Finding the structure of phosphorus in the phase IV

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We have explored the unknown structure of the phosphorus in the phase IV (P-IV phase) based on
the first-principles calculations using the metadynamics simulation method. Starting from
the simple cubic structure, we found a new modulated structure of a monoclinic lattice. The modulation
is crucial to the stability of the structure. Refining further the structure by changing the modulation
period, we have found the structure which shows the X-ray powder pattern in the best agreement
with the experimental one. We can not exclude the possibility that the unknown structure of the
phase IV of phosphorus is an incommensurately modulated one.

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Recent progress in high-pressure physics strengthened
our recognition on the variety of structures of materi-
als. Unexpectedly interesting structures were found in
the high-pressure experiments. The modulated struc-
ture is one of curious structures often found in the high-
pressure phases of elements. Improvement of the high-
pressure techniques has also made it possible to specify
the structure stabilized only in a narrow pressure range.
The modulation of a crystal was found in the group Vb
elements including As, Sb and Bi [1, 2] and in group
Vb elements including S [3], Se [4] and Te [5]. Modu-
lated structures were also reported in halogens, I [6] and
Br [7].

Non availability of sufficient experimental data under
very high pressure constrains high pressure study. There,
people often encounter difficulties in determination of the
lattice structure only from the experimental data. The
theoretical approach gives alternative information on the
lattice structure only from the experimental data. The
structural phase transformation. For the obtained structure,
we checked the relative stability against the sc and sh phases. Next we considered some model structures to
find more refined structure. The structural optimization
was done for each model structures. The calculated X-ray
powder patterns of the optimum structure are compared
with that of the experimental one.

In the study of the metadynamics simulation, which
was first introduced by Laio and Parrinello [13, 14],
we use the Gibbs free energy (GFE) depending upon
the vectors defining the simulation cell and
\( \h \),

\[
G_g(h^t) = \sum_{i<j} \prod_{\nu<\nu'} W \exp(-|h^t - h^{t'}|^2_{ij}/2\delta h^2). \tag{1}
\]

The superscripts \( t \) and \( t' \) denote the current meta-step
and the previous one, respectively. The quantities \( W \) and \( \delta h \) represent the weight and the width of the Gaussian-type function, respectively. The matrix \( h \) is defined by the vectors defining the simulation cell and \( h = (\vec{a}, \vec{b}, \vec{c}) \),

where \( \vec{a}, \vec{b} \) and \( \vec{c} \) are lattice vectors. To eliminate the free rotation of the system, only the symmetric part of the matrix \( h \) is updated, which reduces the number of the independent variables to 6.

The update of the matrix \( h \) is made by the steepest de-
scent method using the driving force $F$ and regarding $\delta h$ as the stepping parameter. The driving force $F$ is obtained as the sum of the original driving force $F_o = -\partial G_o / \partial h$, and the Gaussian driving force $F_g = -\partial G_g / \partial h$. The force $F_o$ can be expressed by an internal pressure tensor $p$, external pressure $P$, and the matrix $h$. One step of updating $h$ is defined as one meta-step.

At each meta-step, in order to equilibrate the system and to estimate $p$, the conventional molecular dynamics (MD) simulations have to be done with the shape of the simulation cell fixed. The internal pressure tensor and the atomic positions at each meta-step can be taken from the output of any constant-pressure MD codes of the first-principles calculation.

The above artificial potential means that if the current $h$ has been visited time after time, which occurs when the system is fluctuating around the local minimum of the GFE surface, $G_g$ accumulates to a large value and the well is gradually filled with the artificial potential $G_o$.

For the simulation of phosphorus, we used the density functional theory in a local density approximation and a norm-conserving pseudopotential, where we employed the expression of Perdew and Zunger for the exchange and correlation energy functional. We checked the pseudopotential comparing the calculated equation of states with the experiments in other phases. We started with the cubic simulation cell whose edge was 4.26 Å and 8 phosphorus atoms are set at the positions which make the sc lattice. We performed the k-space integration using $8 \times 8 \times 8$ mesh points in the first Brillouin zone and set the energy cut-off of the plane wave basis at 40 Ry. We set the external pressure at 120 GPa in the conventional constant-pressure MD, since the P-IV is observed at this pressure. In order to equilibrate the system, we ran this MD simulation for 200 steps at each meta-step and we calculated the average internal pressure tensor from the latter half of 100 steps. In order to perform this metadynamics simulation, we used the cluster machines.

Figure 1 shows the evolution of the cell volume and the angles among lattice vectors. The Gaussian-type potential was switched on at 39th meta-step and off again after 71st meta-step.

FIG. 1: Evolution of the simulation cell volume and the angles among lattice vectors. The Gaussian-type potential was switched on at 39th meta-step and off again after 71st meta-step.

to increase after around 50th meta-step and the volume began to decrease dramatically. After those changes, we switched the Gaussian-type potential off at 71st meta-steps again in order to check whether the system had already surmounted the barrier and had moved to a neighboring local minimum. If the system had not crossed the barrier yet, the angle and the volume would have returned to the starting values of the sc lattice, which are approximately 90° and 74 Å³, respectively. After 71th meta-step, however, the volume fluctuated around 73 Å³ and three angles also continued to fluctuate around 90°, 98° and 90°. This behavior shows that the sc structure transformed into another metastable one.

