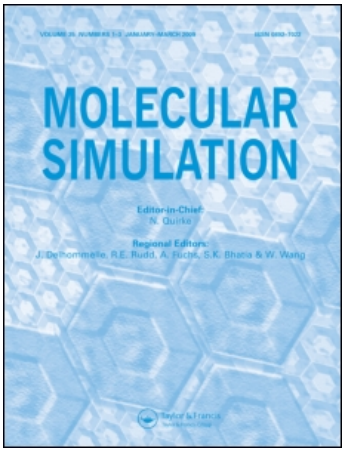

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Structural Transformations of Ice at High Pressures via Molecular Dynamics Simulations II

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STRUCTURAL TRANSFORMATIONS OF ICE AT HIGH PRESSURES VIA MOLECULAR DYNAMICS SIMULATIONS II

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A classical molecular dynamic simulation was performed in order to investigate high pressure phases of ice using recently developed pair and three-body potential model proposed by Kawamura *et al.*. At about 600 GPa and 400 K we have observed an amorphous phase with hydrogen bonds symmetrized formed from a supercooled water by pressuring, and after increasing temperature to 2,400 K, we were able to crystallize it into ice X. After further isobaric heating to 16,000 K we have obtained a new phase in which oxygen atoms form a fcc lattice with protons having a liquid-like self diffusion coefficient.

Keywords: Hydrogen-bond symmetrized amorphous ice; ice X; fcc ice; structural transformation; molecular dynamics; effective interaction for water molecules

1. INTRODUCTION

Ice has more than 10 different stable phases [1]. In the higher pressure regime over 2 GPa, both the phase diagram and the structure of ice become simpler. At a pressure above 2 GPa and temperature above 270 K, ice VII appears whose oxygen atoms form a bcc lattice. Above 80 GPa, hydrogen-bond symmetrized ice (ice X) with the same oxygen lattice as that of ice VII is supposed to appear [6,7]. In such an extremely high pressure regime, the structure of ice is accurately not known yet partly because of the difficulties of

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experiment. Several theoretical studies and molecular dynamics (MD) simulations have been published [16–19].

The aim of the present work is to investigate the properties of high pressure ice phases by MD simulation. Especially, our main interest concerns to what extent the classical potential model we use can reproduce phase transitions of ice.

The potential model we use is the one developed by Kawamura *et al.* [12]. It consists of both two-body and three-body interactions. The latter characterizes this model. If two hydrogen ions near an oxygen ion exist at distances shorter than a certain cutoff length, the three-body force acts along the direction perpendicular to the O-H bond in the plane which contains the three ions so as to regain a proper H-O-H angle. If there are more than two hydrogen ions around an oxygen ion, the three-body force acts on each H_2O pair. Except for the compressibility predicted by this model which is too small, it can reproduce partial pair correlation functions and the power spectrum compatible with experiments at high pressures. With this model we have successfully demonstrated the phase transitions between ice VIII, VII and X [20].

Ice X is characterized by the structure that oxygen ions form a bcc lattice and hydrogen ions are at the mid point of two nearest oxygen ions, namely hydrogen bonds are symmetrized [2–7]. Polian *et al.* have reported that by compression of ice VII at 300 K up to 67 GPa the ice VII-ice X transition occurred at 44 GPa [4]. Hemley *et al.* have reported that up to 128 GPa at room temperature the bcc oxygen lattice continue to exist [5]. Pruzan *et al.* studied the ice VII-ice VIII phase boundary up to the pressure at which ice VIII phase disappears and suggested that ice X might appear above 80 GPa [6,7].

As to the phases in higher pressure regimes there are several MD simulations. Using the classical model which was developed for ice X, Demontis *et al.* have investigated ice phases in higher pressure regime than ice X [16]. They have obtained the result that by pressuring ice X to 100 GPa, the oxygen lattice changes from bcc to fcc and on heating it transforms into a fast-ion proton conductor. Using the *ab initio* constant pressure method, Benoit *et al.* have also studied high pressure ice phases and obtained the result that at room temperature, and pressures around 300 GPa, ice X transforms to ice XI which is a distorted hcp structure [17].

