Tight-binding investigation of oxygen solute hardening in Ti.

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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.
- Corrosion resistance, high strength to weight ratio.
- Ti is used in commercial jet airliners

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.

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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. TiO_2 and bulk Ti)

Invariance theorem with green's function approaches. So good with boundary conditions.

Parameter Optimisation

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

Results of optimisation.

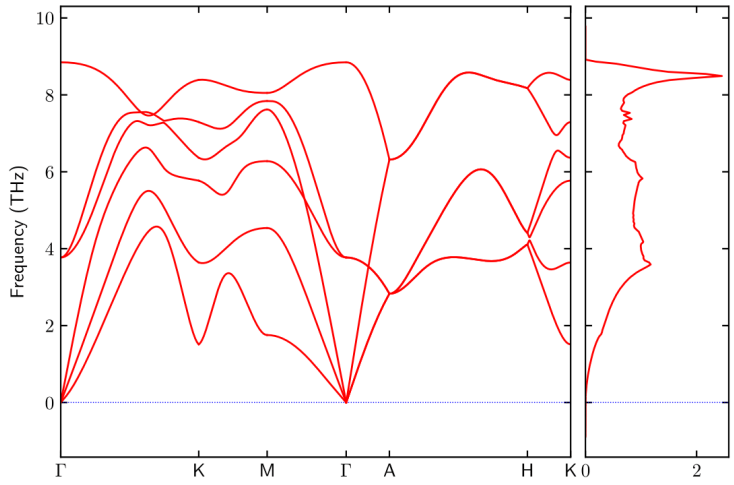
Quantity	TB	target (DFT + empirical)
a_α [bohr]	5.585	5.577
$(c/a)_\alpha$	1.583	1.587
C_{11} [GPa]	171.6	176.1
C_{33} [GPa]	198.9	190.5
C_{44} [GPa]	47.4	50.8
C_{12} [GPa]	94.7	86.9
C_{13} [GPa]	61.2	68.3
a_ω [bohr]	8.93	8.73
c_ω [bohr]	5.39	5.32
a_β [bohr]	6.20	6.18
Γ bandwidth [Ryd]	3.70	5.87

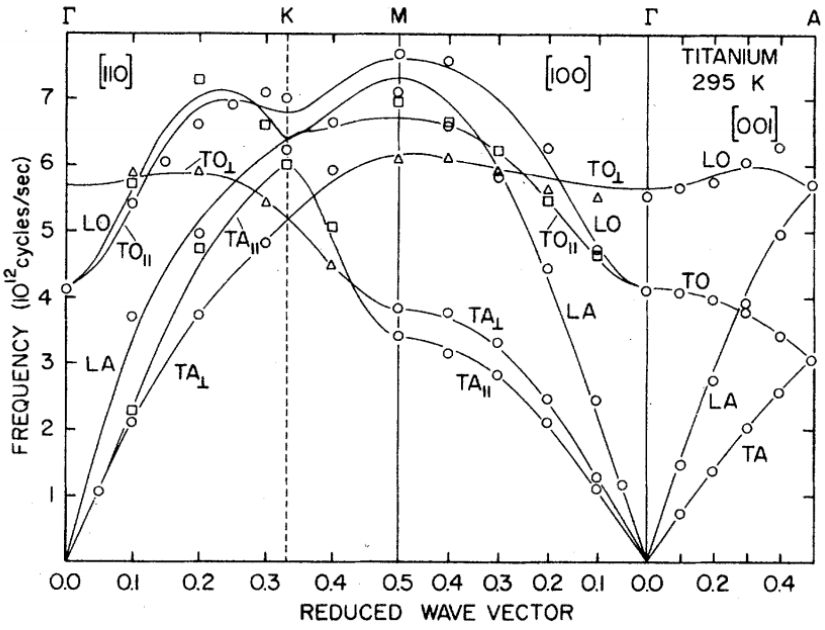
Energy Splittings

Quantity	TB	target
$\Delta E(\omega - \alpha)$ [mRyd]	0.53	-0.73
$\Delta E(4\mathrm{H} - \alpha)$ [mRyd]	1.58	3.17
$\Delta E(6\mathrm{H} - \alpha)$ [mRyd]	2.48	3.72
$\Delta E(\mathrm{fcc} - \alpha)$ [mRyd]	3.78	4.52
$\Delta E(\beta - \alpha)$ [mRyd]	5.35	7.64

