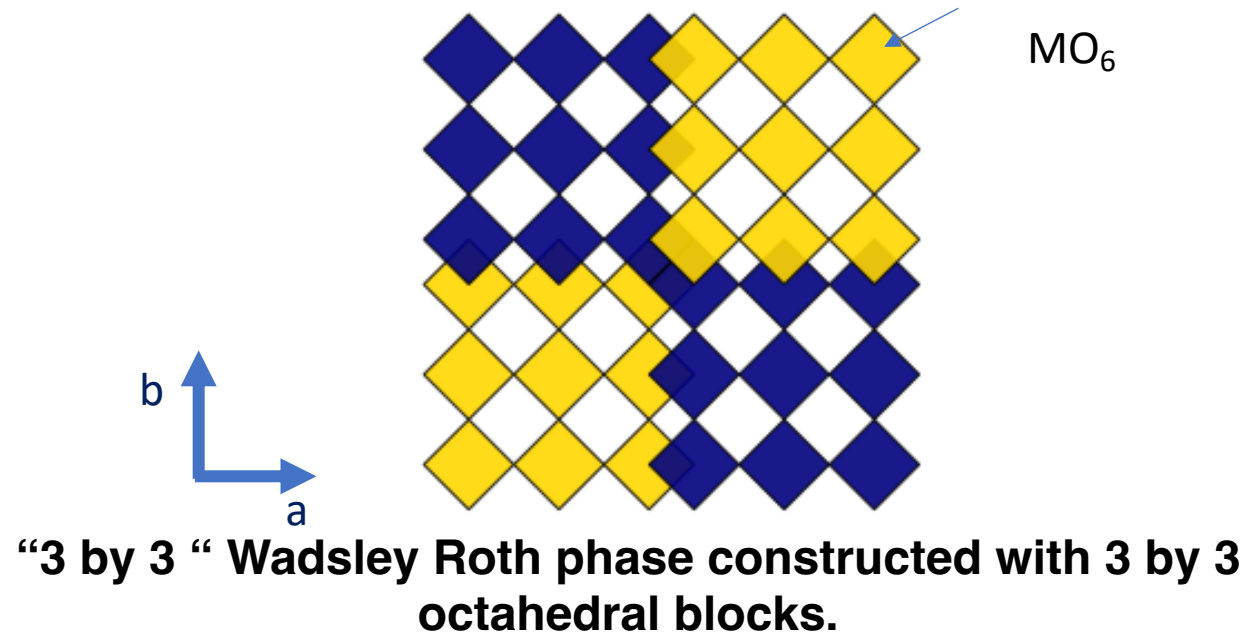


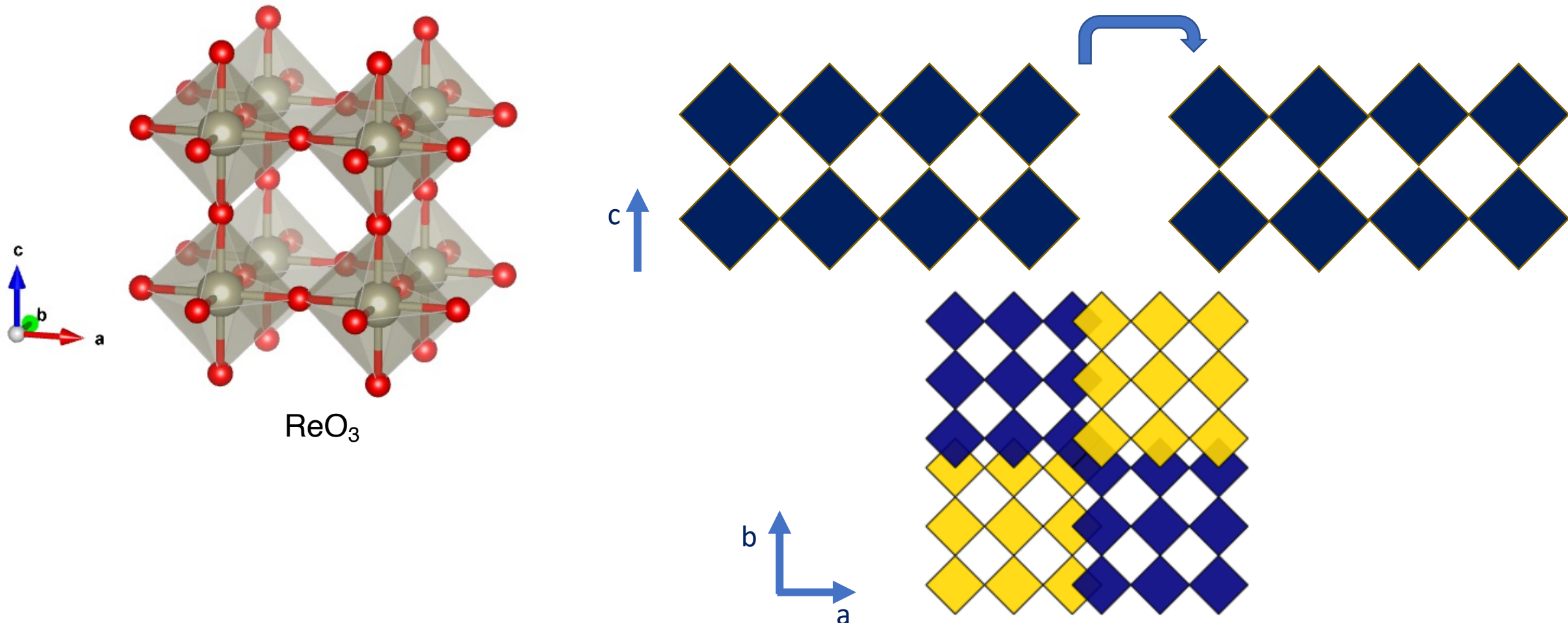
Wadsley-Roth Crystallographic Shear Phase Oxides for Battery Applications

Muna Saber

Wadsley-Roth Crystallographic Shear phases are a family of chemistries constructed from transition metal octahedra sheared along different axes

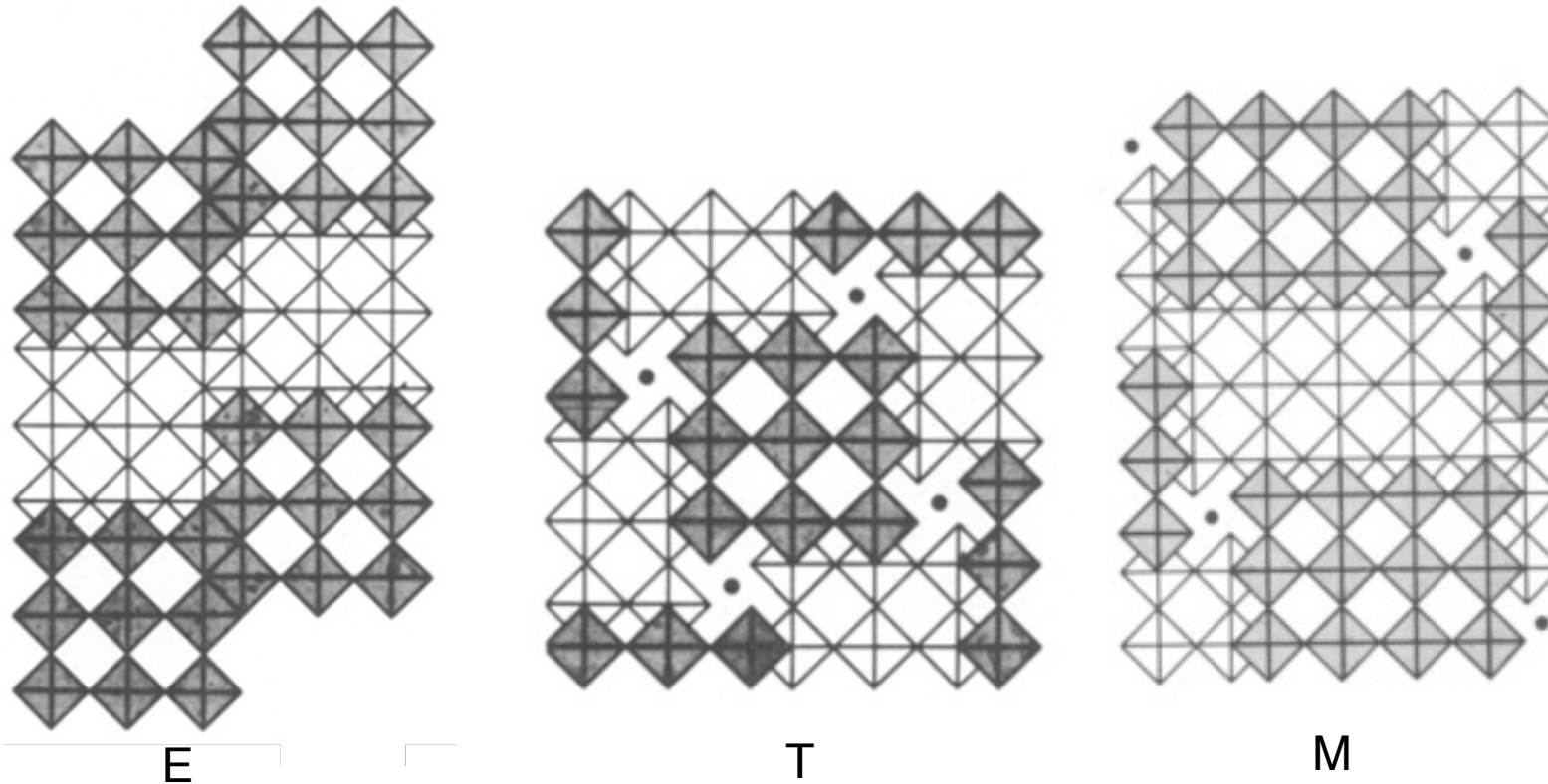


Wadsley-Roth Crystallographic Shear phases are a family of chemistries constructed from transition metal octahedra sheared along different axes



“3 by 3 “ Wadsley Roth phase constructed with 3 by 3 octahedral blocks.

The history of Wadsley-Roth chemistries and their usages as battery electrode materials



- These phases were first synthesized by Wadsley and Roth in the 1960s
- Cava performed a study of lithium insertion into differing Wadsley Roth phases
- Wadsley-Roth phases can be placed into 3 types, E, T, M

Schematics of Wadsley-Roth phases synthesized by Cava for which he did lithium insertion tests¹

1. Cava, R.J., Murphy, D.W. and Zahurak, S.M., 1983. Lithium insertion in Wadsley-Roth phases based on niobium oxide. *Journal of the electrochemical society*, 130(12), p.2345.

