A new approach for the comprehensive analysis of the diffusion process in crystalline ion conductors with point defects

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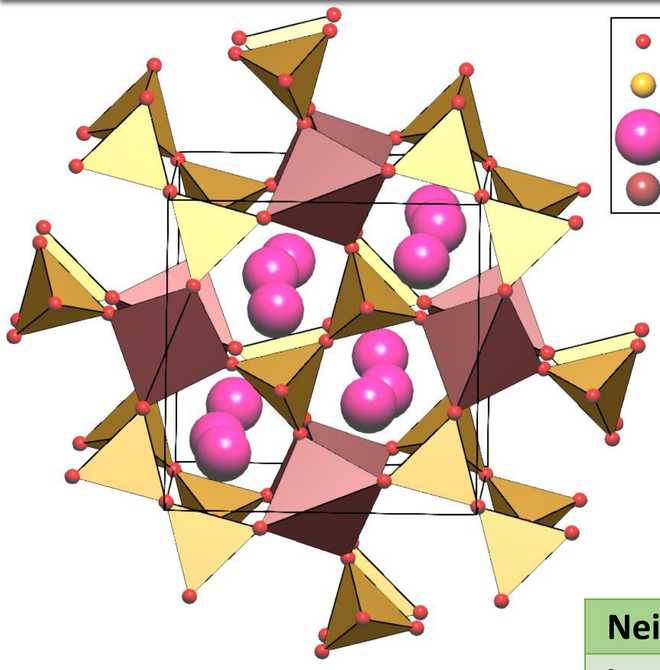
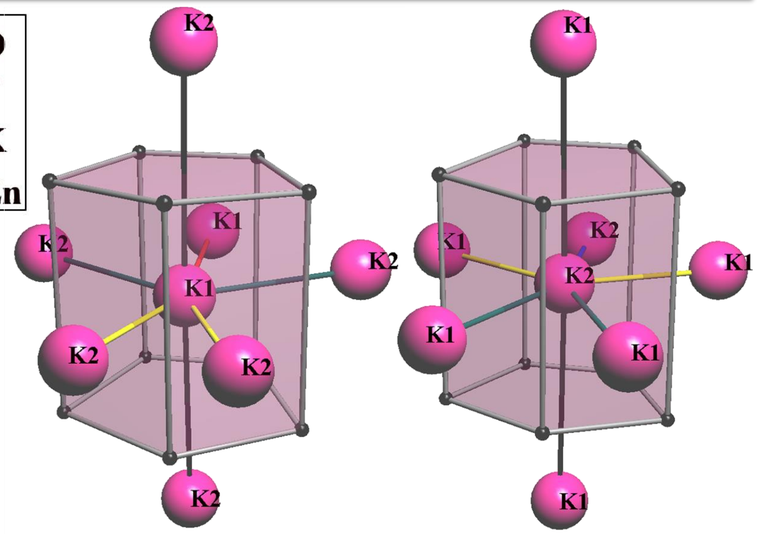
One of the most common approaches for computing the ion transport properties is the nudged elastic band (NEB) method coupled with the density functional theory (DFT). However, the significant computational complexity of the DFT does not allow to apply the NEB (within DFT) for a comprehensive analysis of disordered crystalline materials. It is due to the fact that even at the low doping levels (or point defects concentration) there is a vast range of possible structure configurations. On the other hand, the low-cost computation methods, such as Voronoi partition or bond valence sum landscape analysis, cannot provide reliable results in comparison with sophisticated NEB-DFT approach. In this work, we present an alternative fast and accurate algorithm for calculation of the lowest energy periodic ion migration map in crystalline materials based on the topological analysis of electron density distributions. We demonstrate that the proposed method can be used as a new tool for analysis of ion diffusion processes as well as fine first approximation for the subsequent NEB calculations. Due to the low requirements on the computational resources, the algorithm allows to carry out comprehensive analysis of doped and disordered materials as well as high throughput searching for new crystalline ion conductors.

