THE REVIEW OF PHYSICAL CHEMISTRY OF JAPAN, VOL. 36, NO. 1, 1966

CHEMICAL REACTION AT HIGH TEMPERATURE AND HIGH PRESSURE III

Reaction of Silicon and Phosphorus at High Temperature and High Pressure

BY JIRO OSUGI, RYOSUKE NAMIKAWA AND YOSHIYUKI TANAKA

Several kinds of new high pressure phases in the silicon-phosphorus system have been prepared by direct union of crystalline silicon and red phosphorus under the conditions of temperatures of 1100–1800°C and pressures of 15–50kb. The high pressure equipments are the piston-cylinder of Bridgman type and the compact cubic anvil. The main reaction process in this system under high pressures has been presumed by means of X-ray diffraction. The effects of temperature, pressure, reaction time and the composition of the reactants on the main reaction process have been investigated.

Among the new high pressure phases, a cubic pyrite type silicon diphosphide SiP_2 with a lattice constant of 5.682 Å and a cubic sphalerite (zinc-blende) type silicon monophosphide SiP with a lattice constant of 5.241 Å are included. SiP_2 is prepared at 1100–1500°C under 20–40 kb. SiP may be formed through the following reaction only above about 1700°C under pressures of 40–50 kb; $SiP_2 \longrightarrow SiP + P$. It is one of the characteristics of the silicon-phosphorus system that the reaction is influenced rather sensitively not only by temperature and pressure but also by the composition of reactants and the reaction time.

Introduction

In general, the reactions of group IV B elements (C, Si, Ge, Sn) with group V B elements (P, As) hardly proceed under an atmospheric pressure. Although the existence of SiP, SiAs, GeAs, SnP, $SiAs_2$ and $GeAs_2$ has been known since about 1940, their crystal structure and physical and chemical properties have not so far been investigated sufficiently.

K. Schubert *et al.* (1954)1), J. H. Bryden (1962)2) and T. Wadsten (1965)3) have only recently reported that SiAs and GeAs are monoclinic and $SiAs_2$ and $GeAs_2$ orthorhombic.

In the silicon-phosphorus system. W. Biltz (1938)4) prepared SiP by reacting silicon and phosphorus in a sealed silica tube above 1000°C in the presence of catalyst Tl. P. F. Schmidt and R. Stickler (1964)5) also suggested the presence of SiP phase in the surface layer of heavily phosphorus diffused silicon and reported that its crystal structure is orthorhombic. However SiP_2, which is likely to exist considering the corresponding phases of $SiAs_2$ and $GeAs_2$, has not so far been confirmed.

(*Received August 8, 1966*)

1) K. Schubert, E. Dörre and E. Günzel, *Naturwissenschaften*, **41**, 448 (1954)
2) J. H. Bryden, *Acta Cryst.*, **15**, 167 (1962)
3) T. Wadsten, *Acta Chem. Scand.*, **19**, 1232 (1965)
4) W. Biltz, "Gmelins Handbuch der anorganischen chemie," 8 Auflage, Verlag Chemie, GMBH. (1959)
5) P. F. Schmidt and R. Stickler, *J. Electrochem. Soc.*, **111**, 1188 (1964)

Now, the crystal structures of these anomalously composed phases⁶⁾⁷⁾, whose compositions differ from those expected from the normal valence rule, are much complicated and very low in symmetry, since they have some anion-anion or cation-cation bonds besides cation-anion bonds, whereas normal valence compounds have only cation-anion bonds. It is therefore expected that some considerable pressure effects will come out when these reaction systems are undertaken at high temperatures under very high pressures since high pressure makes higher the coordination number in the crystal and the crystal symmetry.

In the present work the reaction of crystalline silicon with red phosphorus at temperatures of 1100 ~1800°C under pressures of 15~50kb have been undertaken and several high pressure phases with distinctive X-ray diffraction diagrams have been obtained. Among these phases pyrite type SiP_2 and sphalerite type SiP are included. The effects of temperature, pressure, reaction time and the atomic ratio of silicon and phosphorus in the sample on the main reaction have been investigated qualitatively by X-ray diffraction.

