Crystal Imperfections

Perfect Crystals - Natural

Diamonds

~ 3.6x3.2x1.3 cm

Sapphire

~5x3x2 cm

Ruby

~ 2x2x1 cm

Emerald

30x 10x 10 cm

What is the common attribute between them ?

Man made perfect crystals

Si ingot

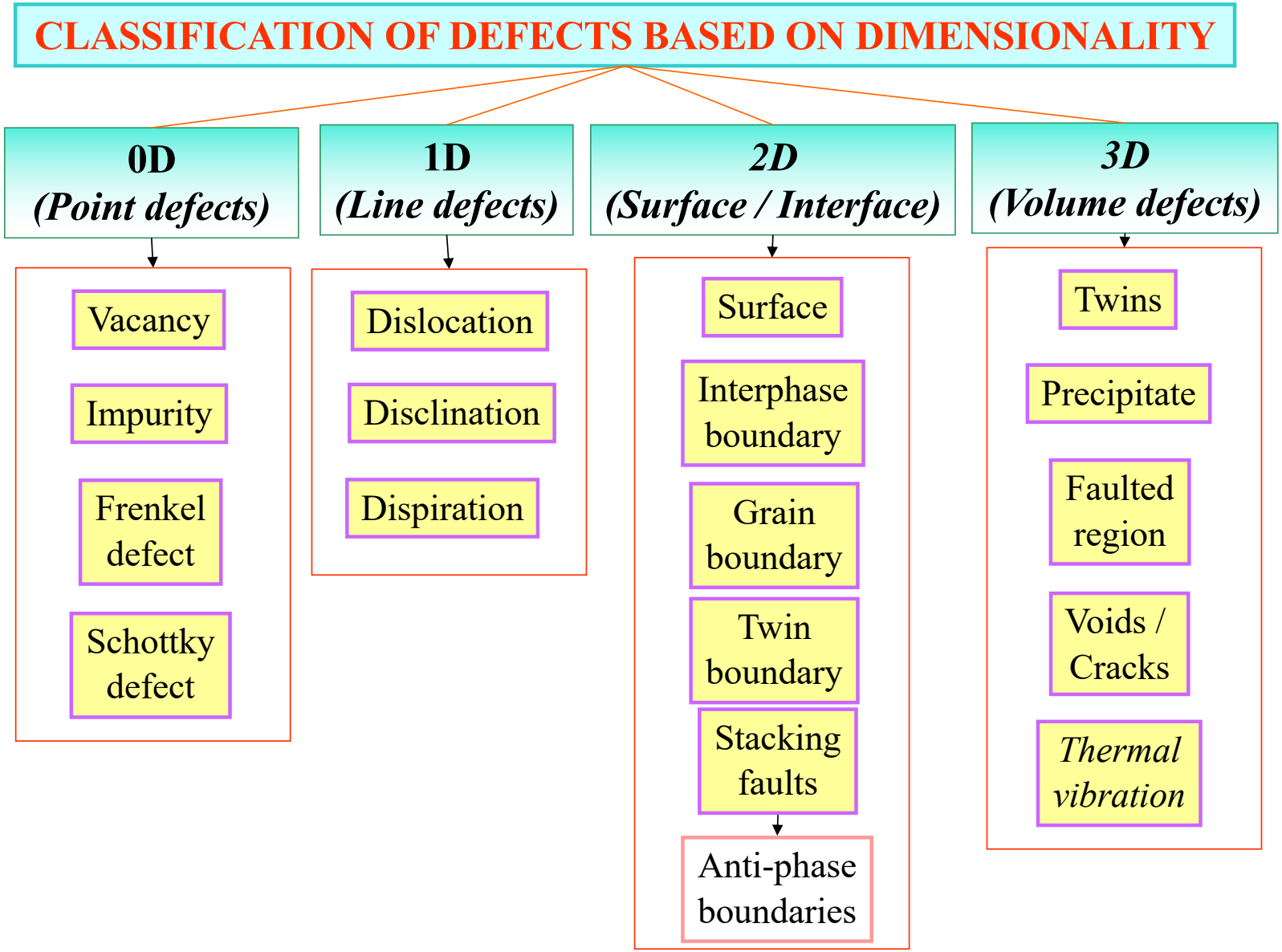
Lab grown diamonds

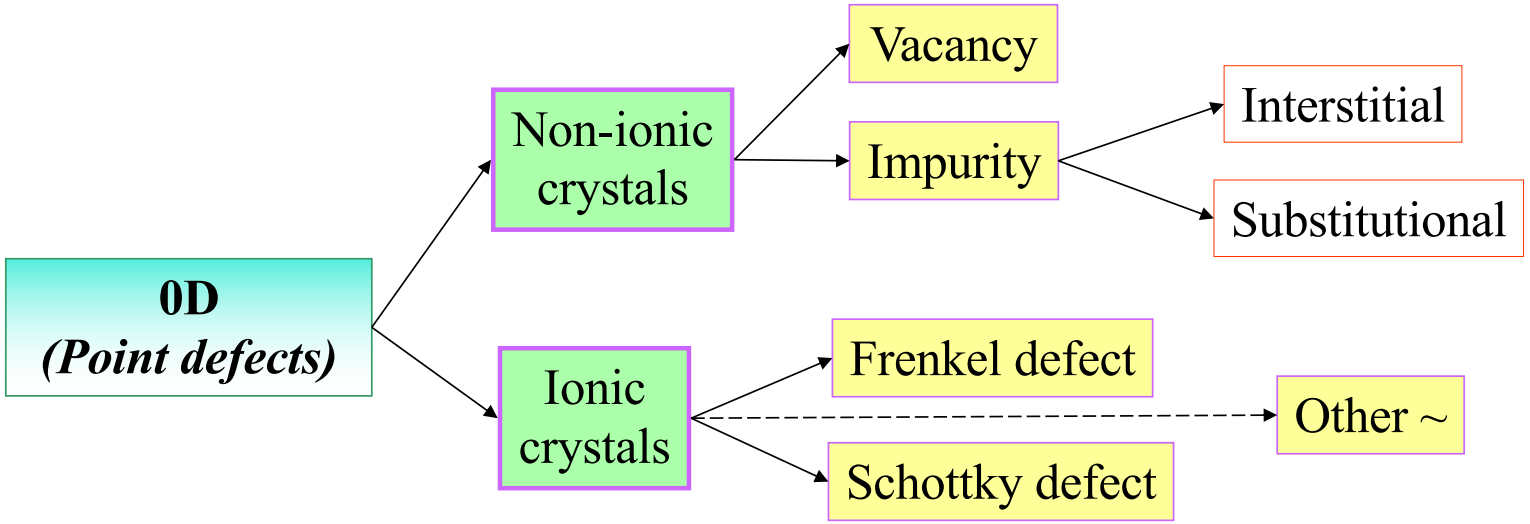
Single crystal quartz

Table of defect densities

Material	Impurity	Material	Impurity
Diamond	Nitrogen impurity 1%	Si wafers	10^2 cm^{-2}
Blue Sapphire	0.01% Ti and Fe	SiC Wafers	$4x10^3 – 5x10^3$ cm^{-2}
Ruby	1% Chromium	GaN wafers	$10^{10}cm^{-2}$

An approximate defect density in steels?


CLASSIFICATION OF DEFECTS BASED ON DIMENSIONALITY
0D
(Point defects)
1D
(Line defects)
2D
(Surface / Interface)
3D
(Volume defects)
Vacancy
Impurity
Frenkel defect
Schottky defect
Dislocation
Disclination
Dispiration
Surface
Interphase boundary
Grain boundary
Twin boundary
Stacking faults
Anti-phase boundaries
Twins
Precipitate
Faulted region
Voids / Cracks
Thermal vibration

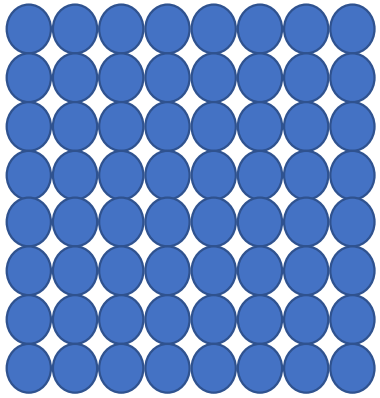


- Imperfect point-like regions in the crystal about the size of 1-2 atomic diameters

