Effect of stress on the interstitial solubility and diffusivity

DAMIEN CONNÉTABLE

CIRIMAT
Toulouse France

GDR COnCOrD, July 2021

materials

nuclear | aeronautic | chemistry

exposure to complex environments

- **mechanical stresses**
- high temperature
- gas (H_2, CO, CO_2, N_2, O_2, H_2O….), liquid
- *etc.*

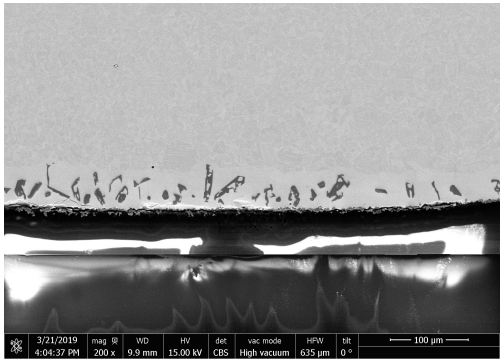
diffusivity, solubility, interactions of interstitial must be known



metal dusting (carbon)



hydrogen embrittlement



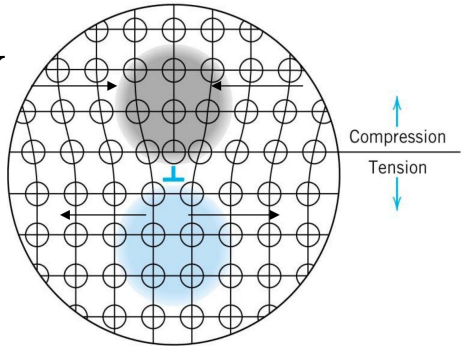
oxide precipitation

kinetics are controlled by the oxygen or nitrogen flux

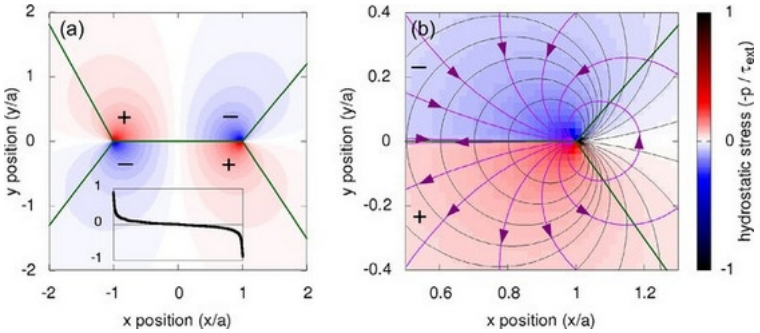
Ex: in Wagner's model for internal oxidation kinetics

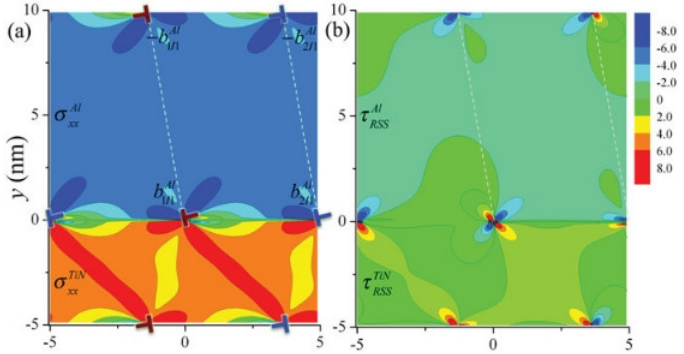
$$k_p \propto N_o D_o$$

coupling between mechanics and chemistry

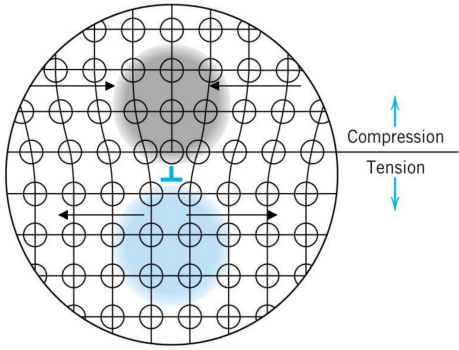


- surfaces/interfaces
- precipitates
- grains boundaries
- dislocations…

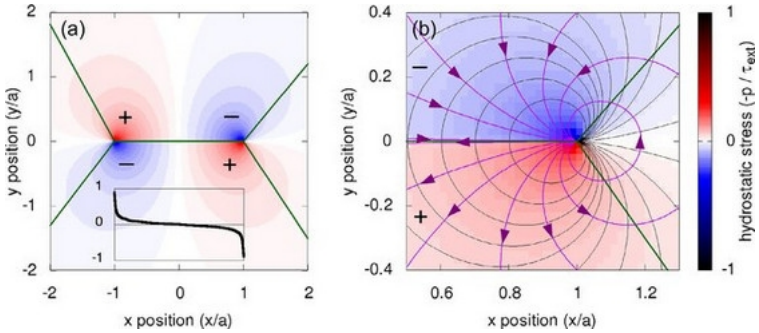


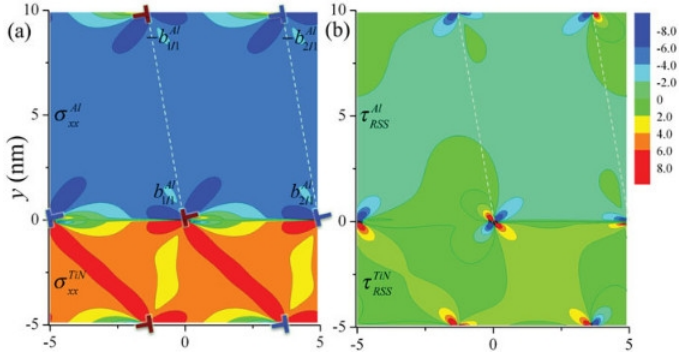


coupling between mechanics and chemistry



- surfaces/interfaces
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How change the diffusivity and solubility?

comparison between atomic scale and elastic model

focus on C, H, O and N interstitial species

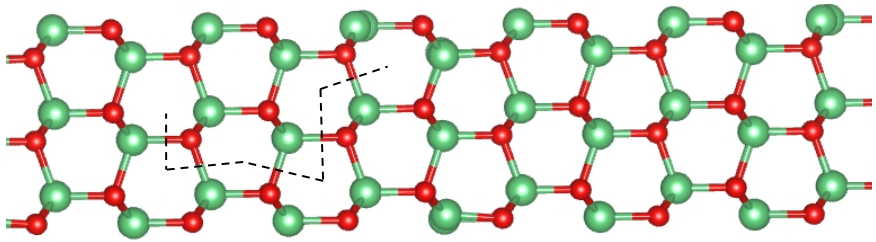
Methodology

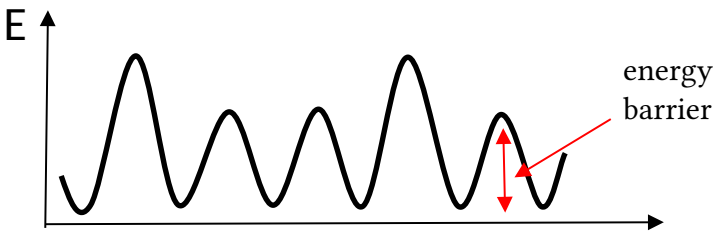
Multi-scale approach

At the atomic scale (DFT calculations):

b-initio VASP ackage imulation ienna

1. **Stable site identification (relaxation+inter-atomic forces):**
   i. Energy, volume of formation, Voronoï, charge transfer, elastic dipole...
   ii. Vibrations, free energy, stability
2. **Mechanisms of diffusion**
   i. Path identification (NEB)
   ii. Jump rates (Γ_{ij})





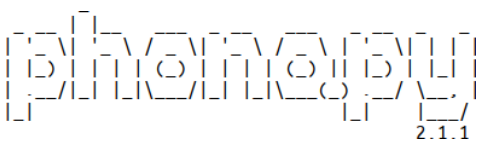
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   ii. Jump rates ($\mathbf{\Gamma_{ij}}$)



At the macroscopic scale:

KMC simulations

Explicit formula of diffusion coefficients

Methodology

Multi-scale approach

Elasticity theory

Insertion induces a distortion of the network

$$E(\epsilon) = E_{pd} + E^i_{pd} + \frac{1}{2} V \mathcal{C}_{ijkl} \epsilon_{ik} \epsilon_{kl} - \mathcal{P}_{ij} \epsilon_{ij}$$

defect energy

energy interaction between defect

elastic deformation energy

elastic constant tensor of the system

elastic dipole tensor of the defect

Multi-scale approach

Elasticity theory

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the stress is defined by

$$\sigma_{ij} = \frac{1}{V} \frac{\partial E}{\partial \epsilon_{ij}} = \mathcal{C}_{ijkl} \epsilon_{kl} - \frac{1}{V} \mathcal{P}_{ij}$$