Experiments by Hemley *et al.* show that an amorphous ice is crystallized by compression alone into a phase which is partially disordered at low temperatures (they call this ice VII'), and by heating, it transforms into ice VIII [13].

A classical MD simulation was also performed to investigate the HDA (high density amorphous) and suggested that peaks in $g(r)$ of the HDA at high

pressures are similar to those for bcc crystal and a pressure induced HDA-ice VII transition is possible [15].

Our main interest is to investigate whether the present model can reproduce such pressure induced ordering and the transition into more ordered phase by increasing temperature.

In the higher pressure regime above ice X, a stimulating problem concerns whether an fcc oxygen lattice or an hcp-like phase is more stable. But there are few investigations in the higher temperature regime above ice X. The main subject of the present simulation is to investigate the type of oxygen lattice in the temperature range above ice X.

2. METHOD

Using 810 particles (270 oxygen ions and 540 hydrogen ions), we have performed MD simulation in a periodic cell. In order to control the temperature of the system Nosé method was used [8,9] and for the pressure control the Parrinello-Rahman algorithm of the MD simulation was employed [10,11]. Coulomb interactions were handled using the Ewald method. The time step is 0.4fs and the fifth order Gear predictor-corrector method of numerical computation is used.

We have used the interatomic potential model proposed by Kawamura and his co-workers [12], which consists of two-body and three-body force terms. The two-body force term consists of the coulomb term, short range repulsive term, van der Waals term, and morse function term representing covalent bonds. The three-body force term is essentially introduced in order to reproduce the correct angle between two O-H bonds in each water molecule. The cutoff length of this interaction is chosen to be 3.0 Å so as to realize the total energy conservation, which is slightly longer than that used for the low-pressure water. Since this term represents the intramolecular H-O-H angle potential, it should effect over the range of the order of the intramolecular O-H distance, which is about 1 Å. However, since the differentiation of the three body potential involves a function which diverges when H-O-H angle is close to 0 or π a technical manipulation can be treated with a larger value of the above cutoff parameter. After this operation the Fermi distribution function which is almost unity when $r_{OH} \leqslant 1.4$ Å and is almost zero when $r_{OH} \geqslant 1.4$ Å is multiplied to determine the effective range of this interaction. With the parameters of this potential fitted so as to reproduce the low-pressure ices (ice I_h, ice II, and ice IX) and water, we have applied the same model to a high pressure regime. We have previously confirmed that this model could successfully reproduce the ice VIII-ice VII-ice X transitions and the ice VI-ice VII transition.

3. RESULTS

We have started the present MD simulation by melting a crystal ice VI at 940 K in constant-(N, V, T) ensemble for 50,000 time steps. After confirming that the system has reached an equilibrium state, the temperature of the system was reduced to 400 K by velocity scaling over the period of 20,000 time steps. After such preparation of the supercooled water, we have imposed a pressure on it rapidly at the rate of 0.1 GPa/step finally to 608.4 GPa under constant-(N, P, T) MD simulation. The partial pair distribution functions obtained was confirmed to be almost independent of such processes: Another supercooled water quenched to 700 K was also prepared with the same procedure and on pressuring at a slower rate of 0.006 GPa/step, resulting in the same $g(r)$'s.

The snapshot of the atoms for the amorphous ice thus obtained is shown in Figure 1 and the partial pair distribution functions g_{OO}, g_{OH}, and g_{HH} are shown in Figure 2. In Figure 1, a number of protons are seen to be connected by two nearest oxygen ions. In Figure 2, the first peak of g_{OH} appears to be at the half the distance of that of g_{OO}, indicating hydrogen-bond symmetrization. Hemley *et al.* have observed the transition of an amorphous ice to a crystalline phase close to ice VII in structure by a compression [13]. However, the conditions adopted in both works are not the same. Pressuring an amorphous ice at an extremely high rate into an extremely high pressure, it may transform to a hydrogen-bond symmetrized phase without crystallization under some condition.

