(Point) Defects in Crystals

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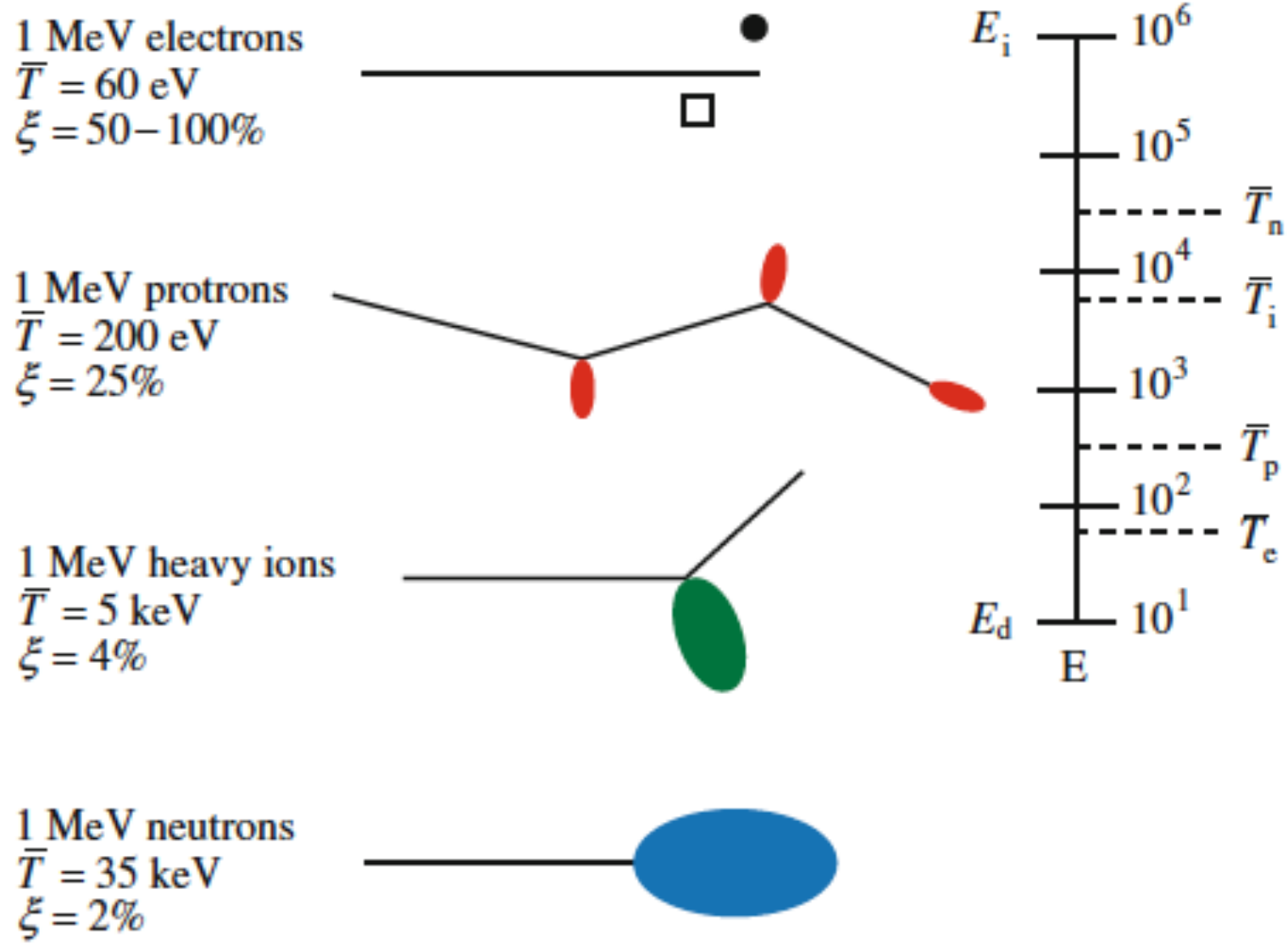
Different radiation produces different cascades

Mass & Charge:

Increasing mass, same charge

Moderate mass, no charge



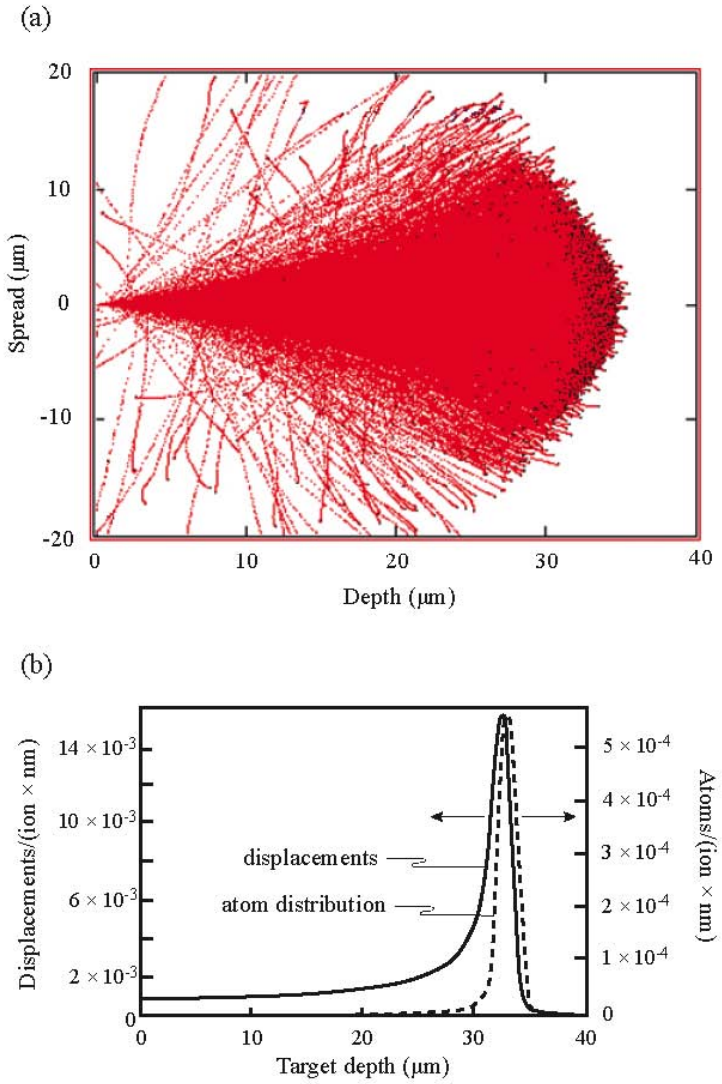
Stopping mechanism:

Simulation methods – BCA + Monte Carlo

SRIM is the most widely used simulation for damage of ions and uses a Monte Carlo approach

- Takes into account:
  - Material composition
  - Material configuration (e.g. layers)
  - Displacement energy of each element in each layer
  - Density
  - Incident ion type & energy
  - Type of calculation

Debated in literature!



