“Quantum-mechanical modelling and development of cathode materials for Li, Na, and K-ion batteries

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Outline

1. *Motivation to study energy materials*
2. *Method and SIMAN code*
3. *Origin of migration barriers in cathode materials*
4. *Layered oxides: surface structure and defects*
5. *Unusual Defects in Olivine* $LiFePO_4$

More than 1 billion gasoline cars on Earth

The Nation

Gas chamber
for execution:

© Emily Kinni

Solution: renewables and electric cars

- Renewable electricity is unpredictable
- Electric cars - the range is limited - the price is high
- Both currently are economically unreasonable

What can change the situation?

Affordable batteries!

How to reduce price of Li-ion ?

Replace Li with abundant Na and K

	Lithium	Sodium	Potassium
Atomic Mass	7	23	39
Crust Abundance (molar, %)	**0.005**	**2.1**	0.78
Voltage vs SHE (V)	-3.04	-2.71	-2.93
Cost of carbonate ($/kg)	**15**	**0.2**	1

- Sodium has larger mass and lower potential, reducing energy density of a battery
- Challenge for fundamental science!

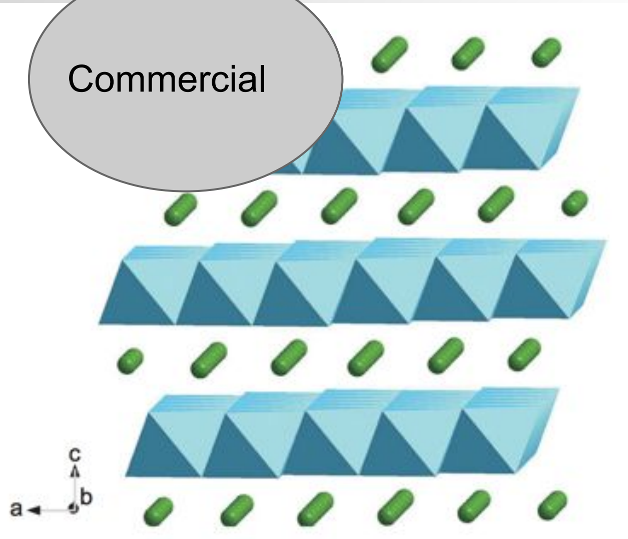
Battery performance depends on materials

Metric	Depends on
Voltage (V)	Chemistry and structure of cathode and anode, working window of electrolyte
Capacity (C)	Chemistry and structure of cathode and anode
Energy density	$E = \int V(C)dC$
Safety	Thermodynamic stability of cathode, anode, and electrolyte, battery construction
Power density	Ionic and electronic conductivity of cathode and anode
Both anode and cathodes are important! In our work we study cathodes	

Main classes of cathode materials

CoO_6 octahedra

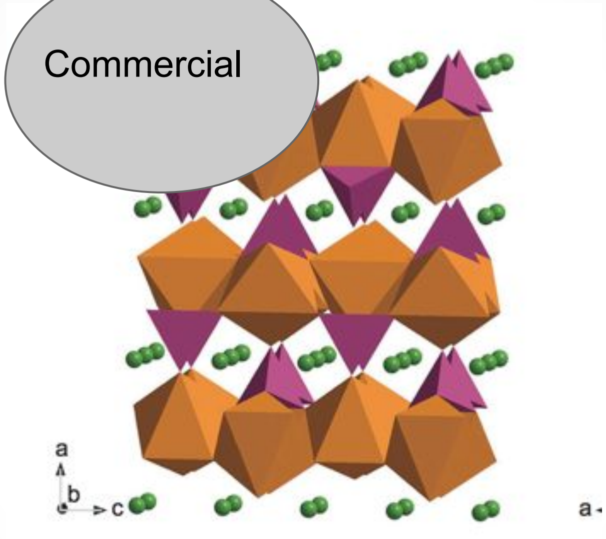
Commercial



$LiCoO_2$, $NaCoO_2$
Layered oxides,
Transition metals are
Co, Mn, Ni
good for Li and Na

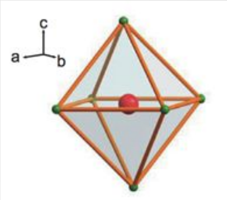
FeO_6 octahedra
PO_4 tetrahedra

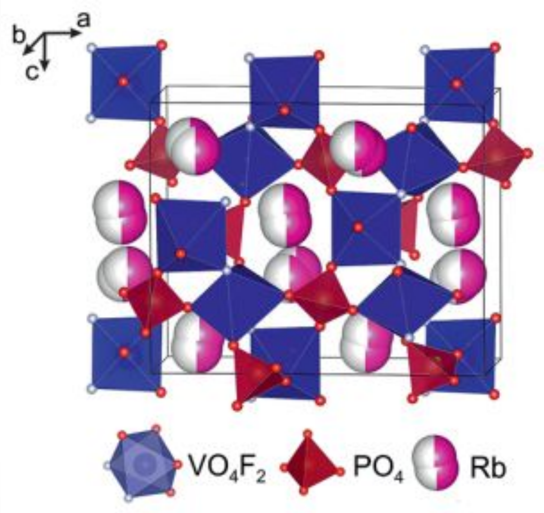
Commercial



$LiFePO_4$, $NaFePO_4$
Olivines
High stability

VO_6
octahedra





Other polyanion materials, e.g. KVPO4F, Na2FePO4F, etc.
SO_4, SiO_4, BO_3 polyanion Li, Na and K

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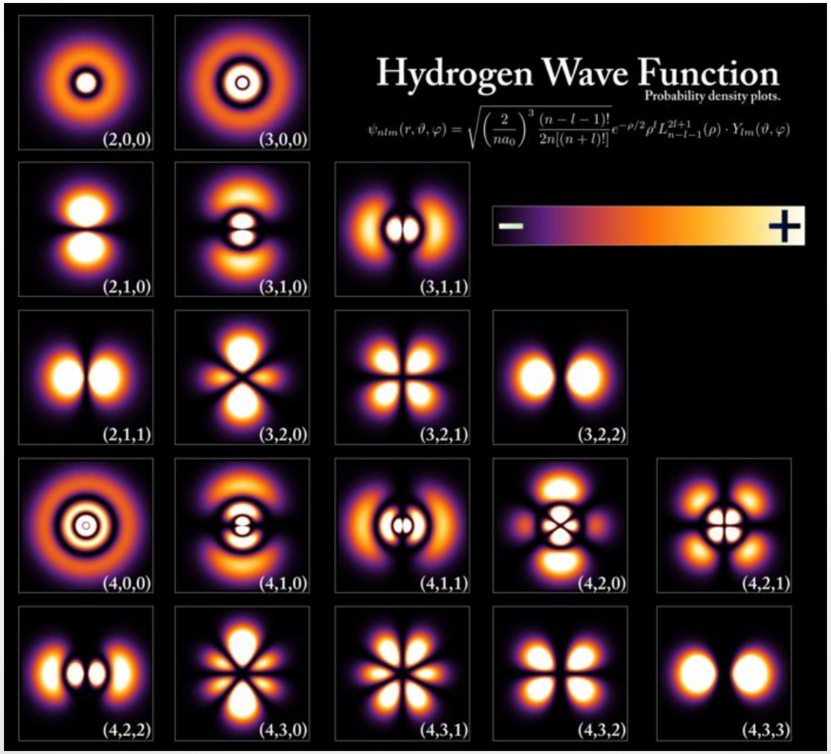
Quantum mechanics - exact description

$$\hat{H}\Psi(\vec{r}_1, \vec{r}_2, \cdots \vec{r}_N) = E\Psi(\vec{r}_1, \vec{r}_2, \cdots \vec{r}_N)$$

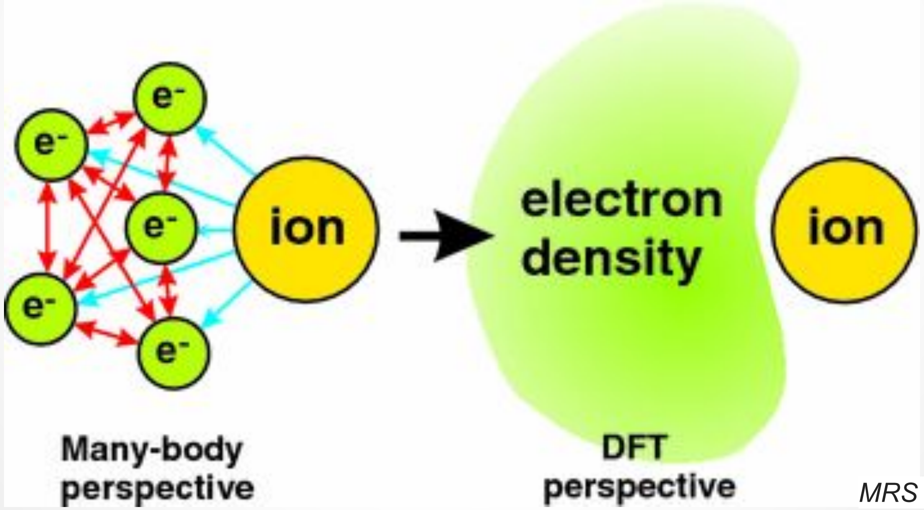
can be solved exactly only for simplest systems like hydrogen atom!



Density functional theory

1. Replace wave function with electronic density (exact)

2. Replace interacting electrons with non-interacting particles.
   a. take interaction into account using effective potential (V_{xc})

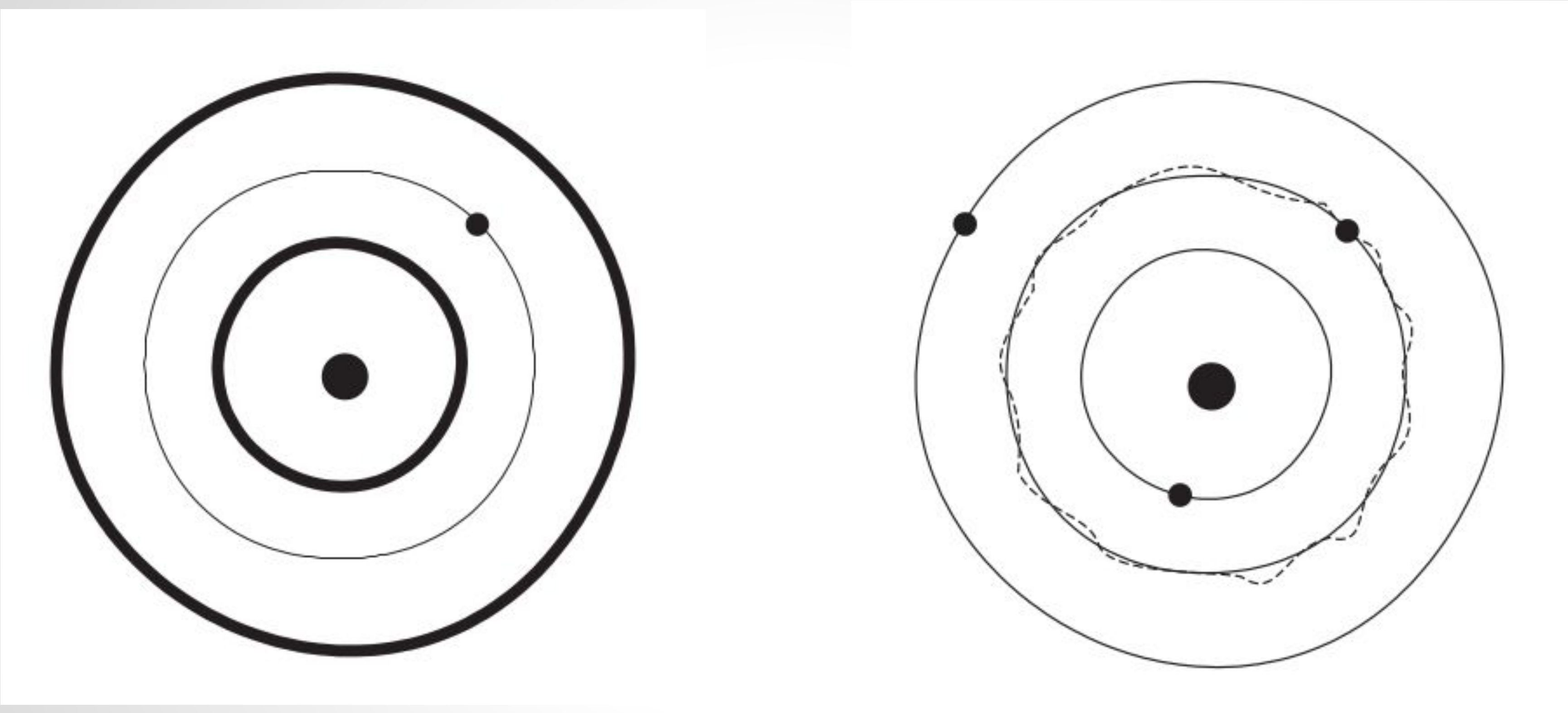


MRS Bulletin 36, no. 3 (2011): 169-174.

First-principles calculations:

Mendeleev Table -> ***Atomic structure and energy***

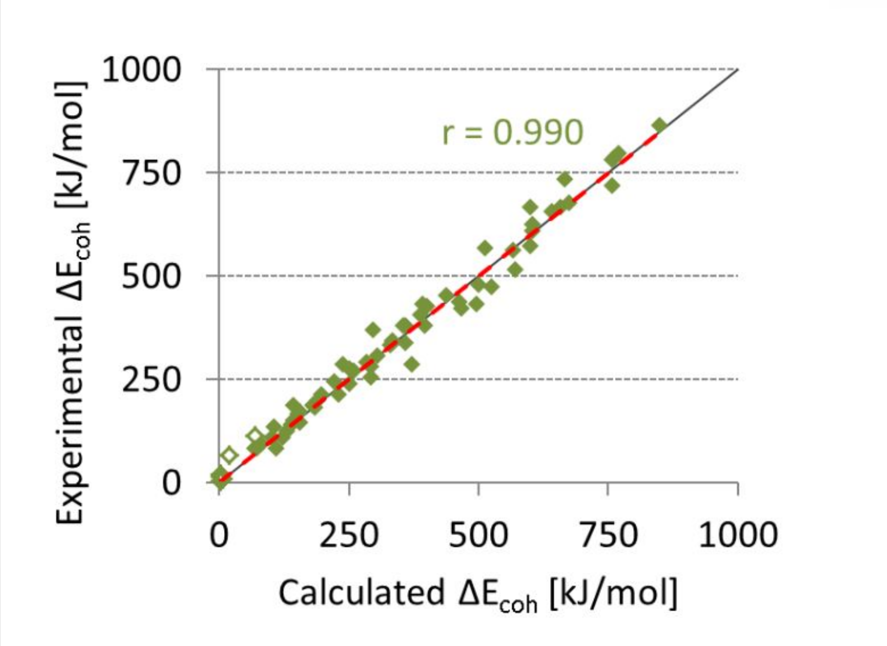
Analogy with central-mass approximation



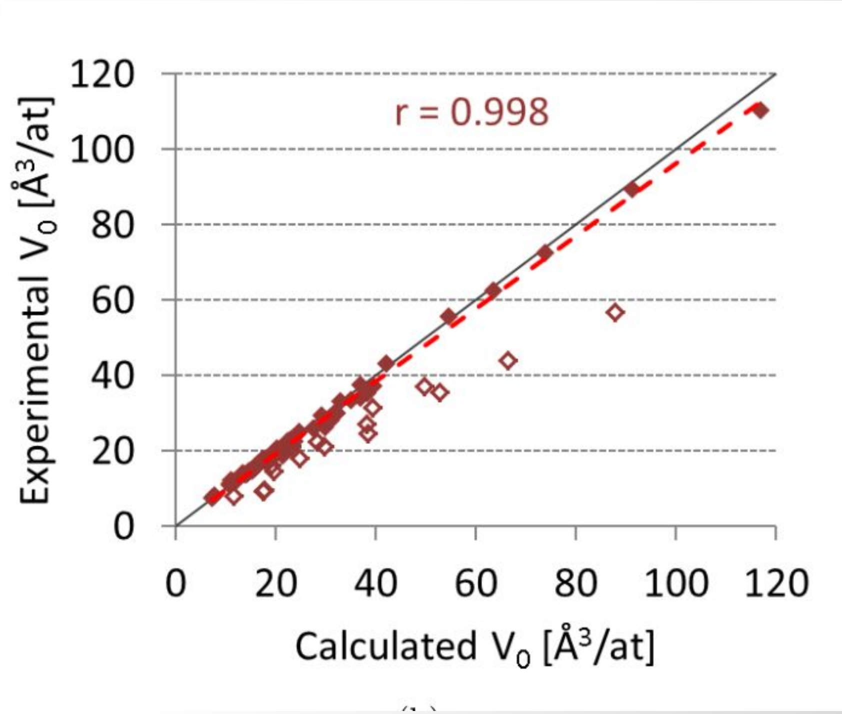
Despite effective field approximation, DFT is very good in predicting experimental properties.

