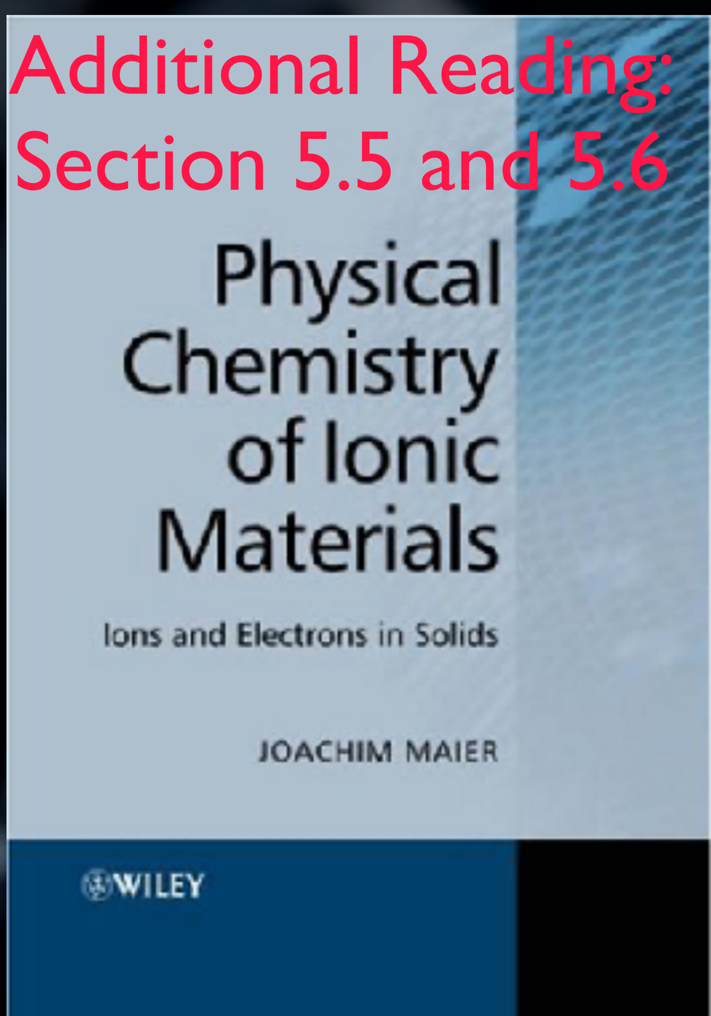
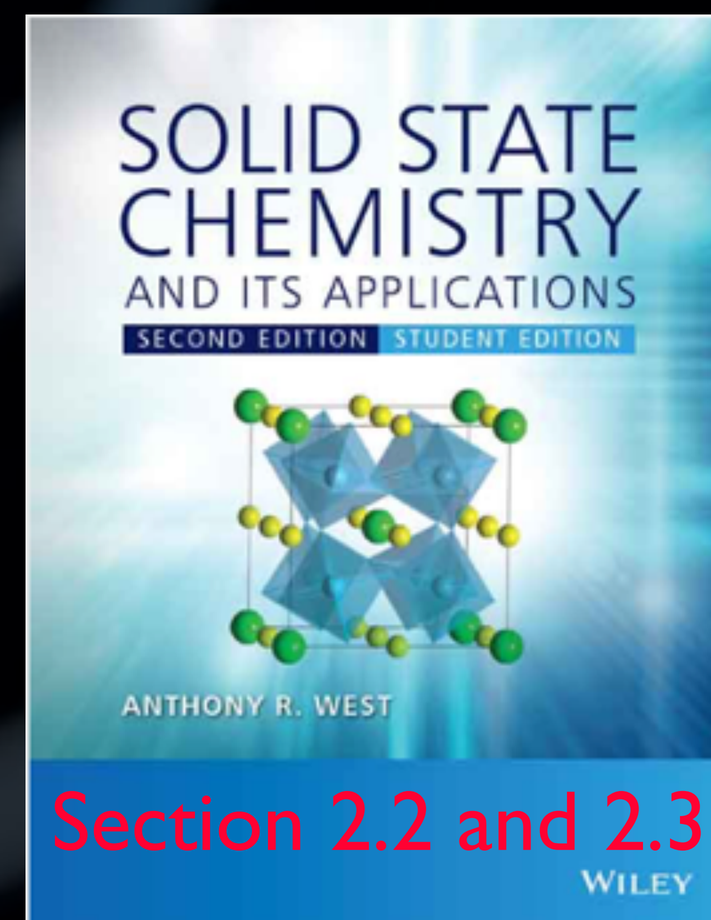
Recap

- Description of defects in crystalline materials
  - Higher dimensional defects - Various Interfaces
  - One-dimensional defects - Dislocations
  - Point defects
- Vacancies in a metallic crystal
  - Entropy of configuration leads to eqm. conc.
  - Temperature dependence of this conc.

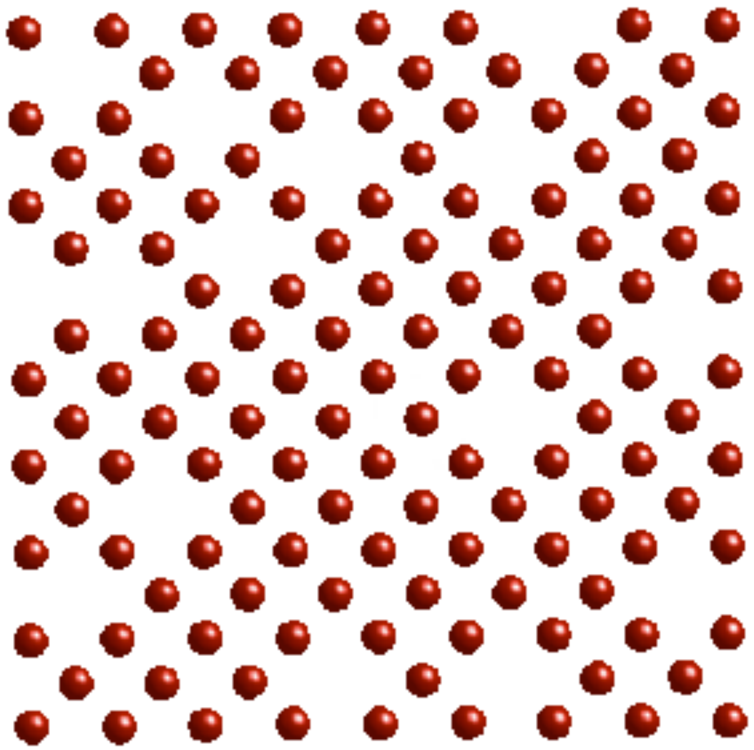
Defects in Ionic/Covalent Materials

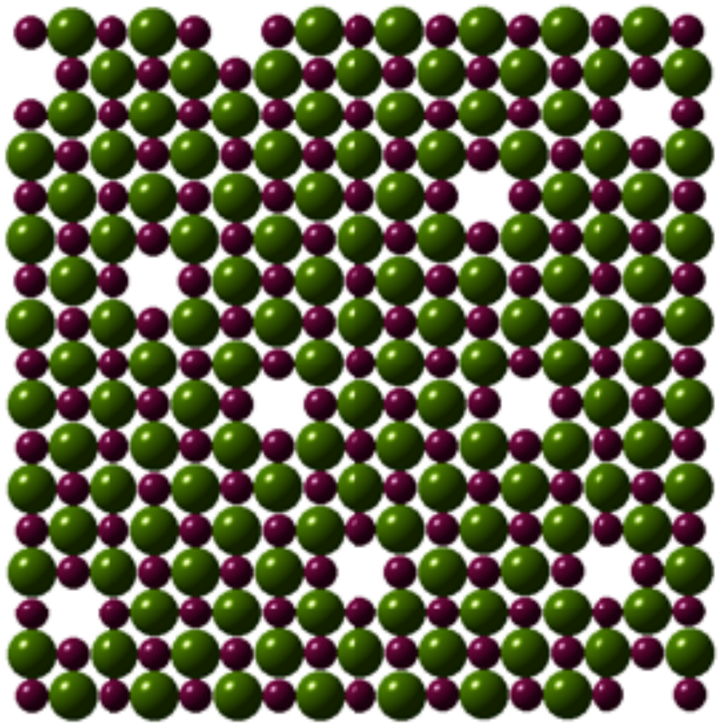
Additional Reading:
Section 5.5 and 5.6



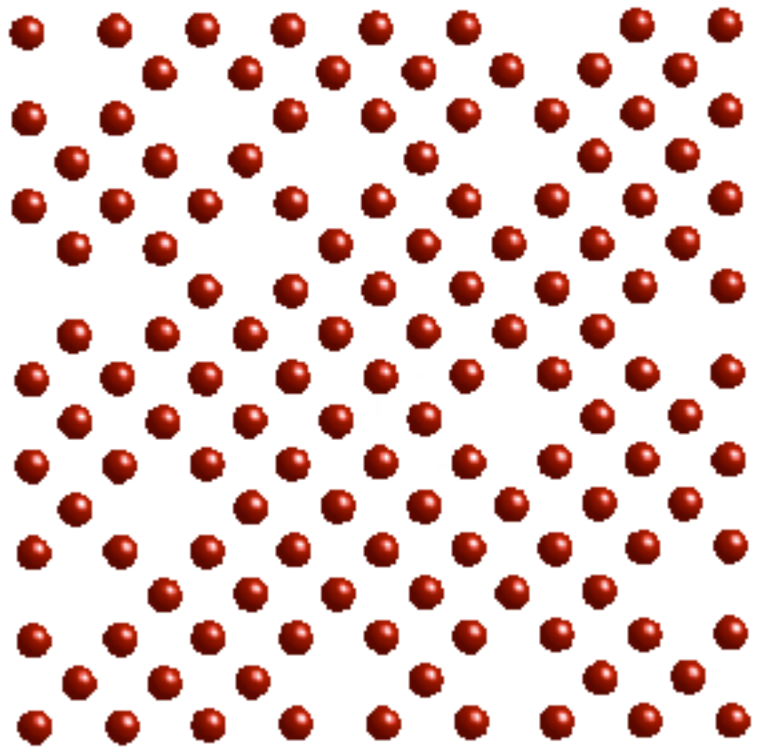
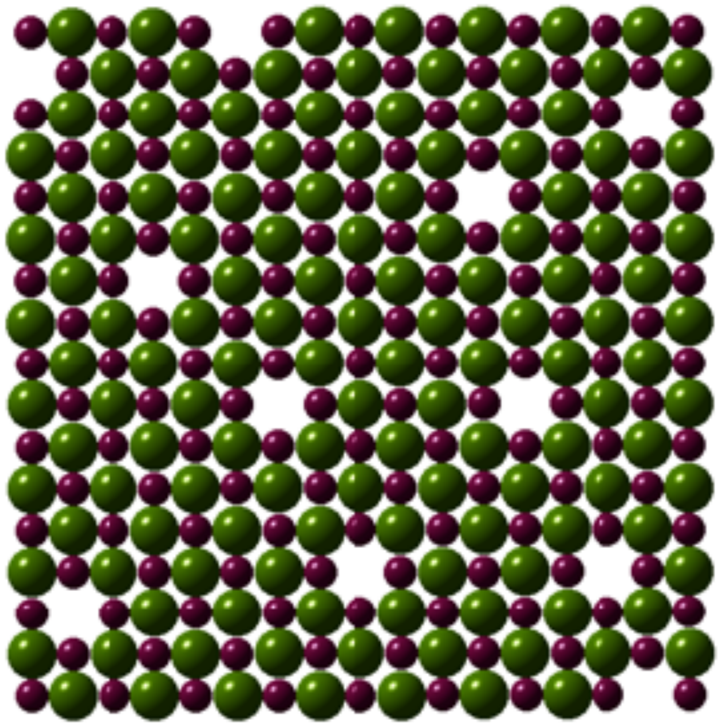
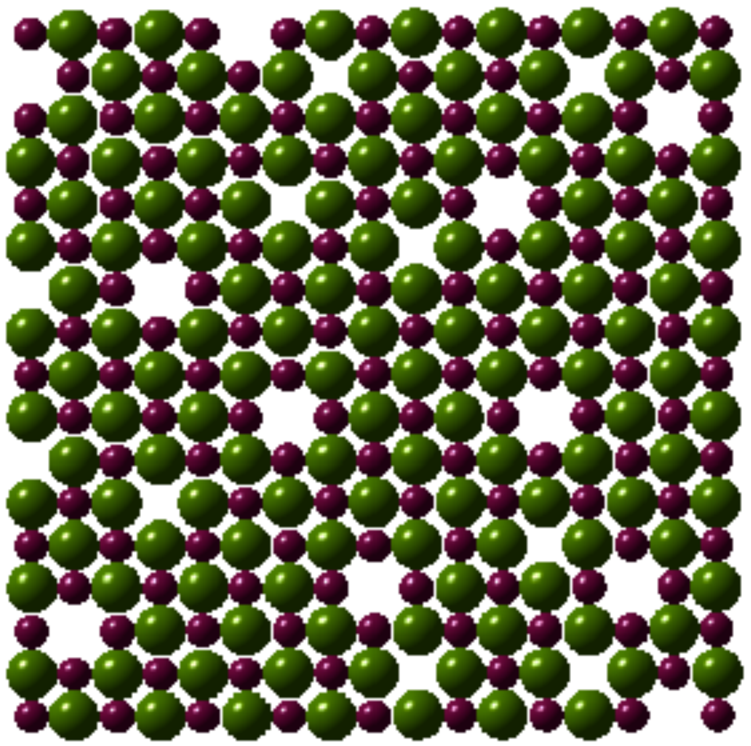


Section 2.2 and 2.3





Metallic *vs* Ionic crystals

Metallic *vs* Ionic crystals

Defects in Ionic Crystals

Local Electroneutrality demands that:

$$\text{Nil} \rightleftharpoons \text{Positive Defect} + \text{Negative Defect}$$

$$\left(\frac{n_{d+}}{n_+}\right) \times \left(\frac{n_{d-}}{n_-}\right) = exp - \frac{\Delta G_m^*}{RT}$$

Composed of bonding and vibrational properties of the defect pair

Many other possibilities for defects exist

Types of Defects in Ionic Crystals

- Stoichiometric
- Non-stoichiometric
- Electronic
- Extrinsic doping

Specific to ionic materials

Extrinsic doping $\longrightarrow$ Common to all materials

Stoichiometric defects

- Internal defect reactions
- Cation to anion ratio maintained in the crystal
  - Remove an ion from its' site and place it at a different site, but within the crystal lattice
    - Frenkel
    - Anion Frenkel
  - Remove/add cations and anions in pairs from their sites/surfaces and place them in surface/interstitial positions
    - Schottky
    - Anti-Schottky

Frenkel Defect Pair Formation

$$\begin{bmatrix} Ag^+ & Cl^- & Ag^+ & Cl^- \\ Cl^- & Ag^+ & Cl^- & Ag^+ \\ Ag^+ & Cl^- & Ag^+ & Cl^- \\ Cl^- & Ag^+ & Cl^- & Ag^+ \end{bmatrix} \rightleftharpoons \begin{bmatrix} & Cl^- & Ag^+ & Cl^- \\ Cl^- & Ag^+ & Cl^- & Ag^+ \\ Ag^+ & Cl^- & \begin{matrix} Ag^+ & \\ & Ag^+ \end{matrix} & Cl^- \\ Cl^- & Ag^+ & Cl^- & Ag^+ \end{bmatrix}$$

Considering only the sections that have changed

$$\begin{bmatrix} Ag^+ & Cl^- \\ Cl^- & Ag^+ \end{bmatrix}^0 + \begin{bmatrix} Ag^+ & Cl^- \\ Cl^- & Ag^+ \end{bmatrix}^0 \rightleftharpoons \begin{bmatrix} & Cl^- \\ Cl^- & Ag^+ \end{bmatrix}^- + \begin{bmatrix} Ag^+ & Cl^- \\ & Ag^+ \\ Cl^- & Ag^+ \end{bmatrix}^+ .$$

-4 AgCl

$$\mathrm{Nil} \leftrightarrow \mathrm{Ag}^{\bullet} + |\mathrm{Ag}|'$$

Notation for defects - Kröger-Vink

General Format : M_s^c

- *M* corresponds to the structural element
  - Atoms
  - Vacancies
  - electrons/holes
- *S* - Lattice site that the structural element occupies
  - Regular site
  - Interstice
- *C* - Charge of the defect relative to site that it occupies

Kröger-Vink notation - *AgCl*

$V_{Ag}' \Rightarrow$ Vacancy on a silver site

$V_{Cl}^{\bullet} \Rightarrow$ Vacancy on a chlorine site

$Ag_i^{\bullet} \Rightarrow$ Silver Interstitial

$Cl_i' \Rightarrow$ Chlorine interstitial

The Frenkel defect reaction becomes: $Ag_{Ag}^{\mathrm{x}} + V_i^{\mathrm{x}} \rightleftharpoons Ag_i^{\bullet} + V_{Ag}'$

Mass Action Law - Frenkel defect

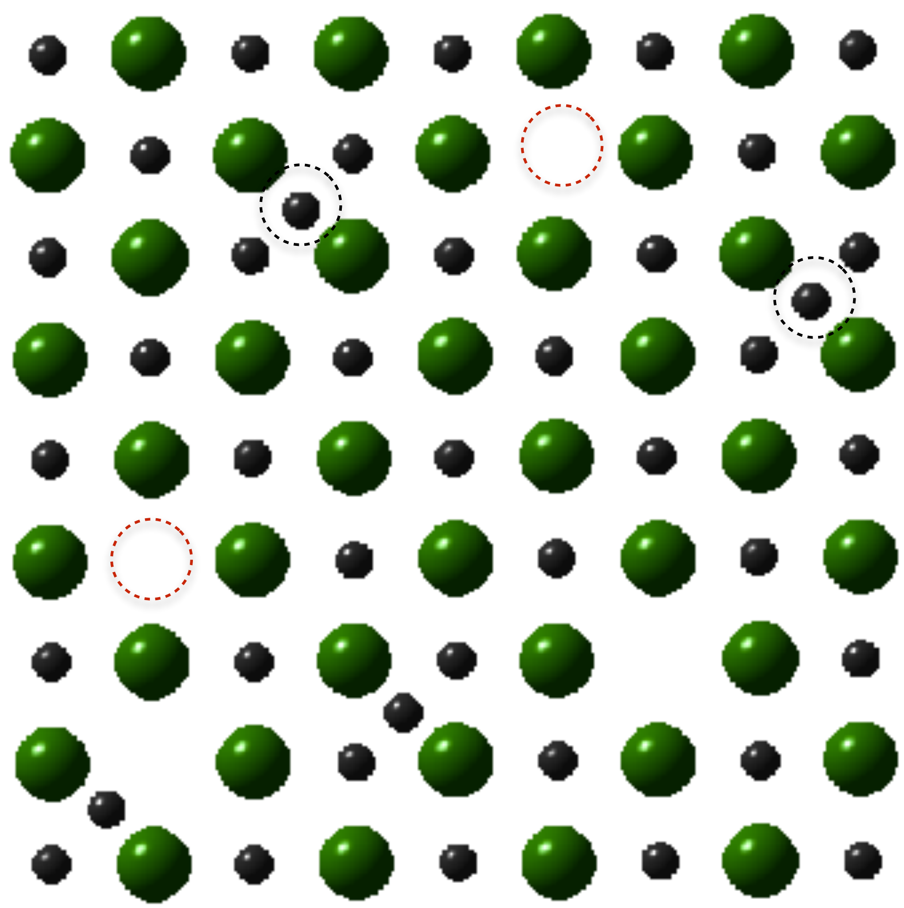
where $K_F = exp(-\frac{\Delta_F G^0}{RT})$

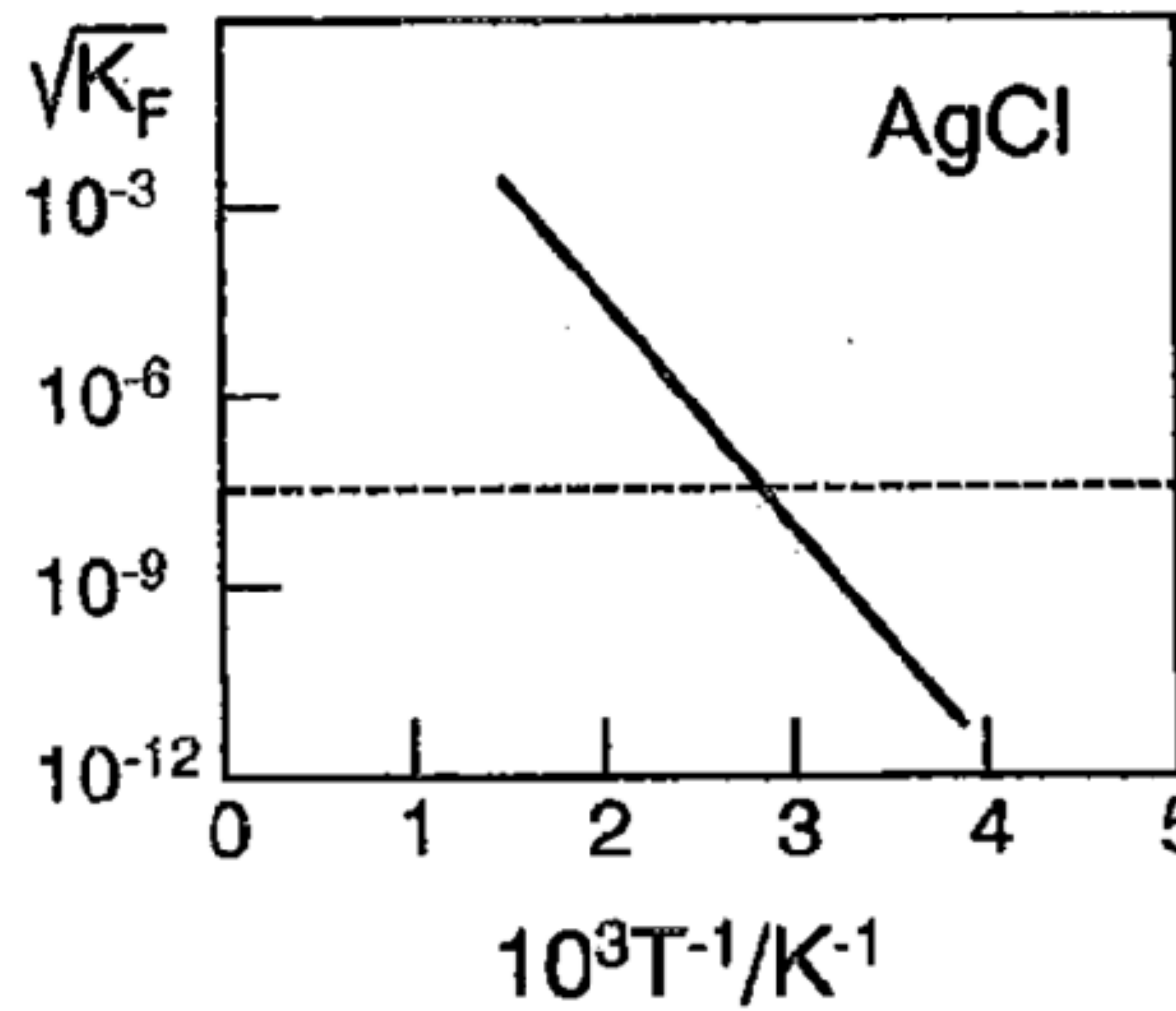
$$[Ag_i^{\bullet}]\left[V_{Ag}^{'}\right] = \alpha N^2 \times K_F$$

$N \rightarrow$ No. of atomic sites/cc

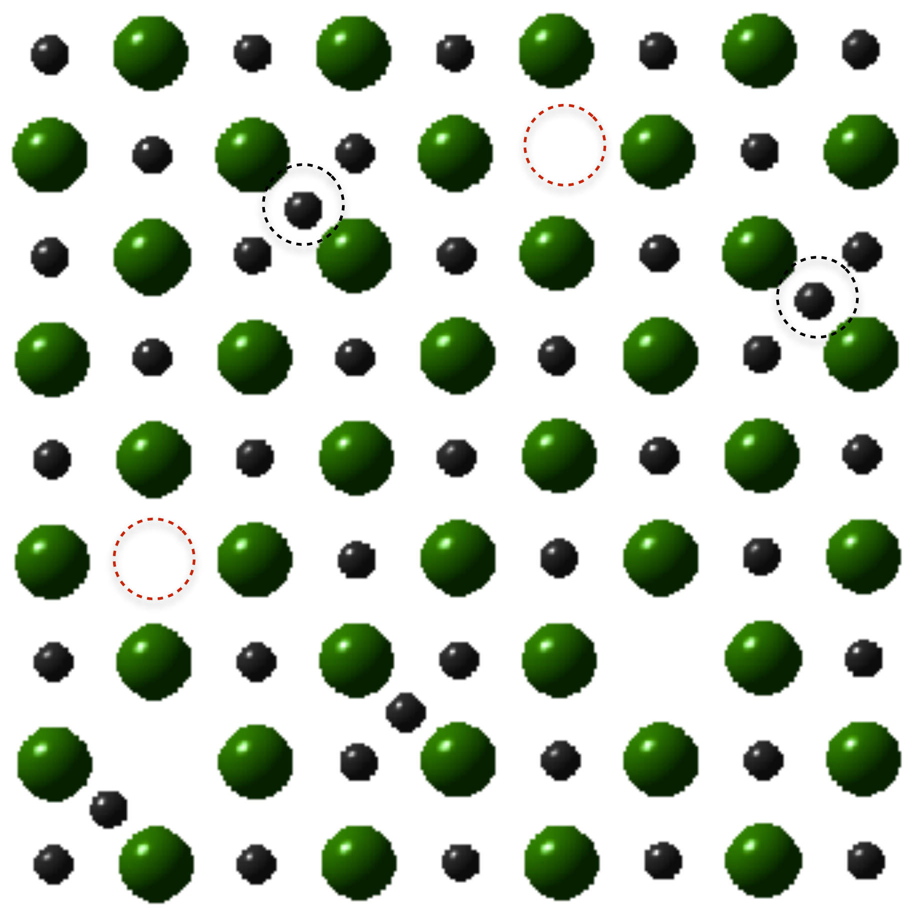
$\alpha \rightarrow$ Interstitial/atomic

