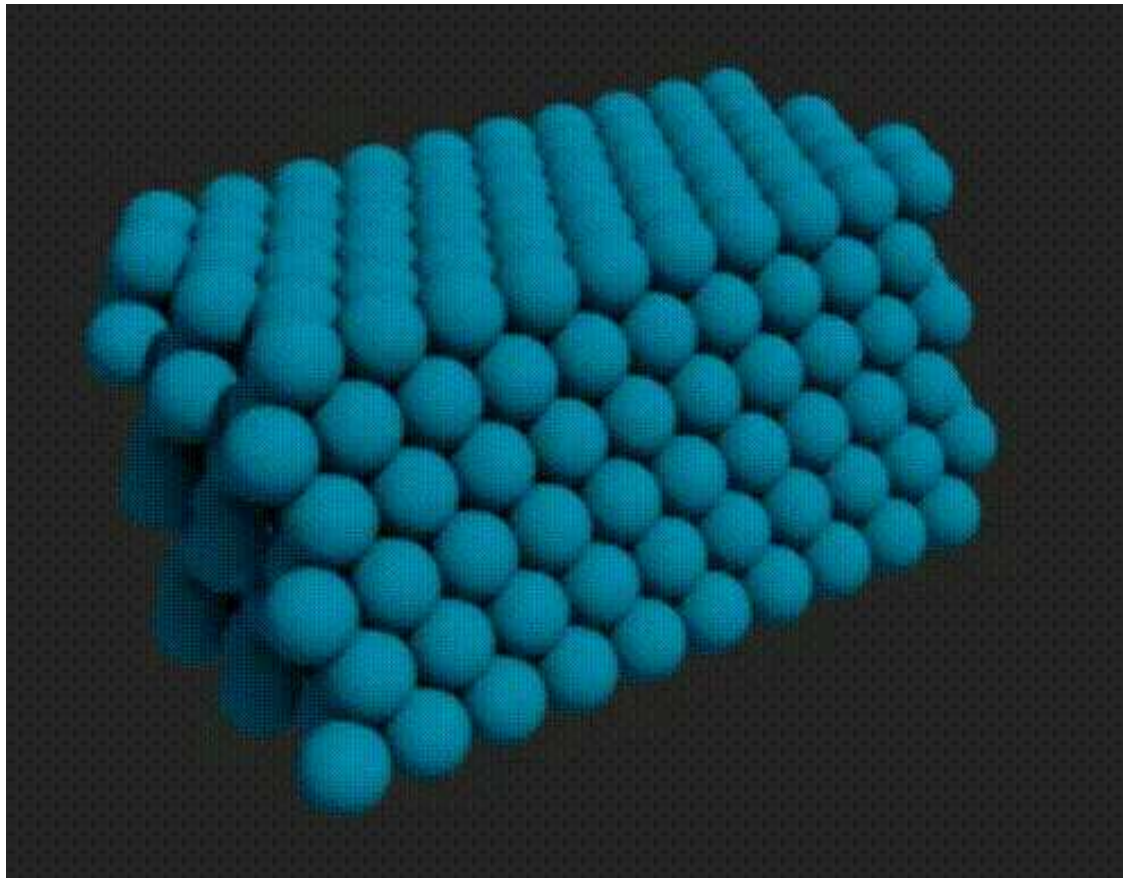
While there are some unfavorable distortions around the dislocation line, the lattice appears “normal” as you get further way from ⊥

Note that unlike point defects, there is no equilibrium concentration of edge dislocations – but they still often arise from **deformations** to the material

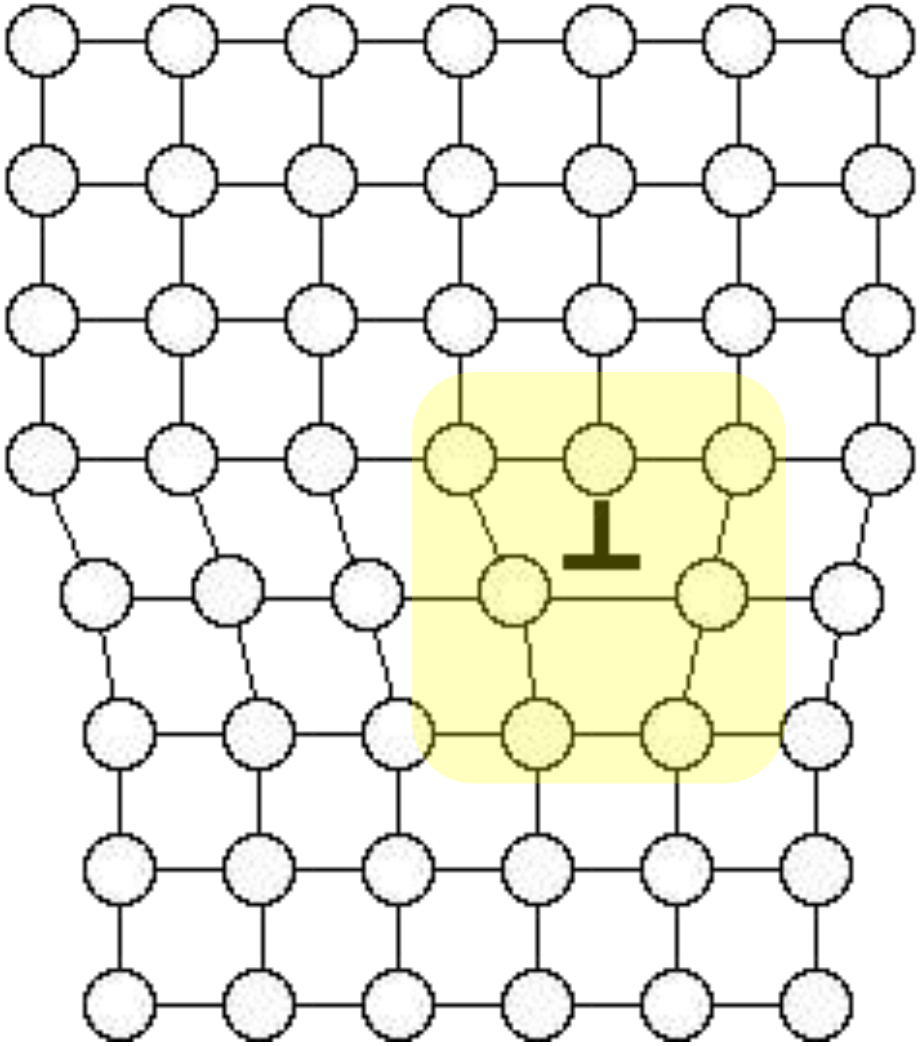
Line defect type 1: *Edge* dislocations

We create and move an edge dislocation by **shearing "left/right"**

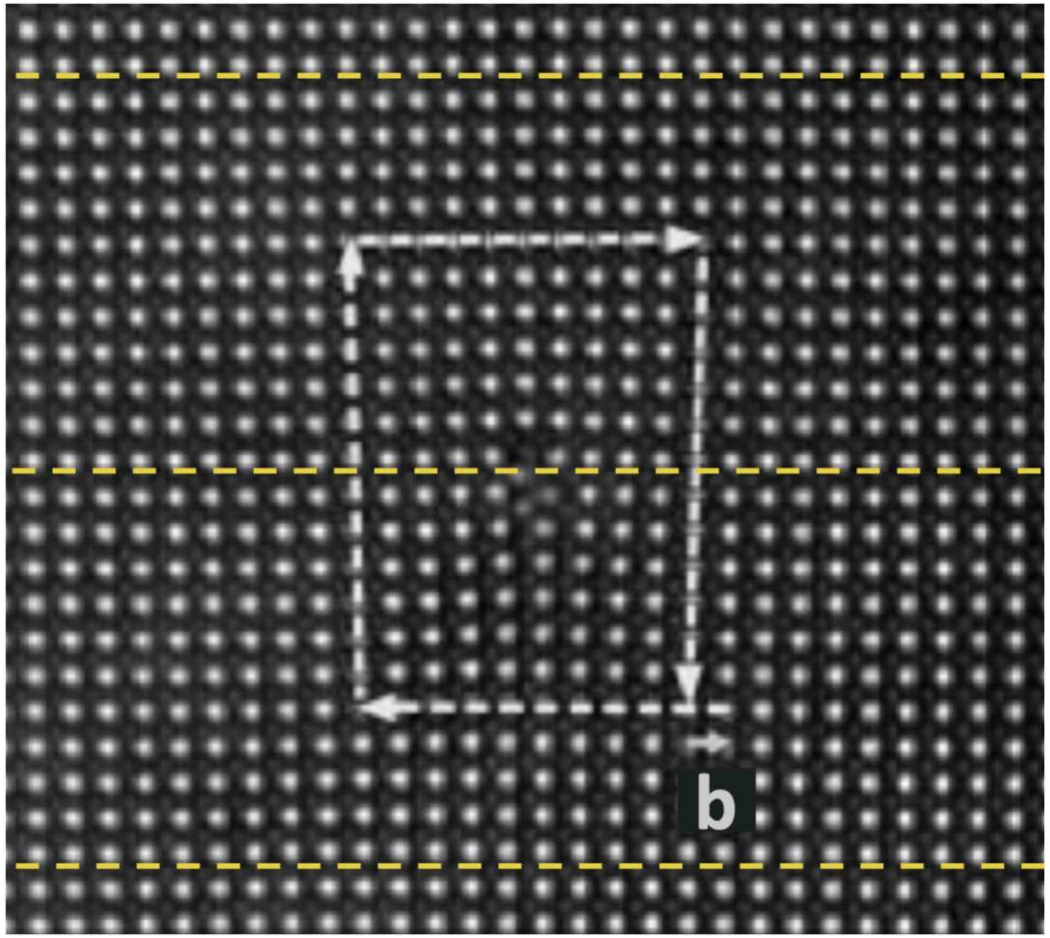




Line defect type 1: *Edge* dislocations

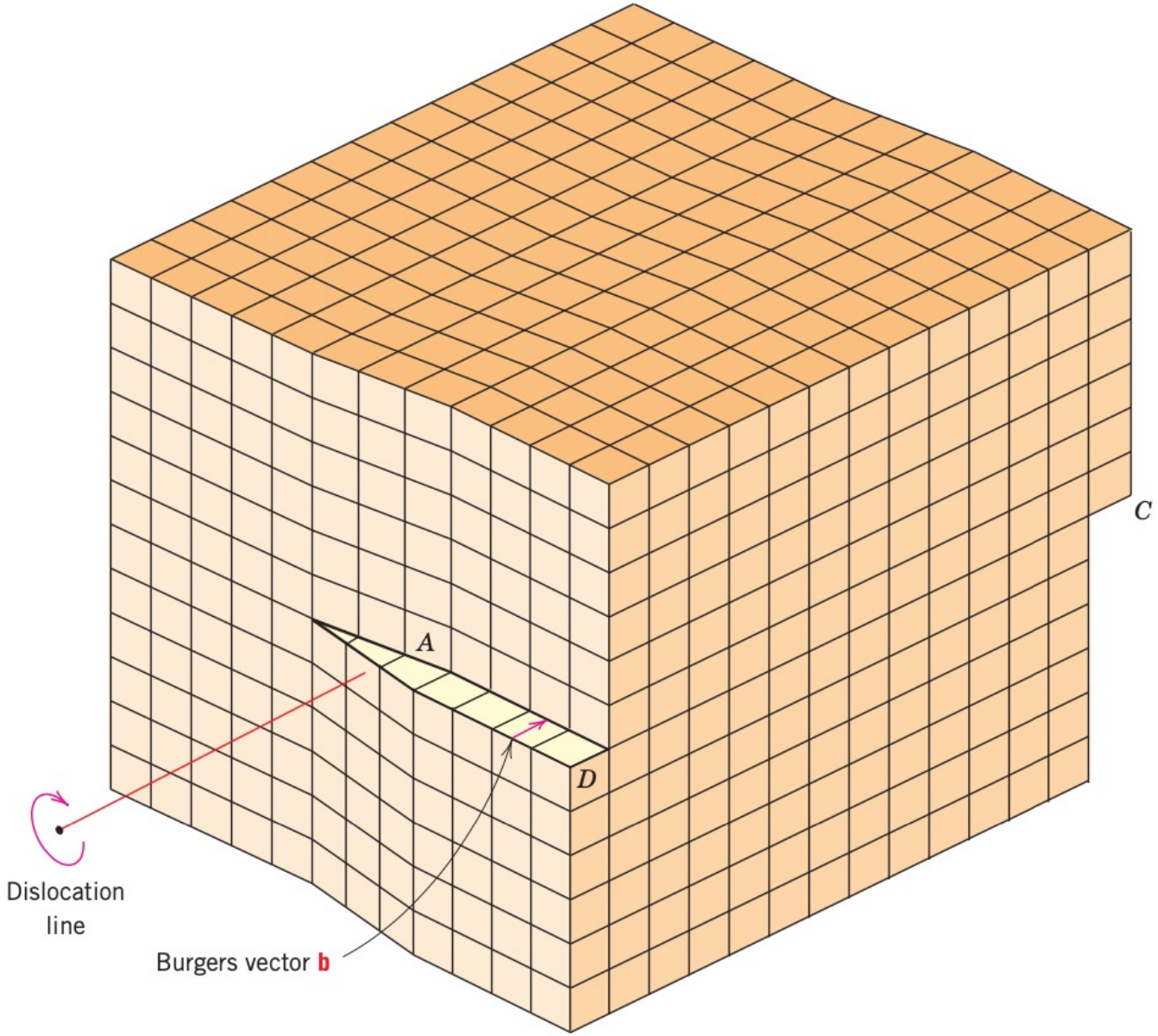


We can directly see these edge dislocations using microscopy!



Hirth and Anderson, PNAS (2025).

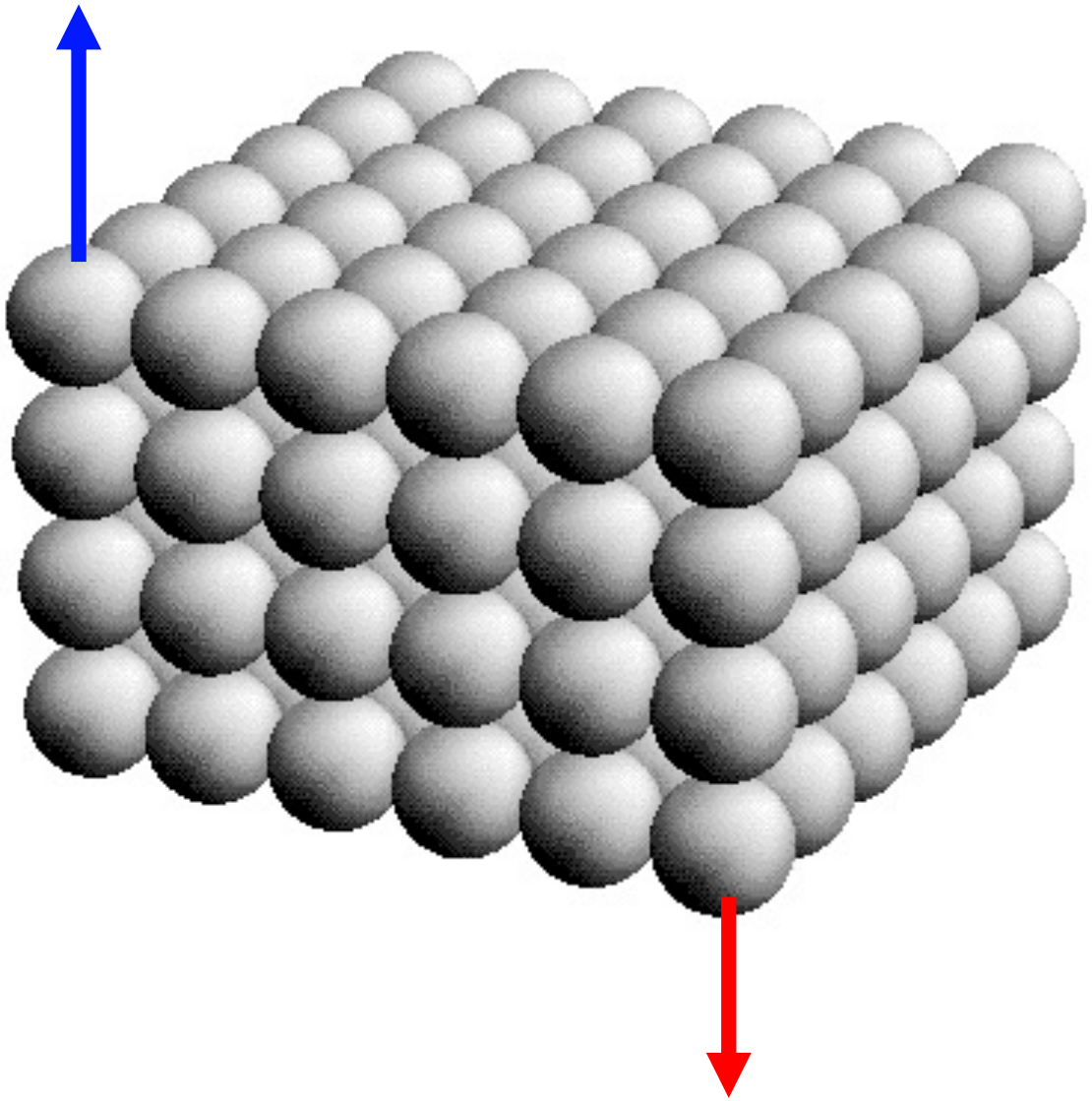
Line defect type 2: *Screw* dislocations

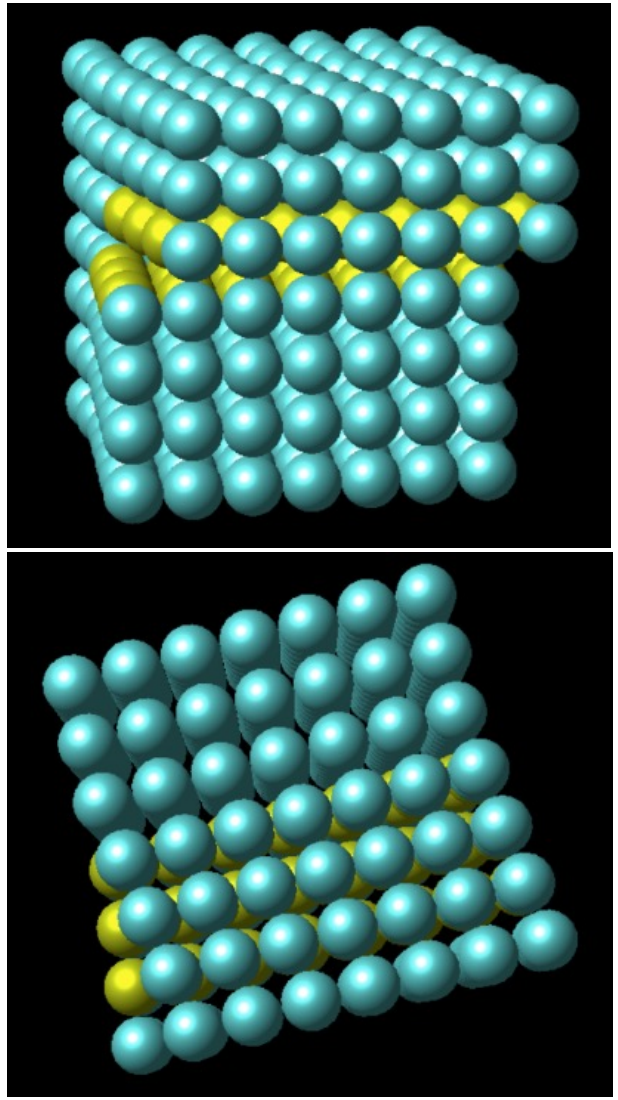


A **screw dislocation** may be thought of as *shifting* an entire portion of the crystal relative to another portion, created by **shearing "up/down"**

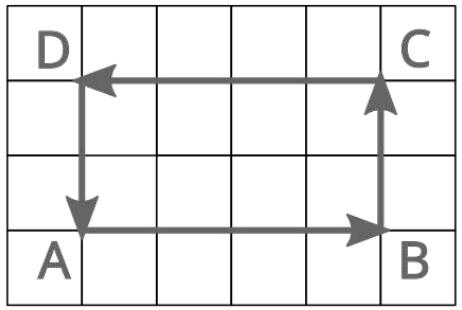
In this case, the **Burgers vector** is parallel to the dislocation line (*not* perpendicular like edge)
…Will show this in a bit

