Superionicity in $\text{Na}_3\text{PO}_4$: A Molecular Dynamics Simulation

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Superionicity in Na$_3$PO$_4$: A molecular dynamics simulation

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Fast ionic conduction in solid Na$_3$PO$_4$ is studied by use of molecular dynamics simulation based on the modified Lu-Hardy approach. We obtain reasonable agreement with experiment for the structural transition and diffusion of the sodium ions. All the sodium ions are found to contribute comparably to the high ionic conductivity. The results of the simulation are discussed in terms of the relative magnitude of the two proposed transport mechanisms: percolation and paddle-wheel. It appears to us that the percolation mechanism dominates the sodium diffusion.

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I. INTRODUCTION

Fast ion conducting crystals have attracted much attention due to their application to solid electrolyte. In particular, sodium orthophosphate (Na$_3$PO$_4$) has served as a model system for investigating the fundamental mechanism of the unusually high ion conductivity, termed “superionicity.” Crystallographic studies revealed that in solid Na$_3$PO$_4$ there are two phases separated by a first order transition at 598 K: The low-temperature α phase has a tetragonal structure; in the high-temperature γ phase, the orientationally disordered phosphate anions form a face-centered cubic (fcc) lattice, which is rather stable up to the melting point ~1723 K, and the sodium cations occupy all the octahedral and tetrahedral interstitial sites of the fcc lattice. Thus, a question immediately comes to mind: “How can the sodium ions diffuse through such a dense packing lattice?” As we can see this is quite different from another model superionic solid, Li$_2$SO$_4$, in which the vacant octahedral interstitials provide natural passages of fast lithium diffusion. Despite extensive effort made to unveil the complex dynamic cation-anion correlation in γ-Na$_3$PO$_4$ for last two decades, the mechanism governing sodium transport in γ-Na$_3$PO$_4$ is still controversial.

The ongoing debate has been focused on the preference of two possible mechanisms: (i) “percolation,” in which the substantial (~3%) volume expansion above the structural transition facilitates the sodium diffusion through the more open structure, and (ii) “paddle-wheel,” in which the sodium ions are impelled via coupling with the reorientation of their neighboring phosphate anions. So far, the experimental identification of the sodium superionicity mechanism was confused by the fact that the structural transition to the high-temperature rotor phase is always accompanied by a sudden increase in volume. Consequently, a mixed mechanism was recently suggested from reverse Monte Carlo modelings of neutron diffraction data.

On the theoretical side, computer molecular dynamics simulations were introduced to probe at the atomistic level structural transitions and ionic transport in solids. A MD simulation of Na$_3$PO$_4$ was recently reported by Har-
TABLE I. Structural parameters and vibration frequencies (\textsuperscript{1}cm) of \textsuperscript{3}PO\textsubscript{4}\textsuperscript{3−} in Na\textsubscript{3}PO\textsubscript{4}.

<table>
<thead>
<tr>
<th></th>
<th>P-O distance (Å)</th>
<th>O-P-O angle (°)</th>
<th>E</th>
<th>(T_2)</th>
<th>(A_1)</th>
<th>(T_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment\textsuperscript{a}</td>
<td>1.550±0.007</td>
<td>109.467±0.512</td>
<td>435</td>
<td>573–586</td>
<td>943</td>
<td>1013–1108</td>
</tr>
<tr>
<td>Theory\textsuperscript{b}</td>
<td>1.568</td>
<td>109.471</td>
<td>425</td>
<td>610</td>
<td>923</td>
<td>1062</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Neutron diffraction data (Ref. 4) and Raman spectroscopy (Ref. 20).
\textsuperscript{b}Hartree-Fock calculations using GAUSSIAN 98 with the 6-31\textsuperscript{g} basis set on the P and O atoms (Ref. 21).

An essential step in the LH approach is partitioning the molecular charge density into the atomic constituents. The charge density of the phosphate anion in solid Na\textsubscript{3}PO\textsubscript{4} was approximated by the Hartree-Fock charge density of gas phase PO\textsubscript{4}\textsuperscript{3−}. This was justified by comparing the calculated molecular geometry and vibrational frequencies of PO\textsubscript{4}\textsuperscript{3−} with experiments on solid Na\textsubscript{3}PO\textsubscript{4}, as shown in Table I.

