

Understanding the phase properties of  $Li_2OHCl$ ,  $Li_2(OH)_{1-x}F_xCl$ , and  $Li_2OHBr$   
with first principles simulations

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## Why study the phase properties of these materials

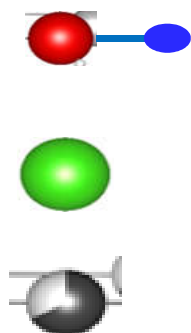
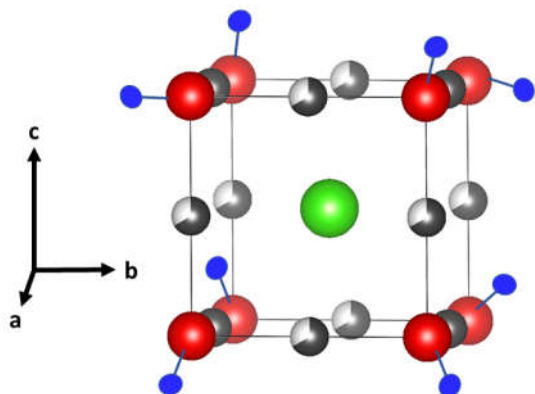
- The materials  $Li_2OHCl$ ,  $Li_2(OH)_{1-x}F_xCl$ , and  $Li_2OHBr$  have been identified as possible electrolyte materials for all solid state Li-ion batteries. Hood et al. Schwering et al. and Li et al.
- The materials  $Li_2OHCl$ ,  $Li_2(OH)_{0.9}F_{0.1}Cl$  have been successfully cycled in electrochemical cells with metallic lithium electrodes. Hood et al and Li et al.
- The material  $Li_2OHCl$  experimentally known to exist two phases. Orthorhombic phase ( $\sim < 312K$ ) and cubic phase ( $\sim > 312K$ ). The cubic phase has enhanced Li-ion conductivity.
- The material  $Li_2OHBr$  is known to exist in the cubic phase as low as 150K
- The material  $Li_2(OH)_{0.9}F_{0.1}Cl$  is known to be stabilized in the cubic phase as low as room temperature.
- The question this work attempts to address is what is the physical differences between these materials that leads to the difference in phase properties.

1. Hood, Wang, Pandian, Keum, and Liang. J. Am. Chem. Soc. (2016), **138**, 1768–1771
2. Schwering, Honnerscheid, Wullen, and Jansen. CHEMPHYSICHEM (2003), **4**, 343 - 348
3. Li, Zhou, Xin, Zhu, Lu, Cui, Jia, Zhou, Zhao, Goodenough. Angew. Chem. Int. Ed. (2016), **55**, 9965-9968

## Structures

- All three materials are known to exist in a disordered cubic phase. Schwering et al

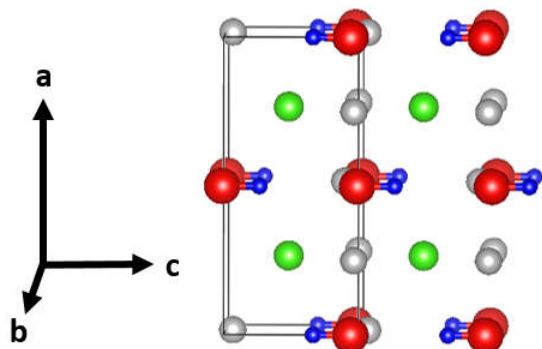
CHEMPHYSICHEM (2003), 4, 343 - 348



OH group, in  $Li_2(OH)_{1-x}F_xCl$  x of these are replaced by a Fluorine  
Cl or Br

2/3 occupied lithium site

- The material  $Li_2OHCl$  is known to exist in an orthorhombic phase



Computational prediction for orthorhombic phase

Howard et al. *Phys Rev Mat* 1. 075406 2017

Why are  $Li_2(OH)_{0.9}F_{0.1}Cl$ , and  $Li_2OHBr$  stabilized in cubic structures compared to  $Li_2OHCl$  ?

- Why are  $Li_2OHBr$  and  $Li_2(OH)_{0.9}F_{0.1}Cl$  stabilized cubic at room temperature? Why don't they form the orthorhombic structure?
- Because  $PV$  is small ( $\sim 10^{-5}$  eV) at atmospheric pressures use the Helmholtz free energy
$$F = \langle E \rangle - TS$$
- This work uses Density functional theory calculations with the LDA within the projector augmented wave formalism (PAW) using the Quantum ESPRESSO code. ATOMPAW used to generate PAW datasets.

