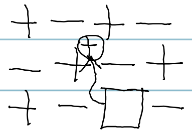
# 6. Kristalldefekte

## 6.1 Defekttypen

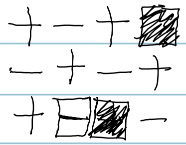
Punktdefekte (0 dim.)
Liniendefekte (1 dim.)
Flächendefekte (2 dim.)
Volumendefekte (3 dim.)

### Punktdefekte

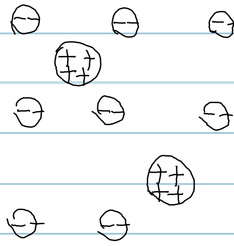
a) intrinsische



Frenkel z.B. AgBr

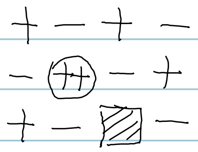


Schottky z.B. NaCl

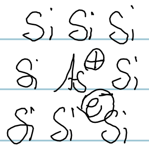


nichtstöchiometrische Verb.
$CeO_{2-x}$

b) extrinsische

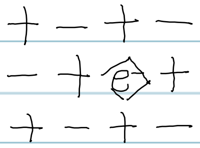


Dotierung
$Ca^{2+}$ in NaCl



Dotierung
As in Si

Farbzentren (F-Zentren)



$\mathrm{Na} \xrightarrow{\mathrm{NaCl}} \mathrm{Na}^{\oplus}_{(s)} + e^{\ominus}_{(s)}$

← gebunden

elektron. Struktur → Teilchen im Kasten (3D)

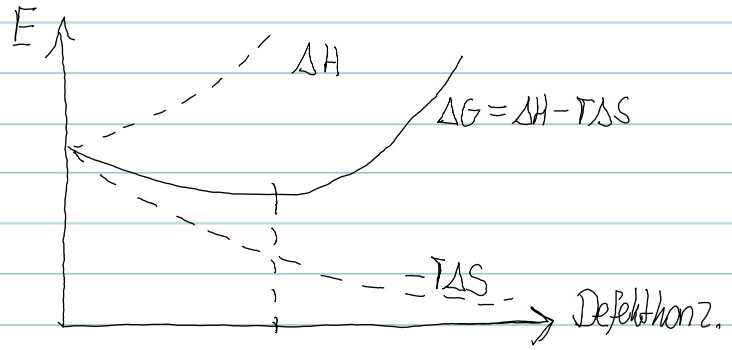
$$E = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2) \rightarrow \Delta E = \frac{3h^2}{8ma^2}$$

z.B. KCl $a = 6,29\,\text{Å}$ → $\Delta E = 2,85\,eV$
$\sim 430\,nm$

## 6.2 Thermodynamik

Defektbildung endotherm

$$\Delta G = \Delta H - T\Delta S \qquad |T\Delta S| > \Delta H$$



Bildungsenthalpien Δh z.B. Frenkel AgBr ~ 1,2eV
Schottky NaCl ~ 2,4eV
Leerstelle Ag ~ 1eV

$$\boxed{\Delta S = k \ln W}$$

z.B. 6 Leerstellung auf 49 Gitterplätzen

$$W = \binom{49}{6} = \frac{49!}{6!\,(49-6)!} = 14 \cdot 10^6$$

$N_V$ Leerstellen $N_L$ Gitterplätze

$$W = \binom{N_L}{N_V} = \frac{N_L!}{N_L!\,(N_L - N_V)!}$$

↳ $\Delta S = k \ln W$     Stirling: $\ln(x!) \approx x \ln x - x$

↳ $\Delta G = N_V \Delta h + kT\left[(N_L - N_V)\ln(N_L - N_V) + N_V \ln N_V - N_L \ln N_L\right]$

$$\frac{\partial \Delta G}{\partial N_V} = 0 = \Delta h + kT \ln\left(\frac{N_V}{N_L - N_V}\right)$$

