**Ab initio Calculations to Understand Ionic Conduction in Lithium Ion Battery Materials**

Mayanak K. Gupta¹, Baltej Singh¹², Prabhat Sree Goel¹, Ranjan Mittal¹² and Samrath L. Chaplot¹²
Solid State Physics Division¹
Homi Bhabha National Institute²

We have performed first principles simulations on lithium ion conductors, namely, Li₂O, LiMPO₄(M=Fe, Mn) and LiAlSiO₄. We are able to identify the specific vibrational mode of lithium ions that become soft at high temperature and which may lead to onset of the superionic behaviour in Li₂O. The mode belongs to the transverse-acoustic phonon branch at the Brillouin-zone boundary and involves large displacement of the lithium ions in the [100] direction. In another battery material, LiMPO₄(M=Fe, Mn), the lattice dynamics calculations reveal instability of some phonon modes when the unit cell volume is increased to that corresponding to elevated temperature, which may result in the onset of diffusion of Li in these compounds. The ab initio molecular dynamics simulations for LiAlSiO₄ reveal the nature of the one-dimensional superionic conduction which involves correlated jump diffusion of lithium ions.

**Keywords:** Ab initio simulation, Phonon, Lattice dynamics, Molecular dynamics

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**Introduction**

Fast ion conductors are one of the functional materials which possess high values of ionic conductivity at relatively modest temperatures. Such compounds find extensive technological applications in solid state batteries, gas sensors and fuel cells. The search for better solid electrolytes (i.e. higher ionic conductivities, higher power densities, low cost, environmentally friendly, etc.) is a particularly active area of research. Discovery and exploitation of new high-performance materials requires a greater fundamental understanding of their properties on the atomic scales, leading to major advances in rechargeable batteries for portable electronics, electric vehicles and large-scale grid storage. Also, global warming and diminishing fossil fuel reserves accelerate the search for efficient energy alternatives. The performance of energy storage devices depends crucially on the properties of their component materials. An excellent example of innovative materials science is the discovery of the rechargeable lithium battery.

Materials research based on computational methods now plays a vital role in characterizing and predicting the structures and properties of complex materials on the atomic scale. The simulations are able to predict the material properties at extreme conditions as well as supplement the experimental studies. Here we review our work based on first principles simulations to understand the diffusion mechanism of Li ion in superionic conductor Li₂O [1-2], LiMPO₄(M=Fe, Mn)[3] and LiAlSiO₄[4-6]. The comparison between the calculated and experimental neutron inelastic spectra for these compounds is shown in Fig 1. The general characteristics of the experimental features are well reproduced by the lattice dynamics calculations. The motivation and significant results from our studies on various compounds are discussed below.

**Soft-phonon mode in Li₂O**

The compound Li₂O belongs to the class of superionic conductors, which exhibit high ionic conductivity above 1200 K. In this case, Li ions are the diffusing species, while oxygen ions constitute the rigid framework. The material finds large applications mostly due to its high melting point, relatively low volatility and high Li atom density. At ambient conditions, Li₂O occurs in the anti-fluorite structure [7-9]. Oxygen ions are arranged in a face centered cubic (FCC) sub lattice with lithium ions occupying the tetrahedral sites.

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![Fig. 1: The comparison of the calculated (at 0 K) and experimental (at 300 K) neutron inelastic scattering spectra for LiAlSiO₄ and LiMnPO₄.](image-url)
The calculated phonon dispersion [1] relation (Fig. 2) at relaxed lattice parameter $a = 4.57 \, \text{Å} \, (0 \, \text{K})$ are in good agreement with the reported experimental data. The compound exhibits superionic transition in the vicinity of 1200 K. Hence, we have performed phonon calculations at various unit cell parameters corresponding to high temperatures. As expected, the phonon frequencies along all three directions are found to soften with the increase of volume[1]. The softening is found to be small for all the modes except for the lowest transverse acoustic (TA) branch along [110] direction at zone boundary.

The eigenvector of unstable transverse acoustic mode of Li$_2$O has been plotted (Fig. 3), which shows displacements of lithium atoms along [001] direction while the oxygen atoms are at rest. It is possible that the softening of these modes might be the precursor to the process of diffusion. At the superionic transition, some of the lithium atoms might just have sufficient energy to move from their ideal positions and start diffusing. Increasing the temperature could lead to migration of lithium ions along [001] direction.

