FIRST PRINCIPLES MODELING OF NOVEL FUNCTIONAL MATERIALS FOR FUEL CELL APPLICATIONS

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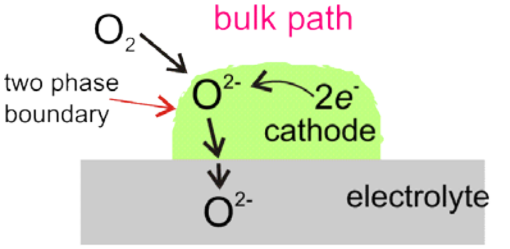
General problem

Improvement of SOFC and permeation membrane performance requires better understanding of oxygen reduction reaction

cathode reaction: $\mathbf{O}_2(g) + 4e^- \rightarrow 2\mathbf{O}^{2-}$

Study and control of possible reaction pathways of oxygen reduction and incorporation reaction



O^{2-}-incorporation via cathode bulk and two phase boundary

Exciting and challenging multidisciplinary field:
-Electrochemistry and materials chemistry,
- surface science of advanced oxides,
-, chemical kinetics,
-large-scale computer simulations

Development of new materials

- **Large scale computer simulations** of materials

in close collaboration with state-of-the art experiments [Max Planck Institute, Stuttgart]:

Combinatorial approach: J.Serra, V.B.Vert,

ChemSusChem 2, 957 (2009) is time-consuming

Limitations of experiments:

Discrimination of processes (O vacancies migration) in the bulk and on surfaces,

A role of different dopands and impurities

Identification of adsorbates at low coverages

Goals of theory:

Atomistic/mechanistic details of oxygen reduction (ORR) at SOFC cathode surface;

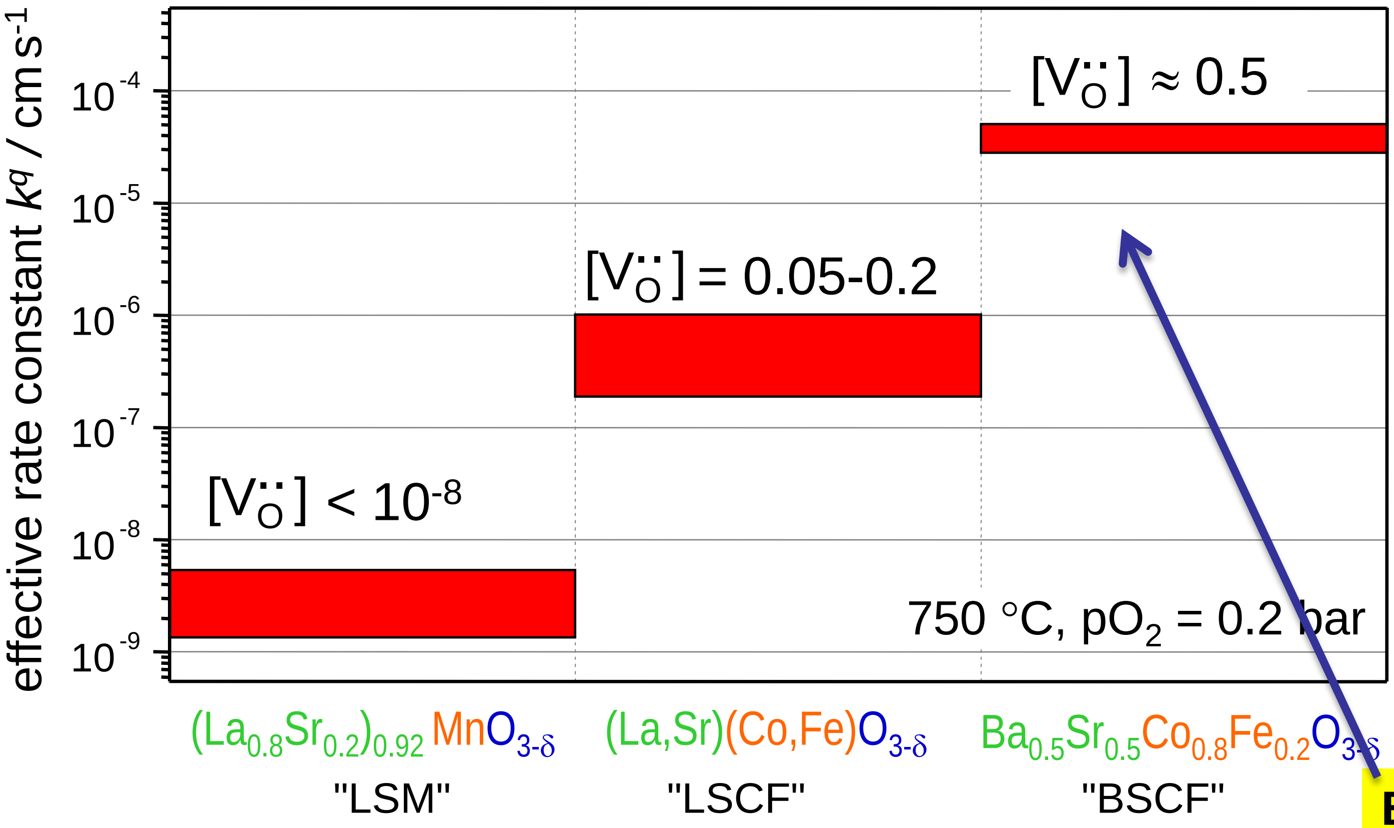
-- **O vacancy formation/migration on the surface/bulk; optimisation of cathode chemical composition**

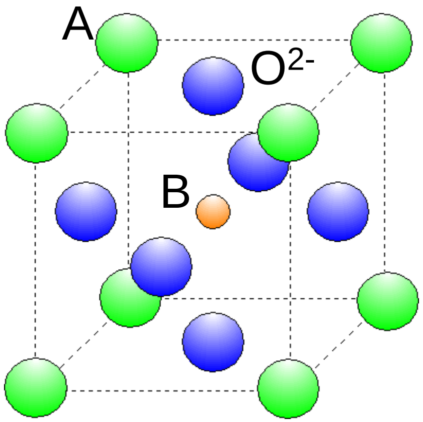
Challenge: what are the rate-determining reaction stages in oxygen reduction reaction

Joint experimental- theoretical study on BSCF-LSCF

- **R.Catlow (ed.) Computational Approaches to Energy Materials, Wiley, 2013, Chapter 6.**
- M. Kuklja et al, PCCP (Perspective) 15, 5443 (2013)
- R. Merkle et al, JECS 159, B 212 (2012)
- Yu. Mastrikov et al, PCCP 15, 911 (2013)
- D. Fuks et al, J. Mater.Chem.A, 1, 14320 (2013)

SOCF perovskites cathode materials comparison





increase of $V_O^{\bullet\bullet}$ concentration

increase of $V_O^{\bullet\bullet}$ mobility

Both migration and formation energies are important!!

F. S. Baumann et al., *J. Electrochem. Soc.* 154 (2007) B931; J. Fleig et al., *Fuel Cells* 8 (2008) 330
L. Wang et al., *J. Electrochem. Soc.* 157 (2010) B1802

Methods: 1. Solid state physics

Density Functional Theory

Plane Wave basis set

Generalised Gradient Approximation (Hubbard U)

Perdew Wang 91 exchange-correlation functional

Projector Augmented Wave method

Davidson algorithm for electronic optimization

Conjugate Gradient method for structure relaxation

Nudged Elastic Bands for energy barriers estimation

Bader charge analysis (**Prof. G. Henkelman** and co-workers, ***Universiy of Texas***)

Spin-polarized calculations

- **2. Quantum chemical approach**
- **CRYSTAL** code with LCAO basis set
- (re-optimised Comp Mat Sci. 29, 165 (2004)

For light atoms (O), all-electron basis set (BS) for heavy atoms (Sr, Pb,Ti and Zr), the **small-core Hay-Wadt pseudopotentials**

- **Hybrid HF-DFT functionals**
- hybrid functionals work very good!
  The gap 3.63 eV(indirect); 3.95 eV(direct): 10% error
- a_0=3.91 A (+ 0.5% error)
- **Supercell model** (up to 320 atoms: 4 x 4 x 4 extended UC)

The most efficient SOFC material: $Ba_{(0.5)}Sr_{(0.5)}Co_{(0.75)}Fe_{(0.25)}O_{3-\delta}$

