Intrinsic Defects

By the end of this lecture, you should be able to:

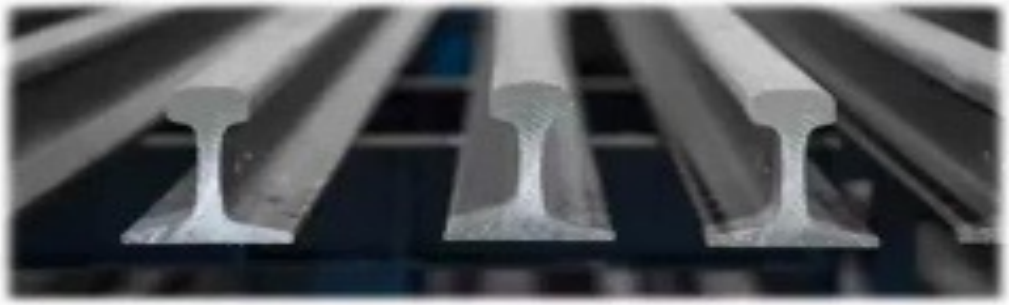
1. Explain why real crystals always contain defects, even under equilibrium conditions.
2. Identify and describe the major types of intrinsic point defects:
   - Vacancies
   - Interstitials
   - Substitutions (intrinsic site-mixing)
   - Schottky defects
   - Frenkel defects
   - Color centers
3. Understand how configurational entropy drives the presence of defects in crystals.
4. Relate defects to important material properties (optical, electronic, mechanical).