Phonon Spectra

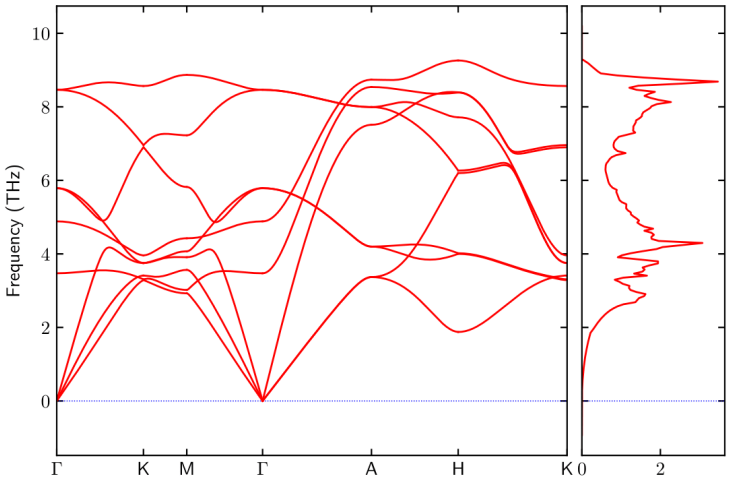
α phase

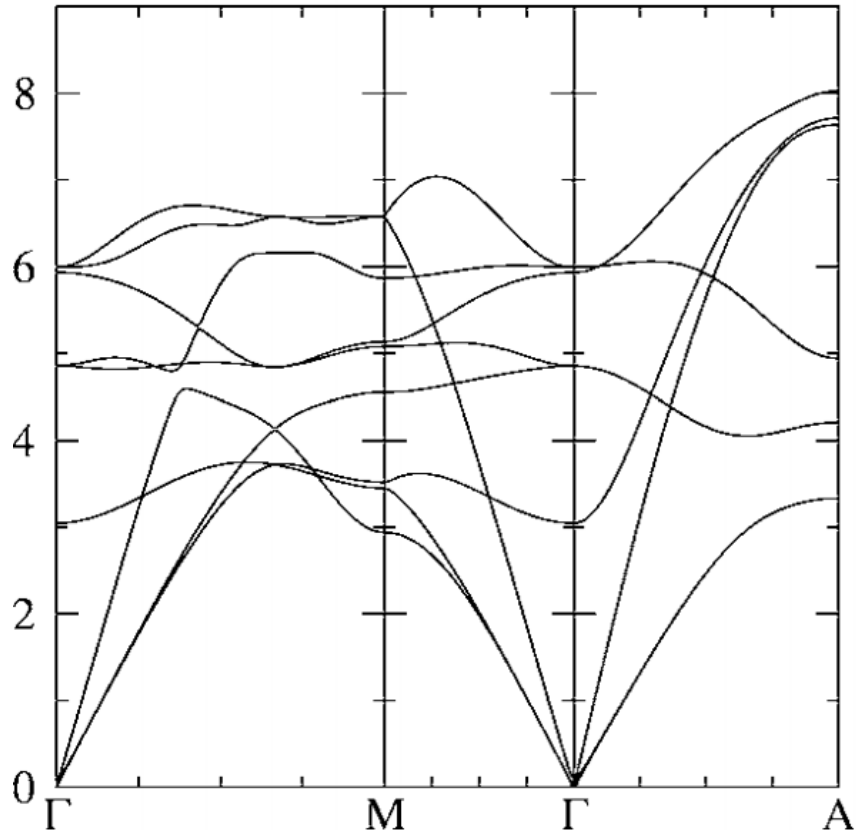




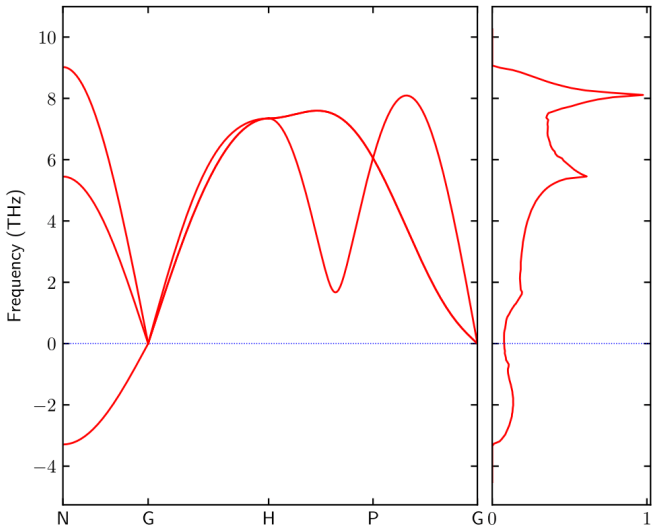
All frequencies are in THz

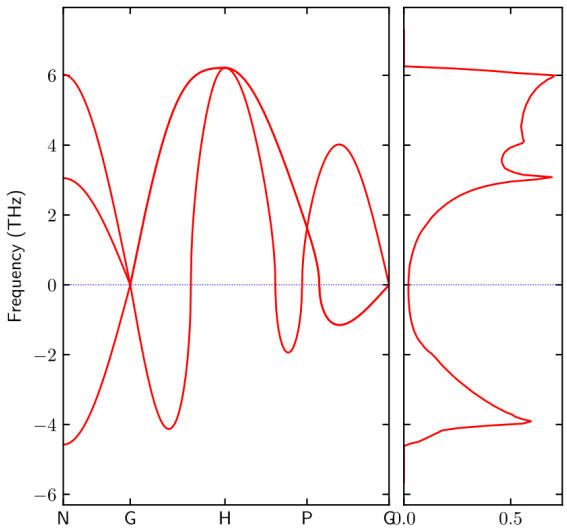
ω phase




8
6
4
2
0
Γ
M
Γ
A

β phase

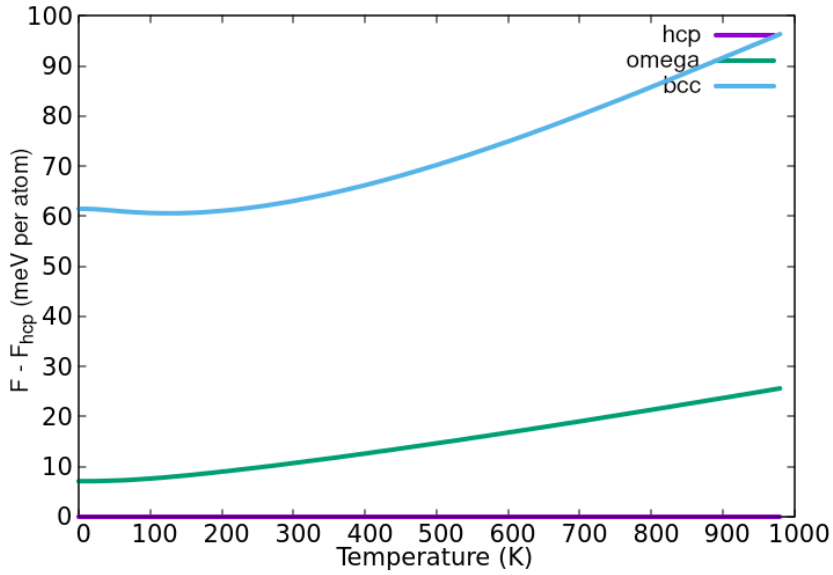

Frequency (THz)
10
8
6
4
2
0
−2
−4
N
G
H
P
G
0
1

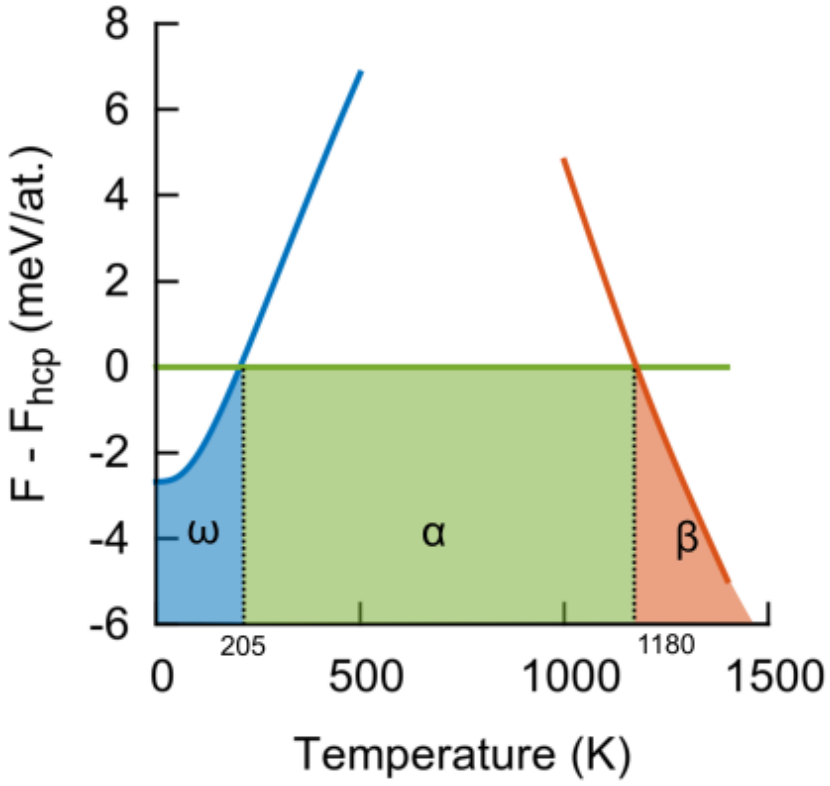

