Incommensurately Modulated Phase of Phosphorus under Pressure

Black phosphorus phase I (orthorhombic, *Cmca*), which is stable under ambient temperature and pressure, transforms to high pressure phase II (rhombohedral, $R\bar{3}m$) at 4.2 GPa, phase III (simple cubic, $Pm\bar{3}m$) at 10 GPa as shown in Fig. 1(a), intermediate phase IV at 107 GPa, phase V (simple hexagonal, *P6/m mm*) at 137 GPa, as shown in Fig. 1(c), and phase VI (bcc, $Im\bar{3}m$) at 262 GPa [1]. The structure of intermediate phase IV remains unsolved. Recently, Ishikawa *et al.* proposed a structural model for phase IV by first-principles calculations using the metadynamics simulation method [2]. They reported a monoclinic structure that has atomic displacement with an A-B-A-C pattern and a unit cell that is 4 times longer along the *c* axis than that of phase III or V. The purpose of this study is to determine the crystal structure of phosphorus phase IV by an angle dispersive powder X-ray experiment and Rietveld analysis.

Powder diffraction patterns of black phosphorus samples at pressures up to 150 GPa were measured using a diamond-anvil high-pressure cell (DAC) with 150 μm culet diamonds and an imaging plate detector (IP) at beamline **BL10XU**. The X-ray wavelength was 0.49654 Å. The X-ray beams were collimated by a 10-μm-diameter pinhole. The typical exposure time was 20 minutes. A one-dimensional powder pattern was obtained by averaging the whole intensities along the Debye-Scherrer rings recorded on the IP.

The diffraction patterns of phase IV were observed from 107 GPa to 137 GPa. By indexing the pattern at 125 GPa, we obtained a C-centered orthorhombic lattice as a possible candidate cell, as shown by blue dashed rectangle in Fig. 1(d). This lattice had a *c* axis length that was 11 times longer than that of phase III or V. After fitting the observed pattern by optimizing the atomic coordinates, a transverse wave along the *c* axis appeared, as shown in Fig. 1(d). However, some peak positions calculated by this model were found to be slightly shifted from the observed positions. Therefore, the structure of phase IV was considered to have an incommensurate modulation. By dividing the length of the *c* axis by 11, the fundamental lattice was obtained as shown by red rectangles in Figs. 1(b) and 1(d). The superspace group of this modulated structure was assigned to be *Cmmm* (00γ)*s*00. By the Rietveld refinement based on the incommensurate model in Fig. 2, the lattice parameters and its volume were determined to be a = 2.772±0.001 Å, b = 3.215±0.001 Å, and c = 2.063±0.001 Å, and V = 18.39±0.02 Å^3, respectively. The modulation wavenumber was also refined to be γ = 0.2673±0.0003, 1/γ = 3.741±0.004. The modulation amplitude corresponds to *xsin1* = 0.148±0.001 in a fractional coordinate and 0.410 Å in real space. The green dotted rectangle in Fig. 1(d) shows the theoretical prediction, that is, the Ishikawa's 4 times supercell [2]. Since the value of 4 is 7% larger than the experimental value for 1/γ, a misfit of the peak

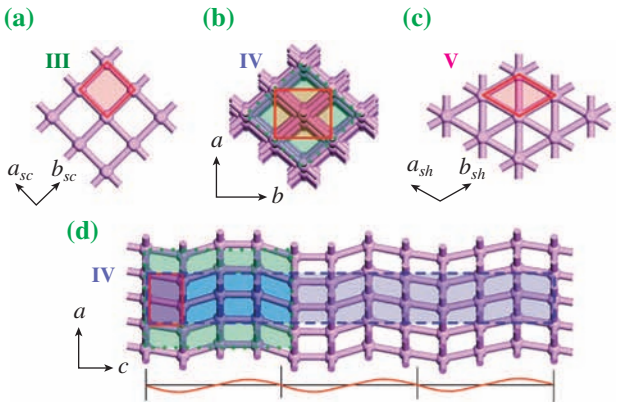

Fig. 1. Crystal structures of phosphorus **(a)** phase III, **(b)** phase IV, **(c)** phase V in *ab* plane, and **(d)** phase IV in *ac* plane with a commensurate approximation. The dashed blue rectangle in **(d)** represents the 11 times supercell. The solid red rectangles in **(b)** and **(d)** show the fundamental lattice for the *Cmmm* (00γ)*s* 00 model. The dotted green rectangle in **(d)** shows a monoclinic lattice predicted by Ishikawa *et al.* [2].

