Acta Cryst. (1959). **12**, 559

The crystal structure of YSi and $Hf_5Ge_3(C)$.

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(*Received* 29 *December* 1958 *and in revised form* 27 *January* 1959)

Introduction

In the course of an intensive study of the silicides and germanides structures it was found interesting to study the silicides and germanides with transition metals of the third and fourth group. In order to increase the amount of useful datas for a future survey of the existence criteria of silicides and germanides the phases YSi and $Hf_5Ge_3(C)$ have been investigated.

Preparation of samples

The yttrium silicide has been prepared by arc melting of the components. The composition of the melt has been checked by chemical analysis. $Hf_5Ge_3(C)$ was prepared by hot pressing a mixture of hafnium–hydride, germanium and 3 at.% carbon. The details of this specimen preparation are given in a previous publication (Parthé & Norton, 1958).

YSi

The Debye–Scherrer powder photograph could be indexed by use of Hesse's method for an orthorhombic unit cell with the lattice parameters

$$a = 4{\cdot}25_1, \quad b = 10{\cdot}52_6, \quad c = 3{\cdot}82_6 \text{ Å}.$$

The unit cell has space for 4 formula units YSi. The theoretical density can be calculated to 4·53 g.cm.$^{-3}$, while the experimental value amounts to 4·33 g.cm.$^{-3}$.

Table 1. *Intensity calculation for* YSi *with* CrB *structure*

Cr $K\alpha$-radiation

hkl	*d*	1000.sin² θ_c	1000.sin² θ_o	I_c	I_o	Remarks
010	—	11·84	—	0	—	—
020	5·248	47·4	—	0·06	—	—
100	—	72·6	—	0	—	—
110	3·940	84·4	83·5	9·80	*m*	—
001	—	89·6	—	0	—	—
021	3·096	136·9	136·7	27·20	*st*	—
111	2·739	174·1	174·6	57·60	*vvst*	—
130	2·704	179·1	178·6	37·00	*vst*	—
040	2·630	189·5	189·4	10·90	*m*	—
131	2·210	268·7	269·9	15·60	*mst*	—
041	2·166	279·0	280·8	10·90	*m*	—
200	2·125	290·4	291·0	13·20	*m*	—
220	1·971	337·7	—	0·01	—	—
002	1·911	358·4	358·8	9·36	*m*	—
150	1·885	368·6	—	0·007	—	—
022	1·798	405·7	—	0·005	—	—
060	1·754	426·2	427·0	1·10	*m*	—
221	1·752	427·3		9·12		
112	1·721	442·8	442·5	1·46	*vvw*	—
151	1·691	458·2	459·9	7·23	*m*	—
240	1·654	479·8	480·8	5·13	*m*	—
061	1·594	515·8	515·7	6·24	*m*	—
132	1·561	537·5	538·4	15·95	*mst*	—
042	1·546	547·8	548·8	5·04	*m*	—
241	1·517	569·4	570·5	9·82	+*m*	—
202	1·421	648·8	651·2	14·30	*vst*	diffuse
170	1·417	652·7		13·30		
310	1·403	665·2	—	0·78	—	—
222	1·372	696·1	—	0·006	—	—
260	1·353	716·6	717·6	2·55	*vvw*	—
152	1·343	727·0	—	0·01	—	—
171	1·328	742·3	—	1·95	—	—
311	1·318	754·8	757·5	19·75	*vst*	diffuse
080	1·315	757·7		0·155		
330	1·313	759·9		13·70		
062	1·2924	784·6	785·4	3·38	*vvw*	—
261	1·2748	806·2	807·8	27·80	*vst*	—
242	1·2503	838·2	838·4	27·00	*vst*	—
081	1·2437	847·3	849·8	14·70	*vvst*	diffuse
331	1·2418	849·5		18·10		
023	1·2391	853·7		11·10		
113	1·2130	890·8	891·0	44·70	*vvst*	—
350	1·1749	949·4	—	0·022	—	—
133	α_1 1·1542	983·8	983·9	> 50·00	*vvst*	—
	α_2 1·1522	987·2	987·6		*vvst*	—

The missing reflections lead to the possible space groups D_{2h}^{17}–$Cmcm$, C_{2v}^{16}–$C2cm$ and C_{2v}^{12}–$Cmc2_1$.

