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The Crystal Structure of Pt_2Ge_3

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A redetermination of the crystal structure of Pt_2Ge_3 has been made using single crystal X-ray techniques. Since the result differs considerably from that obtained earlier by Bhan and Schubert, a complete structure determination is presented.

The unit cell dimensions for the orthorhombic crystals are: $a=16.441$ Å, $b=3.377$ Å, and $c=6.202$ Å. The space group is *Pnma* and the atoms are situated in five sets of the fourfold position 4(*c*). The positional parameters of the atoms are: Pt_I: $x=0.4945$, $z=0.3055$, Pt_{II}: $x=0.1697$, $z=0.2916$, Ge_I: $x=0.4299$, $z=0.9440$, Ge_{II}: $x=0.2303$, $z=0.6615$, and Ge_{III}: $x=0.1138$, $z=0.9143$.

The studies of the platinum metal silicides which are in progress at this institute have also led to some investigations of platinum metal germanides. In a previous investigation of the Pt—Ge system by Bhan and Schubert [1] a crystal structure proposal for Pt_2Ge_3 was presented, but according to these authors the atomic arrangement obtained is not quite satisfactory. Calculations of interatomic distances in Pt_2Ge_3, performed by the present authors, also showed, that some of the distances were much too short. Comparisons between the structures of non-metal-rich silicides and germanides, however, called for a more accurate structure determination and therefore a new structure determination was made. As there is a considerable deviation of the new structure from the first proposal the new results are presented in this paper.

EXPERIMENTAL

Preparations. Alloys of varying compositions in the range of 50 to 80 at-% Ge were prepared from platinum metal powder (Johnson, Matthey and Co Ltd., claimed purity 99.9 %) and germanium (Koch-Light Laboratories Ltd., claimed purity 99.999 %) in an argon arc-furnace. The alloys were annealed in evacuated and sealed silica capsules for about ten days at temperatures of either 860°C or 730°C (depending on the melting point), and then quenched. The variation of the temperature was less than ±0.5°C.

In order to obtain optimal conditions for homogenisation and crystal growth, the liquidus curve was determined in the range of 50 to 80 at.-% Ge. This was carried out by sealing the alloys in evacuated capsules of transparent silica, and placing them in a resistance furnace. The temperature was increased in steps of approximately 10°C until

the first signs of melting were observed. The temperature was held constant for at least 2 h. Temperature was determined potentiometrically with a Pt—Pt10%Rh thermocouple.

The nominal compositions (corrected for the loss of germanium during the melting process), observed melting points, annealing temperatures, and the results of the phase analytical investigations are shown in Table 3.

Powder diffraction investigations. Powder photographs were recorded in a Guinier-Hägg focussing camera using Cu$K\alpha_1$ radiation and silicon as an internal calibration standard ($a=5.43054$ Å).

Single crystal examination. A single crystal fragment, selected from an alloy of the composition $Pt_{40}Ge_{60}$, annealed at 730°C, was used in the examination. The crystal fragment measured about 0.04×0.07 mm in cross section perpendicular to the b axis. The diffraction patterns were recorded in an equi-inclination Weissenberg camera using Zr-filtered MoK radiation. The multiple film technique was employed with thin iron foils interleaved with the films. The crystal was rotated about the b and c axes and the following layers were recorded: $h0l$, $h1l$, $h2l$, $hk0$, $hk1$, and $hk2$. The intensities were estimated by visual comparison with a calibrated intensity scale. No absorption correction was made.

Table 1. All the calculations have been carried out on a CDC 3600 electronic computer using the following programs (all programs are written in Fortran IV).

Program	*Authors*
Least-squares refinement of unit cell dimensions	J. Tegenfeldt, Uppsala, Sweden.
Lorentz-polarization corrections	A. Zalkin, Berkeley, U.S.A., modified by R. Liminga and J.-O. Lundgren, Uppsala, Sweden.
Fourier summations and structure factor calculations	A. Zalkin, Berkeley, U.S.A., modified by R. Liminga and J.-O. Lundgren, Uppsala, Sweden.
Least-squares refinement of positional parameters and temperature factors	P. K. Gantzel, R. A. Sparks and K. N. Trueblood, Los Angeles, U.S.A., modified by A. Zalkin, Berkeley, U.S.A. and by C.-I. Brändén, R. Liminga and J.-O. Lundgren, Uppsala, Sweden.
Interatomic distances	A. Zalkin, Berkeley, U.S.A.

Table 2. Weight analysis from the last cycle of refinement. $\Delta=||F_o|-|F_c||$.