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No stress: $\sigma_{ij} = 0 \Rightarrow \epsilon_{ij} = \frac{1}{V} \mathcal{C}^{-1}_{ijkl} \mathcal{P}_{ij}$

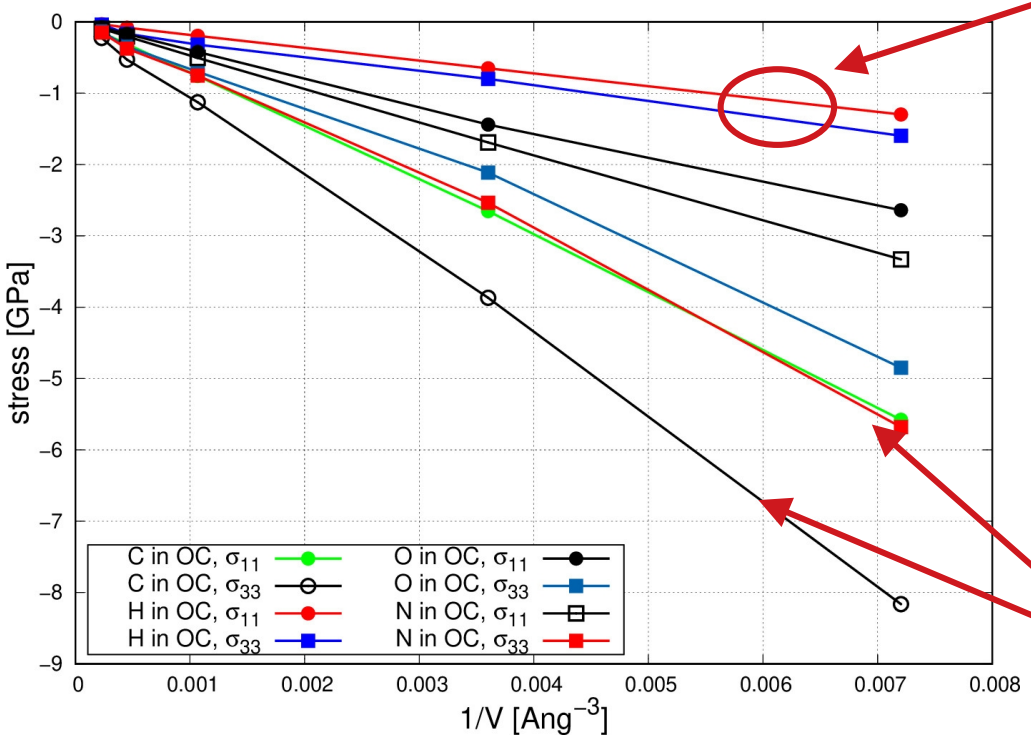
No strain: $\epsilon_{ij} = 0 \Rightarrow \sigma_{ij} = -\frac{1}{V} \mathcal{P}_{ij}$

Methodology

Example: C, H, O and N species in the Ti-hcp system

no strain: $\epsilon_{ij} = 0$

species in octahedral positions



$$\sigma_{ij} = -\frac{1}{V}\mathcal{P}_{ij}$$

$\mathcal{P}_{ij}$ tensors are calculated using DFT simulations

$\mathcal{P}_{11}$ and $\mathcal{P}_{33}$

E. Clouet, *et al. Acta Mater.* **56** (14) (2008) 3450–3460.

Methodology

Multi-scale approach

Elasticity theory

Energy corrections due to the stress (strain)

On solubility: $H(\sigma) = H(0) - \mathcal{S}_{ijkl}\mathcal{P}_{kl}\sigma_{ij}$

On barriers: $H_m(\sigma) = H_m(0) - \mathcal{S}_{ijkl}(\mathcal{P}^{ts}_{kl} - \mathcal{P}^{is}_{kl})\sigma_{ij}$

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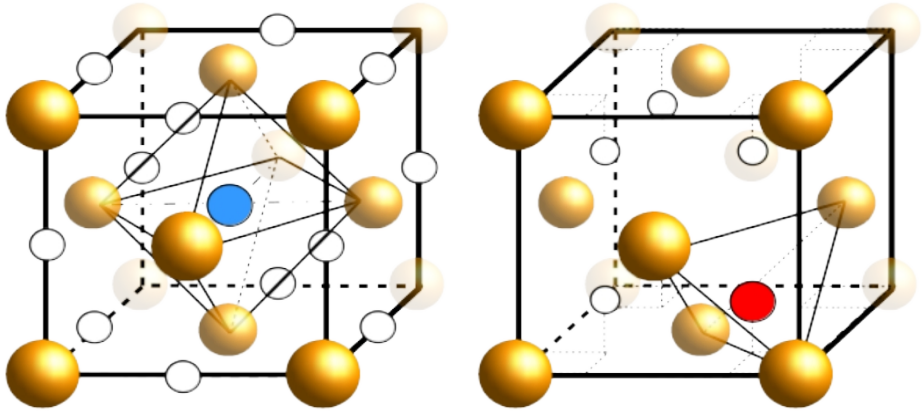
Strain-stress relationship

$$\epsilon_{ij} = \mathcal{S}_{ijkl}(\sigma_{kl} + \frac{1}{V}\mathcal{P}_{kl})$$

Comparison between elastic theory and DFT simulations
application to interstitial species

Hydrogen in Al

Well known interstitial positions in the fcc systems: octahedral (labelled **o**) and tetrahedral (labelled **t**) sites

