PHYSICAL REVIEW B VOLUME 59, NUMBER 13 1 APRIL 1999-I

Simple-cubic–simple-hexagonal transition in phosphorus under pressure

Yuichi Akahama, Mototada Kobayashi, and Haruki Kawamura
Department of Material Science, Faculty of Science, Himeji Institute of Technology 1475-2, Kanaji, Kamigohri, Hyogo, 678-1297, Japan

(Received 5 June 1998; revised manuscript received 15 December 1998)

By using an angle dispersive powder x-ray-diffraction technique with a synchrotron radiation source at the SPring-8, lattice compression of the simple cubic (sc) structure of phosphorus and its phase stability have been studied up to 151 GPa. A phase transition from the sc to the simple hexagonal (sh) structure was observed at 137 GPa via an intermediate phase. In spite of the low packing fraction of atoms, the sc structure was stable over a wide pressure range from 10 to 103 GPa at 300 K and the equation of state of the phase was precisely determined. [S0163-1829(98)06442-X]

I. INTRODUCTION

For phosphorus of the group *Vb* elements, the most stable form at ambient conditions is the so-called black phosphorus which has the $A17$ (orthorhombic, space group: *Cmca*) structure.[1] It has been well known that the $A17$ structure transforms to the $A7$ (rhombohedral: $R\overline{3}m$) structure at 5 GPa and further into the simple cubic (sc: $Pm3m$) structure at 10 GPa.[2,3] The phase transitions are accompanied by drastic changes in its electronic structure, that is, semiconductor-semimetal-metal transitions.[4] Recent pseudopotential band calculations by Morita *et al.*[5] have stimulated numerous experimental studies on the properties of phosphorus. At present, the phase diagram of phosphorus has been constructed over wide temperature and pressure ranges[6] and a superconducting transition has also been found in the metallic sc phase above 10 K.[7,8]

The sc structure is a Bravais lattice with a lower packing fraction of atoms (0.524) than bcc (0.680) and fcc or hcp (0.74). In the periodic table, this structure is rare and occurs only in Po or the high-pressure phases of Ca,[9] P and As.[10] Its phase stability except for P is limited to a narrow pressure region. For this reason, the equation of state of the sc structure is not well known. At first, it was also considered for phosphorus that structural instability such as Peierls' will occur in the sc phase with a slight increase in pressure. However, the high-pressure stability of this phase has been confirmed up to 83 GPa by a previous x-ray-diffraction experiment.[11] How stable is this phase to pressure? A previous electrical resistance measurement has suggested the sign of a phase transition at 80–100 GPa.[4] There has been one theoretical study predicting the sc to bcc phase transition at 135 GPa by Sasaki *et al.*[12]

Iwasaki and Kikegawa[13] have proposed a systematic phase sequence in other group *Vb* elements upon compression, that is, the $A7$-(sc)-distorted bcc-bcc structure, according to recent high-pressure structural studies on As,[10,14,15] Sb,[16,17] and Bi.[18–20] Whether or not phosphorus follows these systematics is the objective of this study. In the study, the x-ray-diffraction experiment of phosphorus has been extended to 150 GPa by using a synchrotron radiation source at the Super Photon ring-8GeV (SPring-8).

In this paper, we report the transition from the simple cubic (sc) to the simple hexagonal (sh) Bravais lattice in phosphorus. The fundamental transition from the sc to sh structure is an interesting observation in the monoatomic system. In Sec. III we present the structural transition from the sc phase to an intermediate phase at 107 GPa and the equation of state of the sc phase. Section IV describes the sc-sh phase transition at 137 GPa.

II. EXPERIMENTAL

The starting material in this study was black phosphorus, of which a single crystal was grown from a red one of 99.9999% purity under high-temperature and high-pressure conditions of 1000 °C and 1.0 GPa, respectively. The crystals have been well characterized to be a high-purity semiconductor.[21] After the crystal was ground into a fine powder, it was used as the sample.

