2004

Superionicity in Na$_3$PO$_4$: A Molecular Dynamics Simulation

Wei-Guo Yin  
*University of Nebraska, Omaha, Nebraska*

Jianjun Liu  
*University of Nebraska, Omaha, Nebraska*

Chun-Gang Duan  
*University of Nebraska at Omaha, cgduan@clpm.ecnu.edu.cn*

Wai-Ning Mei  
*University of Nebraska at Omaha, physmei@unomaha.edu*

R. W. Smith  
*University of Nebraska at Omaha, robertsmith@unomaha.edu*

*See next page for additional authors*

Follow this and additional works at: [https://digitalcommons.unl.edu/physicshardy](https://digitalcommons.unl.edu/physicshardy)

*Part of the Physics Commons*

Yin, Wei-Guo; Liu, Jianjun; Duan, Chun-Gang; Mei, Wai-Ning; Smith, R. W.; and Hardy, John R., "Superionicity in Na$_3$PO$_4$: A Molecular Dynamics Simulation" (2004). *John R. Hardy Papers*, 63.

[https://digitalcommons.unl.edu/physicshardy/63](https://digitalcommons.unl.edu/physicshardy/63)

This Article is brought to you for free and open access by the Research Papers in Physics and Astronomy at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in John R. Hardy Papers by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.
Authors
Wei-Guo Yin, Jianjun Liu, Chun-Gang Duan, Wai-Ning Mei, R. W. Smith, and John R. Hardy
Superionicity in Na₃PO₄: A molecular dynamics simulation

Wei-Guo Yin,1,* Jianjun Liu,1,2 Chun-Gang Duan,1 W. N. Mei,1 R. W. Smith,3 and J. R. Hardy2
1Department of Physics, University of Nebraska, Omaha, Nebraska 68182, USA
2Department of Physics and Center for Electro-Optics, University of Nebraska, Lincoln, Nebraska 68588, USA
3Department of Chemistry, University of Nebraska, Omaha, Nebraska 68182, USA
(Received 20 April 2004; revised manuscript received 2 June 2004; published 24 August 2004)

Fast ionic conduction in solid Na₃PO₄ 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.

DOI: 10.1103/PhysRevB.70.064302 PACS number(s): 66.30.Dn, 64.60.Cn, 61.43.Bn

I. INTRODUCTION

Fast ion conducting crystals have attracted much attention due to their application to solid electrolyte.1–3 In particular, sodium orthophosphate (Na₃PO₄) has served as a model system for investigating the fundamental mechanism of the unusually high ion conductivity, termed “superionicity.” Crystallographic studies4–6 revealed that in solid Na₃PO₄ 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, Li₂SO₄, in which the vacant octahedral interstitials provide natural passages of fast lithium diffusion.7 Despite extensive effort made to unveil the complex dynamic cation-anion correlation in γ-Na₃PO₄ for last two decades,8,9,10 the mechanism governing sodium transport in γ-Na₃PO₄ is still controversial.10

The ongoing debate has been focused on the preference of two possible mechanisms: (i) “percolation,”11 in which the substantial (~3%) volume expansion above the structural transition facilitates the sodium diffusion through the more open structure, and (ii) “paddle-wheel,”12 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.8

On the theoretical side, computer molecular dynamics (MD) simulations were introduced to probe at the atomistic level structural transitions and ionic transport in solids.2,3,7,13 A MD simulation of Na₃PO₄ was recently reported by Har-rison and co-workers:6 Using empirical interatomic potentials, they reproduced the structural transition and predicted that octahedral Na was more mobile than tetrahedral Na,14 contrary to certain experimental analysis in terms of the paddle-wheel mechanism.15 However, whether sodium superionicity existed in their 50-ps simulation was not reported. An obstacle to the simulation of the jump diffusion of sodium in Na₃PO₄ is that the mean residence time for a sodium atom on a lattice site is in the nanosecond range.15 Nevertheless, one would expect an increasing probability to observe sodium superionicity in a shorter time computer simulation if it is performed at temperatures higher than the phase transition temperature, as atomic mean square displacements are enhanced by thermal motion.

The purpose of this paper is to present a systematic investigation of sodium superionicity in Na₃PO₄ by using further improved MD simulation schemes. Important physical quantities, including pair distribution functions, atomic mean square displacements, self-diffusion constants, and pair correlation parameters of atomic motions are calculated and presented. We observed sodium superionicity above 1200 K in 20-ps MD simulation and demonstrated that the fundamental mechanism is primarily percolation.

