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## Revealing the Mechanism of Sodium Diffusion in $\text{Na}_x\text{FePO}_4$ Using an Improved Force Field

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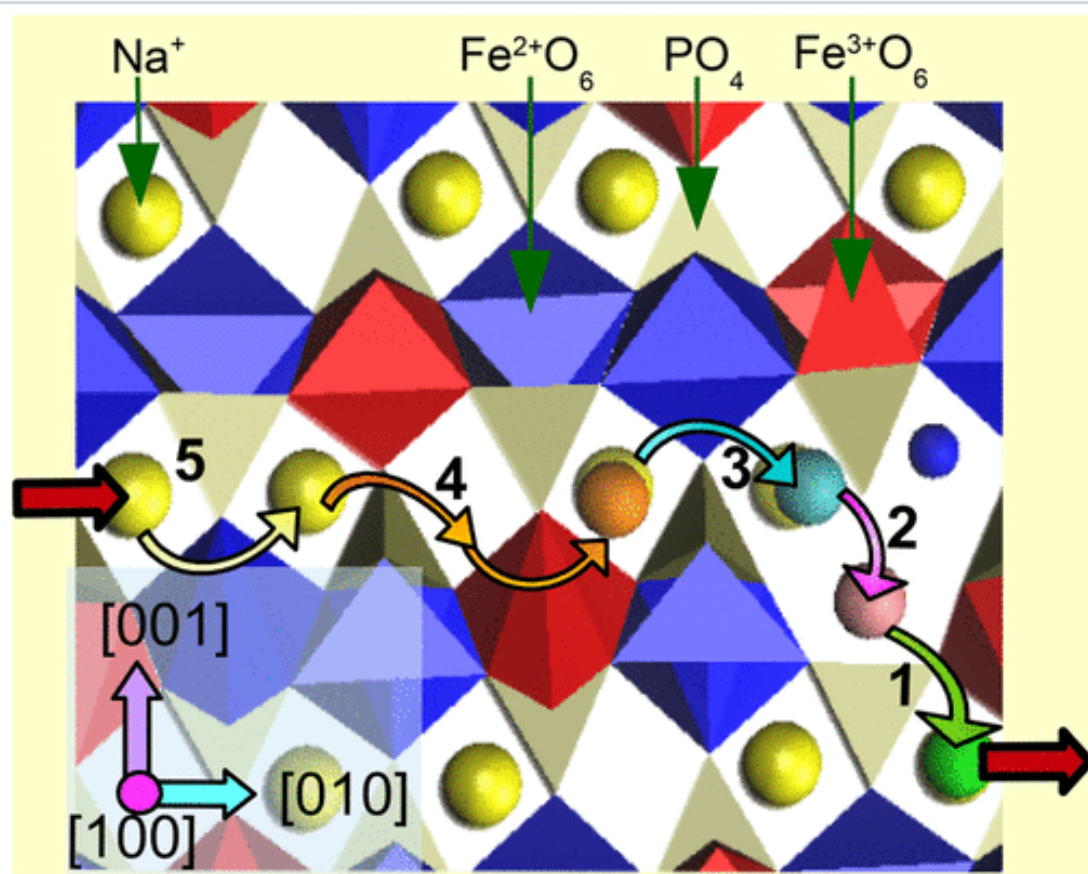
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### Abstract



Olivine  $\text{NaFePO}_4$  is a promising cathode material for Na-ion batteries. Intermediate phases such as  $\text{Na}_{0.66}\text{FePO}_4$  govern phase stability during intercalation-deintercalation processes, yet little is known about  $\text{Na}^+$  diffusion in  $\text{Na}_x\text{FePO}_4$  ( $0 < x < 1$ ). Here we use an advanced simulation technique, Randomized Shell Mass Generalized Shadow Hybrid Monte Carlo Method (RSM-GSHMC) in combination with a specifically developed force field for describing  $\text{Na}_x\text{FePO}_4$  over the whole range of sodium compositions, to thoroughly examine  $\text{Na}^+$  diffusion in this material. We reveal a novel mechanism through which  $\text{Na}^+/\text{Fe}^{2+}$  antisite defect formation halts transport of  $\text{Na}^+$  in the main diffusion direction [010], while simultaneously activating diffusion in the [001] channels. A similar mechanism was reported for  $\text{Li}^+$  in  $\text{LiFePO}_4$ , suggesting that a transition from one- to two-dimensional diffusion prompted by antisite defect formation is common to olivine structures, in general.