Table 1 Crystallographic data for known group IV B (C, Si, Ge, Sn)—V B (P, As) phases under an atmospheric pressure

phases	lattice parameters	crystal structure	references
SiP	$a=6.90$, $b=9.40$, $c=7.68$Å	orthorhombic	(5)
SiAs	$a=15.98$, $b=3.668$, $c=9.529$Å, $\beta=106°$	monoclinic	(3)
GeAs	$a=22.08$, $b=3.77$, $c=9.43$Å, $\beta=43.97°$	monoclinic	(1)
SnP	$a=8.78$, $c=5.98$Å	hexagonal	(8)
$SiAs_2$		orthorhombic	(2)
$GeAs_2$	$a=14.76$, $b=10.16$, $c=3.728$Å	orthorhombic	(2)

Experimentals

Extra pure grade crystalline silicon and red phosphorus were obtained commercially and mixed in various atomic ratios in a mortar. The high pressure apparatuses of Bridgman type piston-cylinder⁹⁾ and compact cubic anvil¹⁰⁾ were used. The pyrophyllite cubic cell geometry, resistance strip-heater arrangement and procedure have been described previously¹¹⁾. The only modification of the cell made in this work was the addition of a pyrophyllite insulating sleeve between the specimen and the glassy carbon heater. After the reaction the sample was powdered in an agate mortar and analysed by X-ray diffraction.

---

6) F. Hulliger and E. Mooser, *J.Phys. Chem. Solids*, **24**, 283 (1963)
7) W. B. Pearson, *Acta Cryst.*, **17**, 1 (1964)
8) G. Katz, J. A. Kohn and J. D. Broder, *Acta Cryst.*, **10**, 607 (1957)
9) J. Osugi, K. Shimizu and Y. Tanaka, *Proc. Japan Acad.*, **40**, 105 (1964)
10) J. Osugi, K. Shimizu, K. Inoue and K. Yasunami, *This Journal*, **34**, 1 (1964)
11) J. Osugi, K. Shimizu and Y. Tanaka, *Proc. Japan Acad.*, **42**, 48 (1966)

Experimental Results

Five kinds of crystalline phases were obtained as reaction products in the Si–P system. Their exact stoichiometric compositions could not be determined by chemical methods at this stage because of their mutual coexistence in the specimen and of the strangeness of their chemical natures.

Thus the symbols SiP (I), SiP (II), SiP (III), SiP (IV) and SiP (V) have been adopted throughout this paper as an abbreviation for these phases.

Crystal Structures

X-ray diagrams taken after releasing the pressure showed that five kinds of new crystalline phases were prepared in the Si–P system. The data are summarized in Table 2, Structures for these phases were determined by analysing the data in this Table, as will be discussed below. The interpretation of these results, however, has not yet been completed.

Table 2 Data of X-ray diffraction diagrams for five kinds of crystalline phases

a) SiP (I)

d(Å)	I/I_0	hkl
6.81	100	0 0 2
3.405	45	0 0 4
2.270	5	0 0 6
1.703	5	0 0 8

b) SiP (II)

d(Å)	I/I_0	hkl
2.840	100	2 0 0
2.547	80	2 1 0
2.325	55	2 1 1
2.014	15	2 2 0
1.717	65	3 1 1
1.644	30	2 2 2
1.522	35	3 2 1
1.243	15	4 2 1

c) SiP (III)

d(Å)	I/I_0	hkl
3.025	100	1 1 1
1.853	90	2 2 0
1.581	70	3 1 1
1.310	5	4 0 0
1.201	10	3 3 1

d) SiP (IV)

d(Å)	I/I_0	hkl
2.527	25	0 0 3
2.319	20	2 2 0
2.179	30	3 0 0
1.996	100	2 0 3
1.982	60	2 2 2
1.932	10	2 1 3
1.894	5	0 0 4
1.733	5	1 1 4
1.410	10	3 0 4
1.294	10	5 0 1

e) SiP (V)

d(Å)	I/I_0	hkl
4.25	30	
3.336	100	
1.816	15	
1.580	35	
1.539	10	

a) SiP (I): An inspection of the X-ray diagrams for this phase showed that only the reflections from $(00l)$ faces with the lattice constant 13.620 Å were observed. This seems to be due to three causes as follows: (1) As Si and P are practically neighbours in the periodic system, their atomic scattering factors f_{Si} and f_P have nearly the same values in the experimental range ($\sin\theta/\lambda=0.113\sim0.834\text{Å}^{-1}$). Therefore every face that is related to the difference in f_{Si} and f_P probably could not be detected. (2) The extinction rule of space group to which the SiP (I) structure belongs. (3) Texture effects. These are especially remarkable in the layer structure, which SiP (I) phase seems to have.

