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Synthesis, Structure, and Superconductivity of New High Pressure Phases in the Systems Ge–P and Ge–As

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Reactions of Ge with P and As were run in a tetrahedral anvil press at conditions ranging from 600–1300C and 15–65 kbars. Three new phases were found in the Ge–P system. Two phases of approximate formulas GeP_5 and GeP_3 have rhombohedral crystal structures related to the A7 arsenic type. The cell dimensions of GeP_5 are $a = 3.467$ (3) Å, $c = 10.04$ (1) Å and of GeP_3 $a = 7.050$ (1) Å, $c = 9.932$ (3) Å. The cell dimensions vary for different preparations indicating ranges of stoichiometry. A new tetragonal form of GeP was prepared by the reaction of Ge + 1.0–1.7 P at 600–800C, 45–65 kbars. The cell dimensions are $a = 3.544$ (2) Å, $c = 5.581$ (1) Å and space group is 14 mm. A similar tetragonal phase was formed in the Ge–As system. The cell dimensions are: $a = 3.715$ (1) Å, $c = 5.832$ (1) Å. The tetragonal crystal structures were solved by least-squares refinement of the powder-diffraction intensity data. Bond distances and angles were calculated. Electrical measurements on single crystals show metallic behavior. Meissner effect measurements show that GeP is superconducting below 1.8–4.2K and GeAs below 3–3.5K.

Introduction

At ambient pressure in the Ge–P system only GeP is known (*1*). The crystal structure is isotypic with GeAs (*2*) and SiAs (*3, 4*) in which the coordinations of the Group IV and Group V elements are normal; i.e., tetrahedral and pyramidal, respectively. These compounds have been described as semiconductors (*5*).

In the Ge–As system the only known phase other than GeAs is $GeAs_2$; however, a solubility limit of 16 at % Ge in As is reported (*2*).

Osugi, *et al.* (*6*) report the formation of sphalerite-type SiP, GeP, and SnP at 1600 to 1800C and 40 to 50 kbars. They have further studied the Ge–P system at high pressure (*7*) and found eight different phases. Their experiments were carried out in a cubic anvil press and a piston cylinder Bridgman-type press. Since they did not separate phases, the determination of stoichiometry was not possible.

In this study, a tetrahedral anvil press of National Bureau of Standards design (*8*) was used. It has a larger sample volume than the cubic device (*9*) and a temperature gradient from the center of the sample pellet to the ends of about 30%. It was found in most cases that phase separation in the form of single crystals was possible. The phases found in this study differ somewhat from those previously reported.

Experimental

All reactions were run in a tetrahedral anvil press of National Bureau of Standards design (*8*). Reactants were contained in a cylindrical boron nitride crucible approximately 0.6 cm long and 0.125 cm^3 in volume, which was surrounded by a graphite sleeve resistance heater and inserted in a pyrophyllite tetrahedron. The calibration points used to establish the pressure developed were the Bi I $\rightarrow$ II, 25.37 ± 0.02 kbars, Bi II $\rightarrow$ III, 26.96 ± 0.18 kbars, Tl II $\rightarrow$ III, 36.69 ± 0.11 kbars, and Ba II $\rightarrow$ III, 59.0 ± 1.0 kbars. All compressions were made on the assembly at room temperature, and the charge was then heated to the desired temperature. The temperature was measured using a Pt–Rh thermocouple, uncorrected for pressure effects, which was placed at the center of the surface of the cylinder. The temperature at the ends is approximately 30% lower. The operating procedure has been explained elsewhere (*10*).

High-purity (5N+) Ge, P, and As were used as reactants. They were ground together in the desired ratios and pelleted prior to reaction. In general, the reactants were cold pressured, then brought to temperature, held for an hour or two, cooled about 400C over a period of 2 hr, and quenched to room temperature in less than 1 min while maintaining pressure. The cooling process enhanced crystal growth.

Because of the temperature gradient, it was frequently found that different phases formed at the ends and center of the pellet. They could generally be physically separated and analyzed. All products were characterized by Debye–Scherrer X-ray powder diffraction at 25C. Films were read on a David Mann film reader Model No. 1222. Unit cell dimensions were refined by a least-squares method with the Nelson–Riley function as one parameter. Densities were measured by a displacement technique in bromoform.