In this paper, we used the modified version of the LH approach where the atomic electron densities on the P and O atoms were obtained by a fitting scheme that preserved the monopole, dipole and quadrupole moments of the PO\textsubscript{4}\textsuperscript{3−}. The resulting charges were 1.863\textsubscript{e} for P and −1.216\textsubscript{e} for O, together with the full ionic charge of +1\textsubscript{e} for Na. With this set of effective charges, the simulated \(\alpha\)–\(\gamma\) transition temperature \(T_c\) was found to be 200 K higher than the experimental value and lattice constants 5% too small. Considering that in the dense packing lattice charge transfer between the Na and the PO\textsubscript{4} is likely to develop, we obtained \(T_c\) ∼ 620 K and the lattice parameters within 3% of experiment, as expected. A broad peak of \(g_{\text{OO}}\) (at 2.6 Å) manifests the tetrahedral shape of the anion groups remains almost unchanged during the simulation. \(g_{\text{NaP}}\) is the flattest as expected. A broad (double peaked) structure in the first peak of \(g_{\text{NaP}}\) results from tetrahedral Na-P and octahedral

![FIG. 1. Temperature variation of (a) lattice constants and (b) volume (per 4 formula units) of Na\textsubscript{3}PO\textsubscript{4} determined by MD simulation.](Image)

TABLE II. Relaxed structural parameters (Wyckoff positions) for α-Na\textsubscript{3}PO\textsubscript{4} (space group P\textsubscript{4}2\textsubscript{1}c). \(a=10.5159(10.8111)\) Å, \(b=a\), \(c=6.5126(6.8183)\) Å. Data given in parentheses are experimental values from room temperature neutron diffraction (Ref. 6).

<table>
<thead>
<tr>
<th>Atom</th>
<th>(X)</th>
<th>(Y)</th>
<th>(Z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(8e)</td>
<td>0.2655(0.2592)</td>
<td>−0.0150(−0.0124)</td>
<td>0.2299(0.2231)</td>
</tr>
<tr>
<td>O1(8e)</td>
<td>0.1688(0.1642)</td>
<td>−0.0387(−0.0750)</td>
<td>0.3687(0.3512)</td>
</tr>
<tr>
<td>O2(8e)</td>
<td>0.3817(0.3768)</td>
<td>−0.0929(−0.0993)</td>
<td>0.1995(0.2049)</td>
</tr>
<tr>
<td>O3(8e)</td>
<td>0.2054(0.2074)</td>
<td>0.0112(0.0162)</td>
<td>0.0194(0.0235)</td>
</tr>
<tr>
<td>O4(8e)</td>
<td>0.3095(0.3050)</td>
<td>0.1104(0.1043)</td>
<td>0.3293(0.3288)</td>
</tr>
<tr>
<td>Na1(8e)</td>
<td>0.2541(0.2556)</td>
<td>0.0372(0.0330)</td>
<td>0.6908(0.6962)</td>
</tr>
<tr>
<td>Na2(8e)</td>
<td>0.2201(0.2229)</td>
<td>0.2366(0.2405)</td>
<td>0.0385(0.0424)</td>
</tr>
<tr>
<td>Na3(2a)</td>
<td>0.0000(0.0000)</td>
<td>0.0000(0.0000)</td>
<td>0.0000(0.0000)</td>
</tr>
<tr>
<td>Na4(2b)</td>
<td>0.0000(0.0000)</td>
<td>0.0000(0.0000)</td>
<td>0.5000(0.5000)</td>
</tr>
<tr>
<td>Na5(4d)</td>
<td>0.0000(0.0000)</td>
<td>0.0000(0.0000)</td>
<td>0.0489(0.0477)</td>
</tr>
</tbody>
</table>
In contrast, the conductivity of the Na is high with the self-
diffusion constant being $1.22 \times 10^{-6}$ cm$^2$/s, comparable favorably with the value, $1.45 \times 10^{-6}$ cm$^2$/s, extracted from neutron scattering experiments performed at $T=1073$ K, which is the highest-temperature experimental datum available to us.