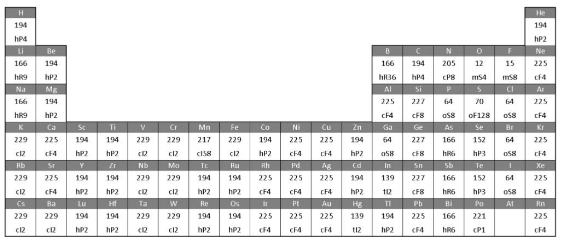
Accuracy of DFT

Cohesive energy



Equilibrium volume





H 194 hP4																	He 194 hP2
Li 166 hR9	Be 194 hP2											B 166 hR36	C 194 hP4	N 205 cP8	O 12 mS4	F 15 mS8	Ne 225 cF4
Na 166 hR9	Mg 194 hP2											Al 225 cF4	Si 227 cF8	P 64 oS8	S 70 oF128	Cl 64 oS8	Ar 225 cF4
K 229 cI2	Ca 225 cF4	Sc 194 hP2	Ti 194 hP2	V 229 cI2	Cr 229 cI2	Mn 217 cI58	Fe 229 cI2	Co 194 hP2	Ni 225 cF4	Cu 225 cF4	Zn 194 hP2	Ga 64 oS8	Ge 227 cF8	As 166 hR6	Se 152 hP3	Br 64 oS8	Kr 225 cF4
Rb 229 cI2	Sr 225 cF4	Y 194 hP2	Zr 194 hP2	Nb 229 cI2	Mo 229 cI2	Tc 194 hP2	Ru 194 hP2	Rh 225 cF4	Pd 225 cF4	Ag 225 cF4	Cd 194 hP2	In 139 tI2	Sn 227 cF8	Sb 166 hR6	Te 152 hP3	I 64 oS8	Xe 225 cF4
Cs 229 cI2	Ba 229 cI2	Lu 194 hP2	Hf 194 hP2	Ta 229 cI2	W 229 cI2	Re 194 hP2	Os 194 hP2	Ir 225 cF4	Pt 225 cF4	Au 225 cF4	Hg 139 tI2	Tl 194 hP2	Pb 225 cF4	Bi 166 hR6	Po 221 cP1	At	Rn 225 cF4

Critical Reviews in Solid State and Materials Sciences 39, no. 1 (2014): 1-24.

What you can predict with DFT?

- Electronic structure and total energies
  - Optimal lattice constants and atomic positions
  - Phase stability
  - Structure and energetics of defects
- Mechanical properties
- Phonons and thermodynamic properties
- etc.

Main limitation is system size, therefore should be careful in comparing to experiment your model system

DFT for battery materials?

Metric	Depends on
Voltage (V)	Chemistry and structure of cathode and anode, working window of electrolyte
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Energy density	$E = \int V(C)dC$
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Power density	Ionic and electronic conductivity of cathode and anode

Both anode and cathodes are important! In our work we study cathodes

Method for electronic structure calculation

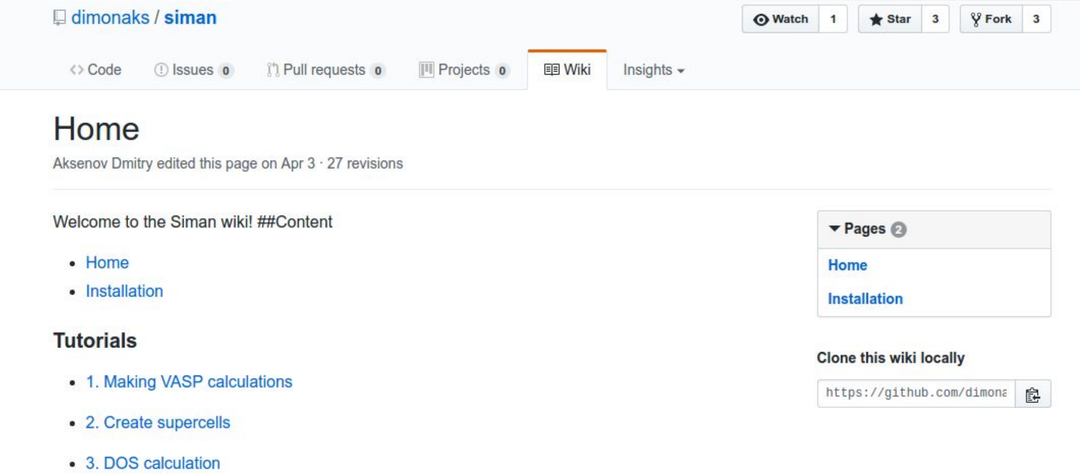
- DFT + U (VASP code)
- U = 6.2 (Ni), 3.4 (Co) , 4.0 (Fe), 3.1 (V) eV
- PAW PBE potentials
- **Spin polarized ferromagnetic**
- Dipole correction for slab
- Energy cut-off 400 eV
- kpoint density 0.03 $Å^{-1}$
- Forces less than 0.05 eV/Å

SIMAN package for automation of DFT calculations

- **SIMAN** package, on github https://github.com/dimonaks/siman (~30 000 lines of code)
  - generation of input files for VASP (DFT) or other codes
  - batch submission of hundreds of jobs and workflows
  - extraction and advanced analysis of output results
  - save results in database using special naming convention

siman 0.9.6

`pip install siman`



Home

Aksenov Dmitry edited this page on Apr 3 · 27 revisions

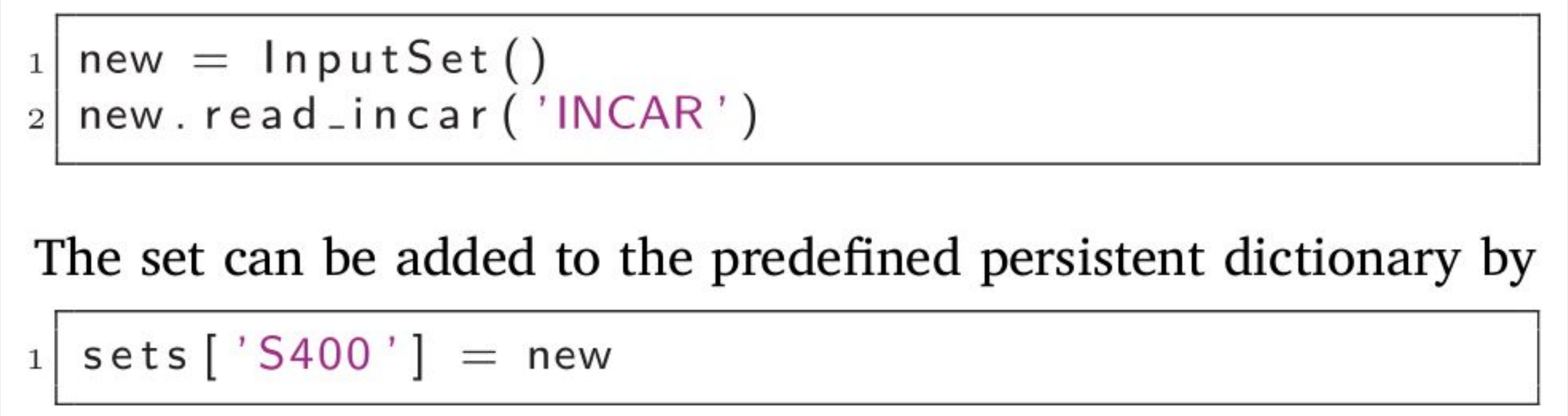
Welcome to the Siman wiki! ##Content

- Home
- Installation

Tutorials

- 1. Making VASP calculations
- 2. Create supercells
- 3. DOS calculation

Optimize volume using Siman at two e-cut



```
new = InputSet()
new.read_incar('INCAR')
```

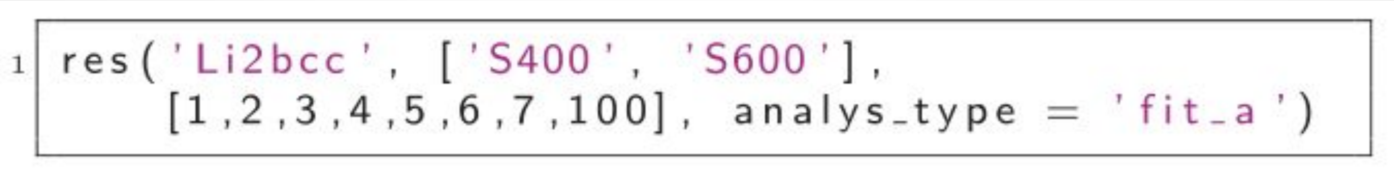
The set can be added to the predefined persistent dictionary by

```
sets['S400'] = new
```

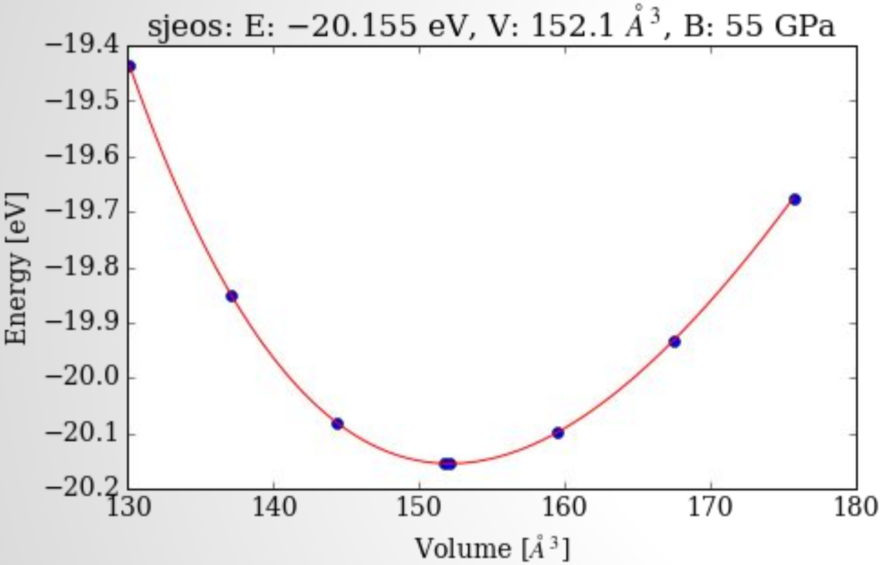
```
read_vasp_sets([('S600','S400', {'ENCUT':600})])
```

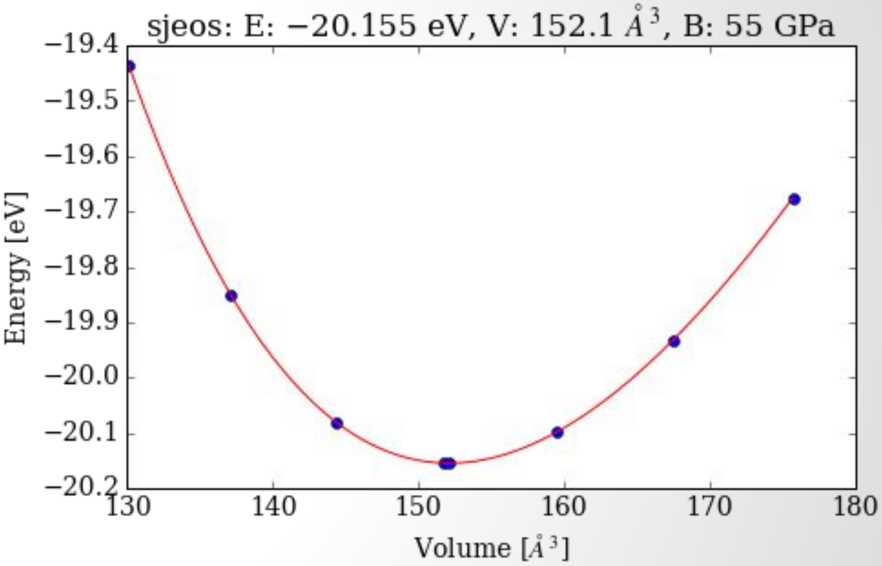
```
add('Li2bcc', ['S400', 'S600'], 1, run = 1,
    calc_method = 'uniform_scale')
```

Results of optimization



```
res('Li2bcc', ['S400', 'S600'],
     [1,2,3,4,5,6,7,100], analys_type = 'fit_a')
```





- In the same manner, each step required in calculations is automated
- Very useful when you have several structures and elements to study

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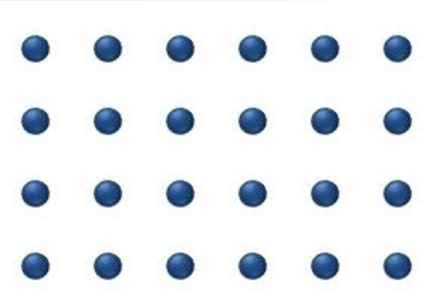
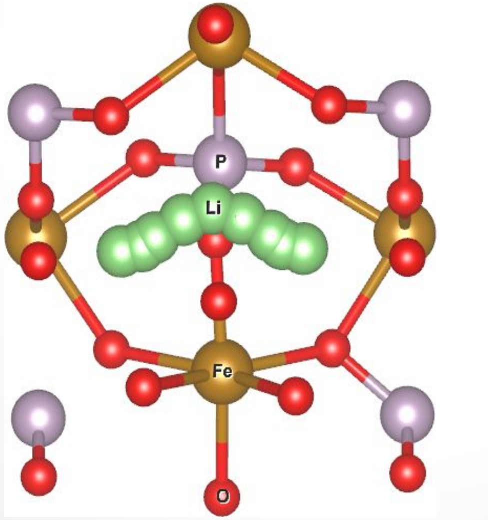
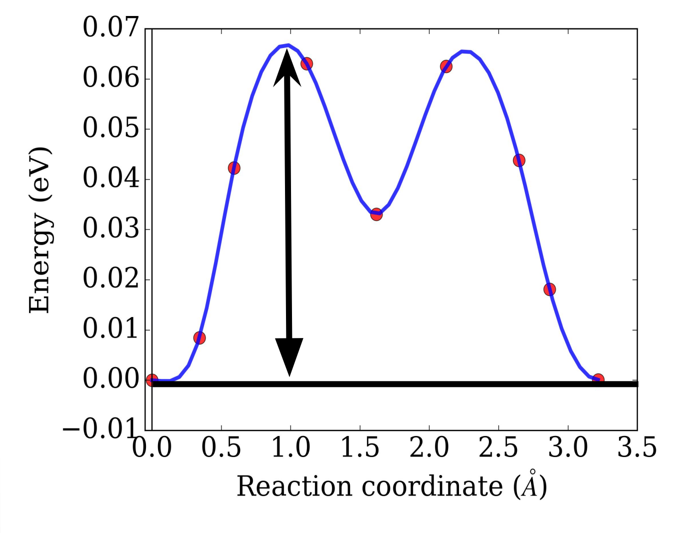
Ionic conductivity determined my migration barriers

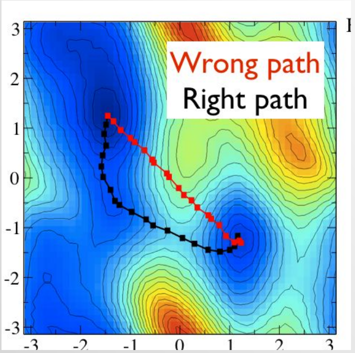
- **Ionic** and electronic conductivity of electrodes determines C-rate
- Ionic conductivity depends on diffusivity of cations
- Migration barrier should be less 0.3-0.4 eV)

$$D = 1/2\Gamma d^2 \qquad \Gamma = \nu^* \exp\left(\frac{-\Delta E}{k_B T}\right)$$



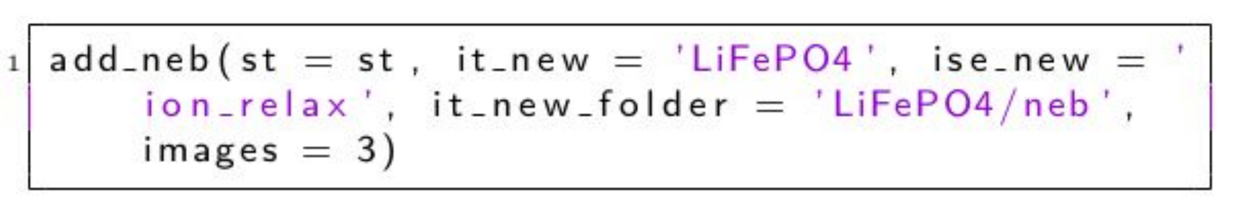






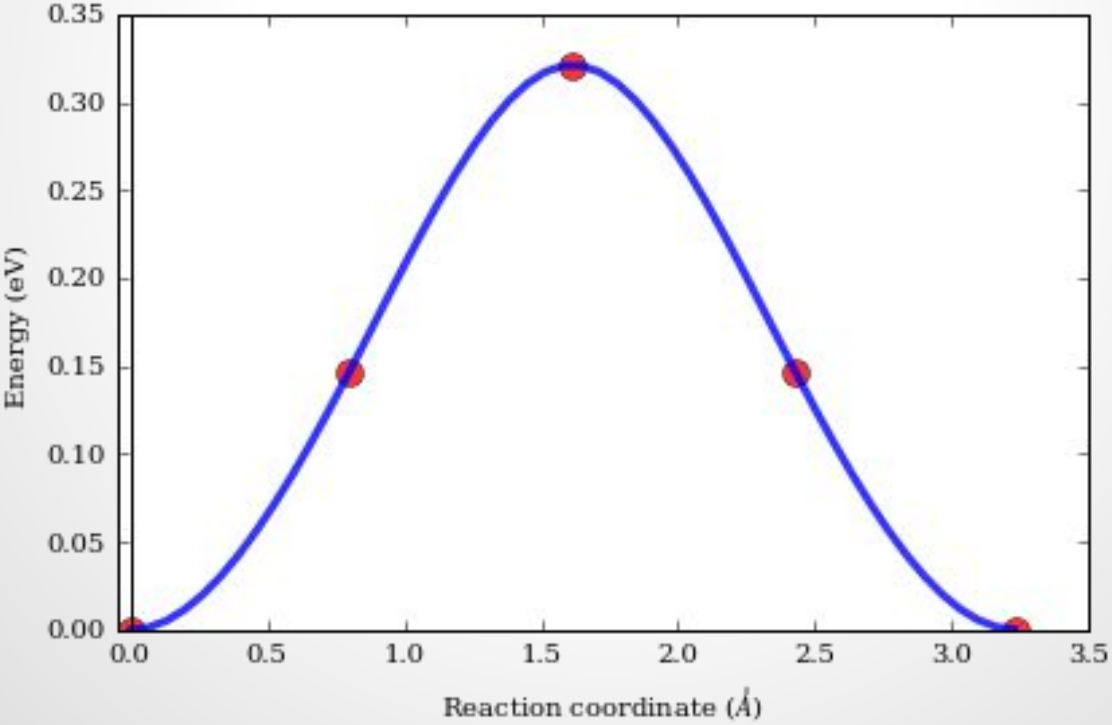
- Migration barrier can be calculated with Nudge elastic band method (NEB)

NEB calculation in SIMAN



```
add_neb(st = st, it_new = 'LiFePO4', ise_new = '
    ion_relax', it_new_folder = 'LiFePO4/neb',
    images = 3)
```

```
res('LiFePO4.n3Li1v1', 'ion_relax', [1,2,3,4,5],
     show = 'fomepp', analys_type = 'neb'   )
```

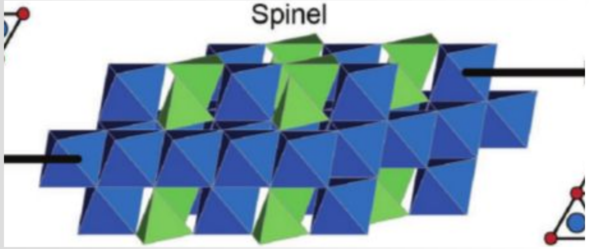


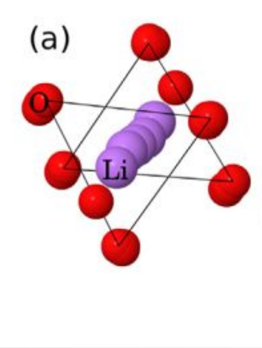
First question

What is the origin of migration barrier in cathode materials ?

