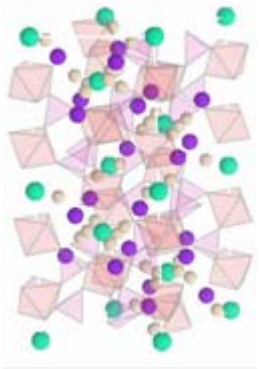
Computer Simulation Studies of Ionic Motion in NaSICon-type Solids



Padma Kumar P.

Department of Physics

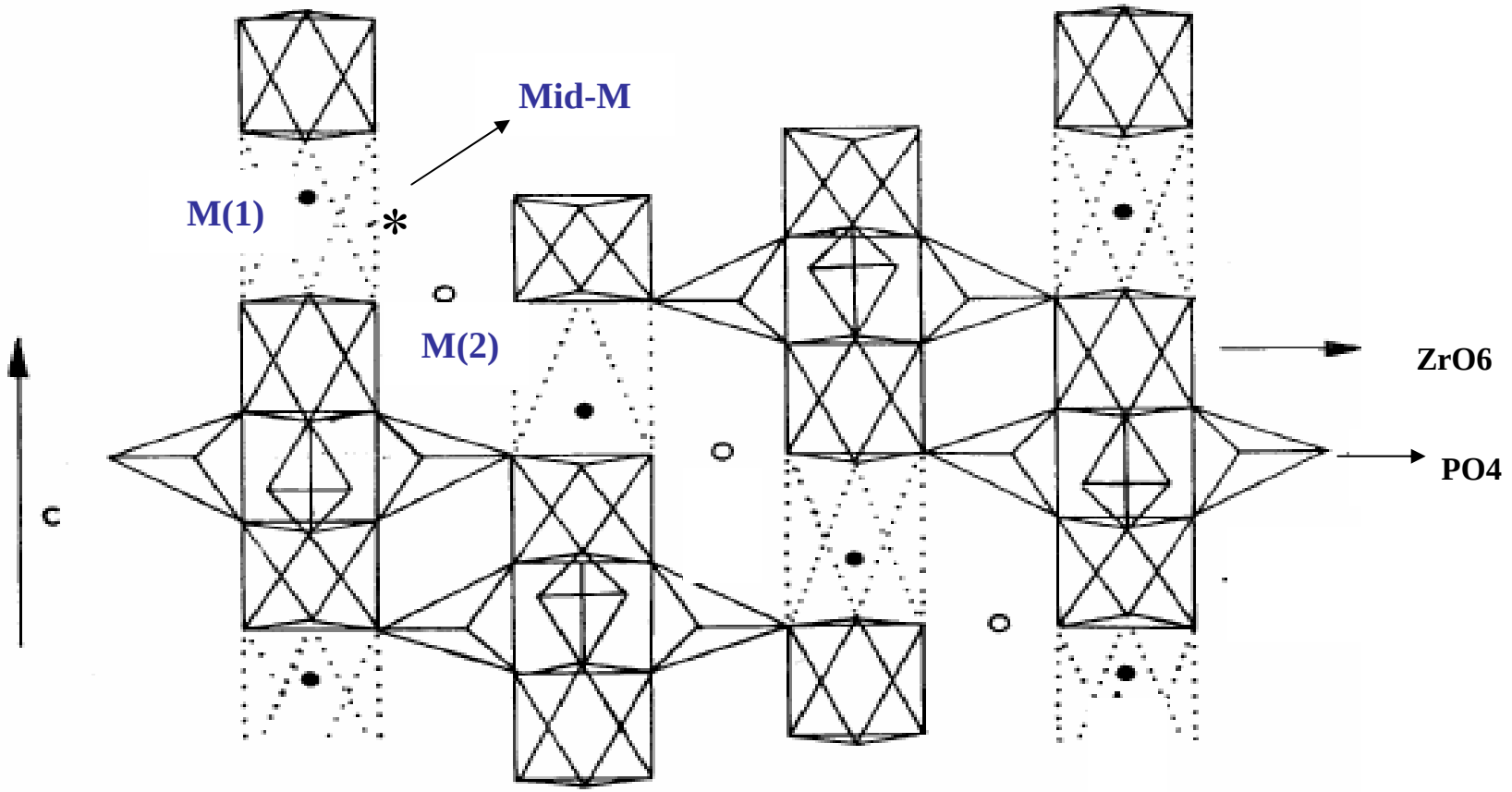
Indian Institute of technology Guwahati

Yashonath S.

Solid State and Structural Chemistry Unit

Indian Institute of Science Bangalore

NaSICon (*Na-SuperIonic CONductor*) Framework



The polyhedral framework structure of $NaZr_2P_3O_{12}$

Several alkali ion ("M") sites with ion channels connecting them!

