Acta Cryst. (1983). B**39**, 158–164

An X-ray Diffraction Study of Lattice Compression and Phase Transition of Crystalline Phosphorus

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(*Received* 19 *July* 1982; *accepted* 23 *September* 1982)

Abstract

Polycrystalline phosphorus has been compressed with sodium chloride as an internal pressure marker in an X-ray diamond-anvil cell. A two-step structural phase transition, orthorhombic → rhombohedral and rhombohedral → simple cubic, has been confirmed. While the rhombohedral (*A*7) structure, found to be common to the Group V*b* elements, forms only in a limited range of pressure, from 5·5 to 10 GPa, the simple cubic (primitive) structure is shown to remain quite stable on compression and no indication of a third transition is detected up to 32 GPa, the highest pressure attained. A least-squares fitting of the lattice-compression data to the Murnaghan equation gives the bulk modulus and its pressure derivative for the three polymorphic phases respectively as follows: 36 ± 2 GPa and 4·5 ± 0·5, 46 ± 4 GPa and 3·0 ± 0·6 and 95 ± 5 GPa and 2·1 ± 0·8. An atomistic model of the first transition between the orthorhombic and rhombohedral structures is proposed and compared with that of the second transition. The stability of the simple cubic structure in the Group V*b* elements under high pressure is discussed.

Introduction

The stable crystalline form of phosphorus at 0·1 MPa (1 bar) and room temperature, called black phosphorus, is orthorhombic (space group *Cmca*) with eight atoms in a unit cell of size $a = 3{\cdot}31$, $b = 10{\cdot}50$ and $c = 4{\cdot}38$ Å† (Hultgran, Gingrich & Warren, 1935). When subjected to high pressure, it undergoes a two-step structural phase transition; the structure first changes into the rhombohedral form and then into the simple cubic form (Jamieson, 1963). The rhombohedral form is the *A*7 structure found to be common to the Group V*b* elements, while the simple cubic form containing one atom in a unit cell is less common among the structures of elements and only polonium is known to crystallize in this structure at low temperatures (Pearson, 1967). The high-pressure structural study by Jamieson was conducted using sodium chloride as an internal pressure marker and referring to the original Bridgman's volumetric data, and the maximum pressure attained was 12 GPa (120 kbar). The transition pressure P_T of the first structural change, however, could not be determined with any confidence, whereas P_T of the second structural change was placed at 11 GPa. Until recently no attempt has been made to measure compressibilities of each polymorphic phase and to extend the structural investigation to pressures in excess of 12 GPa, but two independent measurements of electrical conductivity at liquid-helium temperatures were carried out (Wittig & Matthias, 1968; Berman & Brandt, 1968) and a superconducting transition was found at about 17 GPa. This metallic behavior was attributed to a characteristic of the simple cubic phase (Wittig & Matthias, 1968), whereas, by analogy with the polymorphic sequence found in antimony and bismuth, the superconducting phase of phosphorus was assumed to be isomorphous with SbIII and BiIII (Berman & Brandt, 1968), to which a tetragonal structure was later assigned (Duggin, 1972).

In recent years, much attention has been focused on the structural stability of crystalline phosphorus. Cartz, Srinivasa, Riedner, Jorgensen & Worlton (1979) made a neutron diffraction study on the orthorhombic phase and found a remarkable anisotropy in the lattice compressibility, which was interpreted as a reflex of the directional bonding in the layered structure of black phosphorus. The maximum pressure in their measurement was 2·66 GPa. A theoretical approach was first made by Schiferl (1979) with the aim of reproducing the polymorphic sequence of structures by calculating crystal energy as a function of volume. This approach, however, yielded several results in conformity with the observation. Asahina (1981) improved the method of calculation and could show that the rhombohedral and simple cubic structures are the two stable forms of phosphorus at high pressures and the P_T between these two forms is 10 GPa. However, he could not succeed in

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[†] In the original report, an alternative choice of axes was adopted.

