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## CHEMICAL REACTION AT HIGH TEMPERATURE AND HIGH PRESSURE IV

### High Pressure Phases in the Ge-P System

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Several types of new high pressure phases in the germanium-phosphorus system have been prepared by direct union of germanium and red phosphorus at temperatures of 600~1500°C and pressures of 10~50 kb. 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 pressure 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 are described in comparison with the silicon-phosphorus system under high pressure.

Among the new high pressure phases a disordered sphalerite type GeP with a lattice constant of 5.581 Å and a sphalerite type GeP with a lattice constant of 5.463 Å are included. The sphalerite type GeP is the phase corresponding to the sphalerite type SiP and SnP obtained under high temperature and high pressure. The high pressure phase which corresponds completely to the pyrite type SiP<sub>2</sub> is not observed in the germanium-phosphorus system, but a similar cubic phase with a lattice constant of 5.619 Å, which may have a stoichiometric composition GeP<sub>2</sub>, is confirmed.

The phases in the germanium-phosphorus system are much more complicated than those in the silicon-phosphorus system under high pressure. It may be due to the higher metallic nature of germanium as compared with silicon.

#### Introduction

As for the germanium-phosphorus system, very little attention has been given to the chemical reaction since 1939 because it hardly proceeds under an atmospheric pressure, while there have been several studies on the measurements of the saturation solubility<sup>1)</sup> of phosphorus in germanium and its distribution coefficient<sup>2)~4)</sup>.

In 1939 Biltz *et al.*<sup>5)</sup> reported the preparation of germanium-phosphide, GeP, by direct union of germanium powder and red phosphorus at about 700°C in an evacuated silica tube for about ten days. Although the crystal structure, physical and chemical properties were not investigated in detail, they

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- 2) F. A. Trumbore, *Bell System Tech. J.*, **39**, 205 (1960)
- 3) R. N. Hall, *G. E. Research Laboratory Report* 58-RL-1874
- 4) J. A. Burton, E. D. Kolb, W. P. Slichter and J. D. Struthers, *J. Chem. Phys.*, **21**, 1991 (1953)
- 5) M. Zumbush, M. Heimbrecht and W. Biltz, *Z. anorg. allg. Chem.*, **242**, 237 (1939)

concluded that GeP was not the compound corresponding to silicon-phosphide SiP prepared in a similar manner from the view points of X-ray diffraction, color and chemical properties. The crystal structure of GeP was determined by Wadsten in 1967<sup>6)</sup>. The structure is monoclinic of space group C2/m analogous to those of SiAs and GeAs derived by Wadsten<sup>7)</sup> and Bryden<sup>8)</sup> independently. The unit cell contains 12 formula units GeP and dimensions are  $a=15.14$ ,  $b=3.638$ ,  $c=9.19\text{\AA}$  and  $\beta=101.1^\circ$ . This structure type is built in layers with weak bond between the layers.

GeP<sub>2</sub> is likely to exist in view of the corresponding IV-V compounds such as SiAs, SiAs<sub>2</sub>, GeAs and GeAs<sub>2</sub>, but it has not so far been confirmed.

In the previous paper<sup>9)</sup> the reaction of silicon with phosphorus at high temperature and high pressure was described and it was confirmed that a cubic pyrite type SiP<sub>2</sub>, a cubic sphalerite type SiP and other three high pressure phases were obtained at temperatures of 1100~1800°C and pressures of 15~50 kb. In the Si-P system it is, however, difficult to determine the crystal structures of high pressure phases by means of X-ray diffraction because of the extinctions of the reflections from those faces related to the differences in the atomic scattering factors for silicon and phosphorus,  $f_{Si} - f_P$ , since they are practically neighbours in the periodic system and have much the same values in the atomic scattering factors.

In the present work an investigation on the reaction of germanium with phosphorus at high temperatures of 600~1500°C and high pressures of 10~50 kb was carried out in order to compare the system with the Si-P system under high pressure. The behavior of the Ge-P system at high pressures is quite complex and only its aspects which are fairly clear will be discussed in this paper.

## Experimentals

### Materials

Extra pure grade germanium (50  $\Omega$ -cm, 9-N) and red phosphorus were obtained commercially and mixed in the atomic ratio of Ge : P = 2 : 1, 1 : 1 and 1 : 2 in an agate mortar.