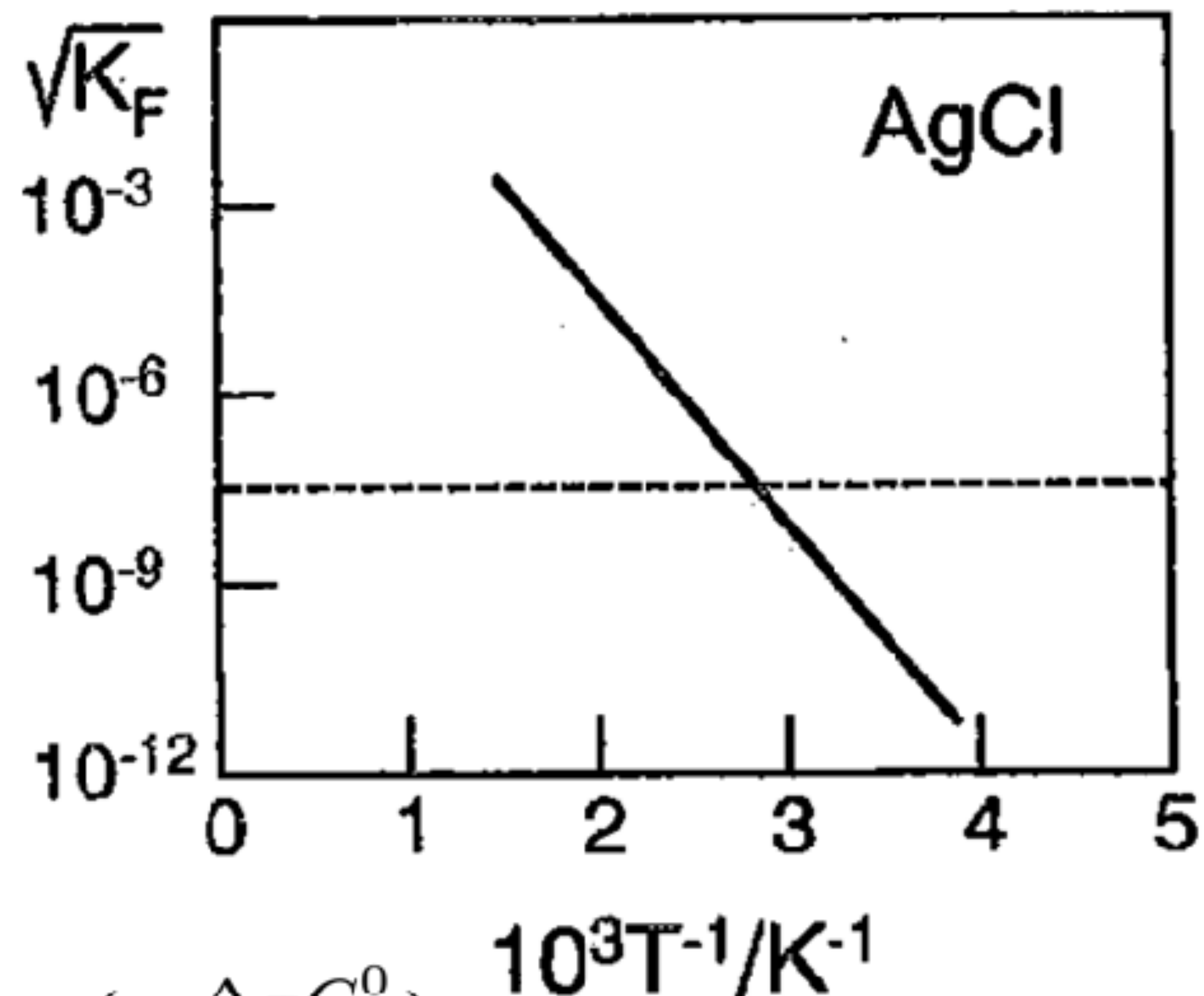
electroneutrality: $[Ag_i^{\bullet}] = [V'_{Ag}] = \sqrt{K_F(T)} \times N\sqrt{\alpha}$





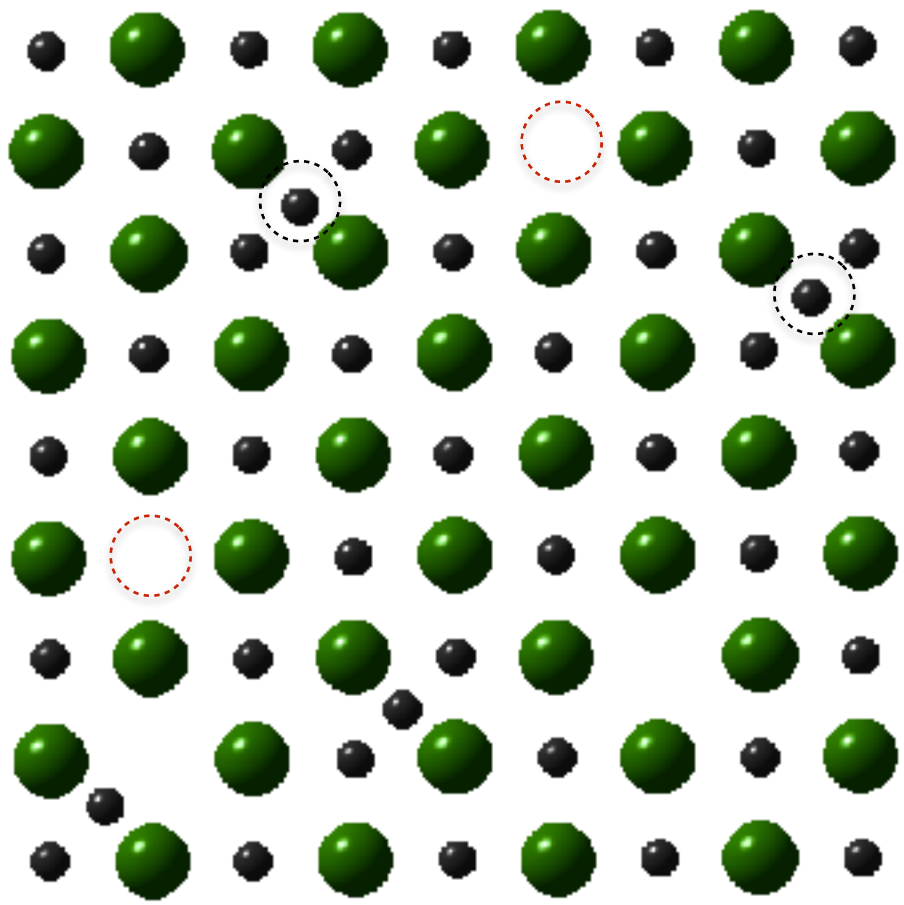
Energetics - Frenkel defect

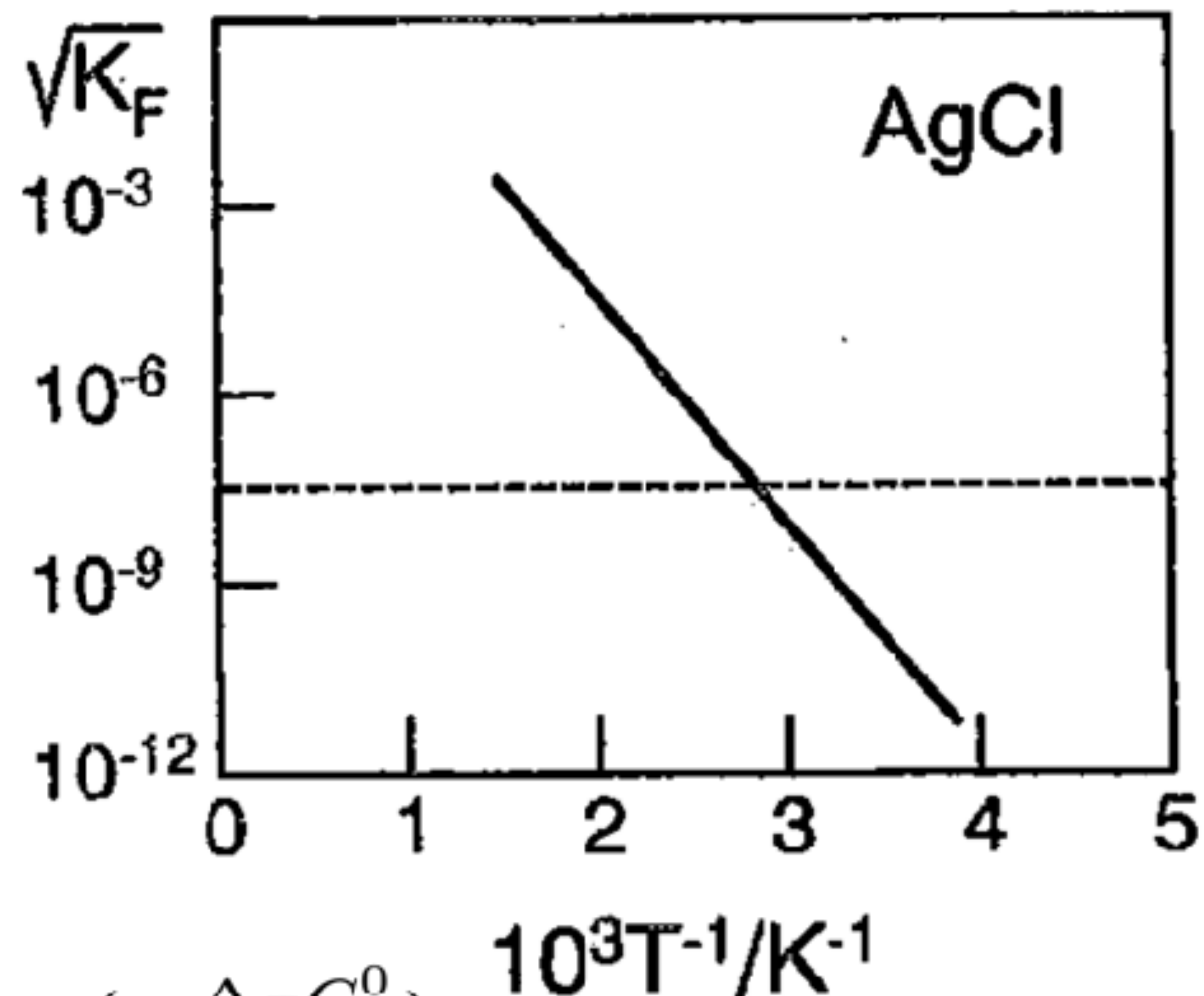




where $K_F = exp(-\frac{\Delta_F G^0}{RT})$

Energetics - Frenkel defect

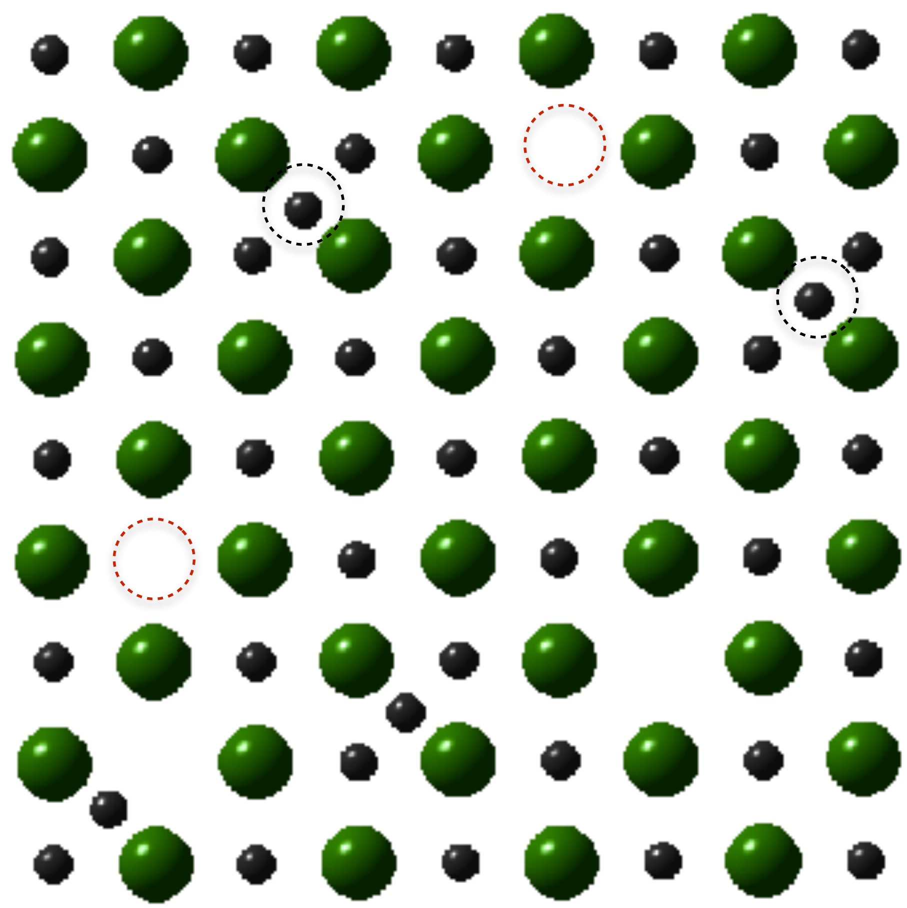


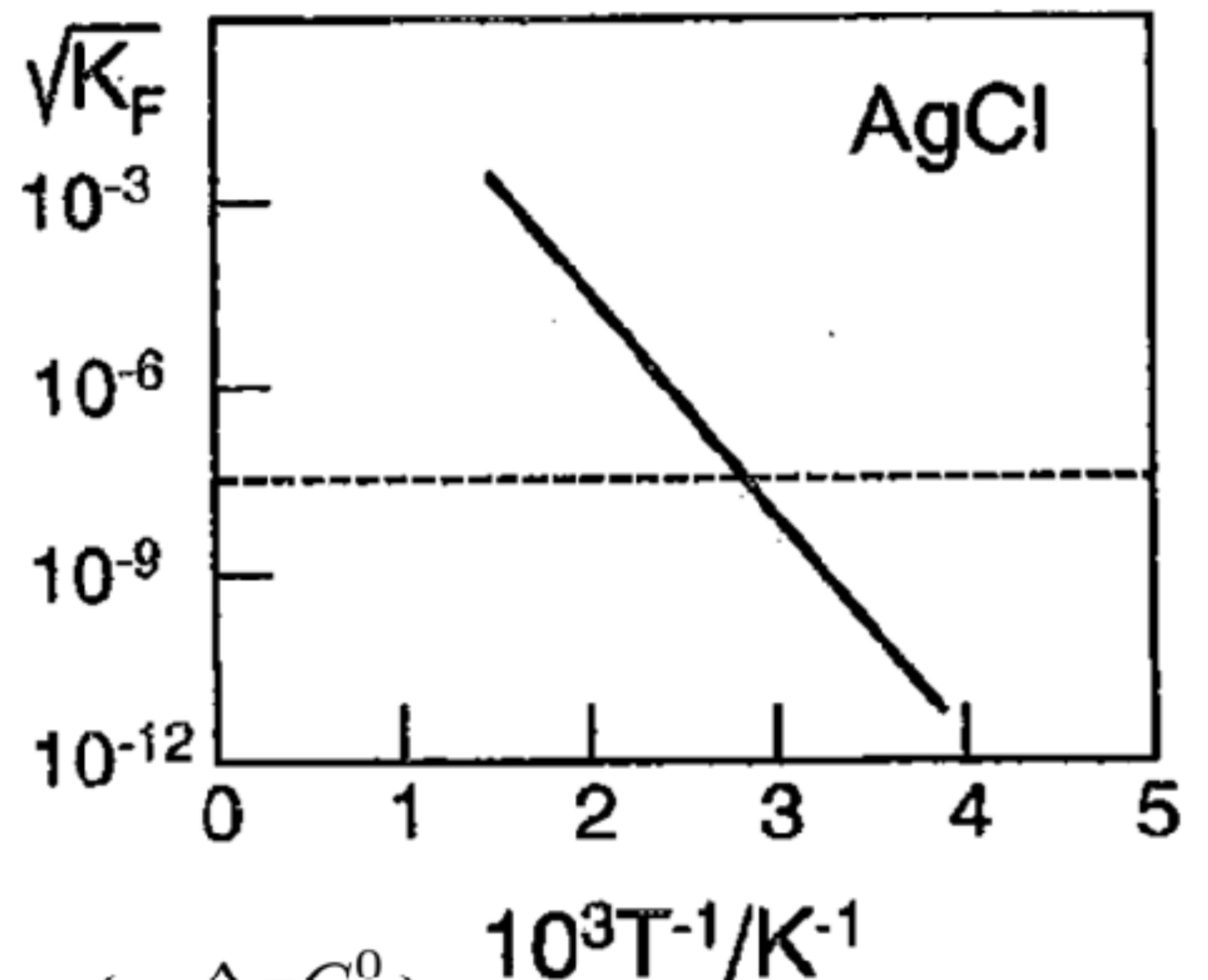


where $K_F = exp(-\frac{\Delta_F G^0}{RT})$

$$\Longrightarrow \left[Ag_i^{\bullet}\right] = \left[V_{Ag}^{'}\right] = N\sqrt{\alpha \times K_F} = \exp\left(\frac{\Delta S_F^0}{2R}\right)\exp\left(-\frac{\Delta H_F^0}{2RT}\right)$$

Energetics - Frenkel defect





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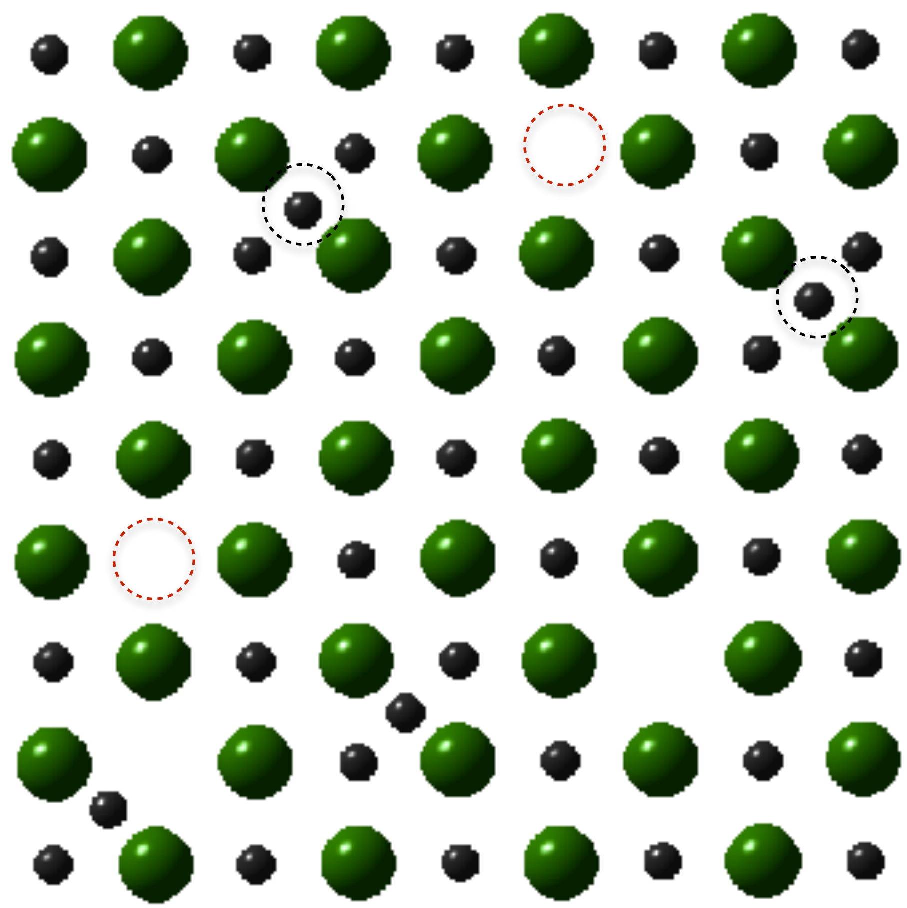
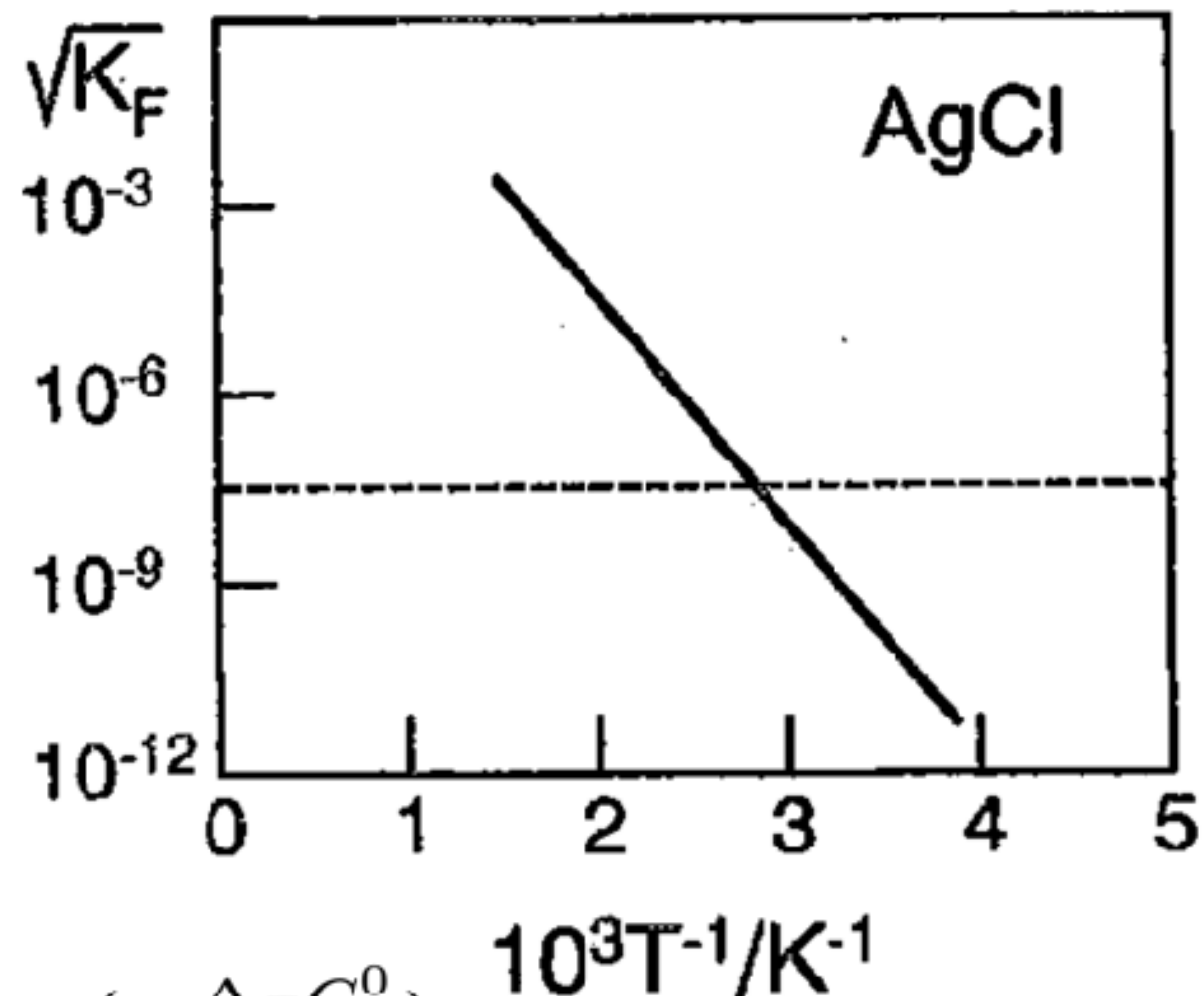
$$\Delta S_F^0 \approx 9.4R$$