The reflections for SiP (I) given in Table 2 (a) are those taken immediately after the experiments. After leaving the sample in powder for 2~3 weeks, however, no reflections corresponding to this phase were observed. This compound is a sublimate and has very stimulative disagreeable smell. It is detected in the gaseous state by gas chromatography. The color is reddish brown in powder. Considering the results discussed above, it is reasonable to posturate that this phase has a layer structure in which the van der Waals forces predominate. This phase is prepared under conditions of 15~20kb and 1100~1400°C. The stoichiometric composition and the exact structure have not yet been determined. This phase, however, is not in agreement with SiP reported by Schmidt *et al*[5].

b) SiP (II): This phase has a cubic structure with $a=5.682\text{Å}$. The X-ray intensities and the extinction of faces(Table 2 b) can be explained when the positions for silicon and phosphorus are assigned as follows:

$$\text{Si}:\ 0\ 0\ 0,\ \frac{1}{2}\,\frac{1}{2}\ 0,\ \frac{1}{2}\ 0\ \frac{1}{2},\ 0\ \frac{1}{2}\ \frac{1}{2}$$

$$\text{P}:\ \pm(x\ x\ x,\ x+\frac{1}{2}\ \frac{1}{2}-x\ \bar{x},\ \bar{x}\ x+\frac{1}{2}\ \frac{1}{2}-x,\ \frac{1}{2}-x\ \bar{x}\ x+\frac{1}{2}),\ x=0.38$$

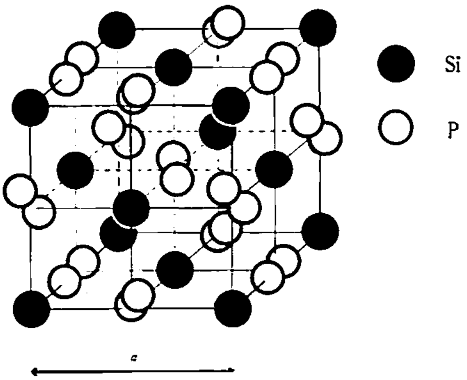

Fig. 1 Crystal structure of pyrite type SiP_2
$a=5.682$ Å

The structure based on this atomic configuration is shown in Fig. 1, which is a pyrite type structure and its space group is $Pa3\text{–}T_h^6$. Therefore the chemical formula of SiP (II) is SiP_2*. In the pyrite type structure silicon and phosphorus atoms lie on a NaCl-like array of elements. A couple of P atoms, P–P, is sited in the direction of the diagonal in the eight cubelets into which the unit cell can be divided. Each Si atom is surrounded by six P atoms and each P atom by three Si and one P atoms. The Si–P bond has some covalent nature. In this structure the lack of spherical symmetry of P–P makes the

---

* See the "Considerations"

crystal symmetry lower to some extent. The extinction of faces (111), (400), (331) and (420) is due to the contribution of the structural factors corresponding nearly to $f_{Si}-f_P$, and that of face (410) to the smallness of the structural factor $F(410)=-8f_P \sin 8\pi x \cdot \sin 2\pi x$. All others obey the extinction rule of the space group for this phase. The interatomic distances for Si-Si, Si-P, and P-P are equal to 4.018, 2.364 and 3.202Å, respectively. The calculated density based on these lattice parameters is 3.26 g/cm^3.

This may be an intermediate phase between SiP (I) and SiP (III). It has an alloy-like appearance and is black in powder.

c) **SiP (III)**: This phase has a cubic structure with $a=5.241$Å. The positions for Si and P are assigned as follows:

$$\mathrm{Si}:\ 0\,0\,0,\ \frac{1}{2}\,\frac{1}{2}\,0,\ \frac{1}{2}\,0\,\frac{1}{2},\ 0\,\frac{1}{2}\,\frac{1}{2}$$

$$\mathrm{P}:\ \frac{1}{4}\,\frac{1}{4}\,\frac{1}{4},\ \frac{3}{4}\,\frac{3}{4}\,\frac{1}{4},\ \frac{3}{4}\,\frac{1}{4}\,\frac{3}{4},\ \frac{1}{4}\,\frac{3}{4}\,\frac{3}{4}$$

Table 2 (c) shows that all reflections corresponding to the indices $h+k+l=4n+2$ besides those to the indices with mixed integers disappear. This is an extinction rule characteristic to diamond structure. Accordingly SiP (III) might be a single component phase of Si or P with diamond structure. But there exist no high pressure modifications of Si and P with this structure having a given lattice constant throughout the experimental conditions. Therefore this phase is sphalerite type structure with space group $F\bar{4}3m-T_d^2$, which has four formula units, SiP, in unit cell as shown in Fig. 2.

