Atomic scale stress corrosion cracking of Ti alloys.

Tigany Zarrouk*

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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.

*tigany.zarrouk@kcl.ac.uk

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: genetic and particle swarm.
- More optimisation necessary. Interim model used for simulations.
- Similar tests can improve the optimisation procedure such that parameters are not overfit to training data.

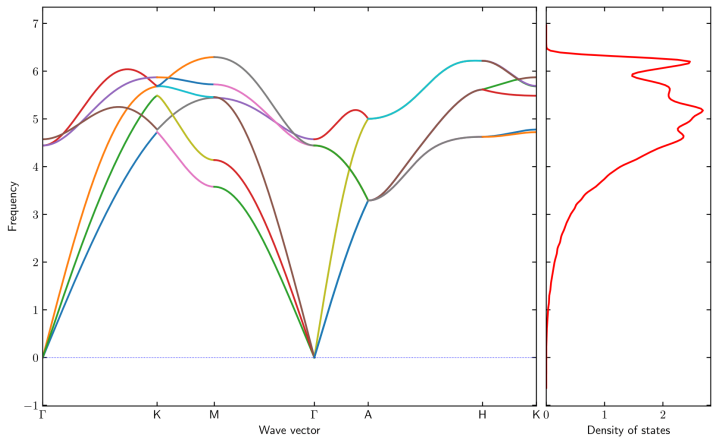
Results of optimisation.

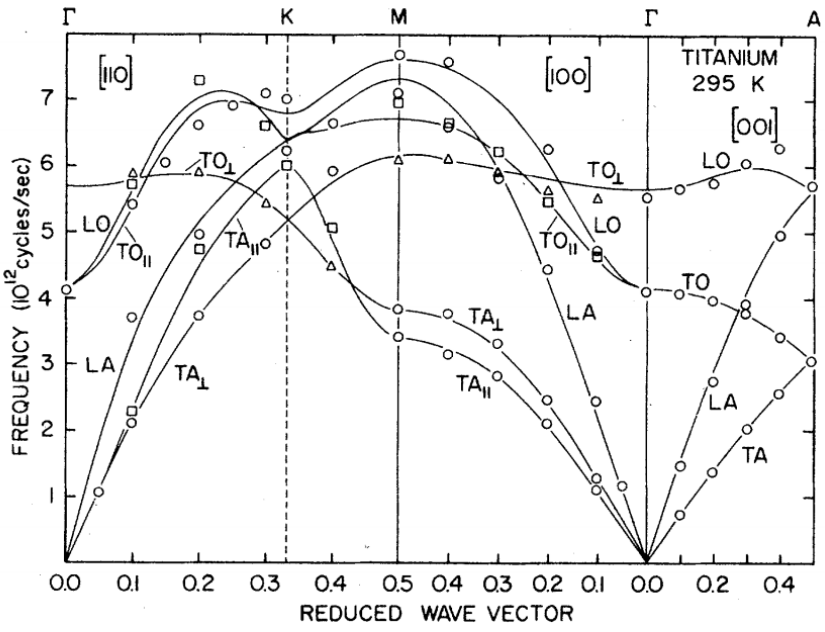
Quantity	TB	BOP	target
a_α [bohr]	5.42	5.20	5.57
c_α [bohr]	8.72	9.15	8.85
C_{11} [GPa]	221.8	218.1	176.1
C_{33} [GPa]	194.2	263.4	190.5
C_{44} [GPa]	58.6	-8.5	50.8
C_{12} [GPa]	71.4	93.6	86.9
C_{13} [GPa]	60.0	54.4	68.3
a_ω [bohr]	8.50	8.34	8.73
c_ω [bohr]	5.27	5.30	5.32
a_β [bohr]	5.92	–	6.17
$\Delta E(\omega - \alpha)$ [mRyd]	5.16	14.34	-0.73
bandwidth [Ryd]	0.41	–	0.42

- BOP difference is probably due to the fact that bond integrals are not exactly the same due to approximate methods.
- Pair potential can be tweaked once the right TB model has been found.
- Energy difference between omega and alpha phase is different.
- nrec = 5

