abICSに実装されている手法の概要

ab Initio Configuration Sampling (abICS)講習会
2022/6/26

笠松秀輔
山形大学
E-mail: kasamatsu@sci.kj.yamagata-u.ac.jp

abICS
ab Initio **C**onfiguration **S**ampling
https://www.pasums.issp.u-tokyo.ac.jp/abics/

Outline

- Target：Disordered but non-random lattice systems
- Conventional methods and their drawbacks
  - Metropolis Monte Carlo algorithm
  - Cluster expansion
- abICS methodology
  - Replica exchange Monte Carlo algorithm
  - On-lattice neural network model
  - Active learning cycles
- Example calculations
  - Temperature-dependence of A/B site inversion in spinel oxides
  - Defect chemistry in proton conducting oxides

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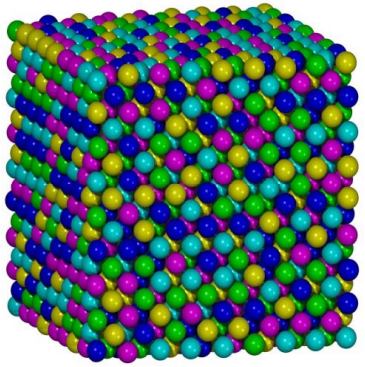
Target :
Disordered but non-random lattice systems

- Short-range order in high-entropy alloys
  - ✓SRO affects the mechanical properties[1]
  - ✓SRO affects the magnetic properties[2]
  - ✓…
- Complex oxides (battery materials, etc.)
  - ✓Ions and ionic defects with varying charges



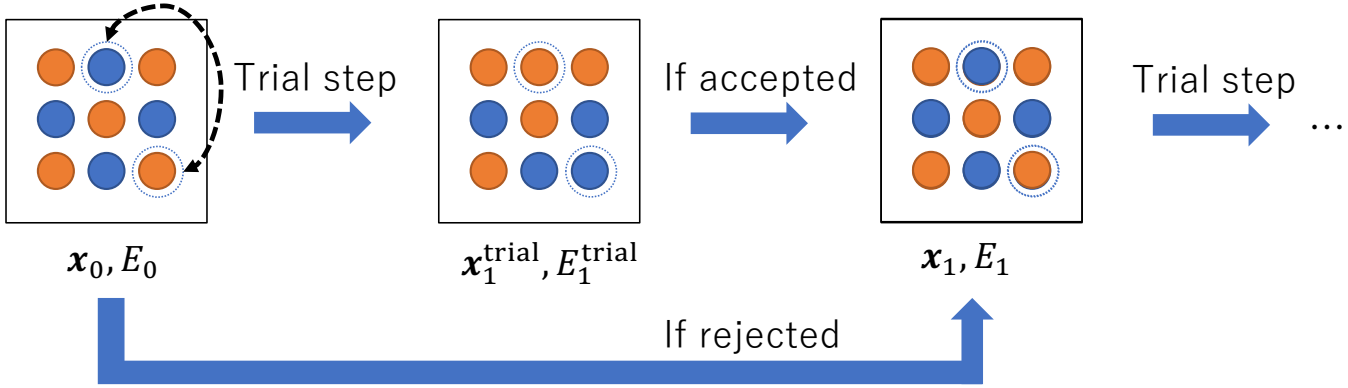
Wang, *Entropy* 15, 5536-5548 (2013)

➡ Exhaustive calculations are impossible
(4-component alloy on 100 sites: ~10^{57} configurations)

➡ Ensemble sampling

[1] R. Zhang et al., Nature 581, 283 (2020).
[2] T. Zuo et al., Acta Mater. 130, 10 (2017).

Thermodynamic importance sampling: Metropolis Monte Carlo algorithm



Metropolis acceptance criterion: $$W\left(\boldsymbol{x}_{i+1} \leftarrow \boldsymbol{x}_{i+1}^{\text{trial}}\right) = \begin{cases} 1, & E_{i+1}^{\text{trial}} < E_i \\ \dfrac{\exp\left(-\frac{E_{i+1}^{\text{trial}}}{kT}\right)}{\exp\left(-\frac{E_i}{kT}\right)}, & E_{i+1}^{\text{trial}} \geq E_i \end{cases}$$

- ✓ $\{\boldsymbol{x}_i\}$ becomes a "chain" of random samples that converges to the equilibrium ensemble at given T naturally considering configuration entropy
- ✓ Too slow at low temperature due to local minima trapping

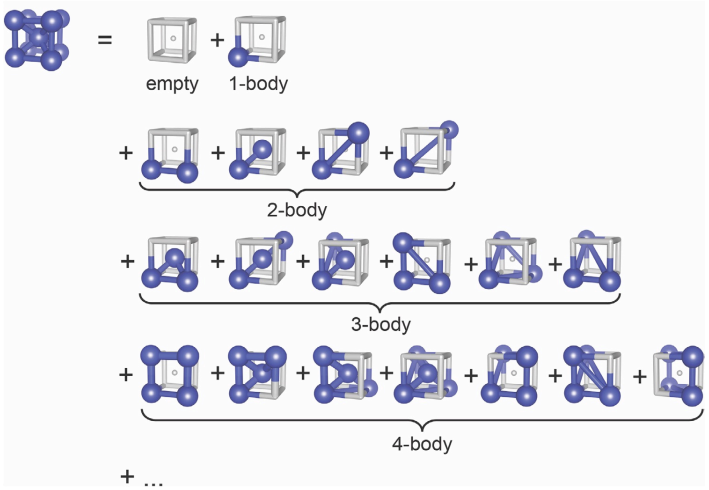
DFT → Lightweight model ?

