

Vibrational effects on the surface energy of III-V compound semiconductors using ab-initio thermodynamics

In Won Yeu^{1,2}, Gyuseung Han^{1,2}, Cheol Seong Hwang², and Jung-Hae Choi^{1*}

¹Center for Electronic Materials, Korea Institute of Science and Technology, Seoul 02792, Korea

²Department of Materials Science and Engineering, and inter-university Semiconductor Research Center, Seoul National University, Seoul 08826, Korea

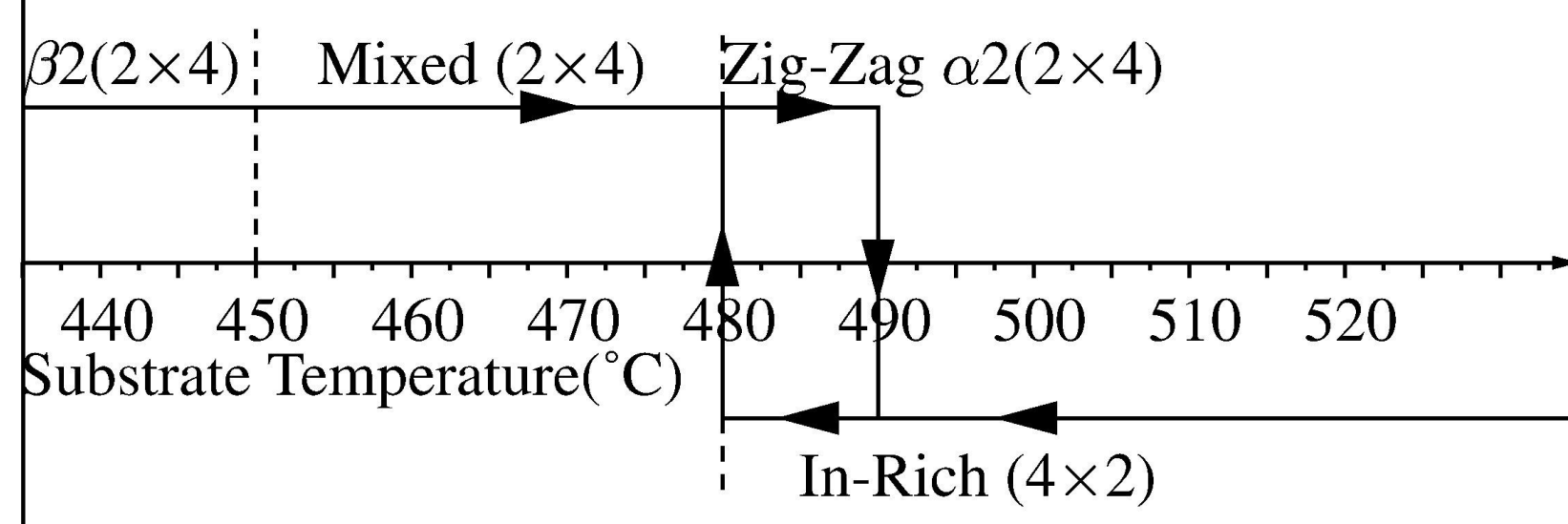
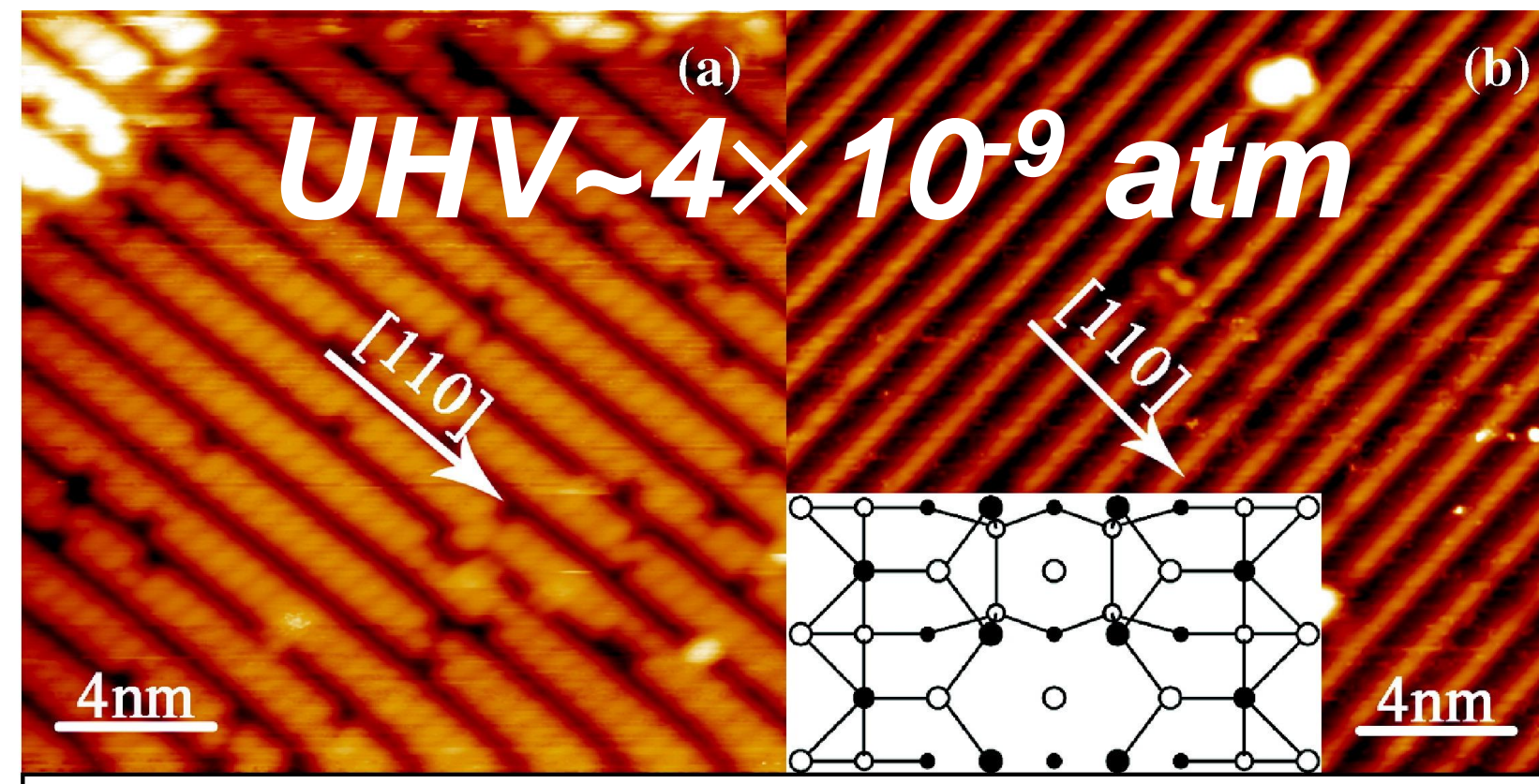