NaSICon - The Big Family

A list of ions that can be substituted at the Na, Zr and P sites

site	ions that can be substituted
Na	H^+, Li^+, K^+, Rb^+, Cs^+, NH_4^+, Cu^+, Ag^+, Tl^+, H_3O^+, Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+2}, Mn^{+2}, Co^{+2}, Zn^{+2}, Pb^{+2}, Fe^{+3}, La^{+3} ...
Zr	Na^+, Ti^{+4}, Ge^{+4}, Sn^{+4}, Th^{+4}, U^{+4}, Nb^{+4}, V^{+3}, Cr^{+3}, Fe^{+3}, Co^{+3}, Ga^{+3}, In^{+3}, Mg^{+2}, Mn^{+2}, Cu^{+2}, Zn^{+2}, Ni^{+2} ...
P	Si^{+4}, As^{+5}, S^{+6} ...

■ Industrial Applications

- ✓**In batteries as solid electrolyte**
- ✓**As refractory materials, in high-T furnaces**
- ✓**Low thermal expansion materials**
- ✓**Nuclear waste disposals**

Etc…

- Most members stabilize in Rhombohedral $R\bar{3}c$

$$a = b \neq c; \alpha = \beta = 90^o; \gamma = 120^o$$

Hong, Mat. Res. Bull., **11**, 173 (1976)

Computer Simulations

Techniques Employed:

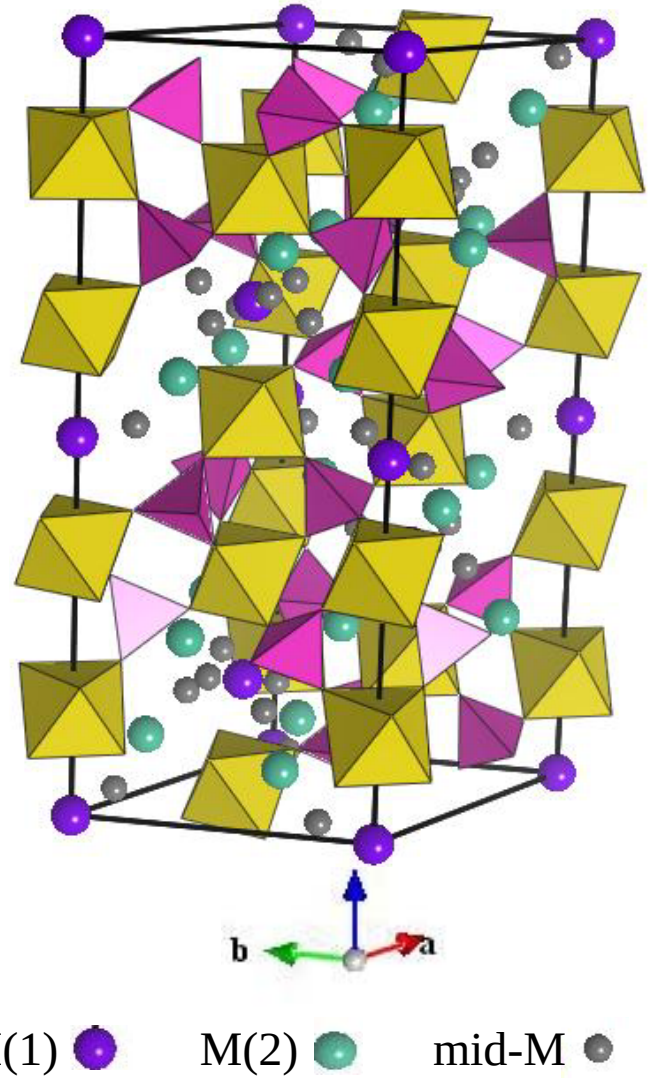
- Molecular Dynamics (MD)
- Monte Carlo (MC)

Systems to discuss:

I. $LiZr_2P_3O_{12}$ ("Li-SICon")

II. **Anomalous Conductivity with ion size**

III. $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ $(0 \leq x \leq 3)$



I) $LiZr_2P_3O_{12}$

Conductivity vs Temperature

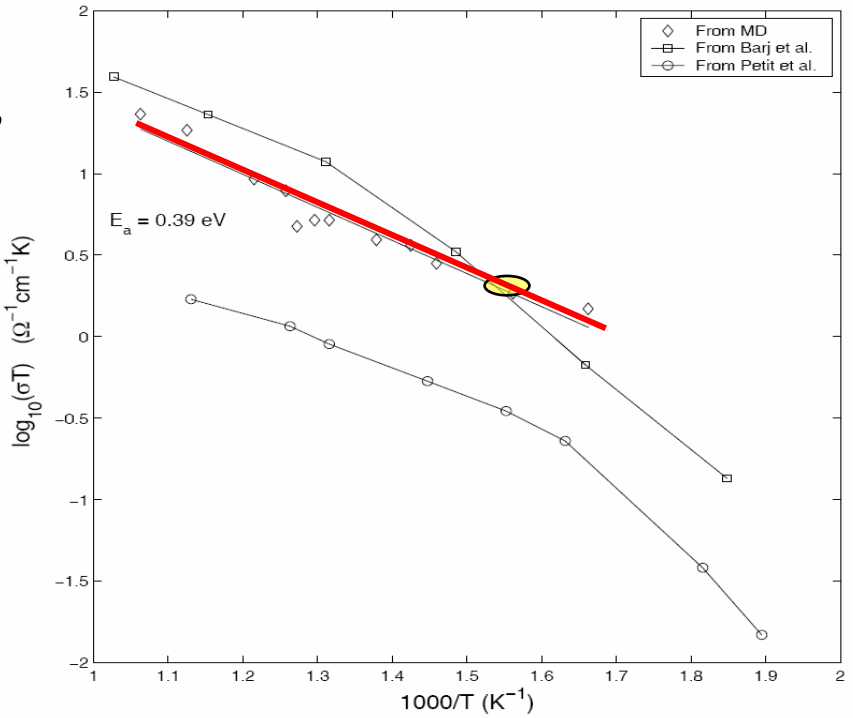
Ionic conductivity (Nernst-Einstein),

$$\sigma = nq^2 D / k_B T$$

n – number of ions per volume

q – charge of the ion

D – self diffusion coefficient



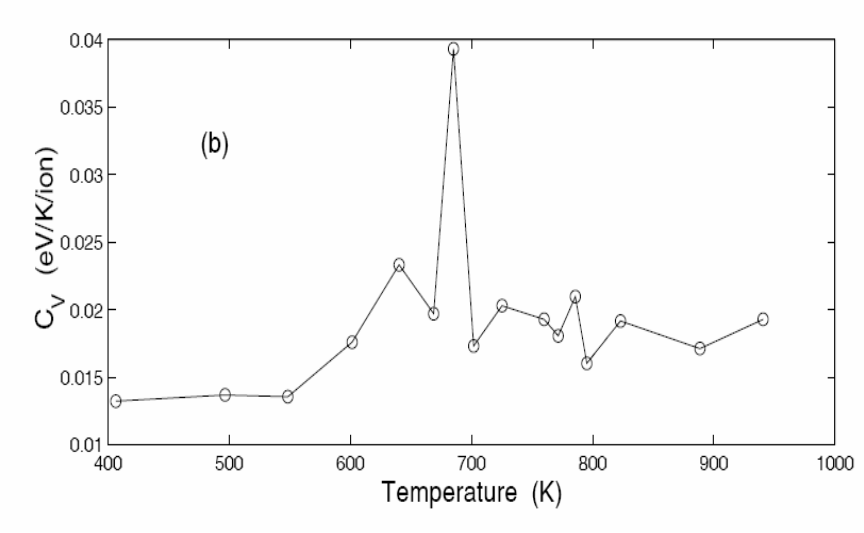
Arrhenius plot of conductivity.

✓The conductivity and activation energies are in good agreement with experiments

Padma Kumar and Yashonath, J. Phys. Chem. B, **105**, 6785 (2001).

Petit et. al., Mat. Res. Bull., **21**, 365 (1986).