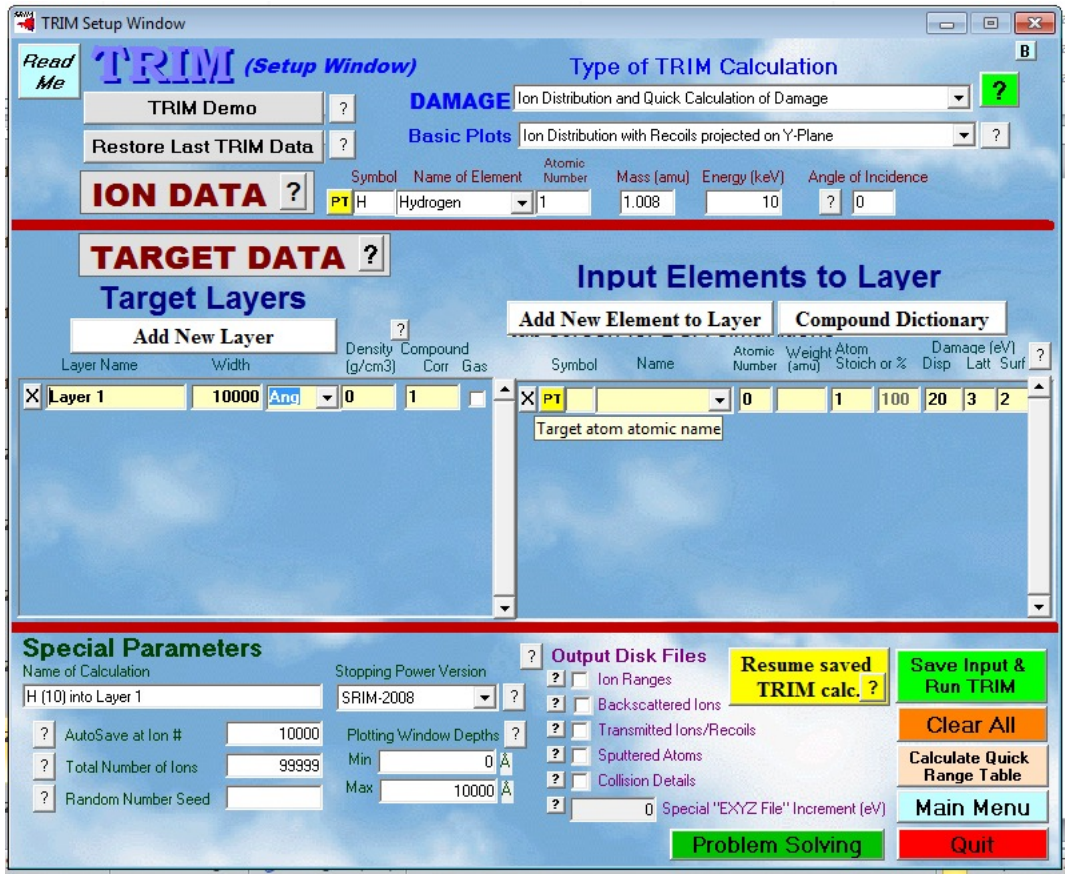
The SRIM software

The SRIM software is freely available at the SRIM web pages

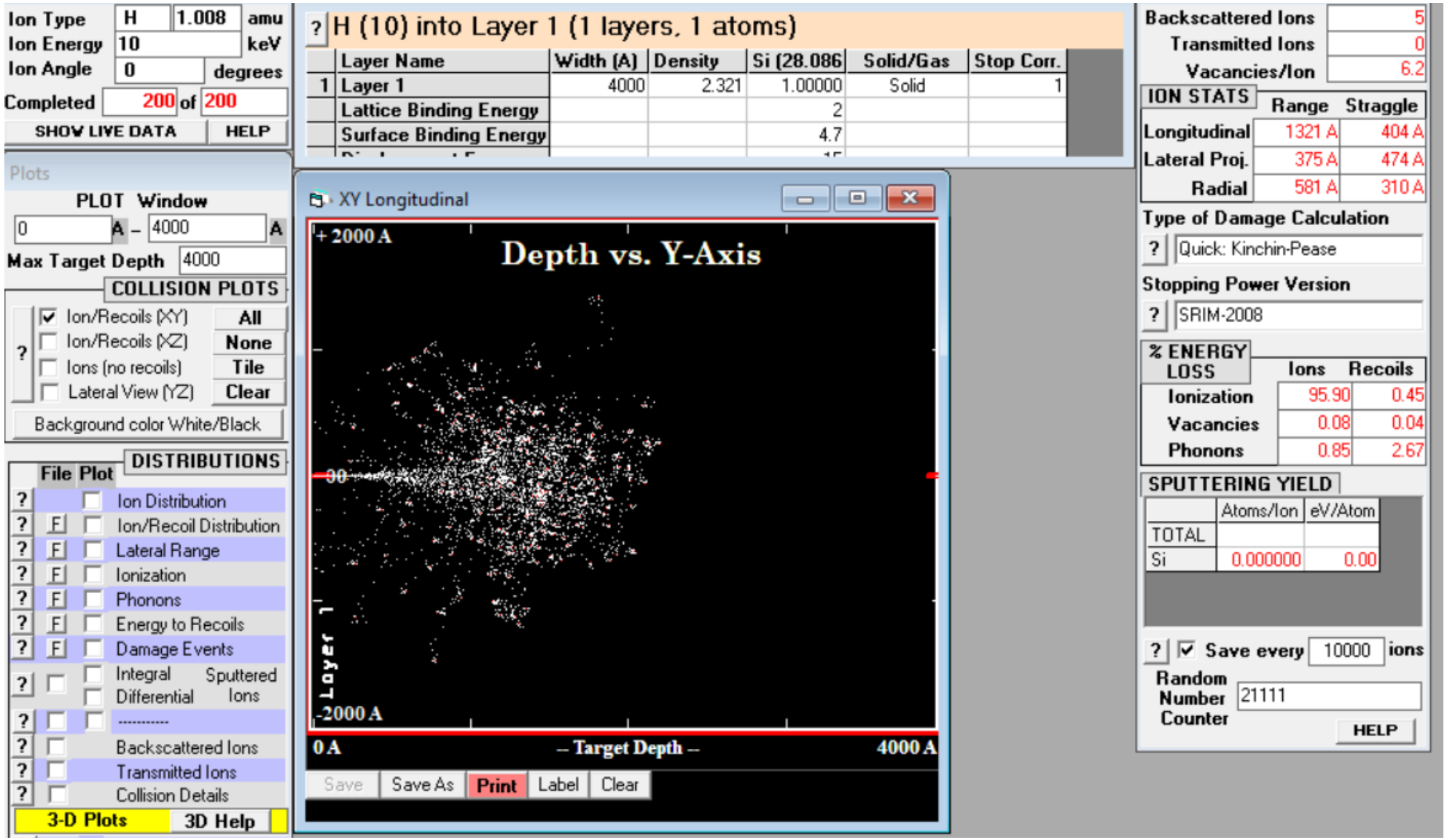
- Often also called TRIM due to the earlier name "Transport and Range of Ions in Matter"

- It can calculate any stopping power (electronic or nuclear) in any material, including compounds and multilayer one
- Includes electronic stopping in all calculations
- Downsides:
  - Only amorphous materials modelled => no channeling
  - No temperature dependence
  - It only works on Windows computers, is not open source , and is programmed in a quite old fashioned way with Visual Basic
  - Because of this, installing it on modern Windows is a hassle
  - Tip: for it to work at all, one needs to set Regional settings to US English in Windows…