We have raised the temperature of the amorphous ice from 400 K to 2,400 K, after which further MD run of 100,000 time steps was performed under constant-(N, P, T). The variation of the pressure, temperature, volume, MD cell length and angle are shown in Figure 3. When temperature was raised (at 2,000 time step in Fig. 3), the volume of the MD cell increased simultaneously and after about 15,000 steps, the system transformed abruptly to another phase. This new phase was stable at least over 80,000 steps after the transition.

The snapshot of the new phase observed is shown in Figure 4. Oxygen atoms form a lattice, while protons are seen to exist near the intermediate position of O-O. Partial pair distribution functions are shown in Figure 5. The positions of peaks of g_{OO} are in good agreement with those of the corresponding ideal bcc peaks. The position of the 1st peak of g_{OH} is half the distance of that of g_{OO}, which means protons are located at the mid-point of the two nearest oxygen ions. The running coordination number (rcn) of the 1st peak of g_{OH} is 4. Thus, it can be concluded that ice X was obtained by heating the hydrogen-bond symmetrized amorphous ice.

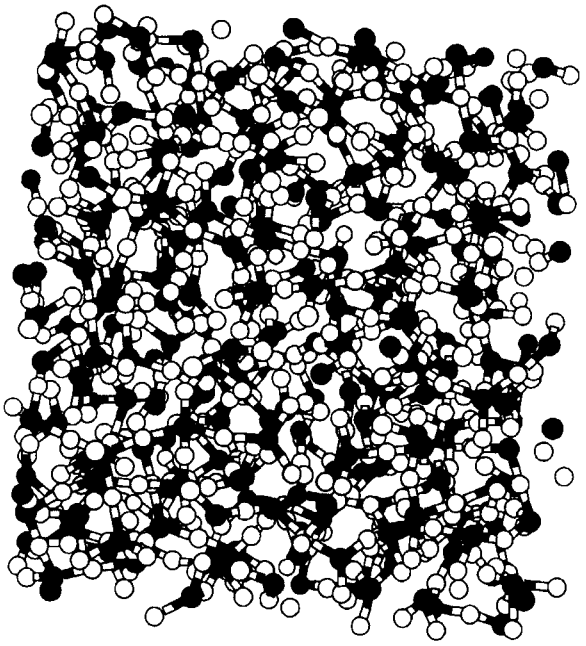

FIGURE 1 Snapshot of hydrogen-bond symmetrized amorphous ice. Black and open circles represent oxygen ions and hydrogen ions, respectively. O-H pairs whose distance is less than 1.17 Å are connected.

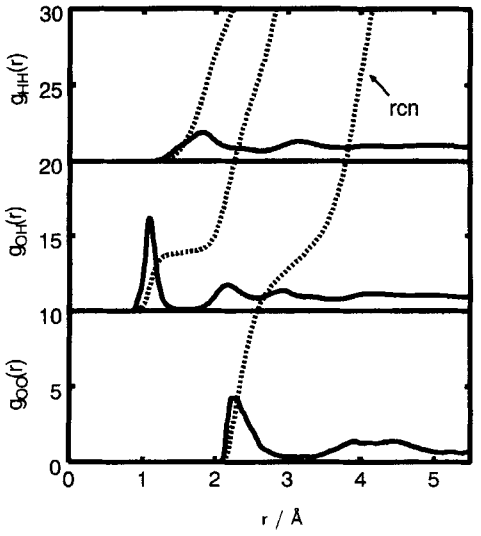

FIGURE 2 Partial pair distribution functions g_{OO}, g_{OH}, and g_{HH} (solid curves) and the corresponding rcn's (running coordination numbers, shown by the dotted curves).