Electrical resistivities were measured by a four-probe technique described previously (*11*). Superconducting transition temperatures were measured by observing the Meissner effect at temperatures above 1.25K.

Results

A. GeP_5

Several reactions were run at reactant ratios of 1 Ge:3.5 P. The primary product at 65 kbars has the approximate formula GeP_5. All reactions and products are summarized in Table I.

The reaction of Ge + 3 P at 900C, 65 kbars, held 1 hr, slow cooled 3 hr to 500C, and quenched yielded large black crystals at the ends of the pellet and an unidentified black center region. The Debye–Scherrer pattern of the end region was indexed on the basis of a rhombohedral cell with hexagonal cell dimensions, $a = 3.467$ (1) Å, $c = 10.04$ (1) Å. The measured density is 3.65 g/cm^3. The density calculated for one formula weight of GeP_5 per unit cell is 3.61 g/cm^3. Resistivity measurements made on a single crystal showed metallic behavior: $\rho_{4.2K} = 8.0 \times 10^{-5}$ ohm-cm; $\rho_{298K} = 1.0 \times 10^{-4}$ ohm-cm.

Reaction of Ge + 3.5 P at the same conditions yielded a similar distribution of products. The crystals were analyzed: Found 64.5% P, 31.1% Ge. Calculated for GeP_5: 68.1% P, 31.97% Ge. Because the sample size was small, the chemical analysis is poor. The deviation may indicate nonstoichiometry. The center region of the pellet gave a poor and unidentified Debye–Scherrer pattern.

The reaction of Ge + 4 P at the same conditions produced a similar product. The hexagonal cell dimensions are: $a = 3.457$ (1) Å, $c = 10.001$ (5) Å and measured density is 3.57 g/cm^3. The deviation in cell dimensions from those of other reactions indicates nonstoichiometry.

The Debye–Scherrer pattern (Table II) is qualitatively similar to that of rhombohedral As in which As is three-fold coordinated and the structure is comprised of puckered, graphite-like sheets. Phosphorus has been reported to have this structure above 50 kbars; however, it is not quenchable and transforms back to black phosphorus (*12*). The cell dimensions are $a = 3.3777$ Å, $c = 8.806$ Å. Since this structure has only six atoms per unit cell in a six-fold position, the Ge atoms must substitute randomly for P. It is surprising that a strict stoichiometry, GeP_5, would be favored over a range of composition. Since an upper limit of 16 at % Ge solubility in As has been reported (*2*), the formula GeP_5 may represent a similar solubility limit. A reaction starting with Ge + 9 P and run at conditions similar to those described above yielded black P and a poorly crystallized product showing a Debye–Scherrer

TABLE I

REACTIONS AND PRODUCTS

Reaction mixture	T (°C)	P (kbars)	Cell dimensions of single crystal product	Type of cell	Proposed formula	Other phases
Ge + 3 P	900–500	65	$a = 3.467(3)$, $c = 10.04(1)$	R	GeP_5	Unidentified
Ge + 4 P	900–500	65	$a = 3.457(1)$, $c = 10.001(5)$	R	GeP_5	Unidentified
Ge + 9 P	900–500	65	$a = 3.2$ Å, $c = 9.98$	R	?	Black P
Ge + 4 P	800–500	30	$a = 6.989(1)$, $c = 9.986(3)$	R	GeP_3	Black P
Ge + 1.7 P	800–400	65	$a = 7.050(1)$, $c = 9.932(3)$	R	GeP_3	Tet. GeP and unidentified
Ge + 1.7 P	800–500	30	$a = 7.054(6)$, $c = 9.90(1)$	R	GeP_3	Low pressure GeP
Ge + P	800–400	65	$a = 3.544(2)$, $c = 5.581(1)$	T	GeP	GeP_3, Ge unidentified
Ge + P	700	45	$a = 3.544(2)$, $c = 5.581(1)$	T	GeP	
Ge + 3 As	900–500	65	$a = 3.72(1)$, $c = 10.73(1)$	H	As(Ge)	GeAs
1.2 Ge + As	800–500	65	$a = 3.712(1)$, $c = 5.832$	T	GeAs	Ge