Frequency (THz)
6
4
2
0
−2
−4
−6
N
G
H
P
G
0.0
0.5

Free Energies

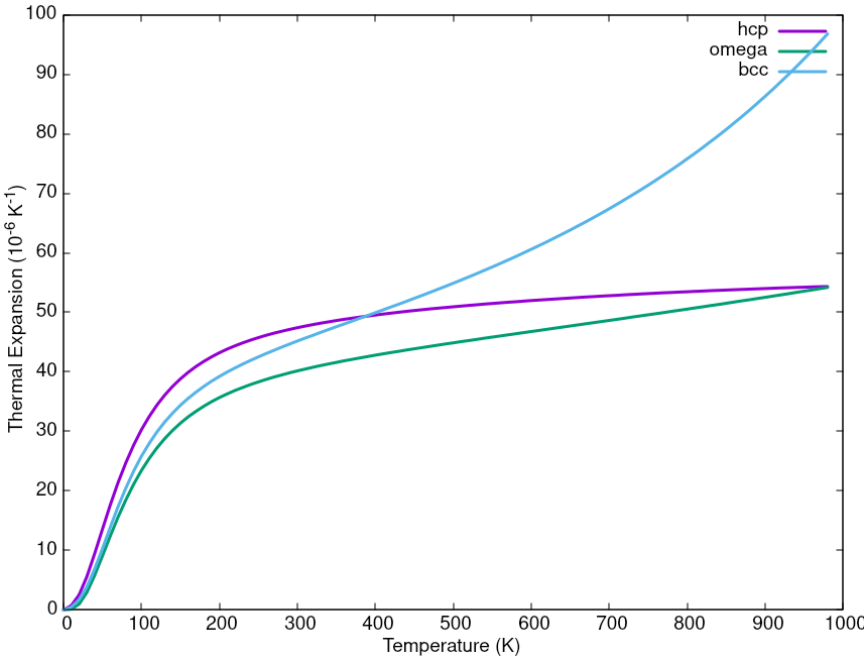
- To find predicted stability of each phase as a function of temperature, one can use the quasi-harmonic approximation.
- One finds the volume dependence of the energy, from which we can convert the Helmholtz free energy into the Gibbs free energy.