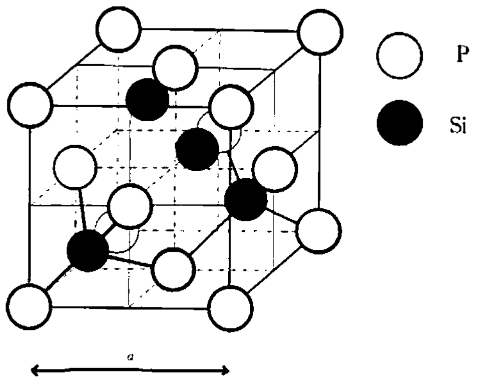

Fig. 2 Crystal structure of sphalerite type SiP
$a=5.241$ Å

Since all of the structural factors $F(hkl)$ of the faces with $h+k+l=4n+2$ are equal to $4(f_{Si}-f_P)$, the structure for this phase is in agreement with the reflections and intensities of its X-ray diagram (Table 2 (c)). The interatomic distances for Si-Si and P-P have the same values 3.708 Å and that for Si-P 2.269Å. The calculated density is 2.73g/cm^3. This phase is prepared under the conditions above 40kb and 1700~1800°C.

d) **SiP (IV) and SiP (V)**: SiP (IV) phase has a tetragonal structure with $a=6.536$Å, $a/c=0.86$. Since this phase may be a product of the decomposition $SiP_2 \rightarrow SiP+P$, SiP (IV) has a possibility of being a new kind of high pressure modification of phosphorus, which has not so far been reported. The stoichiometric composition and the crystal structure for this phase have not been yet determined, since phosphorus formed by the above decomposition also may react with other products coexisting.

SiP (V) phase is most stable among the phases in Si–P system. The number of the reflection lines is, however, scarce, so even the indexing is not possible at this stage.

Main reaction process and effects of temperature, pressure, reaction time and the composition of reactants

The quantitative description of the reaction process in the Si–P system is impossible because of difficulties of the isolation of high pressure phases since they are very changeable in chemical treatments with such reagents as aq. NaOH, aq. HF and aq. HNO_3. Therefore the reaction has been investigated qualitatively by X-ray diffraction. In Figs. 3 and 4 are shown the dependences of the relative intensity of the reflections, such as, SiP (I) (002), SiP_2 (200), SiP (111), SiP (IV) (203) and SiP (V) $d=3.336$ Å, on the reaction time under two typical experimental conditions.

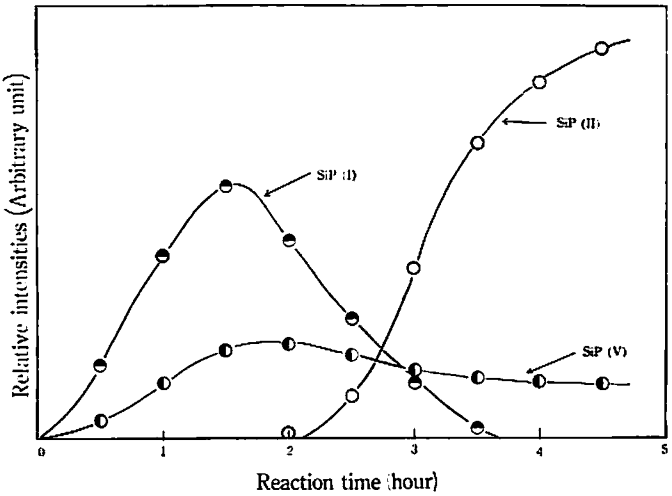

Fig. 3 Dependences of the X-ray relative intensities on the reaction time under the condition of 1400°C and 20 kb in the case of Si : P = 1 : 1 sample

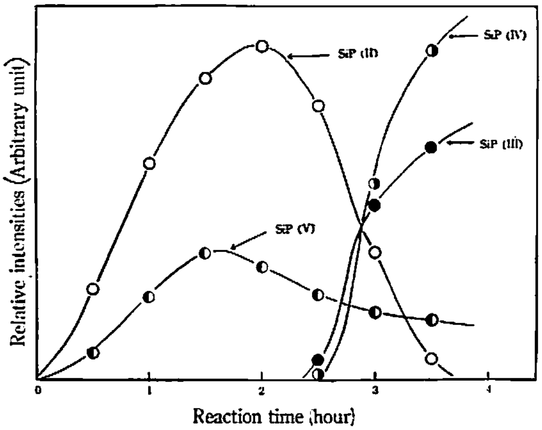

Fig. 4 Dependences of the X-ray relative intensities on the reaction time under the condition of 1700°C and 40 kb in the case of Si : P = 1 : 1 sample

Main reaction process: In comparison with the reaction systems in which normal valence compounds are formed, the reaction of silicon and phosphorus is more sensitively influenced by not only temperature and pressure but also the reaction time and the composition of reactants.