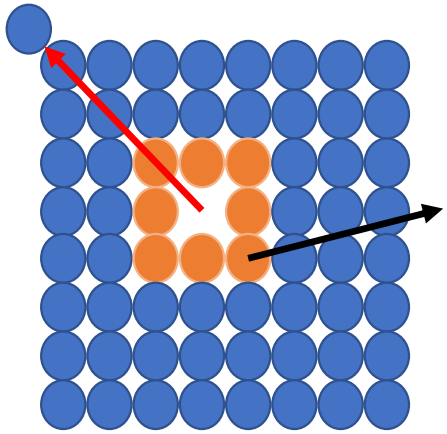
Vacancy

- Missing atom from an atomic site
- Atoms around the vacancy displaced
- Tensile stress field produced in the vicinity

Perfect infinite 2D lattice

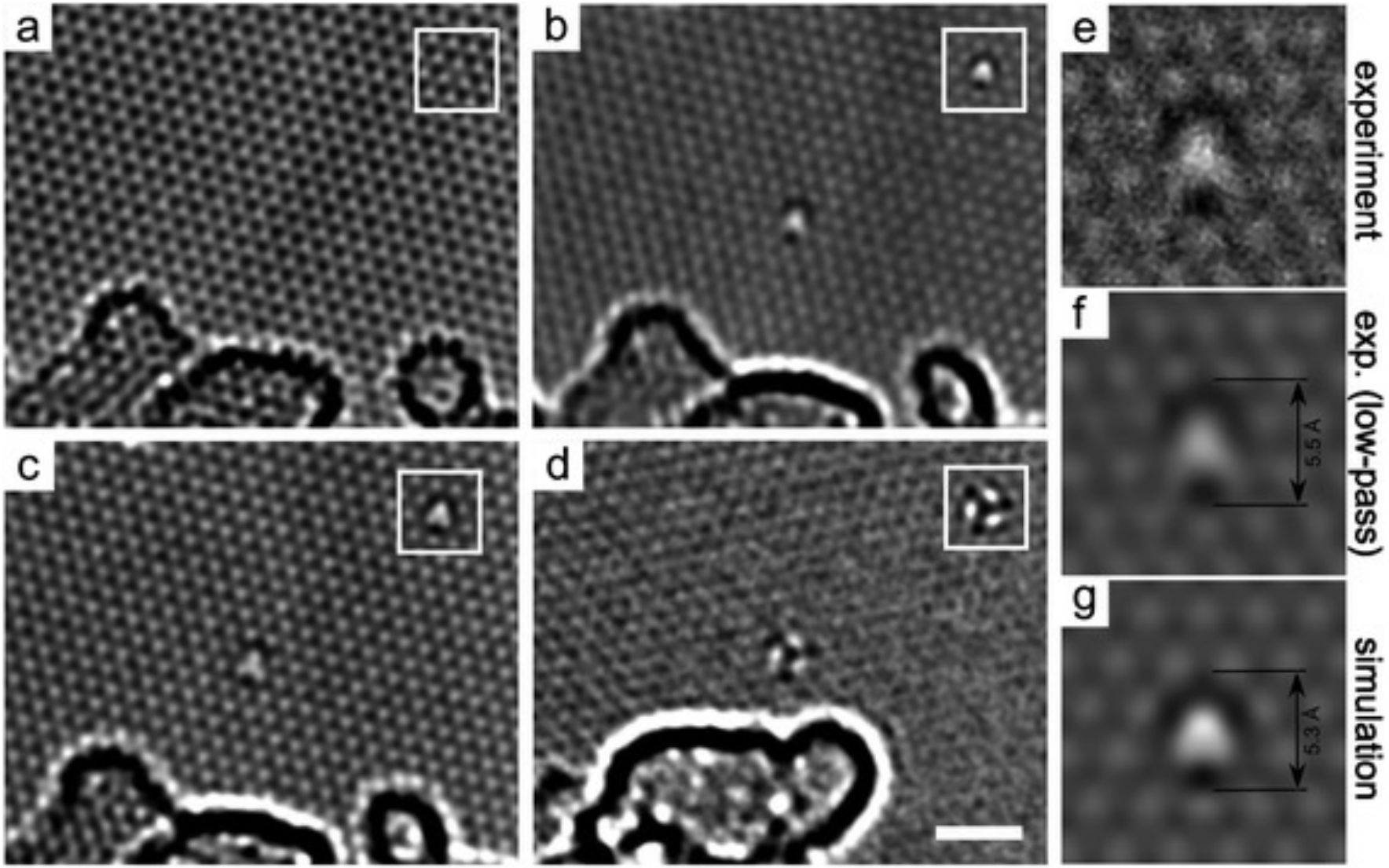


Displaced atom



Feel strained
Differently coordinated

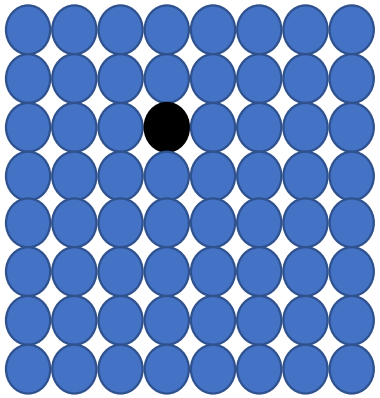
Will the neighboring atoms face tensile or compressive strain ?



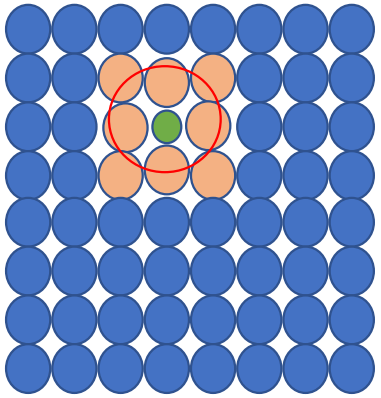
https://pubs.rsc.org/en/content/articlehtml/2014/nr/c4nr01918k