A diamond anvil cell (DAC) was used for the high-pressure generation. Two experimental runs were carried out with different anvil geometries. In both runs, a powder sample was put into a 50-μm-diameter hole of a Ni alloy ($U700$) or a Re gasket with ruby chips as the pressure marker and loaded with single beveled diamond anvils with 150 or 100 μm flats. No pressure transmitting medium was used. The ruby scale[22] was used for pressure determination. Pressure above 100 GPa was determined by the equation of state of Re.[23]

An x-ray-diffraction experiment at room temperature was carried out with a synchrotron radiation source on beam line BL10XU at the SPring-8. Powder patterns were obtained by an angle dispersive method with an image plate detector. The sample was exposed to an x-ray beam monochromated to 0.4957 or 0.4246 Å through a pinhole collimator of 50 or 25 μm diameter. The typical exposure time was 60 min or 3 h. Details of the x-ray experimental techniques and equipment will be described elsewhere. The obtained diffraction images were analyzed by using an integration software by Fujihisa *et al.*[24]

III. THE STABILITY AND EQUATION OF STATE OF THE SC PHASE

The lattice constants and atomic volume of the $A17$ structure of black phosphorus at ambient conditions were *a*

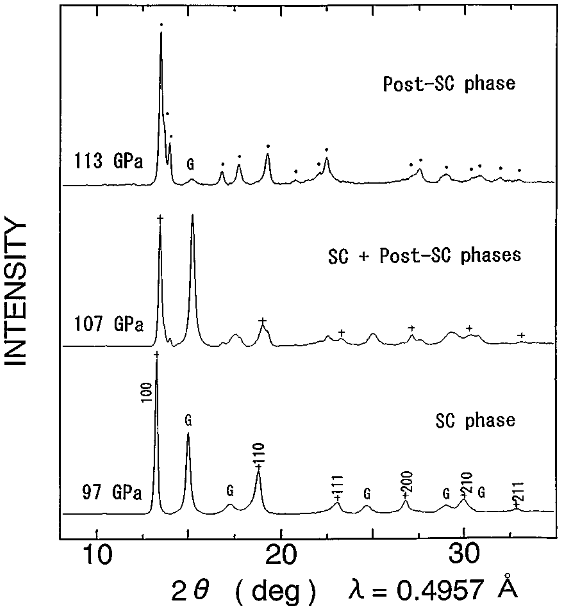

FIG. 1. Powder patterns of phosphorus around the structural transition from the simple cubic to a high-pressure phase, P-IV, at 107 GPa in the first experimental run. Miller indices are assigned to the reflection from the simple cubic phase of phosphorus. The symbol G represents the reflection from a metal gasket. A background due to Compton scattering from the diamond anvils has been subtracted numerically.

$=3.31_9$ Å, $b=10.48_4$ Å, $c=4.37_6$ Å, and $V=19.03_4$ Å^3/atom,[21] respectively, which were consistent with previously reported results.[1] With increasing pressure, the $A17$ structure was completely transformed to the sc structure at 12.7 GPa by way of the $A7$ structure. The diffraction image showed uniform Debye rings. Six reflections from the sample were indexed from 100 to 211. At this pressure, the lattice constant of the sc structure is estimated to be $a=2.387\pm0.001$ Å by the least-squares method. The error corresponds to the standard deviation. This value corresponds to the previous results.[2,3,11] The diffraction pattern of the sc structure with increasing pressure was retained at least up to 97 GPa. The pattern at 97 GPa is illustrated in Fig. 1(a). The observed and calculated d values and relative intensities are listed in Table I. An isotropic thermal parameter of 1.0 was used for the calculation of the intensity. d values of the diffraction lines from the sample are well assigned to the sc lattice with a lattice constant of $a=2.141\pm0.001$ Å, and $V=9.812\pm0.017$ Å^3. The observed relative intensities are different from the calculated ones, though at pressures lower than 62 GPa, the observed and calculated intensities agreed with each other. The observed ones of 100 and 200 reflections are two times larger than the others. This deviation may result from the preferred orientation effect of the sample, which is caused by uniaxial compression due to the nature of DAC.