Interval F_o	$\overline{w\cdot\Delta^2}$ (normalized)	Number of reflexions	Interval $\sin\theta$	$\overline{w\cdot\Delta^2}$ (normalized)	Number of reflexions
0.0— 55.0	0.43	15	0.00—0.46	1.49	80
55.0— 60.3	0.43	16	0.46—0.58	1.24	37
60.3— 69.8	0.83	18	0.58—0.67	1.77	24
69.8— 78.6	1.02	18	0.67—0.74	1.23	15
78.6— 90.1	1.12	19	0.74—0.79	1.39	10
90.1—104.7	1.23	19	0.79—0.84	1.71	4
104.7—124.1	1.27	18	0.84—0.89	0.77	5
124.1—142.2	0.92	19	0.89—0.93	0.40	4
142.2—184.0	2.16	18	0.93—0.97	0.00	0
184.0—309.7	0.59	19	0.97—1.00	0.00	0

Table 3. Cell parameters with standard deviations for binary alloys of the system Pt—Ge in the range of 50 to 100 at.-% Ge (in Ångström units).

Composition, annealing conditions, melting point,	PtGe cell dim.	PtGe st. dev. $\times 10^4$	Pt_2Ge_3 cell dim.	Pt_2Ge_3 st. dev. $\times 10^4$	$PtGe_2$ cell dim.	$PtGe_2$ st. dev. $\times 10^4$	(Ge) cell dim.	(Ge) st. dev. $\times 10^4$
$Pt_{49.9}Ge_{50.1}$ 9 d. 860°C M.p. 1095°C	$a = 5.7227$ $b = 3.6898$ $c = 6.0867$	5 3 5						
$Pt_{45.0}Ge_{55.0}$ 9 d. 860°C M.p. 1035°C	$a = 5.7101$ $b = 3.6828$ $c = 6.0874$	29 19 17	$a = 16.4469$ $b = 3.3772$ $c = 6.2024$	10 3 6				
$Pt_{39.5}Ge_{60.5}$ 9 d. 860°C M.p. 910°C			$a = 16.4411$ $b = 3.3771$ $c = 6.2017$	21 3 7	[a]			
$Pt_{36.4}Ge_{63.6}$ 9 d. 860°C M.p. 890°C			$a = 16.4402$ $b = 3.3748$ $c = 6.2011$	11 2 4	$a = 6.2032$ $b = 5.7790$ $c = 2.9149$	20 13 9		
$Pt_{33.5}Ge_{66.5}$ 10 d. 730°C M.p. 855°C			[a]		$a = 6.1997$ $b = 5.7822$ $c = 2.9145$	6 6 4		
$Pt_{19.7}Ge_{80.3}$ — M.p. 810°C					$a = 6.2034$ $b = 5.7818$ $c = 2.9122$	11 6 5	$a = 5.6583$	1

[a] Traces of the compound were found in the powder diffraction pattern of the sample. The very few lines observed did not allow an accurate determination of the unit cell dimensions.

Calculations. The unit cell dimensions of Pt_2Ge_3 were refined with a least-squares program. In the structure factor calculations the atomic scattering factors for platinum and germanium were obtained from *International Tables* [2] together with the real and imaginary dispersion corrections. The structure was refined by the method of least-squares employing a weighting scheme according to Cruickshank *et al.*[3]: $w = 1/(a + |F_o| + c|F_o|^2)$, where the weighting constants a and c were given the values 60.0 and 0.007, respectively. A weight analysis from the last cycle of the refinement is presented in Table 2. The programs used for the various calculations are listed in Table 1.

Phase analysis of the Ge-rich part of the Pt—Ge system

The unit cell dimensions of the various phases in the non-metal-rich part of the Pt—Ge system are given in Table 3. The table shows that there is no appreciable variation of the unit cell dimensions of Pt_2Ge_3 and $PtGe_2$ and it is therefore concluded that the phases cannot have more than very narrow ranges of homogeneity. The cell dimensions are also in good agreement with those in earlier publications.[1,6]

DETERMINATION OF THE CRYSTAL STRUCTURE OF Pt_2Ge_3

The earlier investigation of Pt_2Ge_3 showed that the structure was orthorhombic with all the atoms situated in the fourfold position 4(*c*) of the space group *Pnma*. The present determination of the structure confirms this symmetry.

By rotating the single-crystal of Pt_2Ge_3 about the *b* and *c* axes and recording the *h*0*l* and *hk*0 layers in a Weissenberg camera the orthorhombic symmetry was verified. Systematic extinctions of the *h*00 reflections were observed for $h=2n+1$ and of the 0*kl* reflections for $k+l=2n+1$. Apart from these observations, a comparison of the *h*0*l* and *h*2*l* layers showed very great similarities. In view of the above facts and since the *b* axis is very short the space group *Pnma* is the most suitable of the two space groups which are possible, *viz.* *Pnma* and $Pn2_1a$.

A calculation of the electron density projection, $\varrho_{obs}(xz)$, based on the coordinates of Pt_2Ge_3 which had been obtained earlier, showed considerable discrepancies. Attempts to refine the atomic positions starting from the arrangement proposed earlier were unsuccessful. A difference projection, $\varrho_{obs}(xz)-\varrho_{calc}(xz)$, was then calculated based on the coordinates of the metal atoms only. The peaks which appeared in the map proved to be the correct positions of the germanium atoms, and these were considerably at variance with those reported previously. A final difference synthesis based on the new atomic positions showed a good agreement between observed and calculated data.