Cluster expansion:
Expansion of the total configuration energy as a sum of contributions from “clusters”

$$E = V_0 + \sum_i V_i \sigma_i + \sum_{ij} V_{ij} \sigma_i \sigma_j + \sum_{ijk} V_{ijk} \sigma_i \sigma_j \sigma_k$$

Successful in few-component metallic alloys but difficult to apply to many component oxides due to **combinatorial explosion in the number of clusters**

- Long-range interactions
- Many-component systems
- Large relaxation



Jin Hyun Chang *et al.*,
J. Phys.: Condens. Matter **31** 325901 (2019)
[CC-BY-3.0]

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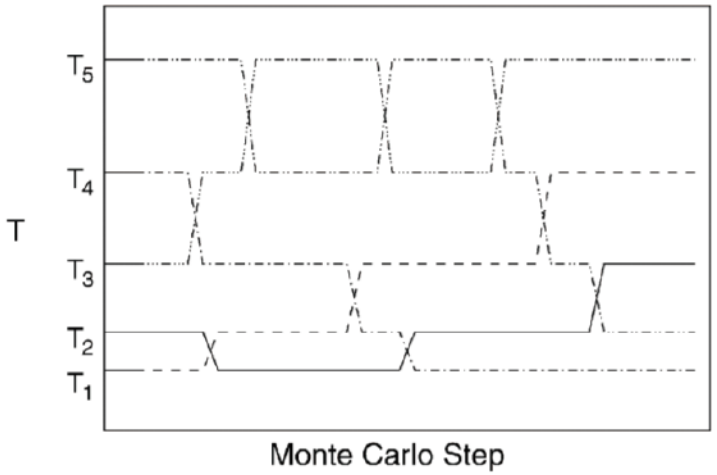
Replica Exchange Monte Carlo (RXMC) Method[*]

1. Prepare copies (replicas) of the system and perform Monte Carlo simulations at different temperatures
2. Perform swapping of temperatures at preset intervals:

$$p = \min\left(1, \exp\left[(E_i - E_j)(\beta_i - \beta_j)\right]\right)$$

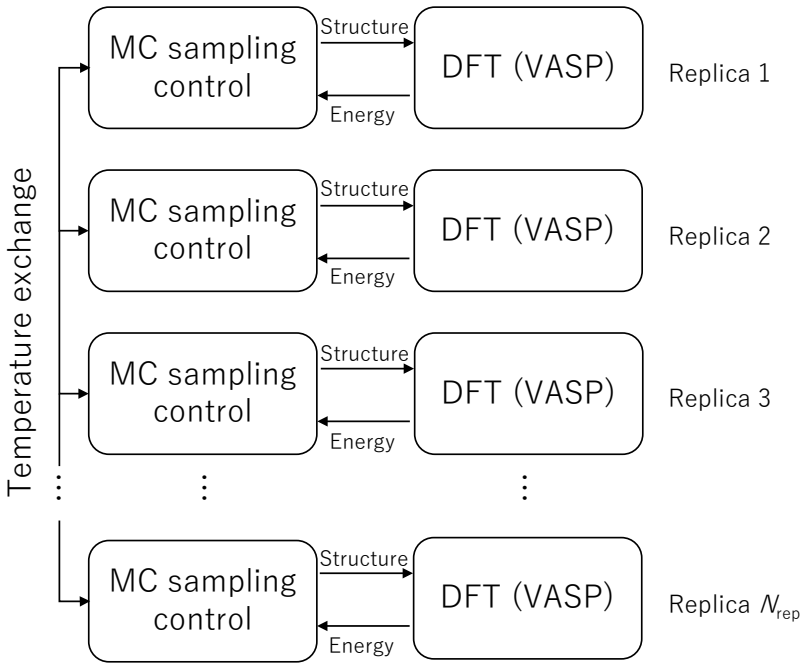


[D. J. Earl and M. W. Deem, PCCP **7**, 3910 (2005).]

✓High-T replicas: global search
✓Low-T replicas: local optimization
✓Well-known in statistical physics (spin models) and classical molecular dynamics

[*] K. Hukushima and K. Nemoto, J. Phys. Soc. Jpn. **65**, 1604 (1996)

abICS version 1: thermodynamic sampling framework using DFT+RXMC



- Direct combination with DFT

- Multilayered parallelism
  →Massively parallel supercomputing

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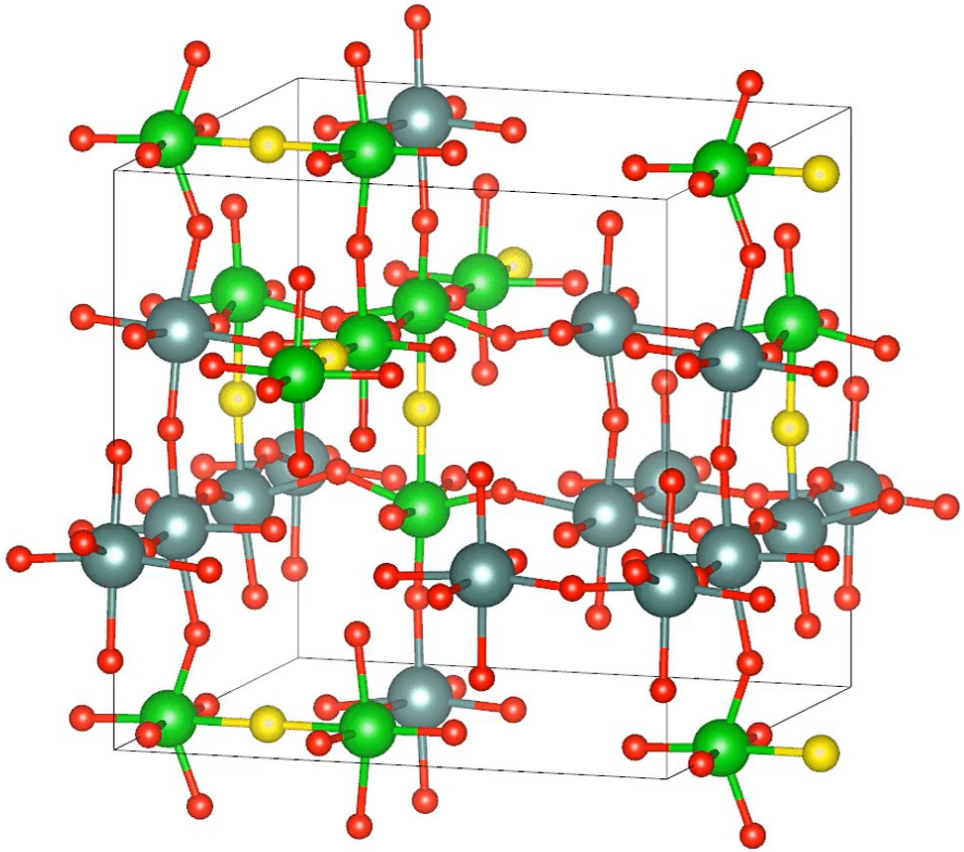
PASUMS