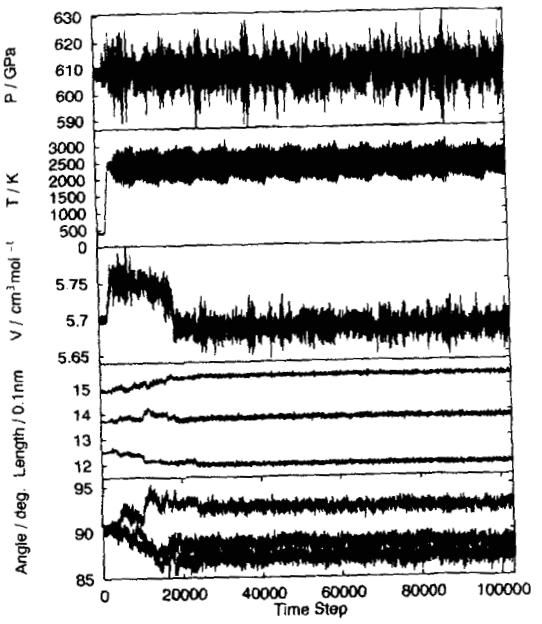

FIGURE 3 Variation of P (pressure), T(temperature), V(volume), MD cell length and angle vs. time steps.

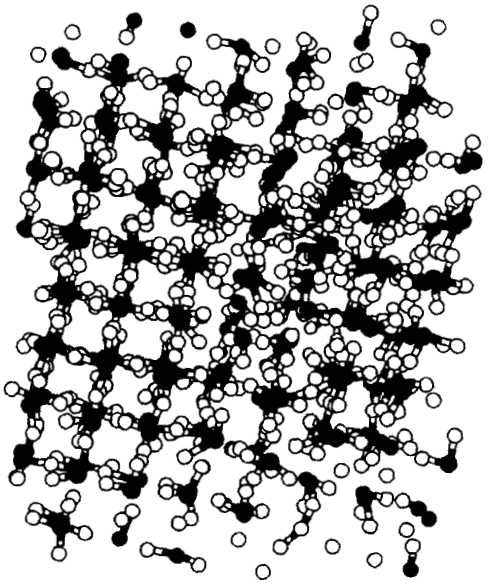

FIGURE 4 Snapshot of atoms for the new phase. The same symbols as in Figure 1 are used.

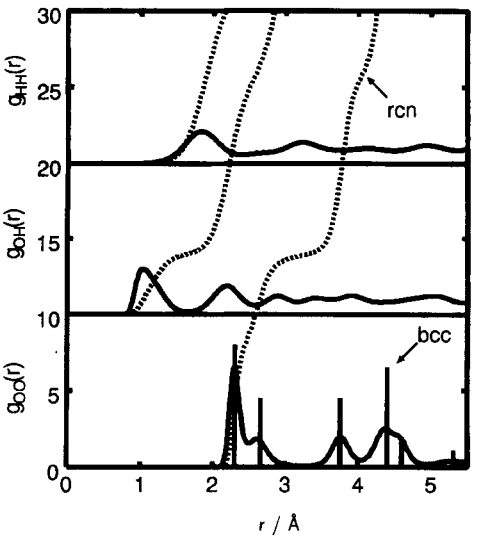

FIGURE 5 Partial pair distribution functions g_{OO}, g_{OH}, and g_{HH} and the corresponding running coordination numbers. "bcc" in g_{OO} denotes the ideal bcc beak, the 1st peak of which is placed at the same position as that of g_{OO}.

We have plotted in Figure 6 the trajectory of oxygen ions and protons during 20,000 time steps after the final time in Figure 3. We see that protons diffuse in the restricted area of a plane perpendicular to x axis with which the oxygen lattice becomes disordered, indicating that defects play an important role in the proton diffusion for the ice X. This tendency was not changed over the further MD run of 80,000 time steps.

