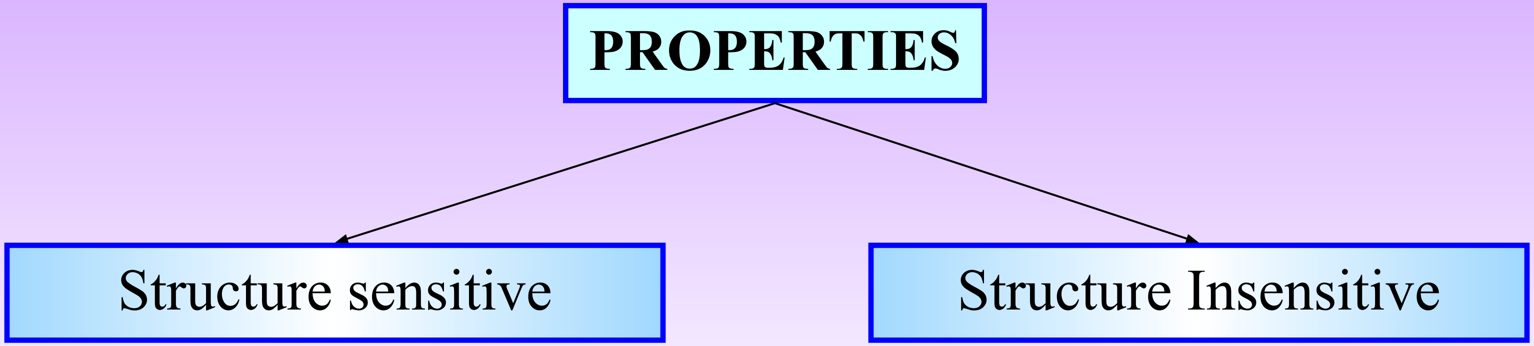
DEFECTS IN CRYSTALS

- Point defects
- Line defects
- Surface Imperfections

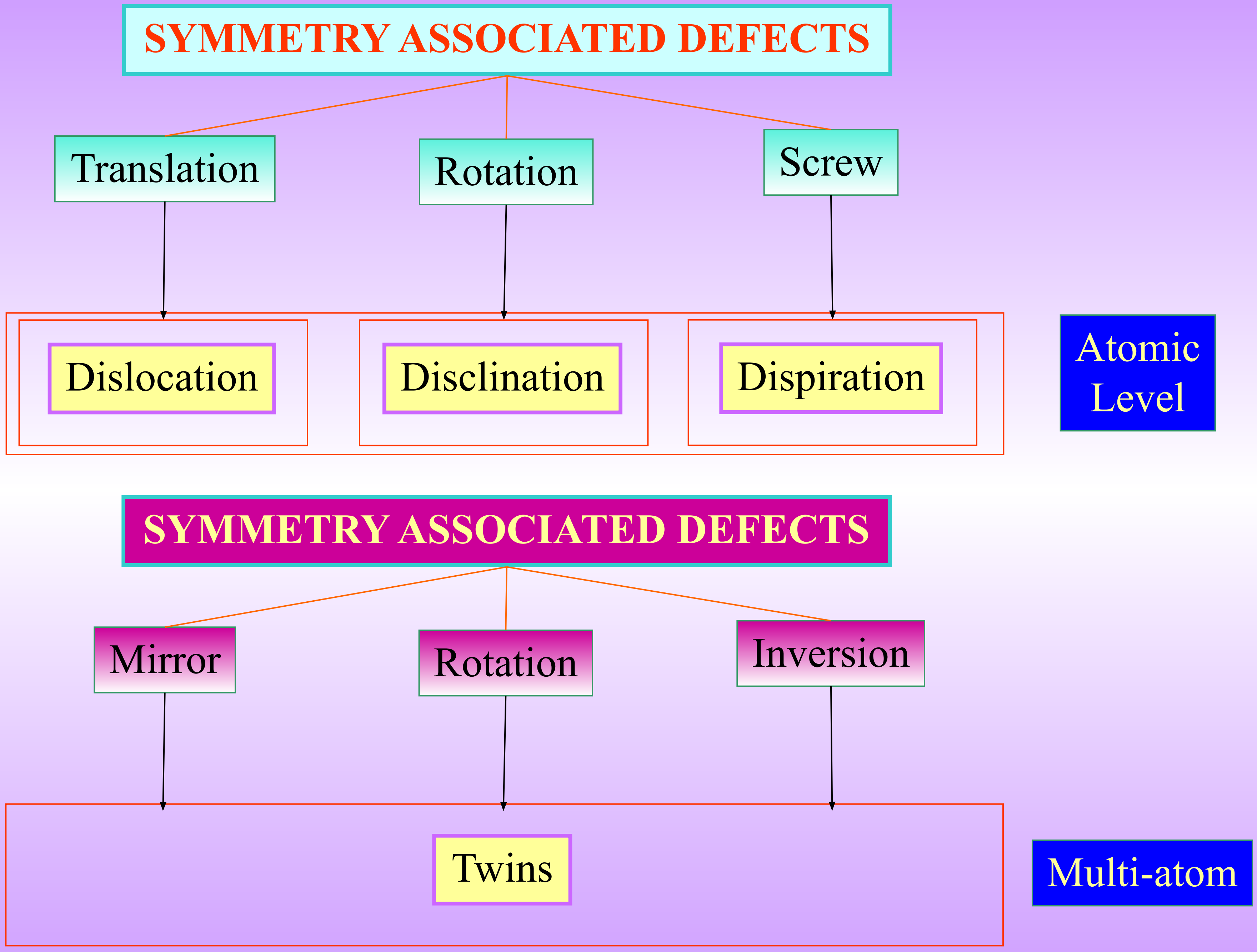


E.g. Yield stress, Fracture toughness

E.g. Density, elastic modulus

CLASSIFICATION OF DEFECTS BASED ON DIMENSIONALITY