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explaining the stability of the orthorhombic structure at 0·1 MPa (1 bar). To further our knowledge, more information on the structure at high pressures, especially on the stability of the simple cubic structure, was required. So long as one considers crystal structures as a packing of atom spheres, the simple cubic structure may not be an ideal atomic arrangement owing to its lower packing density. The question arises to what extent does the non-close-packed structure remain stable at high pressures. In connection with this, it is interesting to note that the existence of the simple cubic phase in antimony is in dispute. Kabalkina, Vereshchagin & Mylov (1964) and Vereshchagin & Kabalkina (1965) reported a transition from the rhombohedral into simple cubic structure at 7 GPa, whereas McWhan (1972) and Schiferl, Cromer & Jamieson (1981) could not detect the transition.

The purpose of the present work is twofold: first, to reinvestigate the crystal structure of phosphorus under compression with the emphasis placed on the confirmation of the existence of the simple cubic phase and, if it is confirmed, to investigate its stability using an apparatus which enables one to explore a much wider range of pressures than that examined in the previous studies. The second purpose is to provide reliable data on compressibility, transition pressure and volume change at the transition, which will be used as parameters for refining the calculation of crystal energy as a function of pressure.

Experimental procedures

Orthorhombic (black) phosphorus was prepared in two different ways. In the first, powdered red phosphorus, 99·999% pure, was held for 24 h at a pressure of 9 GPa and a temperature of 673 K using a Bridgman-anvil type apparatus in our laboratory. In the other, red phosphorus, embedded in a pyrophyllite capsule, was melted under a pressure of 1 GPa in a multi-anvil-type apparatus at Osaka University, cooled slowly across the melting temperature and quenched to ambient conditions. X-ray diffraction examination has shown for both the samples that interplanar spacings and intensities of reflections are in agreement with those reported for black phosphorus by Hultgren *et al.* (1935).

A high-pressure structural investigation was conducted using a gasketed diamond-anvil cell designed by the present authors (Kikegawa & Iwasaki, 1982). It has a semi-spherical anvil support, whose orientation can easily and accurately be adjusted from outside. A powdered sample of black phosphorus intimately mixed with sodium chloride was placed in a hole 0·2 mm in diameter of an Inconnel gasket and squeezed between the diamonds, having a truncated face of 0·5 or 0·6 mm in diameter. Sodium chloride served as an internal pressure marker as well as a pressure-transmitting medium. Filtered Mo $K\alpha$ radiation from a high-power tube with a rotating anode (55 kV and 350 mA) or from a sealed-off tube with fine focus (45 kV and 18 mA), collimated to form a beam 0·1 mm in cross-sectional diameter, was incident on the sample. The diffraction pattern was recorded on a flat film placed at a distance of 55 mm from the sample.

The lattice parameters of phosphorus were determined using the diffraction lines appearing in the 2θ angle range 0 to 40°, the details of which are described separately for each polymorphic phase in the following sections. The main source of systematic error in the lattice-parameter determination was shrinkage of the film and it was corrected by measuring the distance between the shadow edges of the film cassette.

The diffraction lines 200, 220, 222 and 420 of sodium chloride were used for the determination of pressure, referring to Decker's (1971) scale. The error in the pressure values which arises from that in the lattice-parameter measurement of sodium chloride was estimated to be $\pm 2\%$ at low pressures and increased to $\pm 3\%$ at pressures higher than 10 GPa.

Experimental results and their interpretation

(*a*) *Compression of the orthorhombic phase*

The low symmetry and large unit-cell sizes of orthorhombic phosphorus yield a number of diffraction lines distributed over a relatively narrow angle range (Hultgren *et al.*, 1935). But when the diffraction pattern

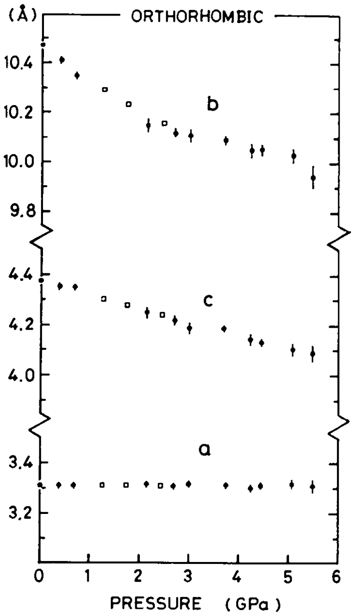

Fig. 1. Lattice parameters of orthorhombic phosphorus plotted against pressure. The bar attached to each datum point represents the estimated error. Some of the data from Cartz *et al.* (1979) are also shown (as open squares) for comparison.

