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Reconstruction and Disorder at Compound Semiconductor Surfaces

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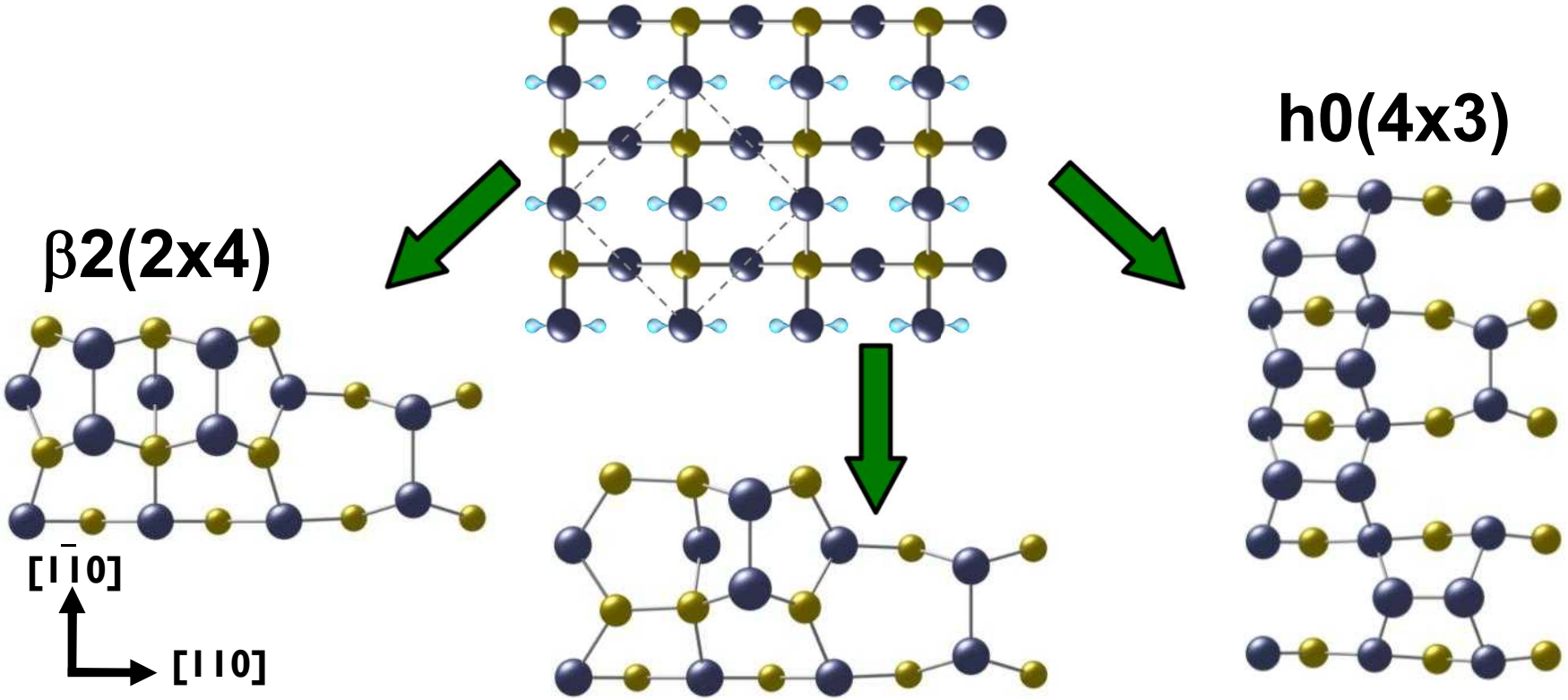
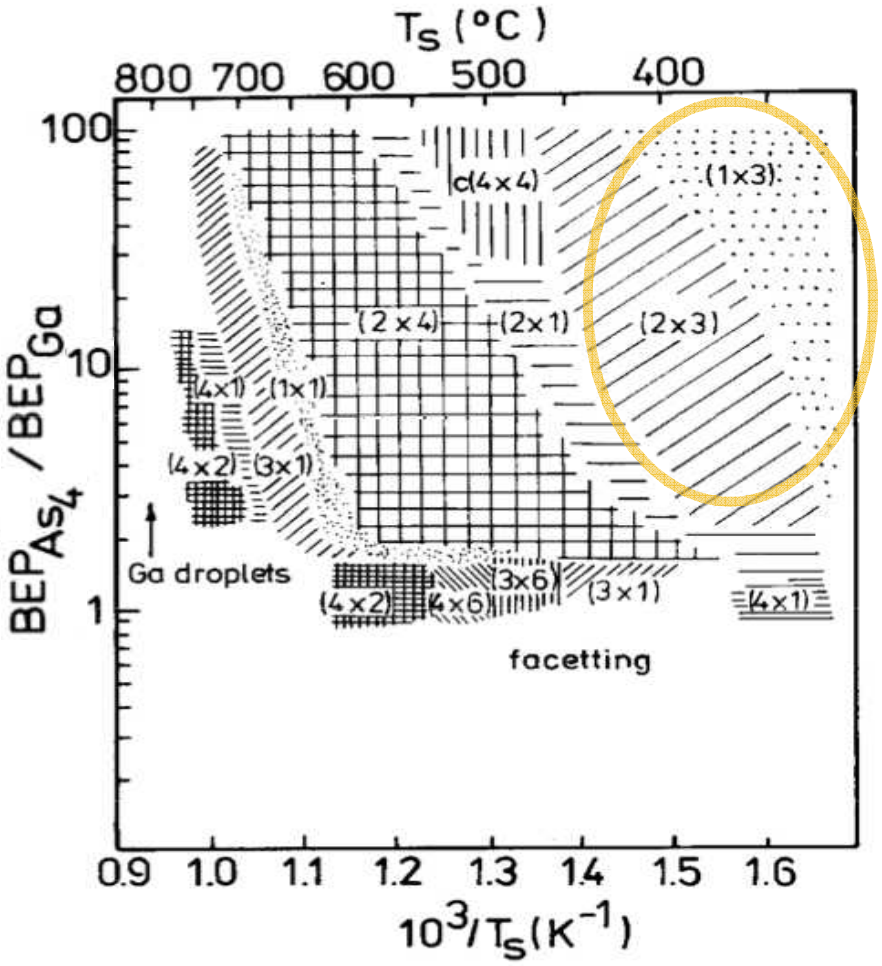
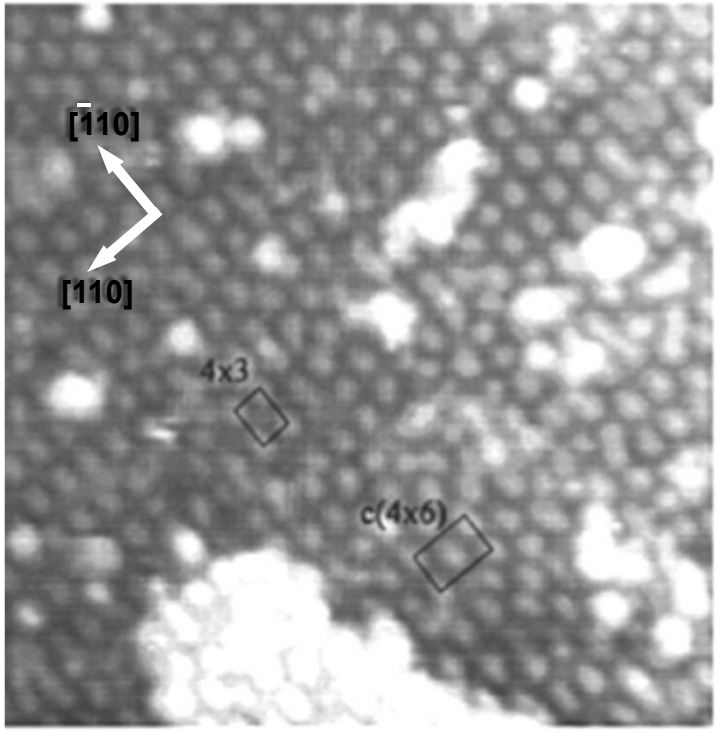
Surface Reconstruction