Substitutional

Perfect infinite 2D lattice



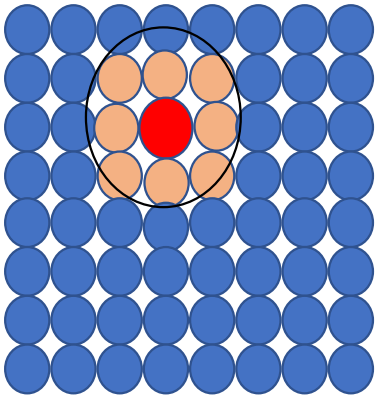
Substitution by a smaller atom



Boron doping in Si

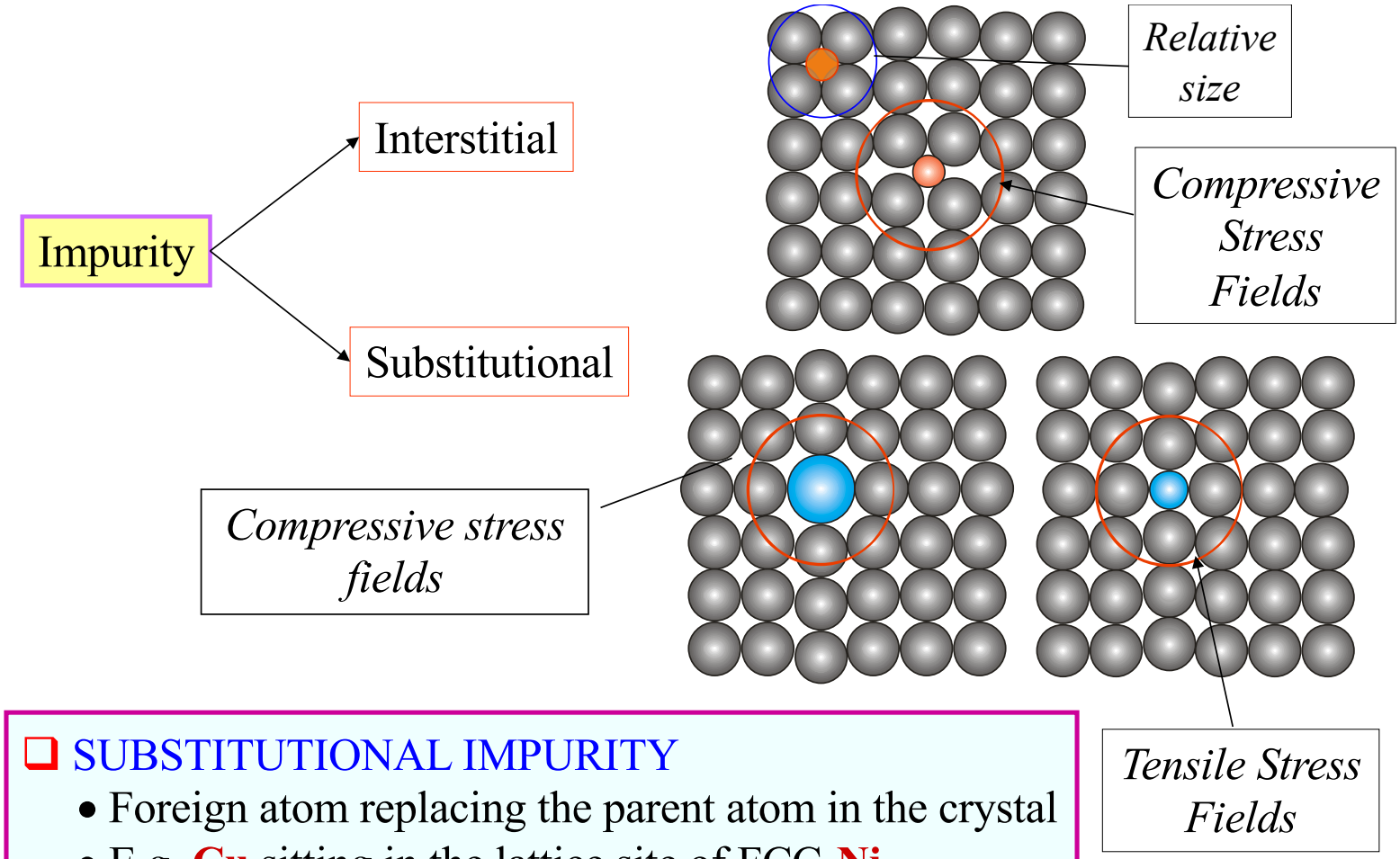
Being a smaller atom,
The neighboring atoms
are in tensile stress