Phonon Spectra

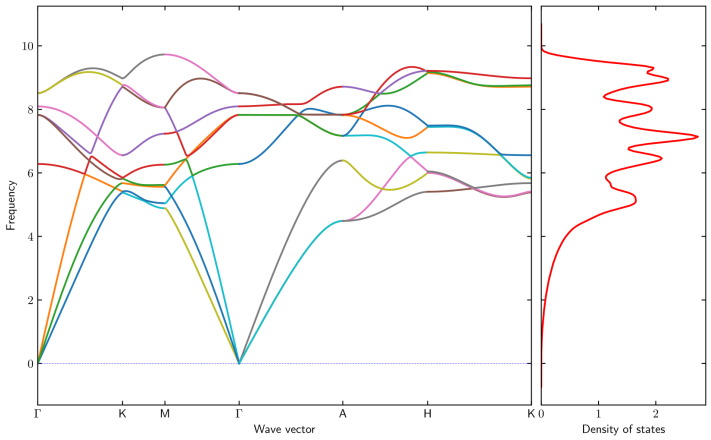
α phase

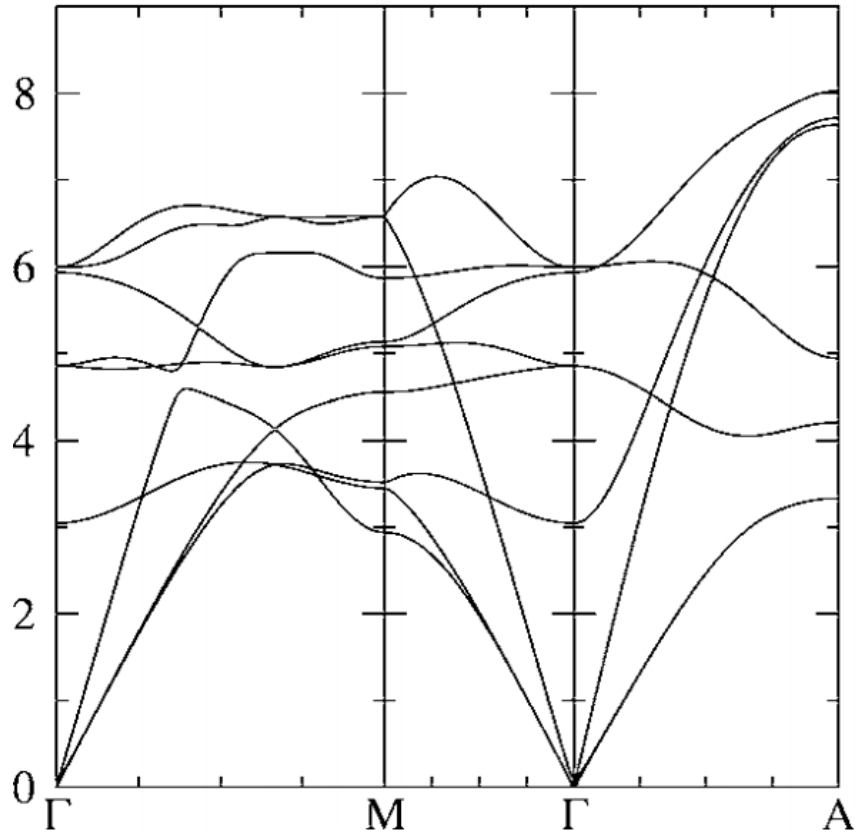




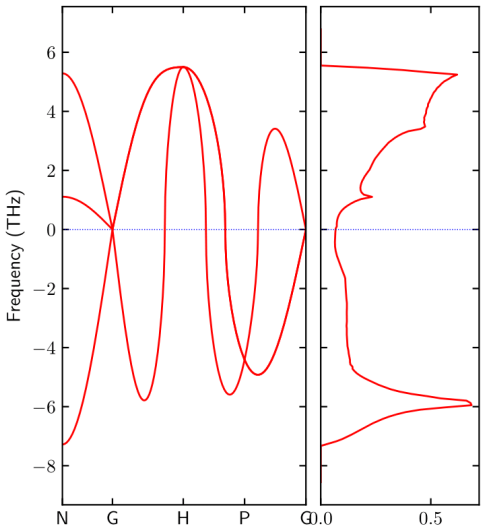
All frequencies are in THz

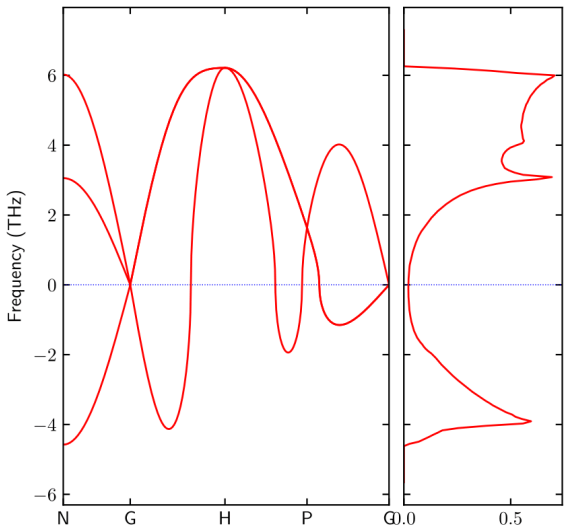
ω phase


Frequency
10
8
6
4
2
0
Γ
K
M
Γ
A
H
K
Wave vector