Defects put to Work

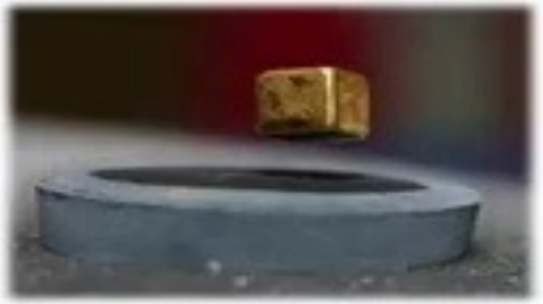
gemstones

Phosphors

Computer chips

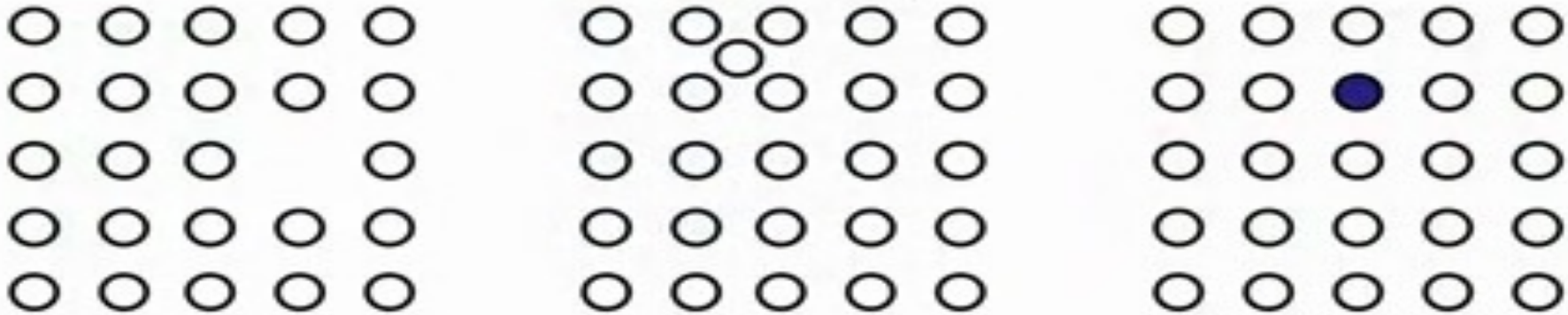


Steel and other alloys



Superconductors

Point Defects

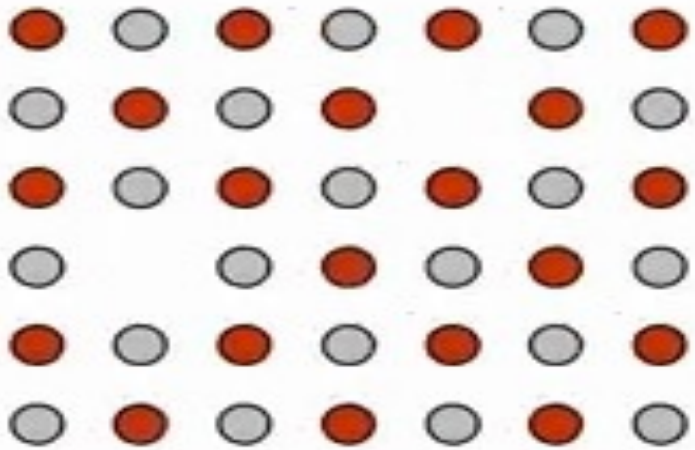


vacancy

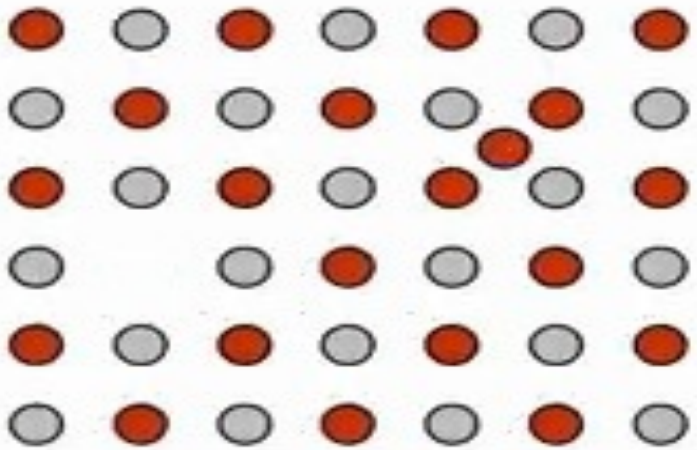
interstitial

substitution

Intrinsic Point Defects in Ionic Compounds



Schottky defect



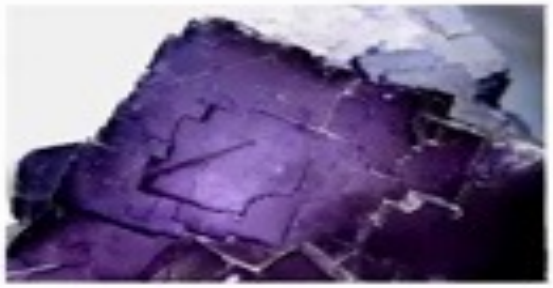
Frenkel defect

Schottky defect - Cation vacancy + anion vacancy

Frenkel defect - Vacancy + interstitial of the same element

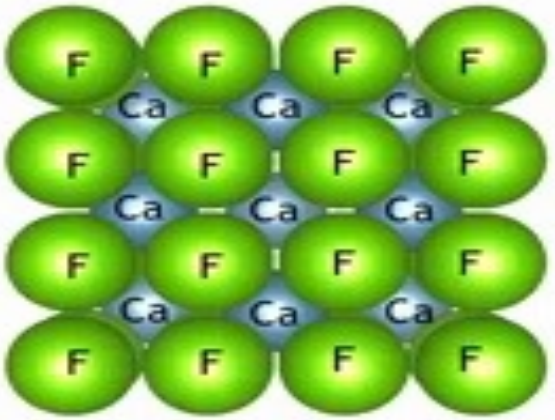
Color Center - Electron trapped on an anion vacancy