Line defect type 2: *Screw* dislocations



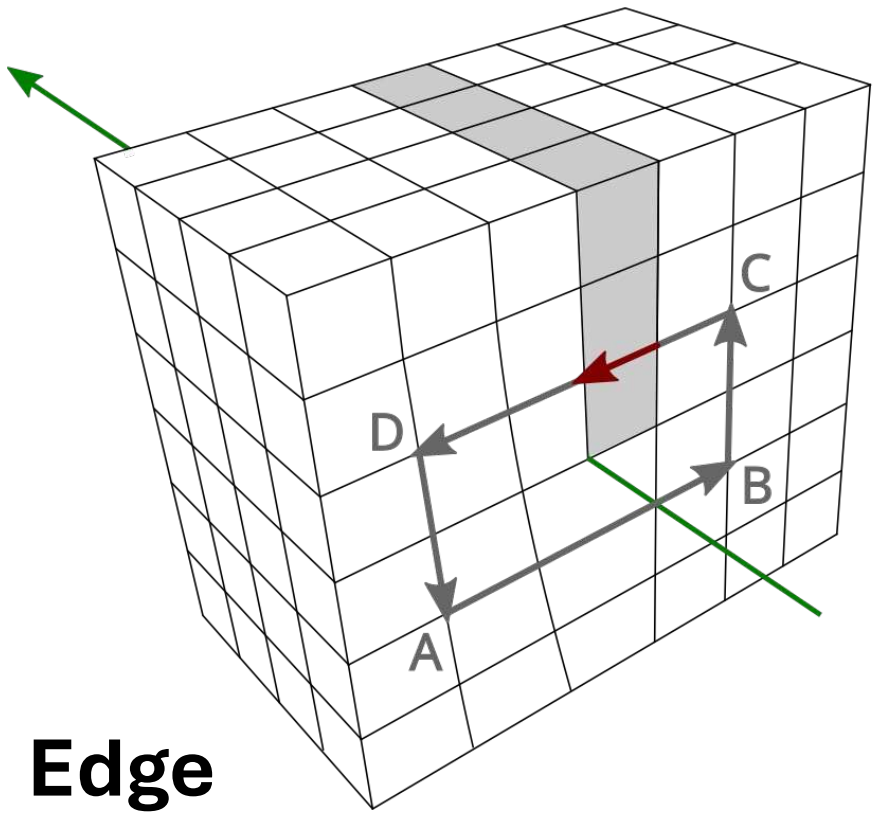


Distinguishing edge versus screw dislocations



Burgers Vector $\vec{b}$

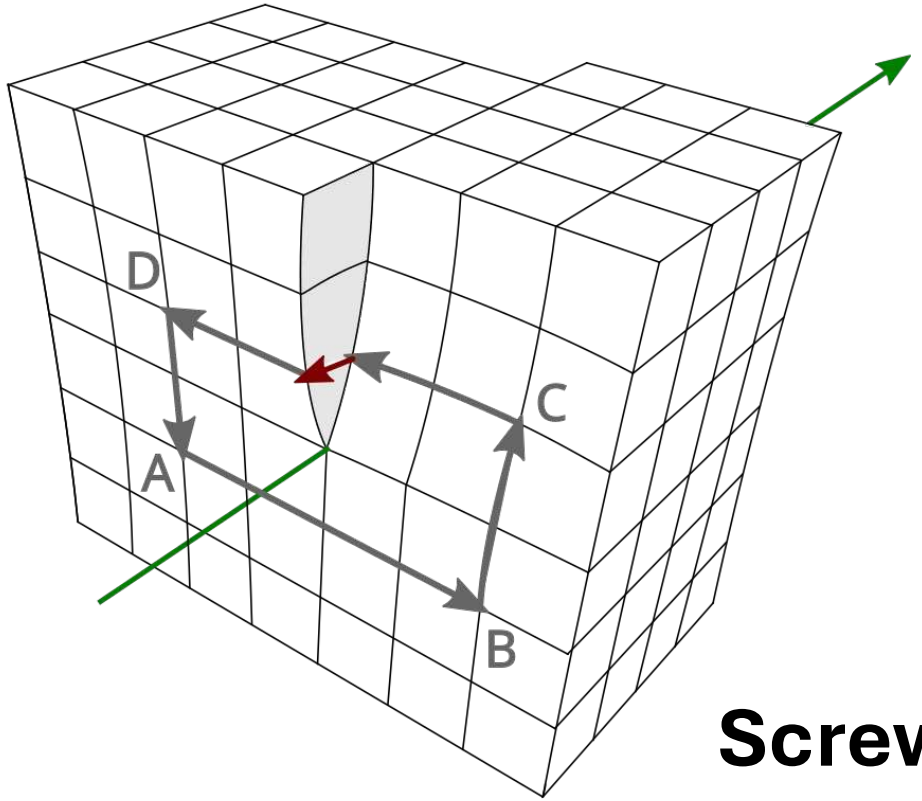
Dislocation Line Vector $\vec{L}$



Edge

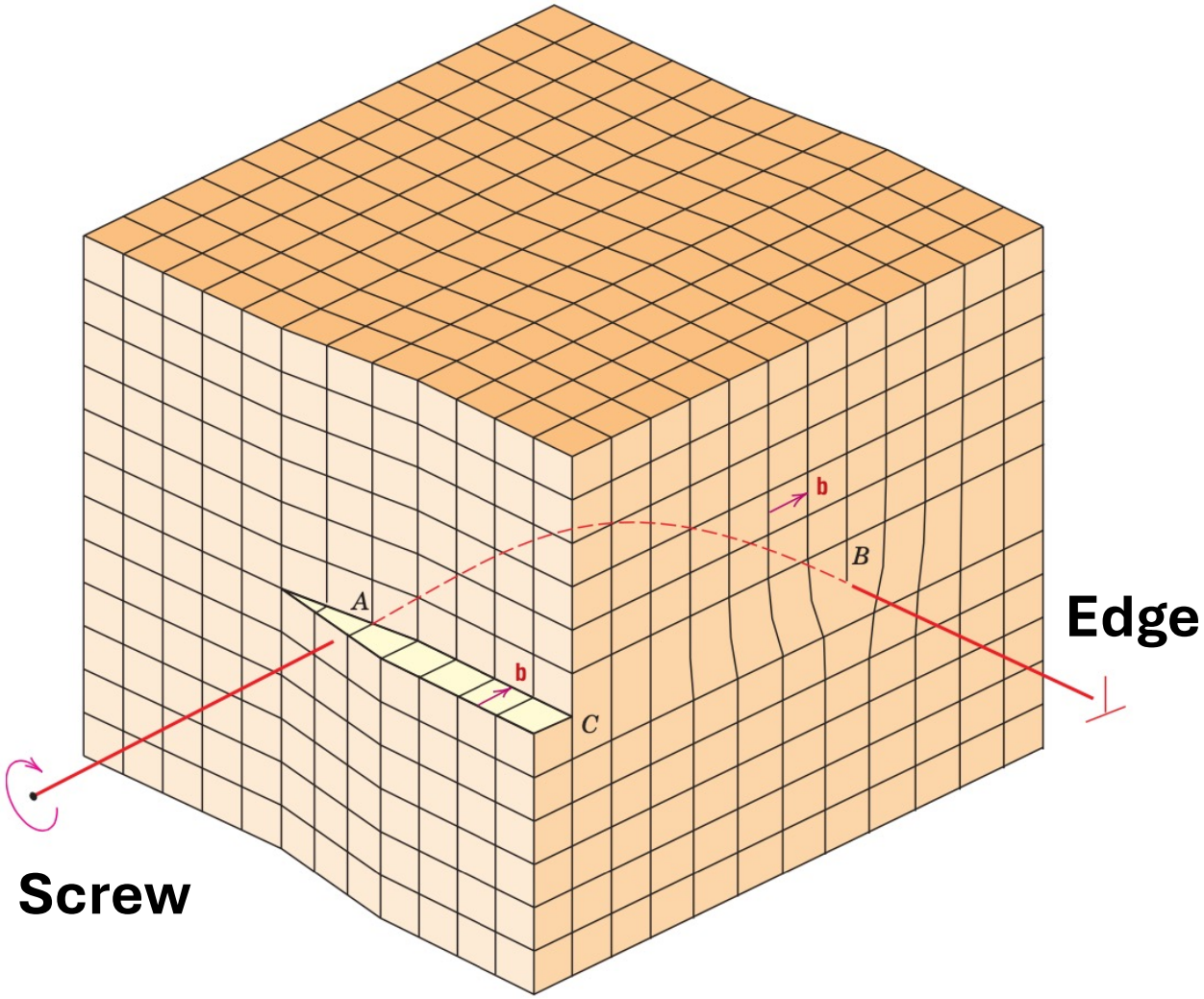
$\vec{b}$

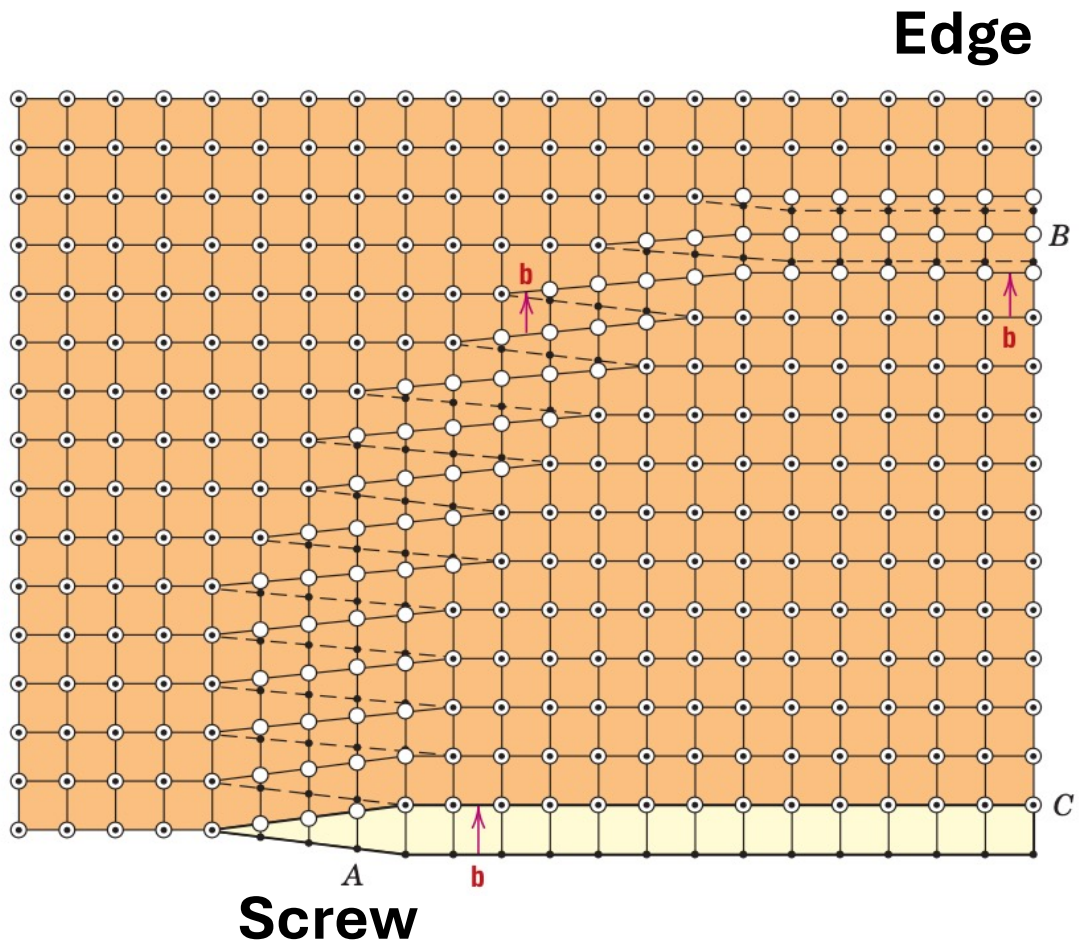
$\vec{L}$



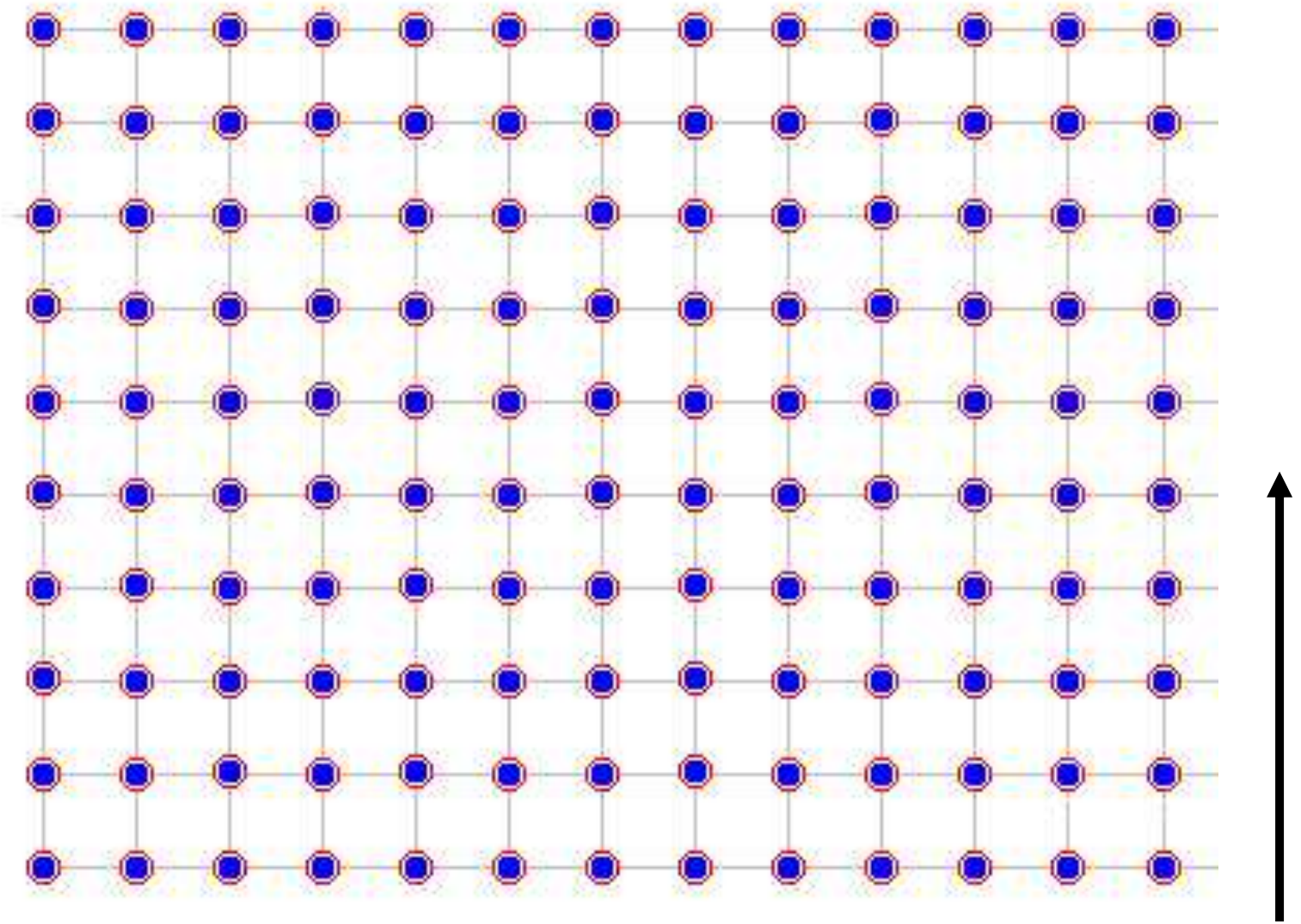
Screw

Mixed (edge + screw) dislocations



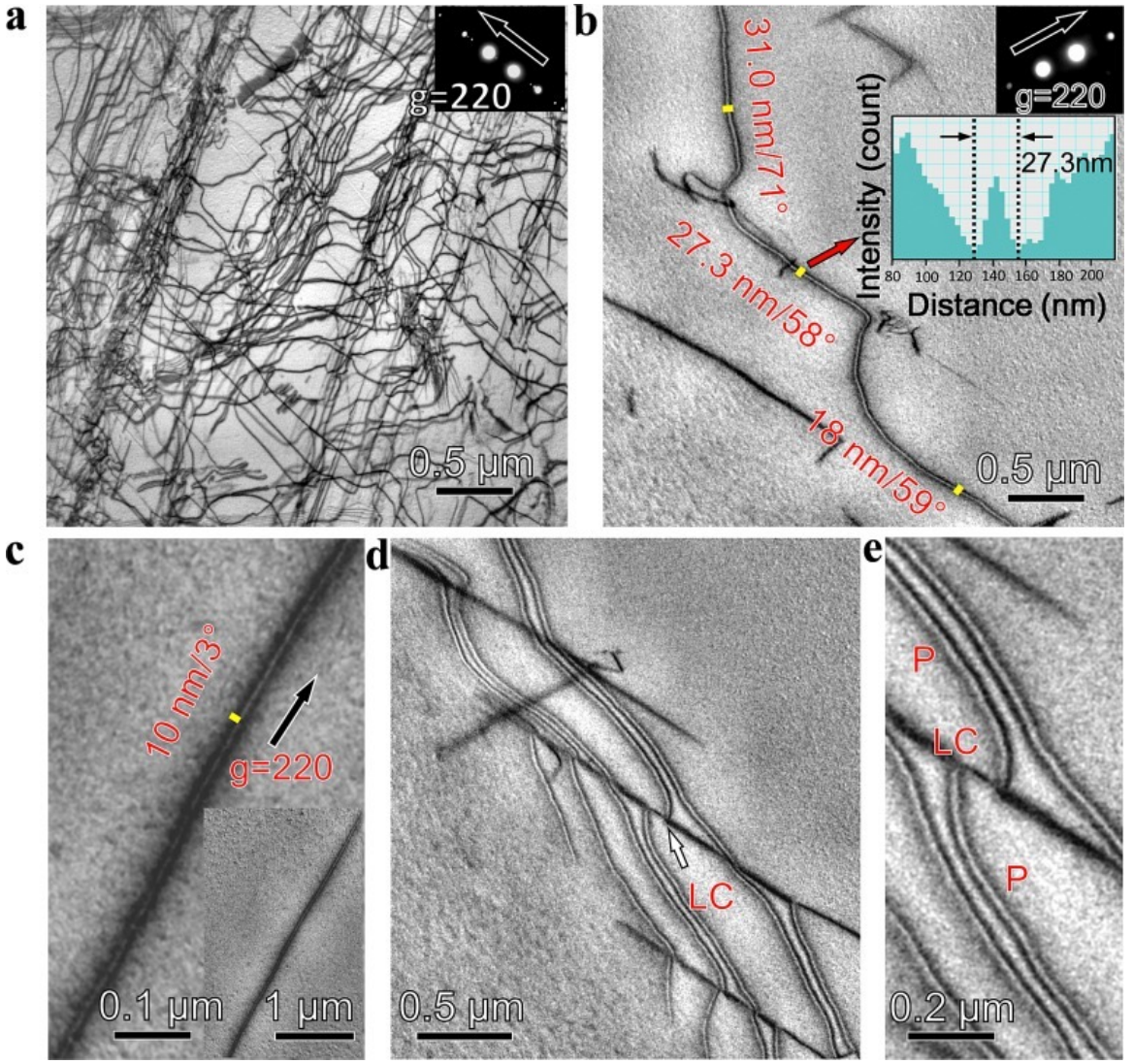


Mixed (edge + screw) dislocations



Mixed dislocations are very commonly observed



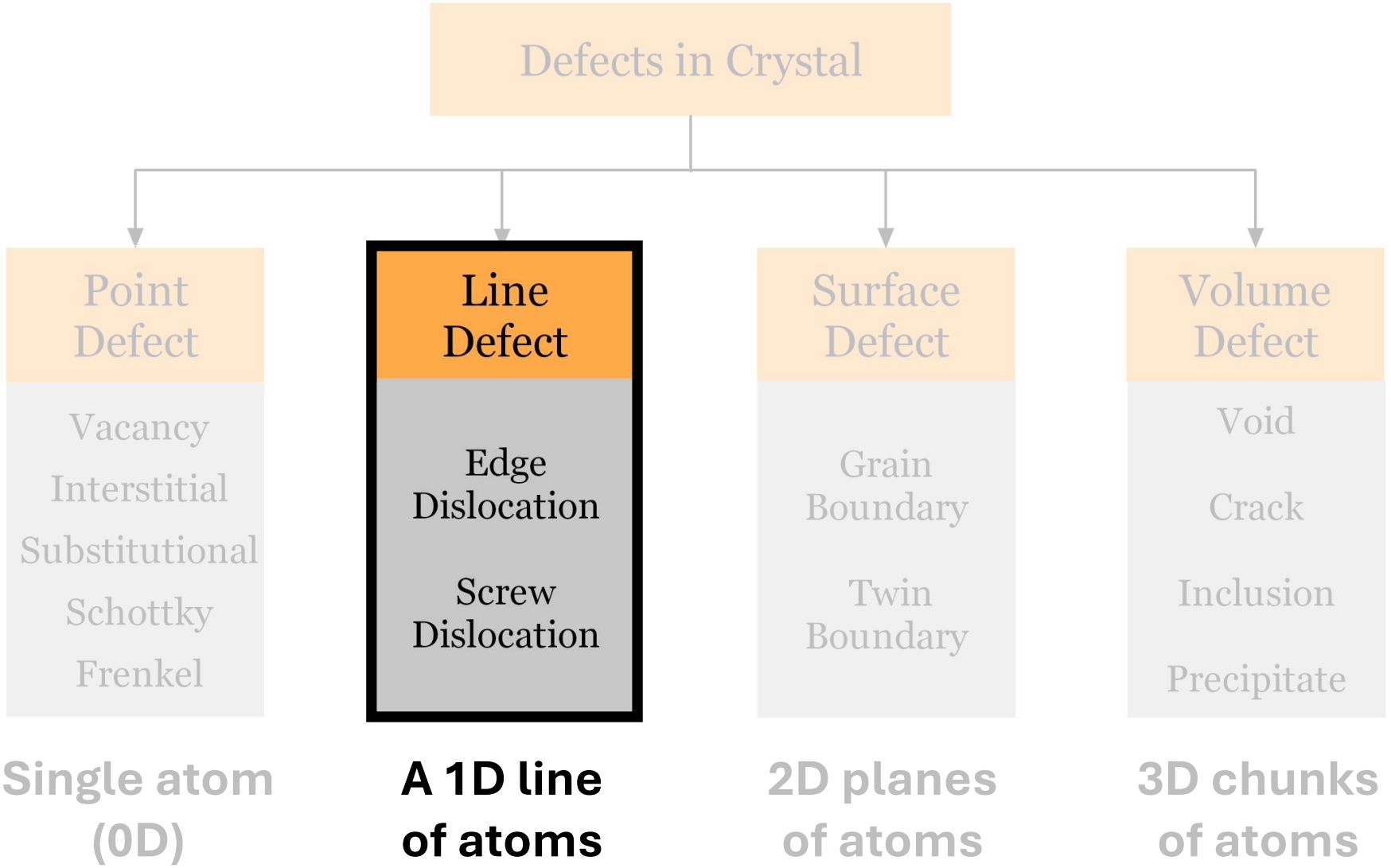


Mixed dislocations are very commonly observed

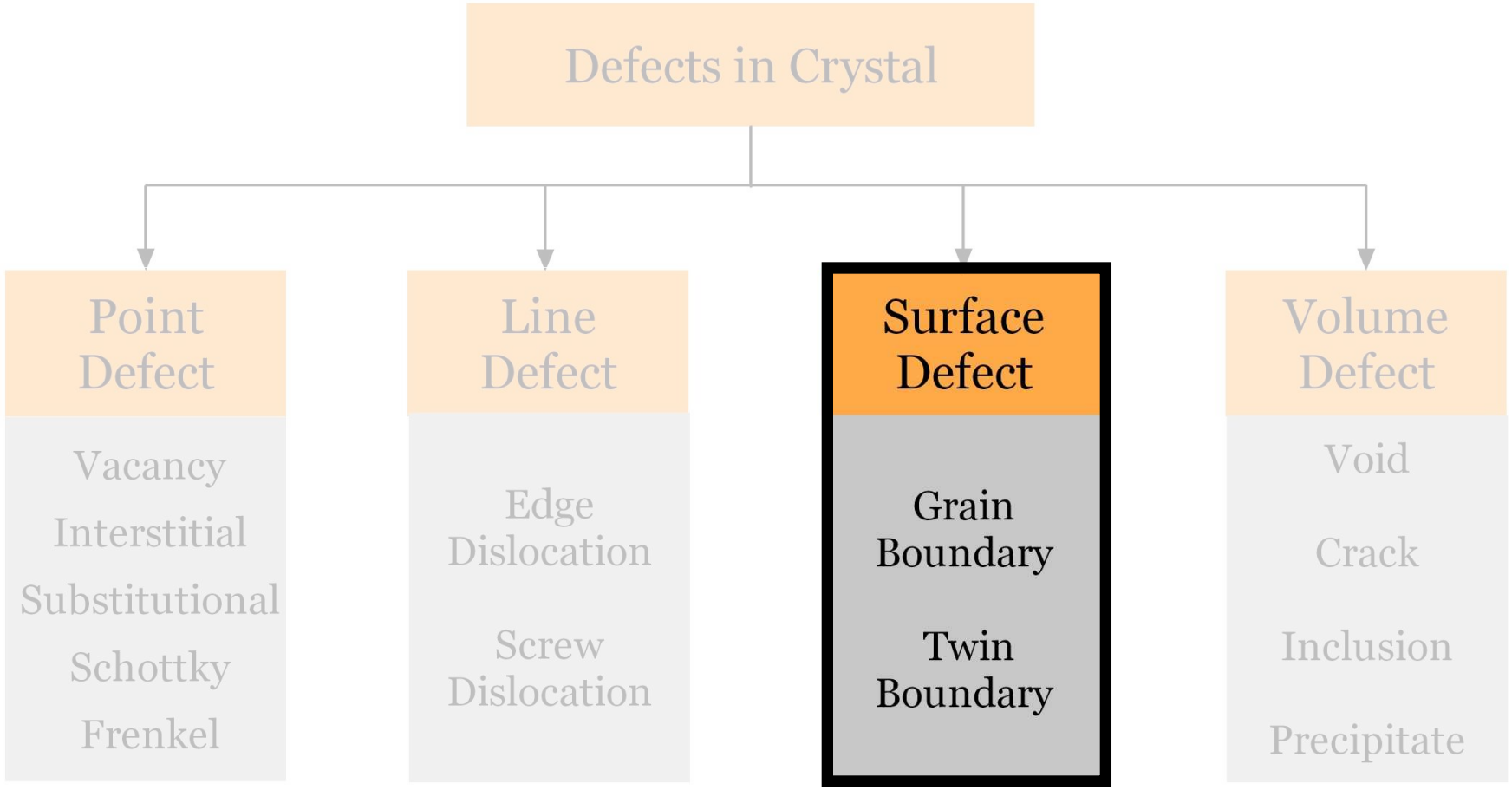


https://www.youtube.com/watch?v=BV1cxwxnhPs

From 1D (linear) to 2D (planar) defects



From 1D (linear) to 2D (planar) defects



Single atom (0D)