0
1
2
Density of states


8
6
4
2
0
Γ
M
Γ
A

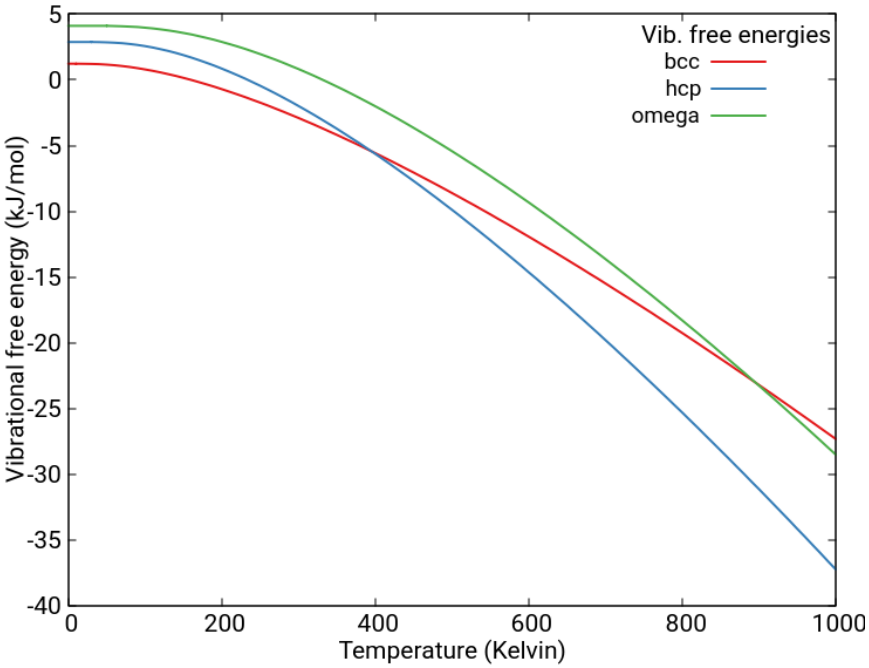
β phase

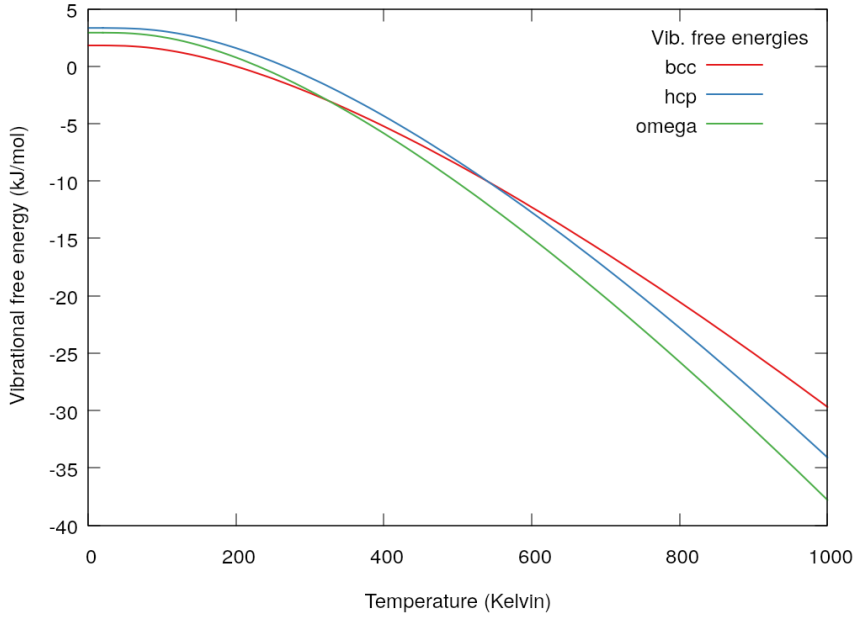

Frequency (THz)
6
4
2
0
−2
−4
−6
−8
N
G
H
P
G
0.0
0.5


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

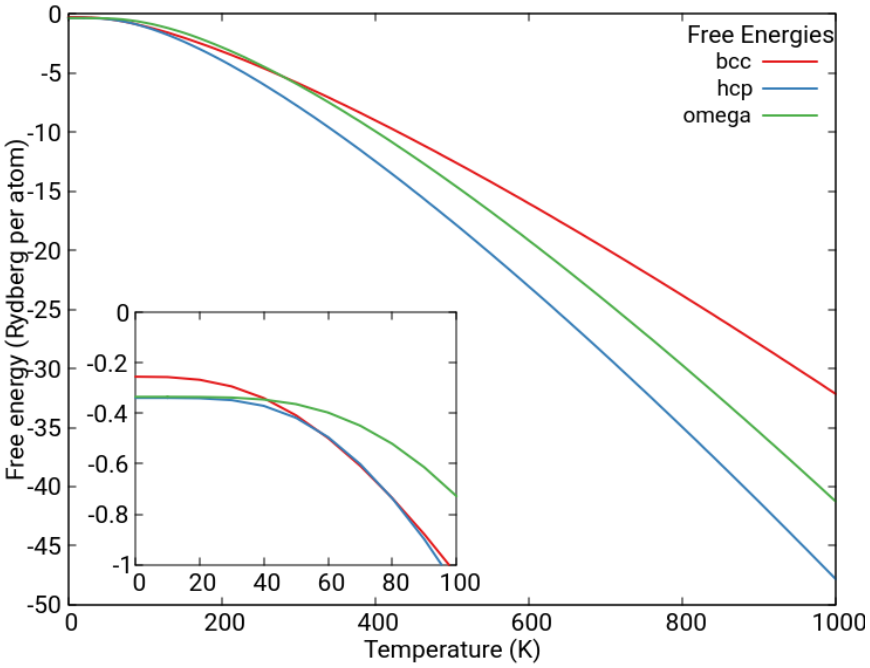