Searching for the neighbor ion positions by means Voronoi decomposition



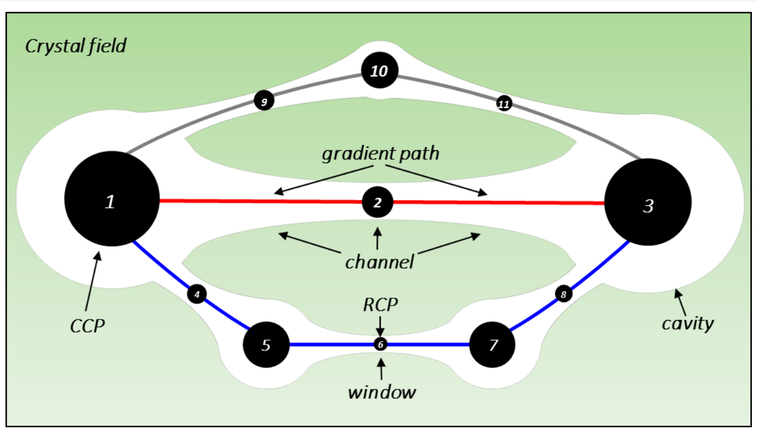
$K_2(ZnP_2O_7)$ (ICSD 95959)



Voronoi polyhedra of K in K-sublattice

Neighbors	K_2-K_2	K_1-K_2	K_1-K_1	K_1-K_2	K_1-K_2
Length (Å)	3.414	3.940	4.188	4.460	5.796

Bader analysis and ion migration path

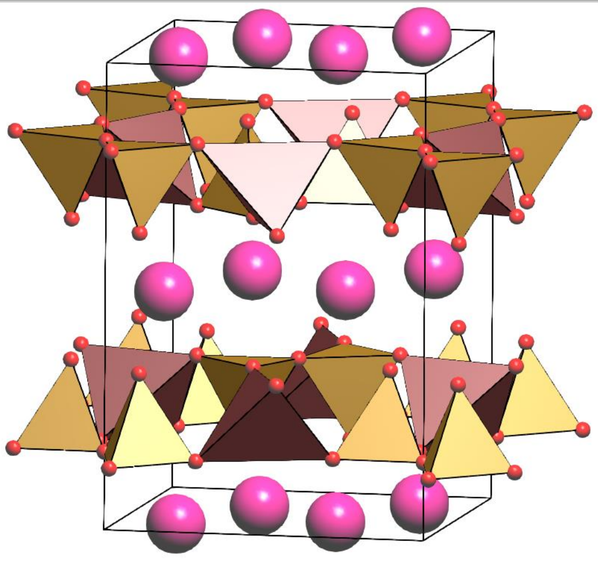


Possible trajectory from 1 to 3	Maximal ρ along the trajectory
1-2-3	$\rho(RCP_2)$
1-9-10-11	$\rho(RCP_{11})$
1-4-5-6-7-8-3	$\rho(RCP_6)$

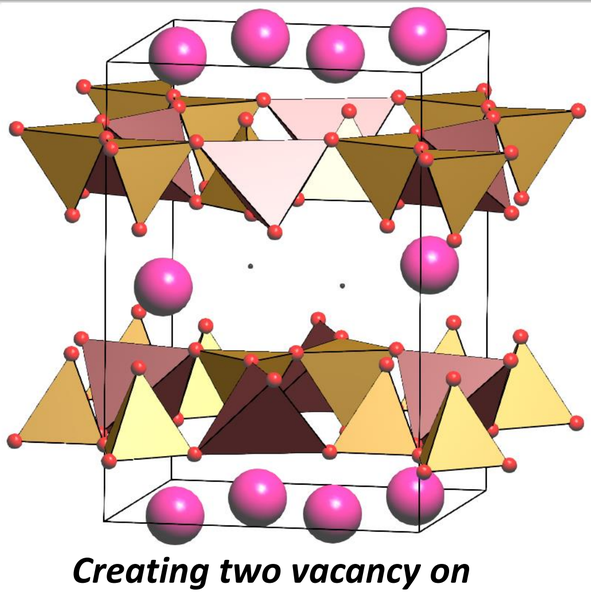
$\rho(CCP_1) < \rho(CCP_3) > \rho(CCP_5) > \rho(CCP_7) > \rho(CCP_{10}) > \rho(RCP_2) > \rho(RCP_9) > \rho(RCP_4) > \rho(RCP_8) > \rho(RCP_{11}) > \rho(RCP_6)$

In our model we consider the ion migration process as moving of negative point charge in the crystal field. Thus the most favorable migration trajectory of the ion between two position is the trajectory with the minimal value of electron density (ρ) along the path. The difference of minimum and maximum value of ρ along the path characterizes the value of the migration barrier.