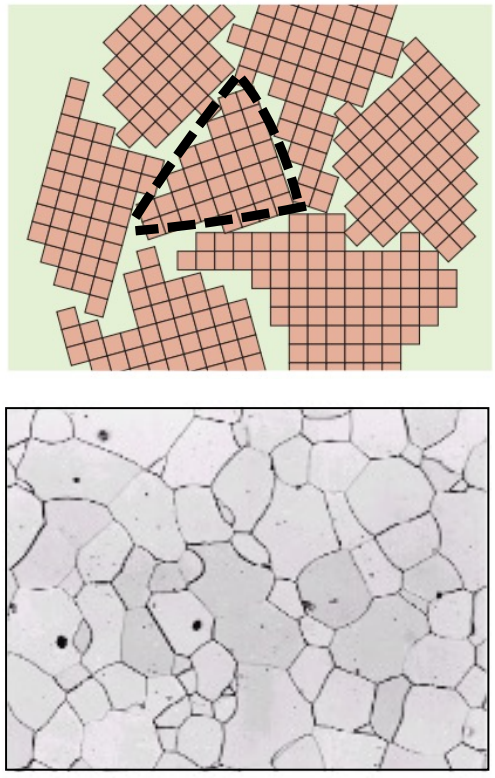
A 1D line of atoms

2D planes of atoms

3D chunks of atoms

Remember: *most* materials are polycrystalline





Grain structure

There are *boundaries* between these crystallographic grains…

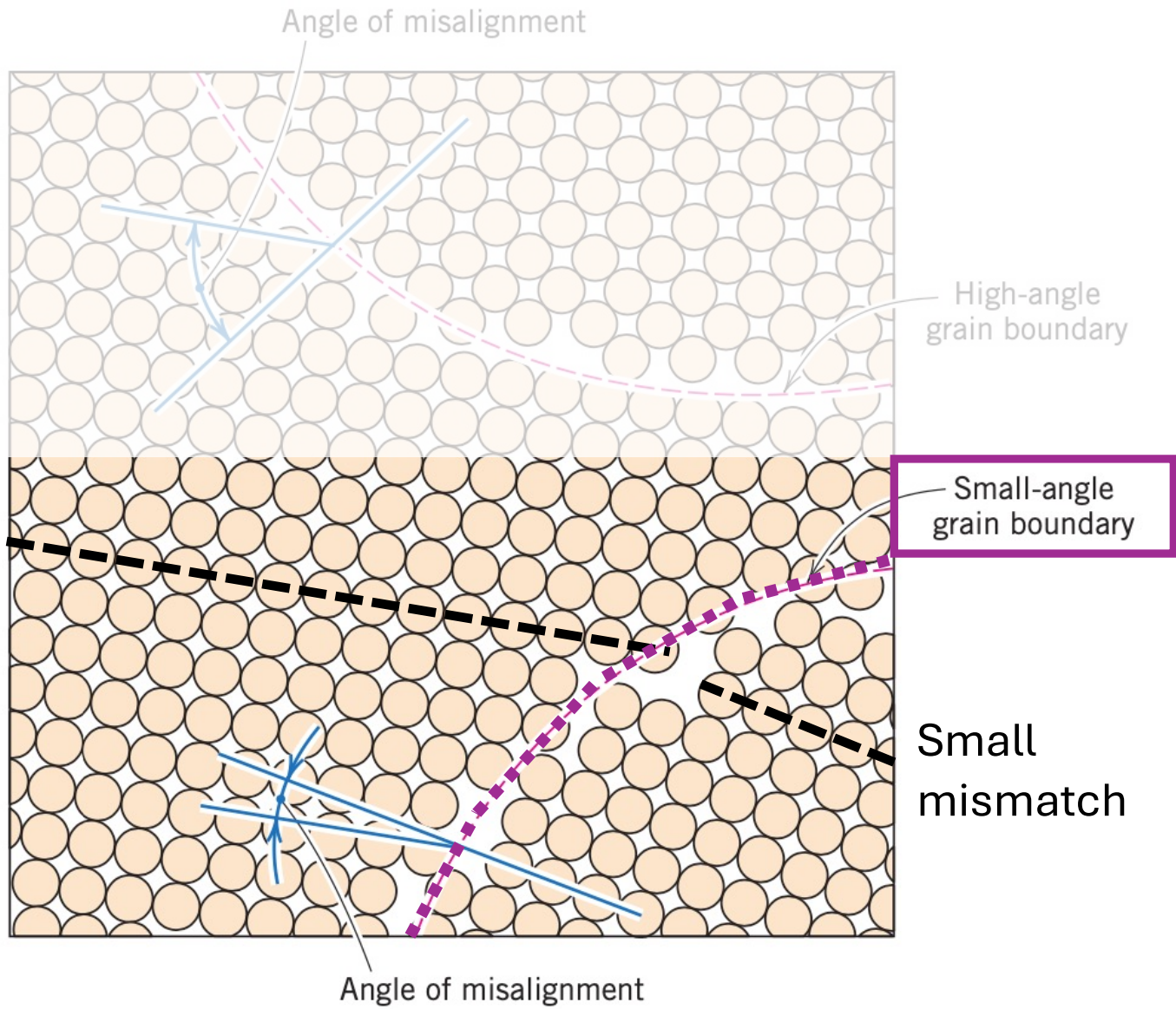
Cleverly named: **Grain Boundaries**

High- versus low-angle grain boundaries

Low-angle grain boundaries have reasonably small mismatch (< 15°) in their orientation

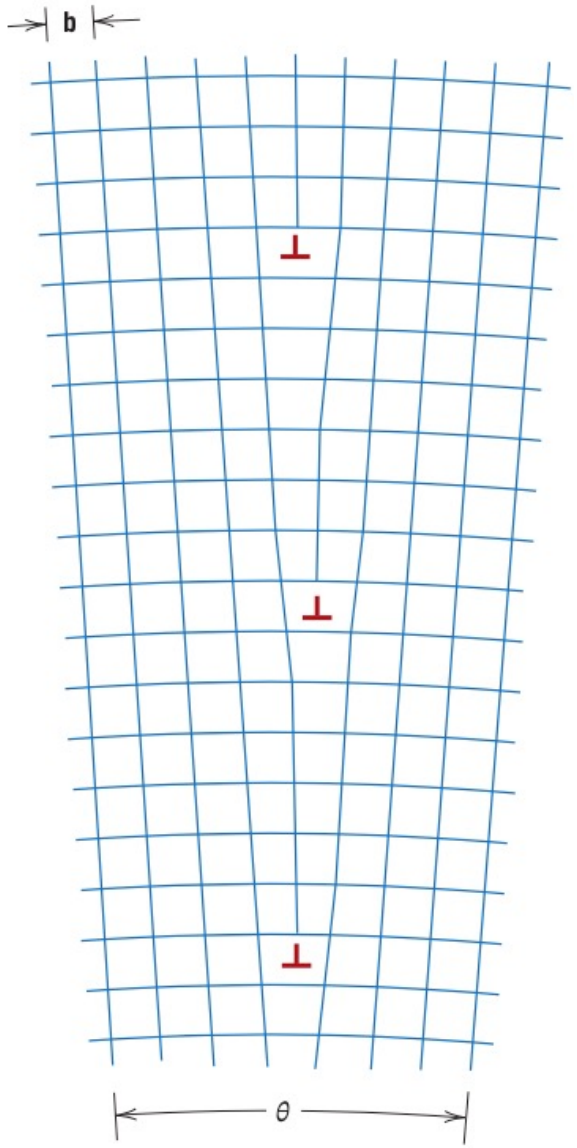
→ **Few broken bonds**

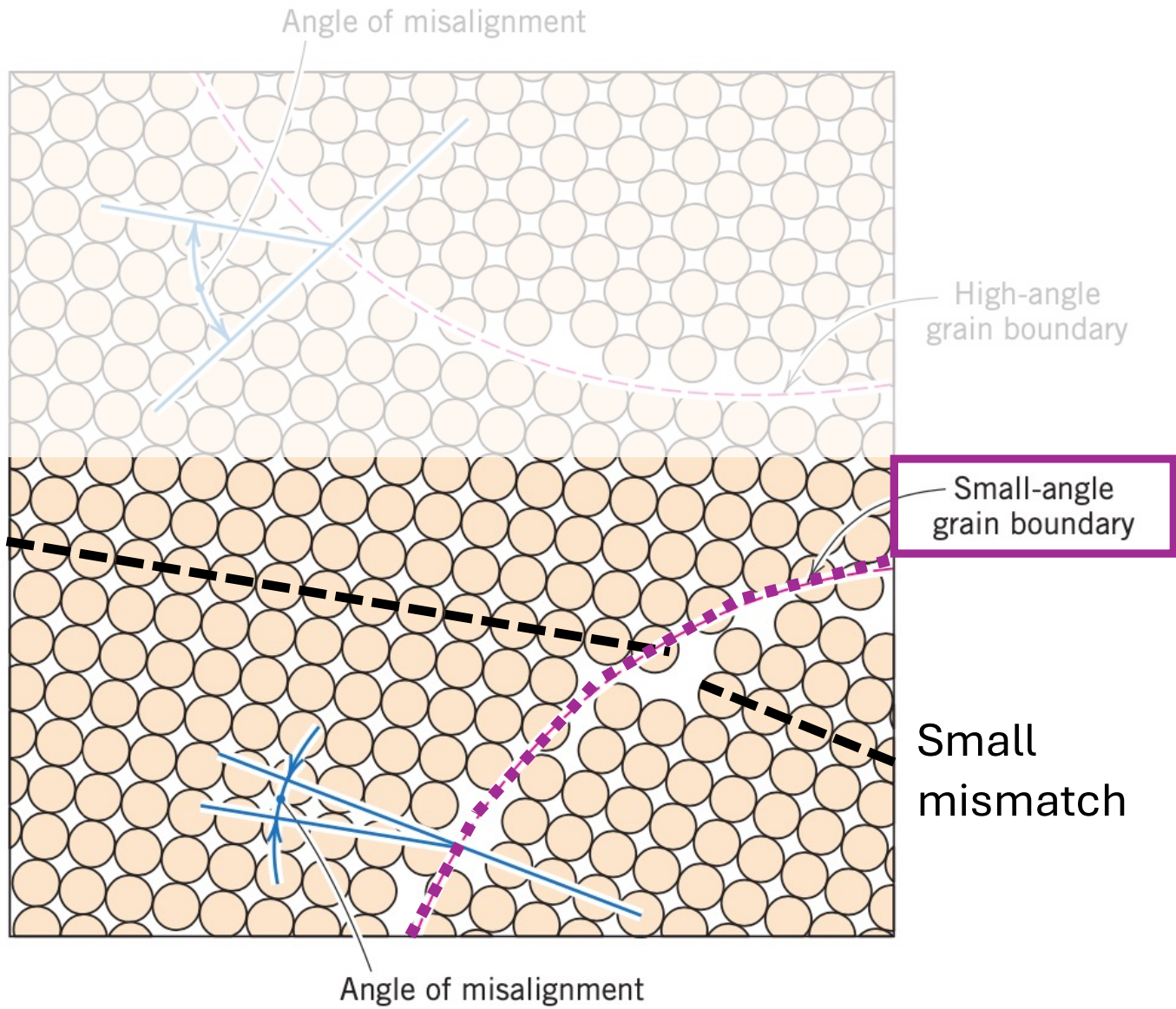
→ **Strong interfacial adhesion**



High- versus low-angle grain boundaries

Low-angle boundaries can may be viewed as a sequence of **edge dislocations**



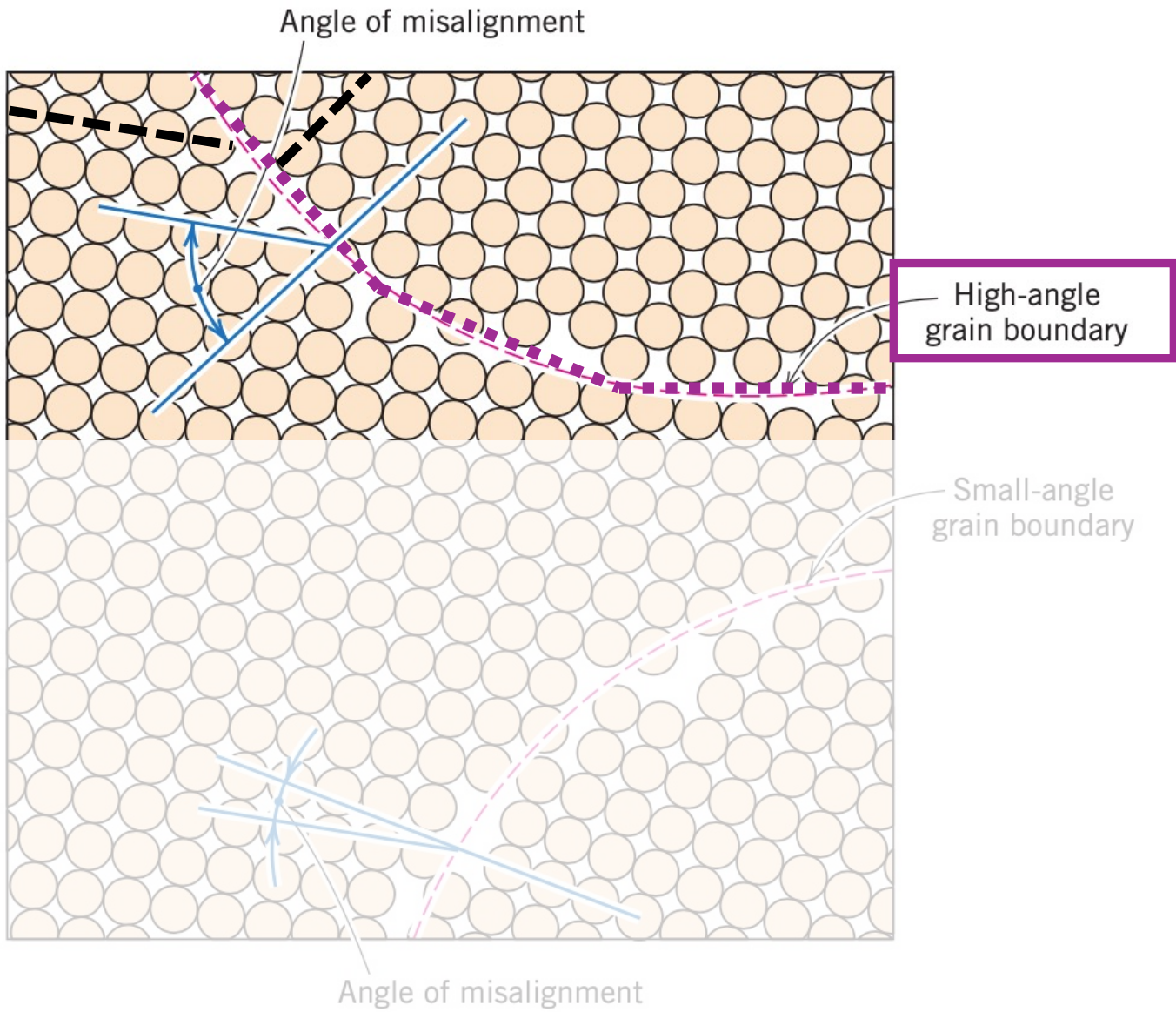


High- versus low-angle grain boundaries

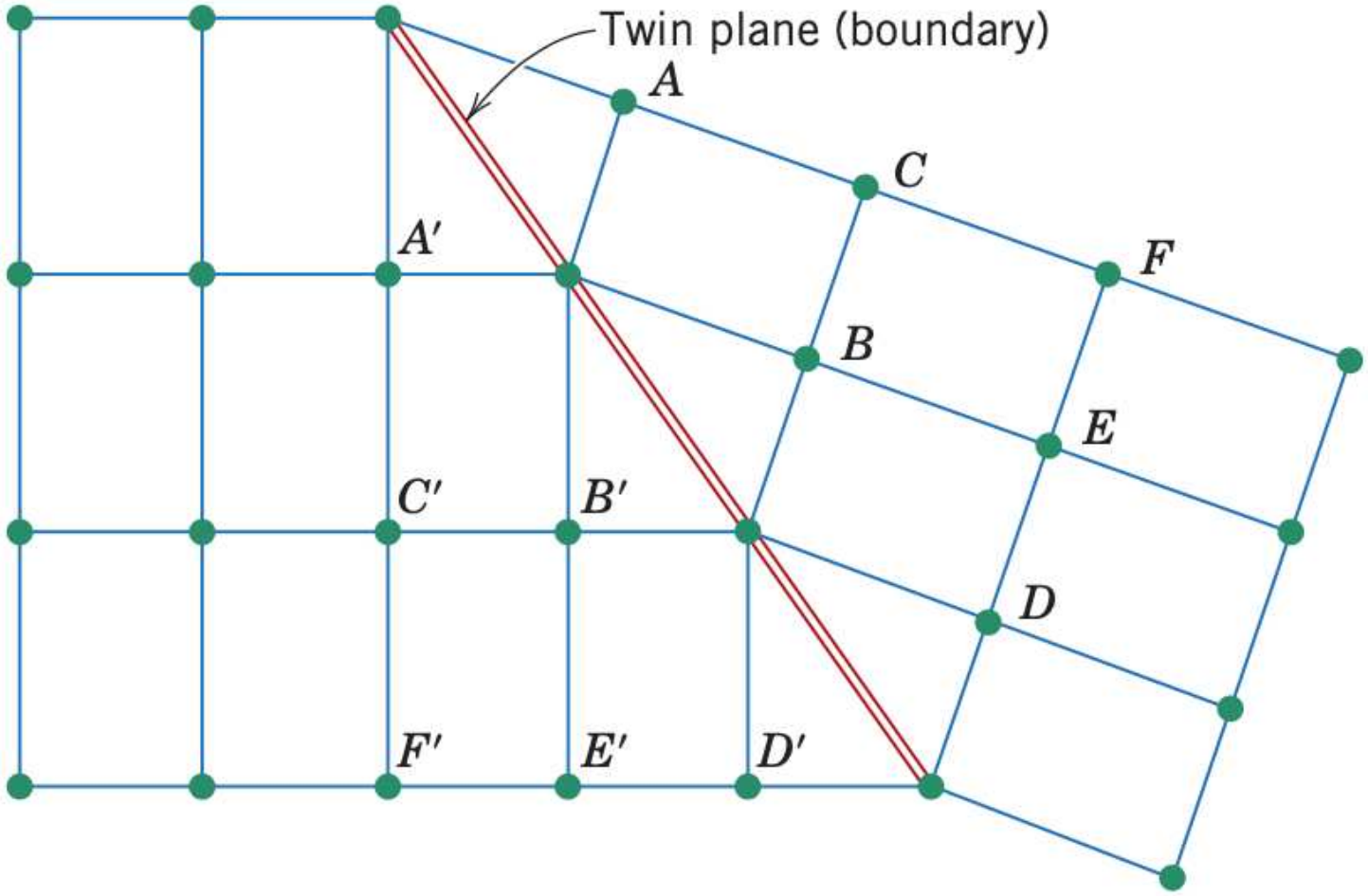
Low-angle grain boundaries have reasonably small mismatch (< 15°) in their orientation
→ **Few broken bonds**
→ **Strong interfacial adhesion**

High-angle grain boundaries have larger mismatch (< 15°)
→ **Many broken bonds**
→ **Weak(er) interfacial adhesion**

Note that even in this case, there can *still* be very strong adhesion at the interface! Think of steel…



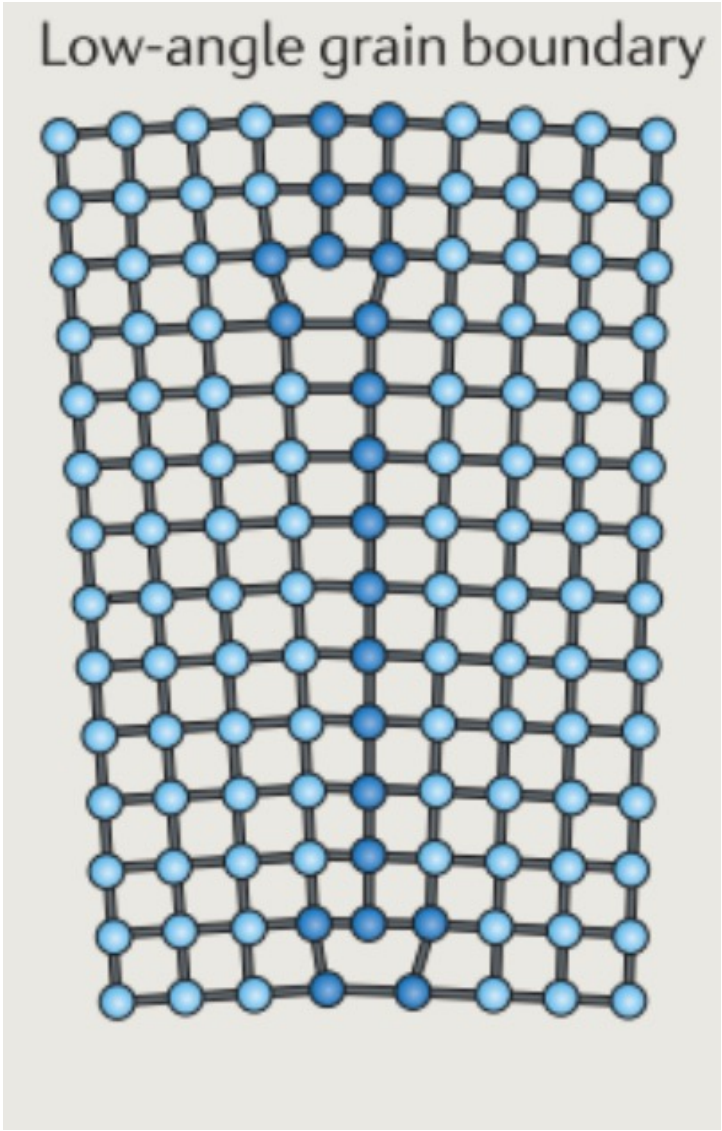
Twin boundaries are special cases of GBs