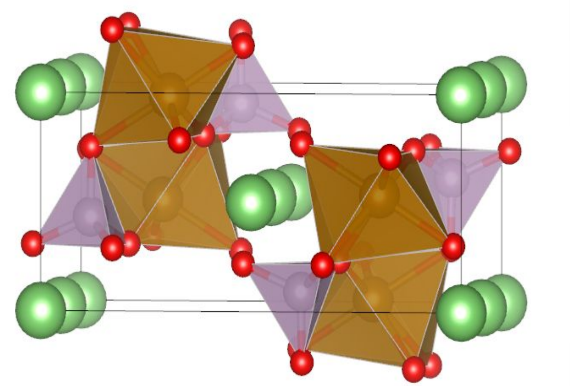
Three classes of cathodes are considered

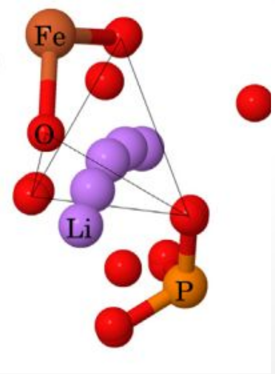
Spinel, $LiMn_2O_4$



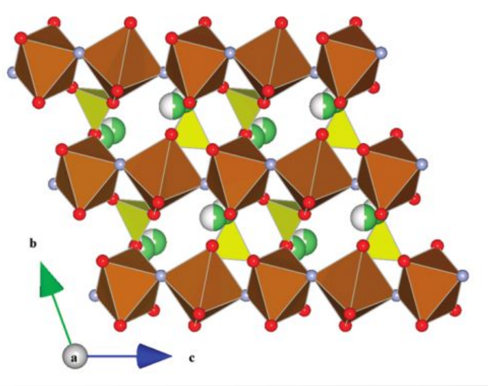


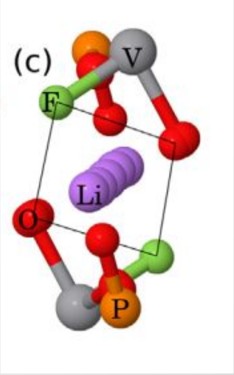
Olivine, $LiFePO_4$, $LiMnPO_4$





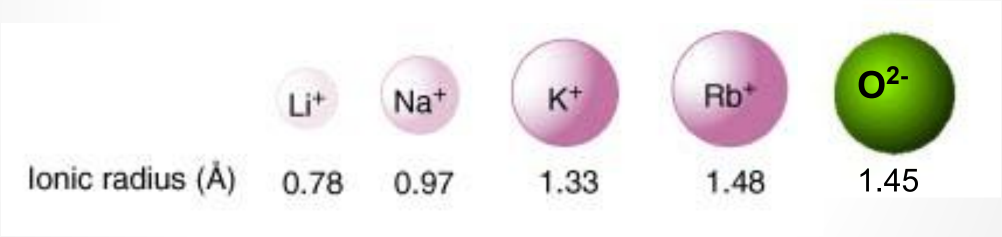
Tavorite, $LiVPO_4F$





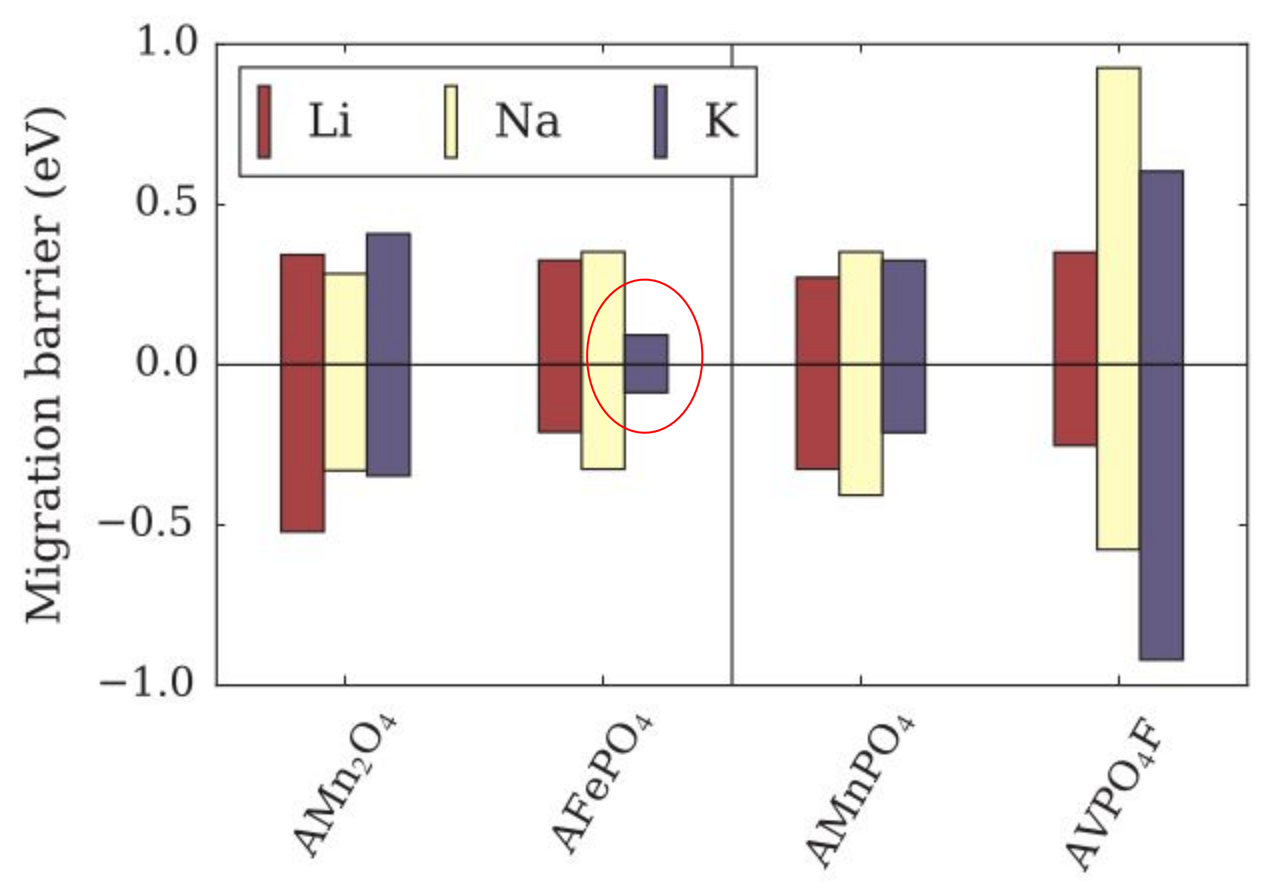
Second question

Is there any difference between Li, Na and K migration?



use the same structures to compare

Migration barriers with NEB method



Intercalated state - Vacancy migration

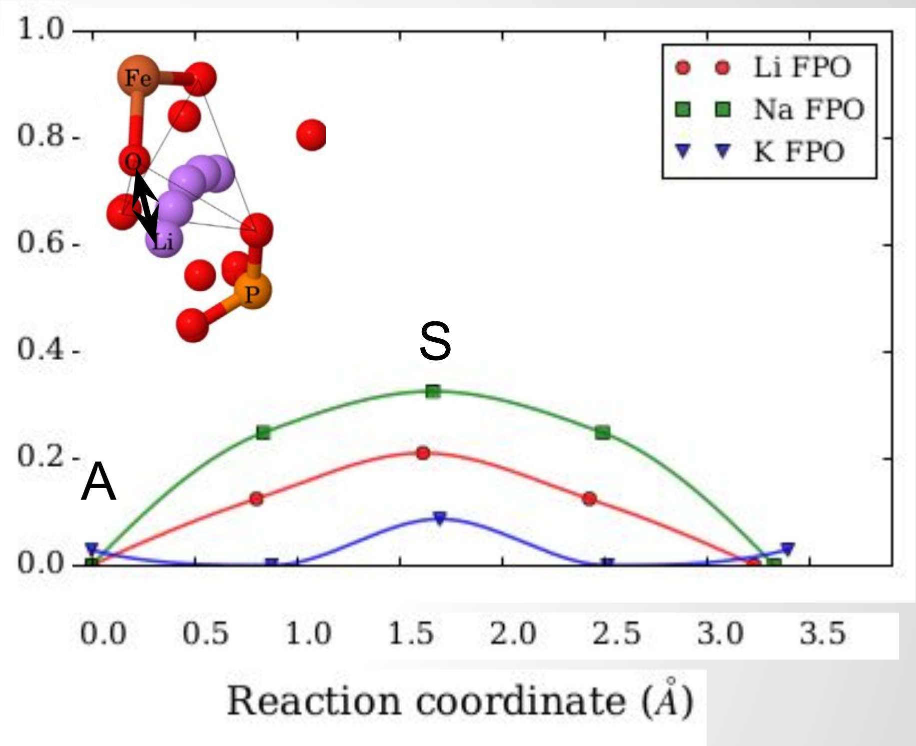
Deintercalated state - interstitial migration

Local contributions to migration barrier

$$E_{DFT} = E_{site} + E_{lattice} \text{ - approximately}$$

$$E_{site} = \sum Z_i/R_i + \sum \lambda_i \exp(-R_i/\rho_i)$$

- R_i - distance between each cation and migrating cation
- site electrostatic energy based on effective charges and Ewald summation
- λ_i and ρ_i are parameters for short range Born-Mayer repulsive interaction [Kunz1992]



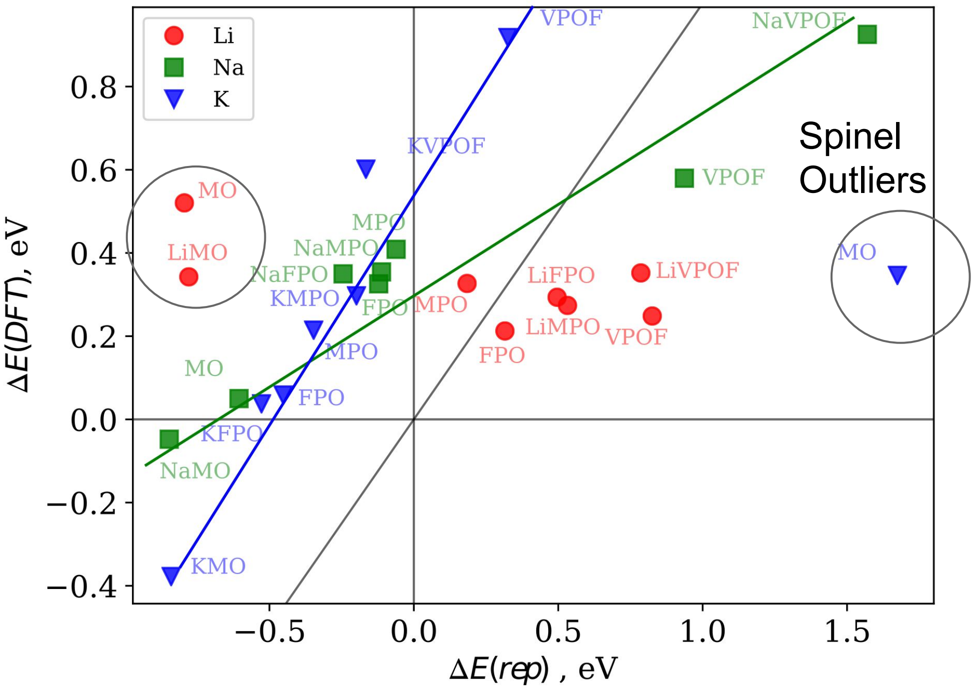
$$dE_{DFT} = E(S, DFT) - E(A, DFT)$$

$$dE_m = E_m(S) - E_m(A)$$

For many cases it is equivalent to migration barrier

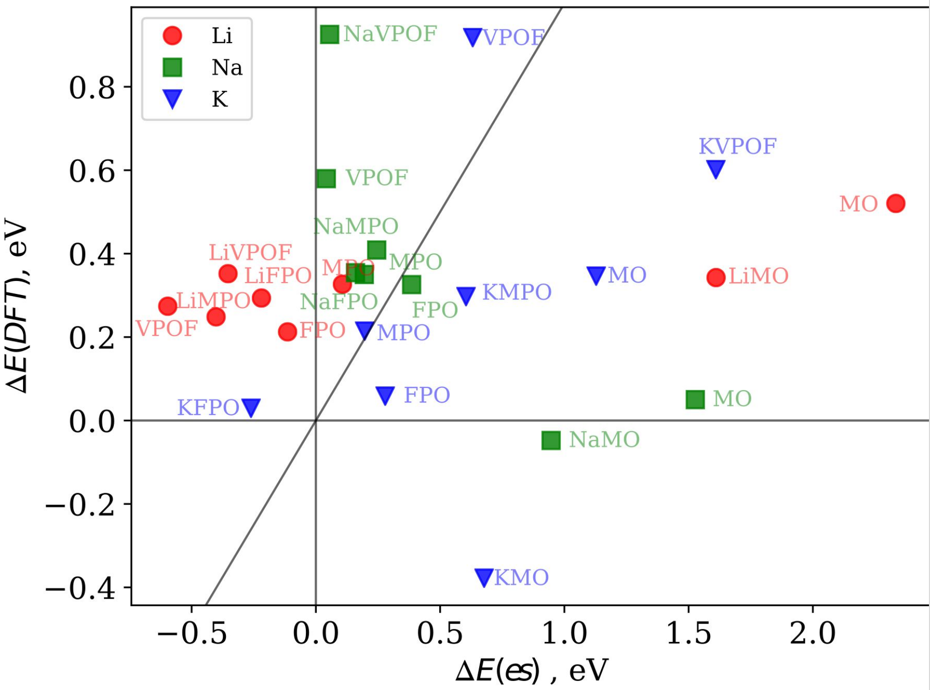
Repulsive and electrostatic site energy

Change of repulsive energy vs dE(DFT)



