

(Point) Defects in Crystals

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Different radiation produces different cascades

Mass & Charge:

Increasing
mass, same
charge

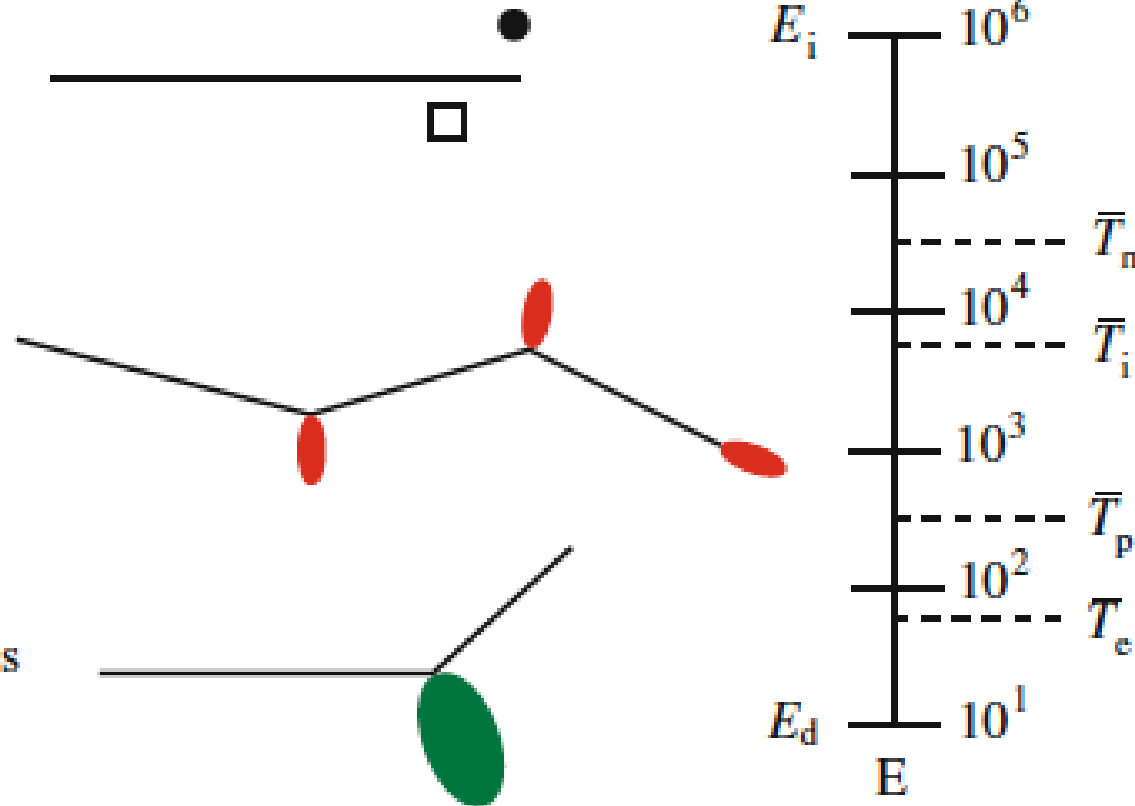
Moderate
mass, no
charge

1 MeV electrons
 $\bar{T} = 60 \text{ eV}$
 $\xi = 50-100\%$

1 MeV protons
 $\bar{T} = 200 \text{ eV}$
 $\xi = 25\%$

1 MeV heavy ions
 $\bar{T} = 5 \text{ keV}$
 $\xi = 4\%$

1 MeV neutrons
 $\bar{T} = 35 \text{ keV}$
 $\xi = 2\%$



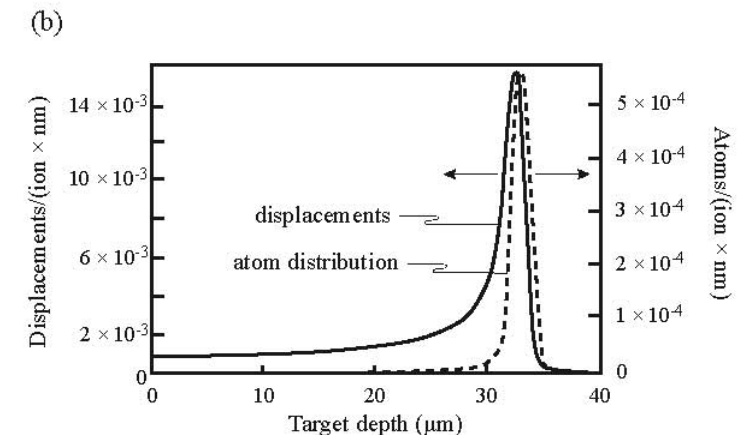
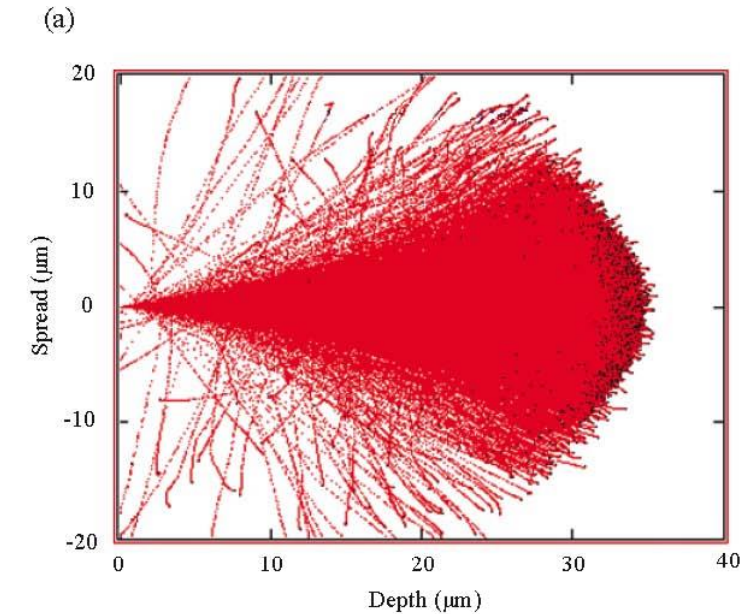
Stopping
mechanism:

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!