Free Energies

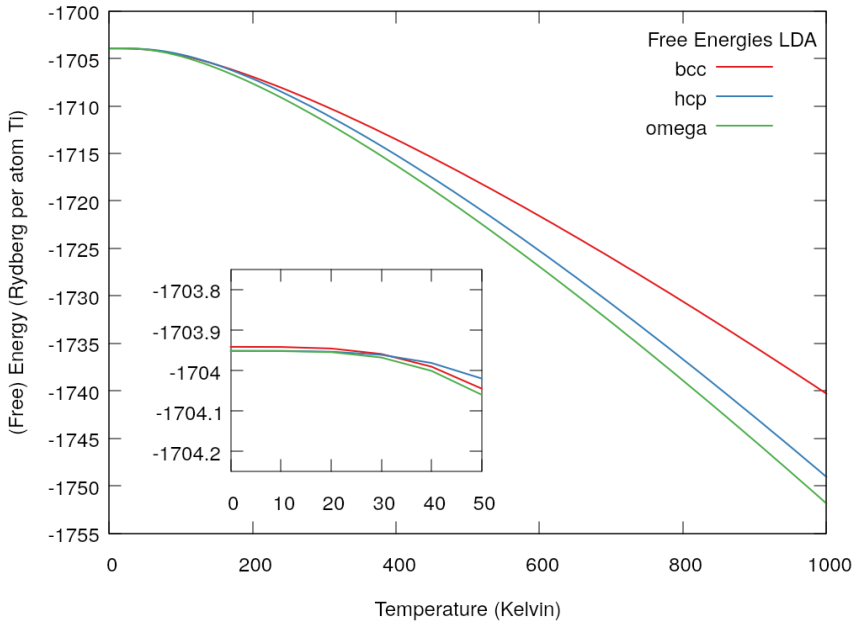
Vibrational Free Energy





Total Free Energy





Free energy contribution from soft phonon modes don't contribute alot to the free energy, hence why at the larger temperatures the bcc phase does not dominate.