TABLE II

DEBYE–SCHERRER X-RAY POWDER DIFFRACTION PATTERN OF GeP_5 AND GeP_3

GeP_5						GeP_3					
$a = 3.457$ Å $c = 10.001$ Å $CuK_{\alpha}(Ni)$, $\lambda = 1.54178$						$a = 7.050$ Å $c = 9.932$ Å					
I/I_0[a]	h	k	l	d(obs.)	d(calc.)	I/I_0[a]	h	k	l	d(obs.)	d(calc.)
20	0	0	3	3.3319	3.3365	35	0	1	2	3.8547	3.8527
10	1	0	1	2.8613	2.8681	35	1	1	0	3.5249	3.5251
100	0	1	2	2.5704	2.5687	30	0	0	3	3.3109	3.3109
30	1	0	4	1.9185	1.9190	10	0	2	1	2.9188	2.9181
50	1	1	0	1.7287	1.7285	100	2	0	2	2.6005	2.6007
5	0	0	6	1.6629	1.6668	10	1	0	4	2.2973	2.3002
	0	1	5		1.6631						
10	1	1	3	1.5339	1.5345	15	1	2	2	2.0910	2.0928
15	2	0	2	1.4339	1.4340	5	3	0	0	2.0336	2.0352
12	0	2	4	1.2849	1.2843	55	0	2	4	1.9260	1.9263
10	1	1	6	1.1986	1.1998	55	2	2	0	1.7622	1.7625
	2	0	5		1.1985	20	2	0	5	1.6641	1.6650
						5	3	1	2	1.6012	1.6028
12	1	2	2	1.1036	1.1036	10	2	2	3	1.5555	1.5558
5	2	4	1	1.0310	1.0309	15	0	4	2	1.4579	1.4590
2	3	0	0	0.9987	0.9980	5	4	0	4	1.2998	1.3004
						5	0	2	7	1.2868	1.2867
						5	2	2	6	1.2064	1.2066
						5	4	2	2	1.1242	1.1239
						5	2	4	4	1.0459	1.0464
						5	6	0	0	1.0186	1.0176
						5	2	2	9	0.9358	0.9354
						5	2	4	7	0.8951	0.8952

[a] Read using the David Mann film reader.

pattern with diffuse lines of the GeP_5-type structure, shifted smaller. An approximate unit cell was calculated from a few diffraction lines: $a = 3.2$ Å, $c = 9.98$ Å. This indicates that solution of Ge in rhombohedral P may occur below the GeP_5 concentration; however, the crystallinity is poor and quenchability seems to be reduced.

B. GeP_3

The reaction of Ge + 4 P at 800C, 30 kbars held 1 hr, cooled 3 hr to 500C, and quenched yielded black crystalline material throughout the pellet. The Debye–Scherrer pattern showed primarily a new phase and black P. The new phase was indexed on the basis of a hexagonal unit cell, $a = 6.989$ (1) Å, $c = 9.986$ (3) Å.

The reaction of Ge + 1.7 P at 800C, 65 kbars held 1 hr, cooled 3 hr to 400C, and quenched yielded black crystals at the ends of the pellet and an unidentified black-gray mass in the center. The Debye–Scherrer pattern of the end region was indexed on the basis of a rhombohedral cell with hexagonal cell dimensions: $a = 7.050$ (1) Å, $c = 9.932$ (3) Å. The possible space groups were determined by Buerger precession camera methods to be $R\bar{3}m$, $R32$, or $R3m$. The Debye–Scherrer pattern (Table II) is like that reported by Osugi *et al.* (*6*) for their product designated GeP (III) which they index tetragonal. The single crystal data confirm the rhombohedral indexing. Density measurements show $\rho = 3.90$ g/cm^3. The value calculated for eight formula units of GeP_3 per unit cell: $\rho = 3.86$ g/cm^3.