For K (MO omitted) and Na proportionality can be identified $R^2 = 0.6$

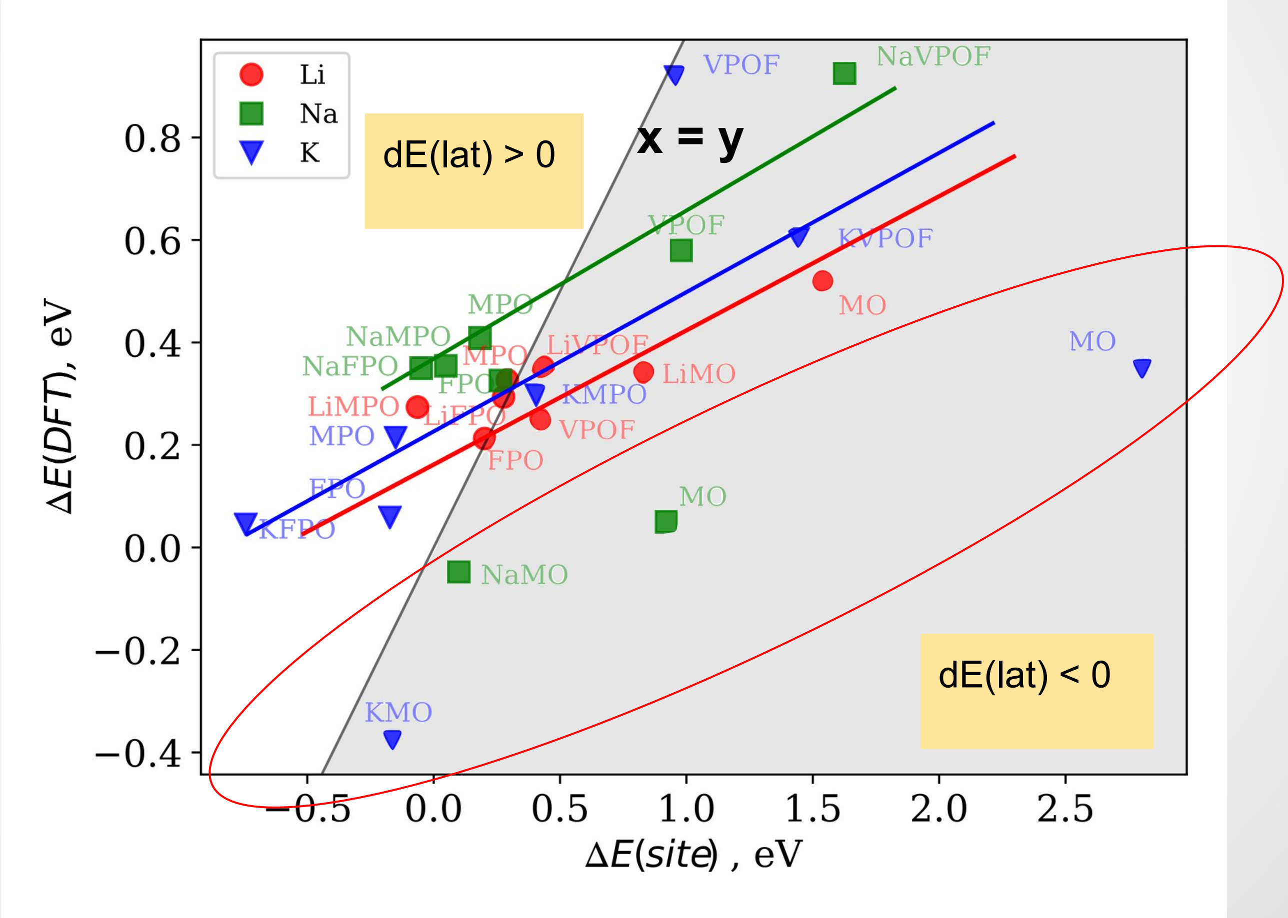
Change of ES energy vs dE(DFT)



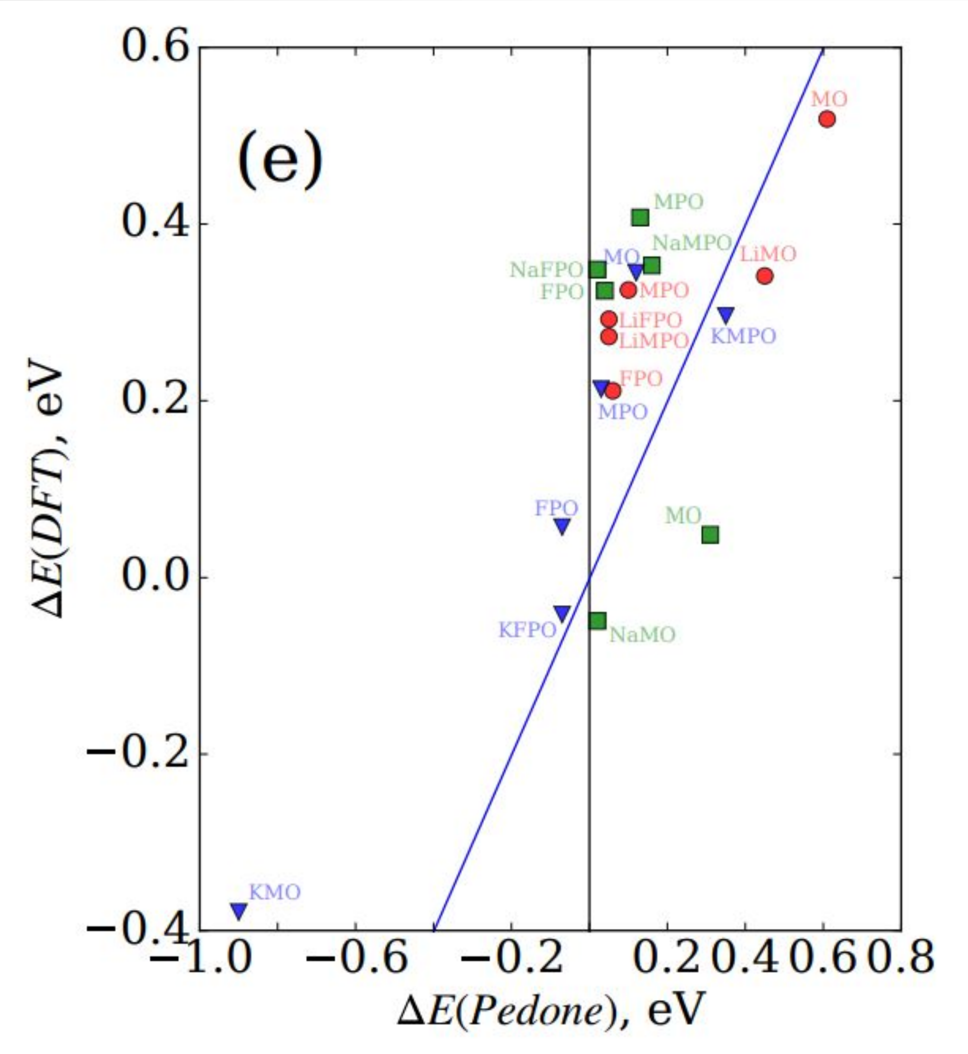
No correlation at all

Sum of repulsive and ES term vs dE (DFT)

$$\Delta E_{lattice} = \Delta E_{DFT} - \Delta E_{site}$$



Empirical Interatomic potentials, $\Delta E_{site} + \Delta E_{lattice}$

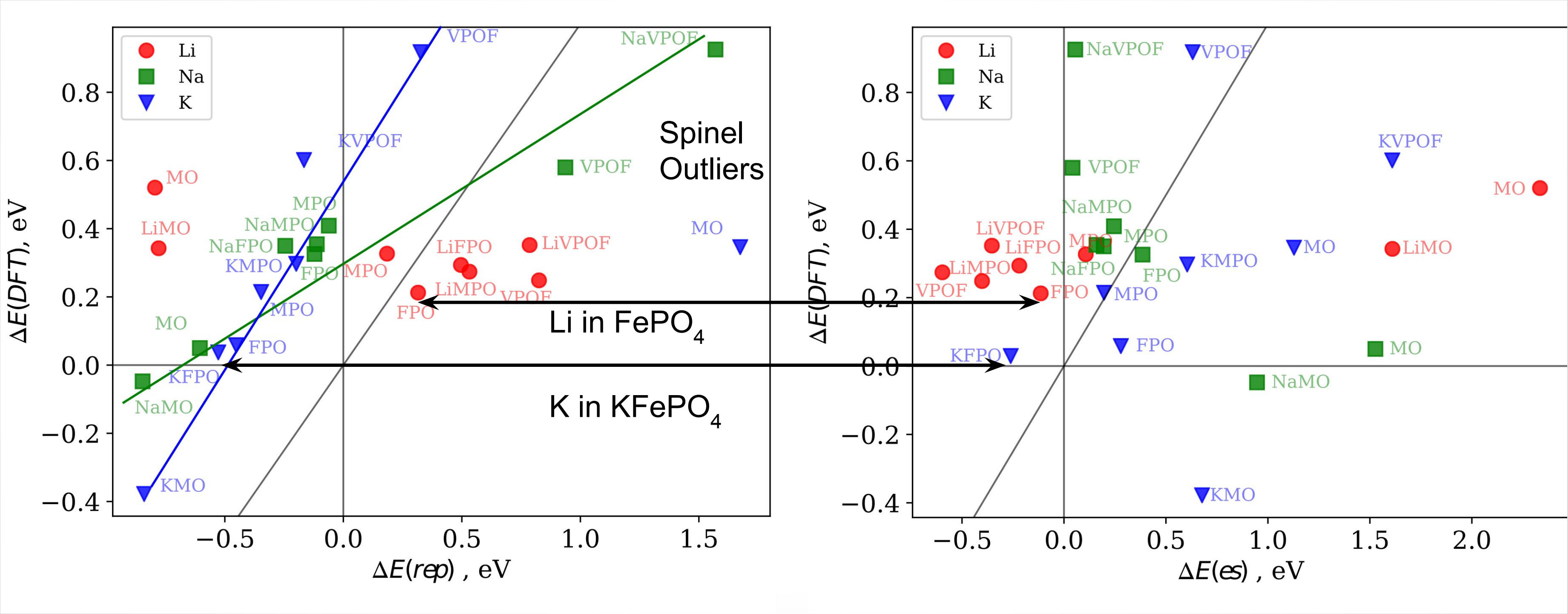


- Without potential parametrization, $R^2 = 0.6$
- Good quantitative description
- Spinel outliers are on line
- The lattice contribution is responsible for reducing energy at saddle point

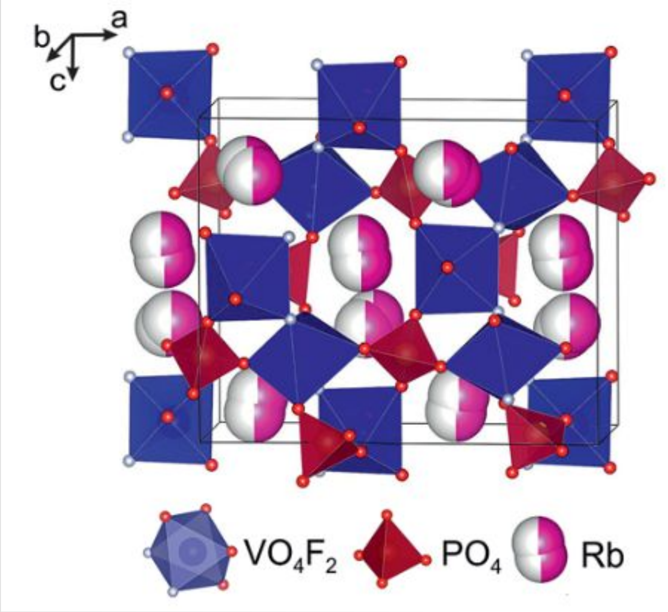
Reasons for low barrier of K

Change of repulsive energy vs dE(DFT)

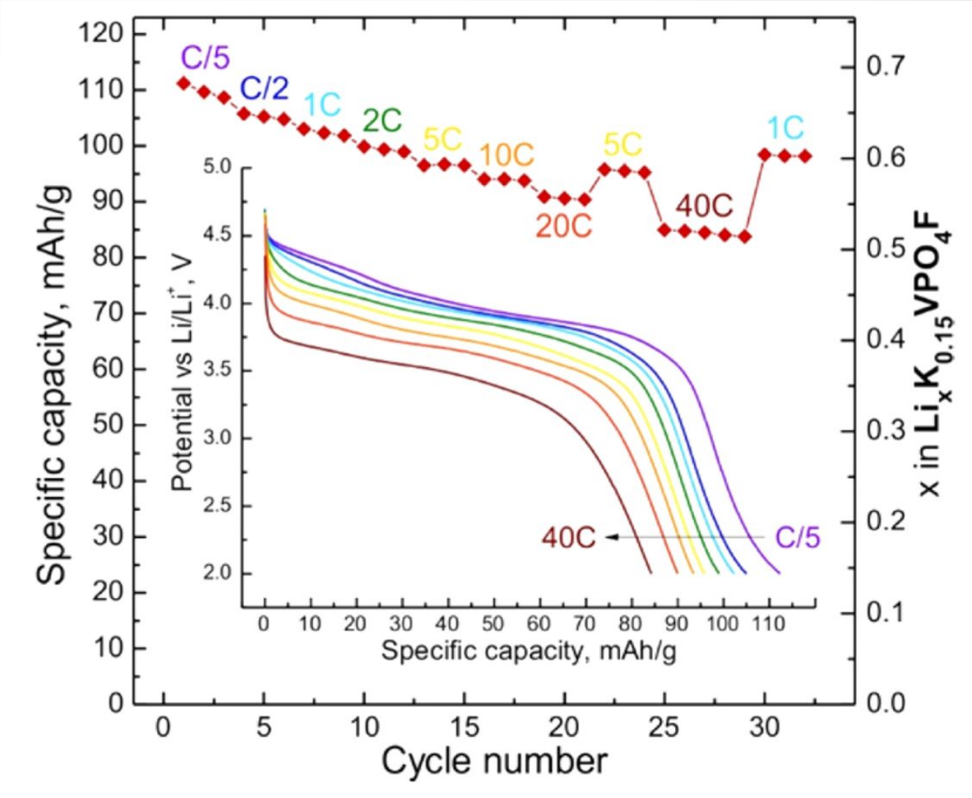
Change of ES energy vs dE(DFT)



$KVPO_4F$ - new cathode material developed at MSU and Skoltech



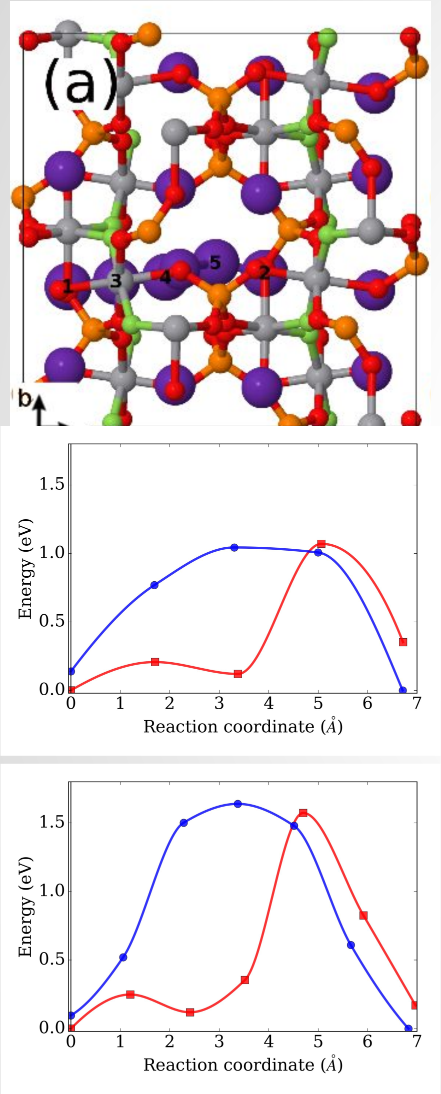
- Relatively low cost
- Possible intercalation of Li, Na, and K
- High intercalation voltage 4 V
- Very high specific rate



75 % of initial capacity at 40C

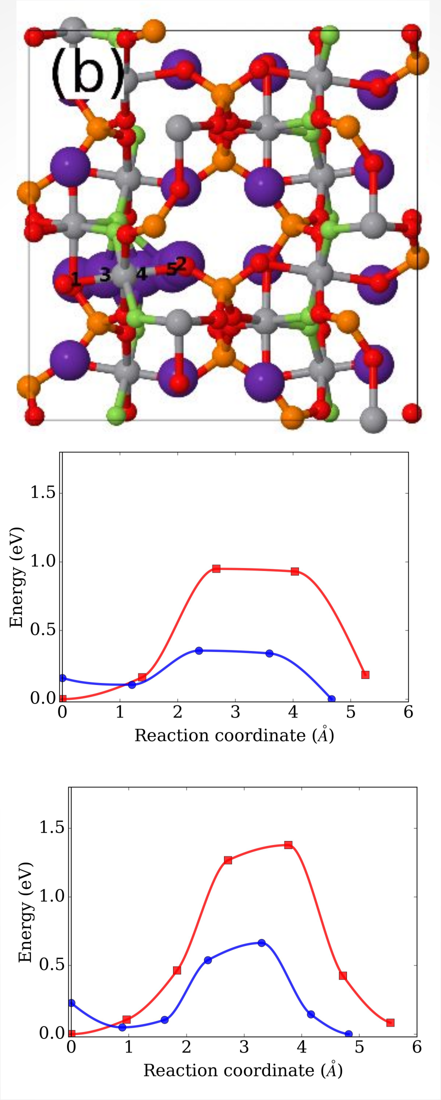
What is the reason for high specific rate?

