

The Crystal Structure of Y_5Si_3 and Y_5Ge_3

BY ERWIN PARTHÉ*

Massachusetts Institute of Technology, Cambridge, Massachusetts, U.S.A.

(Received 21 December 1959)

The crystal structures of Y_5Si_3 and Y_5Ge_3 have been studied by means of rotation and Debye-Scherrer powder photographs. Both compounds crystallize in the $D8_8$ structure type. Y_5Si_3 has the lattice constants $a=8.40_3$ and $c=6.30_3$ Å. The dimensions of Y_5Ge_3 are $a=8.47_1$ and $c=6.35_0$ Å. Both compounds have an unusually large c/a ratio.

Introduction

In the course of a study of the compounds of yttrium, the systems Y-Si and Y-Ge have been investigated. In the case of Y-Si the existence of two compounds was already established. YSi_2 has been mentioned by Brauer & Haag (1952) as a possible orthorhombic variation of the $ThSi_2$ structure. The same compound was the object of a recent complete structure determination which proved the former suggestion (Perri, Binder & Post, 1959). The structure of YSi has been described as belonging to the CrB type (Parthé, 1959). There remained the pattern of another phase in the middle region whose structure is discussed in this paper. An isotypic structure also exists in the system Y-Ge. This is thus far the first yttrium germanide to be reported in the literature. Other phases present in this system will be the object of later publications.

Sample preparation

Yttrium pieces and silicon lumps have been arc melted under helium. The buttons were turned around and remelted three times. The composition of the samples were checked by chemical analysis. The same procedure was repeated for the preparation of the yttrium germanides.

Y_5Si_3

It was possible to isolate a single crystal from a button of yttrium silicide with 37.6 at. % Si. A rotation photograph of this crystal could be indexed with a hexagonal unit cell and the lattice constants

$$a=8.40_3, c=6.30_3 \text{ Å}, c/a=0.750.$$

The density of the compound was determined experimentally to 4.36 g.cm.^{-3} . Assuming the composition Y_5Si_3 and two formula units per unit cell the theoretical density can be calculated to 4.54 g.cm.^{-3} .

The systematic 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 . Assuming space group $D_{6h}^3-P6_3/mcm$ the yttrium atoms have been placed in $4d$ and $6g_1$ with $x_1=0.25$ and the silicon atoms in $6g_{II}$ with $x_{II}=0.61$. The agreement between calculated and observed intensities may be studied in Table I. A structure type with these atomic positions is already known in the literature as $D8_8$ or Mn_5Si_3 type. Only recently another silicide with the $D8_8$ structure has been studied. During the course of that study Weissenberg photographs of a Ti_5Si_3 single crystal were used to calculate the two free parameters more accurately (Nowotny, Auer-Welsbach, Bruss & Kohl, 1959). The free parameters found for Y_5Si_3 are slightly different from those reported for Ti_5Si_3 . It can be reasoned that with $x_1=0.25$ for yttrium and $x_{II}=0.61$ for silicon a better spatial arrangement will be achieved. This fact is not very surprising if we also consider that Ti_5Si_3 and Y_5Si_3 have quite different c/a ratios. The c/a ratio of Ti_5Si_3 , 0.687, is about 10% smaller than that given for Y_5Si_3 . In distinction to Ti_5Si_3 no smear lines have been observed between the equator and the first layer line.

By hot extraction technique the oxygen content of the Y_5Si_3 sample was determined to be 1.3 at.%. It was not possible to synthesize a purer Y_5Si_3 since the only available yttrium metal contained oxygen as impurity. In the neighboring silicon systems with transition metals the Mn_5Si_3 structure type occurs as a ternary phase stabilized by a small amount of oxygen, carbon, etc. These are the so-called Nowotny phases (Parthé, 1957). It has been shown that the Nowotny phase shifts closer to the binary system Me-Si if the group number of the metal decreases and in the case of Ti_5Si_3 it is already a pure binary phase. It is expected from this evidence, that pure oxygen free Y_5Si_3 crystallizes in the binary $D8_8$ structure, which is also able to provide some accommodations for a few oxygen atoms. There are octahedral holes in the $D8_8$ structure at 0, 0, 0 and 0, 0, $\frac{1}{2}$ which are large enough to be occupied by oxygen atoms (Aronsson, 1958). Since the scattering factor of oxygen is so small in comparison to yttrium or silicon the oxygen has not been considered in the intensity calculation.