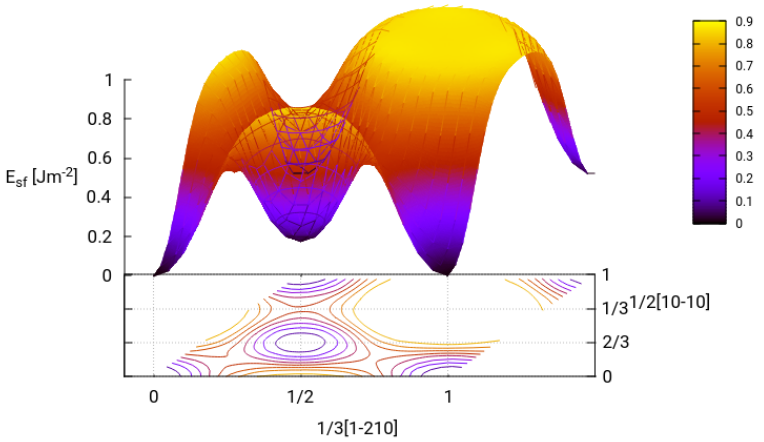
bcc is not favoured and then at around 55-80K it is favoured marginally compared to the hcp structure. After this the hcp structure is favoured with bcc again becoming the one least favourable.

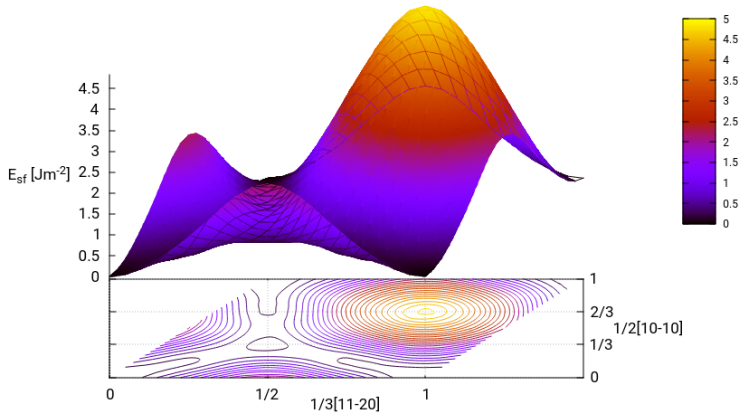
hcp is always more stable than omega in this temperature range.