Upon further loading to 107 GPa, the diffraction pattern indicates the coexistence between the sc phase ($a=2.125\pm0.002$ Å, $V=9.60\pm0.03$ Å^3) and the new high-pressure phase, P-IV, shown in Fig. 1(b). This result suggests a structural phase transition. The pattern at 113 GPa in Fig. 1(c), which was obtained by using a smaller pin-hole collimator with a 35 μm diameter, dramatically changes from the sc structure. The 111 reflection of the sc structure disappears and it is difficult to frame the sc lattice with any lines of observed reflections. At this pressure, the sc phase completely transforms to the P-IV phase. The observed diffraction lines are 16 except for one line from the gasket. Their d values are listed in Table II. The 100 line of the sc phase seems to split into three lines. This result suggests that the crystal symmetry of the P-IV phase is very low. No line with a relative intensity greater than 2% was observed in the 2θ range lower than the triplet. These results point out that the sc phase of phosphorus is not stable above 107 GPa any longer.

Other group Vb elements tend to follow the sequence of an $A7$-(sc)-distorted bcc-bcc structure under high pressure mentioned earlier.[13] The distorted bcc structure is a candidate for the P-IV phase and tetragonal (space group: $P4/n$) with 10 atoms in a unit cell, which well interpreted the dif-

TABLE I. List of the observed and calculated d values and relative intensities for the simple cubic structure of phosphorus and the fcc structure of the $U700$ metal gasket at 96 GPa. An isotropic thermal parameter of 0.1 was used for the calculation of intensity.

		sc of phosphorus $a=2.141\pm0.001$ Å			fcc of metal gasket $a=3.281\pm0.007$ Å	
d_{obs} (Å)	I_{obs} (%)	hkl	d_{cal} (Å)	I_{cal} (%)	hkl	d_{cal} (Å)
2.139	100	100	2.141	100		
1.889	53				111	1.894
1.645	6				200	1.641
1.515	27	110	1.514	66		
1.238	7	111	1.236	23		
1.157	5				220	1.160
1.069	8	200	1.070	10		
0.990	2				311	0.990
0.957	7	210	0.957	26		
0.950	<1				222	0.947
0.875	2	211	0.874	17		

TABLE II. List of observed d values and relative intensities of the intermediate P-IV phase of phosphorus at 113 GPa.

d_{obs} (Å)	I_{obs} (%)	d_{obs} (Å)	I_{obs} (%)
2.104	100	1.268	18
2.076	30	1.055	4
2.030	30	1.041	9
1.864[a]	4	0.990	6
1.689	9	0.941	3
1.604	14	0.931	4
1.478	22	0.900	3
1.372	3	0.872	2
1.292	6		

[a] The line comes from a metal gasket.

fraction patterns of the high-pressure phases of Bi-III,[20] As-III,[14,15] and Sb-II.[17] However, the diffraction pattern of the P-IV phase is not explained by this structure. If the P-IV phase is this structure, the strongest reflection should appear around $2\theta \geqslant 15°$. Because the reflection of the distorted bcc structure approximately corresponds to the 110 reflection of bcc with an atomic volume smaller than 9.6 Å^3. However, this of the P-IV phase is observed around $2\theta = 13°$. Furthermore, no other group Vb element shows the same kind of diffraction pattern. The structure of the P-IV phase is unknown at present.

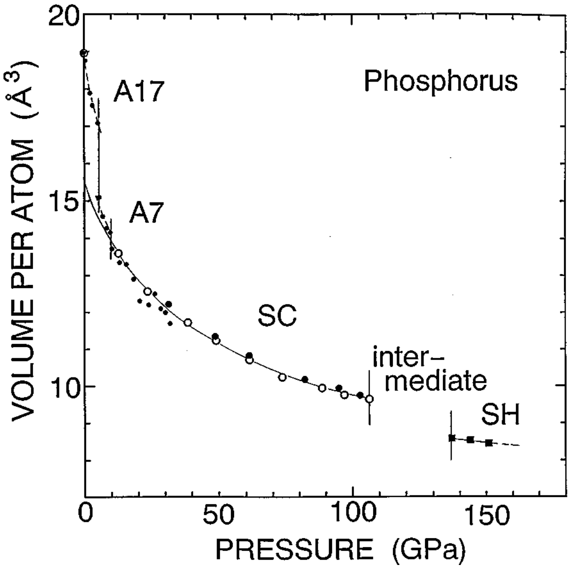

FIG. 2. Pressure dependence of the atomic volume of phosphorus at 300 K. The present data are shown by the open circles (for the first run), and the solid circles and squares (for the second). The small solid circles show the data by Kikegawa and Iwasaki (Ref. 3). The solid line represents the result of a least-squares fit of the Birch-Murnaghan equation of state to the experimental data (see Table IV), $B_0 = 70.7$ GPa, $B_0' = 4.69$, and $V_0 = 15.52$ Å^3.