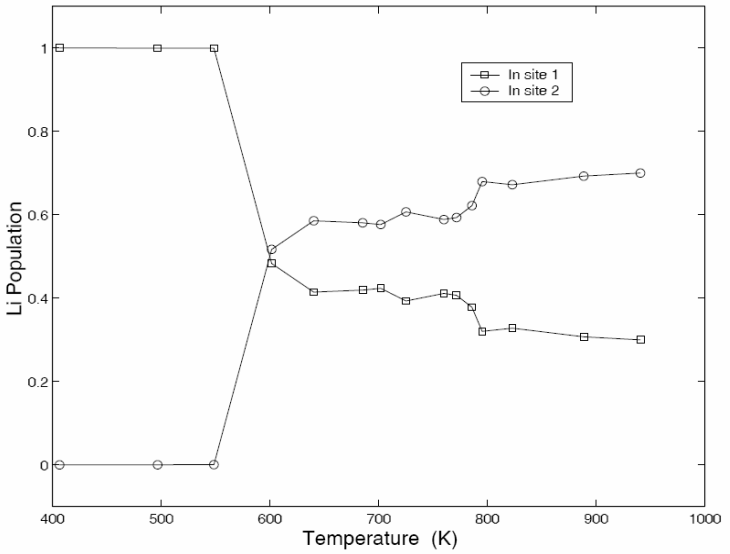
Phase Transitions



Heat capacity *vs* temperature

C_v suggests a higher order transition

Migration of Li-ions from M(1) to M(2) sites

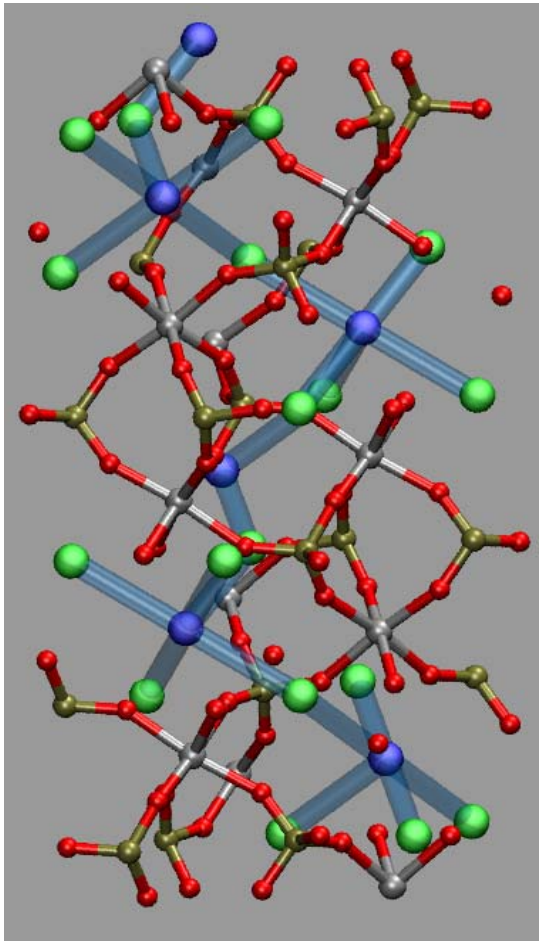


Population of Li in M(1) & M(2) sites with temperature

Microscopics of Ionic Motion

Residence and Hop-times of Li

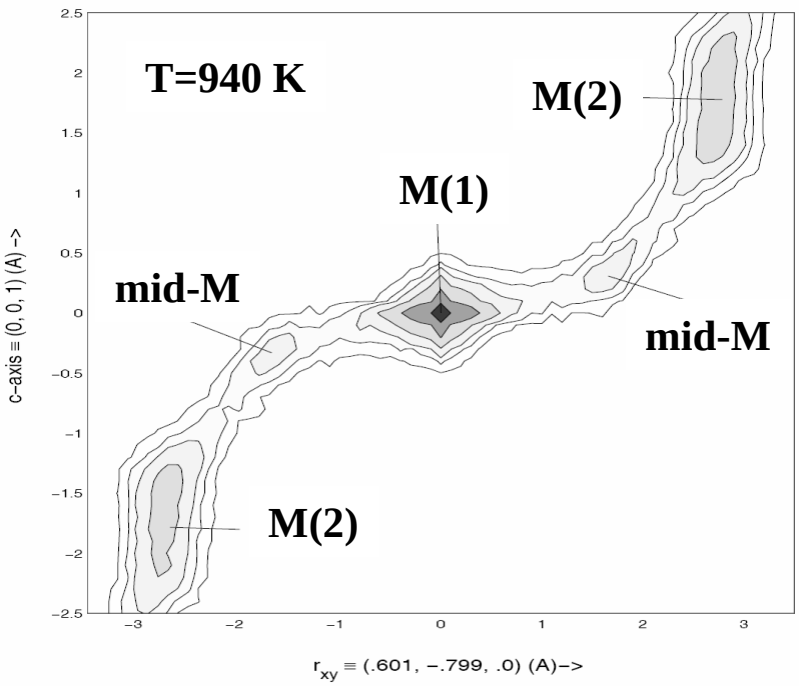
T K	Residence time (ps)		hop times (ps)			
	in **M(1)**	in **M(2)**	1-1	1-2	2-1	2-2
612†	82.1	48.7	none	0.33	0.37	0.51
			(.0000)	(.4993)	(.4980)	(.0027)
940†	5.9	12.9	0.44	0.28	0.28	0.42
			(.0012)	(.4841)	(.4838)	(.0308)