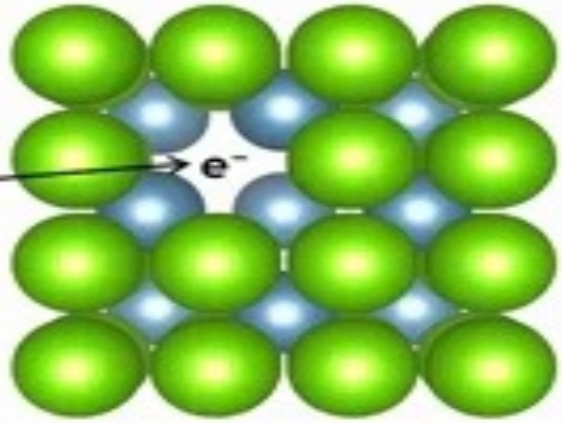
Color Centers



Fluorite, CaF_2

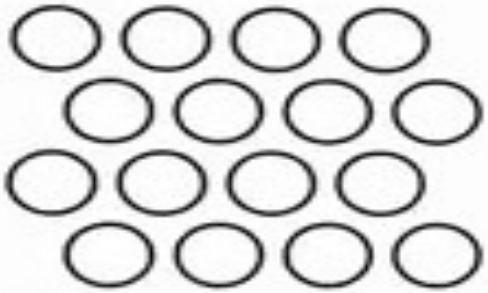
Amethyst, SiO_2





trapped electron
F-center

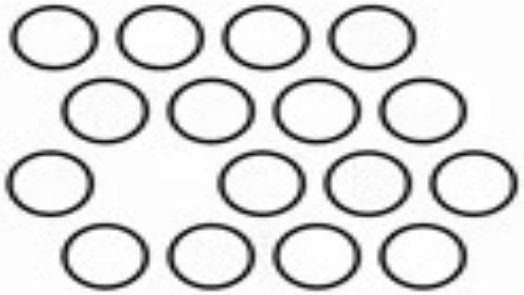
Thermodynamics of Defect Formation

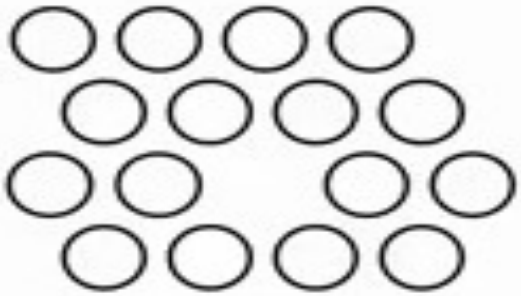


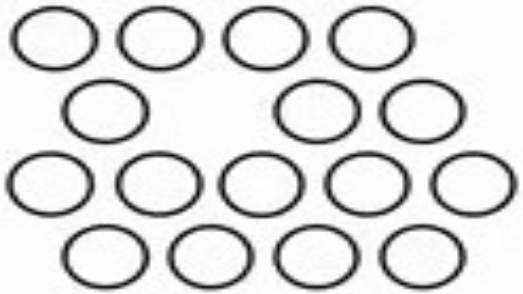
Thermodynamics of Defect Formation

$\Omega = 1$

$S = \ln \Omega = 0$







Thermodynamics of Defect Formation

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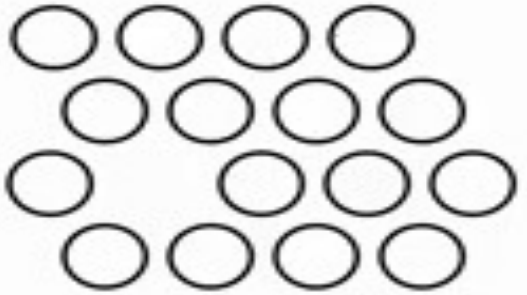
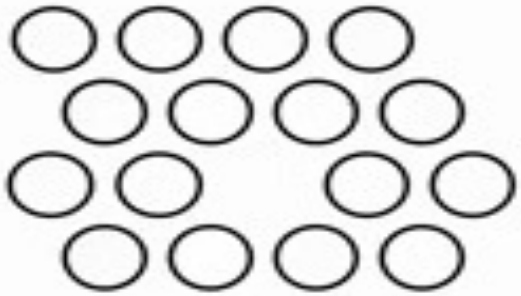


$$\Omega = \frac{(N_0 + n)!}{N_0!\, n!}$$



Defect formation increases the configurational entropy of a crystal

Thermodynamics of Defect Formation

$$\Omega = \frac{(N_0 + n)!}{N_0!\, n!}$$

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

Thermodynamics of Defect Formation

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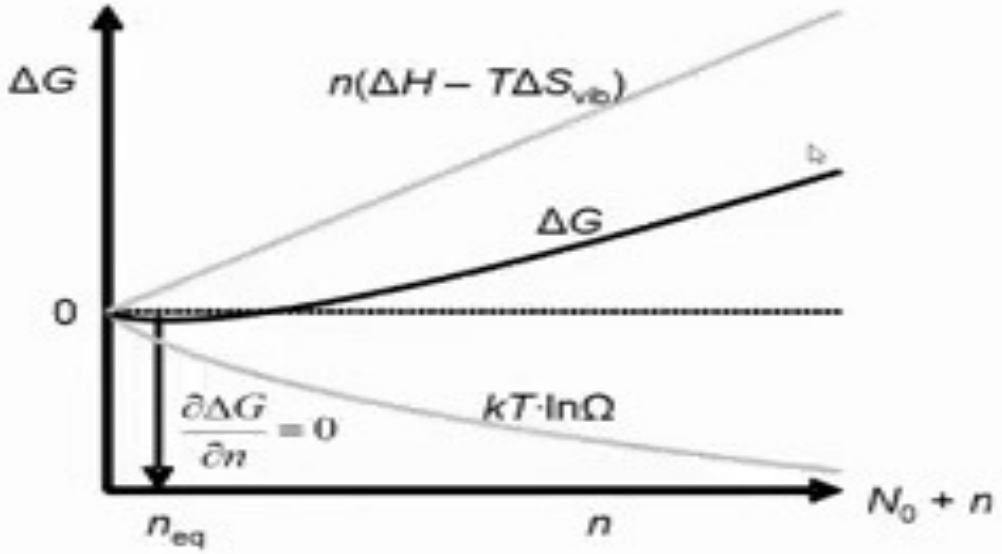
$$\Delta G = n(\Delta H - T\Delta S_{vib}) - kT \cdot \ln \Omega$$

Thermodynamics of Defect Formation

$$\Omega = \frac{(N_0 + n)!}{N_0!\, n!}$$



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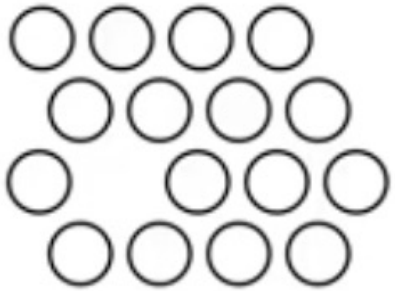
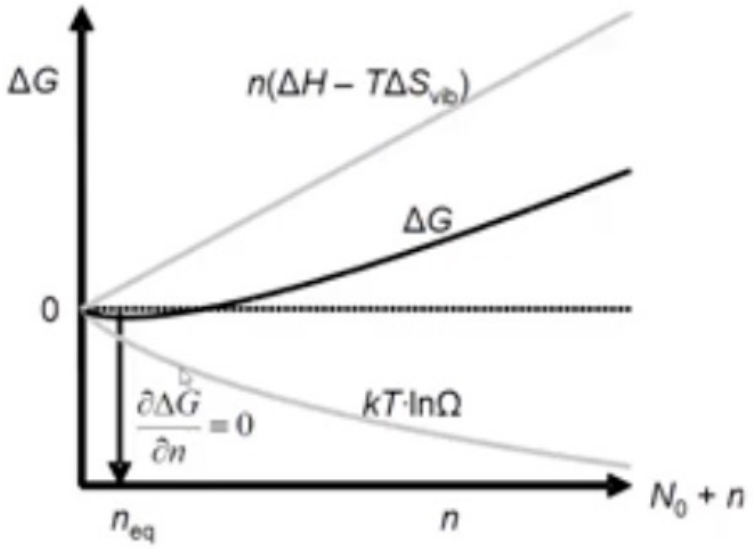
Thermodynamics of Defect Formation



