



# ATOMIC SCALE STRESS CORROSION CRACKING OF TI ALLOYS.

TIGANY ZARROUK

**TIGANY.ZARROUK@KCL.AC.UK**

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# MOTIVATION

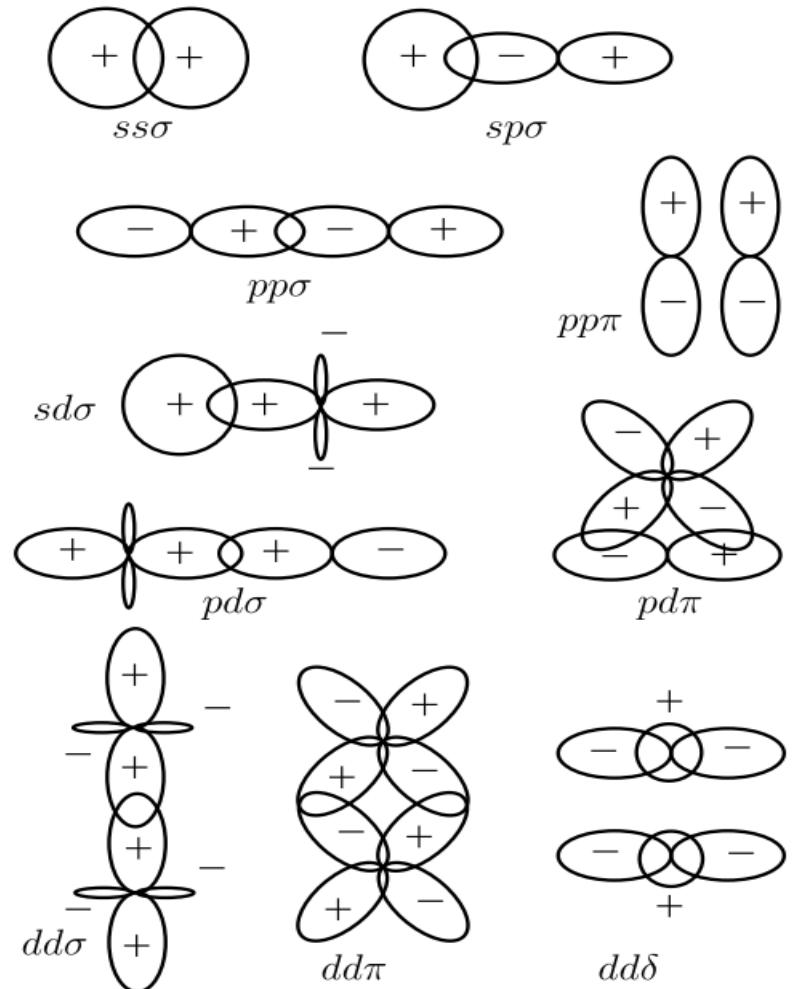
- Titanium alloys are used in highly demanding circumstances.
- Brittle oxide layer can crack.
- Solutes affect dislocation mobility, causing hardening.
- Interaction between oxygen and dislocation cores is not clear.
- Need for atomistic modelling.
- Exploration of Ti/oxide scale interface will give insights into oxygen diffusion, oxygen induces brittleness and stress corrosion cracking in Ti alloys.

# QUANTUM METHODS

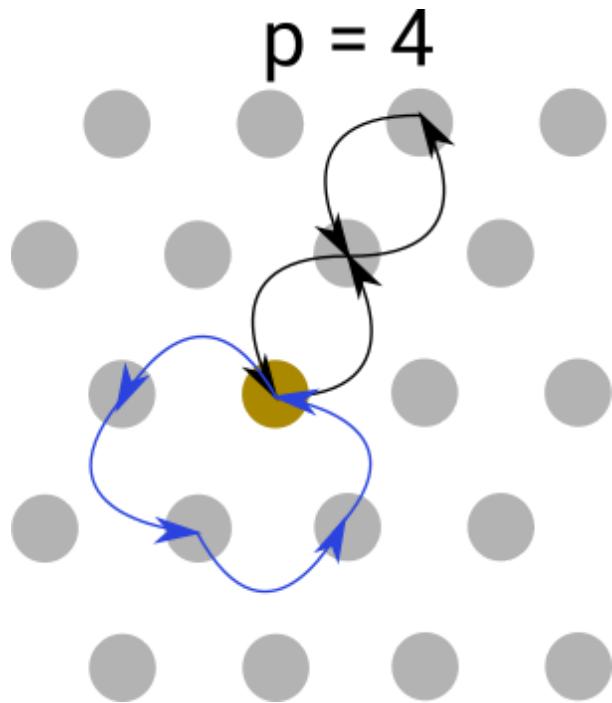
- Density Functional Theory is not feasible.
- System size is limited due to computational cost.
- Boundaries of cell affect relaxation of core more.
- Semi-empirical method is more computationally efficient.

# TIGHT BINDING

- Tight binding is an approximation to DFT.
- Overlaps between atomic orbitals are key parameters.
- Parameters can be fitted to experimental data
- $\mathcal{O}(N^3)$ , but much smaller prefactor compared to DFT.



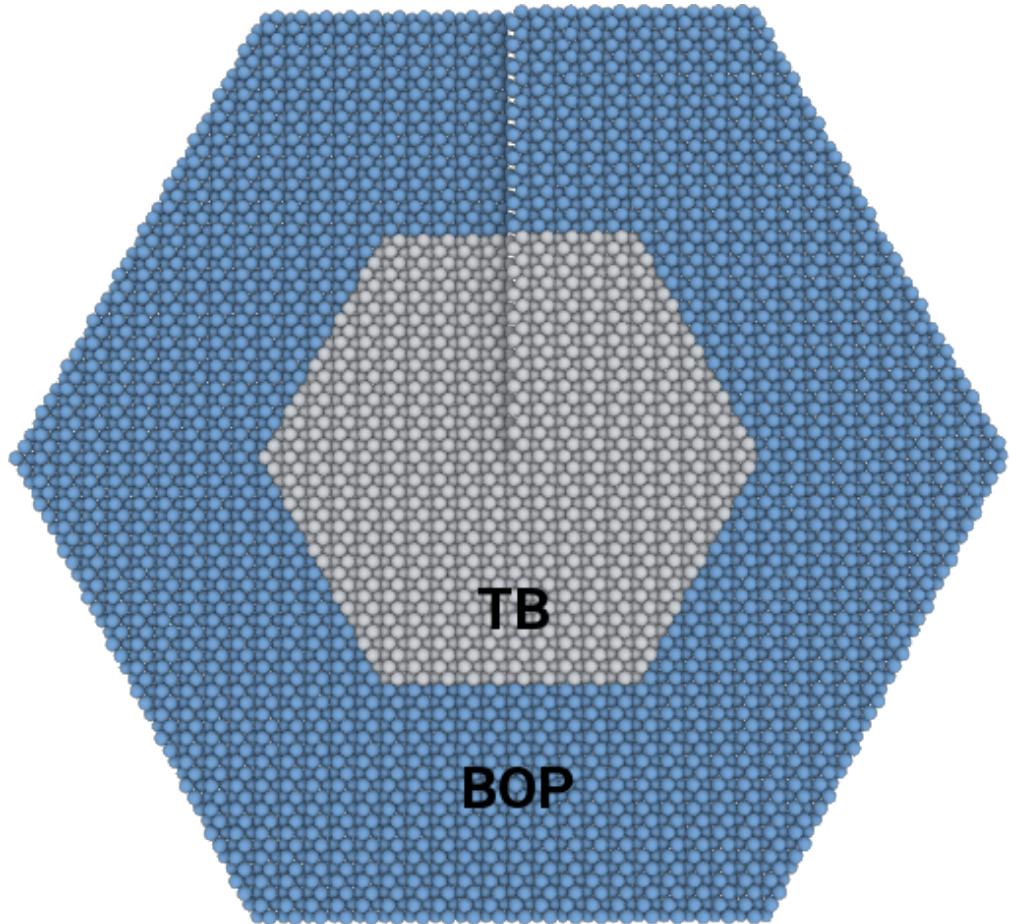
# BOP



- BOP is a faster but less accurate  $\mathcal{O}(N)$  method of interatomic force calculation within tight-binding.
- One builds a local density of states from moments, giving detailed electronic structure information.