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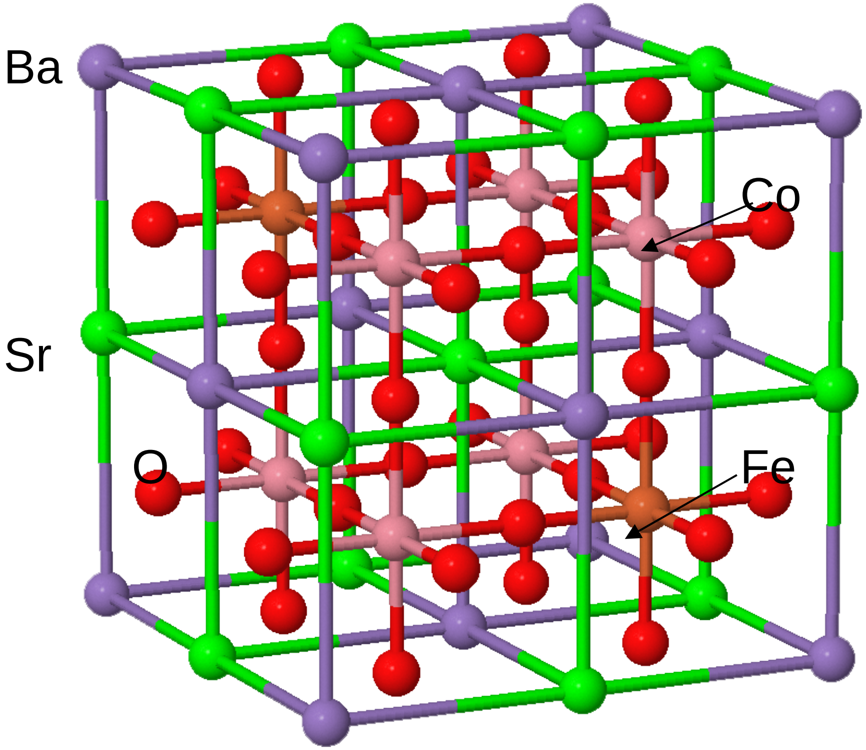
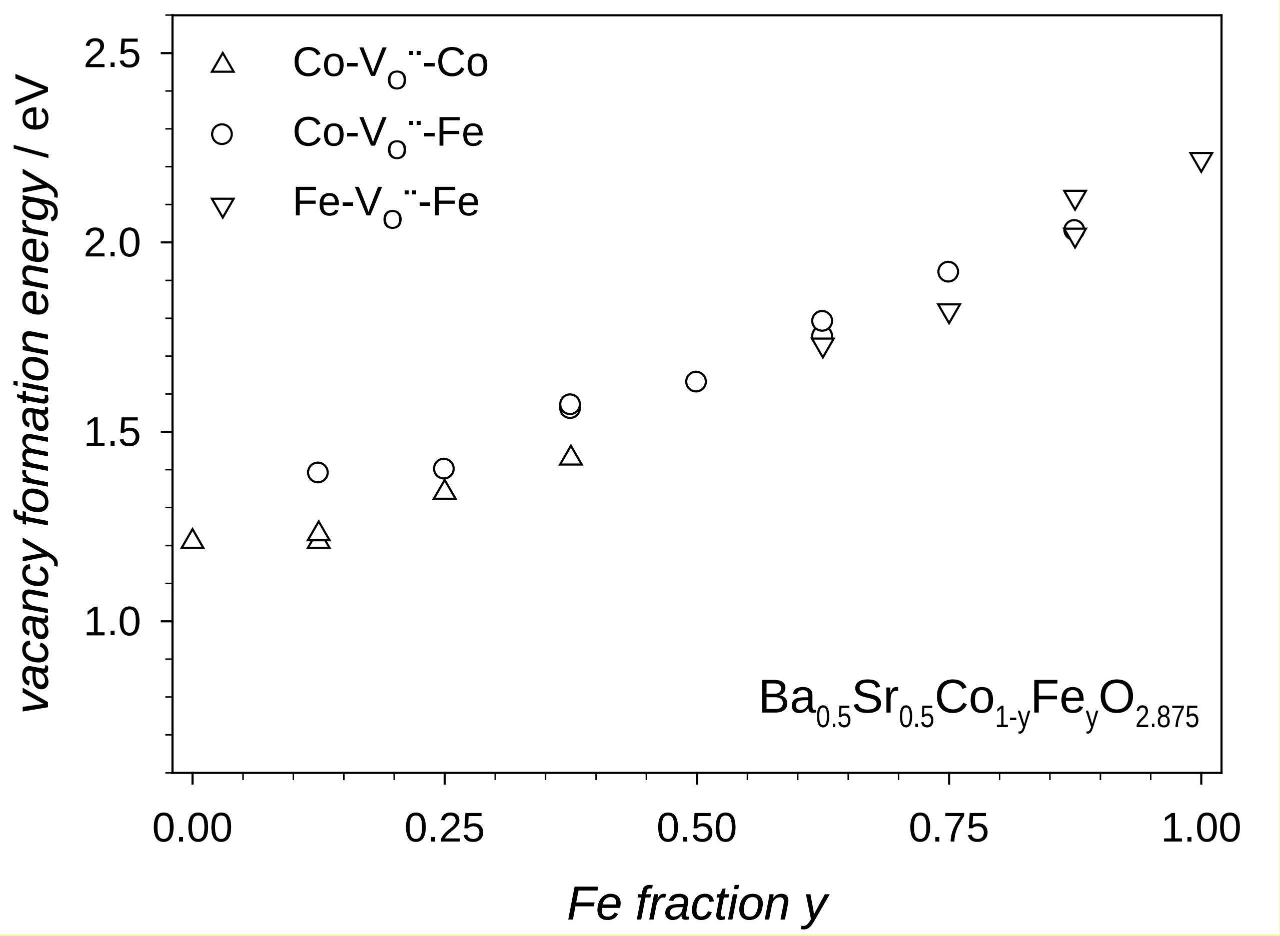


Bulk and defect properties
40 atom supercells (4% of oxygen vacancies) and 320 atoms (0.7%)
Mastrikov et al, En. Env. Sci. 3, 1544 (2010).

Role of chemical composition: defect formation energies [Kotomin et al, Sol. St. Ionics, 188, 1 (2011)]

BSCF



Composition trend

- Vo formation energy increases considerably with Fe concentration (1.2 → 2 eV) [with respect to the free O atoms: ½ O_2],

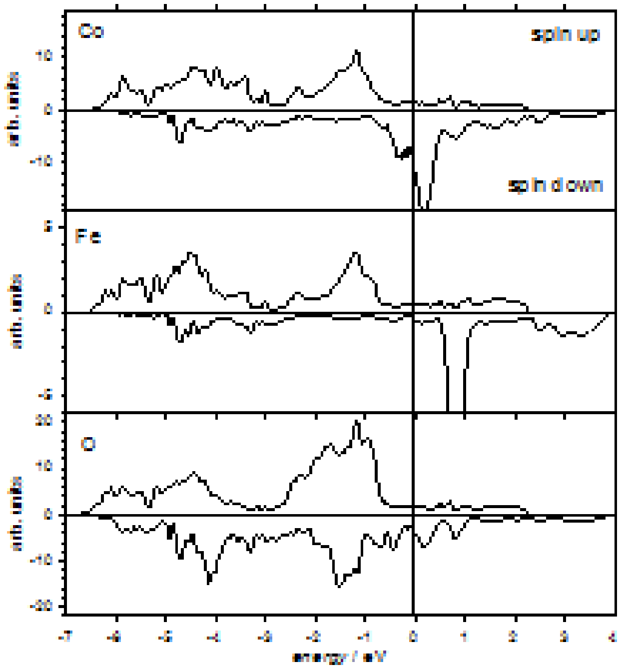
  in agreement with expt observation of defect concentration increase BSF → BSCF (Gauckler et al, PCCP 11, 3090 (2009)

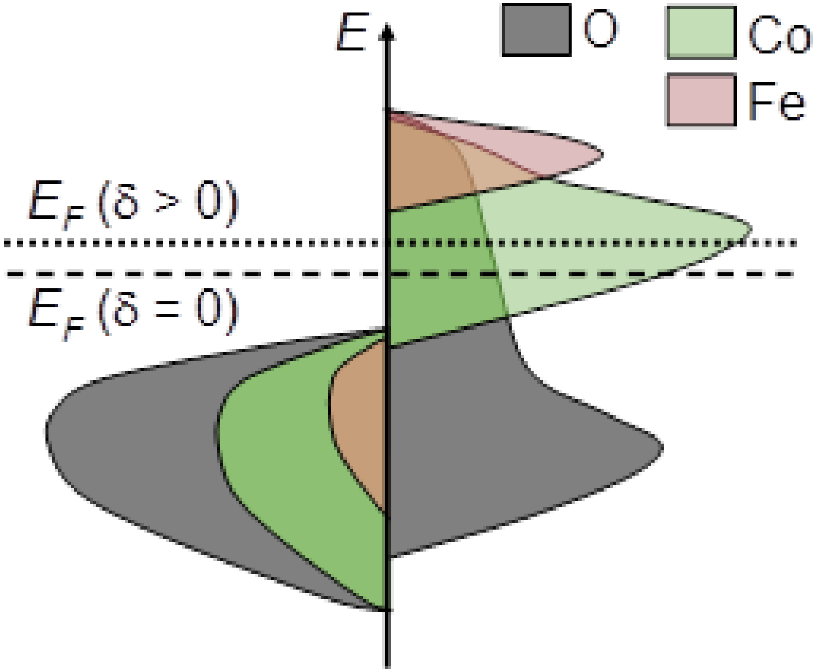
BSCF formation energy much smaller than in

LSM (2.7 eV) and STO (5.9 eV)