When the experimental conditions are changed from the low temperature and pressure to the high in the case of Si : P=1 : 1 atomic ratio sample, the main reaction process could be presumed as follows:

$$\mathrm{Si}+\mathrm{P}\longrightarrow\mathrm{SiP\ (I)}, \qquad (1)$$

$$\mathrm{SiP(I)}\longrightarrow\mathrm{SiP_2}, \qquad (2)$$

$$\mathrm{Si}+\mathrm{P}\longrightarrow\mathrm{SiP_2}, \qquad (3)$$

$$\mathrm{SiP_2}\longrightarrow\mathrm{SiP}, \qquad (4)$$

Besides these reactions SiP (IV) phase are formed probably through reaction (4) or other reactions. This phase would not be a stable final product. SiP (V), which may be formed through the reaction Si+P→SiP (V), is always found throughout the experimental conditions and rather stable, independent of other reactions and products.

Effect of temperature: Reactions (1), (2) and (3) begin to proceed at about 1100°C and are accelerated considerably by rising temperature up to about 1500°C. On the other hand reaction (4) proceeds only above 1700°C under 40–50 kb.

Effect of pressure: It is very important to investigate the reaction in detail in the lower pressure range below 10 kb in order to learn how the reaction process changes with the change of experimental conditions from an atmospheric pressure to high pressure. However, in the lower pressure range below 15 kb, the experiment was not undertaken since phosphorus, which may be the yellow phosphorus and very fluid at the required temperature, could not be contained in the reaction vessel.

Under 15 kb, reaction (1) finishes within 2–3 hours and is followed very slowly by reaction (2). Reaction (2) is accelerated gradually by pressure. Under 25–40 kb, SiP_2 is formed within 1–2 hours at 1300–1500°C through reactions (1) and (2) and/or (3). Above 40 kb, SiP is formed only at higher temperature above 1700°C through reaction (4) probably.

Effect of reaction time: While reaction (1) and (3) almost finish within 3 hours, reactions (2) and (4) proceed very slowly under same conditions as those of (1) and (3) respectively and would not finish within the definite reaction time.

Effect of composition of reactants: In the presence of excess silicon in such cases as Si : P=2 : 1, reaction (1) proceeds mainly within 3–4 hours at 1100–1500°C even under 25–40 kb in which conditions reactions (2) and (3) proceed mainly instead of reaction (1) in Si : P=1 : 1 sample.

In the presence of excess phosphorus in such cases as Si : P=1 : 2, however, SiP_2 is formed rather quickly even under the low pressure range of 15–20 kb. It is one of the characteristics of the Si–P system under high temperatures and high pressures that a minute change of the composition of the reactants brings some interesting changes in the reaction process.

Considerations

SiP (I) phase would be a non-metallic molecular crystal because it is a brown colored sublimate and rather soft in a lump. Similar substances have been reported for non-metallic phases formed between lighter group V B and VI B elements such as P_4S_5, P_4S_3, and P_4Se_3.[12][13]

The color of the powdered samples changes gradually from brown to dark brown with the formation of SiP_2 through reaction (2). SiP_2 and SiP have rather metallic appearances, such as granular tin or zinc.

Considering that the values of f_{Si} and f_P are nearly equal. SiP (II) phase might be SiP_2 or Si_2P. However, in Si : P=1 : 1 sample, X-ray diffraction diagrams with rather strong reflections of excess silicon always coexist with those of SiP (II), whereas excess phosphorus, which should be crystalline black phosphorus in the experimental conditions, is not found. Consequently SiP (II) may be likely SiP_2.

Pyrite type SiP_2 phase is rather dense so that it is reasonable that the reaction SiP (I)$\rightarrow SiP_2$ is accelerated considerably by pressure. On the other hand, the reaction $SiP_2 \rightarrow SiP$ depends upon many factors such as pressure, temperature and reaction time.