Table 1. *Volume per atom of crystalline phosphorus at various pressures*

Pressure (GPa)	Volume (Å^3)	Pressure (GPa)	Volume (Å^3)
Orthorhombic		Simple cubic	
0	$18{\cdot}9_6$	10·3	$13{\cdot}7_2$
0·40	$18{\cdot}7_6$	10·4	$13{\cdot}6_3$
0·70	$18{\cdot}6_3$	10·6	$13{\cdot}8_0$
2·15	$17{\cdot}8_9$	11·2	$13{\cdot}7_0$
$2{\cdot}7_0$	$17{\cdot}6_8$	13·2	$13{\cdot}3_5$
$3{\cdot}0_0$	$17{\cdot}5_6$	13·3	$13{\cdot}1_3$
$3{\cdot}7_0$	$17{\cdot}4_9$	13·6	$13{\cdot}4_3$
$4{\cdot}2_3$	$17{\cdot}1_8$	13·8	$13{\cdot}2_3$
$4{\cdot}4_5$	$17{\cdot}3_2$	14·1	$13{\cdot}2_7$
5·1	$17{\cdot}0_9$	14·6	13·2
5·5	$16{\cdot}8_2$	15·7	13·3
Rhombohedral		17·8	12·6
5·5	$15{\cdot}1_0$	18·4	12·9
5·7	$14{\cdot}9_5$	19·6	12·9
6·3	$14{\cdot}7_7$	19·8	12·9
6·4	$14{\cdot}6_7$	20·7	12·3
6·7	$14{\cdot}6_3$	21·0	12·8
6·9	$14{\cdot}5_9$	21·6	12·7
7·3	$14{\cdot}5_4$	24·1	12·2
7·8	$14{\cdot}4_5$	26·4	12·5
8·4	$14{\cdot}2_8$	28·6	12·1
8·9	$14{\cdot}2_8$	30·4	12·0
9·6	$14{\cdot}2_6$	32·1	11·7
9·7	$14{\cdot}1_6$		

is recorded with the sample placed in the diamond-anvil cell using Mo $K\alpha$ radiation, only fourteen lines are recognized, primarily due to the heavy absorption of the X-ray beam by the anvils and to overlapping with the lines of the internal pressure marker. In spite of the limited number of observable diffraction lines, they suffice for the determination of the lattice parameters at high pressures. First, b was determined from the d values of the 020, 040 and 060 reflections and then a and c from the d values of the remaining reflections using the value of b thus determined.

Fig. 1 shows the lattice parameters of the orthorhombic phase plotted against pressure. The bar attached to each datum point represents the estimated error. The data of Cartz *et al.* (1979) are also shown for comparison. An appreciable anisotropy is observed; b and c rapidly decrease with increasing pressure while a remains almost unchanged. It is to be noted that the compressibility along the b axis is nearly the same as that along the c axis up to a pressure of 2·7 GPa, but then, while the c axis continuously decreases in length, the compressibility along the b axis gradually decreases. At 5·5 GPa, which is determined to be the maximum pressure of the stable existence of the orthorhombic phase, the b and c axes are respectively 4·8 and 6·5% smaller than that at 0·1 MPa.

From the measured lattice parameters, the volume per atom (V) of orthorhombic phosphorus has been calculated as a function of pressure, as shown in Table 1. A least-squares fit of the volumetric data to the Murnaghan equation of the form

$$P=\frac{K_0}{K'}\left[\left(\frac{V_0}{V}\right)^{K'}-1\right] \quad (V_0\text{: volume at } 0{\cdot}1\text{ MPa}) \quad (1)$$

gives K_0 (bulk modulus at 0·1 MPa) = 36 ± 2 GPa and K' (pressure derivative of bulk modulus) = 4·5 ± 0·5.

As for the pressure dependence of the intensities of reflections, an increase or decrease, although not remarkable, has been observed for some diffraction lines. For instance, the 020 reflection gradually loses its intensity with increasing pressure. However, the existence of a preferred orientation of crystallites did not permit accurate determination of the atomic positional parameters as a function of pressure. According to Cartz *et al.* (1979), the variation of the two positional parameters, y and z, up to a pressure of 2·66 GPa is 1·8 and 7·1%, respectively.

