The symmetry-adapted configurational ensemble approach to the computer simulation of site-disordered solids

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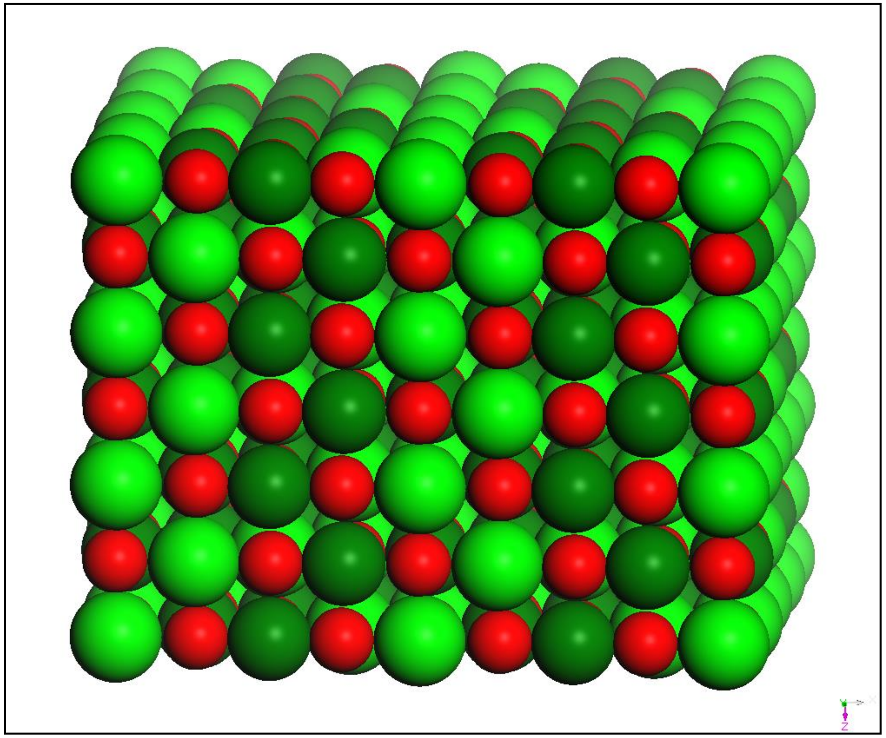


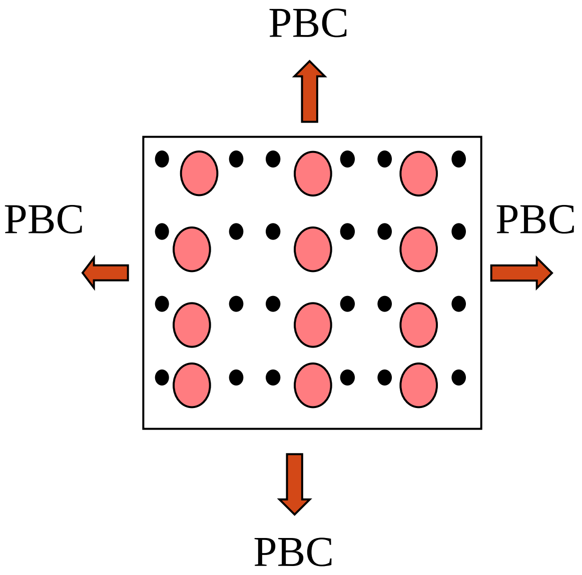
Mol2Net, 2015

University of Reading, UK

Edward Guggenheim (1901- 1970)

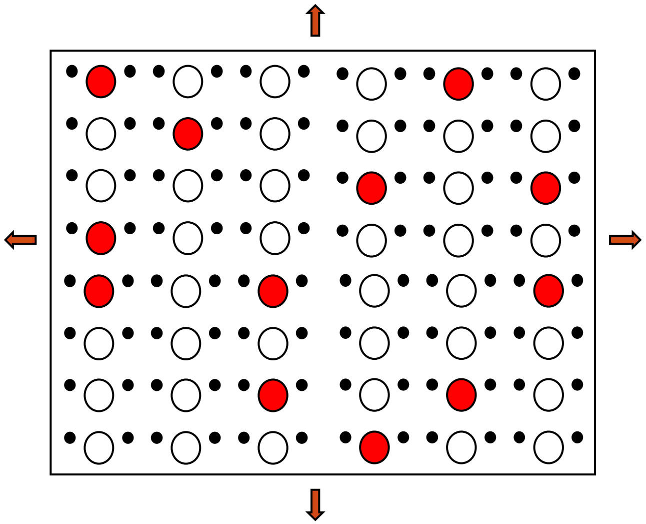
Representations of a site disordered solid

Species A ○ and B ● share the same type of site in the crystal



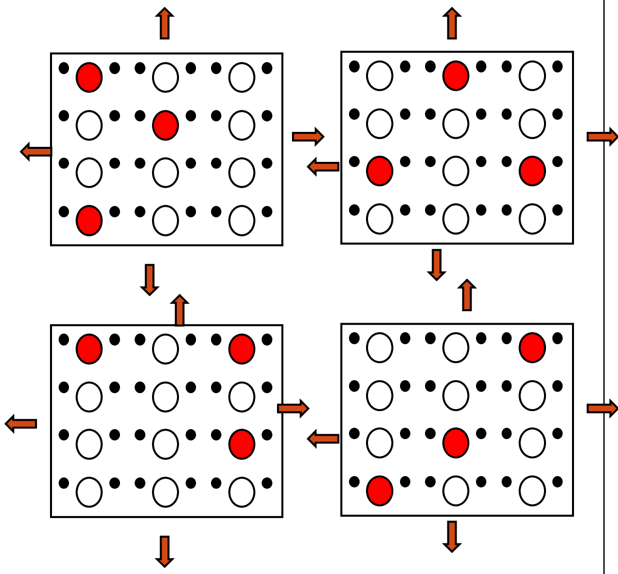
Structure with average ions

- Local structure wrong
- Solution energies usually wrong too



Supercell with random or special quasi-random distribution of ions

- Local structure ok
- Large cell required
- Temperature independent



Configurational ensemble

- Local structure ok
- Computationally cheaper (and parallelisable)
- Temperature dependence via statistical mechanics

Classification of methodologies for modelling site-disorder

Disorder representations →

	Geom. relax.	**Elect. relax.**	**Average-ion**	**Supercell**	**Ensemble**
Energy as a function of site occupancies	No	No	-	-	Ising-like models, Cluster Variation Method (CVM)
Energy from classical interatomic potentials	Yes	No	Mean-field approach in GULP	Random or arbitrary distributions	●
Energy from QM calculations	Yes	Yes	Virtual Crystal Approximation (VCA)	Random or arbitrary distributions, Special quasi-random structures (SQS)	●

R. Grau-Crespo and U. V. Waghmare."Simulation of crystals with chemical disorder at lattice sites"
In: *Molecular Modeling for the Design of Novel Performance Chemicals and Materials*. Ed. B. Rai. CRC Press Inc. (2012).

Why IP or QM in ensemble calculations?

- Some interactions are difficult to parameterise in cluster expansion models (e.g. long-range interactions in ionic solids, strong geometric relaxations, changes in electronic configurations, etc.)

- IP and QM methods provide not just energies but also other properties for each configuration (e.g. local geometries and cell parameters, electronic structure, spectra). Configurational averages can then be obtained.

- They allow to directly evaluate vibrational properties of the disordered solid.

- They also allow to extend the simulations to solid surfaces, which is non-trivial with simpler interaction models.

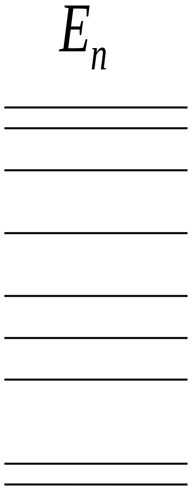
Statistics in the configurational space: basic formulation

$$P_n = \frac{1}{Z}\exp(-E_n / kT)$$

$n = 1, \ldots, N$ (total number of configurations)