Migration of K^+ and Rb^+ in $AVPO_4F$



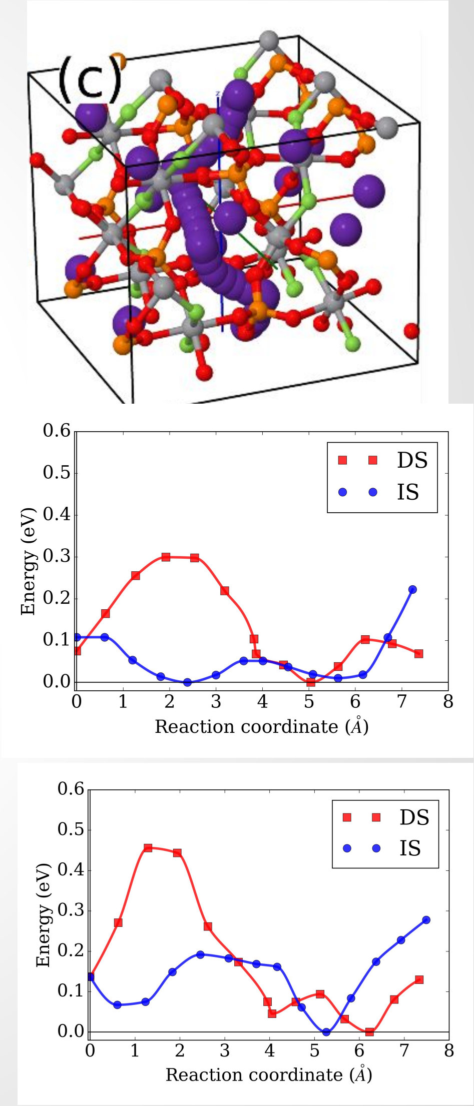
K

Rb



K

Rb



Conclusions

- Migration barrier can be understood through site and lattice contributions
- Simple electrostatic and repulsive site energies allows to estimate barriers
- Low barriers are result of efficient compensation of different contributions, which allows zero-barrier crystal structures

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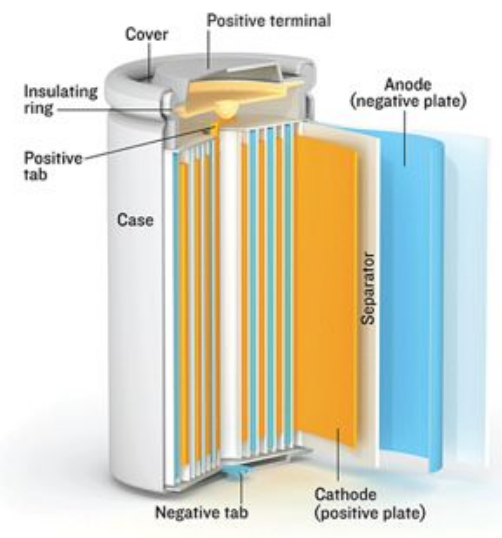
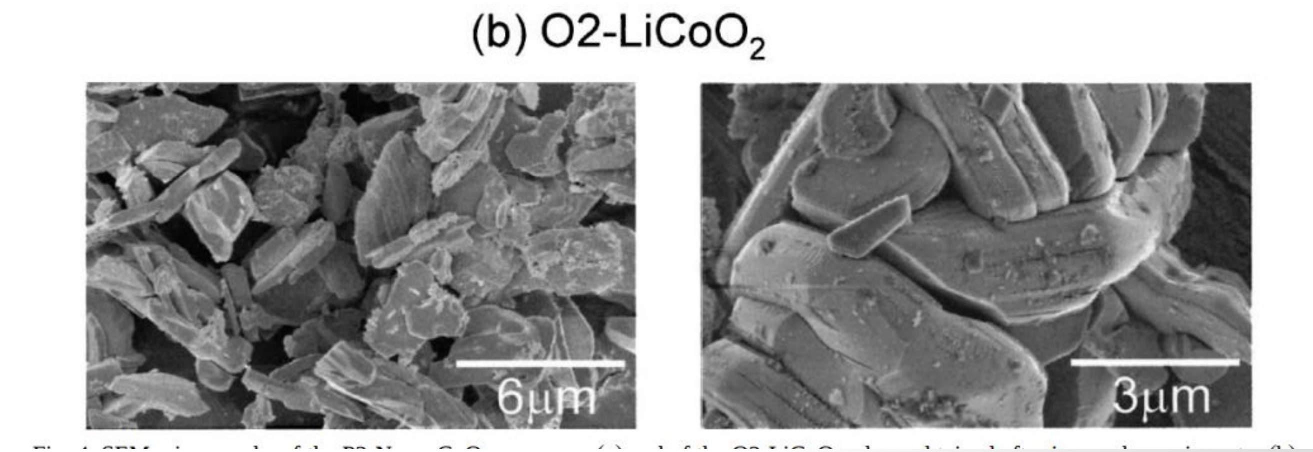
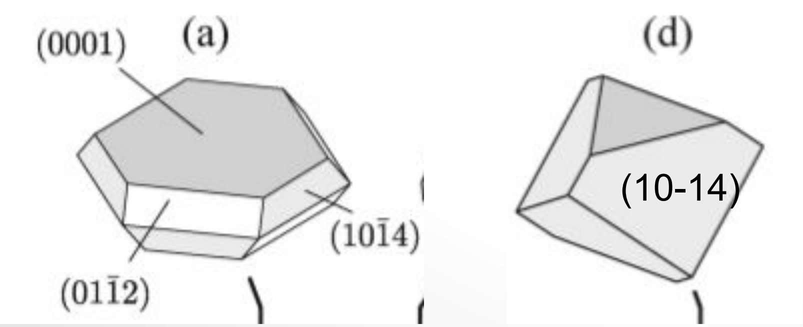
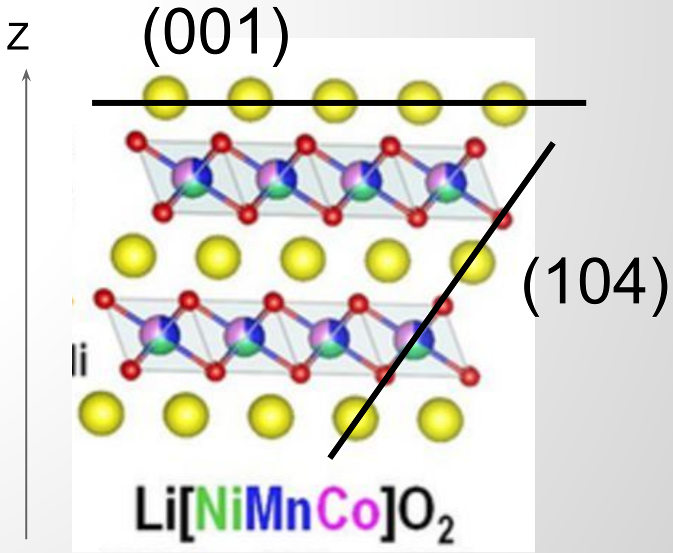
Morphology and surface structure of cathode particles is highly important!




(b) O2-LiCoO$_2$

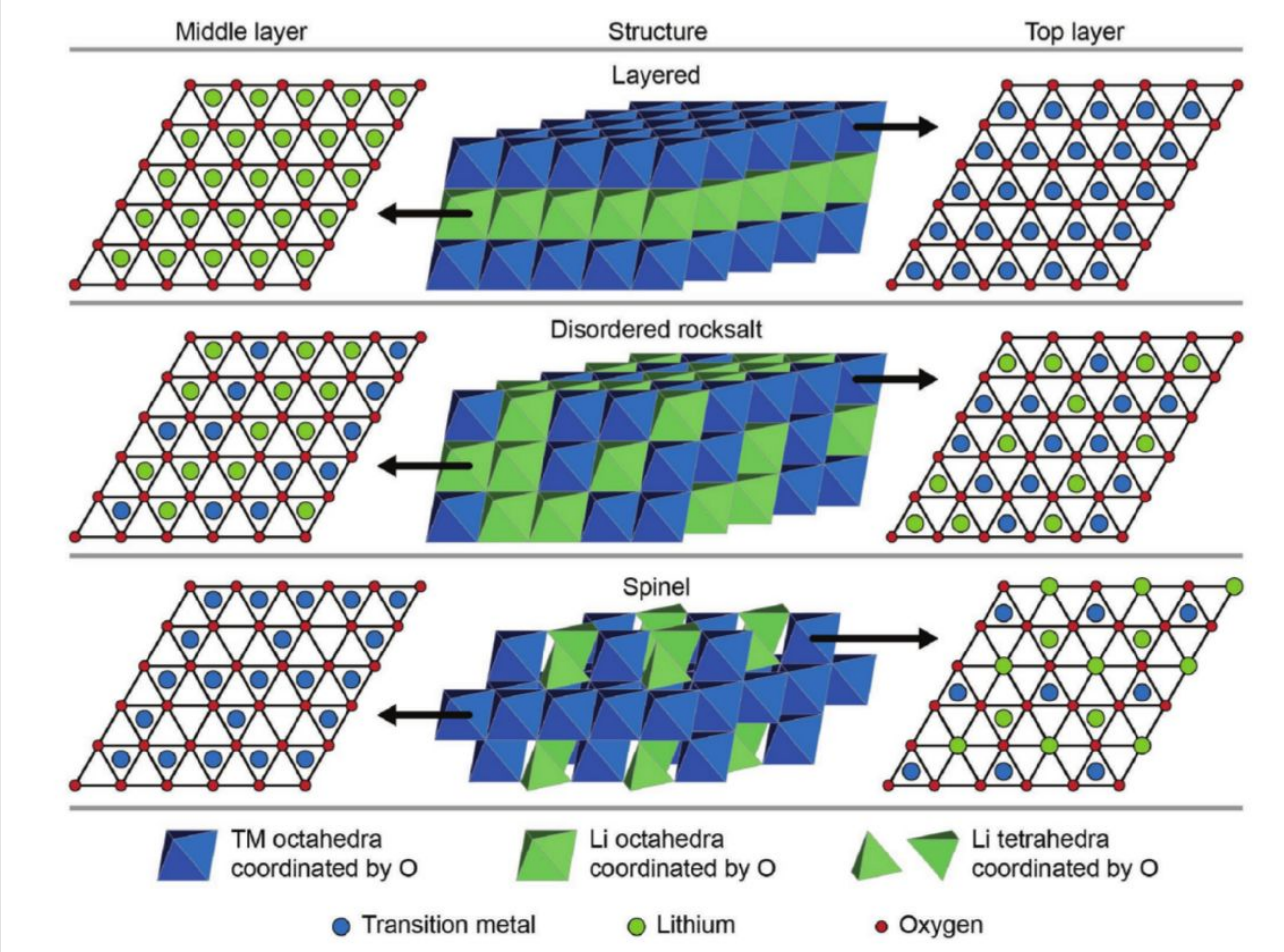




Carlier2001 Kramer2009

What happens on the surface?

Crystal structure of TM oxides



$LiNiO_2$

NiO

$LiNiO_2$ - $Li_{0.5}NiO_2$

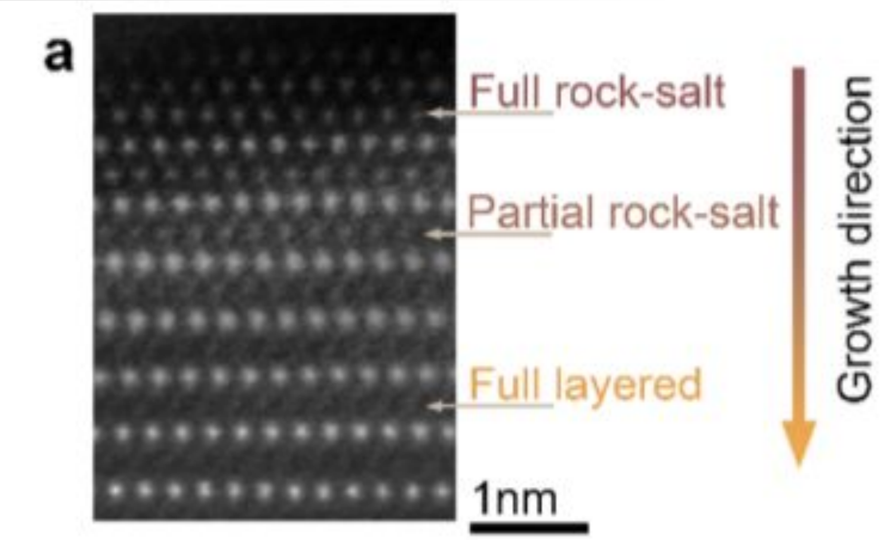
Two main space groups: R-3m and C2/m

From Radin2017

Rocksalt-type surface reconstruction $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (R-3m) - detrimental

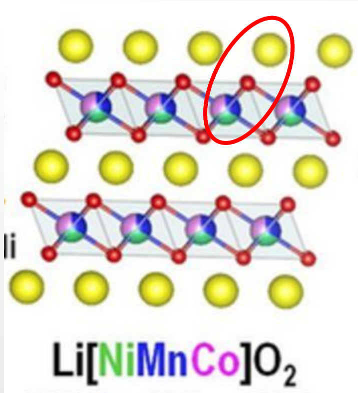
(001) hex -> (111)cub

(104)hex -> (002)cubic



rough due to interlayer mixing

with steps according to inward migration mechanism



No exposure to electrolyte!

Zhang2018

Main question

Is surface reconstruction kinetically controlled or any thermodynamic driving force exists?

↓

Make atomic simulation to study **surface reconstruction** neglecting the influence of electrolyte.

Plan of the study

1. Choose $LiNiO_2$, $LiCoO_2$, $NaNiO_2$, $NaCoO_2$ as studied systems

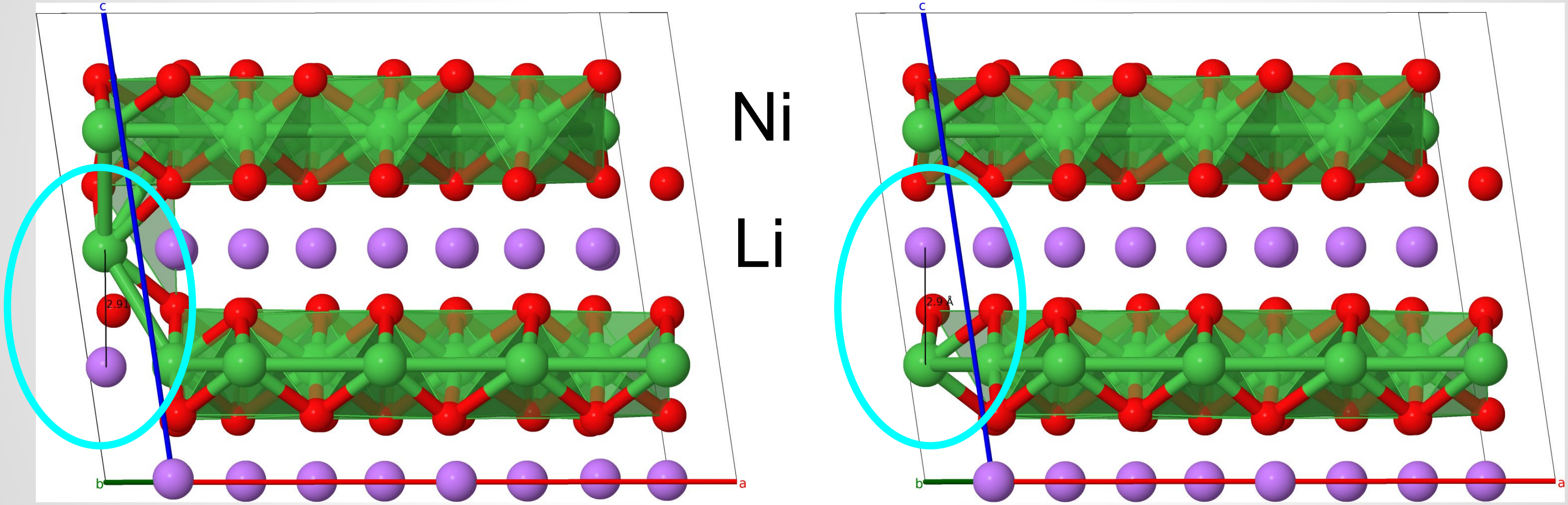
2. Antisite defects in bulk

4. Surface energies - Wulff shapes

3. Surface antisites - reconstruction

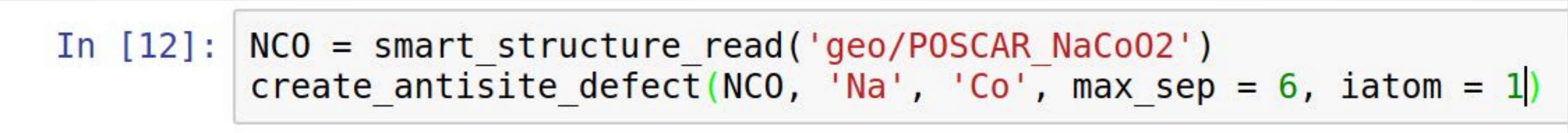
Formation energy of antisites

Very important type of defects in layered oxides, up to 10% in $LiNiO_2$, but much smaller in $LiCoO_2$

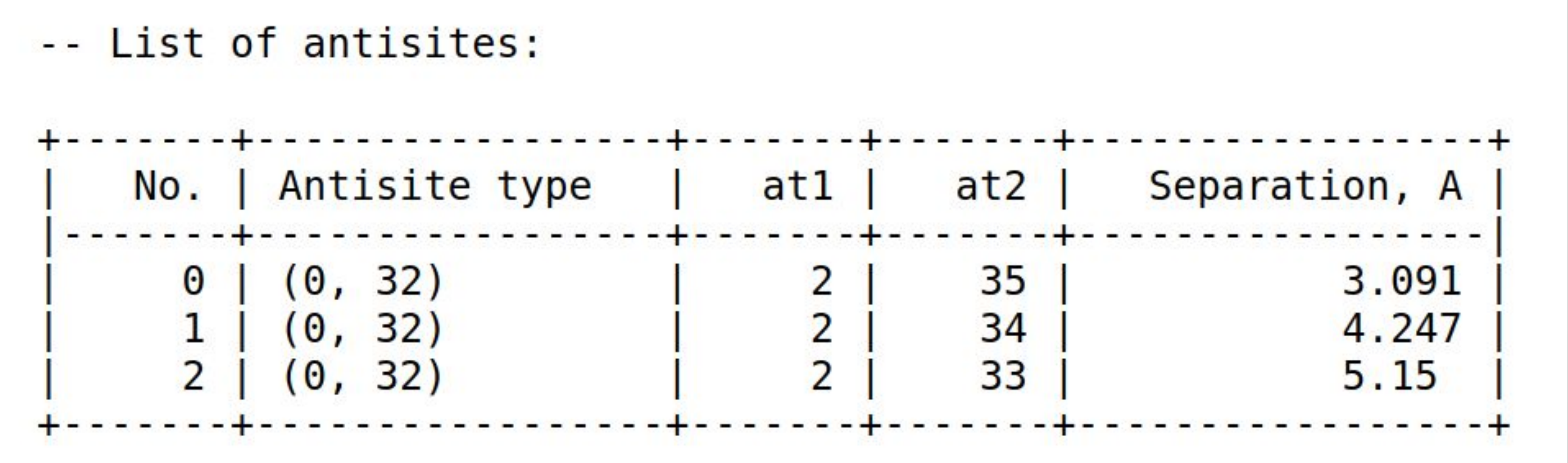


dE_{AS} = E(supercell with antisite) - E (ideal supercell)

Siman code: creating antisite defects



```
In [12]: NCO = smart_structure_read('geo/POSCAR_NaCoO2')
         create_antisite_defect(NCO, 'Na', 'Co', max_sep = 6, iatom = 1)
```



```
-- List of antisites:

+-------+-----------------+-------+-------+-----------------+
|   No. | Antisite type   |   at1 |   at2 |   Separation, A |
|-------+-----------------+-------+-------+-----------------|
|     0 | (0, 32)         |     2 |    35 |           3.091 |
|     1 | (0, 32)         |     2 |    34 |           4.247 |
|     2 | (0, 32)         |     2 |    33 |           5.15  |
+-------+-----------------+-------+-------+-----------------+
```

Antisite pairs formation energies

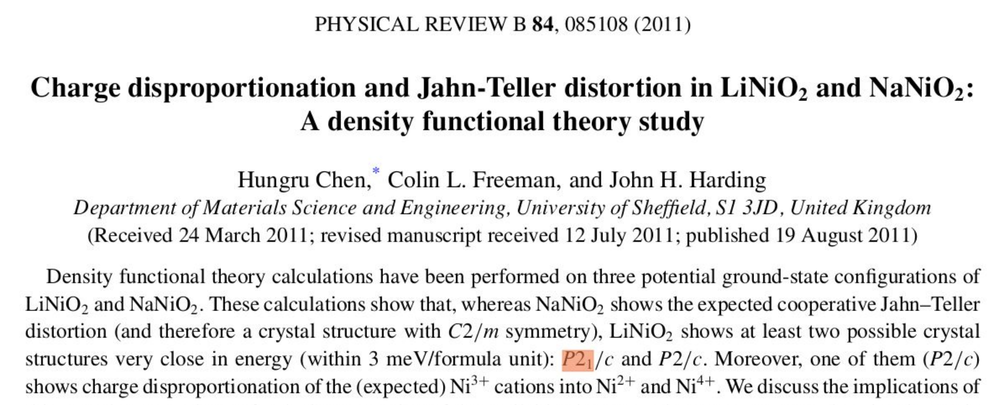
Phase	space group	AS energy
$LiNiO_2$	R-3m	− 0.8 eV
$LiCoO_2$	R-3m	1.9 eV
$NaNiO_2$	C2/m	2.1 eV
$NaCoO_2$	R-3m	2.9 eV

Negative antisite formation energy for $LiNiO_2$!