The center region of the pellet showed a Debye–Scherrer pattern consisting primarily of tetragonal GeP to be described later.

The reaction of Ge + 1.7 P at 800C, 30 kbars held 1 hr, cooled 4 hr to 500C, and quenched yielded black crystalline regions at the ends of the pellet and black needlelike crystals in the center. The end region showed a GeP_3-type Debye–Scherrer pattern with the cell dimensions: $a = 7.054$ (6) Å, $c = 9.90$ (1) Å, and measured density $\rho = 3.84$ g/cm^3. The calculated density is $\rho = 3.86$ g/cm^3. Chemical analysis was poor because the sample size was small: Found: 60.5% P, 37.8% Ge. Calculated for GeP_3: 56.1% P, 43.9% Ge. Resistivity measurements on a single crystal showed metallic conductivity: $\rho_{25K} = 1 \times 10^{-4}$ ohm-cm, $\rho_{4.2K} = 10^{-5}$ ohm-cm.

The center region showed a Debye–Scherrer pattern of low-pressure GeP.

The crystal structure of GeP_3 seems to be related to that of GeP_5 by a doubling of the *a* axis. The doubling might result from an ordering of Ge atoms which have substituted for P in the puckered graphite layers or from a distortion of the basic As-type lattice. The formula GeP_3 is only approximate since the variable cell dimensions and density indicate nonstoichiometry. It does seem unusual that a complete range of Ge substitution does not occur between GeP_5 and GeP_3 since they appear to have related structures.

C. Tetragonal GeP

The reaction of Ge + P at 800C, 65 kbars, held 1 hr, cooled 3 hr to 400C, and quenched yielded a pellet containing four regions. Black crystals on the ends showed a GeP_3-type pattern. In the center an unidentified, poorly crystallized phase was found. Excess Ge was present around the middle of the pellet. Between the central and end regions, a region of large black crystals was present.

The Debye–Scherrer pattern of the crystals (Table III) was indexed on the basis of a tetragonal cell, $a = 3.544$ (2) Å, $c = 5.581$ (1) Å. The most probable space group, determined using a Buerger precession camera, is I4 mm. The density of the crystals was determined: Found: 4.73 g/cm^3; calculated for 2 (GeP) per unit cell, 4.90 g/cm^3. Because of the small size of the sample on which density was measured, the agreement is within the limits of error. Since insufficient single-phase material was obtained, the phase was not analyzed chemically.

The minimum pressure for formation of the tetragonal phase at 700C is approximately 45 kbars.

Electrical measurements on a single crystal show metallic behavior: $\rho_{298K} = 1 \times 10^{-4}$ ohm-cm; $\rho_{4.2K} = 9 \times 10^{-5}$ ohm-cm. Meissner effect measurement showed a superconducting transition between 1.5 and 4.2K.

D. Ge–As System

The reaction of Ge + 3 As at 900C, 65 kbars held 1 hr, slow cooled 3 hr to 500C, and quenched, yielded black crystalline regions at the ends of the pellet and a black-gray region in the center. The Debye–Scherrer pattern of the end region showed a poor quality As-type pattern which was indexed on the basis of a hexagonal unit cell $a = 3.72$ (1) Å, $c = 10.73$ (1) Å. These values are shifted from those of As (*13*) ($a = 3.76$ Å, $c = 10.548$ Å) and indicate solid solution of Ge in the As lattice as described (*2*).

The Debye–Scherrer pattern of the center region showed primarily a pattern similar to that of GeP, tetragonal form, but shifted to larger cell size.

The reaction of 1.2 Ge + As at 800C, 65 kbars held 1 hr, cooled 3 hr to 500C, and quenched yielded a black crystalline region at one end of the pellet and a black, less crystallized region at the other. The Debye–Scherrer pattern of the crystals showed a pure pattern similiar to that of tetragonal GeP. The pattern was indexed on the basis of a tetragonal unit cell $a = 3.712$ (1) Å, $c = 5.832$ (1) Å (Table III). The other region of the pellet was identified as unreacted Ge. The density was measured on the black crystals: Found 6.06 g/cm$_3$, Calculated for 2 (GeAs) per unit cell, 6.10 g/cm^3. The unit cell dimensions were found to vary for different preparations, possibly indicating a small range of stoichiometry.