# EMBEDDING

- Idea is to combine speed of BOP ( $\mathcal{O}(N)$ ) with accuracy of tight-binding  $\mathcal{O}(N^3)$ .
- Increasing the number of atoms gives freedom to:
  - Investigate isolated dislocations.
  - Include solutes at more realistic concentrations.
  - Simulate interfaces near a surface (e.g.  $\text{TiO}_2$  and bulk Ti)



# PARAMETER OPTIMISATION

- Parameter set for TB model optimised by two evolutionary algorithms: genetic and covariance matrix evolution.
- Fitting targets were a mix of experimental and DFT data.

# RESULTS OF OPTIMISATION.

Quantity	TB	BOP	target
$a_\alpha$ [bohr]	5.56	5.54	5.57
$c/a_\alpha$ [bohr]	1.61	1.62	1.58
$C_{11}$ [GPa]	180.7	199.8	176.1
$C_{33}$ [GPa]	206.1	206.9	190.5
$C_{44}$ [GPa]	48.3	37.7	50.8
$C_{12}$ [GPa]	95.2	80.7	86.9
$C_{13}$ [GPa]	66.5	59.6	68.3
$a_\omega$ [bohr]	8.84	8.85	8.73
$c_\omega$ [bohr]	5.38	5.37	5.32
$a_\beta$ [bohr]	6.26	--	6.17
$\Delta E(\omega - \alpha)$ [mRyd]	-1.10	-2.06	-0.73

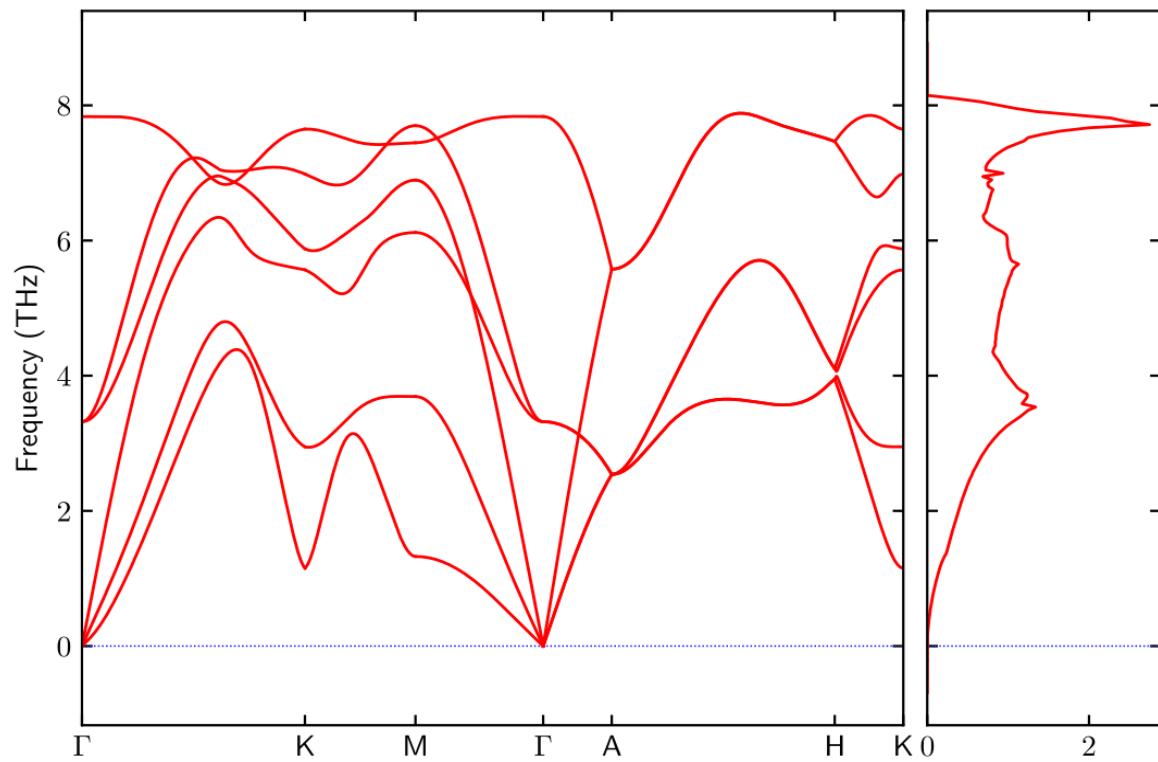
Quantity	TB	BOP	target
bandwidth [Ryd]	0.42		0.42

## ENERGY SPLITTINGS

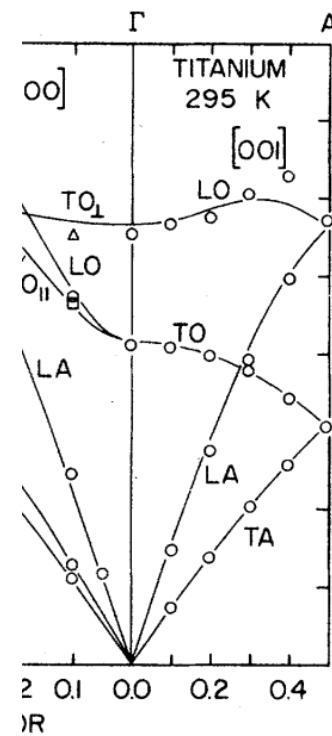
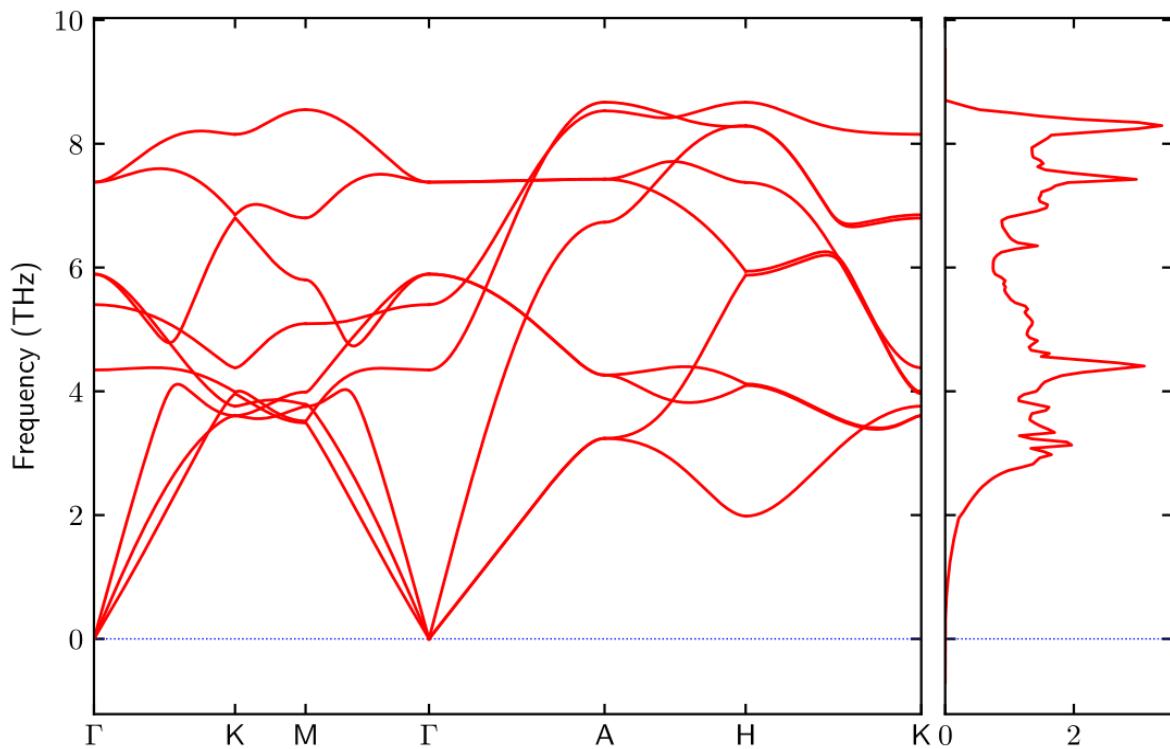
Quantity	TB	target
$\Delta E(\omega - \alpha)$ [mRyd]	-1.10	-0.73
$\Delta E(4\text{H} - \alpha)$ [mRyd]	1.98	3.17
$\Delta E(6\text{H} - \alpha)$ [mRyd]	2.98	3.72
$\Delta E(\text{fcc} - \alpha)$ [mRyd]	4.49	4.52
$\Delta E(\beta - \alpha)$ [mRyd]	9.83	7.64