Substitution by a larger atom



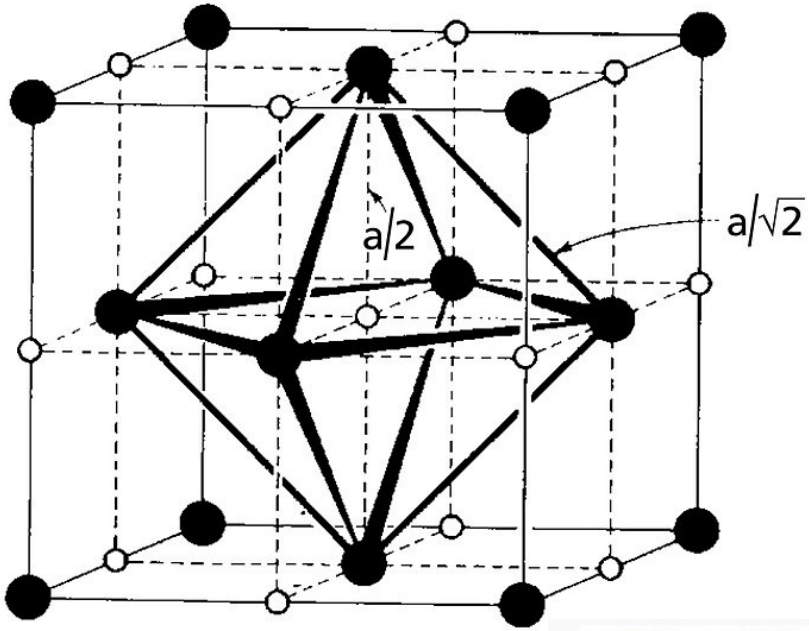
Arsenic doping in Si

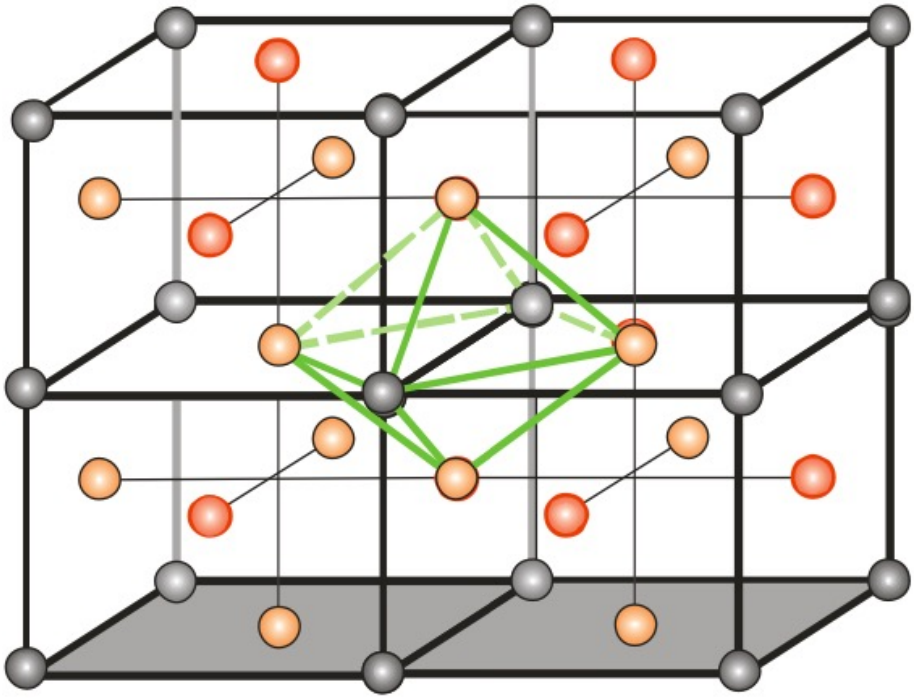
Being a larger atom,
The neighboring atoms
are squeezed.
There exists a
compressive strain field

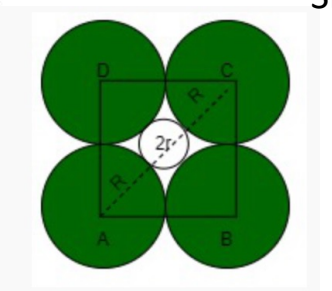


- SUBSTITUTIONAL IMPURITY
  - Foreign atom replacing the parent atom in the crystal
  - E.g. **Cu** sitting in the lattice site of FCC-**Ni**
- INTERSTITIAL IMPURITY
  - Foreign atom sitting in the void of a crystal
  - E.g. **C** sitting in the octahedral void in HT FCC-**Fe**