$N_V \ll N_L \longrightarrow x_V = \frac{N_V}{N_L}$

$0 \approx \Delta h + kT \ln x_V$

$-\Delta h / kT \approx \ln x_V \longrightarrow x_V \approx \exp\left(-\frac{\Delta h}{kT}\right)$

## 6.3 Defektgleichungen

Defekte werden behandelt wie chem. Spezies

↳ Kröger-Vink-Notation

Beispiele:

1) Einbau von $CaCl_2$ in $KCl$

$$CaCl_2 \xrightarrow{KCl} Ca_K^{\bullet} + V_K' + 2\,Cl_{Cl}^{x}$$

2) Einbau von $Y_2O_3$ in $ZrO_2$

$$Y_2O_3 \xrightarrow{ZrO_2} 2\,Y_{Zr}' + 3\,O_O^{x} + V_O^{\bullet\bullet}$$

3) Partielle Reduktion von $CeO_2$

$$2\,Ce_{Ce}^{x} + O_O^{x} \overset{CeO_2}{\rightleftharpoons} 2\,Ce_{Ce}' + V_O^{\bullet\bullet} + \tfrac{1}{2}O_2(g)$$

$$2[V_O^{\bullet\bullet}] = [Ce_{Ce}'] \qquad (1)$$

$$K = \frac{a_{Ce_{Ce}'}^2 \, a_{V_O^{\bullet\bullet}} \, a_{O_2}^{1/2}}{a_{Ce_{Ce}^x}^2 \, a_{O_O^x}}$$

konz. $Ce_{Ce}^x$, $O_O^x$ sehr groß

$$\hookrightarrow K = [Ce_{Ce}']^2 [V_O^{\bullet\bullet}] \, p_{O_2}^{1/2} \qquad (2)$$

(1) in (2)

$$K = \frac{1}{2} [Ce_{Ce}']^3 \, p_{O_2}^{1/2}$$

$$\boxed{[Ce_{Ce}'] \propto p_{O_2}^{-1/6}}$$

## 7. Diffusion in FK

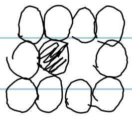
Ursachen: Defektbildung

Bewegung von Atomen → Energiebarriere

$$\Delta g^{\ddagger} = \Delta g_m = \Delta h_m - T\Delta S_m$$

Wahrscheinlichkeit Defekt: $p = \exp(-\Delta h / kT)$

Sprungfrequenz $\gamma_A = \nu_A \exp(-\Delta g_m / kT)$



$$D_A \propto p \cdot \gamma_A$$

$$\hookrightarrow \boxed{D_A = D_A^0 \exp(-E_D / kT)} \qquad E_D = \Delta h + \Delta h_m$$

# Ionenleitung

Leitfähigkeit $\Lambda_i = zFn_i$

$$n_i = \frac{z_i F D_i}{RT}$$

$$\sigma = c_i \Lambda_i = \frac{z_i^2 F_i^2 D_i}{RT} c_i$$

$$\ln(\sigma \cdot T) \text{ vs } 1/T \longrightarrow E_D\,!$$

## Arten von Ionenleitern

intrinsische IL

z.B. NaCl Schottky

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+ − □ −

$$Na_{Na}^{x} + Cl_{Cl}^{x} \xrightarrow{NaCl} V_{Na}' + V_{Cl}^{\bullet}$$

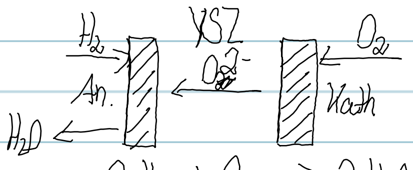
extrinsische IL

z.B. $Y_2O_3$ in $ZrO_2$

$$Y_2O_3 \xrightarrow{ZrO_2} 2Y_{Zr}' + 3O_O^{x} + V_O^{\bullet\bullet}$$

Anwendung: Festelektrolyt-Brennstoffzellen
800°C – 1000°C

$Y_2O_3 / ZrO_2$ (YSZ)



$$2H_2 + O_2 \longrightarrow 2H_2O$$