$$Z = \sum_{n=1}^{N}\exp(-E_n / kT)$$

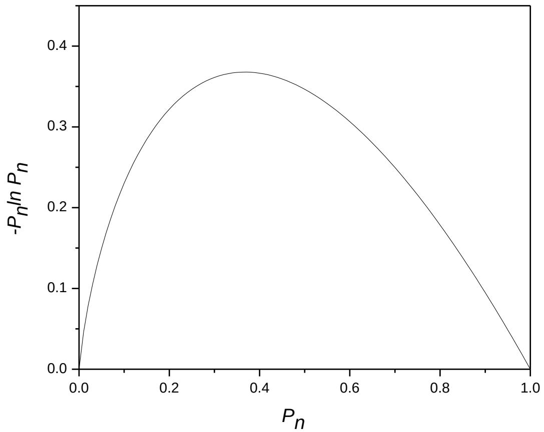
$$F = -kT\ln Z$$



$$E = \sum_{n=1}^{N} P_n E_n$$

For any property $A = \sum_{n=1}^{N} P_n A_n$

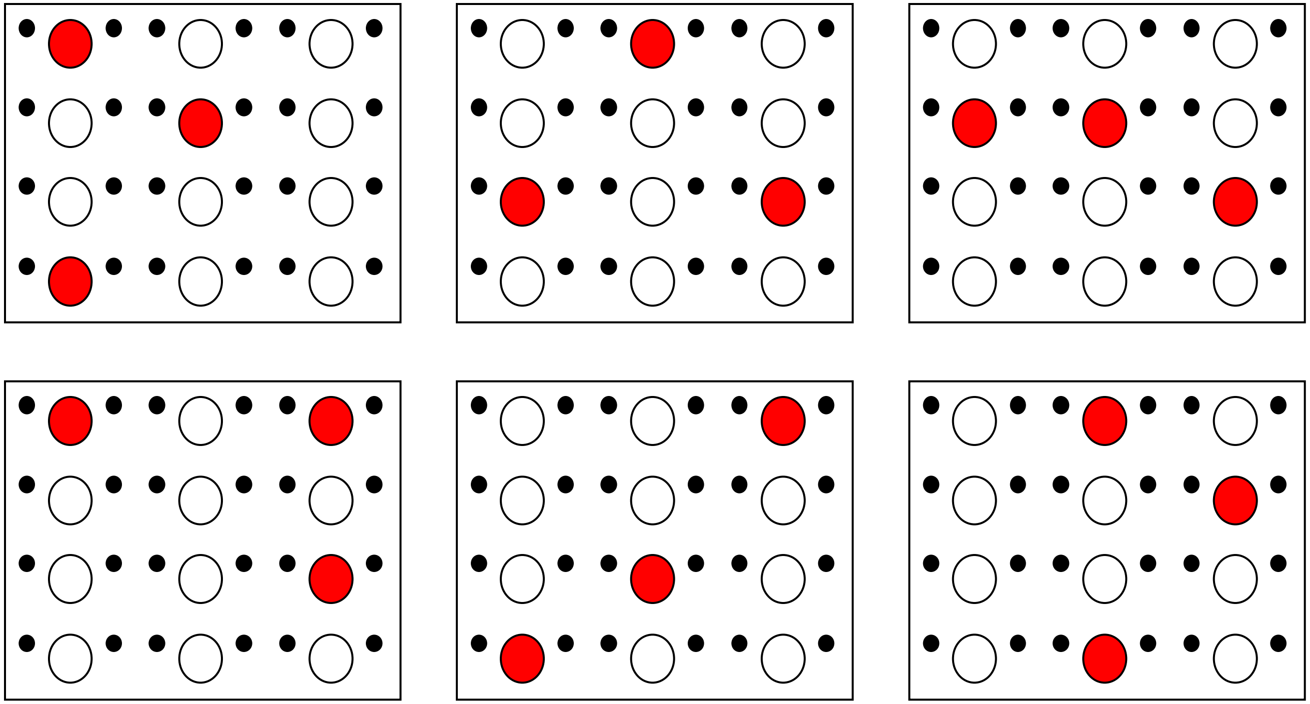
$$S = \frac{E-F}{T} = \ldots = -k\sum_{n=1}^{N} P_n \ln P_n$$



The main problem is the high number of configurations

Example: **3** substitutions in **12** sites
Number of configurations:

$$\frac{12!}{(12-3)!\ 3!} = 220$$



Dealing with the configurational barrier

Random sampling

Importance sampling / Monte Carlo
(sample is biased; statistics is different).

Symmetry-adapted ensembles
(reduces size of configurational space by ~two orders of magnitude)

How to take advantage of the crystal symmetry?

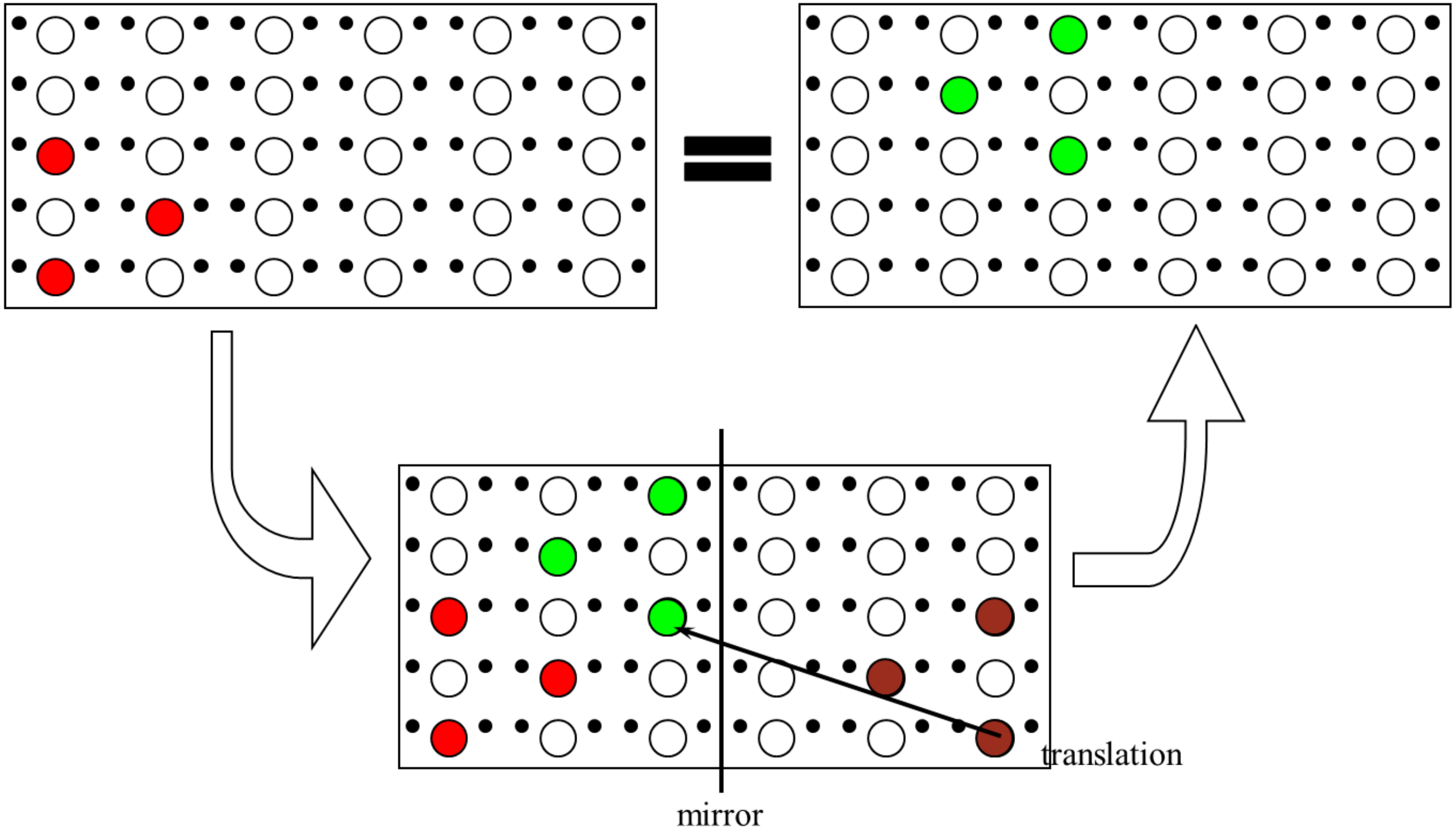
- Only **inequivalent configurations** have to be calculated, if their degeneracies Ω_m are known *a priori*. Then:

$$P_m = \frac{\Omega_m}{Z}\exp(-E_m / kT)$$

- Two configurations are equivalent if they are related by an **isometric transformation**.

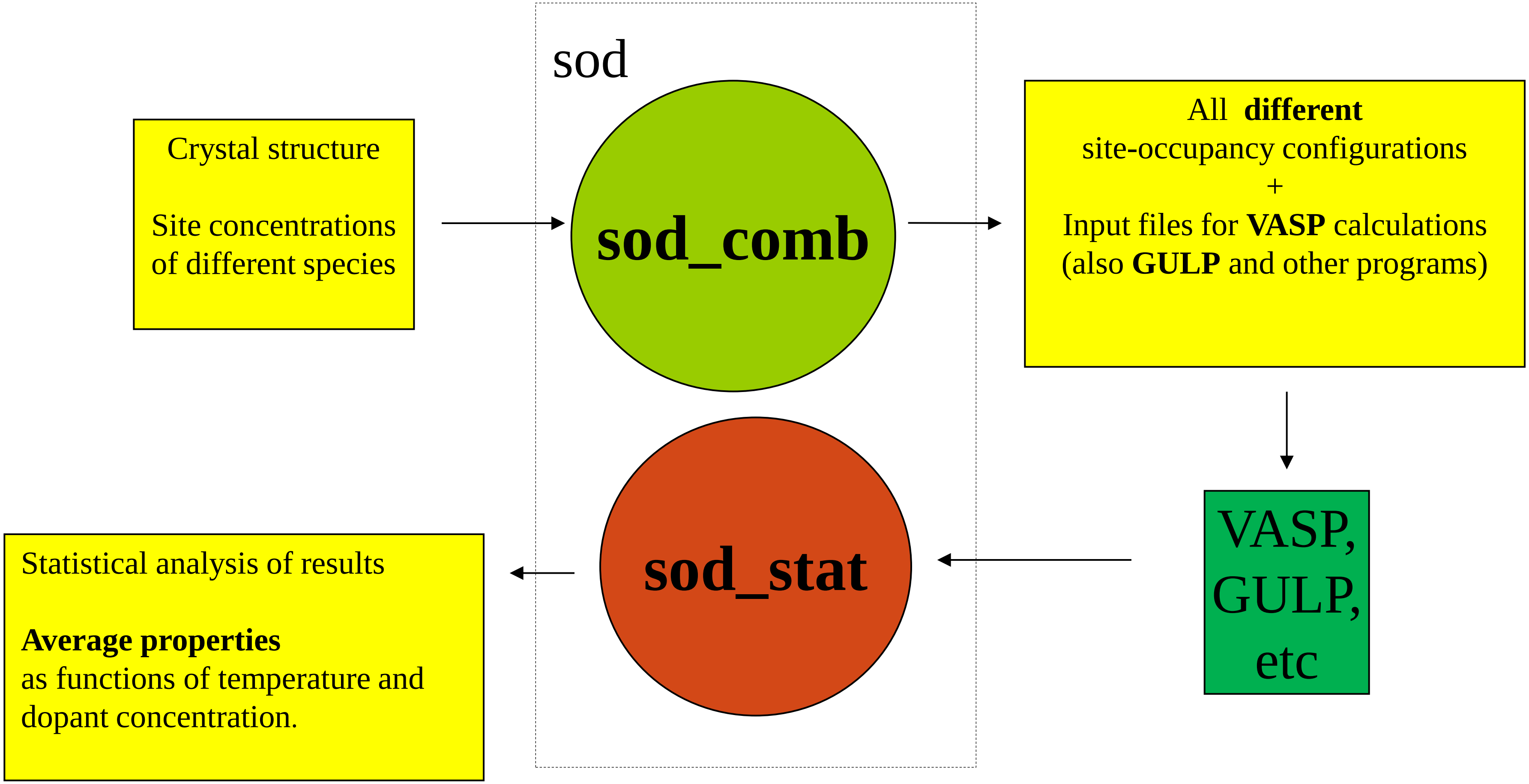
- All possible isometric transformations are contained in the **symmetry group of the parent structure** (including supercell translations).