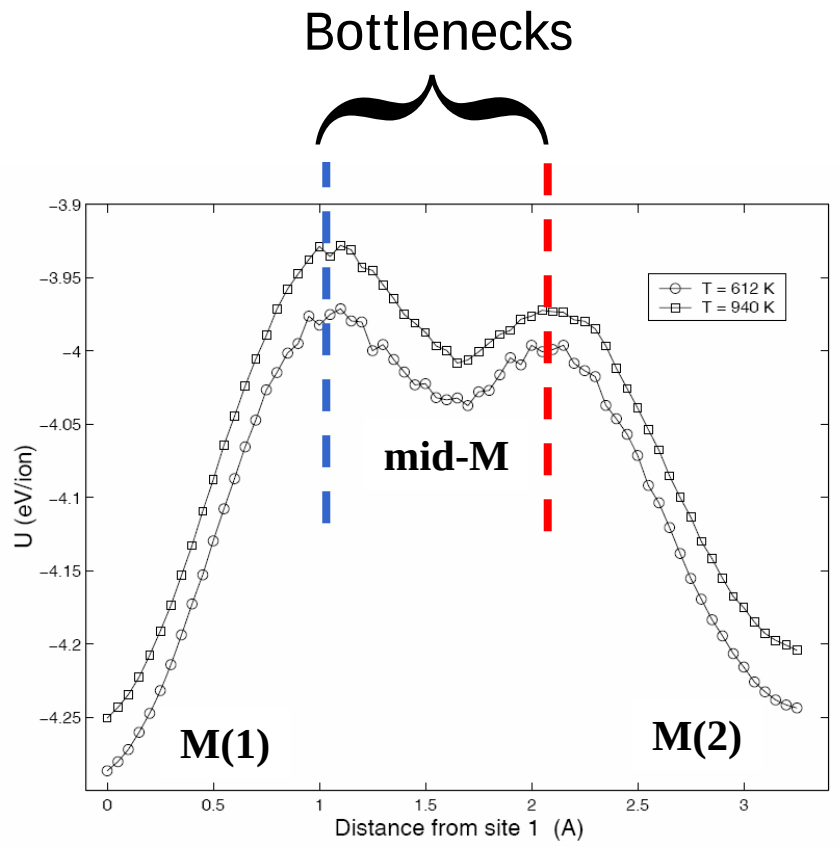
The conduction channel realized in NaSICons: **M(1)-mid-M-M(2)**

I) $LiZr_2P_3O_{12}$

...Microscopics of Ionic Motion



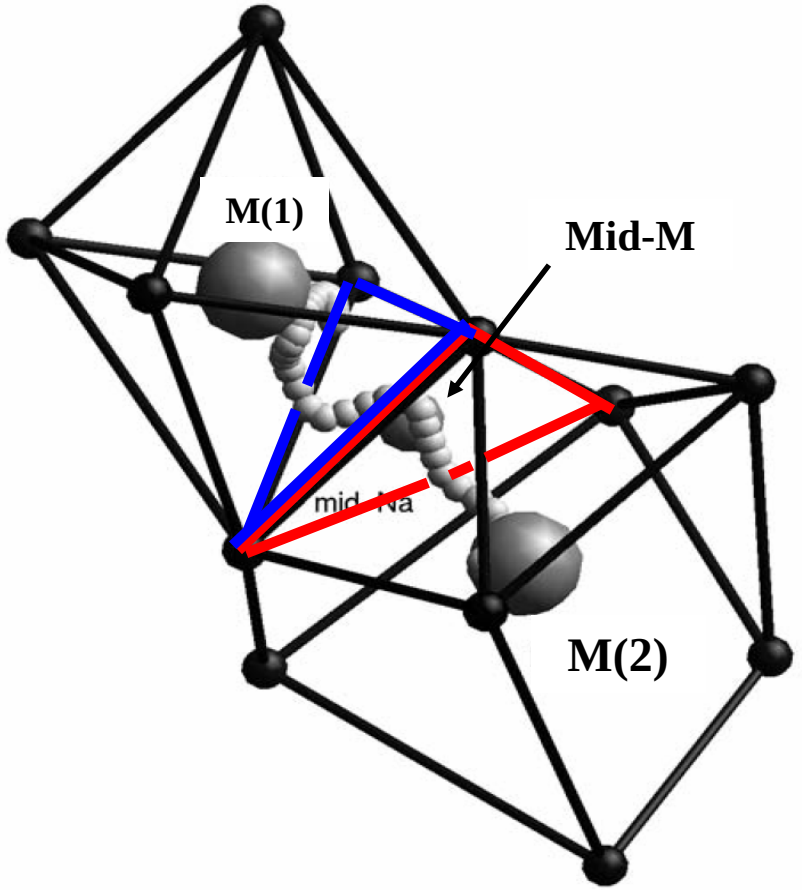
Li atomic density on a plane containing ***one*** M(1) and ***two*** M(2) sites



Potential energy profile of Li transport from M(1) to M(2)

...Microscopics of Ionic Motion

- Two triangular bottle necks for ionic motion.
- Circum radius of the bottlenecks:
  1. Rc = 2.194 Å
  2. Rc = 2.199 Å
- A curved trajectory of ions connecting M(1) – mid-M – M(2)



A typical MD trajectory showing ion hoping from M(1) to M(2).