**ATOMPAW** code (Holzwarth et al. *CPC* **135**, 329 (2001)) <http://pwpaw.wfu.edu>

**QUANTUM ESPRESSO** . (Giannozzi et al. *JPCM* **21**, 394402 (2009); <http://www.quantum-espresso.org>, Gonze et al., *CPC* **180**, 2582 (2009)); <http://www.abinit.org>

## The Helmholtz Free energy approximation

- Helmholtz Free energy,  $F = \langle E \rangle - TS = -k_b T \log(Z)$ .
- $Z = \sum_{i=1}^{\Omega} e^{-\frac{U_i}{k_b T}} Z_{hp}^i = \sum_{i=1}^{\Omega} e^{-\frac{U_i + F_{hp}^i}{k_b T}}$
- This leads to the free energy  $F_{tot} = \langle U_{SL} + F_{hp} \rangle - TS_{\Omega}$ ,
- $\langle U_{SL} + F_{hp} \rangle = \sum_{i=1}^{\Omega} (U_i + F_{hp}^i) \frac{e^{-\frac{U_i + F_{hp}^i}{k_b T}}}{Z}$ ,  $S_{\Omega} = \frac{\langle U_{SL} + F_{hp} \rangle}{T} + k_b \log(Z)$

Where  $U_{SL}$  is the “Static Lattice” energy calculated with ground state DFT

And  $F_{hp}^i$  is the harmonic phonon free energy for configuration  $i$

$$F_{hp}^i = kT \int_0^{\omega_{max}} \ln \left( \sinh \left( \frac{\hbar\omega}{2kT} \right) \right) g_i(\omega) d\omega \quad g_i(\omega) \text{ is the phonon density of states}$$

Fully disordered limit approximation of  $F(T)$

$$S = \frac{\langle U_{SL} + F_{hp} \rangle}{T} + k_b \log(Z) \quad T \rightarrow \infty \quad S = k_b \log(\Omega)$$

$$T \rightarrow \infty \langle U_{SL} + F_{hp} \rangle = \frac{1}{\Omega} \sum_{i=1}^{\Omega} (U_i + F_{hp}^i)$$

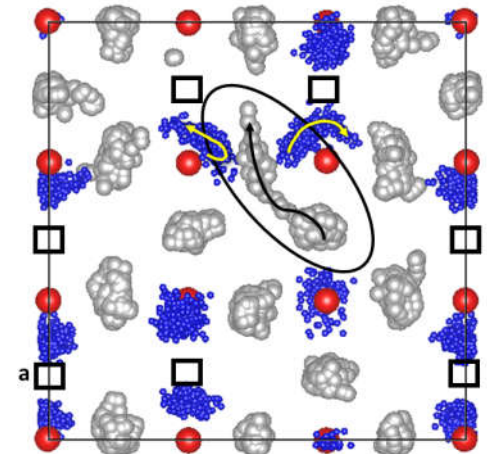
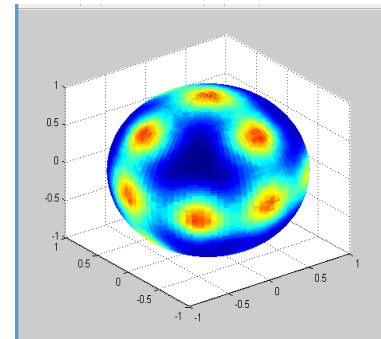
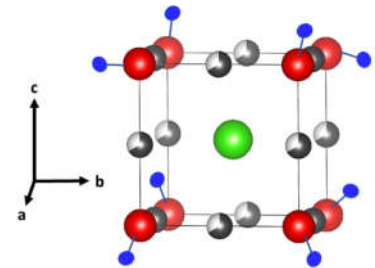
If the OH rotations and lithium lattice are approximately completely coupled