Energetics - Frenkel defect





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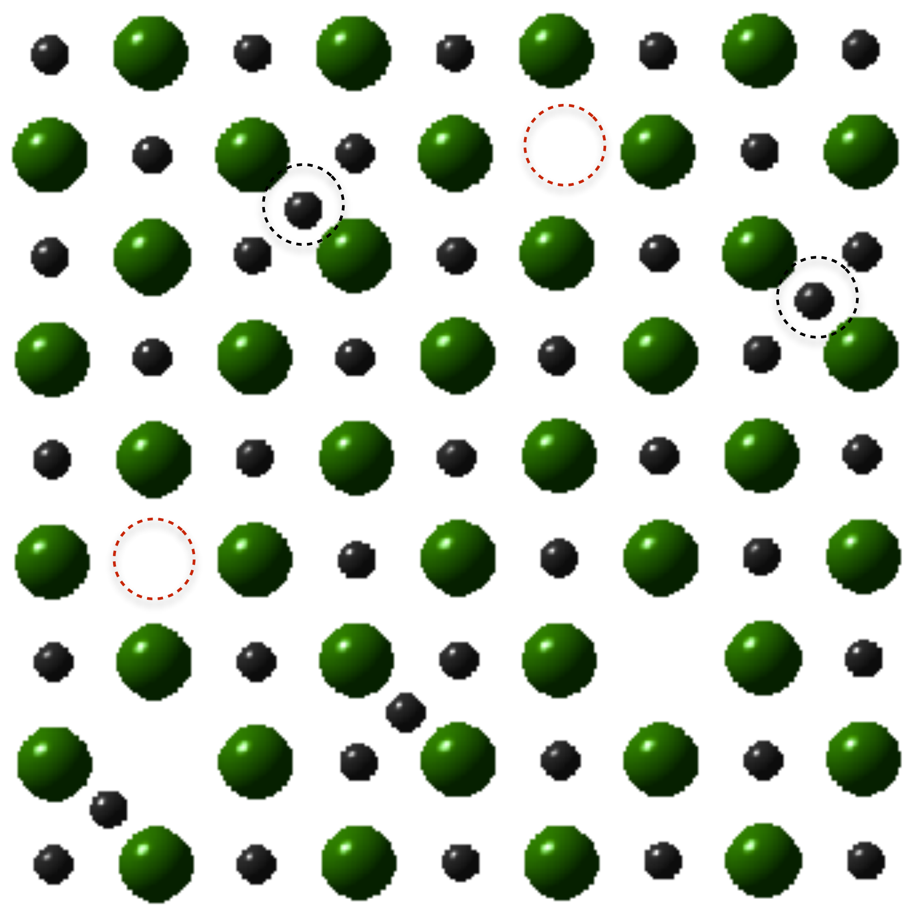
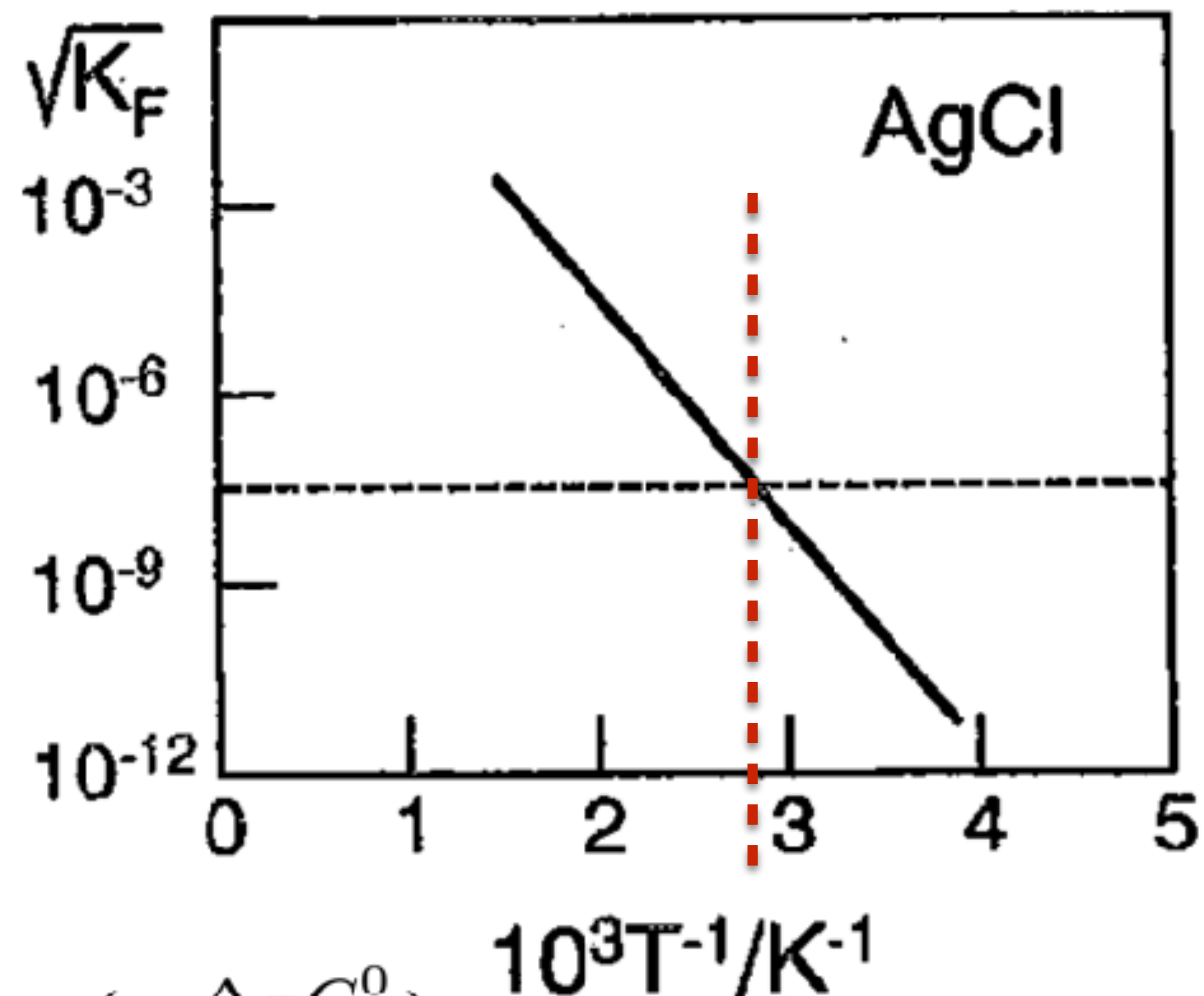
$$\Longrightarrow \left[Ag_i^{\bullet}\right] = \left[V'_{Ag}\right] = N\sqrt{\alpha \times K_F} = \exp\left(\frac{\Delta S_F^0}{2R}\right)\ \exp\left(-\frac{\Delta H_F^0}{2RT}\right)$$

$\Delta S_F^0 \approx 9.4R$ $\Delta H_F^0 \approx$ 140 kJ.mol^{-1}

Energetics - Frenkel defect





$$\text{where } K_F = exp(-\frac{\Delta_F G^0}{RT})$$

$$\Longrightarrow [Ag_i^\bullet] = [V'_{Ag}] = N\sqrt{\alpha \times K_F} = \exp\left(\frac{\Delta S_F^0}{2R}\right) \exp\left(-\frac{\Delta H_F^0}{2RT}\right)$$

$\Delta S_F^0 \approx 9.4R$

$\Delta H_F^0 \approx 140$ kJ.mol^{-1}

Schottky defect - NaCl

$$\begin{bmatrix} Na^+ & Cl^- \\ Cl^- & Na^+ \end{bmatrix} + \begin{bmatrix} Na^+ & Cl^- \\ Cl^- & Na^+ \end{bmatrix} \rightleftharpoons \begin{bmatrix} & Cl^- \\ Cl^- & Na^+ \end{bmatrix}^- + \begin{bmatrix} Na^+ & Cl^- \\ & Na^+ \end{bmatrix}^+ + NaCl$$

Building Element Notation :

$$\mathrm{Nil} \leftrightarrow |\mathrm{Na}|' + |\mathrm{Cl}|^{\bullet} = \mathrm{NaCl}$$

Kroger-Vink Notation :

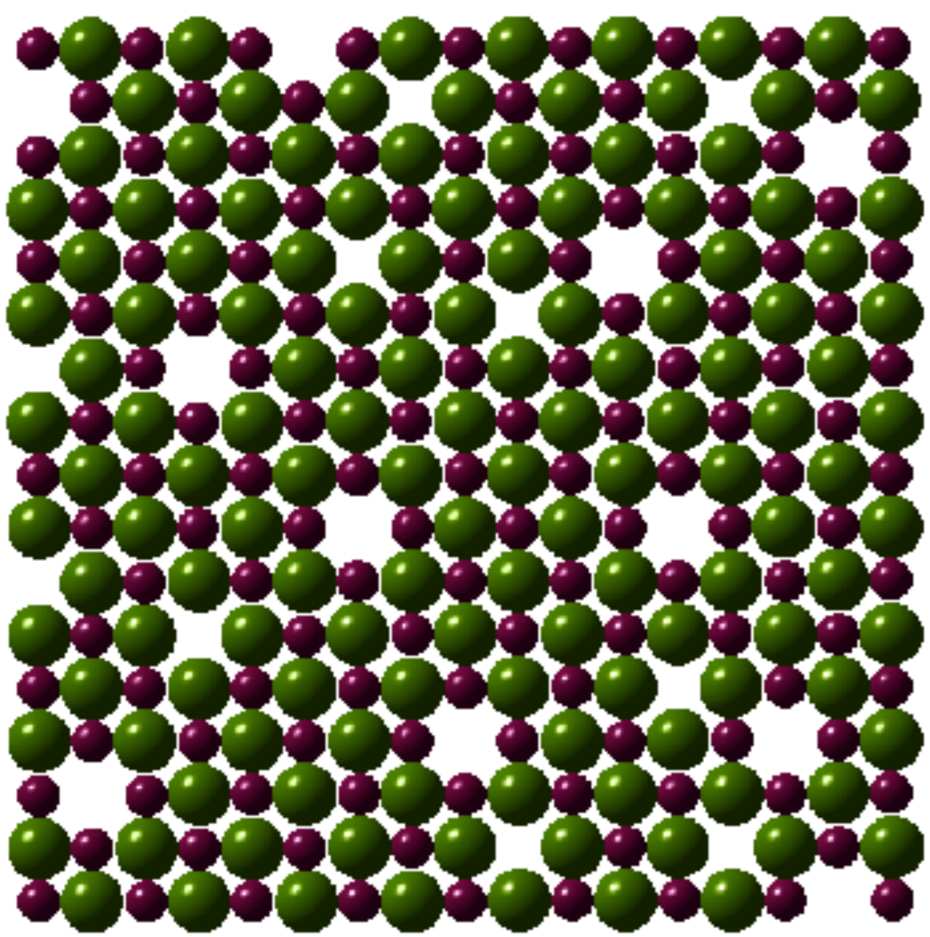
$$Na_{Na}^{\times} + Cl_{Cl}^{\times} + V_{Na,S} + V_{Cl,S} \rightleftharpoons V_{Na}^{'} + V_{Cl}^{\bullet} + Na_{Na,S} + Cl_{Cl,S}$$

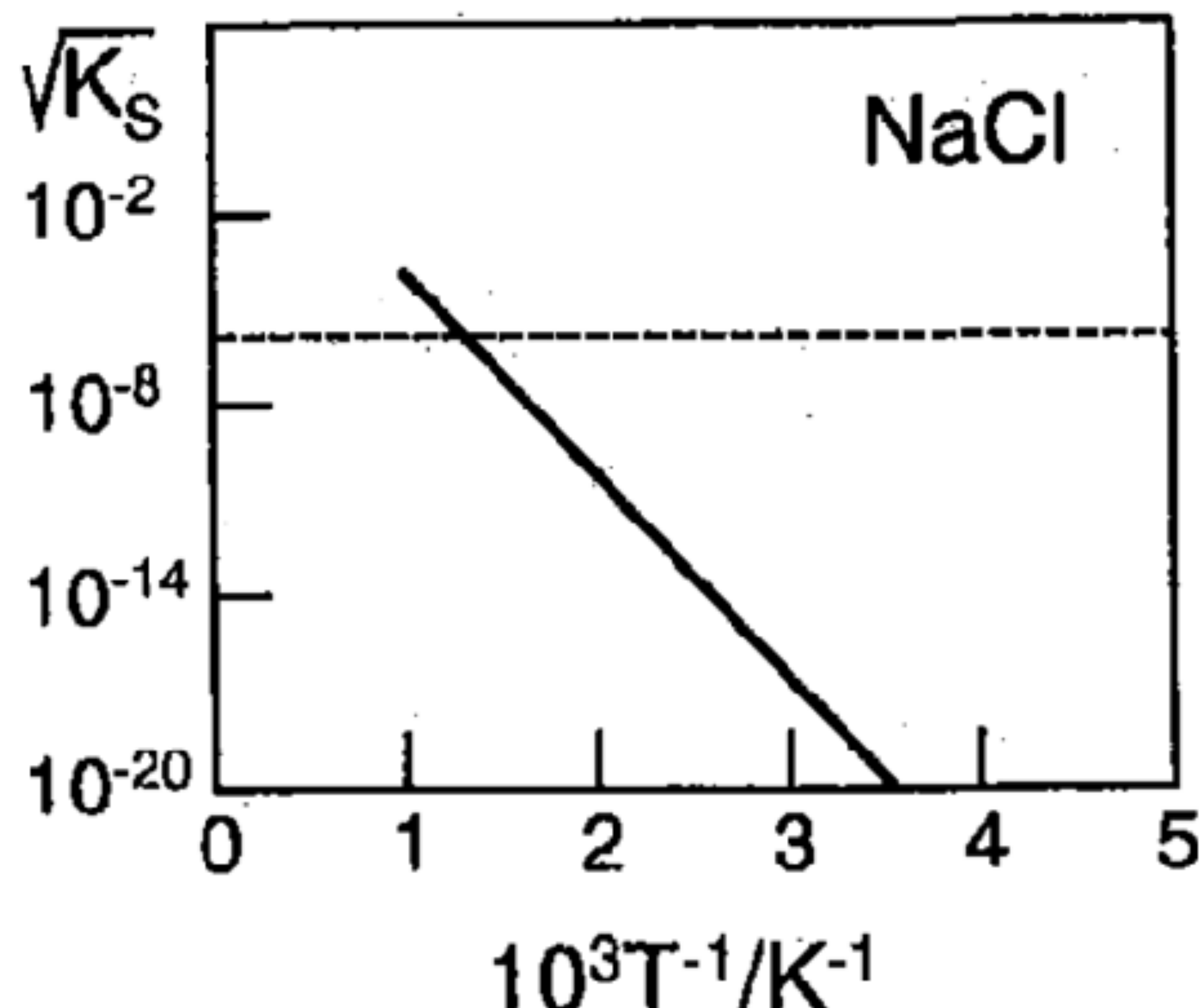
Mass Action Law - Schottky defect

Schottky reaction:

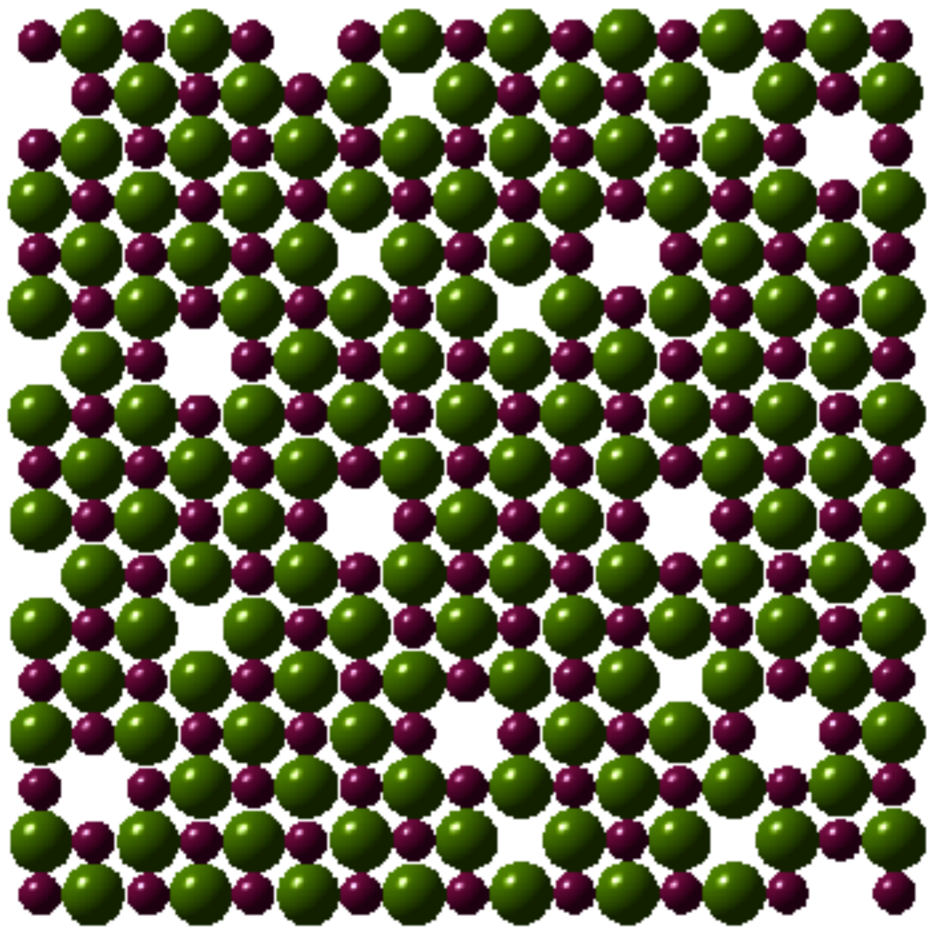
$$Na_{Na}^{\times} + Cl_{Cl}^{\times} + V_{Na,surf} + V_{Cl,surf} \rightleftharpoons V_{Na}^{'} + V_{Cl}^{\bullet} + Na_{Na,surf} + Cl_{Cl,surf}$$

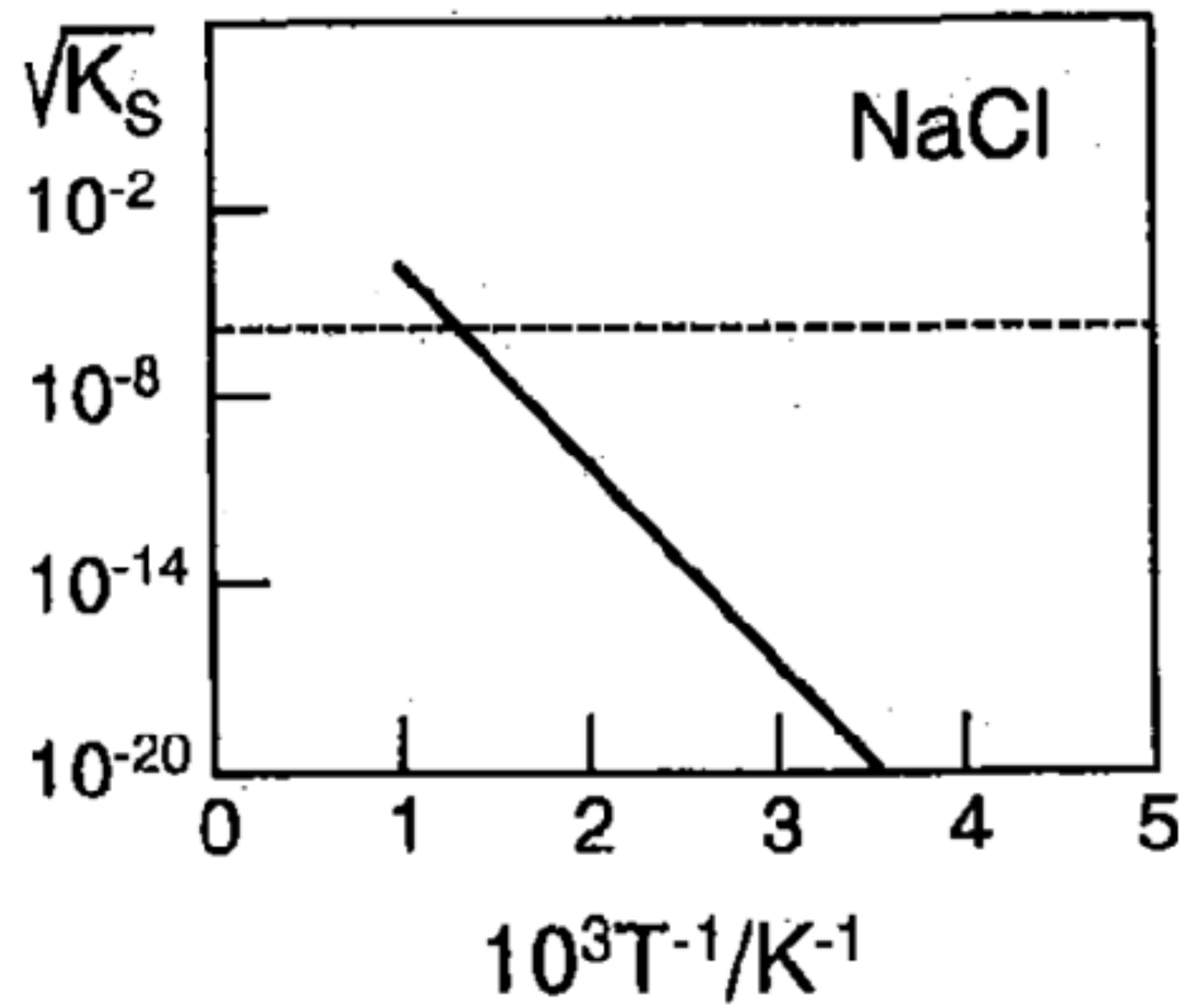
$$\text{electroneutrality: } [V_{Cl}^{\bullet}] = [V_{Na}'] = \sqrt{K_s(T)} \times N$$