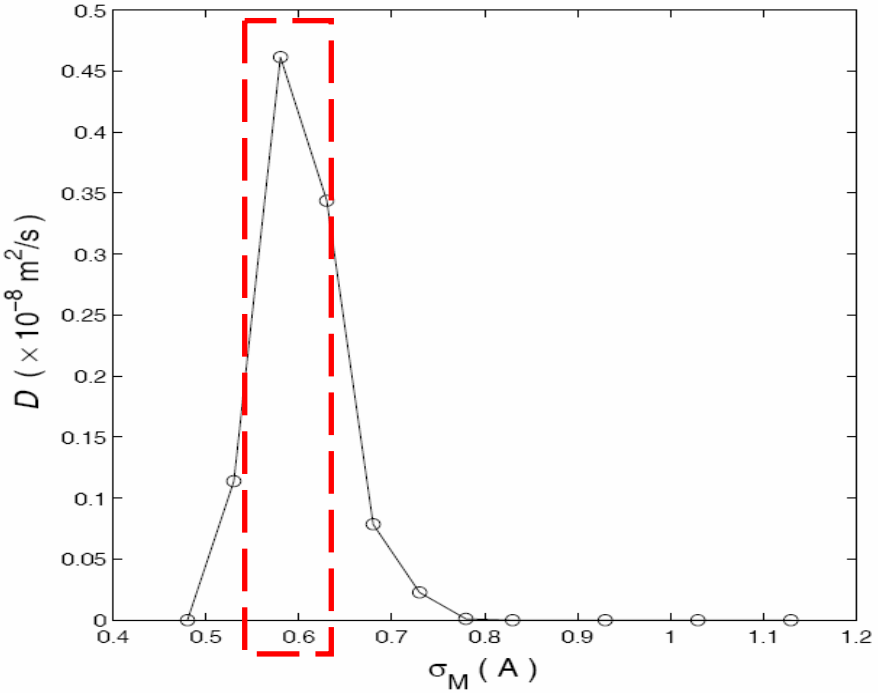
Anomalous conductivity with ion size

Q: What happens if the ions shrink?

A: Obviously, smaller ions diffuse faster!

Interionic potential:

$$\phi(r_{ij}) = \frac{q_i q_j}{r_{ij}} + \frac{A_{ij}(\sigma_i + \sigma_j)^{n_{ij}}}{r_{ij}^{n_{ij}}} - \frac{C_{ij}}{r_{ij}^{6}}$$

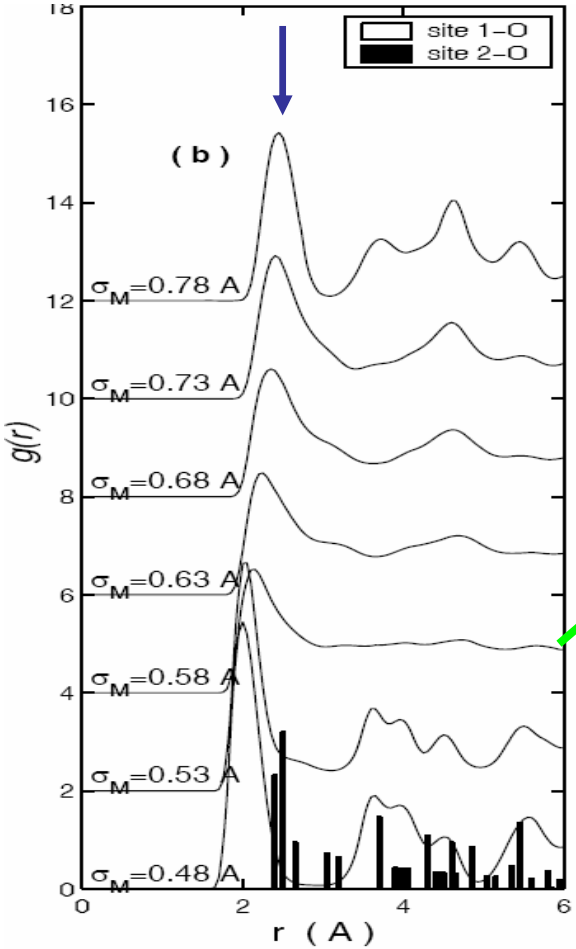


Diffusion profile with ion-size

Padma Kumar and Yashonath, J. Phys. Chem. B, **106**, 3443 (2002).