Reconstruction Stability Diagram





The (2x3)/(4x3)/c(6x4) reconstruction observed on GaAs (001)

Chizhov, Lee, Willis, Lubyshev, and Miller, *Phys. Rev. B*, 56, 1013 (1997).

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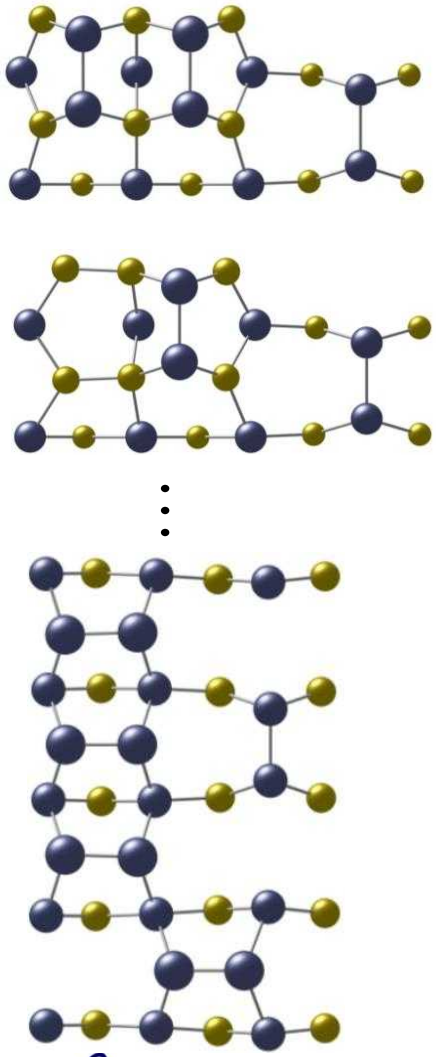
Ab Initio Calculations – Kohn Sham Density Functional Theory



$\mathbf{H\Psi=E\Psi}$

$$E_{tot}\left(Z_1^1, R_1^1, Z_2^1, R_2^1, \square \ , Z_{N^1}^1, R_{N^1}^1\right)$$

$\mathbf{H\Psi=E\Psi}$

$$E_{tot}\left(Z_1^2, R_1^2, Z_2^2, R_2^2, \square \ , Z_{N^2}^2, R_{N^2}^2\right)$$

$\mathbf{H\Psi=E\Psi}$

$$E_{tot}\left(Z_1^M, R_1^M, Z_2^M, R_2^M, \square \ , Z_{N^M}^M, R_{N^M}^M\right)$$