FCC Voids – Octahedral





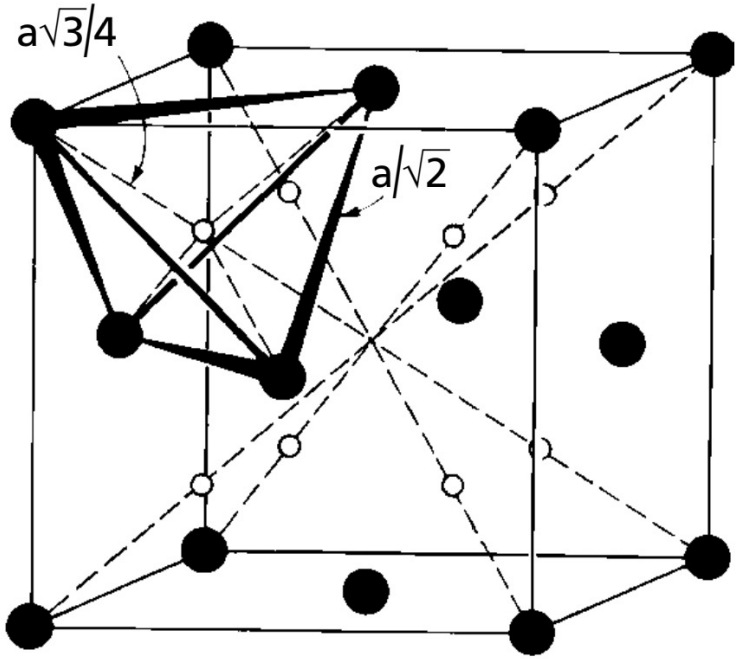


Size of atom that can be squeezed inside an octahedral voild

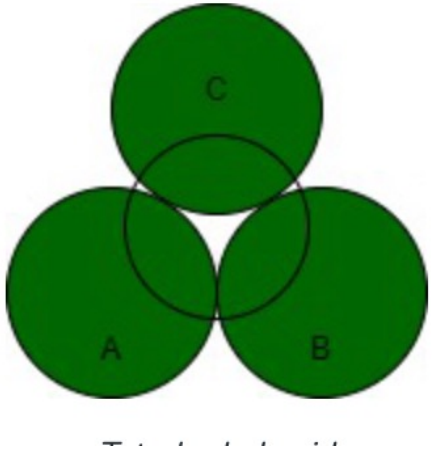
Octahedral void.

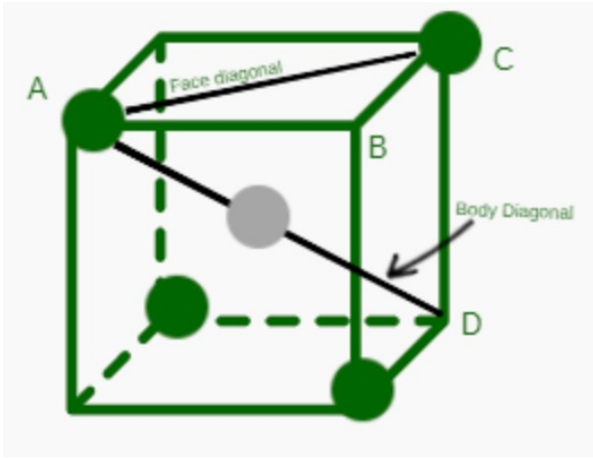
$$\mathrm{r} = 0.414R$$

FCC Voids - Tetrahedral



One void at each corner of the cube.





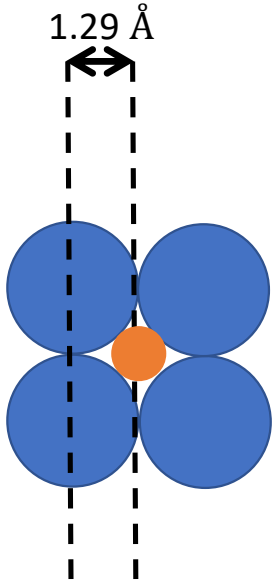
Geometric arguments leads to the size of atom squeezed into tetragonal void

Tetrahedral void.

