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Thorium — Transition Metals Ternary Germanides

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New ternary germanides of the general composition ThM_2Ge_2 were found to exist in the systems Th-Cr-Ge, Th-Mn-Ge, Th-Fe-Ge, Th-Co-Ge, Th-Ni-Ge and Th-Cu-Ge. The crystal structure analysis by means of the x-ray powder diffraction method showed that these compounds are isostructural with the compounds ThM_2Si_2 (M = Cr, Mn, Fe, Co, Ni and Cu), discovered in this laboratory. The tetragonal unit cell contains two formula units. Space group is I4/mmm. The atomic positions of thorium and the transition metal are defined by special position 2(a) and 4(d), respectively, while the variable parameter z determining the position 4(e) of the germanium atoms was obtained by computing the electron density distribution along the c-axis.

INTRODUCTION

A great variety of very interesting and often new crystal structures found in the ternary intermetallic systems, together with the broad interest for such systems from the point of view of the practical application, has put an ever increasing accent on the research in this field. The silicides and germanides as well as carbides, nitrides etc., are of special interest because of its perspective use in nuclear-technology. Besides, these compounds have interesting chemical and physical properties which deserve to be investigated. In this article some new ternary germanides of thorium and transition metals of the first series are described. They were found to be isostructural with the previously discovered ThM_2Si_2 compounds[1].

EXPERIMENTAL

Materials

The following components were used in the elemental form: thorium (Thorium pulver-Nuclearrein, Merck, Darmstadt), chromium (Chromium metal, purity not quoted, The Coleman & Bell Co., USA), iron (Ferrum reductum p.a., Chinoin, Budapest), manganese (Manganese flakes, 99.9%, Light & Co.), cobalt (Cobalt sponge, standard purity, Johnson, Matthey & Co.), nickel (Carbonyl nickel. 99.8%, T. Schuchardt & Co., München), copper (Kupfer gepulvert, elektrolytisch, Merck, Darmstadt) and germanium (Germanium pss., Fluka A. G., Switzerland). Chromium and manganese were chrushed and sieved through a 200 mesh standard sieve.

Mixtures of the corresponding components were cold pressed in small prisms. A thin molybdenum wire was pressed into one end of the compacted mixture and served later for the suspension of the sample in the specially designed electron beam furnace.[2]

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An exothermic reaction was initiated by raising slowly the electron emission current. Samples were then subjected to a thermal treatment at 900°C during 120 hours. This was performed in sealed quartz tubes containing purified argon under reduced pressure. Such treatment did not change the phase composition but usualy introduced an increased amount of thorium oxide.

X-ray Examination

X-ray powder diffraction records were obtained from the most homogeneous parts of the specimens by means of a recording Philips diffractometer equipped with a Geiger counter tube, using filtered CuK radiation. Inevitably present weak diffraction lines of thorium oxide were used as an internal standard for accurate measurements of lattice parameters.

RESULTS

With the exception of $ThCr_2Ge_2$, all compounds were obtained in the single phase form, and showed no unidentified peaks in the powder diffraction records. This indicates that the composition of monophase specimens probably does not correspond to the ideal formula $ThCr_2Ge_2$, which can be explained either in terms of a defect structure or as the distribution of Cr and Ge being statistical rather than in the ratio 1:1. The indexing by means of Bunn charts and the analysis of the systematically absent reflections revealed that these compounds are of the same structure type as ThM_2Si_2 (M = Cr, Mn, Fe, Co, Ni and Cu), prepared in this laboratory. The dimensions of the tetragonal unit cells containing two formula units of ThM_2Ge_2 are presented in Table I. The atomic positions in the space group I4/mmm, are the same as

TABLE I

Unit Cell Dimensions of ThM_2Ge_2

	a (Å)	c (Å)
$ThCr_2Ge_2$	(4.11)	(10.83)
$ThMn_2Ge_2$	4.084 ± 0.002	10.930 ± 0.004
$ThFe_2Ge_2$	4.098 ± 0.002	10.222 ± 0.004
$ThCo_2Ge_2$	4.109 ± 0.002	9.934 ± 0.004
$ThNi_2Ge_2$	4.161 ± 0.002	9.677 ± 0.004
$ThCu_2Ge_2$	4.152 ± 0.002	10.140 ± 0.004