The structure was refined using a full matrix least-squares program. During refinement 16 parameters were varied *viz.* ten position parameters, five individual temperature factors and one scale factor. Before the last cycles of the refinement the ten strongest reflections were omitted in order to reduce extinction effects. Reflections too weak to be measured are not included in the *R* value. Final structural data are given in Table 4. The F_o and F_c values of the *h*0*l* reflections are listed in Table 5. A projection of the structure of Pt_2Ge_3 is shown in Fig. 1. The Roman numerals in the figure correspond to those used for different crystallographic positions in Tables 4 and 6.

Table 4. Final structure data for Pt_2Ge_3.

Space group: *Pnma* (D_{2h}^{16}), $Z = 4$.
$a = 16.4411$ Å, $\sigma(a) = 0.0021$ Å,
$b = 3.3771$ Å, $\sigma(b) = 0.0003$ Å,
$c = 6.2017$ Å, $\sigma(c) = 0.0007$ Å.
Cell volume 344.3 Å^3.

Atom	Position	Pos. parameters and standard deviations				Isotropic temp. fact.	
		x	$\sigma(x)$	z	$\sigma(z)$	B	$\sigma(B)$
Pt_I	4(*c*)	0.49445	0.00018	0.30549	0.00046	0.415	0.038
Pt_{II}	4(*c*)	0.16973	0.00020	0.29162	0.00040	0.383	0.036
Ge_I	4(*c*)	0.42990	0.00056	0.94399	0.00141	0.852	0.125
Ge_{II}	4(*c*)	0.23028	0.00062	0.66151	0.00137	0.724	0.118
Ge_{III}	4(*c*)	0.11383	0.00050	0.91432	0.00119	0.470	0.104

Final *R*-value = 0.100.

Table 5. Observed and calculated structure factors of Pt_2Ge_3. Reflections not included in the refinement are marked with asterisks.