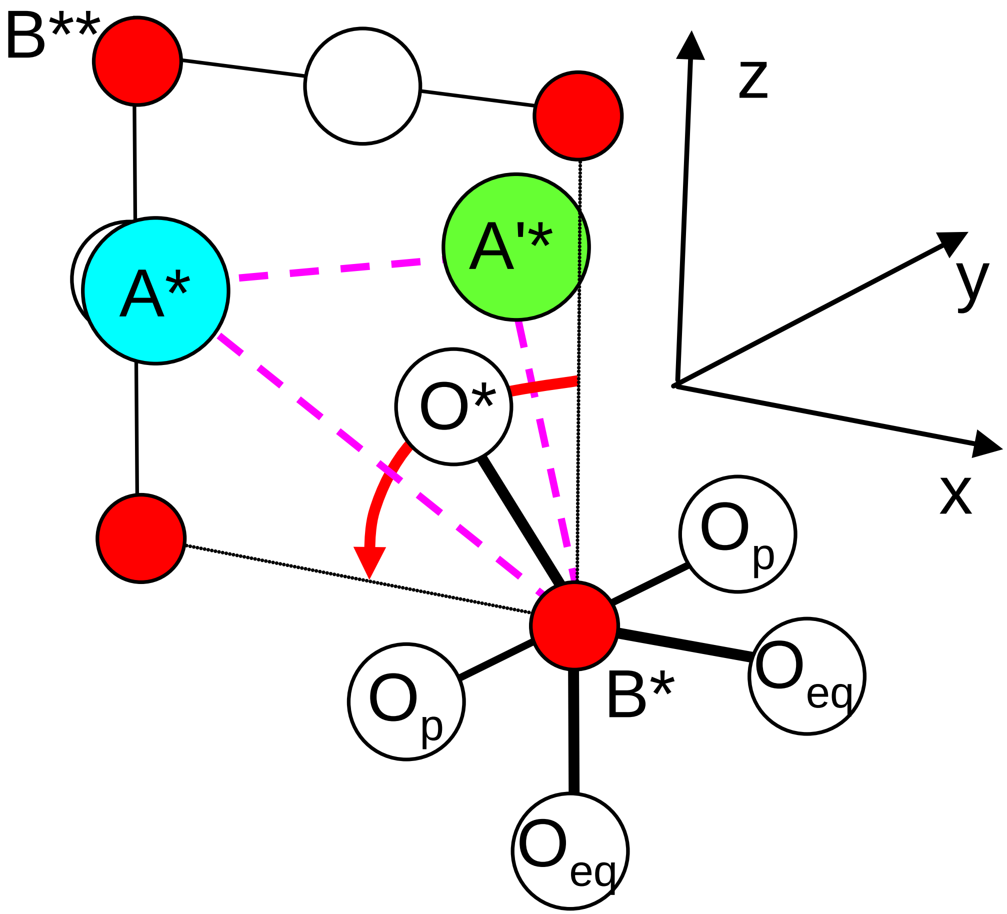
Explanation from DOS analysis

R. Merkle et al, JECS 159, B 219 (2012)



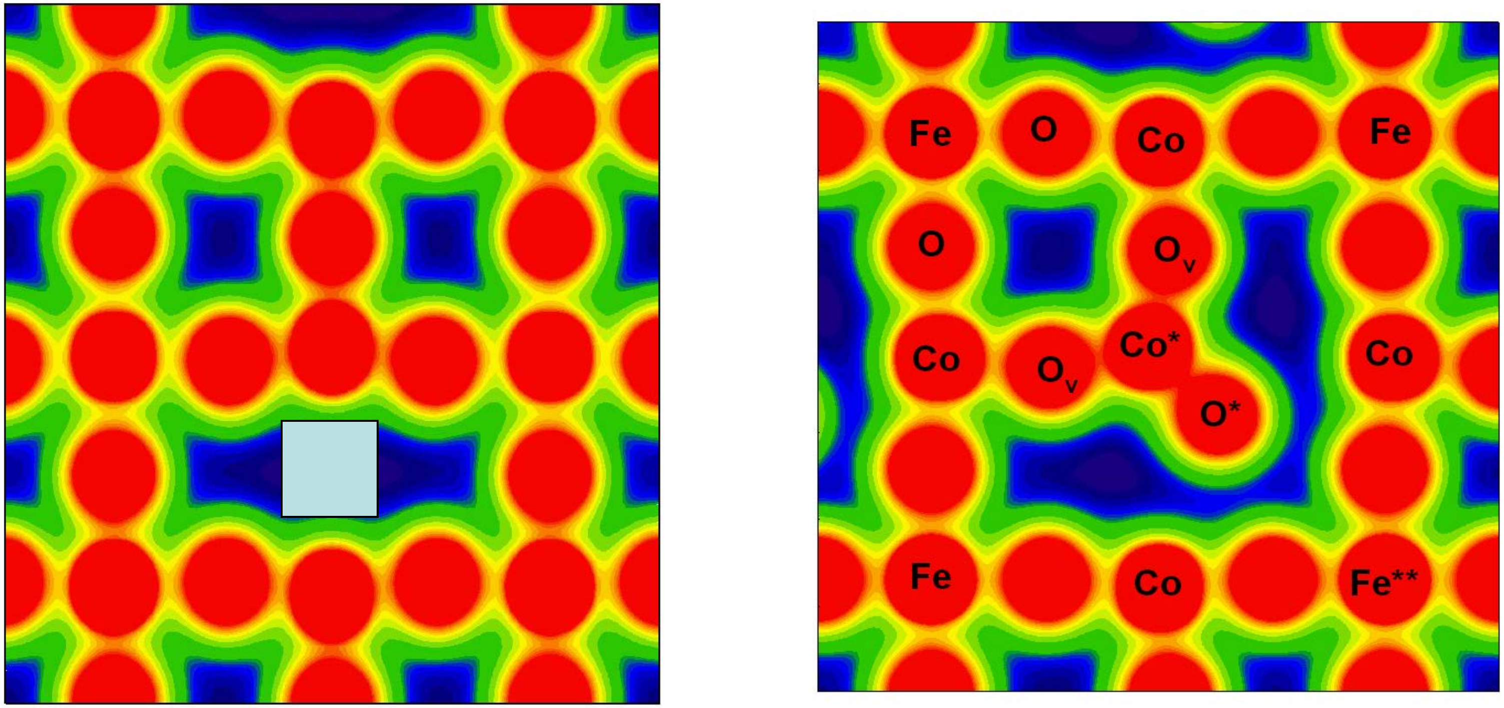


Transition state of O migration



Key factors:
-Lattice expansion
-Charge transfer

BSCF(001) electron density maps

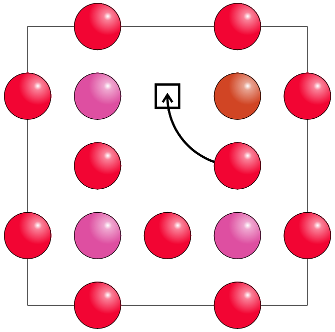


a) Equilibrium state for oxygen vacancy; b) transition state

Merkle et al, JECS **159**, B219 (2012)

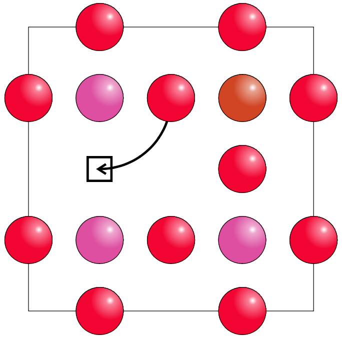
Vacancy migration energy, $\mathrm{Fe}_{0.25}$