Expanded the definitions of Wadsley-Roth phases to group by structure type and unique Li sites for experimentally synthesized phases

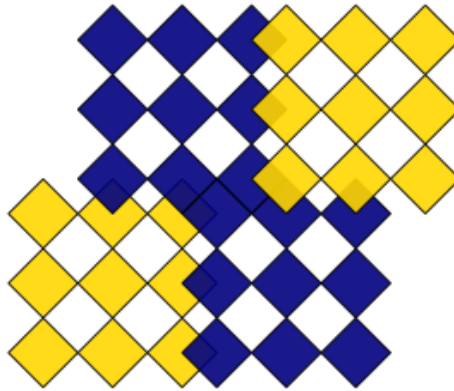
Type E₀[n×m]



Type E₀ [n×∞]



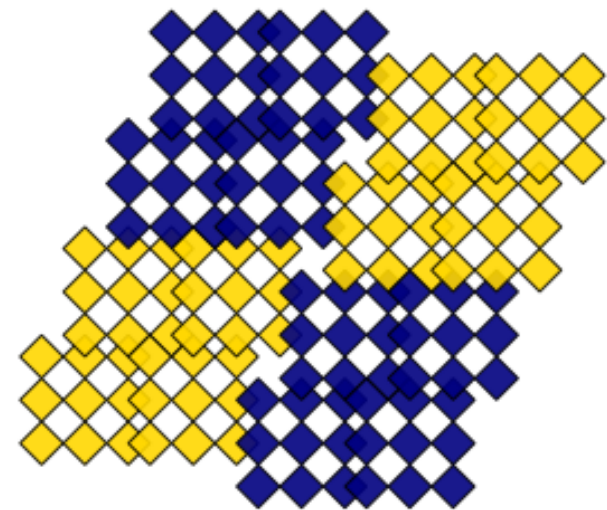
Type E₁ [n×m]



Type T [n×m]

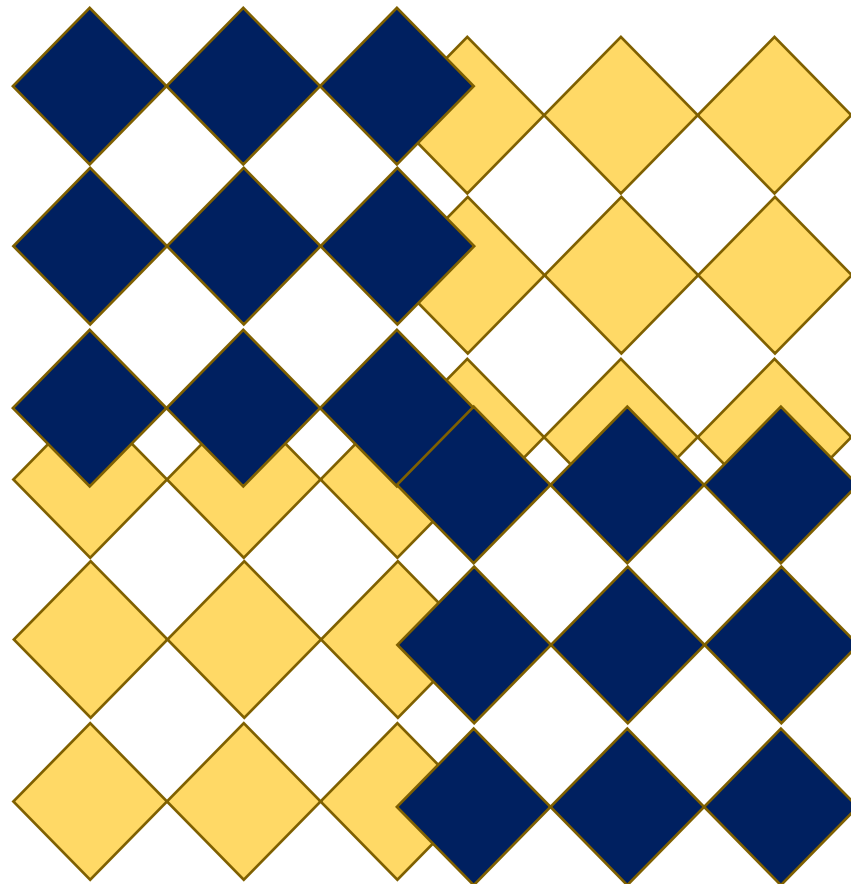


Type M [n×m]



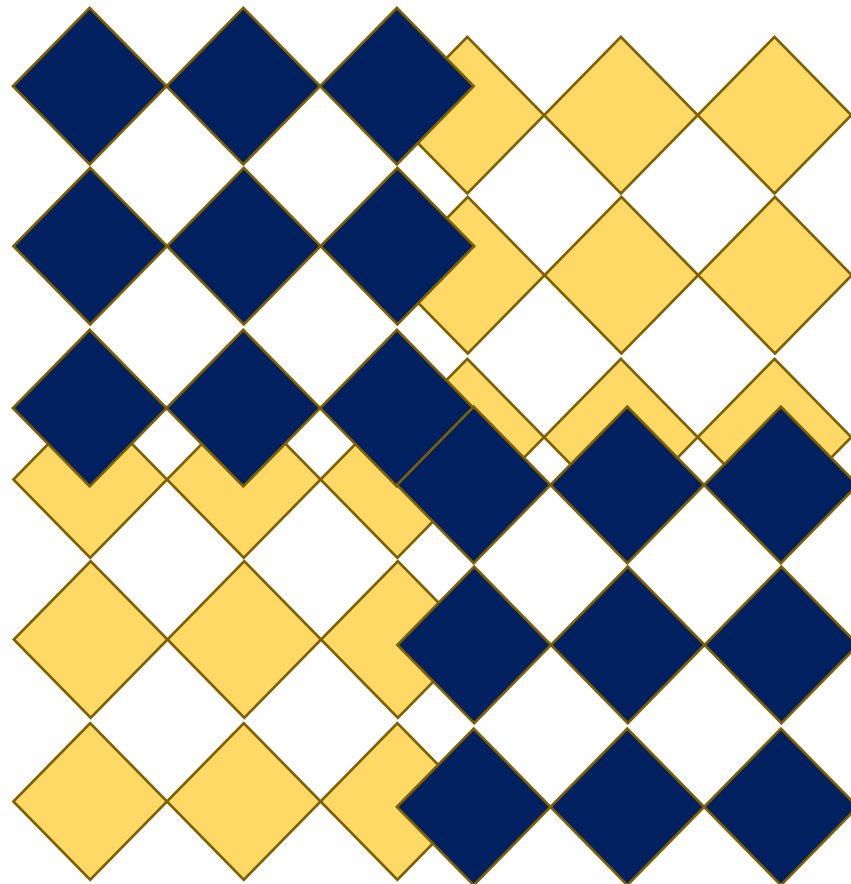
These blocks can be constructed by shifting block of octahedra in different ways

Type E₁ [n x m]



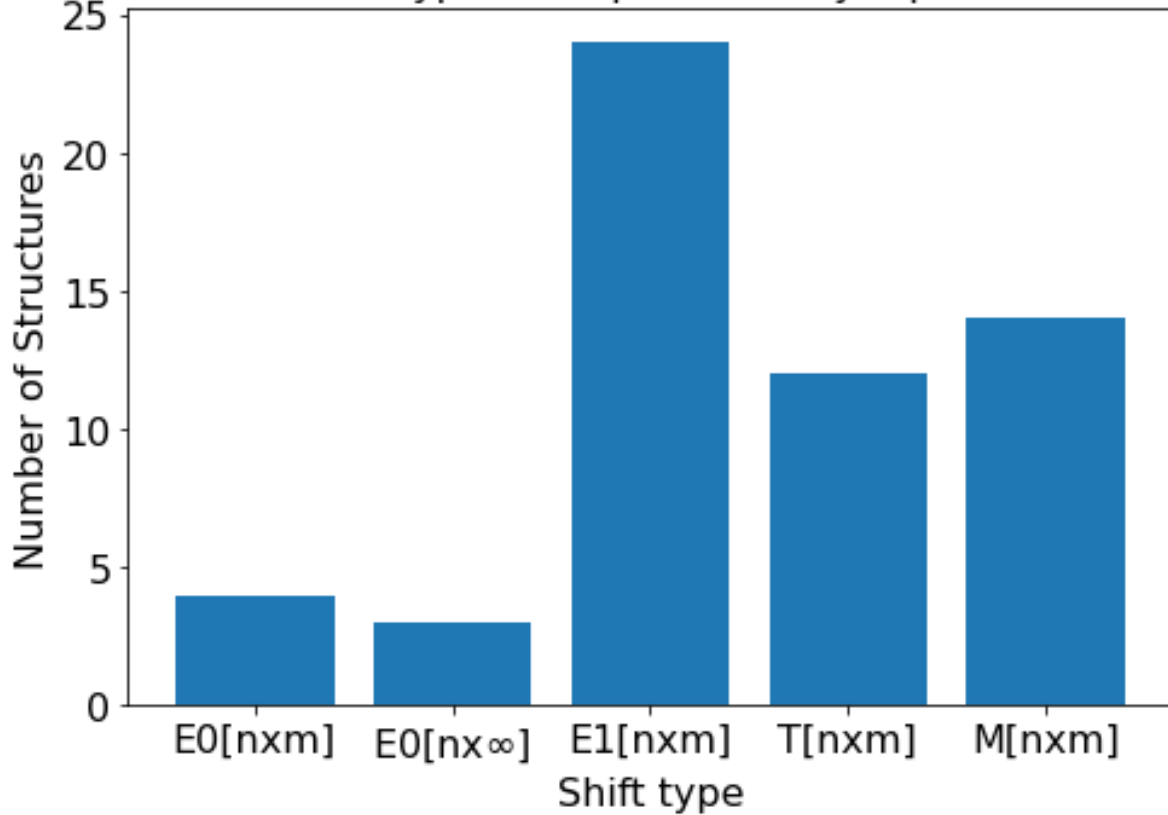
These blocks can be constructed by shifting
block of octahedra in different ways

Type T [nxm]