$$\Omega = \frac{(N_0 + n)!}{N_0!\, n!}$$



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

$$\Delta G = n(\Delta H - T\Delta S_{vib}) - kT \cdot \ln \Omega$$

$$n_{eq} \approx N_0 \exp\left(\frac{\Delta S_{vib}}{k}\right) \exp\left(\frac{-\Delta H}{kT}\right)$$

Summary

- **Perfect crystals** are an idealization; real crystals always contain defects and surfaces.
- **Defects can be beneficial**: gemstone colors, phosphors in LEDs, semiconductor doping, and improved mechanical properties (steel vs. iron).
- **Intrinsic point defects**:
  - **Vacancy** – missing atom.
  - **Interstitial** – extra atom in normally empty site.
  - **Substitution** – atom on the "wrong" site.
  - **Schottky defect** – paired cation + anion vacancies (charge balance).
  - **Frenkel defect** – ion displaced from lattice site into interstitial.
  - **Color centers** – trapped electrons at anion sites, responsible for colors in minerals.
- **Thermodynamic basis**:
  - Formation of defects costs enthalpy (bond breaking).
  - Configurational entropy increases possible arrangements.
  - Equilibrium defect concentration arises from the balance ($\Delta G = \Delta H - T\Delta S$).
  - Defects are always present; concentration grows with higher T and lower ΔH.

Homework

2.1 Given that Cu adopts a ccp structure with a cubic cell parameter of 3.615 Å, confirm that the equilibrium number of vacancies in a 1 cm^3 sample at 1000 °C is around 10^{19}. Note the need to convert between k, in J/K, and R, in J/(K mol), when using molar quantities: $N_A k = R$.

2.2 Calculate the fractional number of vacancy sites in Cu at (a) 300 K, (b) 800 K, and (c) its melting point (1357 K).

2.3 Assuming a unit-cell parameter of 5.62 Å, estimate the equilibrium number of Schottky defects in a 1 mm^3 grain of NaCl at 300 K and at 700 K.

2.6 A brown sample of zinc oxide was found to have the hexagonal wurtzite structure with $a = b = 3.2495$ Å, $c = 5.2069$ Å ($\alpha = \beta = 90°$; $\gamma = 120°$). Chemical analysis gave 80.765% Zn by mass. Density measurements gave 5810 kg/m^3. Determine the formula of the material and state whether it contains oxygen vacancies or interstitial metal atoms.

Homework

2.1 Given that Cu adopts a ccp structure with a cubic cell parameter of 3.615 Å, confirm that the equilibrium number of vacancies in a 1 cm^3 sample at 1000 °C is around 10^{19}. Note the need to convert between k, in J/K, and R, in J/(K mol), when using molar quantities: $N_A k = R$.

$$x_v = \frac{n_{eq}}{N_0 + n_{eq}} = \exp\left(\frac{\Delta S_{vib}}{k}\right)\exp\left(\frac{-\Delta H}{kT}\right)$$

Table 2.1 ΔH_f and ΔS_f for defect formation from ref. [5]. Schottky values concern two vacancies such that the energy per vacancy is similar for all three categories.

Defect type	Material	ΔH_f, kJ/mol	ΔS_f, J/(K mol)
Vacancies	Cu	123	21

The figure of 10^{19} can be derived from the given data and the values in Table 2.1. For a 1 cm^3 crystal, the number of unit cells would be $(0.01/3.615\times10^{-10})^3 = 2.12\times10^{22}$. Each unit cell contains 4 Cu sites. Using values from Table 2.1, the fractional concentration of vacancies is $x_v = \frac{n_{eq}}{N_0 + n_{eq}} = \exp\left(\frac{\Delta S_{\text{vib}}}{k}\right)\exp\left(\frac{-\Delta H}{kT}\right)$ = exp(21/8.3145) × exp[(−123×10³)/(8.3145 × 1273)] = 1.12×10^{-4}. The total number of defects is then 4 × $2.12\times10^{22} \times 1.12\times10^{-4} = 9.5\times10^{18}$.