Co-Vo-Fe



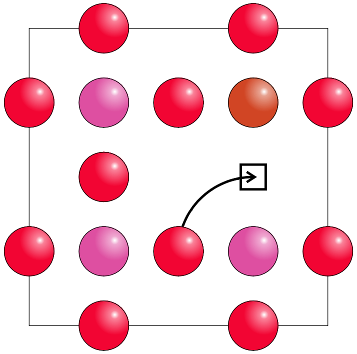
0.46 eV

Co-Vo-Co

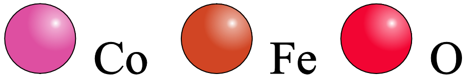


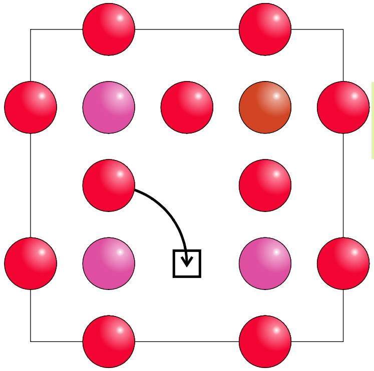
0.52 eV

0.46 eV



Co-Vo-Fe

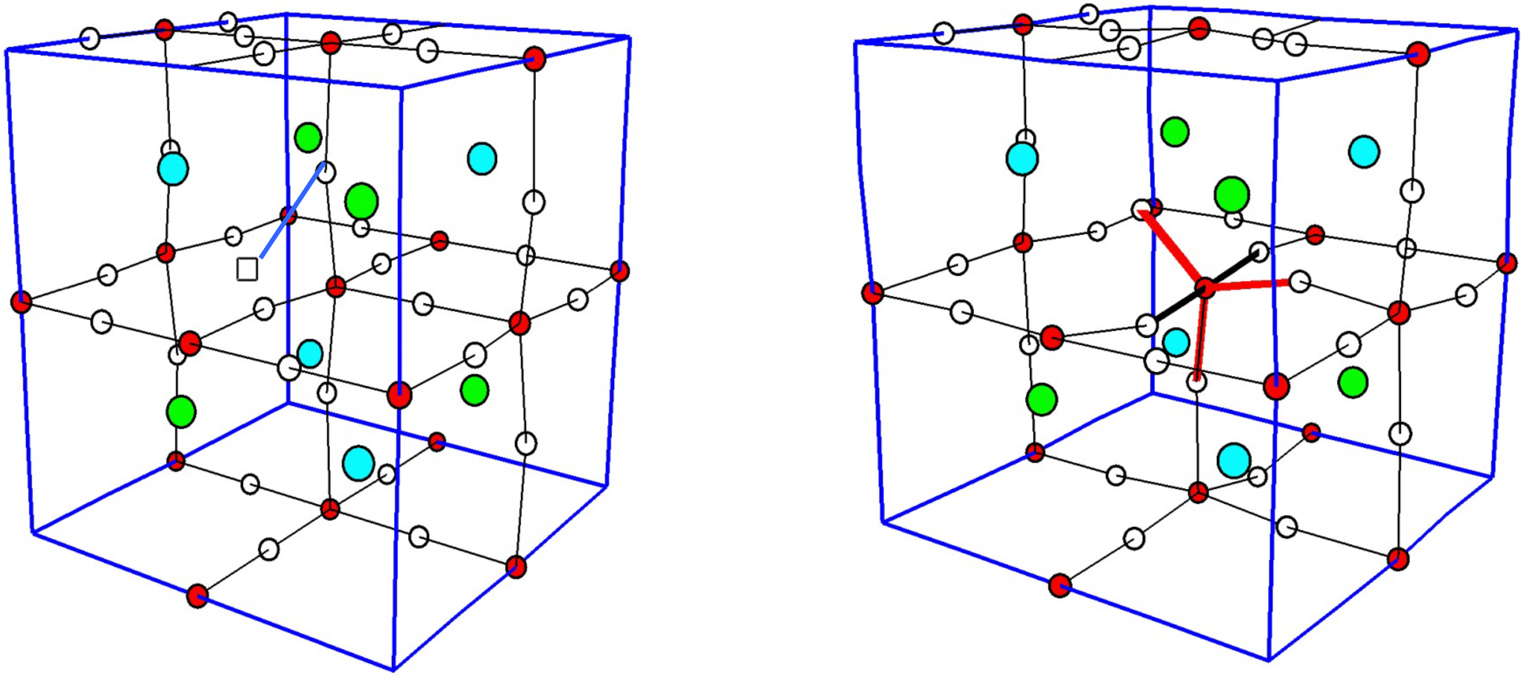




Co-Vo-Co
0.42 eV

For comparison: LMO 0.9 eV

Vacancy migration in BSC: ground and transition states

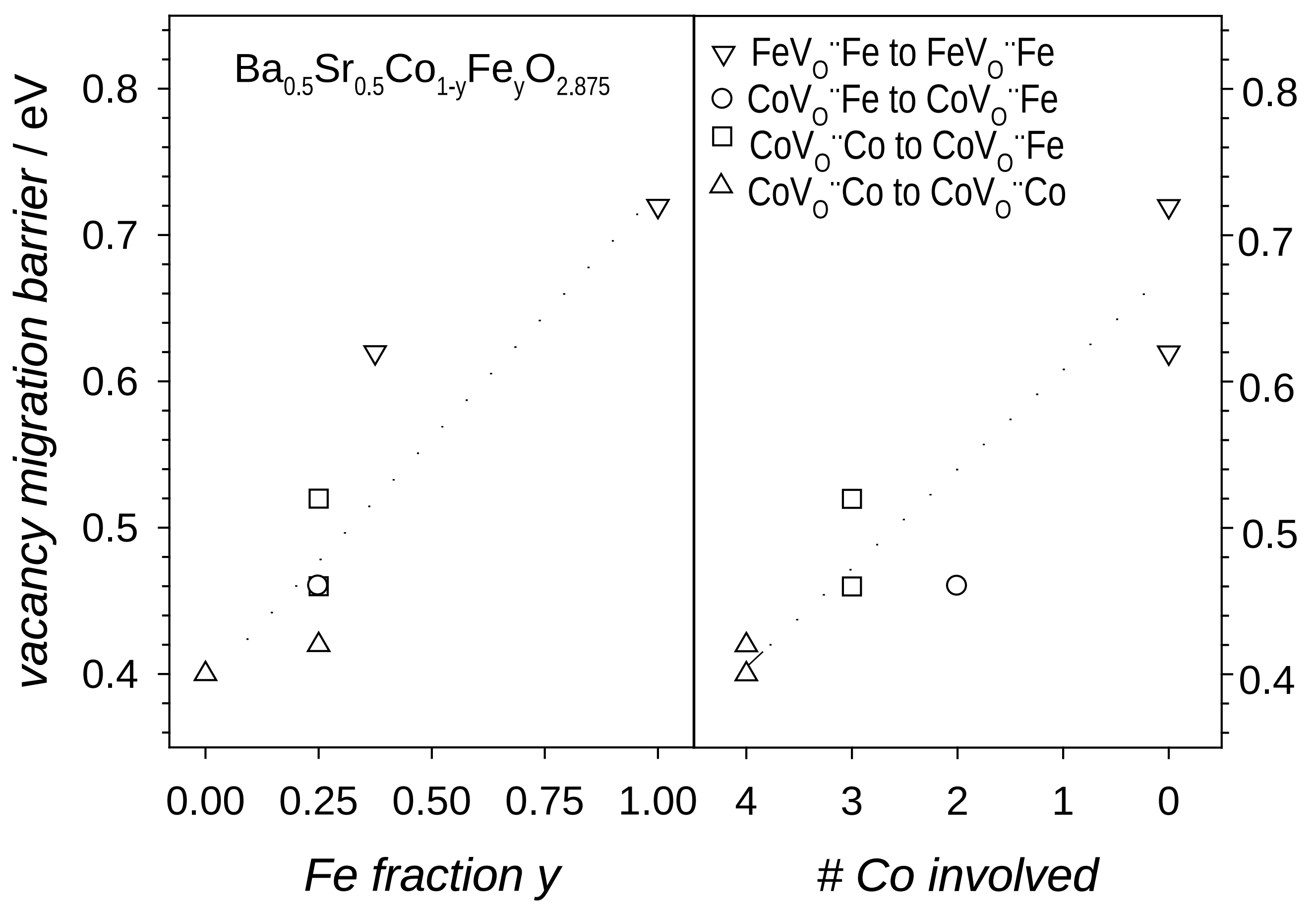


Lattice distortion areas is 6-8 A around the jumping O* ion

Vacancy migration energies

Kotomin, Sol.St.Ionics,**188**,1(2011);Merkle et al,JECS**159**,B219 (2012)]