The SRIM software



The SRIM software



SRIM notes

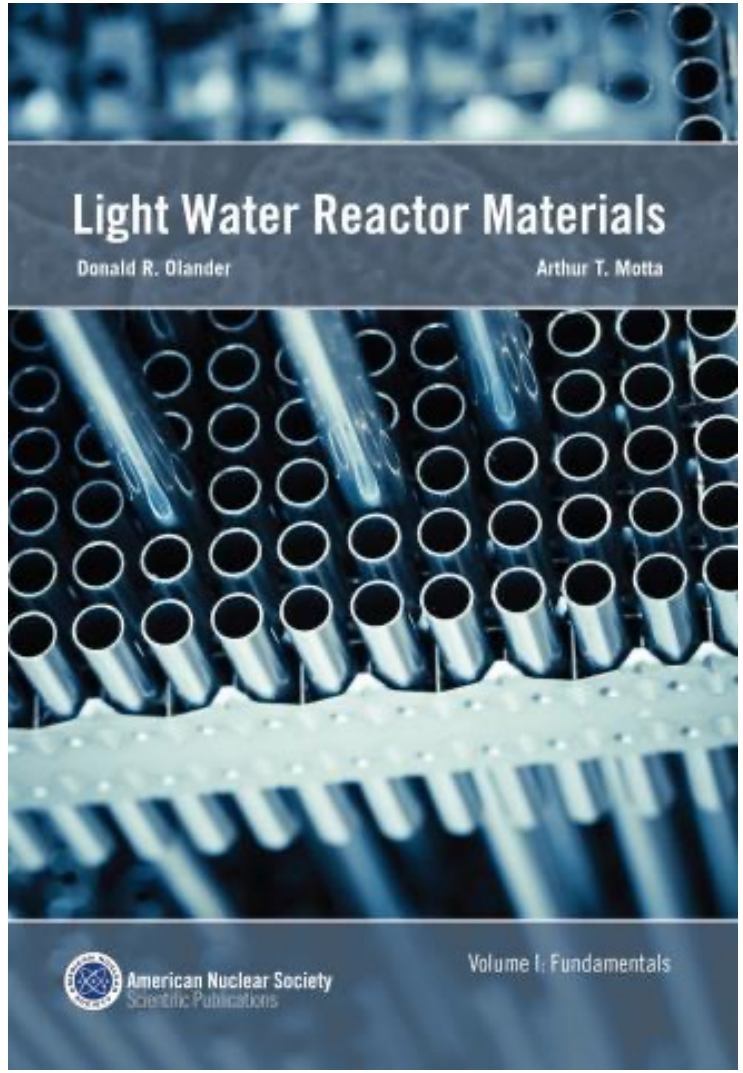
- SRIM can be somewhat speeded up by closing all the output windows, and can be well ran in the background on modern multi core processors
- Several output options exist: ion ranges, nuclear and electronic deposited energy, sputtering yield
- For detailed analyses output of file COLLISON.DAT outputs data on all ions and recoils created during the whole simulation
- Do not use SRIM blindly: there are major caveats and pitfalls in using it, and not knowing them can lead to too much trust in accuracy of results or even outright wrong physics

We have officially finished Part I of the course!

Disclaimer!

- We are passing the threshold into materials science territory
- You might find these helpful from the Motta & Olander book:
  - Chapter 3: Crystallography of nuclear materials
  - Chapter 4: Point defects theory
  - Chapter 5: Diffusion theory

https://na04.alma.exlibrisgroup.com/view/uresolver/01UMICH_INST/openurl?u.ignore_date_coverage=true&portfolio_pid=5310682809000063 81&Force_direct=true



Introduction to Defects

- In the previous section, we learned irradiation from energetic particles creates defects
- We now need to look at the structure and properties of these defects
  - We can classify defects according to their dimensionality
    1.
    2.
    3.
    4.

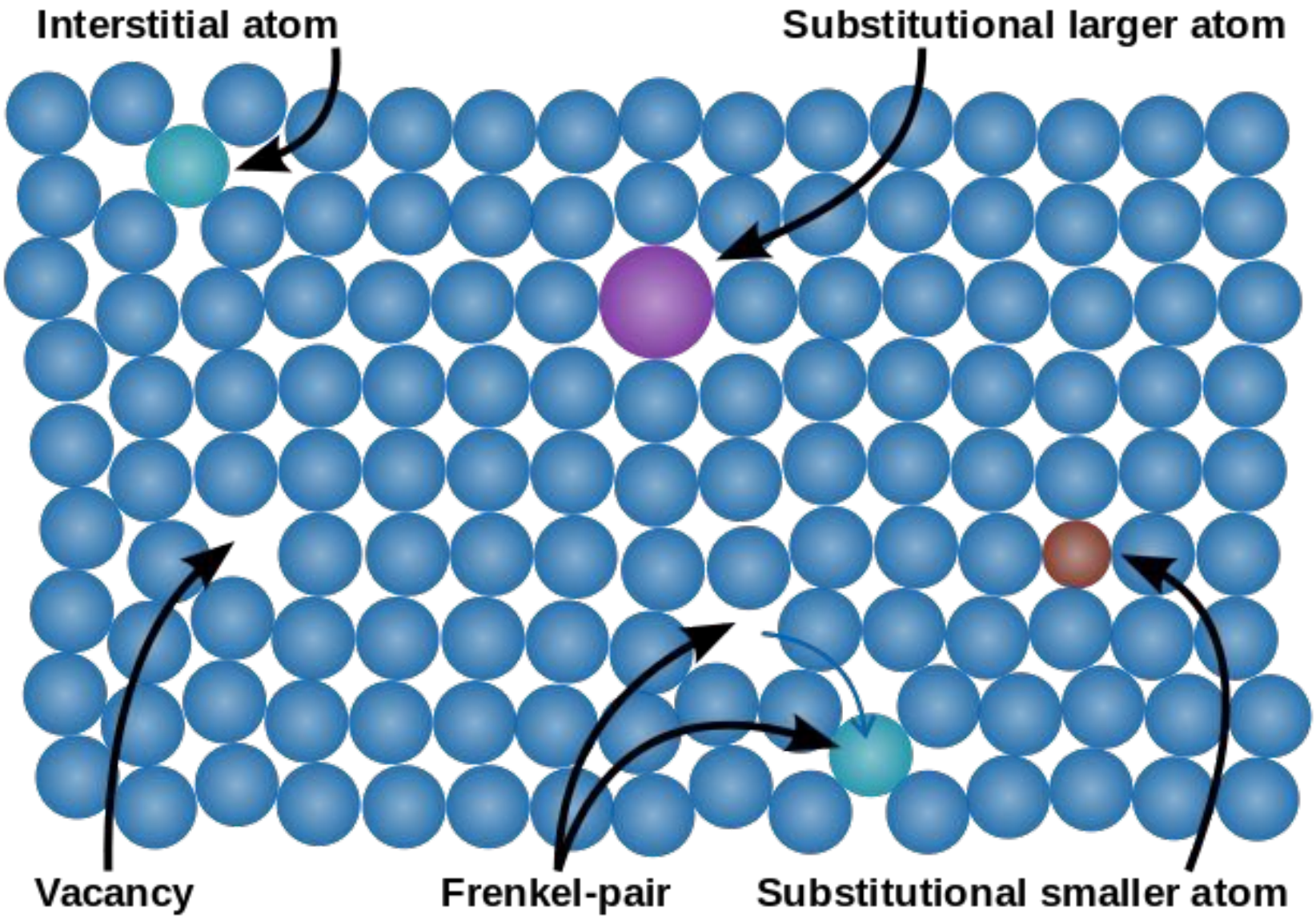
Classification of 0 D defects

- Let's focus on **point defects** – dislocations and other types will come later
- The upper size limit of a "0 D" or point defect is not clear or very well defined
  - But, typically defects with only a few atoms (or vacancies) are considered "0 D" defects
  - This means, typically:

- We can also do sub-classification of point defects:
  - Intrinsic defects:

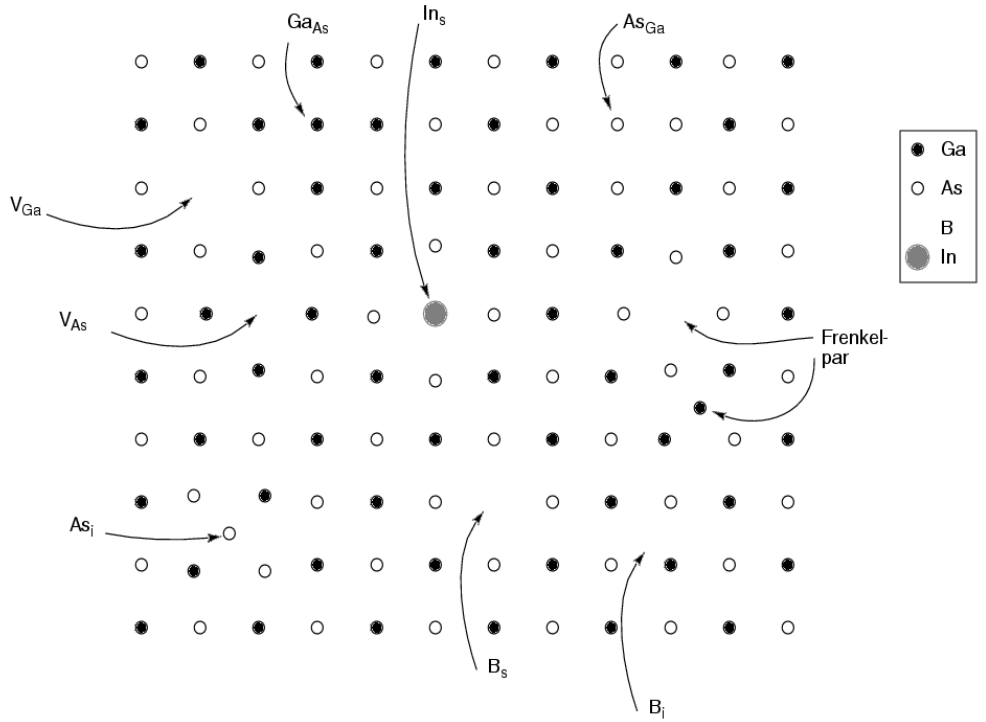
  - Extrinsic defects:

Point Defects



Simple defect notation

- It is handy to adopt a notation when talking about point defects
  - In ionic materials we use the Kroger-Vink notation
- ***V*** for vacancy
  - Subscript for which atom type's place is empty
  - V_2 for divacancy, V_3 for trivacancy, etc.
- ***I*** is for interstitial defects
  - X_i for X atom in an interstitial position
  - Y_s for Y atom on a substitutional atom position
  - X_y for X atoms on a Y atomic site – also known as an antisite



Vacancies

- A vacant or missing atom at a lattice
- The simplest point defect
- All crystalline solids contain vacancies
- The equilibrium number of vacancies in a material depends on temperature (more in next section)
- Produces lattice distortions
- Can coalesce into planar and 3D clusters

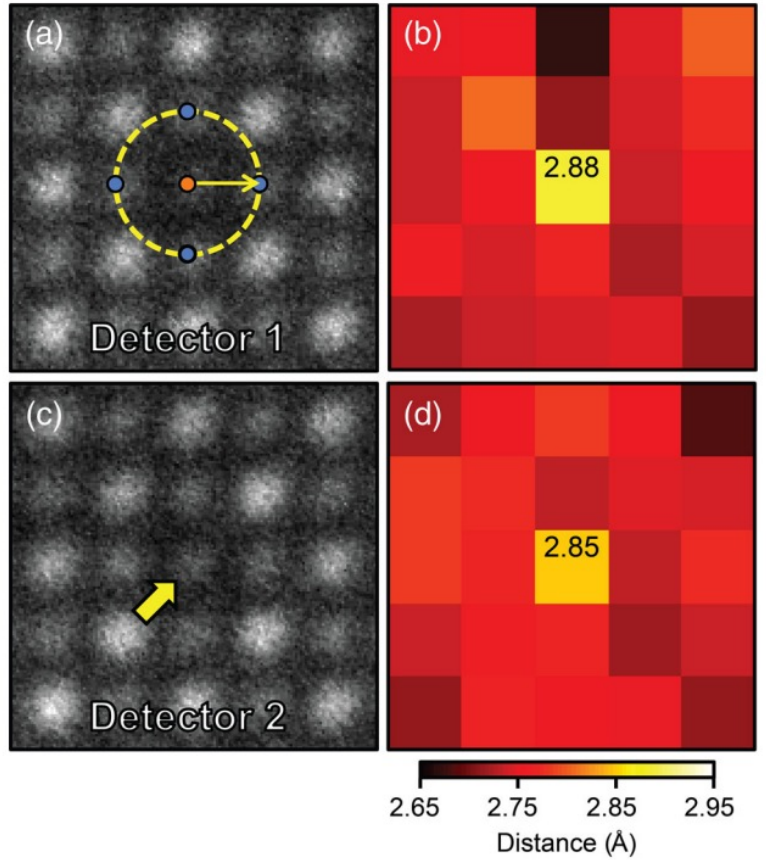


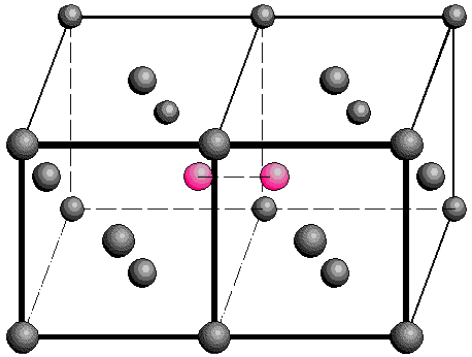
FIG. 3. Local structure relaxation around Sr vacancies. (a,c) Magnified HAADF STEM images near column-A recorded with detectors 1 and 2, respectively. (b,d) Atomic distance maps, where each pixel value indicates the average distance from one cation to its four nearest-neighbor unlike cations, showing Ti-O columns being displaced away from Sr vacancies. The overlay in (a) shows an example of a distance measurement from a Sr column (orange circle) to the Ti-O columns (blue circle).