Extrinsic Defects

Learning Objectives

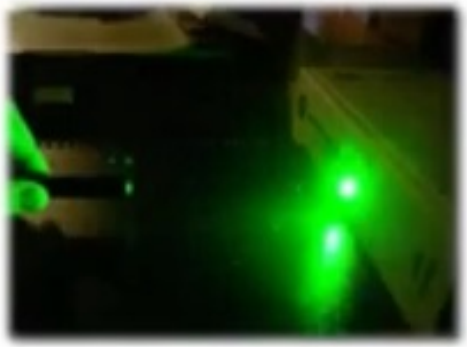
- Define and distinguish **extrinsic defects** from intrinsic defects.
- Differentiate between **isovalent substitution** (e.g., ruby, emerald, YAG lasers) and **alloeovalent substitution**.
- Explain how charge balance is maintained in alloeovalent doping:
  - **Excess positive charge** → anion interstitials or cation vacancies.
  - **Deficit of positive charge** → cation interstitials or anion vacancies.
- Describe technological importance of doping:
  - **Yttria-stabilized zirconia** (oxide ion conductor).
  - **Semiconductors** (donor/electron doping vs. acceptor/hole doping).
  - **Transition metal oxides** (variable oxidation states, batteries, superconductivity, magnetoresistance).
- Interpret **Kröger–Vink notation** to describe defect types, sites, and charges.

Extrinsic Defects (Doping)

- Isovalent substitution
  - Substituting an ion with another ion of the same charge

Ruby
$Al_{2-x}Cr_xO_3$

Emerald
$Be_2Al_{2-x}Cr_xSi_6O_{18}$



Nd-YAG Laser
$Y_{3-x}Nd_xAl_5O_{12}$

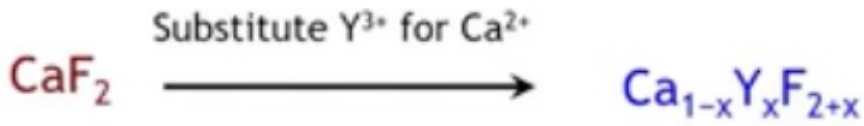
- Aliovalent substitution
  - Substituting an ion with another ion with a different charge

Aliovalent Doping

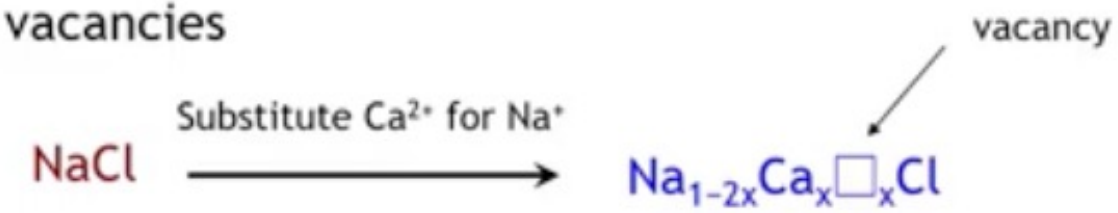
Substituting with a cation of higher charge

The crystal must compensate for the excess positive charge. If we don't allow changes in the oxidation states of the ions, there are two charge compensation mechanisms:

1. Anion interstitials



2. Cation vacancies

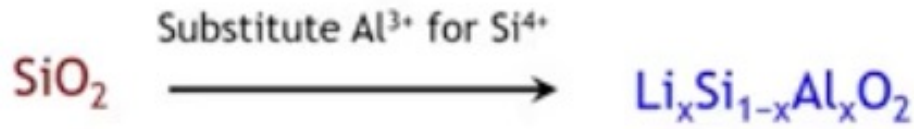


Aliovalent Doping

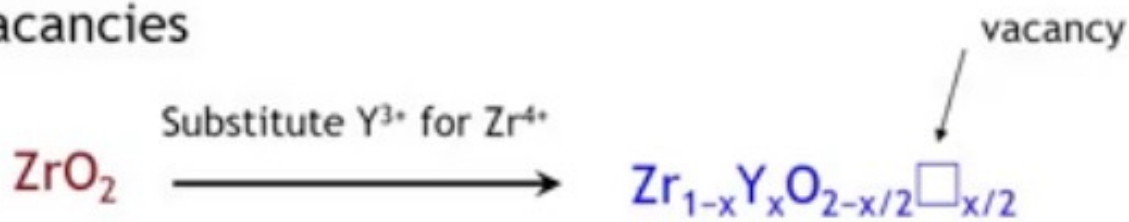
Substituting with a cation of lower charge

The crystal must compensate for the excess negative charge. If we don't allow changes in the oxidation states of the ions, there are two charge compensation mechanisms:

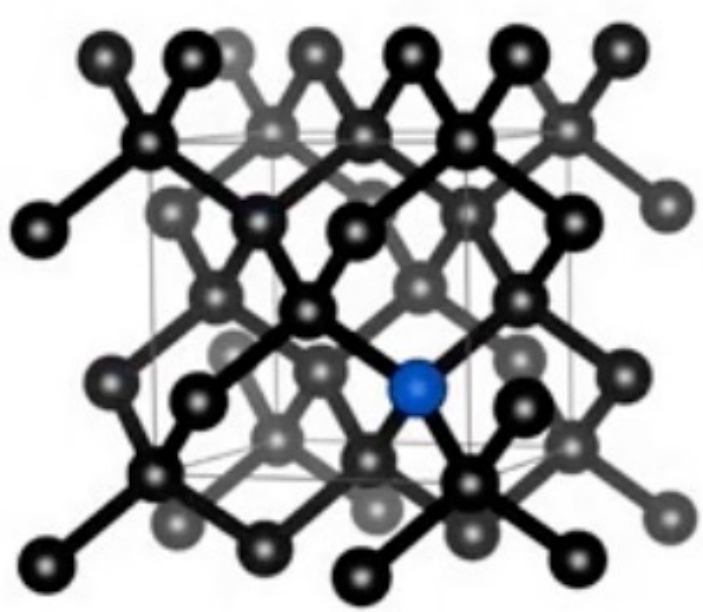
1. Cation interstitials



2. Anion vacancies



Aliovalent Semiconductor Doping



Donor (electron) doping

- Substitutional atom has more valence electrons than the host atom (i.e. P for Si).
- Equivalent of reduction

Acceptor (hole) doping

- Substitutional atom has fewer valence electrons than the host atom (i.e. B for Si).
- Equivalent of oxidation

Controlling oxidation state through doping

Compounds containing transition metal ions, are very sensitive to the oxidation state of the cation. By doping we can control the oxidation state, thereby controlling the properties.

Doping that leads to oxidation

- Cation vacancies

$$LiCoO_2 \xrightarrow{\text{Remove } Li^+} Li_{1-x}CoO_2 \qquad [Co^{+3} \rightarrow Co^{+(3+x)}]$$

- Anion interstitials

$$La_2CuO_4 \xrightarrow{\text{Add } O^{2-}} La_2CuO_{4+x} \qquad [Cu^{+2} \rightarrow Cu^{+(2+2x)}]$$

- Aliovalent doping with lower valent cation

$$La_2CuO_4 \xrightarrow{\text{Sub. } Sr^{2+} \text{ for } La^{3+}} La_{2-x}Sr_xCuO_4 \qquad [Cu^{+2} \rightarrow Cu^{+(2+x)}]$$

Controlling oxidation state through doping

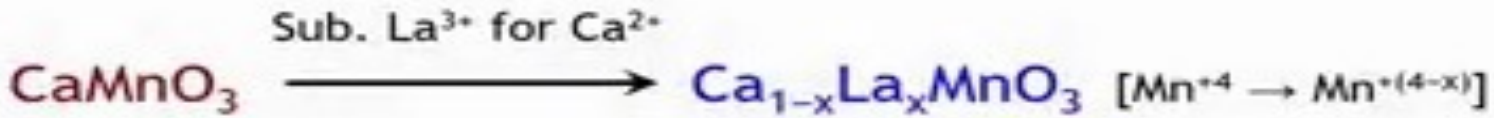
Compounds containing transition metal ions, are very sensitive to the oxidation state of the cation. By doping we can control the oxidation state, thereby controlling the properties.

Doping that leads to reduction

- Cation interstitials

- Anion vacancies

- Aliovalent doping with higher valent cation



Kröger-Vink Notation

Charge of the defect

$\cdot = +1, \quad \cdot\cdot = +2, \quad \cdot\cdot\cdot = +3$

$' = -1, \quad '' = -2, \quad ''' = -3$

$$A_B^C$$

Symbol for defect atom (v for vacancy)

Site in the crystal where the defect occurs (*i* for interstitial, *s* for surface)

Some examples of K-V notation

- Cation vacancies

$$LiCoO_2 \xrightarrow{\text{Remove } Li^+} Li_{1-x}CoO_2$$

- Anion interstitials

$$La_2CuO_4 \xrightarrow{\text{Add } O^{2-}} La_2CuO_{4+x}$$

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Some examples of K-V notation

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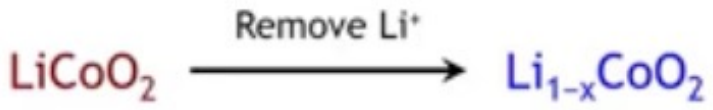
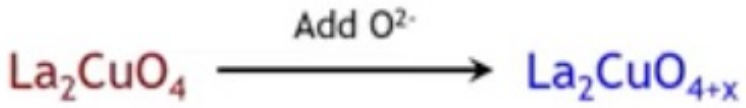
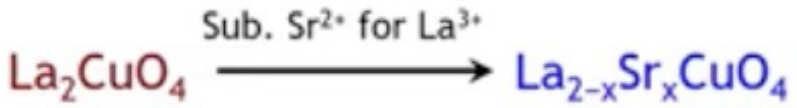