Computational Materials Design



Introduction

Surface reconstruction transition (T,P)



Experimental transition:
c(4x4) → (2x4): ~550 K
(2x4) → (4x2): ~750 K
in the UHV condition.

The conventional density functional theory (DFT) provided a method to obtain the surface energy, γ , as a function of chemical potential, μ . One of the main difficulties of using $\gamma(\mu)$ is that it cannot be directly compared with the experimental results whose variables are T and P .

Entropy effects calculated as a function of T cannot be combined with $\gamma(\mu)$

Vibrational entropy:

$$\gamma(\mu, T) = \gamma^{elec}(\mu) + \Delta\gamma^{vib}(T).$$

$$\gamma^{elec}(\mu) = \frac{(E_{surf}^{elec}) - N_{Ga}(E_{InAs}^{elec}) - (N_{As} - N_{Ga})(E_{As}^{elec})}{A}$$

$$\Delta\gamma^{vib}(T) = \frac{(F_{surf}^{vib}) - N_{Ga}(F_{InAs}^{vib}) - (N_{As} - N_{Ga})(F_{As}^{vib})}{A}$$

$$F_{vib}(T) = \frac{1}{N_k} \sum_{k \in BZ} \sum_{i=1}^M \left\{ \frac{\hbar\omega_i(k)}{2} + k_B T \ln \left(1 - e^{-\frac{\hbar\omega_i(k)}{k_B T}} \right) \right\}$$

Configurational entropy:

$$\text{Fraction of } j \text{ reconstruction, } f_j(\mu, T) = \frac{Z_j(\mu, T)}{Z(\mu, T)}$$

$$Z(\mu, T) = \sum_j Z_j(\mu, T) = \sum_j g_j \exp\left(-\frac{\gamma_j(\mu)A}{k_B T}\right)$$

However, μ depends on T and P :