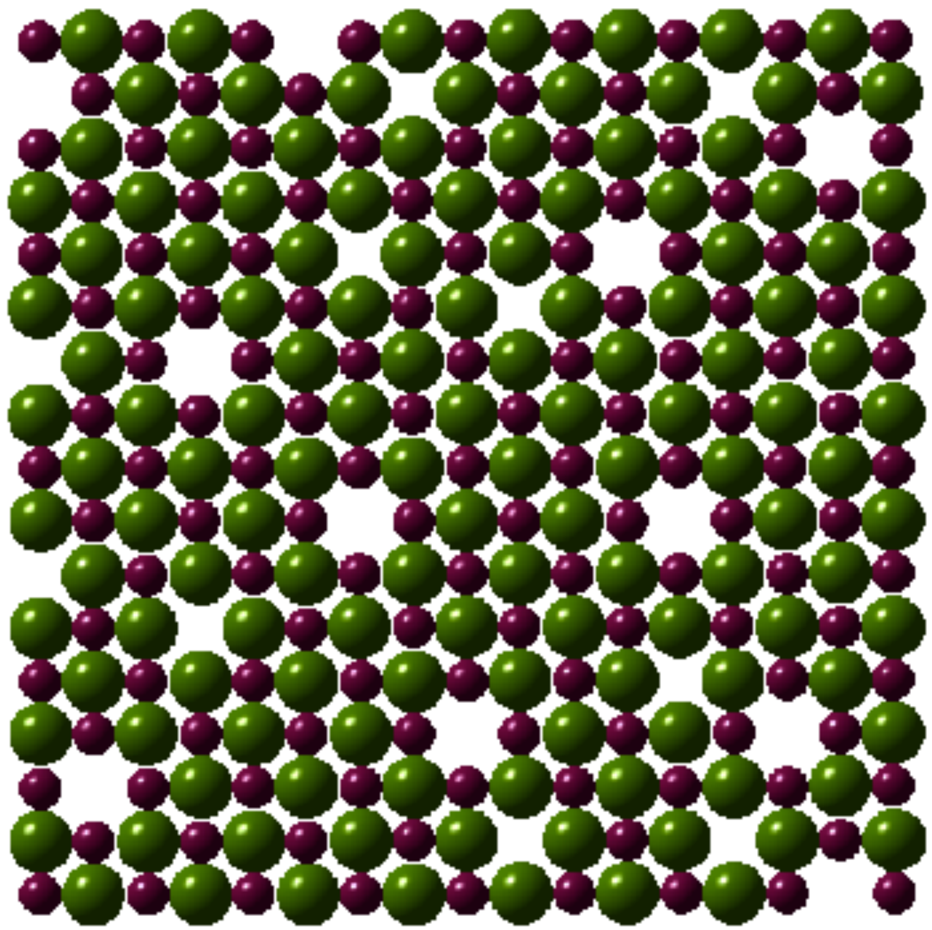


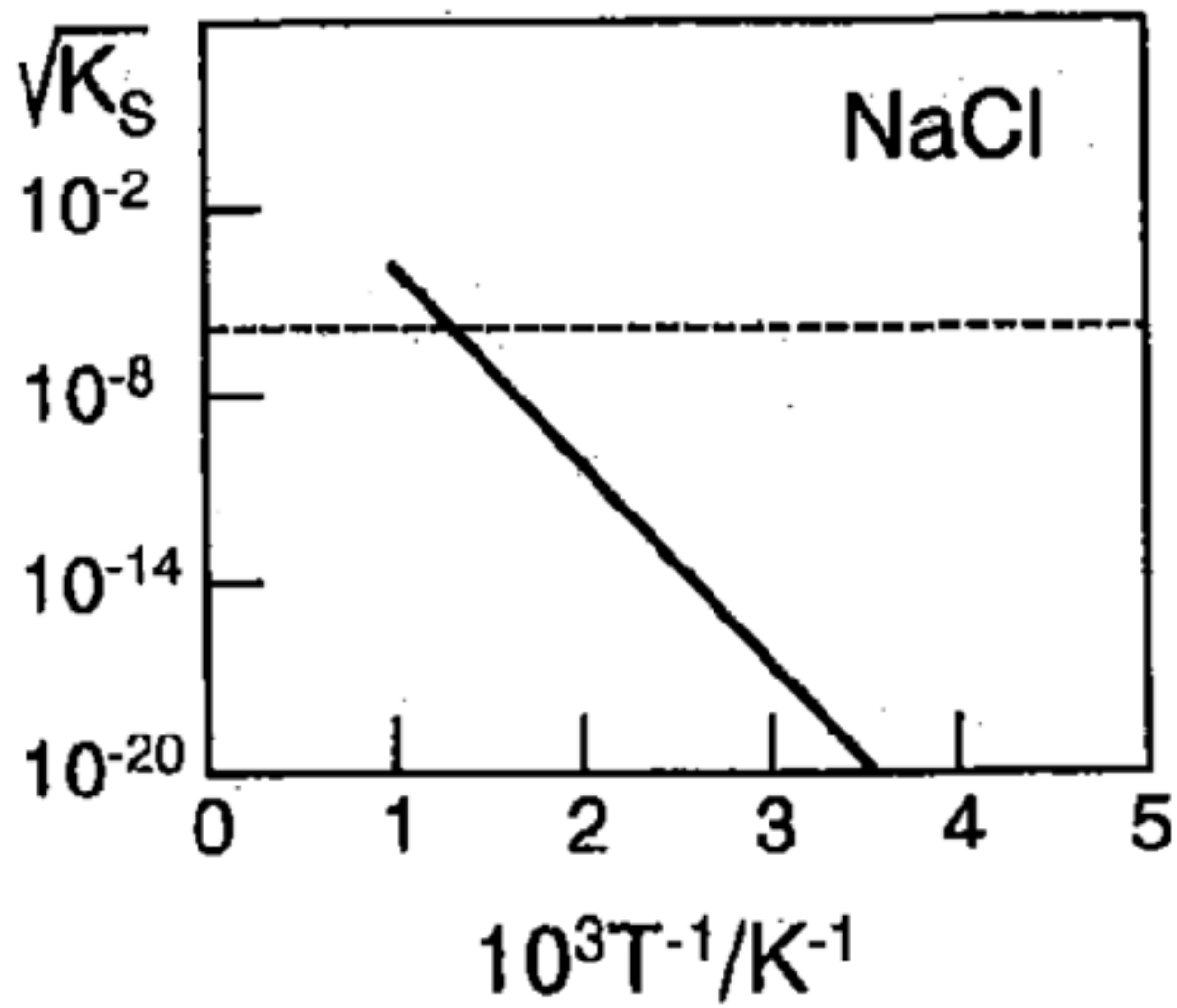
Energetics - Schottky defect





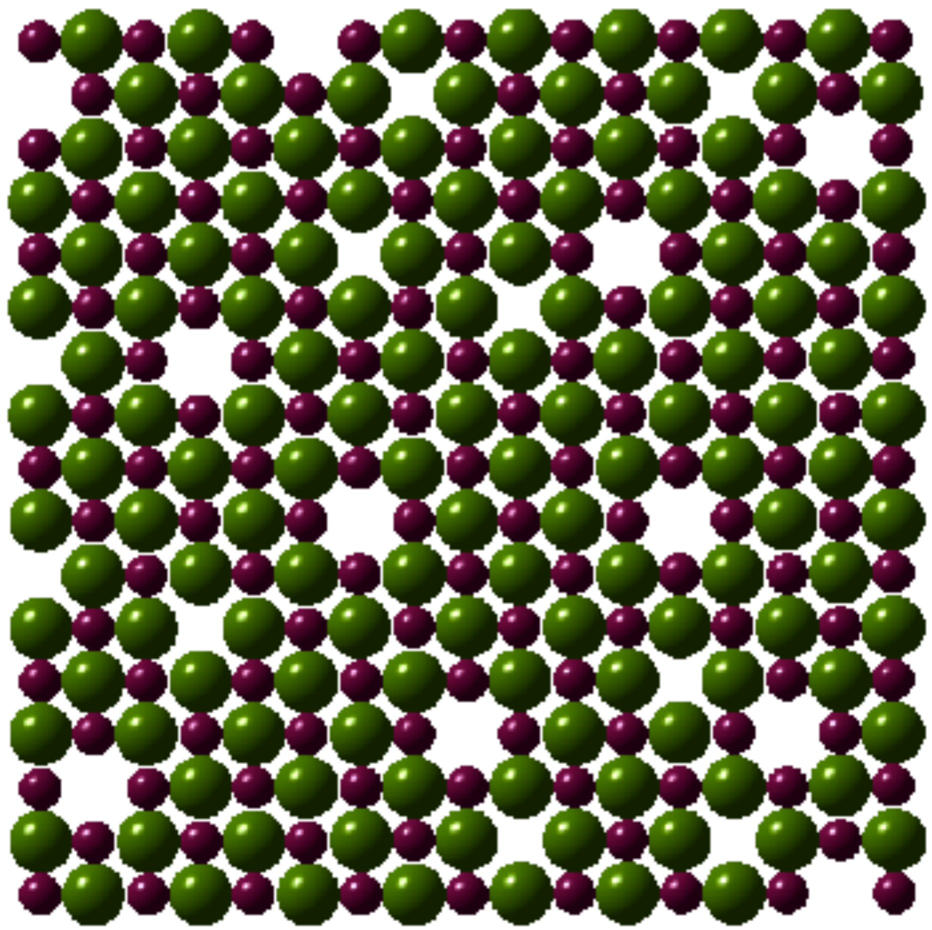
Energetics - Schottky defect

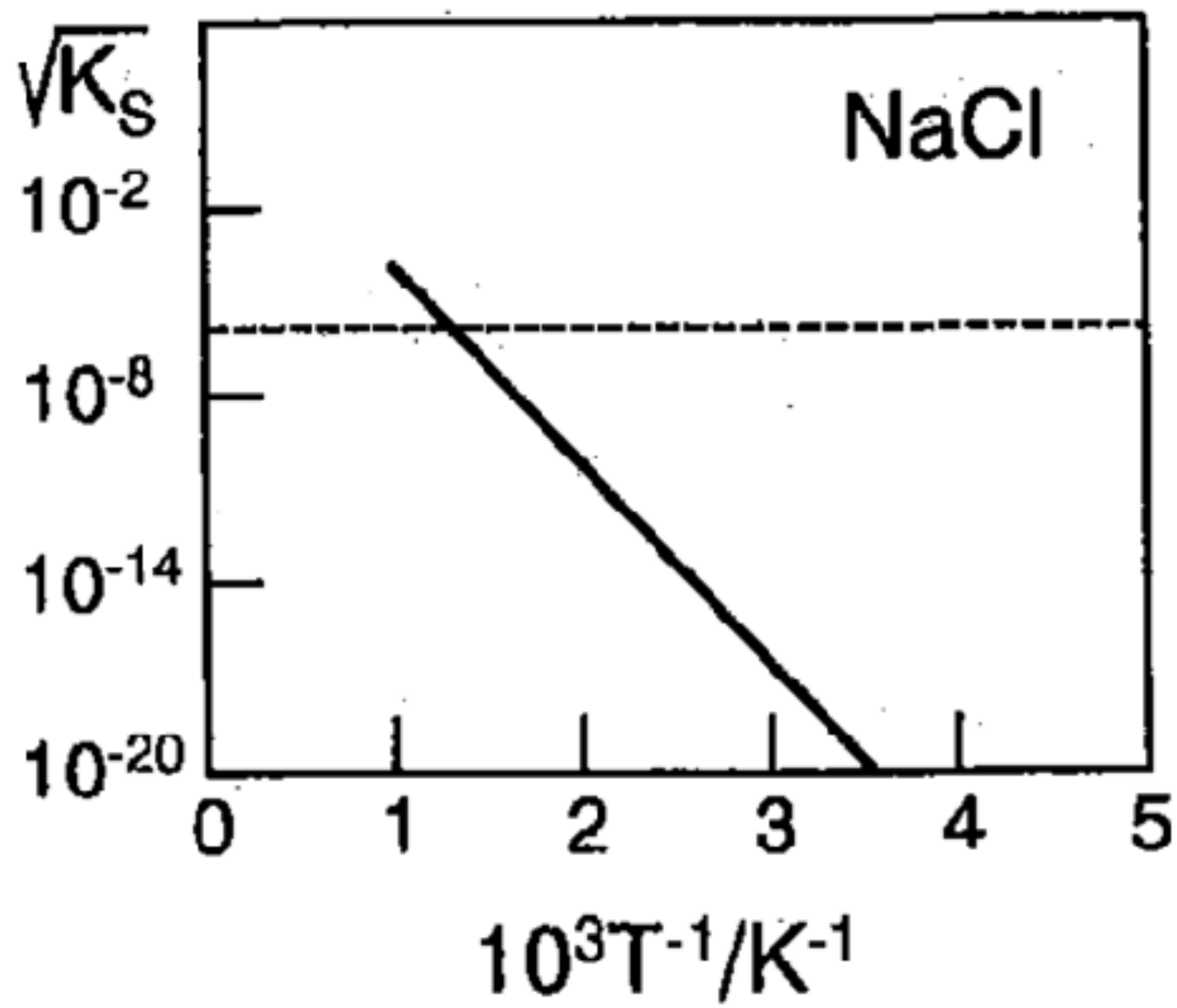




$$\Longrightarrow \left[V_{Cl}^{\bullet}\right] = \left[V_{Na}^{'}\right] = N\sqrt{K_S} = \exp\left(\frac{\Delta S_S^0}{2R}\right)\ \exp\left(-\frac{\Delta H_S^0}{2RT}\right)$$

Energetics - Schottky defect

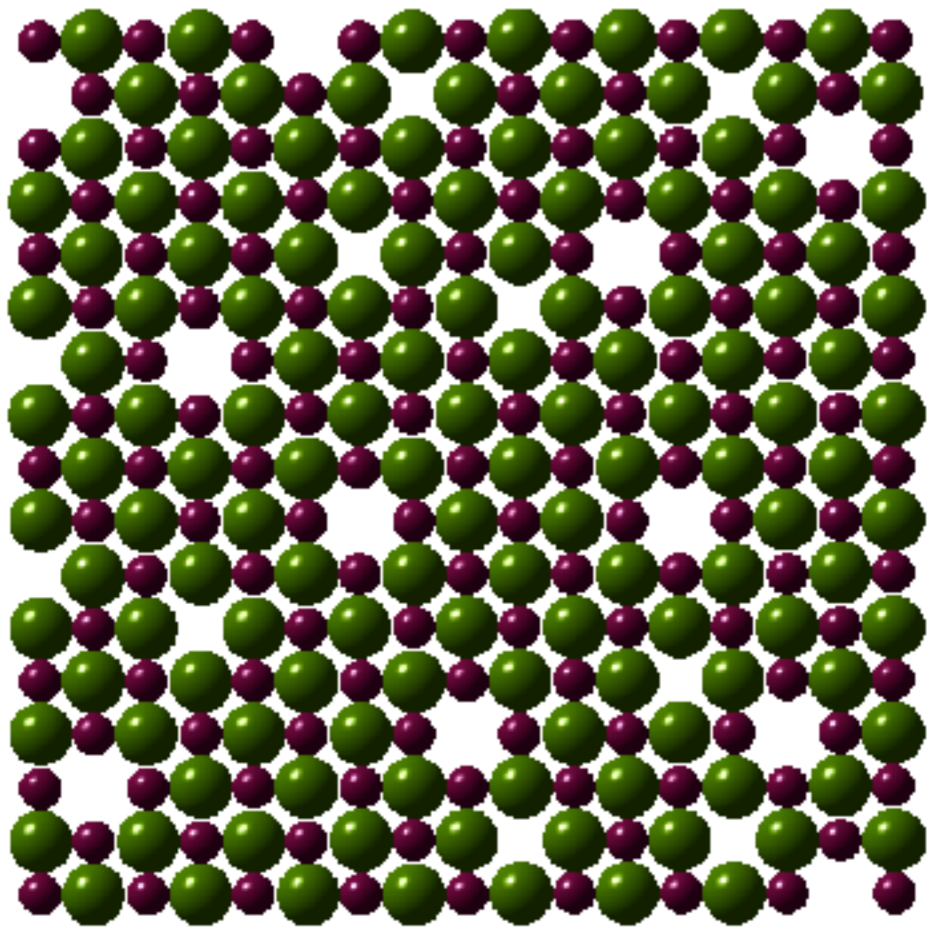


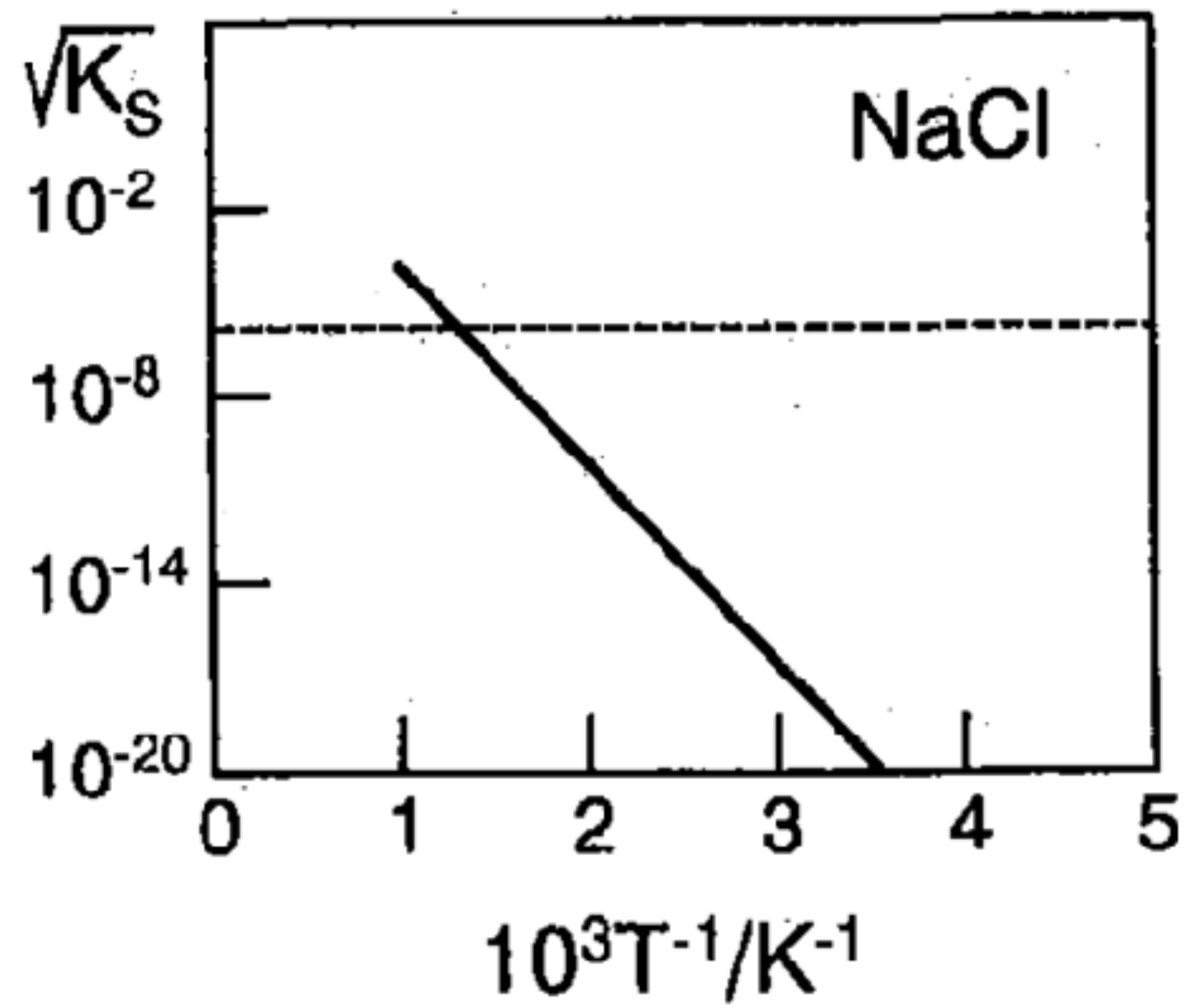


$$\Longrightarrow \; \left[V_{Cl}^{\bullet}\right] = \left[V_{Na}^{'}\right] = N\sqrt{K_S} = \exp\left(\frac{\Delta S_S^0}{2R}\right)\,\exp\left(-\frac{\Delta H_S^0}{2RT}\right)$$

$$\Delta S_S^0 \approx 9.8R$$

Energetics - Schottky defect





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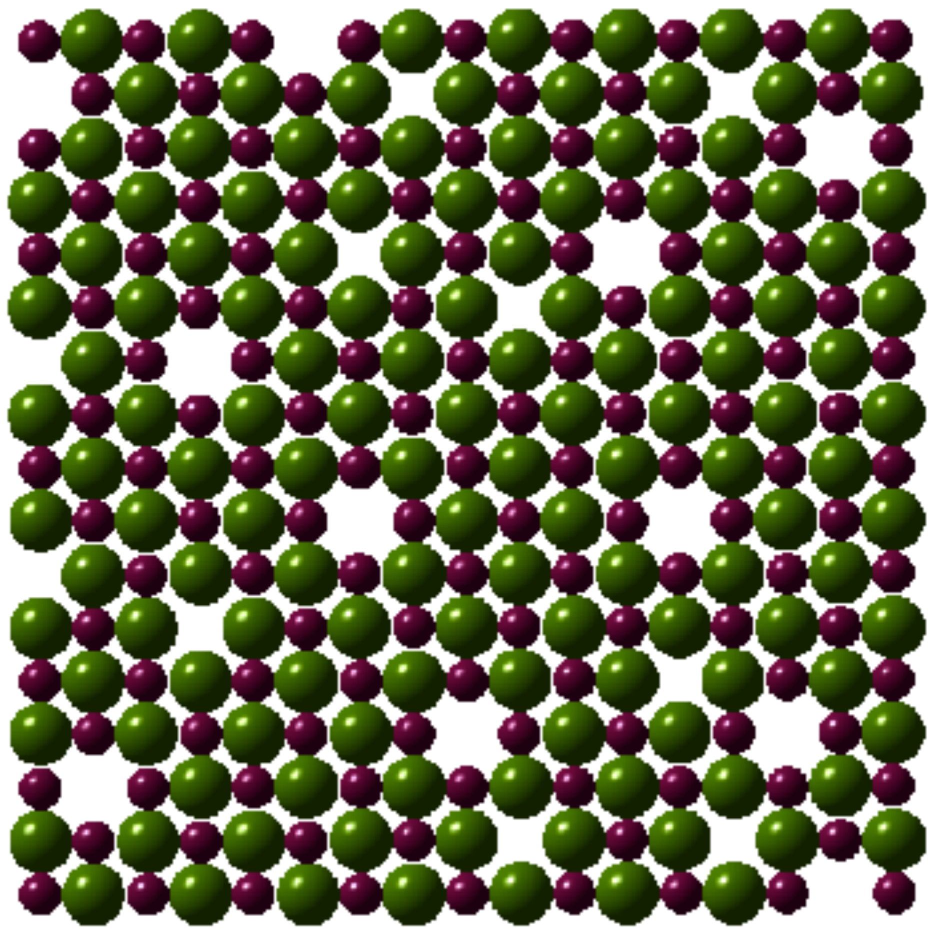
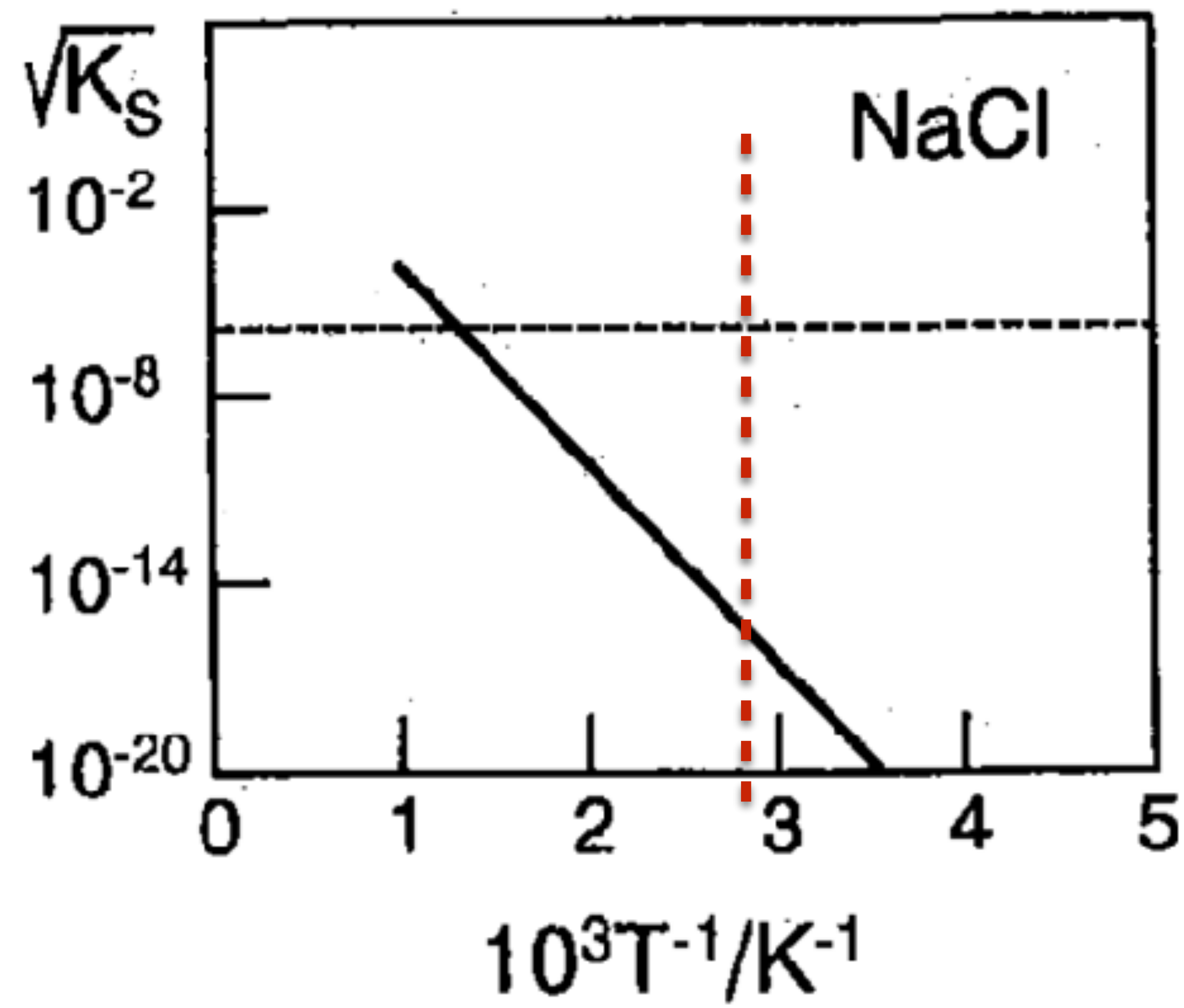
$\Delta S_S^0 \approx 9.8R$

$\Delta H_S^0 \approx$ 240 kJ.mol^{-1}

Energetics - Schottky defect





$$\Longrightarrow \quad [V_{Cl}^{\bullet}] = [V_{Na}^{'}] = N\sqrt{K_S} = \exp\left(\frac{\Delta S_S^0}{2R}\right)\ \exp\left(-\frac{\Delta H_S^0}{2RT}\right)$$

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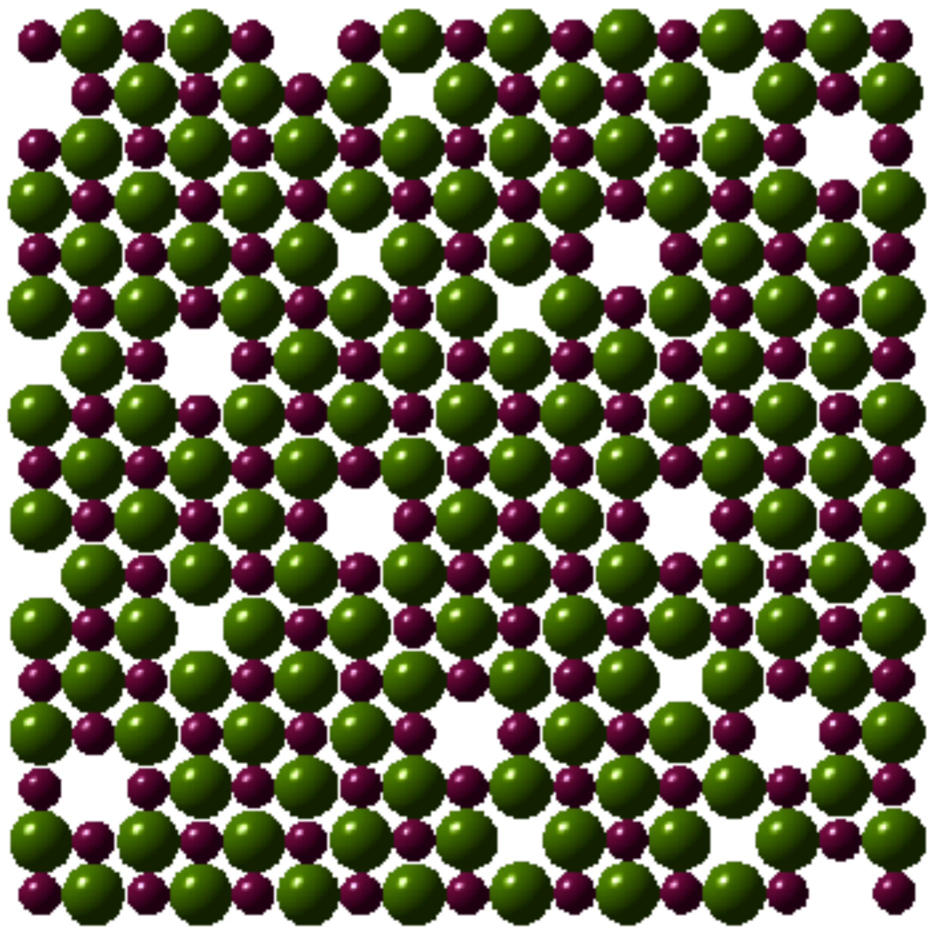
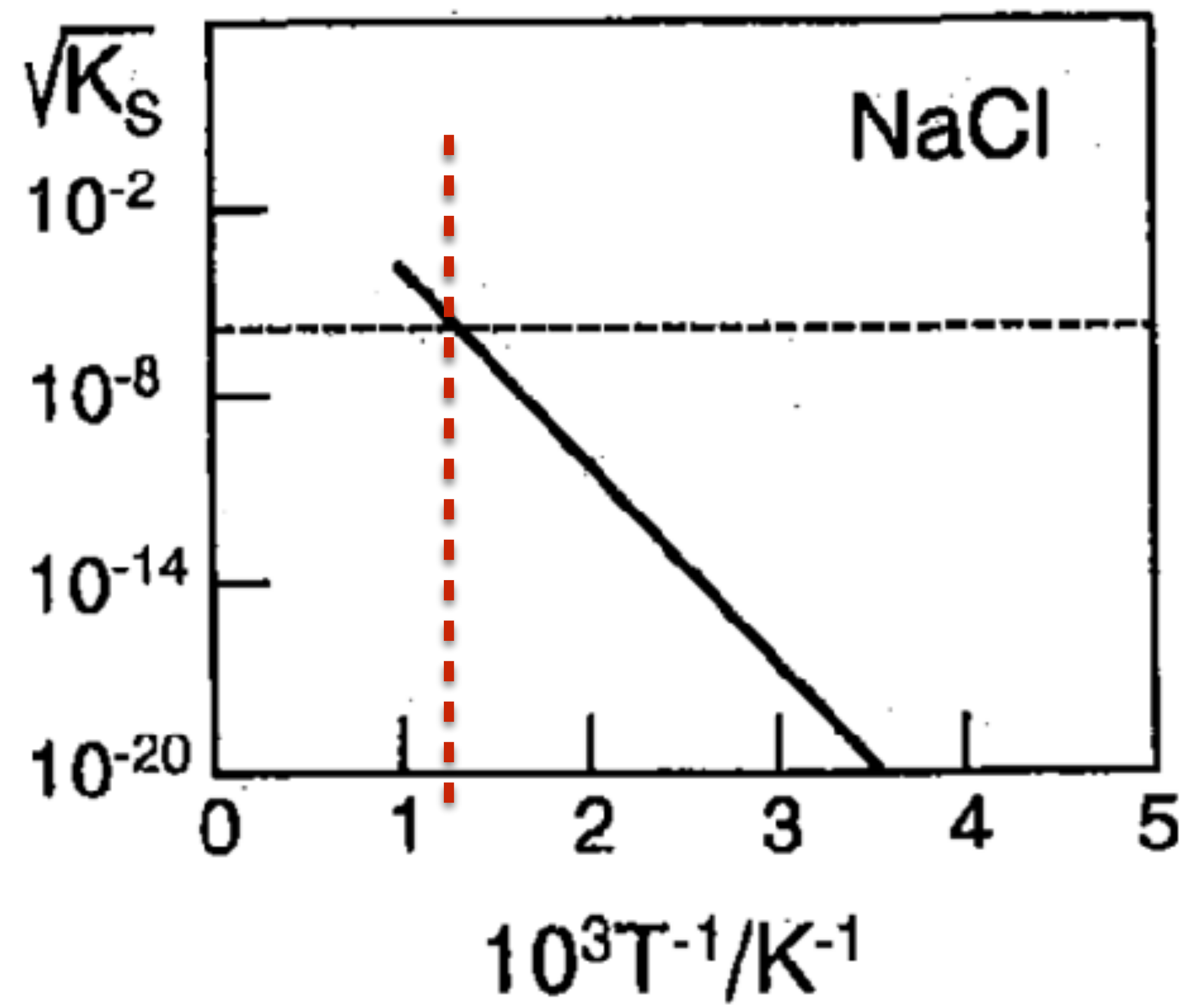
Energetics - Schottky defect