The calculated densities for SiP_2 and SiP are 3.26 and 2.73 g/cm^3, respectively. The changes of the molecular volume for the reactions, ΔV, are given as follows:

$$\mathrm{Si} + 2\,\mathrm{P} \longrightarrow \mathrm{SiP_2}, \quad \Delta V = -7.1\,\mathrm{cm^3/mole}$$

$$\mathrm{SiP_2} \longrightarrow \mathrm{SiP} + \mathrm{P}, \quad \Delta V = +5.6\,\mathrm{cm^3/mole}$$

$$\frac{1}{2}\,\mathrm{SiP_2} + \frac{1}{2}\,\mathrm{Si} \longrightarrow \mathrm{SiP}, \quad \Delta V = +2.0\,\mathrm{cm^3/mole}$$

where Si is crystalline and its density is 2.4 g/cm^3 and P the black phosphorus of which density is 2.69 g/cm^3.

Pressure, therefore, would retard the formation of SiP because of the positive volume change in second and third reactions (and its smaller density.) On the other hand, the crystal structure has a higher symmetry in the sphalerite type SiP than in the pyrite type SiP_2 so that pressure would accelerate the formation of SiP in this view-point. The interatomic distance Si–P are 2.364 Å in SiP_2 and 2.269 Å in SiP respectively. The latter is in better agreement with the value 2.246 Å calculated with univalent radii corrected by electronegativity. Therefore SiP has a higher stability at high temperature under high pressure. In any case very high temperature is required for the rearrangement of crystal structure. The thermodynamical informations of these phases will enable the quantitative discussions.

It was also confirmed that in the reactions of phosphorus with germanium or tin, which are elements in the same group IV B of silicon, sphalerite type GeP (a=5.463 Å) and SnP (a=5.544 Å) are prepared at 1700–1900°C under 40–50 kb. These high pressure phases also have not so far been prepared. The detailed reports on Ge-P and Sn-P systems will be published in the near future.

The sphalerite type structure is usually found in the binary normal valence compounds when the average number of valence electron per atom is 4 in such cases as I–VII, II–VI, and III–V intermetallic compounds. Besides these compounds, recently, H. T. Hall and L. A. Compton[14] reported that an unsymmetrical analog of graphite, B_2O, was synthesized by the reduction of B_2O_3 with B and Li and also by oxidation of B with $KClO_3$ at temperatures of 1200–1800°C under pressures of 50–75 kb and transformed

---

[12] V. S. Houten and E. H. Wiebenga, *Acta Cryst.*, 10, 156 (1957)

[13] E. Keulen and A. Vos, *Acta Cryst.*, 12, 323 (1959)

[14] H. T. Hall and L. A. Compton, *Inorg. Chem*, 4, 1213 (1965)

to diamond like form under about 120kb. The existence of other unsymmetrical analogs of carbon and silicon was also predicted.[15]

In the sphalerite structure the tetrahedral covalent bonding is predominant though the chemical bonding in these structures should be described as arising from the resonance between one or more ionic and covalent valence structures when the difference in electronegativities ΔX between combining atoms is large.

Now, in the sphalerite type SiP obtained under high pressure, the sum of the valence electron is 9 so that one valence should remain unsaturated. The excess electron not utilized in sp^3 hybrid orbital formation would possibly remain very loosely near the P^+ as an oscillating electron instead of a complete free electron in the pure metals. Usually the tetrahedral covalent bonding is intimately concerned with semiconducting properties as shown in I–VII, II–VI, III–V and other intermetallic compounds, however, the sphalerite type SiP would be an intermediate between the extremely covalent semiconductor and the purely metallic alloy since this phase has also unshared valence electron at the same time.

In view of other similar series of chemically analogous compounds such as, BP, AlP, GaP and InP or InP, InAs, InSb and InBi, the metallic properties will likely increase in the order of SiP, GeP and SnP.

As mentioned above the crystal structures of anomalously composed phases are more complicated than those of ionic or covalent crystals and rather changeable in chemical treatments so that the isolation and the sufficient investigation of physical properties of these phases involve considerable difficulties. In spite of many difficulties it is very interesting to investigate these systems under high pressure, since not only the reactions are accelerated by pressure but also some new high pressure phases might be prepared in the comparatively low pressure range and other pressure effects could be expected.

The authors express their hearty thanks to the Department of Education for the Scientific Research Grant.

Laboratory of Physical Chemistry
Department of Chemistry
Faculty of Science
Kyoto University
Kyoto, Japan

---

15) B. R. Pamplin, *J. Phys. Chem. Solids*, **25**, 675 (1964)