GRENVILLE-WELLS, H. J. (1956). *Acta Cryst.* **9**, 709.
HAMILTON, W. C. (1955). *Acta Cryst.* **8**, 185.
HENDRICKS, S. B. (1933). *Z. Kristallogr.* **84**, 85.
HUFFMAN, H. M., PARKS, G. S. & DANIELS, A. C. (1930). *J. Amer. Chem. Soc.* **52**, 1547.
KAUZMANN, W. (1942). *Rev. Mod. Phys.* **14**, 12.
KLUG, A. (1947). *Nature, Lond.* **160**, 570.
LONSDALE, K. (1931). *Proc. Roy. Soc.* A, **133**, 536.
MORGAN, S. O. & YAGER, W. A. (1940). *Ind. Eng. Chem.* **32**, 1519.
PHILLIPS, D. C. (1956). *Acta Cryst.* **9**, 237.
SEKI, S. & CHIHARA, H. (1949). *Sci. Pap. Osaka Univ.* **1**, 1.
WHITE, A. H., BIGGS, B. S. & MORGAN, S. O. (1940). *J. Amer. Chem. Soc.* **62**, 16.

Acta Cryst. (1958). **11**, 14

Crystal Structures of Zr_5Ge_3, Ta_5Ge_3 and Cr_5Ge_3

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The crystal structures of Zr_5Ge_3, Ta_5Ge_3 and Cr_5Ge_3 have been examined by means of Debye–Scherrer diagrams and compared with the corresponding silicides. Cr_5Ge_3 crystallizes in the $T1$ type structure with $a = 9{\cdot}41_3$ Å and $c = 4{\cdot}78_0$ Å. Ta_5Ge_3 crystallizes in the $T1$ structure also, as previously reported, but transforms to the Nowotny structure ($D8_8$ type) with $a = 7{\cdot}58_1$ Å and $c = 5{\cdot}23_5$ Å if 5% of carbon is added. Zr_5Ge_3 crystallizes directly in the Nowotny structure ($D8_8$ type) with $a = 7{\cdot}99_3$ Å and $c = 5{\cdot}59_7$ Å. Apparently the residual impurities are sufficient to stabilize this phase in the latter case. The germanide structures are thus the same as the corresponding silicide structures.

Introduction

A comparison of the structures of the silicides and germanides of the transition metals, in so far as the structures have been determined, shows a complete correspondence of structure types, in spite of the fact that the germanium atom is considerably larger than the silicon atom. In the case of the phases with the formula M_5Si_3 it is known that the expected binary phases are frequently replaced by the so-called Nowotny phase having a $D8_8$ type structure, the stabilization of the latter apparently being brought about by the presence of atoms of carbon, boron, oxygen or nitrogen, often in very small amounts (Parthé, 1957). In order to extend the analogy between the silicides and germanides somewhat further, the compounds Zr_5Ge_3, Ta_5Ge_3 and Cr_5Ge_3 were examined.

Preparation of samples

The specimens were prepared from powders of zirconium hydride, tantalum hydride, chromium, and germanium. The powders were mixed in proper portions in trichlorethylene in a hard-metal ball-mill and the dried powders were hot-pressed in graphite dies. The temperature was 1200° C. and time at temperature about 2 min. Since this temperature was above the melting point of germanium, the pressure was applied slowly.

Cr_5Ge_3

The powder diagram of Cr_5Ge_3 could be indexed to correspond to a tetragonal unit cell with the lattice constants:

$$a = 9{\cdot}41_3 \text{ Å}, \quad c = 4{\cdot}78_0 \text{ Å}, \quad c/a = 0{\cdot}507 \; .$$

The extinctions lead to the space group D_{4h}^8–$I4/mcm$. The agreement between observed and calculated values of the intensities (Table 1) was obtained if the Cr atoms were placed in positions $4(b)$ and $16(k)$ with the parameter $x = 0{\cdot}07_4$ and $y = 0{\cdot}22_3$, while the Ge atoms were in positions $4(a)$ and $8(h)$ with the parameter $x = 0{\cdot}17$. Thus Cr_5Ge_3 has the same structure as Cr_5Si_3, which is of the $T1$ type. The lines of the phase Cr_3Ge were also observed in the specimen.

