実験データとシミュレーションの同化による構造推定

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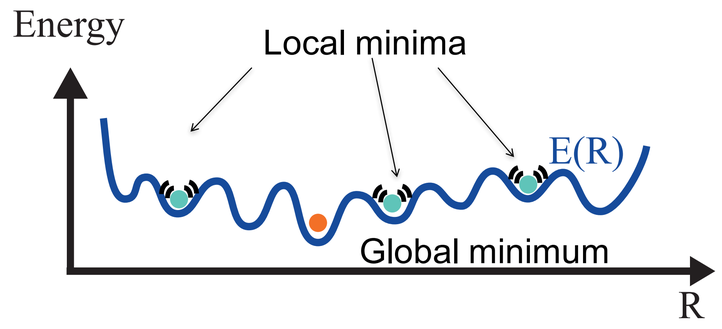
References: N. Tsujimoto, D. Adachi, R. Akashi, S. Todo, S. Tsuneyuki, Phys. Rev. Materials **2**, 053801 (2018)

D. Adachi, N. Tsujimoto, R. Akashi. S. Todo. S. Tsuneyuki, preprint (arXiv:1808.06846)

1. Introduction

"One of the continuing scandals in the physical sciences is that it remains impossible to predict the structure of even the simplest crystalline solids from a knowledge of their chemical composition."

J. Maddox, Nature 335, 201 (1988).



Finding stable structure(s) is difficult because…

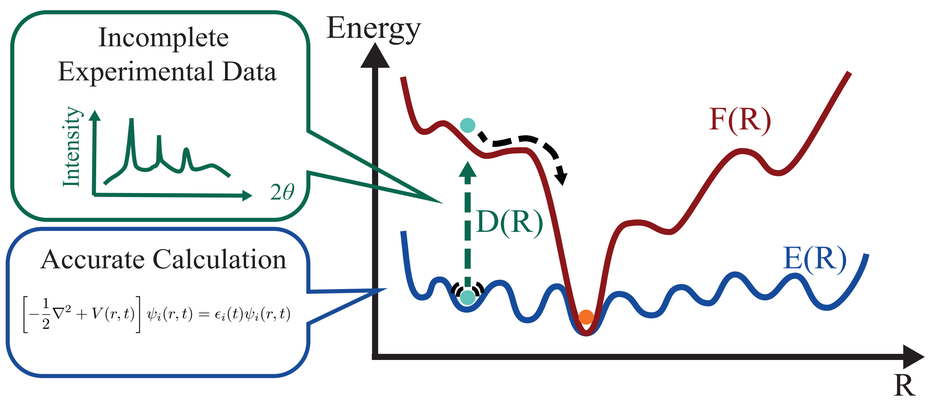
- Potential surface is extremely rugged.
- The search space is high dimensional.

⬇

New approach to predict complicated structures.

2. Combination with insufficient X-ray data

2-1. Basic strategy



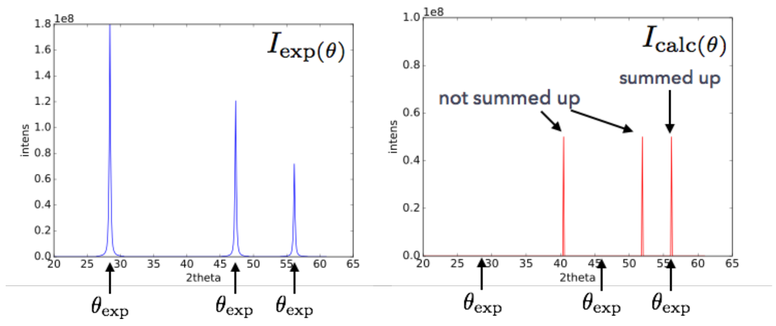
$$F(\mathbf{R}) = E(\mathbf{R}) + \alpha N D[g(\mathbf{R}), g_{\mathrm{obs}}]$$

✓ The penalty function D defined with experimental data can make it easier to find the global minimum of the potential surface E.