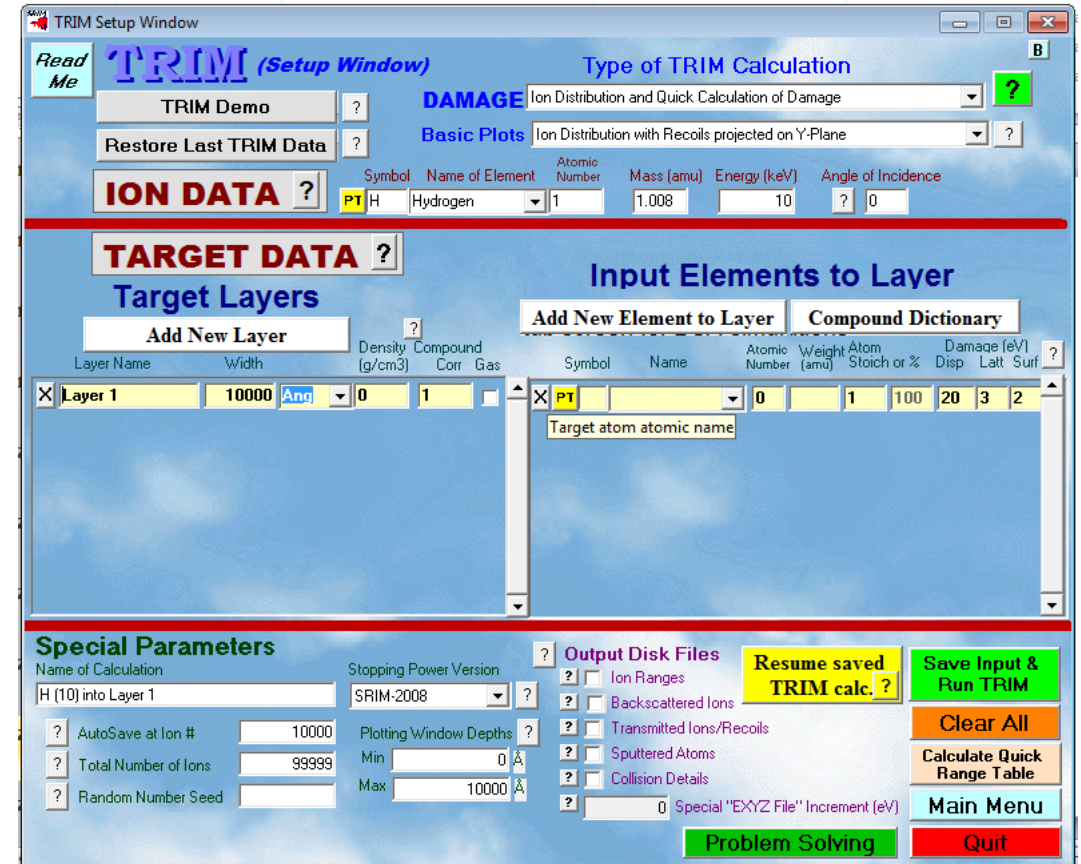


The SRIM software

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

Ion Type **H** 1.008 amu
Ion Energy **10** keV
Ion Angle **0** degrees
Completed **200** of **200**
SHOW LIVE DATA **HELP**

? H (10) into Layer 1 (1 layers, 1 atoms)

Layer Name	Width (A)	Density	Si (28.086)	Solid/Gas	Stop Corr.
1 Layer 1	4000	2.321	1.00000	Solid	1
Lattice Binding Energy			2		
Surface Binding Energy			4.7		

Plots
PLOT Window
0 A - 4000 A
Max Target Depth 4000
COLLISION PLOTS
☒ Ion/Recoils (XY) **All**
☐ Ion/Recoils (XZ) **None**
☐ Ions (no recoils) **Tile**
☐ Lateral View (YZ) **Clear**
Background color White/Black

DISTRIBUTIONS
File Plot
☐ Ion Distribution
☐ Ion/Recoil Distribution
☐ Lateral Range
☐ Ionization
☐ Phonons
☐ Energy to Recoils
☐ Damage Events
☐ Integral Sputtered
☐ Differential Ions
☐ -----
☐ Backscattered Ions
☐ Transmitted Ions
☐ Collision Details
3-D Plots **3D Help**

XY Longitudinal
Depth vs. Y-Axis
+2000 A
-2000 A
0 A - 4000 A
-- Target Depth --
Save Save As **Print** Label Clear

Backscattered Ions 5
Transmitted Ions 0
Vacancies/Ion 6.2

ION STATS
Range Straggle
Longitudinal 1321 A 404 A
Lateral Proj. 375 A 474 A
Radial 581 A 310 A

Type of Damage Calculation
? Quick: Kinchin-Pease

Stopping Power Version
? SRIM-2008

% ENERGY LOSS
Ions Recoils
Ionization 95.90 0.45
Vacancies 0.08 0.04
Phonons 0.85 2.67

SPUTTERING YIELD
Atoms/Ion eV/Atom
TOTAL
Si 0.000000 0.00

? ☒ Save every 10000 ions
Random Number 21111
Counter
HELP



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 COLLISION.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

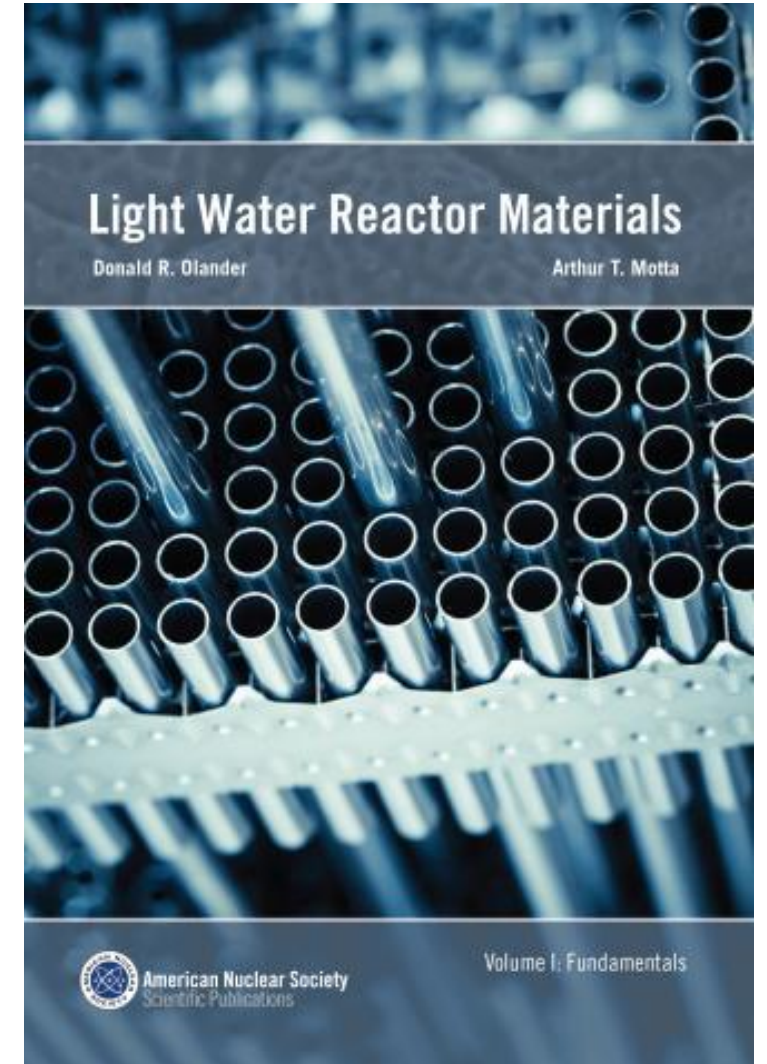
We have officially finished Part I of the course!