Soft-phonon modes in LiMPO$_4$ (M=Fe, Mn)

Another important battery material LiMPO$_4$ (M= Fe, Mn), used as cathode material, crystallize in olivine type orthorhombic Pnma [10] space group analogous to mineral Triphylite structure. The structure comprises of discrete PO$_4$ tetrahedra and highly distorted oxygen octahedra about lithium and transition metal ion, M. The PO$_4$ tetrahedra are irregular, with two significantly different sets of O-O distances. We have performed the lattice dynamics and molecular simulations along with inelastic neutron scattering measurements to understand the diffusion of Li ions.

The calculated phonon frequencies of LiMPO$_4$ (M=Fe, Mn) along all the high symmetry directions (Fig. 2) are found to soften with increase of volume. However, the softening is found to be very large for one of the phonon branches along [100] direction. We find that in both the compounds the zone centre optic mode softens first, followed in quick succession by the zone-boundary mode along [100] direction with increasing volume.

For qualitative understanding of the atomic displacement in LiMnPO$_4$ compounds, we have plotted eigenvectors of unstable modes (Fig. 3). In case of the zone-centre mode at ambient volume the displacements of the Li atoms are maximum, while the amplitudes of other atoms are less but not negligible. The displacement of the lithium ions is only in the x-y plane. In the dynamically unstable regime, the amplitude of Li atoms has increased significantly. The Fe atoms are at rest, while the amplitude of P atoms decreased slightly and O atoms do not show any change. The component of displacement of Li atoms is non-zero along all the three directions but with the highest component along the x-direction.

We find that LiFePO$_4$ shows softening (Fig. 2) at a higher volume in comparison with the Mn counterpart. The percentage change in volume for initiation of phonon instability in LiMnPO$_4$ is much lesser as compared to LiFePO$_4$.

The main interest in these compounds stems from their use as battery materials. Lithium intercalation and subsequent delithiation are the main processes by which energy is transferred during its use as battery material. We have tried to unveil the role of phonons in the initiation of lithium movement crucial for the use of these materials as battery material. Our analysis shows that at ambient temperature, the
likely motion of lithium is in the x-y plane. If conducive conditions prevail, lithium might move in this plane.

**Ab initio molecular dynamics of LiAlSiO₄**

LiAlSiO₄ (β-eucryptite) is a very important one-dimensional superionic conductor. It possesses superionic conductivity along with anisotropic negative thermal expansion (NTE) behaviour[5,6,11,12]. LiAlSiO₄ has a hexagonal structure[13] (space group P6₃22) that expands in the ab-plane and contracts along the c-axis upon heating. It shows an overall very low volume thermal expansion [14,15] and has good mechanical stability. These properties make it a potential electrolyte for Li ion batteries [16]. Lithium is decorated in one-dimensional channels parallel to the hexagonal c-axis.

The room temperature structure has two types of channels[17], namely, ‘S’ type and ‘A’ type. In ‘S’ type channel Li atoms are coplanar with the Si atoms while in ‘A’ type channel Li atoms are coplanar with the Al atoms. There are three secondary (S) and one primary (A) channel in a single unit cell of the room temperature structure[17]. On heating at around 700 K, a phase transition occurs by disordering of Li among all the available sites along the c-axis. The high-temperature phase exhibits a one-dimensional superionic Li conduction.

We have performed ab initio molecular dynamical simulations to understand the mechanism of the high-temperature (HT) phase transition and superionic conduction in the HT phase. The mean square displacements of various atoms (Li, O, Al & Si) are calculated (Fig. 4a) from the time evolution of the trajectory of these atoms at room temperature (300K). The temperature, pressure and energies are well converged in these calculations. The calculated mean square amplitudes (Fig. 4a) show that the Li being lightest element has the highest but Al and Si being heavier has lower mean square amplitudes.

As simulation temperature is increased to 600 K, we see (Fig 4b) that although Al, Si, and O atoms have very small and almost constant values of mean square displacements, Li atom shows a sudden increase after 4 pico seconds. We analyzed the anisotropic mean square displacements (MSD) (Fig. 4c) for Li atoms and found that the MSDs show an anomalous value only along the hexagonal c-axis while it is negligible in the ab-plane. This implies that Li atoms move along the hexagonal c-axis with a jump like behaviour. When the trajectories of all individual atoms (Fig. 4d) are analyzed, we found that groups of three Li atoms are moving altogether. A group of three Li atoms belong to the same channel. The very first channel movement (Fig. 4d) occurs around a simulation time of 4 ps. This is found to be the ‘A’ type channel. All the Li atoms in this ‘A’ type channel are found to have squared-displacement of ~3.6 Å² which corresponds to a displacement of ~1.9 Å. This displacement is equal to c/6. This indicates that the ‘A’ type channel is transformed to the ‘S’ type channel. Afterwards, the Li atoms (three atoms together) in other channels also start moving along c-axis with displacement amplitude of about c/6 and c/3 etc. Hence Li atoms have a possibility to be present in all the available sites along the channels at 600K. All the