BSCF

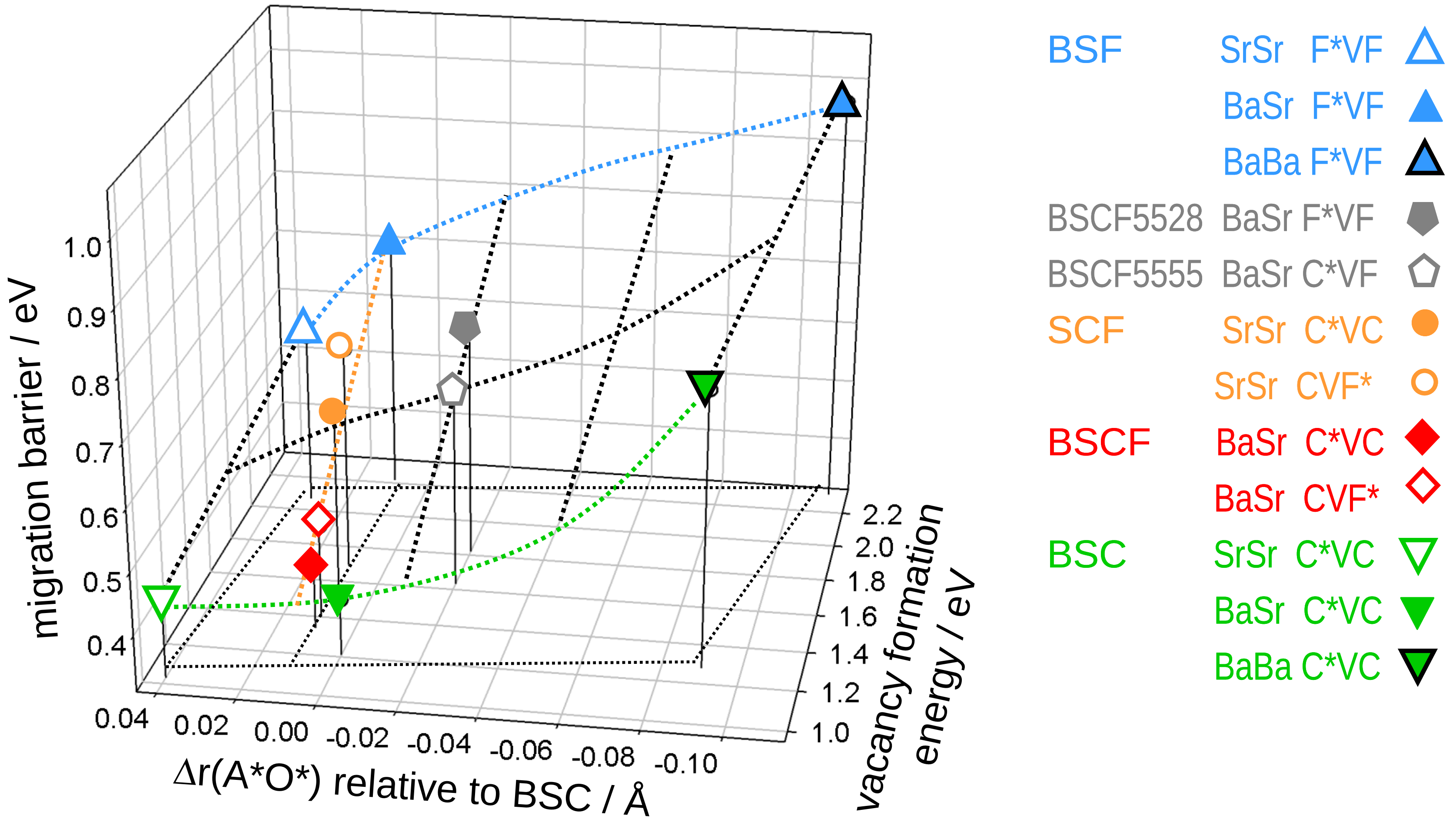


Trend

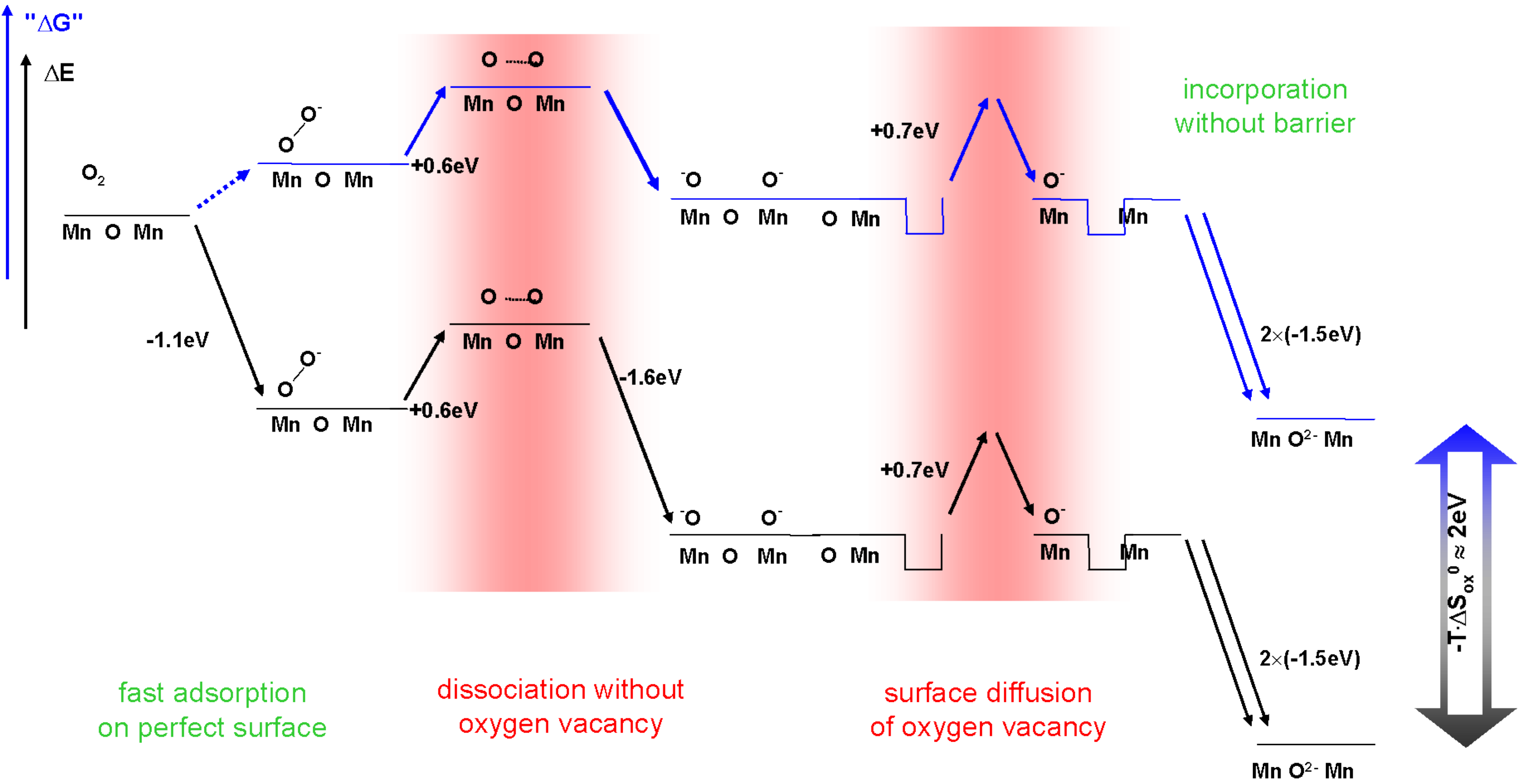
- Migration energies much smaller in BSCF (~0.5 eV) than in LMO, LFO,LCO, STO (0.8-0.9 eV)
- Energy increase with Fe concentration
- What are the main factors behind?

Migration energy depends on both the saddle point geometry and electronic structure (vacancy formation energy)

Merkle et al, JECS **159** (2012) B 219; Kotomin, SSI **188** (2011) 1

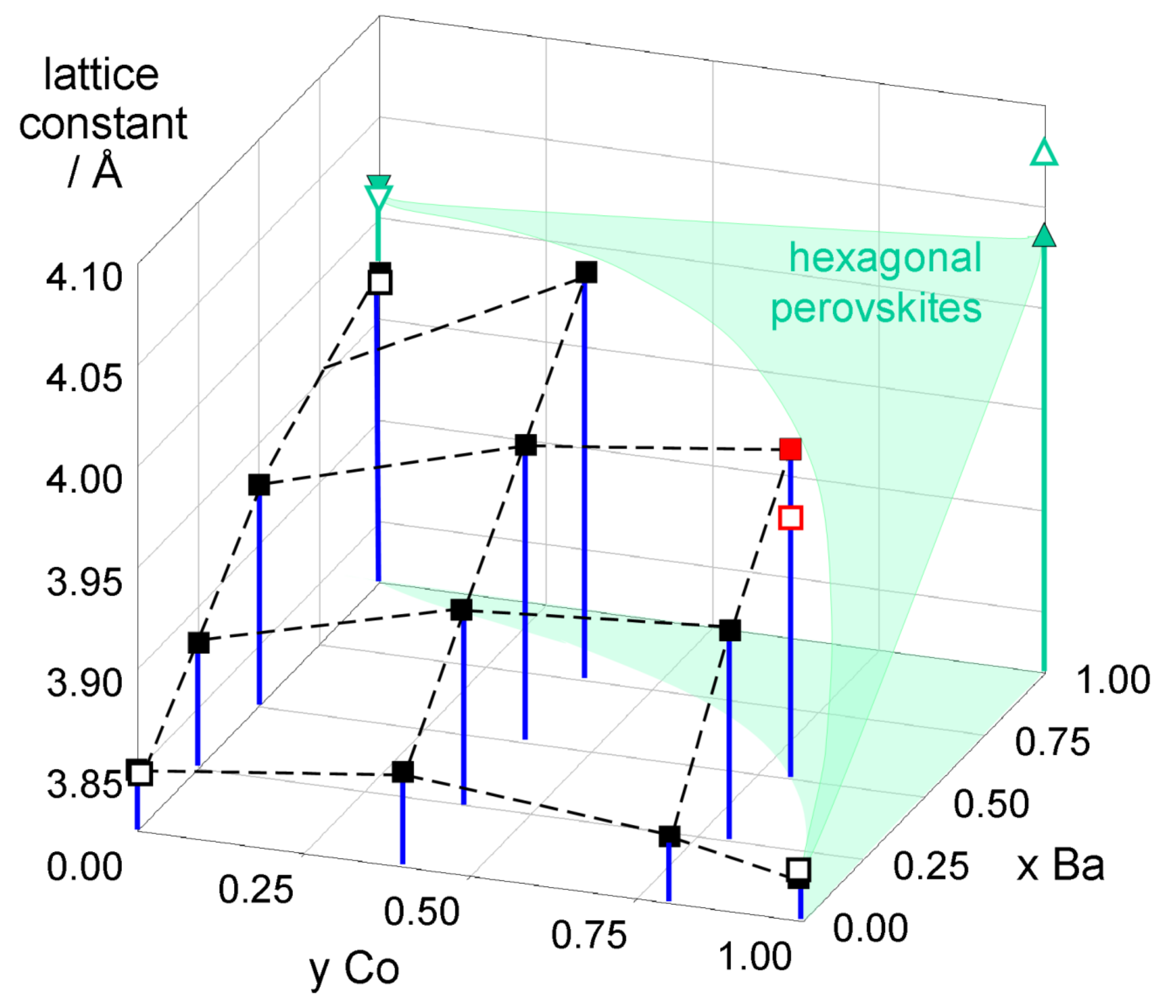


Our goal is modelling of all steps of the ORR in order to find limiting one
Entropy effects important under realistic operational conditions: LSM