* Present address: University of Pennsylvania, Metallurgy Department Philadelphia, U.S.A.

Table 1. *Intensity calculation for Y₅Si₃ with D8₈ structure*

(Cr K α radiation)					
<i>hkl</i>	<i>d</i> (Å)	1000. sin ² θ_c	1000. sin ² θ_o	<i>I_c</i>	<i>I_o</i>
10 $\bar{1}$ 0	7.27	24.78	—	0.88	—
0001	—	33.03	—	0	—
11 $\bar{2}$ 0	4.199	74.34	74.1	2.22	<i>vvw</i>
20 $\bar{2}$ 0	3.636	99.12	99.6	11.48	<i>m</i>
11 $\bar{2}$ 1	3.495	107.37	107.6	13.90	<i>m</i>
0002	3.149	132.12	132.0	3.84	<i>vw</i>
10 $\bar{1}$ 2	2.890	156.90	156.5	16.07	<i>mst</i>
21 $\bar{3}$ 0	2.748	173.46	173.9	17.27	<i>mst</i>
11 $\bar{2}$ 2	2.519	206.46	206.1	36.85	} <i>vvst</i>
21 $\bar{3}$ 1	2.519	206.49		35.77	
30 $\bar{3}$ 0	2.424	223.02	223.3	18.29	<i>mst</i>
20 $\bar{2}$ 2	2.381	231.24	—	0.49	—
2240	2.100	297.36	—	0.60	—
21 $\bar{3}$ 2	2.071	305.58	—	0.00 ₃	—
3140	2.017	322.14	—	0.23	—
2241	1.992	330.39	—	0.38	—
30 $\bar{3}$ 2	1.921	355.14	—	0.18	—
3141	1.921	355.17	—	0.96	—
11 $\bar{2}$ 3	1.878	371.61	370.6	2.04	<i>vvw</i>
4040	1.818	396.48	396.0	1.69	<i>vvw</i>
2242	1.747	429.48	429.6	10.25	<i>m</i>
3142	1.699	454.26	454.7	4.83	<i>vw</i>
21 $\bar{3}$ 3	1.669	470.73	470.3	10.22	} <i>m</i>
32 $\bar{5}$ 0	1.669	470.82		1.98	
32 $\bar{5}$ 1	1.6127	503.85	504.4	7.17	<i>mw</i>
41 $\bar{5}$ 0	1.5872	520.38	520.9	6.17	<i>mw</i>
0004	1.575	528.48	528.8	4.81	} <i>m</i>
4042	1.575	528.60		11.16	
10 $\bar{1}$ 4	1.5392	553.26	—	0.02	—
41 $\bar{5}$ 1	1.5392	553.41	—	0.05	—
2243	1.4844	594.63	—	0.20	—
11 $\bar{2}$ 4	1.474	602.82	—	0.22	—
32 $\bar{5}$ 2	1.474	602.94	—	0.42	—
3143	1.455	619.41	—	0.57	—
5050	1.453	619.50	—	0.33	—
20 $\bar{2}$ 4	1.445	627.60	627.7	1.76	<i>vvw</i>
41 $\bar{5}$ 2	1.418	652.50	652.8	2.27	<i>vvw</i>
3360	1.399	669.06	—	0.48	—
4260	1.3745	693.84	697.0	4.35	} <i>m, d</i>
2134	1.3664	701.94	to	6.21	
3361	1.3662	702.09	703.4	3.99	} —
4261	1.343	726.87	—	0.79	
30 $\bar{3}$ 4	1.320	751.50	751.5	10.60	} <i>mst, d</i>
5052	1.319	751.62		6.97	
3253	1.3066	768.09	767.9	6.88	} <i>m, d</i>
5160	1.3065	768.18		3.61	
3362	1.279	801.18	801.6	7.08	} <i>mst, d</i>
5161	1.278	801.21		8.16	
4153	1.266	817.65	—	0.06	—
2244	1.2596	825.84	—	0.63	—
4262	1.2594	825.96	—	0.34	—
3144	1.2413	850.62	—	0.03	—
6060	1.2120	892.08	—	0.56	—
11 $\bar{2}$ 5	1.2061	900.09	899.3	1.99	} <i>vvw</i>
5162	1.2061	900.30		0.03	
4370	1.1951	916.86	—	0.05	—
4044	1.1903	924.96	924.0	4.29	<i>vw, d</i>
4371	1.1746	949.89	—	0.87	—
3363	1.1645	966.33	965.5	11.74	} <i>mst, vd</i>
5270	1.1645	966.42		3.84	
4263	1.14994	991.11	991.8	4.66	<i>w, vd</i>