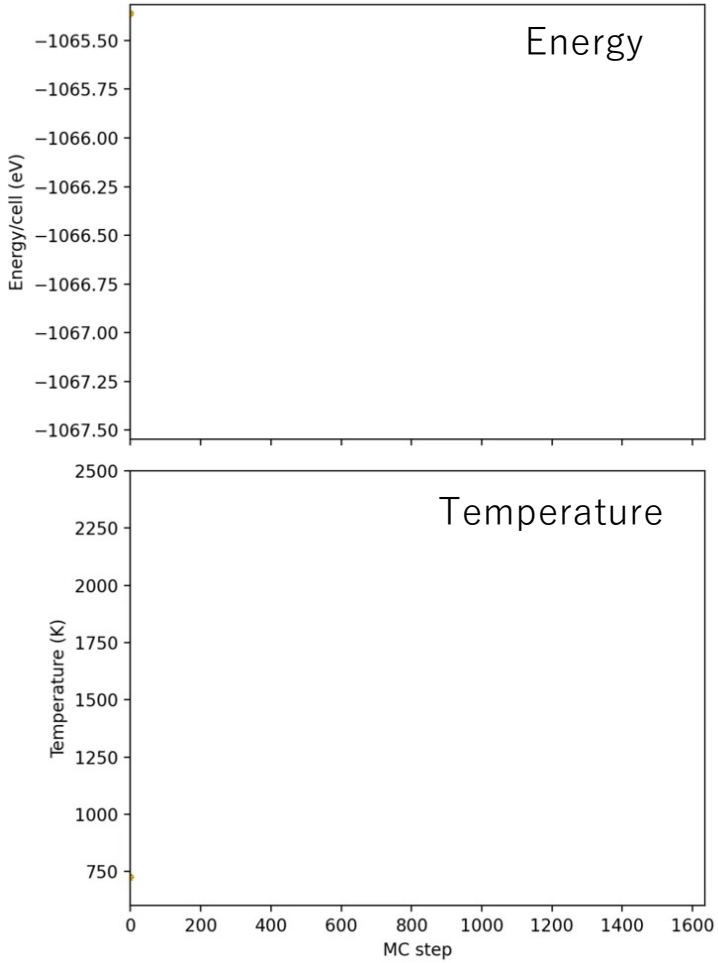
Project for advancement of software usability in materials science

https://www.pasums.issp.u-tokyo.ac.jp/abics/

SK and O. Sugino, J. Phys. Condens. Matter 31, 085901 (2019)

* Showing only BO_6 octahedra with at least one Y or *V*o
* Structures are visualized in 10 step intervals



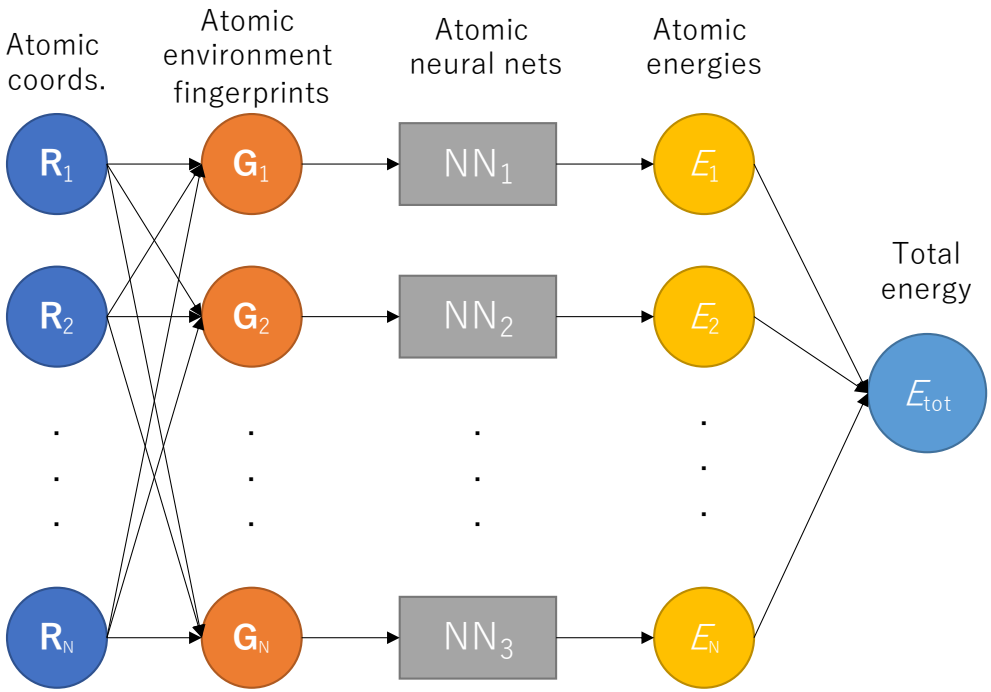


× 16 replicas

SK et al., J. Mater. Chem. A 8, 12674 (2020)

Machine learning potentials (MLP)

- Fit first-principles energies and forces with a flexible ML model and accelerate FPMD simulations
- NNP (Behler & Parinello), GAP (Rappe), MTP (Shapeev), GNN, etc.
- ○ Structural relaxation possible
- ○ Can handle many-component systems
- △ Large amount of training data needed
- △ Relaxation calculations are necessary (cluster expansion is one-shot)