The minimum pressure for formation of the tetragonal phase at 800C is approximately 55 kbars. Excess Ge was found to enhance crystal growth. At lower pressures, the products of several reactions were identified as low-pressure GeAs.

Electrical measurements on crystals of GeAs showed metallic behavior: $\rho_{25K} = 3.8 \times 10^{-3}$ ohm-cm, $\rho_{4.2K} = 2.5 \times 10^{-3}$ ohm-cm. Meissner effect measurements showed transition to the superconducting state at 3–3.5K.

E. Crystal Structure Analysis

The crystal structures of the tetragonal phases GeAs and GeP were solved by refinement of their X-ray powder intensities.

Since the tetragonal unit cell is so small, the possibilities of atomic position are limited. The only possible positions for two atoms in space group I4 mm are $00Z + 1/2\ 1/2\ 1/2$. Relative intensities were collected for GeAs from a diffractometer tracing by obtaining relative weights of the peaks. The sample was prepared by grinding, passing through a 325-mesh screen, and sprinkling on a glass

TABLE III

Debye-Scherrer X-ray Powder Diffraction Patterns of the Tetragonal High Pressure Forms of GeP and GeAs

GeP						GeAs					
$a = 3.544$ Å $c = 5.581$ Å $CuK_\alpha(Ni)$, $\lambda = 1.54178$ [a] $CuK_{\alpha 1}(Ni)$, $\lambda = 1.54051$						$a = 3.715$ Å $c = 5.832$ Å					
I/I_0[a]	h	k	l	d(obs.)	d(calc.)	I/I_0[a]	h	k	l	d(obs.)	d(calc.)
75	1	0	1	2.99369	2.99218	60	1	0	1	3.13337	3.13320
75	0	0	2	2.79533	2.79086	100	0	0	2	2.91870	2.91605
100	1	1	0	2.50726	2.50634	90	1	1	0	2.62777	2.62677
90	1	1	2	1.86521	1.86475	95	1	1	2	1.95223	1.95169
60	2	0	0	1.77245	1.77225	85	2	0	0	1.85783	1.85741
30	1	0	3	1.64820	1.64740	40	1	0	3	1.72405	1.72243
25	2	1	1	1.52528	1.52485	10	2	1	1	1.59727	1.59776
45	2	0	2	1.49642	1.49609	50	2	0	2	1.56672	1.56660
2	0	0	4	1.39504	1.39543	5	0	0	4	1.45761	1.45802
30	2	2	0	1.25345	1.25317	30	2	2	0	1.31306	1.31339
10	1	1	4	1.21927	1.21920	20	1	1	4	1.27487	1.27481
25	2	1	3	1.20668	1.20661	30	2	1	3	1.26293	1.26297
5	3	0	1	1.15721	1.15589	20	2	2	2	1.19736	1.19753
10	2	2	2	1.14342[a]	1.14321	30	3	1	0	1.17438	1.17473
20	3	1	0	1.12042[a]	1.12087	5	2	0	4	1.14642	1.14688
5	2	0	4	1.09687[a]	1.09637	20	1	0	5	1.11322	1.11285
5	3	0	3	.99736[a]	.99739	25	3	1	2	1.08941	1.08963
2	3	2	1	.96826[a]	.96816	5	3	0	3	1.04423	1.04440
20	2	1	5	.91217[a]	.91272	5	2	2	4	.97647	.97584
10	4	0	0	.88602[a]	.88612	10	2	1	5	.95414	.95462
5	3	1	4	.87440[a]	.87387	5	4	0	0	.92893	.92870
5	3	2	3	.86918[a]	.86920	10	1	1	6	.91159[a]	.91160
5	4	1	1	.84967[a]	.84965	10	4	0	2	.88531[a]	.88491
10	4	0	2	.84447[a]	.84457	10	3	3	2	.83844[a]	.83860
5	3	3	0	.83559[a]	.83545	5	4	2	0	.83062[a]	.83066
5	3	0	5	.81179[a]	.81143	5	4	2	2	.79844[a]	.79835
5	3	3	2	.80060[a]	.80035						
10	4	2	0	.79263[a]	.79257						
5	4	1	3	.78037[a]	.78039						

