UC SANTA BARBARA

First-principles thermodynamics and kinetics of layered intercalation compounds for “beyond Li-ion” batteries

Jonas Kaufman & Anton Van der Ven

DOE CSGF Annual Program Review 2021

Why move “beyond Li-ion” to Na/K for batteries?

Na and K are heavier than Li but far more abundant

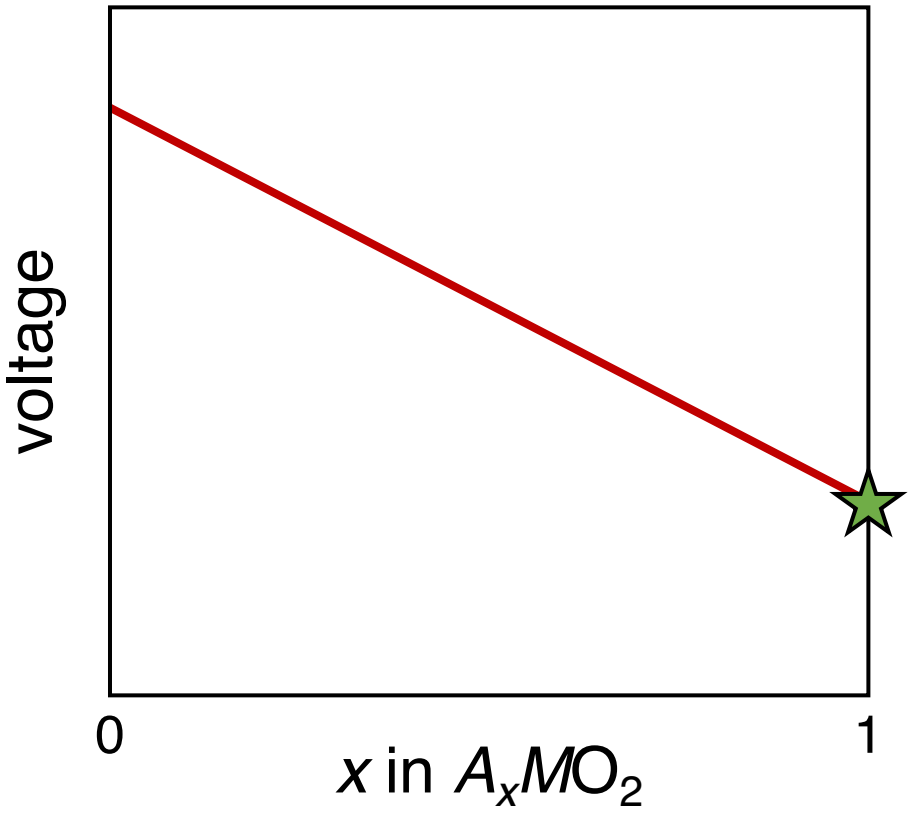
Promising for large-scale energy storage…

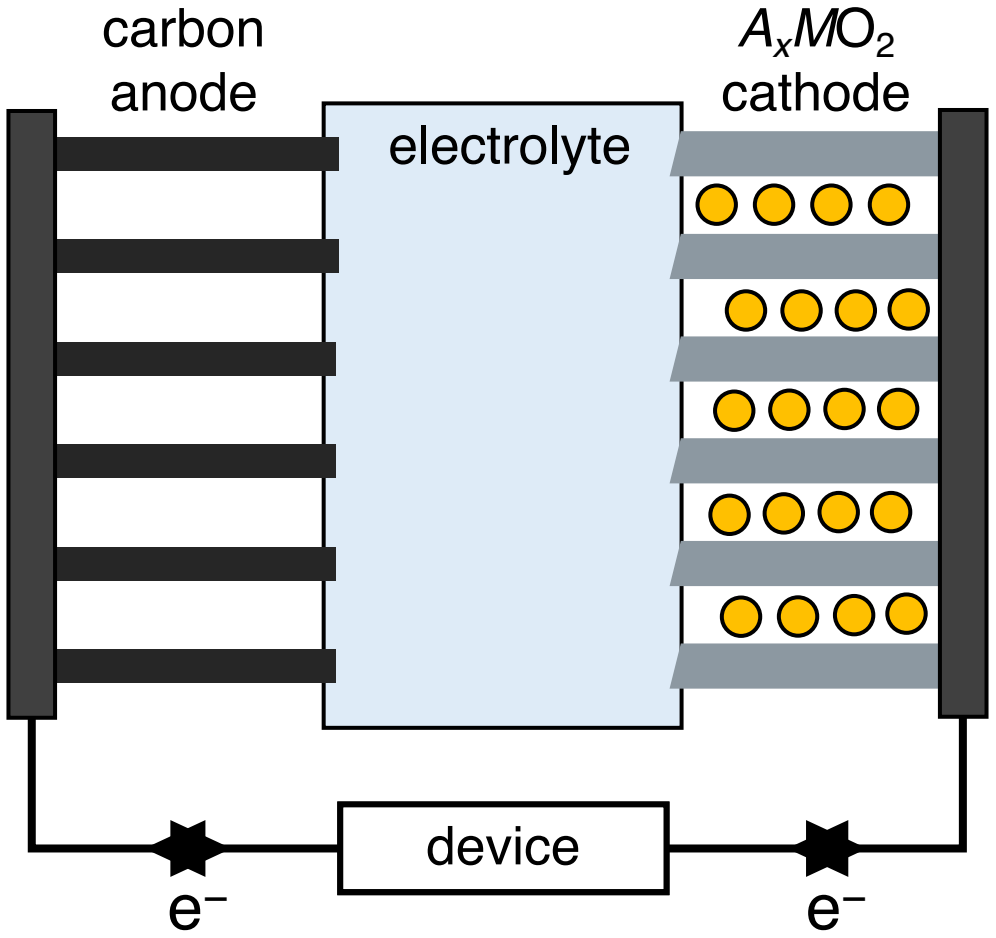
…but electrode materials are usually more susceptible to degradation due to additional **phase transitions**