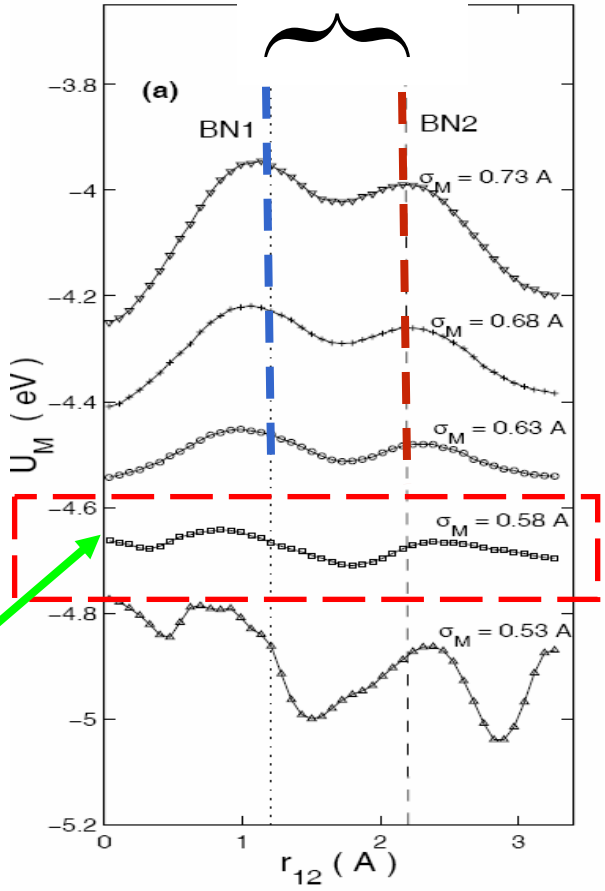
…Anomalous Diffusion

- The preferred ion-oxygen distance shrinks with the size of the mobile ions.
- As this distance match that of the bottleneck radius (Rc ≈ 2.195 Å) the channel offers low barrier for the diffusion of the ions!



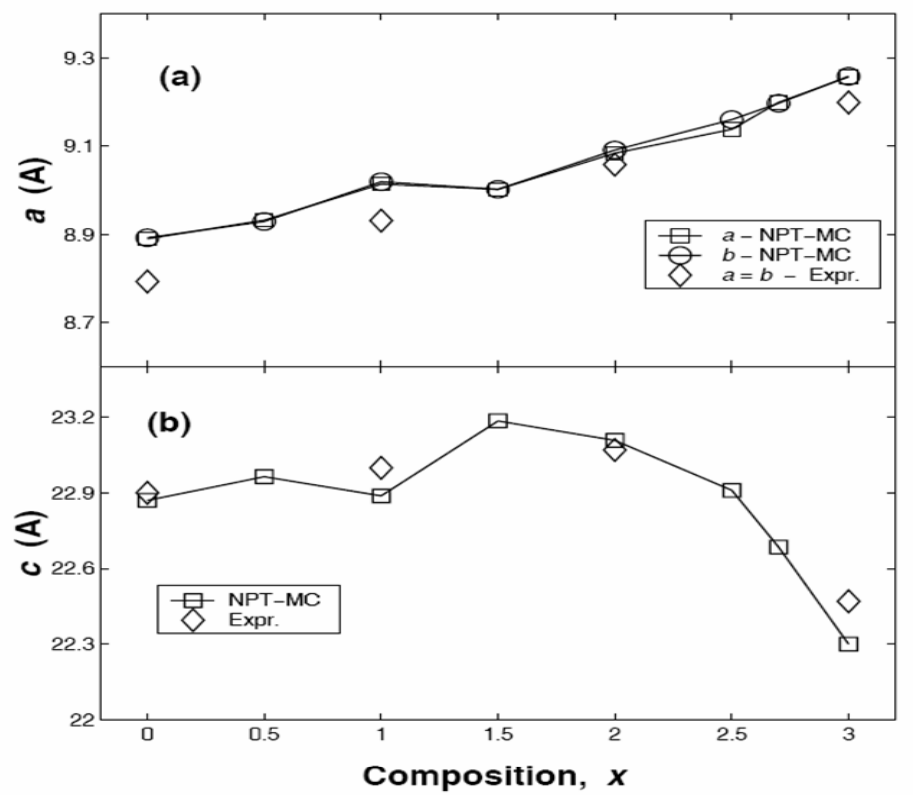
Ion-Oxygen RDFs

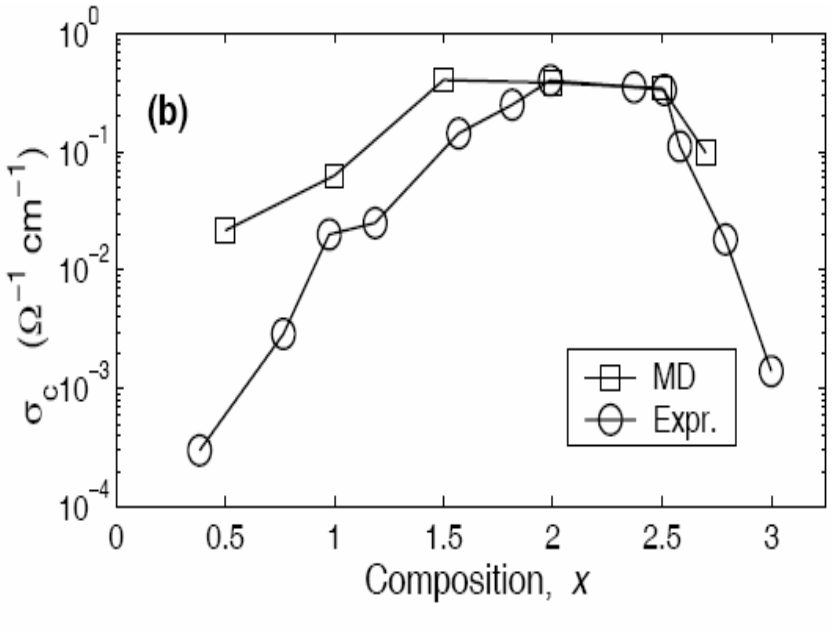
Bottlenecks



Potential energy profile of ion migration from M(1) to M(2)