[a] Read using the David Mann film reader.

slide coated with vaseline. A Norelco diffractometer was used at a scanning rate of 1/4°/min with the chart scaled to 1 inch/1°. Fourteen pieces of data were collected. Relative intensity data for GeP were collected from a Debye–Scherrer film since insufficient material was isolated to prepare an adequate slide for the diffractometer. The film was read especially carefully using the David Mann film reader.

Least-squares refinements were done using a program written by Dr. C. T. Prewitt which handles the sums of non-equivalent overlapping reflections. Atomic scattering factors were obtained from *International Tables for X-Ray Crystallography*, Volume III, Tables 3.3.1A and 3.3.1B. The real and imaginary parts of the anomalous dispersion correction were applied during the refinements. The occupancy factors of all atoms were held at two, and all reflections were weighted at unity. Corrections for Lorentz and polarization factors were made in the refinement. Both Ge and P or As were placed in position $00Z$ with Z held at 0 for Ge and allowed to vary for P or As.

In both refinements, three parameters were

TABLE IV

REFINED PARAMETERS AND BOND DISTANCES AND ANGLES FOR GeP AND GeAs

GeP			GeAs		
Atom	Position	Tempteratur e factor	Atom	Position	Temperature factor
Ge	000	1.0 ± 0.7	Ge	000	1.3 ± 0.6
P	00.427 ± .007		As	00.414 ± 0.04	
Atoms[a]	Distance in Å		Atoms[a]	Distance in Å	
Ge(1)–P(2)	2.38(4)		Ge(1)–As(2)	2.41(3)	
Ge(1)–P(3)	2.54(1)		Ge(1)–As(3)	2.67(1)	
Ge(1)–P(4)	3.20(4)		Ge(1)–As(4)	3.42(3)	
P(3)–Ge(1)–P(2)	99°1′ ± 1.0°		As(3)–Ge(1)–As(2)	100°40′ ± 1°	
P(3)–Ge(1)–P(4)	80°50′ ± 1.0°		As(3)–Ge(1)–As(4)	79°20′ ± 1.0°	
P(5)–Ge(1)–P(3)	88°40′ ± 1.0°		As(5)–Ge(1)–As(3)	88°40′ ± 1.0°	

[a] Atcm Numbers Correspond to the Numbers in Fig. 1.

TABLE V

OBSERVED AND CALCULATED INTENSITIES FOR GeP AND GeAs

GeP					GeAs				
h	*k*	*l*	I/I_0 obs.	*I* calc.	*h*	*k*	*l*	I/I_0 obs.	*I* calc.
1	0	1	80	71.6	1	0	1	27.7	25.6
0	0	2	75	65.7	0	0	2	59.6	53.9
1	1	0	100	112.6	1	1	0	100.0	102.7
1	1	2	68	68.4	1	1	2	52.9	56.7
2	0	0	37	34.0	2	0	0	37.3	31.5
1	0	3	24	25.3	1	0	3	25.0	25.8
2	1	1	18	14.3	2	0	2	25.4	24.2
2	0	2	34	29.5	2	2	0	6.7	7.7
0	0	4	1	3.0					
2	2	0	10	8.7					
1	1	4	6	7.1					
2	1	3	13	14.5					
3	0	1	3	2.3					

varied—one scale factor, the single position parameter, and a single overall temperature factor. The quantity $R = \Sigma|I\,\text{obs} - I\,\text{calc.}/\Sigma I\,\text{obs}$ was reduced to 10.6% for GeP and 7.5% for GeAs. The data are shown in Table V. Refined parameters and bond distances and angles are shown in Table IV. The numbers of the atoms correspond to the numbers on the structure in Fig. 1.

Discussion

It is evident that a large number of phases may be prepared in these systems at high pressure. Osugi *et al.* (*7*) found evidence for eight different phases in the Ge–P system. In this study fewer phases were found; however, the range of pressure and temperature conditions was far from exhaustive.