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=531068280900006381&Force_direct=true



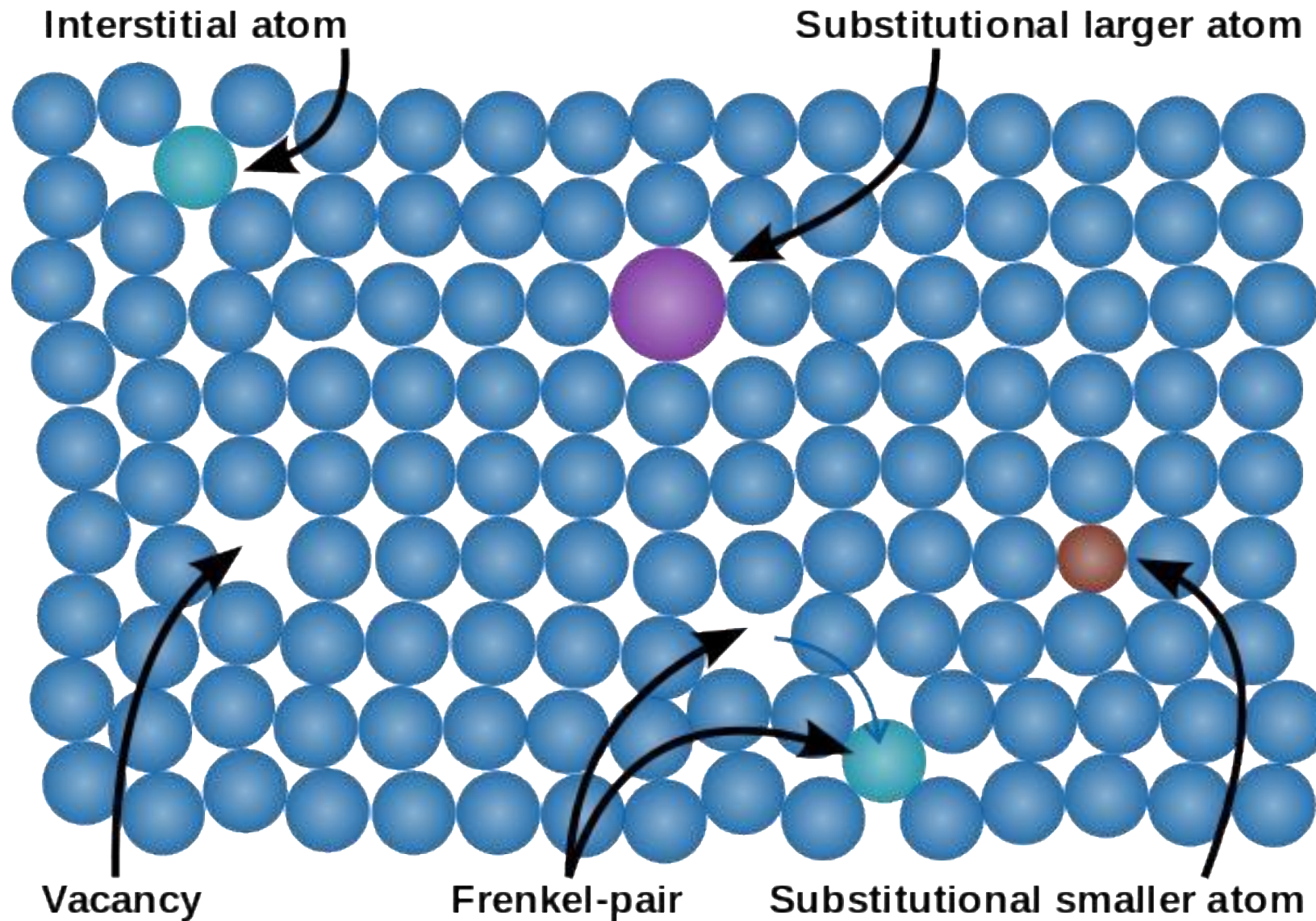
Introduction to Defects

- 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

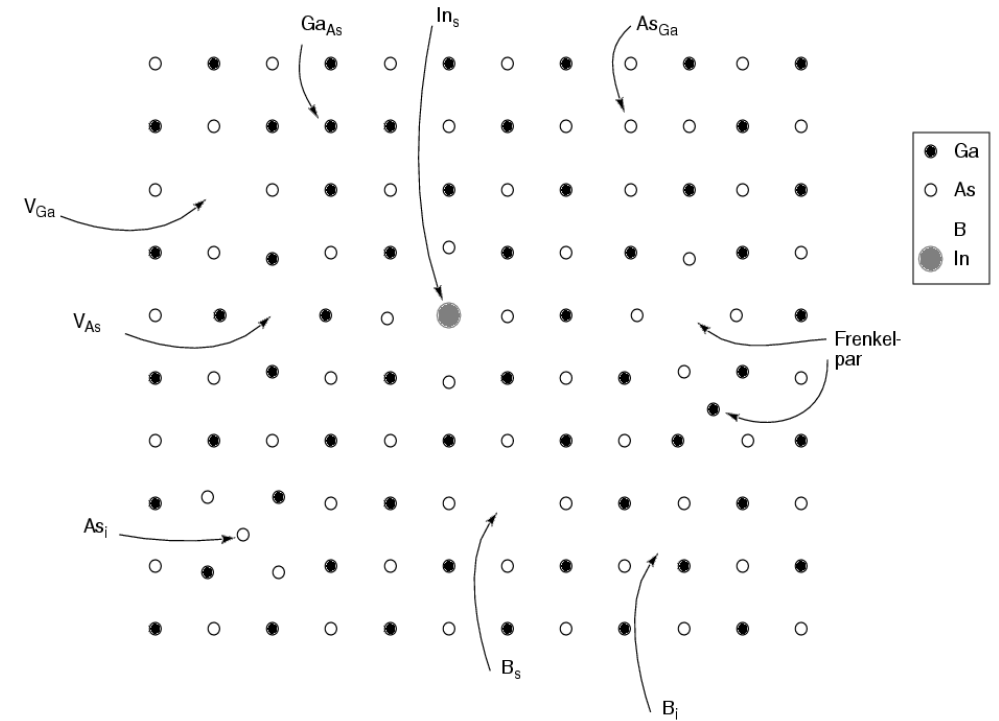
- Let's focus on **point defects** – dislocations and other types will come later
- The upper size limit of a “0 D” or point defect is not clear or very well defined
 - But, typically defects with only a few atoms (or vacancies) are considered “0 D” defects
 - This means, typically:
- We can also do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