TABLE III. List of atomic volume, V(Å^3/atom), of the simple cubic phase of phosphorus at various pressures at room temperature.

P (GPa)	V (Å^3/atom)	P (GPa)	V (Å^3/atom)
12.7 ± 0.5	13.606 ± 0.010	73.7 ± 2.5	10.350 ± 0.015
23.6 ± 1.0	12.588 ± 0.017	88.7 ± 2.0	9.994 ± 0.043
38.8 ± 1.5	11.717 ± 0.003	97.1 ± 1.5	9.812 ± 0.017
49.2 ± 2.0	11.261 ± 0.021	106.6 ± 1.5	9.601 ± 0.031
61.5 ± 2.5	10.784 ± 0.020		

The pressure dependence of the atomic volume of phosphorus is shown in Fig. 2 together with the previous result[3] and Table III lists the numerical results. The present data are in good agreement with the previous data. By using the data over the wide pressure range, the bulk modulus (B_0), its pressure derivative (B_0'), and relative atomic volume (V/V_0) of the sc phase at atmospheric pressure are estimated to be 70.7 ± 0.9 GPa, 4.69 ± 0.10, and 0.815 ± 0.009 ($V = 15.52 \pm 0.16$ Å^3), respectively, from a least-squares fitting to the Birch-Murnaghan equation of state[25] as follows:

$$P = \frac{3}{2} B_0 \left\{ \left(\frac{V_0}{V} \right)^{7/3} - \left(\frac{V_0}{V} \right)^{5/3} \right\} \times \left\{ 1 + \frac{3}{4} (B_0' - 4) \times \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right] \right\}. \tag{1}$$

Error bars to B_0, B_0', and V/V_0 correspond to the estimated standard deviations. With the present experimental technique, uniaxial strain may cause a systematic error if the atomic volume is calculated from the experimental lattice constant. These effects in a cubic system have been discussed by Singh *et al.*[26] According to them, the apparent lattice constant of a cubic crystal varies with a Γ function of the Miller indices of the individual reflections:

$$\Gamma = \frac{h^2k^2 + k^2l^2 + l^2h^2}{(h^2 + k^2 + l^2)^2}. \tag{2}$$

The least affected by uniaxial stress are the $h00$ peaks for which $\Gamma = 0$. The actual values for the lattice constant a must be closer to those obtained directly from the 100 and 200 diffraction lines. In order to estimate the systematic errors, the lattice constants at each pressure were recalculated from d values of both diffraction lines and the least-squares fitting was done using the corrected atomic volumes. The results are $B_0 = 70.4 \pm 1.1$ GPa, $B_0' = 4.51 \pm 0.14$, and $V/V_0 = 0.820 \pm 0.010$. The values of B_0 and B_0' are slightly smaller than the former values and the deviations are roughly within the error bars.

TABLE IV. Bulk modulus (B_0) and its pressure derivative (B_0') at ambient conditions for the $A17$, $A7$, and sc phases. V/V_0 denotes the relative volume of each phase extrapolated to atmospheric pressure, where V_0 (19.03_4 Å^3) stands for the volume of the $A17$ phase at atmospheric pressure.

Phase	V/V_0	B_0 (GPa)	B_0'	Ref.
$A17$	1.000	36 ± 2	4.5 ± 0.5	exp. 3
$A7$	0.872 ± 0.01	46 ± 4	3.0 ± 0.6	exp. 3
sc	0.815 ± 0.009	70.7 ± 0.9	4.69 ± 0.10	this work
	0.798 ± 0.01	95 ± 5	2.1 ± 0.8	exp. 3
	0.721	127.1	4.39	cal. 12

These values are listed in Table IV together with the previous data of the $A17$, $A7$, and sc phases. The present data are consistent with those of the $A17$ and $A7$ phases regarding the relation between each magnitude. The previous experimental B_0 and V/V_0 of the sc phase are different from the present ones. The difference must be due to the fact that the previous ones were estimated from the data in the limited pressure region. The calculated V_0 is smaller than present one but B_0 is larger.