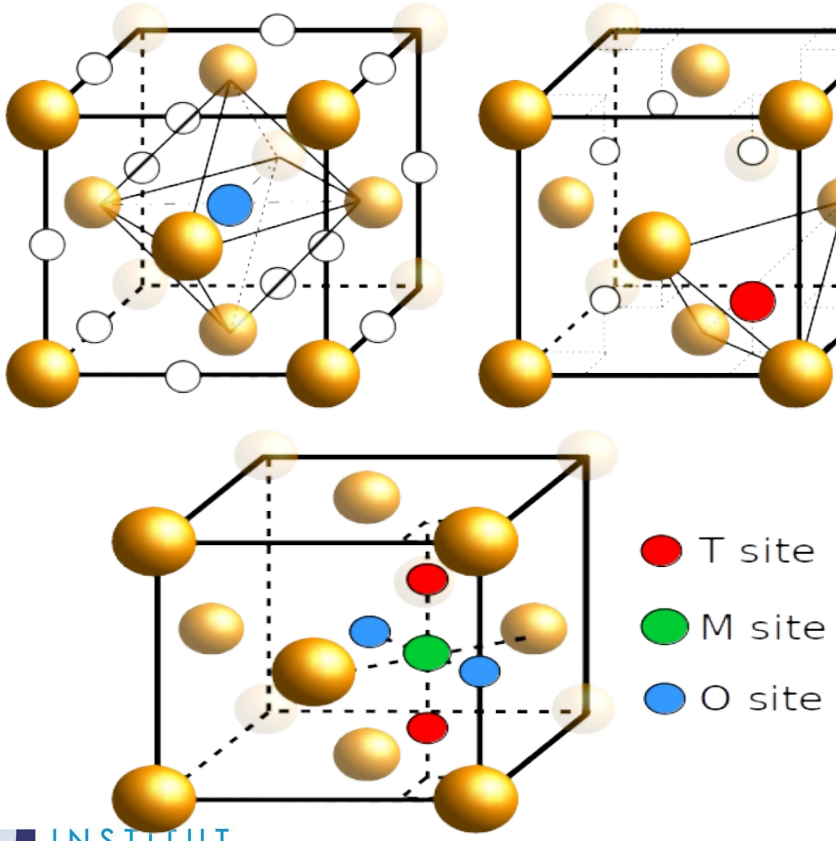


octahedral sites

tetrahedral sites

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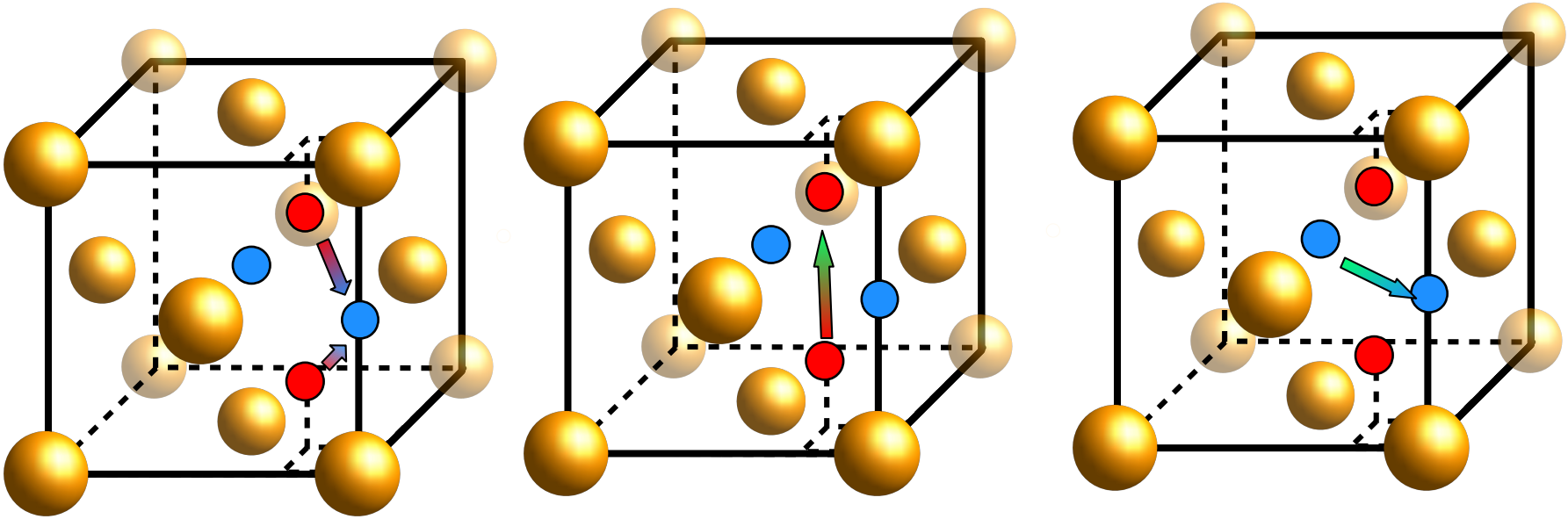


X	site	H_f [eV]	ΔH
H	**tetra**	0.72	0
	octa	0.82	0.10
C	tetra	1.69	0.37
	octa	1.32	0
	M	1.90	0.58
N	tetra	-0.90	0
	octa	0.05	0.85
O	tetra	-3.48	0
	octa	-1.99	1.48
	M	-2.37	1.10

Hydrogen in Al

Diffusion mechanism

3 different jumps

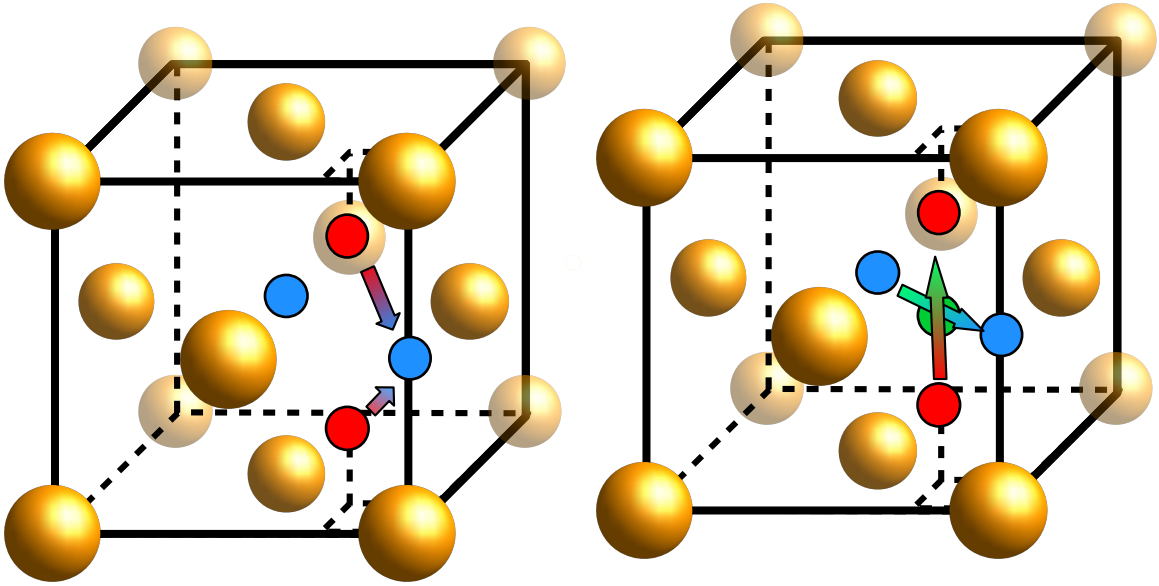


● *t* site

● *o* site

Hydrogen in Al

Diffusion mechanism



● *t* site

● M site

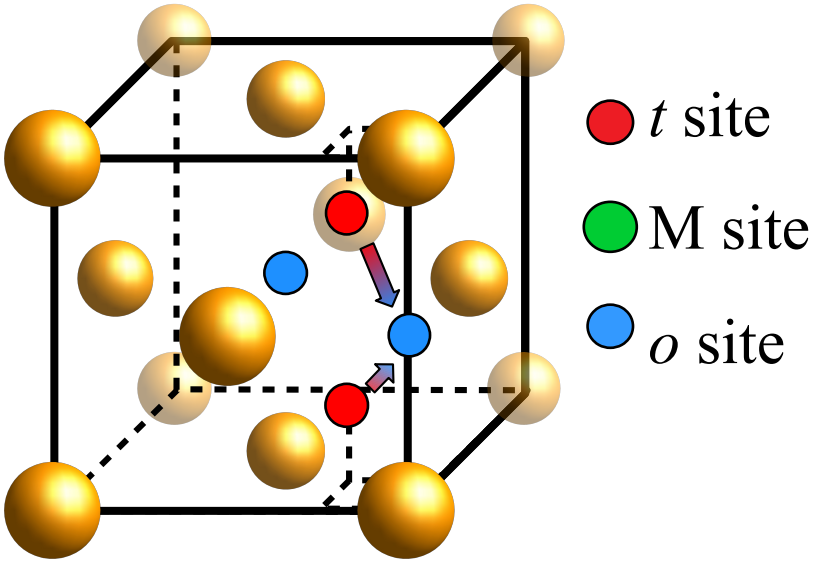
● *o* site

M site is a second-order transition state

not considered in the following

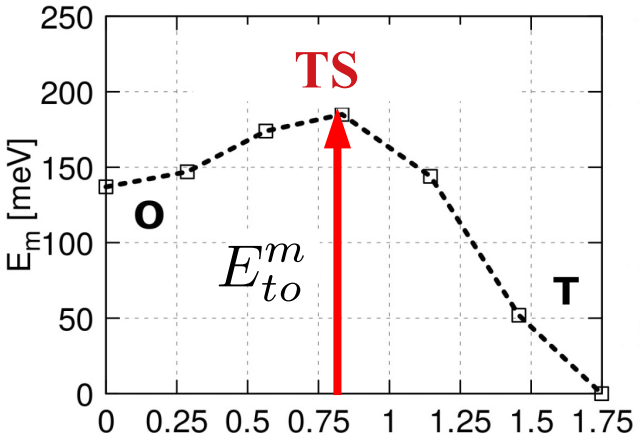
Hydrogen in Al

Diffusion mechanism



only one jump: direct jump between t and o sites

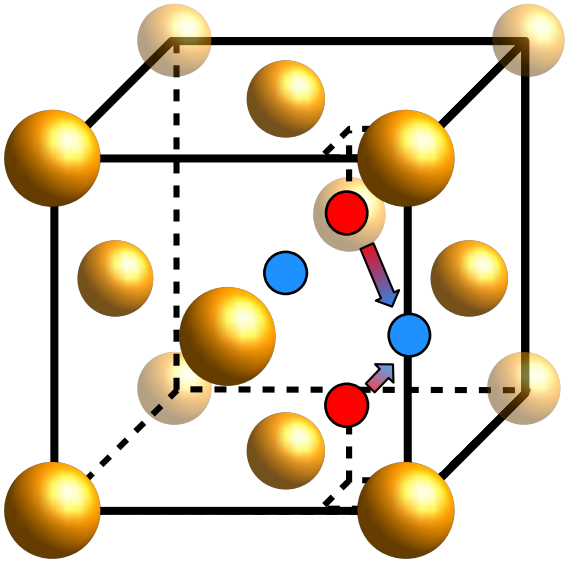
NEB simulations along t-o path



$\Gamma_{ot}[T]$ and $\Gamma_{to}[T]$

Hydrogen in Al

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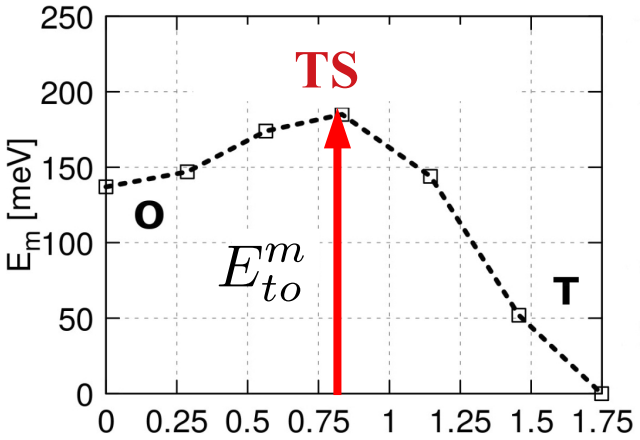
t site