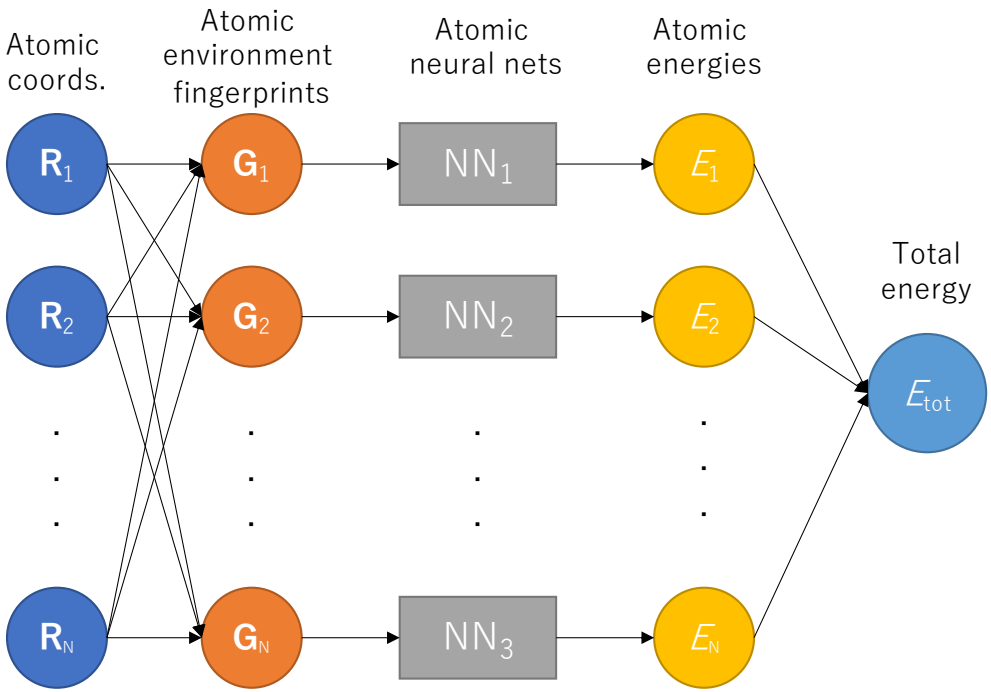
Benchmark on various MLPs：Y. Zhuo et al., J. Phys. Chem. A 2020, 124, 4, 731–745

Our idea :
On-lattice neural network model

- Adaptation of BP-type HDNNP[1, 2]
  Input: Configuration on ideal lattice without relaxation
  Output: Total energy after relaxation

- Easier to train than continuous coordinate NNP
- One-shot calculation for relaxed energies

$$E_{\mathrm{rel}}(\vec{\sigma}) = \sum_{i}^{\mathrm{atoms}} \mathrm{NNP}^{\mathrm{rel}}_{t_i}(f[\vec{\sigma}_i^{R_c}]) \text{ for } \vec{\sigma} \in \{\vec{\sigma}_{\mathrm{lattice}}\}$$



[1] J. Behler and M. Parinello, Phys. Rev. Lett. 98, 146401 (2007).
[2] N. Artrith et al., Phys. Rev. B 96, 014112 (2017).

abICS version2: training and using a NN model with active learning cycles

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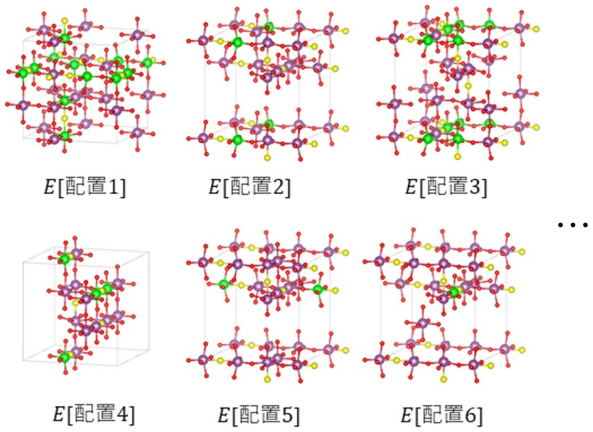
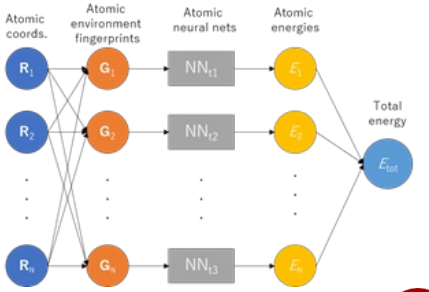
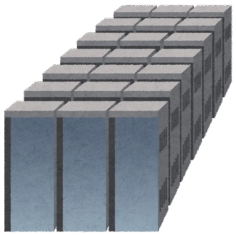


Training data: energies of relaxed configurations



Training a neural network model for high-speed energy calculation

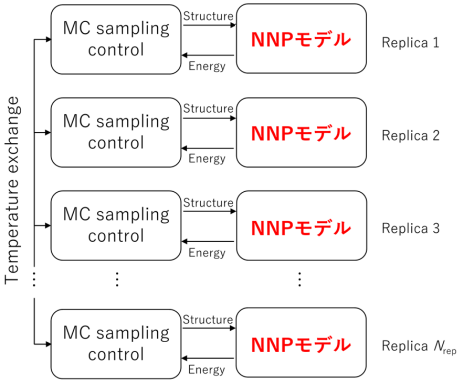
aenet



High-throughput DFT calculations

Add to training data

Thermodynamically relevant configs.



Replica exchange Monte Carlo using NN model

SK et al., arXiv preprint: 2008.02572

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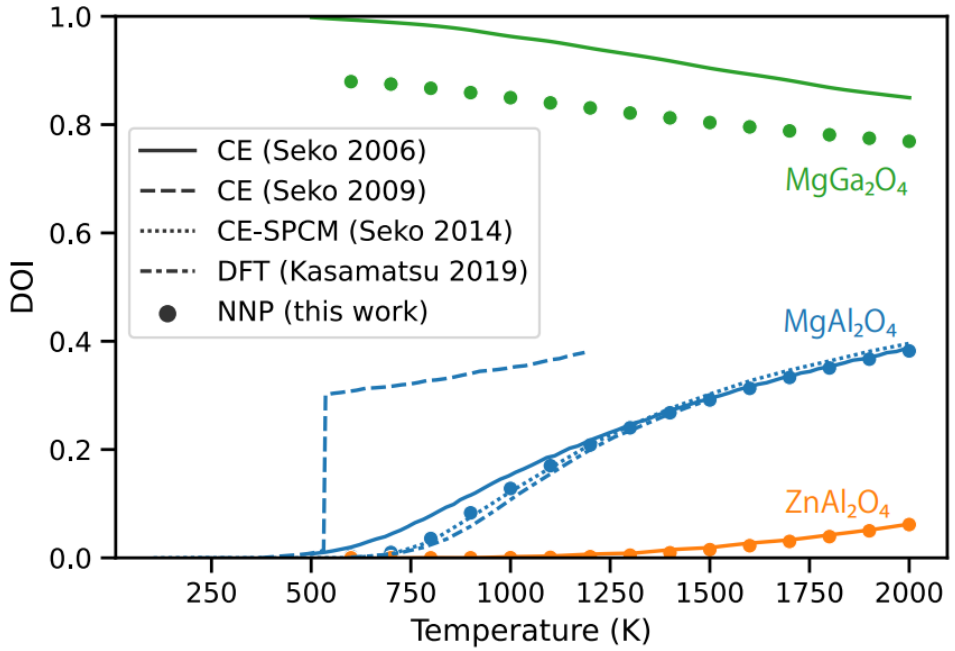
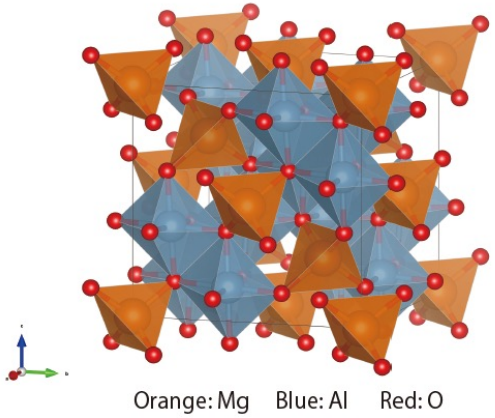
A/B site degree of inversion (DOI) in spinel oxides ($A^{2+}B^{3+}_2O_3$)