A second specimen to which 5 atomic% carbon was added showed the same $T1$ structure of the binary phase Cr_5Ge_3.

Ta_5Ge_3

The specimen prepared from tantalum hydride and germanium confirmed the $T1$ structure of the binary phase Ta_5Ge_3 reported by Nowotny, Searcy & Orr (1956). With the addition of 5 atomic% carbon, however, the powder pattern was different and recogniz-

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Table 1. *Intensity calculation for* Cr_5Ge_3 *with* $T1$ *structure*

Cr $K\alpha$ radiation

hkl	*d* (Å)	$(\sin^2\theta)_c$	$(\sin^2\theta)_o$	I_c	I_o	Remarks
100	—	$14{\cdot}81_5$	—	0	—	
110	6·658	29·63	—	26	—	
001	—	57·45	—	0	—	
200	4·703	59·20	—	4	—	
220	3·323	118·52	119·2	28·6	*vw*	
211	3·158	131·52	130·8	66·8	*w*	
310	2·973	148·15	147·7	40·7	*w*	
002	2·387	229·80	230·6	114·0	*w*	
400	2·350	237·04	236·5	51·5	*vw*	
321	2·289	250·04	250·0	152	*m*	
112	2·246	259·43	—	3·3	—	
330	2·216	266·67	266·8	68·6	*vw*	
202	2·129	289·06	288·7	334	*s*	
420	2·105	296·30	295·0	312	*s*	
411	2·058	309·30	308·9	618	*vvs*	*K* 210 Cr_3Ge
222	1·940	348·32	348·8	167	*m*	
312	1·861	377·95	—	0·5	—	
510	1·845	385·19	—	5·0	—	
431	1·750	427·82	—	$5{\cdot}8_5$	—	
402	1·675	466·84	466·9	52·2	*w*	
440	1·663	474·08	473·8	15·6	*vvw*	
521	1·640	487·08	486·0	90	*mw*	
332	1·624	496·47	496·5	84	*mw*	
530	1·613	503·71	501·7	59	*vw*	
422	1·578	526·10	—	1·5	—	
600	1·568	533·34	533·1	18·5	*vvw*	
213	1·4890	591·12	591·3	9·8	*vw, d*	
620	1·4860	592·60		38·0		
611	1·4710	605·60	—	2·4	—	
512	1·4598	614·99	—	$0{\cdot}3_3$	—	
541	1·4036	664·86	—	0·37	—	
442	1·3604	703·88	705·0	71	*w, d*	
323	1·3589	709·60		72		
631	1·3450	724·12	722·3	96	*vw*	
532	1·3370	733·51	736·3	101	*w, d*	*K* 222 Cr_3Ge
710	1·3300	740·75		46		
550				36·5		
602	1·3105	763·14	762·0	76	*vw*	
413	1·3058	768·90	767·4	547	*s*	
640	1·3045	770·38	—	0·1	—	
622	1·2621	822·40	821·7	254	*ms*	
721	1·2469	842·64	841·6	271	*ms*	
730	1·2352	859·27	858·3	157	*vs*	*K* 321 Cr_3Ge
433	1·2152	887·42	—	1·84	—	
004	α_1 1·1949	α_1 917·76	α_1 918·8	1260	*ms, d*	
	α_2 1·1931	α_2 920·89	α_2 920·7			
523	1·1766	946·68	947·1	697	*vs*	*K* 211 Cr
800	1·1756	948·16	—	10·7	—	
114	1·1754	948·83	—	9·2	—	
651	1·1676	961·16	959·9	32·6	*vvvw*	
712	α_1 1·1630	α_1 968·99	α_1 969·5	1660	*vs*	
552	α_2 1·1611	α_2 972·27	α_2 972·2	1170		
204	1·1574	978·46	979·7	6·9	*vw*	*K* 400 Cr_3Ge

able as that of the Nowotny phase with the $D8_8$ structure. The lattice constants were

$$a = 7{\cdot}58_1 \text{ Å}, \quad c = 5{\cdot}23_5 \text{ Å}, \quad c/a = 0{\cdot}690\,.$$

Agreement between the observed and calculated intensities (Table 2) was obtained if the Ta atoms were placed at positions $4(d)$ and $6(g)_{\text{I}}$ with $x = 0{\cdot}25$ and the Ge atoms at $6(g)_{\text{II}}$ with $x = 0{\cdot}61$. The space group is D^3_{6h}–$C6/mcm$. The carbon atoms were not considered in the intensity calculations. As has been shown previously (Nowotny, Parthé, Kieffer & Benesovsky, 1954) for the analogous phase in the system Mo–Si–C, there might be a metal deficiency on the $4(d)$ position.