# PHONON SPECTRA

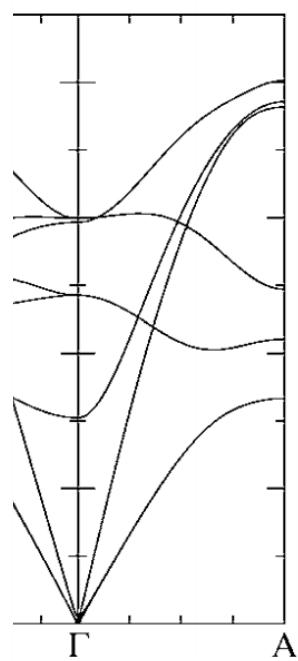
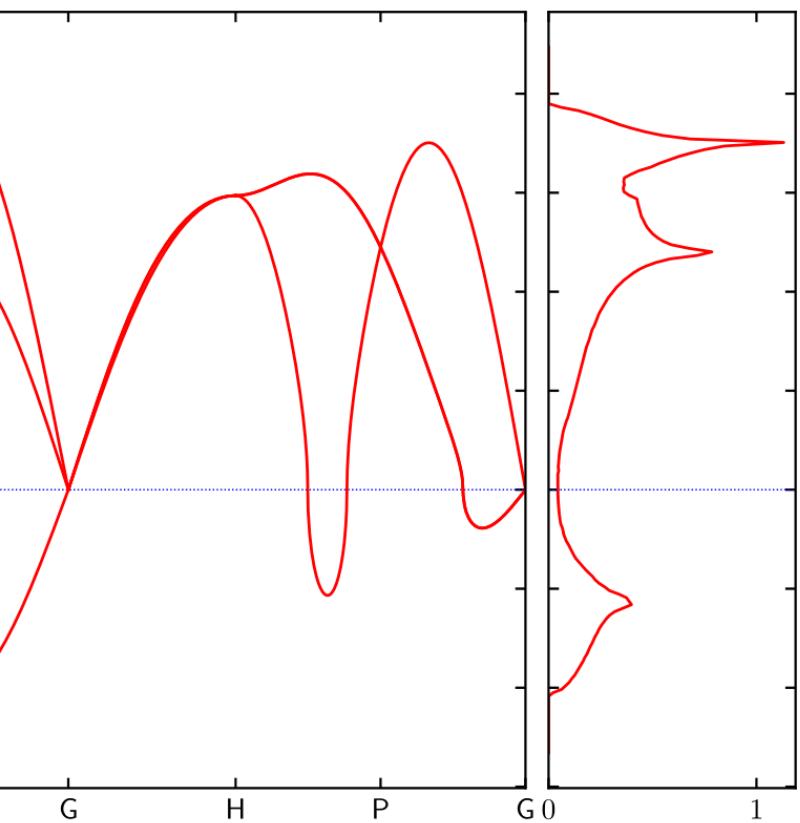
# $\alpha$ PHASE