$$a=8.471, c=6.350 \text{ \AA}, c/a=0.749.$$

A powder photograph of yttrium germanide with 37.4 at.% Ge showed a X-ray pattern similar to Y₅Si₃. The hexagonal cell has the dimensions

With two formula units Y₅Ge₃ per unit cell the theoretical density can be calculated as 5.57 g.cm.⁻³, while the experimental value amounts to 5.40 g.cm.⁻³.

Table 2. Intensity calculation for Y_5Ge_3 with $D8_8$ structure

hkl	d (Å)	(Cr $K\alpha$ radiation)		I_c	I_o
		$1000 \cdot \sin^2 \theta_c$	$1000 \cdot \sin^2 \theta_o$		
10 $\bar{1}$ 0	7.330	24.3832	—	4.99	—
0001	—	32.54065	—	—	—
11 $\bar{2}$ 0	4.2318	73.15	—	0.06	—
20 $\bar{2}$ 0	3.6657	97.53	98.1	3.71	<i>vw</i>
11 $\bar{2}$ 1	3.5214	105.69	—	0.24	—
0002	3.1731	130.16	129.6	12.01	<i>mw</i>
10 $\bar{1}$ 2	2.9121	154.54	153.9	12.00	<i>mw</i>
21 $\bar{3}$ 0	2.7710	170.68	171.3	18.34	<i>m</i>
21 $\bar{3}$ 1	2.5395	203.22	—	57.41	—
11 $\bar{2}$ 2	2.5389	203.31	203.5	54.05	<i>vwst, d</i>
30 $\bar{3}$ 0	2.4438	219.45	219.7	29.89	<i>m</i>
20 $\bar{2}$ 2	2.3991	227.69	228.4	3.23	<i>vw</i>
22 $\bar{4}$ 0	2.1164	292.59	—	0.27	—
21 $\bar{3}$ 2	2.0872	300.84	—	0.02	—
31 $\bar{4}$ 0	2.0333	317.00	317.6	1.49	<i>vwvw</i>
22 $\bar{4}$ 1	2.0077	325.13	325.7	2.45	<i>vw</i>
31 $\bar{4}$ 1	1.9364	349.52	—	6.15	—
30 $\bar{3}$ 2	1.9361	349.61	349.6	0.44	<i>vw</i>
11 $\bar{2}$ 3	1.8923	366.01	—	0.05	—
40 $\bar{4}$ 0	1.8329	390.13	390.9	1.00	<i>vwvw</i>
22 $\bar{4}$ 2	1.7607	422.75	422.6	12.13	<i>w</i>
31 $\bar{4}$ 2	1.7120	447.14	447.7	2.03	<i>vw</i>
32 $\bar{5}$ 0	1.6819	463.28	—	16.24	—
21 $\bar{3}$ 3	1.6815	463.54	463.4	0.47	<i>m</i>
32 $\bar{5}$ 1	1.6258	495.82	496.5	7.92	<i>w</i>
41 $\bar{5}$ 0	1.5998	512.05	512.2	4.73	—
40 $\bar{4}$ 2	1.5871	520.29	to	8.96	<i>w, d</i>
0004	1.5865	520.65	520.9	7.38	—
41 $\bar{5}$ 1	1.5515	544.59	—	0.33	—
10 $\bar{1}$ 4	1.0433	545.03	—	0.15	—
22 $\bar{4}$ 3	1.4960	585.45	585.9	1.19	<i>vwvw</i>
32 $\bar{5}$ 2	1.4860	593.44	—	2.44	—
