

## Incommensurate Structure of Phosphorus Phase IV

Hiroshi Fujihisa,<sup>1</sup> Yuichi Akahama,<sup>2</sup> Haruki Kawamura,<sup>2</sup> Yasuo Ohishi,<sup>3</sup> Yoshito Gotoh,<sup>1</sup> Hiroshi Yamawaki,<sup>1</sup>  
Mami Sakashita,<sup>1</sup> Satoshi Takeya,<sup>1</sup> and Kazumasa Honda<sup>1</sup>

<sup>1</sup>National Institute of Advanced Industrial Science and Technology (AIST), AIST Tsukuba Central 5,  
1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

<sup>2</sup>Graduate School of Material Science, University of Hyogo, 3-2-1 Kouto, Kamigori, Ako-gun, Hyogo 678-1297, Japan

<sup>3</sup>Japan Synchrotron Radiation Research Institute (JASRI), 1-1-1 Kouto, Mikazuki, Sayo-gun, Hyogo 679-5198, Japan  
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There are six known phases for phosphorus at room temperature under high pressure. Only the structure of phase IV, which exists from 107 GPa to 137 GPa, remains unsolved. We performed a powder x-ray diffraction experiment and a Rietveld analysis and successfully determined its structure to be an incommensurately modulated structure by only 1 site of atomic position. High-pressure phases of halogens and chalcogens have previously been shown to have a similar modulated structure; however, phosphorus phase IV is different from them and was shown to be the third case.

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Black phosphorus phase I (orthorhombic,  $Cmca$ , A17) is known to be most stable under ambient temperature and pressure [1,2]. On compression, it transforms to high-pressure phase II (rhombohedral,  $R\bar{3}m$ , A7) at 4.2 GPa and to phase III (simple cubic,  $sc$ ,  $Pm\bar{3}m$ ) at 10 GPa [3]. Akahama *et al.* found successive transitions to the intermediate phase IV at 107 GPa to phase V (simple hexagonal,  $sh$ ,  $P6/mmm$ ) at 137 GPa [4] and found a further transition to phase VI (bcc,  $Im\bar{3}m$ ) at 262 GPa [5]. This is the highest transition pressure known in all materials.

At the first transition from phase I to II, the occurrence of metallization was confirmed by optical [6] and electrical conductivity measurements [7,8]. A low-temperature high-pressure experiment showed that the superconducting temperature of phase I increased from 4.5 K to 13 K on compression [9]. Since phosphorus shows various changes under pressure, many theoretical studies have been performed [10–14].

High-temperature high-pressure behavior of phosphorus was investigated by a multi-anvil apparatus [15]. Katayama *et al.* discovered the first order liquid-liquid transition at 1000 °C and 1 GPa in 2000 [16]. They reported that tetrahedral  $P_4$  molecules in liquid were polymerized above 1 GPa, and their result was supported by a first-principle molecular dynamics simulation [17]. Its phase boundary was determined by an additional high-temperature high-pressure experiment [18].

The structure of the intermediate phase IV remains unsolved among the phases. Ahuja performed first-principle calculations by the full potential linear muffin-tin orbital method and predicted its structure to be  $Imma$ , which is the same as the high-pressure phase of Si [19] with a coordination number (the number of nearest neighbors) of 8. Ehlers and Christensen performed density-functional calculations and predicted its structure to be a Ba IV type host-guest structure [20] with a coordination number of 10. Unfortunately, the x-ray patterns that are

calculated from these structures do not agree with the experimental pattern. Furthermore, the coordination number 10 for the Ba IV structure is not suitable since the preferable value for phosphorus phase IV is 6 to 8. Very recently, Ishikawa *et al.* proposed a new model for phase IV by first-principle calculations using the metadynamics simulation method [21]. They reported a monoclinic lattice and an incommensurate modulation in its structure. The simulated diffraction pattern was similar to the experimental one. The purpose of this study is to determine the crystal structure of phosphorus phase IV by using an angle-dispersive powder x-ray experiment and to compare it to the structures of phases III and V.