### High pressure technique

The high pressure apparatuses of the Bridgman type piston-cylinder and the compact cubic anvil were used in the pressure range up to 15 kb and 20~50 kb respectively. The details of the construction of these apparatuses, pressure calibration, pyrophyllite cubic cell geometry, resistance strip-heater arrangement and experimental procedure had been reported previously<sup>10)~12)</sup>. The specimen was coated with a pyrophyllite insulating sleeve and inserted in a glassy carbon heater. The pyrophyllite cube was dried at about 400°C for 2 hours in order to get off the burst due to the water of crystalliza-

6) T. Wadsten, *Acta Chem. Scand.*, **21**, 593 (1967)

7) T. Wadsten, *Acta Chem. Scand.*, **19**, 1232 (1965)

8) J. H. Bryden, *Acta Cryst.*, **15**, 167 (1962)

9) J. Osugi, R. Namikawa and Y. Tanaka, *This Journal*, **36**, 35 (1966)

10) J. Osugi, K. Shimizu and Y. Tanaka, *Proc. Japan Acad.*, **40**, 105 (1964)

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12) J. Osugi, K. Shimizu and Y. Tanaka, *Proc. Japan Acad.*, **42**, 48 (1966)

tion at very high temperature. The reaction temperature was measured with Pt-PtRh (10%) thermocouple. The thermocouple was made up into a triple bundle only at the pyrophyllite gaskets in order to avoid being cut off by compression throughout the experiments.

After the reaction the sample was powdered in an agate mortar and analysed by X-ray diffraction (Cu-K $\alpha$  radiation).

### Results and considerations

Eight kinds of crystalline phases and other several numbers of non-indexed reflections were revealed by the X-ray analysis in the Ge-P system under high pressure. Their exact stoichiometric compositions could not be determined by the chemical method in consequence of their mutual coexistences in the specimen and of the similarity of their chemical natures. Therefore the symbols GeP (I), GeP (II), ....., and GeP (VIII) have been adopted in this paper as an abbreviation for these phases.

#### Crystal structures

The X-ray diagrams taken after releasing the pressure showed that eight new crystalline phases were prepared in the Ge-P system. The data are summarized in Table 1. The crystal structures for these phases were determined by analysing the data in the table, as will be discussed below. The interpretation of these results, however, has not yet been completed because of their complexities. A summary of crystal structures, lattice constants and experimental conditions for preparation of these phases is shown in Table 2.

In Figs. 1 and 2 are shown the changes of X-ray diagrams with gradual change of experimental conditions from about 600°C and 15 kb to 1400°C and 40 kb.

**GeP (I):** This phase shows weak complicated patterns and always coexists with strong reflections from GeP (II) as shown in Fig. 1a. These reflections due to GeP (I) can be indexed on the basis of a hexagonal structure with lattice constants of  $a=10.02 \text{ \AA}$  and  $c=13.92 \text{ \AA}$ . In view of the lattice constants and the characteristics of X-ray diagrams, this phase may be the phase corresponding to SiP (I)<sup>9)</sup> in the Si-P system under high pressure and have a layer structure. Strong reflection from (002) and (003) faces and the texture effects are always observed in the samples. In any experimental conditions of this work, this phase could not be the main product, though it gave comparatively stronger reflections when formed at about 600°C under 15 kb in the Ge : P = 2 : 1 starting material. This seems to be due to that GeP (I) once formed, which may be not so stable considering the corresponding phase SiP (I), is transformed rapidly to GeP (II) by compression and this transition would be obstructed in the presence of excess germanium similarly as in the case of the Si-P system in which the transition of SiP (I) to SiP<sub>2</sub> is obstructed remarkably in the presence of excess silicon.

**GeP (II) and GeP (II')**: As shown in Figs. 1a and 1b, GeP (II) shows several sharp reflections from a hexagonal crystal with lattice constants of  $a=8.603 \text{ \AA}$  and  $c=12.622 \text{ \AA}$ . This phase may be similar to SiP (I) in view of the fact that both phases are the main products in the first step of the reactions, but not the corresponding phase since the lattice constants are smaller than those of SiP (I) in spite of the larger bond radius of germanium than that of silicon.

