

Under certain conditions, defects are related to the O_2 partial pressure.

↳ Brouwer diagrams: [Defect] vs. P_{O_2} at a given T .

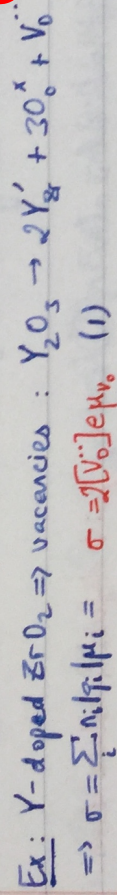
IV. Effect of defects on material properties

1) Defects & conductivity

Defect motion in solids (e.g. by vacancy or interstitial diffusion) $\Rightarrow$ mass & charge transport.

• Electronic conductivity: charge motion under an applied electric field. $\exists$ ionic, electronic, & mixed conductivity.

Ionic conductors: In ionic crystals, defects have charge (e.g. CaF_2) $\Rightarrow \exists$ electronic σ , this is a class of materials called ionic conductors.



But vacancy diffusion is thermally activated due to temp-dependence of diffusivity, D :

$$D = D_0 \exp\left(-\frac{\Delta G_m}{RT}\right) \quad (2)$$

From eq. (1): $[V_o''] \uparrow \Rightarrow \sigma \uparrow$, BUT in, e.g. CaF_2 , $\max(\sigma)$ occurs for low defect content.

When the vacancy content increases, $\exists$ defect association: $Y'_{Zr} + V_o'' \rightarrow \{Y'_{Zr}, V_o''\}$

↳ Defects aren't "free" to be involved in transport processes: at high $[X]$, $\exists$ enough defects for them to interact through Coulomb attraction & form defect pairs & clusters.

Defect reaction: $Y'_{Zr} + V_o'' \rightleftharpoons \{Y'_{Zr}, V_o''\} \Rightarrow K_{ass} = \frac{[Y'_{Zr}, V_o'']}{[Y'_{Zr}][V_o'']} = \exp\left(-\frac{\Delta G_a}{kT}\right)$

Electronic conductors: • Metallic conductors: the valence band isn't filled $\Rightarrow$ e^- are easily promoted to LUMO $\rightarrow \sigma \in [10^2; 10^8] \text{ Scm}^{-1}$

• Semiconductors: $\exists$ an energy gap between HOMO & LUMO, Eg

$$\in [0, 5; 3] \text{ eV.}$$

• Insulator: $E_g > 3 \text{ eV}$

The degree of overlapping of bands defines conduction mechanism. For metals $\sigma \propto T \uparrow$, for insulators & SC: $T \uparrow \Rightarrow \sigma \uparrow$.