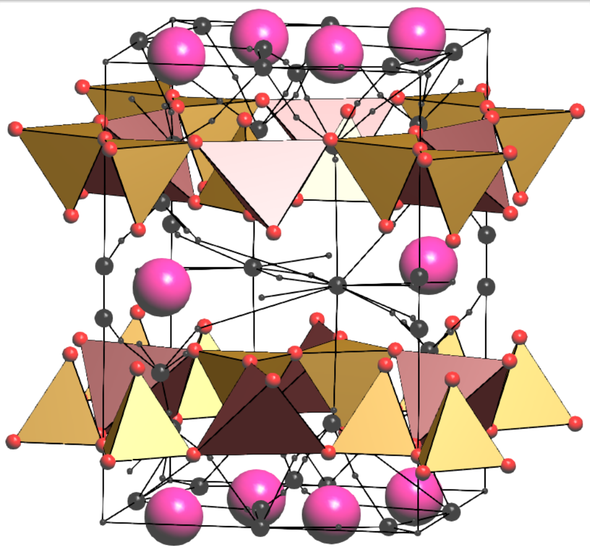
The algorithm of searching for the migration trajectory



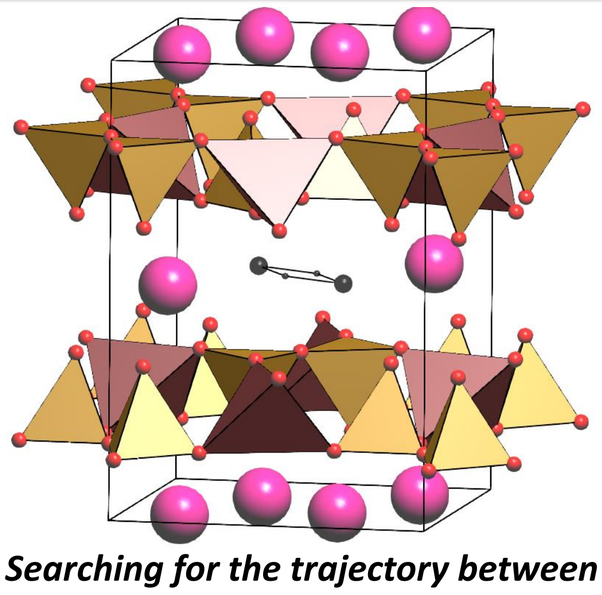
Decreasing the symmetry to P1



Creating two vacancy on the ends of the path

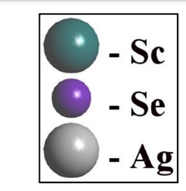


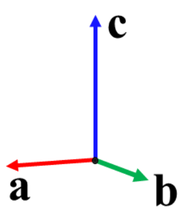
Calculating the ring path net

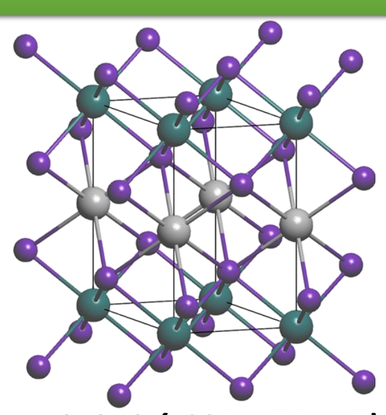


Searching for the trajectory between two CCP in ends of the path

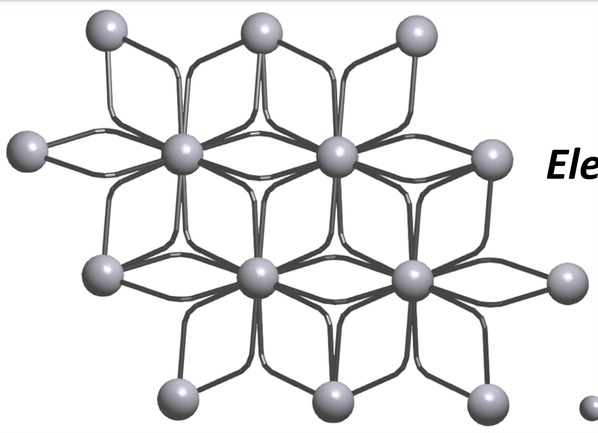
NEB migration trajectory vs ring paths







AgScSe2 (ICSD 155115)