## Chemical Reaction at High Temperature and High Pressure IV

Table 1 Data of X-ray diffraction diagrams for eight kinds of crystalline high pressure phases in the Ge-P system

1 GeP (I)			3 GeP (III)		
$d$ (Å)	$I/I_0$	$hkl$	$d$ (Å)	$I/I_0$	$hkl$
6.96	100	002	4.14	55	002
5.01	40	110	3.54	30	102
4.64	30	003	3.046	100	210
4.14	5	201	2.409	25	220
4.07	20	112	2.260	10	300
3.68	15	202			
3.52	35	004			
2.723	15	204			
2.507	5	220			
2.463	5	221			
2.456	5	303			
2.356	5	222			
2.333	15	006			
2.273	15	312			
2.228	25	304			
2.035	5	224			
1.965	25	403			
1.829	25	323			

2 GeP (II) and GeP (II')				
GeP (II)		GeP (II')		
$d$ (Å)	$I/I_0$	$d$ (Å)	$I/I_0$	$hkl$
6.99	100	6.22	100	002
4.21	25	4.20	30	003
3.67	20	3.58	30	103
3.16	35	3.09	65	004
2.575	15	2.532	15	212
2.104	10	2.076	5	006
1.844	15	1.807	25	401
1.578	5			008

This phase is prepared under the conditions of 600°C and 15 kb and has a layer structure consisting of needle-like colored glass. It is very soft and its color is black in powder and a lump. It may be a non-metallic phase closely related to the molecular crystal. As shown in Fig. 1c, it transforms to GeP (II') with a small contraction of the lattice constants to  $a=8.192\text{Å}$  and  $b=12.44\text{Å}$  by increasing pressure from 15 kb to about 25 kb at 600°C.

The stoichiometric compositions for GeP (II) and GeP (II') would be GeP.

**GeP (III):** GeP (III) is formed under the conditions of 800-1000°C and 30 kb through GeP (II') with more contraction of the crystal lattice. The strongest reflection moves from the reflection at  $2\theta=14^\circ$  in GeP (II) and GeP (II') to that near  $2\theta=30^\circ$  as shown in Fig. 1d. This phase can not be indexed

4 GeP (IV)			5 GeP (V)		
$d$ (Å)	$I/I_0$	$hkl$	$d$ (Å)	$I/I_0$	$hkl$
3.24	15	111	3.22	100	111
2.820	25	200	1.974	35	220
2.515	100	210	1.683	40	311
2.291	10	211	1.395	20	400
1.985	5	220	1.281	10	331
1.872	45	300	1.139	15	422
1.774	50	310	1.074	5	511, 333
1.500	20	321			
1.286	10	330			

6 GeP (VI)			7 GeP (VII)		
$d$ (Å)	$I/I_0$	$hkl$	$d$ (Å)	$I/I_0$	$hkl$
3.16	100	111	3.85	30	102
2.734	10	200	3.55	5	200
1.933	50	220	3.312	100	201
1.647	25	311	2.605	75	212
1.577	5	222	2.291	15	004
1.379	10	400	2.081	10	104
1.252	15	331	1.921	35	204
1.221	10	420	1.811	15	322
1.114	15	422	1.648	40	331
1.050	5	511, 333	1.499	5	422
			1.419	5	500
			1.268	10	513
			1.244	5	441
			1.218	5	530

8 GeP (VIII)		
$d$ (Å)	$I/I_0$	$hkl$
3.03	5	110
3.229	5	200
2.873	35	210
2.635	100	211
2.285	70	220
2.156	25	221, 300
1.945	60	311
1.861	10	222
1.789	5	320

on the basis of a hexagonal structure but a tetragonal one with lattice constants of  $a=6.809 \text{ \AA}$  and  $c=8.280 \text{ \AA}$ . It always coexists with weak reflections from germanium. The color is black in powder.

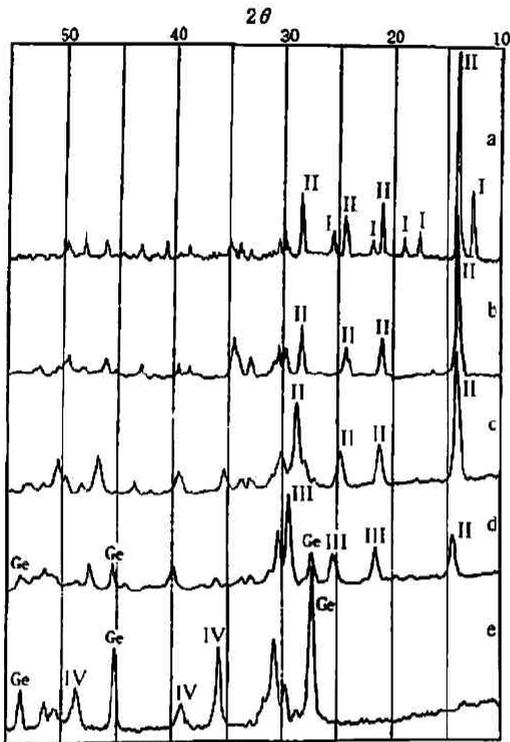


Fig. 1 The changes of X-ray diffraction diagrams with changes of experimental conditions from 600°C, 15 kb to 1200°C, 35 kb