Periodic table scaled by abundance of elements in earth’s crust, by weight

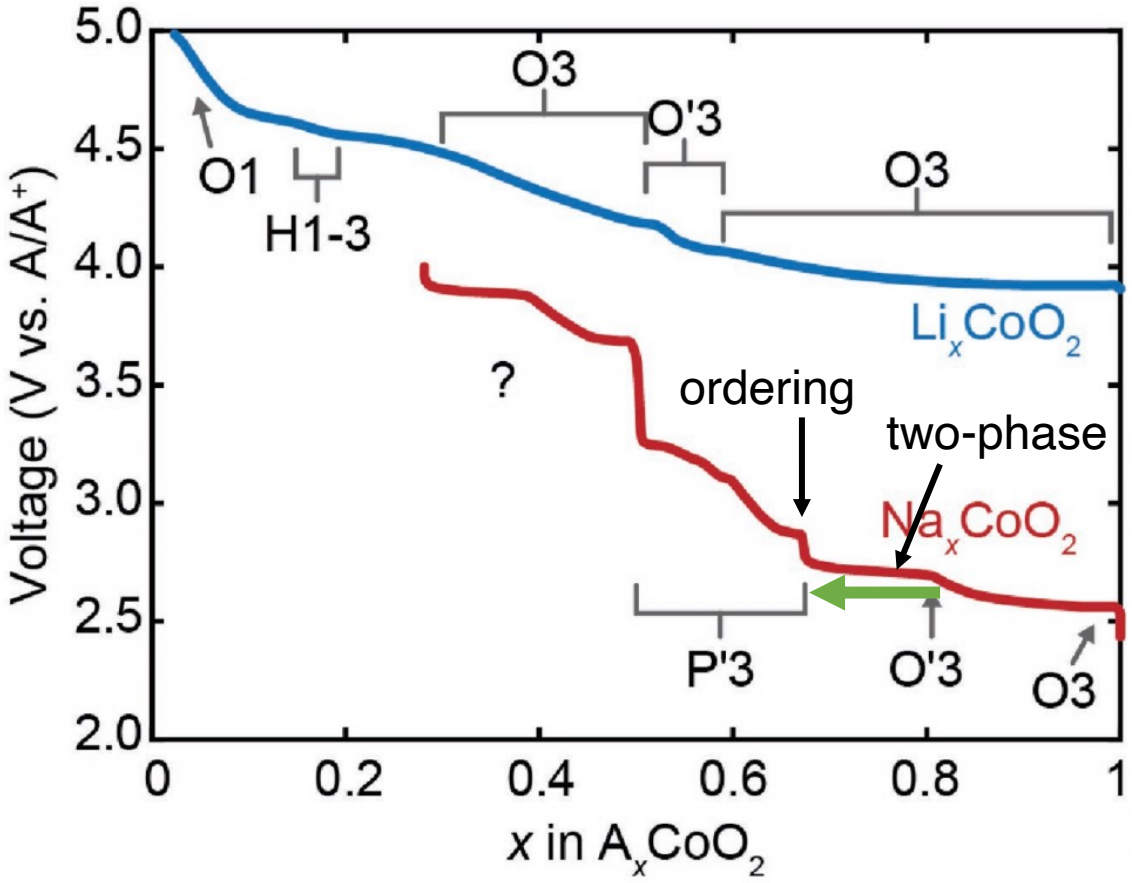
M. J. Winter, Diffusion cartograms for the display of periodic table data, *J. Chem. Educ.* **88** (2011) 1507–1510. DOI: 10.1021/ed1000203

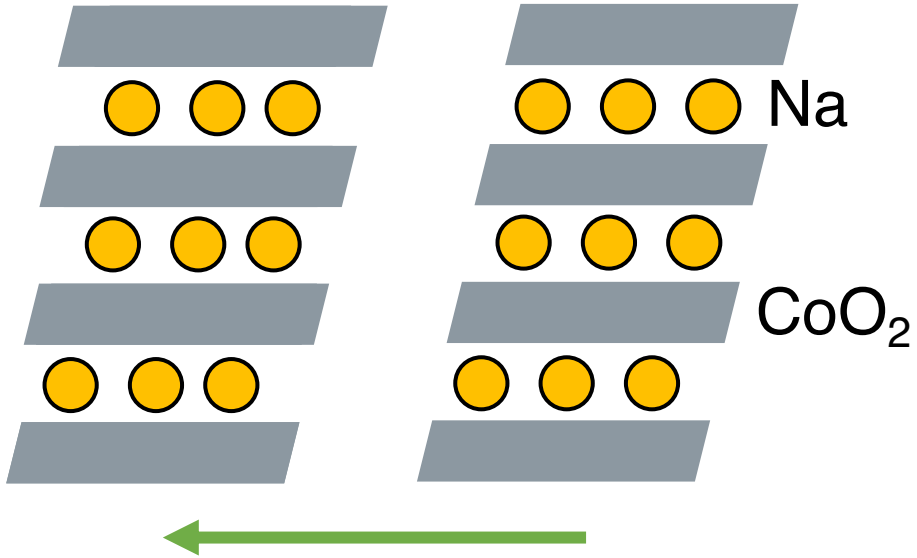
How does a rechargeable battery work?





