Acta Cryst. (1965). **18**, 1085

The crystal structure of Yb_3Ge_5*. By GORDON S. SMITH, QUINTIN JOHNSON, and A. G. THARP†, *Lawrence Radiation Laboratory, University of California, Livermore, California, U.S.A.*

(*Received* 16 *November* 1964)

During a current investigation of compounds formed by lanthanide metals with germanium, powder X-ray diffraction patterns indicated the formation of a germanide of ytterbium unlike previously known germanides and silicides of transition metals. This phase was observed to occur in all preparations with a Ge:Yb gram-atom ratio of 2:1 or slightly lower. We were able to isolate well-formed single crystals of this compound and subsequently determine its formula to be Yb_3Ge_5.

Following the establishment of this composition, a search of the literature for 3:5 compounds disclosed that Yb_3Ge_5 is isotypic with Th_3Pt_5 and Th_3Pd_5 which were recently reported by Thomson (1963).

The preparations were made by arc-melting the components in a Zr-gettered argon atmosphere. Minimum power was used to lower the volatilization of ytterbium metal. Each preparation was turned and remelted several times to homogenize the sample. Oxidation was not apparent in any of the preparations. Excellent powder patterns were obtained without having to anneal the samples.

Oscillation and Weissenberg photographs showed the crystals to be hexagonal, of diffraction symmetry $6/mmm$ with no systematic extinctions. Unit-cell dimensions, determined from the crystal used for intensity measurements, are $a=6{\cdot}80_3\pm0{\cdot}01$, $c=4{\cdot}16_6\pm0{\cdot}01$ Å (λ Mo $K\alpha=0{\cdot}7107$ Å). Integrated intensities for 48 hkl reflections were measured on a General Electric XRD 5 diffractometer equipped with a goniostat and krypton-filled proportional counter. The radiation used was zirconium-filtered Mo $K\alpha$. The crystal shape approximated a parallelopiped, $0{\cdot}03\times0{\cdot}03\times0{\cdot}12$ mm.

Simple considerations of the $h00$ and $00l$ reflections obviated the need for Patterson analysis. A regular alternation in the magnitudes of the $00l$ reflections indicated layers of Ge separated by $c/2$ from layers of Yb, the ratio of Ge atoms to Yb being $\sim1{\cdot}5$. From $h00$, strong for $h=3n$, it was concluded that the x (and y) parameters within the layers were near multiples of $\frac{1}{3}$. Two such models, both formulated in the space group $P\bar{6}2m$ (*International Tables for X-ray Crystallography*, 1952), were derived; one had the stoichiometry Yb_2Ge_3 and the other, Yb_3Ge_5.

Structure factor calculations proved conclusive in favor of the latter, and this structure, moreover, was capable of major refinement *via* the full-matrix least-squares program of Sparks, Gantzel & Trueblood (ACA program no. 317, unpublished). The scattering factors were the Hartree–Fock–Slater values of Hanson, Herman, Lea & Skillman (1964) for the neutral atoms. As an approximation to a weighting scheme appropriate for diffractometric data (Smith & Alexander, 1963), the following formalism was used: $w=F_0^2$ for $F_o<A$, $w=A^{5/4}F_0^{-1}$ for $F_o>A$. On the scale of the structure-factor data in Table 2, A is 122.

After five cycles with isotropic temperature factors, the parameter shifts were negligible, and the R value stood at 7·1 %; 5·8 % if extinction is assumed for the 002 reflection. The final parameters are listed in Table 1. Owing to neglect of absorption as well as anomalous dispersion corrections for both Yb and Ge, the temperature parameters are not physically realistic. For these reasons also we decided not to explore the possibility of any definite departure from the full 3:5 stoichiometry. By way of comparison, Th_3Pd_5 has only a narrow range of homogeneity (Thomson, 1963). Based on Yb_3Ge_5 composition, the calculated density is 8·77 g.cm^{-3}.