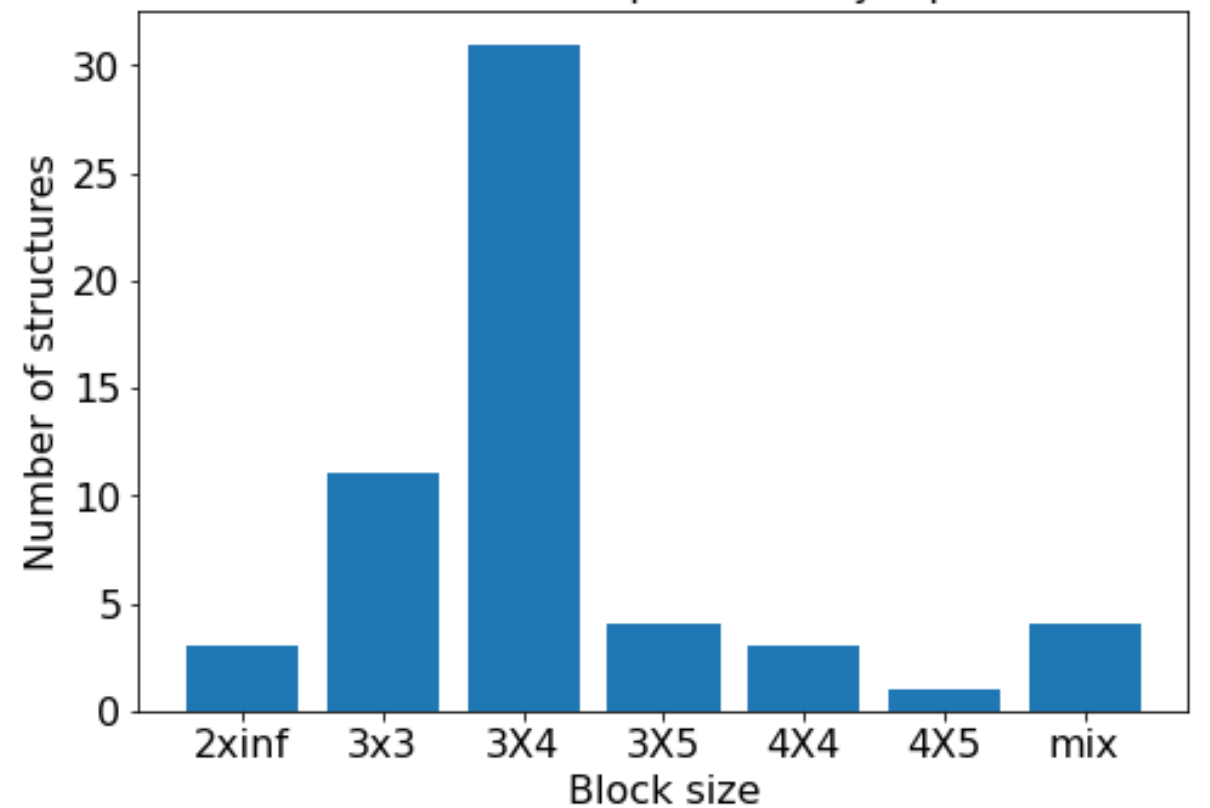


E1 type structures are the most prevalent of the Wadsley-Roth phases but there is a large variety

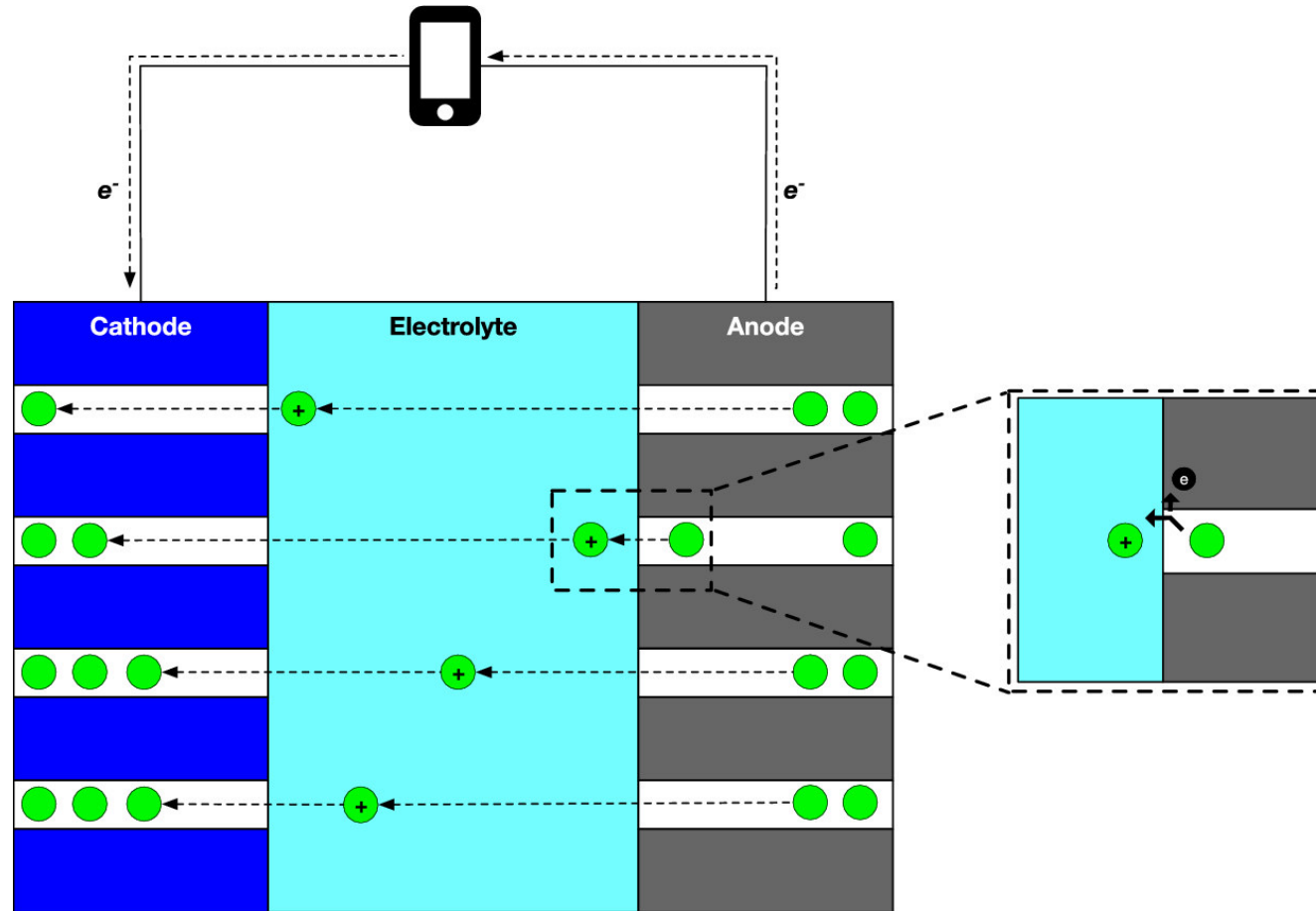
Instances of shift types in experimentally reported structures



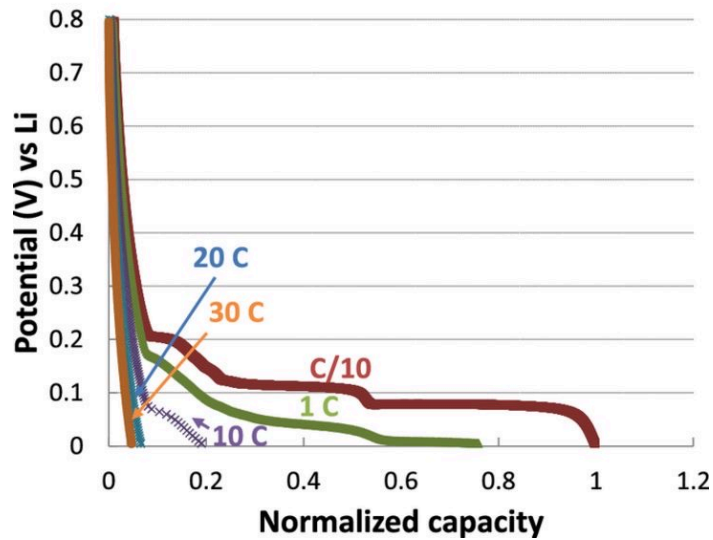
Instances of block sizes in experimentally reported structures



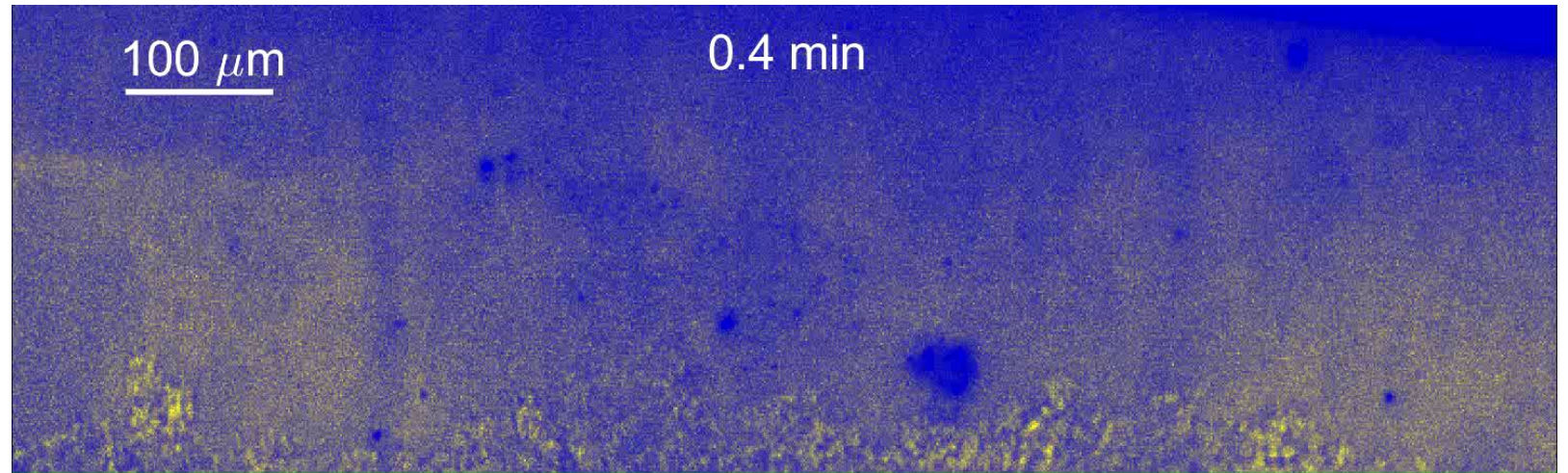
What is a rechargeable battery?