How do electrodes change during cycling?

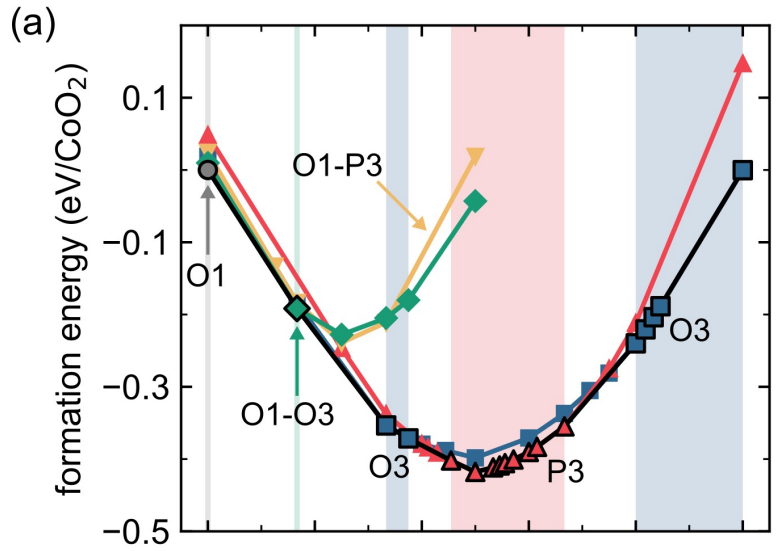


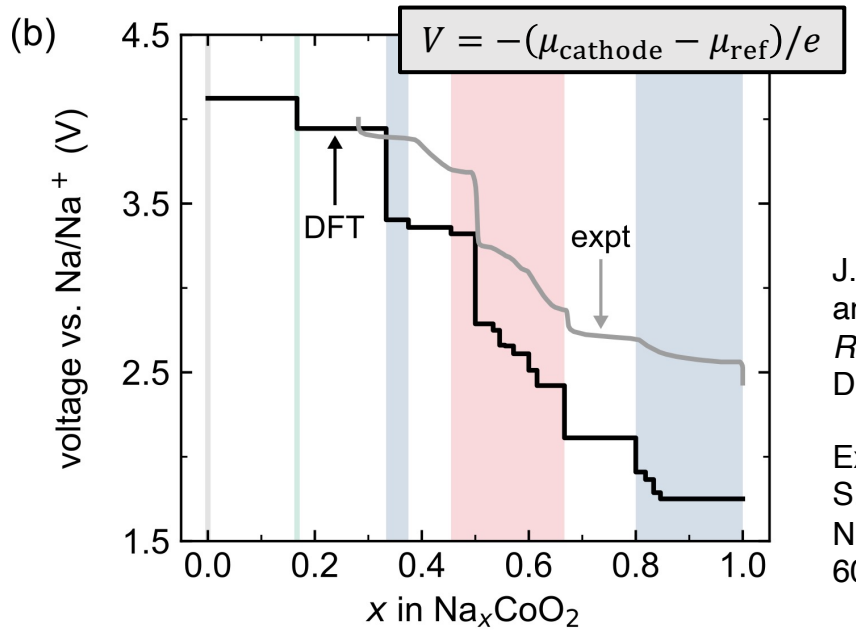


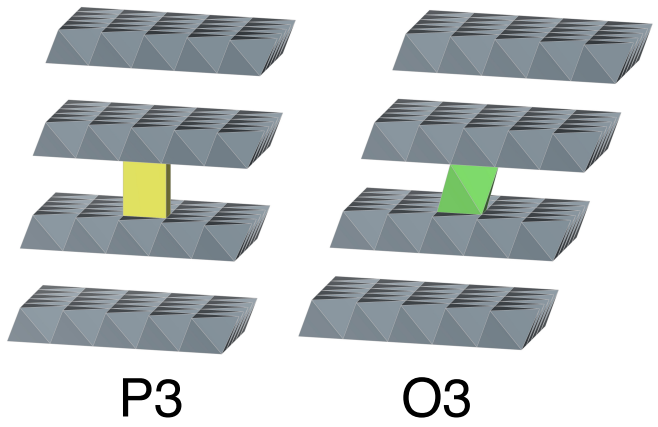
Stacking sequence changes
+
Ion (re)ordering

M. D. Radin, S. Hy, M. Sina, C. Fang, H. Liu, J. Vinckevičiūtė, M. Zhang, M. S. Whittingham, Y. S. Meng, and A. Van der Ven, Narrowing the gap between theoretical and practical capacities in Li-ion layered oxide cathode materials, *Adv. Energy Mater.* **7** (2017) 1602888. DOI: 10.1002/aenm.201602888

Relating electrode voltage to phase stability







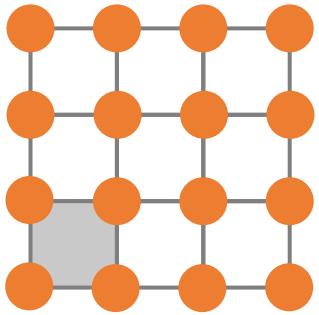
How can we predict phase stability from first principles?