As compared with other elements, the equation of state of the sc phase is similar to that of fcc-Al ($B_0 = 72.7\,\mathrm{GPa}$, $B_0' = 4.3$, and $V_0 = 16.6\,\text{Å}^3$),[27] with a typical free-electron band structure. This means that the total energy vs volume curvature of both phases is correspondence (approximately congruent). Fcc-Al has a high packing fraction of atoms and a longer nearest-neighbor distance of 2.84 Å than that of 2.50 Å of the sc phase for phosphorus. In spite of this, the fact that the compressibilities of both are comparable suggests a nearly free-electron band feature of the sc phase. Considering that Al is near phosphorus in the periodic table, namely, the ion-core configurations of the atoms are almost the same, the present result may reflect the compressibility of the free-electron gases.

This study revealed that the sc phase transforms to a low symmetric structure at 107 GPa. The transition seems to correspond to the previously reported electrical resistance anomaly.[4] The superconducting transition temperature may show a certain change at the transition. According to the theoretical study,[12] the stability of this phase over a wide pressure range between 10 and 97 GPa is due to the fact that the mixing of the $3d$ orbitals into the states around the Fermi level becomes larger upon compression. The observed transition pressure of 107 GPa is lower than the predicted value of 135 GPa.[12] The difference is reasonable because the predicted post-sc structure is bcc. From an analogy based on the observation of As, the transition pressure to bcc for phosphorus has been speculated to be 340 GPa.[14]

IV. THE SC-SH TRANSITION

In order to clarify whether or not phosphorus follows the proposed systematics,[13] the x-ray-diffraction experiments were extended into the 150 GPa regime. In the second experimental run, powder patterns were obtained in a pressure range from 32 to 151 GPa. The sc phase was observed up to 103 GPa. The diffraction pattern at 103 GPa is shown in Fig. 3(a). From six diffraction lines from 100 to 211, the lattice constant and atomic volume were estimated to be $a = 2.1374 \pm 0.0008\,\text{Å}$ and $V = 9.765 \pm 0.010\,\text{Å}^3$. The pressure dependence of the lattice constant of the sc phase was in good agreement with the data in the first run. We should note the remarkable broadening of the 110 diffraction line. On loading to 114 GPa, the sc phase transformed to the P-IV phase. The diffraction pattern of the P-IV phase is shown in Fig. 3(b). The transition pressure in the second run was consistent with the value of 107 GPa in the first run. The reproducibility of the transition was confirmed.

Upon further loading to 137 GPa, the diffraction pattern showed a dramatic change with the appearance of several new diffraction lines. The result indicated a structural transition to a new high-pressure phase, P-V. The transition was completed at 151 GPa. The diffraction pattern at 151 GPa is shown in Fig. 3(c). Nine observed diffraction lines of the sample are well assigned to the simple hexagonal lattice (space group: $P6/mmm$). The lattice includes only one atom in a unit cell. The observed and calculated d values and relative intensities are listed in Table V. Calculated lattice constants and atomic volume are $a = 2.1750 \pm 0.0004\,\text{Å}$, $c = 2.0628 \pm 0.0005$ Å, and $V = 8.452 \pm 0.005$ Å^3, respectively. Relative intensity suggests a strong preferred orientation to the c axis. The 001 and 002 reflections are about four times larger compared with the calculated values. The preferred orientation may be caused by uniaxial compression due to the nature of DAC. A visual observation under a metallugical microscope suggested that the sh phase is as metallic as the sc phase.