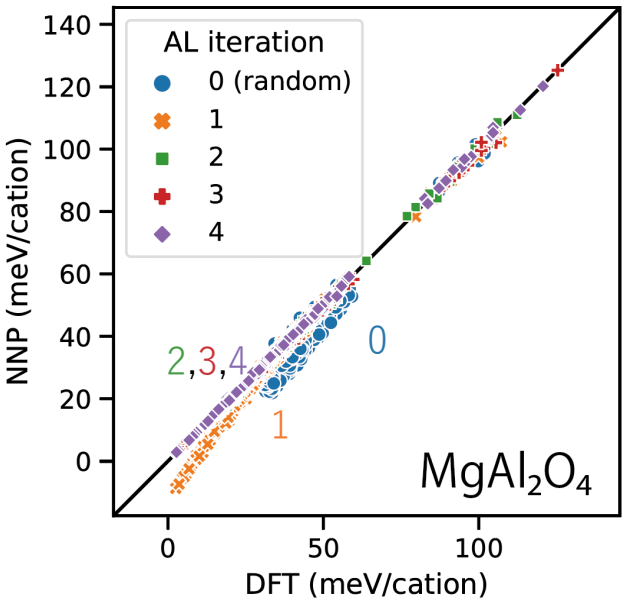


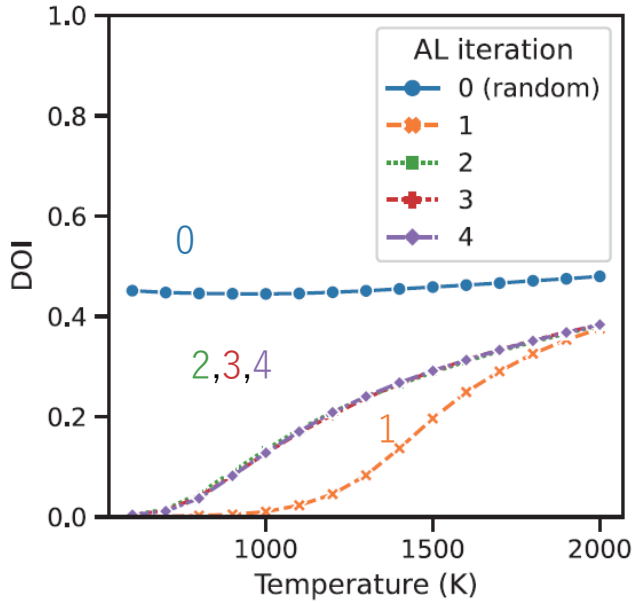
$\times 2 \times 2 \times 2 = 192$ cation sites (448 atoms)

✓ Good agreement with previous works （cluster expansion + MC, DFT-RXMC）and experiment