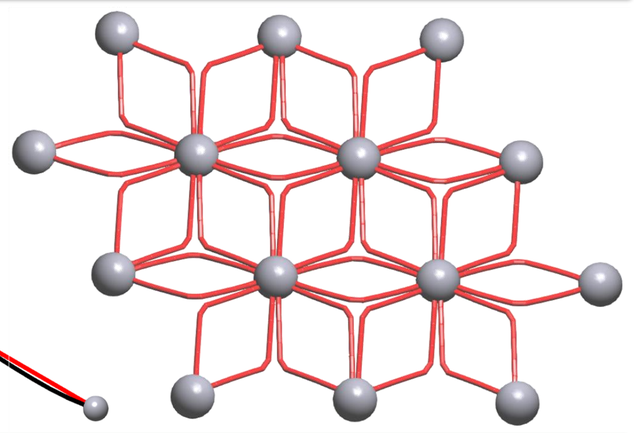


The lowest energy migration map

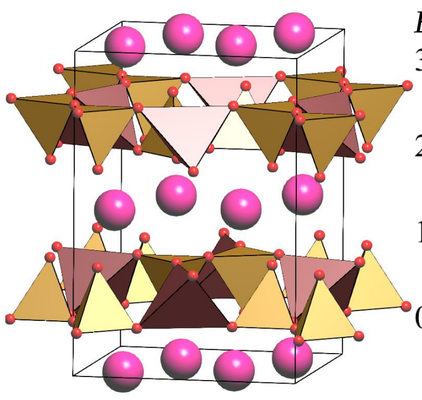
Electron density approach

NEB

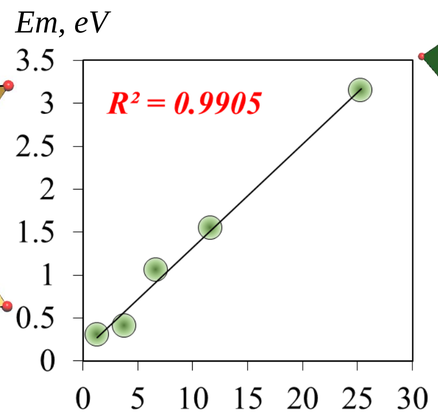
Ion migration trajectory

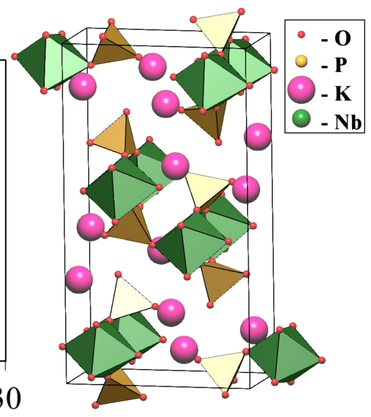


Ion migration energy calculated by means of climbing image NEB within DFT vs migration barrier evaluated by electron density approach

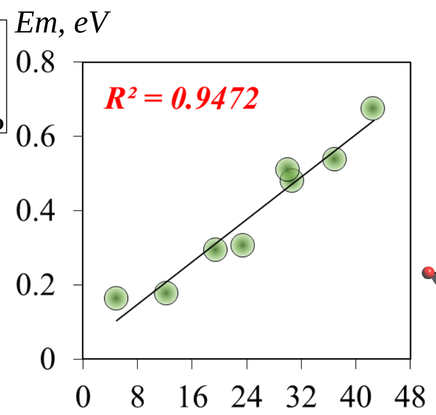


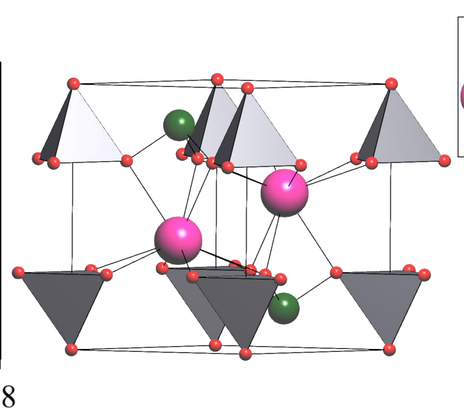
$K_2(ZnP_2O_7)$ (ICSD 95959)



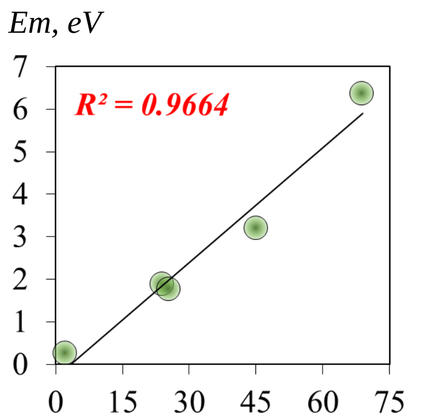


$K_3(NbP_2O_9)$ (ICSD 72873)





$K_2(Al_2Sb_2O_7)$ (ICSD 280310)



Conclusions:

- **We have proposed a new algorithm for the comprehensive analysis of the diffusion process in crystalline ion conductors.**
- **The algorithm was successfully applied for the analysis of ion migration map in crystalline K and Ag ions conductors.**
- **We have shown that the trajectory as well as the value of the migrations barriers calculated by our algorithm have a good agreement with results of climbing image NEB within DFT.**