$\Omega$  is determined by the combinatorics of this lithium lattice

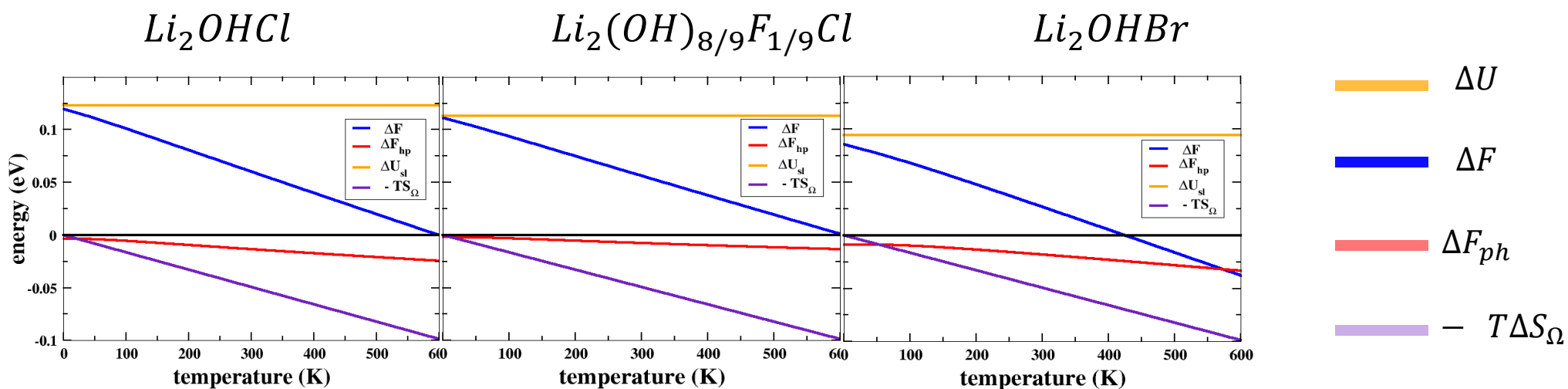
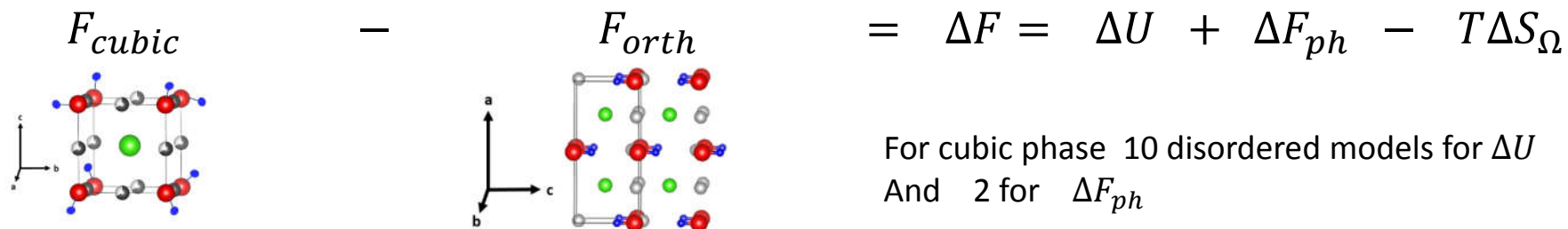
$$\Omega = \frac{(3s^3)!}{(2s^3)!(s^3)!} \quad \text{where } s \text{ is the cubic supercell dimension}$$

Fully disordered (*fd*) approximation

$$F_{fd}(T) = \frac{1}{\Omega} \sum_{i=1}^{\Omega} (U_i + F_{hp}^i) - k_b T \log(\Omega) > F(T)$$



# Comparisons of fully disordered Free energy of cubic and ortho phases





## Disordered subspace approximation

- $F_{dss}(T) = \left[ \frac{1}{m} \sum_{i=1}^m (U_i + F_{hp}^i) - k_b T \{ \log(\Omega) + \log\left(\frac{m}{\Omega}\right) \} \right]_{\min \rightarrow m}$
- $F_{dss}(T) = \mathcal{S} \rightarrow \infty \left\{ \left[ \frac{1}{m'} \sum_{i=1}^{m'} (U_i + F_{hp}^i) - k_b T \{ \log(\Omega) + \log\left(\frac{m'}{\mathcal{S}}\right) \} \right]_{\min \rightarrow m'} \right\}$
- $\mathcal{S}$  is a collection of random samples of the configuration space( $\Omega$ ) and  $m'$  is the number of lowest energy states kept from  $\mathcal{S}$
- $\frac{m'}{\mathcal{S}} \approx \frac{m}{\Omega}$

# Conclusions

- Cubic phase of  $Li_2OHBr$  is predicted to be stabilized because of lower  $\Delta U + \Delta F_{ph}$
- Experimentally known stabilization of the cubic phase of  $Li_2(OH)_{1-x}F_xCl$  is predicted to be subtle effect.  
assuming  $\sim 0.02$  eV error per formula unit. Suggest Orthorhombic phase will form within  $\sim 200-300K$
- A method is laid out to calculate more accurate transition temperatures.

## Future considerations

- Extending on the fully disordered approximation

- $$F_{fd}(T) = \frac{1}{\Omega} \sum_{i=1}^{\Omega} (U_i + F_{hp}^i) - k_b T \log(\Omega)$$

- The partition function will effectively select some subset of the  $\Omega$  configurations

- Order the “energies” from least to greatest

$$U_1 + F_{hp}^1 \leq \dots \leq U_m + F_{hp}^m \leq \dots \leq U_{\Omega} + F_{hp}^{\Omega}$$

- Imagine that a better model is that the system is a subspace (1 ...  $m$ ) of the entire space (1 ...  $\Omega$ )

- Consider the “disordered subspace approximation” (*dss*)

$$F_{dss}(T) = \left[ \frac{1}{m} \sum_{i=1}^m (U_i + F_{hp}^i) - k_b T \left\{ \log(\Omega) + \log\left(\frac{m}{\Omega}\right) \right\} \right]_{\min \rightarrow m} \approx F(T)$$

- $\frac{m}{\Omega}$  is the fraction of the entire space