Halopsinel project progress (late March.)

# STAGE 1: Structure analysis via enumeration using Supercell

* 16m possible structures based on partial occupancies from crystallography, none display local Fd3m character (Pezhman)
* 35 framework structures when supposedly mobile Li ions (8a, 16c, 48f) are removed, none display local Fd3m character
* Based on Ewald energy, structures close in energy… does local structure matter in an MD setup? – DFT paper also predicts frameworks to be close in energy

# STAGE 2: Development of Buckingham potentials

* Used GULP to fit literature Al-Cl potential to ScCl3 structure (trigonal, 148) [DevMethod:space;shell;constk]
* Also managed to get potential from Cu-Cl, produced very similar results,

but took longer to converge, so was discarded

# STAGE 3: 0 K simulations (DFT + GULP)

* Both DFT and GULP relaxations show weird effects
* Li ions move off site and into other sites (DFT: Li ions move to one side of cell; GULP: tetrahedral Li ions move to empty octahedral sites) → Confirms flat energy landscape

# STAGE 4: MD setup trials

* Initial MSDs (3x3x3, 2ns) at 300k messy, overestimates conductivity vs exp.
* Temperature fluctuates & energy of the structure not levelled out
* Played around with settings (drag, tchain, td), but no significant difference
* Found larger cell size (9x9x9) and longer timescales (6 ns equilibration to reach energy minimum, 6 ns for MSD to become linear, 6 ns to calculate diffusion coefficent) is the only way we can estimate conductivity well [also tried 7x7x7, 8x8x8, 9x9x9]
* Worth noting that smaller cells and shorter timescales are okay at higher temperatures

# STAGE 5: Initial conductivity results

* Ran 9x9x9, 16 (6+10) ns calcs at 300, 400, 500, 600 K for lowest energy triclinic and a higher energy monoclinic
* At low temperatures framework seem to remain intact, but Sc-s move at higher temperatures, distorting framework
* Conductivities very similar, especially at higher temperatures, further confirming irrelevance of starting structure
* Haven ratio of 2.40 from DFT paper (indicates correlated ion diffusion) can get results close to experiment at 300 K
* Chloride migration?

# STAGE 6: Long-range order structure results

* Structure with pseudo-random distribution of ions created, to mimic long-range cubic character – 8x8x8 supercells
* Used 10 ns equilibration, 10 ns simulation (all MSDs recorded)
* Different Sc-Cl potential used (previous fitting method found incompatible with In and Y + lower SoS) [DevMethod:P1;shell;vark]
* Results consistent with different randomised structures
* Results at low temperatures no quite on LoBF for higher temperatures on Arrhenius plot
* Conductivities also very similar to scaled-up monoclinic unit cell
* Dipped a toe into cation mixing with 50% In and 50% Y: In has no effect, Y has negative effect
* Analysis to investigate atomic-scale effects, but no useful results as of yet (mobile vs stationary MSD, site\_analysis)
* Lattice parameter still overestimated; Li-Cl potential might need to be refitted

# STAGE 7: Rethinking potentials

* Go back to make sure Buckingham model can be justified
* Standard GULP fitting for LAMMPS MD looking forward: fit to P1 with no shells
* Refit Sc-Cl and Li-Cl; lattice parameter closer, but still too high [DevMethod:P1;noshell]
* Adjusting Sc-Cl not much effect, adjusting Li-Cl much effect, can achieve experimental conductivity – LAMMPS RUN TO DO
* Li-Li (and so Li-Sc and Sc-Sc?) has no effect, Cl-Cl shouldn’t have any effect, but it does – parameters close to experiment, but LAMMPS run gives underestimation
* Is the bloody thing melted? – RDFs