Fig. 2(a) shows a schematic view of the atomic arrangement in orthorhombic phosphorus. It consists of puckered layers stacked in the **b** direction. The decrease in the length of the b axis results in a decrease in the spacing between the puckered layers, while the

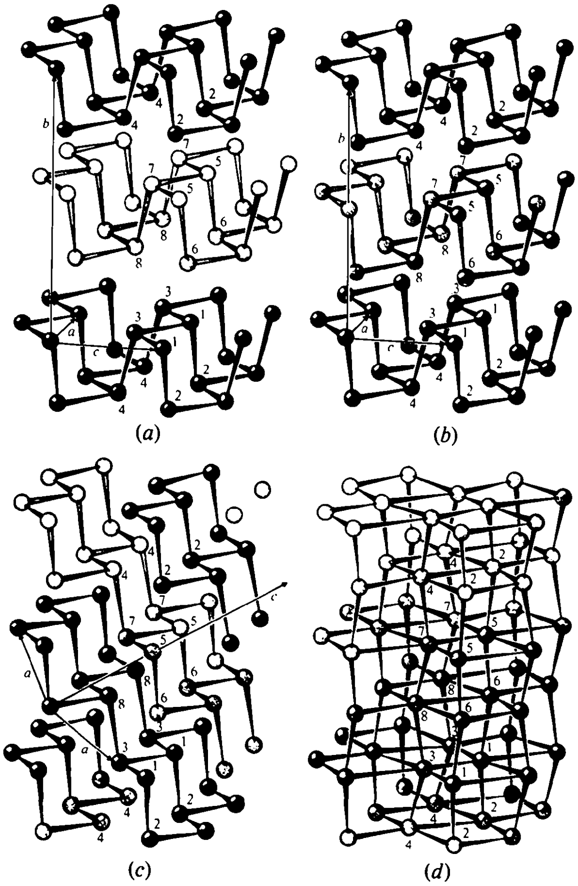

Fig. 2. Atomic arrangements in phosphorus. (a) Orthorhombic form, showing puckered layers stacked in the **b** direction. (b) After displacement of alternate puckered layers by $a/2$. The distances between atoms located on adjacent layers are decreased. (c) Rhombohedral $A7$ form, produced by forming interlayer covalent bonds. (d) Simple cubic form. In order to make clear the structural relation to the rhombohedral form, most of the atoms are shown not exactly positioned on the cubic lattice.

shortening of the c axis signifies an increase in the puckering angle of the layer. Using the lattice parameters determined in the present work and the positional parameters obtained by extrapolating the low-pressure neutron diffraction data (Cartz *et al.*, 1979), approximate values of the principal interatomic distances at 5·5 GPa have been calculated. Those within the layer, which measure the length of the covalent bonds, are 2·19 ± 0·03 Å between the atoms (1) and (3), or (5) and (7), in Fig. 2(*a*) and 2·18 ± 0·03 Å between the atoms (1) and (2), or (7) and (8), which were respectively 2·222 ± 0·008 and 2·277 ± 0·011 Å at 0·1 MPa. Those across the adjacent layers, which measure the length of the van der Waals bonds, are 3·37 ± 0·03 Å between the atoms (3) and (8), or (4) and (7), and 3·53 ± 0·03 Å between the atoms (3) and (6), or (2) and (7), which were respectively 3·559 ± 0·013 and 3·769 ± 0·010 Å at 0·1 MPa.

(*b*) *Transition from the orthorhombic to rhombohedral phase*

The clearest evidence of formation of the $A7$ structure in the sample is the appearance of the 00.3 reflection. In the pattern taken at 5·5 GPa, this reflection is observed, but an overall feature of the pattern shows the coexistence of the low- and high-pressure phases. Increase in pressure up to 5·7 GPa results in complete transformation of the structure. Repeated runs of the pressurization yield nearly identical results and P_T is placed at 5·5 ± 0·5 GPa. No attempt was made to follow the transition on releasing the pressure, since pressure control was difficult. Recent Raman scattering measurements made by Sugai, Ueda & Murase (1981) detected a sharp change in the spectrum at 5·2 GPa, which was interpreted as the change associated with the structural phase transition. It is to be noted that the optical measurement using a liquid pressure-transmitting medium gives nearly the same P_T as that determined by the X-ray diffraction measurement using a solid medium.