The transformations of GeP and GeAs to new high-pressure forms have been shown. Each transformation is accompanied by an increase in density and by an increase of coordination number. The densities of low pressure GeP and GeAs are 4.16 g/cm^3 and 5.33 g/cm^3, respectively, while the calculated values for the high-pressure forms are 4.90 g/cm^3 and 6.10 g/cm^3. The coordination of the

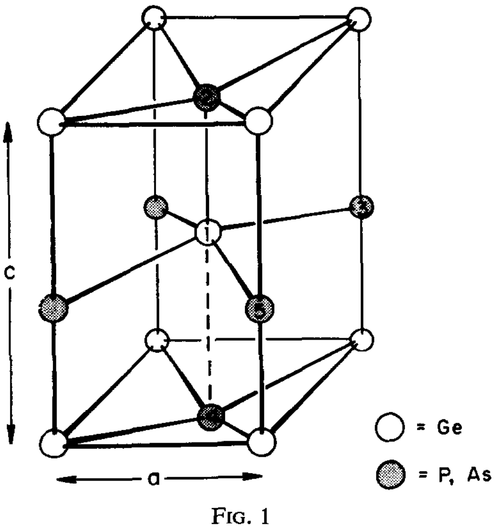

FIG. 1

atoms increased from tetrahedral for Ge and trigonal pyramidal for As and P to distorted octahedral for all.

The tetragonal crystal structure may be described as a distorted NaCl type, since if the single position parameter were 0.5 and if the diagonal in the *a*, *a* plane equaled the *c* axis, it would be NaCl type. The coordination of the atoms is equivalent and distorted octahedral. If one considers that the high-pressure forms of InP and InAs are NaCl type, (*14*) the presence of the extra electron partially localized in the short IVA–VA bond may explain the distortion.

The metallic resistivity of these materials is consistent with the high coordination of the elements since many other post-transition metal compounds exhibit metallic resistivity in their high-pressure forms. Because the crystallographic positions of the atoms are equivalent, the valence of Ge is the unusual +3 if P is considered the normal −3 valence. The presence of the extra Ge electron may account for the electrical properties.

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References

1. M. ZUMBUSCH, M. HEIMBRECHT, AND W. BILTZ, *Z. Anorg. Allgem. Chem.* **242**, 231 (1939).
2. H. STOHR AND W. KLEM, *Z. Anorg. Allgem. Chem.* **244**, 205 (1940).
3. T. WADSTEN, *Acta Chem. Scand.* **19**, 1232 (1965).
4. T. WADSTEN, *Acta Chem. Scand.* **21**, 593 (1967).
5. F. HULLIGER AND E. MOOSER, *J. Chem. Phys. Solids* **24**, 283 (1963).
6. J. OSUGI, R. NAMIKAWA, AND Y. TANAKA, *J. Chem. Soc. Japan Pure Chem. Sect.* **87**, 1169 (1966).
7. J. OSUGI, R. NAMIKAWA, AND Y. TANAKA, *Rev. Phys. Chem. Japan* **37**, 2, 81 (1967).
8. E. C. LLOYD, U. O. HUTTON, AND D. P. JOHNSON, *J. Res. Natl. Bur. Std.* **C63**, 59 (1959).
9. J. OSUGI, K. SHIMIZU, AND Y. TANAKA, *Proc. Japan Acad.* **42**, 48 (1966).
10. T. A. BITHER, C. T. PREWITT, J. L. GILLSON, P. E. BIERSTEDT, R. B. FLIPPEN, AND H. S. YOUNG, *Inorg. Chem.* **5**, 1296 (1966).
11. T. A. BITHER, J. L. GILLSON, AND H. S. YOUNG, *Inorg. Chem.* **5**, 1559 (1966).
12. J. C. JAMIESON, *Science* **139**, 1291 (1963).
13. ASTM—X-Ray Powder Diffraction File Card, 5-0632.
14. J. C. JAMIESON, *Science* **139**, 845 (1963).