For the first trial the space group with the highest symmetry D_{2h}^{17}–$Cmcm$ has been assumed. Placing the yttrium atoms at $4(c)_{\mathrm{I}}$ with $y_{\mathrm{I}} = 0{\cdot}146$ and the silicon atoms at $4(c)_{\mathrm{II}}$ with $y_{\mathrm{II}} = 0{\cdot}440$ yields intensities which check well with the observed intensities. The calculated and observed intensities for Cr $K\alpha$-radiation can be compared in Table 1.

A study of the YSi-structure shows the similarity to the CrB-structure, which had been determined by Kiessling (1949). At the same time there has been published the crystal structure of CaSi (Hellner, 1950). By choosing different axes and origin from those given in Hellner's paper the CaSi-structure becomes virtually identical with the CrB-type (Nowotny & Parthé, 1954; Laves, 1955). Thus CaSi and YSi both crystallize in the same structure type.

A comparison of the yttrium monosilicide with the silicides of the 2nd, 3rd and 4th group metals shows the competition between the FeB and CrB type, which are nearly homeotect structure types. Ca and Y choose the CrB-type, while Ce, Zr, Hf and U prefer the FeB-type. The available data on monosilicides and monoborides suggest that the FeB and CrB-structures occur only in a certain common radius ratio range. In the case of smaller radius ratios we observe the FeSi-type, while in the case of bigger radius ratios the NaCl-type has been found. The conditions for the preference of the CrB-type instead of the FeB-type and vice versa are not yet understood.

$Hf_5Ge_3(C)$

Specimens corresponding to the composition Hf_5Ge_3 with an addition of 3 at.% carbon yield an X-ray pattern which could be indexed to correspond to a hexagonal unit cell with

$$a = 7{\cdot}88_3,\quad c = 5{\cdot}53_7\ \text{Å},\quad c/a = 0{\cdot}702\,.$$

The extinctions lead to the possible space groups D_{6h}^3–$P6_3/mcm$, D_{3h}^2–$P\bar{6}c2$, C_{6v}^3–$P6_3cm$, D_{3d}^4–$P\bar{3}c1$ and C_{3v}^3–$P3c1$. The intensity calculation had been successful by assuming the space group D_{6h}^3–$P6_3/mcm$ and placing the hafnium atoms in $4(d)$ and $6(g)_{\mathrm{I}}$ with $x_{\mathrm{I}} = 0{\cdot}25$ and the germanium atoms in $6(g)_{\mathrm{II}}$ with $x_{\mathrm{II}} = 0{\cdot}61$. The carbon atoms have not been considered for the intensity calculation as the scattering factor for carbon is much smaller than those for germanium and hafnium atoms. The carbon atoms are probably located at the positions 000 and $00\frac{1}{2}$ where there are holes in the structure big enough to insert a carbon atom (Aronsson, 1958). The agreement between observed and calculated intensities may be seen in Table 2.

$Hf_5Ge_3(C)$ crystallizes in the ternary $D8_8$-type. Phases with this structure type have been called in the literature Nowotny-phases. Recently it also had been possible to find a $Hf_5Si_3(C)$ with the ternary $D8_8$-structure type (Nowotny, 1959). This closes the gap in the list of Nowotny-phases with transition metals of the 4th group which was given in a previous publication (Parthé & Norton, 1958).