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

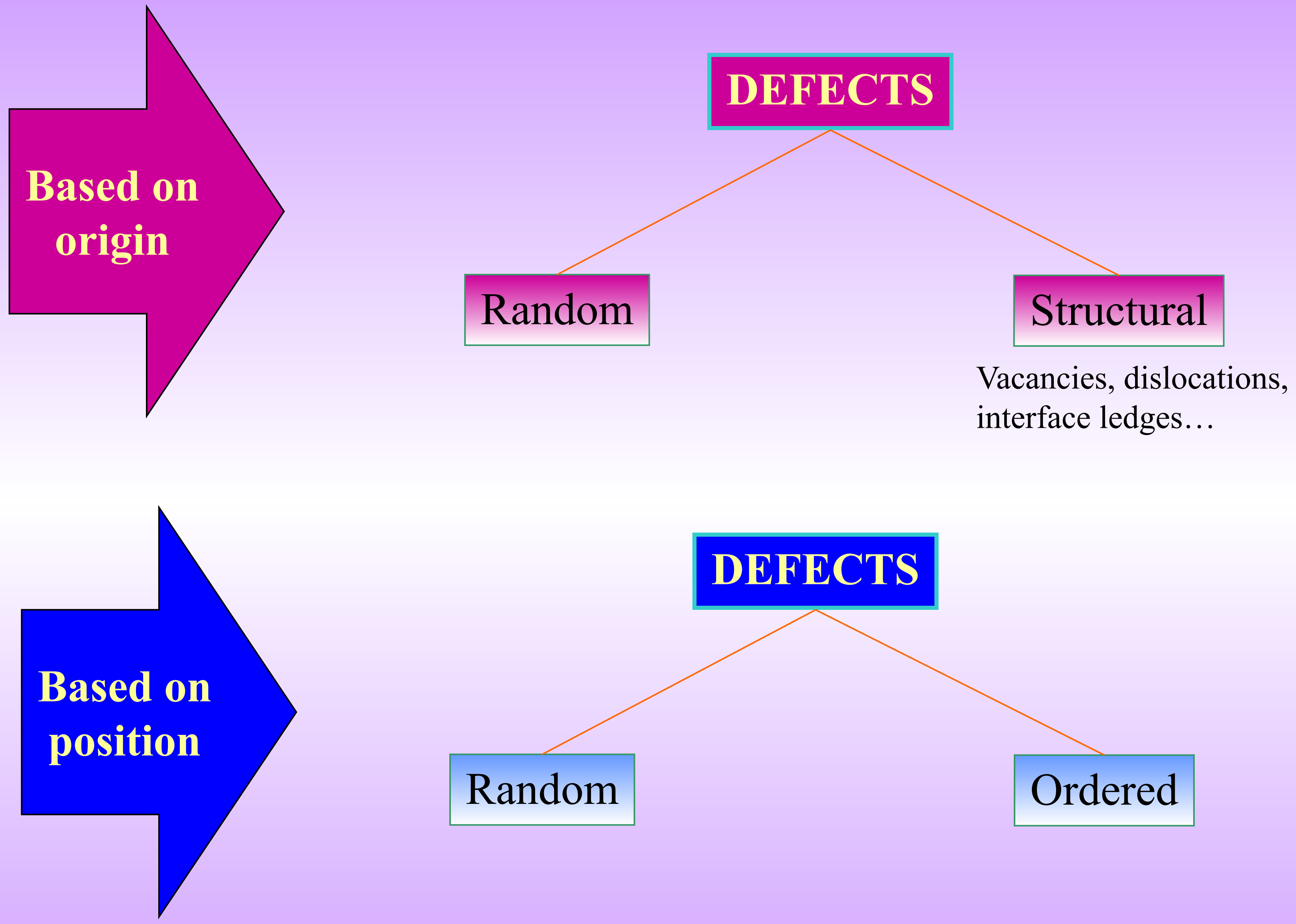

SYMMETRY ASSOCIATED DEFECTS
Translation
Rotation
Screw
Dislocation
Disclination
Dispiration
Atomic Level
SYMMETRY ASSOCIATED DEFECTS
Mirror
Rotation
Inversion
Twins
Multi-atom

Based on symmetry breaking