J. L. Kaufman and A. Van der Ven, Na_xCoO_2 phase stability and hierarchical orderings in the O3/P3 structure family, *Phys. Rev. Mater.* **3** (2019) 015402. DOI: 10.1103/PhysRevMaterials.3.015402

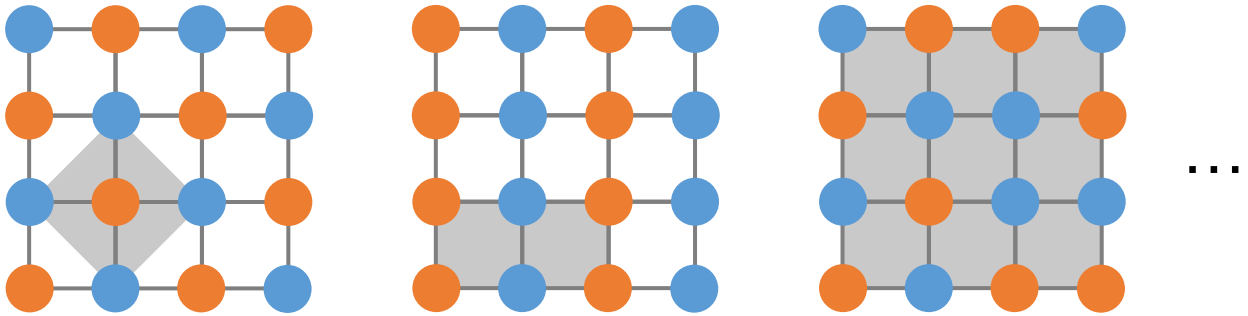
Expt. from: K. Kubota, T. Asari, H. Yoshida, N. Yaabuuchi, H. Shiiba, M. Nakayama, and S. Komaba, Understanding the structural evolution and redox mechanism of a $NaFeO_2$–$NaCoO_2$ solid solution for sodium-ion batteries, *Adv. Funct. Mater.* **26** (2016) 6047–6059. DOI: 10.1002/adfm.201601292

Studying crystals from first principles

primitive parent crystal



Many distinct configurations are possible



…

Which are important?

We need a way to **quickly** calculate the energies of **arbitrary** configurations

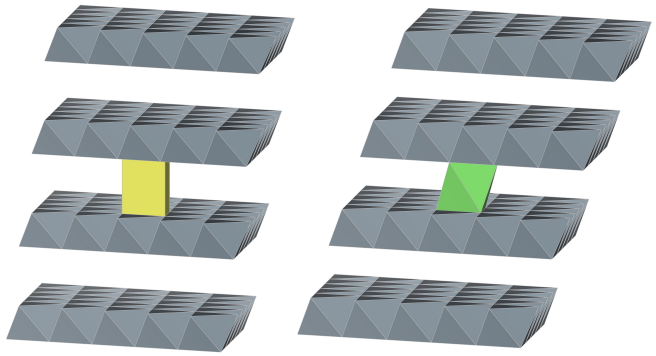
Can express energy (or any property of the crystal) as a *cluster expansion*:

$$E(\vec{\sigma}) = V_0 + \underbrace{\sum_i V_i \sigma_i}_{\text{points}} + \underbrace{\sum_{i,j} V_{ij} \sigma_i \sigma_j}_{\text{pairs}} + \underbrace{\sum_{i,j,k} V_{ijk} \sigma_i \sigma_j \sigma_k}_{\text{triplets}} + \cdots$$

The CASM workflow (github.com/prisms-center/CASMcode)