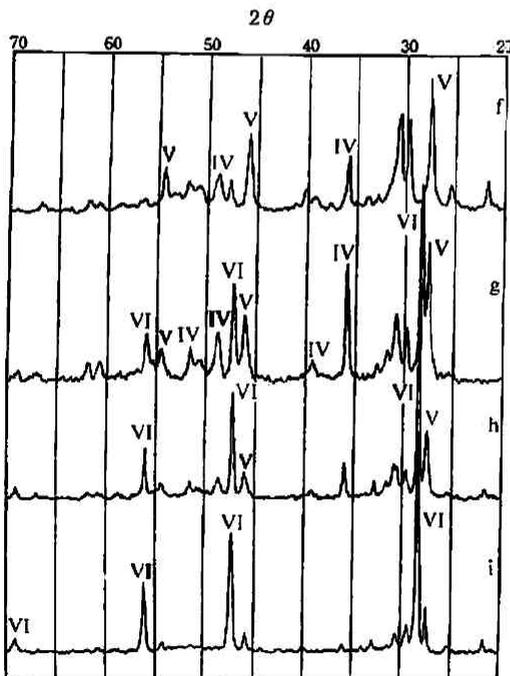


Fig. 2 The changes of X-ray diffraction diagrams with changes of experimental conditions from 1200°C, 30-35 kb to 1400°C, 40 kb

Table 2 Crystallographic data and experimental conditions for preparation of high pressure phases in the Ge-P system

Symbol of phase	Crystal system and lattice constants	Assumed composition	Experimental condition for preparation	
			Temperature(°C)	Pressure (kb)
GeP (I)	hexagonal, $a=10.02 \text{ \AA}$ , $c=13.92 \text{ \AA}$	GeP	600	10
GeP (II)	hexagonal, $a=8.603 \text{ \AA}$ , $c=12.622 \text{ \AA}$	GeP	600	15
GeP (II')	hexagonal, $a=8.192 \text{ \AA}$ , $c=12.44 \text{ \AA}$	GeP	600-800	20-25
GeP (III)	tetragonal, $a=6.809 \text{ \AA}$ , $c=8.280 \text{ \AA}$	?	800-1000	30
GeP (IV)	cubic, $a=5.619 \text{ \AA}$	GeP <sub>2</sub>	1000-1200	35-40
GeP (V)	cubic disordered sphalerite, $a=5.581 \text{ \AA}$	GeP	1200-1400	40
GeP (VI)	cubic sphalerite, $a=5.463 \text{ \AA}$	GeP	1400	40
GeP (VII)	tetragonal, $a=7.101 \text{ \AA}$ , $c=9.129 \text{ \AA}$	?	1200-1400	25-40
GeP (VIII)	cubic, $a=6.451 \text{ \AA}$	?	800	20-25

**GeP (IV):** This phase has a cubic structure with  $a=5.619 \text{ \AA}$ . The stoichiometric composition is presumed to be GeP<sub>2</sub> since the phase shows stronger reflections in the Ge : P = 1 : 2 sample and always coexists with strong reflections from the unreacting germanium in the Ge : P = 1 : 1 sample. It is, however, not the phase corresponding to the pyrite type SiP<sub>2</sub><sup>9)</sup> in the Si-P system because the lattice constant is a little smaller in opposition than that of SiP<sub>2</sub>,  $a=5.682 \text{ \AA}$ , in spite of the larger bond radius of germanium compared with that of silicon. GeP (IV) may be related closely to SiP<sub>2</sub> both in the process of formation and in the X-ray diffraction diagrams as shown in Table 3.

Considering the interatomic distance for Ge-P,  $2.4 \text{ \AA}$ , calculated with univalent radii, GeP (IV) would not have so complicated structure. The structure is not so far determined at this stage. It is prepared under the conditions of 1000~1200°C and 40 kb and has a metallic appearance like a granular tin. The color is gray in powder.