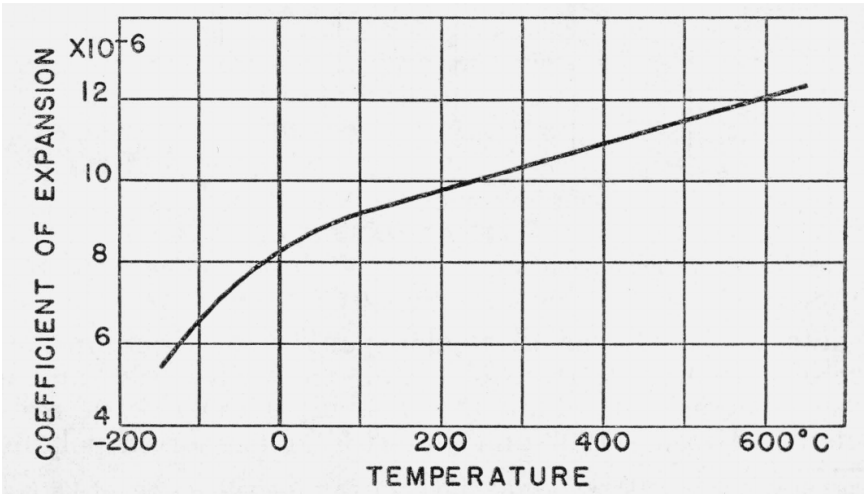
Gibbs Free Energy




8
6
4
2
0
-2
-4
-6
F - F$_{hcp}$ (meV/at.)
ω
α
β
205
1180
0
500
1000
1500
Temperature (K)

Thermal Expansion



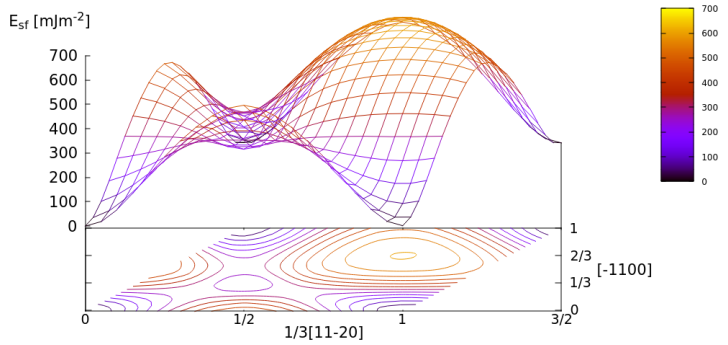


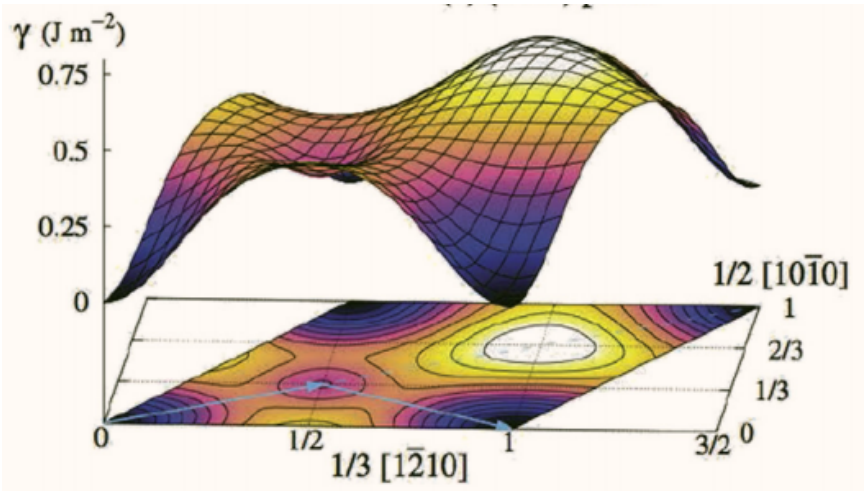
Gamma Surfaces

- γ -surfaces are plots of excess energy with the movement of atoms on a fault plane.

- Stable stacking faults correspond to local minima.
- This provides insight into possible dislocation dissociations.