CASM
A Clusters Approach to Statistical Mechanics

primitive structure(s), degrees of freedom



e.g. Na-vacancy ordering in Na_xCoO_2

configuration enumeration

structures

DFT calculation

iterative prediction

energies

truncated cluster expansion
$\xi\vec{v} = \vec{e}$

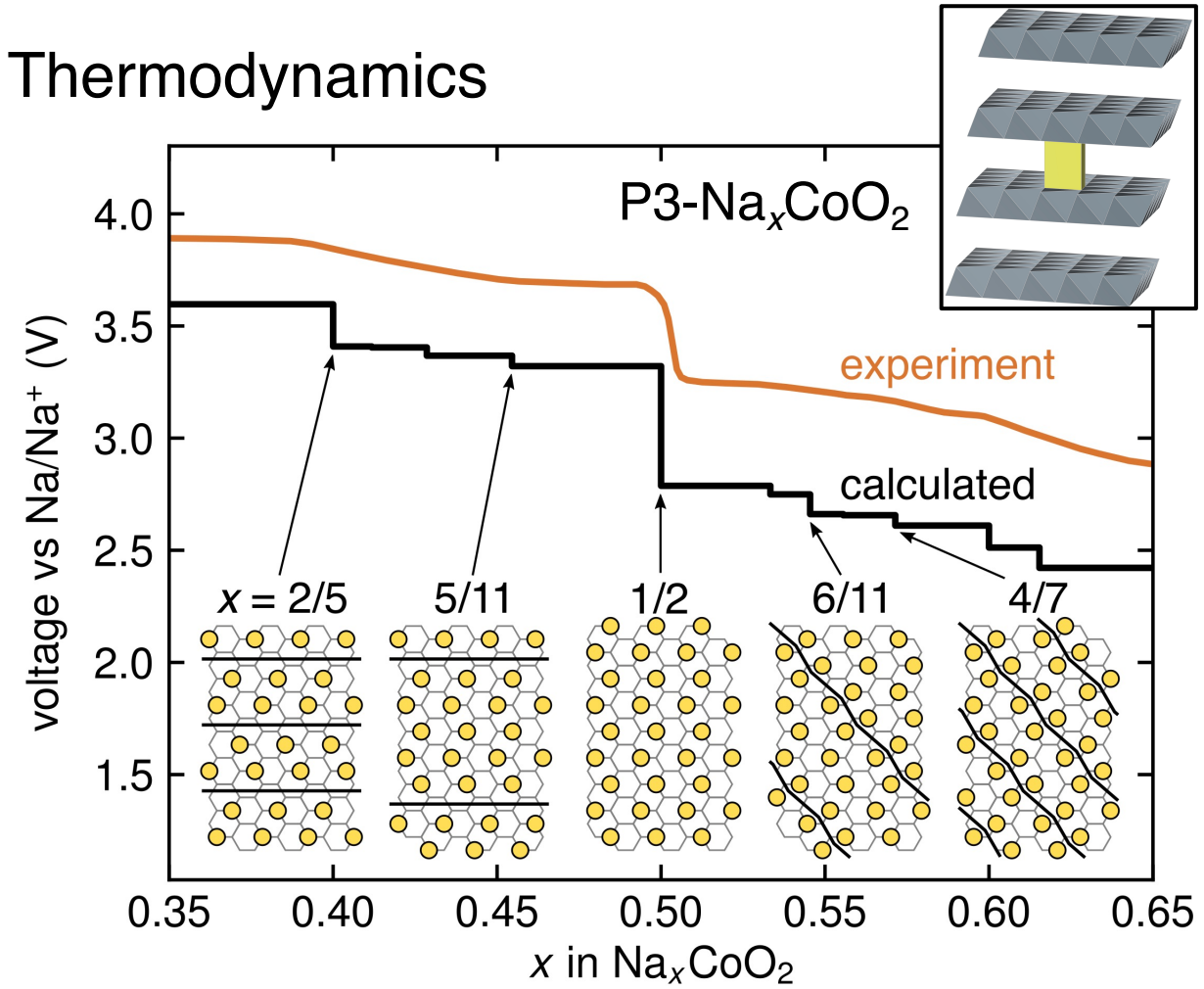
Monte Carlo simulation

finite temperature phase stability

zero temperature phase stability

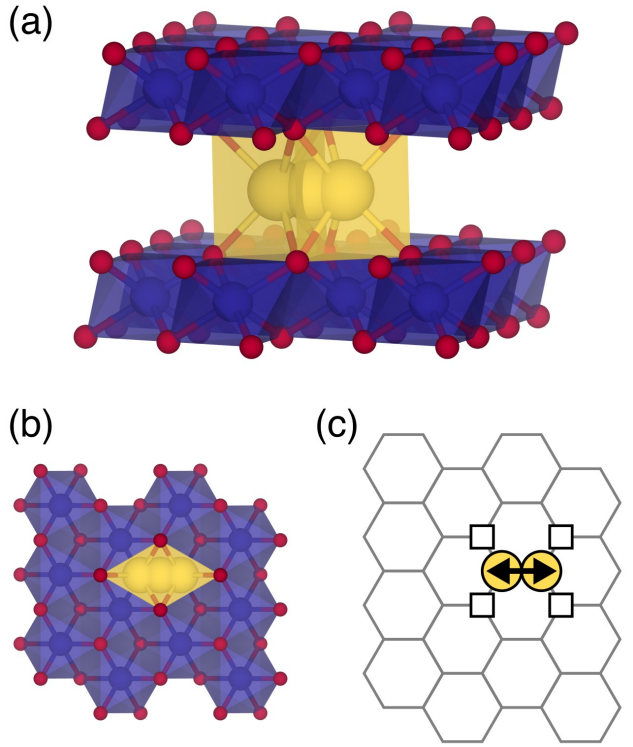
Unusual families of phases predicted in Na_xCoO_2

Thermodynamics



Kinetics

How do transitions between these phases occur?