The structure is derived from the $C32$-AlB_2 type by the systematic removal of one sixth of the Ge atoms, *i.e.* the composition is 3:5 instead of 3:6. As a result the larger hexagonal cell has $a\sim3^{\frac{1}{2}}\times a$ of a hypothetical ytterbium–germanium AlB_2-type structure. A final difference Fourier synthesis gives no indication of a partial occupancy of these vacant sites. Moreover, the positional shifts are such that Ge(2) largely fills up the holes introduced. The coordination is not as high nor as regular as in the AlB_2-type. Table 3 lists these interatomic distances. With atomic radii of 1·94 and 1·37 Å (Teatum, Gschneidner & Waber, 1959) for Yb (valence=2) and Ge, respectively, the observed distances indicate smaller-than-usual sizes for Ge and Yb. We also note that the sum of the atomic volumes (Teatum, Gschneidner & Waber, 1959) for Yb_3Ge_5 exceeds the observed unit cell volume by ~40 %.

This is apparently the only known silicide or germanide to have this formula in a *structural* sense. Lundin (1961) has concluded that several of the rare earth silicides previously reported by Mayer, Banks & Post (1962) and independently by Tharp (1962) to have the AlB_2 structure are actually M_3Si_5 compounds. The unit-cell volumes of these compounds are prohibitively small and cannot contain one formula unit. It would appear preferable to describe these compounds as defect AlB_2 structures of $MSi_{1\cdot67}$ stoichiometry.

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* This work was performed under the auspices of the U.S. Atomic Energy Commission.

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Table 1. *Atomic positions and parameters*

3 Yb in 3(f), x, 0, 0; *etc.*	$x=0{\cdot}3604\pm0{\cdot}0010$	$B=-0{\cdot}05\pm0{\cdot}22$ Å^2
2 Ge(1) in 2(d), $\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{2}$; *etc.*		$B=0{\cdot}08\pm0{\cdot}62$ Å^2
3 Ge(2) in 3(g), x, 0, $\frac{1}{2}$; *etc.*	$x=0{\cdot}7471\pm0{\cdot}0037$	$B=0{\cdot}88\pm0{\cdot}50$ Å^2

Table 2. *Observed and calculated structure factors for* Yb_3Ge_5

hkℓ	$\|F_o\|$	$\|F_c\|$	α, °	hkℓ	$\|F_o\|$	$\|F_c\|$	α, °
010	26·9	19·9	180·00	221	157·8	152·9	233·71
020	25·2	14·0	180·00	231	90·1	86·1	351·04
030	219·4	226·2	0·00	241	54·6	61·9	275·46
040	0·0	7·5	180·00	331	78·2	80·2	343·86
050	64·1	69·1	0·00	002	235·0	289·0	0·00
110	133·4	122·2	122·09	012	19·6	17·6	180·00
120	107·0	98·4	242·88	022	15·7	9·4	180·00
130	64·8	61·6	127·78	032	197·0	198·4	0·00
140	100·8	97·1	98·10	042	0·0	9·9	180·00
150	85·6	77·5	252·15	112	112·9	108·4	120·00
220	152·8	120·3	240·46	122	88·7	83·1	248·20
230	64·2	59·2	7·69	132	58·4	55·9	128·51
240	90·0	89·1	228·53	142	90·2	89·3	94·31
330	130·6	127·3	1·61	222	116·0	116·1	240·63
001	58·8	51·1	0·00	202	53·1	52·2	77·49
011	15·9	16·1	180·00	003	50·4	52·0	0·00
021	100·7	87·6	0·00	013	14·6	10·8	180·00
031	84·2	79·3	0·00	023	69·2	65·6	0·00
041	81·7	71·0	180·00	033	69·2	69·3	180·00
051	73·2	73·5	0·00	113	170·9	168·7	120·51
113	212·2	203·6	119·26	123	39·8	35·9	338·43
121	56·3	48·6	5·75	133	44·1	46·3	126·42
131	57·9	56·4	127·88	223	126·5	127·4	235·43
141	152·5	147·0	138·58	004	185·1	202·0	0·00

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Table 3. *Interatomic distances* Å *for* Yb_3Ge_5

The e.s.d.'s include only the uncertainties in the positional parameters.