From the lattice parameters of the coexisting orthorhombic and rhombohedral phases, the volume change ΔV at the transition is calculated to be 1·72 Å^3 per atom, which is 10·2% of the volume of the orthorhombic phase before the transition.

The rhombohedral structure is known as another type of layered structure of phosphorus with every atom covalently bonded to three neighboring atoms in the same layer. No structural relationship between the two types of layered structures, orthorhombic and rhombohedral, has hitherto been elucidated and here a model is proposed which describes an atomistic mechanism for the transition. As a result of the decrease in the interlayer distance of the orthorhombic structure, there is a chance to form new covalent bonds between the atoms located on the adjacent layers. Transformation, however, may start by the displacement of alternate (010) puckered layers of the orthorhombic structure relative to the others by the distance $a/2$. Fig. 2(*b*) shows the atomic arrangement in the displaced structure and the distances between the atoms located on the adjacent layers, *i.e.* those between the atoms (3) and (8) and those between the atoms (4) and (7), are decreased to 2·94 Å. In the next step, the particular bonds between the atoms located on the same layer, *i.e.* those between the atoms (3) and (4) and those between the atoms (7) and (8), are broken and linkages are formed between the atoms (3) and (8) and between the atoms (4) and (7). Such a reconstruction together with readjustment of some of the bonding angles leads to the rhombohedral $A7$ structure with layers parallel to the (011) plane of the original orthorhombic structure. Fig. 2(*c*) shows the $A7$ structure constructed thus. An X-ray diffraction examination using single crystals would reveal the orientation relationship between the low- and high-pressure phases, *i.e.* $(00.1)_{\rm high} \parallel (011)_{\rm low}$ and $[11.0]_{\rm high} \parallel [100]_{\rm low}$, where the Miller indices of the high-pressure phase are given in terms of a hexagonal lattice.

(*c*) *Compression of the rhombohedral phase*

Fig. 3 shows an X-ray diffraction pattern of the $A7$ phase of phosphorus at 6·7 GPa. Eight diffraction lines are observable. The determination of the lattice parameters, which are expressed here for convenience in terms of a hexagonal lattice, has been made in two steps; first, approximate a and c values have been calculated from the d values of the 11.0 and 00.3 reflections respectively and then they have been refined using the d values of the remaining reflections. a and c at various pressures are shown in Fig. 4. An anisotropy exists in the compressibility and the c axis

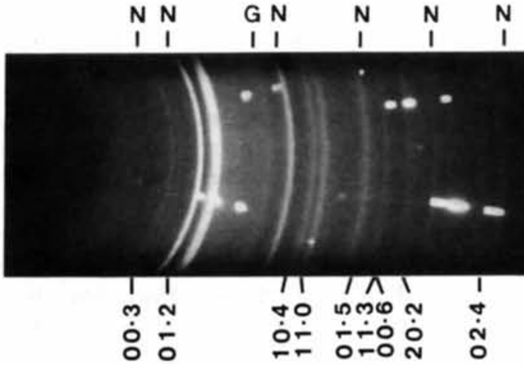

Fig. 3. X-ray diffraction pattern of the rhombohedral form of phosphorus at 6·7 GPa. Indices are given in terms of a hexagonal lattice. The diffraction lines denoted by N and G are those from NaCl and the gasket, respectively. Filtered Mo $K\alpha$ radiation was used.

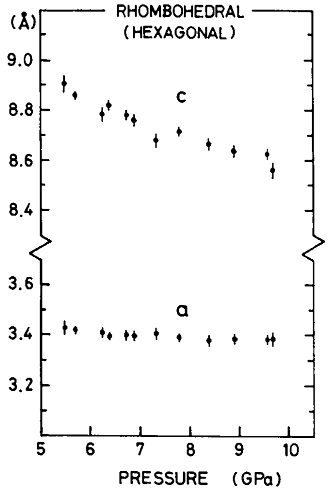

Fig. 4. Lattice parameters of the *A*7 form of phosphorus plotted against pressure.

decreases faster than the *a* axis, resulting in a decrease in the axial ratio. c/a is 2·60 ± 0·01 immediately after the transition and it becomes 2·53 ± 0·01 at 9·7 GPa. It does not reach, however, the critical value $\sqrt{6}$, a value corresponding to the conversion into the simple cubic structure, before the second structural change takes place. A similar observation was reported for the *A*7 antimony (Kolobyanina, Kabalkina, Vereshchagin & Fedina, 1969).