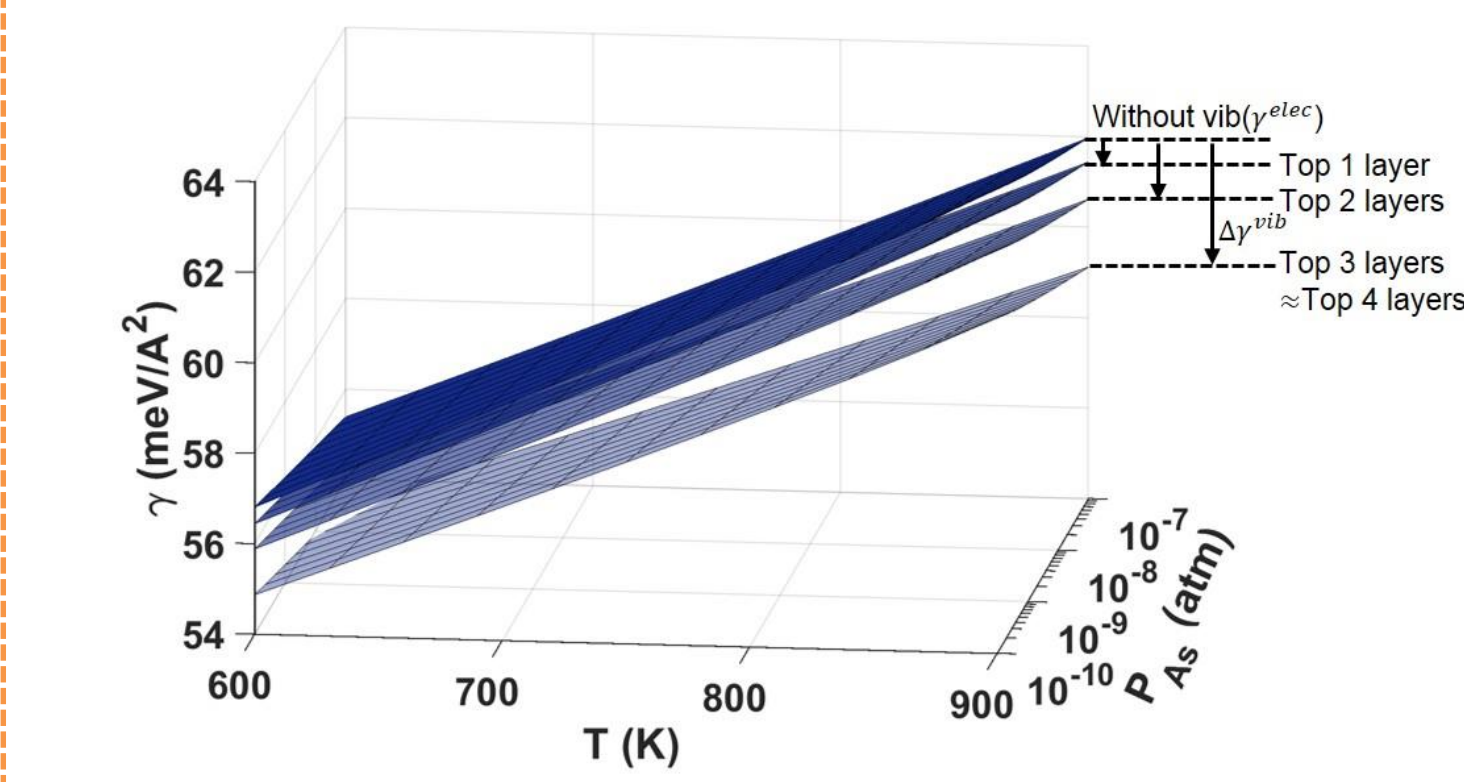
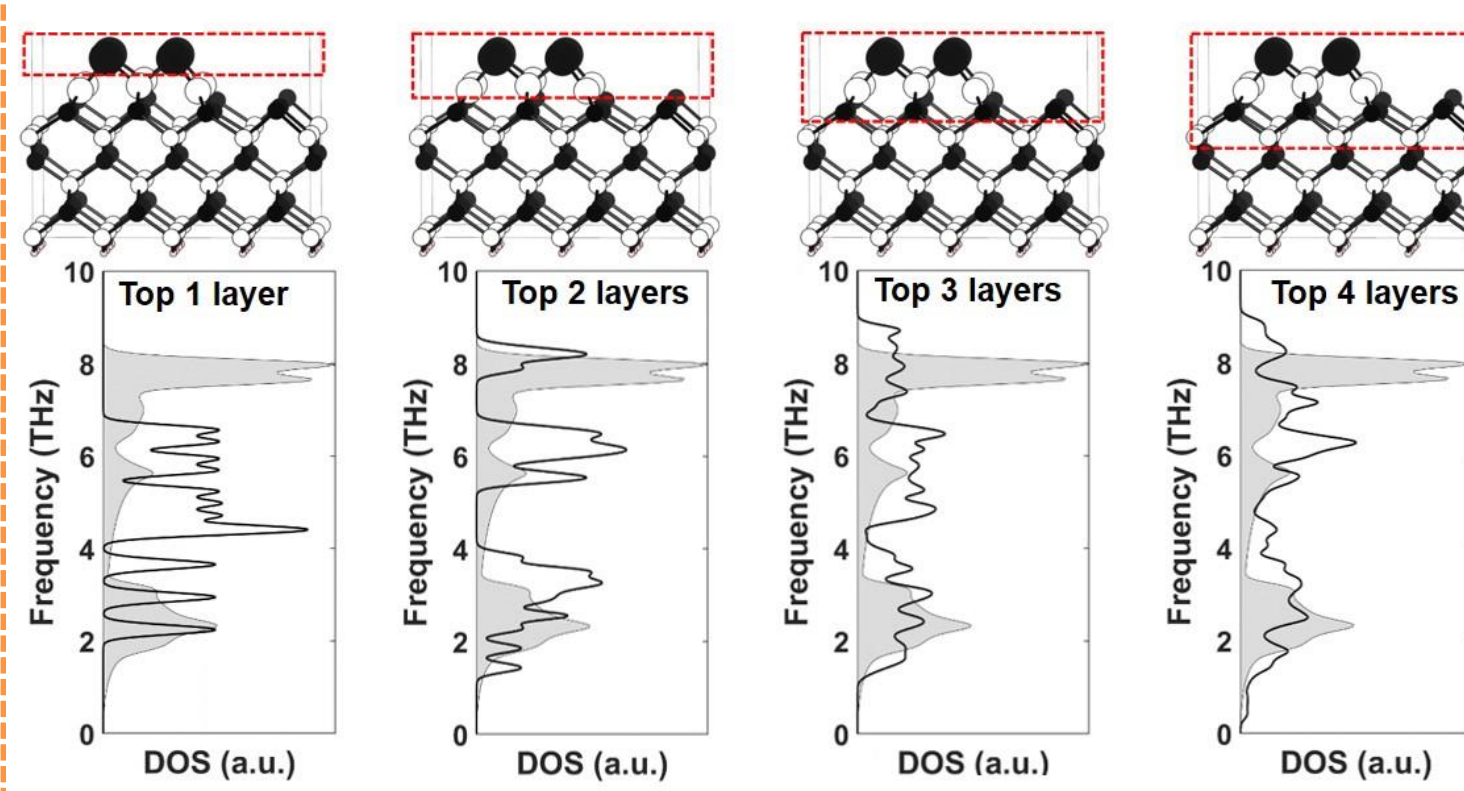
μ and T are not independent variables.