The remainder of this paper is organized as follows: Sec. II describes our potential model and the details of the simulation. In Sec. III we present the results of our MD simulations and discuss the mechanism of sodium transport. Concluding remarks are made in Sec. IV.

II. MODELING AND SIMULATION

Our MD simulation was based on the modified Lu-Hardy (LH) approach16 to efficient simulation of molecular ionic crystals, in which the crystal potential energy surface was calculated within a hybrid quantum chemistry-Gordon-Kim electron gas theory scheme. This first-principles aided approach is essentially a rigid ion model with pairwise intermolecular potentials and has been successfully applied to many molecular crystals, including K₂SeO₂, K₂SO₄, Ca₃SiO₄, NaClO₄, KNO₃, NaNO₂, etc.,16 as well as simulation of superionicity in NaMgF₃.17 Full accounts of this
TABLE I. Structural parameters and vibration frequencies (cm⁻¹) of PO₄³⁻ in Na₃PO₄.

<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>-0.0837(-0.0750)</td>
<td>0.3687(0.3512)</td>
</tr>
<tr>
<td>O2(8e)</td>
<td>0.3817(0.3768)</td>
<td>-0.1028(-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>0.1106(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>

a Neutron diffraction data (Ref. 4) and Raman spectroscopy (Ref. 20).
b Hartree-Fock calculations using GAUSSIAN 98 with the 6-31* 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 Na₃PO₄ was approximated by the Hartree-Fock charge density of gas phase PO₄³⁻. This was justified by comparing the calculated molecular geometry and vibrational frequencies of PO₄³⁻ with experiments on solid Na₃PO₄, 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 PO₄³⁻. The resulting charges were 1.863 e for P and −1.216 e for O, together with the full ionic charge of +1 e for Na. With this set of effective charges, the simulated α–γ transition temperature Tc 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 PO₄ is likely to develop, we obtained Tc ~ 620 K and the lattice parameters within 3% of experiment by slightly reducing the Na charge to +0.9 e and correspondingly changing the O charge to −1.141 e (in order to maintain overall charge neutrality). However, since the charge transfer is a small fraction of the total outer shell charge (0.1 out of 8 for Na), we assumed the Gordon-Kim potentials remained unchanged.

We started our MD simulations with a 2 × 2 × 2 tetragonal supercell of the zero-temperature phase (512 atoms), which was produced by static relaxation of the supercell and verified by simulated annealing. As shown in Table II, the structural parameters of the ground state are in good agreement with neutron diffraction data: the lattice constants are shorter than the experimental values by within 3%. Next, the MD simulations were performed in the constant (zero) pressure Parrinello-Rahman scheme, which allows both the volume and the shape of the MD cell to vary with time. We used the periodic boundary conditions to simulate an infinite crystal, the Ewald method to handle the long-range Coulombic interaction, and a time step of 0.002 ps to integrate the equations of motion. In our heating runs, we raised the temperature of the MD supercell in stages, 50 K each time, up to 2000 K. At each stage, the first 2000 time steps were employed to equilibrate the system, then 10 000 time steps were collected for subsequent statistical analysis.

III. RESULTS AND DISCUSSION

It can be clearly seen in Fig. 1 that the crystal structure changes from tetragonal to cubic at Tc = 620 K with a 2.978% increase in volume, compared with the experimental values of ~600 K and 2.805%. Furthermore, we present the radial pair distribution functions (PDF), gₐβ, calculated for T = 680 K, 980 K, and 1280 K in Fig. 2, showing good agreement with a reverse Monte Carlo modeling of the neutron diffraction data (cf., Fig. 2 in Ref. 8). The first peaks in g₉O (at 1.6 Å) and in g₁O (at 2.6 Å) manifest that the tetrahedral shape of the anion groups remains almost unchanged during the simulation. g₉NaP is the flattest as expected. A broad (double peaked) structure in the first peak of g₉NaP results from tetrahedral Na-P and octahedral Na-O bonds.

FIG. 1. Temperature variation of (a) lattice constants and (b) volume (per 4 formula units) of Na₃PO₄ determined by MD simulation.
Na-P correlations. We notice that there are several detail differences between the MD and RMCPOW data: For example, $g_{NaO}$ from RMCPOW has a weak but definite peak at about 3.4 Å whereas the MD result does not; nevertheless, we observe in Fig. 2 that the dip between the first and second peaks in $g_{NaO}$ is shallow, compared with those deep dips in other PDFs; thus, a weak peak might lurk at about 3.4 Å in $g_{NaO}$ from MD. In addition, Fig. 2 reveals the small temperature dependence of the pair correlations, which confirms that the high temperature phase is rather stable, while the Na are situated predominantly at the cation octahedral and tetrahedral sites of the fcc lattice structure. This naturally suggests that the sodium ions diffuse through hopping processes.15,24