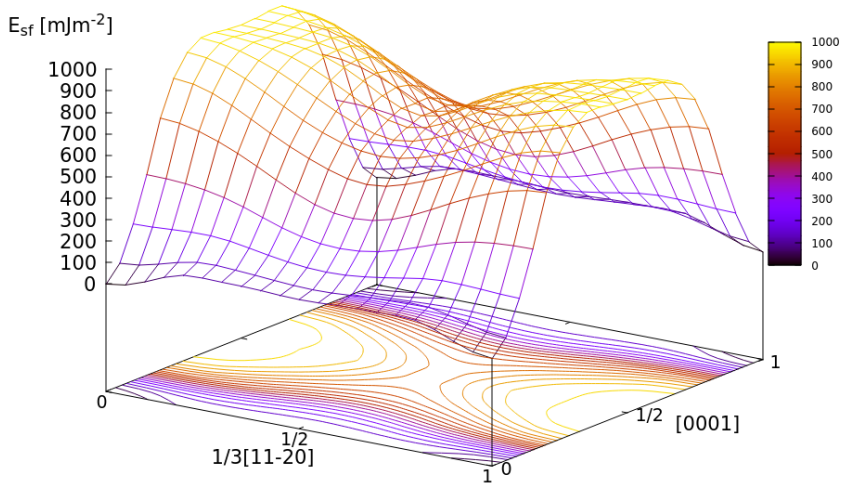
Basal gamma surfaces

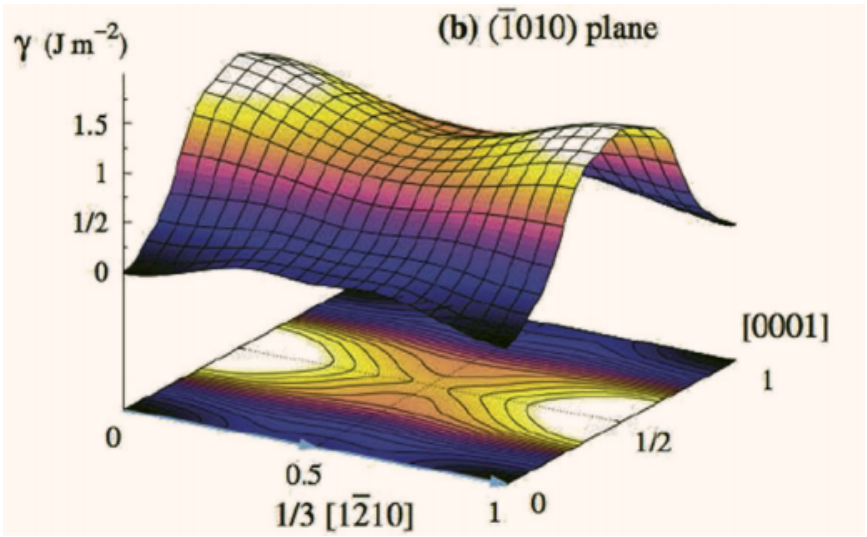




Expected splitting (all models): $\frac{1}{3}[1\bar{2}10] = \frac{1}{3}[1\bar{1}00] + \frac{1}{3}[0\bar{1}10]$

Prismatic gamma surfaces

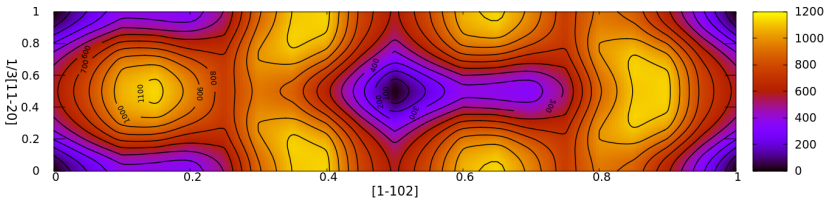




- Expected splitting (all models): $\frac{1}{3}[1\bar{2}10] = \frac{1}{6}[1\bar{2}10] + \frac{1}{6}[1\bar{2}10]$

From TB one can see that the splitting is immediately not exactly the same as that of DFT.

Pyramidal gamma surfaces



One can see a saddle point in the interatomic potential and the tb model. So one can assume that this is a point which relies on subtle electronic structure methods. Like the prismatic splitting above.

Results

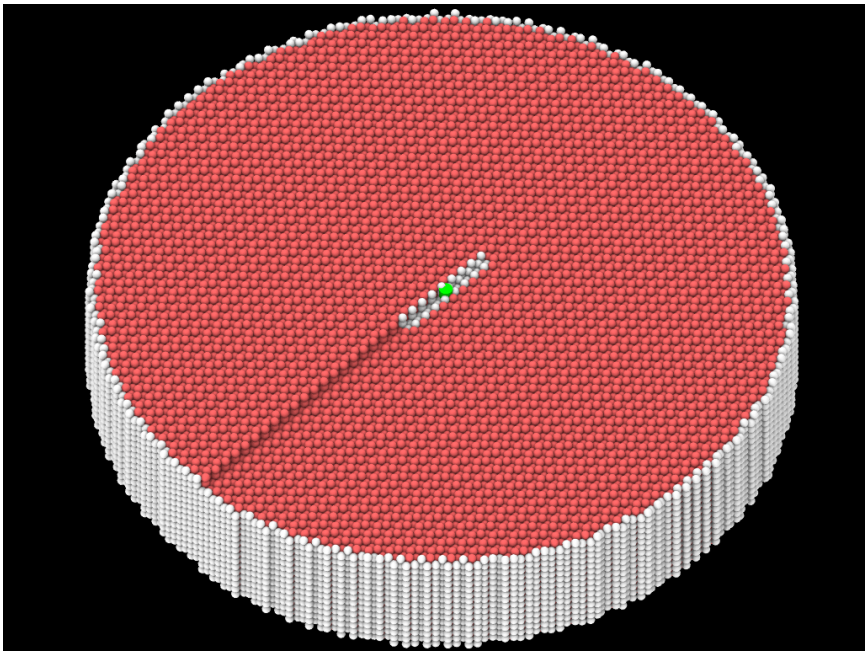
Plane	Fault	TB	[DFT]	[TB]
Basal	I_2	212	260 [1]	290 [2], 110 [3]
Prismatic	γ_P	98	250[1] 233[4]	110[5] , 260[3]
Pyramidal	I_1	332	288 [6]	–
	I_2	737	788 [6]	–