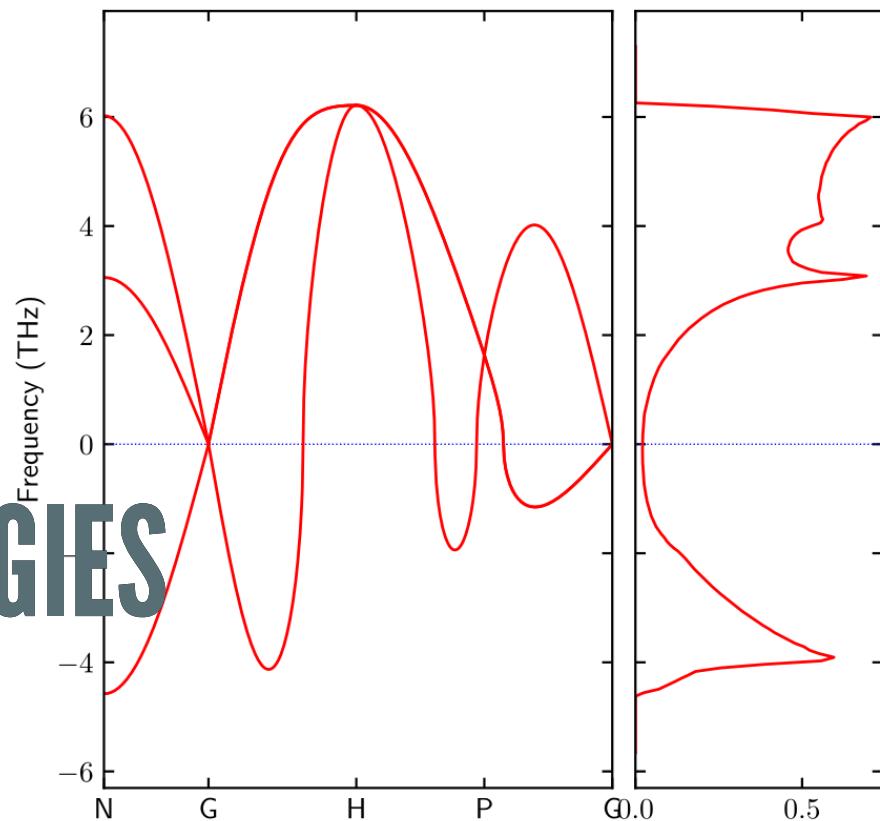
# $\omega$ PHASE



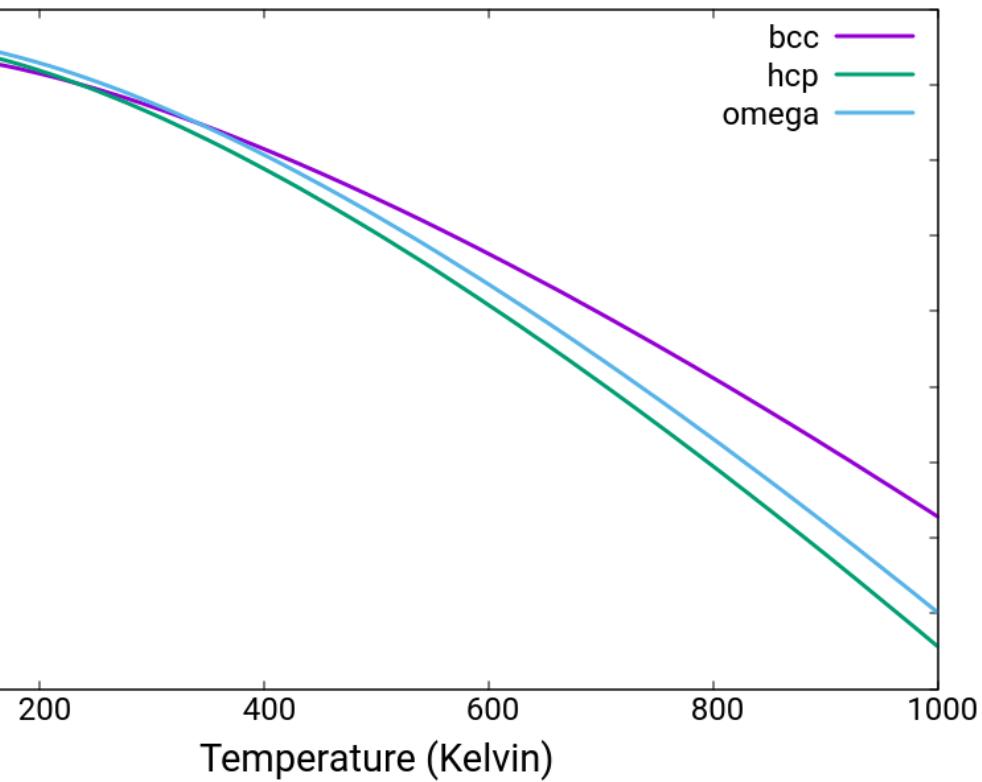
# $\beta$ PHASE



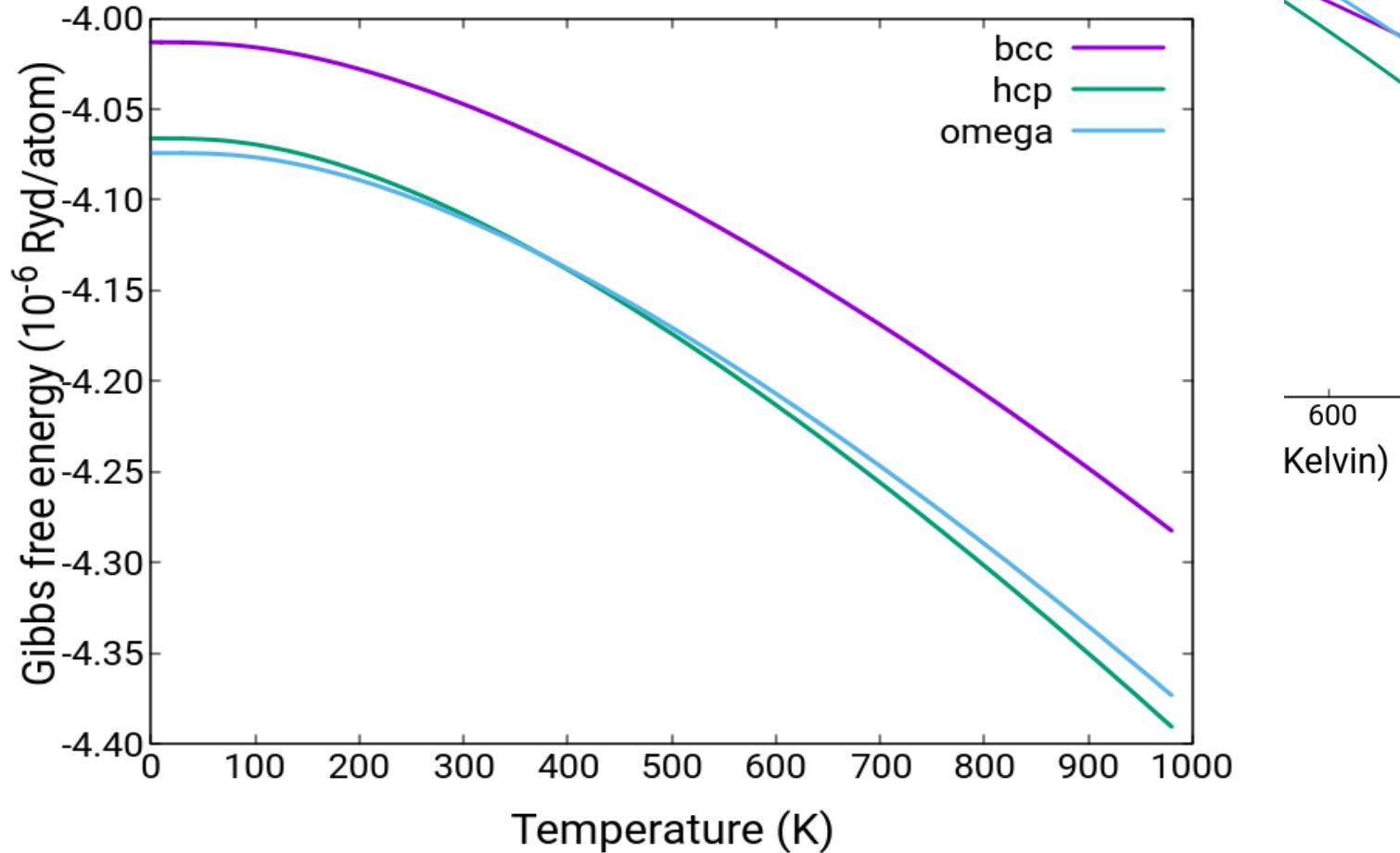
# FREE ENERGIES



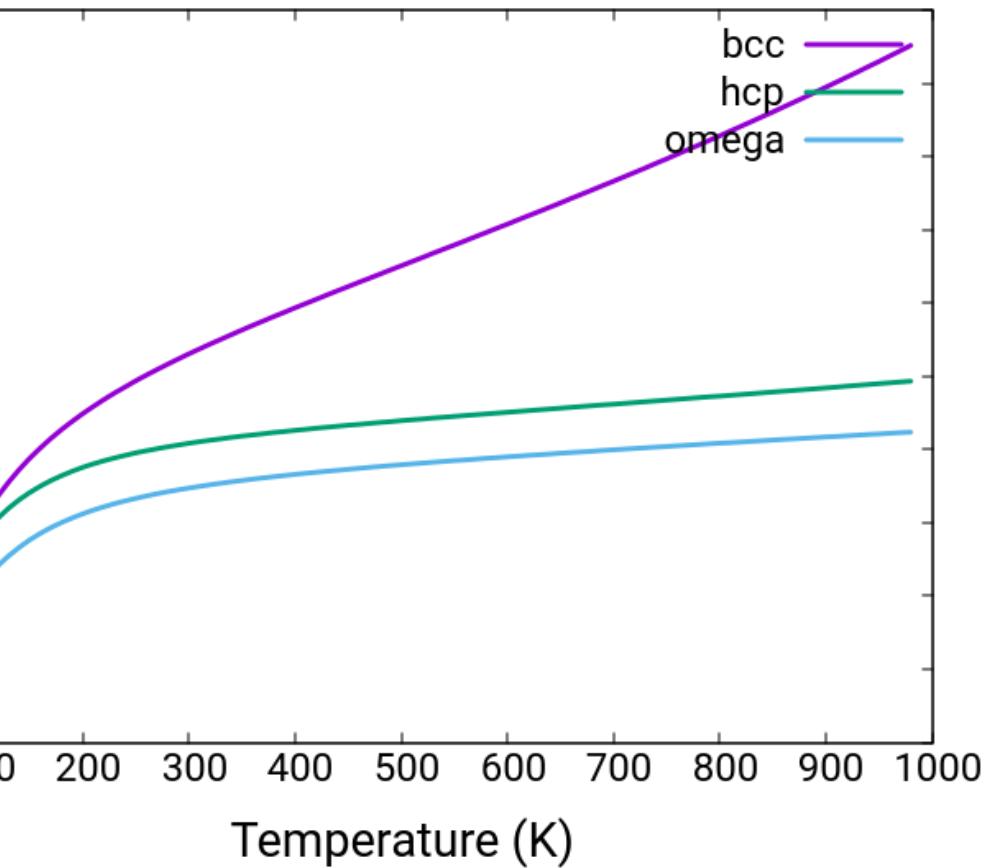
# VIBRATIONAL FREE ENERGY



# GIBBS FREE ENERGY

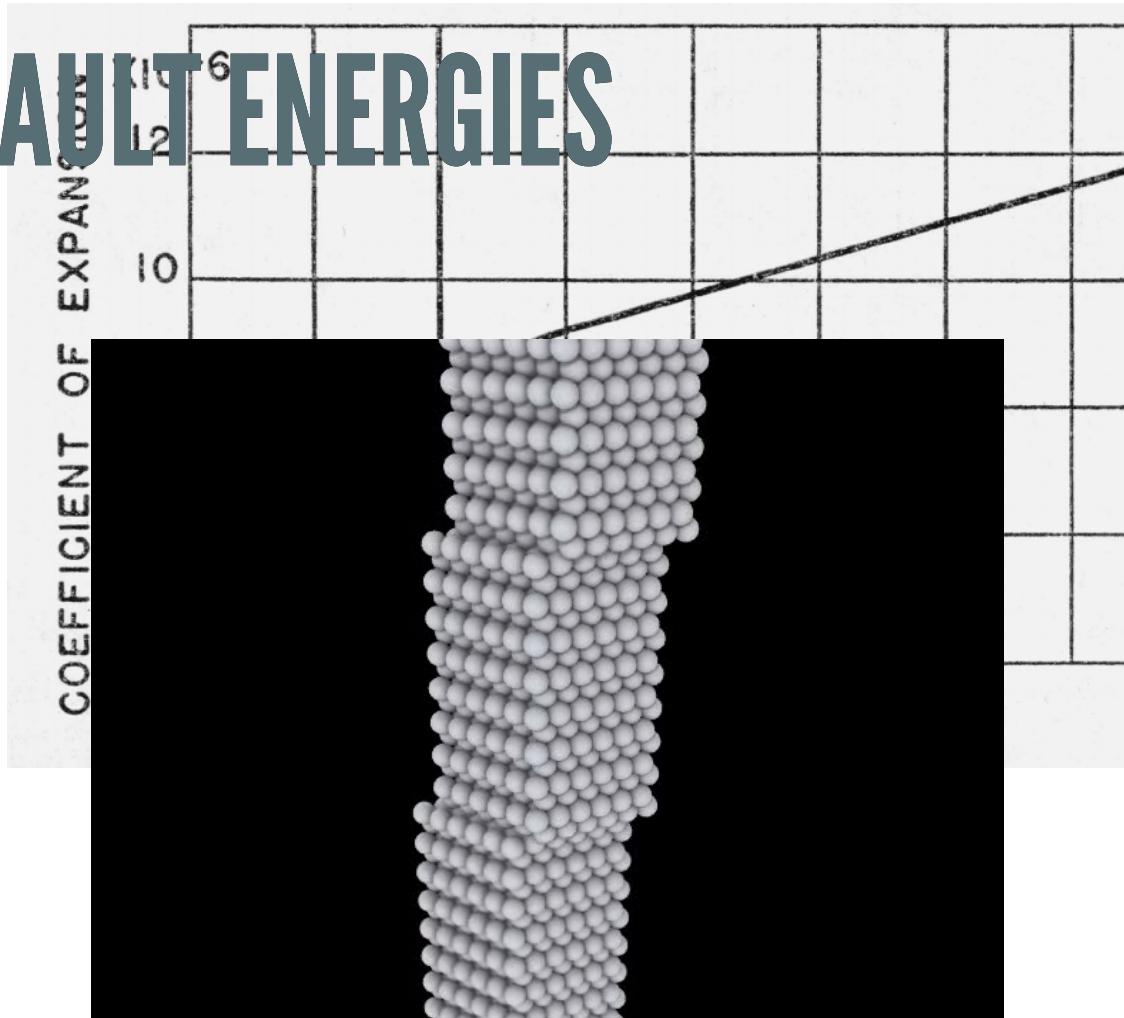


# THERMAL EXPANSION



# STACKING FAULT ENERGIES

- Excess energy of sheared slab.