h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$
2	0	0	***	114.3	31	0	2	77.5	76.2	11	0	5	64.2	58.3	10	0	8	95.7	79.6	16	0	11	147.1	125.9
4	0	0	***	125.4	32	0	2	41.6	34.3 *	12	0	5	86.2	81.5	11	0	8	35.4	20.2 *	17	0	11	41.5	69.1 *
6	0	0	210.5	302.9 **	33	0	2	41.6	19.1 *	13	0	5	137.6	125.0	12	0	8	173.3	152.4	18	0	11	41.4	3.3 *
8	0	0	98.9	119.9	34	0	2	41.3	31.3 *	14	0	5	94.6	83.5	13	0	8	131.5	113.4	19	0	11	41.2	41.1 *
10	0	0	110.1	135.0	35	0	2	40.8	23.6 *	15	0	5	276.3	269.9	14	0	8	58.6	64.0	20	0	11	40.8	1.8 *
12	0	0	269.2	362.9 **	36	0	2	64.5	53.7	16	0	5	32.0	11.6 *	15	0	8	37.6	31.6 *	21	0	11	40.4	10.1 *
14	0	0	24.5	45.2 *	37	0	2	55.1	75.4	17	0	5	32.9	34.2 *	16	0	8	95.4	87.6	22	0	11	41.4	32.4 *
16	0	0	116.2	144.5	1	0	3	165.6	153.8	18	0	5	71.4	78.2	17	0	8	38.7	66.5 *	23	0	11	39.2	20.4 *
18	0	0	250.1	331.5 **	2	0	3	159.1	162.6	19	0	5	34.8	59.8 *	18	0	8	141.7	126.5	24	0	11	38.5	9.0 *
20	0	0	58.2	79.3	3	0	3	354.0	399.4 **	20	0	5	35.5	13.2 *	19	0	8	140.8	128.3	0	0	12	71.9	82.7
22	0	0	33.4	34.7 *	4	0	3	215.9	211.8	21	0	5	41.6	184.2	20	0	8	40.3	5.1 *	1	0	12	41.6	7.5 *
24	0	0	115.2	123.1	5	0	3	27.3	23.6	22	0	5	37.3	10.0 *	21	0	8	40.8	13.5 *	2	0	12	41.5	16.5 *
26	0	0	56.4	45.3	6	0	3	113.9	106.0	23	0	5	38.1	7.4 *	22	0	8	41.1	27.4 *	3	0	12	41.5	11.6 *
28	0	0	39.4	63.0 *	7	0	3	148.1	140.9	24	0	5	39.0	11.2 *	23	0	8	41.4	11.2 *	4	0	12	41.6	10.6 *
30	0	0	122.5	120.5	8	0	3	58.8	60.0	25	0	5	39.7	38.7 *	24	0	8	72.0	67.2	5	0	12	41.6	3.7 *
32	0	0	58.8	64.0	9	0	3	225.5	214.0	26	0	5	40.3	6.1 *	25	0	8	41.6	54.3 *	6	0	12	124.9	124.6
34	0	0	56.9	44.9	10	0	3	48.0	47.8	27	0	5	39.1	96.2 *	26	0	8	41.5	27.4 *	7	0	12	41.6	7.0 *
36	0	0	40.6	63.6 *	11	0	3	128.7	123.7	28	0	5	41.3	17.5 *	27	0	8	41.3	15.5 *	8	0	12	41.6	45.1 *
38	0	0	38.2	54.5 *	12	0	3	73.6	77.1	29	0	5	41.6	14.8 *	28	0	8	41.0	45.4 *	9	0	12	41.6	32.9 *
40	0	0	37.9	12.1 *	13	0	3	67.1	63.3	30	0	5	41.6	16.8 *	29	0	8	40.4	3.1 *	10	0	12	41.6	1.6 *
42	0	0	46.1	39.3	14	0	3	26.8	20.2 *	0	0	6	59.4	49.5	30	0	8	39.6	57.0 *	11	0	12	41.5	37.9 *
1	0	1	***	31.3	15	0	3	300.7	291.2	1	0	6	188.0	174.6	31	0	8	88.7	70.1	12	0	12	129.5	113.8
2	0	1	***	162.1	16	0	3	231.6	222.0	2	0	6	26.7	8.0 *	1	0	9	35.4	4.7 *	13	0	12	41.3	32.5 *
3	0	1	***	109.4	17	0	3	29.7	5.2 *	3	0	6	26.9	35.5 *	2	0	9	35.5	26.1 *	14	0	12	41.1	3.7 *
4	0	1	188.6	207.1	18	0	3	30.8	26.0 *	4	0	6	198.7	182.3	3	0	9	83.5	73.2	15	0	12	40.9	23.1 *
5	0	1	14.7	8.1 *	19	0	3	91.3	96.2	5	0	6	68.5	58.6	4	0	9	121.3	99.6	16	0	12	40.6	15.5 *
6	0	1	15.9	15.4 *	20	0	3	32.8	33.3 *	6	0	6	104.8	82.8	5	0	9	56.9	48.4	17	0	12	40.3	16.2 *
7	0	1	168.5	201.9	21	0	3	112.3	117.3	7	0	6	182.7	173.8	6	0	9	36.2	25.0 *	18	0	12	63.0	56.4
8	0	1	154.9	186.6	22	0	3	110.3	113.5	8	0	6	99.3	75.6	7	0	9	79.5	77.8	19	0	12	39.3	28.3 *
9	0	1	181.7	211.7	23	0	3	35.9	3.4 *	9	0	6	29.2	11.5 *	8	0	9	48.7	38.9	20	0	12	38.7	16.4 *
