Exploring the structure of phosphorus in phase IV using metadynamics simulation

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Abstract

We explored the unknown structure of the phosphorus in phase IV (P-IV phase) using a method of molecular dynamics simulation. The method is based on the first-principles theory and non-Markovian dynamics which was first proposed by Laio and Parrinello. Using an assumption that the structure is approximated by a crystal with 8 atoms in a cell, we found an approximate structure whose x-ray diffraction pattern agrees fairly well with the experimental pattern of the P-IV phase. In the obtained structure, phosphorus atoms occupy the positions in a zigzag pattern which is a kind of modulated structure with short wave-length. The modulation is crucial to the stability of the structure. Possibility of the modulation with longer wave-length is discussed.

1. Introduction

To explore the global structure of free energy surfaces (FES) is challenging and important for the computational material science. In such a circumstance as the first order phase transitions, the FES has local minima separated by large potential barriers. In order to explore these local minima, molecular dynamics (MD) or the Monte Carlo simulations have usually been used. However, when we search the FES for the local minima separated by the large barrier, which can not be surmounted by the thermal fluctuation in a limited simulation time, we have to overpressurize the system to realize a gentle slope of the FES or overheat the system to make the system cross the barrier by the thermal fluctuation. Therefore, we can not directly explore the FES under the realistic condition. Exploration of metastable states or intermediate phases is very difficult.

The simulation technique called the metadynamics (Laio 2002, p.1256, Martoňák 2003, p.075503), however, can overcome this issue, and they showed an example of its application to pressure-induced structural phase transition in Si from diamond to simple hexagonal (sh). The metadynamics is based on the idea that, in order to escape from a local minimum, we may fill its FES well with an artificial Gaussian-type potential energy. Therefore, since we need not change the shape of the FES to surmount the barrier, we can easily and correctly explore the metastable states. Pressure-induced structural phase transitions are often the first order phase transition. If we combine the metadynamics and the first-principles calculation, it is hopeful to find unknown structure which is produced by pressure-induced structural phase transitions.

In this paper, we have tried the first-principles metadynamics simulation to explore the unknown structure of the intermediate phase of phosphorus, the P-IV phase. At ambient pressure, the structure of phosphorus is the A17 (space group No.64), which is so-called "black phosphorus" (Brown 1965, p.684). This A17 structure transforms to the A7 structure (space group No. 166) at 4.5 GPa, and the A7 phase transforms to a simple cubic (sc) phase at 10 GPa (Jamieson 1963, p.1291, Kikegawa 1983, p.158). In 1999, Akahama *et al.* observed a transition from the sc structure to sh one at 137 GPa. Also they found a new phase, the P-IV phase, at pressures just below the sh phase (Akahama 1999, p.8520). The structure of the new P-IV phase has been investigated by means of not only the Rietveld analysis but also theoretical calculations (Ahuja 2003, p.282, Ehlers 2004, p.214112) but the structure is still unclear.

We report the new structure of phosphorus obtained by the use of the first-principles

metadynamics simulations. In Sec. 2, we explain the metadynamics simulation and computational details, and its application to the phosphorus is given in Sec. 3. In Sec. 4 and Sec. 5 we describe the obtained structure and compare its x-ray diffraction patterns with that of the experimental one in the P-IV phase. Summary is given in Sec. 6.

2. Computational details

The metadynamics simulation are powerful to explore the local minima separated by the large barriers on the FES. Following the paper by Martoňák, Laio, and Parrinello (2003, p.12652), we will briefly explain the method of the metadynamics simulation. In the study of pressure-induced structural phase transition, we use the Gibbs free energy (GFE) which depends upon a shape of a simulation cell and add artificial potential energy. This artificial energy is defined by the following Gaussian-type function:

$$G_g^t(\underline{\mathbf{h}}^t) = \sum_{t' < t} W \exp(-\left|\underline{\mathbf{h}}^t - \underline{\mathbf{h}}^{t'}\right|^2 / 2\delta h^2)$$

where t and t' are a current time-step and a previous time-step, respectively. A matrix <u>h</u> indicates the shape of the simulation cell and $\underline{h} = (\vec{a}, \vec{b}, \vec{c})$. \vec{a}, \vec{b} and \vec{c} are lattice vectors of the simulation cell. The quantities W and δh represent the weight and the width of the Gaussian, respectively. The above equation means that if the current <u>h</u> has been visited time after time, G_g accumulates to a large value. This condition corresponds to the situation: While the system is fluctuating around the local minimum of the GFE surface (GFES), the local minimum of the GFES at each time step is gradually filled with the G_g , and then the system moves to the neighboring local minimum.