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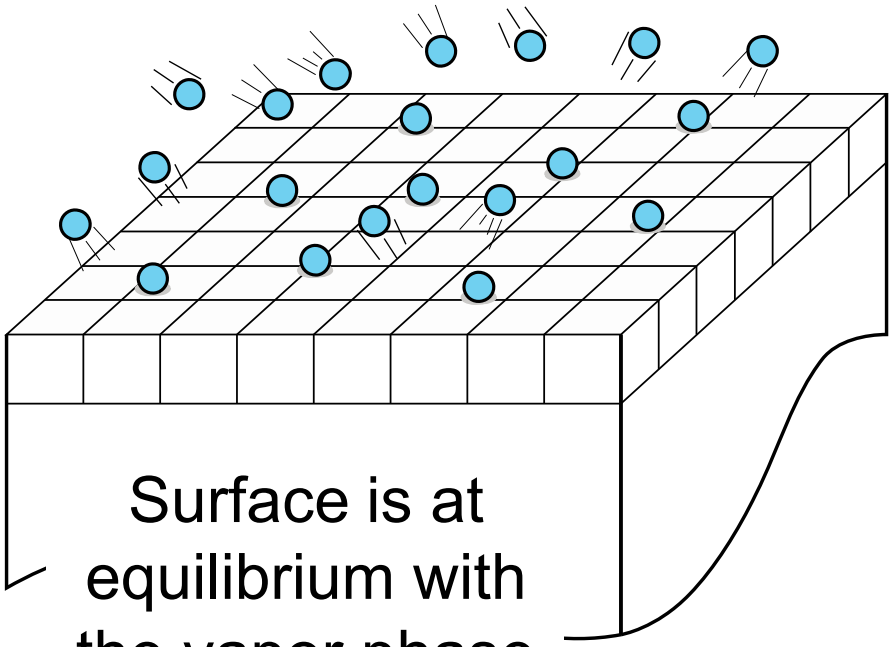
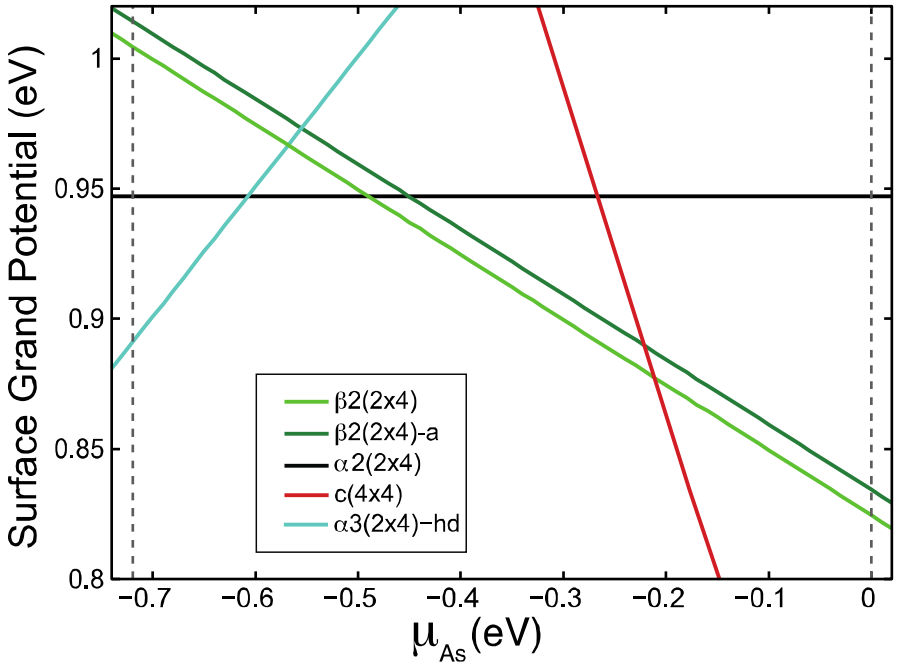
Chemical Potentials Account For Variable Numbers of Each Species



Surface is at equilibrium with the vapor phase



Surface Grand Potential

$$\sigma(\mu_1,\ldots,\mu_n) = \left(E_{tot} - N^{bulk} E_{bulk} - \sum_{\alpha} \mu_\alpha \left(N_\alpha - N_\alpha^{bulk} \right) \right) / A^{surface}$$

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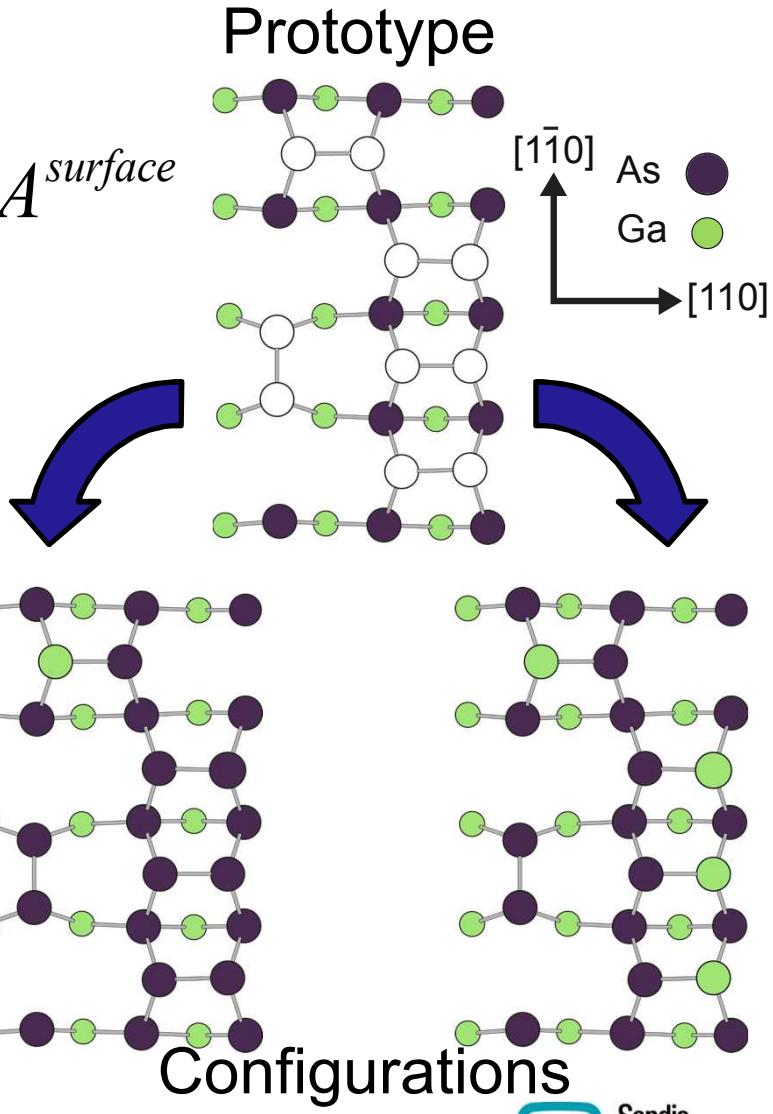
Nonzero Temperature and Disorder

$$\sigma(T,\mu_1,\square\ ,\mu_n)=\sigma(\mu_1,\square\ ,\mu_n)-TS/A^{surface}$$

- **Energy**
  - **Structure**
  - **Species configuration**
- **Entropy**
  - **Vibrational entropy**
  - **Configurational entropy**