May be the problem with $LiNiO_2$ space group?

- **$LiNiO_2$** is often reported in **R-3m** group, where all Ni-O bonds are fixed to 1.99 Å.
- However both Jahn-Teller (**JT**) distortion charge ordering of Ni^{3+} to Ni^{2+} and Ni^{4+} are possible
- For both the energy is reduced

$LiNiO_2$ in P2/c with charge order is most stable



PHYSICAL REVIEW B **84**, 085108 (2011)

Charge disproportionation and Jahn-Teller distortion in $LiNiO_2$ and $NaNiO_2$: A density functional theory study

Hungru Chen,* Colin L. Freeman, and John H. Harding

Department of Materials Science and Engineering, University of Sheffield, S1 3JD, United Kingdom

(Received 24 March 2011; revised manuscript received 12 July 2011; published 19 August 2011)

Density functional theory calculations have been performed on three potential ground-state configurations of $LiNiO_2$ and $NaNiO_2$. These calculations show that, whereas $NaNiO_2$ shows the expected cooperative Jahn–Teller distortion (and therefore a crystal structure with *C*2/*m* symmetry), $LiNiO_2$ shows at least two possible crystal structures very close in energy (within 3 meV/formula unit): $P2_1/c$ and $P2/c$. Moreover, one of them ($P2/c$) shows charge disproportionation of the (expected) Ni^{3+} cations into Ni^{2+} and Ni^{4+}. We discuss the implications of this complex ground state for the interpretation of the available electron and neutron structure data, its electronic and comple

DOI: 10.110

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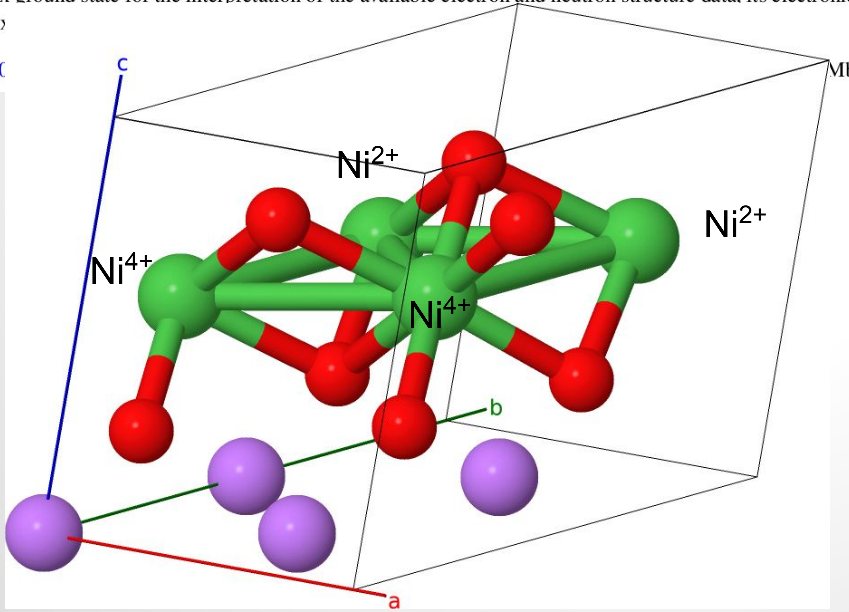


- Charge-disproportionation of Ni^{3+} to Ni^{2+} and Ni^{4+}
- According to our results the total energy reduced by **15 meV/atom**
- 1.5 eV for 100-atom cell!

Antisite pairs formation energies

Phase	space group	AS energy	NN, sep, A
$LiNiO_2$	P2/c	0.73 eV	1nn, 2.86 A
$LiCoO_2$	R-3m	1.9 eV	1nn, 2.82 A
$NaNiO_2$	C2/m	2.1 eV	2nn, 4.17 A
$NaCoO_2$	R-3m	2.9 eV	2nn, 4.22 A

Chen, Hungru, James A. Dawson, and John H. Harding. "Effects of cationic substitution on structural defects in layered cathode materials LiNiO 2." *Journal of Materials Chemistry A*2, no. 21 (2014): 7988-7996.

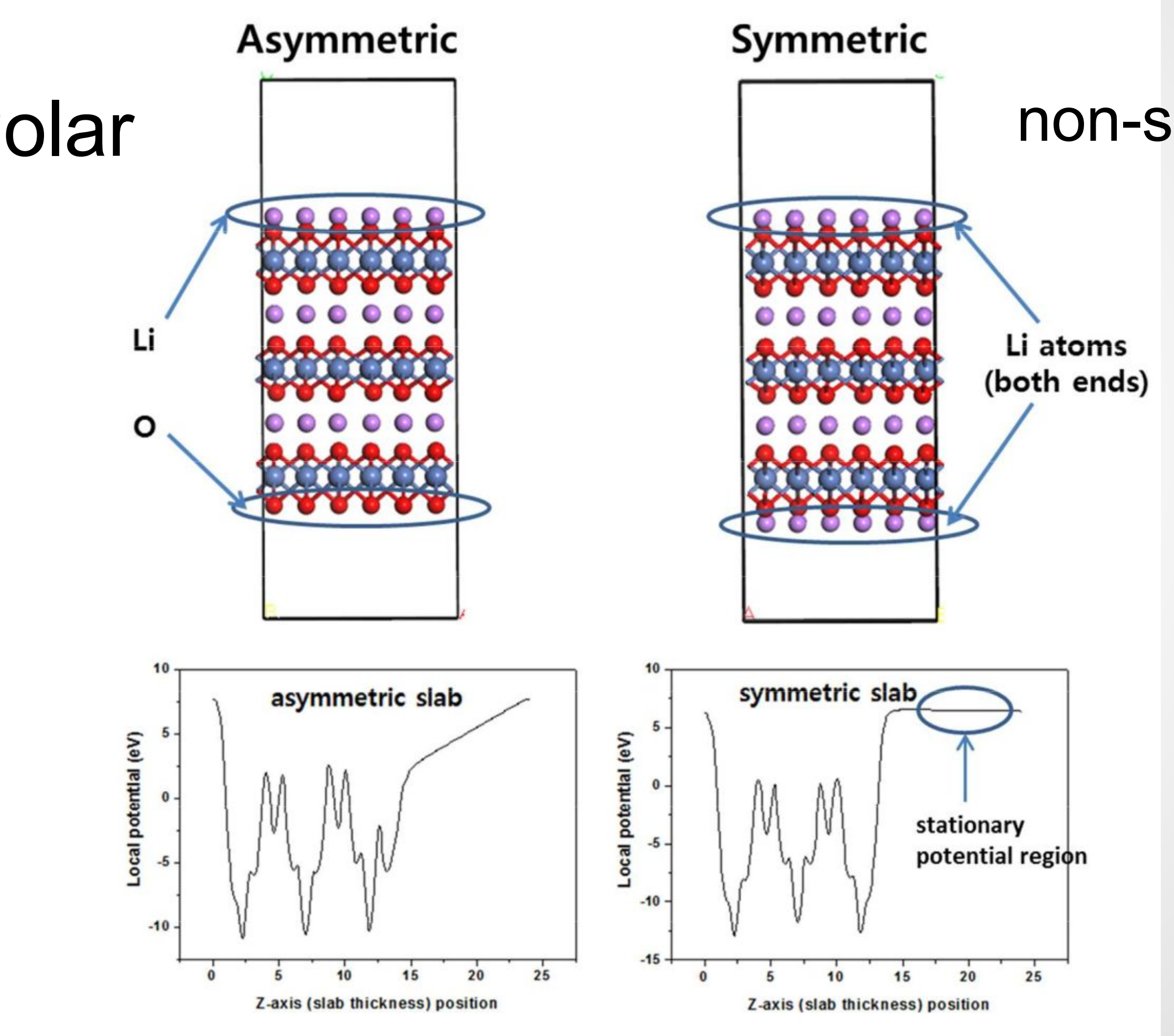
Reasons for different antisite energies

- Ni is Ni^{2+} (HS) state in Ni_{Li} position
- Co is Co^{2+} (HS) state in Co_{Li} position
- Co^{2+} has 0.75 Å, which is closer to Li^{+} radius (0.76 Å) than Ni^{2+} (0.69 Å)
- Superexchange interaction Ni-O-Ni (180°) is responsible for low energy of Ni antisite
- Na^{+} has 1.16 Å

Surface energy calculations

Polar

non-stoichiometric



Cho E., Seo S. W., Min K. ACS applied materials & interfaces. – 2017. – T. 9. – №. 38. – C. 33257-33266./SI

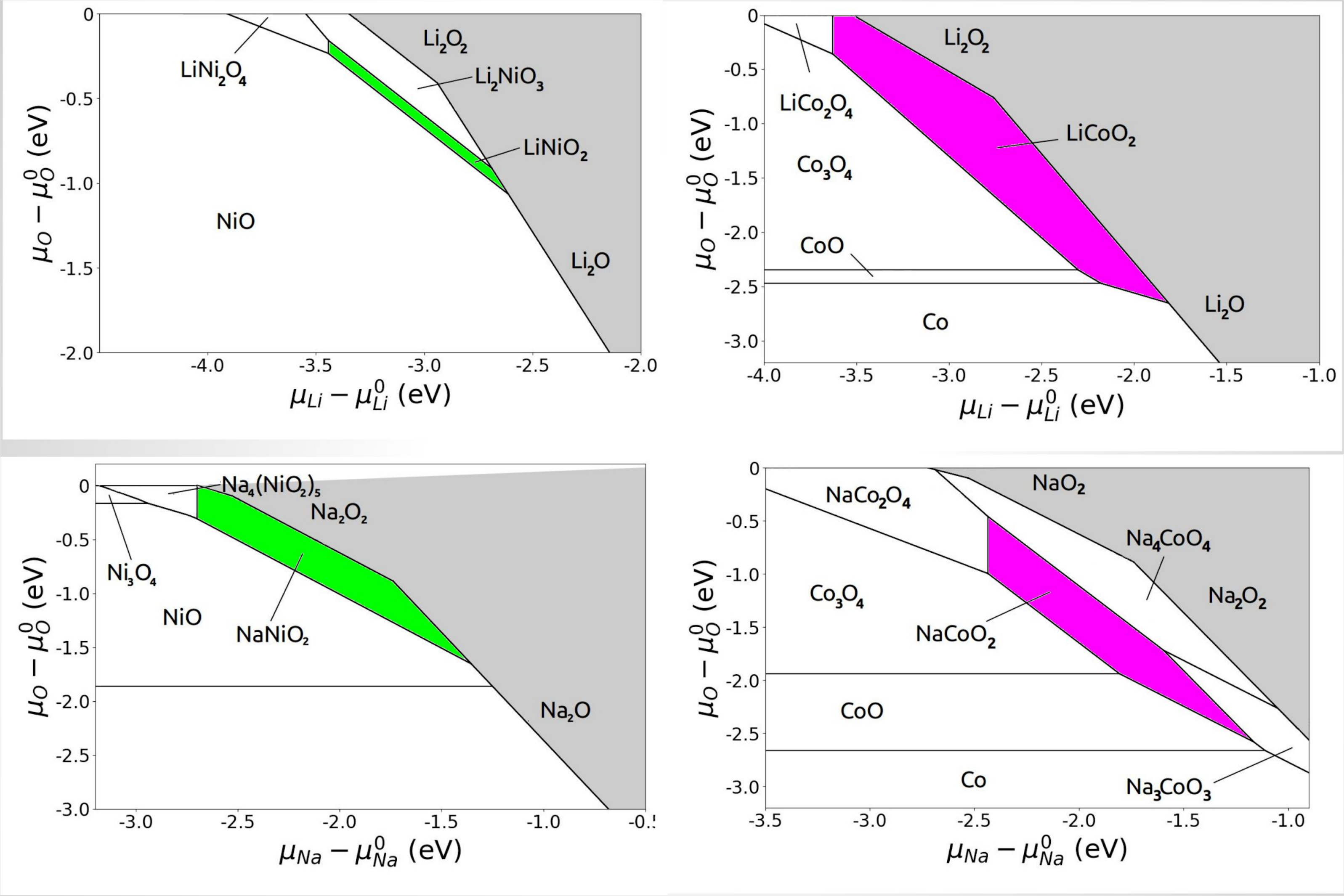
Surface energies

$$\gamma = \frac{1}{2\cdot A}\left[E_{\mathrm{slab}} - N_{\mathrm{Co}}\left(\varepsilon_{\mathrm{b}} - \sum_i \Gamma_i \cdot \mu_i\right)\right]$$

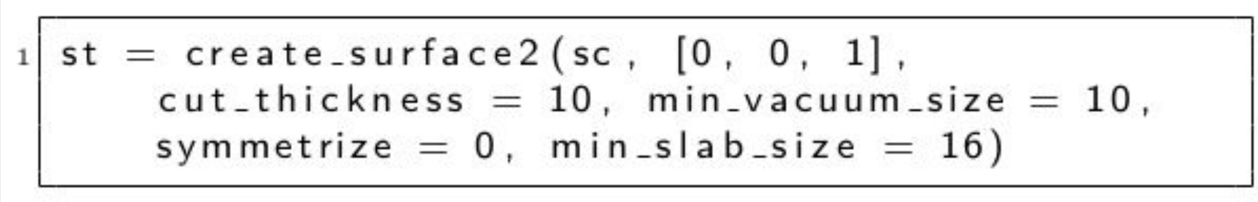
ε_b is energy of bulk cell, Γ_i is excess of i atoms in the slab

Dependence on chemical potential ! phase diagram is required

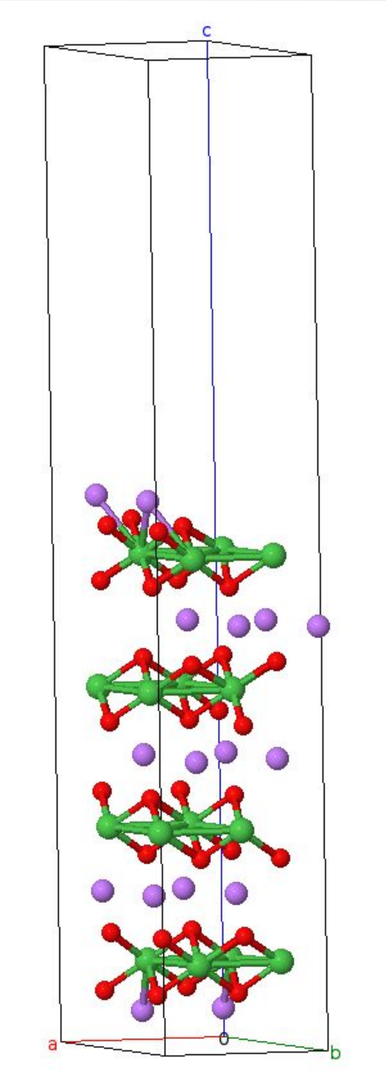
Phase diagrams in chemical potential space