Hence association with symmetry

DEFECTS

- Topological
- Non-topological


Based on origin
DEFECTS
Random
Structural
Vacancies, dislocations, interface ledges…
Based on position
DEFECTS
Random
Ordered

THE ENTITY IN QUESTION

GEOMETRICAL

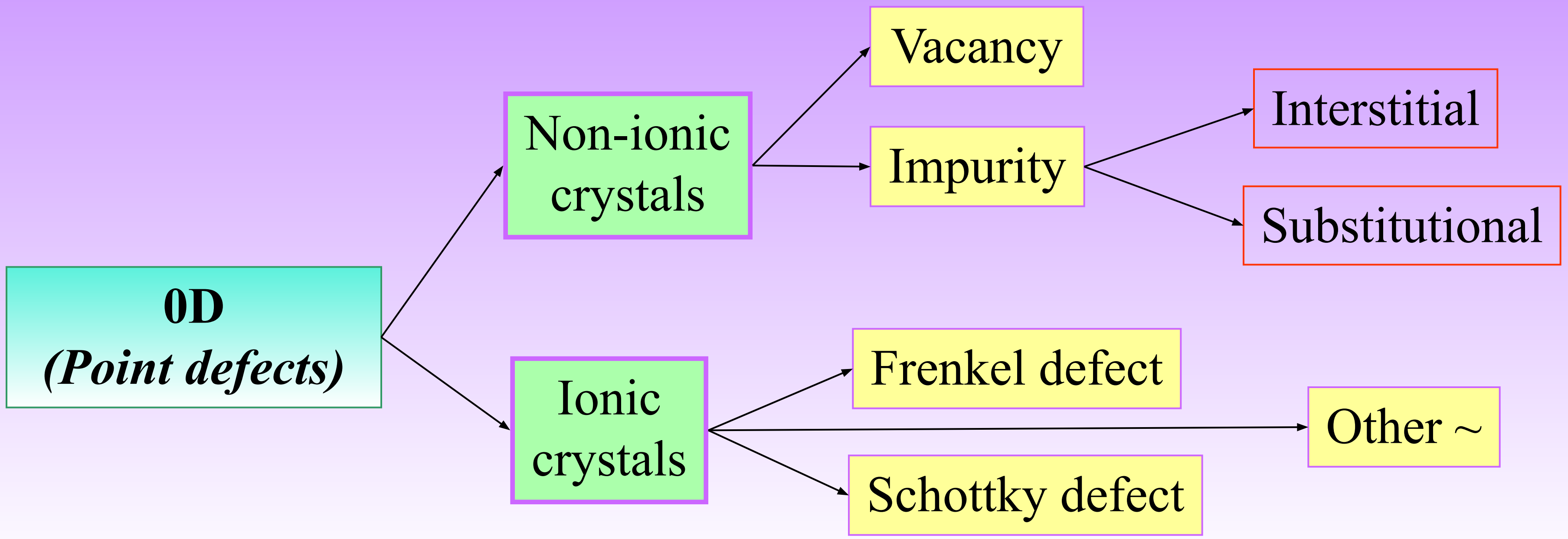
E.g. atoms, clusters etc.