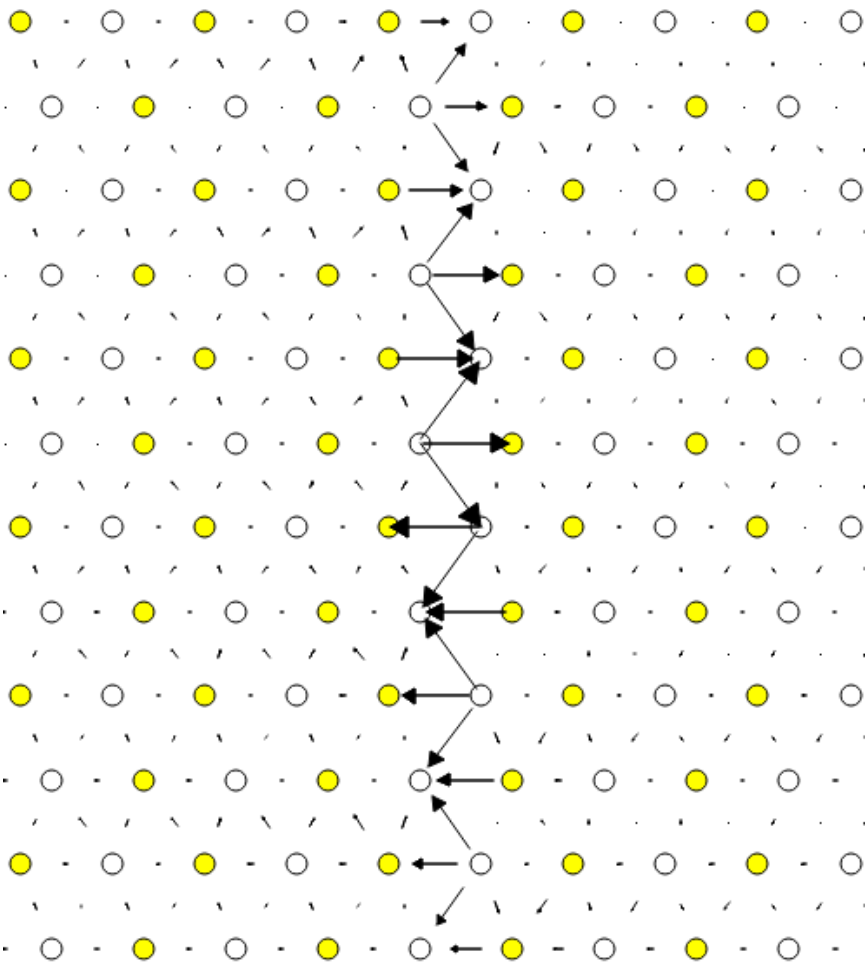
- Units are in mJm^{-2}. Square brackets denote method from literature.
- [1] Benoit (2012), [2] Bere (1999), [3] Girshick (1998)
- [4] Ackland (1992), [5] Legrand (1984), [6] Ready (2019), [7] Chaari (2014)

Core structures

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

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



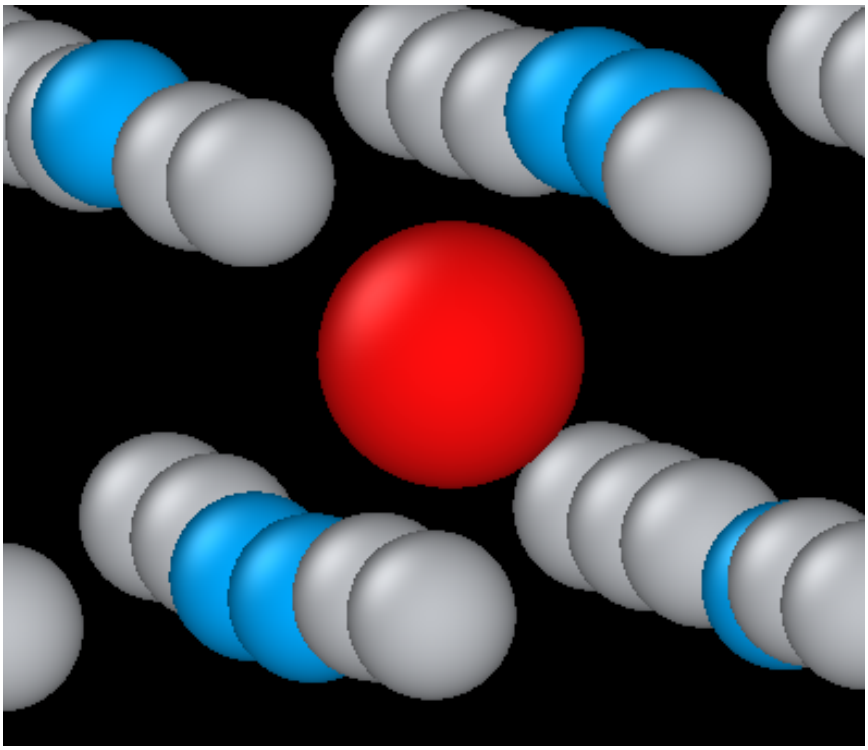

(a)
DFT
MEAM
(b)