http://dx.doi.org/10.1103/PhysRevX.6.041063

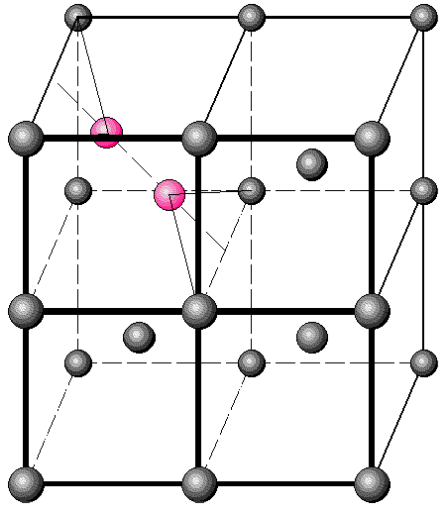
Self Interstitial Atoms (SIA)

- SIAs deform surrounding lattice
- They "share" spot with lattice atom
- Called a dumb-bell configuration
  - Typically, the lowest energy configuration
  - Common radiation damage defects
  - Can affect diffusion characteristics
  - Can sit in different configurations

"Dumbbell" after vintage weights

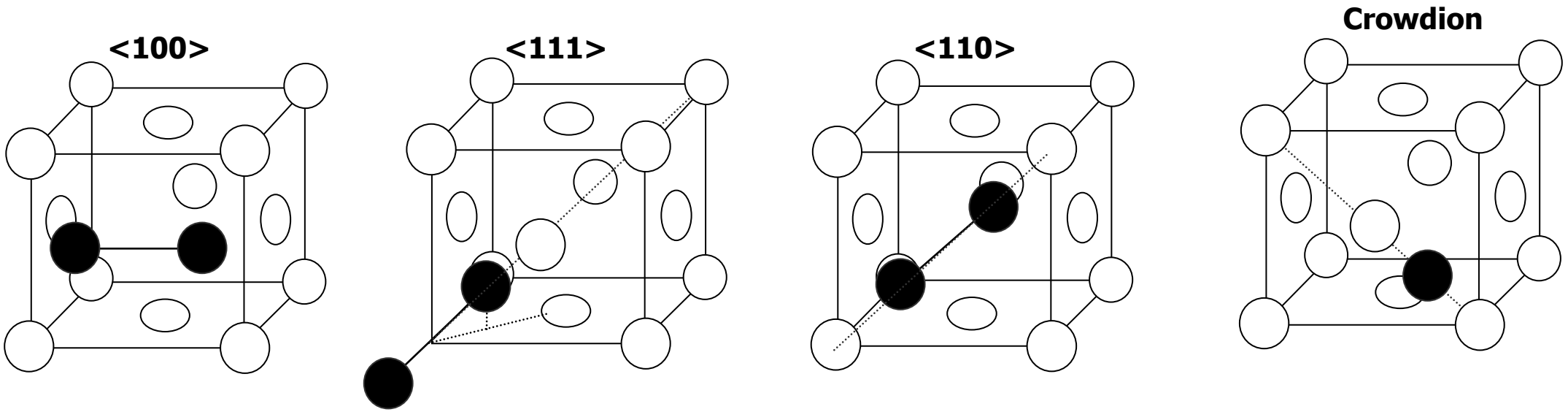


FCC Dumb-bell

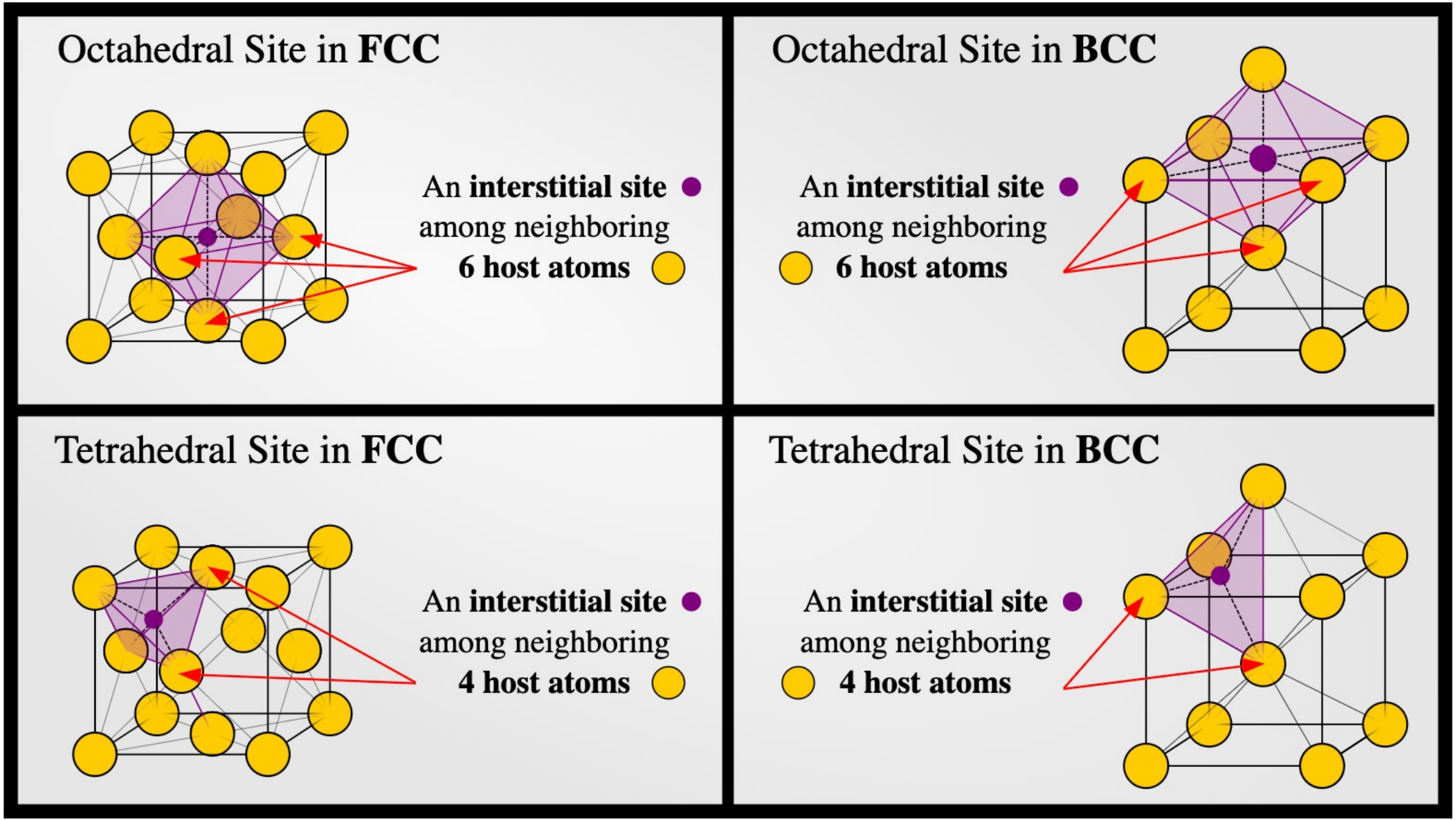


BCC Dumb-bell

Possible FCC Self Interstitial Atom (SIA) Sites



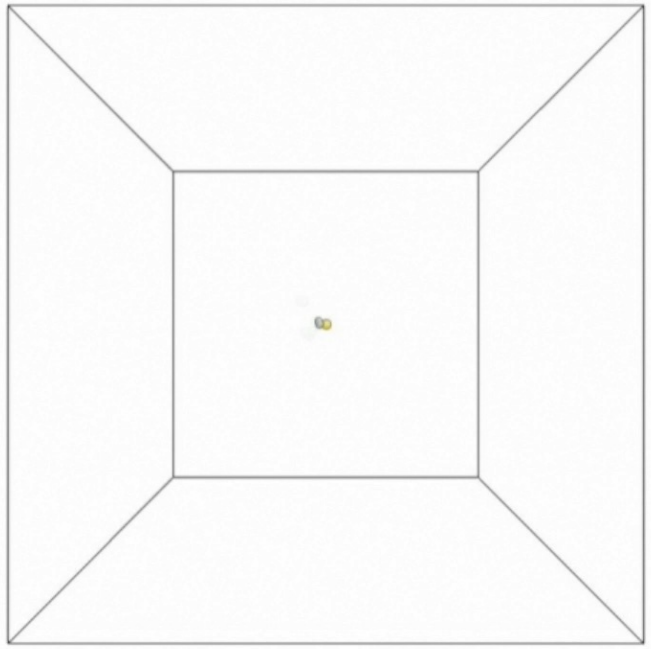
Solute Interstitial Configurations



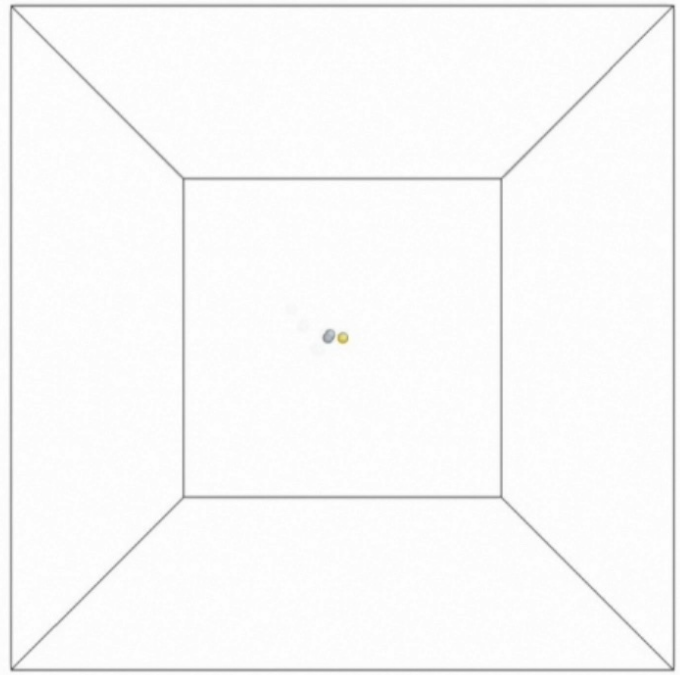
https://msestudent.com/what-is-the-difference-between-fcc-and-bcc-crystal-structure-properties-interstitial-sites-and-examples/

Role of solutes

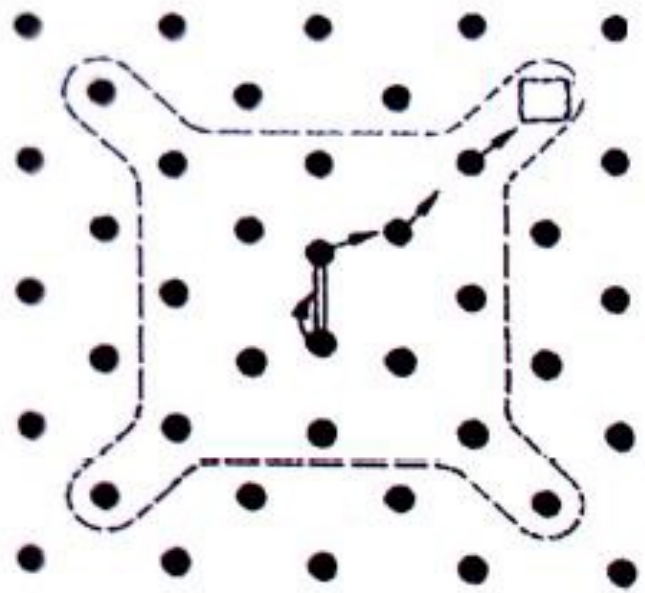