10	0	1	288.7	380.2 **	24	0	3	36.9	17.5 *	10	0	6	29.8	27.5 *	9	0	9	87.1	82.7	21	0	12	38.0	28.4 *
11	0	1	45.6	56.4	25	0	3	37.8	51.9 *	11	0	6	113.3	98.1	10	0	9	132.6	121.2	22	0	12	37.1	15.8 *
12	0	1	22.6	20.0 *	26	0	3	38.7	7.5 *	12	0	6	96.9	83.2	11	0	9	37.9	69.6 *	23	0	12	36.3	40.4 *
13	0	1	85.3	98.0	27	0	3	90.6	105.1	13	0	6	177.3	158.5	12	0	9	74.2	55.6	24	0	12	80.7	71.2
14	0	1	24.7	8.3 *	28	0	3	63.7	67.9	14	0	6	81.1	77.9	13	0	9	38.7	25.3 *	1	0	13	41.3	45.0 *
15	0	1	56.8	58.6	29	0	3	40.9	3.8 *	15	0	6	33.2	33.0 *	14	0	9	39.2	25.1 *	2	0	13	40.4	79.1
16	0	1	131.8	153.6	30	0	3	41.3	1.4 *	16	0	6	34.0	7.8 *	15	0	9	76.7	60.6	3	0	13	71.4	84.8
17	0	1	28.0	15.6 *	31	0	3	41.6	25.3 *	17	0	6	34.8	5.9 *	16	0	9	144.2	89.8	4	0	13	41.2	46.6 *
18	0	1	29.1	56.2 *	32	0	3	41.6	41.8 *	18	0	6	35.6	30.0 *	17	0	9	40.4	17.4 *	5	0	13	68.2	75.0
19	0	1	69.2	89.5	33	0	3	41.5	71.5 *	19	0	6	190.8	187.9	18	0	9	40.8	31.5 *	6	0	13	41.0	5.9 *
20	0	1	31.1	3.2 *	34	0	3	79.6	99.6	20	0	6	37.2	33.2 *	19	0	9	41.1	29.8 *	7	0	13	40.9	43.3 *
21	0	1	32.4	57.8 *	35	0	3	40.4	42.4 *	21	0	6	37.9	16.0 *	20	0	9	41.3	44.5 *	8	0	13	40.8	26.5 *
22	0	1	189.7	212.1	36	0	3	39.5	11.9 *	22	0	6	106.0	99.7	21	0	9	41.5	39.7 *	9	0	13	78.7	71.8
23	0	1	34.6	6.3 *	37	0	3	38.4	27.9 *	23	0	6	39.4	0.9 *	22	0	9	124.9	101.3	10	0	13	70.0	56.2
24	0	1	35.7	16.1 *	0	0	4	82.2	65.2	24	0	6	40.1	14.2 *	23	0	9	41.6	60.1 *	11	0	13	40.2	33.8 *
25	0	1	36.7	37.5 *	1	0	4	40.2	33.4	25	0	6	121.8	121.7	24	0	9	41.5	15.4 *	12	0	13	39.7	1.5 *
26	0	1	37.7	27.9 *	2	0	4	40.5	27.5	26	0	6	41.1	15.7 *	25	0	9	41.2	1.0 *	13	0	13	59.3	70.1
27	0	1	38.7	42.7 *	3	0	4	71.0	58.1	27	0	6	41.4	8.6 *	26	0	9	40.9	23.7 *	14	0	13	58.2	34.0 *
28	0	1	145.3	182.1	4	0	4	21.5	10.2 *	28	0	6	41.6	14.9 *	27	0	9	40.3	23.2 *	15	0	13	51.2	54.5
29	0	1	40.3	26.6 *	5	0	4	196.4	180.7	29	0	6	41.6	18.5 *	28	0	9	110.4	106.3	16	0	13	38.1	66.7 *
30	0	1	40.9	15.9 *	6	0	4	181.1	166.6	30	0	6	41.5	41.0 *	29	0	9	38.7	30.9 *	17	0	13	37.5	29.5 *
31	0	1	41.5	22.0 *	7	0	4	282.2	283.2 **	31	0	6	126.7	128.6	30	0	9	37.7	35.7 *	18	0	13	36.9	30.4 *
32	0	1	41.6	31.1 *	8	0	4	103.9	88.6	1	0	7	29.5	28.5 *	34	0	9	61.5	68.5	19	0	13	36.1	26.3 *
33	0	1	41.6	37.7 *	9	0	4	59.7	42.1	2	0	7	81.1	65.2	0	0	10	147.6	153.0	20	0	13	35.2	34.5 *
34	0	1	94.9	101.7	10	0	4	25.1	12.2 *	3	0	7	220.1	187.2	1	0	10	38.1	39.3 *	21	0	13	34.3	60.6 *
35	0	1	41.0	12.9 *	11	0	4	25.6	30.6 *	4	0	7	30.0	5.5 *	2	0	10	60.4	53.7	22	0	13	57.5	52.7
36	0	1	40.3	33.3 *	12	0	4	134.7	127.5	5	0	7	30.2	11.8 *	3	0	10	57.4	53.0	0	0	14	39.3	48.5 *
37	0	1	39.3	27.4 *	13	0	4	215.4	221.8	6	0	7	53.0	51.5	4	0	10	57.6	53.1	1	0	14	39.3	34.3 *
38	0	1	38.0	35.5 *	14	0	4	28.4	5.0 *	7	0	7	53.1	56.3	5	0	10	38.5	28.0 *	2	0	14	39.2	33.3 *
39	0	1	36.5	4.6 *	15	0	4	58.6	51.6	8	0	7	31.3	0.4 *	6	0	10	203.1	196.5	3	0	14	39.1	10.2 *
40	0	1	86.9	101.8	16	0	4	30.2	11.0 *	9	0	7	310.1	285.0	7	0	10	38.9	47.4 *	4	0	14	38.9	37.4 *