The powder x-ray diffraction experiments were carried out using a monochromatic synchrotron radiation source on the BL10XU station at SPring-8, Hyogo, Japan. Powder diffraction patterns of the black phosphorus samples [22] were collected by an angle-dispersive method with a diamond anvil cell (DAC) and an imaging plate detector (IP). The experimental runs above 150 GPa were performed 6 times to check the reproducibility of the diffraction pattern. Diamond anvils of a 150- $\mu\text{m}$  culet and a tungsten carbide backing plate with a slit aperture were used to obtain Debye-Scherrer rings. Pressures were determined using the diamond anvil Raman gauge [23], which is based on the equation of the state of platinum [24]. The error of the pressure was estimated to be 2%, i.e.,  $\pm 2.5$  GPa at 125 GPa. The x-ray wavelength was 0.49654 Å. The x-ray beams were collimated by a 10  $\mu\text{m}$  diameter pin-hole. The typical exposure time was 20 minutes, and all the runs gave consistent results. A one-dimensional powder pattern was obtained by averaging the diffraction intensities along the ring [25]. Small spots on the image were omitted from the averaging.

As previously reported, phase I transformed successively to phase II, III, IV, V, and to VI as the pressure increased. The diffraction peaks of phases IV and V began

to appear at 107 GPa and 137 GPa, respectively. The atomic volume of phase IV at 125 GPa was estimated to be  $9.1 \pm 0.2 \text{ \AA}^3$  by extrapolating the atomic volumes of phases III and V. We were not able to obtain any good indexing candidates with a lattice constant below  $10 \text{ \AA}$ . By expanding the search range, *C*-centered orthorhombic lattice parameters of  $a = 2.772 \text{ \AA}$ ,  $b = 3.215 \text{ \AA}$ ,  $c = 22.69 \text{ \AA}$ , and its volume of  $V = 202.2 \text{ \AA}^3$  were found. This lattice contains 22 atoms judging from the estimated atomic volume of  $9.1 \text{ \AA}^3$ . Its primitive monoclinic lattice of  $a = c = 2.123 \text{ \AA}$ ,  $b = 22.69 \text{ \AA}$ ,  $\beta = 98.46^\circ$ , and  $V = 101.1 \text{ \AA}^3$  contains 11 atoms. After optimizing the atomic coordinates of 11 atoms to fit the observed pattern, a wavy structure appeared as shown in Fig. 1. An atomic displacement is visible along the *a* axis in Fig. 1(a) and the transverse wave along the *c* axis in Fig. 1(b). However, some peak positions that are simulated from this model still shifted. Therefore, the structure of phase IV must be an incommensurately modulated type by only 1 site of atomic position (ic1).

By dividing the length of the *c* axis of the *C*-centered lattice by 11, the smaller cell of  $c = 2.063 \text{ \AA}$ , containing 2 atoms, was obtained. The space group of this basic structure was *Cmmm* with the atom at the 2a (0,0,0) site. All the peaks could be fitted accurately by introducing the superspace group *Cmmm* (00 $\gamma$ ) *s*00 with  $\gamma = 0.267$ . The profile in Fig. 2 displays the Rietveld fit by the program Jana2000

