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Superionicity in Na_3PO_4: A molecular dynamics simulation

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Fast ionic conduction in solid Na_3PO_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.[1–3] In particular, sodium orthophosphate (Na_3PO_4) has served as a model system for investigating the fundamental mechanism of the unusually high ion conductivity, termed "superionicity." Crystallographic studies[4–6] revealed that in solid Na_3PO_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 $\sim$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_2SO_4, 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-Na_3PO_4 for last two decades,[6,8,9] the mechanism governing sodium transport in γ-Na_3PO_4 is still controversial.[10]

The ongoing debate has been focused on the preference of two possible mechanisms: (i) "percolation,"[11] in which the substantial ($\sim$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 Na_3PO_4 was recently reported by Harrison 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 Na_3PO_4 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 Na_3PO_4 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) approach[16] 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 K_2SeO_4, K_2SO_4, Ca_2SiO_4, $NaClO_4$, KNO_3, $NaNO_2$, etc.,[16] as well as simulation of superionicity in $NaMgF_3$.[17] Full accounts of this

TABLE I. Structural parameters and vibration frequencies ($^{-1}$cm) of PO_4^{3-} in Na_3PO_4.

	P-O distance (Å)	O-P-O angle (°)	E	T_2	A_1	T_2
Experiment[a]	1.550±0.007	109.467±0.512	435	573–586	943	1013–1108
Theory[b]	1.568	109.471	425	610	923	1062

[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).

approach and its modified version have been given elsewhere.[16,18,19]

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_3PO_4 was approximated by the Hartree-Fock charge density of gas phase PO_4^{3-}. This was justified by comparing the calculated molecular geometry and vibrational frequencies of PO_4^{3-} with experiments on solid Na_3PO_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_4^{3-}.[16] The resulting charges were $1.863e$ for P and $-1.216e$ for O, together with the full ionic charge of $+1e$ 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_4 is likely to develop, we obtained T_c $\sim$620 K and the lattice parameters within 3% of experiment by slightly reducing the Na charge to $+0.9e$ and correspondingly changing the O charge to $-1.141e$ (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.[22]

We started our MD simulations with a $2\times2\times2$ 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,[23] 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.

TABLE II. Relaxed structural parameters (Wyckoff positions) for α-Na_3PO_4 (space group $P\overline{4}2_1c$). $a=10.5159(10.8111)$ Å, $b=a$, $c=6.5126(6.8183)$ Å. Data given in parentheses are experimental values from room temperature neutron diffraction (Ref. 6).

Atom	X	Y	Z
P(8*e*)	0.2655(0.2592)	−0.0150(−0.0124)	0.2299(0.2231)
O1(8*e*)	0.1688(0.1642)	−0.0837(−0.0750)	0.3687(0.3512)
O2(8*e*)	0.3817(0.3768)	−0.1028(−0.0993)	0.1995(0.2049)
O3(8*e*)	0.2054(0.2074)	0.0112(0.0162)	0.0194(0.0235)
O4(8*e*)	0.3095(0.3050)	0.1106(0.1043)	0.3293(0.3288)
Na1(8*e*)	0.2541(0.2556)	0.0372(0.0330)	0.6908(0.6962)
Na2(8*e*)	0.2201(0.2229)	0.2366(0.2405)	0.0385(0.0424)
Na3(2*a*)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
Na4(2*b*)	0.0000(0.0000)	0.0000(0.0000)	0.5000(0.5000)
Na5(4*d*)	0.0000(0.0000)	0.0000(0.0000)	0.0489(0.0477)

III. RESULTS AND DISCUSSION

It can be clearly seen in Fig. 1 that the crystal structure changes from tetragonal to cubic at $T_c\simeq620$ K with a 2.978% increase in volume, compared with the experimental values of $\sim$600 K and 2.805%.[6] Furthermore, we present the radial pair distribution functions (PDF), $g_{\alpha\beta}$, calculated for $T=680$ K, 980 K, and 1280 K in Fig. 2, showing good agreement with a reverse Monte Carlo modeling (RMCPOW) of the neutron diffraction data (cf., Fig. 2 in Ref. 8). The first peaks in g_{PO} (at 1.6 Å) and in g_{OO} (at 2.6 Å) manifest that the tetrahedral shape of the anion groups remains almost unchanged during the simulation. g_{NaNa} is the flattest as expected. A broad (double peaked) structure in the first peak of g_{NaP} results from tetrahedral Na-P and octahedral