TABLE II

Interatomic Distances in ThM_2Ge_2 (Å)

	M =	Cr	Mn	Fe	Co	Ni	Cu
	z =	(0.374)	0.385	0.371	0.372	0.367	0.379
Th 2(a)	8 M 4(d)	(3.40)	3.41_1	3.27_6	3.22_3	3.19_1	3.27_7
	8 Ge 4(e)	(3.22)	3.15_4	3.18_3	3.18_9	3.21_8	3.18_2
	2 Ge 4(e)	(4.05)	4.20_8	3.79_2	3.69_5	3.55_1	3.84_3
M 4(d)	4 M 4(d)	(2.91)	2.88_8	2.89_8	2.90_5	2.94_2	2.93_6
	4 Ge 4(e)	(2.46)	2.51_9	2.39_3	2.38_5	2.36_8	2.45_4

TABLE III

Diffractometer Data for $ThNi_2Ge_2$

h k l	$\sin^2\Theta_o$	$\sin^2\Theta_c$	I_o	I_c
0 0 2	0.0253	0.0254	18.3	11.4
1 0 1	0.0407	0.0407	73.3	71.9
1 1 0	0.0687	0.0686	69.6	75.5
1 0 3	0.0914	0.0914	190.6	204.6
1 1 2	0.0939	0.0940	171.1	189.3
0 0 4	0.1016	0.1015	22.0	16.2
2 0 0	0.1368	0.1373	90.4	119.7
2 0 2	0.1625	0.1627	12.2	5.7
1 1 4	—	0.1702	—	1.0
2 1 1	0.1778	0.1779	26.9	21.4
1 0 5	0.1927	0.1927	58.6	50.4
0 0 6	0.2281	0.2281	97.8	2.3
2 1 3		0.2283		100.4
2 0 4	0.2384	0.2384	17.1	17.5
2 2 0	0.2741	0.2741	30.5	38.0
1 1 6	0.2966	0.2966	33.0	41.9
2 2 2	—	0.2995	—	2.4
3 0 1	—	0.3147	—	3.4
2 1 5	0.3296	0.3297	53.8	41.2
1 0 7	—	0.3506	—	2.1
3 1 0	0.3427	0.3427	15.9	13.6
2 0 6	0.3655	0.3651	30.5	4.5
3 0 3		0.3654		22.8
3 1 2	0.3679	0.3680	48.8	42.7
2 2 4	0.3756	0.3755	9.8	8.2
0 0 8	0.4058	0.4055	9.8	9.5
3 1 4	—	0.4440	—	0.2
3 2 1	—	0.4518	—	5.2
3 0 5	0.4669	0.4668	12.2	12.2
2 1 7	—	0.4818	—	2.7
1 1 8	0.4742	0.4740	9.8	7.6
2 2 6	0.5026	0.5022	30.5	3.1
3 2 3		0.5025		30.3
2 0 8	0.5428	0.5426	22.0	26.4
1 0 9	0.5481	0.5474	12.2	3.9
4 0 0		0.5483		13.6
3 1 6	0.5711	0.5708	28.1	33.8
4 0 2	—	0.5736	—	1.0
4 1 1	—	0.5889	—	4.0
3 2 5	0.6041	0.6039	19.5	19.4
3 3 0	—	0.6168	—	3.4
3 0 7	—	0.6188	—	1.1
0, 0, 1 0	—	0.6336	—	—
4 1 3	0.6397	0.6396	22.0	25.2
3 3 2	coinc.	0.6421	8.0	coinc. 12.0
4 0 4	—	0.6496	—	4.7
2 2 8	0.6798	0.6796	17.1	24.7

those ascribed to the analogous series of silicides, *i.e.* 2Th in (a), 4M in (d) and 4Ge in (e)[3]. The correlation of the observed and calculated relative intensities allows the possibility of the partially statistical distribution of smaller atoms over the points (d) and (e). The prolonged heat treatment as described in the experimental part of this article, improved the agreement