Lithium-ion battery anodes suffer from low power density and safety issues



Lithium intercalation into graphite at variable c-rates for the first cycle, normalized³



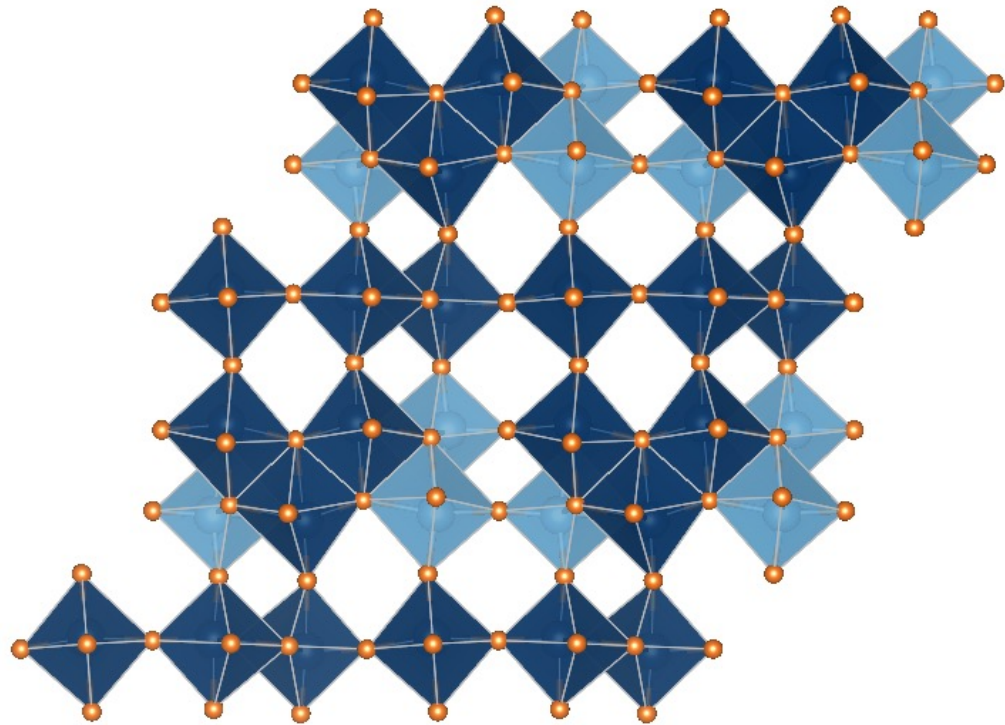
Lithium dendrite formation on a lithium anode⁴

3. Takahashi, K. and Srinivasan, V., 2015. Examination of graphite particle cracking as a failure mode in lithium-ion batteries: a model-experimental study. *Journal of The Electrochemical Society*, 162(4), p.A635.

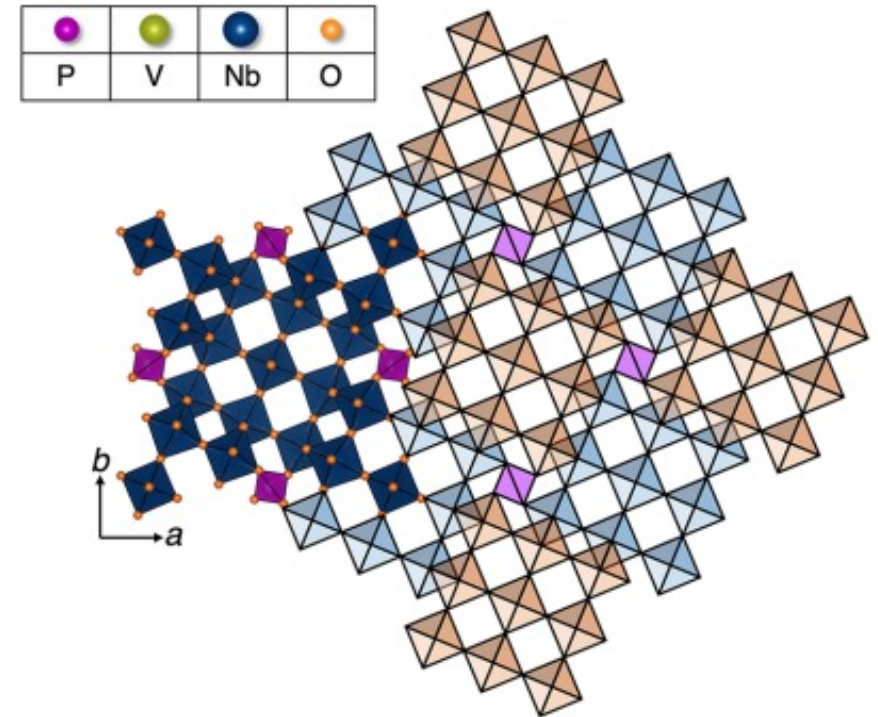
4. Yu, S.H., Huang, X., Brock, J.D. and Abruña, H.D., 2019. Regulating key variables and visualizing lithium dendrite growth: an operando X-ray study. *Journal of the American Chemical Society*, 141(21), pp.8441-8449.

Why are Wadsley-Roth phases being examined for lithium-ion battery applications?

Operates at 1-2V vs Li/Li+ -> Low SEI/dendrite formation
High power density



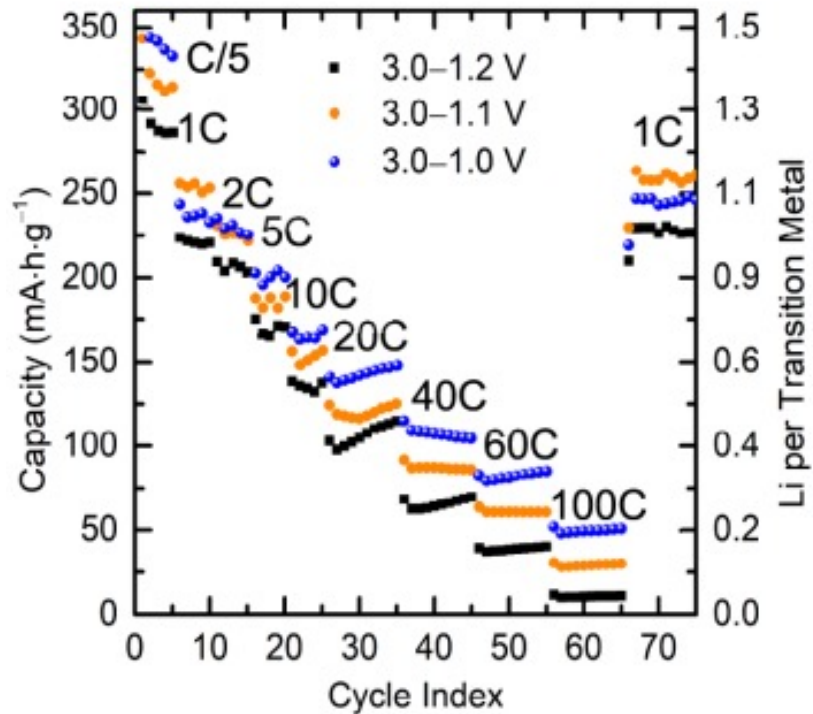
Crystal structure for one of the phases of the Wadsley-Roth structure, TiNb_2O_7



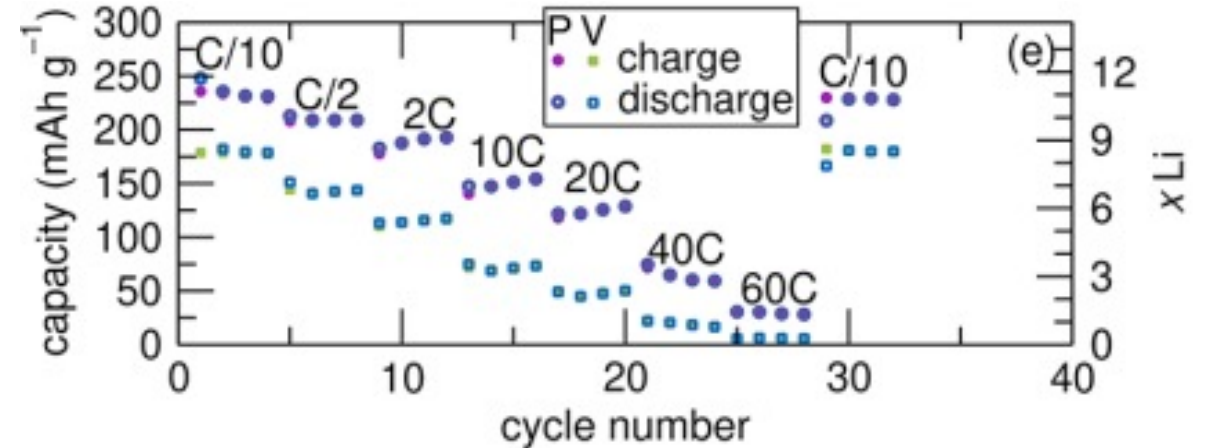
Crystal structure for the Wadsley-Roth phase, $\text{PNb}_9\text{O}_{25}$

5. Preefer, M.B., Saber, M., Wei, Q., Bashian, N.H., Bocarsly, J.D., Zhang, W., Lee, G., Milam-Guerrero, J., Howard, E.S., Vincent, R.C. and Melot, B.C., 2020. Multielectron redox and insulator-to-metal transition upon lithium insertion in the fast-charging, Wadsley-Roth phase $\text{PNb}_9\text{O}_{25}$. *Chemistry of Materials*, 32(11), pp.4553-4563.

Why are Wadsley-Roth phases being examined for lithium-ion battery applications?



Variable rate cycling data for the Wadsley-Roth phase structure, TiNb₂O₇⁶



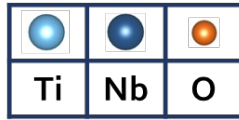
Variable rate cycling data for the Wadsley-Roth phase structure, PNB₉O₂₅⁷

6. Preefer, M.B., Saber, M., Wei, Q., Bashian, N.H., Bocarsly, J.D., Zhang, W., Lee, G., Milam-Guerrero, J., Howard, E.S., Vincent, R.C. and Melot, B.C., 2020. Multielectron redox and insulator-to-metal transition upon lithium insertion in the fast-charging, Wadsley-Roth phase PNB₉O₂₅. *Chemistry of Materials*, 32(11), pp.4553-4563.

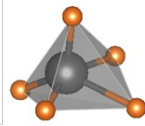
7. Griffith, K.J., Seymour, I.D., Hope, M.A., Butala, M.M., Lamontagne, L.K., Preefer, M.B., Koçer, C.P., Henkelman, G., Morris, A.J., Cliffe, M.J. and Dutton, S.E., 2019. Ionic and electronic conduction in TiNb₂O₇. *Journal of the American Chemical Society*, 141(42), pp.16706-16725.

What types of Li sites are stable in these Wadsley-Roth phases?