- Stable stacking faults provides insight into possible dislocation dissociations.



# RESULTS

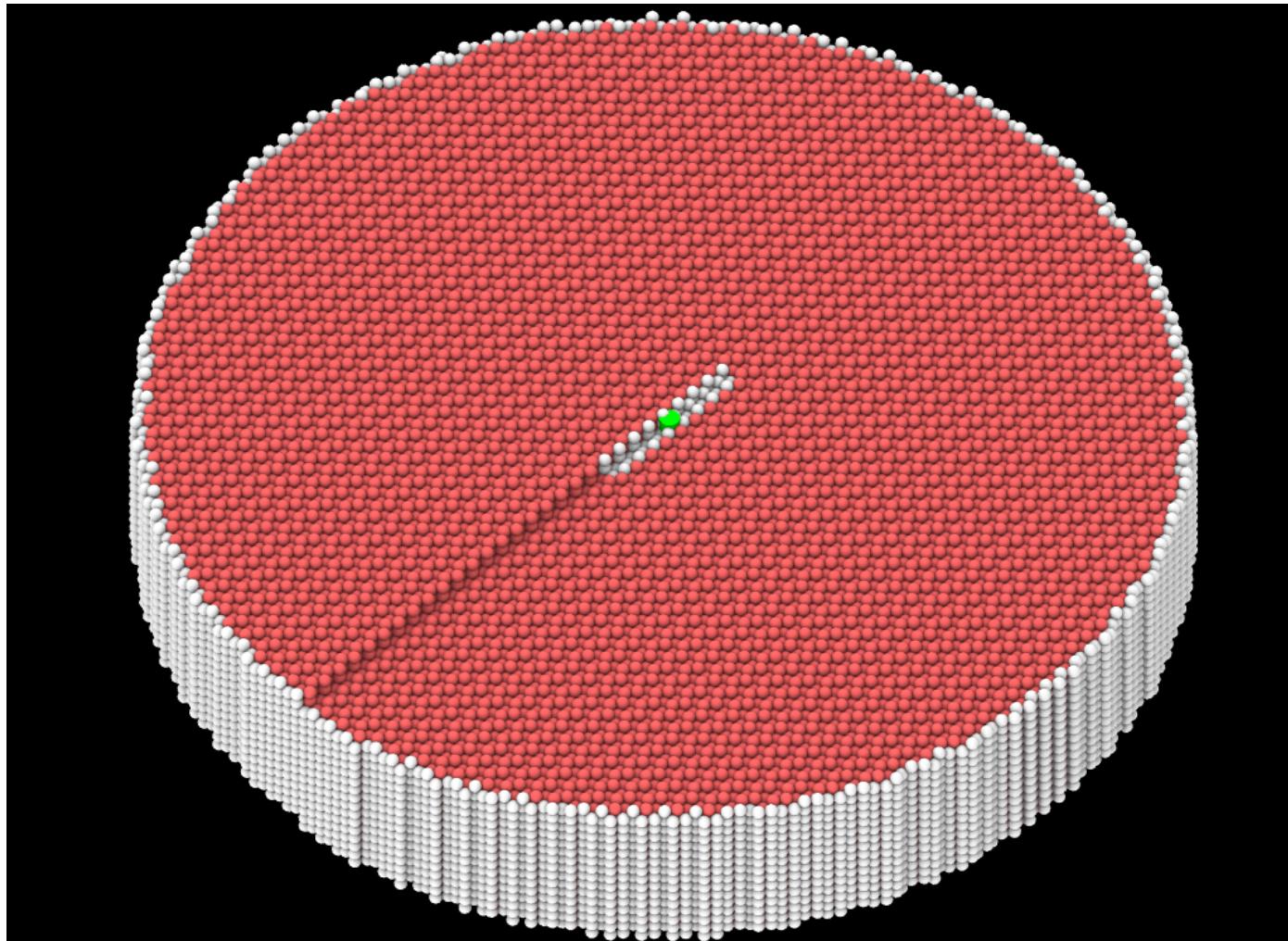
Plane	Fault	TB	DFT
Basal	$I_1$	198	148 <sup>[1]</sup>
	$I_2$	242	260 <sup>[1]</sup>
Prismatic	$\gamma_P$	45	250/233 <sup>[1,2]</sup>

- Units are in  $mJm^{-2}$ . Square brackets denote method from literature.
- [1] Benoit (2012), [2] Bere (1999)