In Table 1, the volume per atom of the rhombohedral phase is shown as a function of pressure. Least-squares fitting of the data to equation (1) has been made, V_0 thereby being treated as an adjustable parameter. It yields $K_0 = 46 \pm 4$ GPa, $K' = 3{\cdot}0 \pm 0{\cdot}6$ and $V_0 = 16{\cdot}6 \pm 0{\cdot}2$ Å^3 per atom. The K_0 value of the *A*7 phosphorus is larger than that of its *A*7 cognates arsenic (38 GPa),* antimony (41 GPa)* and bismuth (31 GPa).*

There is one atomic positional parameter *z* for the *A*7 structure (Schubert, 1964). It can be shown that a value $z = 0{\cdot}223 \pm 0{\cdot}003$ gives intensities of reflections which are in agreement with those photometrically measured on the X-ray diffraction pattern taken at 6·7 GPa. Table 2 shows a comparison of the calculated and measured intensities. An appreciable pressure dependence of the relative intensities of the reflections is detected, the 10.4 and 02.4 reflections increasing their intensities and the 00.3, 01.5 and 11.3 reflections decreasing. At 9·7 GPa, the measured intensities of reflections can be explained assuming that the *z* parameter is increased to 0·228 ± 0·003. It does not reach, as the axial ratio does not, the critical value 0·250 corresponding to the conversion into the simple cubic structure.

Table 2. *Diffraction data for rhombohedral phosphorus at* 6·7 GPa

Sample characterization: as described in the text.
Technique: Mo $K\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å, Zr-filtered; flat film, diffraction pattern shown in Fig. 3; powdered specimen packed in the diamond-anvil cell; range of 2θ, from 5 to 38°; internal standard NaCl, $a = 5{\cdot}840$ Å at 0·1 MPa and 298 K; intensity measured by microphotometer (peak heights).

$2\theta_{exp}$ (°)	I_{exp}/I_0	d_{exp} (Å)	*hk.l*	$\Delta 2\theta$* (°)	I_{cal}/I_0
14·03	5	2·91	00.3	0·079	7·5
	–	–	10.1		4·7
16·69	100	$2{\cdot}44_8$	01.2	−0·031	100
23·35	25	$1{\cdot}75_6$	10.4	0·040	26
24·12	25	$1{\cdot}70_1$	11.0	−0·025	19
27·22	10	1·51	01.5	−0·039	15
28·04	15	$1{\cdot}46_7$	11.3 00.6	0·043	6·0 1·1
	–	–	02.1		0·7
29·49	15	$1{\cdot}39_6$	20.2	−0·025	19
33·81	10	$1{\cdot}22_2$	02.4	0·001	8·9
	–	–	10.7		10
	–	–	20.5		6·4

$I_{cal} = |F|^2 \times \mathrm{Lp} \times m$. The positional parameter $u = 0{\cdot}223$.
Indices are assigned in terms of a hexagonal lattice.

* $2\theta_{exp} - 2\theta_{cal}$.

Using the lattice parameters and the atomic positional parameters linearly extrapolated, approximate values of the principal interatomic distances in the rhombohedral structure of phosphorus at 5·5 GPa are calculated. They are 2·20 ± 0·03 Å between the atoms (1) and (3), or (5) and (6), within the same layer and 2·81 ± 0·03 Å between the atoms (1) and (6), or (2) and (5), across the adjacent layers [Fig. 2(*c*)]. The transition from the orthorhombic to rhombohedral structure at 5·5 GPa thus induces, within the estimated error, a negligible change in the covalent bond distance. At 9·7 GPa, these distances are respectively 2·22 ± 0·03 Å and 2·66 ± 0·03 Å.