Taking advantage of the supercell symmetry



site **o**ccupancy **d**isorder

sod (**s**ite – **o**ccupancy **d**isorder) package



sod

Crystal structure

Site concentrations of different species

sod_comb

All **different** site-occupancy configurations
+
Input files for **VASP** calculations (also **GULP** and other programs)

VASP, GULP, etc

sod_stat

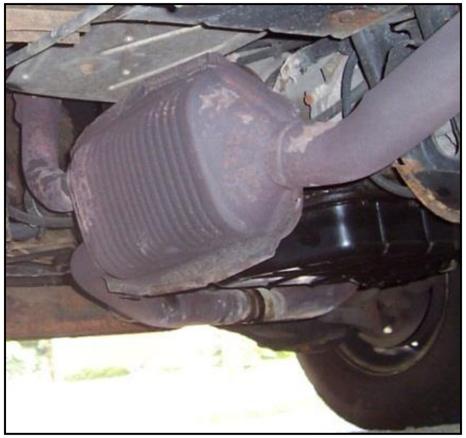
Statistical analysis of results

Average properties as functions of temperature and dopant concentration.

Grau-Crespo et. al. *Journal of Physics - Condensed Matter* **19** (2007) 256201

Bulk and surface of ceria-zirconia solid solutions

(with U. Waghmare and N. H de Leeuw)



$Ce_{1-x}Zr_xO_2$ has replaced pure ceria in three-way car exhaust catalysts

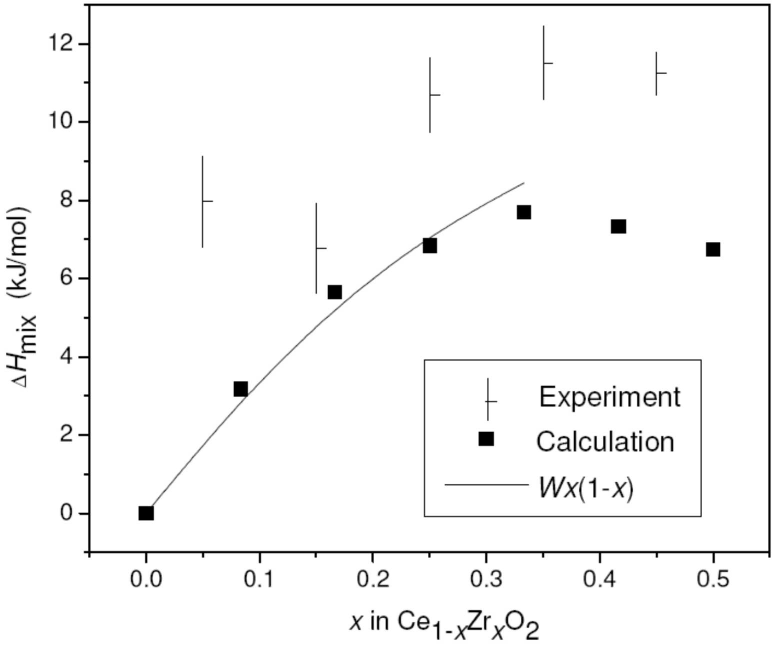
What happens to the cation distribution at the high temperatures (up to 1373 K) of close coupled converters?

SOD+VASP (DFT) calculations

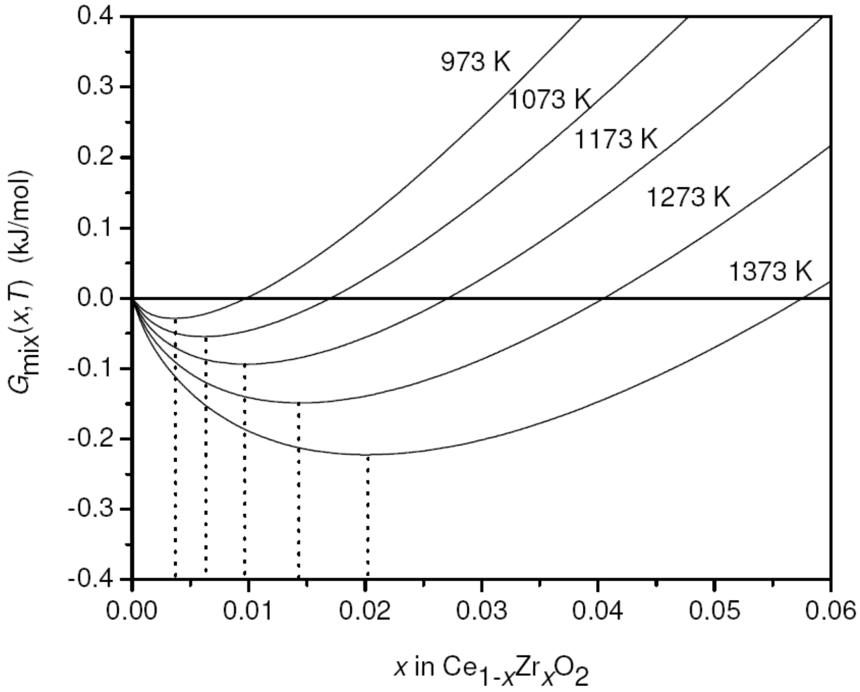
Enthalpy of mixing:

The formation of the solid solution is strongly endothermic

Free energy of mixing:

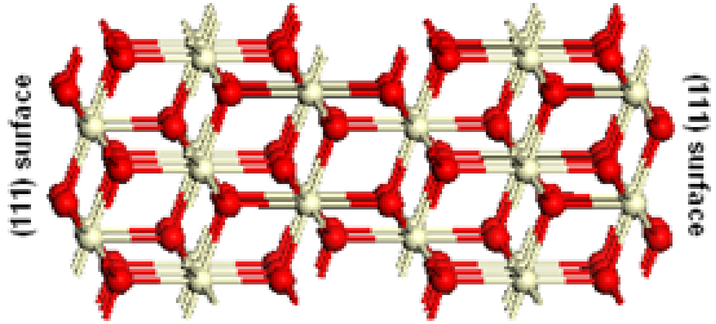


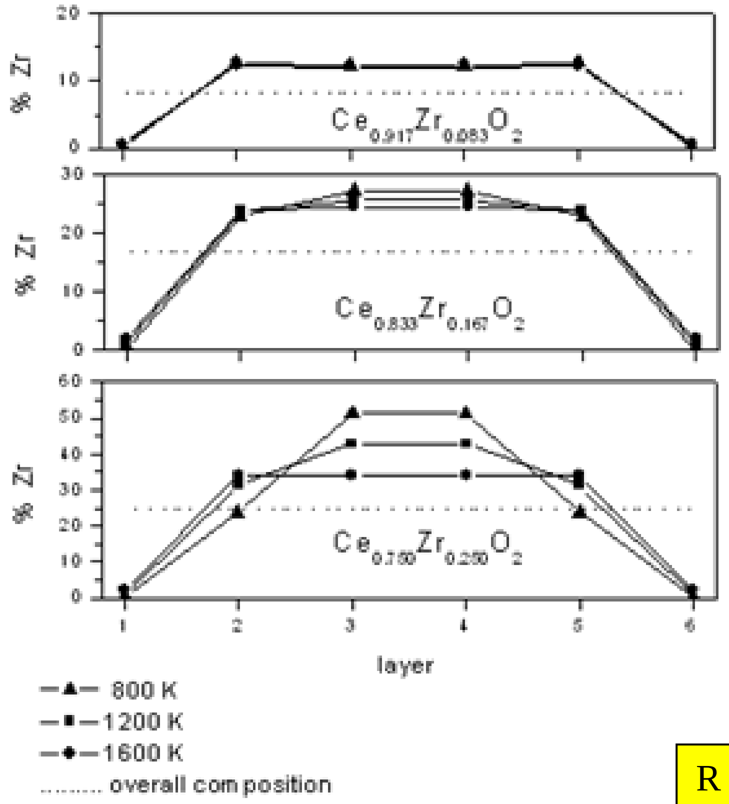
Calorimetric experiments:
Lee, Navrotsky *et al*. J. Mater. Res. (2008)



Solid solutions used in applications are metastable
(Maximum stable Zr content at 1373 K is ~2 mol%)

Ceria – zirconia surface calculations (SOD + VASP)