PHYSICAL

E.g. spin, magnetic moment

THE OPERATION DEFINING A DEFECT CANNOT BE A SYMMETRY OPERATION OF THE CRYSTAL

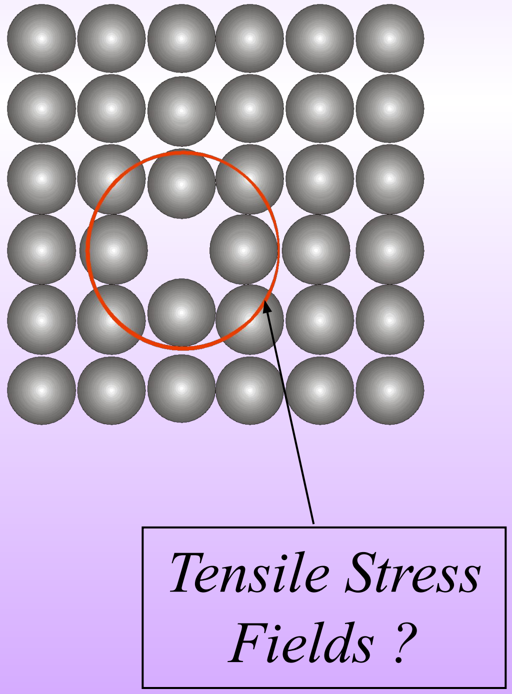
A DEFECT *"ASSOCIATED"* WITH A SYMMETRY OPERATION OF THE CRYSTAL
→ TOPOLOGICAL DEFECT