Zr_5Ge_3

The specimen prepared from zirconium hydride and germanium powders without carbon addition showed the pattern of the $D8_8$ Nowotny phase directly with no other lines. The lattice constants were

$$a = 7{\cdot}99_3 \text{ Å}, \quad c = 5{\cdot}59_7 \text{ Å}, \quad c/a = 0{\cdot}700\,,$$

Table 2. *Intensity calculation for* $Ta_5Ge_3(C)$ *with* $D8_8$ *structure*

Cr $K\alpha$ radiation

hkil	*d* (Å)	$(\sin^2\theta)_c$	$(\sin^2\theta)_o$	I_c	I_o
$10\bar{1}0$	6·56	30·4	—	3·92	—
0001	—	47·9	—	0	—
$11\bar{2}0$	3·78	91·4	—	3·82	—
$20\bar{2}0$	3·27	122	121·5	27·7	*mw*
$11\bar{2}1$	3·07	139·3	139·1	26·0	*mw*
0002	2·61	192	190·8	11·3	*w*
$21\bar{3}0$	2·48	213	213·2	49·6	*s*
$10\bar{1}2$	2·43	222	221·9	35·4	*m*
$21\bar{3}1$	2·24	261	260·7	110·0	*vvs*
$30\bar{3}0$	2·18	274	273·0	59·0	*s*
$11\bar{2}2$	2·14	284	284·0	95·2	*vs*
$20\bar{2}2$	2·04	314	—	1·92	—
$22\bar{4}0$	1·893	365	—	1·56	—
$31\bar{4}0$	1·819	396	—	0·98	—
$21\bar{3}2$	1·799	405	—	0·013	—
$22\bar{4}1$	1·781	413	413·2	1·70	*vvw*
$31\bar{4}1$	1·717	444	442·5	4·16	*vvw*
$30\bar{3}2$	1·675	466	—	0·216	—
$40\bar{4}0$	1·639	487	486·0	6·75	*vw*
$11\bar{2}3$	1·583	523	522·7	4·44	*vvw*
$22\bar{4}2$	1·533	557	555·7	37·1	*ms*
$32\bar{5}0$	1·505	578	576·5	7·22	*vw*
$31\bar{4}2$	1·492	588	586·8	18·3	*w*
$32\bar{5}1$	1·447	626	626·0	35·0	*ms*
$41\bar{5}0$	1·431	639	637·8	31·0	*ms*
$21\bar{3}3$	1·426	645	644·5	52·1	*s*
$40\bar{4}2$	1·389	679	677·6	62·8	*s*
$41\bar{5}1$	1·381	687	—	0·475	—
$50\bar{5}0$	1·311	762	762·0	3·88	*vw*
0004	1·307	767	767·9	4·12	*w*
$32\bar{5}2$	1·304	770		5·00	
$22\bar{4}3$	1·282	797	798·1	2·72	*vvw*
$10\bar{1}4$		797		0·32	
$33\bar{6}0$	1·262	823	825·3	6·00	*vw, d*
$31\bar{4}3$	1·258	828		9·05	
$41\bar{5}2$	1·256	831	832·0	30·9	*w, d*
$42\bar{6}0$	1·239	853	851·1	66·0	*ms*
$11\bar{2}4$	1·236	858	—	2·66	—
$33\bar{6}1$	1·226	871	871·6	67·0	*ms*
$20\bar{2}4$	1·214	889	890·8	31·3	*w, d*
$42\bar{6}1$	1·205	901	901·4	22·3	*vvw, d*
$50\bar{5}2$	1·1721	954	α_1 950·9 α_2 953·9	354	*vvs*
$21\bar{3}4$	1·1563	980	980·1	736	*vvs, d*

which are possibly more precise than those reported by Carlson, Armstrong & Wilhelm (1956).

