First Principles Simulation of Li2(OH)Cl

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Introduction

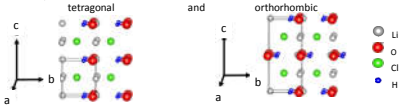
- Li2(OH)Cl is a material studied for its possible use as a solid state Li-ion electrolyte
- It is experimentally observed to exist in two phases , a low temperature orthorhombic and a high temperature cubic
- The cubic phase is a fast Li-ion conductor
- In this work the structure of both phases was studied. Molecular dynamics of the cubic phase was performed to understand more about the Li-ion mobility

Methods

- Density functional theory using the projector augmented wave formalism
  Data sets generated with ATOMPAW, simulations done with Quantum Espresso
- Quasi harmonic phonons(QHA) calculations were used for structure analysis of possible low temperature phases
  90Ry ecut, 12X12X12 and 12X12X6 K-point grids,
- Lattice constants include approximate 1.02 LDA correction
- Density functional molecular dynamics in the microcanonical ensemble from ~350K-650K
  45 Ry ecut , 1 Kpoint at 0.5 0.5 0.5, 1fs time step

Low temperature structure search

- Two possible structures
  tetragonal and orthorhombic



- Tetragonal structure inherently in disagreement with experiment. Orthorhombic lattice parameters in disagreement with experiement and 0.02eV per formula higher in energy than tetragonal
- Quasi harmonic phonon calculations

$F_{QH}(T) = \ minimum(\ E_{internal}(a,b,c) + F_{phonon}(a,b,c,T)\ )_{a,b,c}$

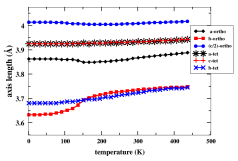
$E_{internal}(a,b,c)$ is the internal/structural ground state energy calculated by DFT at (a,b,c)

$F_{phonon}(a,b,c,T)$ is the harmonic phonon free energy at the fixed lattice constants (a,b,c)

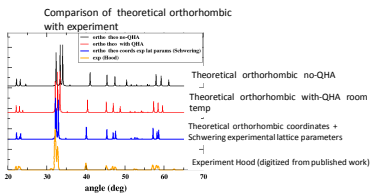
- $F_{phonon}(a,b,c,T) = kT \int_0^{\omega_{max}} \ln\left(\sinh\left(\frac{\hbar\omega}{2kT}\right)\right) g(a,b,c,\omega) d\omega$
  where $g(a,b,c,\omega)$ is the harmonic phonon density of states at fixed lattice parameters a,b,c
  k is the Boltzmann constant, T the temperature

- In practice calculate $F_{phonon}(a,b,c,T)$ on a grid of lattice constants and interpolate to find the free energy minimum
  - tetragonal calculated on 4X4X4 grid of lattice constants grid spacing 0.1 Ang
  - orthorhombic on 5X6X5 grid of lattice constants with grid spacing 0.07 Ang

Theoretical tetragonal and orthorhombic lattice parameters as function of temperature



Comparison of theoretical orthorhombic with experiment



- Theoretical vs Experimental lattice constants at room temp
  Schwering predicts a 4 formula unit unit-cell this work predicts a 2 formula unit unit-cell . It is hypothesized that the lattice parameters in this work correspond to Schwering's as a -> c/2 , b -> a, c -> b

QHA 271K Theoretical	Experimental
a-3.87 Å	c/2 - 3.87 Å
b-3.73 Å	a - 3.82 Å
c-8.02 Å	b - 8.00 Å

References

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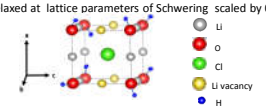
Molecular Dynamics

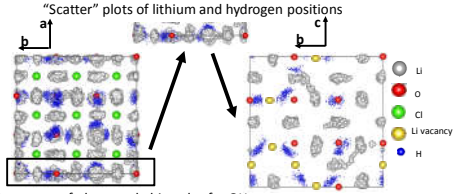
- Initial configurations started from randomly placing lithium on the available sites and randomly orienting the OH groups in 3X3X3 supercells.
  - Relaxed at lattice parameters of Schwering scaled by 0.98



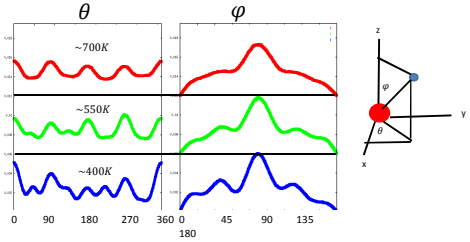
- Two starting configurations Initialized for target temperatures 300-600K
- Scatter plot provides qualitative information .
  - snap shot of lithium and hydrogen approximately every 10fs for a 2ps run
  - display ideal locations of Cl and O

$\sim 550K$

"Scatter" plots of lithium and hydrogen positions



- Histograms of theta and phi angles for OH groups



Insights from MD into lithium ion conductivity

- For a fast ionic conductor, conductivity can be expressed in terms of the "tracer" or tracked particle diffusion constant