On further heating of the crystalline phase to the temperature of 16,000 K a transformation to another phase was observed (at 10,000 time step in Fig. 7). The length and angle of the MD cell change rather as often during the MD run as oxygen ions form bcc or fcc lattice. Finally a phase in which oxygen ions form fcc lattice was obtained. The snapshot and the partial pair distribution functions g_{OO}, g_{OH}, and g_{HH} are shown in Figures 8 and 9, respectively. In Figure 8, oxygen ions are seen to form a lattice, while protons are likely to be distributed at random. We can see from g_{OO} in Figure 9 that oxygen ions form a thermally agitated fcc lattice and from g_{HH} in Figure 9 that protons are almost in a gas state with no correlation between them. The trajectory of oxygen ions and that of protons are shown in Figure 10. Oxygen ions still form a lattice, while protons diffuse like in a gas phase in the MD cell in accordance with the behavior of g_{HH}. The self diffusion coefficient of protons was

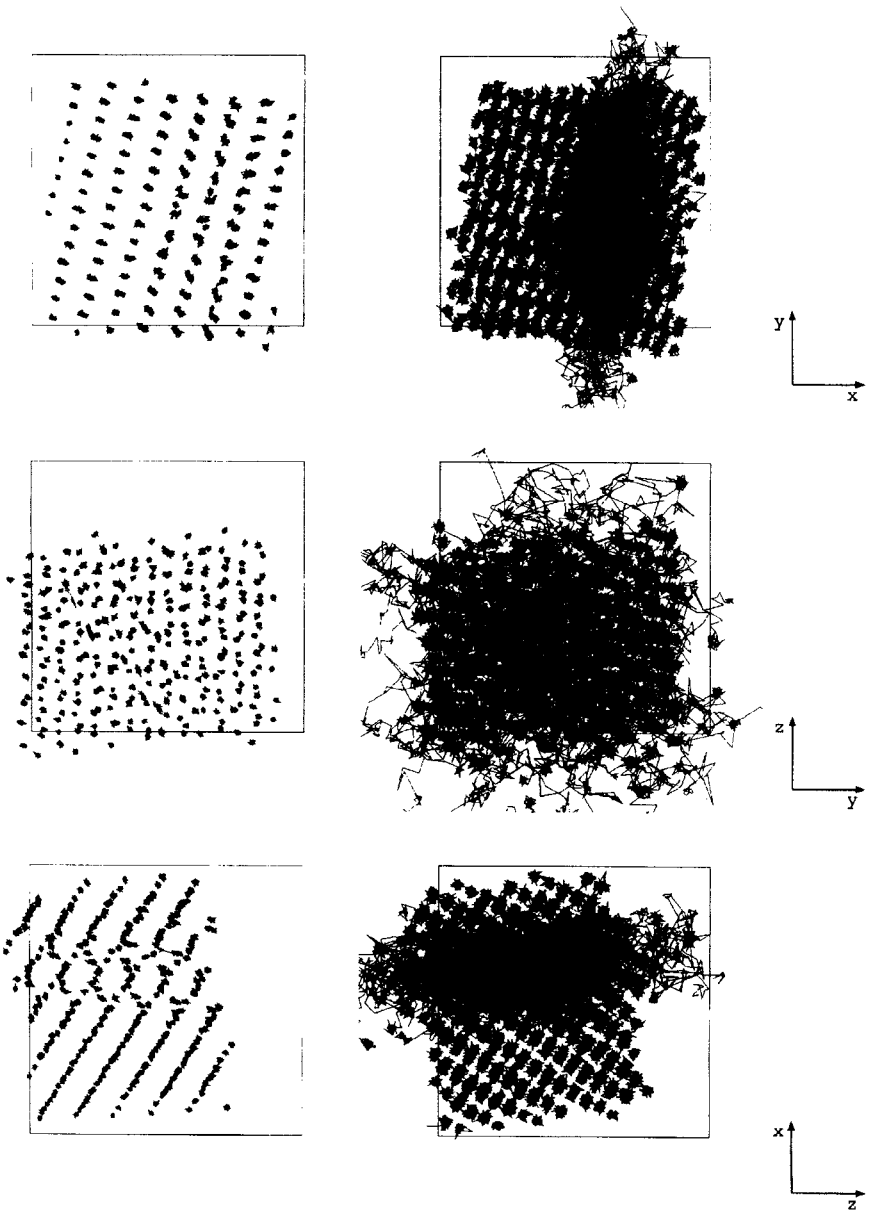

FIGURE 6 The trajectry of oxygen ions (left) and hydrgen ions (right) seen from z direction (upper), x direction (middle), and y direction (lower), respectively. The most upper figures correspond to Figure 4. The frames are for guide to eyes.