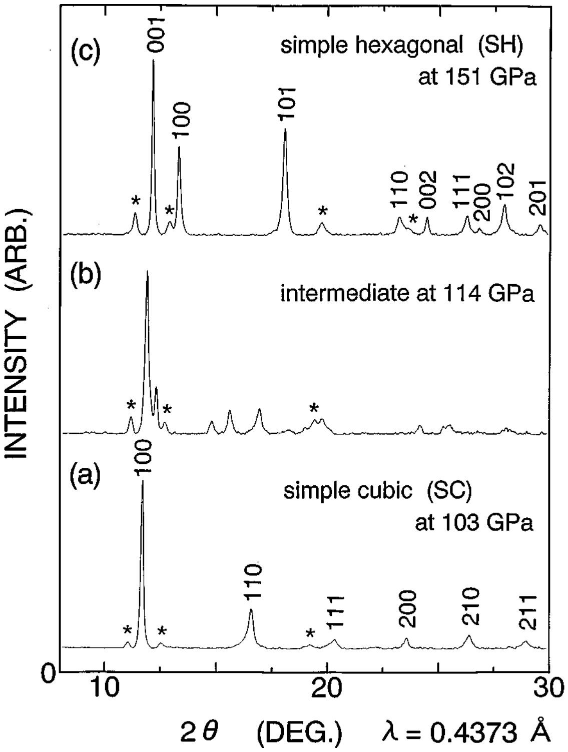

FIG. 3. Typical powder diffraction patterns of the high-pressure phases of phosphorus at RT, (a) the simple cubic (sc) phase at 103 GPa, (b) an intermediate phase (P-IV) at 114 GPa, and (c) the simple hexagonal (sh) phase at 151 GPa in the second experimental run. They were obtained with an x-ray beam of $\lambda = 0.4373\,\text{Å}$. A background due to Compton scattering from the diamond anvils has been subtracted numerically. Miller indexes in (a) and (c) are assigned to the reflections from the sc and sh phases, respectively. The asterisk (*) represents the reflection from a Re gasket.

The pressure dependence of the atomic volume of phosphorus is shown in Fig. 2. The sc phase transforms to the sh phase by way of the P-IV phase. Since the P-IV phase exists in a narrow pressure region from 107 to 137 GPa, it must be an intermediate phase between the sc and sh phase. The roughly estimated volume reduction between the sc and sh phases is $\Delta V = 0.74\,\text{Å}^3$ ($\Delta V/V_0 \sim 4\%$) at 103 GPa. The relatively large volume reduction comes from an increase in the coordination number as discussed below. The relative volume at 151 GPa reached 0.444.

TABLE V. List of the observed and calculated d values and relative intensities for the simple hexagonal structure of phosphorus and the hcp structure of the Re gasket at 151 GPa.

		sh of phosphorus $a = 2.1750 \pm 0.0004$ Å $c = 2.0628 \pm 0.0005$ Å			hcp of metal gasket $a = 2.5483 \pm 0.0007$ Å $c = 4.089 \pm 0.013$ Å	
d_{obs} (Å)	I_{obs} (%)	hkl	d_{cal} (Å)	I_{cal} (%)	hkl	d_{cal} (Å)
2.2096					100	2.2069
2.0645	100	001	2.0629	46.6		
1.9421					101	1.9421
1.8834	49	100	1.8837	100		
1.3913	60	101	1.3910	58.7		
1.2740					110	1.2742
1.0865	10	110	1.0875	8.6		
1.0314	10	002	1.0314	2.1		
0.9614	10	111	0.9620	8.2		
0.9424	4	200	0.9418	3.5		
0.9047	16	102	0.9047	5.4		
0.8570	7	201	0.8568	3.6		

The sh structure is also as rare as the sc structure in the monoatomic system and occurs only in the high-pressure phases of Si (Refs. 28 and 29) and Ge.[30] The sh lattice can be easily derived from the sc one by monoclinic distortion along the [110] direction to the sc lattice. Figure 4 illustrates the derivation. The sh lattice is achieved when the monoclinic angle γ becomes 120°. Therefore, the structure of the P-IV phase may be found in the process of this distortion. The broadening of the 110 diffraction line observed in the sc phase may also be attributed to a precursor behavior of the structural transition from the sc to the sh phase. If the mechanism is true, the transition pressure may be sensitive to a shear stress. We should note that in this experiment no pressure transmitting medium was used.

By the transformation from the sc to sh lattice, the coordination number increases from 6 to 8. As the result, a relatively large volume reduction of 13% is expected, that is, from a^3 to $\sqrt{3/2}\,a^3$. However, the observed volume reduction is $\Delta V = 0.74\,\text{Å}^3$ and corresponds to 7.6% of the atomic volume of the sc phase at 103 GPa. The result that the value is smaller than the expected one is due to the elongation of the lattice constant a of the sh phase compared with that of the sc phase. An interesting thing is that the c/a ratio of phosphorus is 0.948 and deviates from 1.0. The ratio was almost independent of pressure. The behavior of the ratio has also been reported for Si and Ge. According to the pseudopotential band calculation for Si by Chang and Cohen,[31] the fact that the c/a ratio is less than 1 means a large pileup of covalent charge along the c direction and suggests the existence of pressure-sensitive soft phonon modes. They have discussed that the soft modes and a modification of the c/a ratio reduce effectively the energy barrier from the sh to the hcp phase and these are likely the origin of the phase transition. Actually, the sh phase transformed to the hcp phase.[28] The transition may be expected in phosphorus.