Yb – 4 Ge(2)	3·015 ± 0·006 Å
– 4 Ge(1)	3·016 ± 0·002
– 2 Ge(2)	3·356 ± 0·021
– 4 Yb	3·778 ± 0·005
– 2 Yb	4·166
Ge(1) – 3 Ge(2)	2·585 ± 0·017
– 6 Yb	3·016 ± 0·002
– 3 Ge(1)	3·928
Ge(2) – 2 Ge(1)	2·585 ± 0·017
– 2 Ge(2)	2·979 ± 0·044
– 4 Yb	3·015 ± 0·006
– 2 Yb	3·356 ± 0·021

Acta Cryst. (1965). **18**, 1086

The rate of refinement of coordinates for the minimum residual method in three dimensions.

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(*Received* 2 *November* 1964)

Bhuiya & Stanley (1963) proposed a method of refinement in which each parameter, u_j, is varied in turn from $u_j - n\Delta u_j$ to $u_j + n\Delta u_j$ in $2n$ increments of Δu_j. The lowest value of the residual, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, within the range of variation is noted and the corresponding value of u_j is taken as the best value of the parameter within the permitted range of variation. This method has worked very well in two-dimensional studies and the rate of refinement in two dimensions has been studied in detail by Stanley (1964) who showed that, for small errors, the rate of refinement could be related to the average error in the coordinates on the basis of the figures given by Luzzati (1952) for the residual as a function of error in coordinates and sin θ.

Tables 1 and 2 give values of the residual R for centrosymmetric and non-centrosymmetric space groups, for three-dimensional data, as a function of the standard devi-

Table 1. *Values of* $(\bar{1})R$ *as a function of* $\sigma(r)$ *and* B

$\sigma(r)$ \ B	0.0	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0
0.00	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.02	0.114	0.109	0.105	0.100	0.096	0.092	0.088	0.084	0.080	0.077	0.074
0.04	0.219	0.211	0.202	0.194	0.186	0.177	0.170	0.162	0.166	0.149	0.143
0.06	0.314	0.302	0.291	0.279	0.268	0.256	0.246	0.235	0.226	0.217	0.209
0.08	0.398	0.384	0.370	0.356	0.342	0.328	0.315	0.302	0.291	0.280	0.270
0.10	0.471	0.456	0.439	0.424	0.408	0.393	0.378	0.363	0.350	0.337	0.326
0.12	0.534	0.518	0.501	0.484	0.466	0.450	0.433	0.418	0.403	0.390	0.377
0.14	0.587	0.570	0.553	0.535	0.517	0.500	0.483	0.467	0.451	0.437	0.423
0.16	0.630	0.614	0.597	0.579	0.561	0.544	0.526	0.510	0.494	0.479	0.465
0.18	0.667	0.651	0.634	0.616	0.599	0.582	0.564	0.548	0.532	0.517	0.503
0.20	0.696	0.681	0.665	0.648	0.631	0.614	0.597	0.581	0.565	0.551	0.536
0.22	0.720	0.705	0.690	0.674	0.658	0.642	0.626	0.610	0.595	0.580	0.566
0.24	0.738	0.725	0.711	0.696	0.681	0.665	0.650	0.635	0.620	0.606	0.592
0.26	0.752	0.740	0.727	0.714	0.700	0.685	0.671	0.657	0.643	0.629	0.616
0.28	0.764	0.753	0.741	0.729	0.716	0.702	0.689	0.676	0.663	0.650	0.637
0.30	0.772	0.763	0.752	0.741	0.729	0.717	0.704	0.692	0.679	0.667	0.656
0.32	0.780	0.771	0.762	0.751	0.740	0.729	0.717	0.706	0.694	0.683	0.672
0.34	0.786	0.778	0.769	0.760	0.750	0.739	0.729	0.718	0.707	0.696	0.686
0.36	0.791	0.784	0.776	0.767	0.758	0.749	0.739	0.729	0.719	0.709	0.699
0.38	0.795	0.788	0.781	0.773	0.765	0.756	0.747	0.738	0.729	0.720	0.711
0.40	0.798	0.793	0.786	0.779	0.771	0.763	0.755	0.746	0.738	0.729	0.721
0.42	0.801	0.796	0.790	0.786	0.777	0.769	0.761	0.754	0.746	0.738	0.730
0.44	0.804	0.799	0.794	0.788	0.781	0.775	0.767	0.760	0.753	0.745	0.738
0.46	0.807	0.802	0.797	0.791	0.785	0.779	0.773	0.766	0.759	0.752	0.745
0.48	0.809	0.805	0.800	0.795	0.789	0.783	0.777	0.771	0.764	0.758	0.752
0.50	0.817	0.807	0.802	0.798	0.792	0.787	0.781	0.775	0.770	0.763	0.757