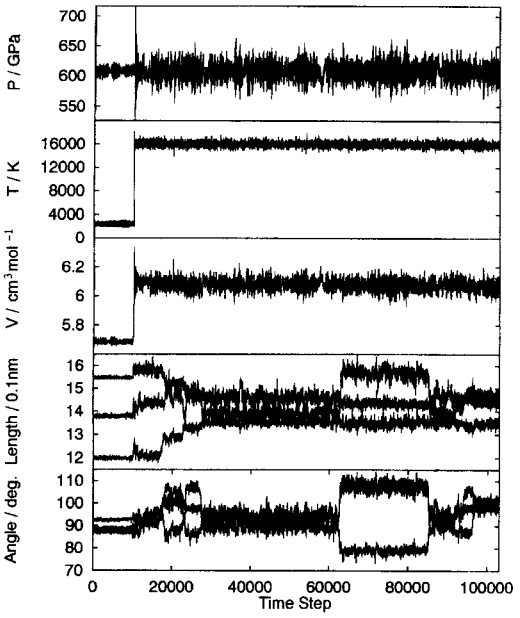

FIGURE 7 Variation of P (pressure), T(temperature), V(volume), and MD cell length and angle vs. time steps.

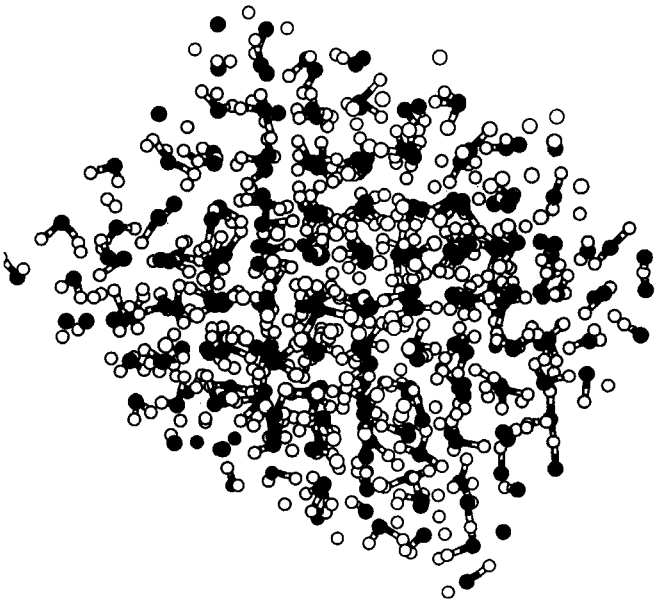

FIGURE 8 Snapshot of an fcc ice seen from [100] direction of the fcc oxygen lattice.

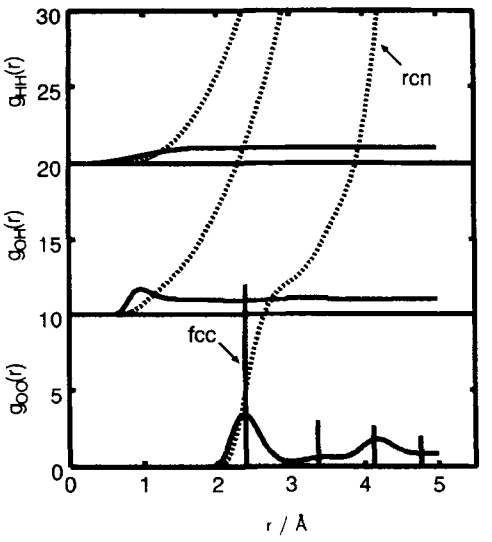

FIGURE 9 Partial pair distribution functions g_{OO}, g_{OH}, and g_{HH} and the corresponding running coordination numbers. "fcc" in g_{OO} denotes the ideal fcc peak, the 1st peak of which is placed at the same position as that of g_{OO}.