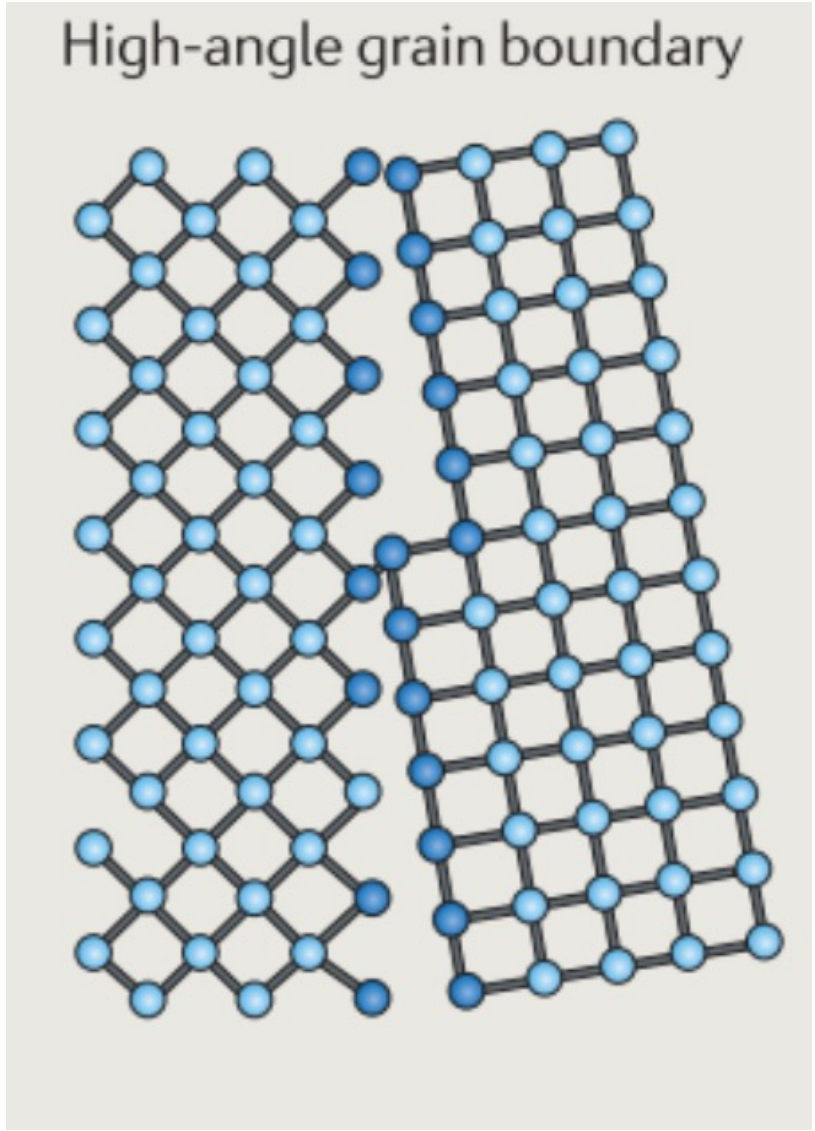


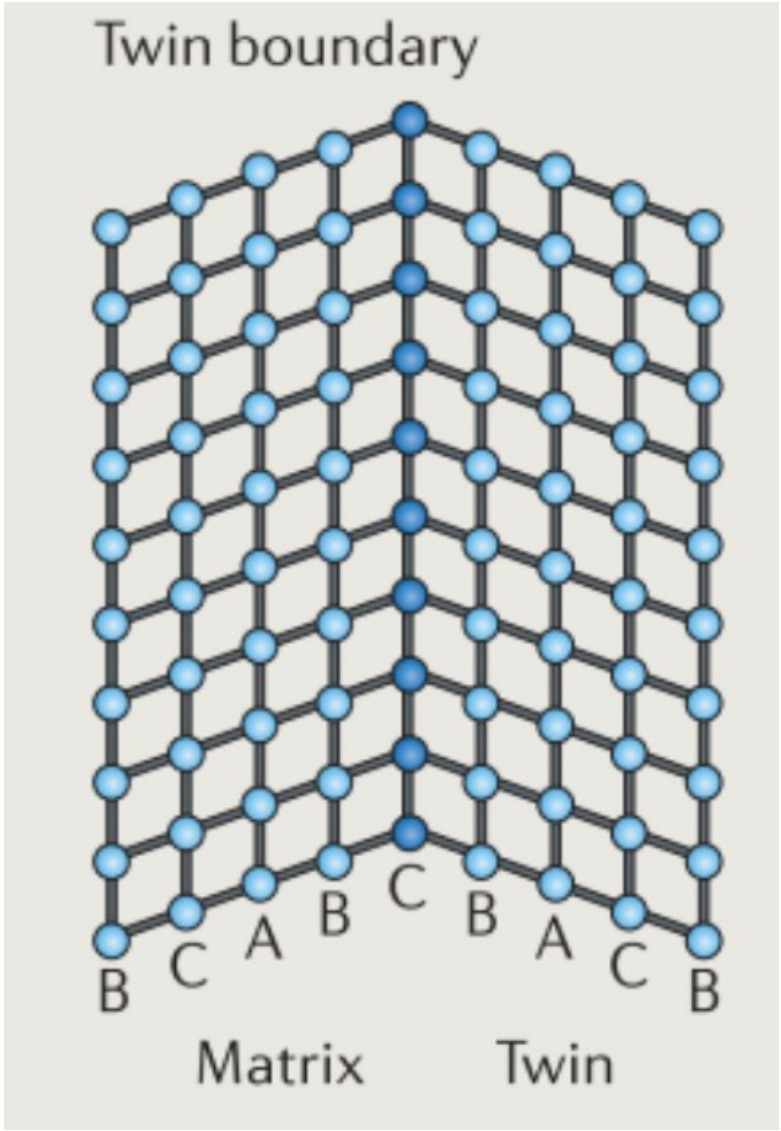
This angle of misorientation is high, yet there is still **perfect nearest-neighbor bonding at the interface**

This is what's known as a **twin boundary** → it has *mirror symmetry* on either side of the interface

Twin boundaries are special cases of GBs

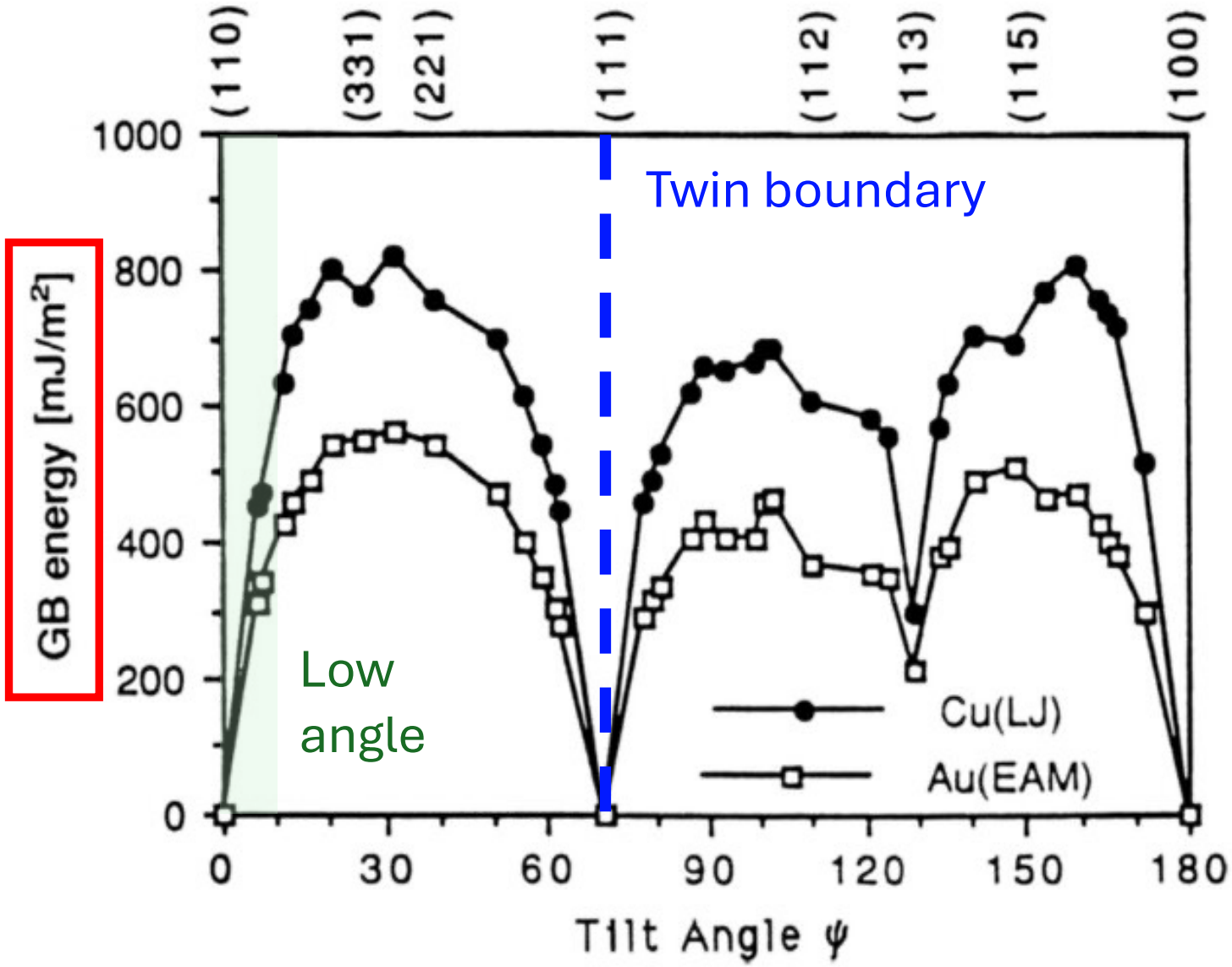




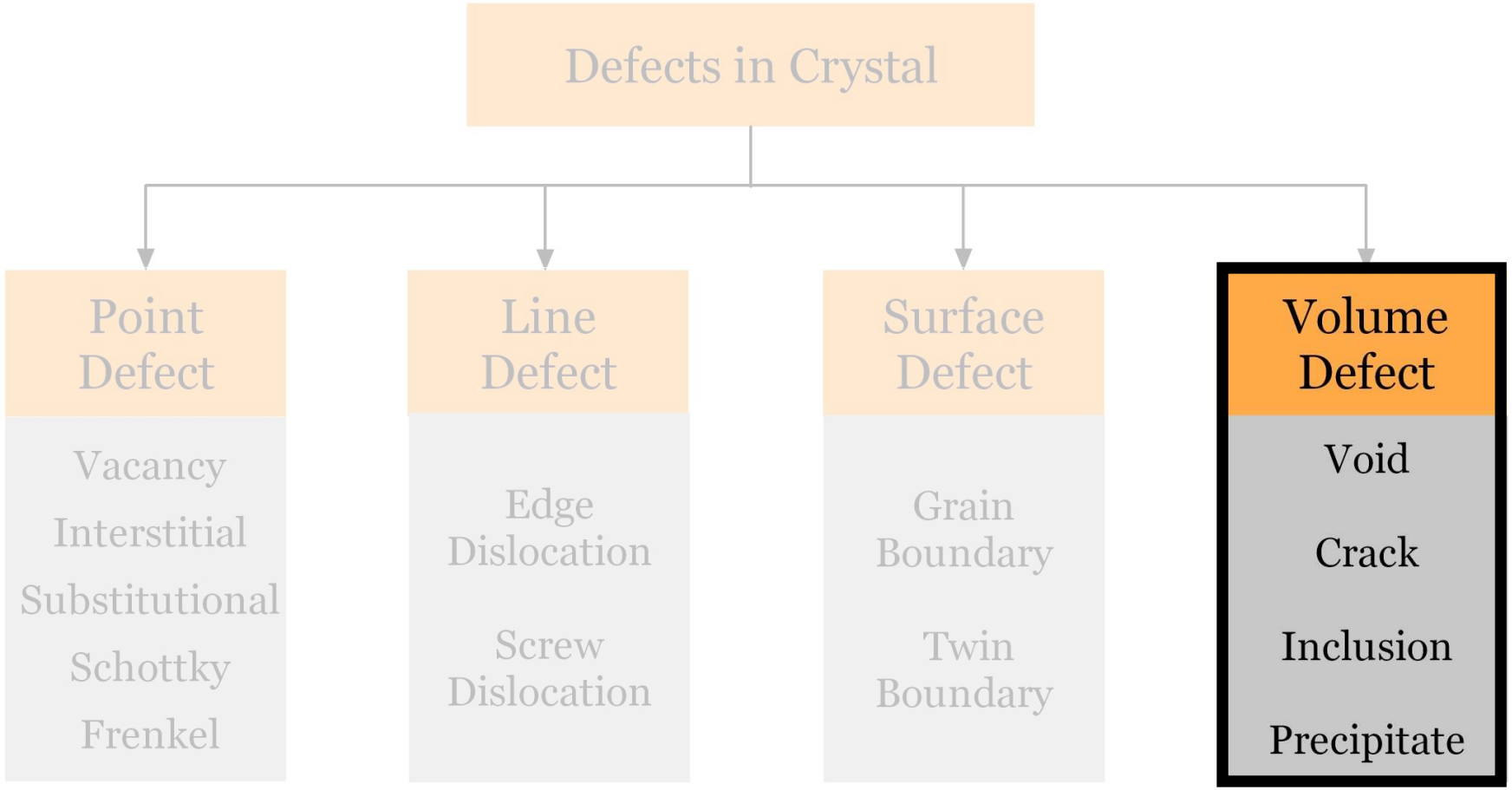


Twin boundaries are special cases of GBs

Measure excess energy at the interface

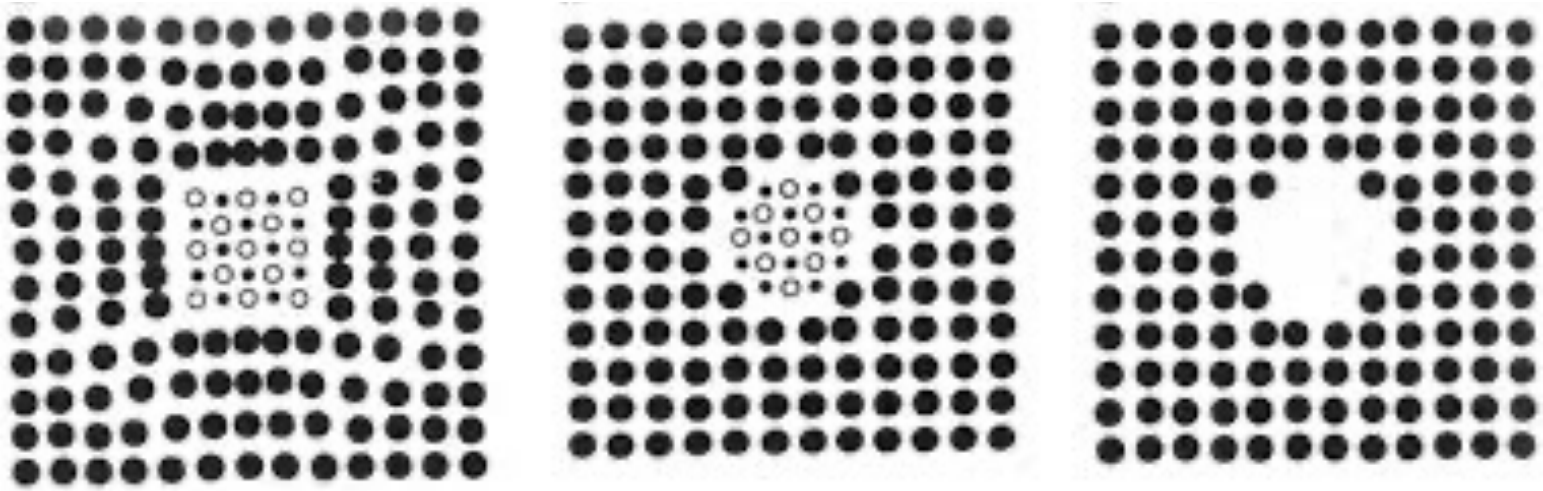


From 2D (planar) to 3D (volume) defects



From 2D (planar) to 3D (volume) defects

These are fairly straightforward: just think of them as “holes” or ”extra stuff” in the material



Volume Defect

Void

Crack

Inclusion

Precipitate

3D chunks of atoms

Characterizing 2D and 3D defects

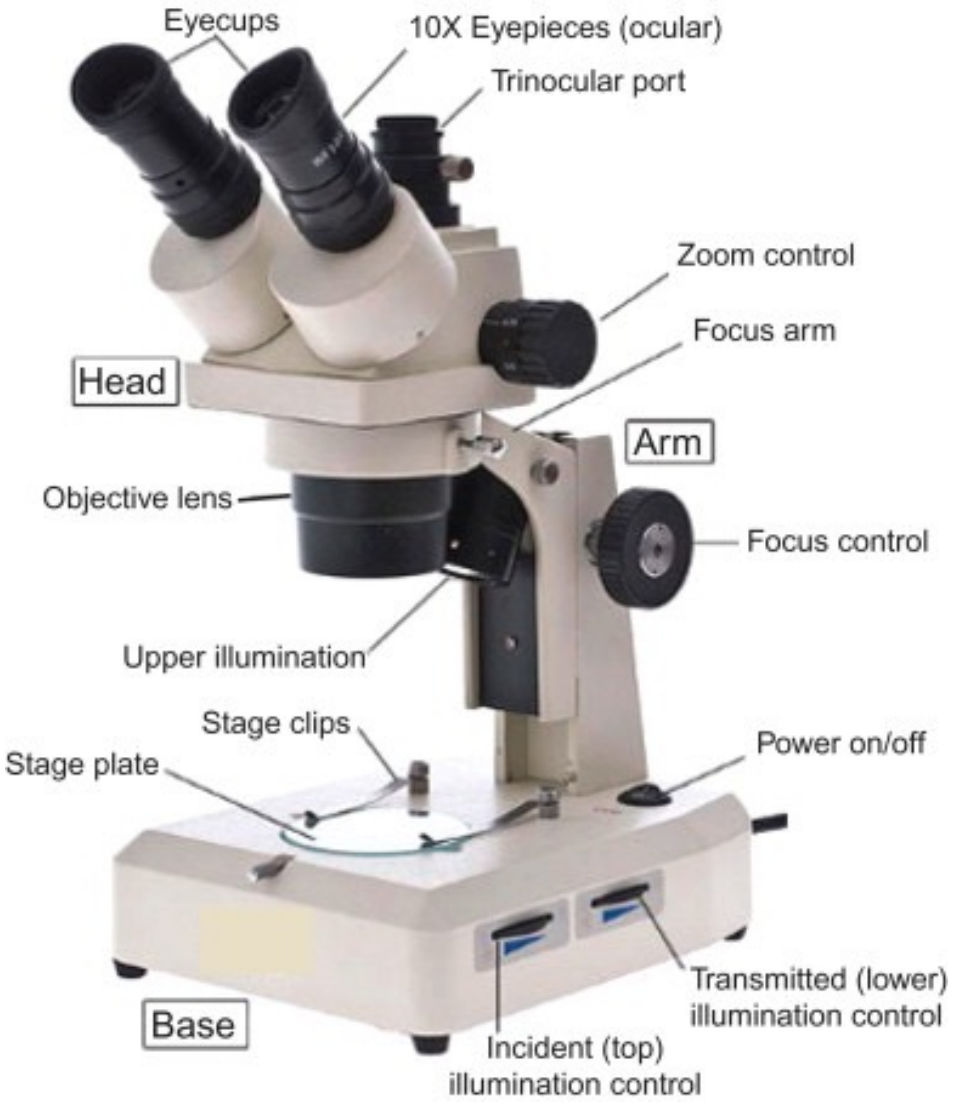


Grain structure (microstructure) is important. How do we observe it?

Surface Defect
Grain Boundary
Twin Boundary

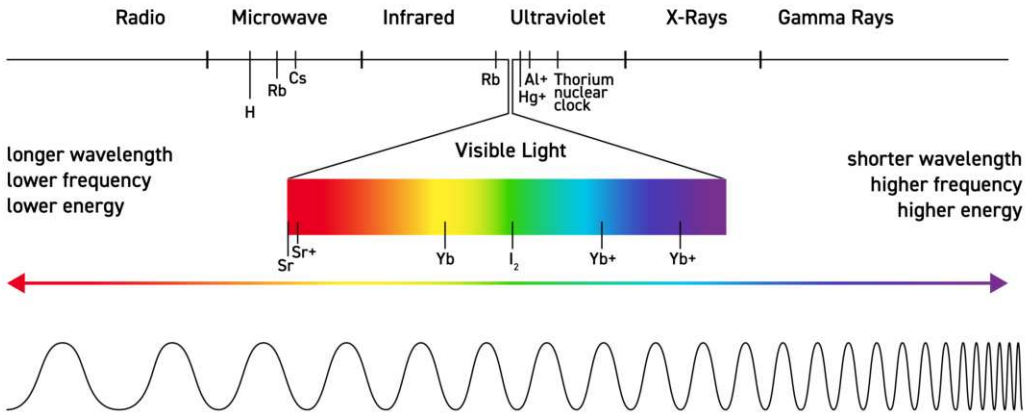
Volume Defect
Void
Crack
Inclusion
Precipitate

Optical microscopy: basic principles

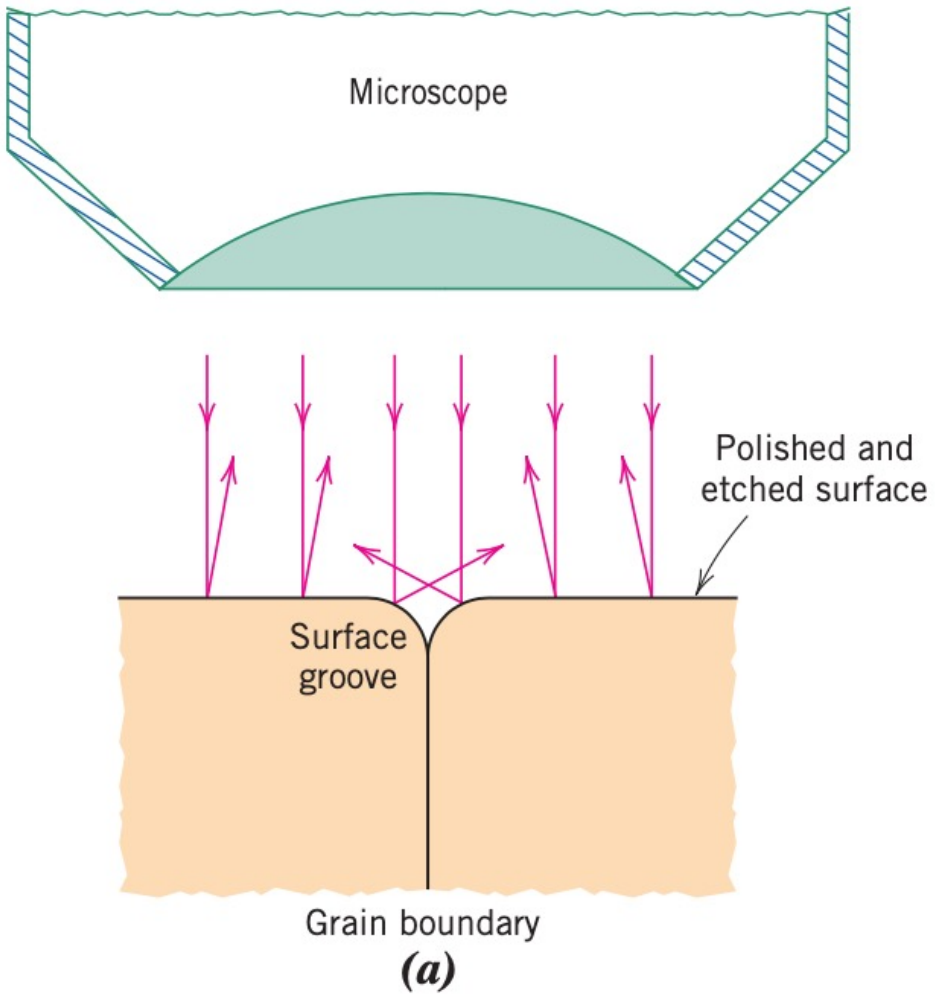


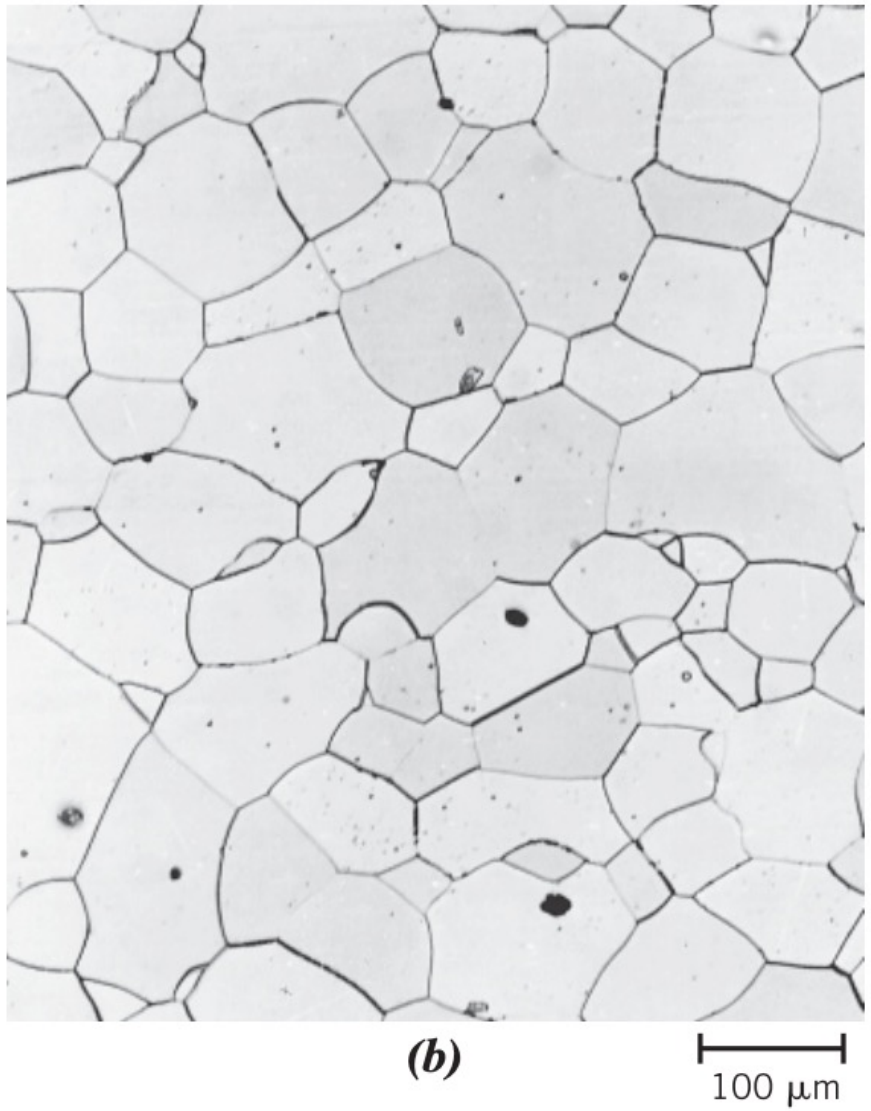
This is probably what you think of when you hear "microscopy"