# CORE STRUCTURES

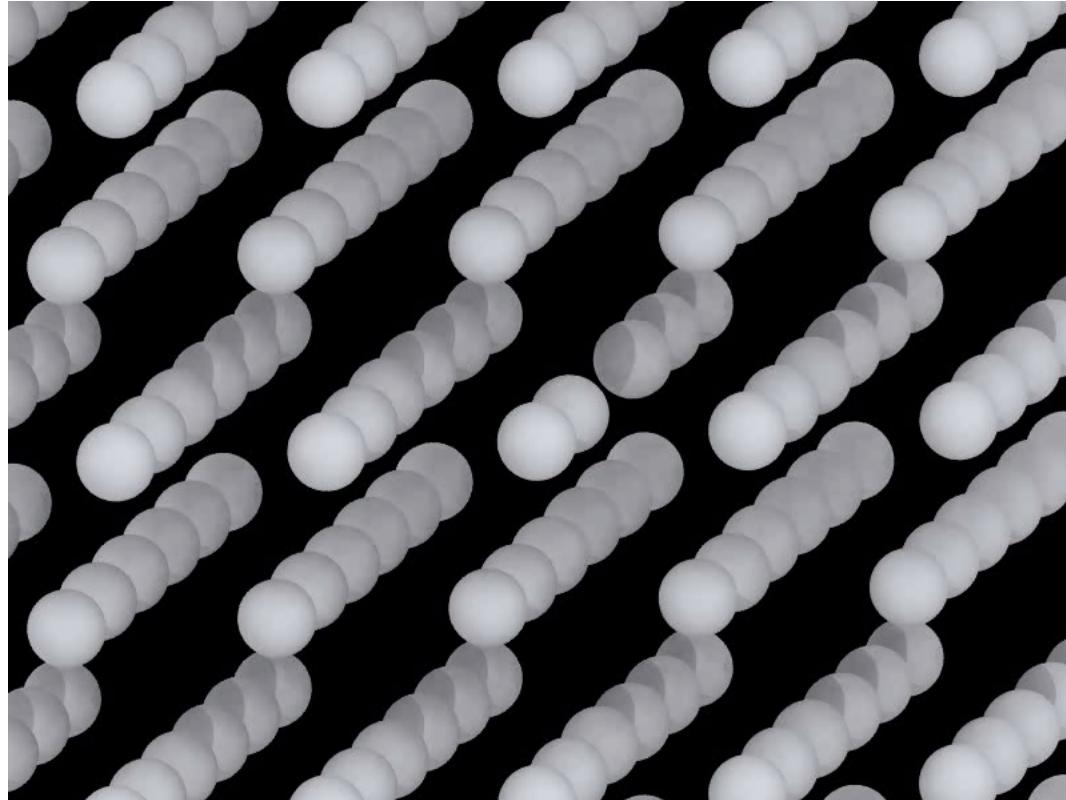
- Dislocation cores are sensitive to boundary conditions.
- Sufficient resolution of core structure is necessary to ascertain how dislocation glide is modified.

$\frac{1}{3} \langle 11\bar{2}0 \rangle$  SCREW



# **FORMATION AND DISSOLUTION ENERGIES**

# VACANCY FORMATION ENERGY



$$\Delta E_f^{\text{vacancy}}$$

[eV]

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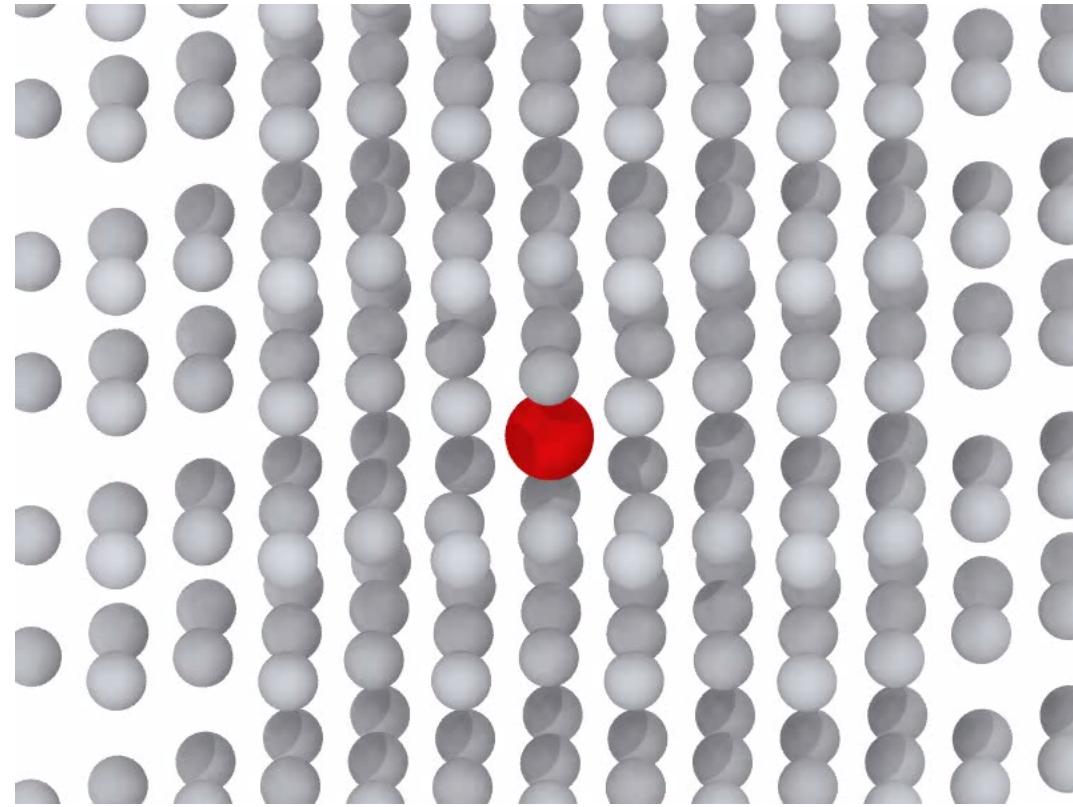
Tight Binding

2.66

GGA-DFT Trinkle (2006)

2.03

# DISSOLUTION ENERGIES



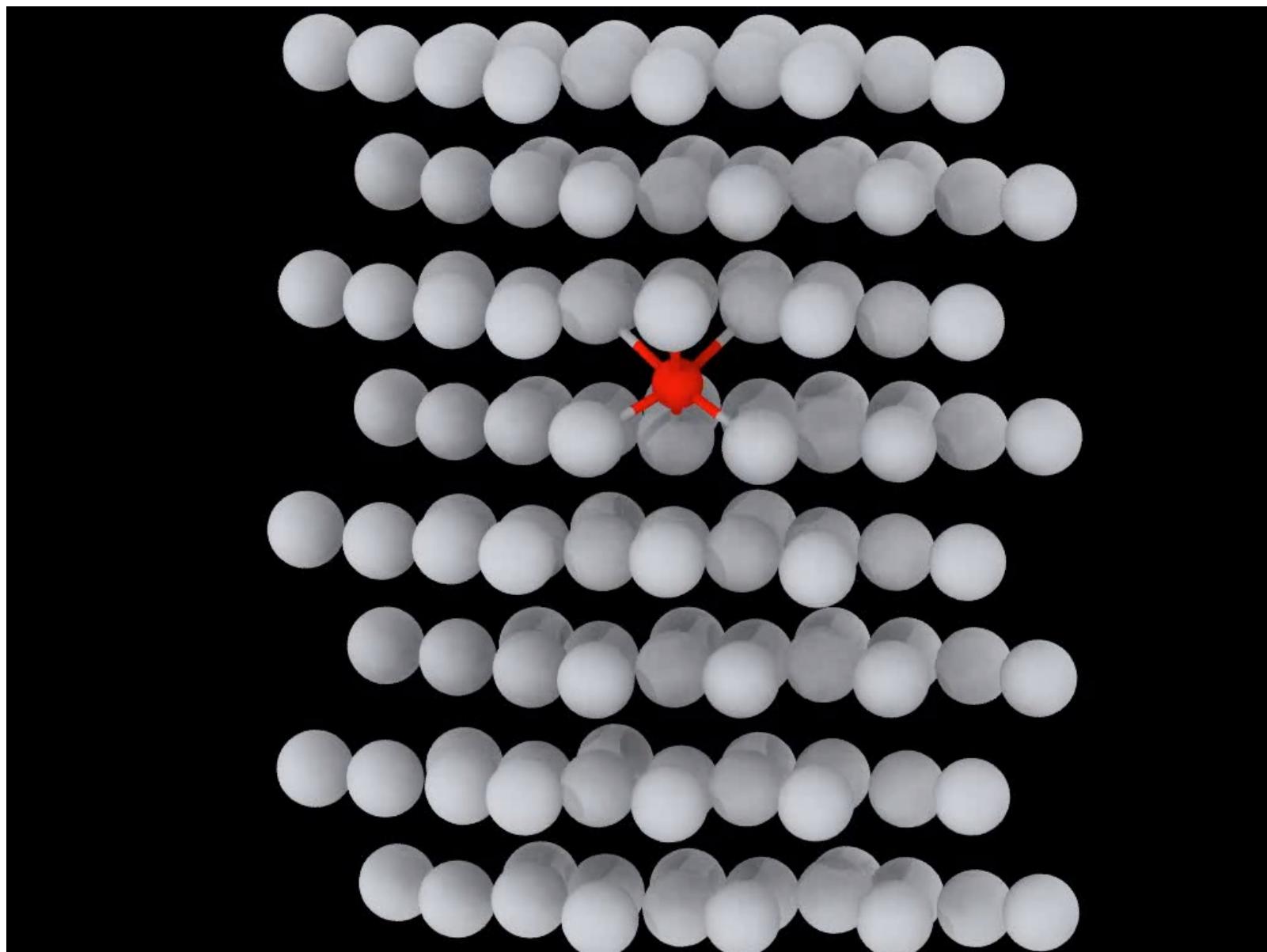
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$$\Delta E_f^{\text{solution}} (\text{Tetra.} - \text{Octa.}) \text{ [eV]}$$