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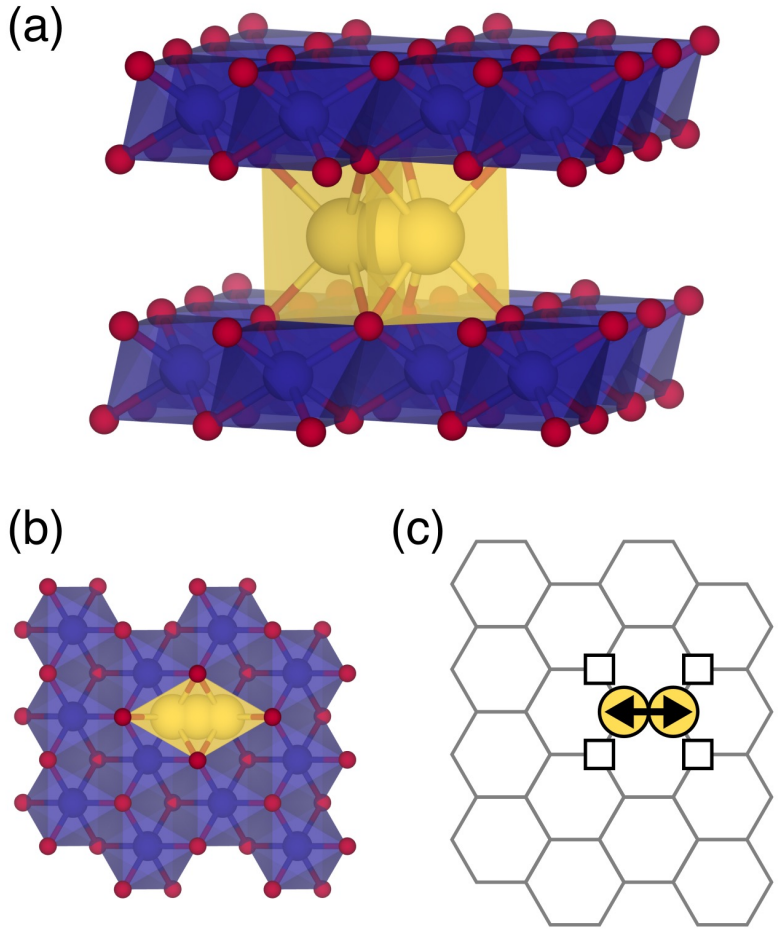
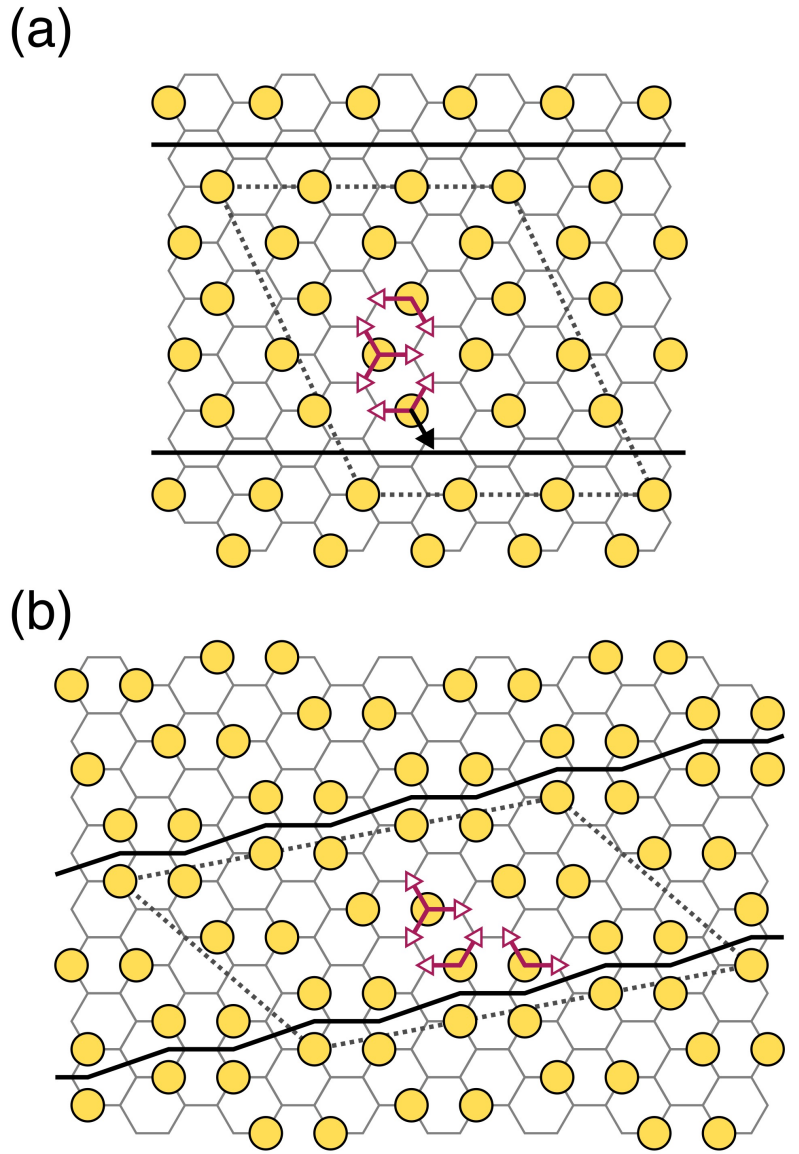
Most simple Na hops are invalid in perfect orderings