v'_{Li}

- Anion interstitials

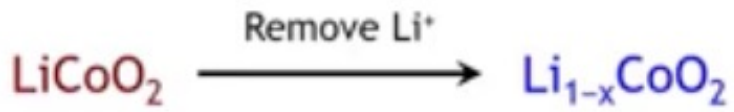


- Aliovalent doping with lower valent cation



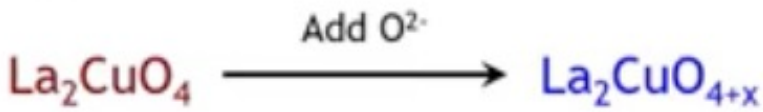
Some examples of K-V notation

- Cation vacancies



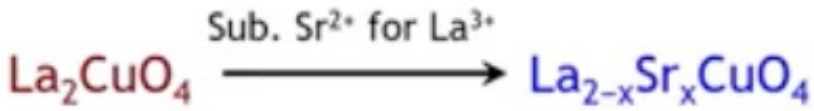
v'_{Li}

- Anion interstitials



O''_i

- Aliovalent doping with lower valent cation

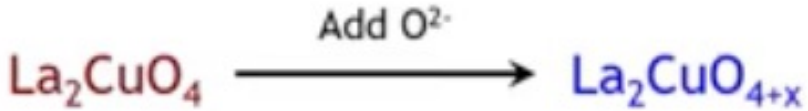


Some examples of K-V notation

- Cation vacancies

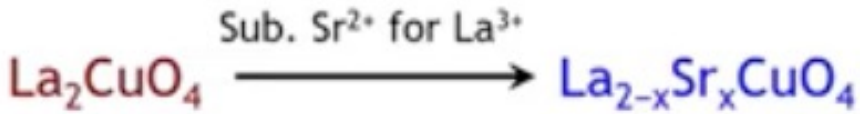
v'_{Li}

- Anion interstitials



O''_i

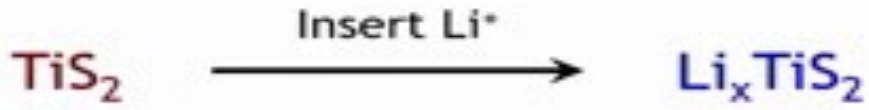
- Aliovalent doping with lower valent cation