Uses the interaction between **visible light ($\lambda \approx$ 340-750 nm)** and matter to visualize its structure



Optical microscopy: visualizing microstructure



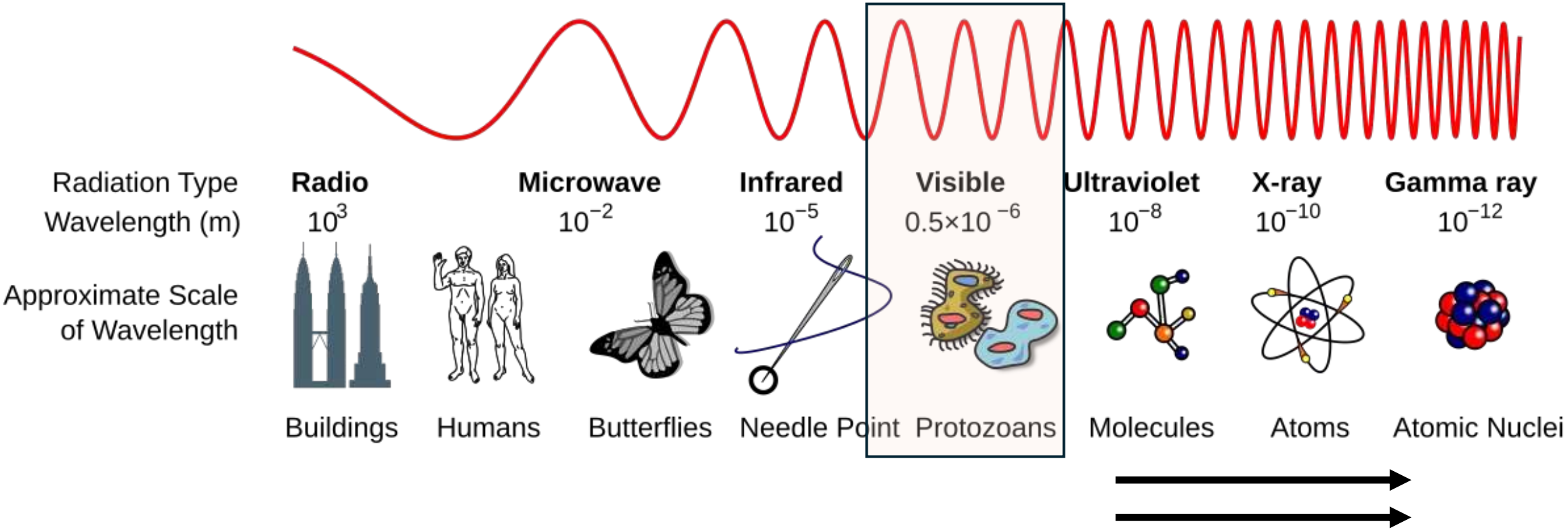


Grain boundaries appear as dark lines in optical microscopy since they **scatter light differently**

Good for 2D defects, not so much for the much smaller 0D and 1D defects

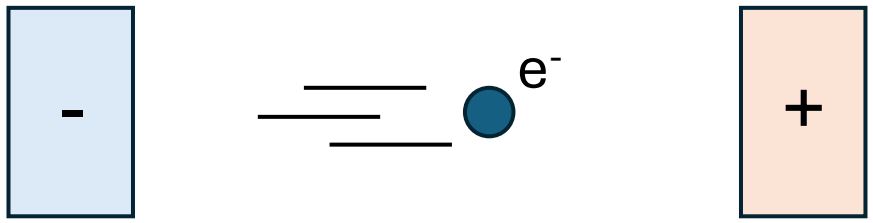
Limitations of optical microscopy

Visible light has a wavelength on the order of **~100 nm**, which ***cannot*** **be used to probe individual atoms or defects**



We need something with a shorter wavelength

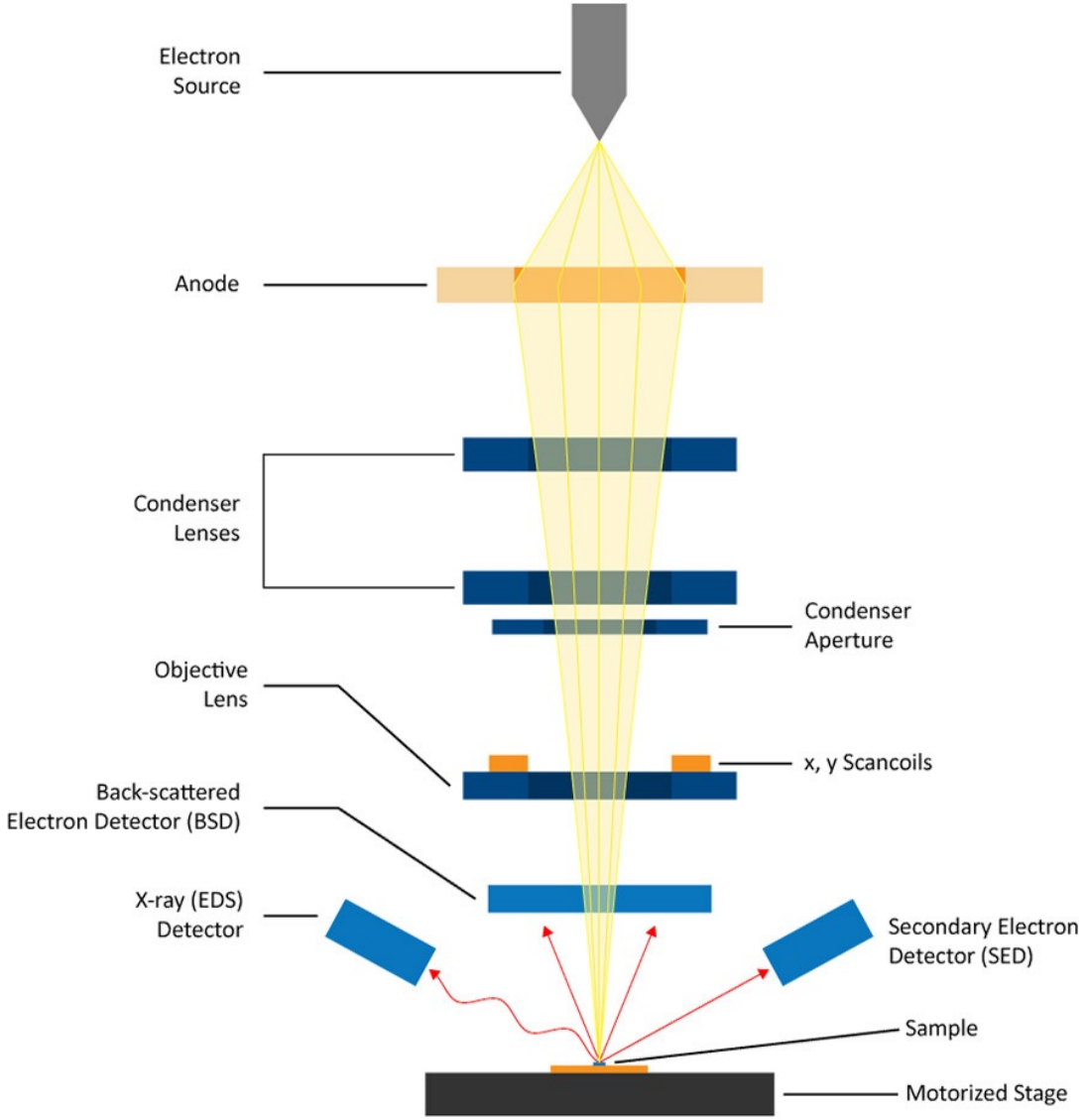
Electron microscopy gives much higher magnification



De Broglie wavelength:
$\lambda = hp$

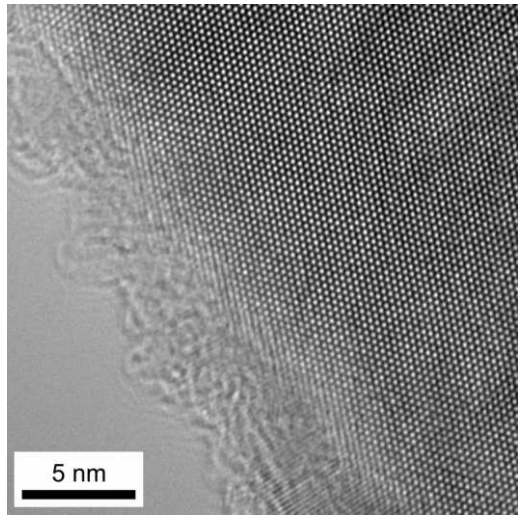
With a high enough momentum (p), **electrons have a wavelength < 1 nm**

Gives magnification as high as 1,000,000×



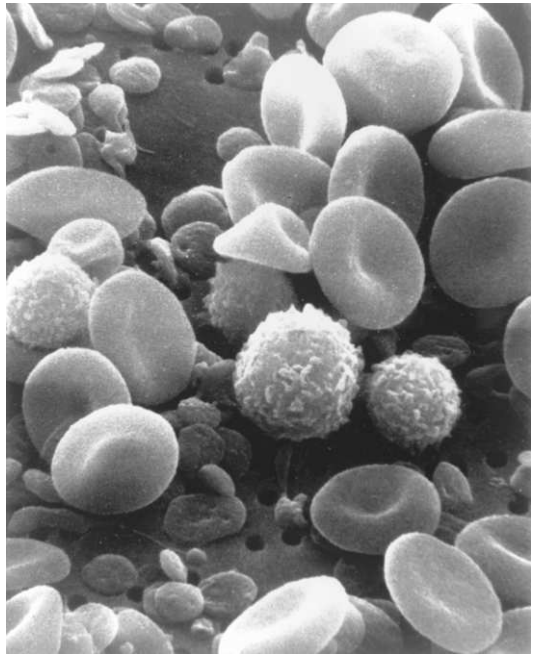
Electron microscopy gives much higher magnification

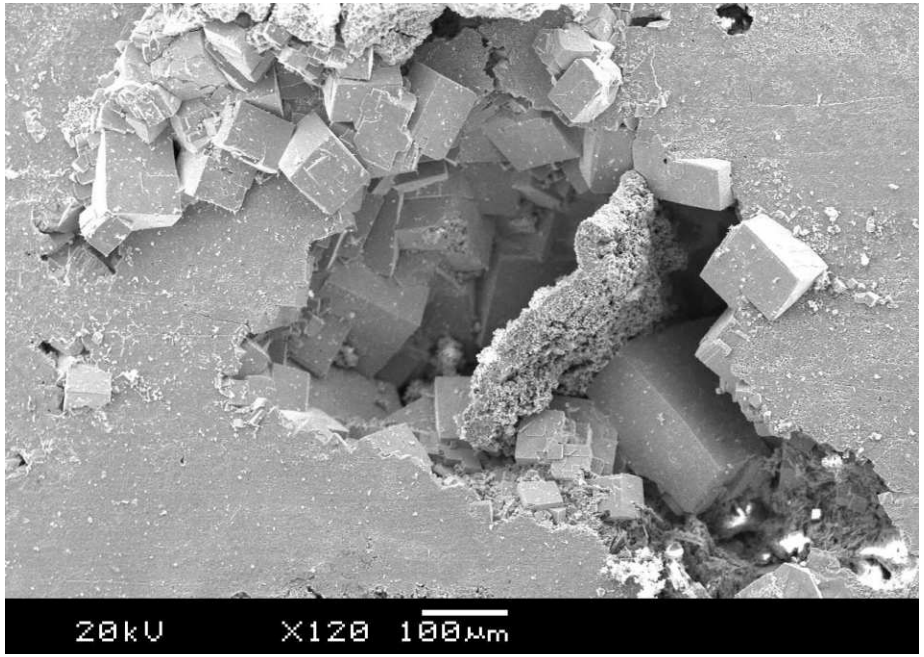
TEM images

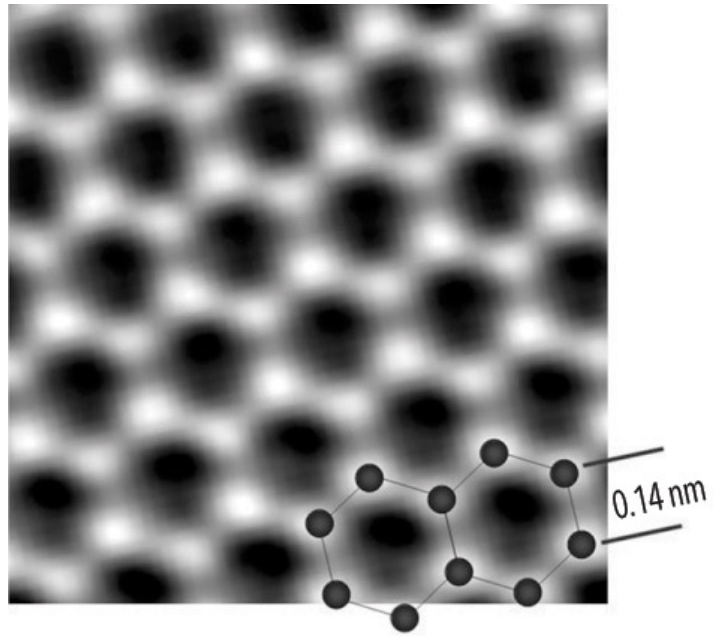




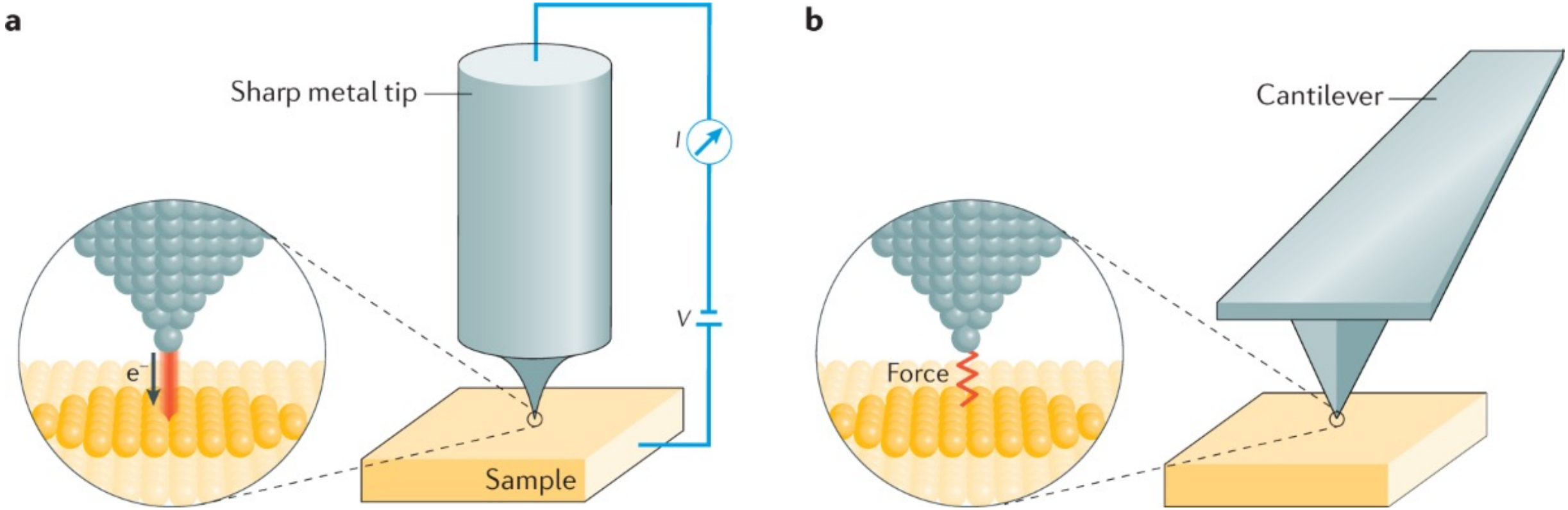
SEM images





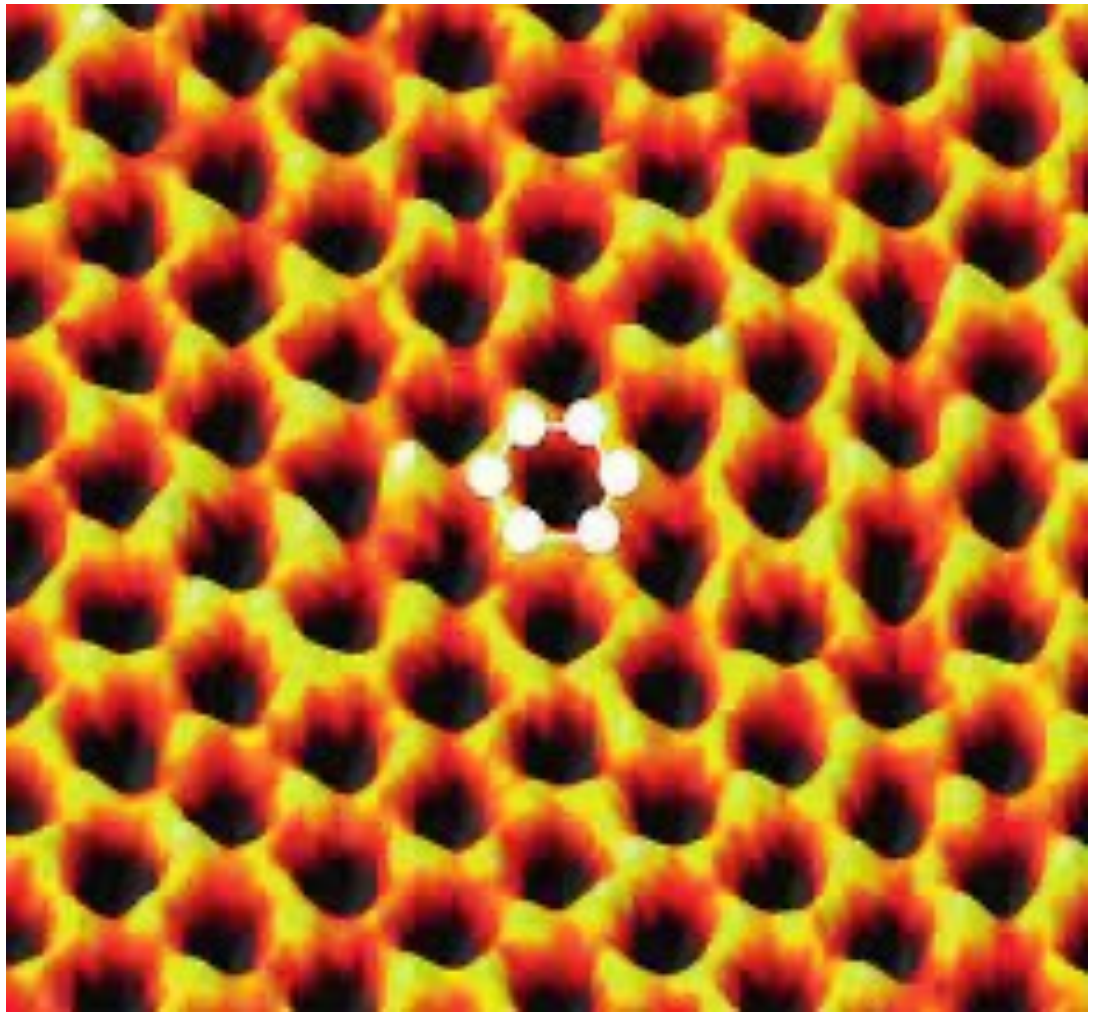


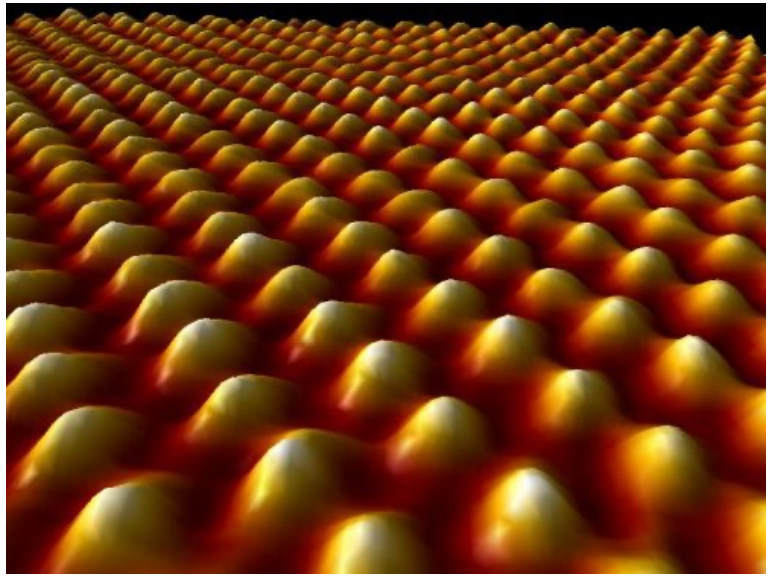
Another option: Scanning probe microscopy



In SPM, you run a very narrow tip over the surface and monitor its deflection

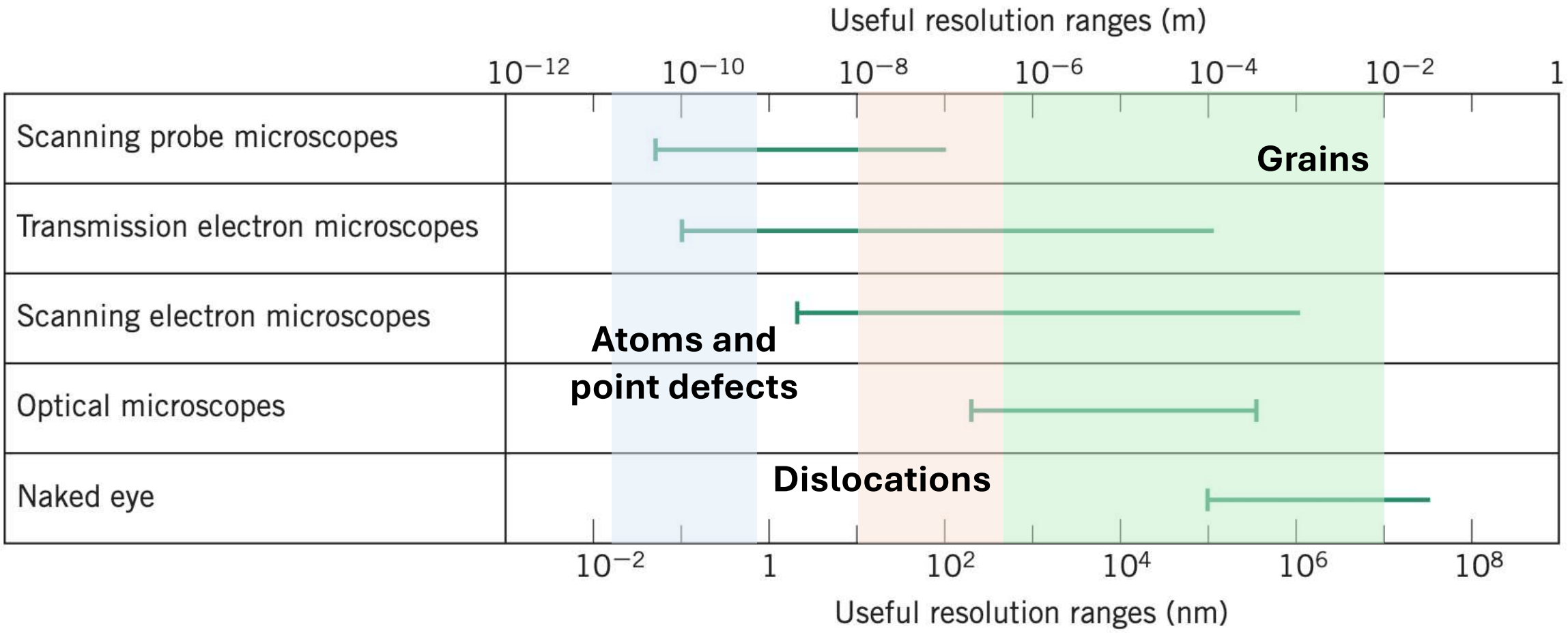
Another option: Scanning probe microscopy