Calculation methods

Surface vibrational energy:

$$\gamma(T, P) = \gamma^{elec}(T, P) + \Delta\gamma^{vib}(T).$$

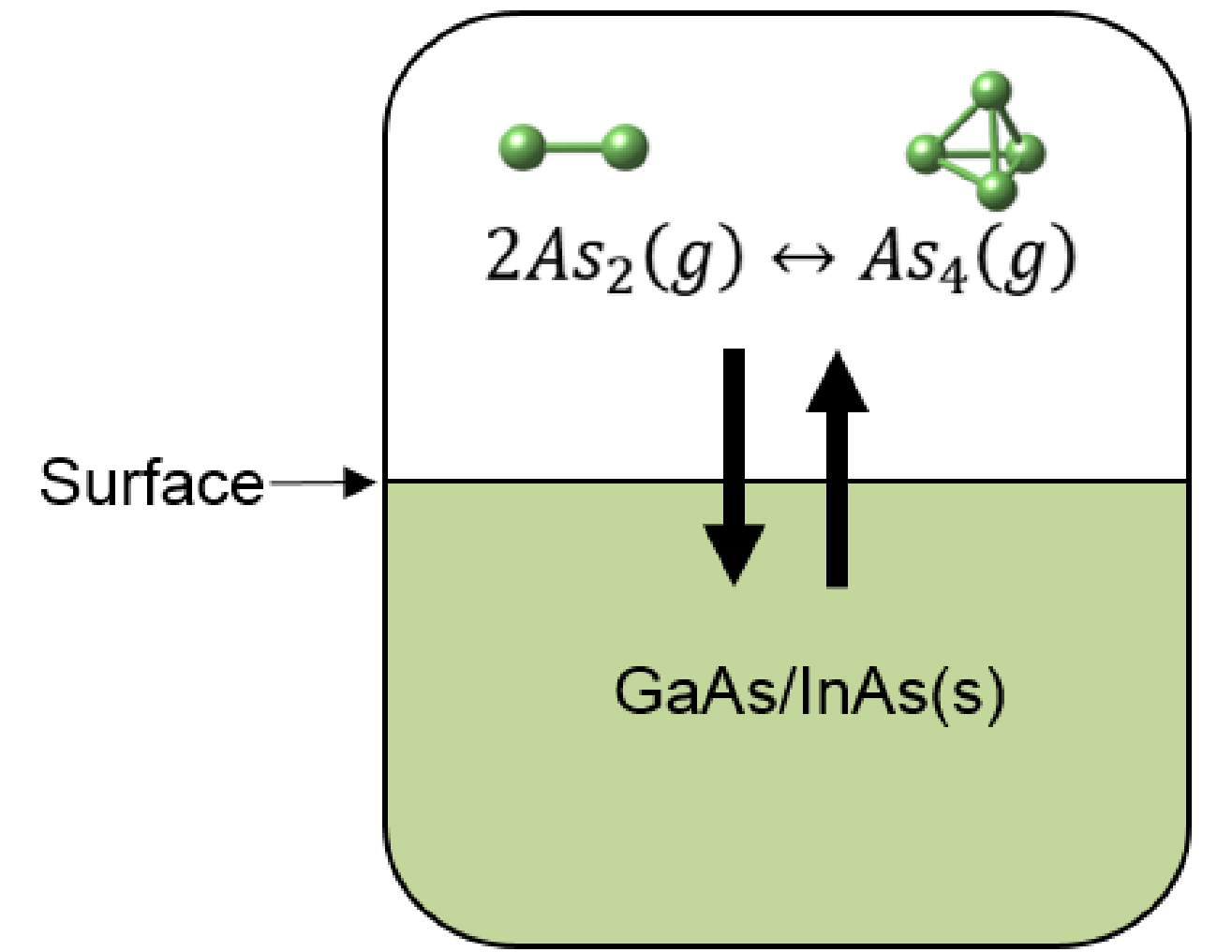
Converged by considering Top 3 layers.



Equilibrium:

$$\gamma^{elec}(\mu) \rightarrow \gamma^{elec}(T, P) \text{ by}$$

$$\mu_{As}(GaAs/InAs) = \mu_{As}(g)(T, P).$$



Chemical potential of Gas:

$$\mu_{i(gas)}(T, P) = (-k_B T \ln Q_{i(gas)}^{tot} + PV) / N.$$

$$Q_{i(gas)}^{tot} = \frac{1}{N!} (q^{trans} q^{rot} q^{vib} q^{elec})^N,$$

$$\mu_{i(gas)}(T, P) = \mu_{i(gas)}^0(T, P^0) + k_B T \ln \frac{P_{i(gas)}}{P^0}.$$

$$F_{trans} = -k_B T \ln \left[\left(\frac{2\pi m}{h^2} \right)^{3/2} \frac{(k_B T)^{5/2}}{p} \right]$$

translation

$$F_{rot} = -k_B T \ln \left(\frac{\pi^{1/2}}{\sigma} \sqrt{\frac{2I_A k_B T}{h^2}} \sqrt{\frac{2I_B k_B T}{h^2}} \sqrt{\frac{2I_C k_B T}{h^2}} \right)$$