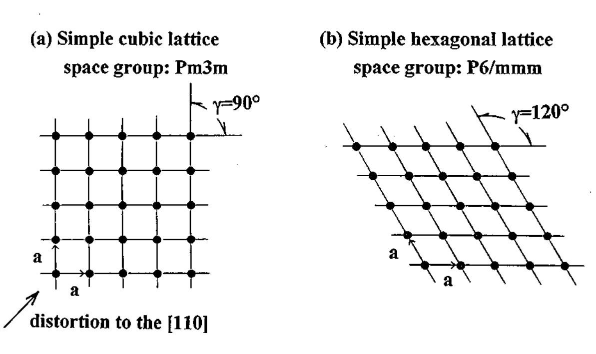

FIG. 4. Atomic arrangements of the simple cubic lattice (a) and the simple hexagonal lattice (b) projected onto the (001) plane. The simple hexagonal lattice of phosphorus can be derived from the simple cubic lattice by a monoclinic distortion along the [110] direction. The transition from the simple cubic to the simple hexagonal structure is completed with a monoclinic angle γ of 120°. As the result the coordination number N_c increases from 6 to 8.

The sh structure does not occur in the structural sequence of other group Vb elements. Namely, phosphorus did not follow the proposed structural sequence.[13] It rather seems to follow the sequence of Si, that is, sh-intermediate-hcp-fcc.[32] Phosphorus atom does not have d electrons in the core just like Si. McMahan and Moriarty[33] have reported the structural phase stability in third-period simple metals by first-principles techniques. They predicted sequences of high-pressure structural phase transitions for Mg, Al, and Si. Whether or not their prediction is extended to phosphorus and transforms to hcp and further to fcc structure is our next question.

V. CONCLUSION

We have shown that the sc phase transforms to an intermediate phase at 107 GPa where the relative volume V/V_0 is 0.506. By using the data over the wide pressure range, the equation of state of the sc phase, that is, the bulk modulus (B_0), its pressure derivative (B_0'), and relative atomic volume (V/V_0) of the sc phase at atmospheric pressure were determined to be 70.7 ± 0.9 GPa, 4.69 ± 0.10, and 0.815

± 0.009 ($V = 15.52 \pm 0.16$ Å^3), respectively.

The present study also revealed that the sc phase of phosphorus transformed to the sh phase at 137 GPa via an intermediate phase, P-IV. Phosphorus showed a different structural sequence from other group *Vb* elements. The difference may be attributed to the absence of *d* orbitals in the core of the phosphorus atom as proposed by Sasaki *et al.*[12] The simplest and most fundamental transition from the sc to sh Bravais lattice is a special example in the monoatomic system. In order to clarify the mechanism of this transition, the determination of the structure of the intermediate P-IV phase is indispensable, and also a theoretical study is strongly desired.

ACKNOWLEDGMENTS

The authors would like to thank all members of the High-Pressure Working Group for their contribution to building the experimental system for the high-pressure x-ray diffraction at the SPring-8. They also thank Dr. Y. Katayama, Dr. M. Ishii, and Dr. Y. Ohishi, and I. Nakahata, N. Matsui, and K. Nakano for their help in the experiments at the SPring-8. This work was partly supported by a Grant-in-Aid for Scientific Research (Grant No. 10440093) from the Ministry of Education, Science and Culture, Japan and done under Proposal Nos. 1997B0083-ND and 1998A0149-CD of the SPring-8.

---

[1] A. Brown and S. Rundquist, Acta Crystallogr. **19**, 684 (1965).

[2] J. C. Jamieson, Science **139**, 129 (1963).

[3] T. Kikegawa and H. Iwasaki, Acta Crystallogr., Sect. B: Struct. Sci. **B39**, 158 (1983).

[4] M. Okajima, S. Endo, Y. Akahama, and S. Narita, Jpn. J. Appl. Phys., Part 1 **23**, 15 (1984).