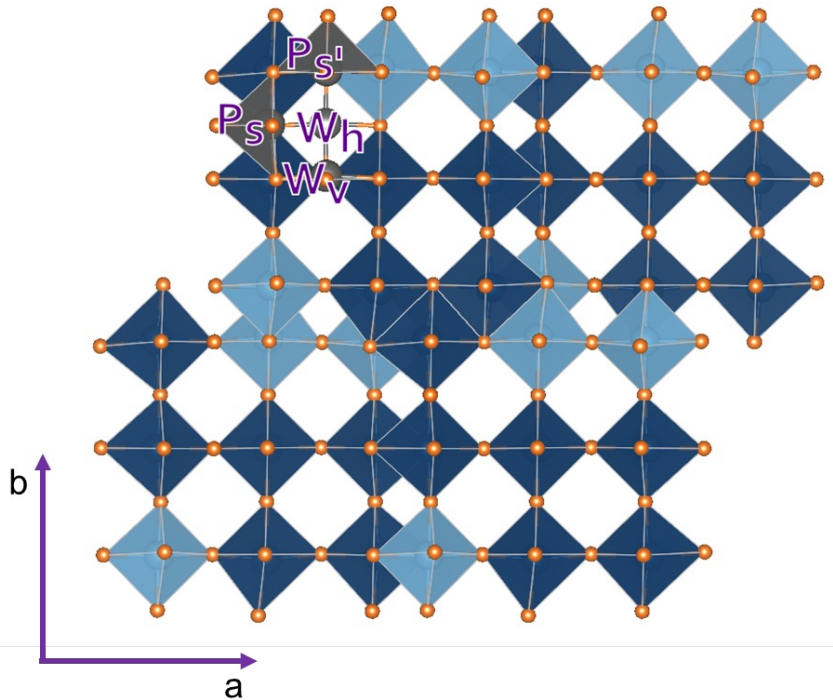
Type E₁



Site P_x



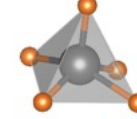
Site W_x



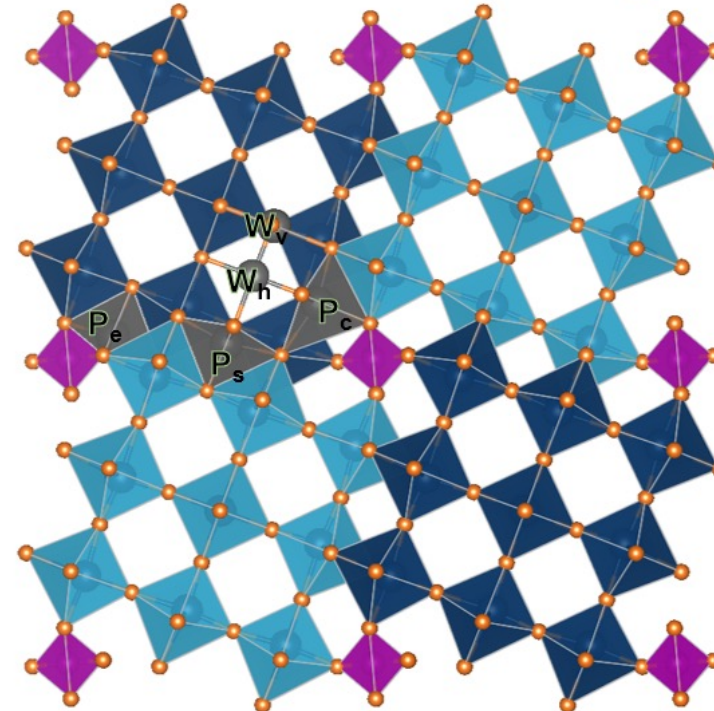
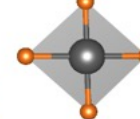
Type T



Site P



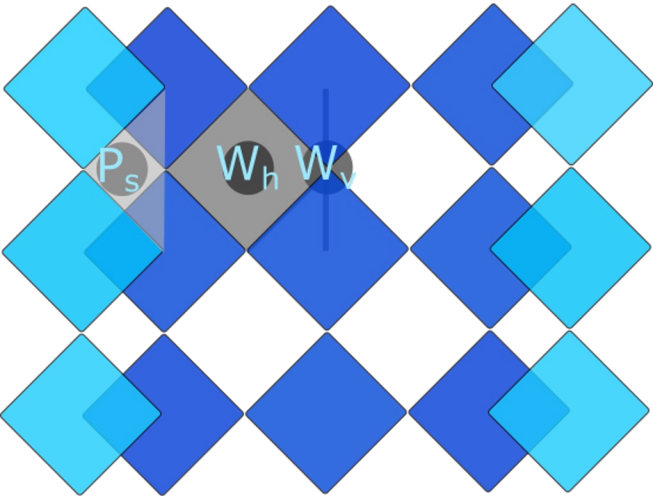
Site W



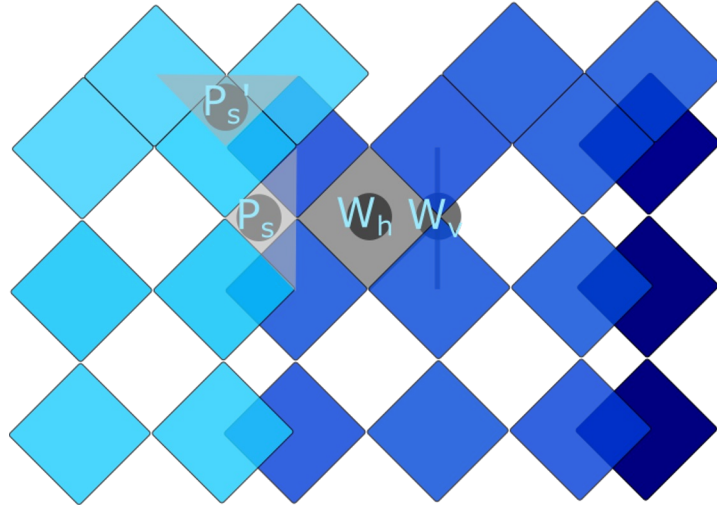
How do Li Site stabilities differ between structures?

Li ion sites present are structure dependent

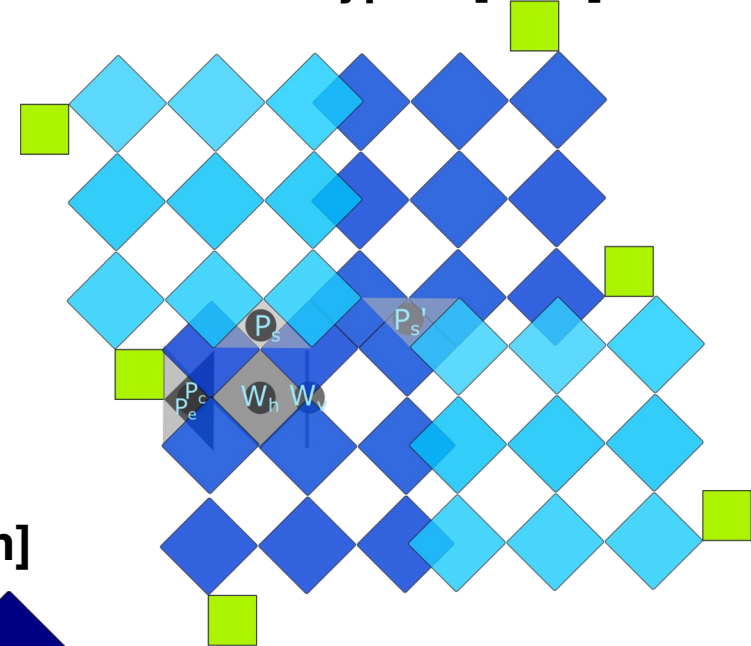
Type $E_0[n \times \infty]$



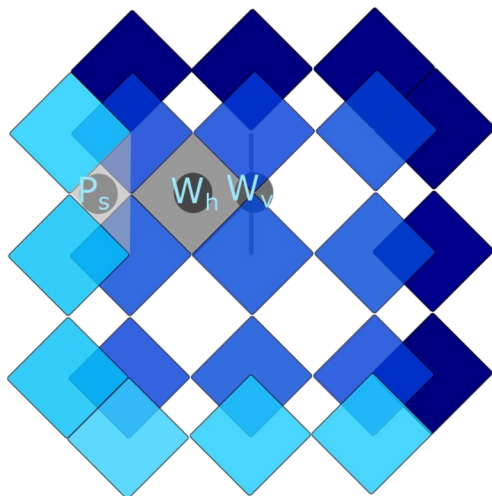
Type $E_1[n \times m]$



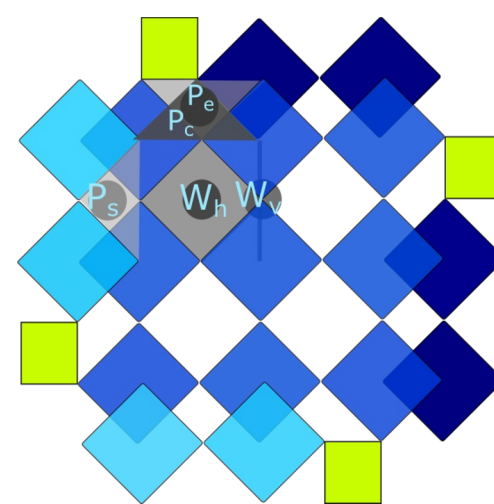
Type $M[n \times m]$



Type $E_0[n \times m]$

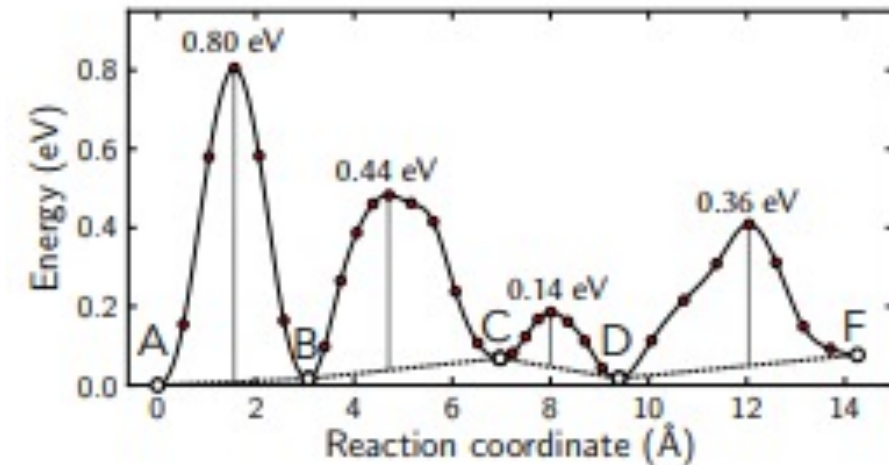
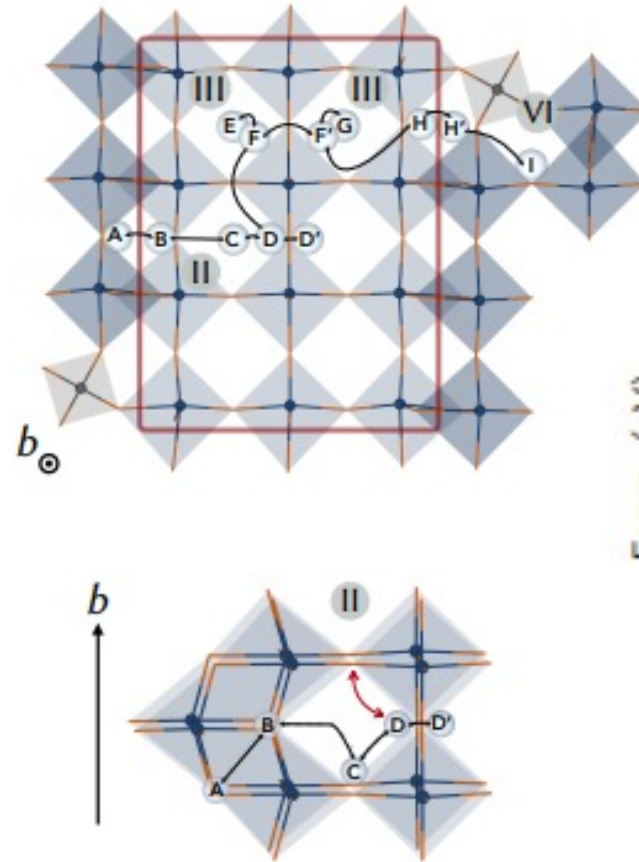