TABLE IV

Diffractometer Data for $ThCr_2Ge_2$

h k l	$\sin^2\Theta_o$	$\sin^2\Theta_c$	I_o
0 0 2	0.0203	0.0202	28
1 0 1	0.0402	0.0403	18
1 1 0	0.0703	0.0704	30
1 0 3 0 0 4	0.0805	0.0808 0.0809	100
1 1 2	0.0905	0.0907	76
2 0 0	0.1403	0.1407	22
1 1 4	—	0.1512	—
2 0 2 1 0 5	0.1618	0.1609 0.1615	45
2 1 1 0 0 6	0.1813	0.1809 0.1819	5
2 1 3 2 0 4	0.2215	0.2214 0.2216	28
1 1 6	0.2523	0.2523	11
2 2 0 1 0 7	0.2824	0.2814 0.2828	10
2 2 2 2 1 5	0.3022	0.3016 0.3022	25
3 0 1	—	0.3216	—
2 0 6 0 0 8	0.3235	0.3226 0.3234	10
3 1 0	0.3513	0.3517	5
3 0 3 2 2 4	0.3620	0.3621 0.3623	16

between the observed intensities and those which were calculated for the assumed positions. Final decision can not be made because of the nearly equal scattering powers of transition metals and germanium. The possible tendency of transition metal atoms to pairing, which in this case is suggested by the less pronounced nonmetallic character of germanium, as compared to silicon, should not be neglected.

The variable parameter z for the position (e) was obtained by computing the electron density distribution along the c-axis by using all reflections recorded with the signs determined by the thorium atom. The Fourier series $\varrho\,(x, y, z)_{\substack{x=0\\y=0}} \sim \Sigma\, F(hkl)\cos 2\pi lz$ were computed by means of Beevers-Lipson strips. The resulting distribution of the electron density along the c-axis for all compounds gave clearly resolved maxima indicating the position of germanium atoms. Table II gives the numerical values for the parameter z and the interatomic distances. It can be noticed that the parameter z assumes the same values as in the structure of ThM_2Si_2. Since it was not possible to determine these values for $ThFe_2Si_2$ and $ThCo_2Si_2$ because of the unfavourable peak to background ratio, we may assume that the z-values for $ThFe_2Ge_2$ and $ThCo_2Ge_2$ hold equally well in the former case. The comparison between the observed and the calculated intensities for $ThNi_2Ge_2$, together with the corresponding values $\sin^2\Theta$ are given in Table III. The data for other compounds are listed in Tables IV—VIII.

TABLE V

Diffractometer Data for $ThMn_2Ge_2$

h k l	$\sin^2\Theta_o$	$\sin^2\Theta_c$	I_o
0 0 2	0.0200	0.0199	12
1 0 1	0.0406	0.0406	28
1 1 0	0.0712	0.0713	38
0 0 4	0.0805	0.0795	85
1 0 3		0.0804	
1 1 2	0.0911	0.0910	100
2 0 0	0.1424	0.1423	46
1 1 4	—	0.1506	—
1 0 5	0.1600	0.1597	50
2 0 2	0.1625	0.1621	8
0 0 6	—	0.1788	—
2 1 1	0.1828	0.1828	11
2 0 4	0.2226	0.2217	73
2 1 3		0.2226	
1 1 6	0.2503	0.2499	19
1 0 7	0.2791	0.2789	5
2 2 0	0.2846	0.2846	22
2 1 5	0.3021	0.3020	32
2 2 2		0.3044	
0 0 8	0.3179	0.3178	7
2 0 6	—	0.3211	—
3 0 1	—	0.3251	—
3 1 0	0.3558	0.3557	9
2 2 4	0.3645	0.3640	14
3 0 3		0.3648	
3 1 2	0.3755	0.3756	22
1 1 8	0.3894	0.3890	5
2 1 7	0.4215	0.4212	3
3 1 4	—	0.4352	—
1 0 9	—	0.4378	—
3 0 5	0.4443	0.4443	9
2 0 8	0.4601	0.4601	17
2 2 6	—	0.4634	—
3 2 1	0.4674	0.4673	3
0 0 10	—	0.4966	—
3 2 3	0.5068	0.5071	12
3 1 6	0.5342	0.5345	12
3 0 7	—	0.5635	—
1 1 10	0.5687	0.5678	10
4 0 0		0.5692	
2 1 9	—	0.5801	—
3 2 5	0.5865	0.5866	15
4 0 2	—	0.5890	—
2 2 8	0.6023	0.6024	10
4 1 1	—	0.6097	—
1 0 11	—	0.6370	—
2 0 10	0.6395	0.6389	4
3 3 0		0.6403	
4 0 4	0.6488	0.6486	8