2-2. Design of penalty function D

$$D(\mathbf{R}) = 1 - \lambda(\mathbf{R}) \qquad \text{"Crystallinity"}\ \lambda = \frac{\sum_{\theta_{\mathrm{exp}}} \int_{\theta_{\mathrm{exp}-\Delta}}^{\theta_{\mathrm{exp}+\Delta}} I_{\mathrm{calc}}(\theta)d\theta}{\int I_{\mathrm{calc}}(\theta)d\theta}$$

Ex.) $\lambda = \frac{1}{3}$



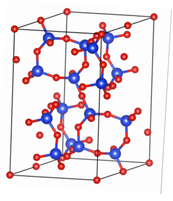
Crystal structure prediction with the accurate atomic energy calculation supported by limited information of diffraction data.

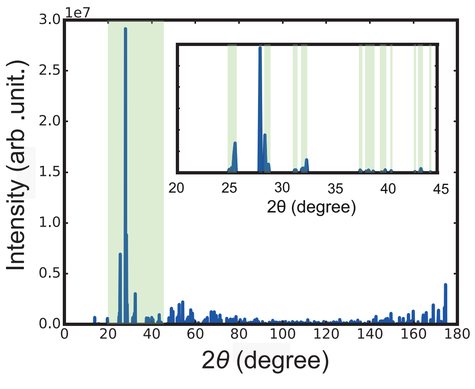
➡

- ✓ Robust against the noise and difficulties in experiments.
- ✓ Higher efficiency than usual crystal structure prediction.
- ✓ Any of the optimization methods can be applied.
- ✓ Any experimental data can be used.

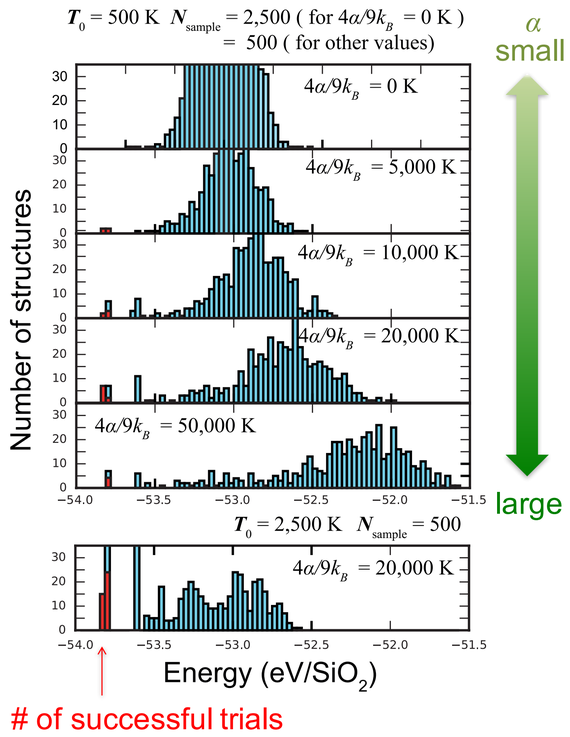
2-3. Demonstration for SiO_2 coesite

96 atoms (48 atoms/unitcell)





Exp. Data
used in this simulation



α small ⬇ large

# of successful trials

- ✓ High efficiency with suitable value of α.
- ✓ Works well also for low quartz and low cristobalite.