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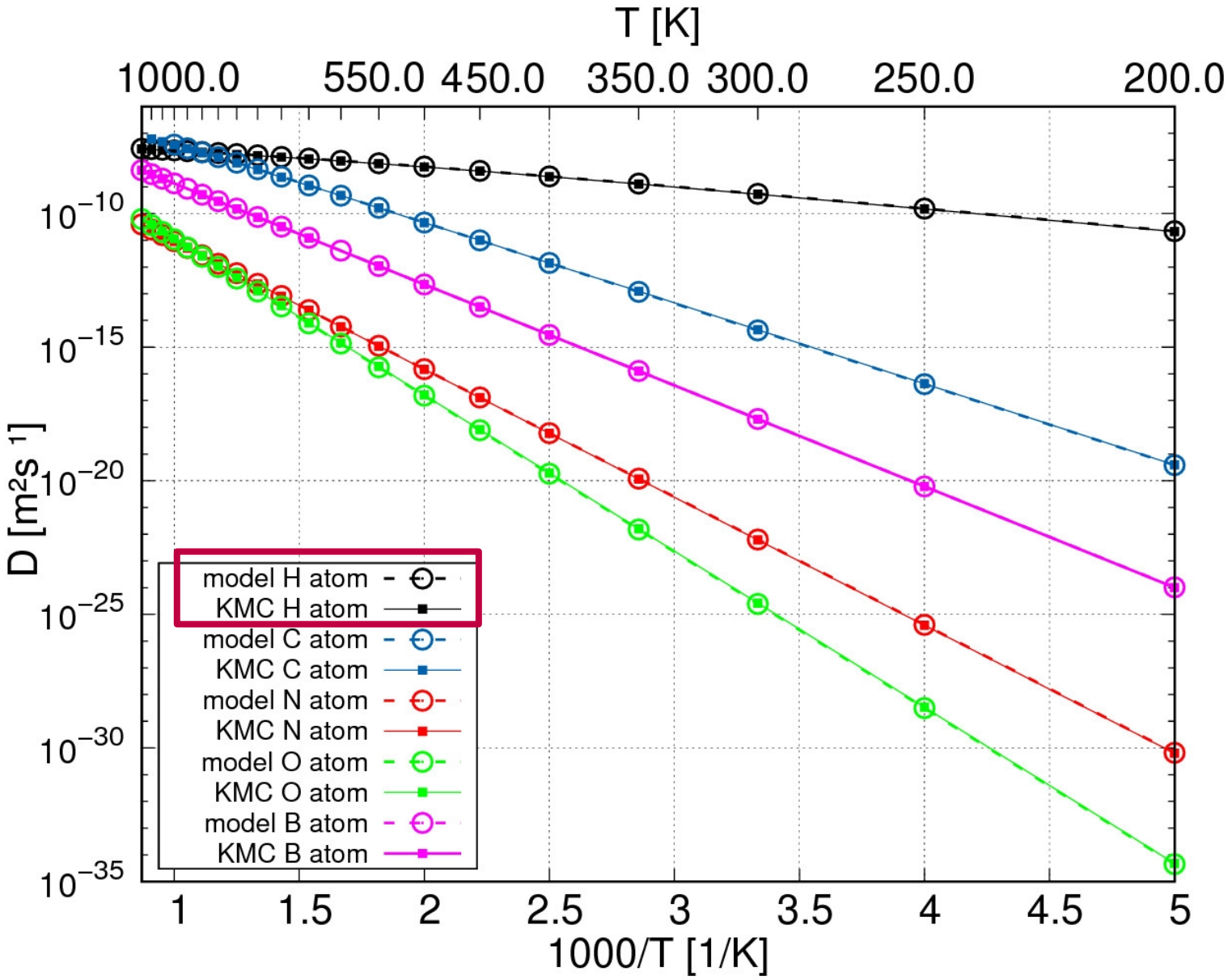
$\Gamma_{ot}[T]$ and $\Gamma_{to}[T]$

H coefficient diffusion

$$D[T,p] = \frac{a^2[p]}{2} \frac{\Gamma_{ot}[T]\Gamma_{to}[T]}{\Gamma_{to}[T] + 2\Gamma_{ot}[T]}$$

Hydrogen in Al

diffusion coefficients



Hydrogen in Al

Bulk properties:

Lattice parameters (a_o), elastic constants (C_{ijkl})

	Al	Ni	Cu	Pd
a_0	4.04/4.05	3.52/3.52	3.62/3.61	3.94/3.87
$\mathscr{C}_{11}$	105/116	272/253	193/168–173	202/234
$\mathscr{C}_{44}$	33/31	125/122	85/61–76	60/71
$\mathscr{C}_{12}$	65/65	158/158	134/118–129	153/176
$\mathscr{C}'$	20/25	57/47	29/24	25/29
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Comparison theo/exp*.

*C. Kittel, Introduction to Solid State Physics, Wiley, New York, 1996.

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Comparison theo/exp*.

For interstitial species:

Elastic dipoles of stable sites ($\mathcal{P}^x_{ij}$) and transition state ($\mathcal{P}^{ts}_{ij}$)

$$\mathcal{P}^t_{ij} = \mathcal{P}^t_{11}\delta_{ij}$$

$$\mathcal{P}^o_{ij} = \mathcal{P}^o_{11}\delta_{ij}$$

$$\mathcal{P}^{ts}_{ij} = \begin{pmatrix} \mathbf{2.26} & \mathbf{-0.27} & \mathbf{-0.27} \\ \mathbf{-0.27} & \mathbf{2.26} & \mathbf{-0.27} \\ \mathbf{-0.27} & \mathbf{-0.27} & \mathbf{2.26} \end{pmatrix}$$

D. Connétable, *et al. JALCOM* **879** (2021) 160425.

Hydrogen in Al

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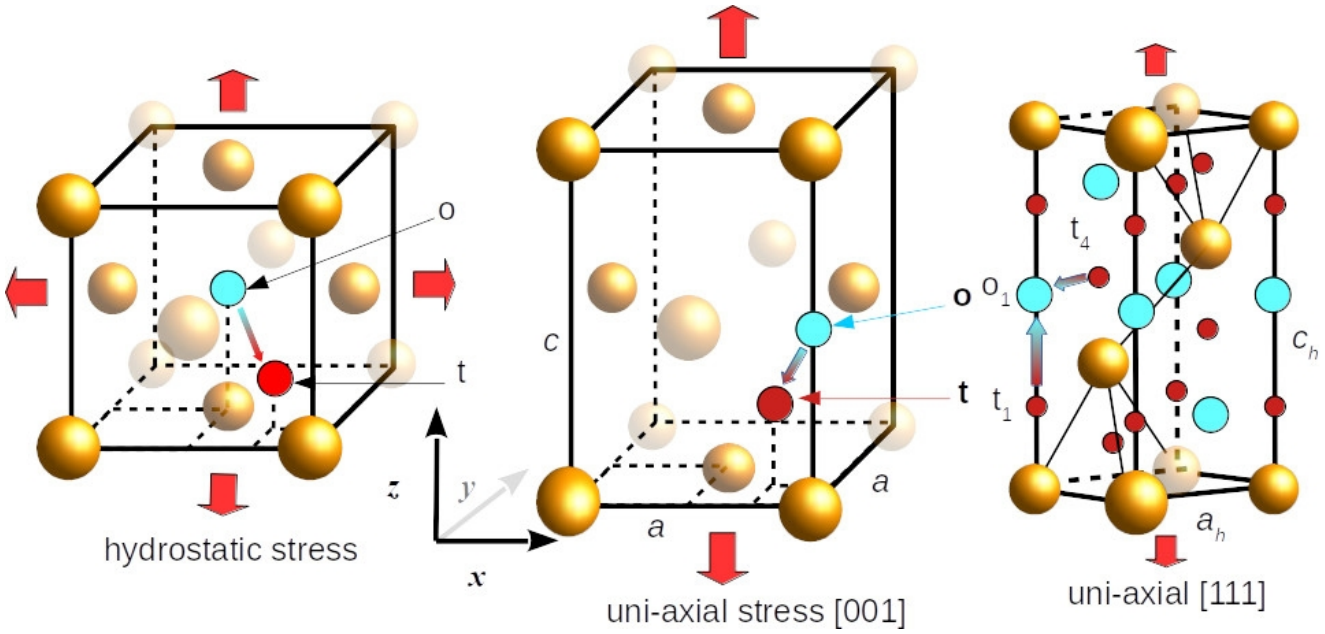
where

$$\mathcal{P}^t_{11} = 2.15 \text{ eV} \qquad \mathcal{P}^o_{11} = 1.28 \text{ eV}$$