Systematic Enumeration of Low Energy Prototypes

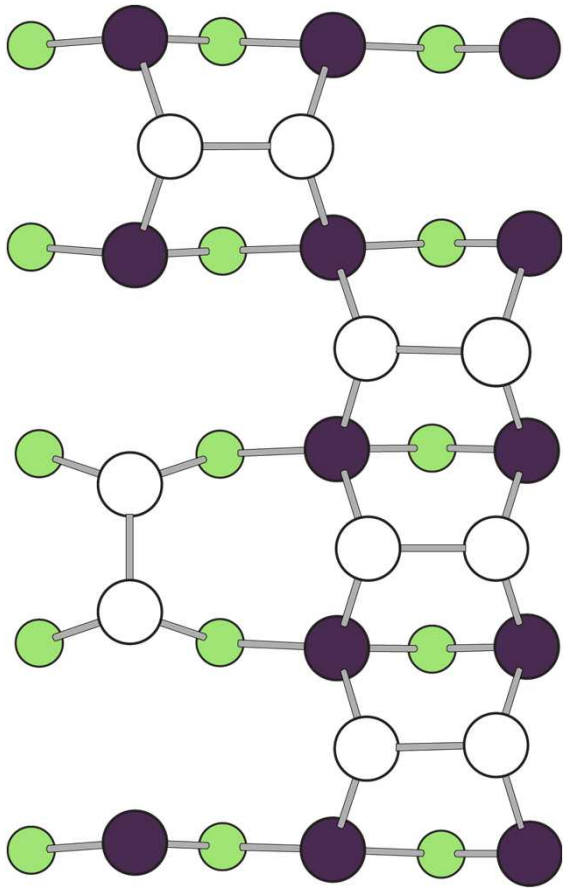
Identify rules that describe observed structural trends

Enumerate all distinct prototypes that obey rules

Calculate energies of promising structures from first principles

Collect low-energy prototypes to study configurations

Prototype



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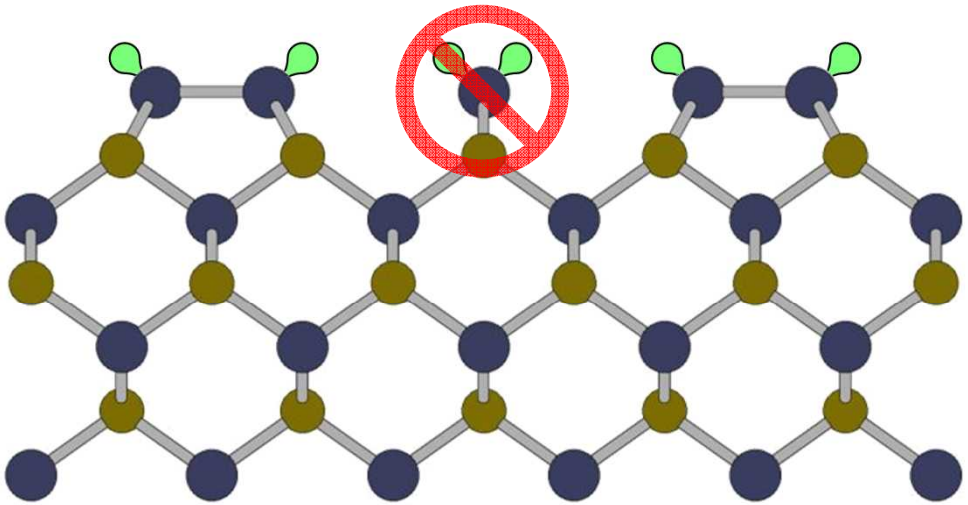
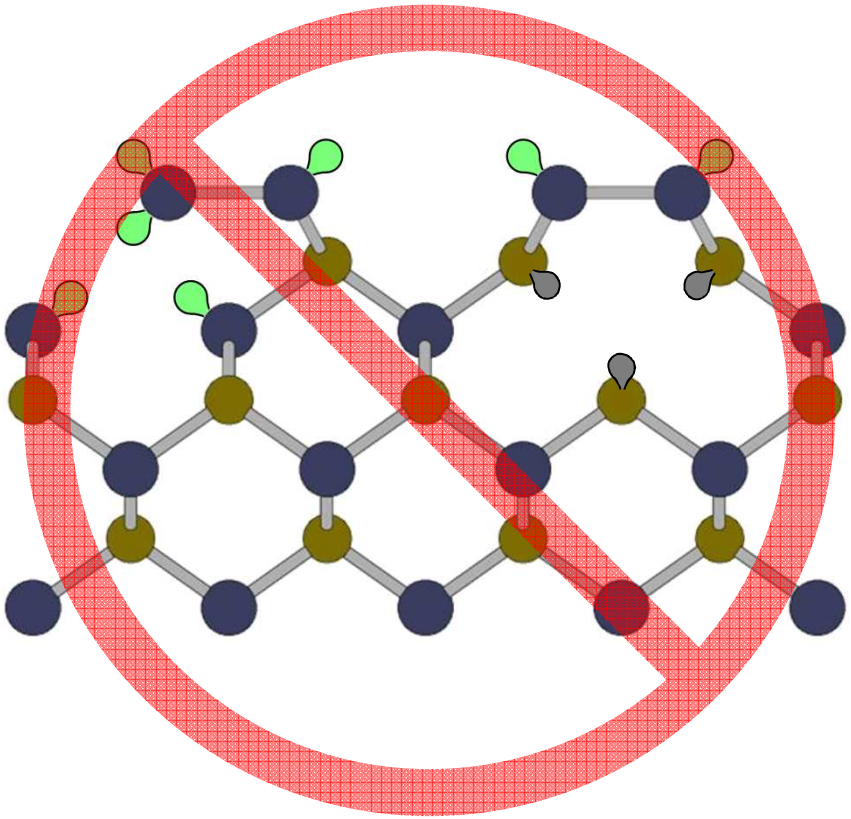
Structural trends