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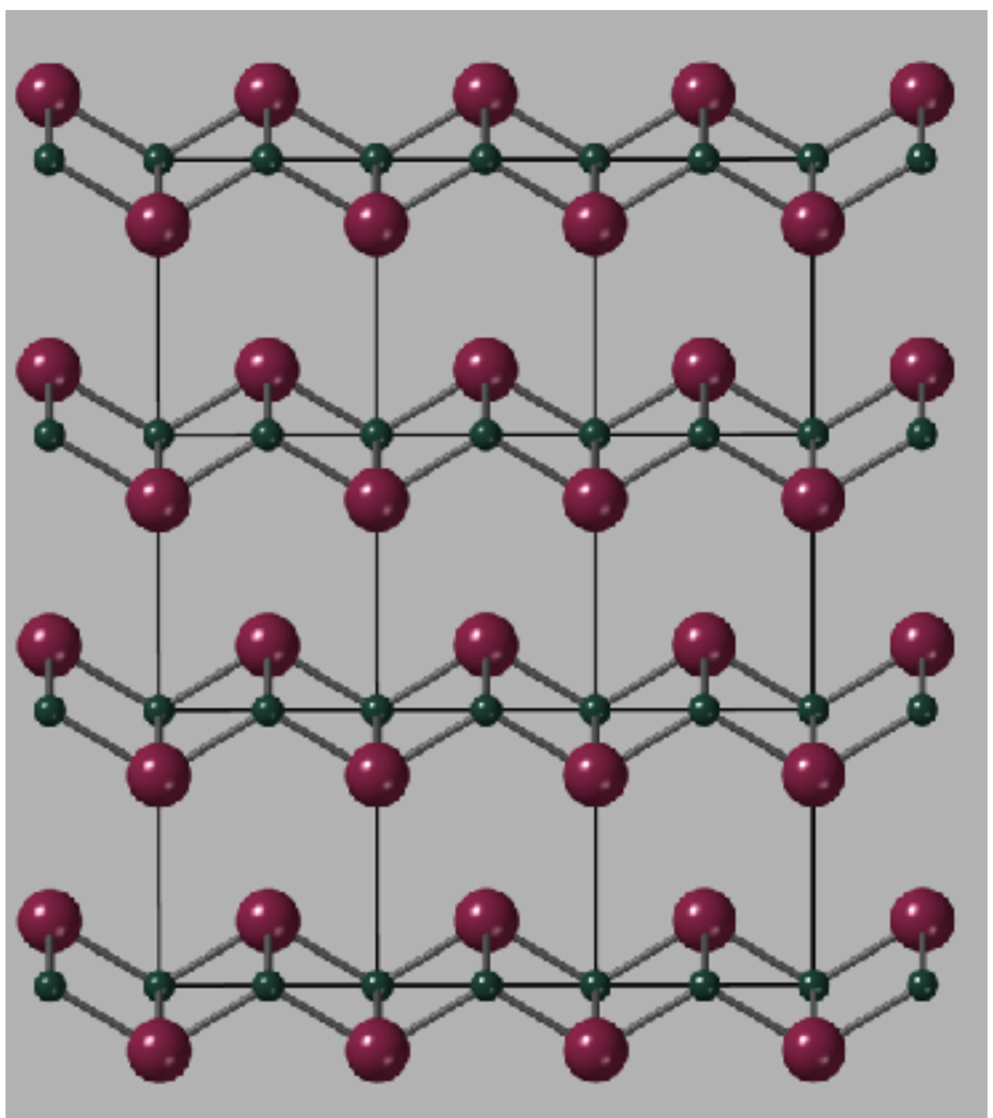
$\Delta S_S^0 \approx 9.8R$ $\quad$ $\Delta H_S^0 \approx 240$ kJ.mol^{-1}

Other stoichiometric internal reactions

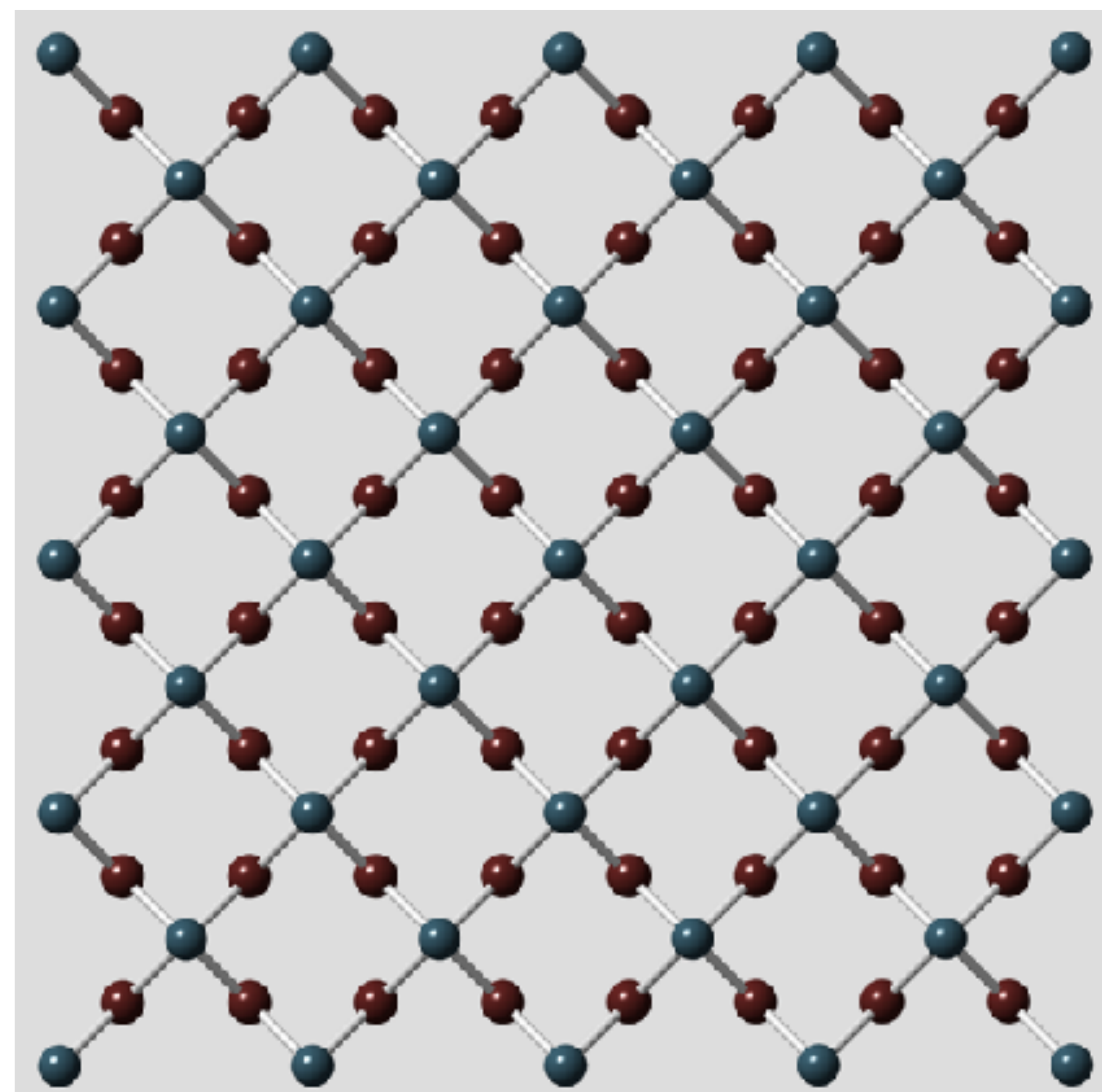
Anti-Schottky

$$PbO + 2V_i^{\mathrm{x}} \rightleftharpoons Pb_i^{\bullet\bullet} + O_i''$$



Anion Frenkel

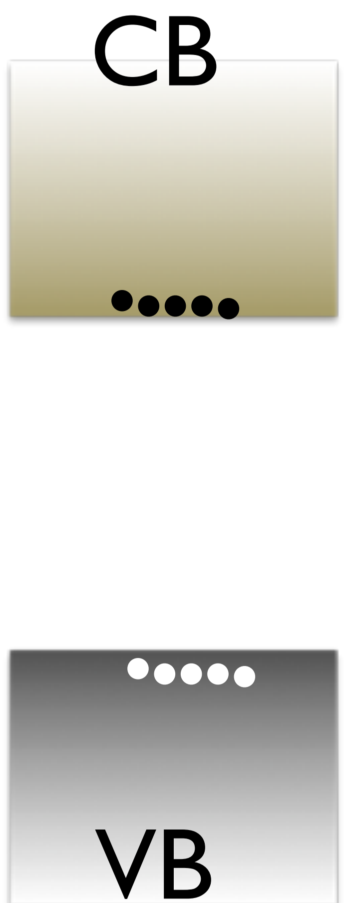
$$F_F^{\mathrm{x}} + V_i^{\mathrm{x}} \rightleftharpoons V_F^{\bullet} + F_i'$$

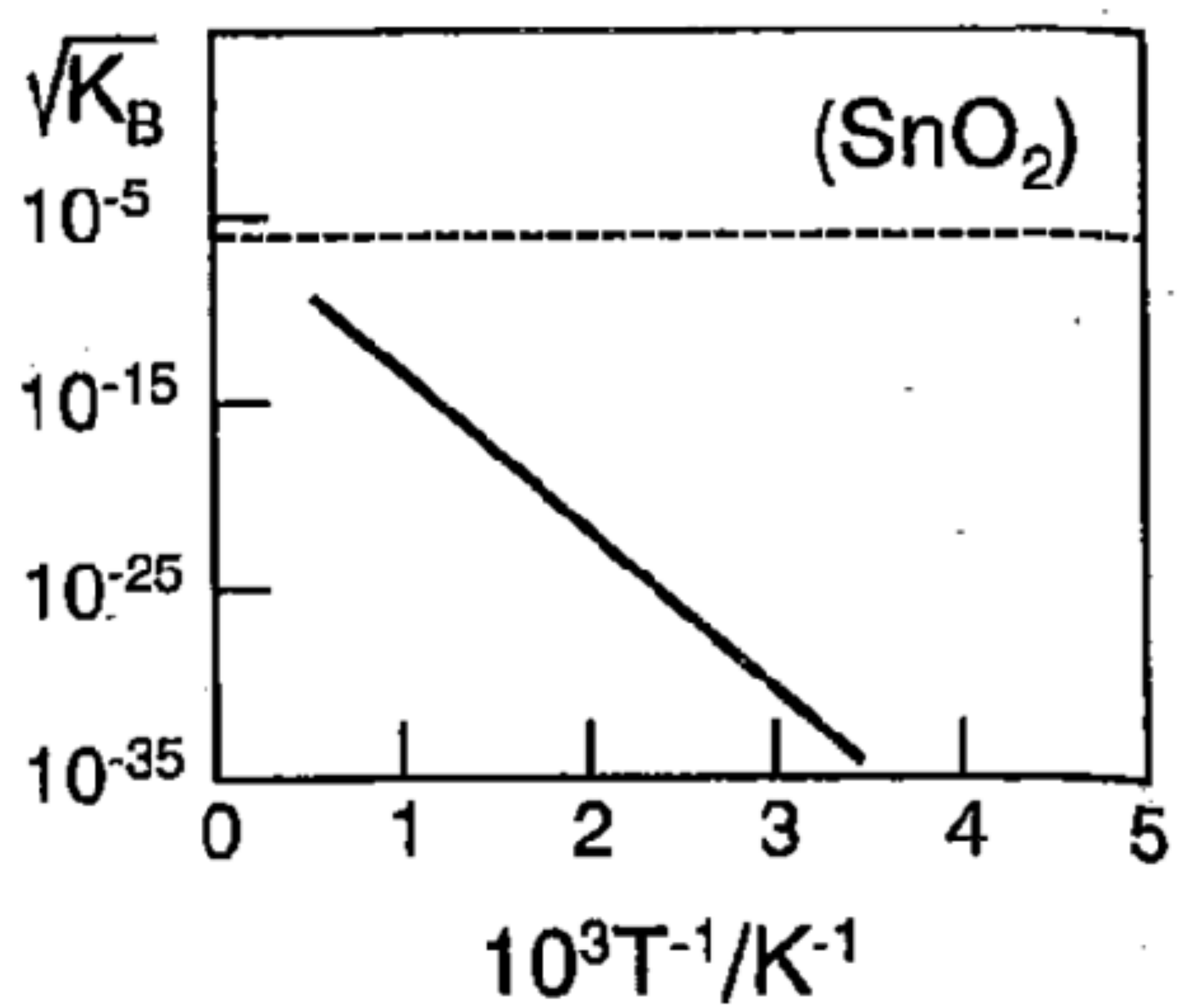


Electronic defects

Band-to-band: $e^{\times}_{\mathrm{VB}} + h^{\times}_{CB} \rightleftharpoons h^{\bullet}_{\mathrm{VB}} + e'_{\mathrm{CB}}$

electroneutrality: $[e'] = [h^{\bullet}] = \sqrt{K_B(T)} \times N_c N_v$





Internal Defect Reactions - MX

Defect creation processes occurring due to non-zero T without involvement of neighboring phases

Example Materials	Defect Rxn	Kroger-Vink Notation
AgCl	Frenkel (F)	$Ag_{Ag}^{x} + V_i^{x} \rightleftharpoons Ag_i^{\bullet} + V_{Ag}'$
NaCl	Schottky (S)	$Na_{Na}^{x} + Cl_{Cl}^{x} \rightleftharpoons V_{Cl}^{\bullet} + V_{Na}' + NaCl$
CsF	Anion-Frenkel ($\bar{\mathrm{F}}$)	$F_F^{x} + V_i^{x} \rightleftharpoons V_F^{\bullet} + F_i'$
PbO	Anti-Schottky ($\bar{\mathrm{S}}$)	$PbO + 2V_i^{x} \rightleftharpoons Pb_i^{\bullet\bullet} + O_i''$
All	Band-Band (B)	$Nil \rightleftharpoons h^{\bullet} + e'$

Internal Defect Reactions - MX

Defect creation processes occurring due to non-zero T without involvement of neighboring phases

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PbO	Anti-Schottky ($\bar{\mathrm{S}}$)	$PbO + 2V_i^{x} \rightleftharpoons Pb_i^{\bullet\bullet} + O_i''$
All	Band-Band (B)	$Nil \rightleftharpoons h^{\bullet} + e'$

Acid-base

Redox

Extrinsic defect incorporation

Extrinsic defect incorporation

Doping

Alloying

Extrinsic defect incorporation

Doping

Alloying

Interstitial

C in Fe

O_2 in UO_2

Extrinsic defect incorporation

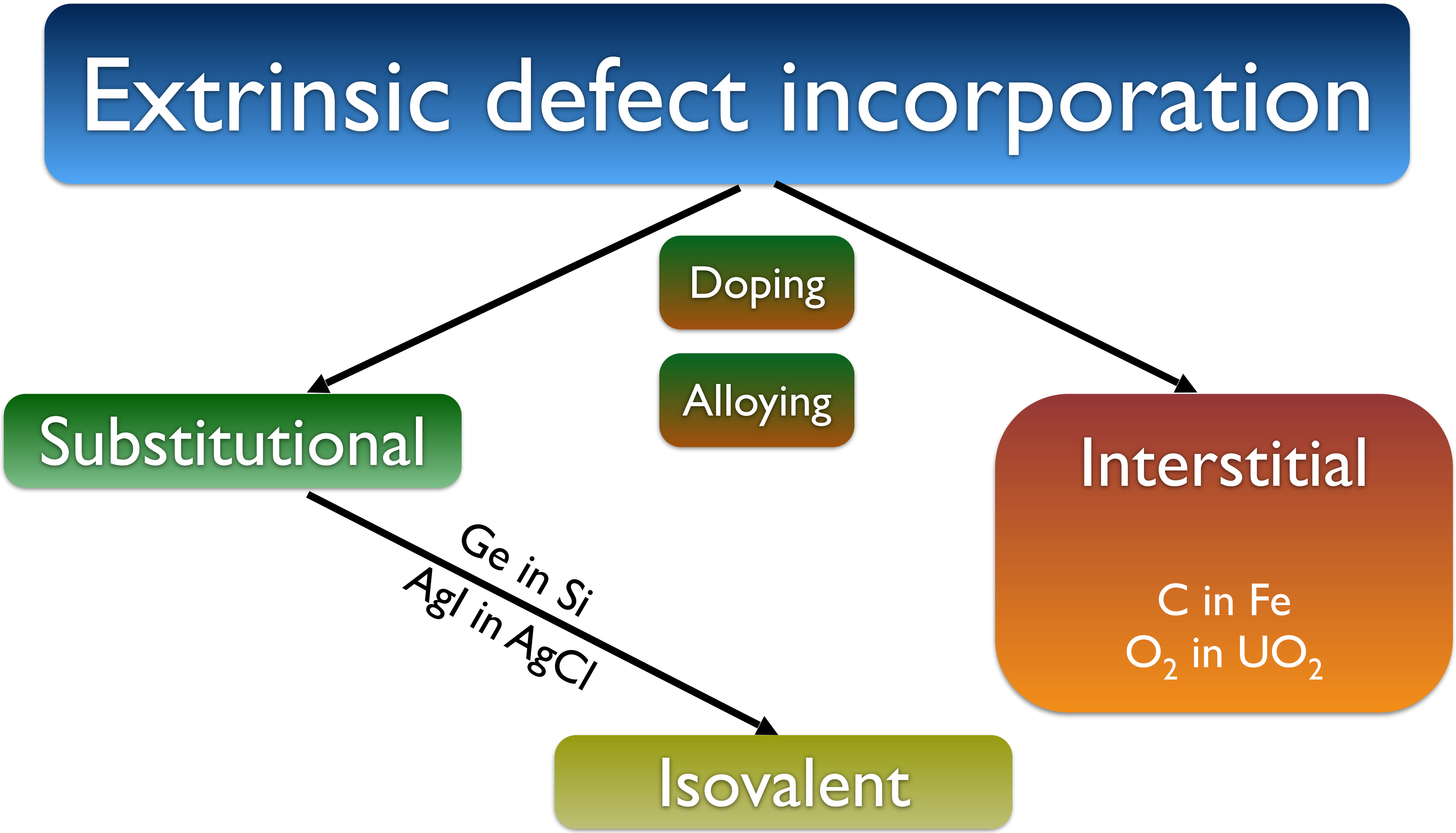
Substitutional

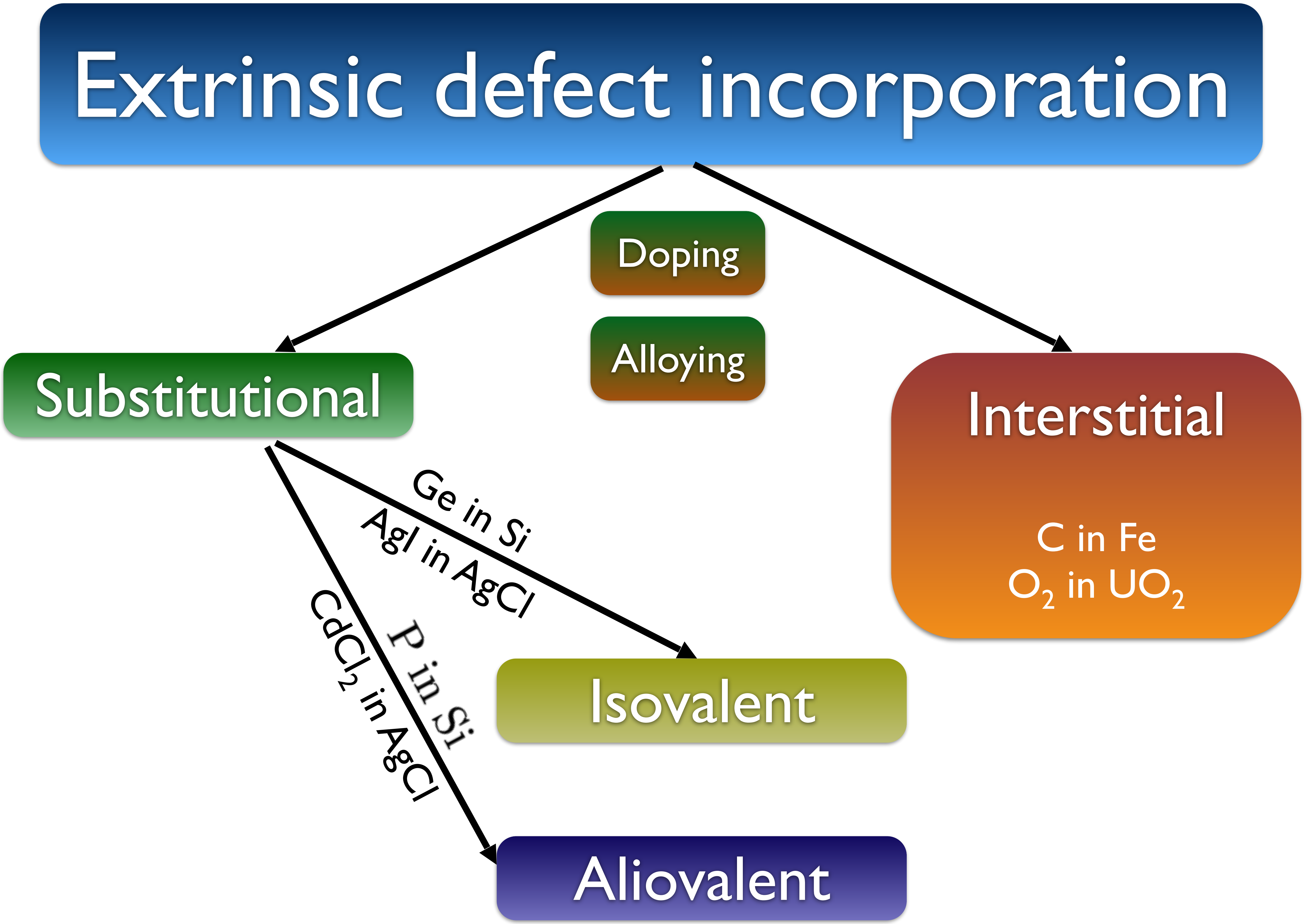
- Doping
- Alloying

Interstitial

C in Fe

O_2 in UO_2


Extrinsic defect incorporation
Doping
Alloying
Substitutional
Interstitial
Ge in Si
AgI in AgCl
C in Fe
O_2 in UO_2
Isovalent



Extrinsic defect incorporation
Doping
Alloying
Substitutional
Interstitial
C in Fe
O_2 in UO_2
Ge in Si
AgI in AgCl
P in Si
$CdCl_2$ in AgCl
Isovalent
Aliovalent