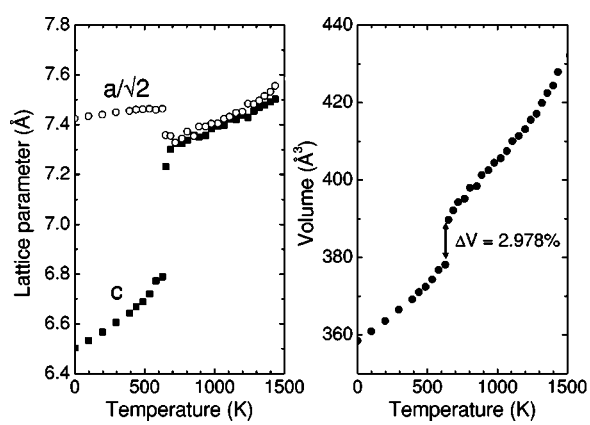

FIG. 1. Temperature variation of (a) lattice constants and (b) volume (per 4 formula units) of Na_3PO_4 determined by MD simulation.

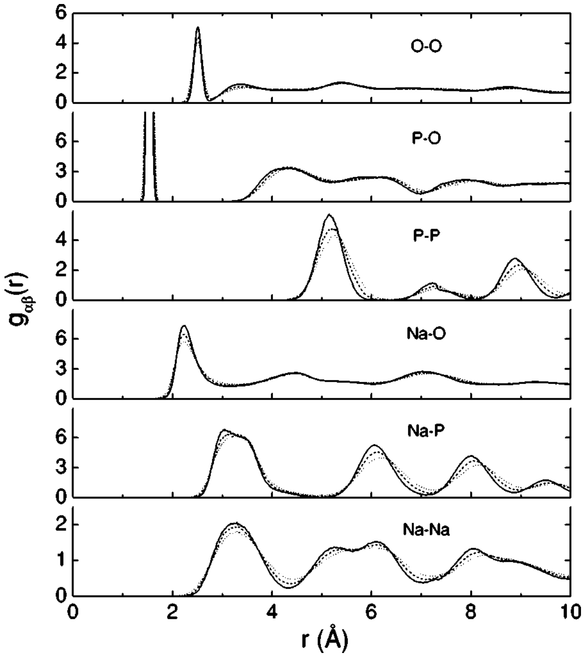

FIG. 2. Pair distribution functions, $g_{\alpha\beta}(r)$, for Na_3PO_4 at T $=680$ K (solid lines), 980 K (dashed lines), and 1280 K (dotted lines) from MD simulation.

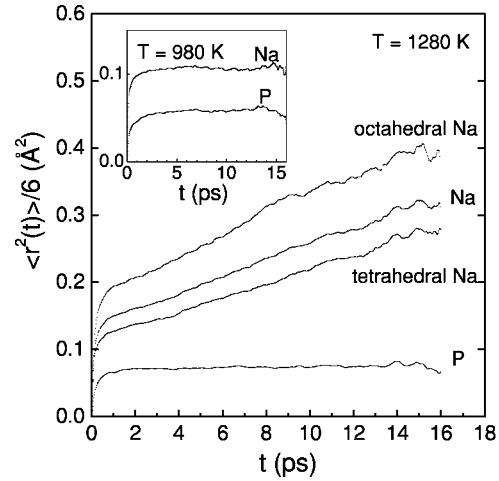

FIG. 3. Time-dependent mean square atomic displacements $\langle r^2(t)\rangle/6$ for the P and Na atoms at $T=1280$ K. The Debye-Waller thermal ellipsoid of the P has a width of 0.073 Å^2. The tetrahedral, octahedral, and all Na have a constant of self-diffusion D $=1.07, 1.22, 1.52\times10^{-6}$ cm^2/s, respectively. Inset: Results for T $=980$ K.

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,[13]

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

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 $=\frac{1}{6}\lim_{t\to\infty}[\mathrm{d}\langle r^2(t)\rangle/\mathrm{d}t]$ can be obtained from the slope of a $\langle r^2(t)\rangle/6$ versus t 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 1.22×10^{-6} cm^2/s, comparable favorably with the value, 1.45×10^{-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 $\times10^{-6}$ and 1.52×10^{-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 $T^*\simeq1200$ K; this striking feature indi-

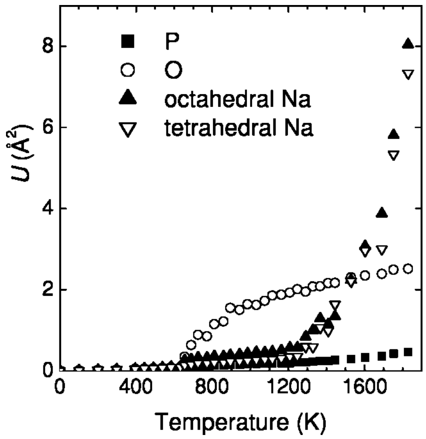

FIG. 4. Temperature variation of the mean square atomic displacements U.