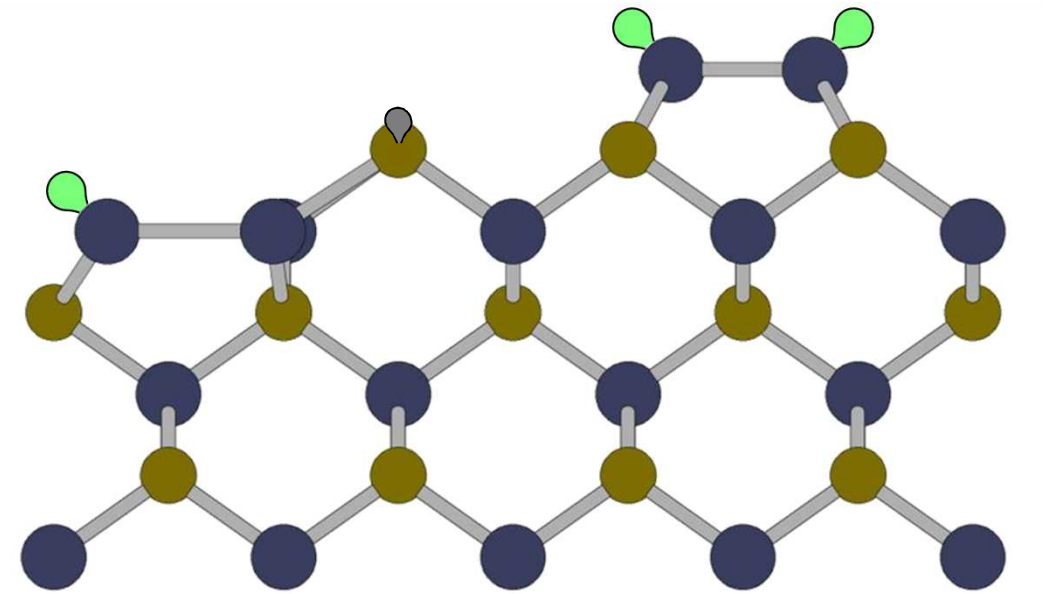
I. Only three-fold and four-fold coordination is allowed.

Structural trends



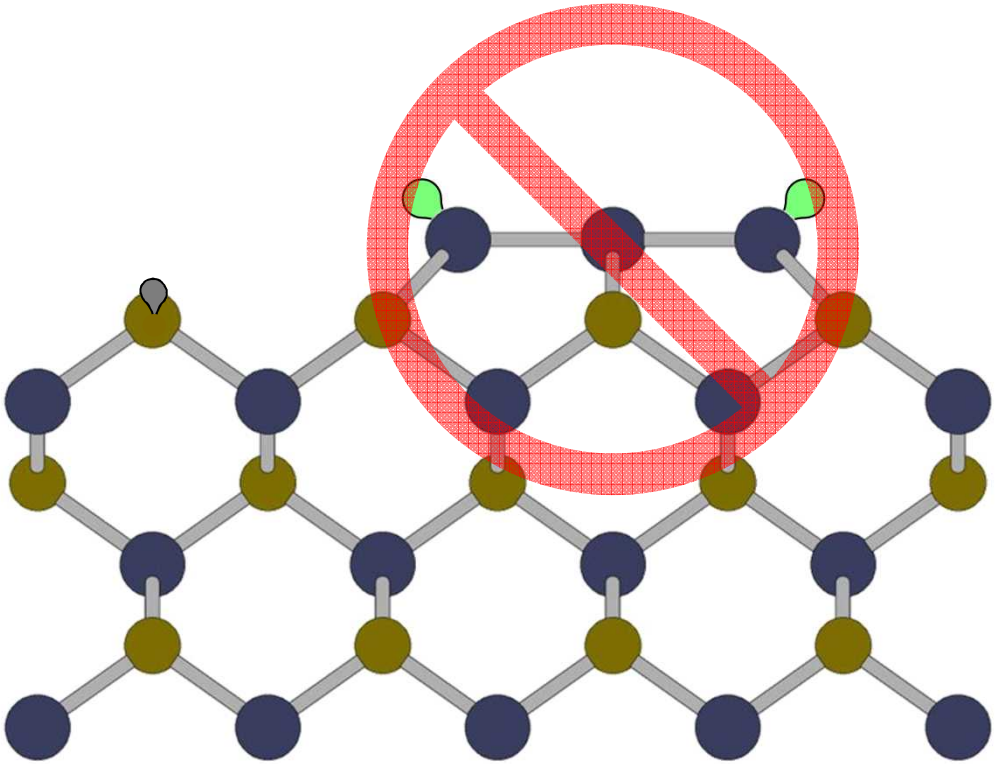
II. There are no subsurface vacancies.