4.1 Behavior of iron and chromium in a 20 keV cascade in Fe-10% Cr alloy with Cr as an oversized solute. In this simulation, chromium (green) is modeled as an oversized solute in iron, resulting is a large number of small interstitial (grey), Cr-containing clusters. (courtesy, B. Wirth, University of California, Berkeley)



4.2 Behavior of iron and chromium in a 20 keV cascade in Fe-10% Cr alloy with Cr as an undersized solute. This is the same cascade and alloy as in Movie 4.1 but with Cr modeled as an undersized solute in iron. This condition leads to stronger trapping by iron interstitials compared to the case where chromium is modeled as an oversized solute. (courtesy, B. Wirth, University of California, Berkeley)



What is the fate of point defects?



Point Defect Thermodynamics

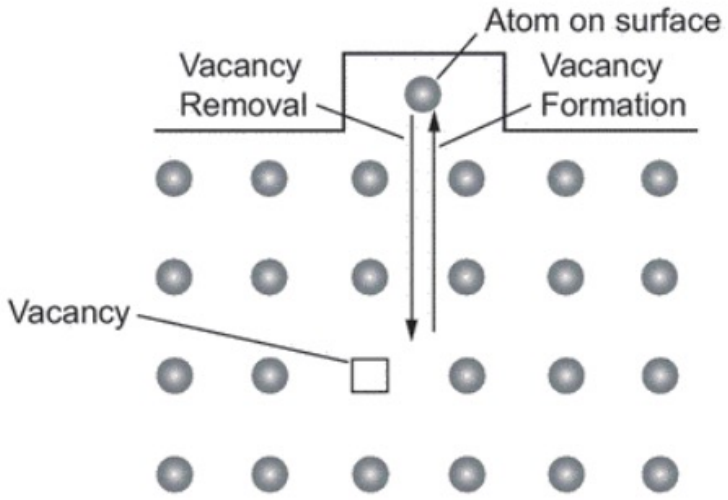


FIGURE 4.3: *Vacancy formation.*

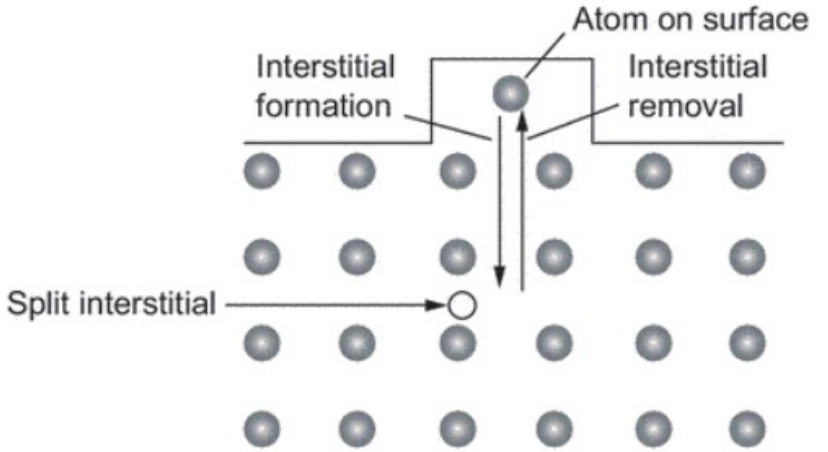


FIGURE 4.4: *SIA formation.*

- Even a crystalline material in equilibrium (e.g. not irradiated) will still contain **point defects** (although one type, v or i, might be more stable)
  - This is due to the Gibbs energy of formation:

Enthalpy for point defects

- The enthalpy change due to the creation of point defects, h_j, is given as:

Entropy for point defects

- The entropy term can be divided into two parts:

$$s = s_{vib} + s_{mix}$$

- Where

$$s_{vib} = k_b ln(v/v')^{\alpha}$$

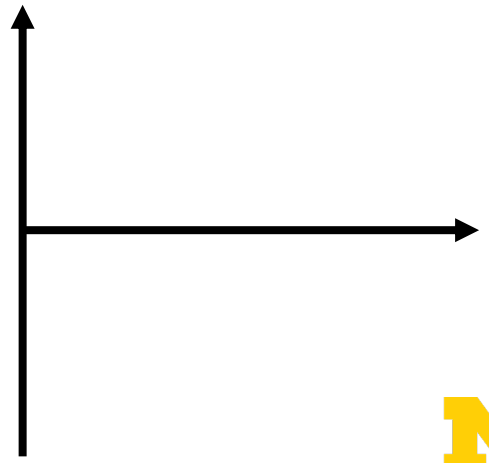
- And

$$s_{mix} = -k_b \left[\left(\frac{N}{N+N_v} \right) ln \left(\frac{N}{N+N_v} \right) + \left(\frac{N_v}{N+N_v} \right) ln \left(\frac{N_v}{N+N_v} \right) \right]$$

$$= -k_b [(1-C_v) ln(1-C_v) + C_v ln C_v]$$

Point Defects Formation: Vacancy

- **Vacancy formation:**
  - The Gibbs energy, G_v, of a solid containing N_v moles of vacancies and N moles of atoms is:



Point Defects Formation: Interstitial

- **Interstitial formation:**
  - Using the same analysis, we then get:

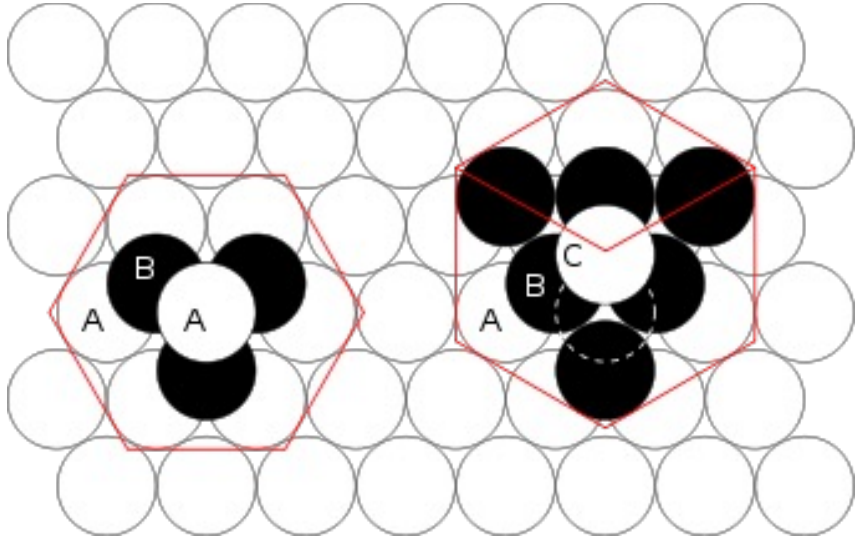
Example problem – to make a point

Point defect properties

	Symbol	Unit	Al	Cu	Pt	Mo	W
Interstitials							
Relaxation volume	V^i_{relax}	Atomic vol.	1.9	1.4	2.0	1.1	
Formation energy	E^i_f	eV	3.2	2.2	3.5		
Equilibrium concentration at T_m^*	$C_i(T_m)$	-	10^{-18}	10^{-7}	10^{-6}		
Migration energy	E^i_m	eV	0.12	0.12	0.06		0.054
Vacancies							
Relaxation volume	V^v_{relax}	Atomic vol.	0.05	-0.2	-0.4		
Formation energy	E^v_f	eV	0.66	1.27	1.51	3.2	3.8
Formation entropy	S^v_f	k	0.7	2.4			2
Equilibrium concentration at T_m^*	$C_v(T_m)$	-	$9x10^{-6}$	$2x10^{-6}$			$4x10^{-5}$
Migration energy	E^v_m	eV	0.62	0.8	1.43	1.3	1.8
Activation energy for self diffusion	Q_{vSD}	eV	1.28	2.07	2.9	4.5	5.7
Frenkel pairs							
Formation energy	E^{FP}_f	eV	3.9	3.5	5		


Questions?

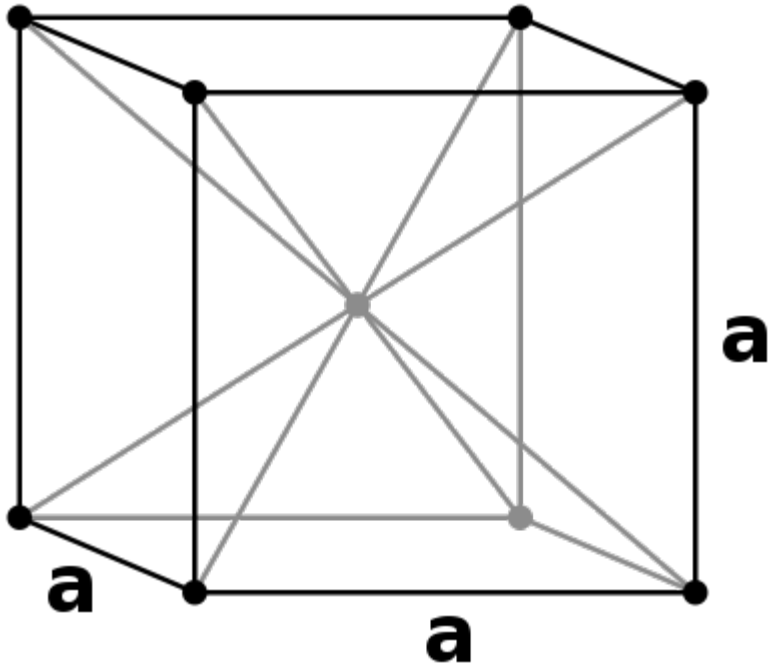
Atomic Packing

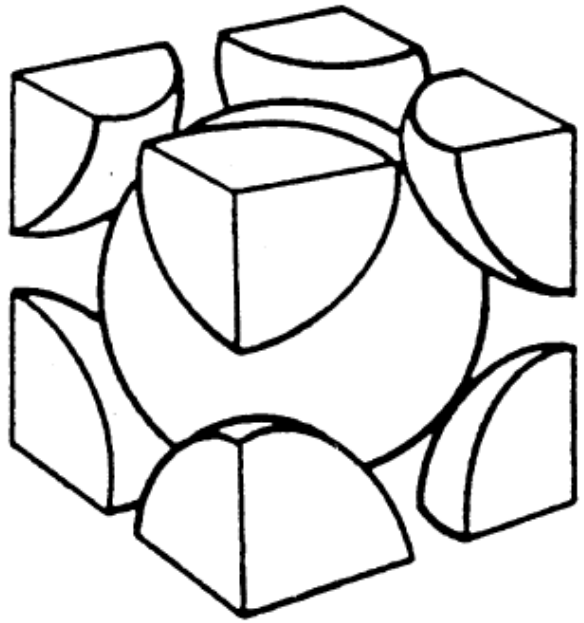


- Atoms are ‘packed’ or ‘stacked’ to form a matrix of the material
- Different stacking sequences will lead to different lattice configurations
- Atomic Packing Factor (APF) is the fraction of volume occupied by the atomic spheres in a crystal system (leads to variations in theoretical densities)
  - BCC: .68; FCC: .74; HCP: .74