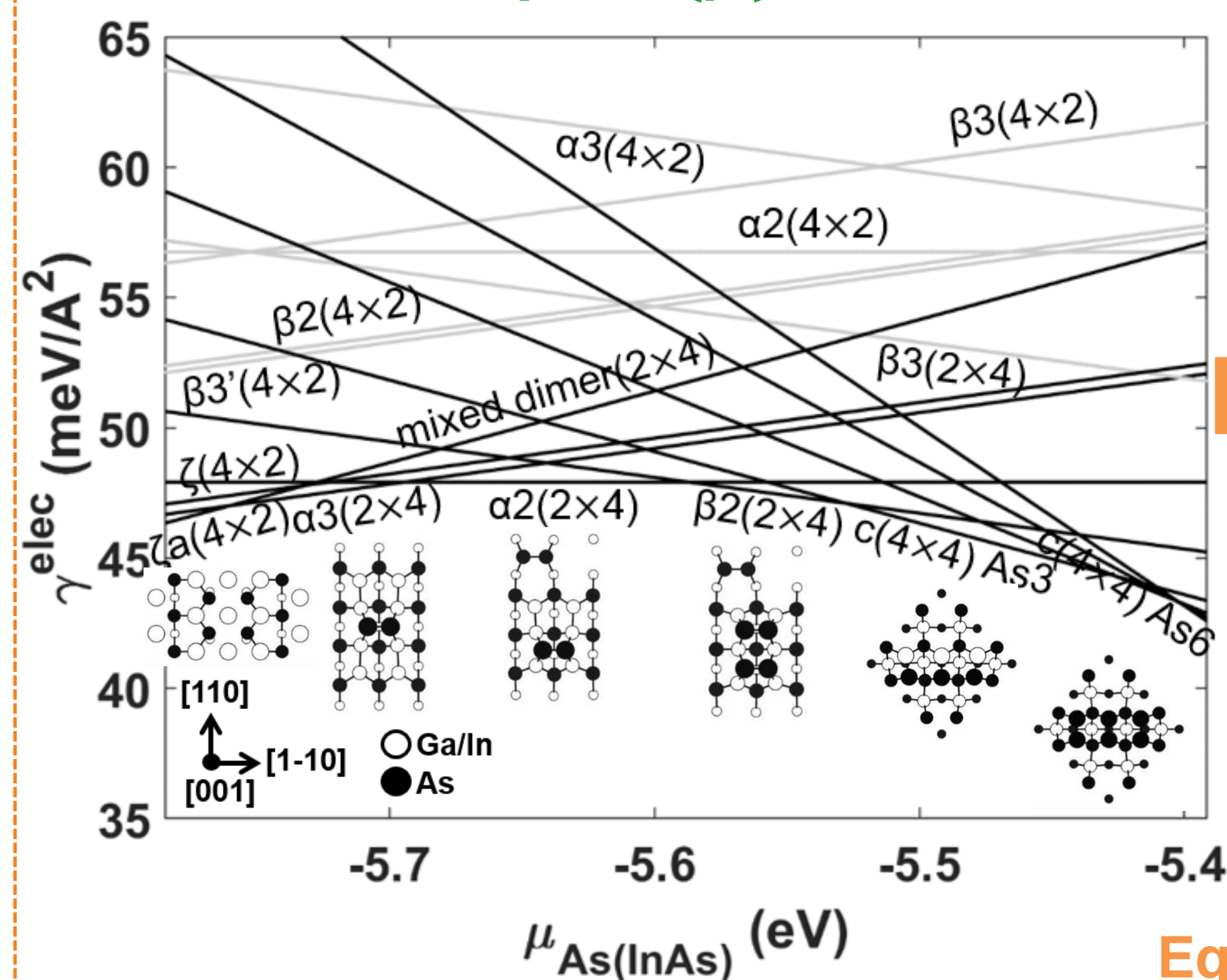
rotation

$$F_{vib} = \sum_{i=1}^M \frac{\hbar\omega_i}{2} + \sum_{i=1}^M k_B T \ln \left(1 - e^{-\frac{\hbar\omega_i}{k_B T}} \right)$$

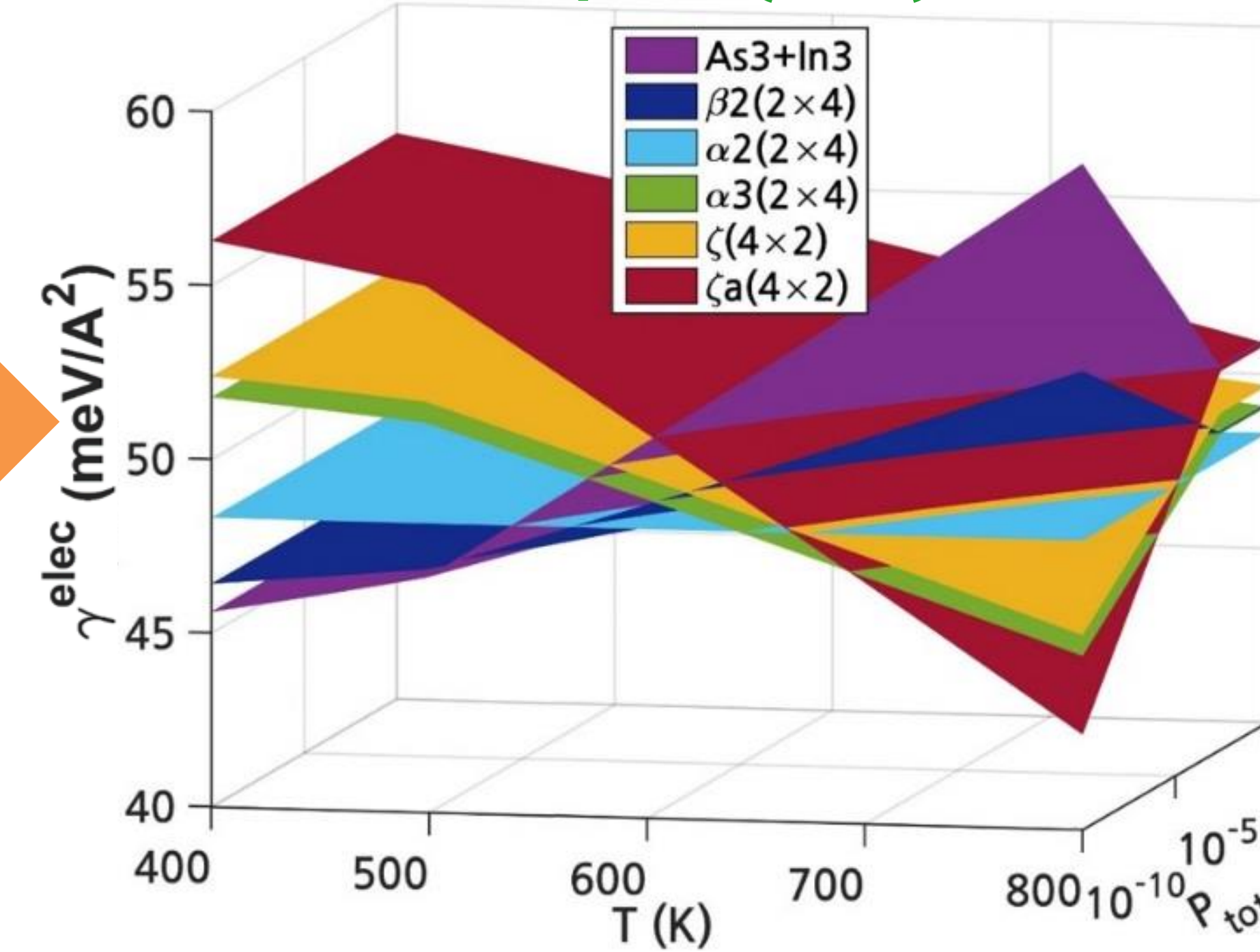
vibration (M=3N-5 or 3N-6)

