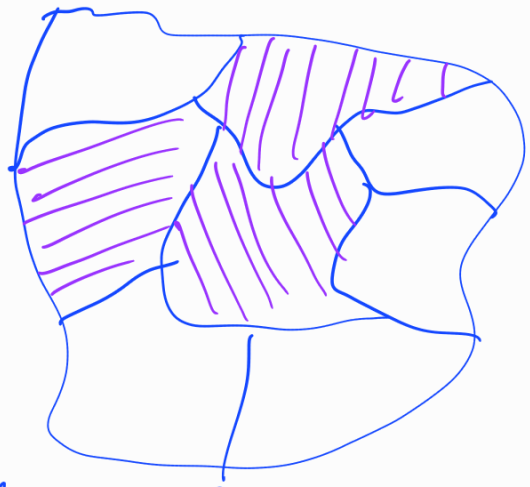
Defects: 0D: vacancy, interstitials, self-interstitials, impurities (subs, int)

1D: dislocations

2D: grain boundaries

3D: precipitate, void, bubble,



Thermodynamics of defects (4, 1 ...)

Was

Gibbs free energy

$G = H - TS$

H: enthalpy

S: entropy

G should be minimal.

Case of vacancy

Formation enthalpy $H_v^f \sim 2eV$ (Fe)

Q: What happens if $H_v^f < 0$?

Material does not crystallize!

Assume: N_a = # atoms

N_v = # vacs.

$N_a \gg N_V$ ← dilute limit

$$H = N_V H_V^f$$

Entropy: $S = k_B \ln \Omega$ ($k_B = 1{,}28 \cdot 10^{-23}\ J/K = 8{,}62 \cdot 10^{-5}\ eV/K$)

↑ disorder

1) Conf entropy = S_{mix}

2) formation entropy = S_V^f

$$S = S_{mix} + N_V S_V^f$$

Stirling ↓

$$S_{mix} = k_B \ln \Omega = k_B \ln \frac{(N_a + N_V)!}{N_a!\, N_V!} \simeq$$

$$= k_B \left((N_a + N_V) \ln (N_a + N_V) - N_V \ln N_V - N_a \ln N_a \right)$$

$\{\ln(x!) = x \ln x - x\}$

$$G = N_V H_V^f - T \left(S_{mix} + N_V^f S_V^f \right).$$

Minimize G: $\frac{dG}{dN_V} = 0 = H_V^f - T S_V^f -$

$$-T k_B \left(\ln (N_a + N_V) - \ln N_V \right) = H_V^f - T S_V^f - T k_B \cdot$$

$\ln \frac{N_a + N_V}{N_V}$

$1/c_V$

$$\Rightarrow \boxed{c_V = e^{S_V^f / k_B} e^{-H_V^f / k_B T} = e^{-G_V^f / k_B T}}$$