SPM results in **topographic** data with atomic resolution

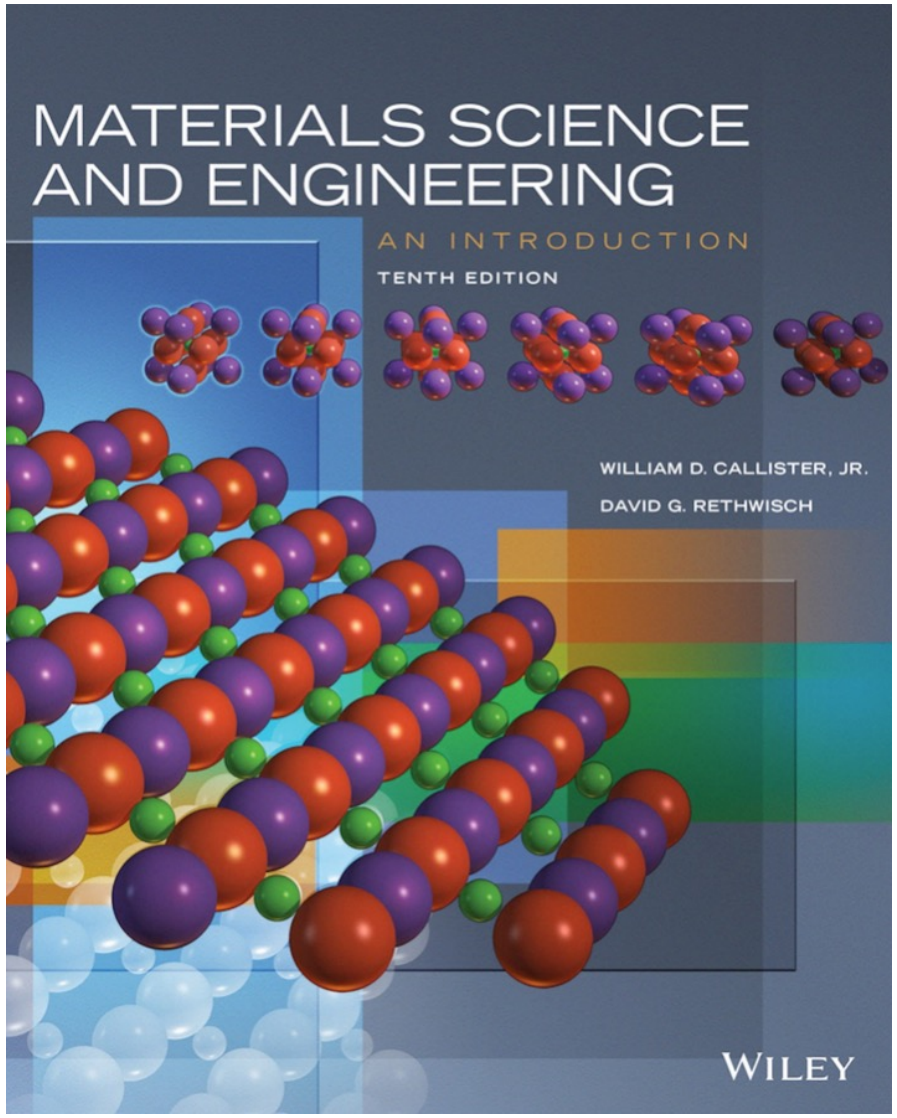
Summary of microscopic techniques



Any questions?

...Let's see how much time we have...

Reading for this subject



Chapter 5 Diffusion

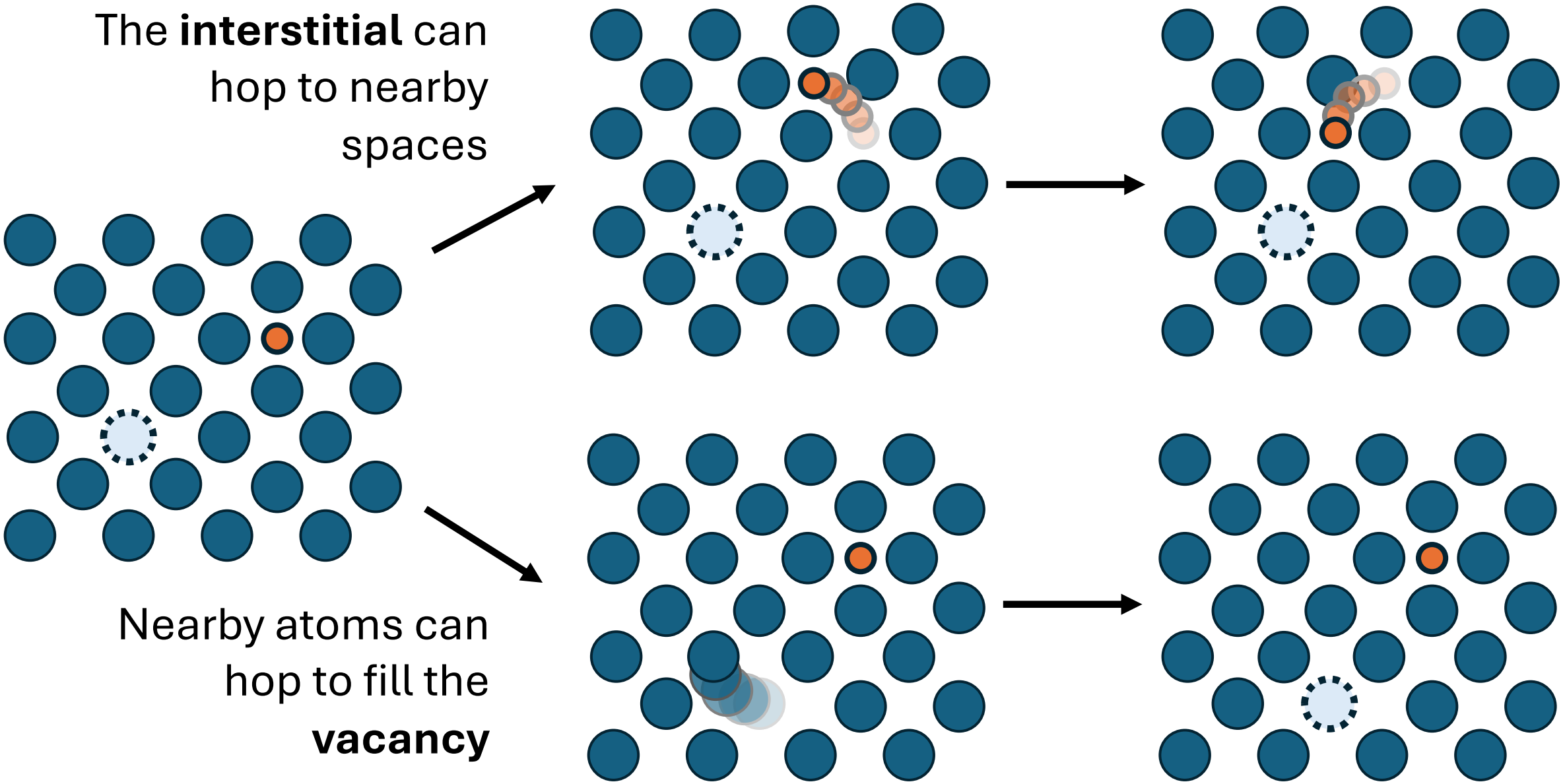
This discussion will closely follow **Chapter 5** of Callister, **pages 122-139** of the 10th edition.

Supplementary Texts:

- *Diffusion in Solids* by Shewman
- *Kinetics of Materials* by Balluffi

Motion of point defects

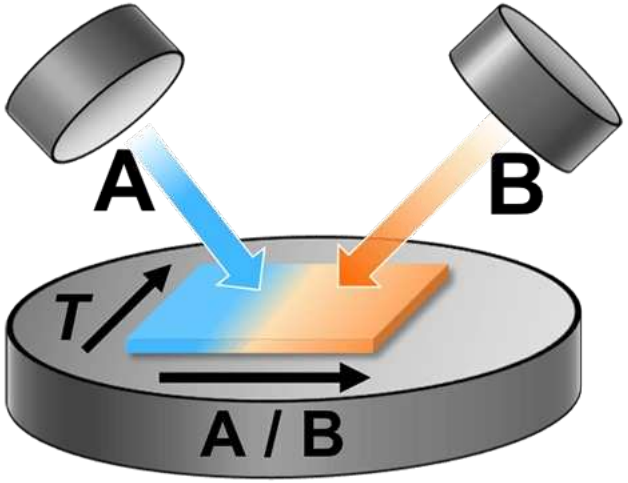
The **interstitial** can hop to nearby spaces



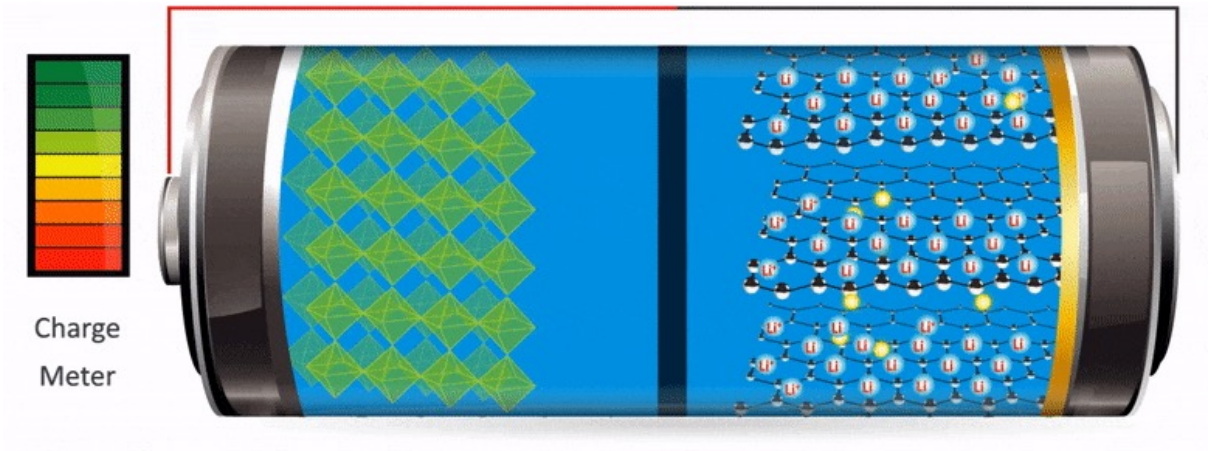
Nearby atoms can hop to fill the **vacancy**

Motion of point defects = *Diffusion*

Diffusion is the transport of mass by atomic motion – very prevalent!



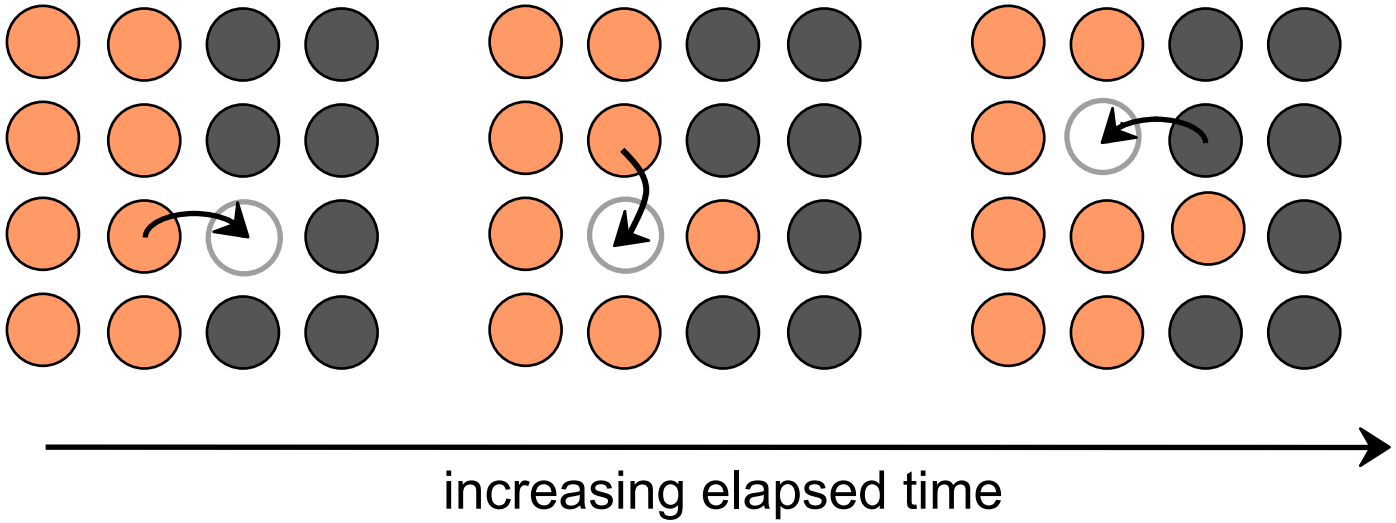




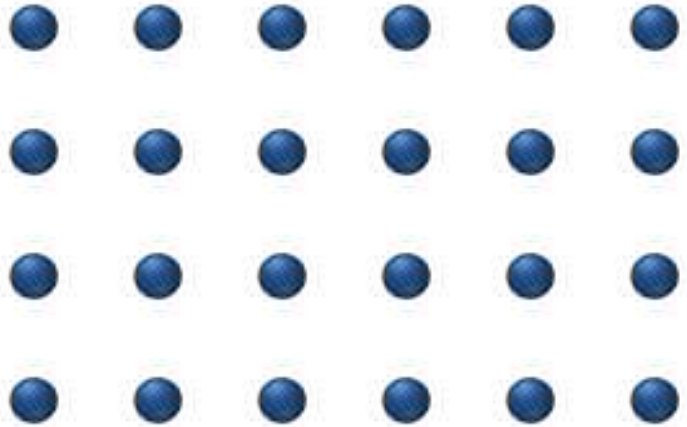


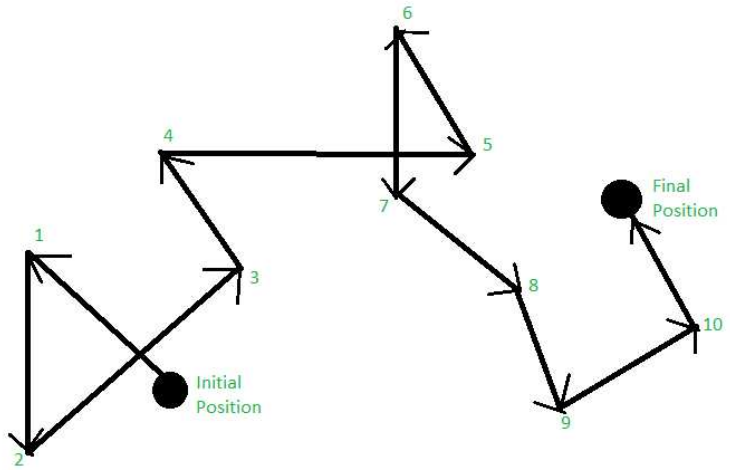
What causes diffusion to occur?

Vacancy diffusion



Interstitial diffusion





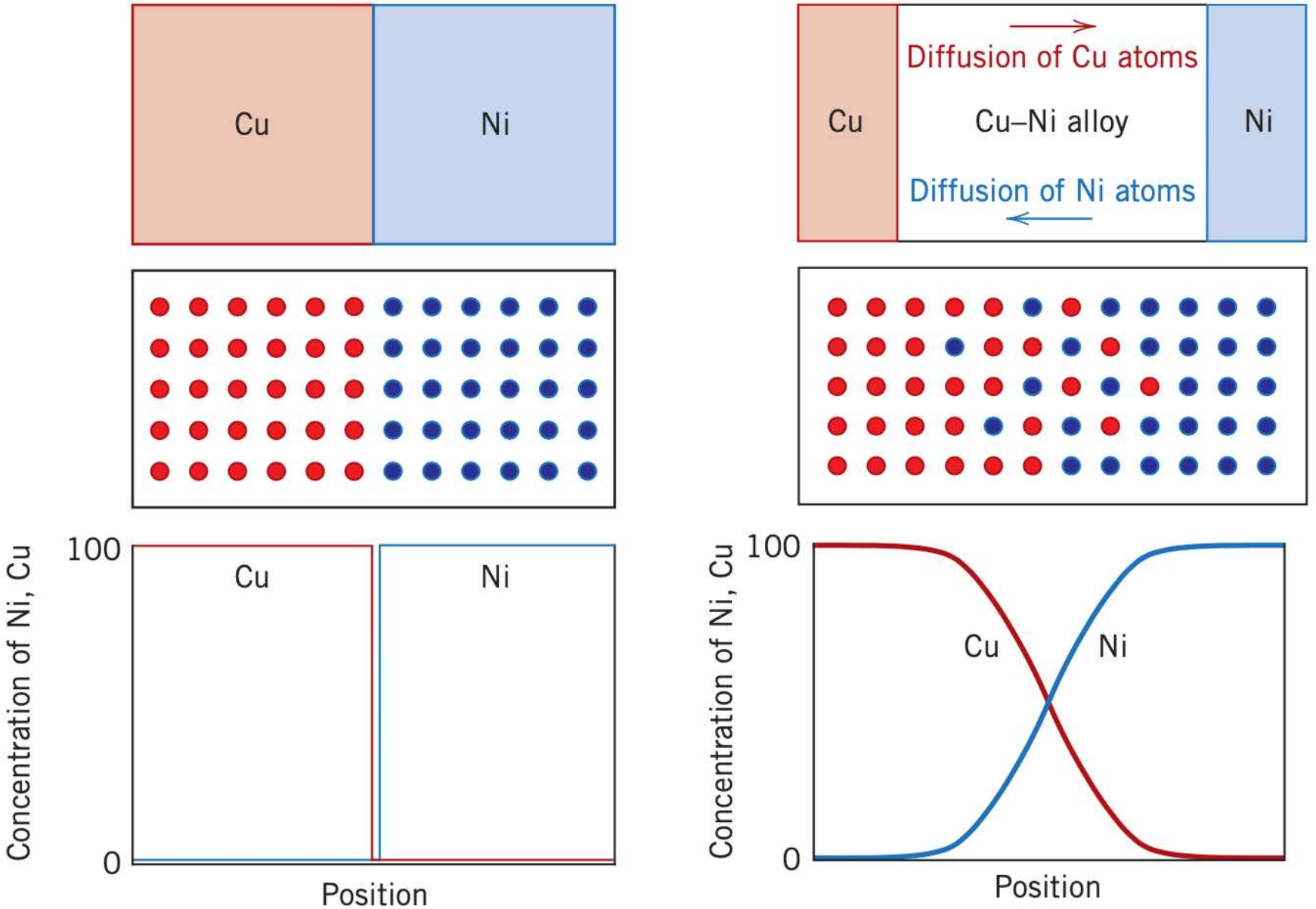
- **Thermal motion** causes defects to “hop around”
- If these hops were to happen randomly, there would (on average) be no net displacement
- But often there is a **driving force for diffusion**

One driving force: a difference in concentration



MIT Open Courseware: https://www.youtube.com/watch?v=j4m0Ye5Qgcg

One driving force: a difference in concentration



Atoms tend to migrate from regions of high concentration to regions oflow concentration

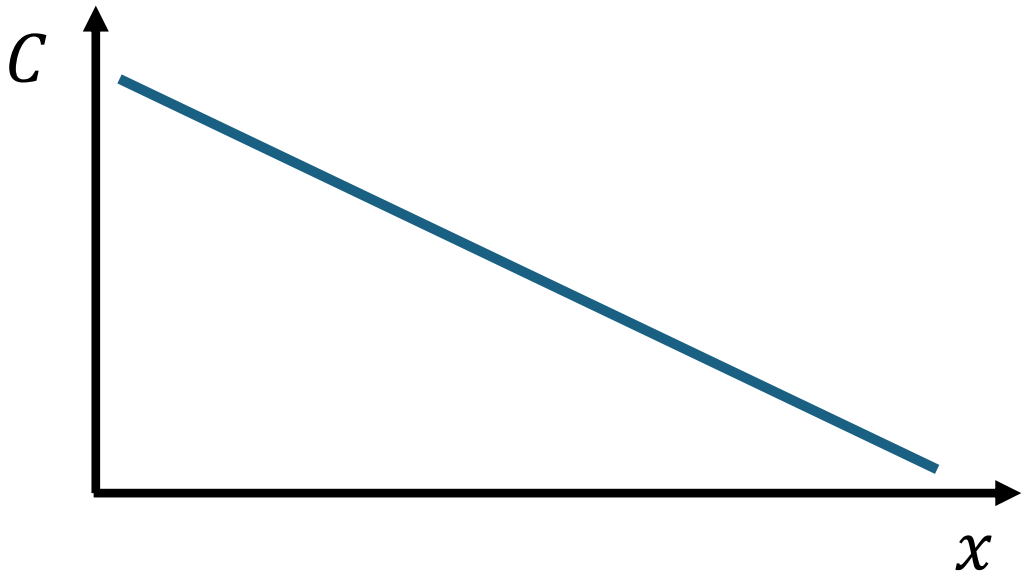
Cu ↔ Ni referred to as *interdiffusion*

Can we quantify the *rate* of diffusion?