Type $T[n \times m]$



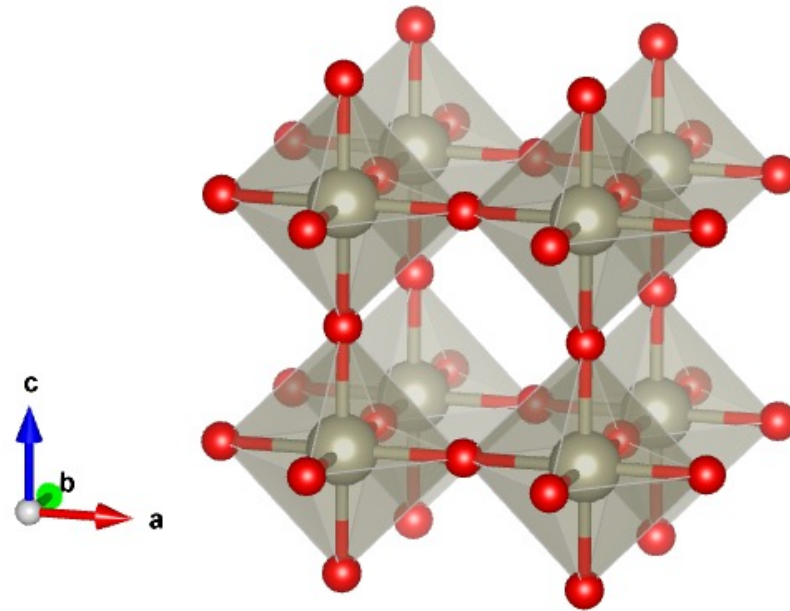
Li diffusion at the dilute limit in TiNb_2O_7 and $\text{Nb}_{12}\text{WO}_{33}$ is anisotropic

- As determined by Kocer et. al, diffusion in the T[4x3] block structure $\text{Nb}_{12}\text{WO}_{33}$, NEB studies indicate lower kinetic energy barriers for the window sites. A similar finding occurred for TiNb_2O_7
- The paper also shows that kinetic energy barriers between face sharing Ps sites is very high, indicating there may be anisotropic diffusion of Li



8. Koçer, C.P., Griffith, K.J., Grey, C.P. and Morris, A.J., 2020. Lithium diffusion in niobium tungsten oxide shear structures. *Chemistry of Materials*, 32(9), pp.3980-3989.

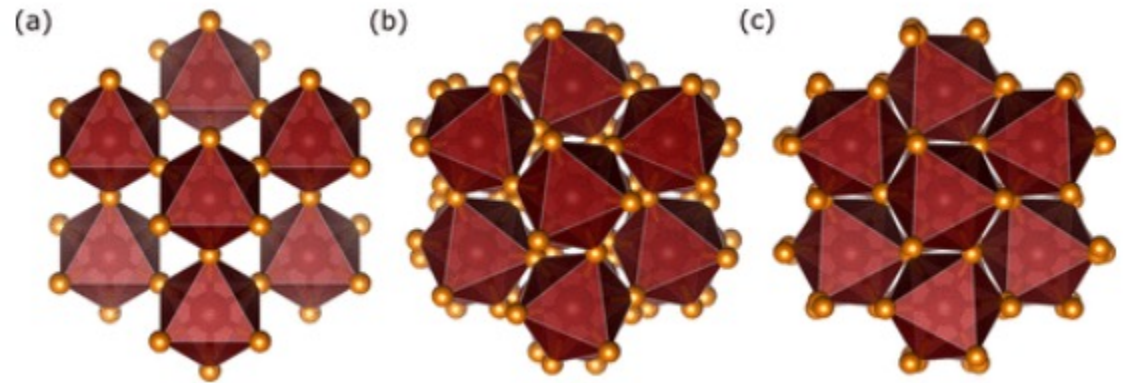
If window sites show the lowest kinetic energy barriers, why isn't ReO_3 used as an anode material?



ReO_3 type structure

If window sites show the lowest kinetic energy barriers, why isn't ReO_3 used as an anode material?

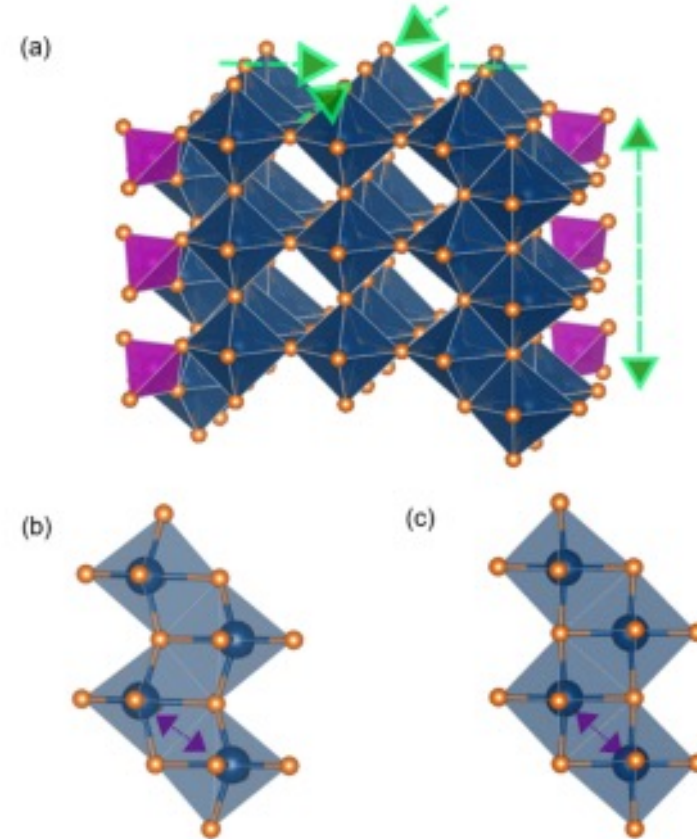
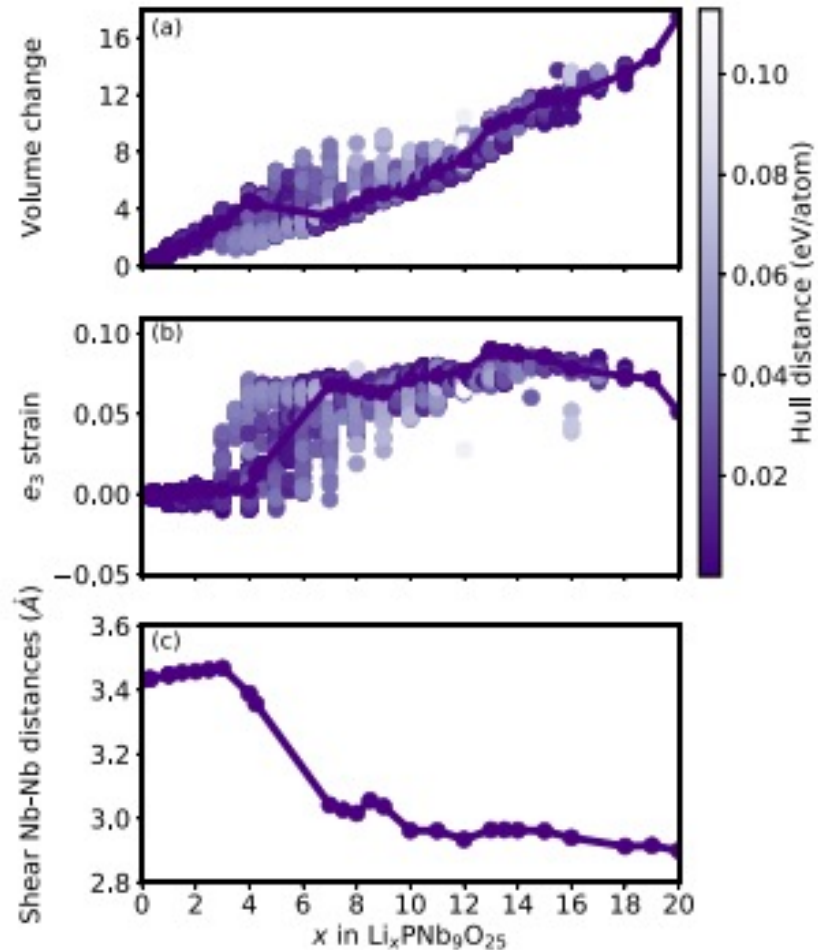
Li does not reversibly intercalate into ReO_3 since insertion of LI is followed by twisting of the ReO_3 .



Octahedral Rotations in ReO_3 upon Li insertion⁹

9. Bashian, N. H., Zhou, S., Zuba, M., Ganose, A. M., Stiles, J. W., Ee, A., ... & Melot, B. C. (2018). Correlated polyhedral rotations in the absence of polarons during electrochemical insertion of lithium in ReO_3 . *ACS Energy Letters*, 3(10), 2513-2519.

Wadsley-Roth phases are stabilized by their edge-sharing octahedra



Wadsley-Roth phases can be synthesized with differing block sizes, ways that the blocks are shifted and degrees of disorder

Parameters that can change in Wadsley-Roth phases:

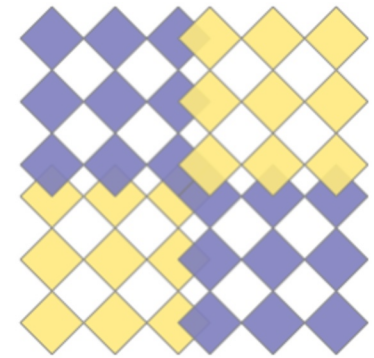
- Block size
- TM Disorder
- Cation Species
- Structure type



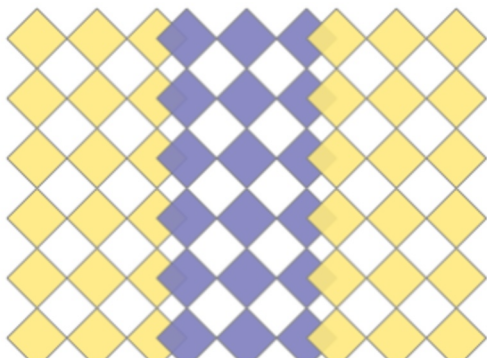
“3 by 3 “ Wadsley Roth phase constructed with 3 by 3 octahedral blocks.