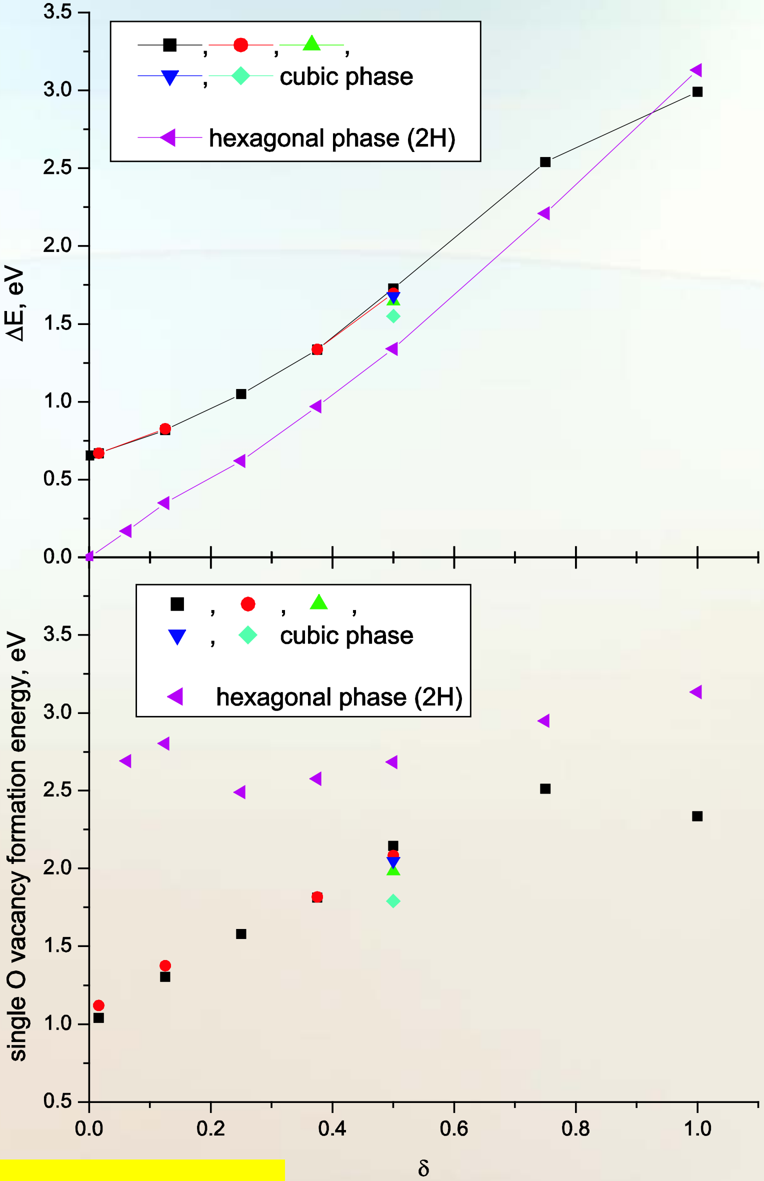
Mastrikov et al, J. Phys. Chem. C 114, 3017 (2010); Wang J.Mat. Res. 27, 2012

Cubic vs hexagonal?



Chemical expansion coefficient is close to expt value

BSCF: cubic vs hexagonal?



Kukla et al J Phys Chem C 116 (2012)

CONCLUSIONS

- First-principles computer modeling could be useful tool for understanding „composition-property“ relation in complex perovskite solid solutions (where simple models fail)
- especially at surfaces/interfaces (defect formation energies and mobilities, charge distribution, etc.) and transition states of processes
- Intuitive conclusions are not always correct, e.g.

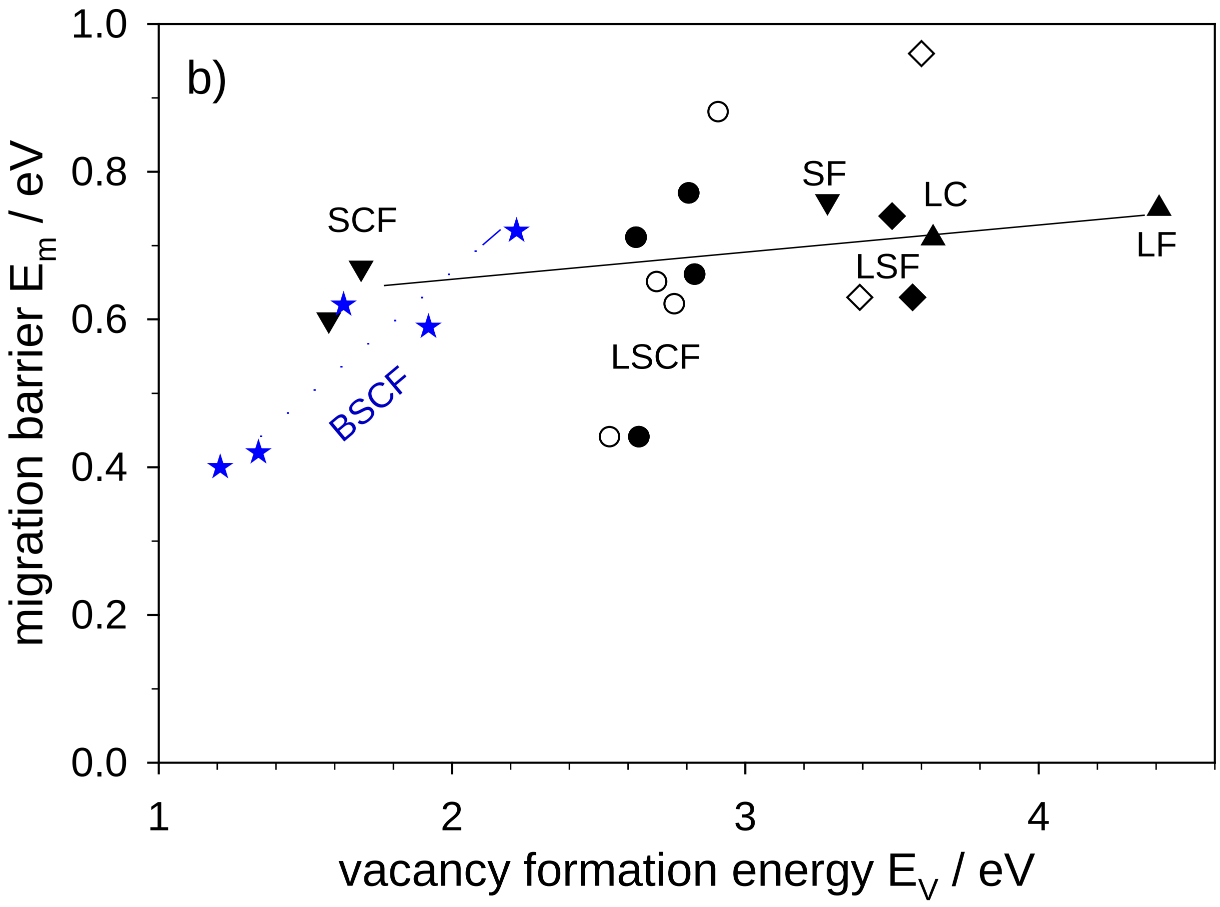
defect formation energies at surfaces and in bulk

- Structural stability aspects!! Kuklja et al, J Phys Chem C 116, 18605 (2012)

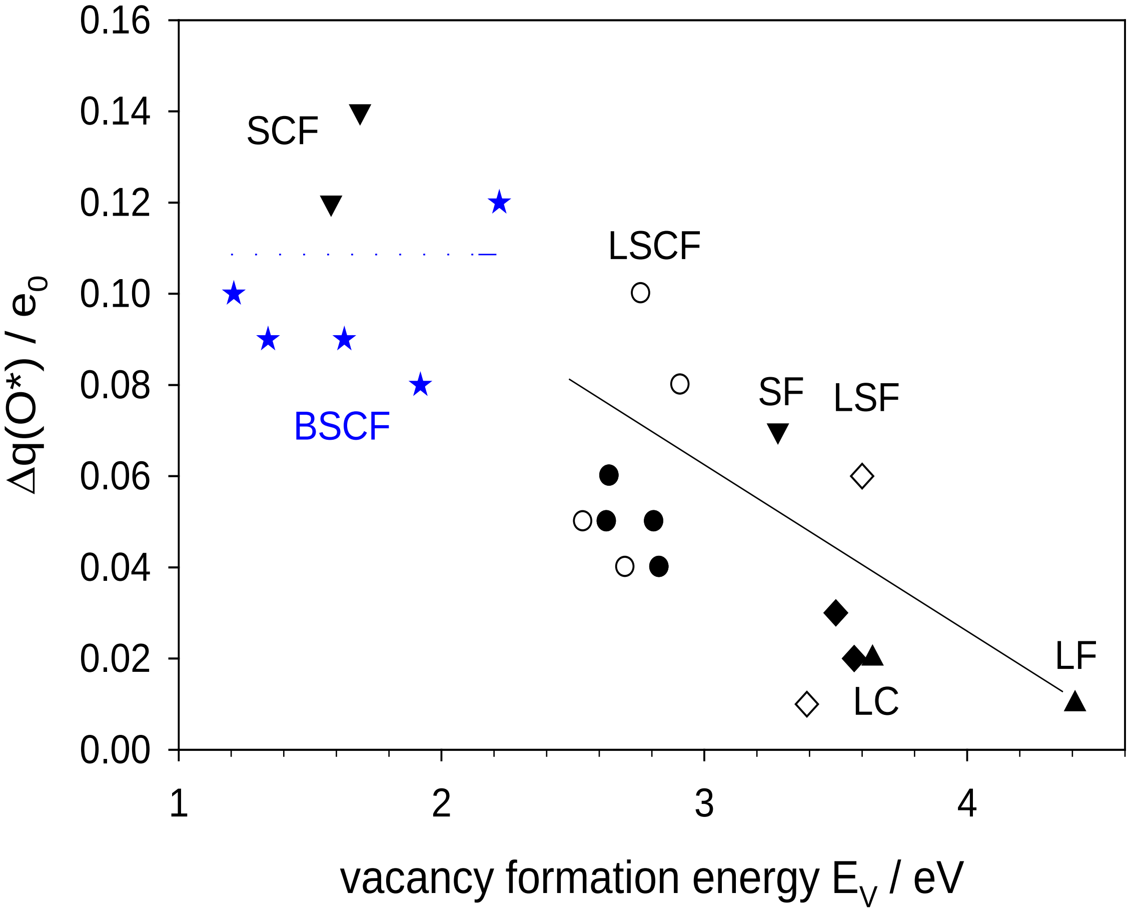
- Many thanks due to:
- R.Evarestov (St Petersburg University)
- D.Gryaznov, Yu.Mastrikov (University of Latvia)
- M. Kuklja (Maryland University, USA)
- D. Fuks (Ben Gurion University, Israel)
- J.Maier, R. Merkle (Max Planck Institute, Stuttgart)