Table 3 Comparison of the data of X-ray diffraction diagrams for SiP<sub>2</sub> and GeP (IV)

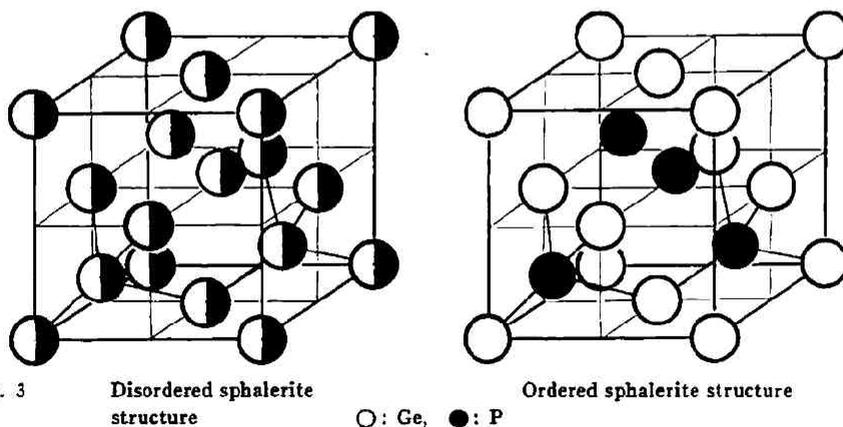
SiP <sub>2</sub> (cubic pyrite)		GeP (IV) (cubic)		
$d$ (Å)	$I/I_0$	$d$ (Å)	$I/I_0$	$hkl$
—	—	3.24	15	111
2.840	100	2.82	25	200
2.547	80	2.515	100	210
2.325	55	2.291	10	211
2.014	15	1.985	5	220
—	—	1.872	45	300
—	—	1.774	50	310
1.717	65	—	—	311
1.644	30	—	—	222
1.522	35	1.500	20	321
—	—	1.286	10	330
1.243	15	—	—	421
$a=5.682 \text{ \AA}$		$a=5.619 \text{ \AA}$		

**GeP (V) and GeP (VI):** GeP (V) has a cubic structure with  $a=5.581 \text{ \AA}$ . Table 1 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 this phase might be a single component phase of germanium or phosphorus with diamond structure. But there exists no high pressure modification of germanium and phosphorus with this structure having a given lattice constant throughout the experiments. Therefore it may be a product of the reaction of unreacting germanium with GeP (IV) or other coexisting phases. GeP (V) may have disordered sphalerite structure and a stoichiometric composition GeP.

GeP (VI) has a cubic structure with  $a=5.463 \text{ \AA}$ . All reflections corresponding to the indices with mixed integers disappear. This is an extinction rule characteristic to sphalerite structure. Therefore this phase corresponds to the cubic sphalerite type SiP<sup>9)</sup>. Since there exist small deviations in the intensities of super lattice reflections with indices  $h+k+l=4n+2$  according to the changes of experimental conditions and the compositions of the starting materials, the disordering might come about in the positions for germanium and phosphorus. In the Si-P system it is impossible to determine whether the cubic SiP has an ordered sphalerite structure or a disordered sphalerite structure since all the structural factors  $F(hkl)$  of the faces with  $h+k+l=4n+2$  are equal to  $4(f_{Si}-f_P)$  and super lattice reflections disappear because  $f_{Si}$  and  $f_P$ , the atomic scattering factors for silicon and phosphorus, are nearly equal. However in the Sn-P system a sphalerite type SnP with a lattice constant  $a=5.544 \text{ \AA}$  is also formed under the conditions of about  $1700^\circ\text{C}$  and  $40\sim 50 \text{ kb}$ . Therefore these three high pressure phases SiP, GeP and SnP may be the corresponding phases having sphalerite structure. The data of X-ray diffraction diagrams for the sphalerite type SnP are shown in Table 4.

The calculated density is  $4.22 \text{ g/cm}^3$ . The interatomic distances for Ge-Ge and P-P have the same values  $3.863 \text{ \AA}$  and that for Ge-P  $2.365 \text{ \AA}$ .