Differentiating structural properties by transition metal disorder

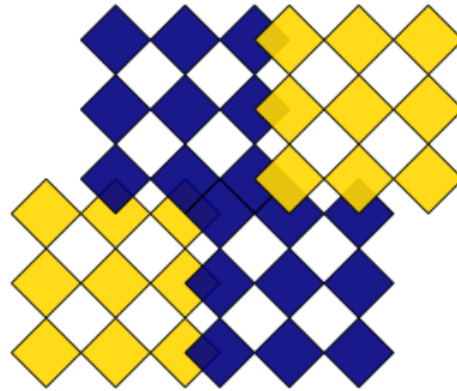
Type E₀[n×m]



Type E₀ [n×∞]



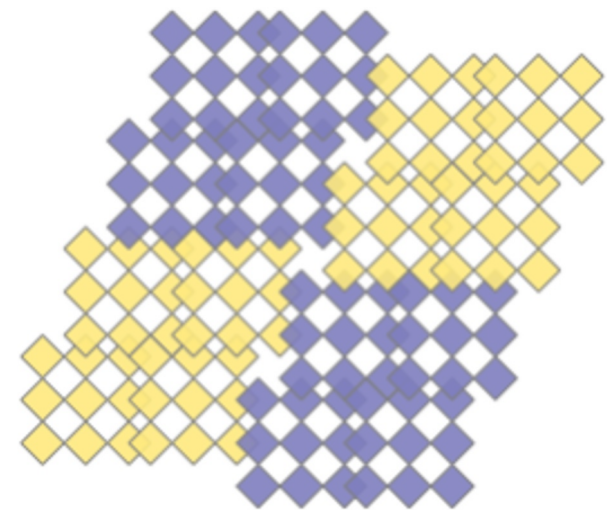
Type E₁ [n×m]



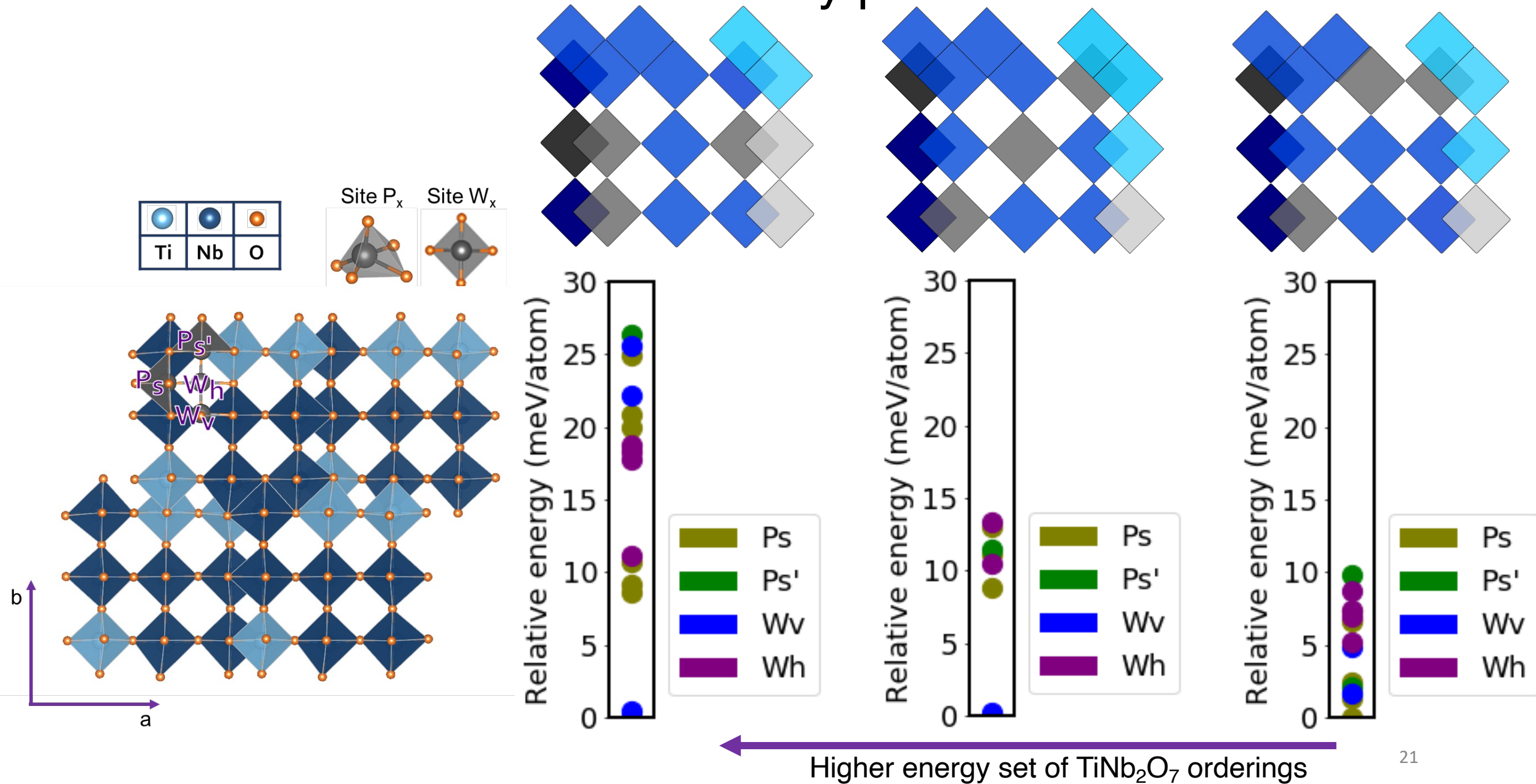
Type T [n×m]



Type M [n×m]

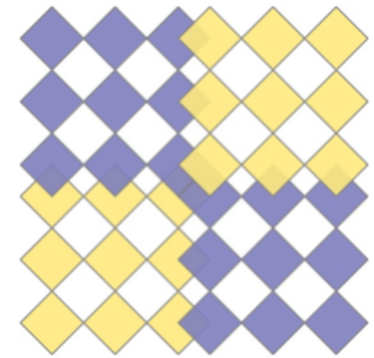


How can disorder affect battery performance?

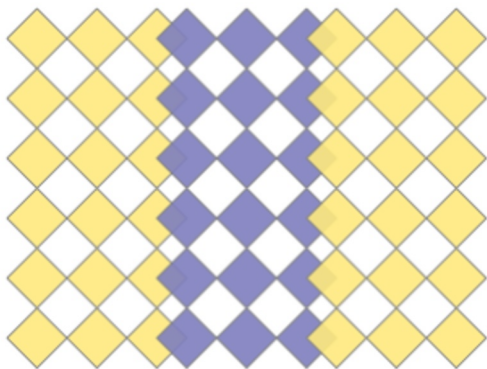


Differentiating structural properties by structure type

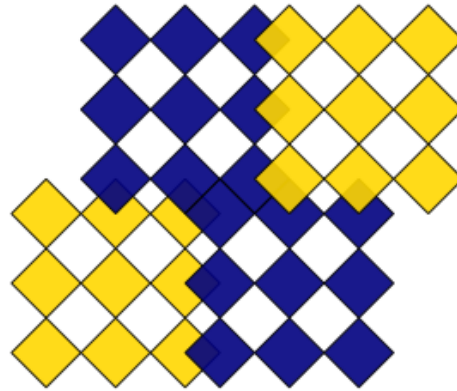
Type E₀[n×m]



Type E₀ [n×∞]



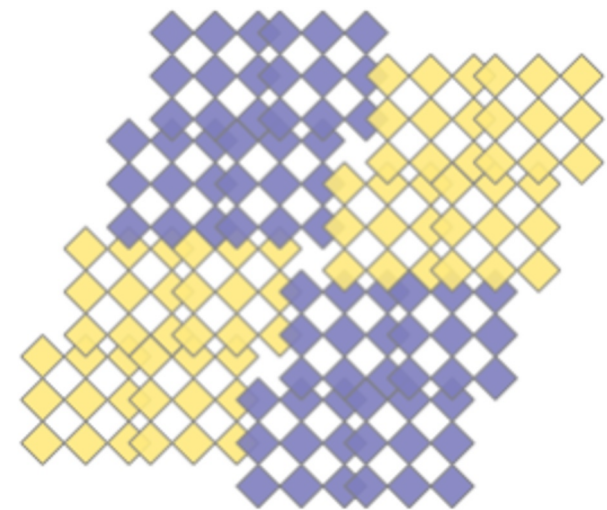
Type E₁ [n×m]



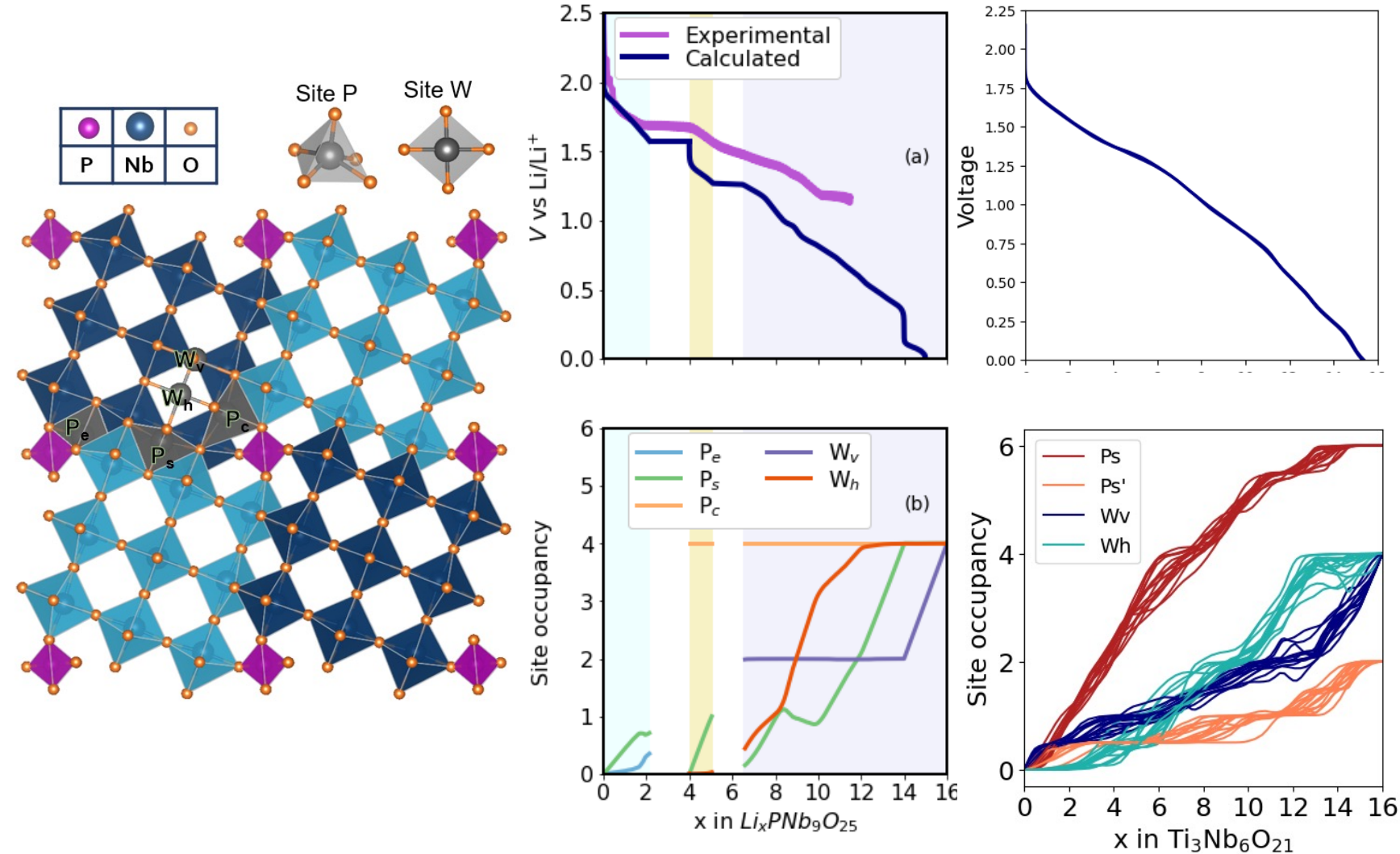
Type T [n×m]