In order to cross barriers, the driving force must be the sum of the original driving force \underline{F}_o and the Gaussian driving force \underline{F}_g : $\underline{F}^t = \underline{F}^t_o + \underline{F}^t_g$. The ij element of these forces is represented by

$$\underline{\mathbf{F}}_{oij}^{t} = -\partial G_{o}^{t} / \partial \underline{\mathbf{h}}_{ij}^{t} = \Omega^{t} \{ [(\underline{\mathbf{p}}^{t} - p_{\text{ext}}) \underline{\mathbf{h}}^{t^{-1}}]_{ij} + [(\underline{\mathbf{p}}^{t} - p_{\text{ext}}) \underline{\mathbf{h}}^{t^{-1}}]_{ji} \} \left(1 - \frac{1}{2} \delta_{ij} \right)$$
$$\underline{\mathbf{F}}_{g_{ij}}^{t} = -\partial G_{g}^{t} / \partial \underline{\mathbf{h}}^{t}_{ij} = \sum_{t' \leq t} \frac{W}{\delta h^{2}} (\underline{\mathbf{h}}^{t} - \underline{\mathbf{h}}^{t'}) e^{-\left|\underline{\mathbf{h}}^{t} - \underline{\mathbf{h}}^{t'}\right|^{2} / 2\delta h^{2}}$$

where $\Omega = \det(\underline{h})$ and p_{ext} are the volume of the simulation cell and the external pressure, respectively. A tensor p is the internal pressure tensor. Using the total force \underline{F} , the simulation cell is updated by the steepest descent method:

$$\underline{\mathbf{h}}^{t+1} = \underline{\mathbf{h}}^{t} + \delta h \, \underline{\mathbf{F}}^{t} / \left| \underline{\mathbf{F}}^{t} \right|$$

where δh is used as a stepping parameter. We call this one process by one meta-step. At each meta-step, in order to equilibrate the system and estimate p, we have to perform the conventional MD simulations with the shape of the simulation cell fixed.

In our calculations, we employed the conventional simulation using the interatomic forces obtained by the first-principles calculation, where we employ the density functional theory within the framework of a local density approximation (LDA) and a norm-conserving pseudo-potential. For the exchange and correlation energy functional we used the expression of Perdew and Zunger (1981, p.5048). We used the PWscf package (Baroni) for this calculation. The internal pressure tensor and the atomic positions at each meta-step are taken from the output of the PWscf program.

3. Implementation of the simulation for the phosphorus-IV phase.

For the simulation of the phosphorus, we used the cubic simulation cell containing 8 atoms which occupy the sc atomic positions, and performed the k-space integration using 8 × 8 × 8 mesh points in the first Brillouin zone (BZ). We set the pressure at 120 GPa in the constant pressure conventional MD, since the P-IV phase is the most stable phase at this pressure. In order to equilibrate the system, we run this MD simulation of 200 steps at each meta-step and we calculated the average internal pressure tensor from the latter half of 100 steps. First we run the simulation of few tens of meta-steps switching the Gaussian-type potential energy off in order to explore the minimum of the starting GFES well. We used 10 mÅ, as the stepping parameter δh . Then we switch it on to changing the Gaussian-type potential parameter W from 0 mRy to 1 mRy. We changed δh from 10 mÅ, to 20 mÅ to accelerate the simulation.

In order to perform these metadynamics simulations, we made use of machines HITACHI HA8000 at the Institute for Molecular Science (IMS).

4. Results

Figure 1 shows the change of three angles among the vectors defining the simulation cell and its volume. We performed simulations without the Gaussian-type potential for 39 metasteps in order to check whether the sc structure is stable or not. The values of the angles and the volume are nearly maintained at those of the sc lattice during these steps. This means that the sc structure resides in a local minimum and it is separated from the other local minima by the barriers on the GFES. We note that the metadynamics simulation with the Gaussian-type potential switched off is nearly equivalent to the conventional MD simulations. Thus the transition from the sc phase to other phase may be hard to be simulated by the normal MD around 120 GPa.