Example - Isovalent Substitutional

Al_2O_3

Cr_2O_3

Example - Isovalent Substitutional

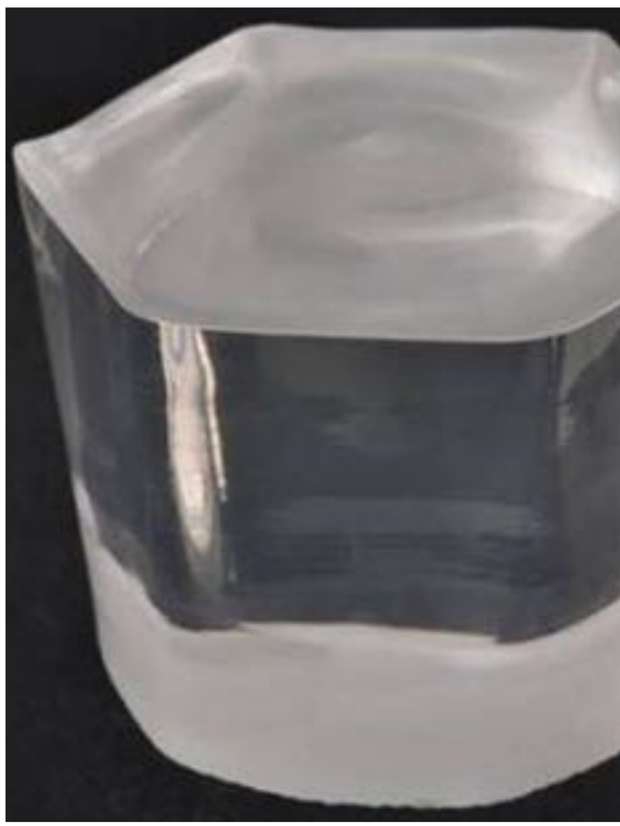
Al_2O_3

Cr_2O_3

Increasing Cr_2O_3

Example - Isovalent Substitutional

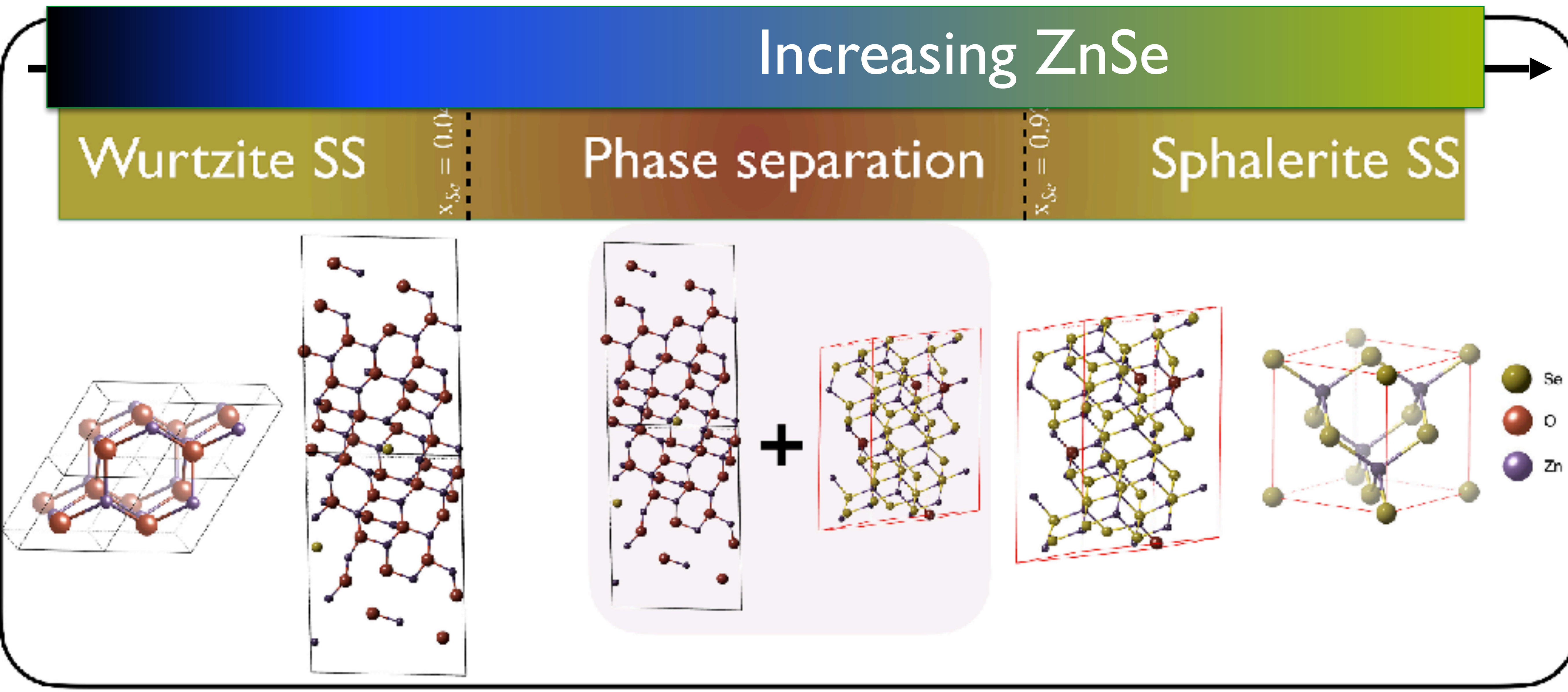
Al_2O_3



Cr_2O_3

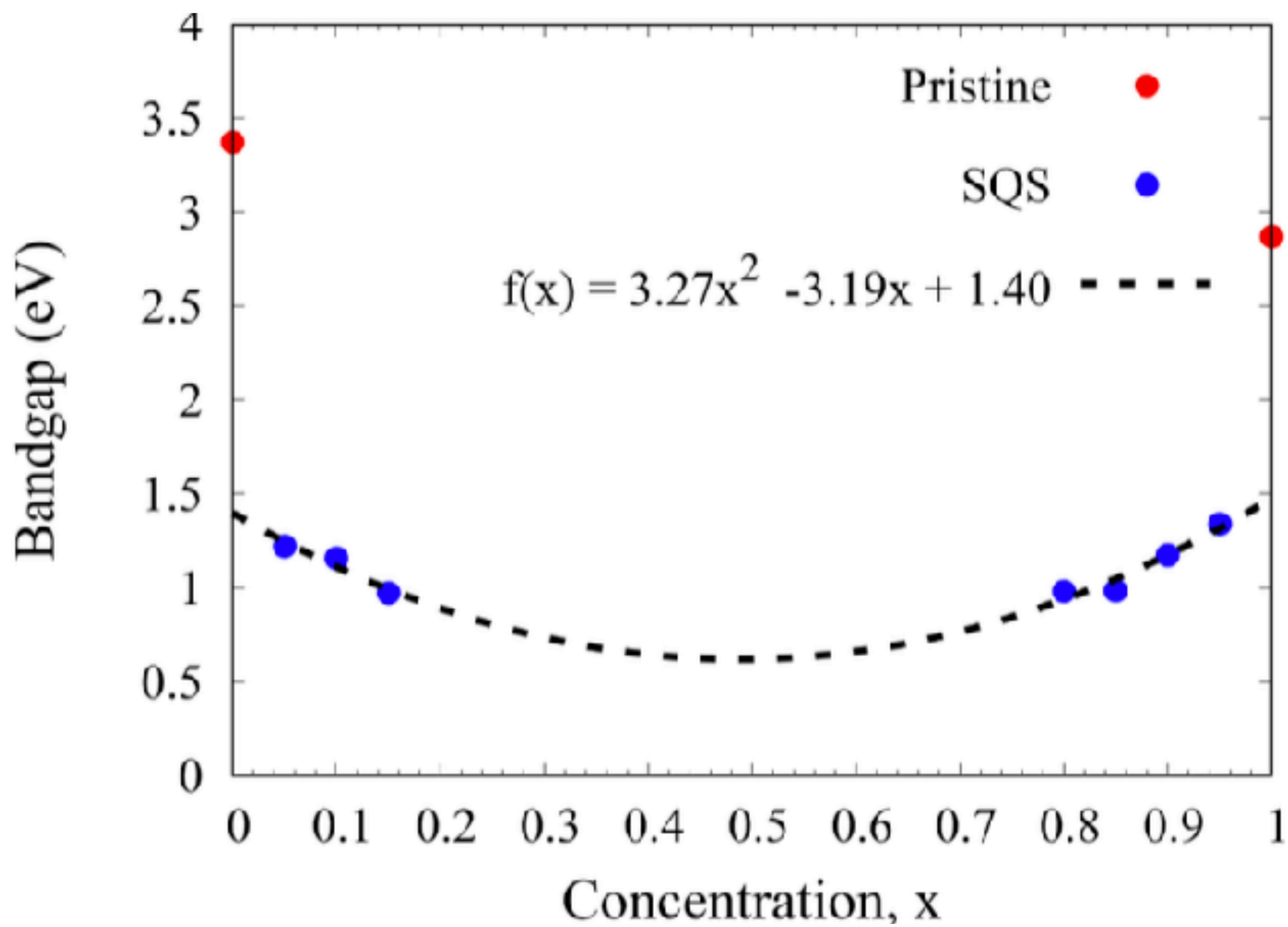
Increasing Cr_2O_3

Example - Isovalent Substitutional



Arini et al., Journal of Applied Physics, **134**, 235702 (2024)

Example - Isovalent Substitutional



Arini et al., Journal of Applied Physics, **134**, 235702 (2024)

Aliovalent Incorporation

Atoms with different valence than the site

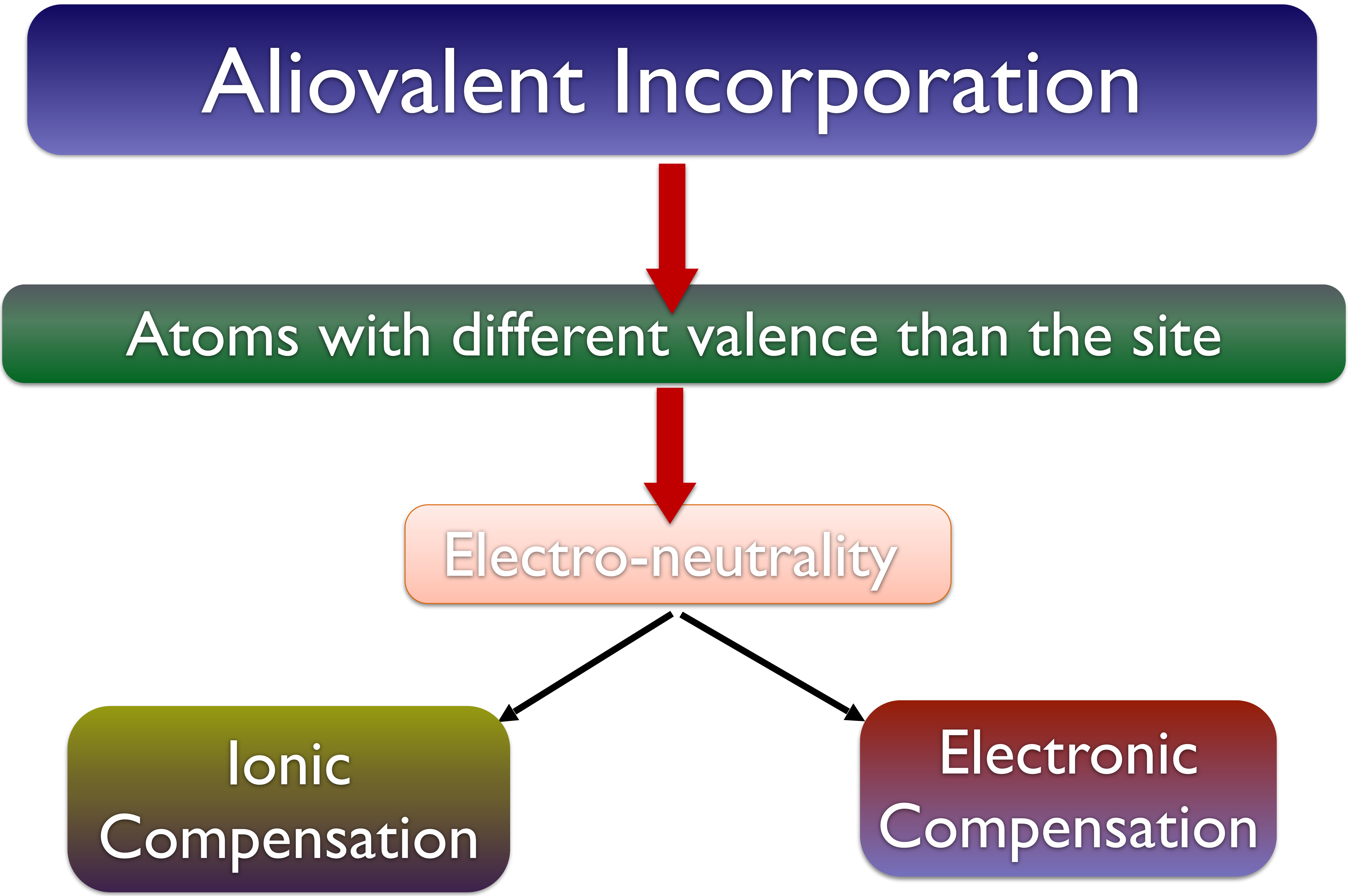
Electro-neutrality

Aliovalent Incorporation

Atoms with different valence than the site

Electro-neutrality

Ionic Compensation


Aliovalent Incorporation
Atoms with different valence than the site
Electro-neutrality
Ionic Compensation
Electronic Compensation

Class Test 3

(10 marks)

AgCl crystallizes in the cF lattice with a lattice parameter of 0.5622 nm. Cl forms the ccp framework with Ag in the octahedral interstices.

Defect	Formation enthalpy ($kJ.mol^{-1}$)	Formation entropy ($kJ.mol^{-1}$)
Schottky	400	9.8R
Frenkel	140	9.4R

Determine the volume of AgCl at room temperature (T = 300 K) when you will find a single chlorine vacancy in the material.

Defect Reactions - Rules

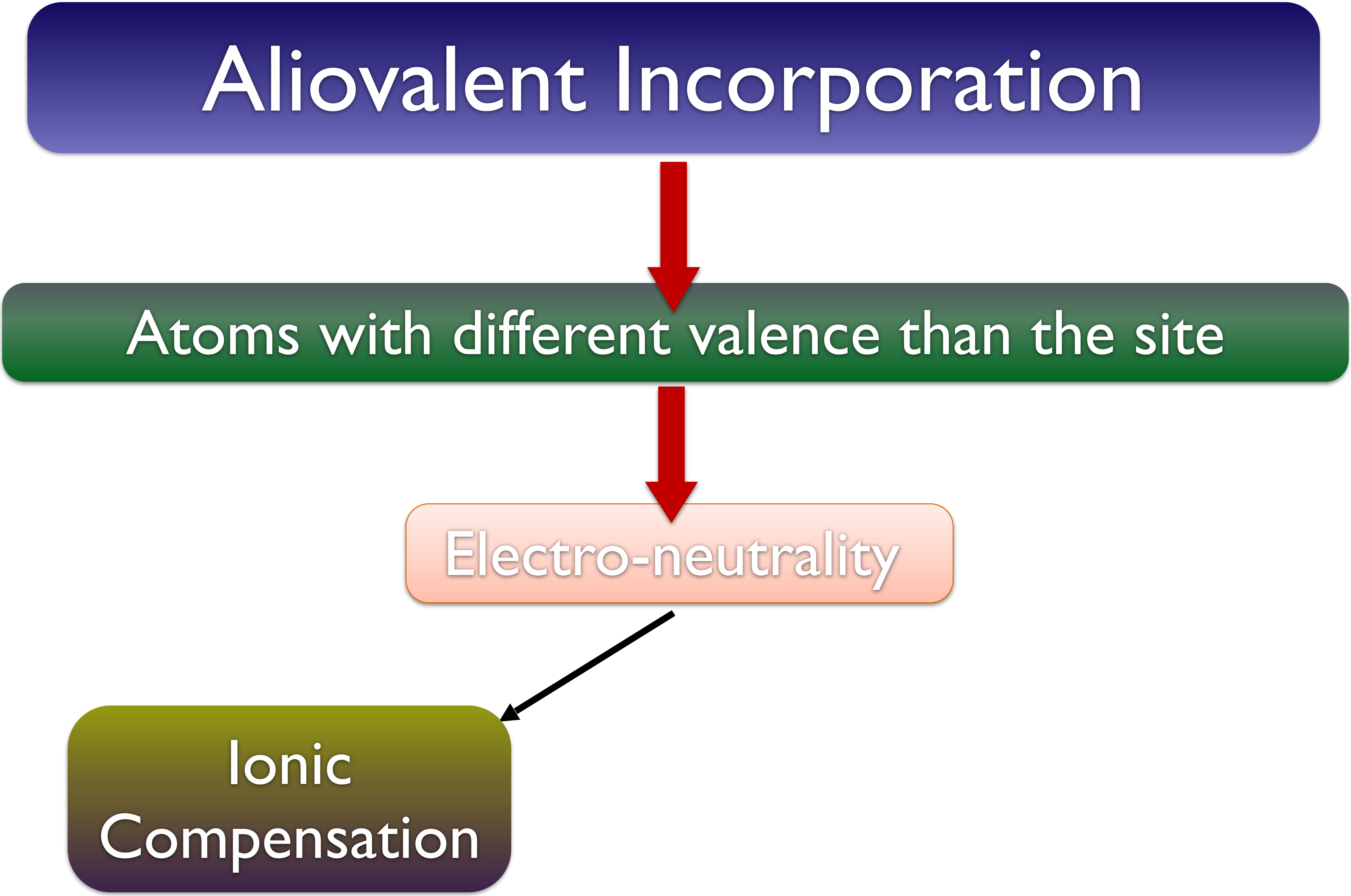
- *Site relation:*
  - The number of M sites in a compound M_aX_b must always be in correct proportion to the number of X sites
  - Total number of each type of site may change
- *Site creation:*
  - Must not affect the site relation described in rule above
- *Mass balance:*
  - Mass balance must be maintained as in any chemical reaction

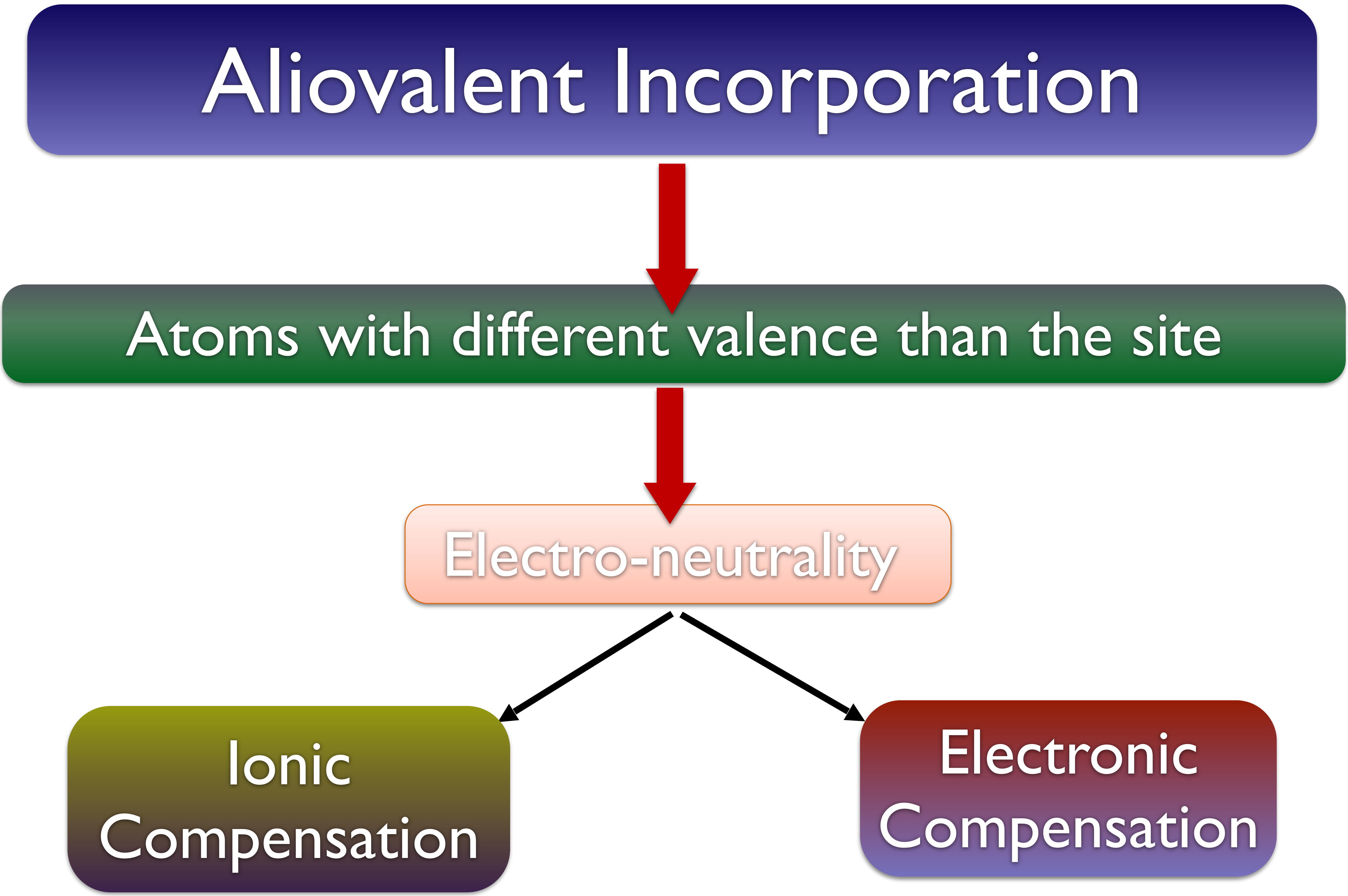
  Note: subscript in the defect symbol indicates the site under consideration and is of no significance for the mass balance
- *Electroneutrality:*
  - The crystal must remain electrically neutral
  - Only neutral atoms or molecules are exchanged with other phases outside the crystal under consideration; within the crystal neutral particles can yield two or more oppositely charged defects
- *Surface sites:*
  - Atom M displaced from the bulk to surface increases the number of M sites

Aliovalent Incorporation

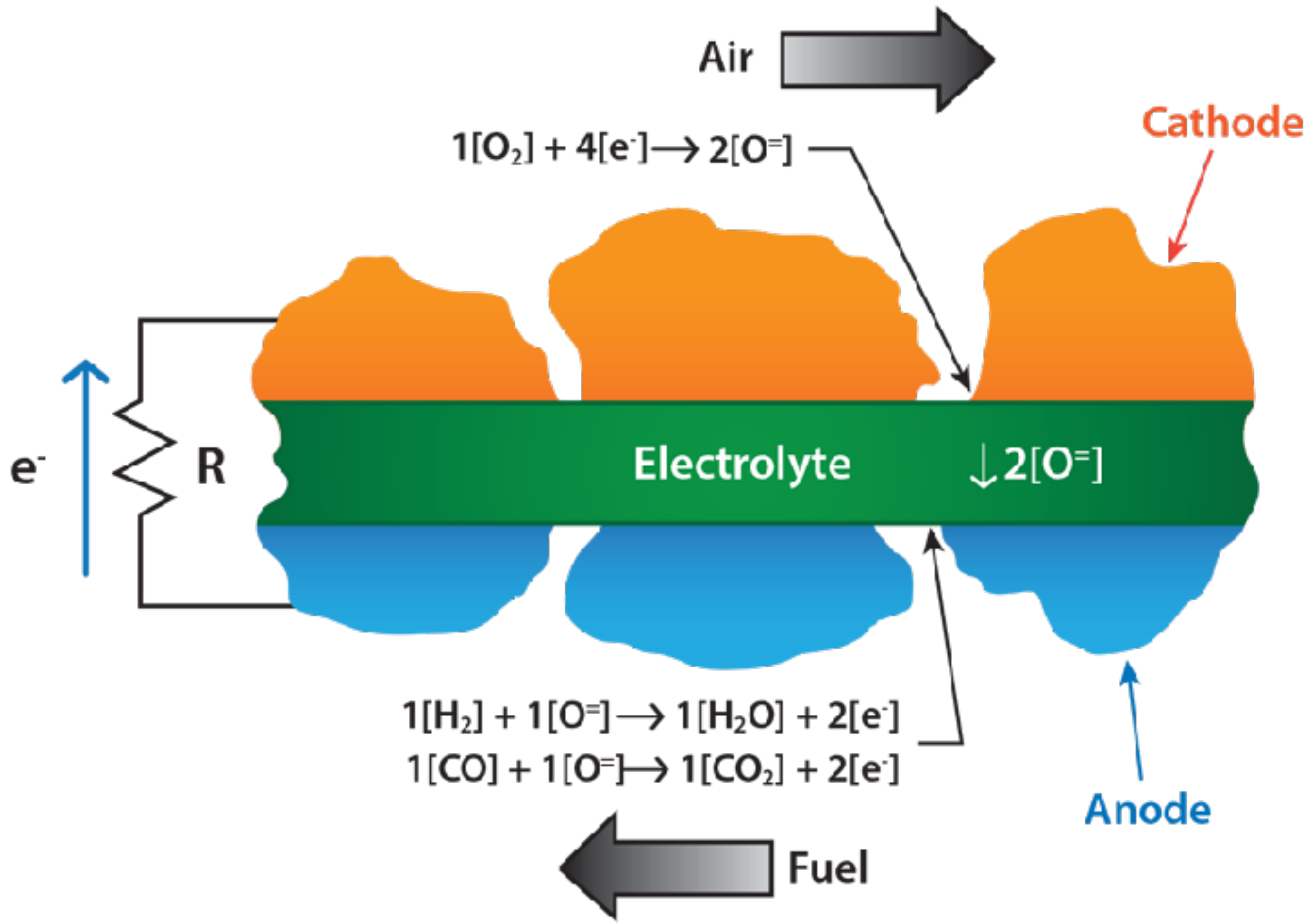
Atoms with different valence than the site

Electro-neutrality


Aliovalent Incorporation
Atoms with different valence than the site
Electro-neutrality
Ionic Compensation


Aliovalent Incorporation
Atoms with different valence than the site
Electro-neutrality
Ionic Compensation
Electronic Compensation