S. Kasamatsu, Y. Motoyama, K. Yoshimi, U. Matsumoto, A. Kuwabara, and T. Ogawa, submitted (arXiv: 2008.02572)

Active learning cycles



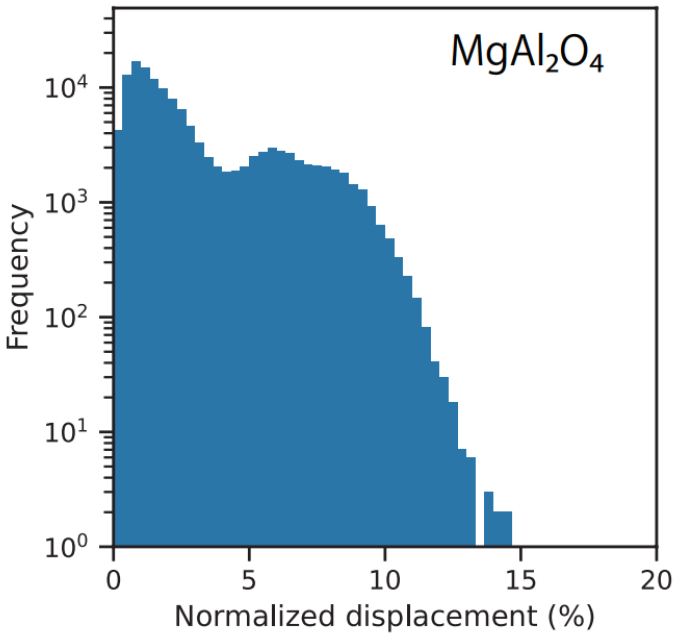


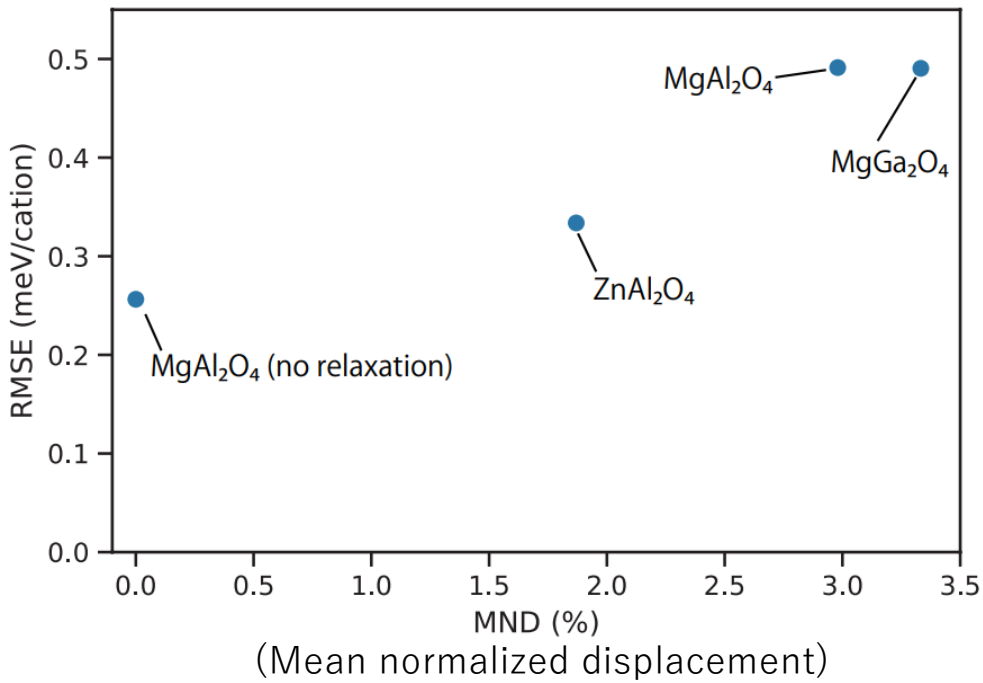
✓ By repeating AL cycles (300 DFT calcs./cycle), the energy precision improves (RMSE < 1 meV/cation) and physical quantities of interest (DOI vs. T) converges

Notes on model size and computational resources

- ✓DFT relaxations comprise the majority of total computation
- ✓Training for $MgAl_2O_4$ example with 192 cations (448 atoms) required about 3 cycles with 300 DFT relaxations each
- ✓DFT relaxations on 300 configurations (VASP GGA-PBE calc. with PW cutoff of 400 eV) takes only ~2 hours when using 144-node queue on Ohtaka
- ✓Today, we will work with a smaller cell size (24 cations) due to time constraints (please see paper for examination of finite-size effects)

Relaxation vs. model precision





✓ Local strain is as large as 10%, but prediction accuracy is very high ~ 0.5 meV/cation

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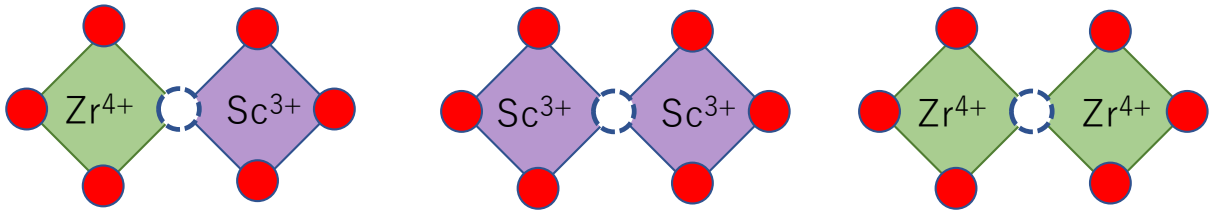
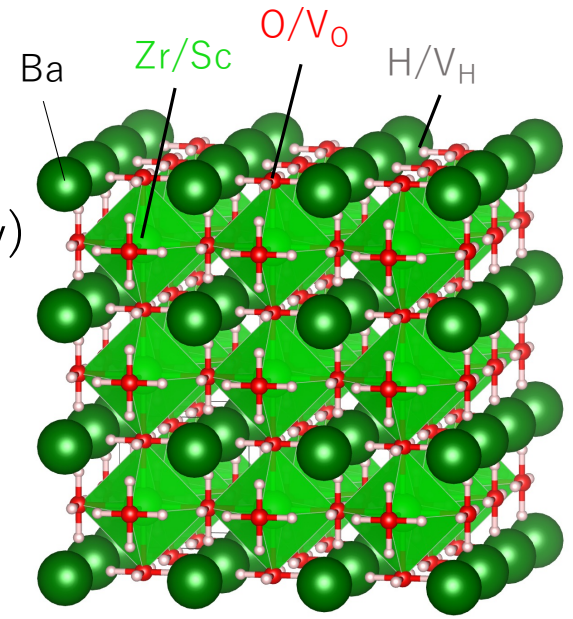
Application to thermodynamics of hydration in $BaZr_{0.78}Sc_{0.22}O_{2.89}V_{O0.11}$

- ✓ Proton conducting oxide (0.01 S/cm @ 400 °C)
  [J. Hyodo et al., Adv. Energy. Mater. **10**, 2000213 (2020).]
  Substitution of Zr^{4+} by Sc^{3+}
  ⇒Oxygen vacancies are formed (charge neutrality)
  ⇒Hydration on oxygen vacancies
  ⇒proton conduction