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Tight Binding	1.50
GGA-DFT Kwasniak (2013)	1.23

# MOLECULAR DYNAMICS



## TIGHT-BINDING: FUTURE WORK

- Finish embedding calculations to see how core structure changes with O content.
- Calculate the Peierls barrier on prism, and  $\pi$  planes.
- Calculate secondary Peierls barrier for kink migration with and without oxygen.
- Add rutile layer. See how dislocations and oxygen interact with structure.
- Simulate high pressure Ti-H<sub>2</sub>O system.

# DEFECT CLUSTERS

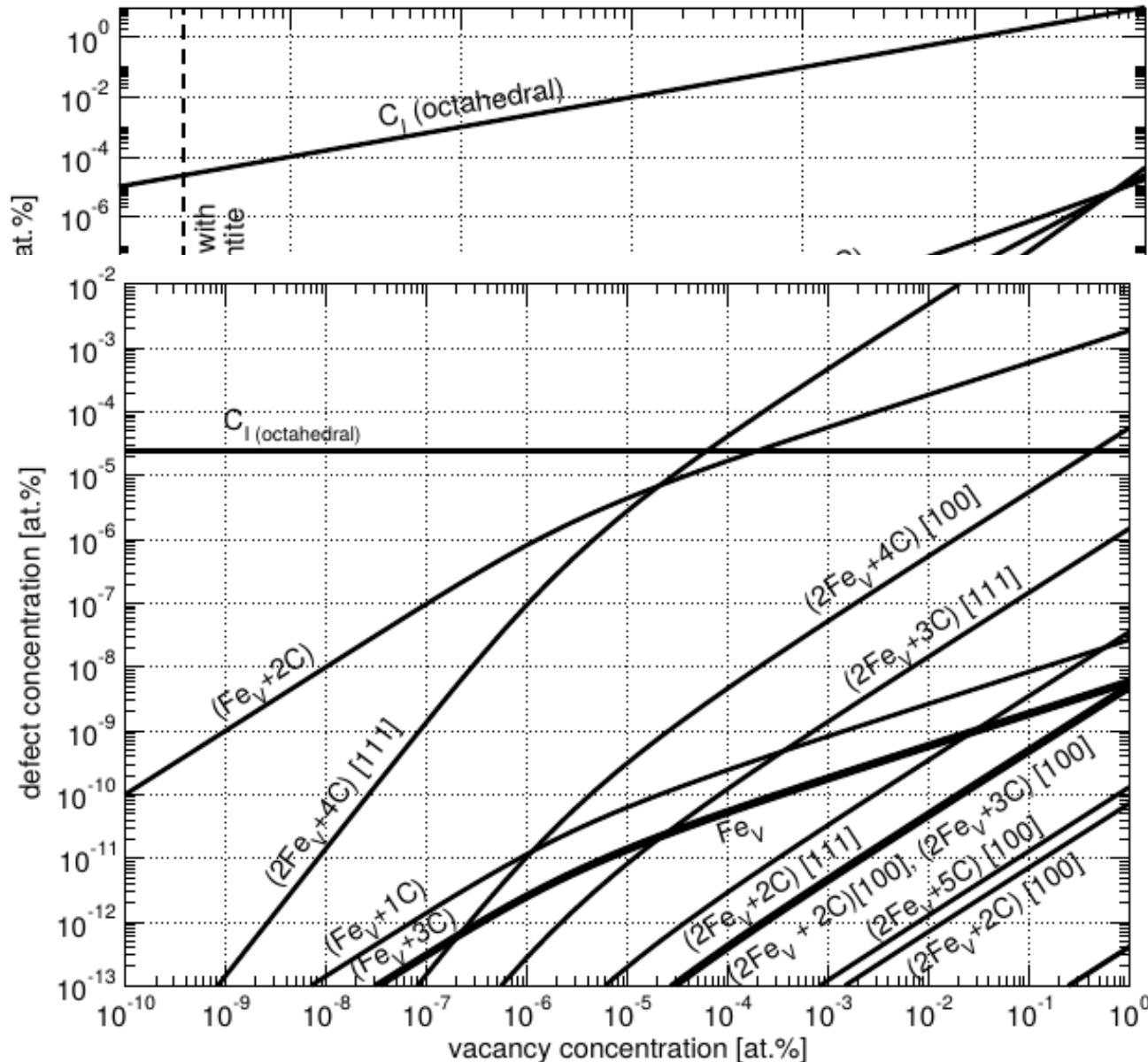
- Increase in oxygen content in Ti-7wt.%Al causes higher number density of  $\alpha_2$  precipitates at 550° C (Felicity's results).
- Oxygen acting as a defactant might stabilise defect complexes ( $Ti_V + nO$ ).
- This can cause more defects resulting in the increased number of precipitates due to more nucleation sites.
- First starting out with pure Ti and  $\alpha_2$ . Still working on extension to Ti-7wt.%Al.

## CALCULATION DETAILS

- Först *et al.* [3] calculated energetics of defect complexes with associated local force-constant matrix.
- Partial thermodynamic equilibrium imposed (thermal equilibrium for one species and not the other).
- Defect concentration plotted as a function of carbon/vacancy concentration only at 160° C.
- Extension: apply the quasiharmonic approximation/do thermodynamic integration for better accuracy at higher temperatures (550° C - 950° C).