Structural trends



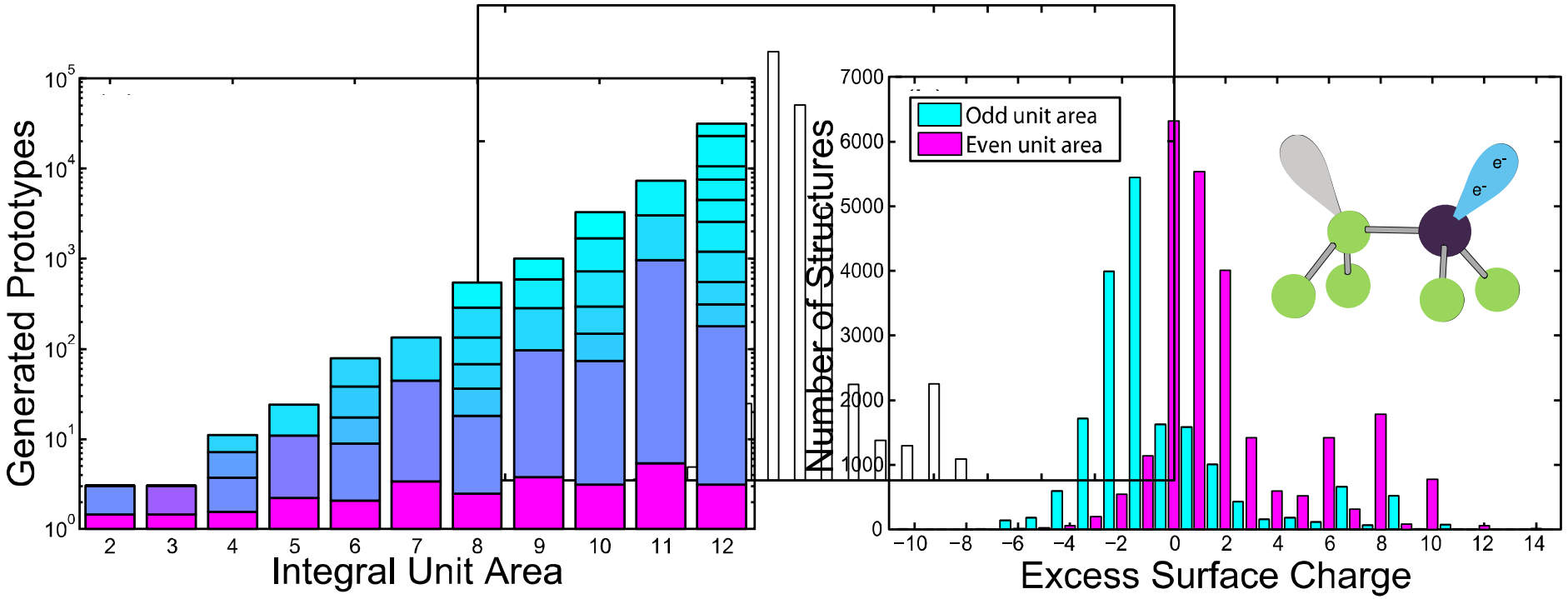
III. Under-coordinated atoms can bond to in-plane neighbors.

Structural trends



IV. An atom can have no more than one in-plane bond.

Screen Results Using the "Electron Counting Model"



There are over 40,000 new structural prototypes with unit area ≤12.

Charge neutral prototypes make up only about 15% of those generated.

J. Thomas *et al., Phys. Rev. B,* 82, 165434, (2010).

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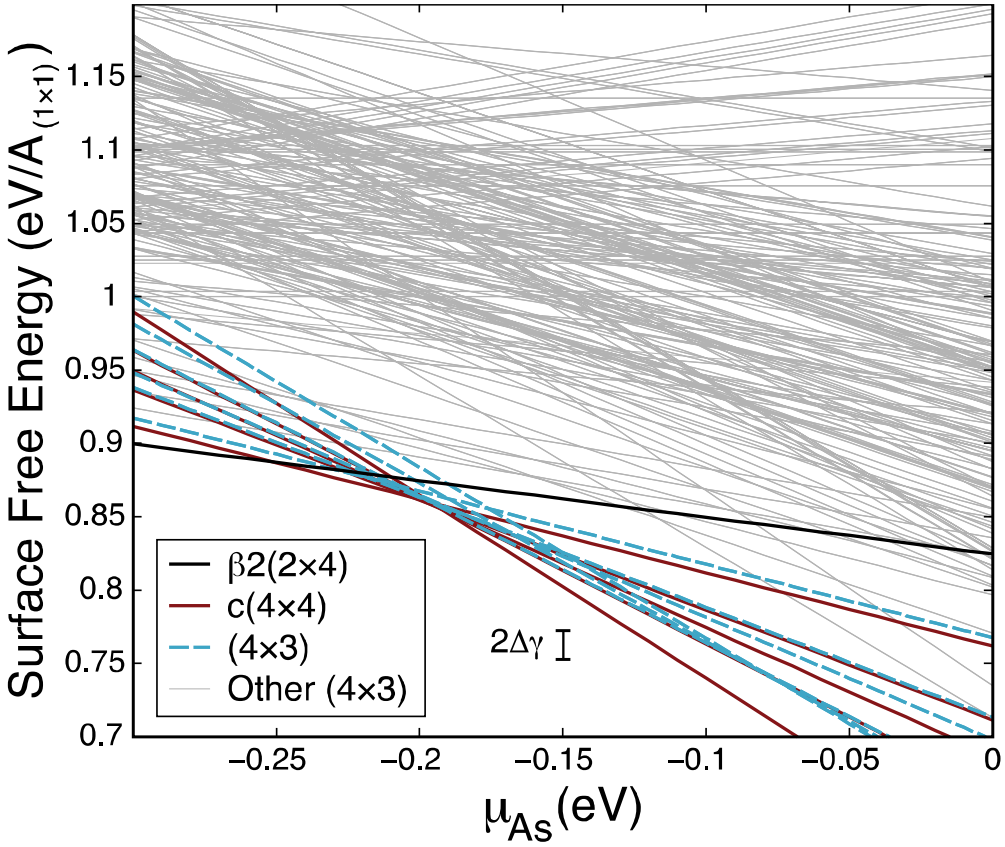
GaAs (001) Groundstate Search

Experimentally Observed Unit Cells

124 Reconstruction Prototypes

$H\Psi=E\Psi$



Charge-neutral structural prototypes for observed geometries: 20 c(8x2), 20 c(4x4), 23 (4x2), 23 (2x4), and 124 (4x3).