On the basis of the same calculations as before, the agreement between observed and calculated intensities was obtained as shown in Table 3. In this case it appears that even the residual impurities in the powders or the slight carbon pick-up from the graphite die is sufficient to suppress the formation of the binary phase that might be expected and to stabilize the ternary Nowotny phase.

Table 3. *Intensity calculation for* Zr_5Ge_3 *with* $D8_8$ *structure*

Cr $K\alpha$ radiation

hkil	*d* (Å)	$(\sin^2\theta)_c$	$(\sin^2\theta)_o$	I_c	I_o
$10\bar{1}0$	6·90	27·4	—	4·35	—
0001	—	41·9	—	0	—
$11\bar{2}0$	3·99	82	—	0·02	—
$20\bar{2}0$	3·44	110	—	3·47	—
$11\bar{2}1$	3·25	124	—	0·41	—
0002	2·79	167·5	168·5	8·68	*w*
$21\bar{3}0$	2·61	192	193·5	16·2	*m, d*
$10\bar{1}2$	2·59	195		9·10	
$21\bar{3}1$	2·36	234	234·0	48·3	*s*
$30\bar{3}0$	2·31	246	248·5	26·2	*s, d*
$11\bar{2}2$	2·29	249		41·1	
$20\bar{2}2$	2·17	277	276·1	2·35	*vw*
$22\bar{4}0$	$1{\cdot}99_5$	329	—	0·27	—
$31\bar{4}0$	$1{\cdot}92_0$	356	355·5	1·23	*vvw*
$21\bar{3}2$	$1{\cdot}91_1$	359	—	0·01	—
$22\bar{4}1$	$1{\cdot}88_0$	371	370·6	2·00	*vvw*
$31\bar{4}1$	$1{\cdot}81_5$	398	397·8	4·92	*w*
$30\bar{3}2$	$1{\cdot}78_1$	413	—	0·30	—
$40\bar{4}0$	$1{\cdot}73_1$	438·5	439·1	0·93	*vvvw*
$11\bar{2}3$	$1{\cdot}69_1$	459	—	0·07	—
$22\bar{4}2$	$1{\cdot}62_4$	496	496·5	10·4	*m*
$32\bar{5}0$	$1{\cdot}58_7$	520	—	0·51	—
$31\bar{4}2$	$1{\cdot}58_3$	523	522·7	1·90	*vvw*
$32\bar{5}1$	$1{\cdot}52_6$	562	569·6	8·60	*ms, vd*
$21\bar{3}3$	$1{\cdot}51_7$	569		15·8	
$41\bar{5}0$	$1{\cdot}50_7$	576		5·53	
$40\bar{4}2$	1·471	605	605·7	10·8	*m*
$41\bar{5}1$	1·456	618	—	0·40	—
0004	1·397	671	671·0	9·9	*mw*
$50\bar{5}0$	1·382	685	687·3	2·87	*mw*
$32\bar{5}2$	1·380	687		3·68	
$10\bar{1}4$	1·369	698	—	0·20	—
$22\bar{4}3$	1·362	706	706·6	1·83	*vw*
$31\bar{4}3$	1·337	733	734·7	5·80	*w*
$33\bar{6}0$	1·330	740	743·9	1·25	*w*
$41\bar{5}2$	1·327	743		7·30	
$11\bar{2}4$	1·319	753	—	0·003	—
$42\bar{6}0$	1·306	767	767·9	14·0	*m*
$20\bar{2}4$	1·295	781	782·5	1·5	*m*
$33\bar{6}1$	1·294	782		12·4	
$42\bar{6}1$	1·272	809	810·6	11·2	*w, d*
$51\bar{6}0$	1·242	850	852·3	12·8	*s, d*
$50\bar{5}2$	1·240	852		45·0	
$21\bar{3}4$	1·232	863	863·3	23·7	*ms, d*
$51\bar{6}1$	1·212	892	891·8	40·2	*ms, d*
$32\bar{5}3$	1·208	897	898·3	34·8	*ms, d*
$33\bar{6}2$	1·201	907	907·6	31·2	*ms*
$30\bar{3}4$	$1{\cdot}195_8$	917	918·4	86·0	*vs, d*
$42\bar{6}2$	$1{\cdot}184_4$	934	933·9	11·4	*w, d*
$41\bar{5}3$	1·1726	953	—	3·08	—