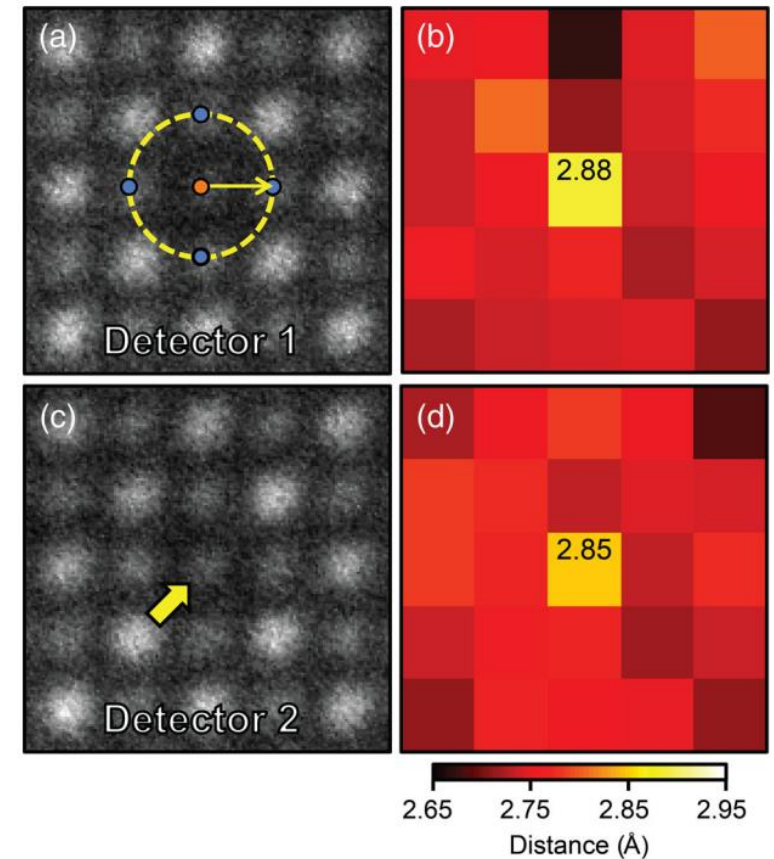


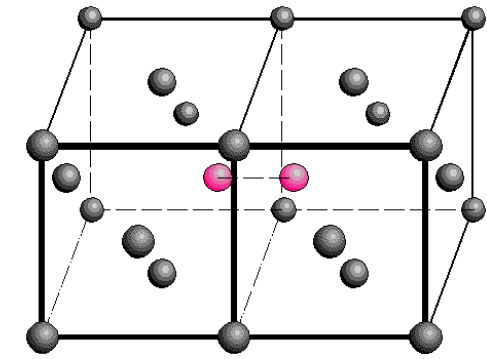
FIG. 3. Local structure relaxation around Sr vacancies. (a,c) Magnified HAADF STEM images near column-A recorded with detectors 1 and 2, respectively. (b,d) Atomic distance maps, where each pixel value indicates the average distance from one cation to its four nearest-neighbor unlike cations, showing 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).

Self Interstitial Atoms (SIA)

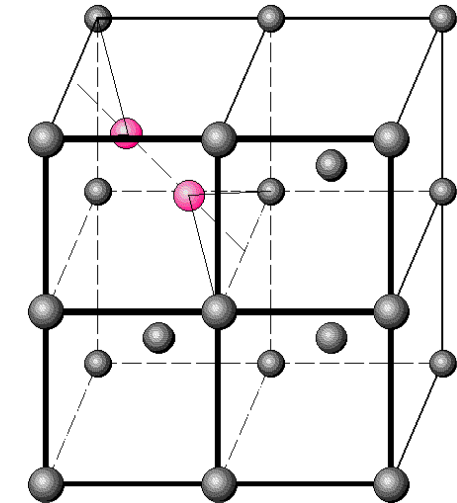
- SIAs deform surrounding lattice
- They “share” spot with lattice atom
- Called a dumb-bell configuration
 - Typically, the lowest energy configuration
 - Common radiation damage defects
 - Can affect diffusion characteristics
 - Can sit in different configurations



“Dumbbell” after vintage weights

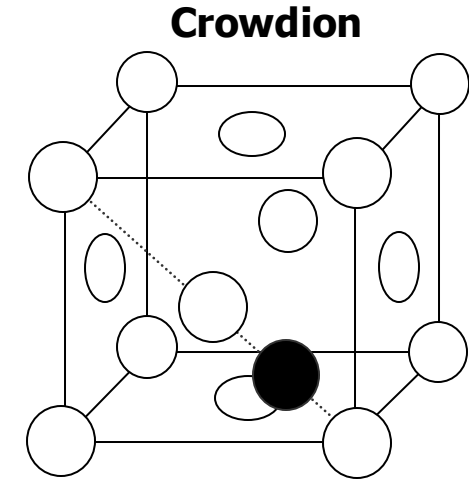
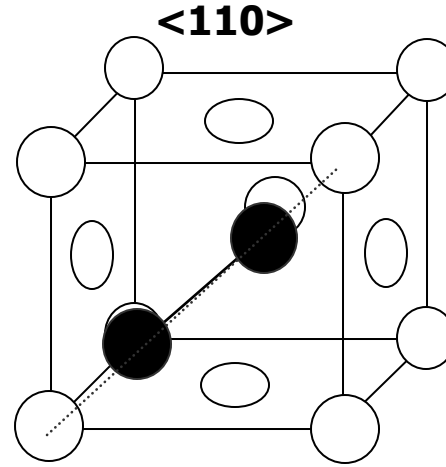
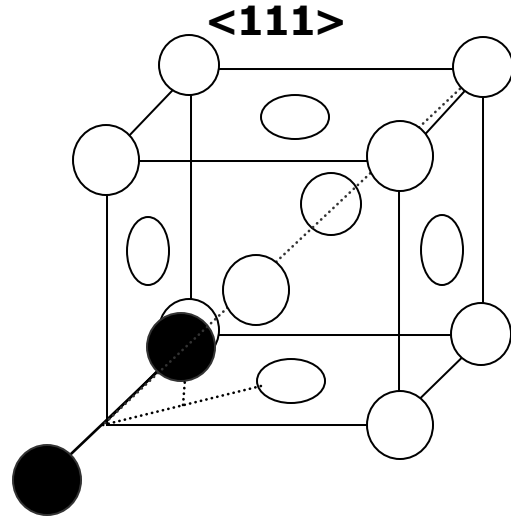
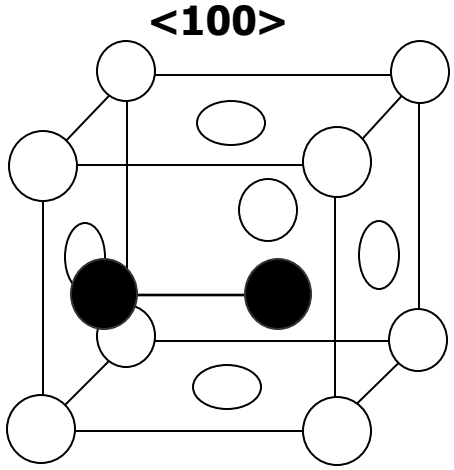