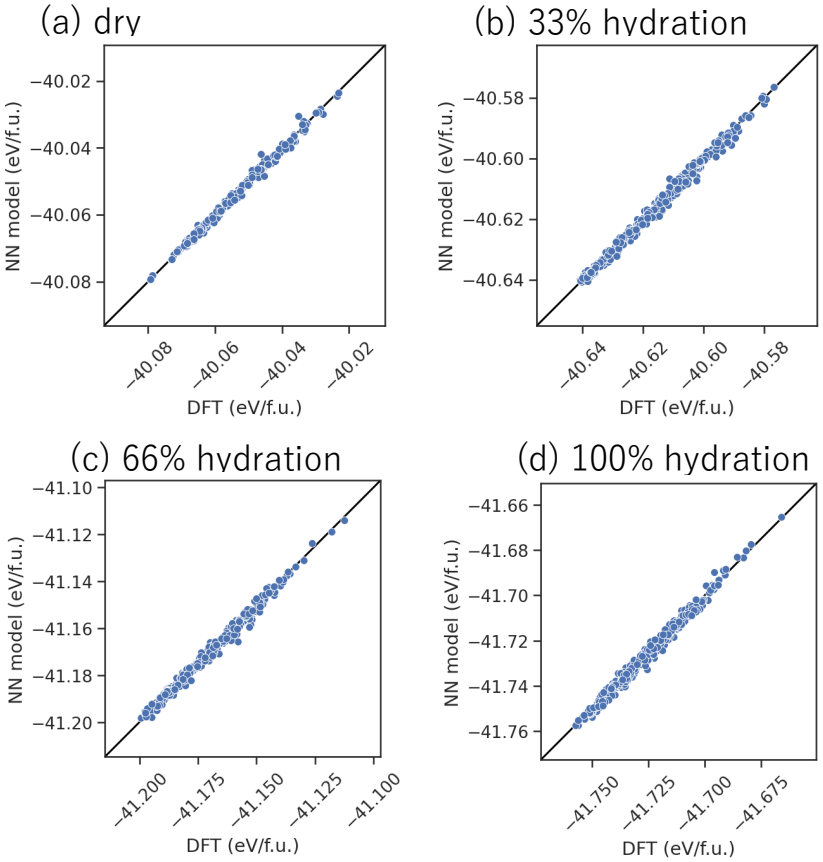


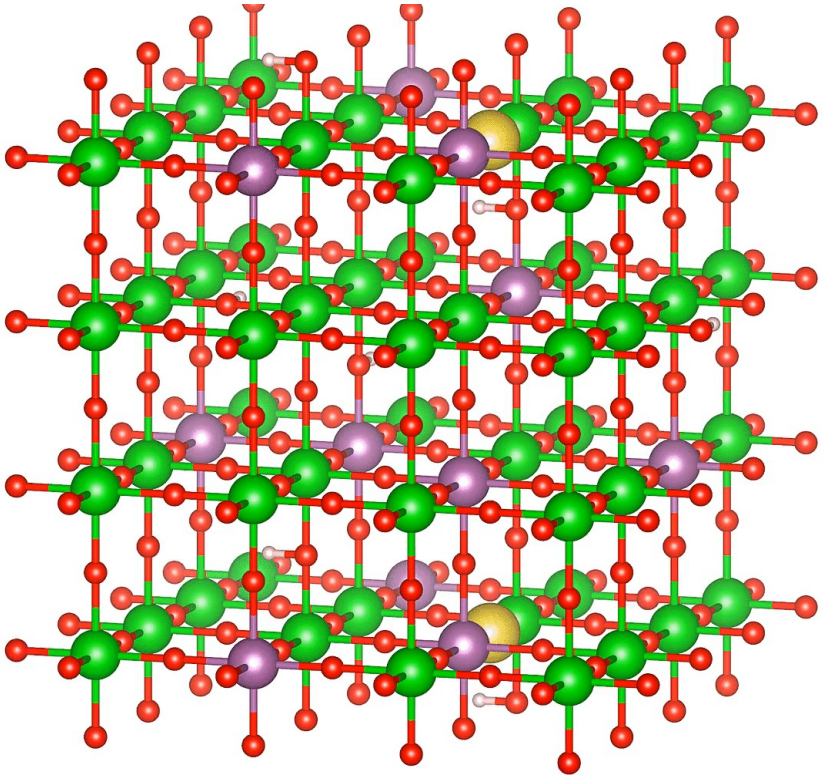
✓6 components !

- ✓ Which of these vacancies contribute to hydration?

K. Hoshino, SK et al., in preparation

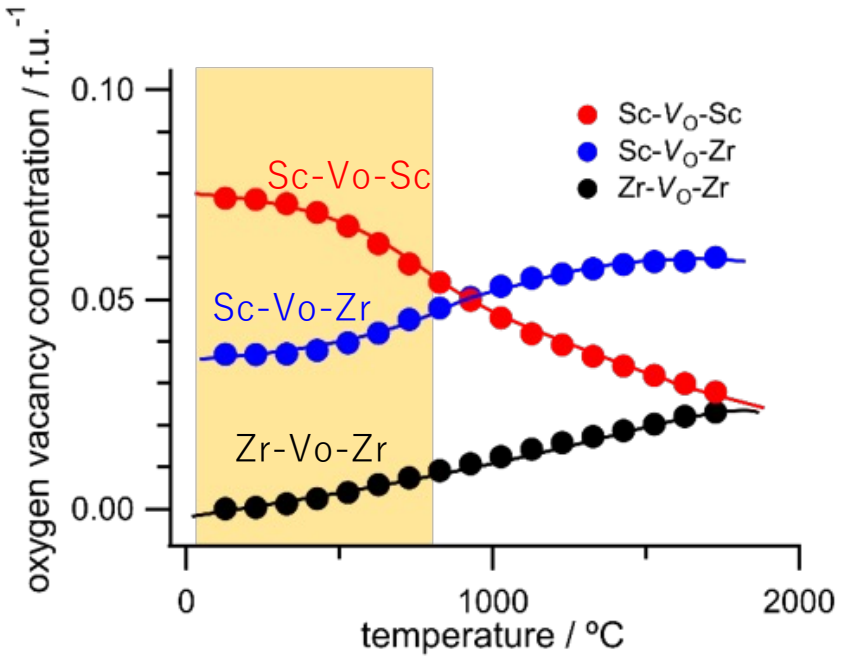
Final model precision

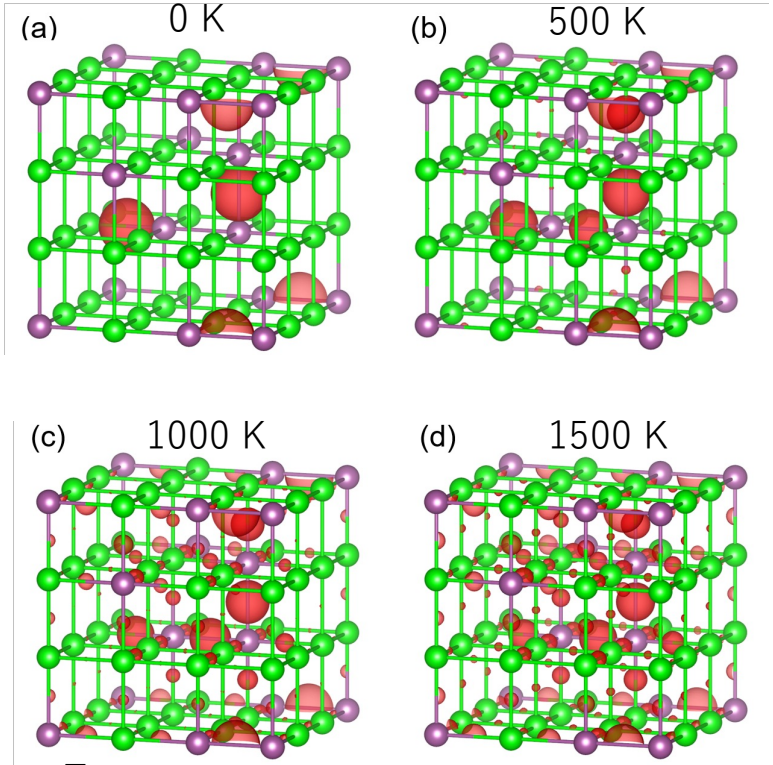




RMSE: 1.9 meV/f.u.