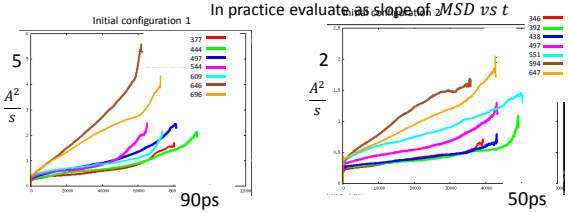
$$\sigma = \frac{n(Qe)^2 D^*}{kTVH_r}$$

- Where n is the number of mobile ions, Q is the charge of the ions e is the fundamental charge, k is Boltzmann's constant, T the temperature, V the volume H_r the Haven ratio and D^* given as

$$D^* = \frac{1}{6nt}\lim_{t\to\infty}\left\langle \sum_{i=1}^{n} (R_i(t) - R_i(0))^2 \right\rangle_{t_o} = \frac{1}{6t}\lim_{t\to\infty} MSD(t)$$

Where $MSD(t)$ is the mean square displacement of the mobile ions

In practice evaluate as slope of $MSD\ vs\ t$



Generalized Kubo expression for Ionic conductivity

$$\sigma = \frac{e^2}{kTV}\int_0^\infty \langle J(t)\cdot J(0)\rangle_{to} dt = \frac{e^2}{kTV}\lim_{t\to\infty}\frac{1}{6t}\langle \delta\rho(t)^2\rangle_{to}$$

where $J(t) = \sum_i Q_i v_i(t)$ and

$$\delta\rho(t) = \sum_i Q_i R_i(t) \ - \ \sum_i Q_i R_i(0)$$

Theoretical considerations for fast ionic conductor

- Split $\delta\rho(t)$ into a mobile $\delta\rho_M(t)$ and a non-mobile term $\delta\rho_{NM}(t)$

$$\sigma = \frac{e^2}{kTV}\lim_{t\to\infty}\frac{1}{6t}\langle \delta\rho_M(t)^2 + 2\,\delta\rho_M(t)\cdot\delta\rho_{NM}(t) + \delta\rho_{NM}(t)^2\rangle_{to}$$

- Non mobile implies ions are confined to a local minimum therefore $\delta\rho_{NM}(t)^2$ is bounded by some constant C_{NM}
- Closer inspection of middle term

$$2\,\delta\rho_M(t)\cdot\delta\rho_{NM}(t) = 2\,|\delta\rho_M(t)|\,|\delta\rho_{NM}(t)|\cos\theta_{M,N}$$

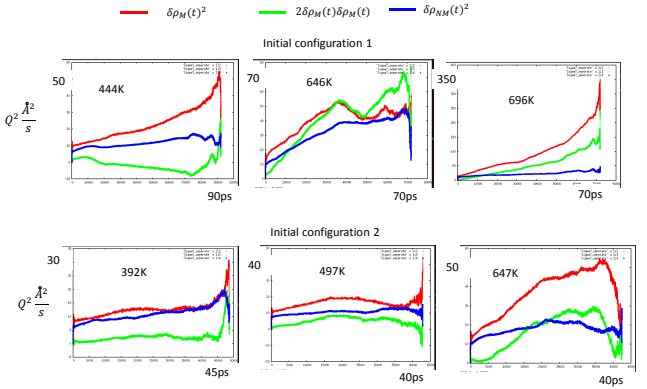
- This can only grow as fast as

$$\pm 2C_{NM}\sqrt{\delta\rho_M(t)^2}$$

- $\delta\rho_M(t)^2$ goes as $C_M t$ at long times, therefore $\pm 2C_{NM}\sqrt{\delta\rho_M(t)^2} = \pm 2C_{NM}\sqrt{C_M t}$
- This says for a fast ionic conductor in terms of the Kubo relation

$$\sigma = \frac{e^2}{kTV}\lim_{t\to\infty}\frac{1}{6t}\langle \delta\rho_M(t)^2\rangle_{to}$$, evaluated as slope at long t

In practice convergence time is long i.e. not yet explicitly demonstrated



Arrenhius plots $\log(\sigma T)\ vs\ 1/T$

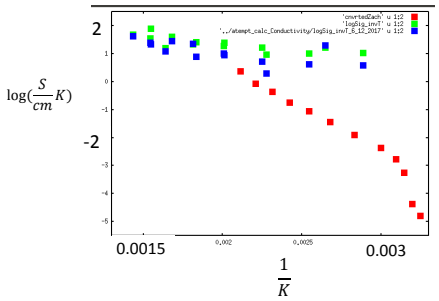
- In tracer picture

$$\log(\sigma T) = \log\left(\frac{n(Qe)^2 D^*}{kV}\right) - \log(H_r)$$

First term on right is plotted

Note: not well converged

$\log\left(\frac{n(Qe)^2 D^*}{kV}\right)$ $\log(\sigma T)$ theoretical $\log(\sigma T)$ experiment (Hood)



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