FCC Dumb-bell



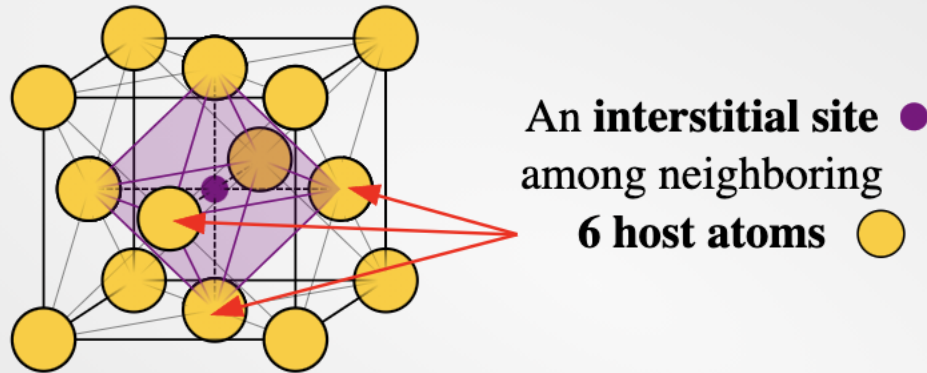
BCC Dumb-bell

Possible FCC Self Interstitial Atom (SIA) Sites

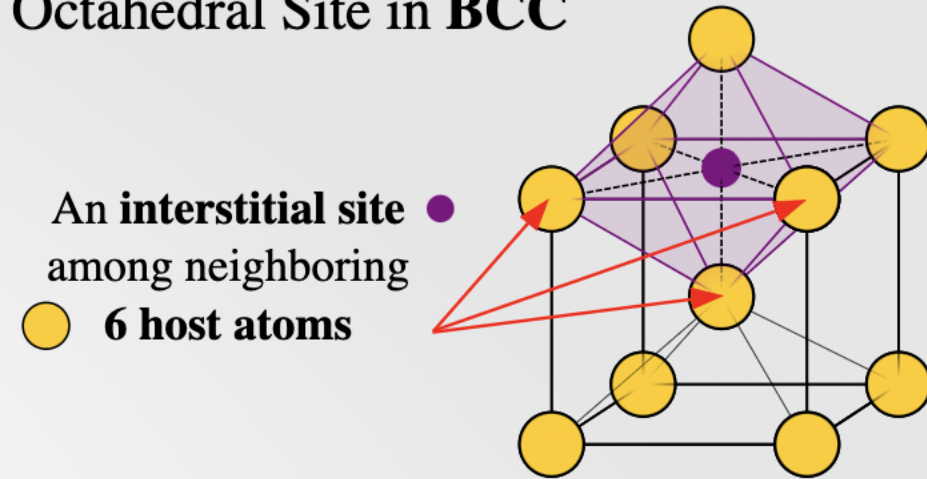


Solute Interstitial Configurations

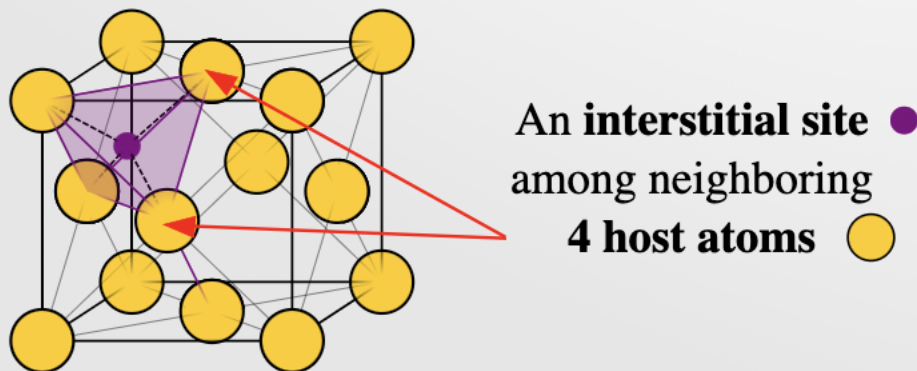
Octahedral Site in FCC



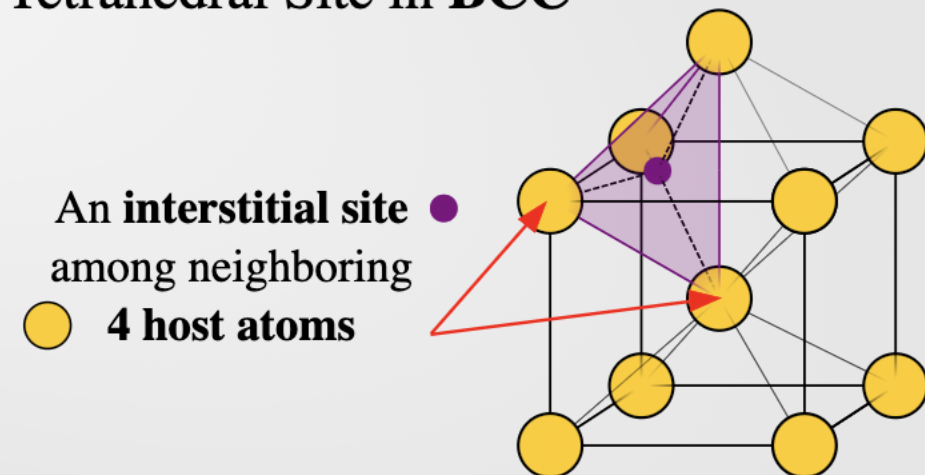
Octahedral Site in BCC



Tetrahedral Site in FCC

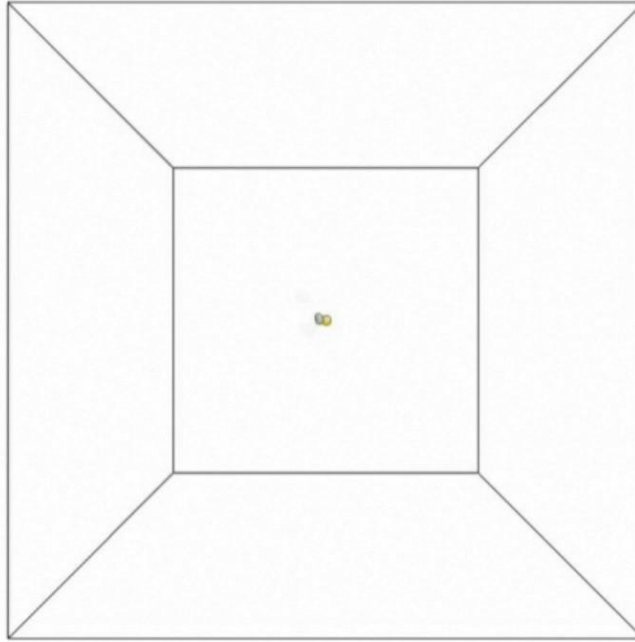


Tetrahedral Site in BCC

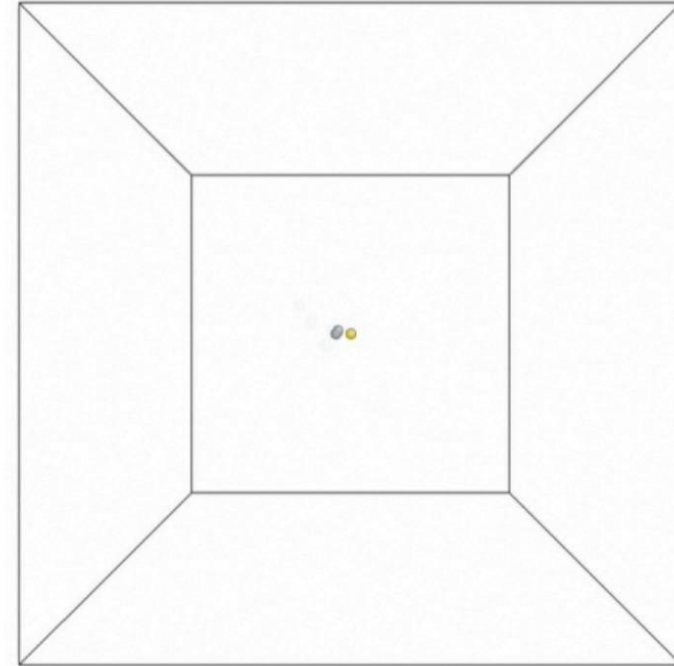


Role of solutes

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 in a large number of small interstitial (grey), Cr-containing clusters. (courtesy, B. Wirth, University of California, Berkeley)