After obtaining the correct phase transition behavior, we proceeded to study ion transport and calculated the time-dependent atomic mean square displacement,15

$$\langle r^2(t) \rangle = \frac{1}{N} \sum_{j=1}^{N} \langle |\mathbf{r}_j(s+t) - \mathbf{r}_j(s)|^2 \rangle,$$

where the atomic index has been omitted and $N$ is the number of one kind of atoms. $\mathbf{r}_j(t)$ is the instantaneous position of atom $j$ at time $t$, and the angular brackets denote an average over time $s$. The atomic self-diffusion constant $D = \frac{1}{6} \lim_{r \to 0} \frac{d}{dr} \langle r^2(t) \rangle$ can be obtained from the slope of a $\langle r^2(t) \rangle/6$ versus $r$ plot. We present the results for $T=980$ K and 1280 K in Fig. 3. At $T=1280$ K, the Na and P atoms have quite different diffusion behavior: The P primarily vibrate around their equilibrium positions with a small Debye-Waller thermal ellipsoid width 0.073 Å$^2$, confirming again that the fcc lattice formed by the phosphates is rather stable. 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,15 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 tetrahedral 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 $T' = 1200$ 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. Temperature variation of the mean square atomic displacements $U$.

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 hy-
pothetical “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$_4$
anions got much heavier or lighter—thus moved slower or
faster—there should be a significant effect on $U_{Na^+}$. However,
from Fig. 6(a) we compare the triangles with the solid
squares and see very little effect. Although the vibration
speed of the center of mass of the PO$_4$ also changes with
volume, the rotation of the PO$_4$ is irrelevant to the so-
dium 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$_4$
and the previous “real” ones (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 hy-
pothetical “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$_4$
anions got much heavier or lighter—thus moved slower or
faster—there should be a significant effect on $U_{Na^+}$. However,
from Fig. 6(a) we compare the triangles with the solid
squares and see very little effect. Although the vibration
speed of the center of mass of the PO$_4$ also changes with
mass, unlike the paddle-wheel mechanism which involves
direct head-on collision between the O and Na atoms, the
center of mass vibrations of the PO$_4$ group just produces an
overall lattice expansion which has a weak effect on the Na
motion. In addition, consistent evidence can be found in
Figs. 6(b) and 6(c), where we present the mean square dis-
placements $U_Q$ and $U_P$ of the O and P, respectively. There
are three noticeable features: First, changing the O and P
masses has little effect on $U_Q$ and $U_P$ as well as $U_{Na^+}$. This
suggests that the system can be appropriately described
within the harmonic approximation. Secondly, changing vol-
ume 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, $U_Q$ changes little with volume. This implies
that the rotational motion of the PO$_4$ is irrelevant to the so-
dium superionicity. Therefore, we conclude that the sodium
superionicity is mainly governed by the percolation.

ACKNOWLEDGMENTS

We are grateful to L. L. Boyer and John Flocken for help-
ful discussions. This work was supported by the Nebraska
Research Initiative, the Nebraska EPSCoR-NSF Grant No.
EPS-9720643, and Department of the Army Grants Nos.
DAAG 55-98-1-0273 and DAAG 55-99-1-0106. W.N.M.
thanks the Office of Naval Research for support.

---

*Present address: Physics Dept., Brookhaven National Laboratory,
Upton, NY 11973. Electronic address: wyin@bnl.gov
1S.-Y. Chung, J. T. Bloking, and Y.-M. Chiang, Nat. Mater. 1, 123
(2002).
2M. Parrinello, A. Rahman, and P. Vashishta, Phys. Rev. Lett. 50,
1073 (1983).
4E. Lissel, M. Jansen, E. Jansen, and G. Will, Z. Kristallogr. 192,
5D. M. von Wienc and M. Jansen, Z. Anorg. Allg. Chem. 461,
101 (1980).
6R. J. Harrison, A. Putnis, and W. Kockelmann, Phys. Chem.
7M. Ferrario, M. L. Kein, and I. R. McDonald, Mol. Phys. 86,
8P. Zetterström, R. L. McGreevy, A. Mellergård, and J. Eriksen,
14The Na ions situated on the tetrahedral (octahedral) interstitial
sites of the fcc lattice are referred to as tetrahedral (octahedral)
Na.
16W.-G. Yin, C.-G. Duan, W. N. Mei, J. Liu, R. W. Smith, and J. R.
17L. X. Zhou, J. R. Hardy, and H. Z. Gao, Geophys. Res. Lett. 24,
25 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.