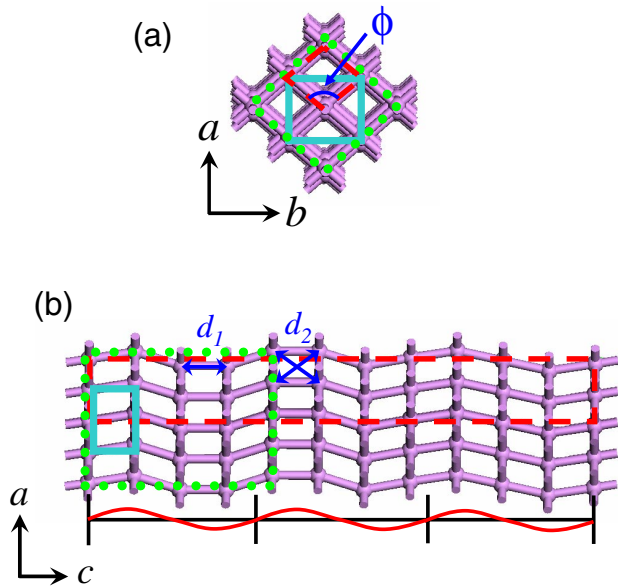


FIG. 1 (color online). Structural model of phosphorus phase IV at 125 GPa in (a) *ab* and (b) *ac* planes with a commensurate approximation. The dashed square represents a monoclinic primitive cell with 11 atoms.  $\phi$  is a monoclinic angle and corresponds to the lattice angles for phases III and V. Solid square shows the basic lattice for the *Cmmm* (00 $\gamma$ ) *s*00 model. The dotted rhombus in (a) and the square in (b) show a monoclinic lattice reported by Ishikawa *et al.* [21].

[26] with this superspace group. Very small peaks at  $15.0^\circ$  and  $15.4^\circ$  were assigned to second order satellites of (1 1 1  $\bar{2}$ ) and (1 1 0 2). The inverted  $\gamma$  was 3.74, a 7% smaller value than 4, and incommensurate. The triplicated value of 3.74 was 11.22 and was only 2% larger than 11. This explains why the commensurate model with 11 atoms could fit the pattern and the appearance of the 3 cycles of sine waves in Fig. 1(b). After the Rietveld refinement, the lattice parameters and its volume were determined to be  $a = 2.772 \pm 0.001 \text{ \AA}$ ,  $b = 3.215 \pm 0.001 \text{ \AA}$ ,  $c = 2.063 \pm 0.001 \text{ \AA}$ , and  $V = 18.39 \pm 0.02 \text{ \AA}^3$ . Its atomic volume of  $9.19 \pm 0.01 \text{ \AA}^3$  was in the range of the estimated value of  $9.1 \pm 0.2 \text{ \AA}^3$ . The modulation wave number was refined to be  $\gamma = 0.2673 \pm 0.0003$ ,  $1/\gamma = 3.741 \pm 0.004$ . The modulation amplitude was  $x \sin 1 = 0.148 \pm 0.001$  in fractional coordinate and  $0.410 \text{ \AA}$  in real space.

The dotted rhombus in Fig. 1(a) shows an *ac*-plane of Ishikawa's monoclinic lattice [21]. This is  $\sqrt{2} \times \sqrt{2}$  times larger than our *ab* plane in the ic1 model. The atomic displacement of their structure is along the  $\langle 101 \rangle$  direction and corresponds to our *a* direction. Their *b* axis corresponds to 4 times the length of the *c* axis in our basic