0	0	2	301.7	348.3 **	17	0	4	31.1	5.9 *	10	0	7	113.1	95.8	8	0	10	62.0	58.4	5	0	14	38.9	12.6 *
1	0	2	124.3	117.7	18	0	4	32.1	41.0 *	11	0	7	32.9	36.6 *	9	0	10	39.5	8.1 *	6	0	14	38.7	36.4 *
2	0	2	29.4	22.7	19	0	4	90.6	101.0 *	12	0	7	33.5	6.2 *	10	0	10	84.2	77.8	7	0	14	38.5	67.5 *
3	0	2	231.6	230.2	20	0	4	34.1	15.6 *	13	0	7	33.1	8.9 *	11	0	10	40.0	61.3 *	8	0	14	38.3	37.3 *
4	0	2	184.2	192.6	21	0	4	35.0	33.0 *	14	0	7	60.2	60.2	12	0	10	142.4	124.5	9	0	14	37.9	7.5 *
5	0	2	139.4	125.1	22	0	4	36.0	6.0 *	15	0	7	127.6	113.6	13	0	10	40.6	29.2 *	10	0	14	37.5	20.5 *
6	0	2	336.9	425.8 **	23	0	4	37.0	38.9 *	16	0	7	56.9	56.9	14	0	10	40.8	18.1 *	11	0	14	37.1	26.5 *
7	0	2	121.0	120.8	24	0	4	37.9	72.9 *	17	0	7	36.8	14.3 *	15	0	10	41.0	5.6 *	12	0	14	36.6	34.6 *
8	0	2	90.2	84.5	25	0	4	171.0	221.7	18	0	7	37.5	30.8 *	16	0	10	41.3	48.5 *	13	0	14	36.1	40.9 *
9	0	2	34.0	32.0	26	0	4	39.5	58.3 *	19	0	7	37.1	45.6 *	17	0	10	41.5	45.0 *	14	0	14	35.6	1.4 *
10	0	2	68.0	72.4	27	0	4	40.2	17.1 *	20	0	7	38.8	7.2 *	18	0	10	137.9	123.6	15	0	14	34.8	36.3 *
11	0	2	22.5	7.7 *	28	0	4	40.8	19.3 *	21	0	7	149.0	132.3	19	0	10	41.6	9.1 *	16	0	14	34.2	12.0 *
12	0	2	251.9	283.0	29	0	4	41.2	28.6 *	22	0	7	84.9	80.8	20	0	10	41.6	27.2 *	17	0	14	33.3	19.0 *
13	0	2	127.3	125.5	30	0	4	41.5	41.7 *	23	0	7	37.9	38.9 *	21	0	10	65.6	50.2	18	0	14	32.4	36.0 *
14	0	2	25.5	6.1 *	31	0	4	95.4	105.0	24	0	7	71.0	60.4	22	0	10	41.3	29.2 *	19	0	14	32.2	53.6
15	0	2	26.6	23.0 *	32	0	4	41.5	12.9 *	25	0	7	41.3	41.3 *	23	0	10	41.0	11.6 *	20	0	14	30.3	38.2 *
16	0	2	27.6	25.2 *	33	0	4	41.2	35.6 *	26	0	7	41.2	47.9 *	1	0	11	90.2	98.7	1	0	15	35.4	21.2 *
17	0	2	28.7	38.3 *	34	0	4	40.6	4.4 *	27	0	7	95.4	96.1	2	0	11	63.8	70.5	2	0	15	35.3	11.7 *
18	0	2	160.8	195.5	35	0	4	39.8	31.9 *	28	0	7	41.5	57.5 *	3	0	11	40.4	23.6 *	3	0	15	35.2	78.6
19	0	2	133.4	153.0	36	0	4	39.8	17.2 *	29	0	7	41.5	56.2 *	4	0	11	114.5	105.3	4	0	15	34.9	76.5
20	0	2	31.9	1.7 *	37	0	4	79.5	91.5	30	0	7	40.9	17.1 *	5	0	11	40.6	32.7 *	5	0	15	34.8	32.4 *
21	0	2	75.6	85.6	1	0	5	73.0	58.2	0	0	8	248.9	245.1	6	0	11	40.7	4.9 *	6	0	15	34.6	15.2 *
22	0	2	93.3	113.5	2	0	5	89.1	75.6	1	0	8	164.1	155.3	7	0	11	41.2	54.0	7	0	15	34.3	31.6 *
23	0	2	35.1	42.9 *	3	0	5	379.7	395.7 **	2	0	8	99.1	99.4	8	0	11	41.0	26.6 *	8	0	15	33.9	47.3 *
24	0	2	111.5	135.5	4	0	5	50.1	14.4	3	0	8	32.7	15.4 *	9	0	11	41.1	38.4 *	9	0	15	33.6	81.4
25	0	2	78.9	86.6	5	0	5	122.0	104.2	4	0	8	32.4	7.4 *	10	0	11	61.8	57.3	10	0	15	33.4	33.5 *
26	0	2	38.1	39.5 *	6	0	5	120.2	101.9	5	0	8	66.2	75.3	11	0	11	71.6	64.4	11	0	15	32.4	6.9 *
27	0	2	39.0	5.6 *	7	0	5	97.3	89.8	6	0	8	134.6	129.2	12	0	11	41.5	9.2 *	12	0	15	31.7	17.4 *
28	0	2	39.0	9.0 *	8	0	5	26.1	9.7 *	7	0	8	53.3	49.4	13	0	11	41.5	34.6 *	13	0	15	31.4	33.5 *
29	0	2	60.8	70.3	9	0	5	256.7	231.2 **	8	0	8	59.1	57.7	14	0	11	41.6	37.0 *	14	0	15	30.3	31.3 *
30	0	2	71.1	94.5	10	0	5	54.7	49.6	9	0	8	34.5	22.6 *	15	0	11	41.6	30.2 *	15	0	15	57.0	52.9