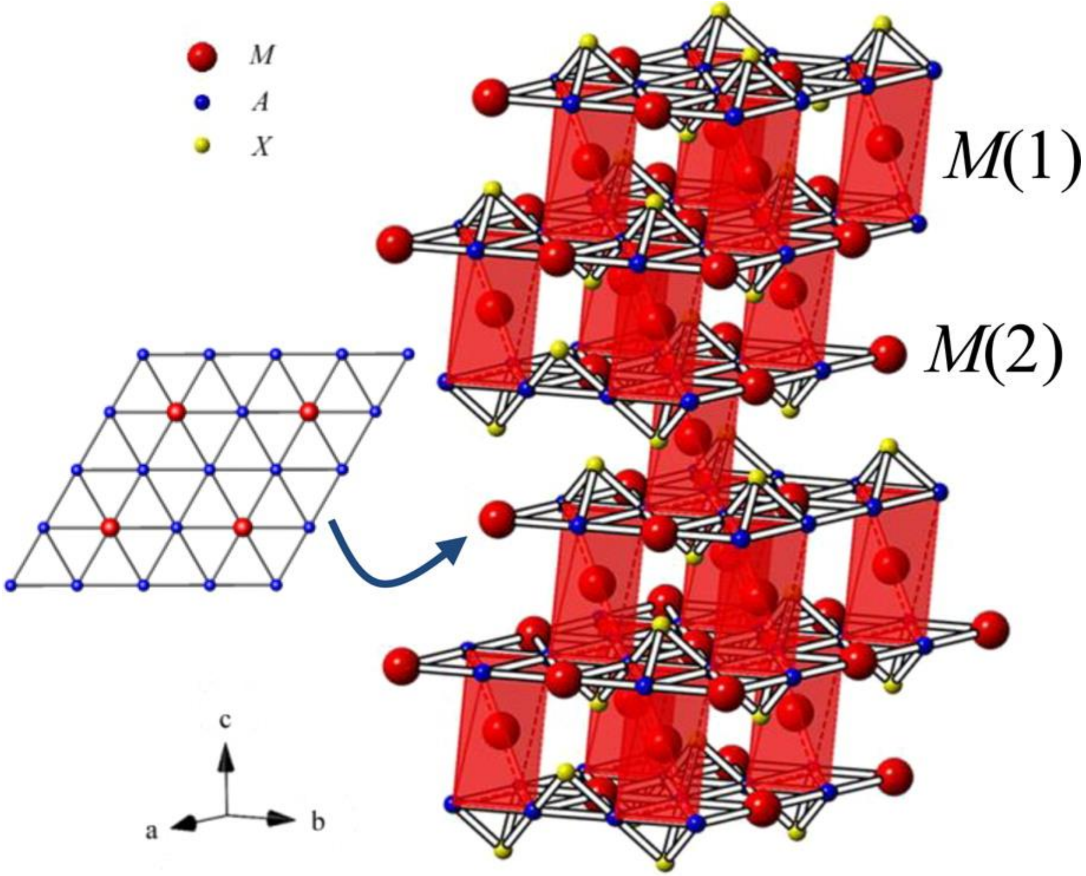
$$f = \sum_{n=1}^{N} P_n f_n$$

Calculated Zr content at different layers as a function of composition and temperature

R Grau-Crespo, NH de Leeuw, S Hamad, UV Waghmare, *Proc. Royal Soc. A* 467, 1925-1938 (2011)

$Co_3Sn_{2-x}In_xS_2$ solid solutions

in collaboration with the group of Prof. Anthony V. Powell (Reading)

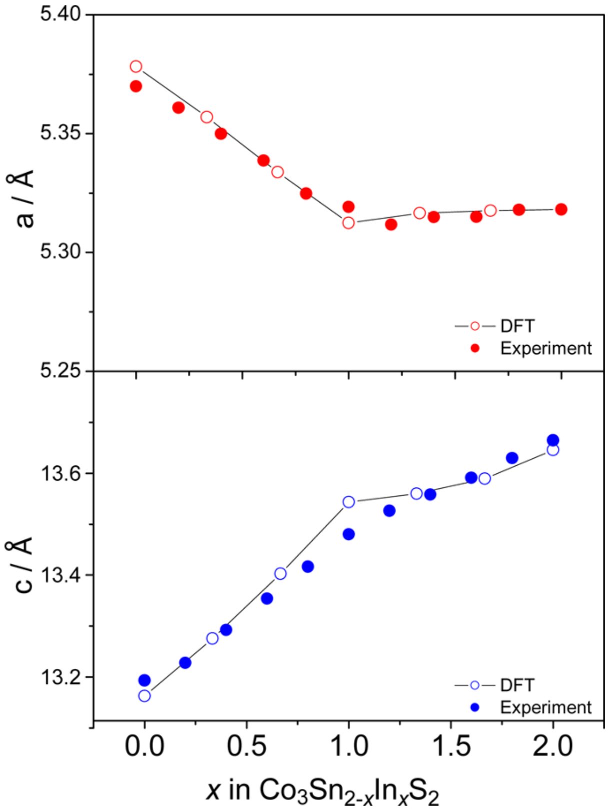


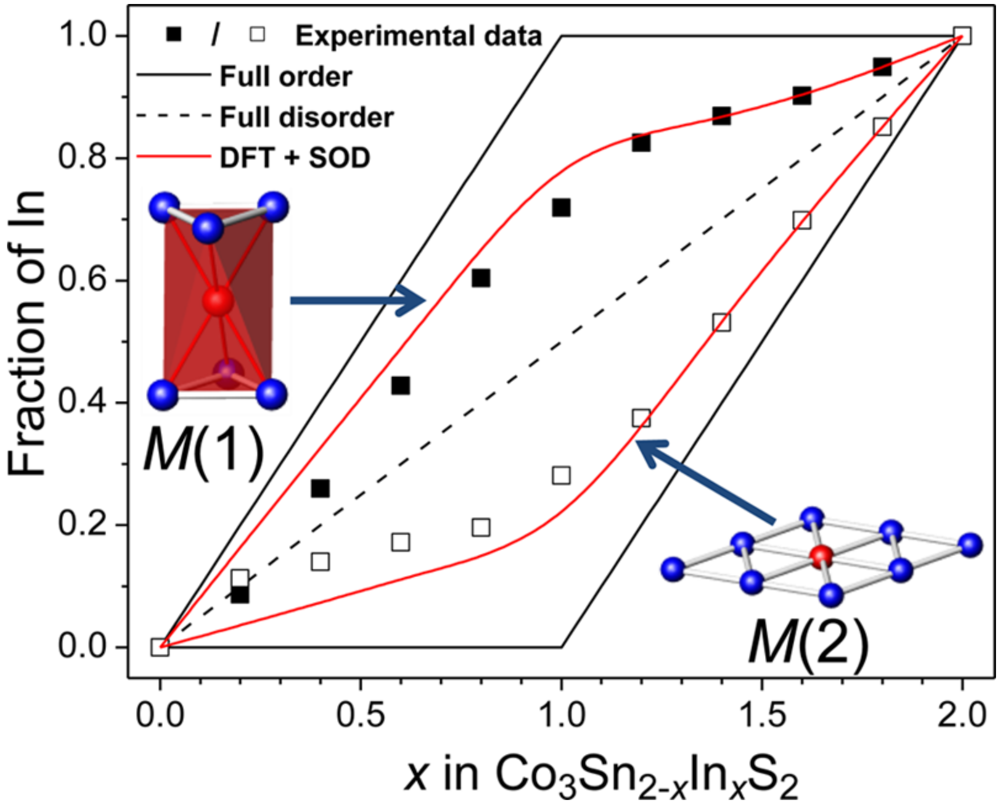
- Shandites are a family of structurally-related materials of general formula $A_3M_2X_2$ (A = Ni, Co, Rh, Pd; M = Pb, In, Sn, Tl; X = S, Se).

- Low thermal conductivity due to their sudo 2-dimensional layered structure

- In doping of Sn in $Co_3Sn_{2-x}In_xS_2$ was performed changing the electron count by two across the composition range

$Co_3Sn_{2-x}In_xS_2$ solid solutions





Chem. Mater. **2015**, *27* (11), 3946–3956.