11 $\bar{2}$ 4	1.4856	593.80	593.7	0.005	<i>vw</i>
50 $\bar{5}$ 0	1.4662	609.58	—	3.35	—
31 $\bar{4}$ 3	1.4660	609.84	610.8	1.98	<i>vw</i>
20 $\bar{2}$ 4	1.4561	618.18	—	0.59	—
41 $\bar{5}$ 2	1.4285	642.21	642.8	3.72	<i>vw</i>
33 $\bar{6}$ 0	1.4109	658.34	—	0.66	—
42 $\bar{6}$ 0	1.3854	682.73	683.2	6.81	—
33 $\bar{6}$ 1	1.3773	690.88	to	5.51	<i>w, d</i>
21 $\bar{3}$ 4	1.3769	691.33	691.1	6.43	—
42 $\bar{6}$ 1	1.3536	715.27	716.0	4.68	<i>vw</i>
50 $\bar{5}$ 2	1.3310	739.74	—	14.67	—
30 $\bar{3}$ 4	1.3307	740.10	739.3	16.48	<i>m, d</i>
51 $\bar{6}$ 0	1.3167	755.88	—	8.32	—
32 $\bar{5}$ 3	1.3169	756.14	756.7	7.47	<i>w, d</i>
51 $\bar{6}$ 1	1.2893	788.42	—	9.83	—
33 $\bar{6}$ 2	1.2892	788.50	788.9	5.98	<i>w</i>
41 $\bar{5}$ 3	1.2760	804.91	—	0.35	—
42 $\bar{6}$ 2	1.2697	812.89	—	1.83	—
22 $\bar{4}$ 4	1.2694	813.24	813.3	0.28	<i>vwvw</i>
31 $\bar{4}$ 4	1.25089	837.63	837.2	1.81	<i>vwvw</i>
60 $\bar{6}$ 0	1.22190	877.79	—	0.51	—
51 $\bar{6}$ 2	1.21627	886.04	—	0.18	—
11 $\bar{2}$ 5	1.21570	886.67	—	0.05	—
43 $\bar{7}$ 0	1.20535	902.18	—	0.26	—
40 $\bar{4}$ 4	1.19956	910.78	909.6	2.34	<i>vwvw</i>
43 $\bar{7}$ 1	1.18410	934.72	935.1	4.49	<i>vw</i>
52 $\bar{7}$ 0	1.17395	950.94	—	6.06	—
33 $\bar{6}$ 3	1.17382	951.20	950.9	13.74	<i>mw, d</i>
42 $\bar{6}$ 3	α_1 1.15977	α_1 974.4	α_1 974.4	16.86	<i>mw</i>
		α_2 977.7	α_2 977.6		<i>w</i>
52 $\bar{7}$ 1	α_1 1.15509	α_1 982.28	982.5	36.16	—
	α_2	985.62	—	—	—
32 $\bar{5}$ 4	α_1 1.15483	α_1 982.73	986.0	3.68	<i>mst, d</i>
	α_2	986.07	—	—	—
21 $\bar{3}$ 5	α_1 1.15468	α_1 982.99	986.0	63.27	<i>m, d</i>
	α_2	986.34	—	—	—

The space group $D_{6h}^3-P6_3/mcm$ has again been assumed. The yttrium and germanium atoms have been placed in the same positions as in Y_5Si_3 . The agreement between calculated and observed intensities as seen in Table 2 is very good. Thus Y_5Ge_3 also crystallizes in the $D8_8$ structure and like Y_5Si_3 has the unusually large c/a ratio.