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

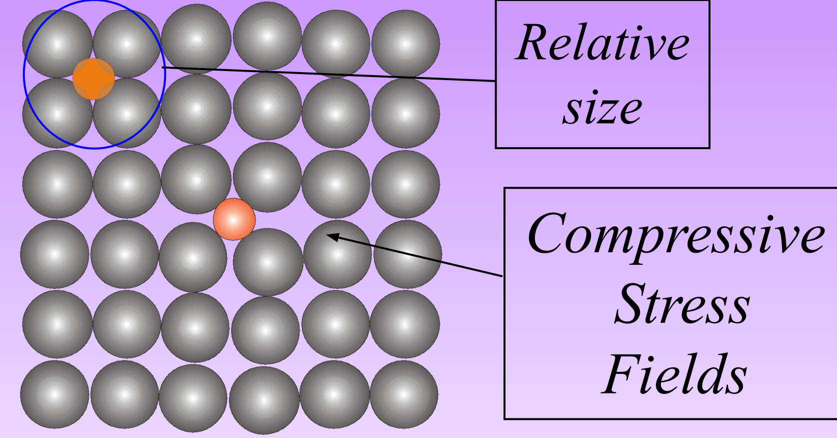
Vacancy

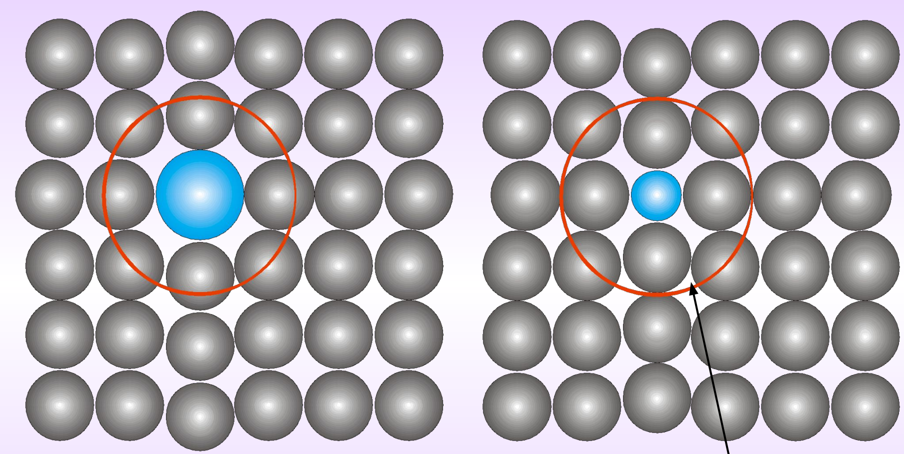
- Missing atom from an atomic site
- Atoms around the vacancy displaced
- Tensile stress field produced in the vicinity



Impurity → Interstitial

Impurity → Substitutional





- **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**

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%)

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

- $r_{Tetrahedral\ void} / r_{BCC\ atom} = 0.29 \cdot r_C = 0.71$ Å
- $r_{Fe\text{-}BCC} = 1.258$ Å $\Rightarrow$ $r_{Tetrahedral\ void} = 0.29 \times 1.258 = 0.364$ 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%)

ENTHALPY OF FORMATION OF VACANCIES

- Formation of a vacancy leads to missing bonds and distortion of the lattice
- The potential energy (Enthalpy) of the system increases
- Work required for the formaion of a point defect →
  Enthalpy of formation (ΔH_f) [kJ/mol or eV / defect]
- Though it costs energy to form a vacancy its formation leads to increase in configurational entropy
- ⇒ above zero Kelvin there is an equilibrium number of vacancies

Crystal	Kr	Cd	Pb	Zn	Mg	Al	Ag	Cu	Ni
kJ / mol	7.7	38	48	49	56	68	106	120	168
eV / vacancy	0.08	0.39	0.5	0.51	0.58	0.70	1.1	1.24	1.74

- Let n be the number of vacancies, N the number of sites in the lattice
- Assume that concentration of vacancies is small i.e. $n/N \ll 1$

  $\Rightarrow$ the interaction between vacancies can be ignored

  $\Rightarrow$ $\Delta H_{formation}$ (n vacancies) = n . $\Delta H_{formation}$ (1 vacancy)
- Let ΔH_f be the enthalpy of formation of 1 mole of vacancies

$$\Delta G = \Delta H - T\,\Delta S$$

$$\Delta S = \Delta S_{thermal} + \Delta S_{configurational}$$

Larger contribution ($\Delta S_{configurational}$)

$$\Delta G \text{ (putting n vacancies)} = n\Delta H_f - T\,\Delta S_{config}$$

$$\frac{\partial \Delta G}{\partial n} = \Delta H_f + n\frac{\partial \Delta H_f}{\partial n} - T\frac{\partial \Delta S_{config}}{\partial n}$$

(zero: $\frac{\partial \Delta H_f}{\partial n}$)

$$\frac{\partial \Delta S_{config}}{\partial n} = k\ln\left(\frac{N-n}{n}\right)$$