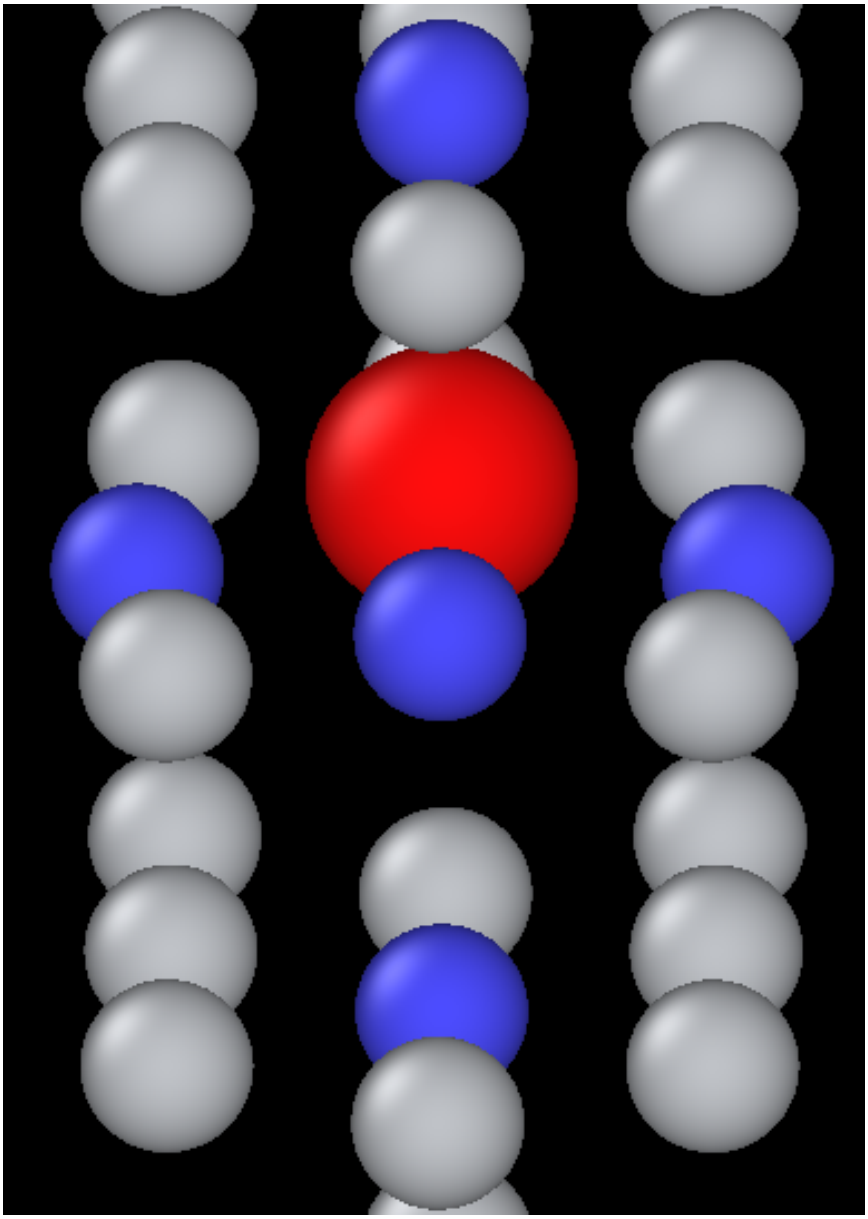
Formation and Dissolution energies

Vacancy formation Energy

$\Delta E_{\mathrm{f}}^{\mathrm{vacancy}}$	[eV]
Tight Binding	2.34
GGA-DFT Trinkle (2006)	2.03
GGA-DFT Connetable (2011)	1.97
Exp. Hashimoto (1984)	1.27

Dissolution Energies





$\Delta E_{\mathrm{f}}^{\mathrm{solution}}$(Tetra. − Octa.)	[eV]
Tight Binding	1.60
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 π 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_2O system.