Discussion

As mentioned above, the $D8_8$ structure occurs in silicides and germanides with transition metals of the fourth to the sixth group of the periodic system. The metal atoms in the $4d$ and $6g$ positions are not touching each other in these compounds. In Y_5Si_3 on the other hand, the distance between $4d$ and $6g_I$ has been calculated to be 3.57 Å, while the value of 3.62 Å can be taken from tables for the diameter of a yttrium atom. This compression of the a axis is the reason for the unusually large c/a ratio in Y_5Si_3 and Y_5Ge_3 which has not been observed by other compounds with $D8_8$ structure. It will be shown in another paper that in the case of Y_5Si_3 and Y_5Ge_3 an increased transfer of electrons of the $6g_I$ atoms to the $4d$ position should be observed. This increased electron transfer causes

the shortened distance between the atoms in the $4d$ position and the $6g_I$ position of the $D8_8$ structure, and hence the unusually high c/a ratio.

The author wishes to thank Prof. John T. Norton for his stimulating interest. He also would like to express his gratitude to Dr M. V. Nevitt at Argonne National Laboratory for the arc melting of the samples. He further acknowledges the contributions of Mr W. 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.
 BRAUER, G. & HAAG, H. (1952). *Z. Anorg. Chem.* **267**, 198.
 NOWOTNY, H., AUER-WELSBACH, H., BRUSS, J. & KOHL, A. (1959). *Mh. Chem.* **90**, 15.
 PERRI, J. A., BINDER, I. & POST, B. (1959). *J. Phys. Chem.* **63**, 616.
 PARTHÉ, E. (1957). *Powder Metall. Bull.* **8**, 23.—Errata and additions (1958). *Powder Metall. Bull.* **8**, 70.
 PARTHÉ, E. (1959). *Acta Cryst.* **12**, 559.

Acta Cryst. (1960). **13**, 871

Experimentelle Untersuchungen zur Brechungskorrektur bei Präzisionsgitterkonstantenmessungen an Pulverpräparaten

VON MANFRED WILKENS

Institut für Metallphysik am Max-Planck-Institut für Metallforschung, Stuttgart, Deutschland

(Eingegangen am 15. Januar 1960)

The displacements through refraction of the diffraction maxima of gold, relative to those of aluminium, were measured for three radiations (Cu, Co and Cr K). In the back-reflexion region only the wavelength change in the interior of the powder grains is important. In the low- and medium-angle regions the effect due to the change in direction of the ray on entering the grain is also detectable, and depends strongly on the grain size and shape. All these findings are in accordance with theory.

Einleitung

In einer vorangegangenen Mitteilung wurde über statistische Abschätzungen bezüglich der Brechungskorrektur (im Folgenden kurz BK genannt) bei Präzisionsgitterkonstantenmessungen an Pulverpräparaten berichtet, Wilkens (1960a). Danach liegt die BK im allgemeinen zwischen zwei Grenzen, die aus idealisierten Präparatmodellen abgeleitet wurden.

1) Bei sehr kleinen Teilchen mit Linearabmessungen $L < 1/\mu$ (μ = Absorptionskoeffizient) braucht nur die Veränderung der Wellenlänge im Kristallinneren berücksichtigt zu werden, unabhängig von der Gestalt der Teilchen.

$$d_{\text{korr}} = d_{\text{gemessen}} \left(1 + \frac{\Delta d}{d} \Big|_{\text{Br}} \right); \frac{\Delta d}{d} \Big|_{\text{Br}} = \delta; \quad (1)$$

d = Netzebenenabstand.

$$\delta = 4.47 \cdot 10^{-6} \lambda^2 Z/V. \quad (1a)$$

Z = Zahl der Elektronen pro Elementarzelle;

V = Volumen der Elementarzelle in Å³;

λ = Wellenlänge in Å.

2) Bei sehr grossen Teilchen mit $L \gg 1/\mu$, die von ebenen Flächen begrenzt sind, gibt zusätzlich dazu die Richtungsänderung der Wellennormalen beim Durchtritt durch die Teilchenoberflächen einen