As shown in Fig. 2, GeP (V) may be an intermediate between GeP (IV) and the sphalerite type GeP. In this phase the contraction of the crystal lattice with increasing pressure is not observed. It is not necessarily impossible to regard GeP (V) as the disordered state of GeP (VI), in which the reflections corresponding to the indices  $h+k+l=4n+2$  are the super lattice reflections, considering



the following facts: (1) A close relation is observed among the X-ray diagrams of germanium, GeP (V) and GeP (VI). (2) In the order-disorder transition of  $\text{Cu}_3\text{Au}^*$  under high pressure<sup>13)</sup>, for example, it is confirmed that the disordering of  $\text{Cu}_3\text{Au}$  results in a volume increase and therefore pressure stabilized the ordered state. However the difference of the lattice constants between GeP (V) and GeP (VI) in the present work, 0.118 Å, is too large in comparison with the values of  $10^{-2}\sim 10^{-3}$  Å order observed in the general order-disorder transitions under atmospheric pressure. Therefore GeP (V) may not be the pure disordered state of GeP (VI) as shown in Fig. 3.

In the In-Te<sup>14)</sup> system it is reported that a pressure-induced NaCl type In-Te phase exists in the region  $\text{In}_{0.80}\text{Te}$  to  $\text{In}_{1.15}\text{Te}$  and a substantial number of vacancies are produced by high pressure in In sites. The lattice constant of this high pressure phase changes from  $a=6.179$  Å for stoichiometric InTe to  $a=6.040$  Å for  $\text{In}_{0.80}\text{Te}$  with change in In concentration. The difference of the lattice constant 0.139 Å is comparable to the value 0.118 Å between GeP (V) and GeP (VI). Therefore deviation of the composition from stoichiometric GeP may be induced in GeP (V) or GeP (VI) by high pressure.

Both phases are prepared under the conditions of 1200~1400°C and 40 kb and have such an alloy-like appearance as granular tin. It can be easily pulverized and the color is gray in powder.

$d$ (Å)	$I/I_0$	$hkl$
3.215	100	111
2.776	70	200
1.959	45	220
1.667	20	311
1.610	30	222
1.383	5	400
1.272	5	331
1.239	10	420
1.129	10	422
1.065	5	511, 333
0.983	5	440
0.936	10	531

Table 4 Data of X-ray diffraction diagrams for the sphalerite type SnP

Pressure dependence of the resistances of GeP (II) and GeP (VI) at room temperature are shown in Fig. 4. The homogeneity of the samples were ensured by X-ray diffraction. The dimensions of the sample after the runs are about 1mm×1mm in area and 1mm in length. The two anvils afforded electric contact to the sample through the platinum foil electrodes. The resistance measurements were made using a TOA PM-8 type vacuum tube voltmeter.

For the pressures up to 30kb, the electrical resistance of GeP (II) decreases gradually with pressure and is nearly constant above 30kb. The resistivity is of the order of  $10^0 \Omega\text{-cm}$ . The electrical

\* In the order-disorder transition of  $\text{Cu}_3\text{Au}$  the lattice constant changes from 3.76 Å of the disordered fcc lattice to 3.748 Å of the ordered cubic lattice.

13) M. C. Franzblau and R. B. Gordon, *J. Appl. Phys.*, **38**, 103 (1967)

14) S. Geller, A. Jayaraman and G. W. Hull, Jr., *J. Phys. Chem. Solids*, **25**, 353 (1965)

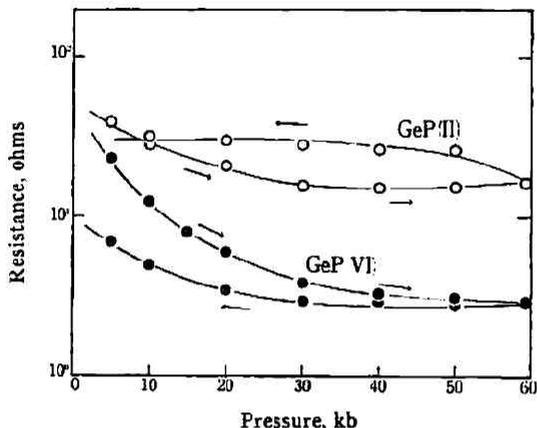


Fig. 4 Pressure dependence of the resistances of GeP (II) and GeP (VI) at room temperature

resistivity of GeP (VI) at low pressure is nearly equal to that of GeP (II) but it decreases with pressure up to 40 kb from the order of  $10^0$  to  $10^{-1}$   $\Omega$ -cm. The pressure dependence of the resistance of GeP (VI) is comparatively large. The resistivity of GeP (VI) is quite small so that GeP (VI) seems to be an alloy rather than a semiconductor. If GeP (VI) has a complete sphalerite structure, the resistivity should be much smaller than the value  $10^{-1}$   $\Omega$ -cm measured in the present work since the sum of the valence electron is 9 in GeP so that one valence should remain unsaturated. Therefore GeP (VI) may have a sphalerite structure which contains statistically distributed vacancies in such cases as  $\gamma$ - $\text{In}_2\text{Te}_3$ <sup>15)</sup> or the pressure-induced NaCl-type  $\text{InTe}$ <sup>14)</sup>.