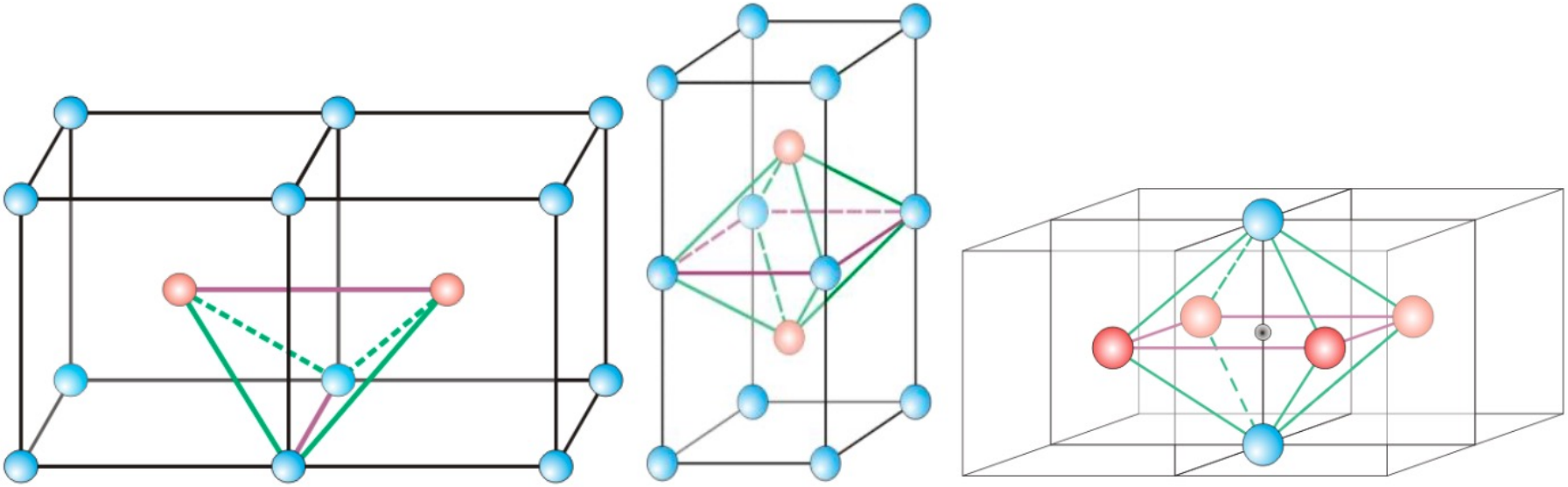
$$\mathrm{r} = 0.225R$$

Interstitial **C** sitting in the octahedral void in HT FCC-**Fe**

- $r_{Octahedral\ void} / r_{FCC\ atom} = 0.414$
- $r_{Fe\text{-}FCC} = 1.29$ Å $\Rightarrow$ $r_{Octahedral\ void} = 0.414 \times 1.29 = 0.53$ Å
- $r_C = 0.71$ Å
- $\Rightarrow$ Compressive strains around the C atom
- Solubility limited to 2 wt% (9.3 at%)

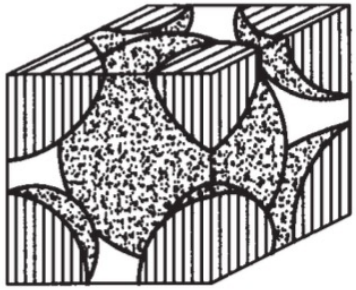


What happens in BCC ? (Iron at low temperatures)

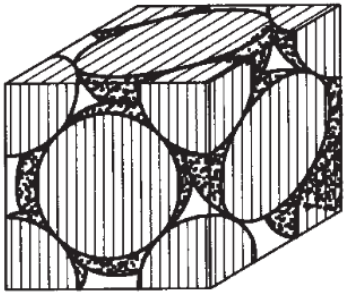


Two tetrahedral voids for each line of the cube – 12 TV
One octahedral void for each plane – 3 OV
For each line, there is another octahedral shared by four - 3

Voids Comparison



	BCC	FCC
Tetrahedral void centers	Face (1/2,1/4,0) and equivalent	Body diagonals(1/4,1/4,1/4) and (3/4,3/4,3/4)
Number of tetrahedral voids	12	8
Tetrahedral void sizes	0.29 R	0.225R
Octahedral voids sizes	0.15 R	0.414R
Number of Octahedrons	6	4
Octahedron centers	Mid point of edges (0,0,1/2) and equivalent	Body center(1/2,1/2,1/2) and cell edges (1/2,0,0) and equivalent



What does these information tell us about the carbon solubility in Iron at different temperatures ?

Interstitial **C** sitting in the octahedral void in LT BCC-**Fe**

- $r_{\text{Tetrahedral void}} / r_{\text{BCC atom}} = 0.29 \bullet r_C = 0.71$ Å
- $r_{\text{Fe-BCC}} = 1.258$ Å $\Rightarrow$ $r_{\text{Tetrahedral void}} = 0.29 \times 1.258 = 0.364$ Å
- ► But C sits in smaller octahedral void- displaces fewer atoms
- $\Rightarrow$ Severe compressive strains around the C atom
- Solubility limited to 0.008 wt% (0.037 at%)

- Remember, voids in BCC are all distorted.
- Octahedral is asymmetric with two atoms very close