DFT calculations performed using Vienna *ab initio* Simulation Package

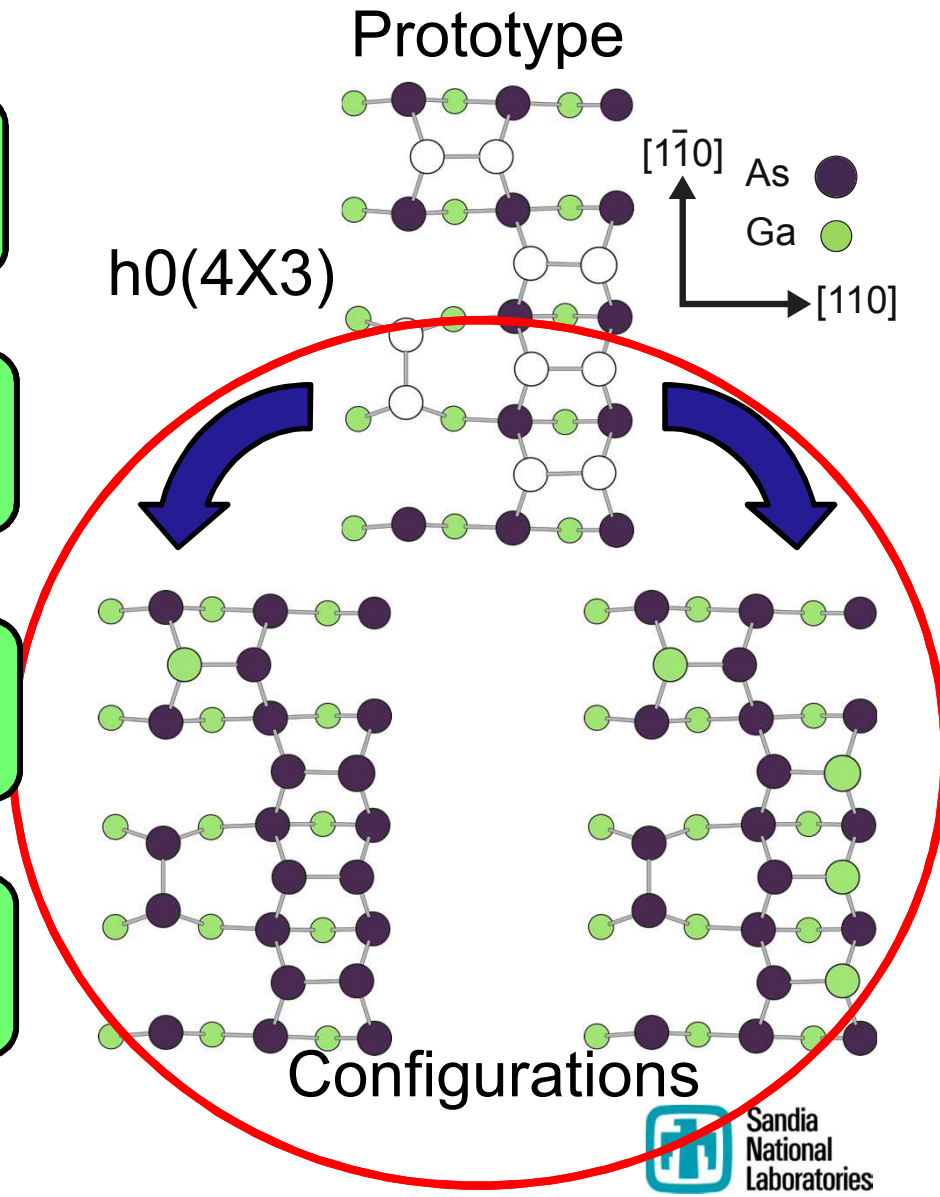
Systematic Sampling of Configurations For Low Energy Prototypes

Build a training set of configurations using DFT

Fit the cluster expansion to the training set

Perform Monte-Carlo using cluster expansion energies

Calculate quantities of interest (composition, free energy, …)



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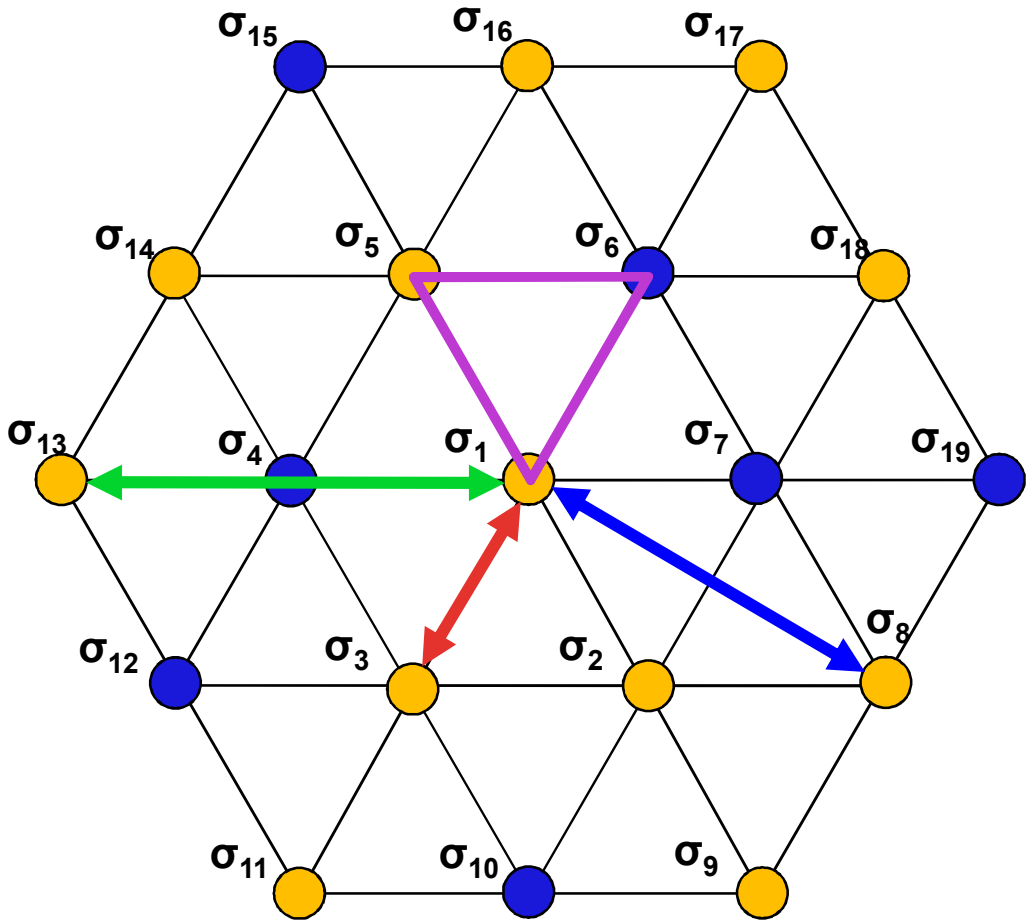
The Cluster Expansion

Interactions between sites are described by products of σ_i.