**GeP (VII) and GeP (VIII):** GeP (VII) has definite reflections from a tetragonal structure with  $a=7.101 \text{ \AA}$  and  $c=9.129 \text{ \AA}$  only in the Ge : P = 1 : 2 sample. It is rather stable in the pressure range 25~40 kb at about 1200°C.

GeP (VIII) has weak reflections from a cubic structure with  $a=6.451 \text{ \AA}$  under about 25 kb at 800°C only in the Ge : P = 1 : 2 sample and have probably a primitive cell. This phase shows a small distortion to a tetragonal structure by increasing pressure. The value  $c/a=1.06$  is calculated by use of Megaw's equation which is often applied to the perovskite type compounds.

**Other non-indexed reflections:** There exist several non-indexed reflections besides the phases mentioned above.

Under the conditions of 1500°C and 40 kb, the X-ray diffraction diagrams with a very low crystallinity are obtained in the Ge : P = 1 : 1 sample. This phase may be a high pressure phase in the last step of the reaction in the experimental conditions. It coexists with GeP (V) and GeP (VI), which have also low crystallinities in this condition.

It is expected that the diamond and the sphalerite structures transform to denser form at high temperatures and very high pressures since they have comparatively wide vacant spaces in the lattices. Therefore this would be the phase obtained from the sphalerite type GeP though even indexing is impossible at this stage. Only spacings and intensities are shown in the following table.

15) H. Hahn and G. Frank, *Z. anorg. allg. Chem.*, 278, 333 (1955)

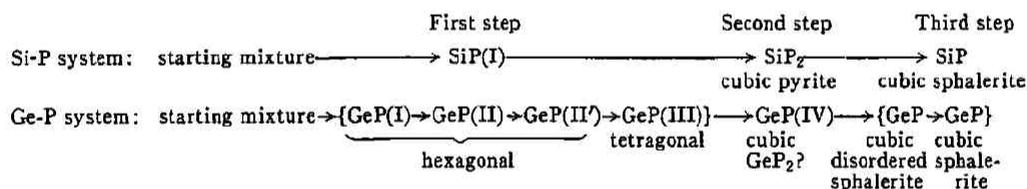
As mentioned above, these high pressure phases always coexist each other in the sample. This may be due to the conditions of the chemical equilibria in the reaction processes.

$d$ (Å)	$I/I_0$	$d$ (Å)	$I/I_0$
3.60	30	1.940	15
3.055	20	1.840	80
2.762	100	1.770	20
2.184	35	1.742	50
2.125	10	1.670	35
2.021	15	1.652	10

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

The quantitative description of the reaction process in the Ge-P system can not be made because of difficulties of the isolation of high pressure phases since they are very changeable in chemical treatments with such as aq. NaOH, aq. HF and aq. HNO<sub>3</sub>. Therefore the reaction under high pressure has been investigated qualitatively by X-ray diffraction in comparison with the reaction in the Si-P system.

**Main reaction process:** The main reaction processes in the Si-P and Ge-P system at high temperatures and high pressures are shown schematically as follows in the case of Si : P or Ge : P = 1 : 1 starting materials.



From the crystallographic point of view, the reaction processes consist of three main steps in both systems. In the Si-P system there exists only one phase in each step and the contraction of lattice constants with increasing pressure is not observed through the experiment. On the other hand, in the Ge-P system, the transition from hexagonal GeP (I) to tetragonal Ge-P (III) in the first step of the reaction is carried out through three sub-steps. There exists a disordered sphalerite type GeP as an intermediate between cubic GeP (VI) and the sphalerite type GeP. Thus the characteristics of the high pressure phases in the Ge-P system is that they have comparatively non-directional metal-like natures in bonding and the crystal structures change rather easily and delicately. This differences may arise from the higher metallicity of germanium compared with silicon.