Results

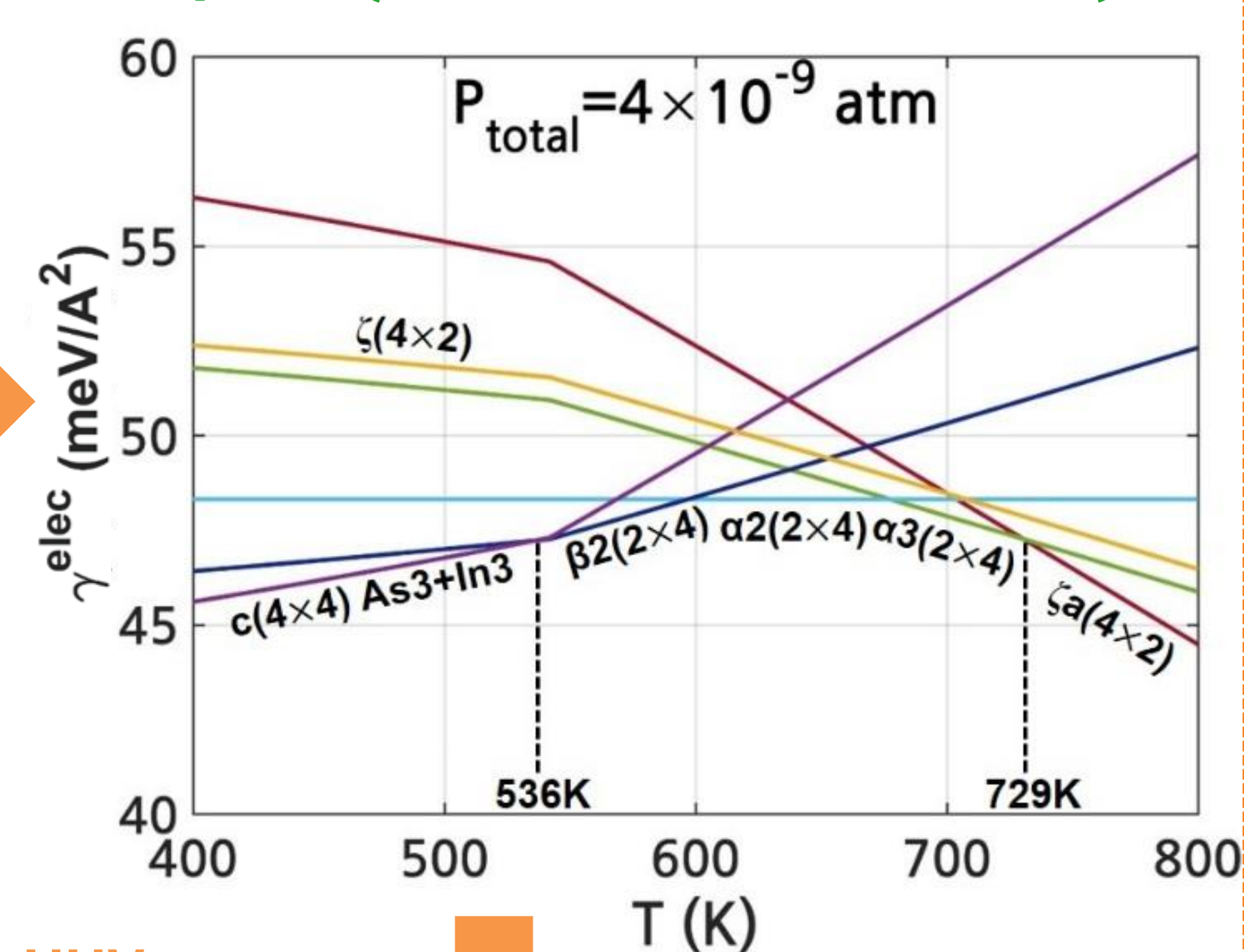
$\gamma^{elec}(\mu)$



$\gamma^{elec}(T, P)$



$\gamma^{elec}(T; P = 4 \times 10^{-9} \text{ atm})$