[5] A. Morita, Appl. Phys. A: Solids Surf. **A39**, 227 (1986), and references therein.

[6] T. Kikegawa, H. Iwasaki, T. Fujimori, S. Endo, Y. Akahama, T. Akai, O. Shimomura, T. Yagi, S. Akimoto, and I. Shirotani, J. Appl. Crystallogr. **20**, 406 (1987).

[7] H. Kawamura, I. Shirotani, and K. Tachikawa, Solid State Commun. **49**, 879 (1984).

[8] J. Wittig, B. Bireckoven, and T. Weidlich, in *Solid State Physics under High Pressure*, edited by S. Minomura (KTK Science Publisher, Tokyo, 1985), p. 217.

[9] H. Olijnyk and W. B. Holzapfel, Phys. Lett. **100A**, 191 (1984).

[10] T. Kikegawa and H. Iwasaki, J. Phys. Soc. Jpn. **56**, 3417 (1987).

[11] T. Akai, S. Nagatomo, S. Endo, Y. Akahama, and S. Narita, in *Proceedings of the 24th High Pressure Conference of Japan, 1983*, edited by Tanaka (Seikyosha, Fukuoka, 1983), p. 152.

[12] T. Sasaki, K. Shindo, K. Niizeki, and A. Morita, J. Phys. Soc. Jpn. **57**, 978 (1988).

[13] H. Iwasaki and T. Kikegawa, Acta Crystallogr., Sect. B: Struct. Sci. **B53**, 353 (1997).

[14] R. G. Greene, H. Luo, and A. L. Ruoff, Phys. Rev. B **51**, 597 (1995).

[15] H. Iwasaki, Phys. Rev. B **55**, 14 645 (1997).

[16] K. Aoki, S. Fujiwara, and M. Kusakabe, J. Phys. Soc. Jpn. **51**, 3826 (1982).

[17] H. Iwasaki and T. Kikegawa, High Press. Res. **6**, 121 (1990).

[18] R. M. Brugger, R. B. Bennion, and T. G. Worton, Phys. Lett. **24A**, 714 (1967).

[19] K. Aoki, S. Fujiwara, and M. Kusakabe, Solid State Commun. **45**, 161 (1983).

[20] J. H. Chen, H. Iwasaki, T. Kikegawa, K. Yaoita, and K. Tsuji, *Proceedings of the XIV AIRAPT International Conference on High Pressure Science and Technology*, Colorado Springs, 1993, edited by S. C. Schmidt *et al.* (AIP, New York, 1994), p. 421.

[21] S. Endo, Y. Akahama, S. Terada, and S. Narita, Jpn. J. Appl. Phys., Part 2 **21**, L482 (1982).

[22] H. K. Mao, P. T. Bell, J. W. Shaner, and D. J. Steinberg, J. Appl. Phys. **49**, 3276 (1978).

[23] Y. K. Vohra, S. J. Duclos, and A. L. Ruoff, Phys. Rev. B **36**, 9790 (1987).

[24] O. Shimomura, K. Takemura, H. Fujihisa, Y. Fujii, Y. Ohishi, T. Kikegawa, and Y. Amemiya, Rev. Sci. Instrum. **63**, 967 (1992).

[25] F. Birch, Phys. Rev. **71**, 809 (1947).

[26] A. K. Singh and C. Balasingh, J. Appl. Phys. **48**, 5338 (1978).

[27] K. Syassen and W. B. Holzapfel, J. Appl. Phys. **49**, 4427 (1978).

[28] H. Olijnyk, S. K. Sikka, and W. B. Holzapfel, Phys. Lett. **103A**, 137 (1984).

[29] J. Z. Hu and I. L. Spain, Solid State Commun. **51**, 263 (1984).

[30] Y. K. Vohra, K. E. Brister, S. Desgreniers, and A. L. Ruoff, Phys. Rev. Lett. **56**, 1944 (1986).

[31] K. J. Chang and M. L. Cohen, Phys. Rev. B **31**, 7819 (1985).

[32] S. J. Duclos, Y. K. Vohra, and A. L. Ruoff, Phys. Rev. B **41**, 12 021 (1990).

[33] A. K. McMahan and J. A. Moriarty, Phys. Rev. B **27**, 3235 (1983).