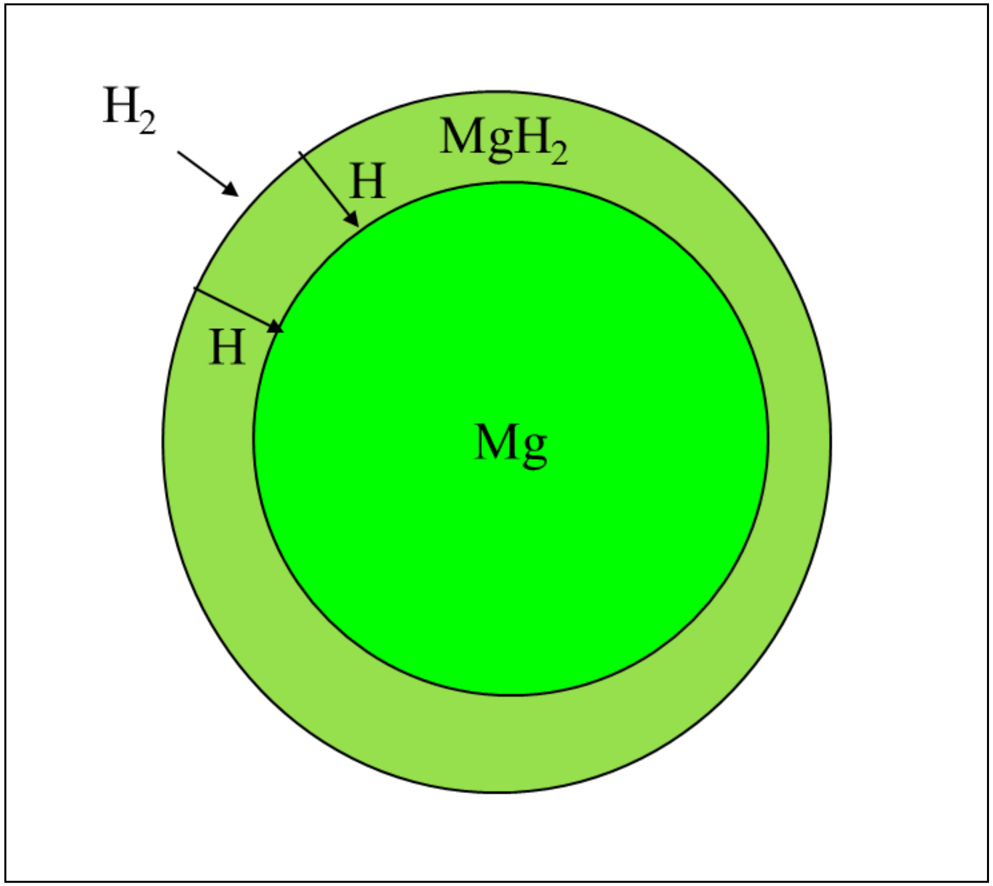
Hydrogen vacancies in MgH_2

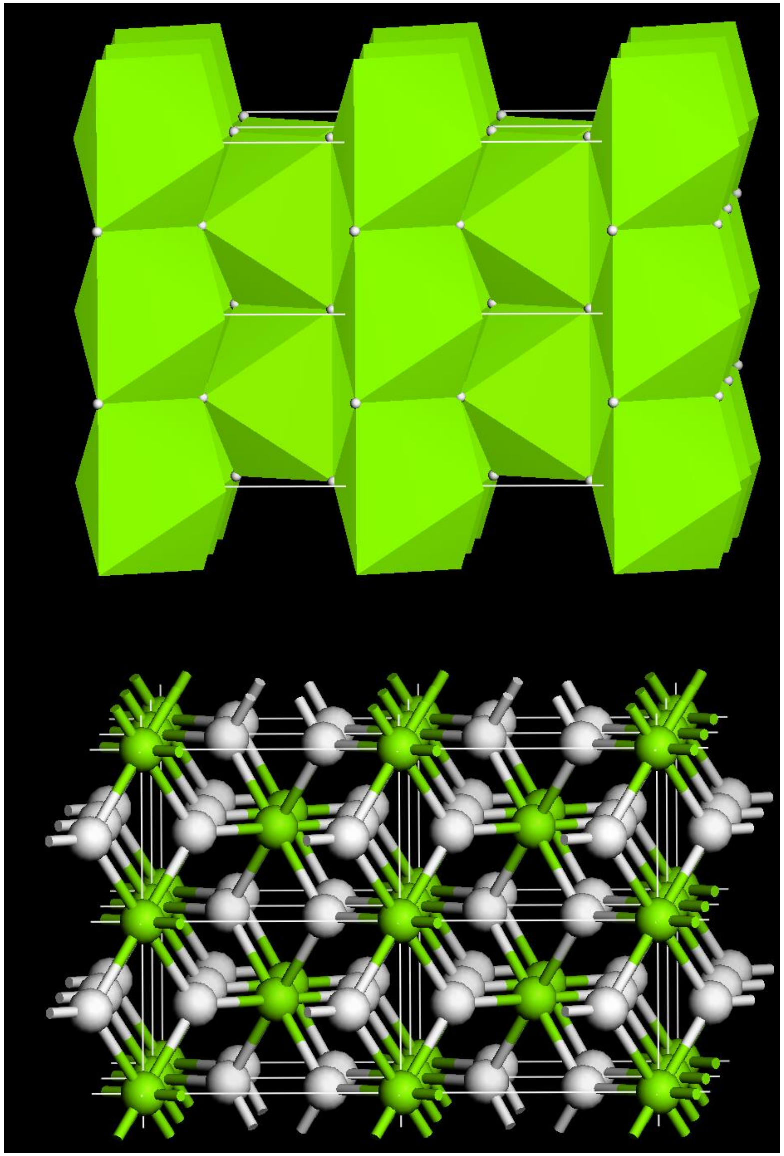
(With Umesh Waghmare, Kyle Smith and Tim Fisher)

α phase:
Metallic Mg with interstitial H

β phase:
Ionic MgH_2

Very slow H diffusion in β phase!





MgH$_2$ rutile-like structure

Chains of MgH$_6$ octahedra sharing edges along the c axis.

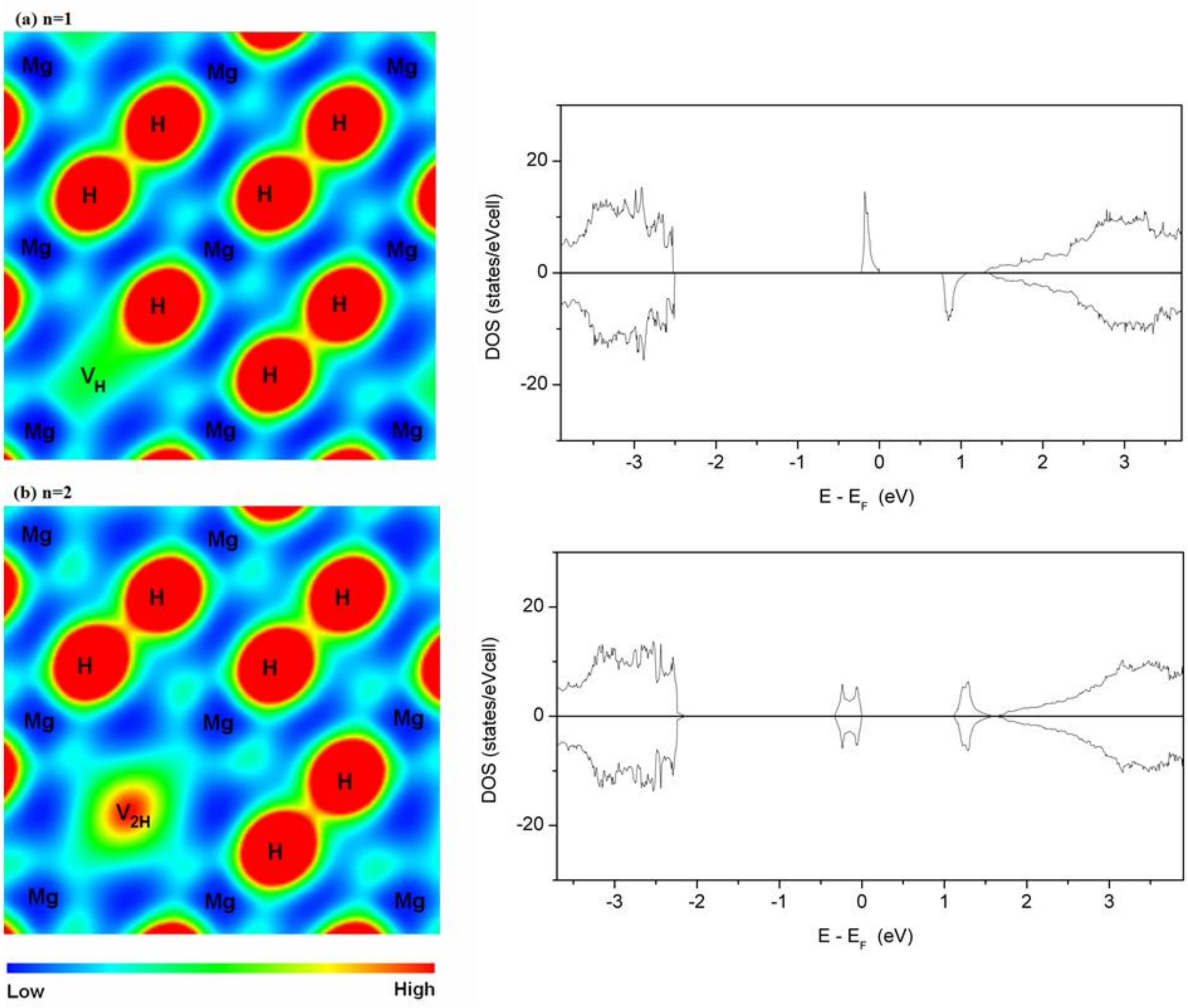
2x2x2 supercell employed in calculations:

16 Mg and **32-*n*** H atoms,

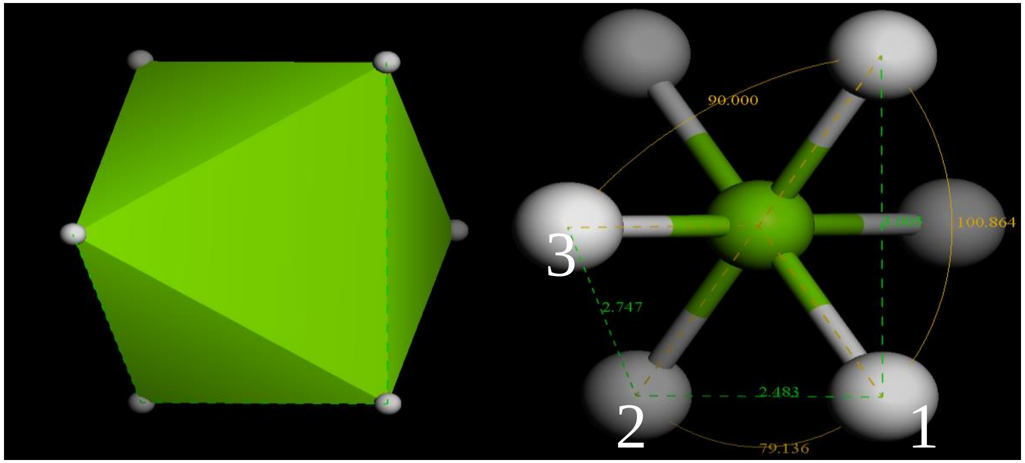
n is the number of vacancies in the supercell