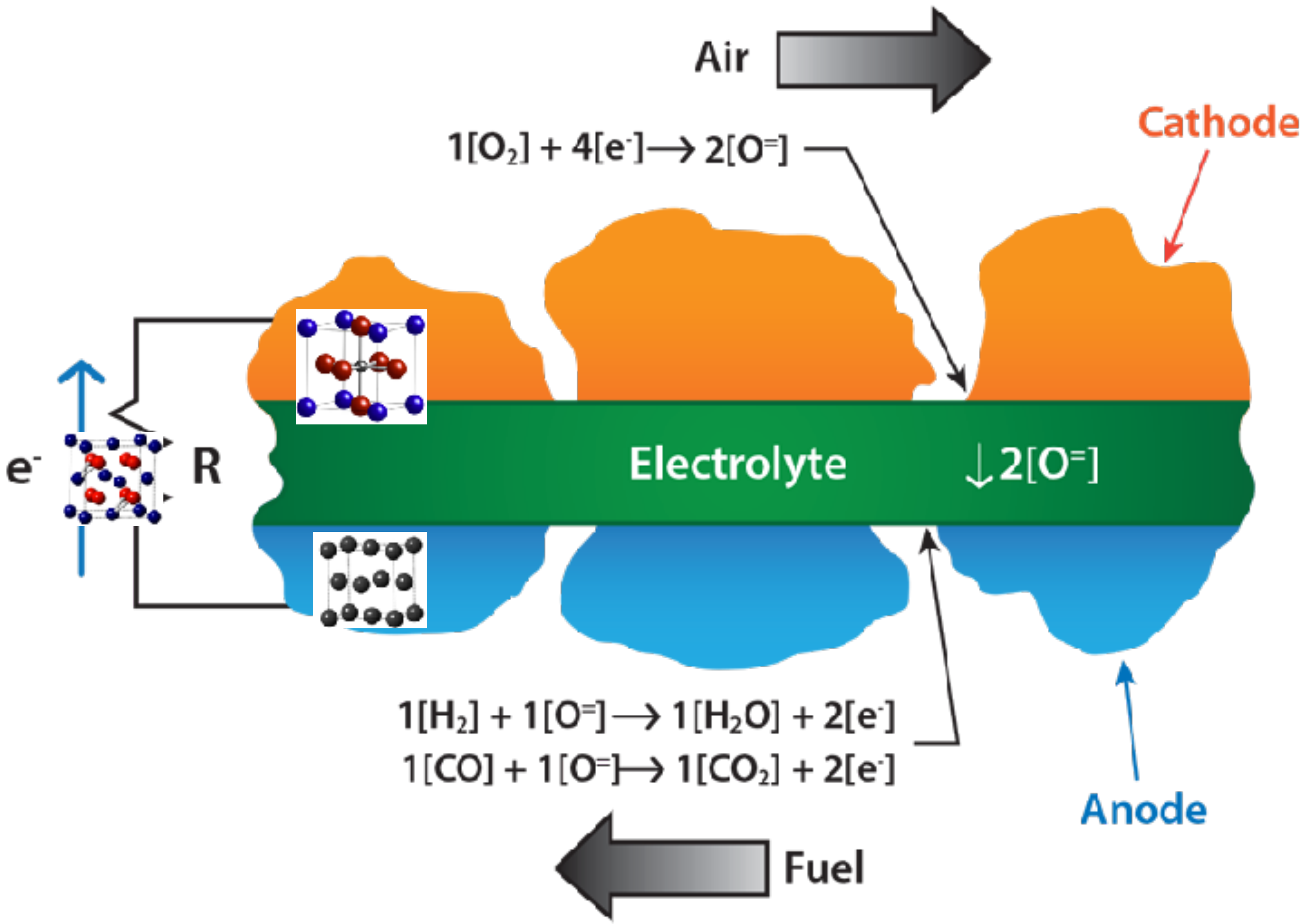
Anion Vacancies
Solid Oxide Fuel Cell electrolyte



https://www.netl.doe.gov/research/coal/energy-systems/fuel-cells/operating-principles

Anion Vacancies

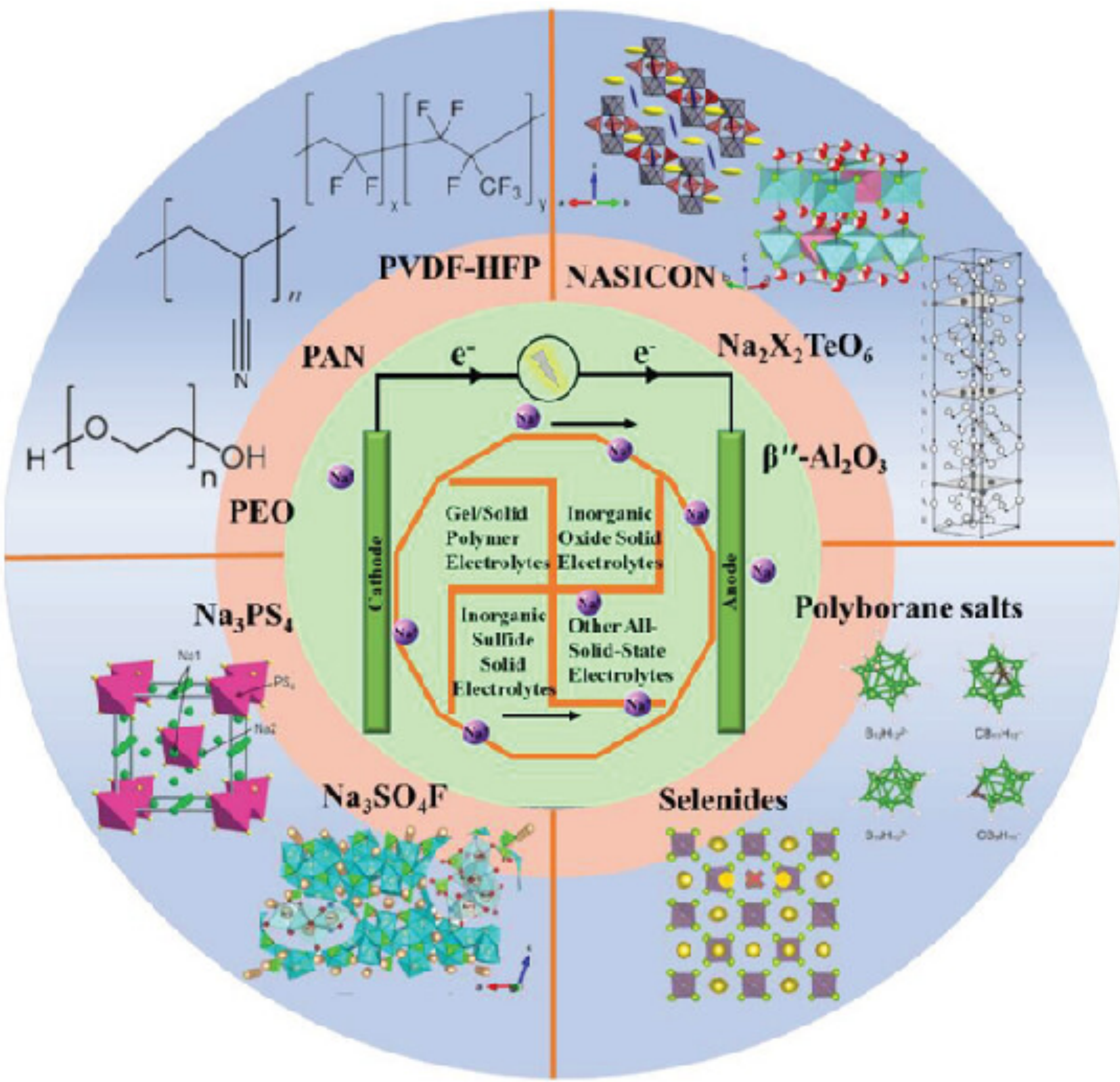
Solid Oxide Fuel Cell electrolyte



https://www.netl.doe.gov/research/coal/energy-systems/fuel-cells/operating-principles

Cation Interstitials

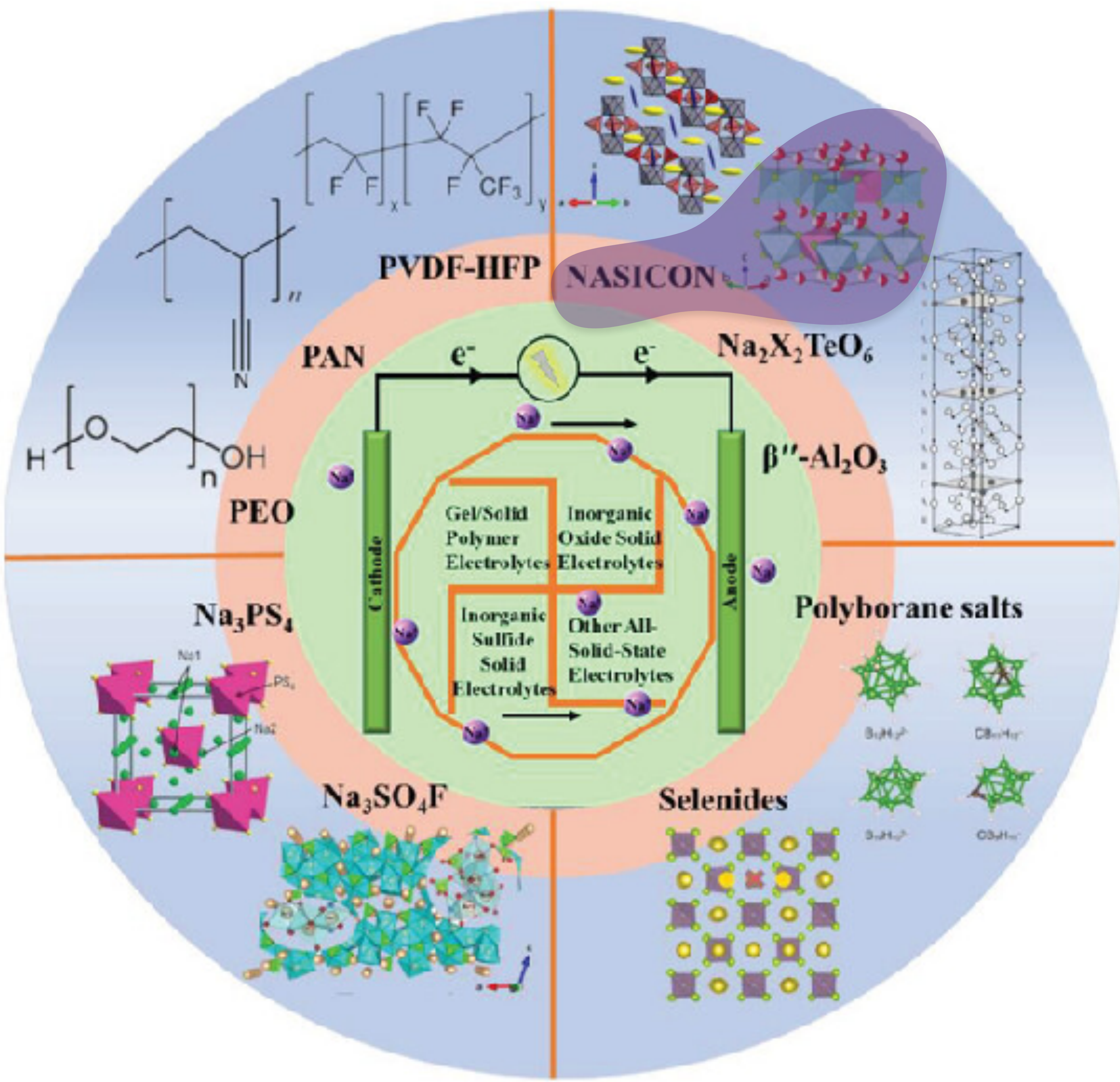
Solid electrolytes for Na-ion Batteries



Cation Interstitials

Solid electrolytes for Na-ion Batteries

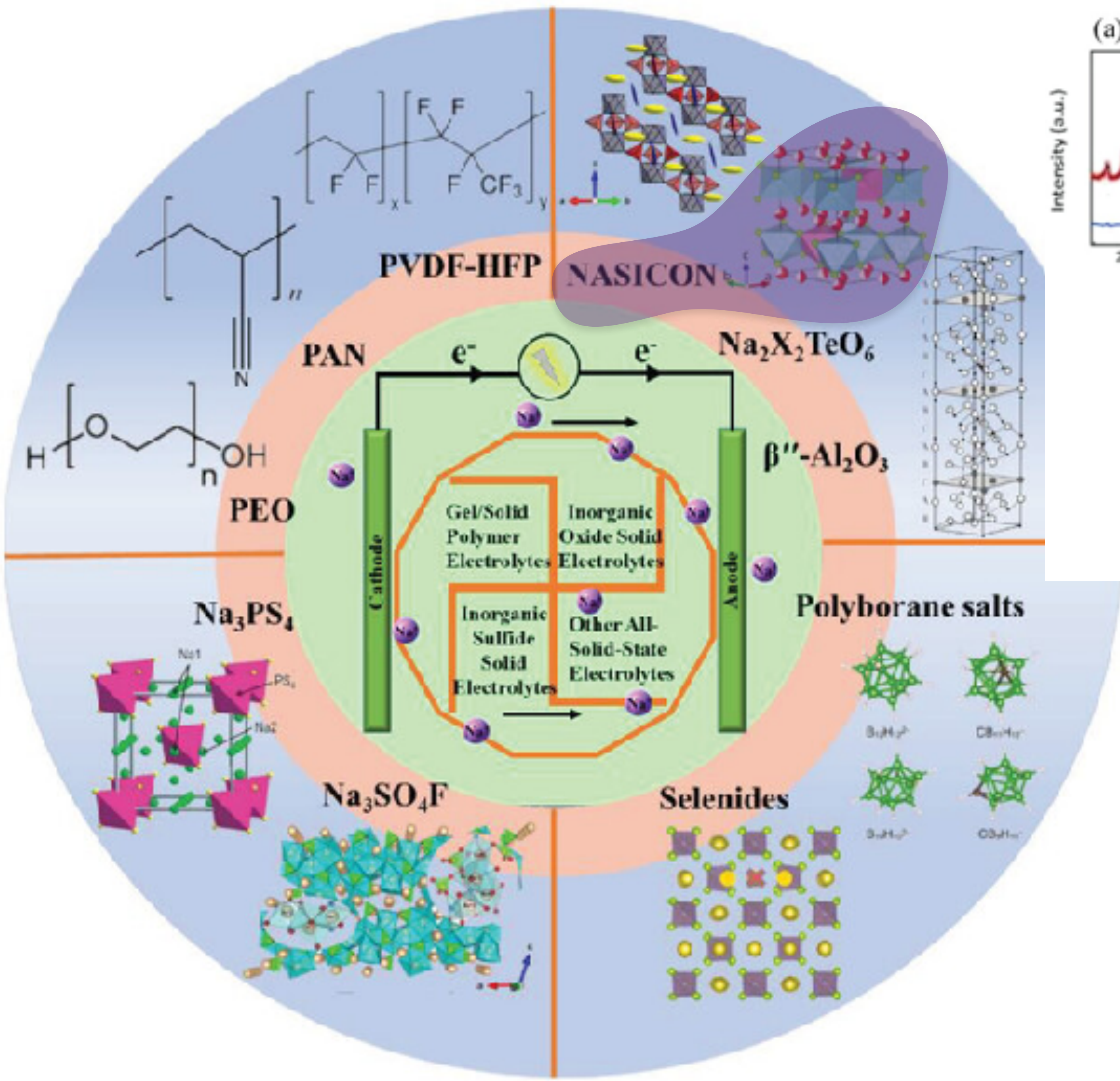
Sodium(**Na**) Super-Ionic (**SI**) Conductor (**Con**)

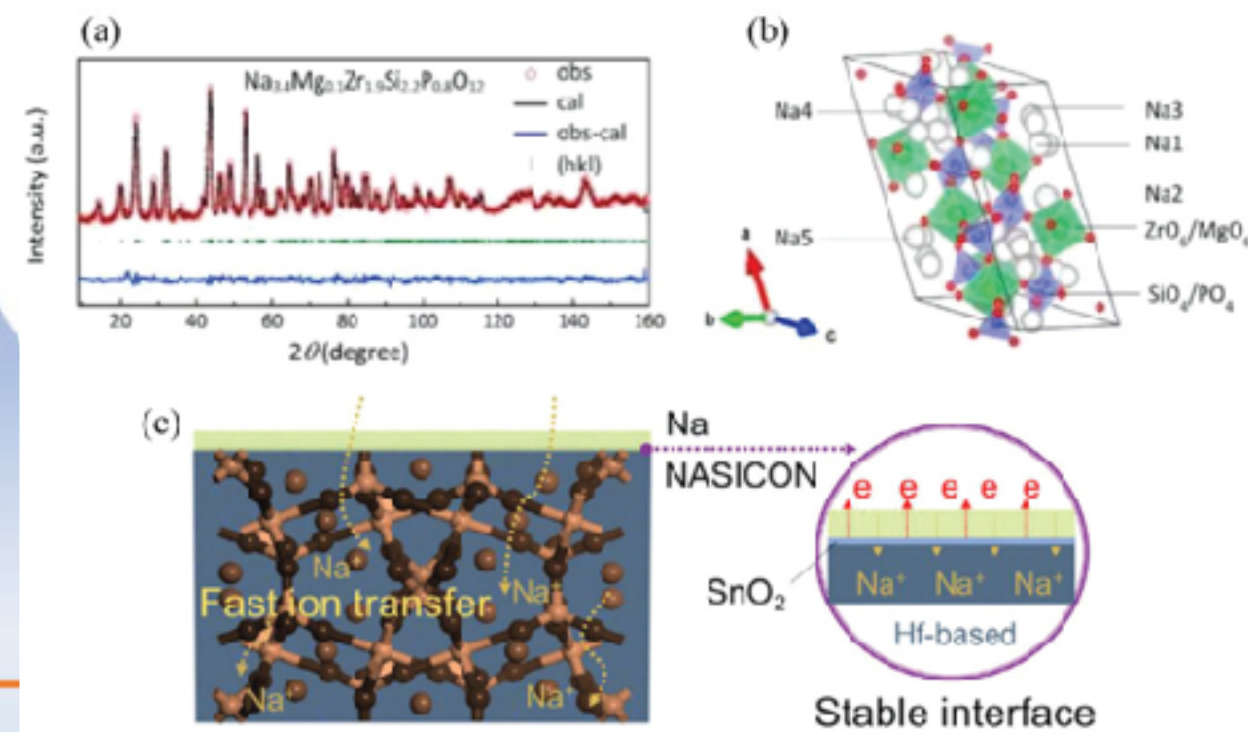


Cation Interstitials

Solid electrolytes for Na-ion Batteries

Sodium(**Na**) Super-Ionic (**SI**) Conductor (**Con**)

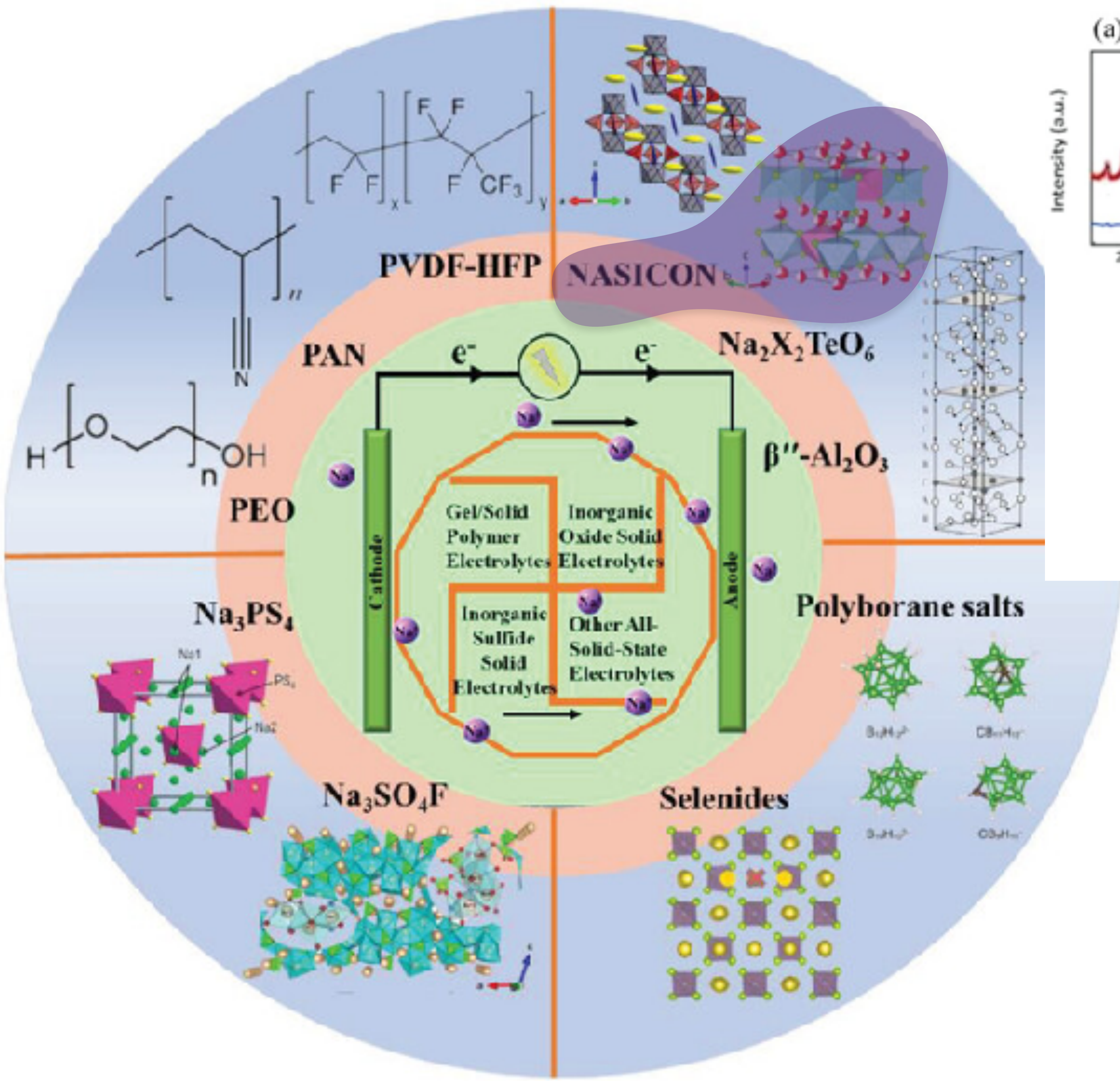


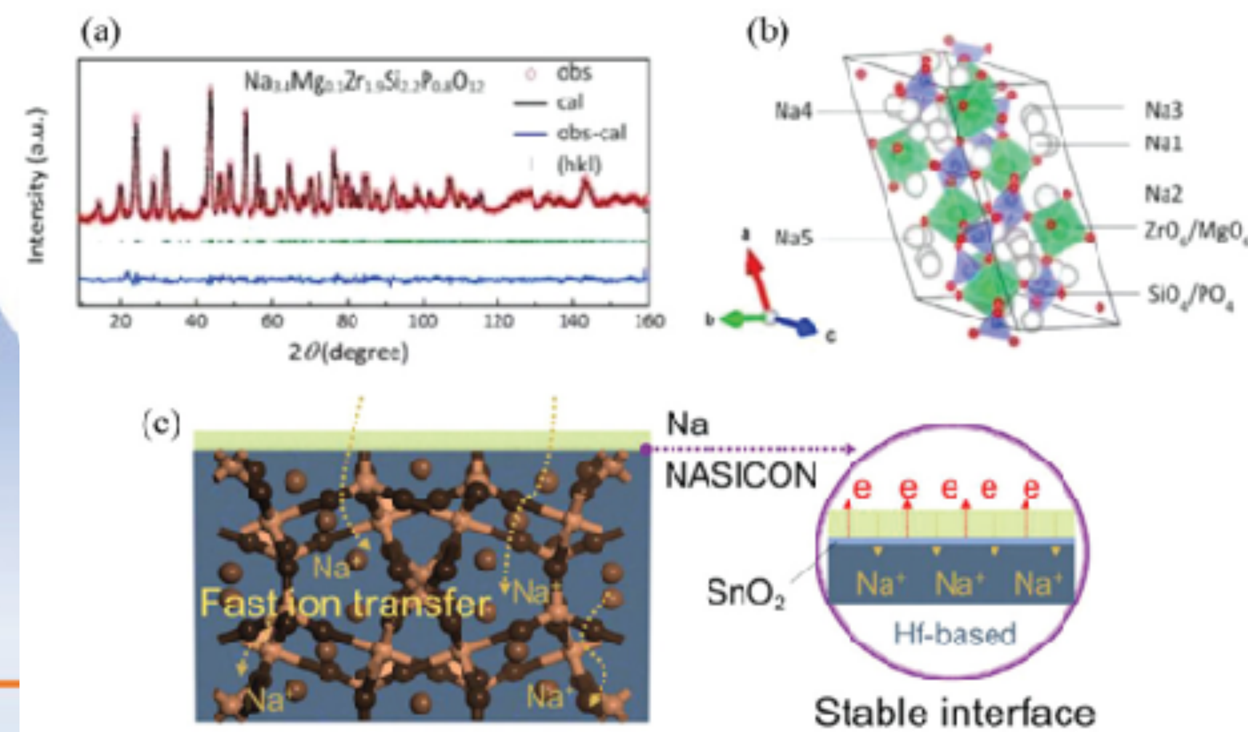


Cation Interstitials

Solid electrolytes for Na-ion Batteries

Sodium(**Na**) Super-Ionic (**SI**) Conductor (**Con**)