**Effects of temperature and pressure:** At 800°C under 15 kb the formation of GeP (II) finishes within 1~2 hours and other reactions in the first group proceed at 600~1000°C and 10~25 kb. The experiment in the lower pressure range below 10 kb was not undertaken since phosphorus was very fluid at the required temperature and could not be contained in the reaction vessel. In the lower tempera-

ture range below 600°C the formation of GeP (II) is considerably retarded but there is no condition under which GeP (I) is the main product instead of GeP (II). The transition from GeP (II') to GeP(III) requires the conditions of 900~1100°C and 25~30 kb.

The second and the third steps of the reactions are attained under the conditions of 1100~1200°C, 35~40 kb and about 1400°C, 40 kb respectively.

In the Si-P system the transformation from SiP (I) to SiP<sub>2</sub> is considerably easy to make while that from SiP<sub>2</sub> to SiP is difficult. On the other hand, each step in the Ge-P system proceeds comparatively easily under high pressure. The consecutive delicate changes of the crystal structures in the first and the third steps of the reaction can be observed only in the suitable experimental conditions. Under the severe conditions they are passed by very quickly, or neglected.

**Effect of reaction time:** The reactions in the Ge-P system have considerable reactivity and finish within 1~2 hours. The reaction time has a large effect on the delicate changes in the first and the third steps of the reaction. Each phase shown in Figs. 1 and 2 was obtained by sampling at an interval of 30 minutes under the suitable conditions.

**Effect of composition of reactants:** In the Si-P system the presence of excess silicon in such cases as Si : P = 2 : 1 sample retards the transition from SiP (I) to SiP<sub>2</sub> remarkably even under sufficiently severe conditions in which the transition is carried out easily in the Si : P = 1 : 1 sample.

In the Ge-P system, on the other hand, each transition proceeds without being retarded in the presence of excess germanium.

In the presence of excess phosphorus in such a case as Ge : P = 1 : 2 sample, GeP (VII) and GeP(VIII), which are not observed in the Ge : P = 1 : 1 sample, are prepared.

Thus in the Si-P system the change of the composition of the reactants do not bring about any crystallographic change on the high pressure phases but has a decisive influence on the proceeding of the reaction. In the Ge-P system it has effects on the X-ray intensities of the super lattice reflections, while it has hardly any effect on the process of the reaction. From this point of view the Ge-P system under high pressure has the characteristics of "metallic phases" rather than those of "non-metallic compounds".

The authors have described the high pressure phase in the Ge-P system. According to Zintl's empirical rule<sup>16)</sup>, it is known that non-metallic intermetallic compounds must contain an anion-forming element, *i. e.* an element with at least half-filled valence shells or sub-shells. Thus the anion formers lie to the right of the Zintl border, in groups IVB to VIIB of the periodic table. In the intermetallic compounds, the compounds, for which the difference in electronegativities between the component atoms is  $\Delta X > 1.0 \sim 0.8$ , will be ionic, those, for which the difference is  $0.4 \sim 0.5 < \Delta X < 0.8 \sim 1.0$ , will be covalent and those for which the difference is  $\Delta X < 0.3 \sim 0.4$  will be rather covalent or metallic.

In general, group IVB, VB, and VIB elements are apt to form with more positive elements the covalent intermetallic compounds which have compositions determined from the normal valence rule. This tendency is marked in the systems consisting of higher electronegative elements in IVB, VB and VIB groups and higher positive elements. In the covalent intermetallic compounds there often exist

16) E. Zintl and E. Husemann, *Z. Physik Chem.*, **B51**, 138 (1933)

$sp^3$  or  $p^3$  bonds and so the chemical bondings have directional character. The coordination number and the crystal structure that they can adopt, therefore, are restricted as compared with metallic phases. Thus the effect of high pressure on the crystal structures of covalent intermetallic compounds may be smaller than on those of anomalously composed semiconductors.<sup>17)18)</sup>

In the IV-V compounds IVB elements are considerably non-metallic for the positive components of the systems and so they have small tendencies to form covalent intermetallic compounds.  $\Delta X$  has the same value, 0.3, both in the Si-P and in the Ge-P system. Under an atmospheric pressure they adopt the complicated structures to saturate the valences and manage to have semiconducting properties. It is, therefore, expected that they transform easily to more metallic phases with high pressures since high pressure makes higher the coordination number in the crystal and crystal symmetry.

As mentioned above, it is very difficult to investigate completely the Ge-P system under high pressure because of its complexity but it is characteristic that the system shows quite clearly the effect of pressure on the crystal structures of high pressure phases.

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