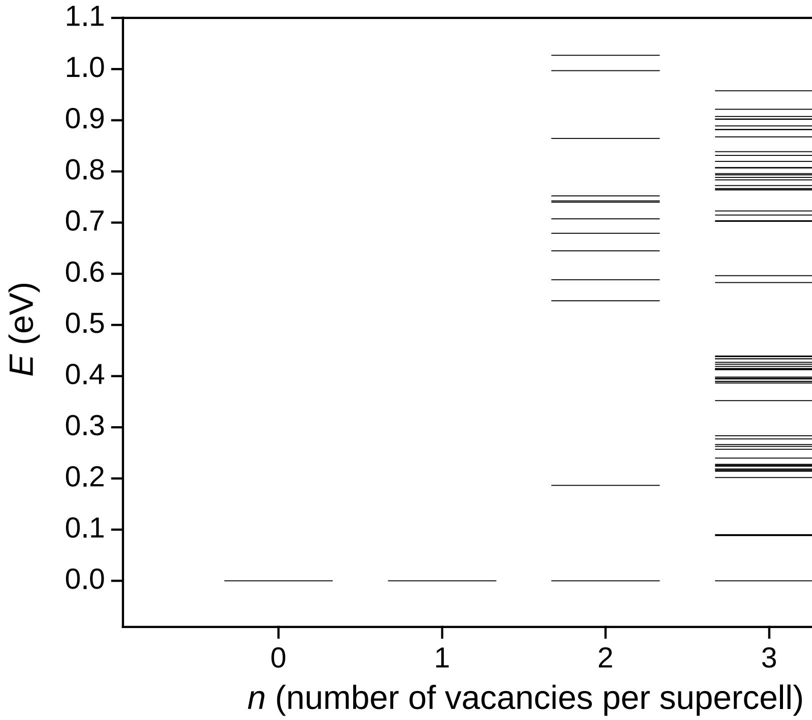
DFT (VASP) calculations – there are F centres

Electronic structure of H vacancies in MgH_2



Configuration energies





Vacancy species:

VFE(eV)

1	mono-vacancy	1.41
1+2	di-vacancy of type I	1.04
2+3	di-vacancy of type II	1.13
1+2 +3	tri-vacancy	1.07

Introducing the grand-canonical formulation:

Probability of the m^{th} configuration with n vacancies is:

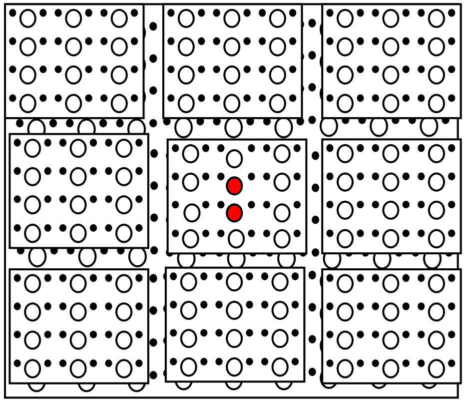
$$P_{nm} = \frac{\Omega_{nm}}{\Xi} \exp\left(-\frac{E_{nm} - n\mu}{k_B T} \right)$$

μ is the H chemical potential in the gas phase:

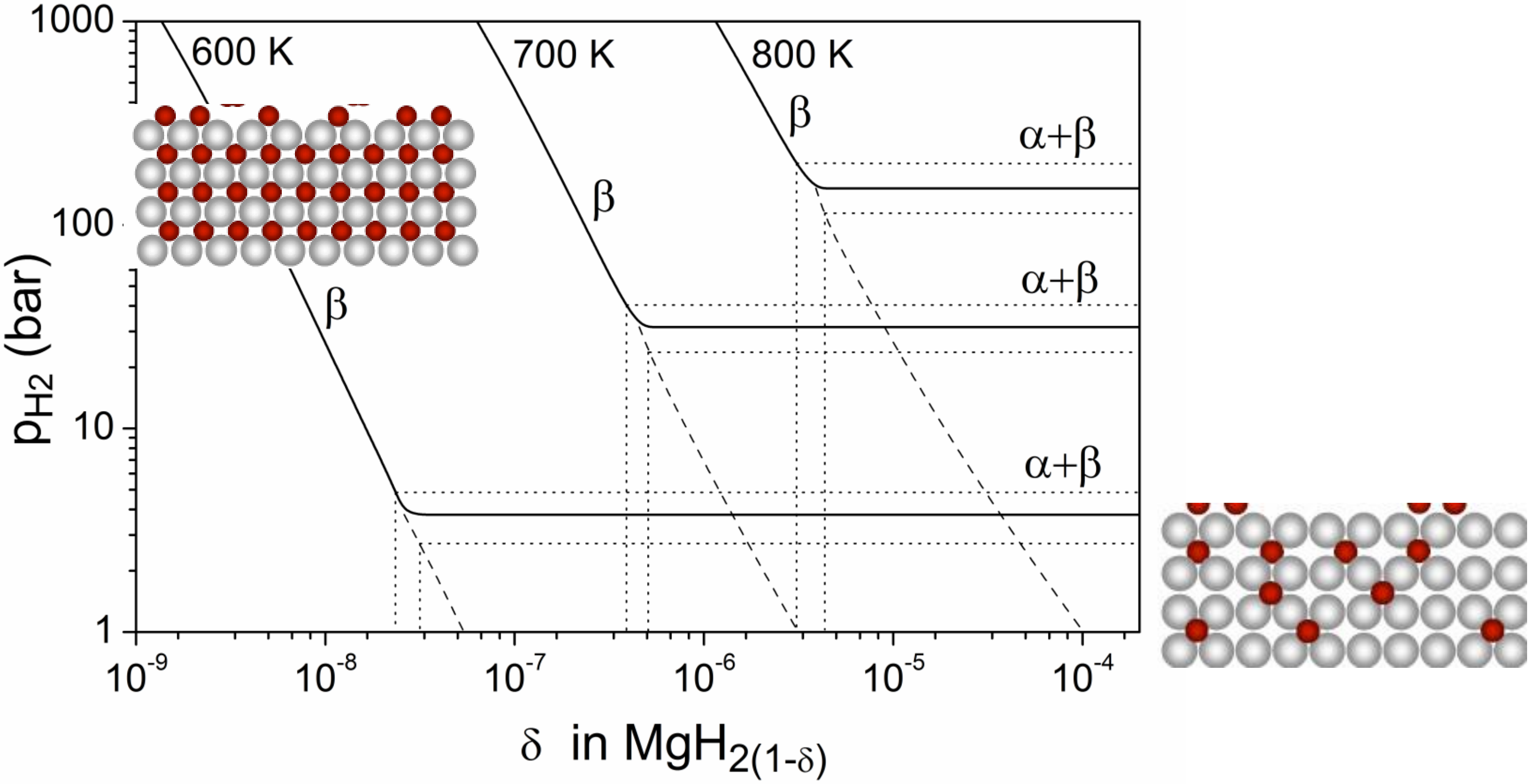
$$\mu = -\frac{1}{2} g_{\mathrm{H}_2}(T, p_{\mathrm{H}_2}) \approx -\frac{1}{2}\left(E_{\mathrm{H}_2}^{DFT} + ZPE + \Delta g_{\mathrm{H}_2}(T, p_0) + k_{\mathrm{B}} T \ln \frac{p_{\mathrm{H}_2}}{p_0} \right)$$

Equilibrium concentration of vacancies as a function of p_{H2} and T:

$$\delta = \frac{1}{N} \sum_n n \sum_m P_{nm}$$



Theoretical pressure – composition isotherms in MgH_{2-x}



- Very low concentration of vacancies, which explains slow diffusion kinetics
- More mono-vacancies than di-vacancies!

Phys. Rev. B 80 174117 (2009)

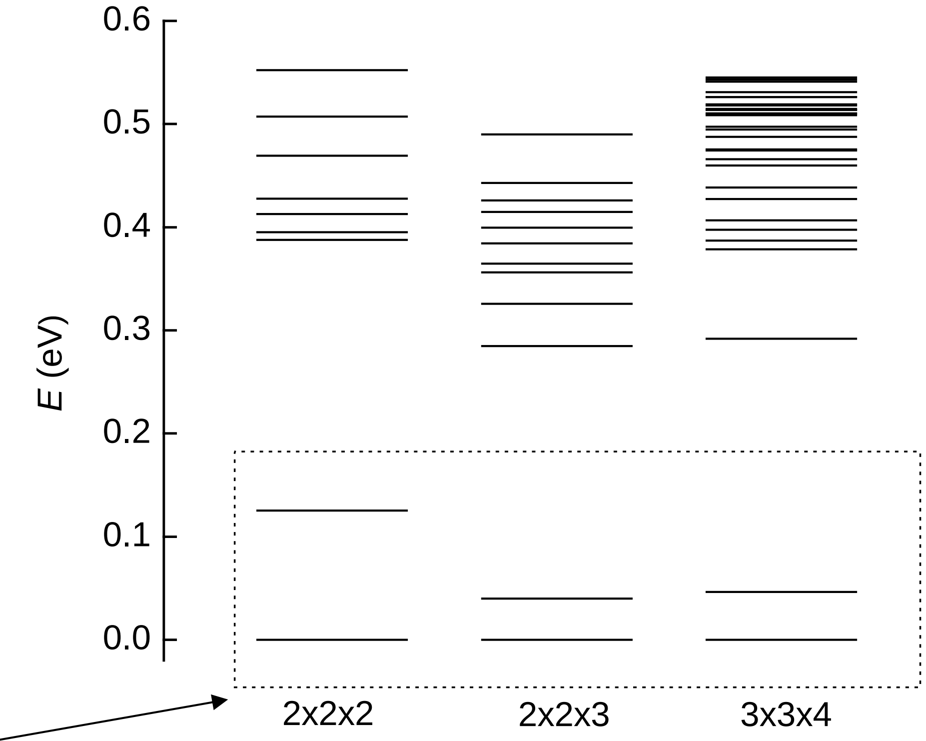
An alternative mechanism for vacancy formation: doping with monovalent ions