![FIG 4 The calculated mean-squared displacements (<u^2>) of various atoms of RT phase of β-eucryptite as a function of time (a) at 300K and (b) 600K. (c) Anisotropic mean-squared displacement (<u^2>) of Li averaged over all the Li atoms in the supercell and (d) u_0 of each individual Li atoms along c-axis at 600K as a function of time[4].](image-url)
channels become equivalent with a distribution of Li atoms at all the available sites. This gives rise to the high-temperature phase transition in β-eucryptite [13]. This transition was experimentally reported [13,18] at 698-758 K. In the high temperature phase, all channels become equivalent and hence the new symmetry reduces the 'a' (or 'b') lattice parameter to half of their original values. Experimentally[18] the high temperature structure of β-eucryptite is also known to have Li atoms positional disordering along the hexagonal c-axis.

The simulations performed at 800 K in the HT phase indicate increase in Li channel movements. At 800 K (Fig. 5a & Fig. 6a), the compound is already in high temperature structure, so all the Li containing channels are equivalent. The channel movement begins at smaller simulation time in comparison to that for 600 K, and some channels start moving coherently at the same time. The increasing squared displacements \( u^2 \) of Li atoms in these channels signify the diffusion in Li channels along the hexagonal c-axis. When temperature is raised to 1000 K (Fig. 5b & Fig. 6b), more numbers of channels are seen to be diffusing at even smaller simulation times. During the diffusion, there is correlation between the Li atoms in each channel which can be seen at 1000K (Fig. 5b & Fig. 6b). The diffusion of Li channels in this compound is found to be one-dimensional jump-like rather than continuous diffusion. At sufficiently high temperature of 1200 K (Fig. 6c), some of the Li atoms also started diffusing in the ab-plane; hence at high temperatures the intra-channel correlation of Li atoms decreases.

We have calculated the average diffusion coefficient for all the

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**Fig. 5:** The calculated \( u^2 \) of each individual Li atoms of HT-phase of β-eucryptite as a function of time along c-axis at (a) 800K (in 331 supercell), (b) 1000K (in 331 supercell)[4]

(a) \( T=800K, \) HT Phase Supercell (3×3×1)

(b) \( T=1000K, \) HT Phase Supercell (3×3×1)

**Fig. 6:** Trajectory of Li atoms in channels of β-eucryptite (HT-Phase) at (a) 800K and (b) 1000K. Key: AlO\(_4\)-Blue, SiO\(_4\)-Red, Initial Position of Li- Black, Time Evolution of Li- Green balls[4]
Li atoms in the supercell. The calculated diffusion coefficient (Fig. 7a) shows a sharp increase in magnitude around 600K. The calculated value of diffusion coefficient has magnitude ($\approx 10^{-7}$ m$^2$/s) comparable to that of atoms in liquids. So, the high temperature structure of $\beta$-eucryptite possesses a superionic Li conduction which is one dimensional in nature. The activation energy for Li jump diffusion can be obtained from the Arrhenius plot of diffusion coefficient. The calculated activation energy (Fig 7b) for diffusion of Li atoms is 0.33 eV which agrees with those calculated[6] from the nudged elastic band method (0.3-0.4 eV) and with the experimental[19] values of 0.6-0.8 eV.

Conclusions

First principles calculations of Li$_2$O, LiMPO$_4$ (M=Fe, Mn) and LiAlSiO$_4$ have been successfully used to understand the atomic vibrations and their role in ionic diffusion in these compounds. The calculated phonon dispersion relation in Li$_2$O and LiMPO$_4$, (M=Fe, Mn) as a function of volume suggests a significant phonon instability which may be related to initiating the diffusion of lithium ions. For LiAlSiO$_4$, ab-initio molecular dynamical simulations are used to understand the mechanism of the high-temperature phase transition and superionic conduction. The simulations for LiAlSiO$_4$ reveal one-dimensional jump-like diffusion of lithium ions in the compound.

References

20. S. Hull, T. W. D. Farley, W. Hayes, and M. T. Hutchings,