Table 2. *Intensity calculations for* $Hf_5Ge_3(C)$ *with* $D8_8$ *structure*

Cr $K\alpha$ radiation

hkil	*d* (Å)	$1000.(\sin^2\theta)_c$	$1000.(\sin^2\theta)_o$	I_c	I_o
$10\bar{1}0$	6·83	28·15	—	4·18	—
0001	—	42·8	—	0	—
$11\bar{2}0$	3·94	84·4	—	3·70	—
$20\bar{2}0$	3·41	112·6	113·6	28·0	*w*
$11\bar{2}1$	3·21	127·2	127·8	26·9	*w*
0002	2·77	171·2	172·5	13·85	*vw*
$21\bar{3}0$	2·58	197·0	199·1	53·60	*s, d*
$10\bar{1}2$	2·56	199·3		27·65	
$21\bar{3}1$	2·34	239·8	240·2	120·0	*vs*
$30\bar{3}0$	2·27	253·3	255·5	61·3	*vs, d*
$11\bar{2}2$	2·26	255·6		112·0	
$20\bar{2}2$	2·15	283·8	—	2·34	—
$22\bar{4}0$	$1{\cdot}97_0$	337·8	—	1·66	—
$31\bar{4}0$	1·89	365·9	—	1·16	—
$21\bar{3}2$	$1{\cdot}88_7$	368·2	—	0·02	—
$22\bar{4}1$	$1{\cdot}85_5$	380·6	—	1·92	—
$31\bar{4}1$	$1{\cdot}79_0$	408·7	409·7	4·84	*vvw*
$30\bar{3}2$	$1{\cdot}75_7$	424·5	—	2·12	—
$40\bar{4}0$	$1{\cdot}70_6$	450·4	451·2	5·26	*vvw*
$11\bar{2}3$	1·67	469·6	470·3	4·52	*vvw*
$22\bar{4}2$	$1{\cdot}60_5$	509·0	508·7	35·0	*m*
$32\bar{5}0$	$1{\cdot}56_5$	534·8	532·0	6·37	*vvw*
$31\bar{4}2$	1·561	537·1	538·4	15·87	*w*
$32\bar{5}1$	$1{\cdot}50_6$	577·6	579·9	31·40	*s, d*
$21\bar{3}3$	1·50	582·2		44·50	
$41\bar{5}0$	1·489	591·1	592·8	27·10	*m*
$40\bar{4}2$	1·452	621·6	622·7	51·50	*s*
$41\bar{5}1$	1·438	633·9	—	0·46	—
0004	1·383	684·8	685·7	28·30	*m*
$50\bar{5}0$	1·365	703·7	705·0	3·14	*vvw*
$32\bar{5}2$	1·363	706·0		3·86	
$10\bar{1}4$	1·356	712·9	—	0·22	—
$22\bar{4}3$	1·346	723·0	723·9	1·98	*vvvw*
$31\bar{4}3$	1·320	751·1	753·0	6·17	*vvw*
$33\bar{6}0$	1·313	760·0	760·5	4·23	*mw*
$41\bar{5}2$	1·311	762·3		20·50	
$11\bar{2}4$	1·305	769·2	—	1·39	—
$42\bar{6}0$	1·289	788·2	788·2	45·0	*ms*
$20\bar{2}4$	1·282	797·4	802·3	16·20	*ms*
$33\bar{6}1$	1·278	802·8		43·20	
$42\bar{6}1$	1·261	831·0	833·3	13·20	*vvw, vd*
$51\bar{6}0$	1·225	872·6	872·7	58·60	*vs, d*
$50\bar{5}2$	1·223	874·9		122·5	
$21\bar{3}4$	1·219	881·8	880·8	100·0	*s*
$51\bar{6}1$	$1{\cdot}196_5$	915·5	916·5	197·0	*s, vd*
$32\bar{5}3$	$1{\cdot}193_4$	920·0		310·0	
$33\bar{6}2$	$1{\cdot}186_3$	931·2	930·4	198·0	*s, vd*
$30\bar{3}4$	$1{\cdot}181_9$	938·1	937·3	320·0	*vs, vd*
$42\bar{6}2$	$1{\cdot}168_7$	959·4	—	13·2	—
$41\bar{5}3$	$1{\cdot}158_6$	976·3	—	6·4	—

The author wishes to express his sincere gratitude to Prof. John T. Norton for many encouraging discussions. He also acknowledges the contributions of Mr Warren Holbrook to the experimental portion of the program. This investigation was sponsored by the Atomic Energy Commission under contract No. AT(30-1)-981. This support is gratefully acknowledged.

Literature

Aronsson, B. (1958). *Acta Chem. Scand.* **12**, 31.
Hellner, E. (1950). *Z. anorg. Chem.* **261**, 226.
Kiessling, R. (1949). *Acta Chem. Scand.* **3**, 595.
Laves, F. (1955). *Smithells Metals Reference Book*, 2nd ed., p. 218. New York: Interscience Publishers.
Nowotny, H. & Parthé, E. (1954). *Planseeber.* **2**, 34.
Nowotny, H. *et al.* (1959). *Mh. Chem.* To be published.
Parthé, E. & Norton, J. T. (1958). *Acta Cryst.* **11**, 14.