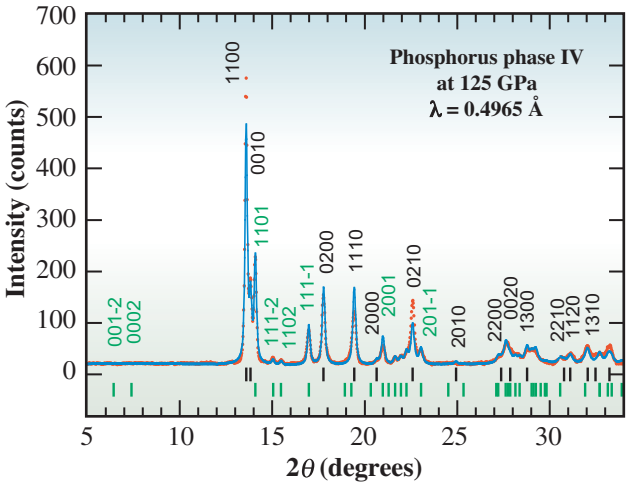

Fig. 2. Diffraction pattern of phosphorus phase IV observed at 125 GPa (brown dots) and the Rietveld fit with the proposed *Cmmm* (00γ)*s* 00 model (blue curve). The upper and lower tick marks show the peak positions of the fundamental and satellite reflections, respectively.

positions indeed exists between the observed data and the pattern calculated from the Ishikawa's model. However, their model is essentially consistent with our experimental result from the viewpoint of forming a particular superlattice structure.

Figure 3 shows the pressure dependence of the lattice parameters 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 $\sqrt{a^2+b^2}/2 \cdot \sqrt{2}\,a_{sc}$ for phase III split into *a* and *b* in phase IV. The coordination number of 6 for phase III was maintained in phase IV. As a result of the modulation, the interatomic distances along the *c* axis were distributed from 2.06 Å to 2.15 Å at 125 GPa. The *a* length of 2.74 Å in phase IV at around 140 GPa shrunk to a_{sh} 2.18 Å in phase V. The coordination number increased from 6 to 8 at the IV-V transition. Consequently, our proposed model of the phase IV structure suggests the meaningful explanation for the mechanism of the phase transition from phase III to V.

An incommensurate displacive modulation by only one site of the atomic position was first discovered in a high pressure phase of iodine [3] as a superspace group $Fmmm\ (00\gamma)s00$. The second one was $I'2/m\ (0q0)s0$ for chalcogens [4]. The present $Cmmm\ (00\gamma)s00$ for phosphorus phase IV is the third incommensurate displacive modulation. Comprehensive studies regarding pressure-induced incommensuration are needed.

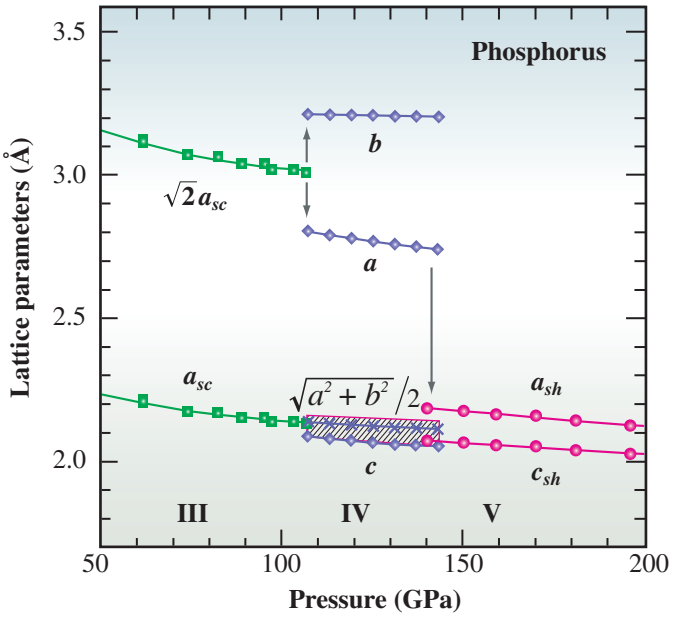

Fig. 3. Pressure dependence of the lattice parameters for phosphorus phases III, IV, and V. The squares, diamonds, and circles denote the lattice parameters for each phase. The crosses correspond to the nearest distance in the *ab* plane in phase IV. The pink-hatched area above the *c* axis length shows the nearest distance along the *c* axis, which is elongated by the modulation.

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References

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