Discussion

In Table 4 is shown the presently known information on the parallelism of the structures of silicides and germanides. It appears that in every case where the germanide has been prepared, its structure type is the same as that of the corresponding silicide. The present results show that in Ta_5Ge_3 the situation is exactly analogous to the silicide case; namely that the *T*1 binary phase is stable with low carbon content but that the $D8_8$ Nowotny ternary phase is stabilized if the carbon content is increased. In the case of Zr_5Ge_3 the $D8_8$ phase is stable even with very small impurity content, as is also true of the silicide. Again, in the case of Cr_5Ge_3 the binary *T*1 phase is stable even with appreciable carbon content, which parallels the corresponding silicide; but it still remains to be shown

Table 4. *Silicides and germanides with transition metals of the 4th to 6th group of the period system*

Compound formula	M_3X		M_5X_3						MX		MX_2							
Structure type	*DA*15		*T*1		*T*2		$D8_8$		*B*20		*C*54		*C*49		*C*40		*C*11	
	S	G	S	G	S	G	S	G	S	G	S	G	S	G	S	G	S	G
Titanium	−		−		−		+	+	−		+	+	−	−	−	−	−	−
Zirconium	−	−	−	−	−	−	+	+	−	−	−	−	+	+	−	−	−	−
Hafnium											−		+		−		−	
Vanadium	+	+	+		−		+		−		−		−		+		−	
Niobium	−		+	+	+		+	+	−		−	−	−	−	+	+	−	−
Tantalum	−		+	+	+	+	+	+	−		−	−	−	−	+	+	−	−
Chromium	+	+	+	+	−		+		+	+	−		−		+		−	
Molybdenum	+	+	+	+	+		+		−		−		−				+	+
Tungsten	−		+		+		(+)		−		−		−				+	

+ : structure is formed.
− : structure is not formed.
S = silicide; G = germanide.

whether the $D8_8$ phase could be stabilized at higher carbon contents. It seems clear, however, that the stability of the *T*1 binary phase with respect to the $D8_8$ phase increases with increasing group number in the periodic table. Further studies of the germanides will undoubtedly strengthen this interesting and important analogy between these two groups of intermetallic compounds.

References

Carlson, O. N., Armstrong, P. E. & Wilhelm, H. A. (1956). *Trans. Amer. Soc. Met.* **48**, 843.

Nowotny, H., Parthé, E., Kieffer, R. & Benesovsky, F. (1954). *Mh. Chem.* **85**, 255.

Nowotny, H., Searcy, A. W. & Orr, J. E. (1956). *J. Phys. Chem.* **60**, 677.

Parthé, E. (1957). *Powder Metallurgy Bulletin.* **8**, 23.

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The Crystal Structure of L-Leucyl-L-Prolyl-Glycine*

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The crystal structure of the tripeptide leucyl-prolyl-glycine 'mono'-hydrate has been determined by Fourier and least-squares analysis of complete three-dimensional intensity data from copper radiation. The crystals are monoclinic with space group $P2_1$; the unit-cell dimensions are: $a_0 = 9{\cdot}44$, $b_0 = 6{\cdot}72$, $c_0 = 12{\cdot}10$ Å, $\beta = 100{\cdot}2°$. With the exception of a twist required by the presence of the proline ring, the peptide chain is in a highly extended configuration. A surprising feature is the presence of only approximately 80% of a water molecule of crystallization per molecule of tripeptide. In addition, one atom in the pyrrolidine ring of the proline residue is disordered, being located with apparently equal probability on either side of the plane of the other four ring atoms.

Introduction

Accurate determinations of the crystal structures of amino acids and simple peptides are of fundamental importance in arriving at the configurations of polypeptide chains in protein molecules. Such determinations yield information concerning the dimensions of the various components of the polypeptide chain, the methods of packing of the side chains, and the role of hydrogen bonding in determining the spatial arrangements of the chains. The confidence which can be placed in predictions of these various structural features of a protein—and, hence, the confidence with which the structure of a protein as a whole can be predicted—depends directly on both the number and the accuracy of the experimental results derived from the simpler compounds.

The amino acid proline is an important constituent

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