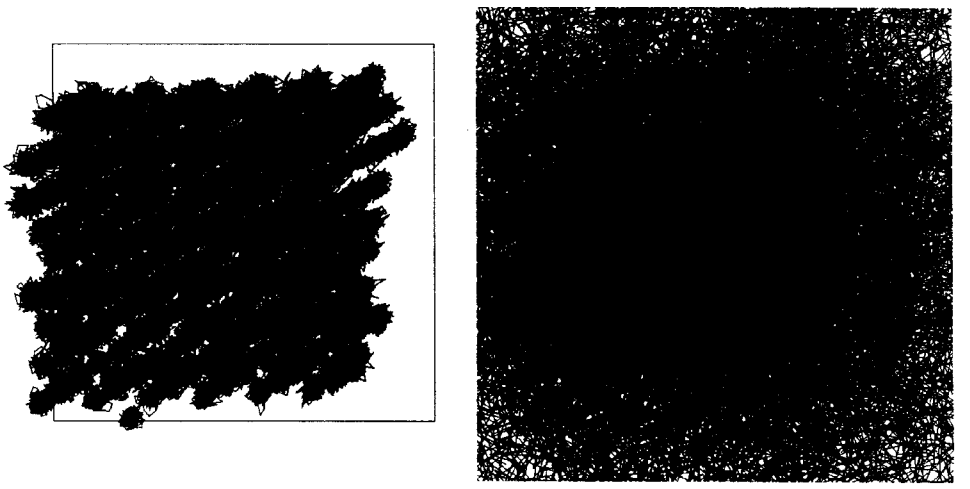

FIGURE 10 The trajectry of oxygen ions 10,000 steps (left) and hydrgen ions during 200 steps (right). The frames are for guide to eyes.

calculated from the slope of the mean-square displacement to yield 8.96×10^{-3}cm^2/sec, which is more than 10^2 times larger than a typical liquid-like value because of the extremely high temperature of the system of consideration.

4. CONCLUSION AND DISCUSSION

The following results were obtained:

(1) By rapid compression of a supercooled water, a hydrogen-bond symmetrized amorphous ice was obtained, this is in contrast to the experimental suggestion of the crystallization of HDA under pressure. However with an extremely high pressuring rate, it may be observable.

(2) Following heating of the symmetrized hydrogen-bond amorphous ice, it crystallized into ice X. Amorphous ices can be crystallized by increasing temperature, which is commonly observed in experiments [13, 14]. However, this is not trivial in MD simulation, because crystallization of a rather small system (liquid) is generally difficult to observe. The present result of the MD simulation is meaningful, which shows a partial crystallization from the amorphous ice. In the ice X obtained, the bcc oxygen lattice was not completely ordered but involved a disordered planar area. The hydrogen ions diffuse near the disordered area, indicating that defects of oxygen lattice plays an important role in proton diffusion in the crystalline ice X.

(3) Ice X is considered to be stable at least above 80 GPa [6, 7]. The phase boundary of ice X is not yet obtained. Whether there is an fcc phase or a distorted hcp phase above the pressure range of ice X is very interesting. By raising the temperature of high pressure ice X, the possibility of a new phase like an fcc lattice arises. The present MD simulation shows that at a high temperature ice X melts and at a pressure where ice X is stable a new phase appears whose oxygen lattice forms fcc with diffusing hydrogen ions similar to a superionic conductor.

(4) Using the original Kawamura potential, we were able to reproduce transitions such as ice VI-ice VII by pressuring, ice VIII-ice VII by heating, ice VIII-ice VII-ice X by pressuring, and hydrogen-bond symmetrized amorphous ice-ice X-fcc ice by heating. Though this model was originally developed for low pressure ice phases and water, it works excellently in the high pressure regime as well. However, since the compressibility of this potential is too small, the parameters of the model potential should be corrected.

Acknowledgements

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