(*d*) *Transition from the rhombohedral to the simple cubic phase*

A change in crystal structure from the rhombohedral to the simple cubic form manifests itself in the merging of the pair of diffraction lines, 10.4 and 11.0. Since the *A*7 structure can be regarded as a distorted simple cubic structure, a continuous increase in the rhombohedral axial angle and a continuous change in the relative positions of the two sublattices smoothly converts the former structure into the latter (Schiferl, 1979). Fig. 2(*d*) shows the atomic arrangement of this structure, which is no longer a layered structure. What is really observed in the pressurization process is, however, not a continuous but a discontinuous change in the diffraction pattern and P_T is placed at 10·0 ± 0·6 GPa. When one observes through the diamond, the sample color changes from black to white silver at the

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* Calculated from the data of Morosin & Schirber (1972).

transition. ΔV calculated from the lattice parameters is 0·53 Å^3 per atom, 3·7% of the volume before the transition. On the other hand, ΔV measured at the corresponding transition of antimony is as small as 0·5% (Kolobyanina *et al.*, 1969). It is to be noted that, whereas the layer(rhombohedral)–non-layer(simple cubic) transition in phosphorus involves a minor rearrangement of atoms accompanied by a smaller ΔV, the layer(orthorhombic)–layer(rhombohedral) transition proceeds with extensive reconstruction of the atomic configuration accompanied by a larger ΔV.

As a result of the increase in the coordination number upon formation of the simple cubic structure, the nearest-neighbor distance is changed from 2·22 ± 0·03 Å at 9·7 GPa to 2·39 ± 0·01 Å at 10·3 GPa, the latter being considered as the distance characteristic of metallic bonding in phosphorus.

(*e*) *Compression of the simple cubic phase*

Fig. 5 shows an X-ray diffraction pattern of phosphorus at 10·3 GPa. The compression experiment has been extended beyond 30 GPa at which the internal pressure marker, sodium chloride, undergoes structural transition. The X-ray diffraction pattern of phosphorus remains unchanged,* except for a slight shift of the diffraction lines due to volume contraction, and no indication of a supposed transition at a pressure around 17 GPa (Duggin, 1972) has been observed. This makes a striking contrast to the behavior of the simple cubic phase of antimony, which forms at a pressure of 7·0 GPa and immediately transforms into the SbIII phase at 8·6 GPa (Kolobyanina *et al.*, 1969).

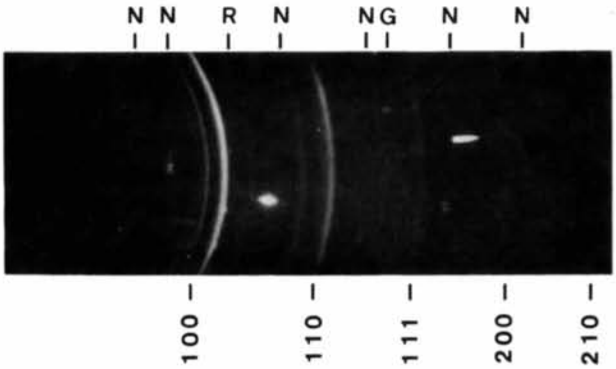

Fig. 5. X-ray diffraction pattern of the simple cubic form of phosphorus at 10·3 GPa. The diffraction lines denoted by *N* and *R* are those from NaCl and ruby, respectively.

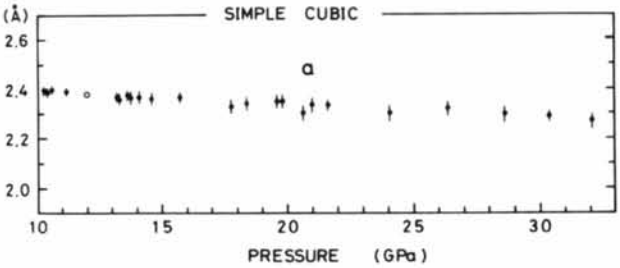

Fig. 6. Lattice parameter of the simple cubic form of phosphorus plotted against pressure. The datum point from Jamieson (1963) is also shown by an open circle for comparison.