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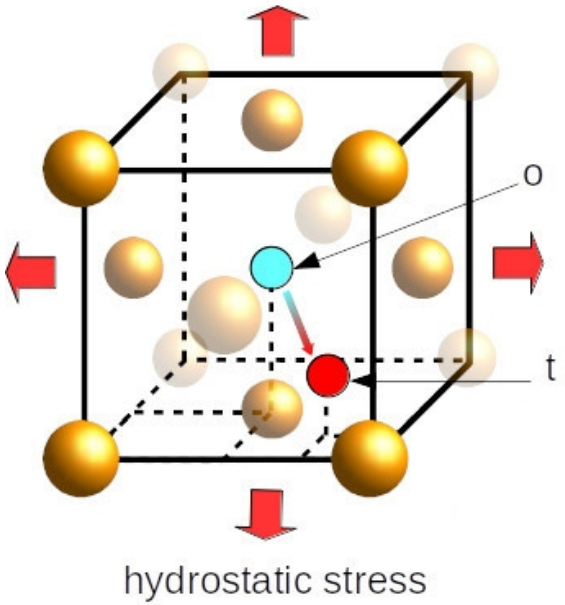
Stress effect



SG: 225 139 166-h

➡ reduction of symmetry, lift degeneracy

Stress effect: hydrostatic strain

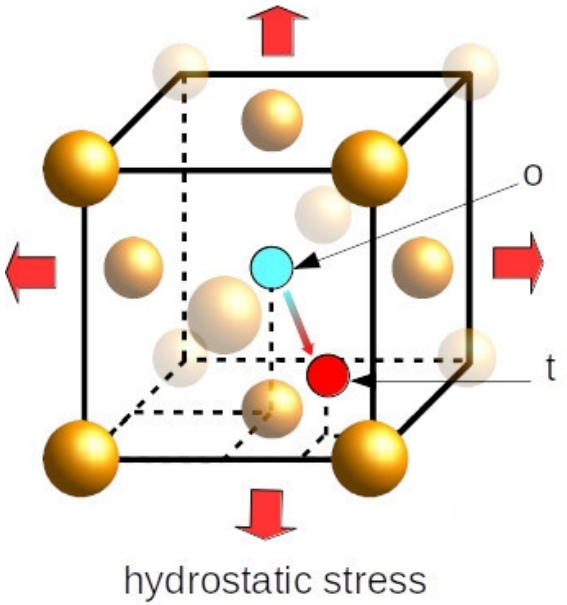


Two sites are stable for H in Al: *t* and *o*

under hydrostatic loading: symmetry preserved (SG 225)

$$D[T,p] = \frac{a^2[p]}{2} \frac{\Gamma_{ot}[T,p]\Gamma_{to}[T,p]}{\Gamma_{to}[T,p] + 2\Gamma_{ot}[T,p]}$$

Stress effect: hydrostatic strain



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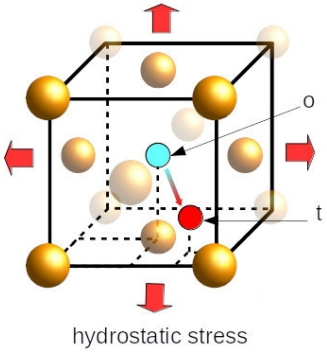
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Two effects:

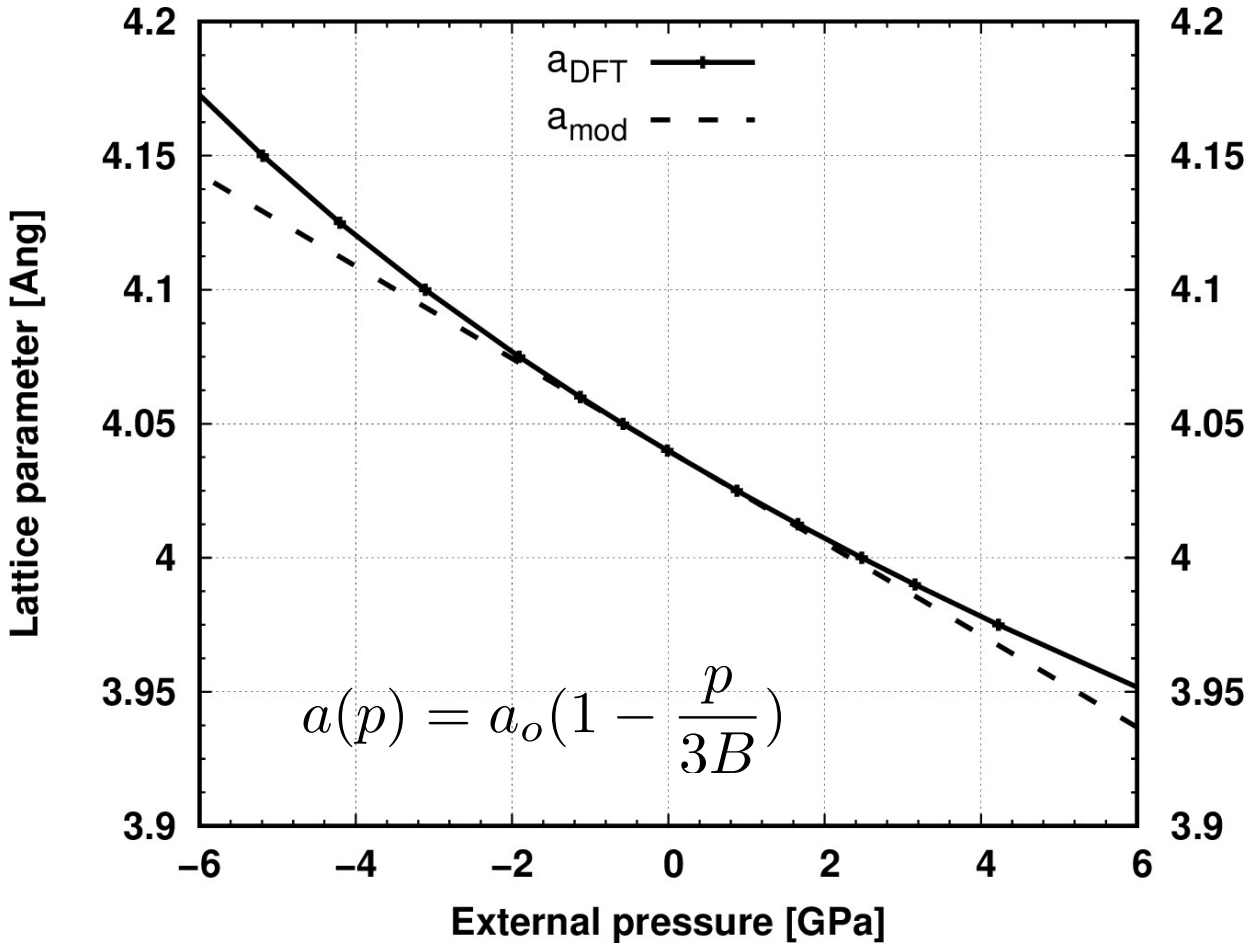
- modify lattice parameter a[p]
- change energy barriers, phonons and thus Γ_{xy}