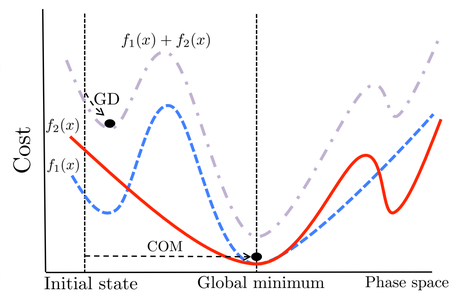
3. Combined optimization method

3-1. Algorithm of COM

$$x_i \leftarrow x_i - \mathrm{sign}_i F_i \Delta t$$

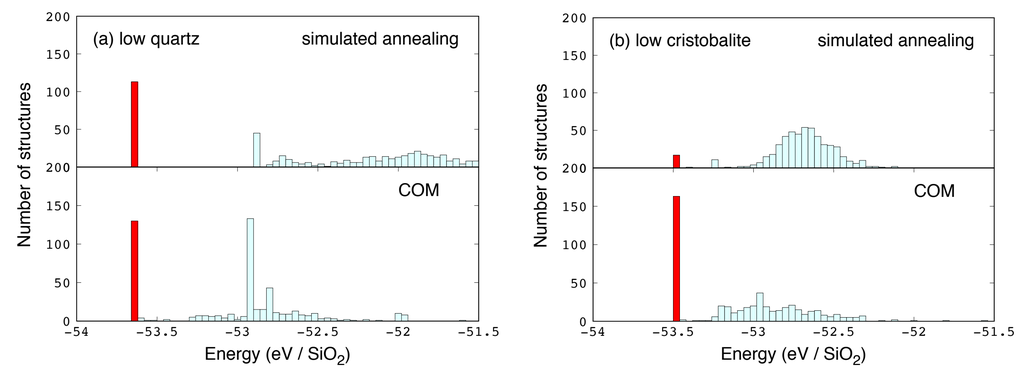
$$F_i = \sqrt{\left(\frac{\partial f_1}{\partial x_i}\right)^2 \Big/ \left|\frac{\partial f_1}{\partial x}\right|^2 + \left(\frac{\partial f_2}{\partial x_i}\right)^2 \Big/ \left|\frac{\partial f_2}{\partial x}\right|^2}$$

$$\mathrm{sign}_i = \begin{cases} +1 & \text{if } \frac{\partial f_1}{\partial x_i} \geq 0 \text{ and } \frac{\partial f_2}{\partial x_i} \geq 0, \\ -1 & \text{if } \frac{\partial f_1}{\partial x_i} \leq 0 \text{ and } \frac{\partial f_2}{\partial x_i} \leq 0, \\ \text{unchanged} & \text{otherwise.} \end{cases}$$



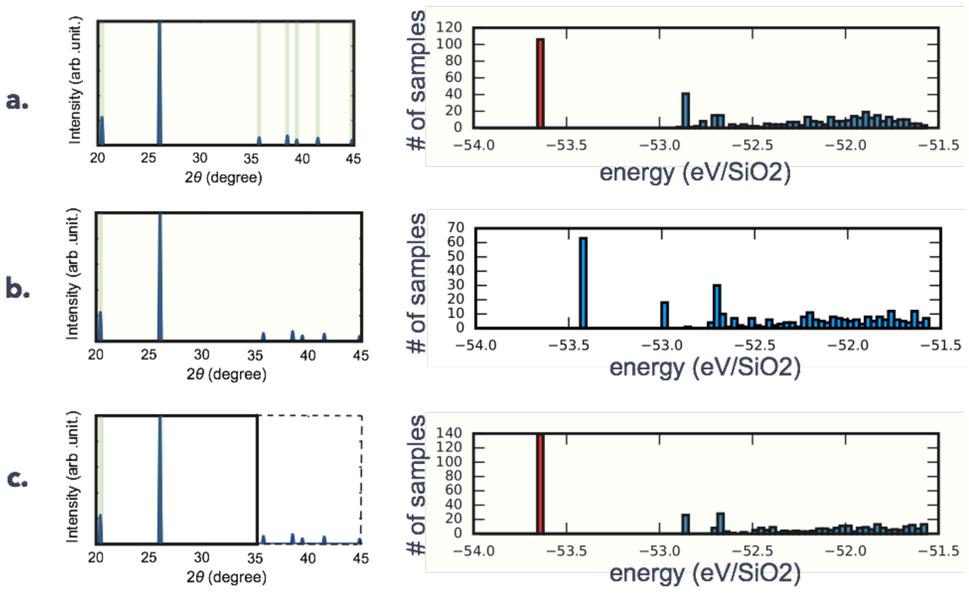
- ✓ Our cost function is a sum of two functions that share the same global minimum but have different local-minima distributions.
- ✓ Optimization stops only when the global minimum point is reached.

3-2. Benchmark results for SiO_2 polymorphs



4. Dealing with small and noisy peaks

3-1. Small peaks in X-ray diffraction of low quartz



- ✓ It is better to exclude angle ranges in which peaks can't be distinguished from background.
- ✓ It's better to take only large peaks into account.

5. Summary

- ✓ New methods for crystal structure prediction are proposed.
- ✓ Hybrid cost function: potential energy and penalty function "crystallinity."
- ✓ Can be applied to the case where the X-ray diffraction data is insufficient: limited range of angles, large noise, etc.
- ✓ Successfully reproduced three well-known polymorphs of SiO_2: coesite, low quartz, low cristobalite.
- ✓ Combined optimization method (COM) is proposed to enhance the success rate of simultaneous optimization