LSCF: almost no correlation!

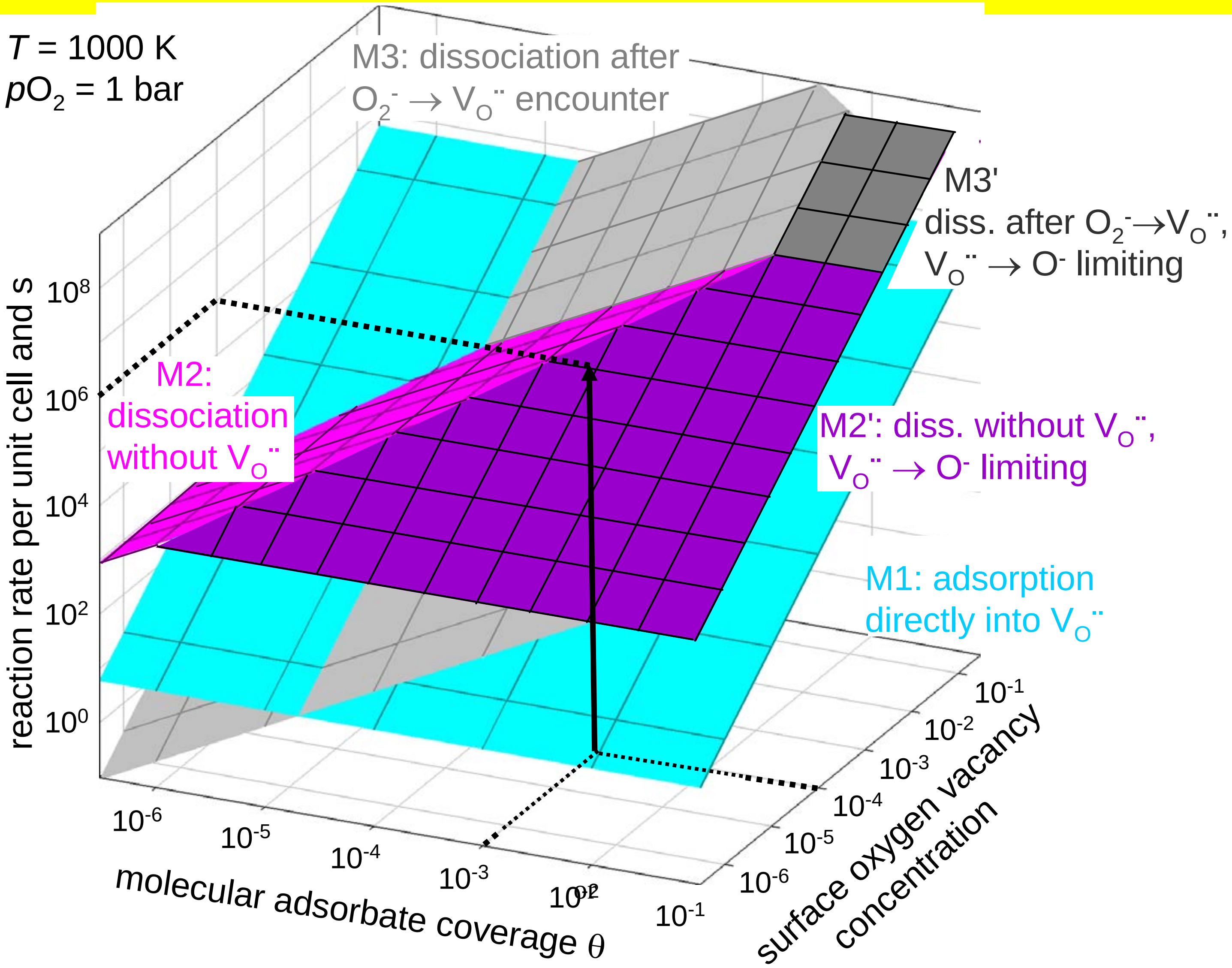
Mastrikov et al, PCCP 15, 911 (2013)



…and negligible charge transfer



Variation of oxygen exchange rates for MnO2- termination



T = 1000 K
pO_2 = 1 bar

M3: dissociation after $O_2^- \rightarrow V_O^{\cdot\cdot}$ encounter

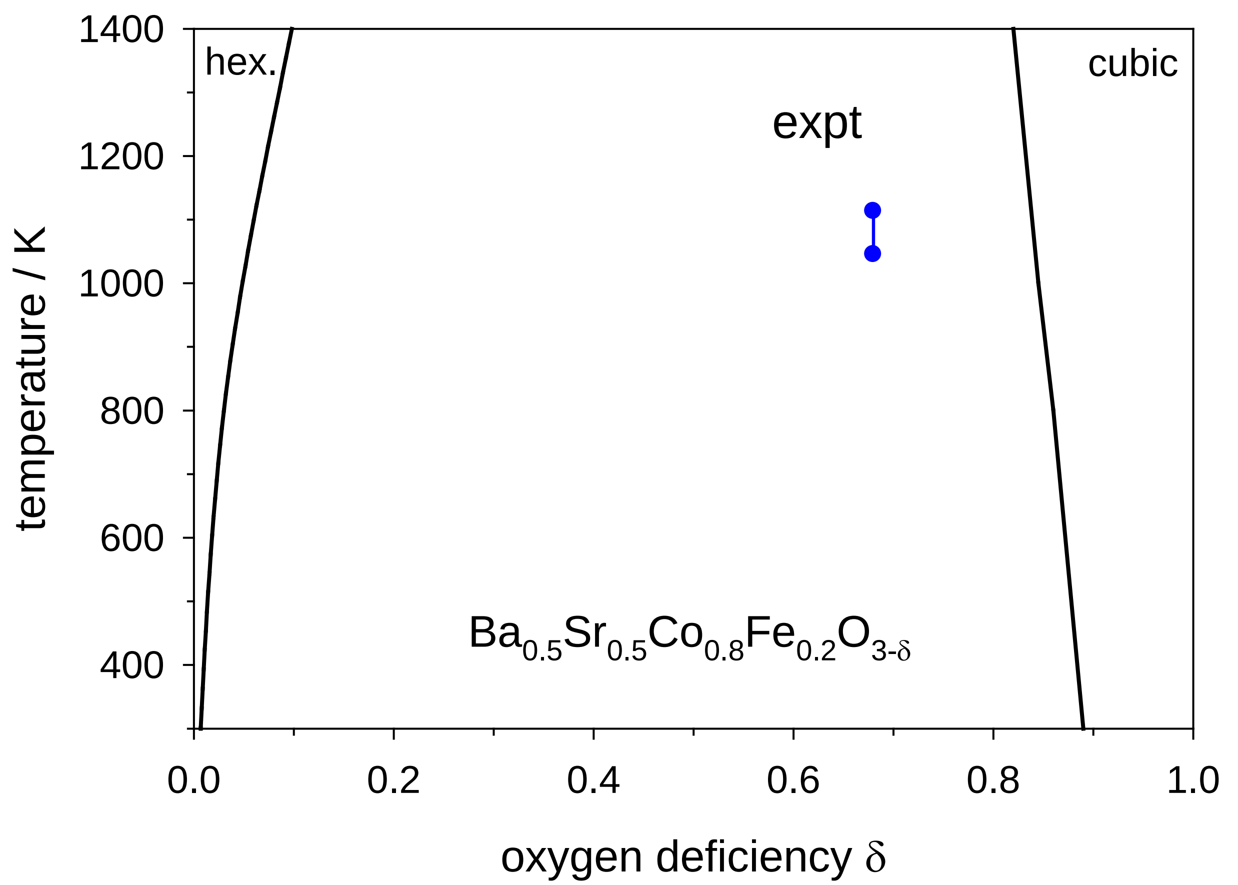
M3' diss. after $O_2^- \rightarrow V_O^{\cdot\cdot}$, $V_O^{\cdot\cdot} \rightarrow O^-$ limiting