Stress effect: hydrostatic strain

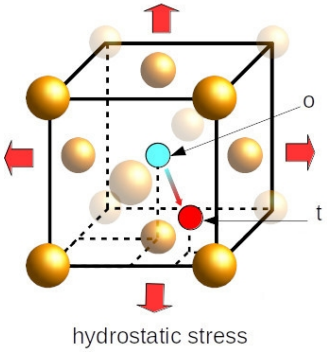


hydrostatic stress

Effect on lattice parameter

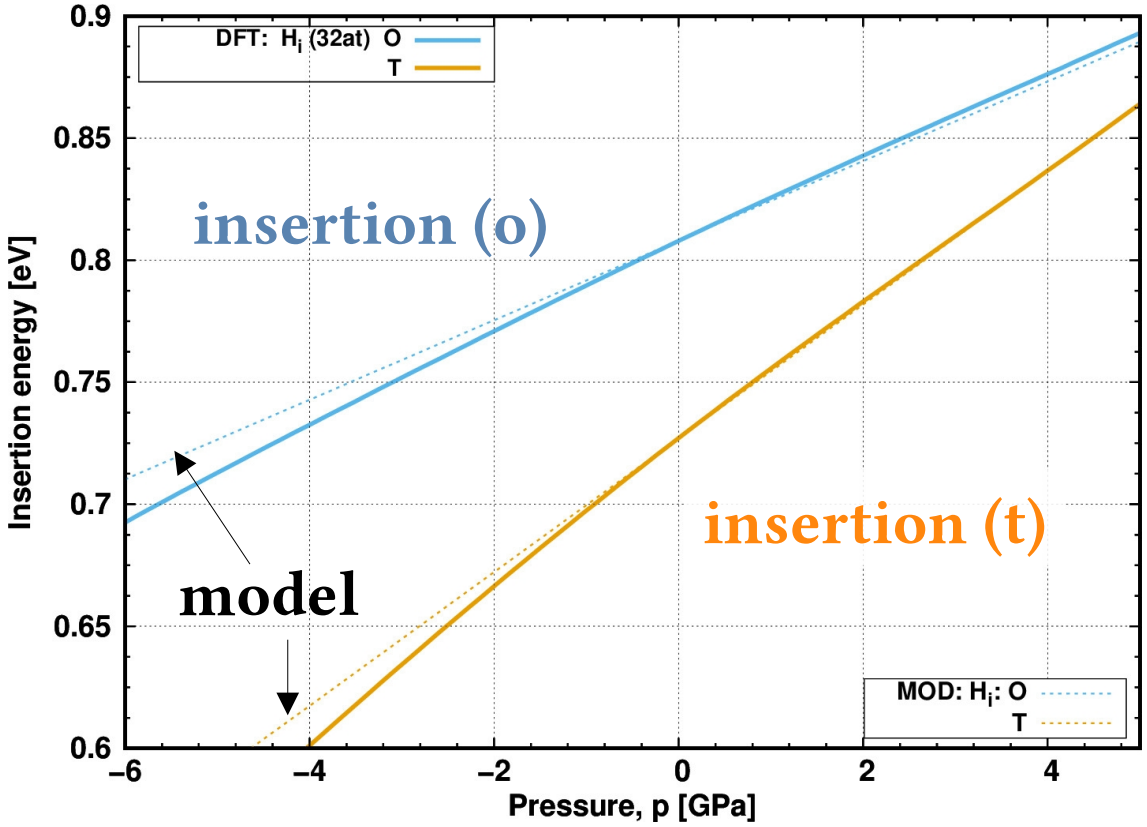


Stress effect: hydrostatic strain



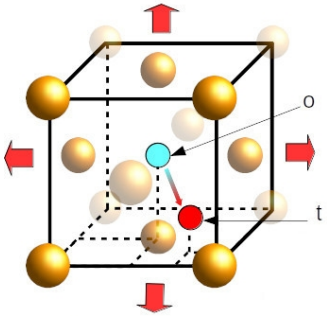
hydrostatic stress

Effect on energies (**insertion** and migration)



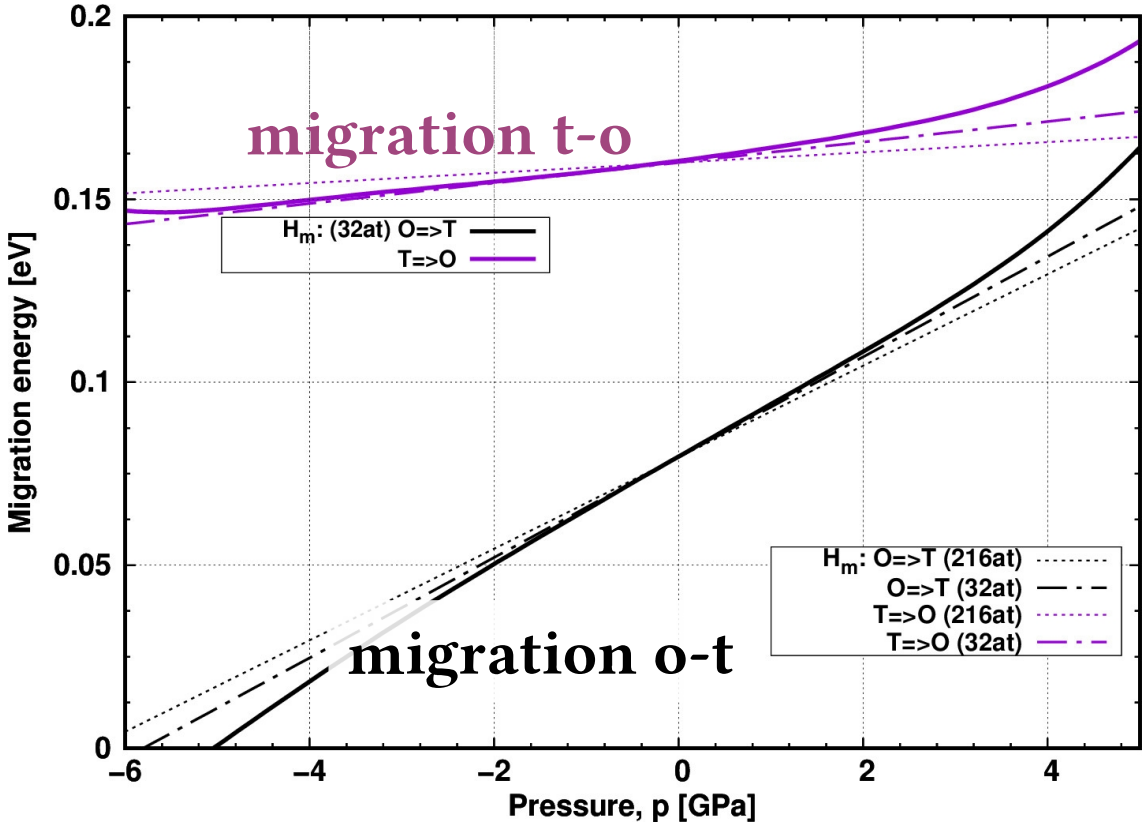
$$\Delta H^{o,t} = p\mathcal{S}_{1111}\mathcal{P}_{11}^{o,t}$$

Stress effect: hydrostatic strain



hydrostatic stress

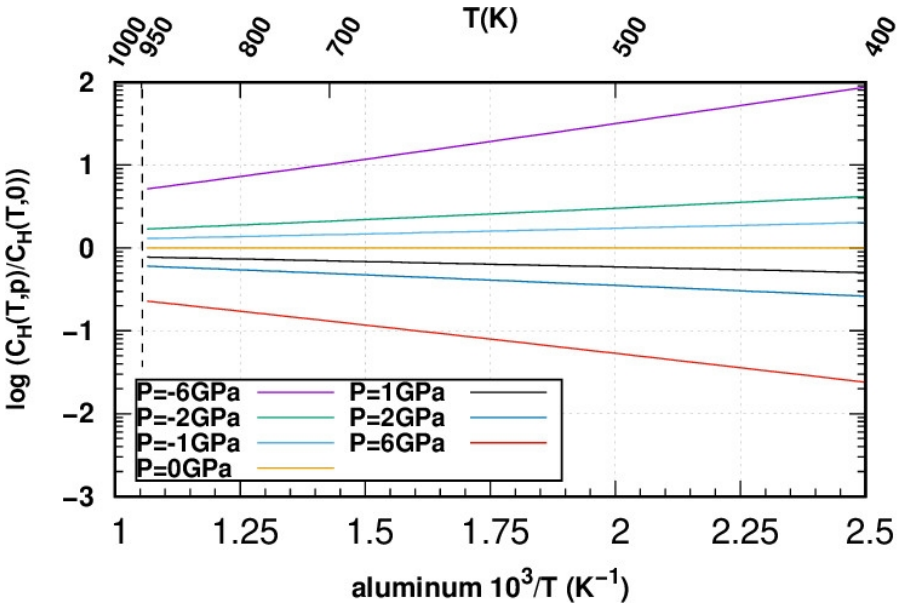
Effect on energies
(insertion and **migration**)