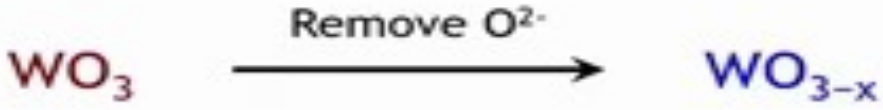
Sr'_{La}

Some examples of K-V notation

- Cation interstitials



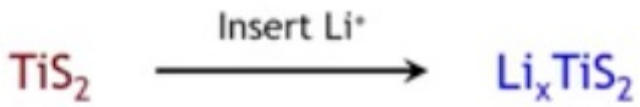
- Anion vacancies



- Aliovalent doping with higher valent cation

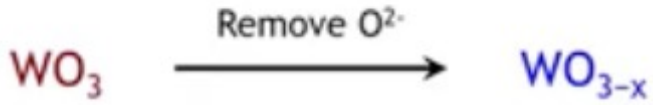
Some examples of K-V notation

- Cation interstitials

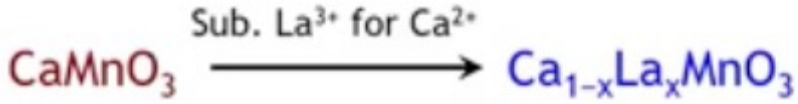


$Li_i^{\bullet}$

- Anion vacancies

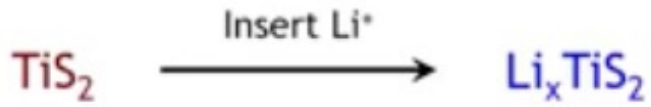


- Aliovalent doping with higher valent cation



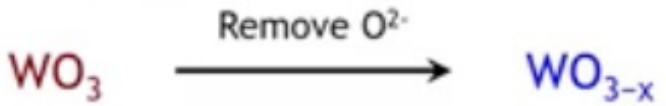
Some examples of K-V notation

- Cation interstitials



$Li_i^{\bullet}$

- Anion vacancies

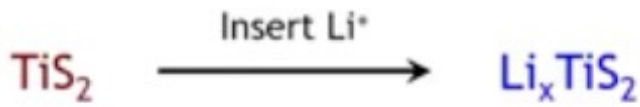


$v_O^{\bullet\bullet}$

- Aliovalent doping with higher valent cation

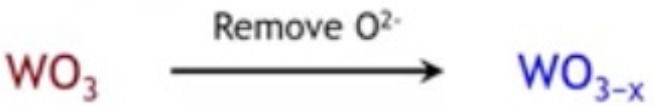
Some examples of K-V notation

- Cation interstitials



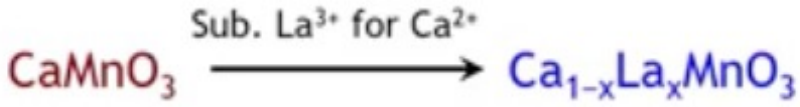
$Li_i^{\bullet}$

- Anion vacancies



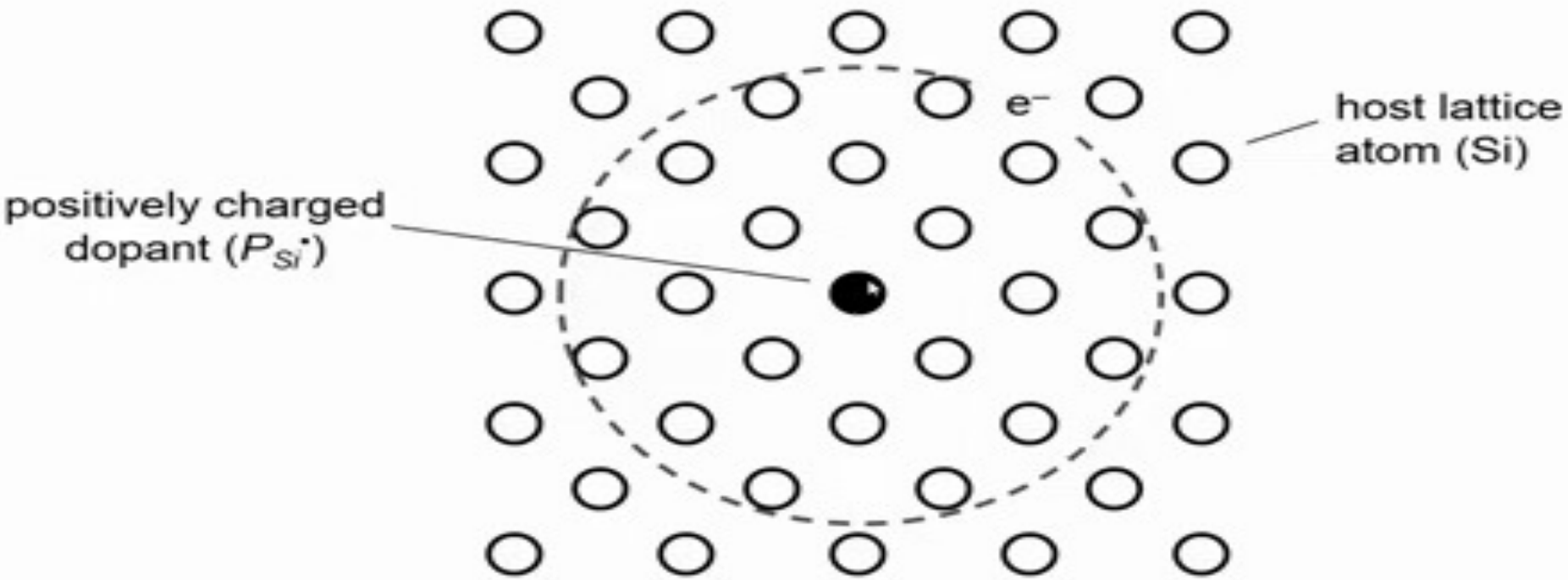
$v_O^{\bullet\bullet}$

- Aliovalent doping with higher valent cation



$La_{Ca}^{\bullet}$

Aliovalent Semiconductor Doping



Summary

- **Extrinsic defects** arise from introducing foreign atoms into a lattice.
- Two substitution types:
  - **Isovalent substitution**: no net charge imbalance.
  - **Alloeovalent substitution**: different charge, requiring compensating defects.
- Compensation mechanisms include **interstitials**, **vacancies**, or **oxidation state changes** of transition metals.
- Key examples:
  - Ruby/emerald coloration, YAG lasers.
  - Y-stabilized ZrO_2 for oxygen conduction.
  - Semiconductor doping (n-type, p-type).
  - Battery cathodes ($LiCoO_2$), superconductors (La_2CuO_4), bronzes (WO_{3-x}), colossal magnetoresistance oxides.
- **Kröger–Vink notation** provides a systematic language for defect chemistry.

Homework

2.7 Suggest oxidation states for the metal ions in each of the following materials: (a) FeO, $Fe_{0.872}O$, Fe_3O_4, FeS_2; (b) FeTe, $Fe_{1.1}Te$; (c) LaOFeAs, $LaO_{0.9}F_{0.1}FeAs$; and (d) $YBaFe_2O_5$, $NdBaFe_2O_{5.5}$, and $NdBaCo_2O_6$.

2.8 Suggest oxidation states for the metal ions in each of the following materials: (a) TiS_2, $Li_{0.7}TiS_2$; (b) $LaMnO_3$, $La_{0.8}Sr_{0.2}MnO_3$, $La_{0.5}Ca_{0.5}MnO_3$; (c) La_2CuO_4, $La_{1.85}Ba_{0.15}CuO_4$, $La_2CuO_{4.075}$; and (d) $BaPbO_3$, $BaBiO_3$, $Ba_{0.6}K_{0.4}BiO_3$.

2.15 State the Kröger–Vink notation for the predominant defects in each of the materials in Table 2.2.

3.1 Write Kröger–Vink symbols for the following fully charged point defects in NiO: metal vacancy, oxygen vacancy, lithium acceptor, aluminum donor.

3.2 Name the following defects in TiO_2 and write their Kröger–Vink symbols: Al and Nb dopants at the Ti site; F and N dopants at the O site; oxygen and titanium atoms out of their regular sites.