M2: dissociation without $V_O^{\cdot\cdot}$

M2': diss. without $V_O^{\cdot\cdot}$, $V_O^{\cdot\cdot} \rightarrow O^-$ limiting

M1: adsorption directly into $V_O^{\cdot\cdot}$

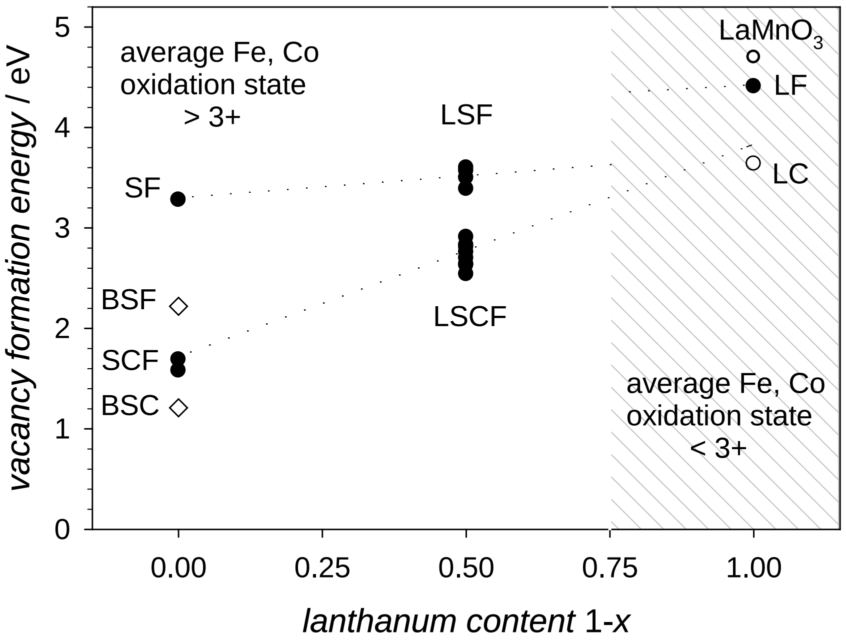
Phase diagram (ab initio TD)



Phase diagram of hexagonal/cubic BSCF 5582 from thermodynamic modeling

Diffusion in LSCF: contrast to BSCF

Mastrikov et al, PCCP 15, 911 (2013)



Oxygen vacancy formation energy *Ev* as a function of lanthanum content *1-x* in $La_{1-x}Sr_xCo_{0.8}Fe_{0.2}O_{2.875}$ (circles),
several data for a given cation composition refer to different cation configurations around the vacancy.
For comparison, *Ev* of BSF, BSC22,24 and orthorhombic $LaMnO_3$ are included (open symbols).

A role of Sr doping in Vo formation energy in $La_{(1-x)}Sr_xFeO_{3-d}$

- Two limiting cases: $LaFeO_3$ (oxidation state 3) and $SrFeO_3$ (oxidation state 4)
- each Sr (+2) atom brings a hole: Fe→+4
- Each oxygen vacancy Vo kills 2 holes: Fe(+3) or even Fe2+
- The Fe oxidation state is strongly affecting Vo formation energy (nonstoichiometry)
- The control parameter: d/2 vs x

Whats does *ab initio* mean?

- Two global approaches: HF and DFT
- DFT: exchange-correlation functionals→
- LDA-type (only density)
- GGA (also density gradients)
- GGA+U (Hubbard U– on-site correlations)
- HF-DFT hybrids: semi-empirical or not

Example: calculated band gap for defect-free ortho-$LaFeO_3$

Expt	2.1 eV
LDA	metal
LDA+U	2.3 eV
GGA	0.75 eV
GGA+U	2.53 eV
HSE (hybrid)	3.6 eV

PS. LSF is a semiconductor up to 90% Sr.

THE CALCULATED Vo FREE FORMATION ENTHALPY IN $La_{1-x}Sr_xFeO_{3-\delta}$

GGA calcs

X,%	δ,%	ΔH	Oxidation state Fe	expt
0 (LF)	12.5	4.26 (GGA)	2.75	5.0
50.0	12.5	3.5 (GGA)	3.25	0.99
100 (SF)	50	3.28 (GGA)	4.0	0.7

Mastrikov, PCCP 2013

THE CALCULATED Vo FREE FORMATION ENTHALPY IN $La_{1-x}Sr_xFeO_{3-\delta}$

GGA+U, 900 K

X,%	δ,%	ΔH (900 K)	Oxidation state	expt
0 (LF)	12.5	3.99 (4.41)	2.75	5.0
25	12.5	0.69± 0.17 (1.1)	3.00	1.2
50	12.5	0.01± 0.28 (0.41)	3.25	0.99

Carter, Chem Mater 2013

THE CALCULATED Vo FREE FORMATION ENTHALPY IN $La_{1-x}Sr_xFeO_{3-\delta}$

Hybrid PBE0 calculations, 1200 K

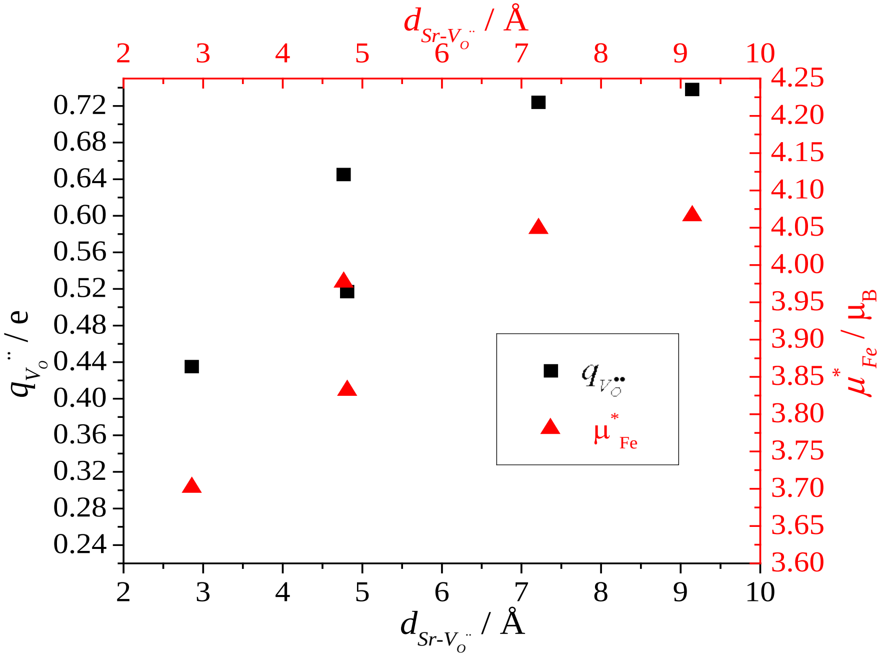
X,%	δ,%	ΔH (1200 K)	Oxidation state	expt
0 (LF)	12.5	4.26 (GGA) 3.99 (GGA+U)	2.75	5.0
12.5	12.5	2.2	2.875	3.0
12.5 25	6.25 12.5	0.89 0.69(GGA+U)	3.00	1.2
50.0	12.5	0.15	3.25	0.99
		3.5 (GGA)		
		-0.01(GGA+U)		
100 (SF)	50	3.28 (GGA)	4.0	0.7

GGA- Mastrikov, PCCP 2013; GGA+U – Carter, Chem Mater 2013

Hybrid calculations give the best agreement with expt but…

DISPERSION OF FORMATION ENERGIES IS QUITE LARGE:

6 types of Vo vacancies in 12.5% Sr
Formation energies are ranged 0.68-1.09 eV



4 types of Vo for 50% Sr, energy are ranged **0.04-0.27** eV !!

Problem of averaging : kinetic MC

GENERAL CONSLUSIONS

1. Neither „*ab initio*“ method is perfect….
2. … but hybrid functional are more reliable
3. Choice of a realistic model is non-trivial:
   inhomogeneous defect-dopant distributions,
   soft modes/unharmonicity in perovskites
   and phase transformations
4. Charged defects, especially in thin films is another challenge.

Transition state complexity:

- Simple geometry arguments based on a critical ionic (Shannon radii) **fail**, high Ba ion polarizability and the electronic structure are important factors.
- 3 key factors determining migration barrier through A-A‘-B triangle are:
- Displacements of A-type ions from jumping O*
- Displacement (tilting) of a whole BO_4O^*
- Covalency of B-O* chemical bond
- clear correlation between oxygen migration and vacancy formation energies

Thank you for your attention!

- **2. Quantum chemical approach**
- **CRYSTAL 2014** code with LCAO basis set
- (re-optimised Comp Mat Sci. 29, 165 (2004)

For light atoms (O), all-electron basis set (BS) for heavy atoms (Sr, Pb,Ti and Zr), the **small-core pseudopotentials**

- **Hybrid HF-DFT functionals** work very good for band gaps
- Bond populations and atomic charge analysis
- Well suited for slabs
- **Ghost basis set on vacant sites**

Methods: 1. Solid state physics

Density Functional Theory

Plane Wave basis set

Generalised Gradient Approximation (Hubbard U)

GGA, GGA+U, PBE0 hybrid exchange-correlation functional

Projector Augmented Wave method

Conjugate Gradient method for structure relaxation

Nudged Elastic Bands for energy barriers estimation

Bader charge analysis

Spin-polarized calculations

Factors determining O diffusion?