(Kröger–Vink notation)

$$\mathrm{Li}_{\mathrm{Mg}}^{'} + V_H^{\bullet}$$

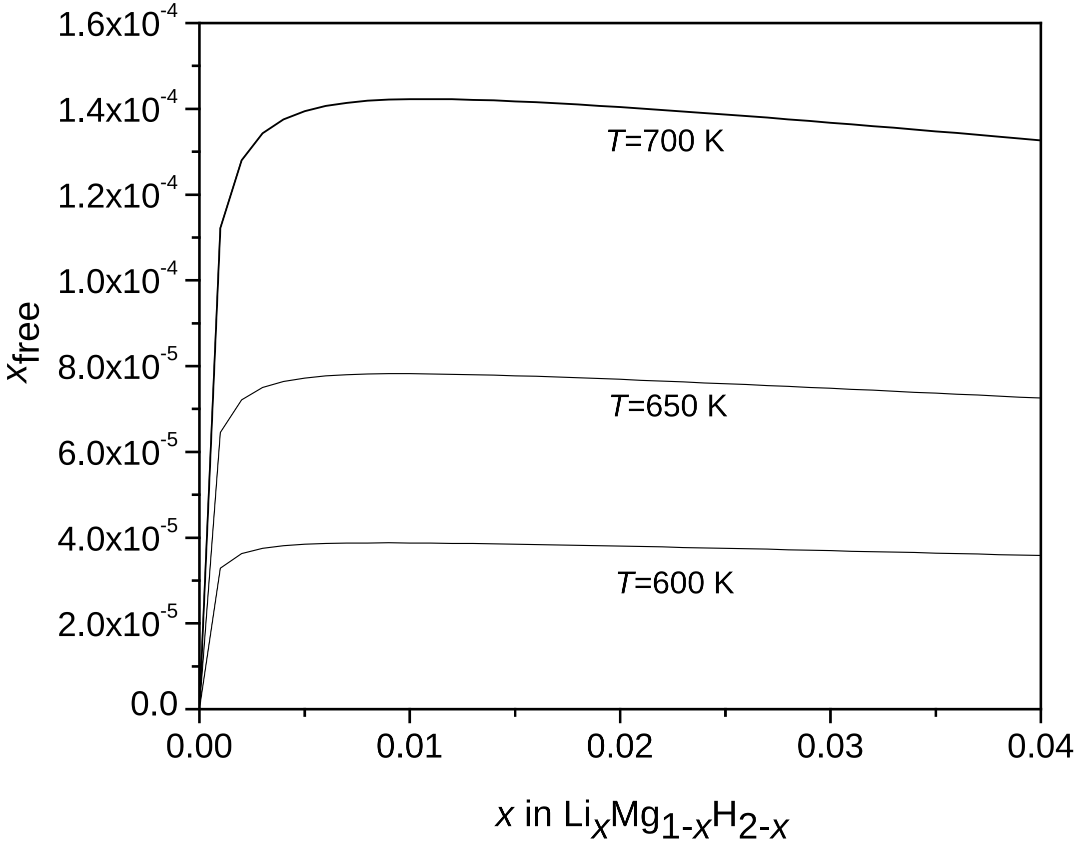
Negative”
$\mathrm{Li}^{+}/\mathrm{Mg}^{2+}$
substitution

Positive”
H vacancy



Vacancies trapped by dopants

Concentration of *free* vacancies *vs* dopant molar fraction

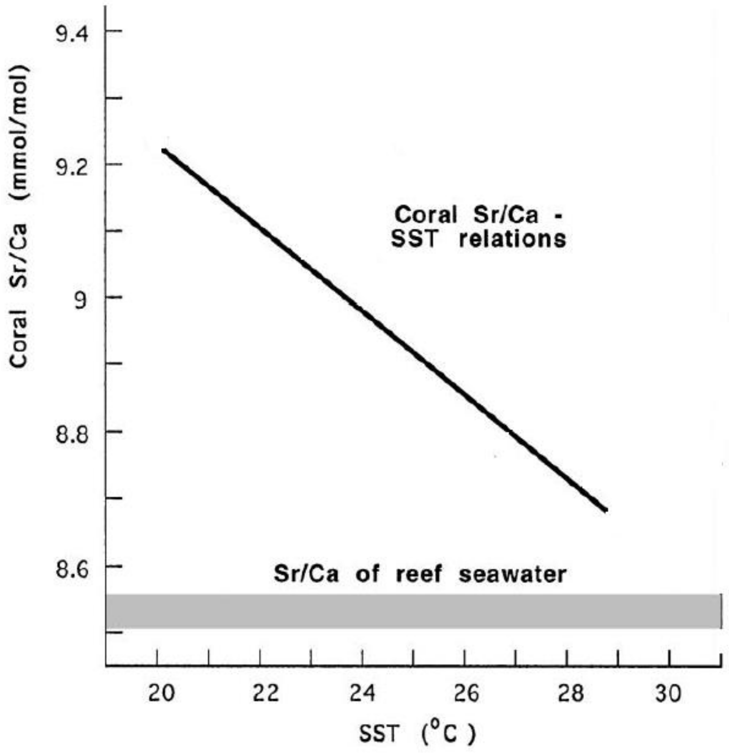


Diffusion cannot be improved with Li doping beyond ~1% !!!!

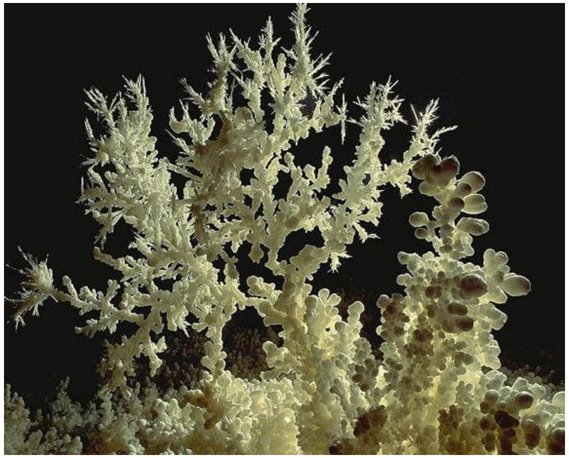
K. Smith, T. S. Fisher, U. V. Waghmare and R. Grau-Crespo, *Phys. Rev. B* 82, 134109 **(2010)**

Impurities in aragonite:
Measuring climate change from coral fossils

(in collaboration with Nora de Leeuw's group)



Adapted from Gagan et al.
Quaternary Science Reviews
19 (2000) 45-64



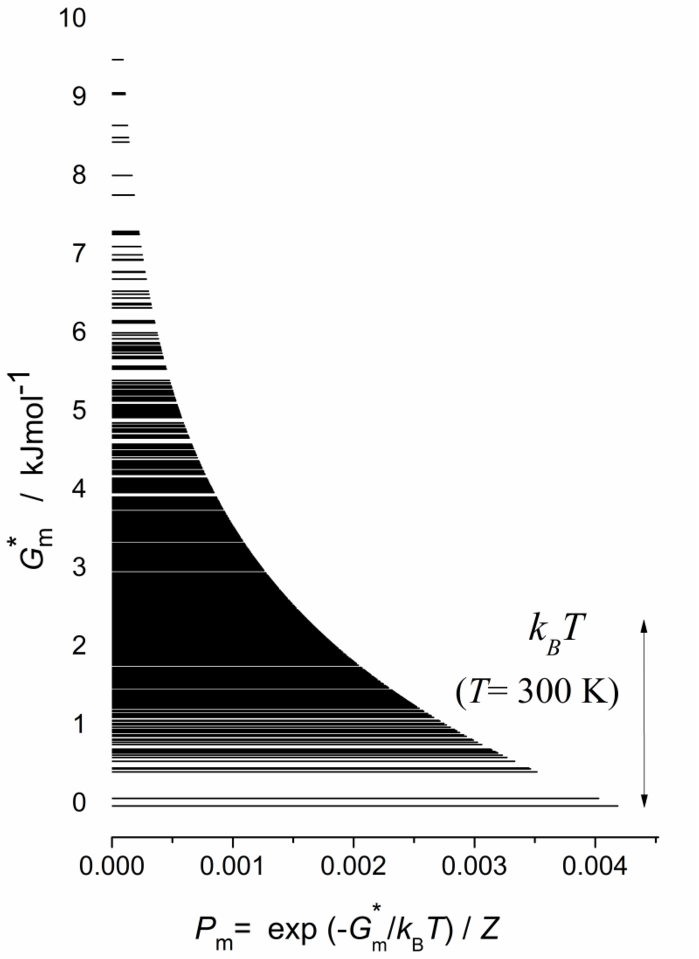
- Sr content of coral fossils correlates with sea surface temperature (SST) during biomineralization (paleothermometer)

- Doubts about thermodynamic stability of this Sr content in coral skeleton material (aragonite $CaCO_3$)

- formation of strontianite $SrCO_3$?

Configurational spectrum for $Sr_{0.125}Ca_{0.875}CO_3$,

Highly but not *completely* disordered.