$$\Delta H_m^{xy} = pS\Delta\mathcal{P}^{x-y}$$

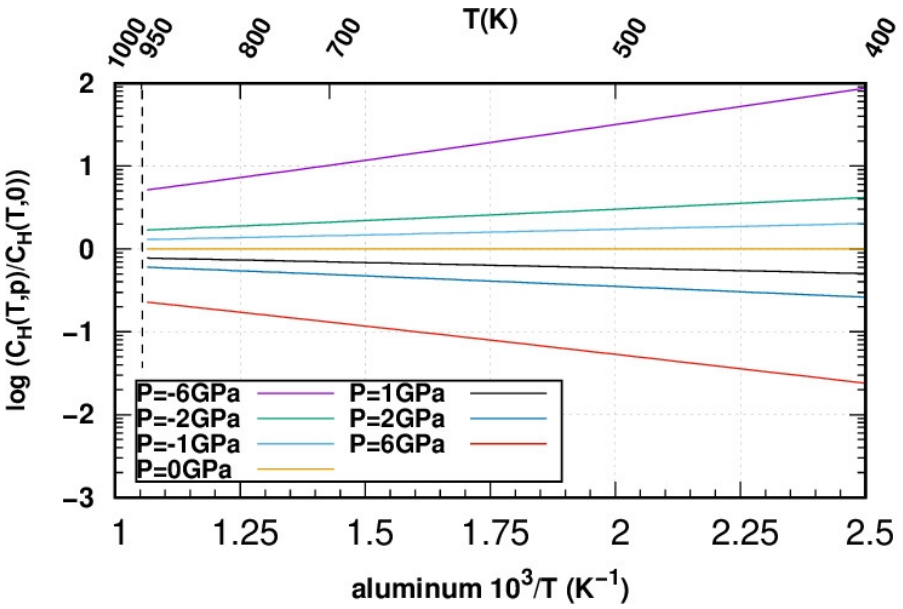
Stress effect: hydrostatic strain

H solubility

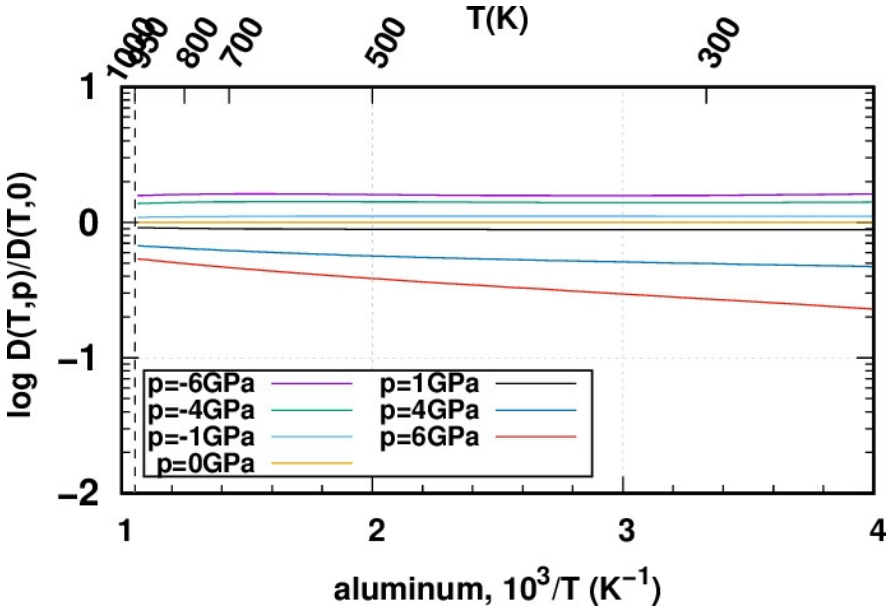


Stress effect: hydrostatic strain

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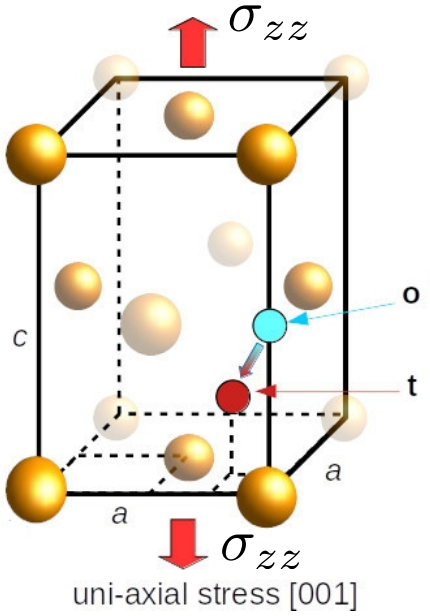


H diffusivity



effect more pronounced on the solubility than on the diffusivity

Stress effect: 001 uniaxial strain



symmetry break

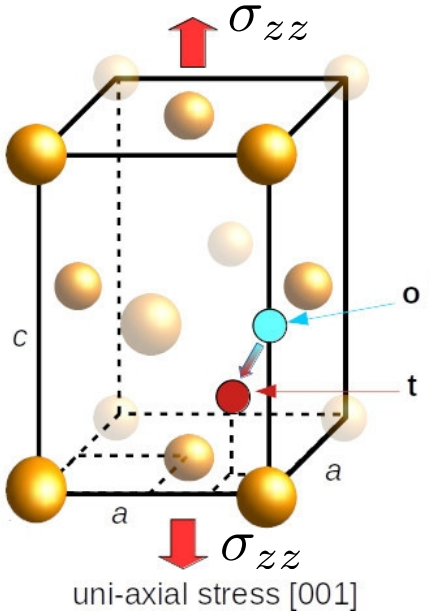
SG 225 ➡ SG 123

new set of equations

symmetry break of D

➡ only one jump, symmetry break due to the lattice parameters

Stress effect: 001 uniaxial strain



symmetry break

SG 225 ➡ SG 123

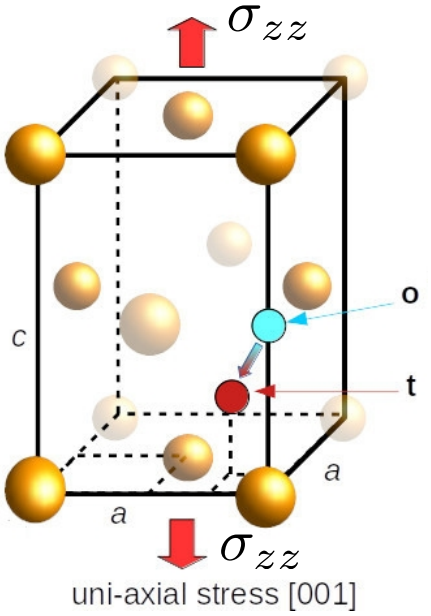
new set of equations

symmetry break of D

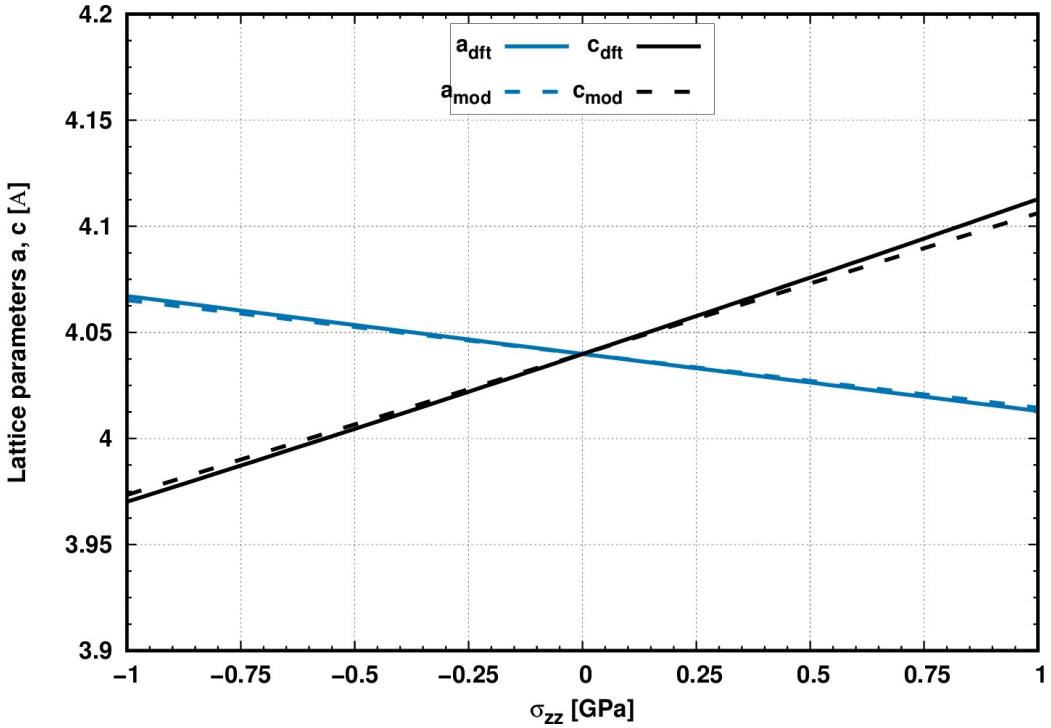
➡ only one jump, symmetry break due to the lattice parameters

$$\begin{cases} D_a[T,\sigma_{zz}] = \dfrac{a^2[\sigma_{zz}]}{2}\dfrac{\Gamma_{ot}[T,\sigma_{zz}]\Gamma_{to}[T,\sigma_{zz}]}{\Gamma_{to}[T,\sigma_{zz}]+2\Gamma_{ot}[T,\sigma_{zz}]} \\ D_c[T,\sigma_{zz}] = \dfrac{c^2[\sigma_{zz}]}{2}\dfrac{\Gamma_{ot}[T,\sigma_{zz}]\Gamma_{to}[T,\sigma_{zz}]}{\Gamma_{to}[T,\sigma_{zz}]+2\Gamma_{ot}[T,\sigma_{zz}]} \end{cases}$$

Stress effect: 001 uniaxial strain



uni-axial stress [001]



$$a, b = a_o \left[1 - \frac{\mathcal{C}_{12}}{6\mathcal{B}\mathcal{C}'} \sigma_{zz} \right]$$

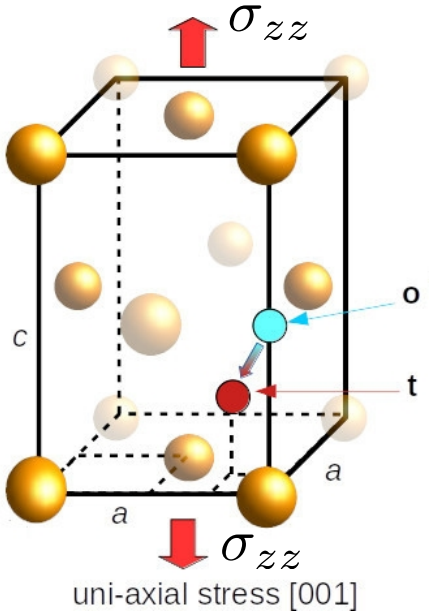
$$c = a_o \left[1 + \frac{\mathcal{C}_{12} + \mathcal{C}_{11}}{6\mathcal{B}\mathcal{C}'} \sigma_{zz} \right]$$