We also examined the different behaviors of the octahedral and tetrahedral Na.$^{25}$ As shown in Fig. 3, we observe that both tetrahedral and octahedral Na ions are highly diffusive at $T=1280$ K; their self-diffusion constants are $1.07 \times 10^{-6}$ and $1.52 \times 10^{-6}$ cm$^2$/s, respectively. The octahedral Na is more mobile than the tetrahedral Na. We attribute this to the fact that the octahedral Na have some more spacious environment—the shortest octahedral Na-P distance is slightly larger than the shortest tetrahedral Na-P distance, thus favoring the percolation mechanism. Our finding is qualitatively different from Harrison et al.‘s conclusion that the tetrahedral Na were tightly constrained within their interstitial sites. We also noticed that Harrison et al.‘s conclusion was based on their simulation performed at $T=1000$ K for 50 ps, and similar results can be drawn from our simulation at $T=980$ K (see the inset of Fig. 3). Hence, we found there is a characteristic temperature $T^*$ (considerably higher than $T_c$) above which sodium superionicity becomes observable during a MD simulation over the picosecond range. $T^*$ can be identified in Fig. 4, where we show the temperature variation of the mean square displacement $U=\langle |\mathbf{u}_i|^2 \rangle$, where $\mathbf{u}_i$ is the thermal displacement of atoms $i$ from its average position and the angular brackets refer to an ensemble average over a time of 20 ps. In Fig. 4, there are three noticeable features: (i) The O mean square displacement increases by 278% above 600 K, consistent with the picture that the rotational motion of the PO$_4$ has been largely enhanced above the phase transition temperature. (ii) The displacement of octahedral Na is generally larger than that of tetrahedral Na. (iii) Both tetrahedral and octahedral Na displacements increase dramatically above $T^*\approx1200$ K; this striking feature indi-
cates that sodium superionicity becomes observable in our 20-ps simulations.

The local motion of the Na ions is illustrated in Fig. 5, where the ellipsoids represent the root-mean-square deviations of the atoms from their average positions and thus indicate the thermal motions of these atoms. It is evident in Fig. 5(d) that the pathway of sodium jumping is primarily between octahedral and tetrahedral sites. Such Na ions motion can be understood in the following way: the direct connection between the interstitial sites are from octahedra to tetrahedra since they share faces, while the octahedra are linked only by edge and the same is true for the tetrahedra. Thus, there is no qualitative difference in the behavior of tetrahedral and octahedral Na. In real crystals, a certain number of lattice vacancies like Schottky or Frenkel defects are always present and certainly they should play substantial roles in the sodium diffusion. However, in our simulation of pure Na3PO4 with use of the periodic boundary conditions, the lattice vacancies are absent since all the interstitial sites of the fcc lattice are filled. Consistently, Fig. 5 suggests that the Na jump diffusion is likely to happen via ion interchange.26

In order to identify the underlying mechanism of the sodium superionicity observed in the simulation, we performed additional tests. On the one hand, to address the issue of the volume dependent characteristic of the percolation mechanism, we restarted our simulations from \( T=980 \) K with the shape of the MD supercell fixed. This corresponds to a high

![Fig. 4](image_url)  
**FIG. 4.** Temperature variation of the mean square atomic displacements \( U \).

![Fig. 5](image_url)  
**FIG. 5.** (Color online) Average atomic positions of the P (black), O (red), octahedral Na (green), and tetrahedral Na (blue) viewed from the \( c \) direction of the MD supercell at (a) \( T=300 \) K, (b) \( T=980 \) K, (c) \( T=1280 \) K, and (d) \( T=1280 \) K with only the Na displayed.
pressure experiment. As shown in Fig. 6(a), comparing the new results of the mean square displacement of the Na, $U_{Na^+}$ (open circles) and the previous "real" ones (solid squares), we found that the sodium superionicity has been significantly suppressed. Hence, the volume increase above the structural transition is a very important factor. On the other hand, to detect the paddle-wheel mechanism, we performed two hypothetical "isotope" experiments: we just doubled the masses of the P and O in one and reduced them by half in the other. Suppose the diffusive sodium cations were impelled by the PO$_4$ rotors that acted as the paddle wheels. If the PO$_4$ masses has little effect on $U_{Na^+}$ and $U_p$ as well as $U_{Na}$. This suggests that the system can be appropriately described within the harmonic approximation. Secondly, changing volume has considerable effect on $U_p$ above $\sim 1200$ K, similar to $U_{Na}$. This is because in the harmonic approximation the nearest-neighbor ions tend to move in phase with each other. Thirdly, $U_O$ changes little with volume. This implies that the rotational motion of the PO$_4$ is irrelevant to the sodium superionicity. Therefore, we conclude that the sodium superionicity is mainly governed by the percolation.

**IV. SUMMARY**

To summarize, we have observed in molecular dynamics simulation the fast ion conducting rotor phase of Na$_3$PO$_4$. We obtain reasonable agreement with experiment for the structural transition and diffusion of the Na ions. Both tetrahedral and octahedral sodium ions are found to contribute comparably to high sodium conductivity. The microscopic mechanism for sodium superionicity has been demonstrated to be primarily percolation. We propose to test our finding by high pressure experiments.

**ACKNOWLEDGMENTS**

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14 The Na ions situated on the tetrahedral (octahedral) interstitial sites of the fcc lattice are referred to as tetrahedral (octahedral) Na.


The octahedral Na in the high temperature phase come from those labeled as Na1 in Table II, while the tetrahedral Na are composed of all the other sodium ions.