For minimum $\rightarrow$ $$\frac{\partial \Delta G}{\partial n} = 0$$

$$\Rightarrow \qquad \frac{\Delta H_f}{kT} = \ln\left(\frac{N-n}{n}\right)$$

Assuming n << N

Considering only configurational entropy

$$\frac{n}{N} = \exp\left(-\frac{\Delta H_f}{kT}\right)$$

User R instead of k if ΔH_f is in J/mole

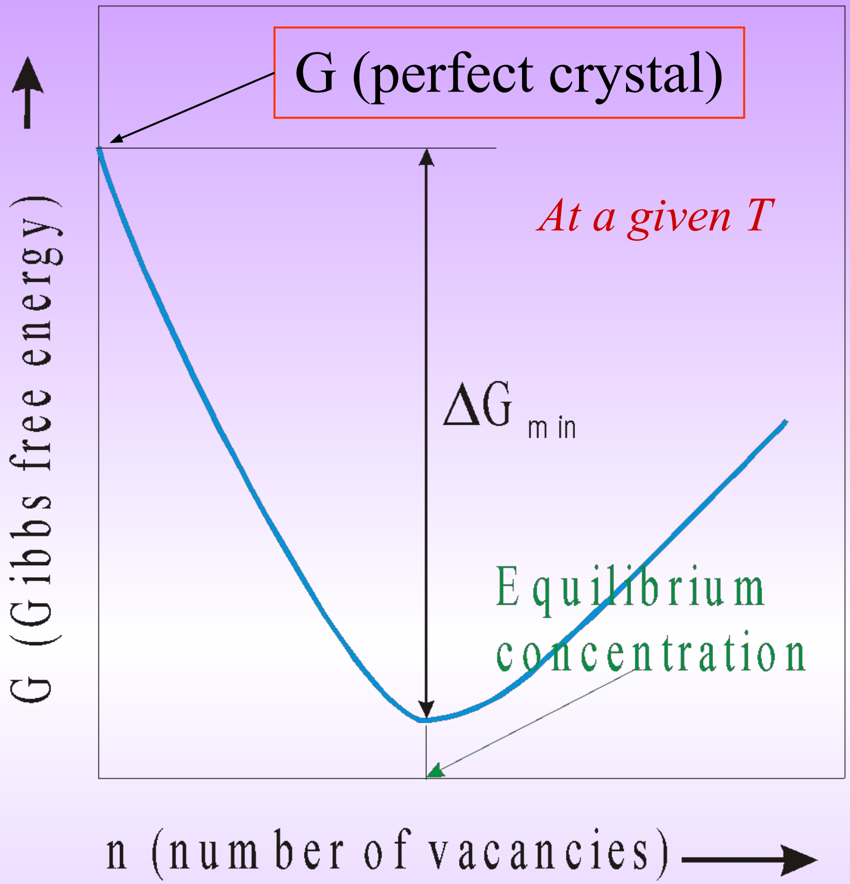
Using

$$\Delta S = \Delta S_{thermal} + \Delta S_{configurational}$$

?

$$\frac{n}{N} = \exp\left(\frac{1}{k}\frac{\partial \Delta S_{thermal}}{\partial n}\right)\exp\left(-\frac{\Delta H_f}{kT}\right)$$

Independent of temperature, value of ~3



T (ºC)	n/N
500	1×10^{-10}
1000	1×10^{-5}
1500	5×10^{-4}
2000	3×10^{-3}
ΔH_f = 1 eV/vacancy = 0.16×10^{-18} J/vacancy	

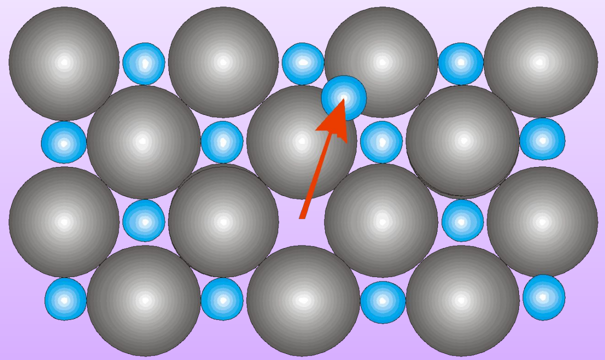
- Certain equilibrium number of vacancies are preferred at T > 0K