Defect Clusters

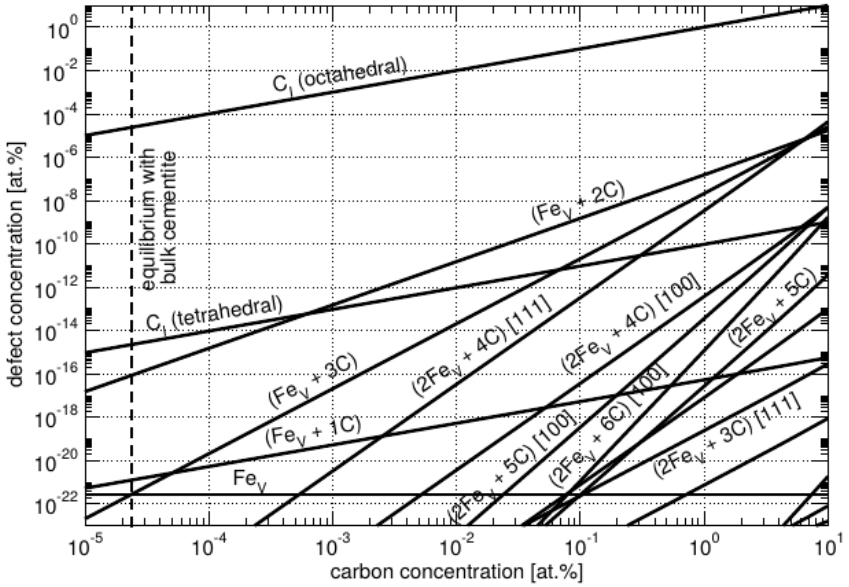
- Increase in oxygen content in Ti-7wt.%Al causes higher number density of α_2 precipitates at 550° C (Felicity's results).
- Oxygen acting as a defactant might stabilise defect complexes (Ti_v + nO).
- This can cause more defects resulting in the increased number of precipitates due to more nucleation sites.
- First starting out with pure Ti and α_2. Still working on extension to Ti-7wt.%Al.

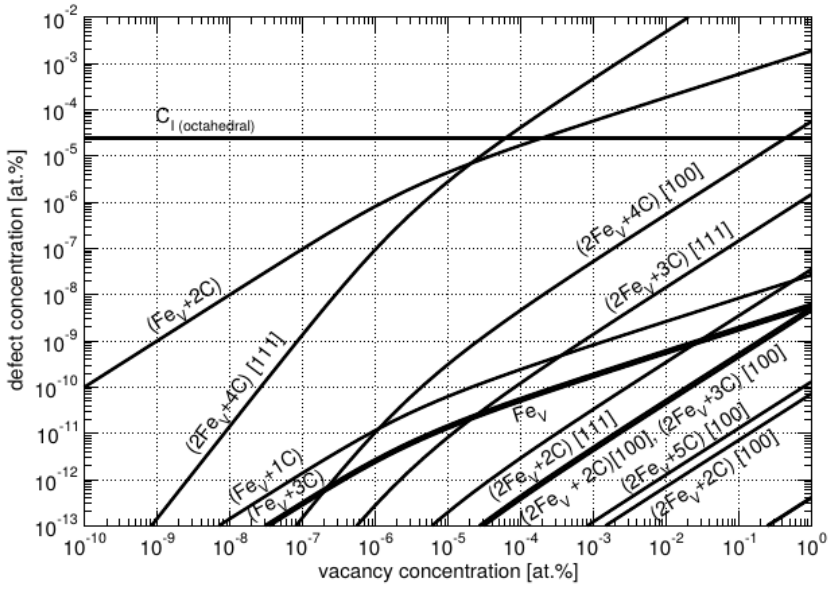
Calculation Details

- Först *et al.* [6] 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).

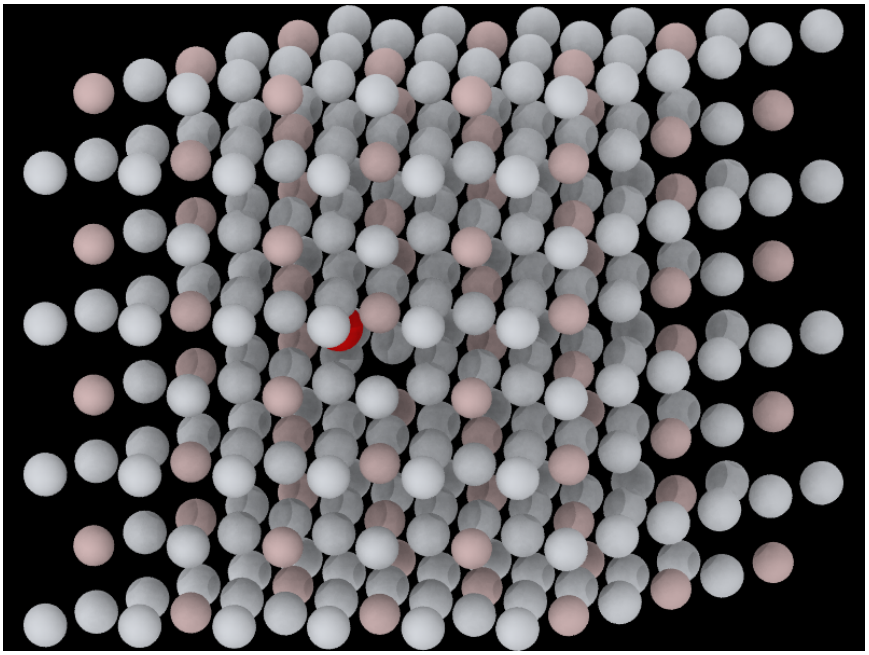
[6] *Point Defect Concentrations in Metastable Fe-C Alloys*, Först *et al*, Phys. Rev. Lett. 96, 2006

Plots in Fe-C





Ti_3Al 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.

Additional references

- Ghazisaeidi, Trinkle (2012), *Core structure of a screw dislocation in Ti from density functional theory and classical potentials.*
- Rodney, Ventelon (2016), *Ab initio modelling of dislocation core properties in metals and semiconductors.*
- Chaari, Clouet (2014), *First order pyramidal slip of 1/3 screw dislocations in zirconium*