SIMAN: creating slabs with surfaces



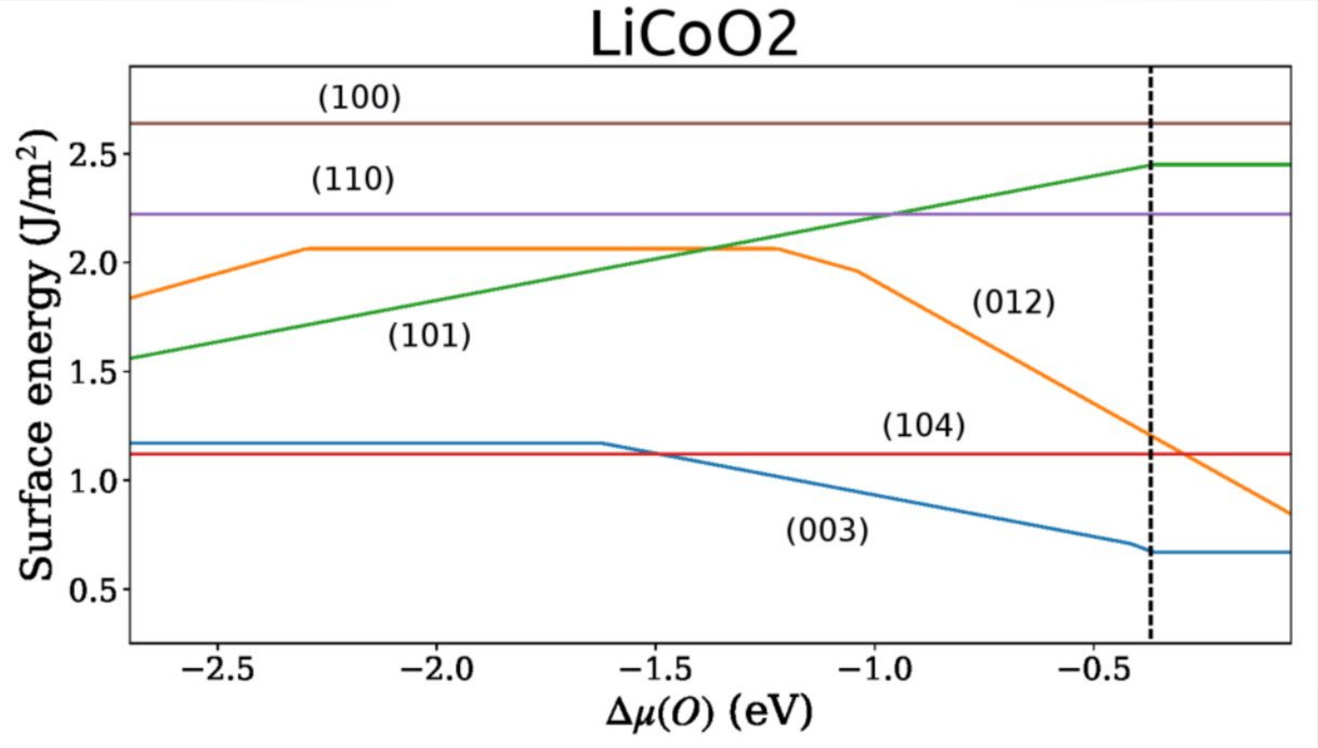
```
st = create_surface2(sc, [0, 0, 1],
     cut_thickness = 10, min_vacuum_size = 10,
     symmetrize = 0, min_slab_size = 16)
```



Considered surfaces, example of $LiCoO_2$

R-3m: non-polar (104), (110), (100), polar : (012), (003), (101), (111)

C2/m: non-polar (104), (10-1), (100), (111), (10-2); polar - (003), (012), (110)

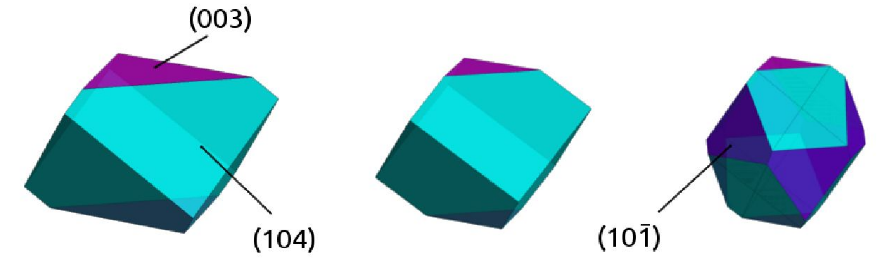


Dependence of surface energy on chemical potential

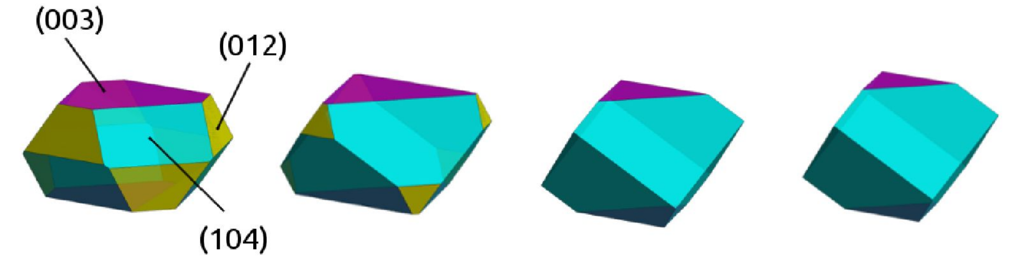
Wulff construction depending on chemical potential

Wulff construction - minimizes the total surface energy for a given particle volume

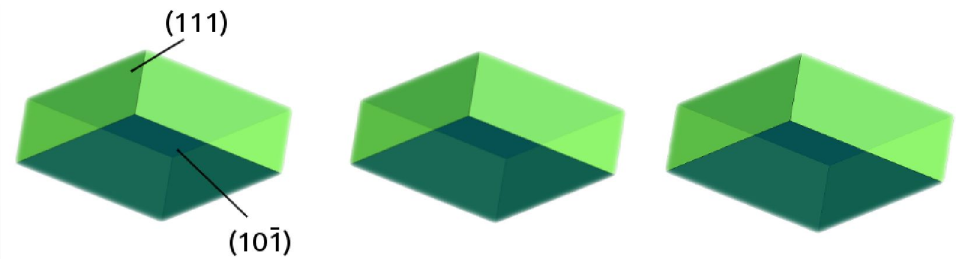
$LiNiO_2$



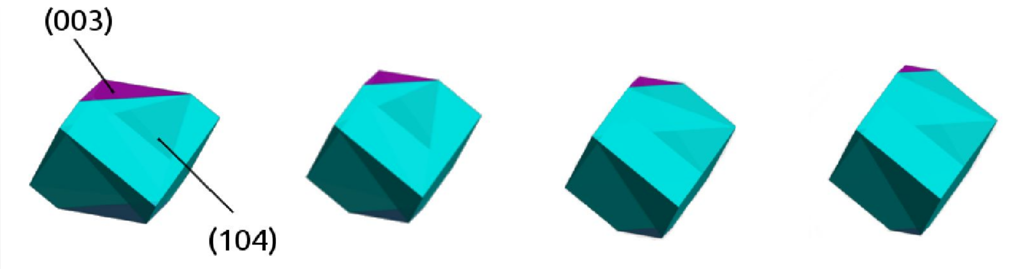
$LiCoO_2$



$NaNiO_2$



$NaCoO_2$



Surface energy (J/m^2) of considered oxides

Surface	$LiNiO_2$ (R-3m)	$LiCoO_2$ (R-3m)	$NaNiO_2$ (C2/m)	$NaCoO_2$ (R-3m)
(001) ½ ML	0.65	1.2	1.35	1.35
(104)/ (10-1)	0.55	1.1	0.35	0.87

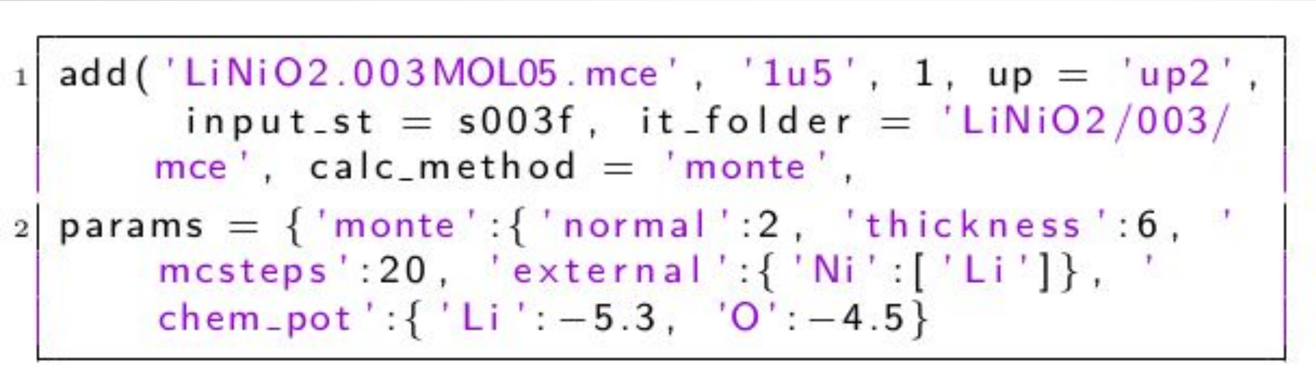
SIMAN: Code for surface reconstruction

- Monte-Carlo for atom swapping
  - Swap atoms in the specified layers, for example Li and Ni in $LiNiO_2$
  - Swap atoms with external reservoir
  - Swap atoms with vacancies
  - Metropolis criteria for accepting moves

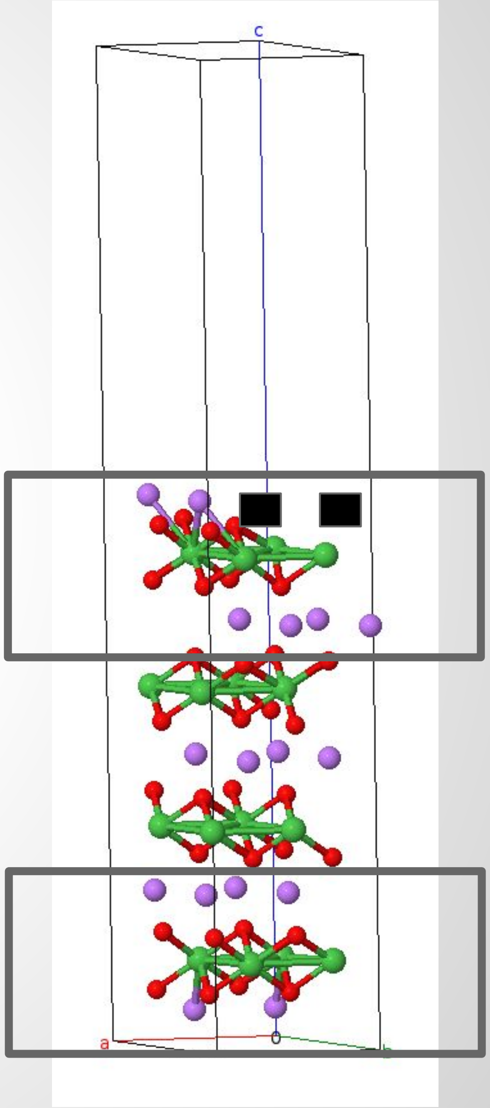
P = exp(dE/kT), P >1 or P > rand(0,1) - accept

- Check the coordination after swapping
  - if Ni-O average distance increased more than specified criteria than ignore

Monte-Carlo is integrated in SIMAN code



```
add('LiNiO2.003MOL05.mce', '1u5', 1, up = 'up2',
     input_st = s003f, it_folder = 'LiNiO2/003/
   mce', calc_method = 'monte',
params = {'monte':{'normal':2, 'thickness':6, '
   mcsteps':20, 'external':{'Ni':['Li']}, '
   chem_pot':{'Li':-5.3, 'O':-4.5}
```



Layers for
Monte-Carlo swaps

Fixed atoms

Conclusions

- Since surface reconstruction requires increase of surface energy it should be kinetically activated (effect of electrolyte?)
- Due to thermodynamic reasons reconstruction in Co oxides is comparable to Ni oxides
- Na-based oxides are more resistant to reconstruction (is it good or bad?)
- Project took several thousands calculations, which would be impossible without **Automation** !

Outline

1. Motivation to study energy materials

2. Method and SIMAN code

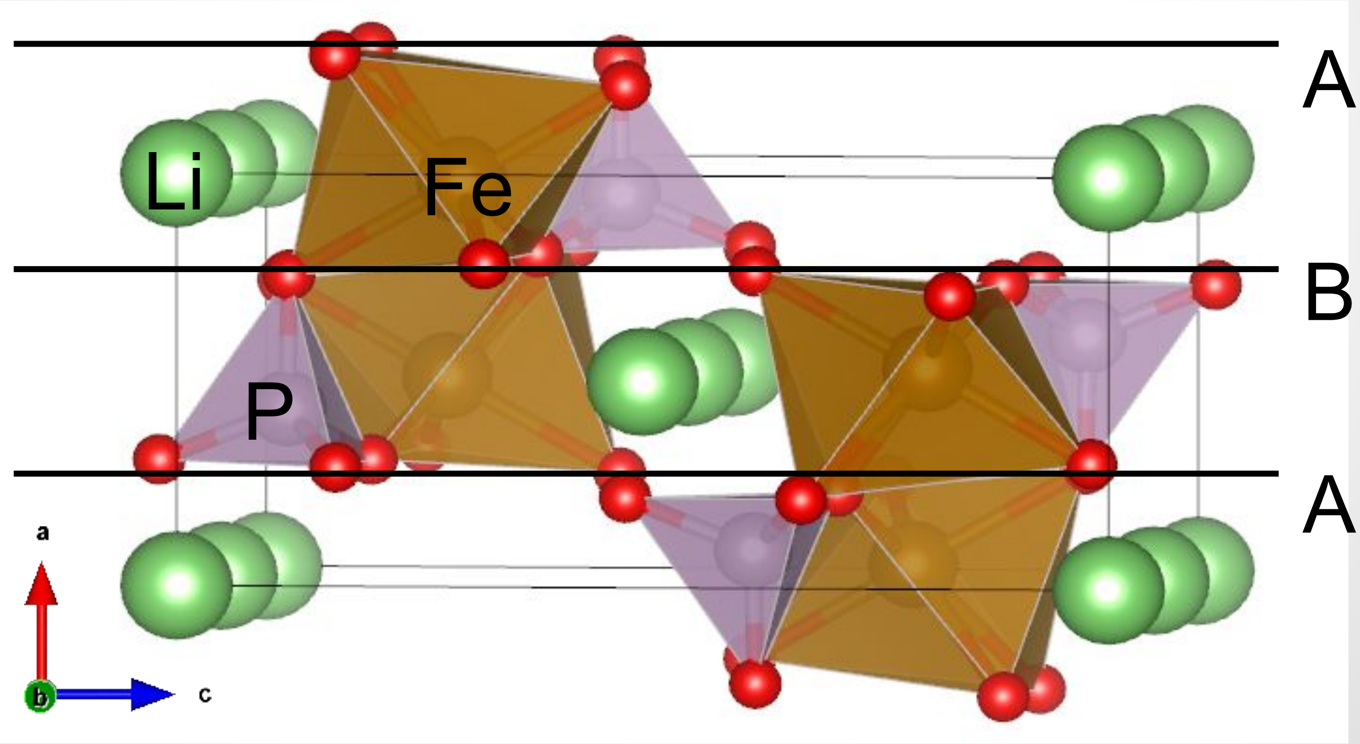
3. Origin of migration barriers in cathode materials

4. Layered oxides: surface structure and defects

5. Unusual Defects in Olivine $LiFePO_4$

$LiFePO_4$ cathode material (Pnma)

Formula	name	a	b	c
$Mg_{1.8}Fe_{0.2}SiO_4$	olivine	4.76	5.99	10.23
$LiFePO_4$	triphylite	4.70	6.00	10.33



Experimentally observed compositions obtained with hydrothermal synthesis

$Li_{0.93}Fe_{1.07}P_{0.84}$

$Li_{0.95}Fe_{1.05}P_{0.87}$

$Li_{0.98}Fe_{1.02}P_{0.88}$

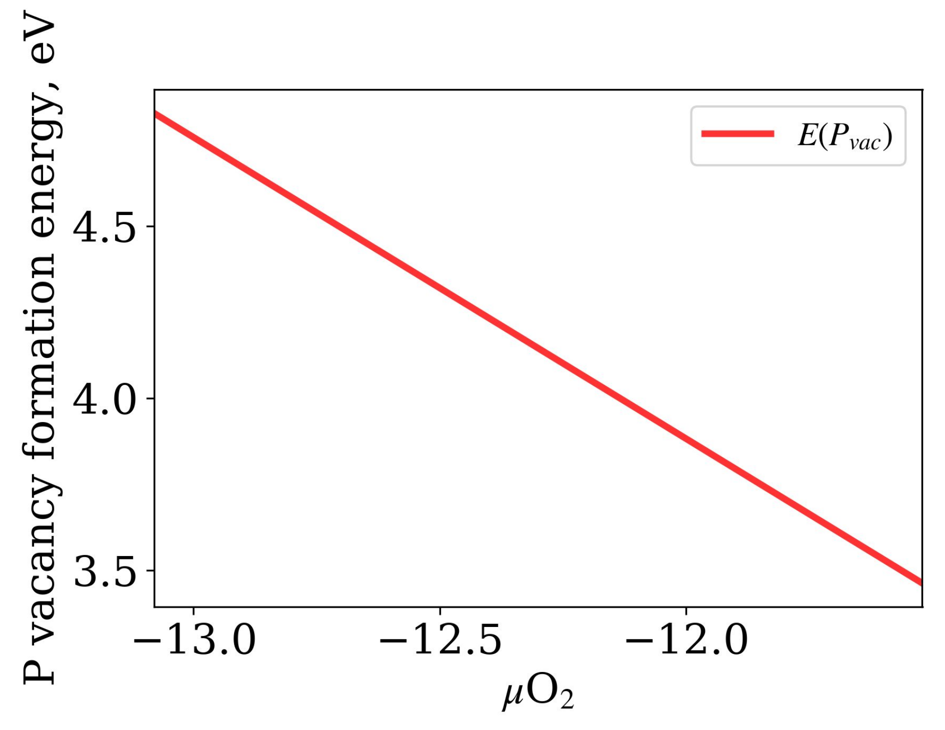
Up to 15% of P vacancies!