* denotes reflections too weak to be measured. The F_o-values for these are given as $1/\sqrt{2}\cdot F_{min}$ for the reflection in question.

** denotes the strongest reflections, which have been omitted in order to reduce extinction.

*** denotes reflections not observable on account of camera geometry.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE OF Pt_2Ge_3

The crystal structure of Pt_2Ge_3 can be described in terms of the structure elements present in the *B*31 and *C*35 structure types. As there are representatives of both structure types in the Pt—Ge system, *viz.* PtGe and $PtGe_2$, the latter are illustrated in Figs. 2*a* and 2*b*. The characteristic structure element of PtGe is the strongly deformed octahedral arrangement of Ge atoms

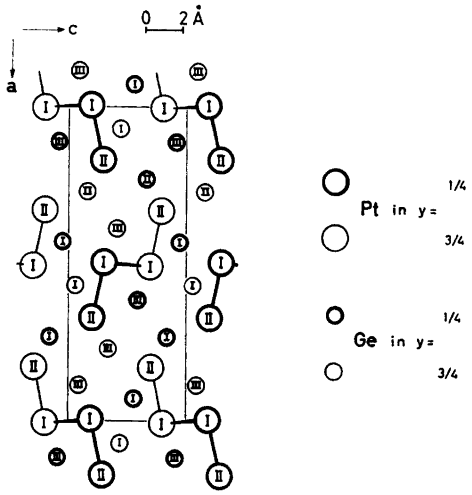

Fig. 1. The crystal structure of Pt_2Ge_3 viewed along the *b* axis.

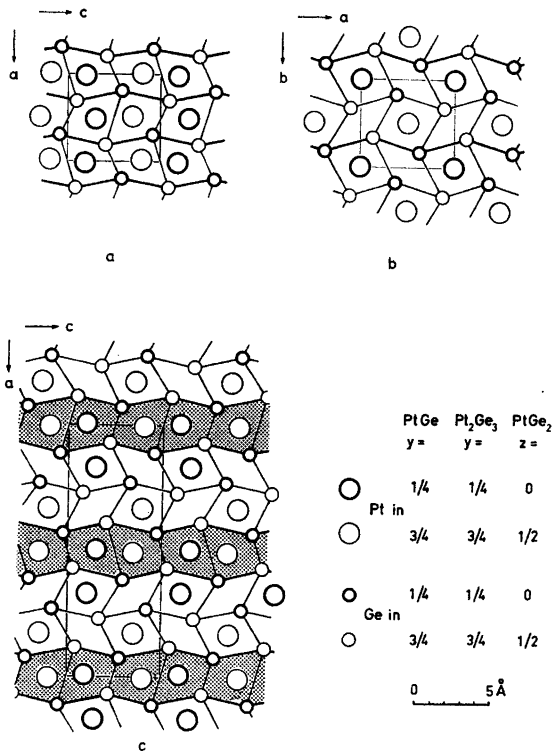

Fig. 2. Schematic representations of the structures of (a) PtGe, (b) $PtGe_2$, and (c) Pt_2Ge_3 viewed along the short axes. The faint lines indicate the unit cells, whereas the heavy lines connect Ge atoms which form deformed octahedra.

about the metal atoms, whereas the two characteristic structure elements of $PtGe_2$ are an octahedral coordination polyhedron of Ge atoms about the metal atom and a strongly deformed octahedron of Ge atoms without any atom inside. In the structure of Pt_2Ge_3 there are regions where the atomic arrangement is almost identical with that in the PtGe ($B31$) structure. In Fig. 2*c* a schematic representation of Pt_2Ge_3 is given and the shaded areas show the same atomic arrangement as the areas between two successive zigzag lines in direction of the *c* axis in Fig. 2*a*. The heavy zigzag lines in the diagram of $PtGe_2$ (Fig. 2*b*) enclose a region where the atomic arrangement is the same as that between the shaded areas in Fig. 2*c*. Thus the structure of Pt_2Ge_3 can be regarded as composed of layers related to PtGe and $PtGe_2$ alternating in the direction of the *a* axis.

The close relationship between the three platinum germanides, PtGe, Pt_2Ge_3, and $PtGe_2$, gives reason for comparing the axial ratios of the three structures. The *b* and *c* axes of PtGe correspond to the *b* and *c* axes of Pt_2Ge_3, whereas there are two possibilities in the comparison of $PtGe_2$ with PtGe and Pt_2Ge_3. The *c* axis of $PtGe_2$ corresponds to the *b* axis of the two other structures but both the *a* and *b* axes are comparable with the *c* axis of PtGe and Pt_2Ge_3. A plot of the axial ratios of the three germanides against atomic percent germanium gives a linear relation (see Fig. 3) if the *b*/*c* ratio is chosen for $PtGe_2$. The *a*/*c* ratio of $PtGe_2$ does not lie on a straight line as can be seen from the figure.