Ionic Crystals

- Overall electrical neutrality has to be maintained

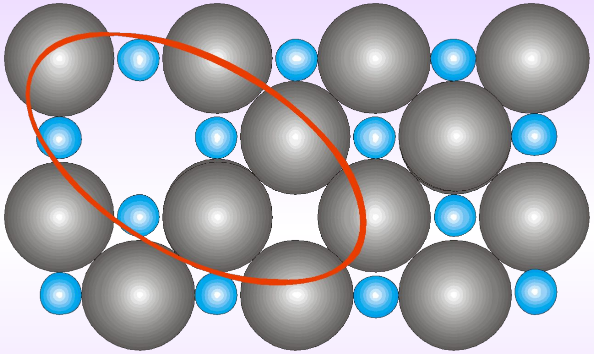
Frenkel defect

- Cation (being smaller get displaced to interstitial voids
- E.g. AgI, CaF_2



Schottky defect

- Pair of anion and cation vacancies
- E.g. Alkali halides

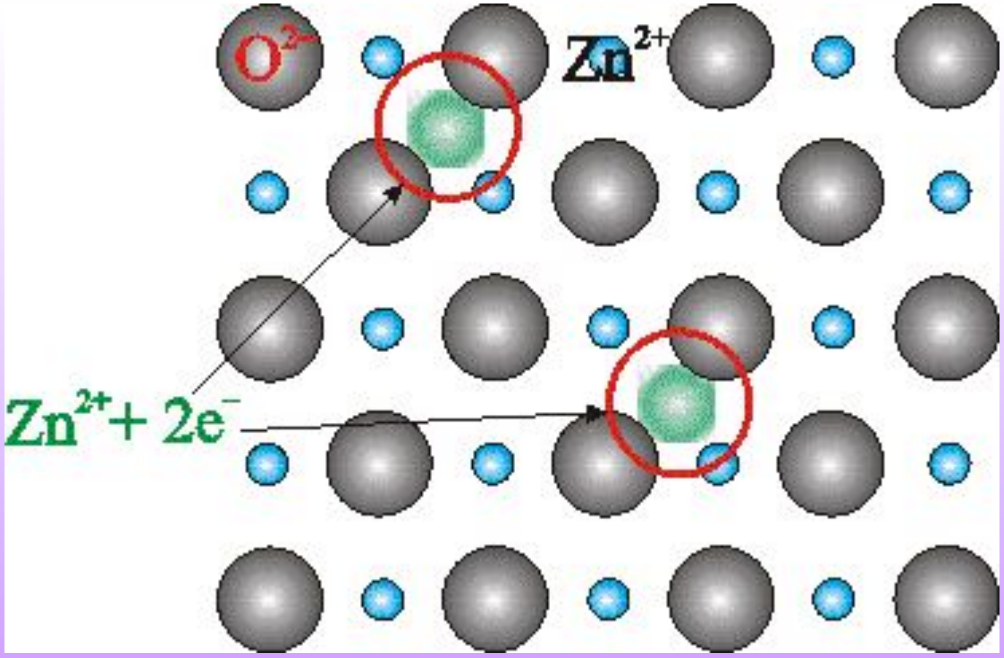


Other defects due to charge balance

- If Cd^{2+} replaces Na^{+} → one cation vacancy is created

Defects due to off stiochiometry

- ZnO heated in Zn vapour → Zn_yO *(y >1)*
- The excess cations occupy interstitial voids
- The electrons ($2e^-$) released stay associated to the interstitial cation



- FeO heated in oxygen atmosphere → Fe_xO *(x <1)*
- Vacant cation sites are present
- Charge is compensated by conversion of ferrous to ferric ion:

  $Fe^{2+} \rightarrow Fe^{3+} + e^-$
- For every vacancy (of Fe cation) two ferrous ions are converted to ferric ions → provides the 2 electrons required by excess oxygen