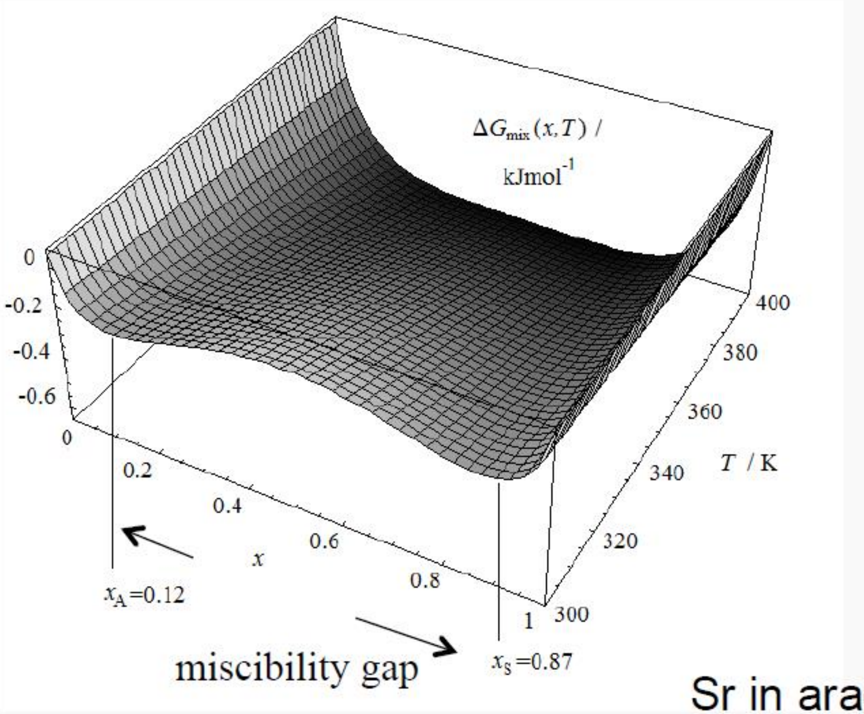


- Classical interatomic potential calculations using GULP
- Vibrational effects included in the thermodynamic analysis.
- Full range of compositions in the solid solution.

Free energies of mixing

(including configurational and vibrational contributions)

$$\Delta G_{\text{mix}} = G[\text{Sr}_x\text{Ca}_{1\text{-}x}\text{CO}_3] - (1-x)G[\text{CaCO}_3] - xG[\text{SrCO}_3]$$



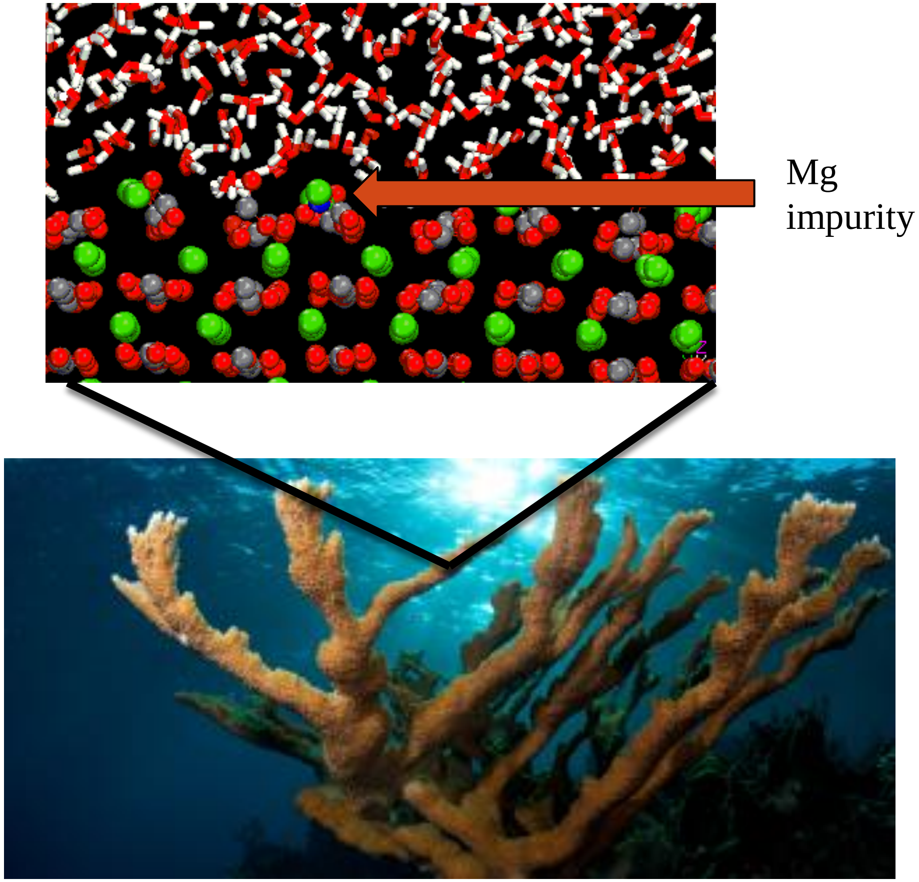
$$G[\text{Sr}_x\text{Ca}_{1\text{-}x}\text{CO}_3] = \overset{\text{ideal}}{\overline{k_\text{B}T[x\ln x + (1-x)\ln(1-x)]}} + \underline{x(1-x)[A_0 + A_1(1-2x) + \dots]}$$

Excess (E. A. Guggenheim, 1937

Sr in aragonite **thermodynamically stable** with respect to phase separation

Mg in aragonite CaCO$_3$

The grand-canonical approach in equilibrium with **aqueous solution**



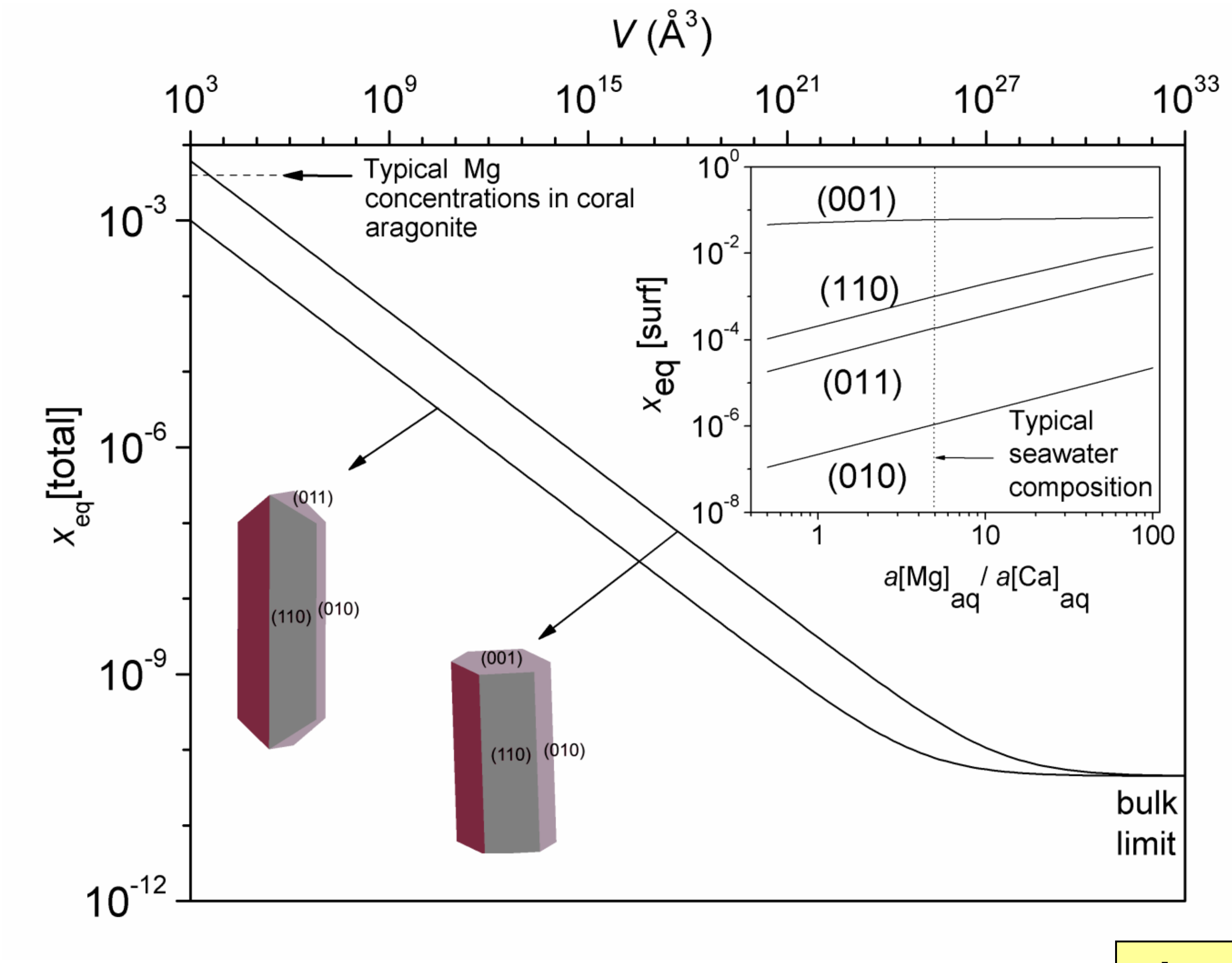
- Mg in corals offers more resolution in paleothermometry correlations

- But trends less reproducible – Mg not in aragonite bulk

- In surface?

Chem. Eur J. (2012)

Equilibrium Mg content in aragonite depends on particle size and morphology (and of Mg content in solution - inset)



Chem. Eur J. (2012)

Other applications of the SOD methodology:

https://sites.google.com/site/rgrauc/sod-program

Including materials for:

- Batteries (Saiful Islam’s group in Bath)
- Solar cells (Aron Walsh’s group in Bath)
- Thermoelectric (Sands’s group in Purdue, USA)
- Superconductivity (Illas’s group in Barcelona)
- Biomaterials (Nora de Leeuw’s group)
- And more minerals (Angeles Fernandez, Oviedo)

Acknowledgements

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- Prof. Umesh Waghmare (JNCASR, Bangalore, India)
- Prof. Tim Fisher (Purdue University, USA)

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UK Materials Chemistry Consortium and for access to the UK National Supercomputing Facilities.

Grau-Crespo's Research group, Summer 2015