Fick's first law of diffusion

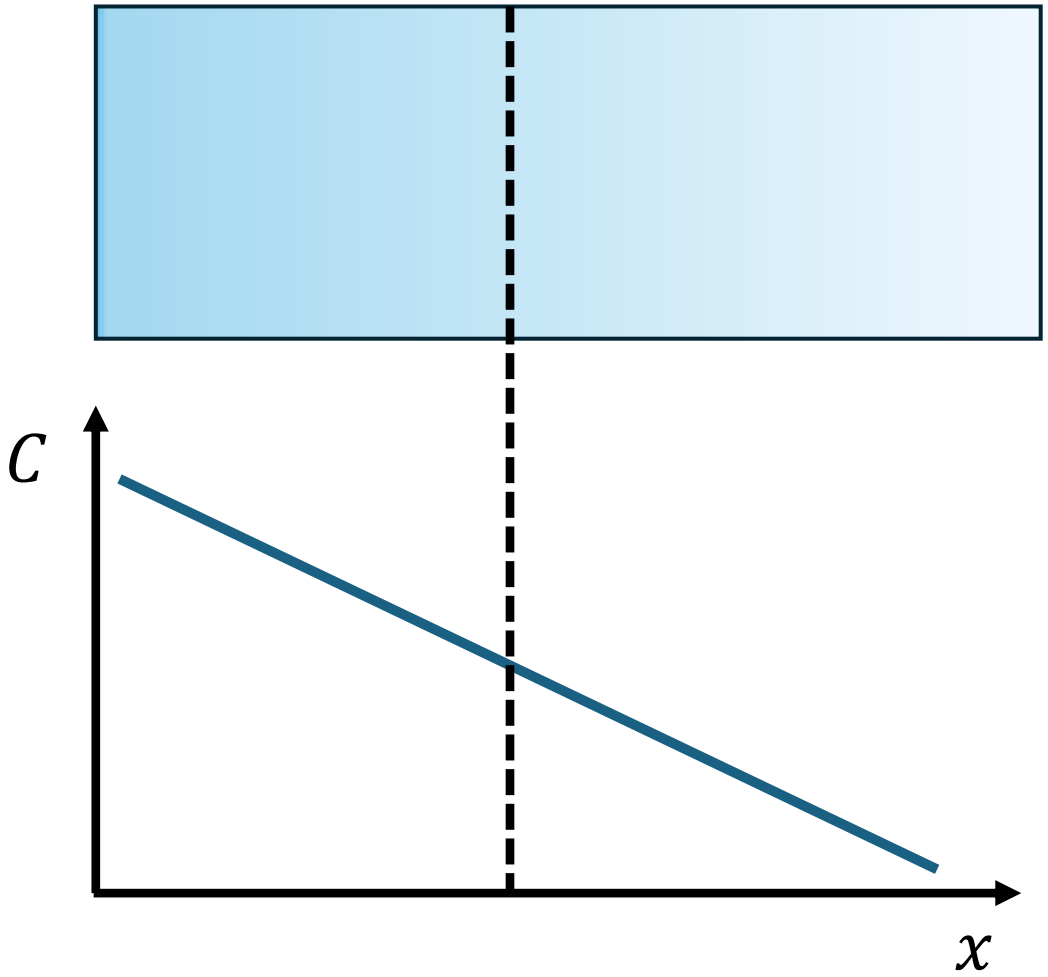
Consider a material with varying concentration (C) of species A





Fick's first law of diffusion

Consider a material with varying concentration (C) of species A

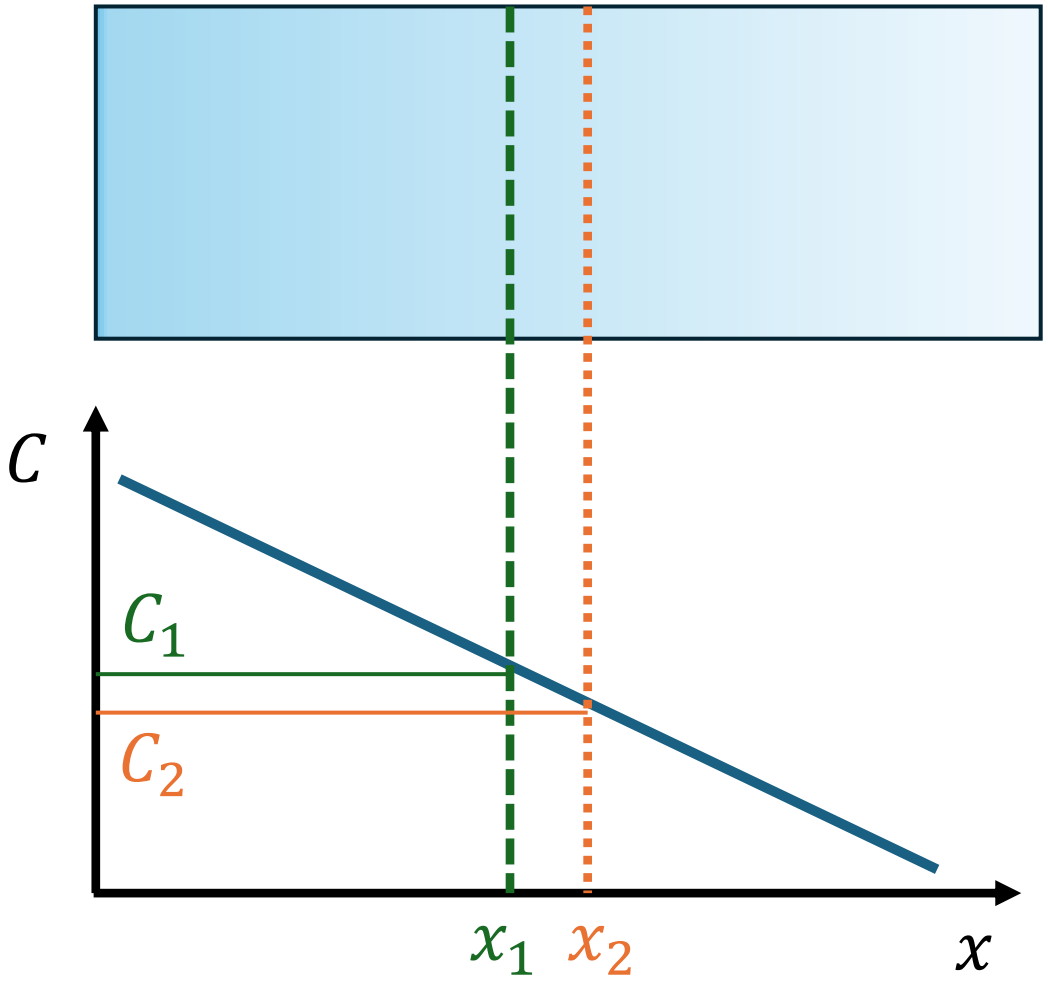


We want to know the ***flux* (J)** of species A through the dashed line. In other words, **how many atoms cross this line per unit time?**

$$\boldsymbol{J = \frac{(\text{amount})}{(\text{area})(\text{time})}}$$

Fick's first law of diffusion

Consider a material with varying concentration (C) of species A



We want to know the ***flux* (J)** of species A through the dashed line. In other words, **how many atoms cross this line per unit time?**

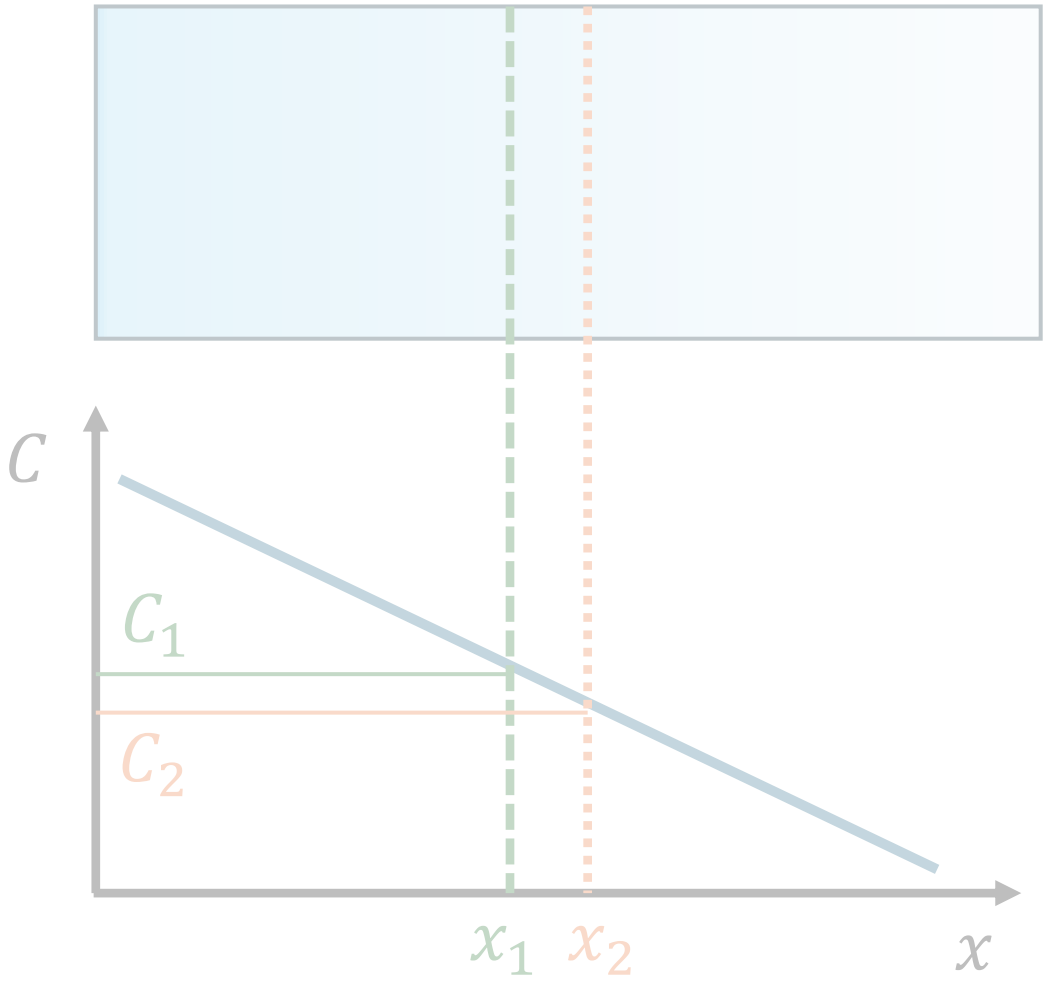
The flux is related to the composition difference:

$$J \propto \frac{C_2 - C_1}{x_2 - x_1} \rightarrow -\frac{\partial C}{\partial x}$$

(negative sign because atoms want to move toward *lower* concentration)

Fick's first law of diffusion

Consider a material with varying concentration (C) of species A



The proportionality is accounted for by the **diffusion coefficient (*D*):**

$$J = -D\frac{\partial C}{\partial x}$$

This is Fick's first law!

Describes how mobile the atoms are

$$J \propto \frac{C_2 - C_1}{x_2 - x_1} \rightarrow -\frac{\partial C}{\partial x}$$

(negative sign because atoms want to move toward *lower* concentration)

The diffusion coefficient varies with temperature

$$D = D_0 \exp(-Q_d/RT)$$

A pre-factor that depends on the diffusing species and host lattice

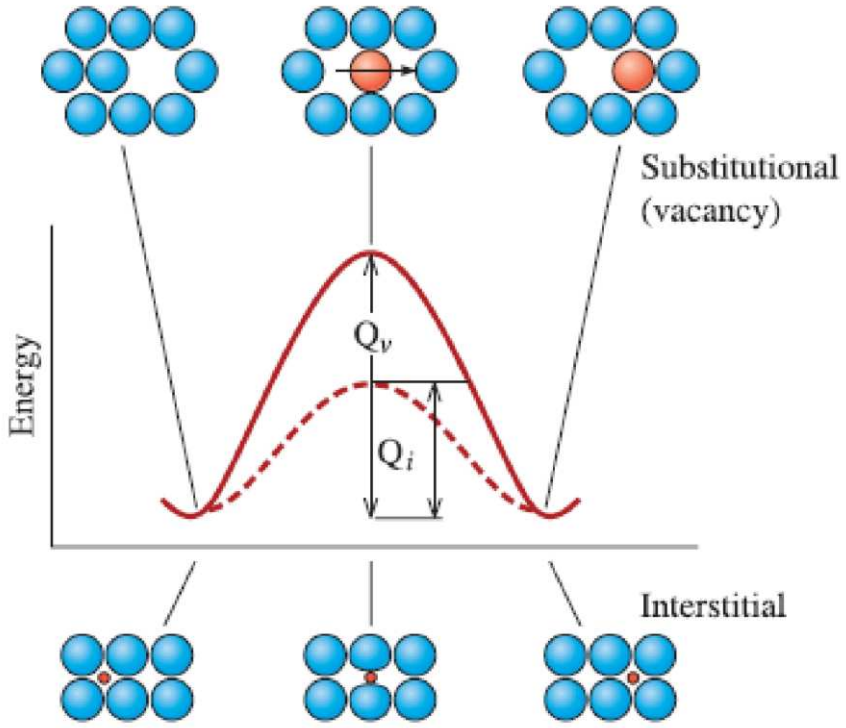
The **activation energy** for diffusion

Temperature

Think of the activation energy as a **barrier** for diffusion:

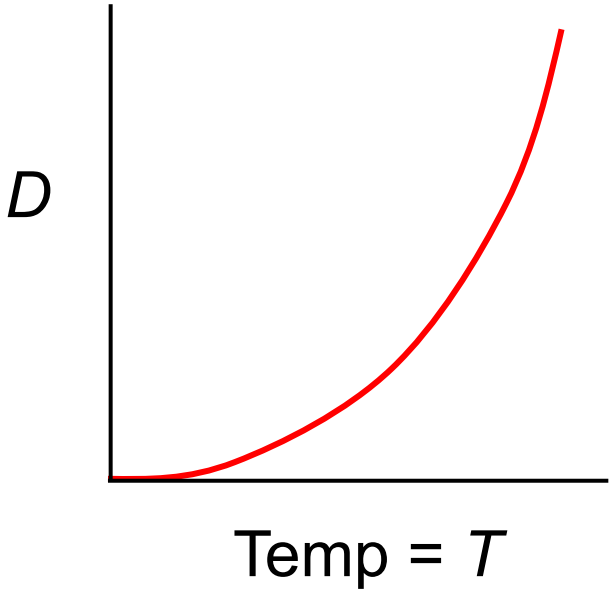
Lower barrier → faster diffusion

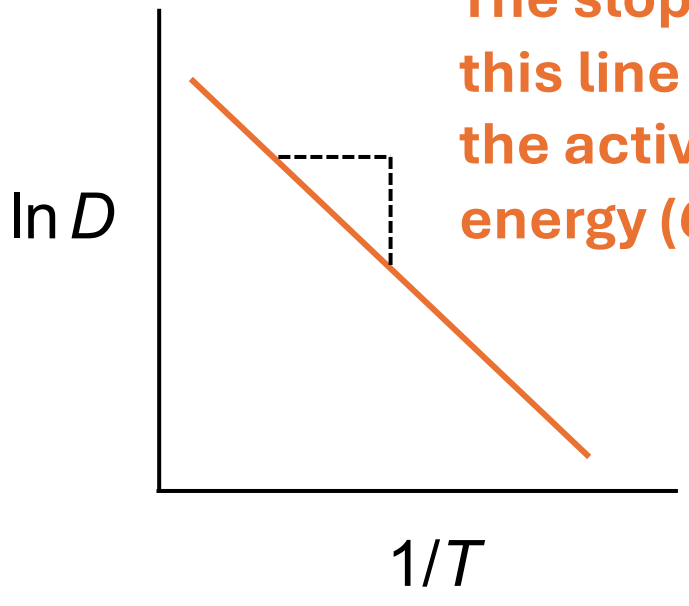
Higher temperature → more likely to overcome this barrier



This is atomic-scale, but we can study it by measuring diffusion – a bulk property

Determining the activation energy



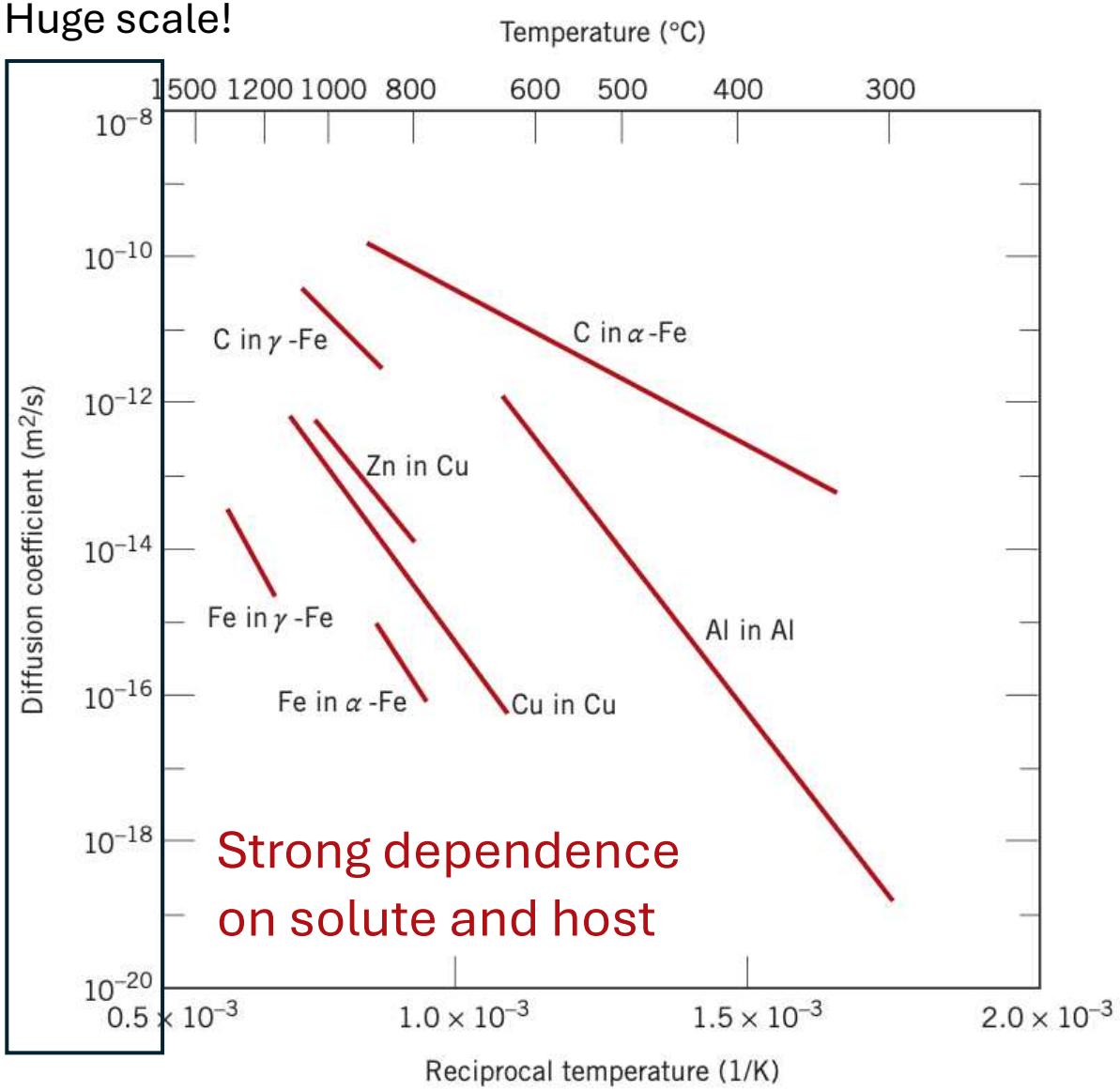


The slope of this line gives the activation energy (Q_d)

$$D = D_0 \exp\left(-\frac{Q_d}{RT}\right) \xrightarrow[\text{of both sides}]{\text{take natural log}} \ln D = \ln D_0 - \frac{Q_d}{RT}$$

Some real diffusion coefficients

Huge scale!



Very wide range of diffusion coefficients!

Diffusing Species	*Host Metal*	D_0 (m^2/s)	Q_d (*J/mol*)
	Interstitial Diffusion		
C[b]	Fe (α or BCC)[a]	1.1×10^{-6}	87,400
C[c]	Fe (γ or FCC)[a]	2.3×10^{-5}	148,000
N[b]	Fe (α or BCC)[a]	5.0×10^{-7}	77,000
N[c]	Fe (γ or FCC)[a]	9.1×10^{-5}	168,000
	Self-Diffusion		
Fe[c]	Fe (α or BCC)[a]	2.8×10^{-4}	251,000
Fe[c]	Fe (γ or FCC)[a]	5.0×10^{-5}	284,000
Cu[d]	Cu (FCC)	2.5×10^{-5}	200,000
Al[c]	Al (FCC)	2.3×10^{-4}	144,000
Mg[c]	Mg (HCP)	1.5×10^{-4}	136,000
Zn[c]	Zn (HCP)	1.5×10^{-5}	94,000
Mo[d]	Mo (BCC)	1.8×10^{-4}	461,000
Ni[d]	Ni (FCC)	1.9×10^{-4}	285,000
	Interdiffusion (Vacancy)		
Zn[c]	Cu (FCC)	2.4×10^{-5}	189,000
Cu[c]	Zn (HCP)	2.1×10^{-4}	124,000
Cu[c]	Al (FCC)	6.5×10^{-5}	136,000
Mg[c]	Al (FCC)	1.2×10^{-4}	130,000
Cu[c]	Ni (FCC)	2.7×10^{-5}	256,000
Ni[d]	Cu (FCC)	1.9×10^{-4}	230,000

Usually, interstitial > vacancy diffusion

An example problem

At 300 °C, the diffusion coefficient for Cu in silicon is: $\boldsymbol{D_{300\,^{\circ}\mathrm{C}} = 7.8\times10^{-11}}$ **m²/s**

And the activation energy for Cu hopping is: $\boldsymbol{Q = 0.43}$ **eV**

What do you expect the **diffusion coefficient to be at 350 °C**?

An example problem

At 300 °C, the diffusion coefficient for Cu in silicon is: $D_{300\,°C} = 7.8\times10^{-11}$ m²/s

And the activation energy for Cu hopping is: $Q = 0.43$ eV

What do you expect the **diffusion coefficient to be at 350 °C**?

Unknown

$$D = D_0 \exp(-Q_d/RT)$$

Known Known

Rearranged:

$$D_0 = D \exp(Q_d/RT) = (7.8\times10^{-11}\ \text{m}^2/\text{s})\ \exp\left(\frac{-0.43\ \text{eV}}{(8.62\times10^{-5}\ \text{eV/K})(573\ \text{K})}\right)$$

$$D_0 = 2.34\times10^{-7}\ \text{m}^2/\text{s}$$

An example problem

At 300 °C, the diffusion coefficient for Cu in silicon is: $D_{300\,°C} = 7.8\times10^{-11}$ m²/s

And the activation energy for Cu hopping is: $Q = 0.43$ eV

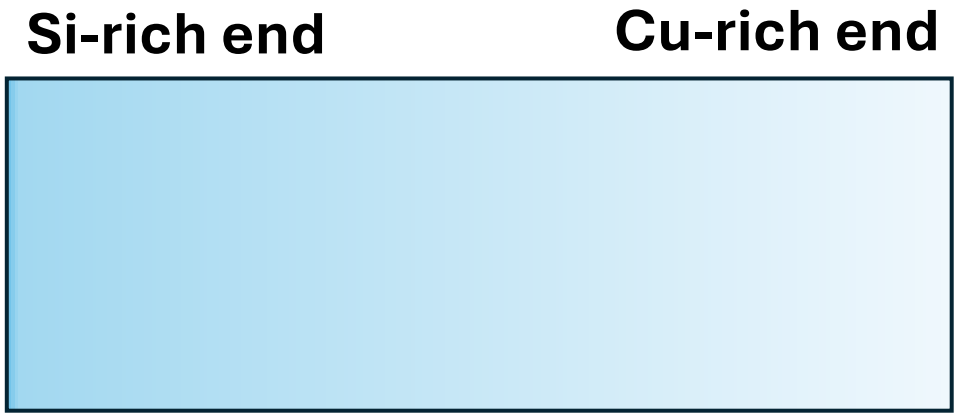
What do you expect the **diffusion coefficient to be at 350 °C**?