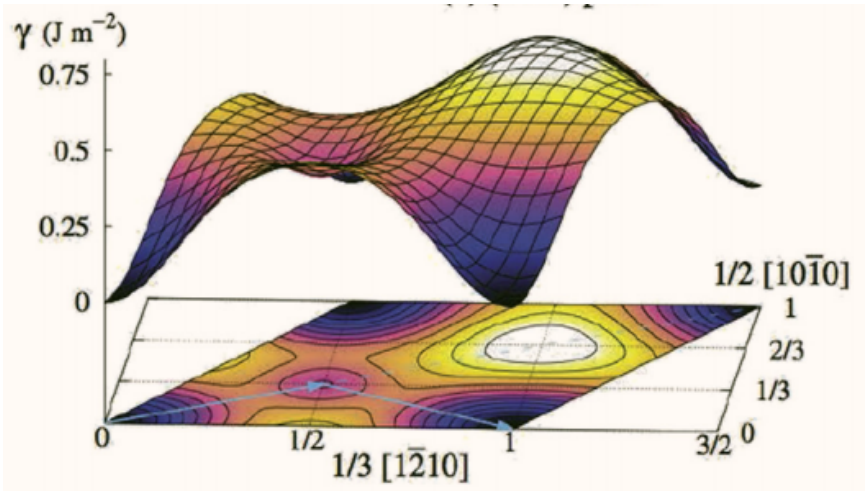
Gamma Surfaces

- 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

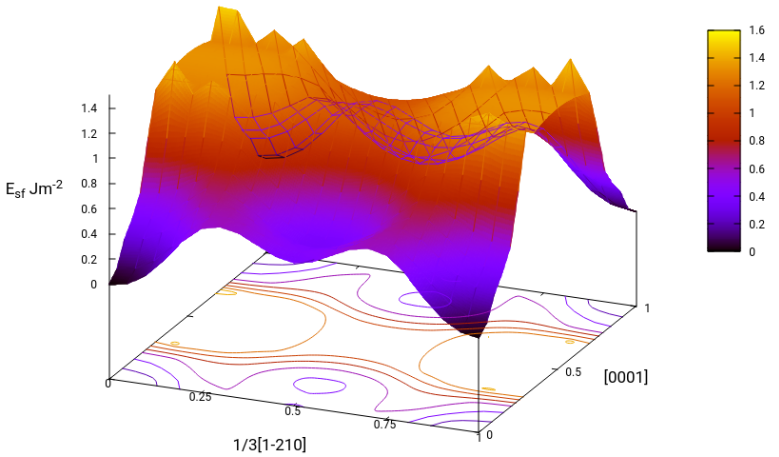


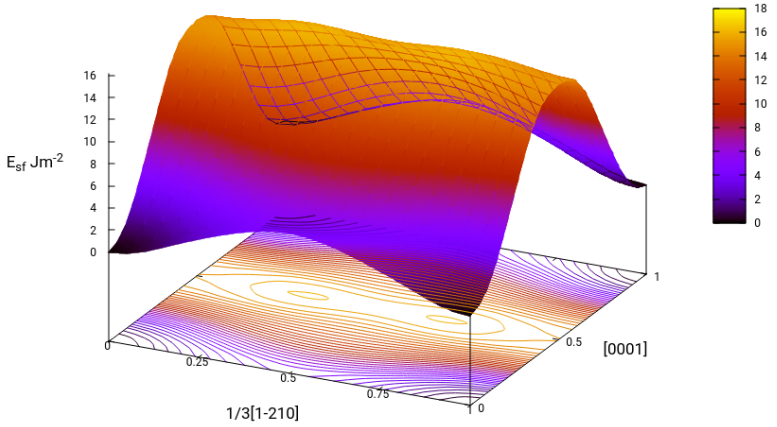


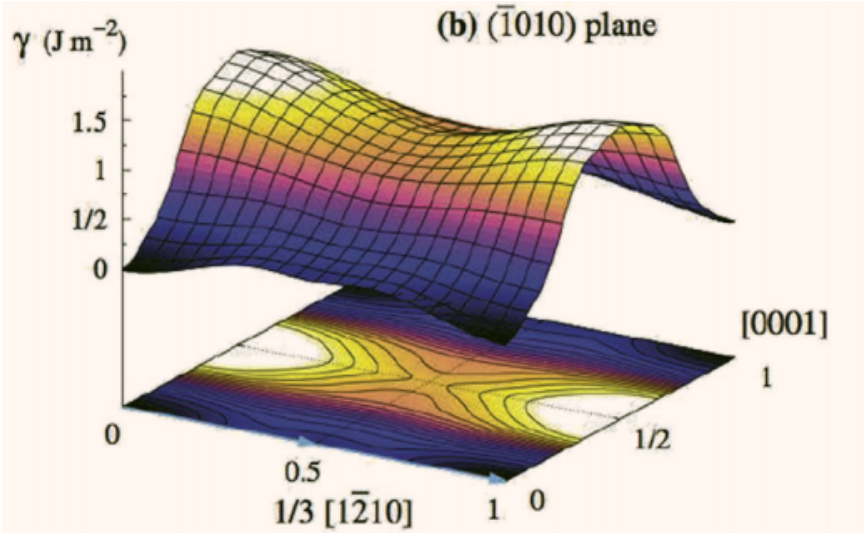


Expected splitting (all models): $\frac{1}{3}[1\bar{2}10] = \frac{1}{3}[1\bar{1}00] + \frac{1}{3}[0\bar{1}10]$

Prismatic gamma surfaces



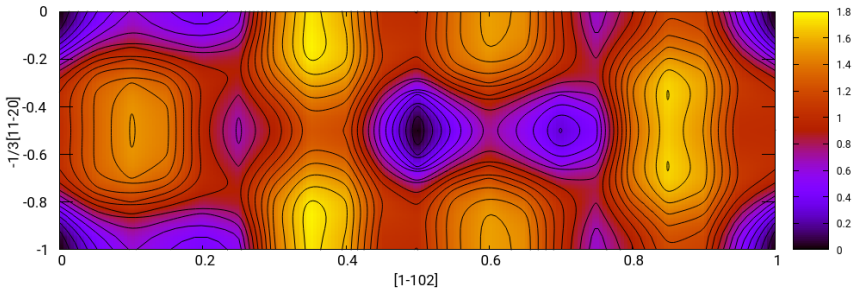




- Theoretical splitting: $\frac{1}{3}[1\bar{2}10] = \frac{1}{6}[1\bar{2}10] + \frac{1}{6}[1\bar{2}10]$
- Expected splitting (TB): $\frac{1}{3}[1\bar{2}10] = (\frac{1}{6}[1\bar{2}10] + 0.15[0001]) + (\frac{1}{6}[1\bar{2}10] - 0.15[0001])$
- Expected splitting (BOP): None.