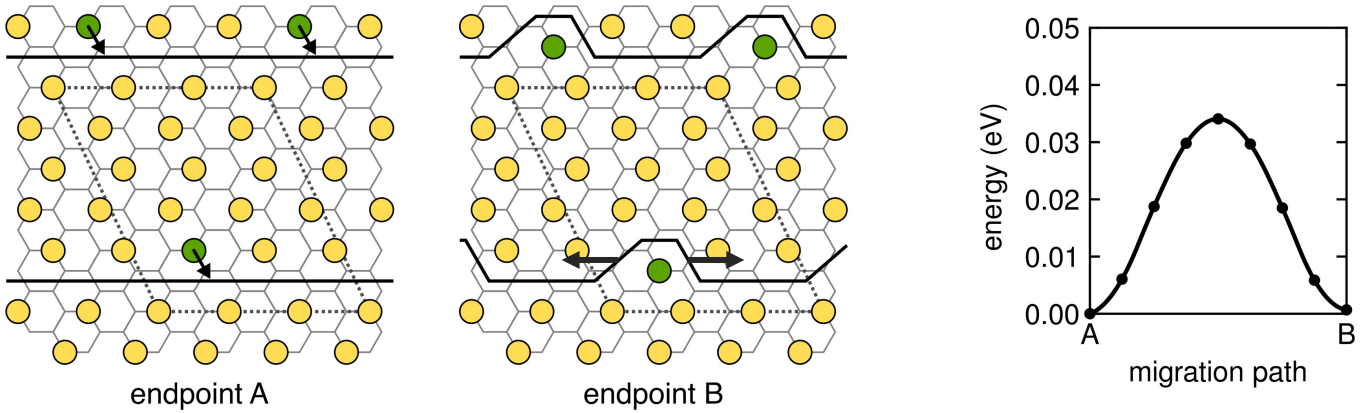
$x < 1/2$ representative ordering ($x = 5/11$)

$x > 1/2$ representative ordering ($x = 6/11$)

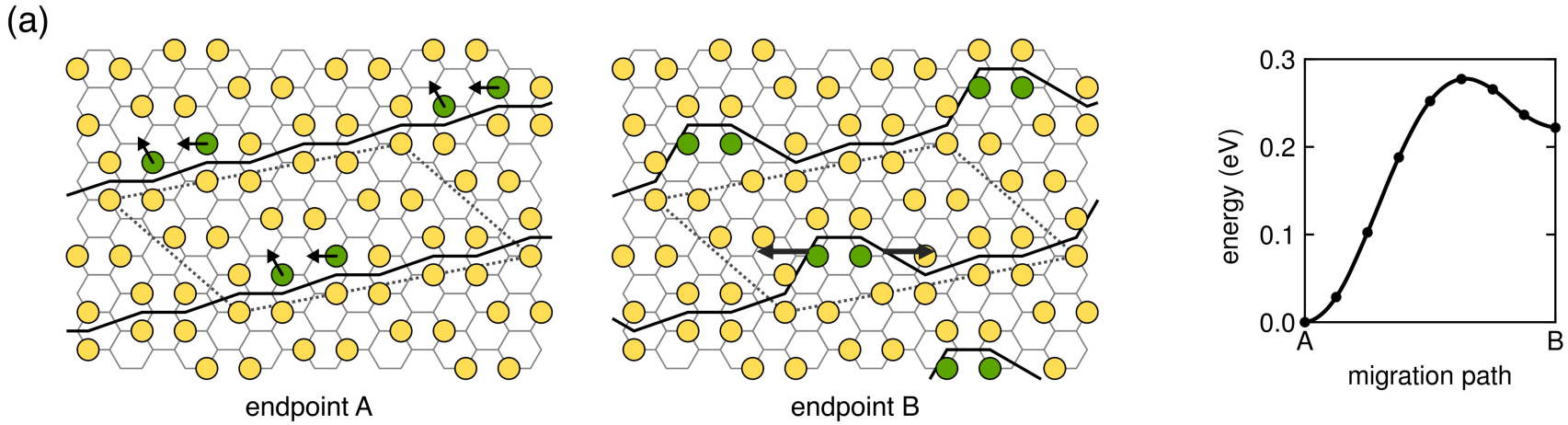
J. L. Kaufman and A. Van der Ven, Antiphase boundary migration as a diffusion mechanism in a P3 sodium layered oxide, *Phys. Rev. Mater.* **5** (2021) 055401. DOI: 10.1103/PhysRevMaterials.5.055401

APBs can migrate via kink formation/expansion

$x < 1/2$:



$x > 1/2$:



J. L. Kaufman and A. Van der Ven, Antiphase boundary migration as a diffusion mechanism in a P3 sodium layered oxide, *Phys. Rev. Mater.* **5** (2021) 055401.
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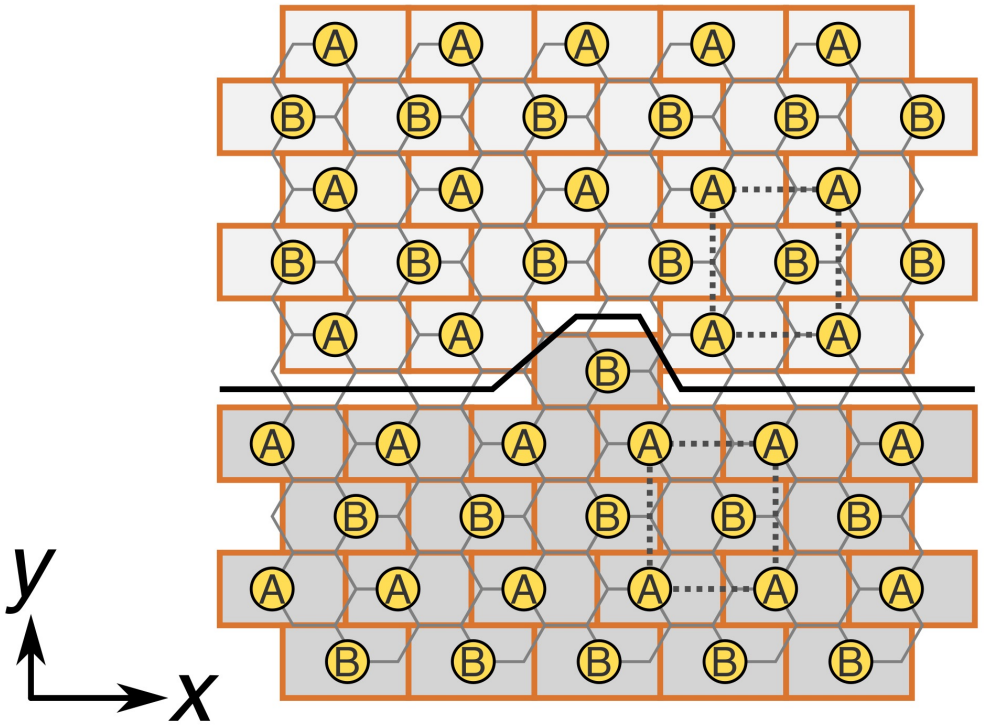
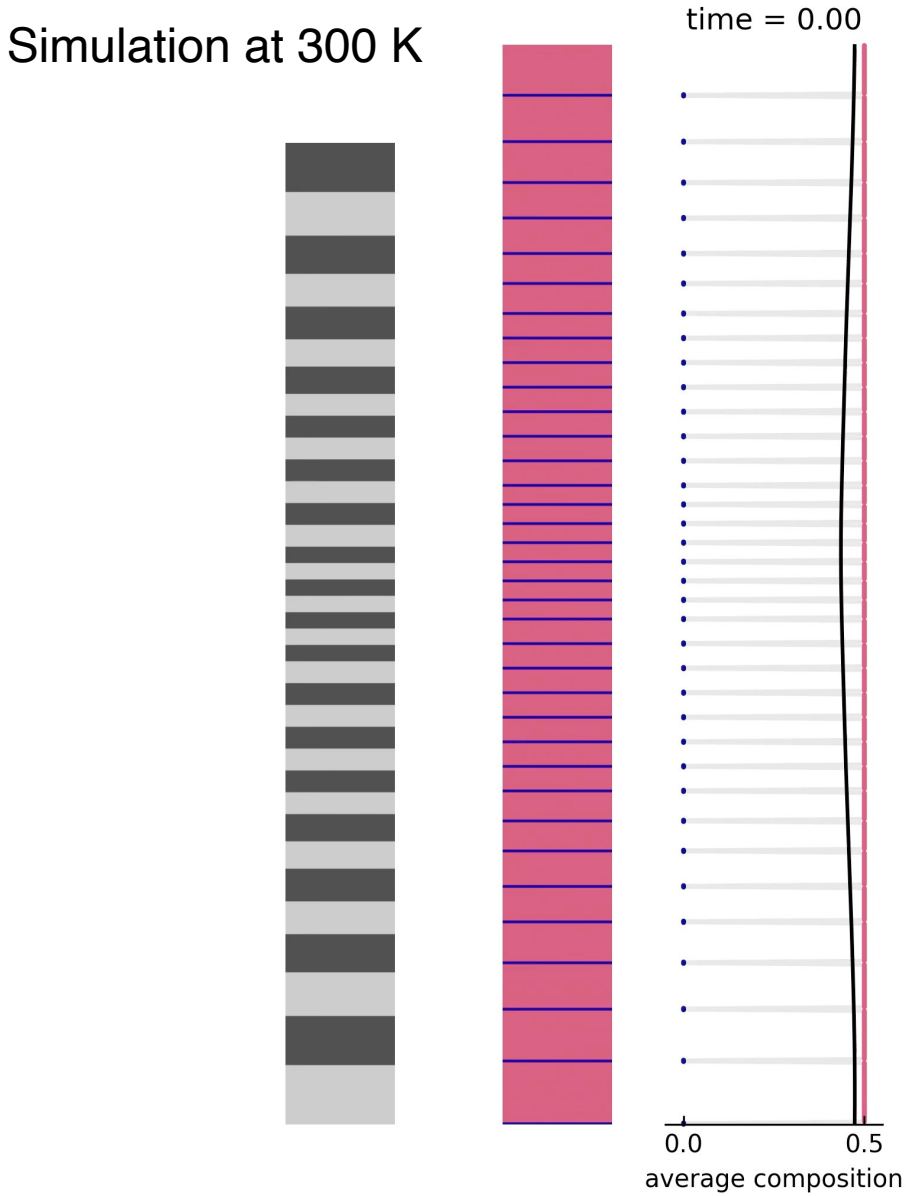
Kinetic Monte Carlo model can simulate diffusion





Acknowledgements

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