Equilibrium

$$\mu_{As(g)}(T, P) = \mu_{As(InAs)}$$

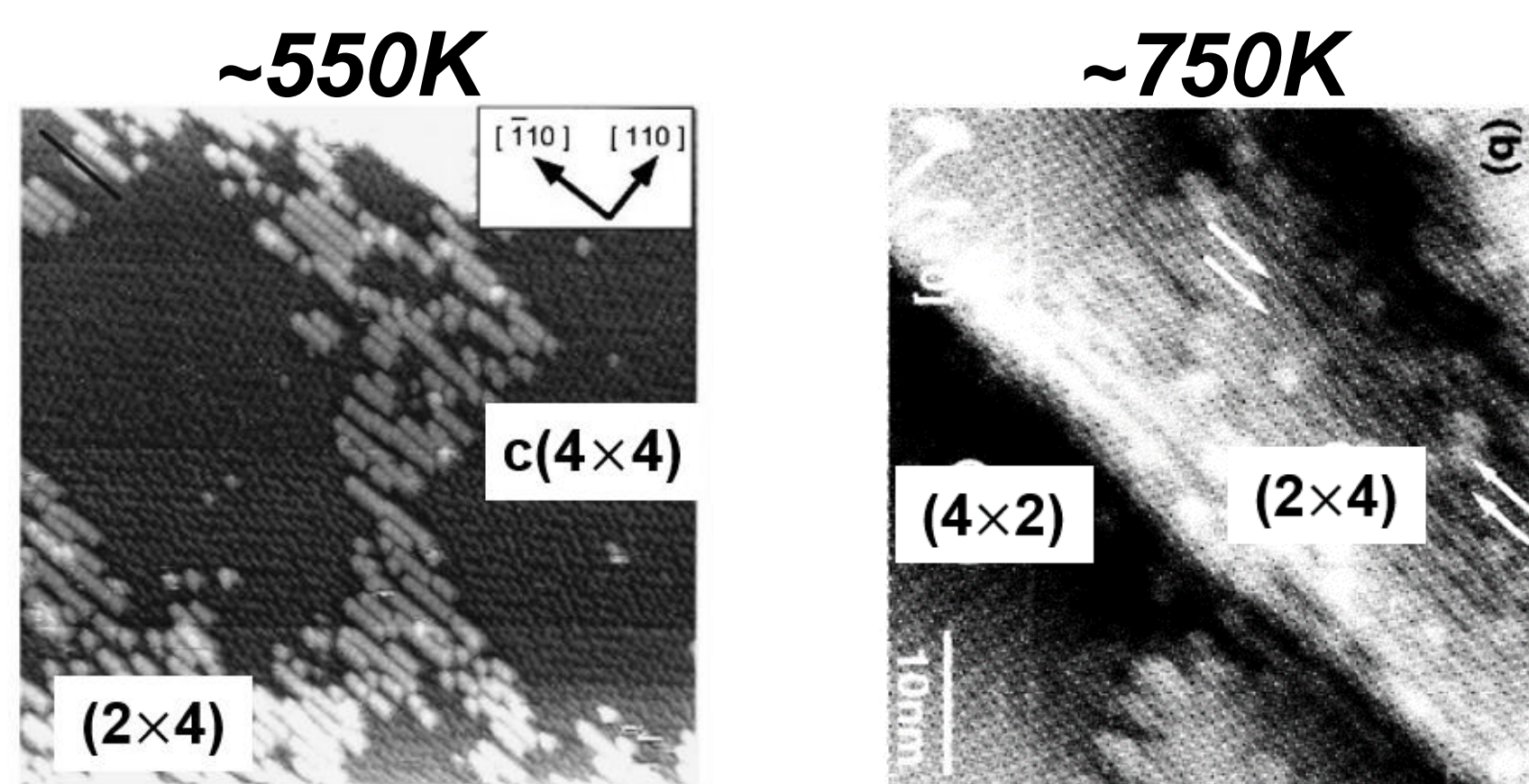
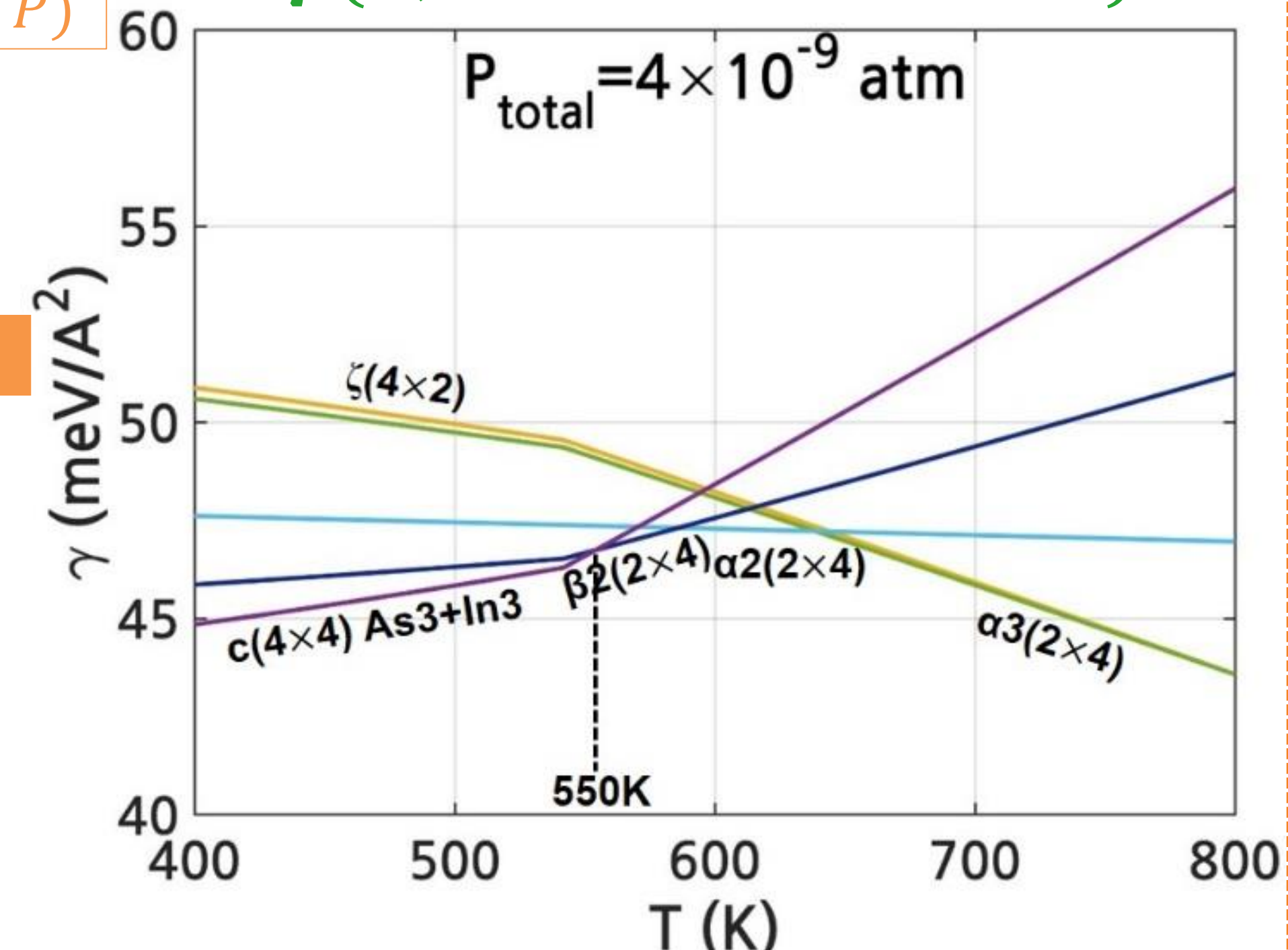
P fixed to UHV