Another notable fact observed for the simple cubic phase of phosphorus is its small compressibility, as Fig. 6 suggests, in which the *a* parameter of the simple cubic structure is plotted as a function of pressure. The parameter has been determined from the *d* values of the 100, 110 and 111 reflections. At a pressure of 32 GPa, the highest pressure attained in the present work,† *a* is measured to be 2·27 ± 0·02 Å, which is smaller than that at 10·3 GPa by only 5%. In Table 1, the volume per atom of the simple cubic phase of phosphorus is shown. Least-squares fitting of the volumetric data to equation (1) yields $K_0 = 95 \pm 5$ GPa, $K' = 2{\cdot}1 \pm 0{\cdot}8$ and $V_0 = 15{\cdot}2 \pm 0{\cdot}2$ Å^3.

Discussion

The simple cubic structure of phosphorus is shown to be quite stable at high pressures and no indication of transformation into structures having a higher packing density of atoms is observed. Asahina (1981) theoretically showed, by means of a third-order perturbation expansion method using the atom pseudopotential, that at moderate pressures the rhombohedral structure is stable owing to its lower electron band energy, but with increasing pressure an increase in the Madelung energy tends to favor an atomic arrangement of higher symmetry and the simple cubic structure having metallic character forms. The reason why phosphorus takes among other structures the simple cubic one may be found in the configuration of the outer electrons. There are two 3*s* and three 3*p* electrons in a phosphorus atom and they both can take part in the bonding of a crystal by constructing hybridized orbitals. However, under high pressure the energy level of the 3*s* electrons is depressed so deeply that the degree of hybridization is low and the bonding orbitals retain much of the *p*-like character, and the geometrical nature of the *p*-electron orbitals leads to the structure in which every atom has the coordination number six. We designate here the metallic substance in which the *p* electrons play a dominant role in cohesion as a *p* metal in order to distinguish from the metals in

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* A recent communication by Dr Yagi of the University of Tokyo shows that the simple cubic structure is stable even at 58 GPa.

† This value for the pressure was determined assuming that the high-pressure *B*2 form of sodium chloride decreases its volume in line with an extrapolated equation-of-state curve of the low-pressure *B*1 form.

which the *s* electrons (alkali metals) or *d* electrons (transition metals) are responsible for the cohesion. In general, these metals crystallize in the body-centered cubic, face-centered cubic or hexagonal close-packed structures. It should be noted that polonium, which takes the simple cubic structure at low temperatures, has four *p* electrons in its outermost orbitals. It is not clear at present, however, why metallic phosphorus exhibits high resistance against compression and its structure is stable over a wide range of pressure.

Arsenic, antimony and bismuth have an identical configuration of outer electrons to that of phosphorus, but in these elements the simple cubic structure does not form or, even if it does form, it is stable only in a limited range of pressure. The difference in the stability of the simple cubic structure between phosphorus and the other three elements may arise from the difference in the degree of hybridization of the outer *s*- and *p*-electron orbitals, and in the heavier elements the *p*-like character of the bonding electrons is weak under high pressure (Shindo, 1982).

Measurements of various physical properties of simple cubic phosphorus will be of interest because they can provide information on how the *p* metal behaves differently from the *s* and *d* metals. High-pressure techniques may be used to find other *p* metals in the elements having similar outer-electron configurations.

The superconducting transition of phosphorus was found at a pressure of 17 GPa. It does not correspond to any of the P_T's determined in the present work. If the superconducting transition is associated with the structural change from the rhombohedral to the simple cubic, as was first suggested by Wittig & Matthias (1968), P_T must increase from 10 GPa at room temperature to 17 GPa on going down to liquid-helium temperature. That is, the boundary between the rhombohedral and simple cubic phases in the pressure–temperature diagram of phosphorus must have a negative slope. This is highly likely, because the corresponding phase boundary in antimony has a negative slope and the phase field of the rhombohedral form increases in its width with decreasing temperature (Pistorius, 1976). In connection with this, it is worth noting that the phase boundary between BiI (rhombohedral) and BiII (monoclinic) also has a negative slope. An attempt to fix the rhombohedral/simple cubic phase boundary of phosphorus as a function of temperature is in progress in our laboratory.

The present work has been motivated by suggestions by Professor A. Morita of Tohoku University whom we thank for his interest. We also thank Professor S. Endo of Osaka University for providing black-phosphorus samples of good quality, and Professor K. Shindo of Iwate University and Dr H. Asahina of Tohoku University for valuable discussions.

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