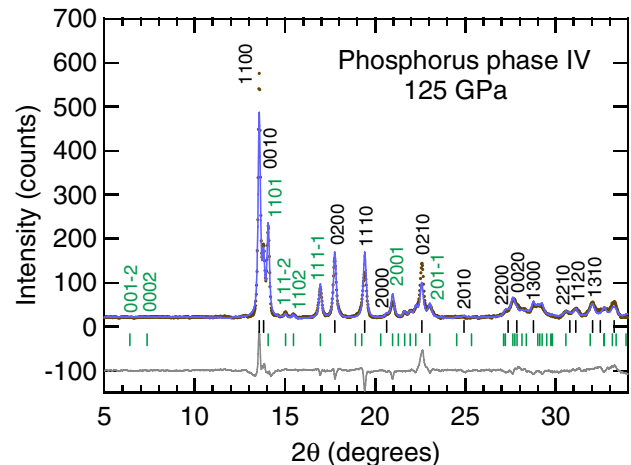


FIG. 2 (color online). The observed diffraction pattern of phosphorus phase IV at 125 GPa (dots) and the calculated profile (curve) after the Rietveld refinement. The tick marks show the calculated peak positions for the proposed *Cmmm* (00 $\gamma$ ) *s*00 structure. The differences between the observed and calculated profiles are shown below the tick marks. The March-Dollase preferred orientation function was used for the fitting. We tested preferred orientation vectors along the  $\langle 100 \rangle$ ,  $\langle 010 \rangle$ ,  $\langle 001 \rangle$ ,  $\langle 011 \rangle$ ,  $\langle 101 \rangle$ ,  $\langle 110 \rangle$ , and  $\langle 111 \rangle$  directions, and we found that the  $\langle 001 \rangle$  direction gave the best result. The reliability factor of  $R_{wp} = 17.4\%$  without the preferred orientation factor decreased to  $R_{wp} = 11.2\%$  with preferred orientation along the  $\langle 001 \rangle$  direction. The preferred orientation parameter *R* converged to  $1.262 \pm 0.007$ . The modulation amplitude  $x \sin 1$ , which is only one atomic parameter in this model, changed from  $0.153 \pm 0.002$  to  $0.148 \pm 0.001$ . The shift of  $0.005$  ( $0.01 \text{ \AA}$  in real space) does not affect the present result.

lattice. Thus, their monoclinic model is identical to our ic1 model, except for the  $\gamma$  value.

Figure 3 shows the dependence of the lattice parameters on pressure for phases III, IV, and V. The nearest interatomic distance for phase III ( $a_{sc}$ ) was connected continuously to that for phase IV in the  $ab$  plane written as  $\sqrt{a^2 + b^2}/2$ . However, the monoclinic angle  $\phi$  jumped discontinuously from  $90^\circ$  to  $97.8^\circ$  with pressure at the III-IV transition, and the  $\sqrt{2}a_{sc}$  for phase III split into  $a$  and  $b$  in phase IV. The coordination number 6 for phase III was maintained in phase IV since  $a$  for phase IV was still further than the nearest distances around  $2.2 \text{ \AA}$ . From 113 GPa to 137 GPa,  $a$ ,  $b$ , and  $c$  shrunk 1.5%, 0.2%, 1.2%, respectively. The largest shrinkage of the  $a$  axis corresponds to an increase in  $\phi$ . The  $a$  length of  $2.74 \text{ \AA}$  in phase IV shrunk to an  $a_{sh}$  of  $2.18 \text{ \AA}$  in phase V at 140 GPa, and  $\phi$  jumped from  $99^\circ$  to  $120^\circ$ . The coordination number increased from 6 to 8 at the IV-V transition. Akahama *et al.* reported that the structure of phase IV would be found between the monoclinic angle ( $\gamma$  in their report) of  $90^\circ$  to  $120^\circ$  [4]. This theory was proved to be correct when the modulation along the  $c$  axis was ignored.

The modulation wave number  $\gamma$  showed a gradual decrease of 0.268 to 0.266 in a pressure range from 113 GPa to 137 GPa. The modulation amplitude shifted from 0.132 to 0.149 in the same range. If there is no modulation, the interatomic distances along the  $c$  axis,  $d_1$  in Fig. 1(b), become the same as the length of the  $c$  axis. However,

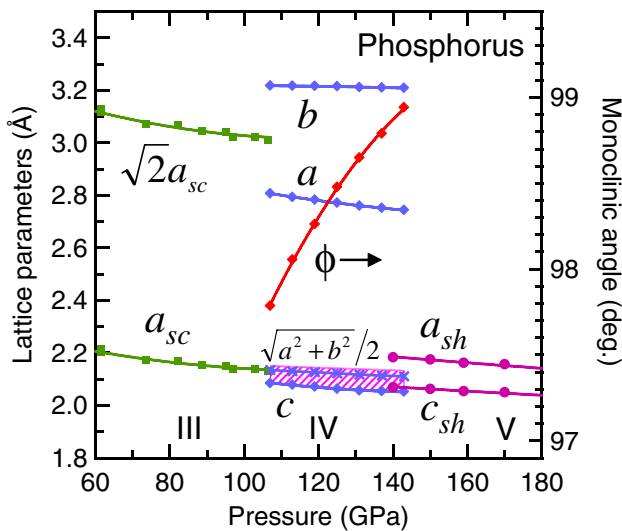


FIG. 3 (color online). Dependence of the lattice parameters on pressure for phosphorus phases III, IV, and V.  $\phi$  represents the angle for the monoclinic lattice shown in Fig. 1. The squares, diamonds, and circles denote the lattice parameters for each phase. The crosses correspond to the nearest distance in the  $ab$  plane in phase IV and are equal to the length of the lattice in the primitive monoclinic cell. The hatched area above the length of the  $c$  axis shows the nearest distances  $d_1$  in Fig. 1(b) along the  $c$  axis.