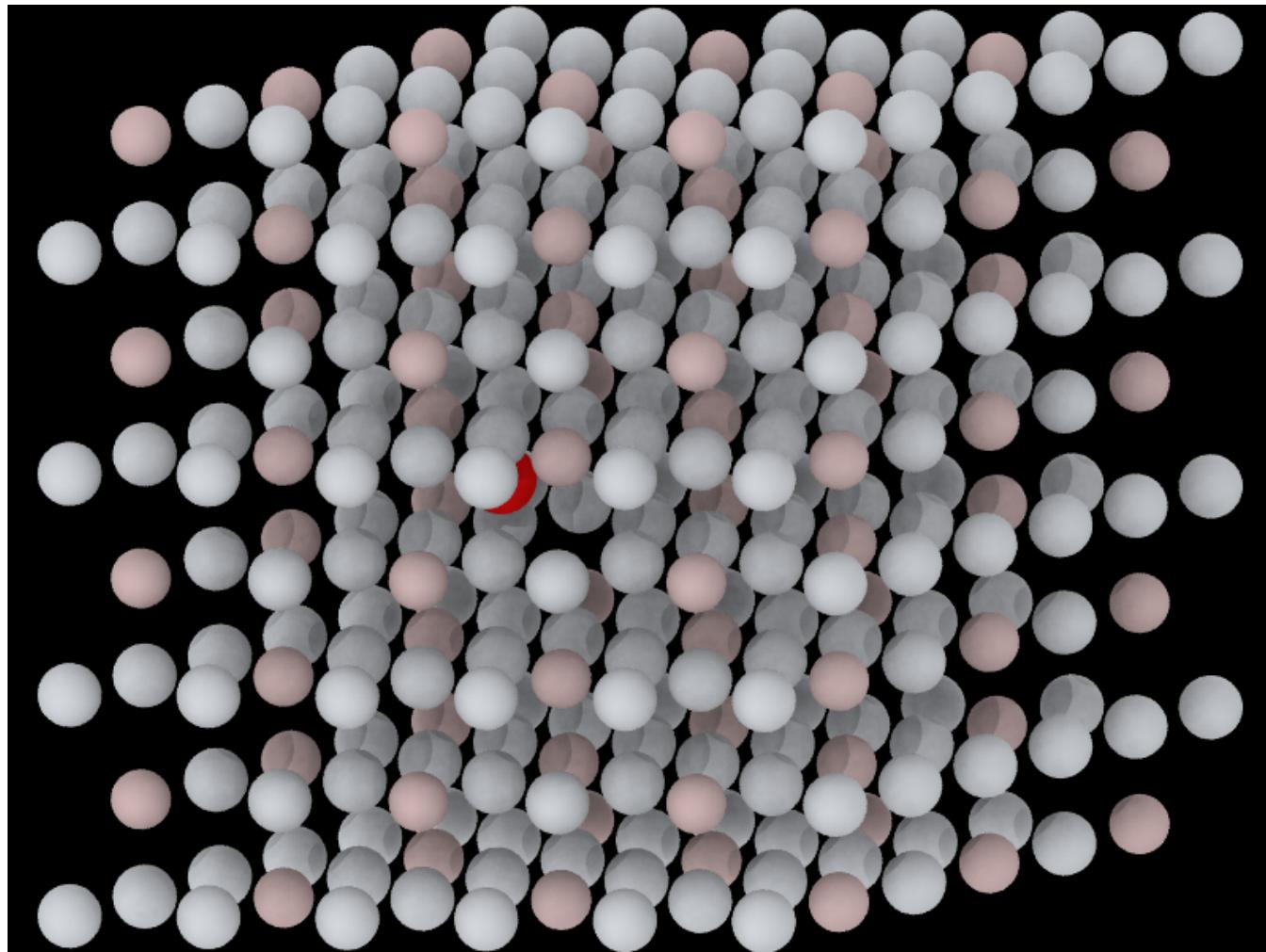
[3] *Point Defect Concentrations in Metastable Fe-C Alloys*, Först *et al*, Phys. Rev. Lett. 96, 2006

# PLOTS IN FE-C

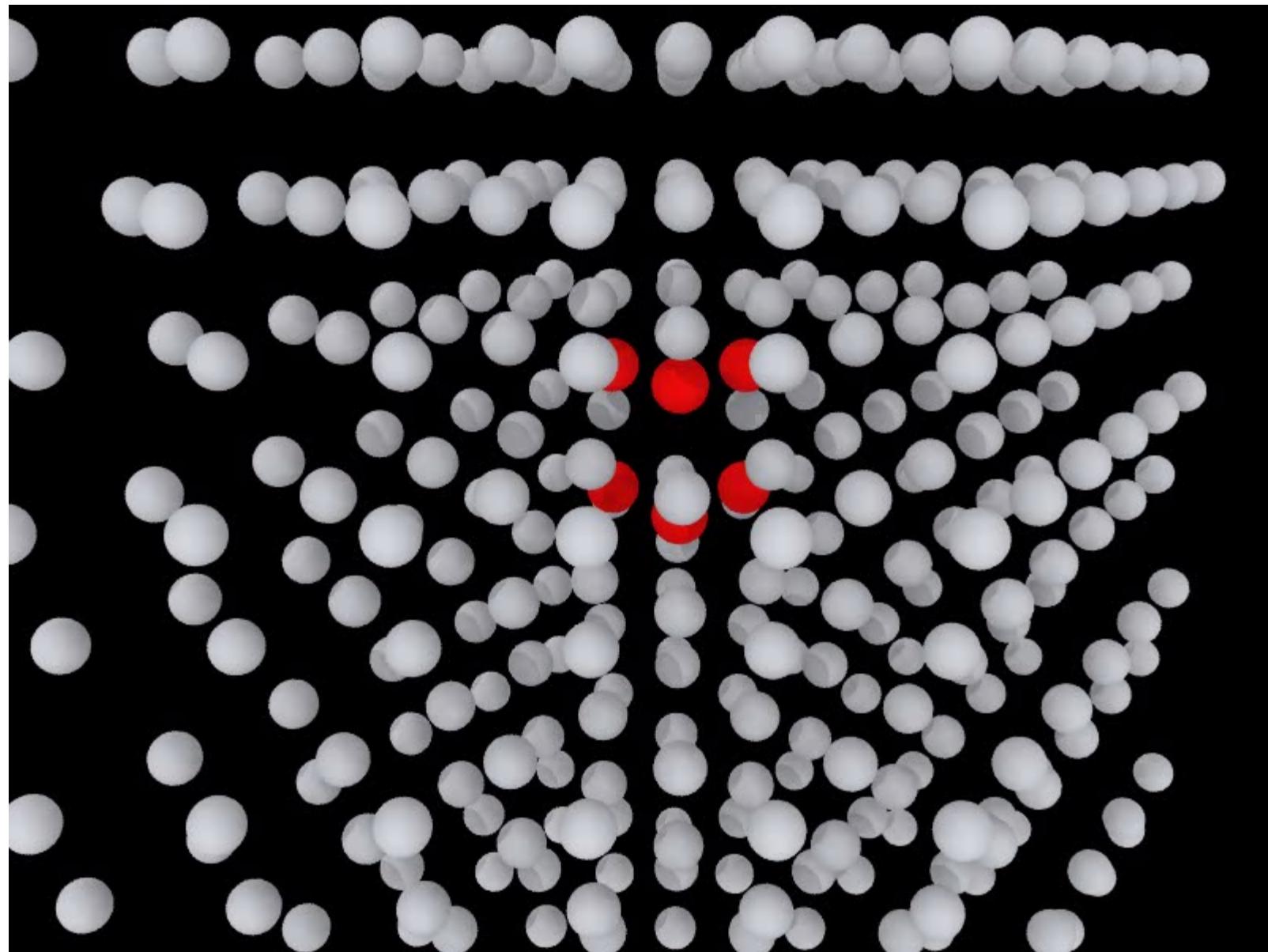




# Ti<sub>3</sub>Al CELLS



# TI CELLS



## DEFECT CLUSTERS: FUTURE WORK

- Finish Ti and  $Ti_3Al$  defect cluster calculations in DFT.
- Possibly extend to Ti-7wt%Al with SQS structures.
- See how much of an effect anharmonicity has on predictions.

# SUMMARY

- Successfully made TB model of Ti which reproduces DFT results with only d-orbitals.
- Transferable:
  - Correct energetic ordering for study of different phases.
  - Correct elastic properties and good scaling for defect simulations.
  - Integer number of electrons for charge transfer models (electrochemistry).
- BOP formulation produces similar results with only linear scaling.
- Embedding calculations should resolve single dislocation core ground-state at realistic O concentrations.
- To do: Embed O-disl, Ti/TiO<sub>2</sub> interface, defect clusters.