Table 2. *Values of* $(1)R$ *as a function of* $\sigma(r)$ *and* B

$\sigma(r)$ \ B	0.0	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0
0.00	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.02	0.073	0.070	0.068	0.065	0.062	0.059	0.056	0.054	0.051	0.049	0.047
0.04	0.144	0.138	0.132	0.127	0.121	0.116	0.110	0.106	0.101	0.097	0.093
0.06	0.211	0.203	0.195	0.187	0.179	0.171	0.163	0.156	0.149	0.143	0.137
0.08	0.272	0.262	0.252	0.242	0.232	0.222	0.213	0.204	0.195	0.187	0.180
0.10	0.325	0.314	0.303	0.291	0.280	0.268	0.256	0.247	0.238	0.229	0.220
0.12	0.370	0.359	0.346	0.334	0.322	0.310	0.298	0.287	0.276	0.266	0.257
0.14	0.409	0.397	0.384	0.371	0.359	0.346	0.334	0.322	0.311	0.300	0.290
0.16	0.441	0.429	0.416	0.404	0.391	0.378	0.365	0.353	0.342	0.331	0.321
0.18	0.467	0.456	0.443	0.431	0.418	0.405	0.393	0.381	0.369	0.358	0.348
0.20	0.488	0.477	0.466	0.454	0.441	0.429	0.417	0.405	0.394	0.383	0.372
0.22	0.505	0.495	0.484	0.473	0.461	0.449	0.437	0.426	0.415	0.404	0.394
0.24	0.518	0.509	0.499	0.488	0.477	0.466	0.455	0.444	0.434	0.423	0.413
0.26	0.529	0.520	0.511	0.501	0.491	0.480	0.470	0.460	0.450	0.440	0.431
0.28	0.537	0.529	0.521	0.512	0.502	0.493	0.485	0.473	0.464	0.455	0.446
0.30	0.544	0.536	0.528	0.521	0.512	0.503	0.494	0.485	0.476	0.467	0.459
0.32	0.549	0.543	0.536	0.528	0.520	0.512	0.504	0.495	0.487	0.479	0.471
0.34	0.553	0.547	0.541	0.534	0.527	0.519	0.512	0.504	0.496	0.489	0.481
0.36	0.557	0.552	0.546	0.540	0.533	0.526	0.519	0.512	0.505	0.498	0.491
0.38	0.560	0.555	0.550	0.544	0.538	0.532	0.525	0.519	0.512	0.505	0.498
0.40	0.563	0.558	0.553	0.548	0.543	0.537	0.531	0.525	0.518	0.512	0.506
0.42	0.565	0.561	0.557	0.552	0.547	0.541	0.536	0.530	0.524	0.518	0.513
0.44	0.567	0.563	0.559	0.555	0.550	0.545	0.540	0.535	0.529	0.524	0.519
0.46	0.569	0.565	0.562	0.558	0.553	0.549	0.544	0.539	0.534	0.529	0.524
0.48	0.570	0.567	0.564	0.560	0.556	0.552	0.547	0.542	0.538	0.533	0.528
0.50	0.572	0.569	0.566	0.562	0.558	0.554	0.550	0.546	0.541	0.537	0.533