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 Na_3PO_4 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

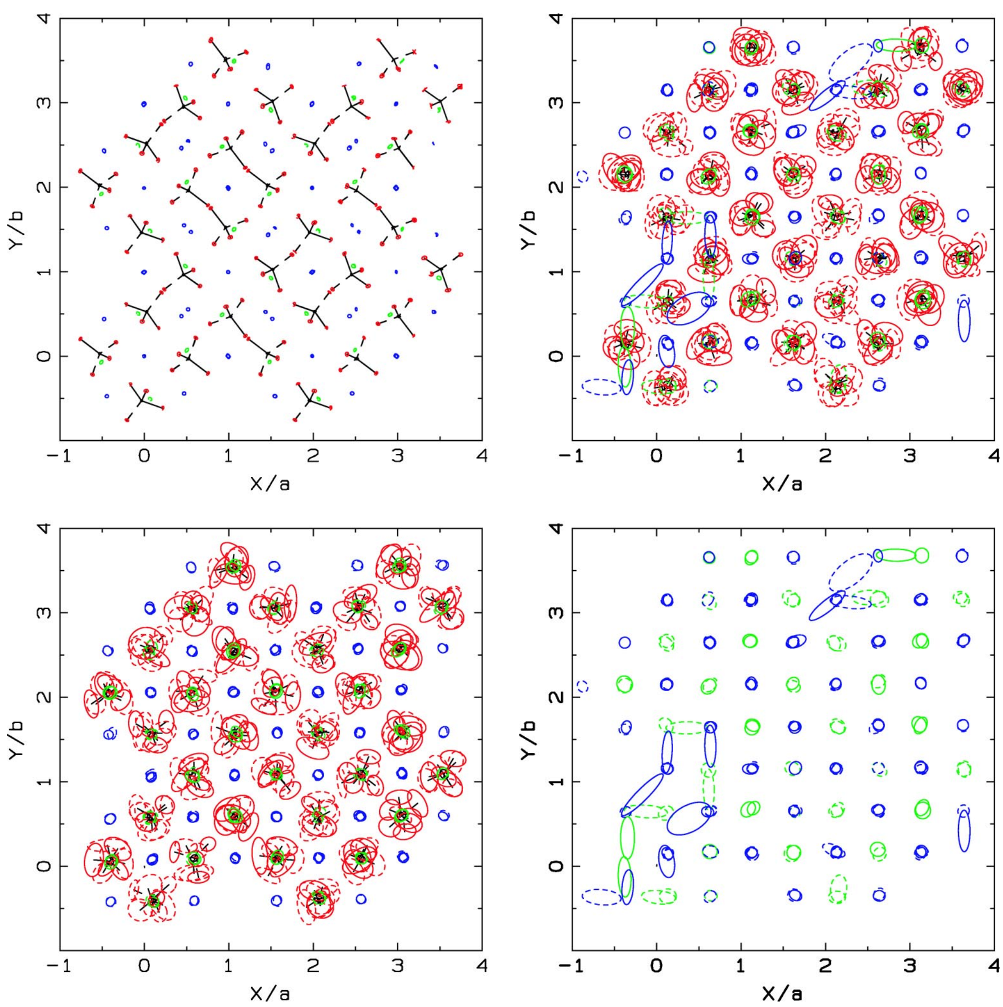

FIG. 5. (Color online) Average atomic positions of the P (black), O (red), octahedral Na (green), and tetrahedral Na (blue) viewed from the c direction of the MD supercell at (a) $T=300$ K, (b) $T=980$ K, (c) $T=1280$ K, and (d) $T=1280$ K with only the Na displayed.

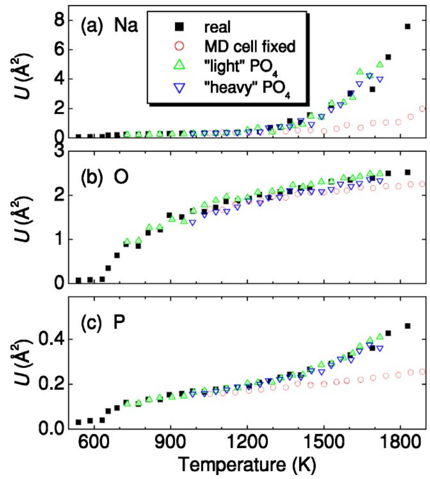

FIG. 6. (Color online) Temperature variation of the mean square atomic displacements U in MD simulations with different conditions (see text). (a), (b), and (c) for Na, O, and P, respectively.

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:[7] 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 displacements U_O 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_O 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 ~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.[27] 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_3PO_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.

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