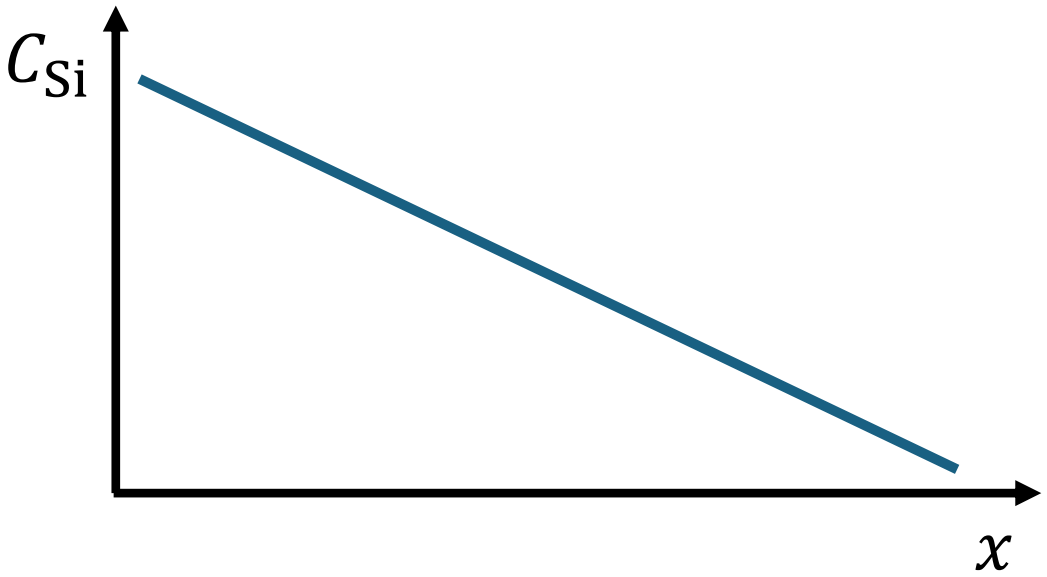
$$D_{350\,°C} = (\underbrace{2.34\times10^{-7}\ \text{m}^2/\text{s}}_{D_0})\exp\left(\frac{-0.43\ \text{eV}}{(8.62\times10^{-5}\ \text{eV/K})(623\ \text{K})}\right)$$

$$D_{350\,°C} = 14.1\times10^{-11}\ \text{m}^2/\text{s}$$

We've roughly *doubled* our rate of Cu diffusion by raising the temperature 50 °C

An example problem



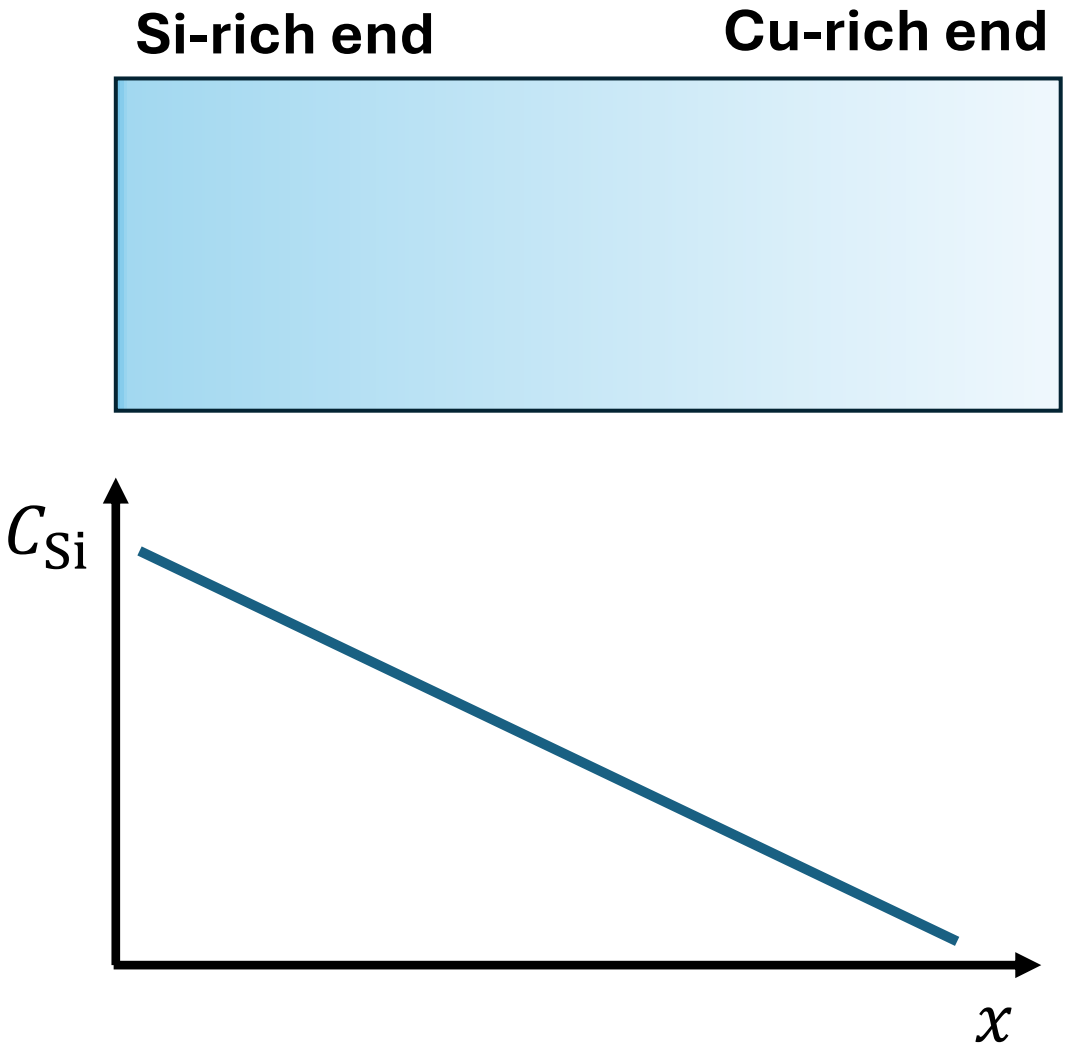


$$D_{350\,^{\circ}\mathrm{C}} = 14.1\times10^{-11}\ \mathrm{m^2/s}$$

Suppose the Si concentration varies uniformly, is equal to **1.2 kg/m³ at *x* = 5 mm**, and equal to **0.8 kg/m³ at *x* = 10 mm**

What is the flux of Si to the right?

An example problem



$$D_{350\,^{\circ}\mathrm{C}} = 14.1\times10^{-11}\ \mathrm{m^2/s}$$

Suppose the Si concentration varies uniformly, is equal to **1.2 kg/m³ at x = 5 mm**, and equal to **0.8 kg/m³ at x = 10 mm**

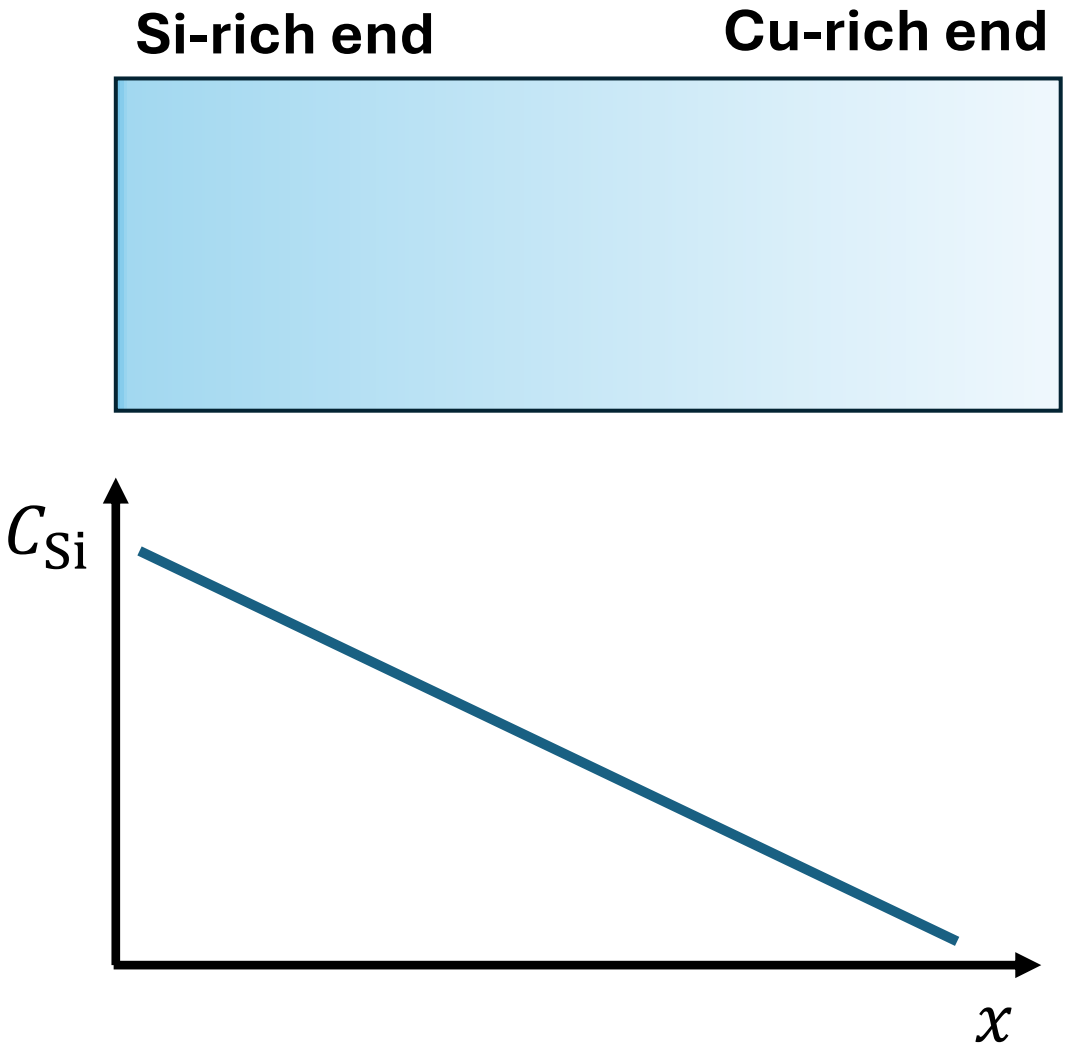
What is the flux of Si to the right?

$$J = -D\frac{\partial C}{\partial x}$$ **Fick's first law**

$$J = -14.1\times10^{-11}\ \mathrm{m^2/s}\left(\frac{1.2-0.8}{0.01-0.005}\right)$$

$$J = 1.13\times10^{-8}\ \mathrm{kg/m^2\cdot s}$$

An example problem

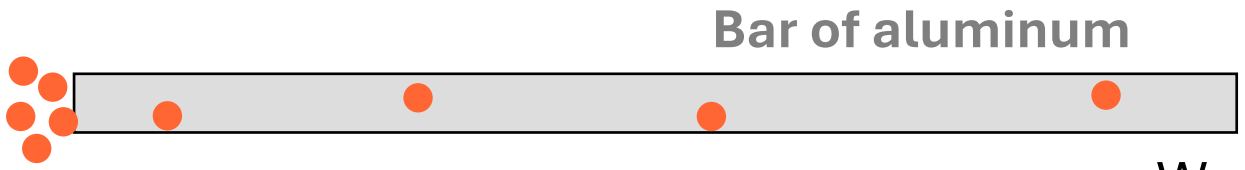


We have so far assumed our concentration profile is *not* changing with time.

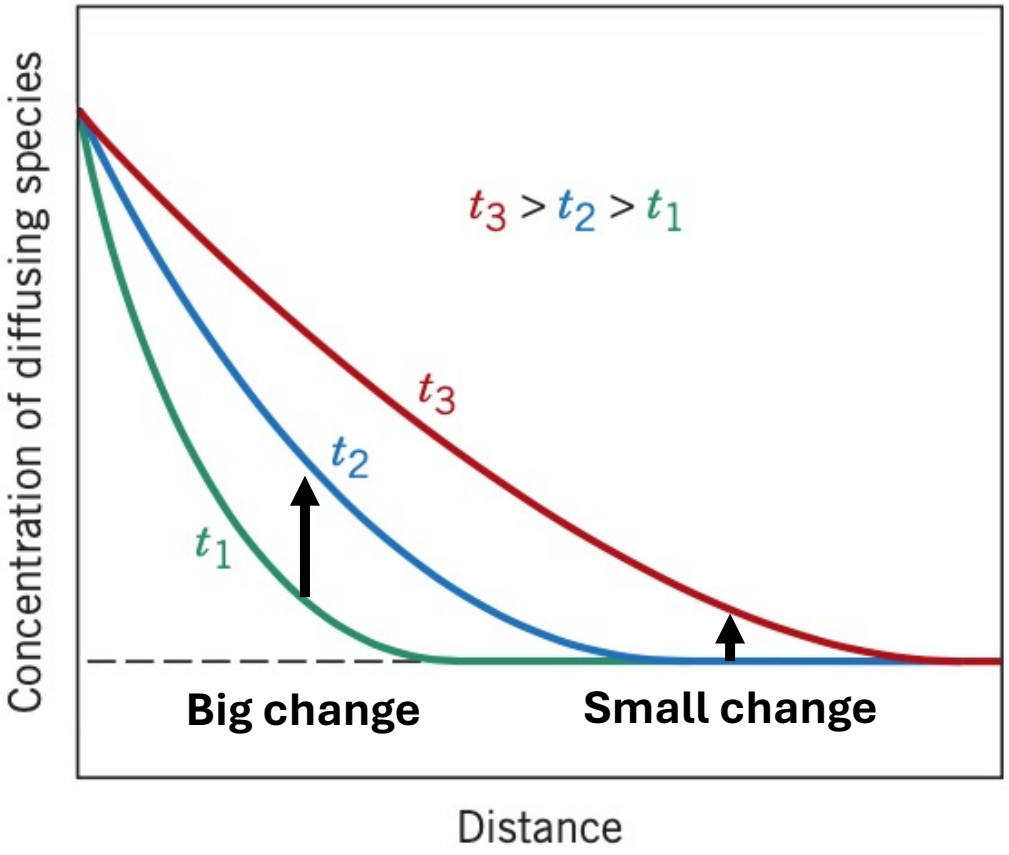
In other words: it is **steady-state…**

What if this is not the case?

Non-steady-state diffusion ↔ Fick's 2nd law



We expect the Cu atoms to spread out more over time



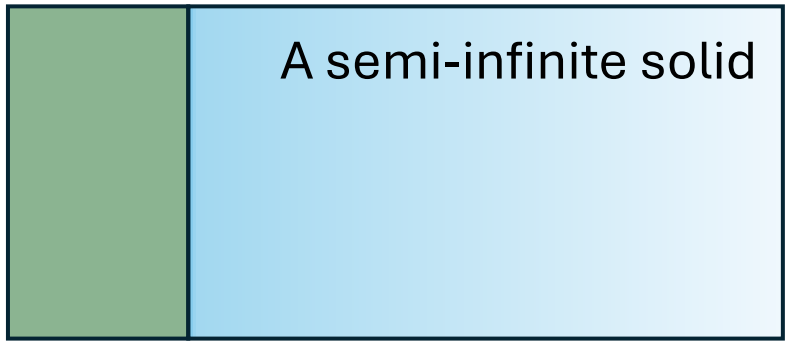
This is quantitatively described by **Fick's 2nd law:**

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

How the concentration changes over time

The curvature of the concentration profile

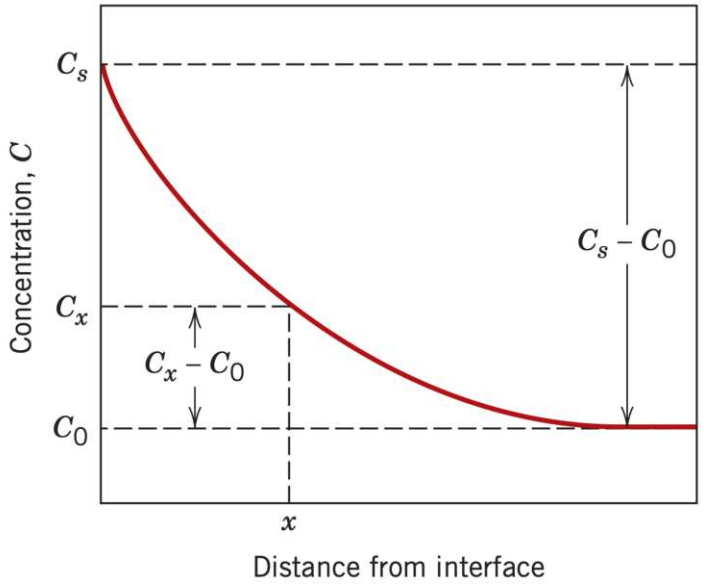
One solution to Fick's 2nd law



Constant source (*e.g.*, a gas with fixed pressure)

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial t^2}$$

This is a PDE that can be quite annoying to solve, which we won't do here…But let's look at one special case where a solution is known



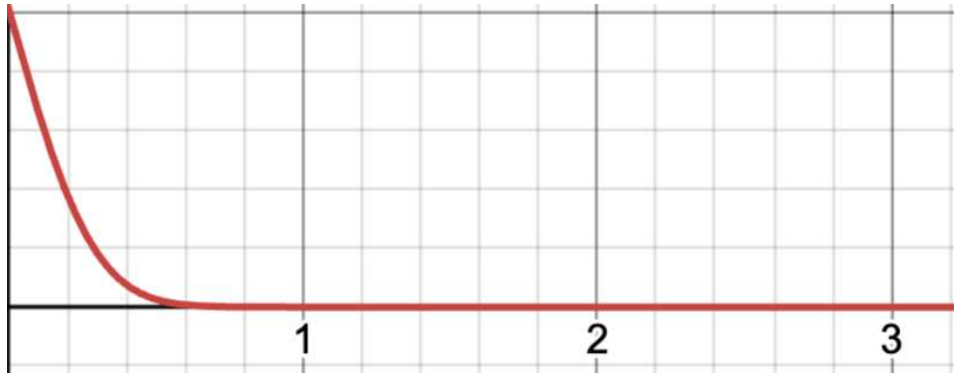
$$\frac{C_x - C_0}{C_s - C_0} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

C_s = concentration at the source

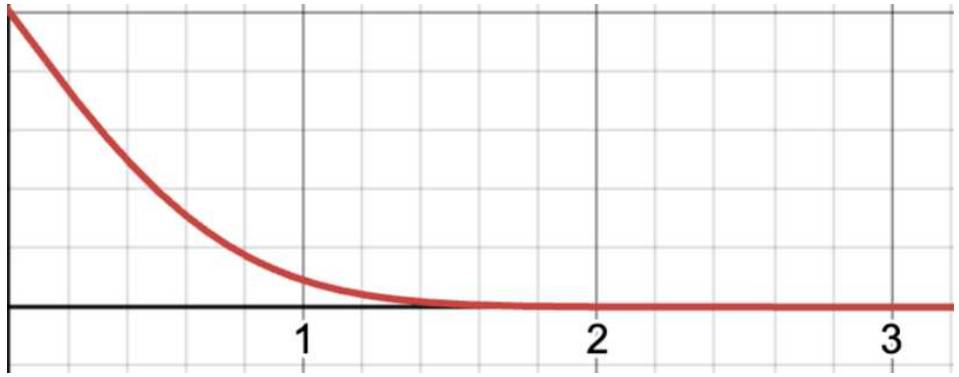
C_0 = concentration far away from source

C_x = concentration at some in-between distance

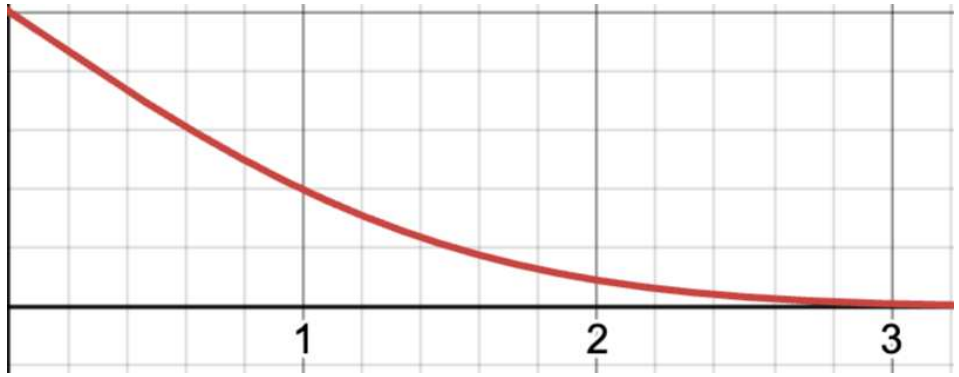
Try plotting a few of these with Desmos



t_1



t_2

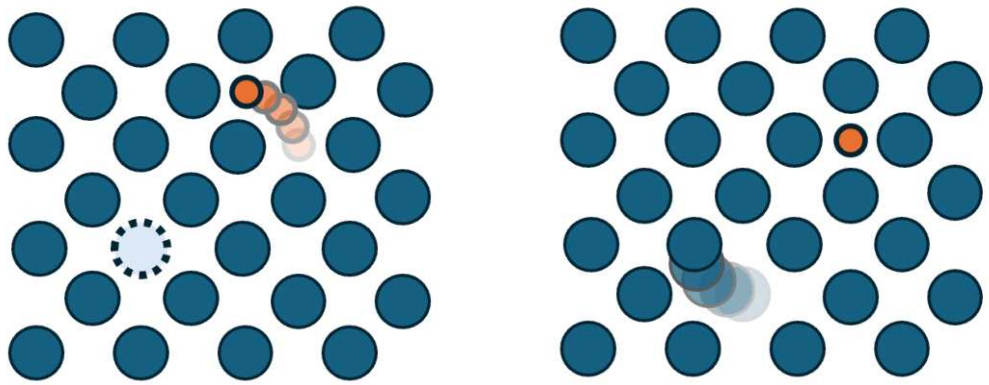


t_3

Concentration is fixed at $x = 0$ but spreads out to the right as time evolves

$$\frac{C_x - C_0}{C_s - C_0} = 1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Summary of diffusion topics

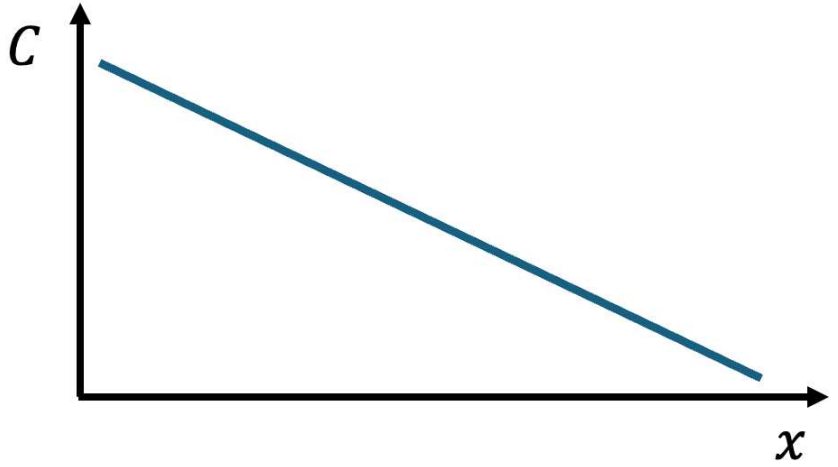


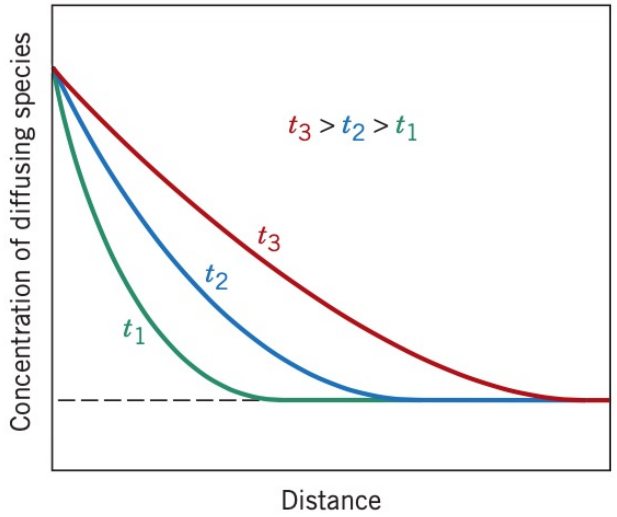
Diffusion is the transport of matter through atomic-scale migration of point defects

$$D = D_0 \exp(-Q_d/RT)$$

Steady-state diffusion is described by Fick's 1st law:

$$J = -D\frac{\partial C}{\partial x}$$





$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial t^2}$$

Non-steady-state diffusion is described by Fick's 2nd law