due to the modulation, the distances were distributed from  $2.06 \text{ \AA}$  to  $2.15 \text{ \AA}$  at 125 GPa. A width of the distribution was approximately  $0.08 \text{ \AA}$  and was almost constant through phase IV as shown by the hatched area. The distances along the  $\vec{a}/2 + \vec{b}/2 + \vec{c}$  and the  $-\vec{a}/2 + \vec{b}/2 + \vec{c}$  directions,  $d_2$  in Fig. 1(b), showed a wide distribution from  $2.73 \text{ \AA}$  to  $3.29 \text{ \AA}$  at 125 GPa. This range is almost the same as the range between  $a$  and  $b$ , and it is located in the second nearest neighbor region. Therefore, the coordination number for phase IV was confirmed to be 6.

Figure 4 shows the dependence of the atomic volume on pressure at room temperature. The volume of phase IV is located between that of phases III and V. The volume showed a gradual decrease of  $9.34 \text{ \AA}^3$  to  $9.07 \text{ \AA}^3$  in a pressure range from 113 GPa to 137 GPa. The volume gaps at III-IV and IV-V transitions were 2.6% and 5.5%, respectively. The latter takes the larger value and would correspond to the change of the coordination number and the bonding state.

The first ic1 type of incommensurately modulated structure reported was an  $Fmmm(00\gamma)s00$  for the high-pressure phase of iodine [27,28]. Bromine has been reported to have the same structure by the Raman experiment [29]. The second one was an  $I'2/m(0q0)s0$  for chalcogen of Te, Se, and S [30–32]. The present  $Cmmm(00\gamma)s00$  for phosphorus phase IV is the third case and has the highest transition pressure among incommensurate structures in all solids.

Ackland and Fox mentioned that a Kohn anomaly would induce an incommensurate modulation in selenium [33]. Degtyareva *et al.* proposed another theory that an incommensuration of sulfur is due to a charge-density wave [34].

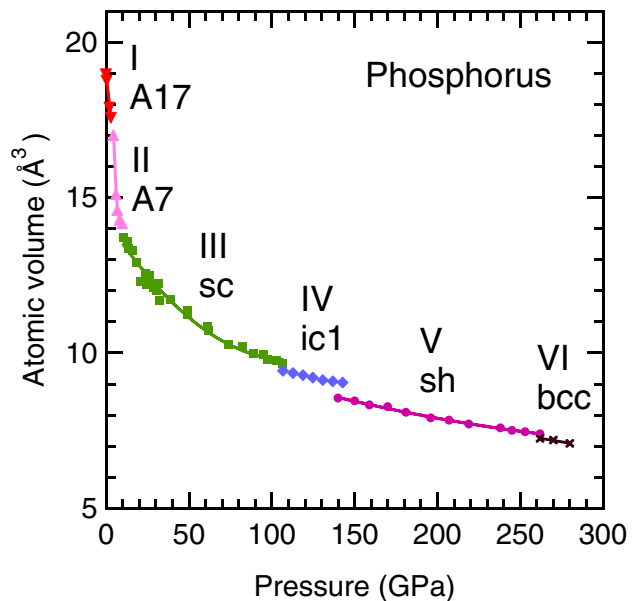


FIG. 4 (color online). Dependence of the atomic volume on pressure for phosphorus phases I to VI.

For phosphorus phase IV, Ishikawa *et al.* reported incommensuration in their recent calculation [21]; however, the details were not given. Further theoretical studies regarding incommensuration are necessary, and phosphorus phase IV can be used since its atomic number is the smallest among the ic1 structures that have been found and is quite suitable for the calculations.

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