Fit interaction parameters to a database of DFT energies.

Monte-Carlo used to sample configurations.

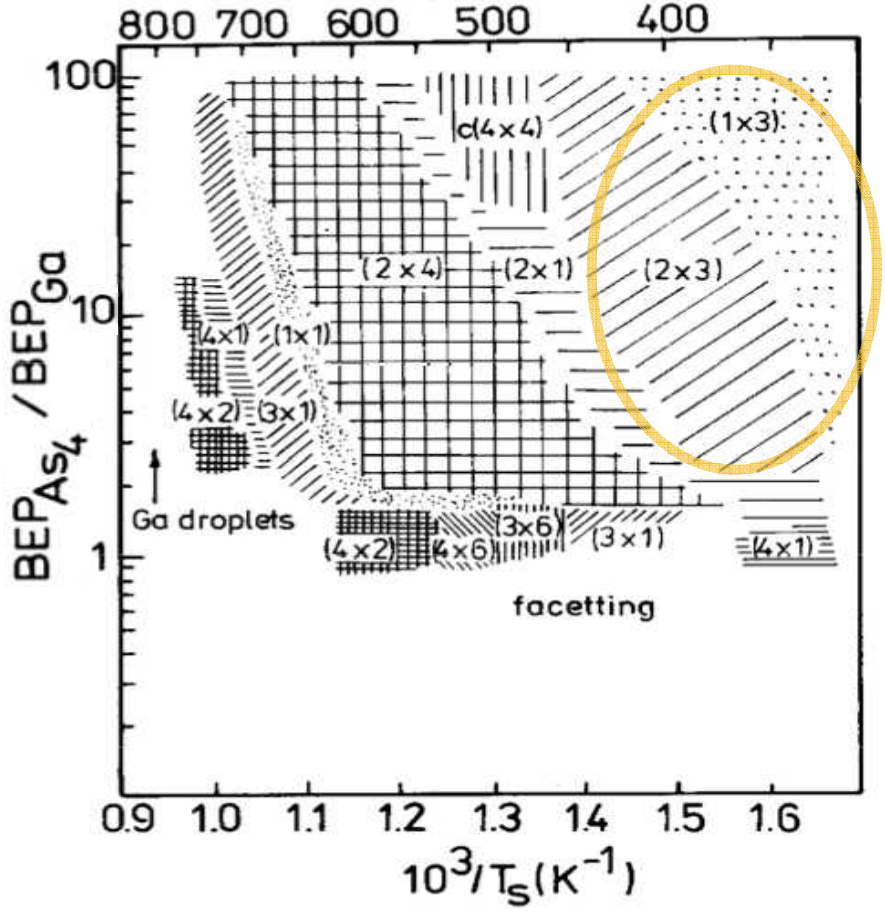


$$E = J_1\sigma_1 + J_{1,3}\sigma_1\sigma_3 + J_{1,8}\sigma_1\sigma_8 + J_{1,5,6}\sigma_1\sigma_5\sigma_6 + \ldots$$

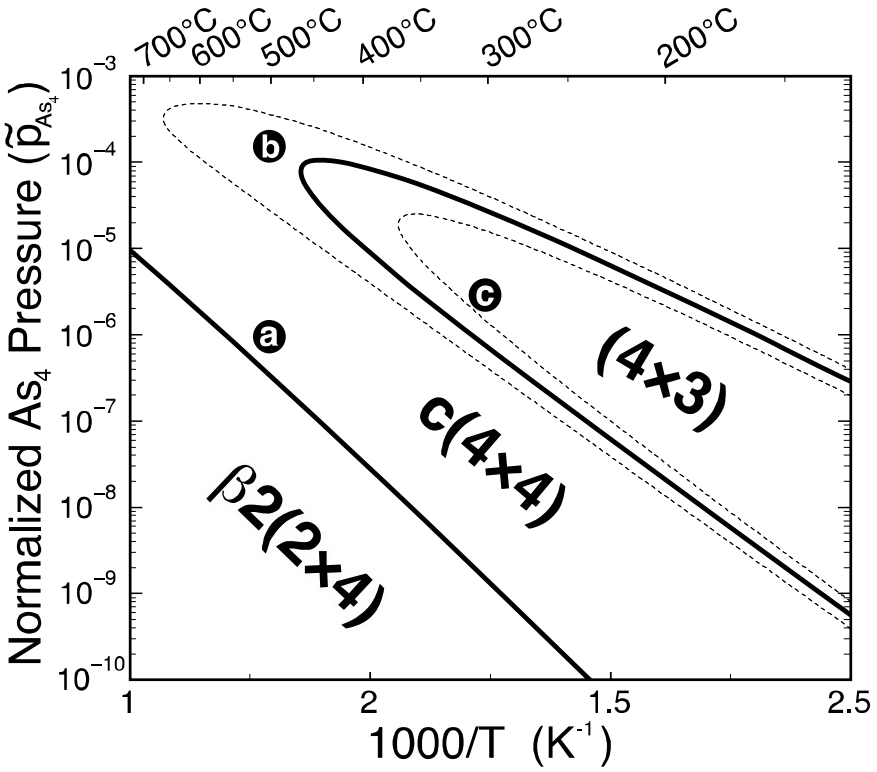
Cluster expansion constructed using CASM code.

Theoretical (4X3) Consistent with Experiment

Observed GaAs (001) Phase Diagram



Calculated GaAs (001) Phase Diagram



Chizhov, Lee, Willis, Lubyshev, and Miller, *Phys. Rev. B*, 56, 1013 (1997).

J.C. Thomas, J.M. Millunchick, N.A. Modine, A. Van der Ven, Submitted to PRL.

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Conclusions

- We have developed a systematic method for predicting equilibrium surface atomic structure based on coupling DFT, rule-based enumeration, the Cluster Expansion, and Monte-Carlo
- A complete surface structure consists of a “Prototype” and a “Configuration”
- Our approach captures the effects of disorder due to non-zero temperature and alloying
- NEXT: We aim to systematically couple surface reconstruction and strain