The shortest Pt—Pt distance in Pt_2Ge_3 is about 7 % longer than the Pt—Pt distance in platinum. The shortest Ge—Ge distance is 2.475 Å, which is only slightly more than twice the germanium "single bond" radius. The formation of pairs of non-metal atoms with a short interatomic distance is characteristic for some transition metal compound, MeX_2, with elements of the 4th and 5th groups. It can be noted that the shortest Ge—Ge distance in $OsGe_2$ [4] is about 2.38 Å and thus appreciably less than the "single bond" distance in germanium. The shortest Pt—Ge distance in Pt_2Ge_3 is 2.480 Å and the average Pt—Ge distances for the six Ge atoms surrounding each of the platinum atoms are 2.567 and 2.511 Å for Pt_I and Pt_{II}, respectively. (In the earlier version of the structure the shortest Pt—Ge distance was 2.06 Å and the average Pt—Ge distance for Pt_I was 2.304 Å). The sum of the Goldschmidt metal radius for twelve-coordination for platinum and the tetra-

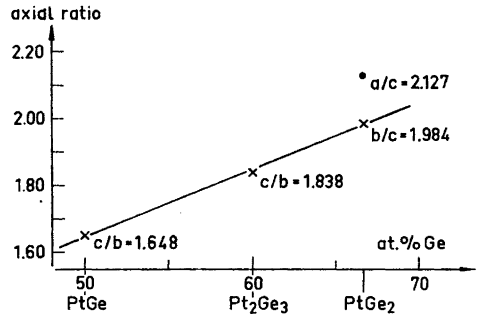

Fig. 3. Axial ratios of platinum germanides.

Table 6. Interatomic distances and standard deviations for Pt_2Ge_3 (in Ångström units).

Atoms	Dist.	St.dev.	Atoms	Dist.	St.dev.
Pt_I — Pt_{II}	2.944	0.004	Ge_I —2 Ge_{III}	3.446	0.010
—2 Pt_I	2.950	0.005	— Ge_{II}	3.720	0.013
—2 Pt_I	3.377	0.000	— Ge_{III}	3.753	0.012
			—2 Ge_{III}	3.763	0.010
Pt_I — Ge_I	2.480	0.009			
—2 Ge_{III}	2.545	0.006	Ge_{II} —2 Pt_{II}	2.491	0.008
—2 Ge_I	2.606	0.007	— Pt_{II}	2.501	0.009
— Ge_{III}	2.622	0.008	— Pt_{II}	4.032	0.009
— Ge_I	4.099	0.009			
			Ge_{II} — Ge_{III}	2.475	0.012
Pt_{II} — Pt_I	2.944	0.004	—2 Ge_{II}	3.377	0.000
—2 Pt_{II}	3.377	0.000	—2 Ge_I	3.407	0.012
			—2 Ge_{III}	3.431	0.011
Pt_{II} —2 Ge_{II}	2.491	0.008	—4 Ge_{II}	3.590	0.004
— Ge_{II}	2.501	0.009	— Ge_I	3.720	0.013
— Ge_{III}	2.514	0.008			
—2 Ge_I	2.535	0.007	Ge_{III} — Pt_{II}	2.514	0.008
— Ge_{III}	3.970	0.008	—2 Pt_I	2.545	0.006
—2 Ge_{III}	4.012	0.008	— Pt_I	2.622	0.008
— Ge_{II}	4.032	0.009	— Pt_{II}	3.970	0.008
			—2 Pt_{II}	4.012	0.008
Ge_I — Pt_I	2.480	0.009			
—2 Pt_{II}	2.535	0.007			
—2 Pt_I	2.606	0.007	Ge_{III} — Ge_{II}	2.475	0.012
— Pt_I	4.099	0.009	—2 Ge_{III}	3.377	0.000
			—2 Ge_{II}	3.431	0.011
Ge_I —2 Ge_I	2.941	0.015	—2 Ge_I	3.446	0.010
—2 Ge_I	3.377	0.000	— Ge_I	3.753	0.012
—2 Ge_{II}	3.407	0.012	—2 Ge_I	3.763	0.010

hedral covalent radius for germanium is 2.60 Å. Table 6 gives a list of interatomic distances in Pt_2Ge_3.

It is interesting to compare the Pt_2Ge_3 structure with the structures of the two rhodium silicides Rh_4Si_5 and Rh_3Si_4 as described in Ref. 5. In all three structures it is possible to discern regions having a *B*31 type of atomic arrangement. Between these regions more "non-metal-rich" regions are inserted. While the "non-metal-rich" parts of the Pt_2Ge_3 structure have a *C*35 type of atomic arrangement, the corresponding parts of the Rh_4Si_5 and Rh_3Si_4 structures are quite different. In spite of the close similarities, the Pt_2Ge_3 structure can therefore hardly be classified as a member of the same structure family as the rhodium silicides.

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REFERENCES

1. Bhan, S. and Schubert, K. *Z. Metallk.* **51** (1960) 327.
2. *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III.
3. Cruickshank, D. W., Philling, D. E., Bujosa, A., Lovell, F. M. and Truter, M. R. *Computing Methods and the Phase Problem*, Pergamon, Oxford 1961, p. 32.
4. Weitz, G., Born, L. and Hellner, E. *Z. Metallk.* **51** (1960) 238.
5. Engström, I. *Acta Chem. Scand.* **22** (1968) 3127.
6. Pfisterer, H. and Schubert, K. *Z. Metallk.* **41** (1950) 358.

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