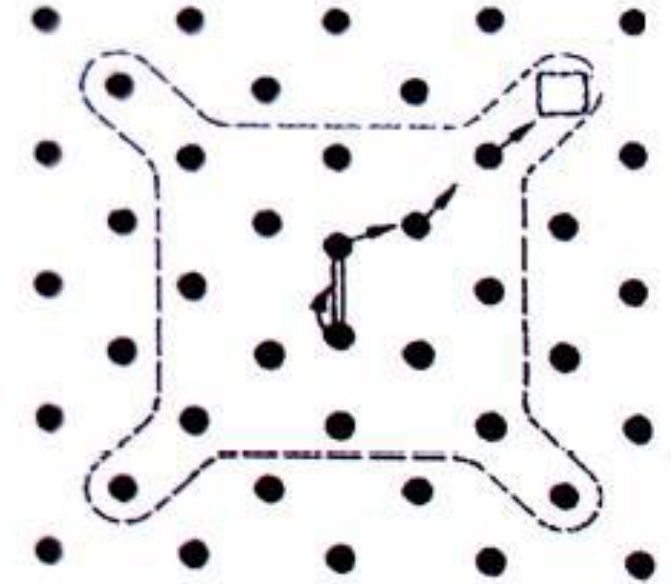
4.2 Behavior of iron and chromium in a 20 keV cascade in Fe-10% Cr alloy with Cr as an undersized solute. This is the same cascade and alloy as in Movie 4.1 but with Cr modeled as an undersized solute in iron. This condition leads to stronger trapping by iron interstitials compared to the case where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



The Henry Ford Museum of American Innovation in Dearborn, Michigan, boasts an impressive collection of artifacts within its vast exhibition hall. How many square feet does this hall encompass?



What is the fate of point defects?