Figure 2 shows the structure obtained by the above run, where $\vec{a}$, $\vec{b}$ and $\vec{c}$ are the lattice vectors of the simulation cell. This structure has a unit cell with the lattice parameters $a = 4.22$ Å, $b = 4.15$ Å, $c = 4.22$ Å, $\alpha = 90.86°$, $\beta = 97.76°$ and $\gamma = 90.26°$. The left hand
FIG. 3: Modulated structures with different modulation periods along the b-axis. The pattern M1 is of a non-modulated structure, and M2 the structure obtained by our metadynamics simulation (ABAB⋯). The modulation periods of M4 (ABAC⋯) and M8 (ABCBADED⋯) patterns are twice and four times as long as that of the M2, respectively.

TABLE I: Comparison of the total energies per atom for a non-modulated structure (M1) and three modulated structures (M2, M4 and M8). We used the unit cell with the lattice vectors, \( \vec{a}/2, 4\vec{b} \) and \( \vec{c}/2 \) in the calculation of the total energy for all of these four structures.

| Structure | Total energy [Ry/atom] |
|-----------|-------------------------|
| M1        | -13.1624                |
| M2        | -13.1638                |
| M4        | -13.1642                |
| M8        | -13.1637                |

The side figure is the projection onto the ac plane. It shows the distortion of the simulation cell from the cubic into the cell with an angle 97.76°. When we look lattice from a side, we find a zigzag modulation of the ac plane along the b-axis with displacement in the direction of [110] as is shown in the ABAB.. in the right hand side figure. This is an important feature. The ABAB⋯ modulation pattern is crucial for the stability of the distortion of the angle \( \beta \). When we removed the zigzag modulation pattern and performed the simulation for the relaxation of the structure, we observed that the structure returned to the initial sc structure.

The structure obtained by the metadynamics is a modulation pattern with period consisting of two planes. Our simulation, however, was performed using the system with 8-atoms in a simulation cell, and with the periodic boundary condition. Hence there remains a question that the small simulation cell may limit the modulation period to a shorter one. In fact, the X-ray powder pattern of the zigzag modulated structure and that of the experimental one show some discrepancies. To answer this question, we tried some more first-principles calculations for the refinement of the structure.

We extended our study to two more structures which have commensurate modulations: an ABAC⋯ and an ABCBADED⋯. The modulation period of the ABAC⋯ and that of the ABCBADED⋯ are twice and four times as long as that of the ABAB⋯, respectively. These structures are denoted as M4 and M8 and shown in Fig. 3. The pattern M1 is a non-modulated structure, and M2 is the structure obtained by the metadynamics simulation. We calculated the total energies and the X-ray powder patterns.

To compare the total energy among these structures, we used the same unit cell with the lattice vectors, \( \vec{a}/2, 4\vec{b} \) and \( \vec{c}/2 \), where \( \vec{a}, \vec{b} \) and \( \vec{c} \) are those of the simulation cell obtained by the metadynamics simulation. The 8 atoms were located only along the b axis in the unit cell with displacements corresponding to the modulation pattern (Fig. 3). This choice of the unit cell avoids the numerical
errors coming from the use of the different size of the unit cells. For the k-space integration, we used $16 \times 4 \times 16$ mesh points in the first Brillouin zone. Amplitude of modulation for each structure was optimized by the relaxation of the atomic positions.

Calculated total energies are listed in Table I. All modulated structures, M2, M4, and M8 have lower energy per atom than the unmodulated structure, M1, which shows any modulation periods from M2 to M8 are more favorable than the M1. Among the above three modulated structures, the energy of the M4 is the lowest in our study of the commensurate approximation. Though the enthalpy of the M4 is very close to that of the sc, it is in fact lower than that of the sc at 120 GPa, according to our results. If we plot the total energy as a function of the modulation period and optimize the period as was done by Ehlers et al. [12], an incommensurately modulated structure is expected.

In figure 4 we compare the X-ray powder patterns of our structures with that of the experimental one. The experimental pattern of the P-IV (top figure) was obtained from Akahama et al.’s 8. It shows the feature that the splits of the strongest peak at $2\theta = 13^\circ$ and the three peaks in the range from $2\theta = 17^\circ$ to $19^\circ$ are observed. In our M2 structure, these features are missing and unnecessary peaks exist at $2\theta = 15^\circ$ and $25^\circ$. However, this disagreement is much improved with increase of the modulation period. Intensities of the unnecessary peak at $2\theta = 15^\circ$ in the M2 structure, which was brought about by the zigzag modulation, and another unnecessary one at $2\theta = 25^\circ$ in the same M2 structure, which appeared owing to the distortion of the simulation cell from the cubic, are decreased in the M4 and M8 structures and the split of the strongest peak appears also in the M4 and M8 structure. About the intensity of the three peaks in the range from $2\theta = 17^\circ$ to $19^\circ$, the X-ray powder pattern of the M4 shows most improved agreement with the experimental one among the 4 patterns studied. From the comparison of the total energies and the X-ray powder patterns, we conclude that the modulation period is close to that of the M4 structure in the P-IV.

In this study, we explored the structure of phosphorus in the phase IV using the first-principles metadynamics simulation and identified the new structure. This structure is the monoclinic with the modulation pattern. Furthermore we found the refined structure showing the best agreement with the X-ray powder pattern. Although we have not fully studied the possibility of the incommensurate modulation, we conclude that phosphorus takes the modulated structure with possible incommensurate modulation. The simple idea of Akahama et al. 8 stating that the structure of the P-IV may be on the path from the sc to sh via monoclinic distortion along the [110] direction is partly supported because the unmodulated structure is of space group $P2_1$ and of one atom per unit cell. The structure of the P-IV is not so complicated as one suggested by and Ehlers et al. 12. The modulation stabilizes the monoclinic distortion of the lattice. It is highly probable that the Vb, VIb, and VIIb group elements commonly show modulated structures in a narrow pressure range when they undergo the pressure induced structural transition between simple stable structures.

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