First Principles Simulation of Li2(OH)Cl

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Introduction

1. 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.

2. The cubic phase is a fast Li-ion conductor.

3. 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

1. Density functional theory using the projector augmented wave formalism.

2. Data sets generated with QUANTUMWAVE simulations done with Quantum Expresso.

3. Quasi harmonic phonon(QH) calculations were used for structure analysis of possible low temperature phases 398 K exc, 1253223 and 1251266 vacancy pairs.

4. Lattice constants include approximate 1.02 IA correction.

5. Density functional molecular dynamics in the microcanonical ensemble from ~30K-920K 45 Ry excited, 1 femtosecond 0.5-0.5, 10h. time step.

Quasi harmonic phonon calculations

- F_s(q) = \frac{1}{2} \sum_{alpha=\alpha,b,c} \frac{\gamma_{\alpha}}{\omega_{\alpha}} \cos(q_a a + q_b b + q_c c)\omega_{\alpha}

- E_{\text{eigen}}(q) = \sum_{\alpha=\alpha,b,c} \frac{\gamma_{\alpha}}{2} \omega_{\alpha}^2 + \frac{\omega_{\alpha}^2}{2} \cos(q_a a + q_b b + q_c c)\omega_{\alpha}

- \omega_{\alpha} is the phonon frequency at the fixed lattice parameters (a,b,c)

- F_s(q) is the quasi harmonic free energy at the fixed lattice parameters (a,b,c)

6. In practice calculate F_s(q) on a grid of lattice constants and interpolate to find the free energy minimum.

- tertagonal calculated on 6X6X6 grid of lattice constants giving 0.1 Ang.

- orthorhombic on 5X4X5 grid of lattice constants with grid spacing 0.07 Ang.

Theoretical tetragonal and orthorhombic lattice parameters from experiment

- theoretical: a=3.871, c=1.027
- experimental: a=3.821, c=7.012

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{\rho D}{\mu}

- As the number of mobile ions, Q is the charge of the ions, \rho is the fundamental charge, \mu is the Bohr magneton, T is the temperature, if the volume V, the Hansen ratio and \gamma given:

- D' = D(V) = \frac{\int \langle \rho, 0 \rangle - \langle \rho, 0 \rangle^2}{\langle \rho, 0 \rangle^2} = \frac{1}{\langle \rho, 0 \rangle^2} \int \rho^2

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

- In practice evaluated as slope of JMSD vs t

Generalized Kubo expression for ionic conductivity

- \sigma = \frac{e^2}{h} \int \langle \rho, 0 \rangle^2 \langle e, 0 \rangle^2 = \frac{e^2}{h} \int \langle \rho, 0 \rangle^2 \langle e, 0 \rangle^2 \gamma_0^2

where \langle \rho, 0 \rangle = \sum \langle \rho, 0 \rangle and

\sigma = \sum \langle \rho, 0 \rangle^2 \langle e, 0 \rangle^2

Theoretical considerations for fast ionic conductor

- Split \rho, (Q) into a mobile \rho_{\text{m}}(Q) and a non-mobile term \rho_{\text{nm}}(Q)

- Non mobile impurity ions are confined to a local minimum therefore \rho_{\text{nm}}(Q) is bounded by some constant C_{\text{nm}}

- Closer inspection of mobile term

- This can only grow as fast as

- \sum_{Q} C_{\text{nm}}^2 \leq C_{\text{nm}} \Delta Q

- \Delta Q(0) goes as \gamma^{1/2} at long times, therefore

- \sum_{Q} C_{\text{nm}}^2 \leq C_{\text{nm}} \gamma^{1/2}

- This says for a fast ionic conductor in terms of the Kubo relation

- \sigma = \frac{e^2}{h} \sum \langle \rho, 0 \rangle^2 \langle e, 0 \rangle^2 \gamma_0^2 = \frac{1}{\gamma_0} \sum \langle \rho, 0 \rangle^2 \langle e, 0 \rangle^2

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

- \rho_{\text{m}}(Q)

- 2\rho_{\text{m}}(Q)\rho_{\text{nm}}(Q)

- C_{\text{nm}} \gamma^{1/2}

- 2\rho_{\text{m}}(Q)\rho_{\text{nm}}(Q)

- C_{\text{nm}} \gamma^{1/2}

- C_{\text{nm}} \gamma^{1/2}

- C_{\text{nm}} \gamma^{1/2}

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