Point Defect Thermodynamics

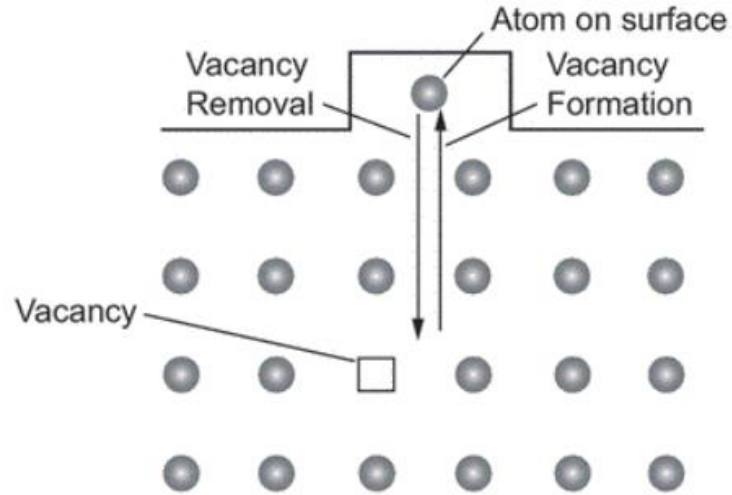


FIGURE 4.3: *Vacancy formation.*

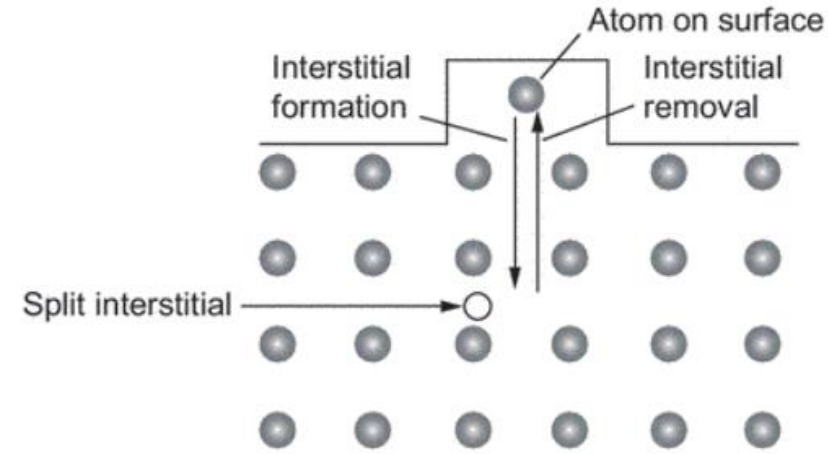


FIGURE 4.4: *SIA formation.*

- 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

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

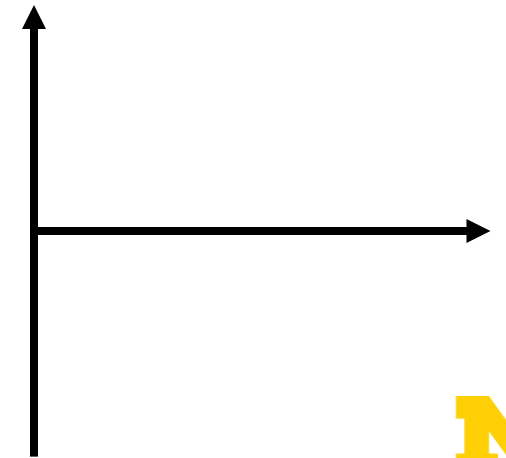
- And

$$\begin{aligned} S_{mix} &= -k_b \left[\left(\frac{N}{N + N_v} \right) \ln \left(\frac{N}{N + N_v} \right) + \left(\frac{N_v}{N + N_v} \right) \ln \left(\frac{N_v}{N + N_v} \right) \right] \\ &= -k_b [(1 - C_v) \ln(1 - C_v) + C_v \ln C_v] \end{aligned}$$

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

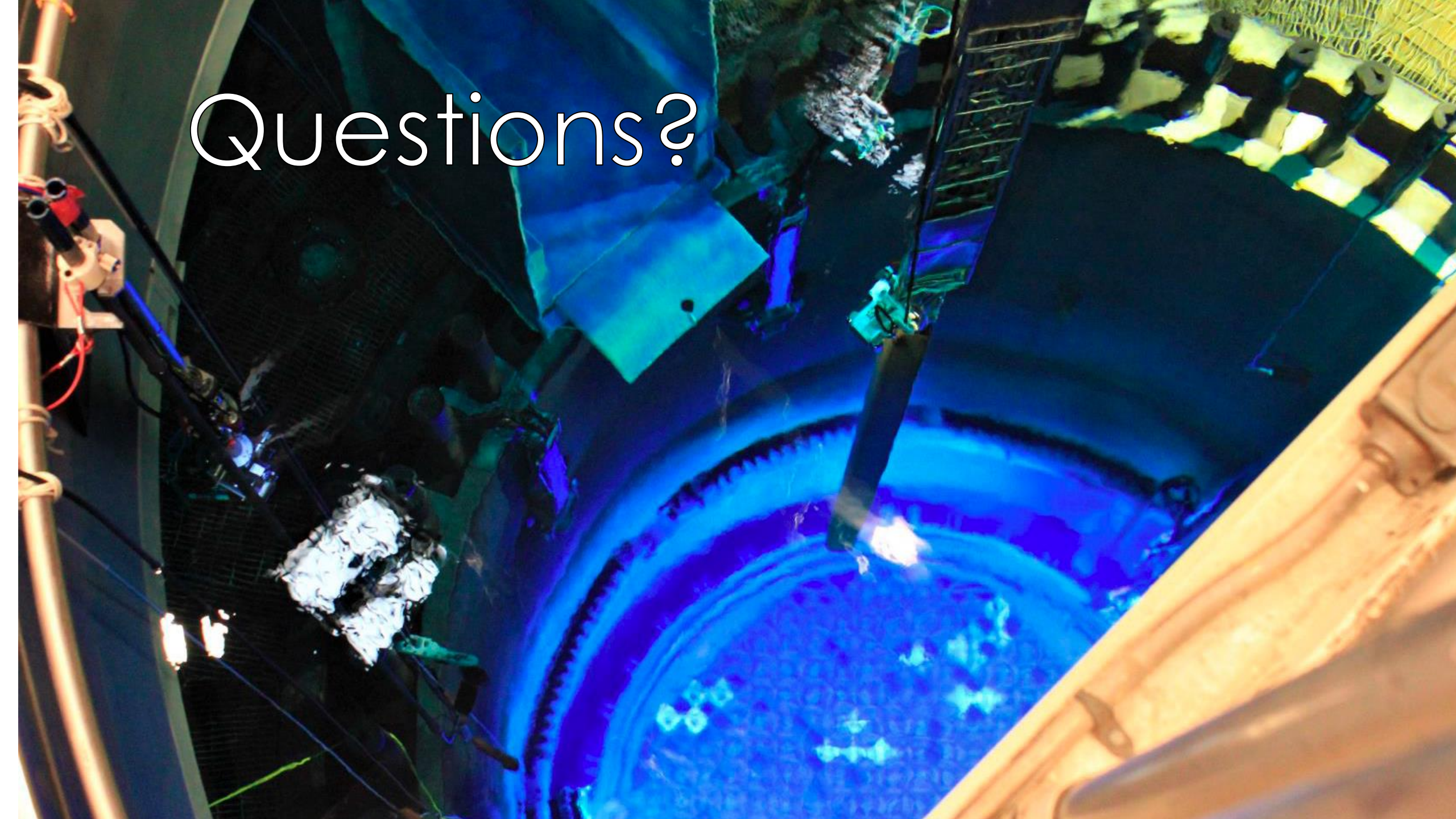
- **Interstitial formation:**
 - Using the same analysis, we then get:

Example problem – to make a point

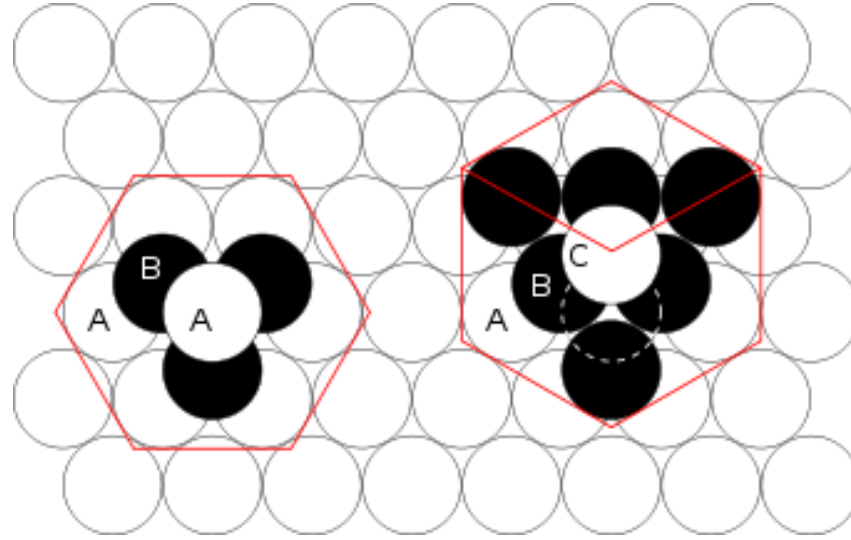
Point defect properties

	Symbol	Unit	Al	Cu	Pt	Mo	W
Interstitials							
Relaxation volume	V_{relax}^i	Atomic vol.	1.9	1.4	2.0	1.1	
Formation energy	E_f^i	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_m^i	eV	0.12	0.12	0.06		0.054
Vacancies							
Relaxation volume	V_{relax}^v	Atomic vol.	0.05	-0.2	-0.4		
Formation energy	E_f^v	eV	0.66	1.27	1.51	3.2	3.8
Formation entropy	S_f^v	k	0.7	2.4			2
Equilibrium concentration at T_m^*	$C_v(T_m)$	-	9×10^{-6}	2×10^{-6}			4×10^{-5}
Migration energy	E_m^v	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_f^{FP}	eV	3.9	3.5	5		

Questions?