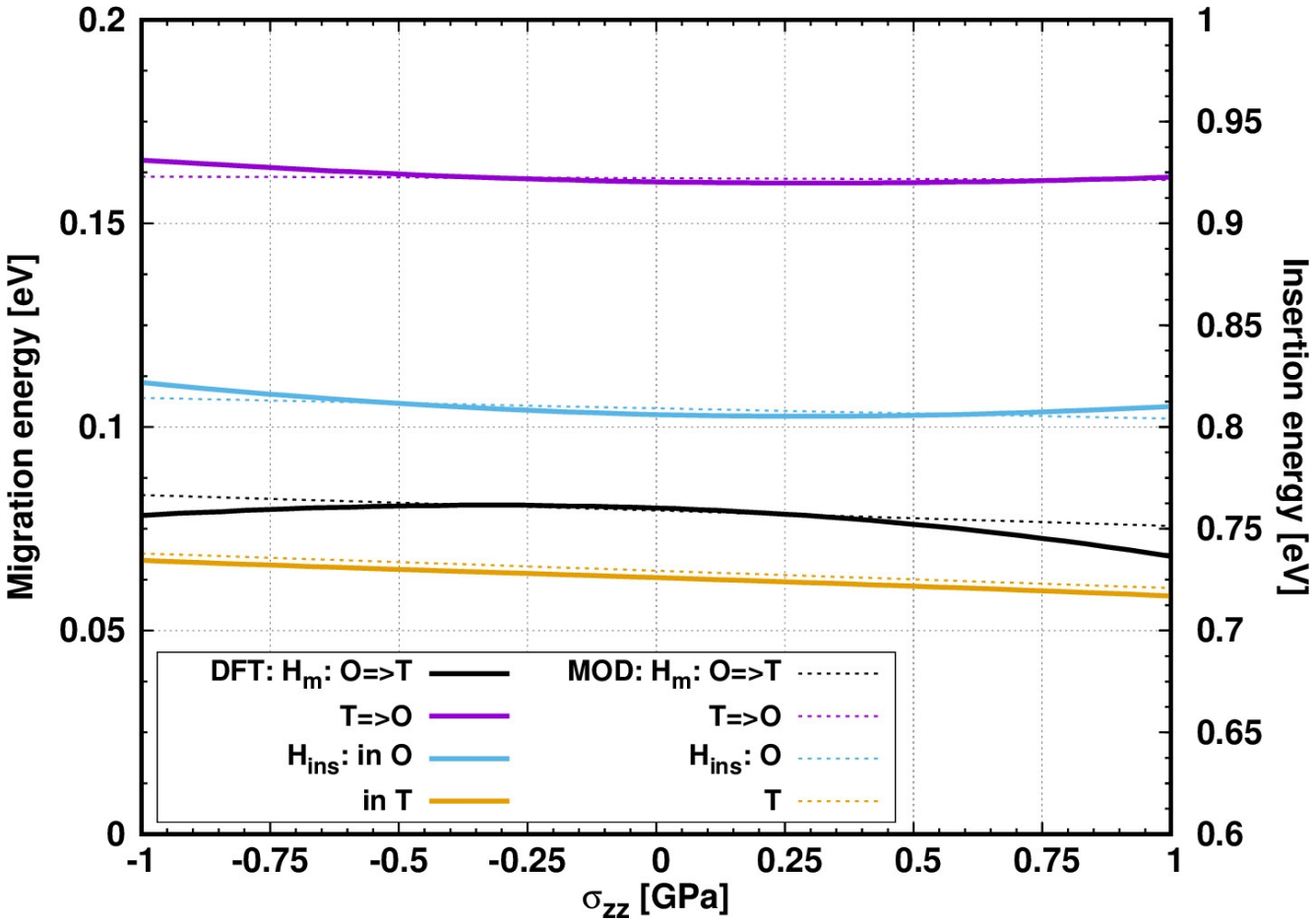
$\mathcal{B}$ bulk modulus

$\mathcal{C}'$ shear modulus

Elastic effects in excellent agreement with DFT values

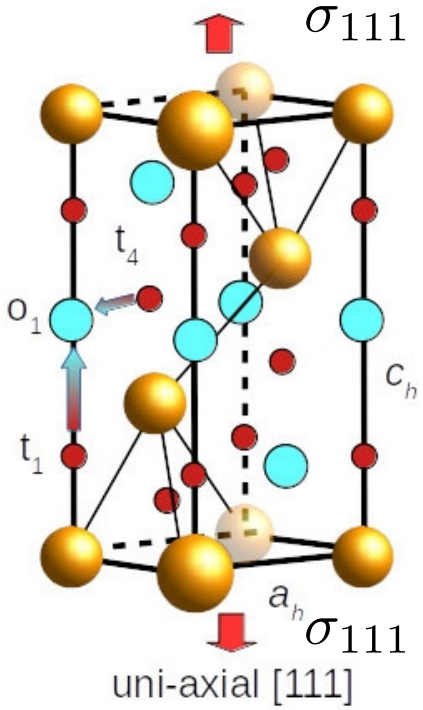
Stress effect: 001 uniaxial strain





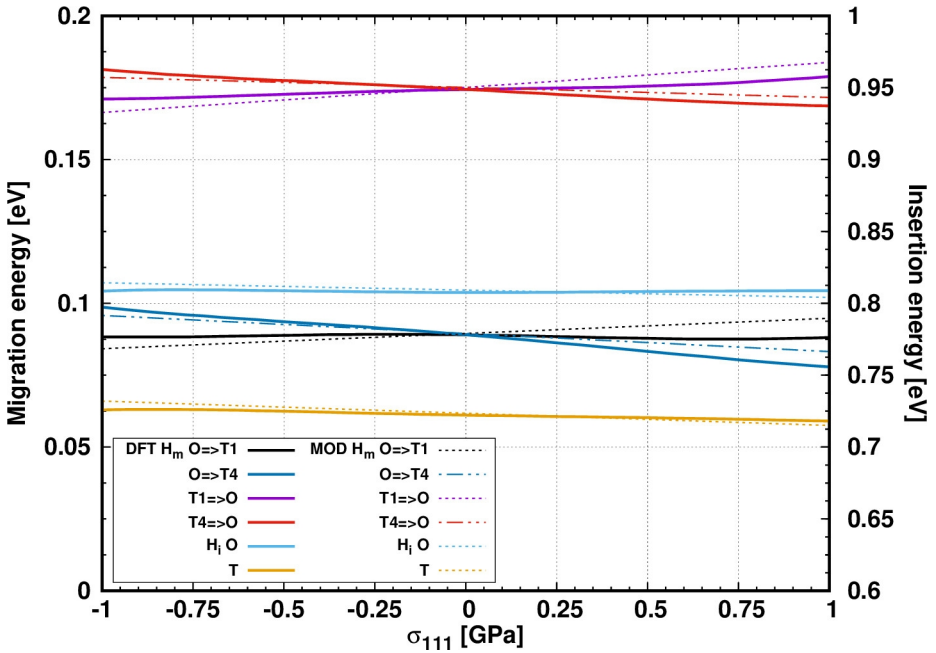
excellent agreement DFT-elastic theory
small effect, negligible on diffusion and solubility

Stress effect: 111 uniaxial strain



$$D_{X,Y} = \frac{2a_h^2}{3} \frac{\Gamma_{o_1t_4}\Gamma_{t_1o_1} + \Gamma_{o_1t_1}\Gamma_{t_4o_1} + 6\Gamma_{o_1t_4}\Gamma_{t_4o_1}}{2\Gamma_{o_1t_1} + 6\Gamma_{o_1t_4} + \Gamma_{t_1o_1} + 3\Gamma_{t_4o_1}}$$

$$D_Z = \frac{c_h^2}{3} \frac{\Gamma_{o_1t_4}\Gamma_{t_1o_1} + \Gamma_{o_1t_1}\Gamma_{t_4o_1}}{2\Gamma_{o_1t_1} + 6\Gamma_{o_1t_4} + \Gamma_{t_1o_1} + 3\Gamma_{t_4o_1}}$$



Conclusion

Excellent agreement between DFT/elastic model

Stress effect is maximal in the case of hydrostatic stress

Small anisotropy in fcc systems

Quantify diffusion coefficients

Work in progress...

Elasto-diffusion coefficients can also be computed

$$d_{ijkl} = \frac{\partial D_{ij}}{\partial \epsilon_{kl}}$$

Effect of the concentration

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