Lattice Configurations

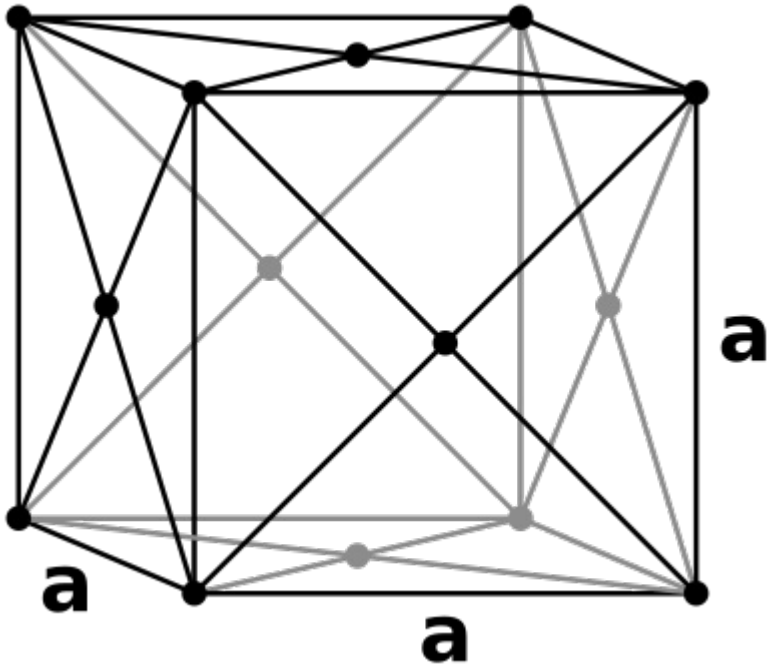
- Body Centered Cubic (BCC): An atom at each corner of a cube and an atom in the center
  - Common microstructure in pressure vessel steels
  - Typically magnetic if the solvent is Iron
  - Good swelling resistance

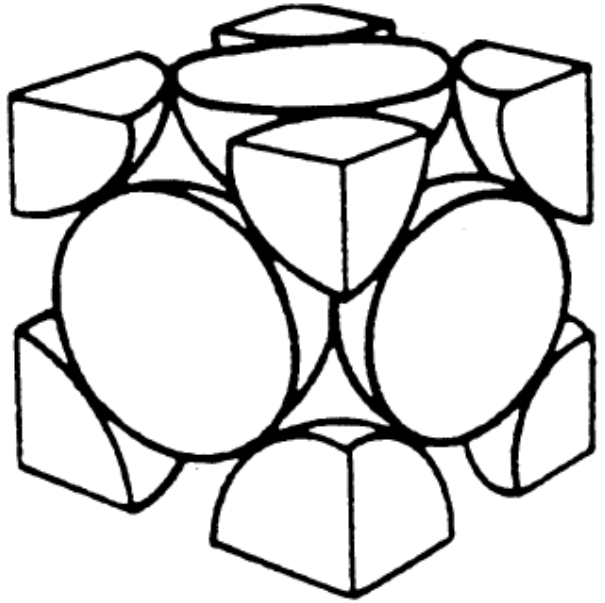




Lattice Configurations

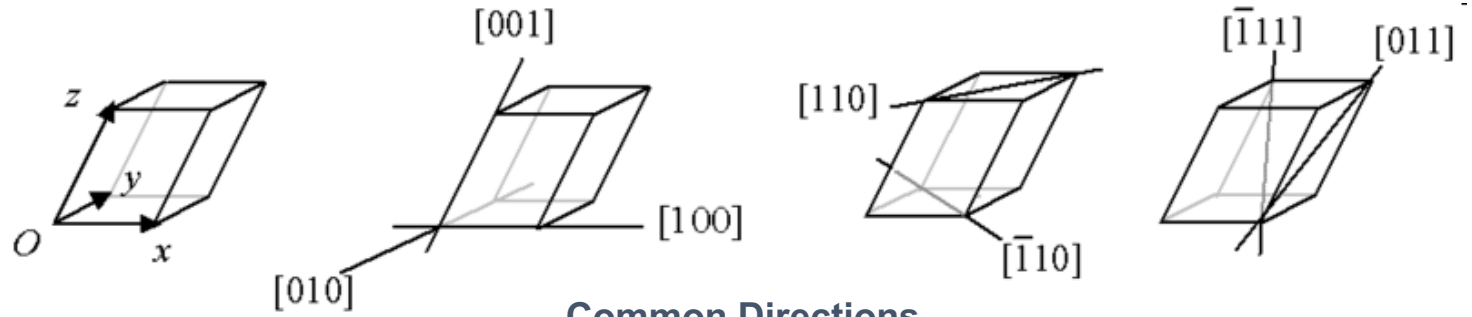
- Face Centered Cubic (FCC): An atom at each corner of a cube and an atom at each face
  - Common microstructure in PWR former plates
  - Typically non-magnetic if the solvent is Iron
  - Good creep resistance



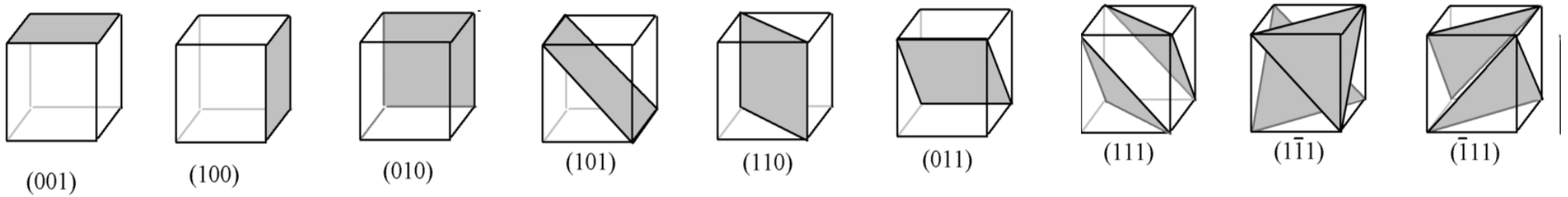


Crystallography

- Miller indices are used to describe crystallographic points, directions, and planes:
  - 3-D axis assignment based off the material's unit cell
  - For more information read Callister



Common Directions



Common Planes