Type M[n×m]



Voltage and Site occupancy show significant differences as we vary WR structure type



10. Saber, M., Preefer, M.B., Kolli, S.K., Zhang, W., Laurita, G., Dunn, B., Seshadri, R. and Van der Ven, A., 2021. Role of Electronic Structure in Li Ordering and Chemical Strain in the Fast Charging Wadsley–Roth Phase PNb_9O_{25} . *Chemistry of Materials*, 33(19), pp.7755-7766.

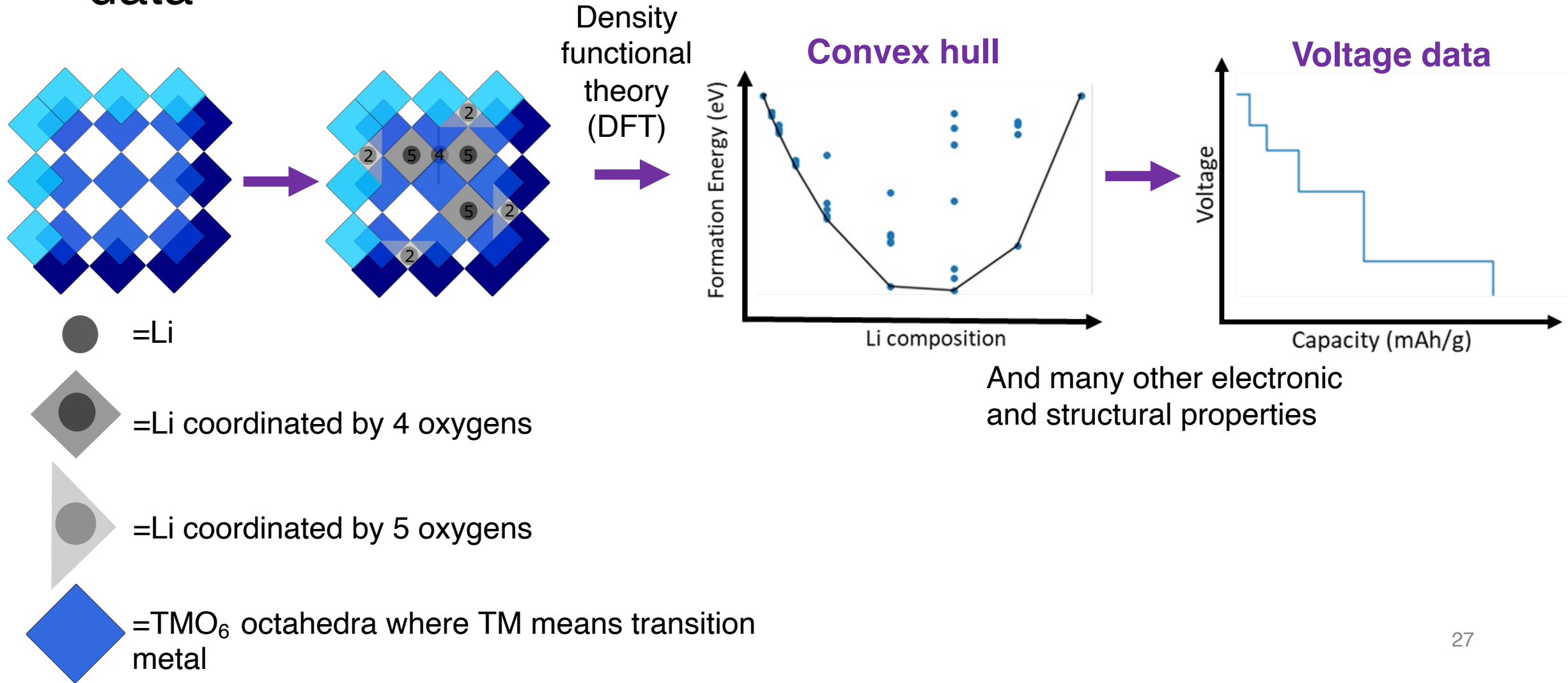
Conclusions

- Different Wadsley-Roth phases are oxides with crystallographic shear along a block of transition metal octahedra
- Different sets of Wadsley-Roth phases can be differentiated by the relative shifts of their “blocks” and the size of the sets of corner sharing octahedra units.
- Synthesized WR phases used for battery applications tend to be of the E1[nxm] structure type
- SOJT distortions are generally seen on the edges of the blocks when the transition metals are fully oxidized
- Disorder may be a method for tuning site occupancies and therefore the voltage profile
- Different structure types show differences in voltage profile though work still needs to be done to deconvolute this affect from the affect from disorder

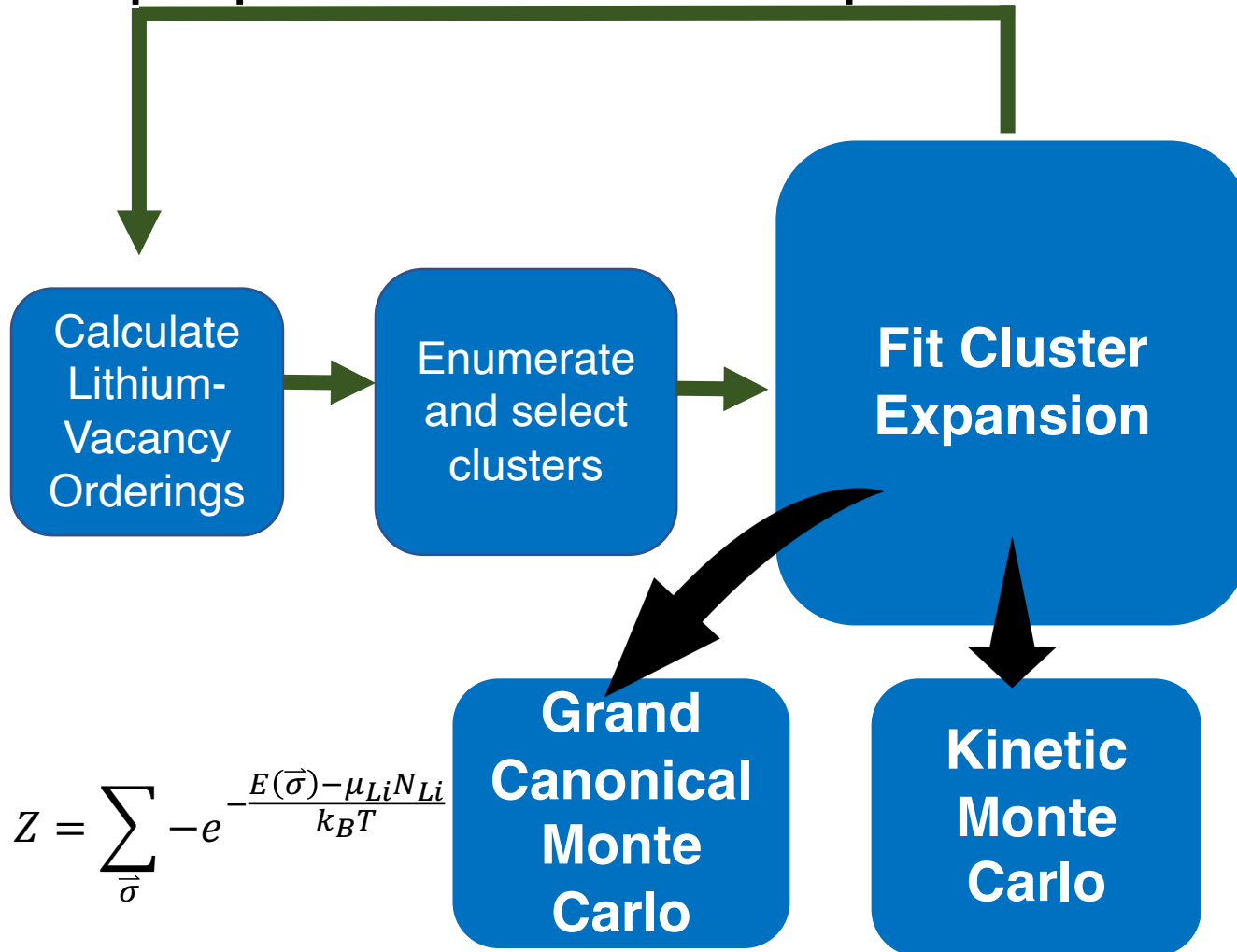
Questions?

Back up slides

General Methodology: We can examine 0K thermodynamic properties and electronic structure using density functional theory (DFT) calculations as training data



The DFT training data can be used to fit an equation called a cluster expansion that can be used to examine thermodynamic properties at finite temperature



$$Z = \sum_{\vec{\sigma}} -e^{-\frac{E(\vec{\sigma}) - \mu_{Li} N_{Li}}{k_B T}}$$

Cluster expansion equation

$$E(\vec{\sigma}) = V_0 + \sum_a V_a \phi_a(\vec{\sigma}) \quad \text{with} \quad \phi_a(\vec{\sigma}) = \prod_{j \in a} \sigma_j$$

$\vec{\sigma}$ is a vector of occupation variables where $\vec{\sigma} = \sigma_1, \sigma_2, \dots, \sigma_N$

A caveat on Li site stabilities

- In some structures there is a high energy minima that is five coordinated between sets of octahedra.