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	BOP	[DFT]	[TB]	[BOP]
Basal	I_2	19	127	260 [1]	290 [2]	110 [3]
Prismatic	γ_P	299	4618	250/233 [1,4]	110[5]	260[3]
Pyramidal	I_1	288	–	288 [6]	–	–
	I_2	671	–	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)

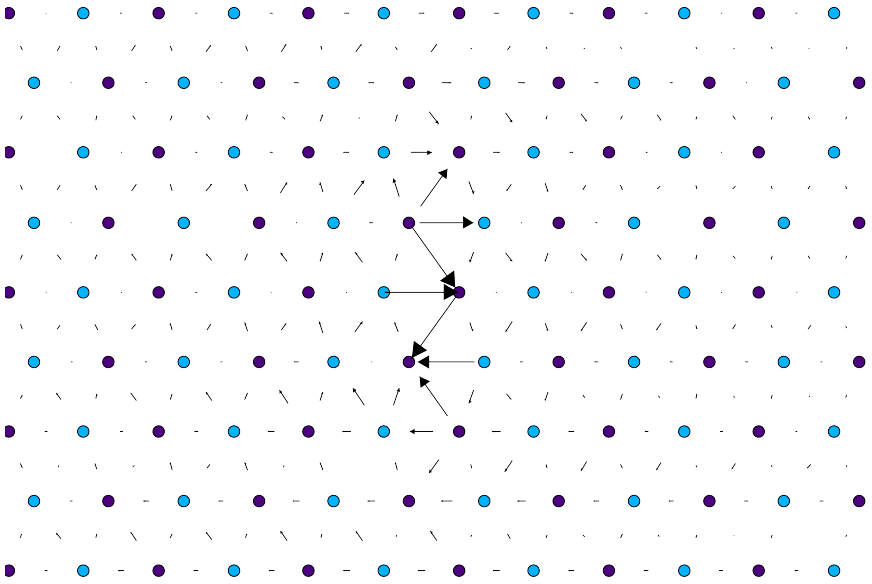
Pyramidal plane large minima at 0.5, 0.5, 0.0.
For I_1 fault I get 288 For the other fault, I get 671 mJm^{-2}
Smaller minima is at 0.7, 0.5, 288 mJm^{-2}
In pseudopotential one gets 288 as well!
Pair potential for the BOP on fitting needs to be tweaked for accurate results.

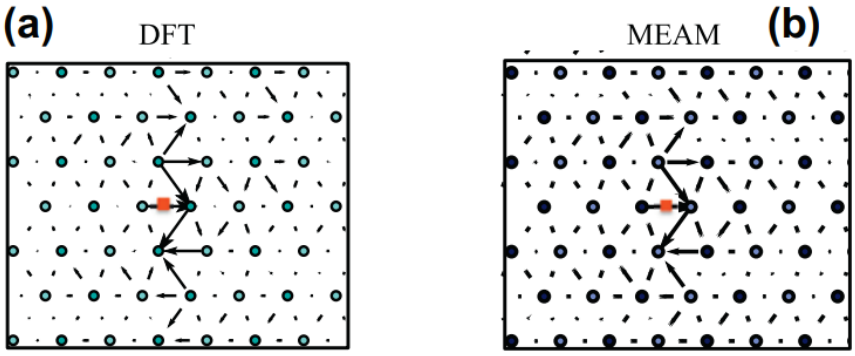
Core structures

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

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

`file:///home/tigany/Documents/docs/Management/Images/core_relax_initial.gif`





Oxygen-core quadrupole

Vacancy formation energy

$\Delta E_{\mathrm{f}}^{\mathrm{vacancy}}$	[eV]
Relaxed	1.01
(Exp.) Hashimoto (1984)	1.27
(DFT) GGA-PAW: Angsten (2013)	1.95

Molecular Dynamics

Future Work

- Obtain a model of Ti that more closely matches empirical quantities.
- 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.

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*