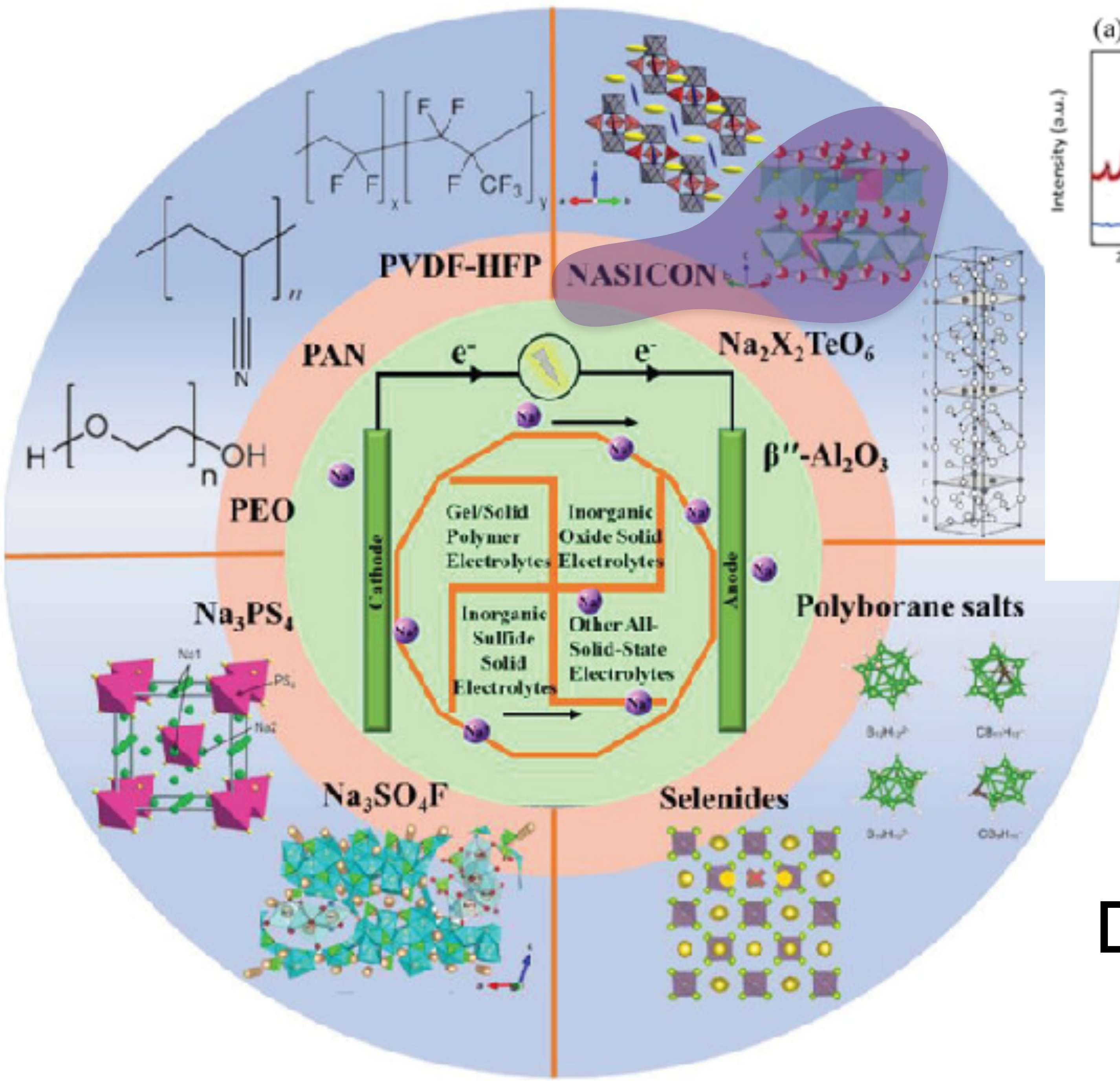


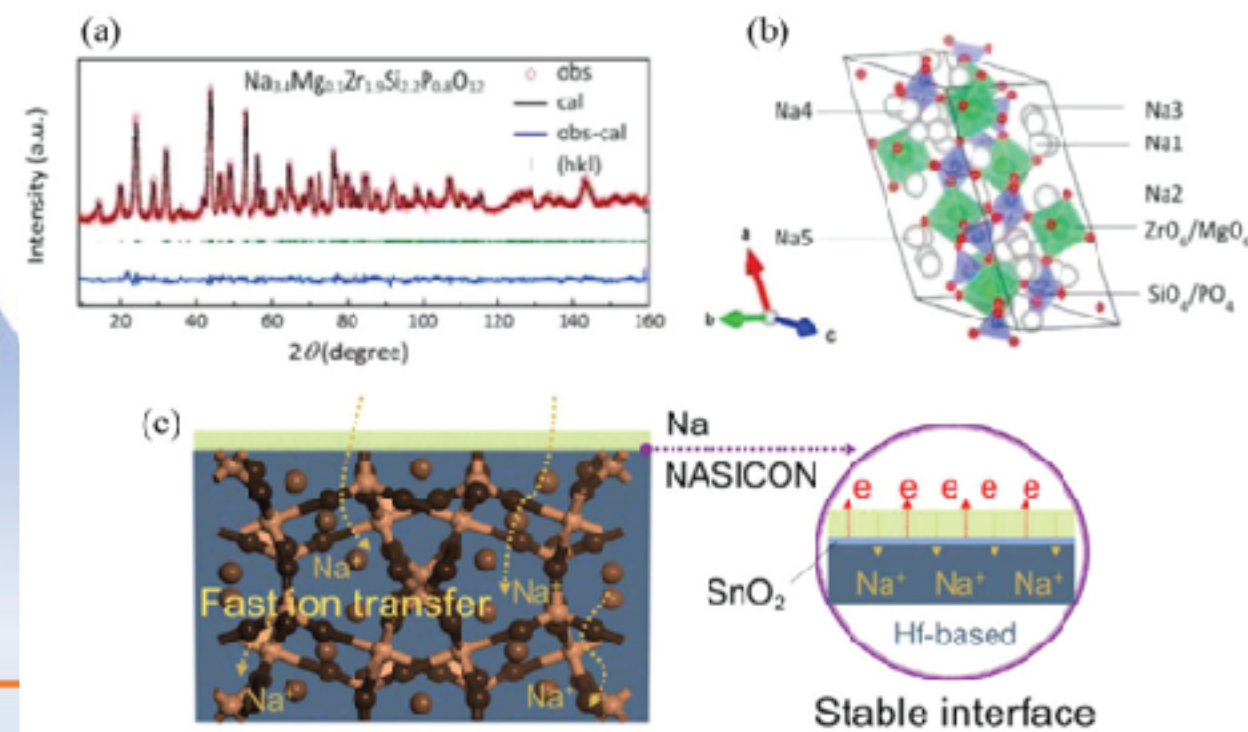
Host Material: $NaZr_2(PO_4)_3$

Cation Interstitials

Solid electrolytes for Na-ion Batteries

Sodium(**Na**) Super-Ionic (**SI**) Conductor (**Con**)

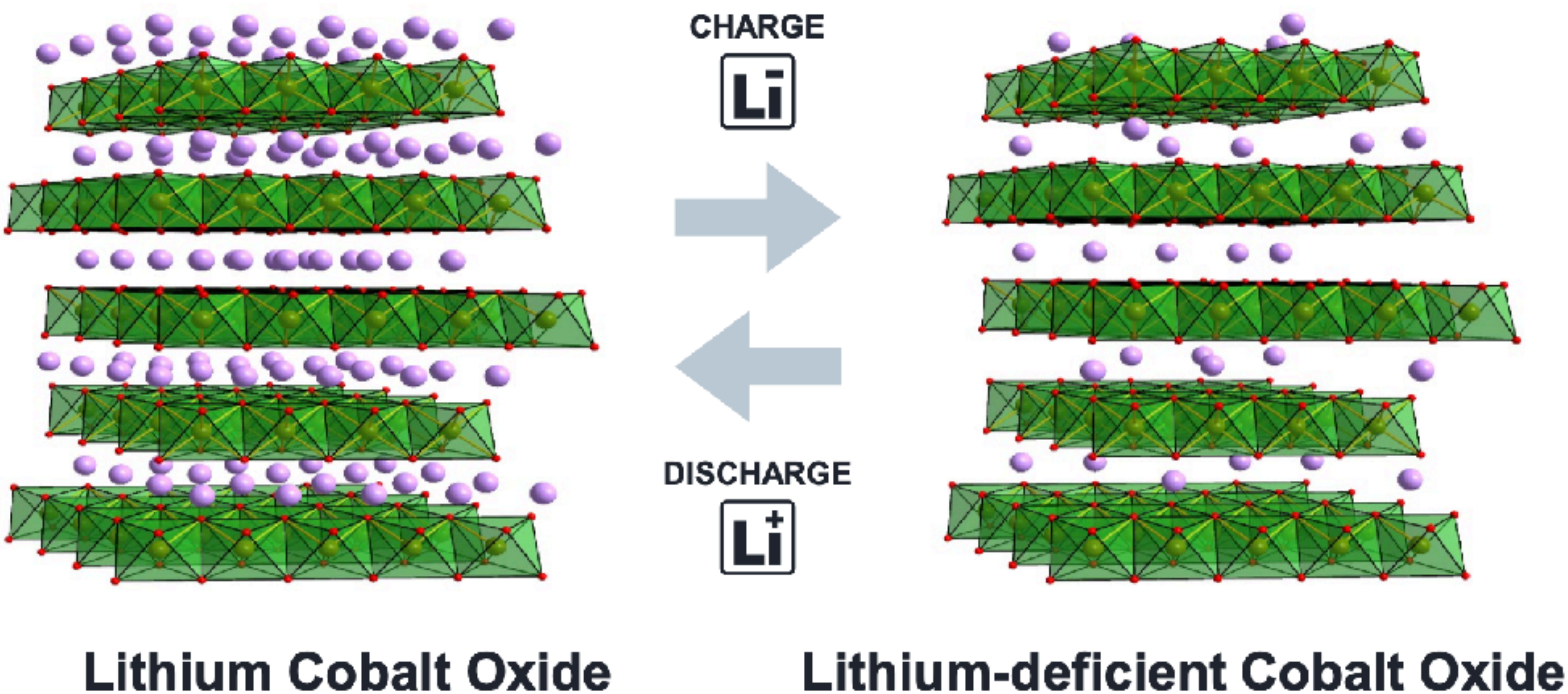




Host Material: $NaZr_2(PO_4)_3$

Dopant Material: $Na_4Zr_2(SiO_4)_3$

Electronic compensation
Li ion battery electrodes



Electronic compensation

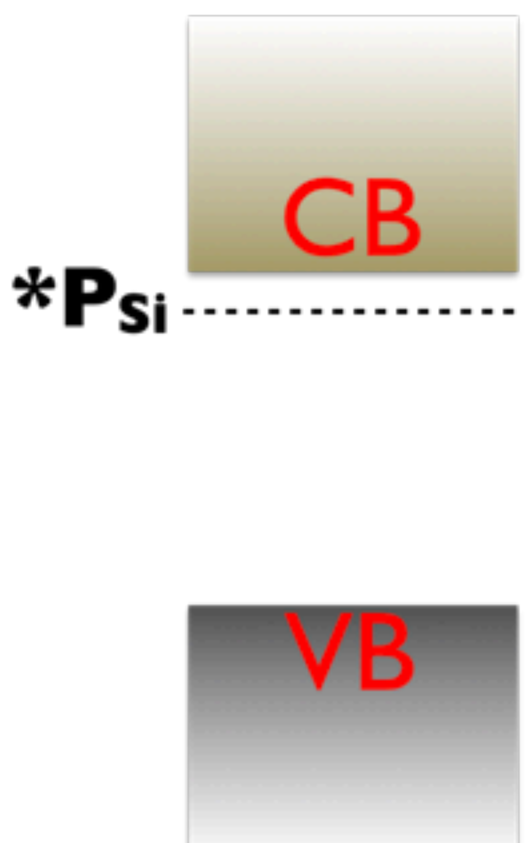
Solar Photovoltaic Absorber

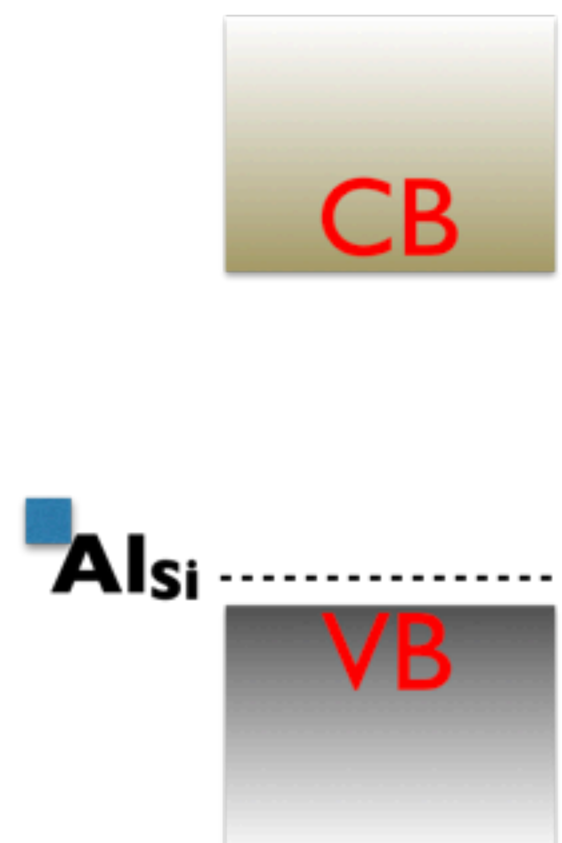
Si $\longrightarrow$ *Ne* 3s2 3p2

P $\longrightarrow$ *Ne* 3s2 3p3

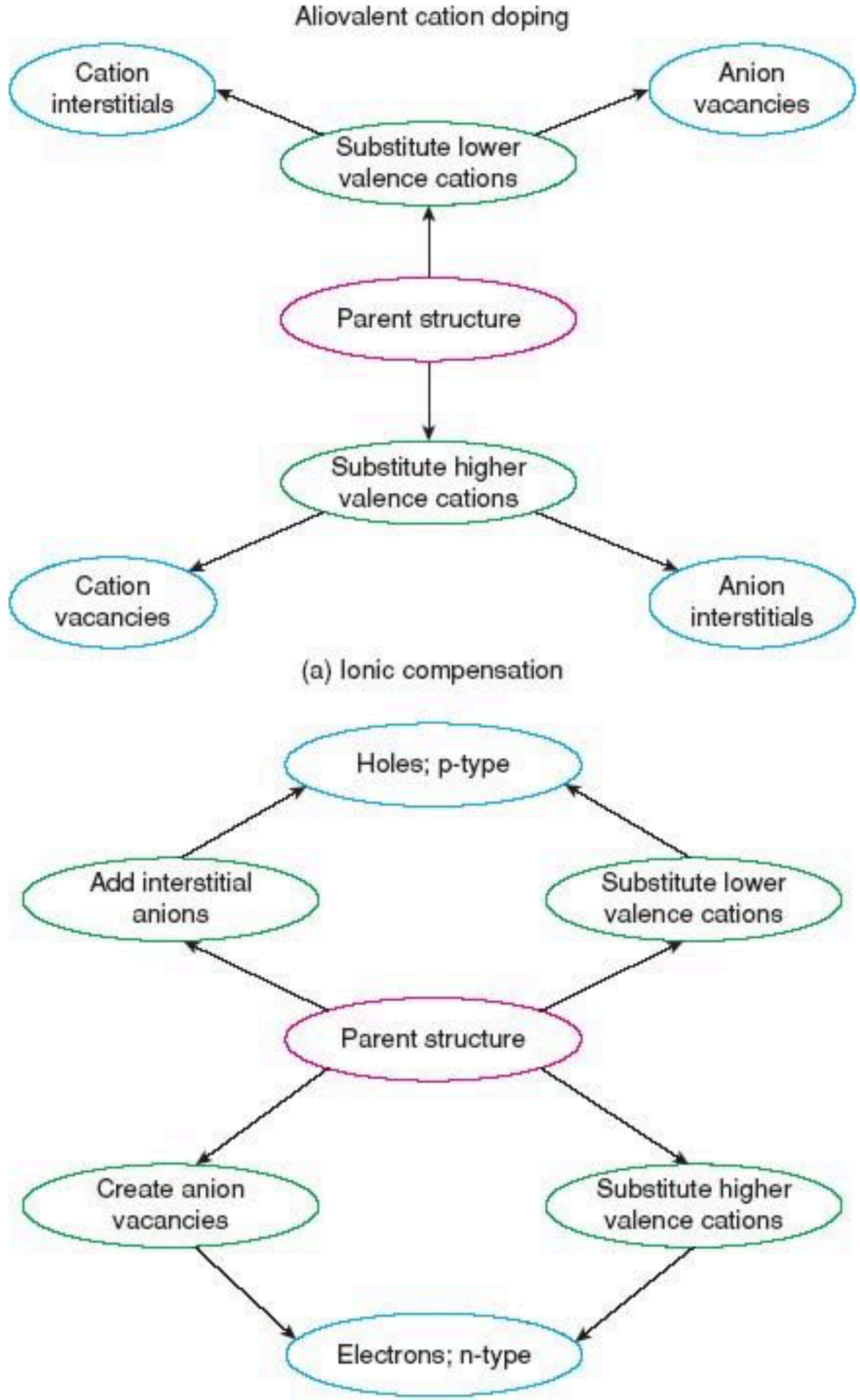
Si $\longrightarrow$ *Ne* 3s2 3p2

Al $\longrightarrow$ *Ne* 3s2 3p1





Summary

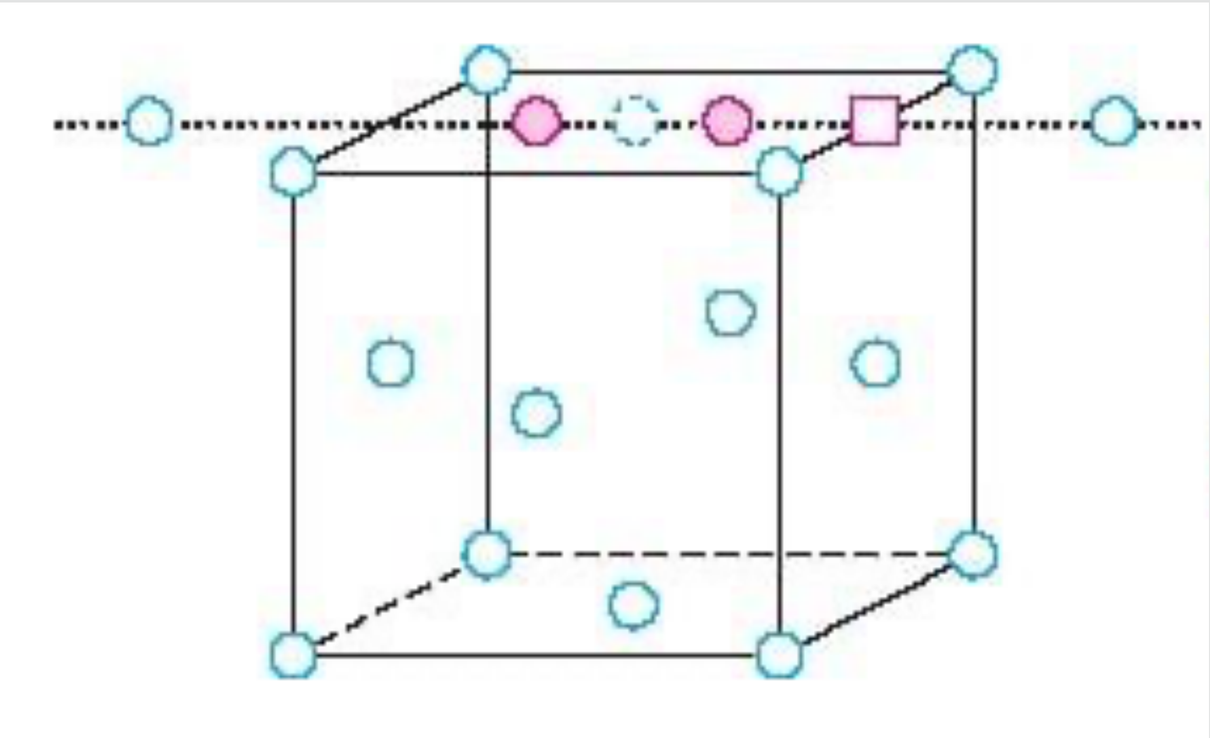


(a) Ionic compensation

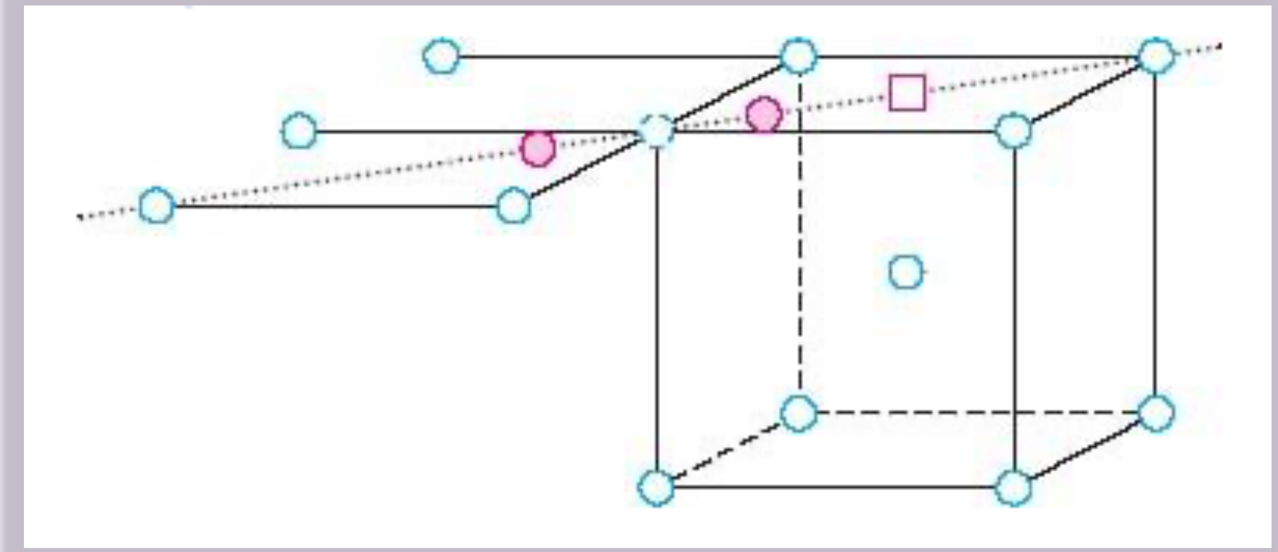
(b) Electronic compensation

Read other examples in Section 2.3.3. of A.R. West

Defect Clusters

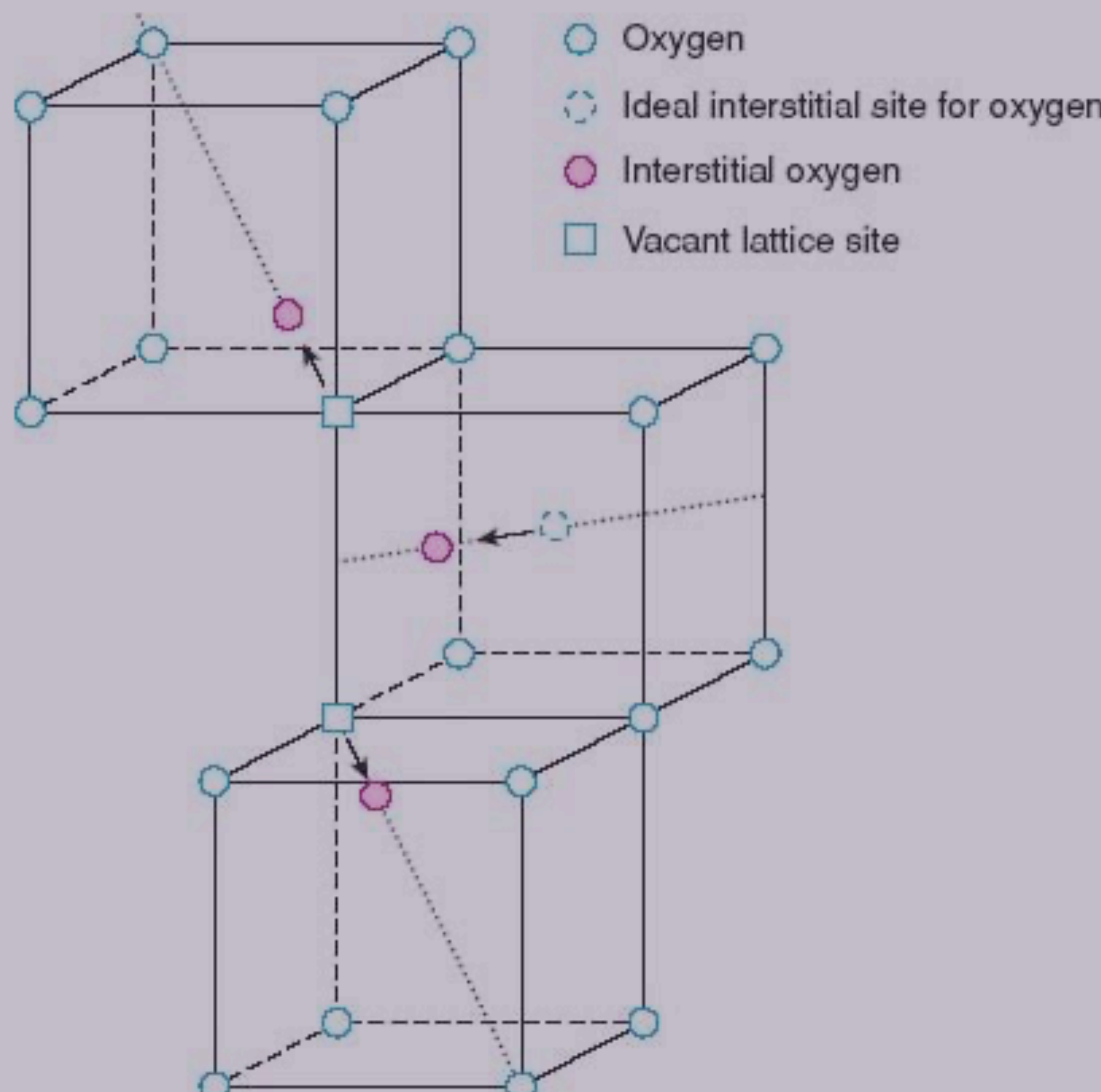


- Interstitial Pt atom at octahedral site in fcc Pt
- Displaced towards top face Pt atom
- Displaces top face Pt atom
- Two Pt atoms on distorted interstitial site - cluster



- Interstitial Fe atom at octahedral site in bcc Fe
- Displaced towards vertex Fe atom
- Displaces vertex Fe atom
- Two Fe atoms on distorted interstitial site - cluster

Defect Complexes in Oxides – UO_2



- UO_2 - ccp U^{4+} with O^{2-} in tetrahedral interstices
- Non-stoichiometry - UO_{2+x}
- Ideal interstitial site is the octahedral site
- Displaced along <110>
- Displaces two other site O^{2-}
- 3 O_i on distorted interstitial sites + 2 V_O - cluster

Electronic properties of materials

- Concept of atomic and molecular orbitals, AO and MO
- MO to bands in crystalline solids - Tight binding, Free electron, and nearly free electron models
- Metals, semiconductors, insulators
- Electrical behaviour of metals and semiconductors
- **Section 3.3, 3.4, 8.1, 8.2, 8.4 in A.R. West**