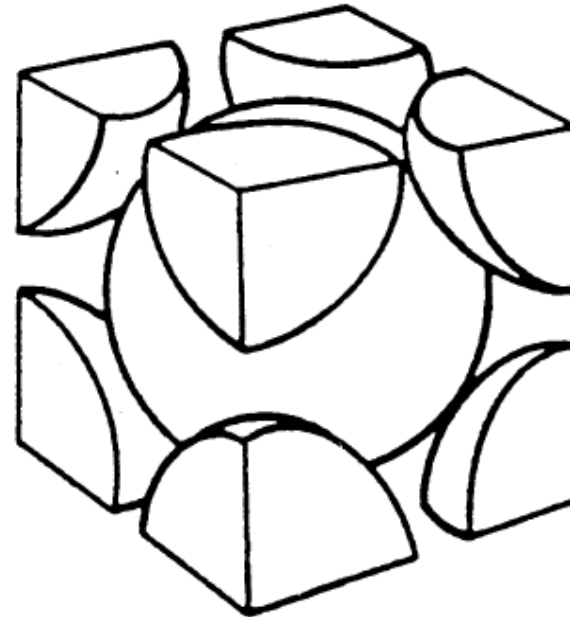
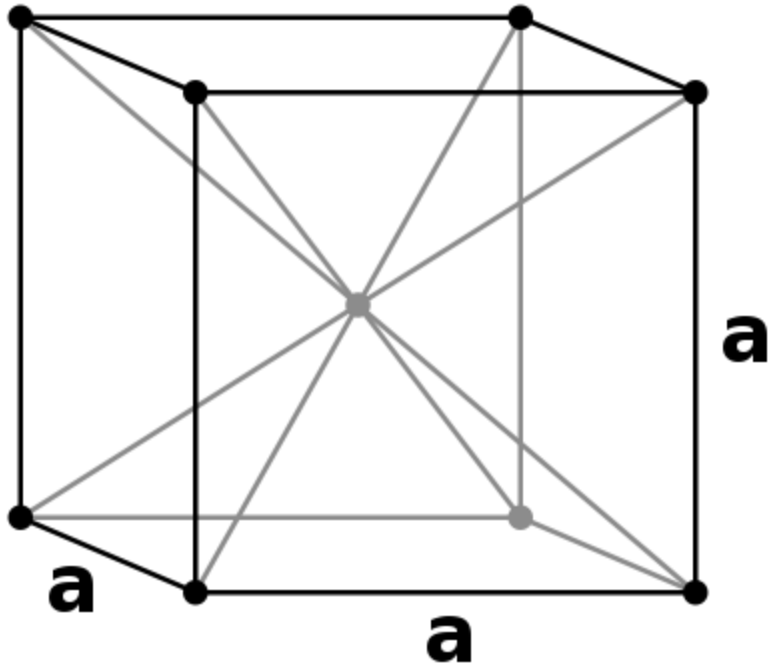
Atomic Packing



- 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

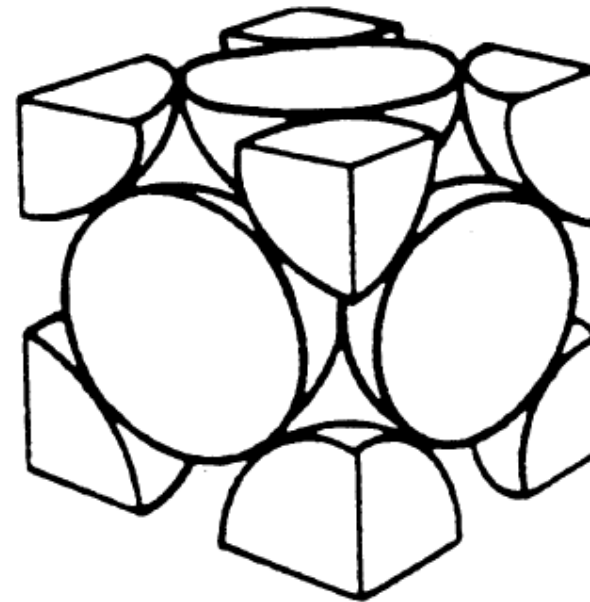
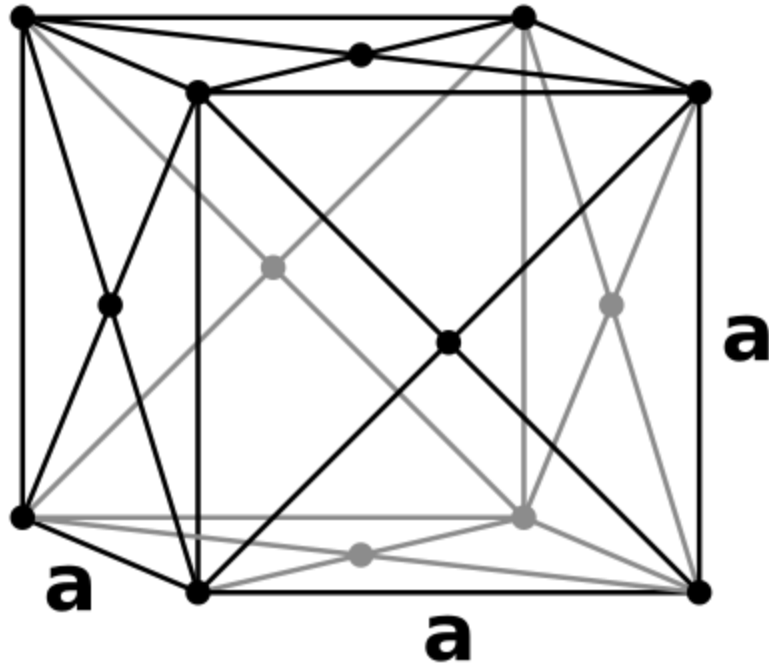
Lattice Configurations

- 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