Is it possible in $LiFePO_4$?

Sumanov, Vasily D., Dmitry A. Aksyonov, Oleg A. Drozhzhin, Igor Presniakov, Alexey V. Sobolev, Iana Glazkova, Alexander A. Tsirlin et al. "“Hydrotriphylites” Li1–x Fe1+ x (PO4) 1–y (OH) 4 y as Cathode Materials for Li-ion Batteries." *Chemistry of Materials* 31, no. 14 (2019): 5035-5046.

Formation energy of P vacancies

$$dE = [E(LiFeP_{1-x}Vac_xO_4) – E(LiFePO_4) + x\mu(P)]/x$$

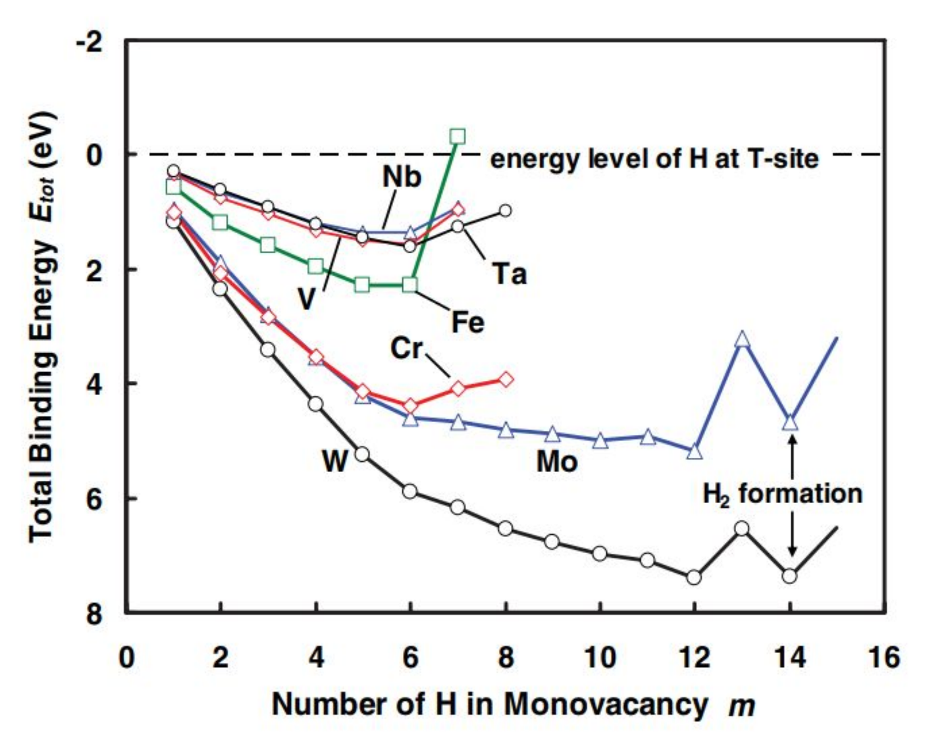


C_{vac} = exp(-3.5/kT) ~ 10^{-36} at T = 473 K - no vacancies are possible

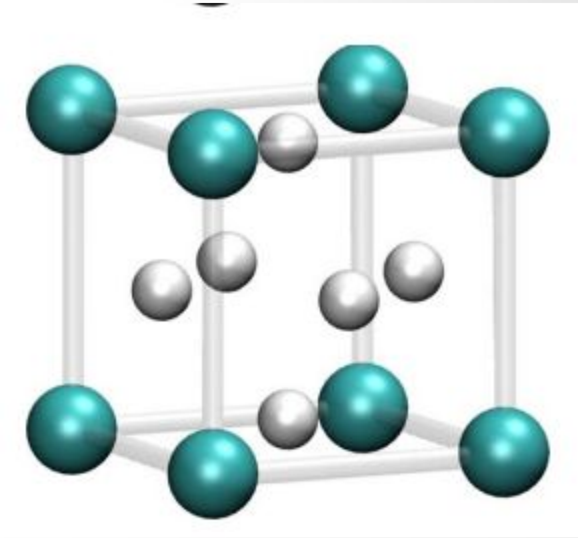
How the P vacancy energy can be reduced?

In metals, hydrogen is trapped in vacancies

E.g. in tungsten up to 12 H go into vacancy



PHYSICAL REVIEW B 85, 094102 (2012)

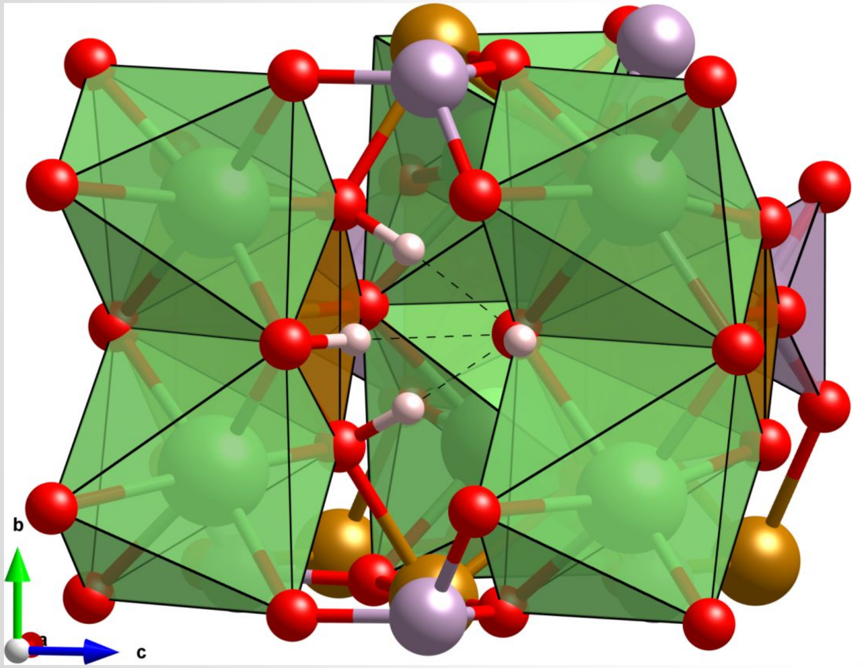


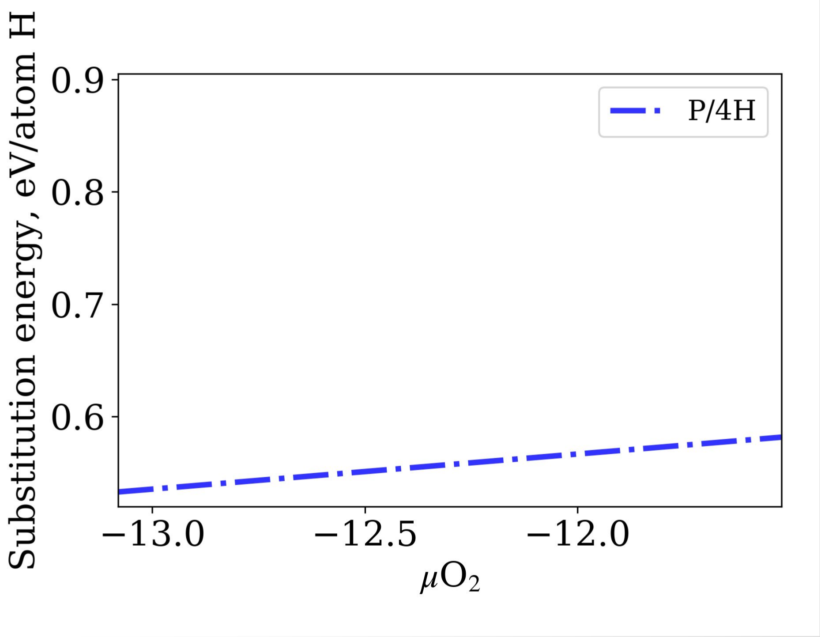
8 H in vacancy in tungsten

PHYSICAL REVIEW B 82, 094102 2010

What if 4 hydrogens substitute one P?

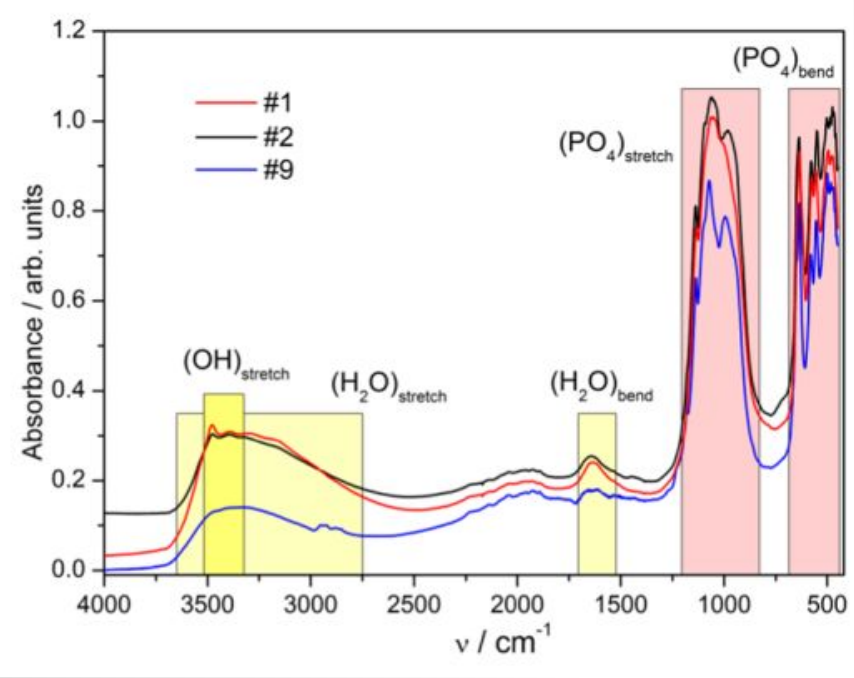
$$E_{sub} = [E(LiFeP_{1-x}Vac_xH_{4x}O_4) - E(LiFePO_4) + x\mu(P) - 4\mu(H)]/4x$$





Hydrogen stabilize P vacancy reducing it’s formation energy from 4.8 eV to 2.1 eV

Experimental confirmation of 4H defect

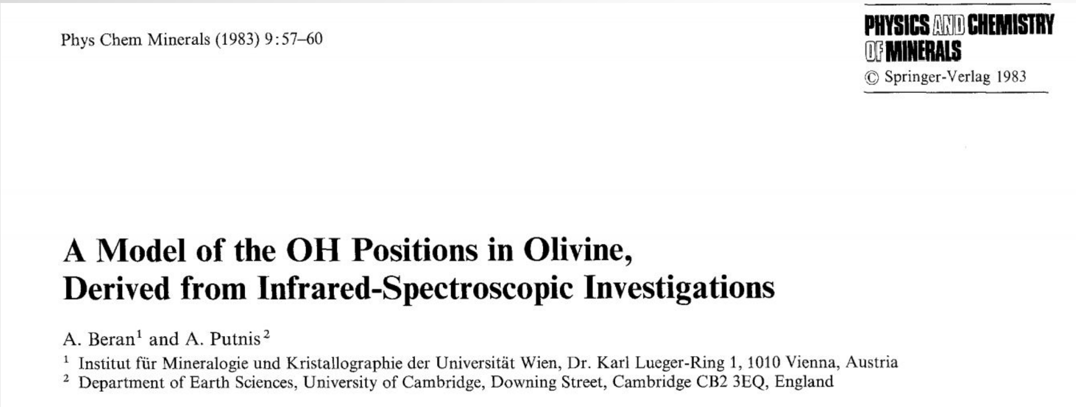


- After theoretical prediction the existence of 4H defects was confirmed experimentally at our center using both Mossbauer and Infrared spectroscopy.

- However, the exact atomic structure of defect is known only from DFT calculations

Sumanov, Vasily D., Dmitry A. Aksyonov, Oleg A. Drozhzhin, Igor Presniakov, Alexey V. Sobolev, Iana Glazkova, Alexander A. Tsirlin et al. "“Hydrotriphylites” Li1–x Fe1+ x (PO4) 1–y (OH) 4 y as Cathode Materials for Li-ion Batteries." *Chemistry of Materials* 31, no. 14 (2019): 5035-5046.

In mineral world hydrogarnet defect in Mg_2SiO_4 is known for a long time



Phys Chem Minerals (1983) 9:57–60

PHYSICS AND CHEMISTRY OF MINERALS
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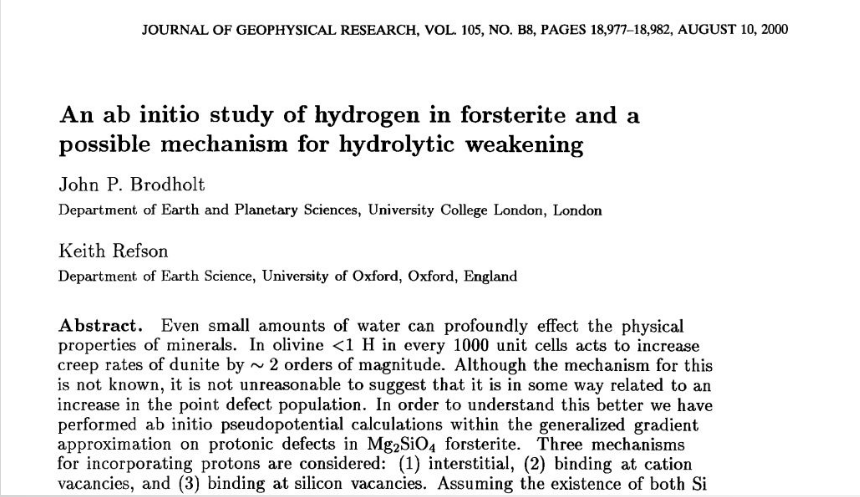
A Model of the OH Positions in Olivine, Derived from Infrared-Spectroscopic Investigations

A. Beran[1] and A. Putnis[2]

[1] Institut für Mineralogie und Kristallographie der Universität Wien, Dr. Karl Lueger-Ring 1, 1010 Vienna, Austria
[2] Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, England

- First experimental evidence of hydrogarnet type defect in olivine was obtained by Beran and Putnis in **1983** (though P/3H)
- DFT calculations for P/4H in Mg_2SiO_4 was done in **2000** by Brodholt and Refson



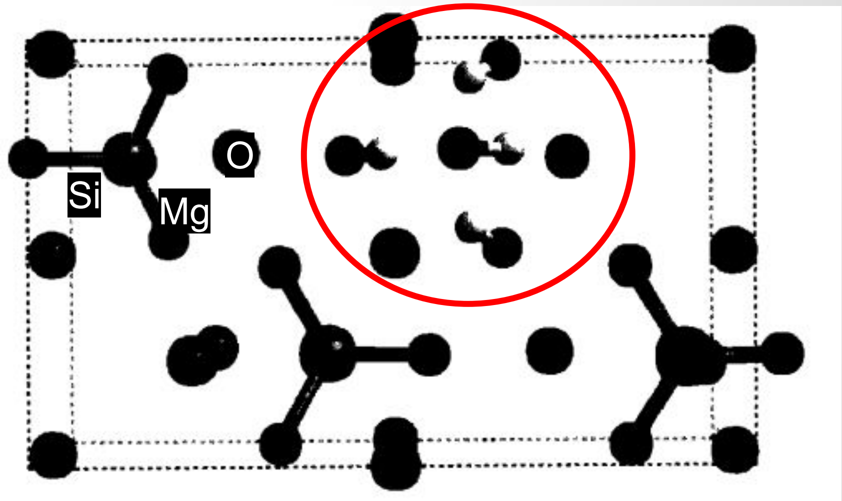
JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 105, NO. B8, PAGES 18,977–18,982, AUGUST 10, 2000

An ab initio study of hydrogen in forsterite and a possible mechanism for hydrolytic weakening

John P. Brodholt
Department of Earth and Planetary Sciences, University College London, London

Keith Refson
Department of Earth Science, University of Oxford, Oxford, England

Abstract. Even small amounts of water can profoundly effect the physical properties of minerals. In olivine <1 H in every 1000 unit cells acts to increase creep rates of dunite by ~ 2 orders of magnitude. Although the mechanism for this is not known, it is not unreasonable to suggest that it is in some way related to an increase in the point defect population. In order to understand this better we have performed ab initio pseudopotential calculations within the generalized gradient approximation on protonic defects in Mg_2SiO_4 forsterite. Three mechanisms for incorporating protons are considered: (1) interstitial, (2) binding at cation vacancies, and (3) binding at silicon vacancies. Assuming the existence of both Si



Conclusions on $LiFePO_4$

- 4H/P is the most favourable for hydrogen to incorporate into $LiFePO_4$
- Despite more than ~5000 papers published on LiFePO4 for battery application we shown for the first evidence of OH defects in this material
- The screening of potential energy surface, consideration of numerous configurations and their characteristics required ~1000 of DFT/DFT+U calculations

Acknowledgments

PhD **A.Boev,**

Belgorod State
University

Dr. **S.Fedotov,**

Skoltech

Prof.

A, Zhugayevych

Skoltech

Prof.
K.Stevenson,

Skoltech

Prof.
A.Abakumov,

Skoltech

Thank you for your attention!