In order to explore the metastable structures near the sc local minimum, we perform the metadynamics simulation switching the Gaussian on after 39 meta-steps. We changed W to 1 mRy and δh to 20 mÅ. Then one of the three angles starts to increase after 50 meta-steps and the volume dramatically decreases around 70 meta-steps. After those changes, we switch the Gaussian off again in order to check whether the system has already surmounted the barrier and moved to a neighboring local minimum. After that the volume fluctuated around the value of 73.0 Å³ and three angles around the values of about 98°, 90° and 90°, respectively. This behavior is thought that the sc structure transformed into another metastable structure.

Figure 2 shows the structure obtained by the above run. The projection onto the z-x plane (left figure) shows the distortion of the simulation cell from cubic into that with an angle 98°. The projections onto the x-y plane and the y-z plane are shown in the right upper figure and the right lower figure, respectively. The important feature of this new structure is that the atoms are located in a zigzag pattern. In order to check whether these zigzag locations of atoms are related to the stability of the distorted unit cell or not, we relocated the atoms in the zigzag pattern to the position of no zigzag modulation (reference structure) without changing the shape of the cell and investigated the stability of the structure by the relaxation of the



Fig. 1 Change of angles among vectors defining the simulation cell and the cell volume by the first-principles metadynamics simulation. One of the three angles and the volume dramatically change after switch-on of the Gaussian-type potential. The potential was switched on at 39 meta-steps and off again at 70 meta-steps.



FIG. 2 The new structure obtained by the first-principles metadynamics simulation. One of three angles of the simulation cell is 98° (left figure) and the other two are 90°. Phosphorus atoms are located in a zigzag pattern.



Fig.3 The x-ray powder pattern of the P-IV phase. Experiment (upper figure), our structure (middle figure) and the sc (lower figure). Experimental one is taken from Akahama *et al.* (1999, p.8520). That of our structure is calculated using RIETAN-2000 (lzumi, 2000, p.198).

structure. As a result, this structure returned to the initial sc structure. This shows the zigzag pattern of the locations of the atoms are crucial for the stability of its structure.

5. Comparison with the experiment

In Figure 3 we compare the x-ray powder patterns. The upper figure is the powder pattern of the P-IV phase (Akahama 1999, p.8520) and the middle figure shows the simulated x-ray diffraction patterns of our structure by the RIETAN-2000 (Izumi 2000, p.198). Both patterns show that the 111 diffraction of the sc structure disappears and the diffraction lines increase from $2\theta = 27^{\circ}$ to 35° . However, the splitting of the 100 diffraction into three lines is not seen in our pattern. This shows that our structure has higher symmetry than that of the P-IV phase. In this simulation, we used the simulation cell having 8 atoms, but the disagreement of the diffraction patterns may improved by the consideration of the simulation cell size.

Next we calculated the powder pattern of the reference structure discussed above to see how it looks like. In Fig. 4 we compare the x-ray powder patterns. The middle figure is pattern of the structure found in the present simulation and the lower one is that of the reference



Fig. 4 The comparison of the x-ray powder pattern with that of a reference structure. Experiment (upper figure) (Akahama, 1999, p.8520), our structure (middle figure) and a reference structure (lower figure). The reference structure is defined removing zigzag modulation in our structure (See the text for the defini-

structure. Owing to the zigzag modulation, the new peaks appear which is due to a lowering of the symmetry. In particular, the appearance of the peak near 2 θ = 15° (a kind of satellite peak) may have the key to understand the structure for the P-IV phase. The zigzag pattern is modulation with smallest period. Thus, if larger unit cells are employed in our simulation, the modulation with larger wave-length than the zigzag structure may be possible. Then the satellite peak will shift towards the largest peak. It can explain why the largest peak of the P-IV phase splits into 3 lines.

6. Summary

We performed the metadynamics simulations using the first-principles calculations for interatomic interactions in order to explore unknown structure of the phosphorus IV phase. We found the structure which is thought to be an intermediate structure between sc and sh and is modulated with the zigzag pattern. The reference structure can be obtained by changing one of the three 90° angles among primitive translational vectors to 98°, but this structure is unstable without the modulation of the zigzag pattern (Fig.2). The simple hexagonal structure is obtained by setting this angle at 120°.

We could perform the first-principles metadynamics simulations to study the unknown structure of the phosphorus in phase IV, because the unit cells of all sc, sh and our structure consist of small number of atoms. The limitation remains that we may not be able to treat large enough simulation cell due to limited computational resources. The metadynamics simulation combined with the first-principles calculation, however, has a power to predict unknown phases at high pressures which have not yet been observed.

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