$\zeta a(4 \times 2)$ is identified to be unstable

Vibrational entropy

$$\gamma(T; P) = \gamma^{elec}(T; P) + \Delta\gamma^{vib}(T)$$

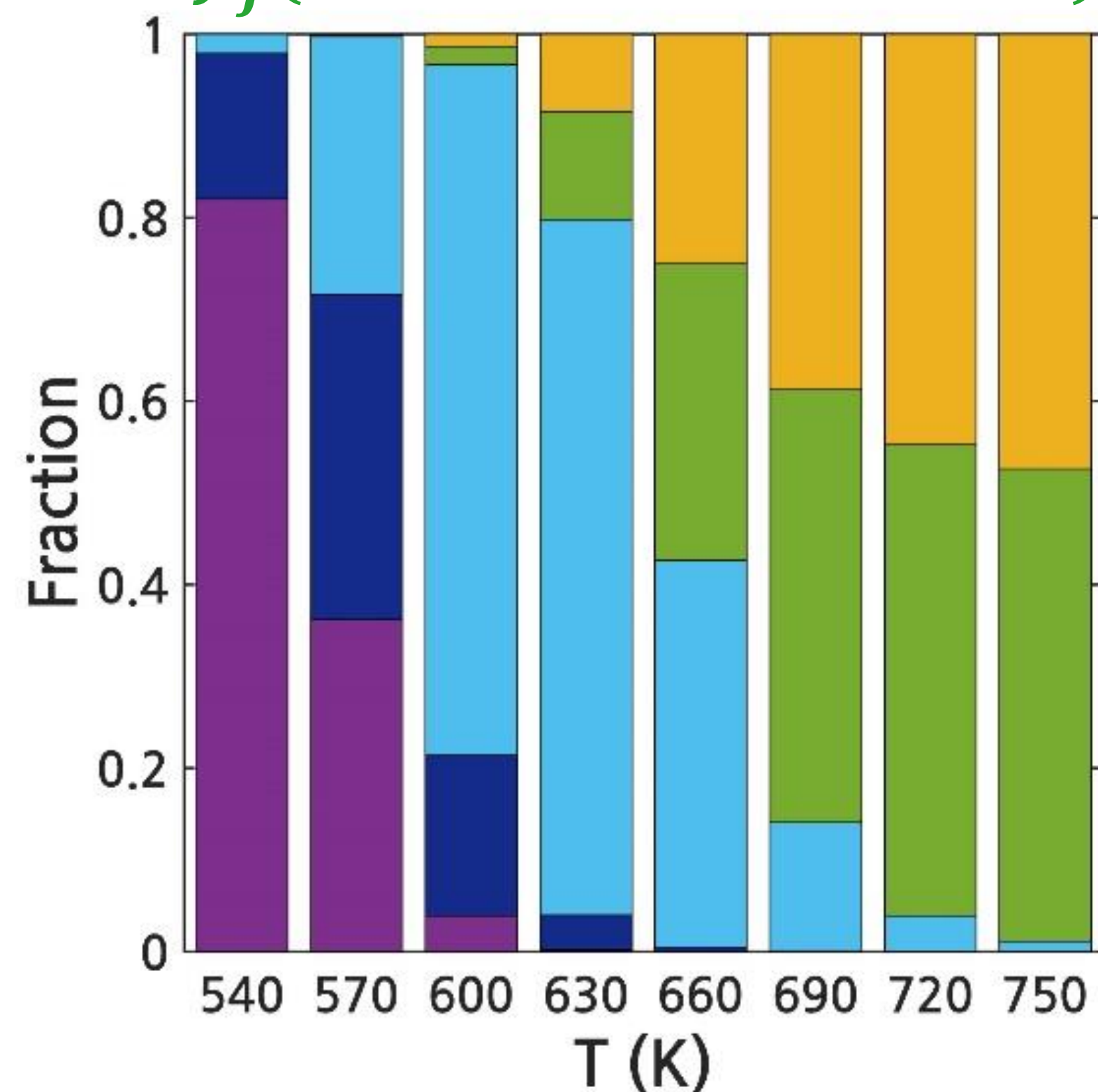
$\gamma(T; P = 4 \times 10^{-9} \text{ atm})$



Some reconstructions which are unstable in terms of electronic surface energy (γ^{elec}) become energetically stable at high T (entropy effects).

Such a correspondence between the calculations and experiments for a given T and P has not been available in the previous DFT calculations.

$f_j(T; P = 4 \times 10^{-9} \text{ atm})$



Configurational entropy

$$f_j(T; P) = \frac{Z_j(T; P)}{Z(T; P)}$$