Ratio of oxygen vacancy environments

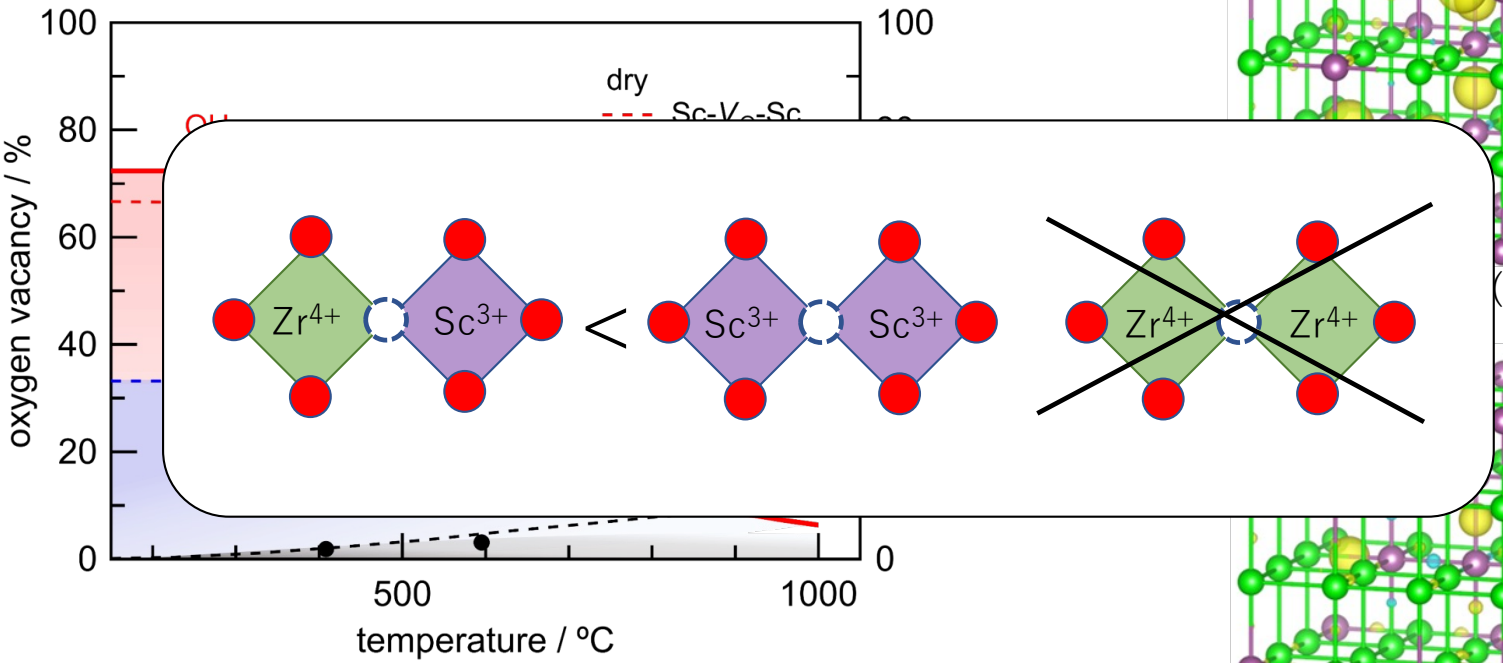




- ✓ Strong Sc-V_O leads to high Sc-V_O-Sc concentration at low T
- ✓ Sc-V_O-Zr becomes the majority at higher T due to entropy
- ✓ Zr-V_O-Zr seldom exists (high hydration activity was suggested*)

[*] Takahashi et al.,
J. Phys. Chem. C 122, 6501 (2018)

Active vacancy sites for hydration



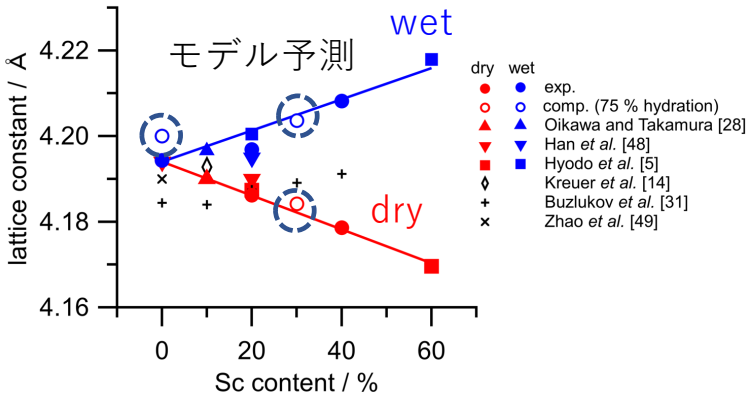
(596 °C)

66% hydration (408 °C)

- ✓ Hydration first occurs preferentially at Sc-V_O-Zr
- ✓ At higher water uptake, Sc-V_O-Sc becomes the majority

Physical quantities other than coordination numbers and energies

- The neural network can be trained to predict extensive properties in the same manner as energy (e.g. lattice volume; not yet included in abICS)
- Calculate average cluster correlations from the sampled configurations



⇒Construct supercell models to reproduce these correlations (cf. SQS)

⇒Perform DFT calculations on a small number of supercell models

T. Fujii et al., Phys. Chem. Chem. Phys. 23, 5908 (2021)

Summary

- We proposed an on-lattice neural network model for mapping configurations on a lattice to relaxed energies
- Efficient training was realized through an active learning scheme
- First-principles configuration sampling on many-component oxides is now possible!

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