Cell dimensions & Conductivity with composition, x





- Monotonic variation of ***a***
- Anomalous variation of ***c***
- ***C*** Maximum occur around x=2

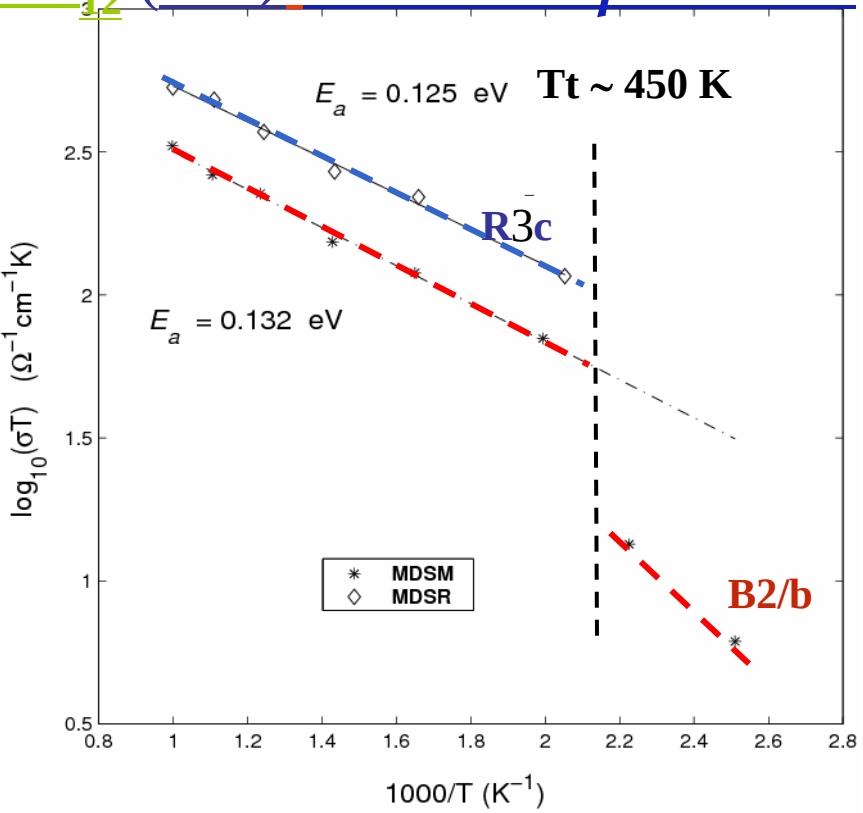
- **σ** Maximum occur around x=2 !

Padma Kumar and Yashonath, J. Am. Chem. Soc, **124**, 3828 (2002).

Conductivity of $Na_3Zr_2Si_2PO_{12}$ (x=2) with Temperature

MD Starting from the distorted L. T. monoclinic structure

MD Starting from the H. T. rhombohedral structure



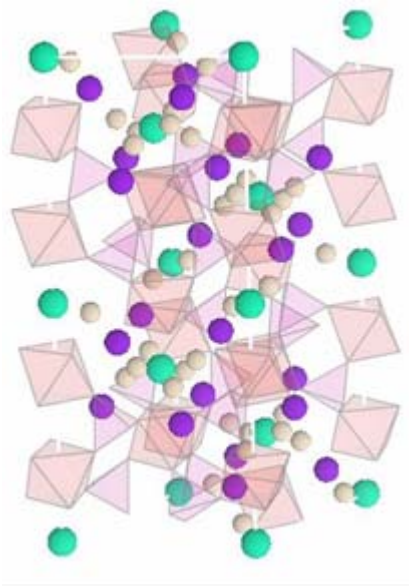
Arrhenius plot of conductivity.

Ph Colomban, Solid State Ionics, 21, 97 (1986).

Conclusions

- Atomistic computer simulations offer an excellent ***complimentary*** technique to understand microscopics ion transport, such as,
  - **The mechanism of normal ⇔ superionic transition.**
  - **The nature of ion transport (jump vs smooth diffusion).**
  - **Microscopic energetics of ionic motion.**
  - **Understand site preferences of small ions.**
  - **Identify the preferred conduction channel**.

- Have some degree of capability to predict the factors that enhance ion transport in solids.
  - **Useful in tailor making of fastion conductors.**



Thank you