Preliminary results of the measurement of magnetic susceptibilities, using the Gouy method, indicate a very interesting dependence of magnetic moments on the transition metal atom. The general trend is very similar to that found in the series of the transition metal and rare earth ions[4]. We met

TABLE VI

Diffractometer Data for $ThFe_2Ge_2$

h k l	$\sin^2\Theta_o$	$\sin^2\Theta_c$	I_o
0 0 2	0.0226	0.0227	10
1 0 1	0.0410	0.0411	55
1 1 0	0.0707	0.0708	59
1 0 3	0.0867	0.0866	142
0 0 4	0.0910	0.0910	16
1 1 2	0.0935	0.0935	134
2 0 0	0.1413	0.1415	65
1 1 4	—	0.1618	—
2 0 2	—	0.1643	4
1 0 5	0.1777	0.1776	35
2 1 1	0.1824	0.1823	12
0 0 6	—	0.2044	2
2 1 3	0.2280	0.2277	70
2 0 4	0.2324	0.2322	15
1 1 6	—	0.2751	—
2 2 0	0.2824	0.2826	15
2 2 2	0.3056	0.3053	5
1 0 7	—	0.3135	—
2 1 5	0.3187	0.3186	32
3 0 1	—	0.3236	—
2 0 6	0.3463	0.3457	5
3 1 0	0.3525	0.3533	5
0 0 8	—	0.3634	—
3 0 3	0.3692	0.3691	10
2 2 4	—	0.3735	—
3 1 2	0.3757	0.3756	25
1 1 8	0.4348	0.4341	7
3 1 4	—	0.4441	—
2 1 7	—	0.4549	—
3 0 5	0.4601	0.4599	10
3 2 1	—	0.4649	—
2 2 6	—	0.4870	—
1 0 9	—	0.4952	—
2 0 8	0.5054	0.5047	15
3 2 3	0.5106	0.5104	22
3 1 6	0.5578	0.5577	15
4 0 0	0.5653	0.5653	10

TABLE VII

Diffractometer Data for $ThCo_2Ge_2$

h k l	$\sin^2\Theta_o$	$\sin^2\Theta_c$	I_o
0 0 2	0.0240	0.0241	26
1 0 1	0.0412	0.0412	76
1 1 0	0.0704	0.0704	72
1 0 3	0.0894	0.0894	200
1 1 2	0.0946	0.0945	186
0 0 4	0.0964	0.0964	22
2 0 0	0.1405	0.1408	102
2 0 2	—	0.1649	—
1 1 4	—	0.1665	—
2 1 1	0.1821	0.1817	20
1 0 5	0.1856	0.1857	46

h k l	$\sin^2\Theta_o$	$\sin^2\Theta_c$	I_o
0 0 6	—	0.2164	—
2 1 3	0.2302	0.2298	98
2 0 4	0.2370	0.2368	18
2 2 0	0.2811	0.2811	32
1 1 6	0.2868	0.2867	38
2 2 2	—	0.3052	—
3 0 1	—	0.3223	—
2 1 5	0.3259	0.3260	50
1 0 7	—	0.3297	—
3 1 0	—	0.3514	—
2 0 6	—	0.3570	—
3 0 3	0.3704	0.3704	20
3 1 2	0.3755	0.3755	40
2 2 4	—	0.3773	—
0 0 8	0.3841	0.3848	20
3 1 4	—	0.4476	—
1 1 8	—	0.4550	—
3 2 1	—	0.4628	—
3 0 5	0.4665	0.4666	14
2 1 7	—	0.4703	—
3 2 3	0.5108	0.5109	34
1 0 9	—	0.5221	—
2 0 8	0.5253	0.5253	27
4 0 0	0.5623	0.5622	15
3 1 6	0.5677	0.5678	26
4 1 1	—	0.6034	—
3 2 5	0.6067	0.6071	18

TABLE VIII

Diffractometer Data for $ThCu_2Ge_2$

h k l	$\sin^2\Theta_o$	$\sin^2\Theta_c$	I_o
0 0 2	0.0231	0.0231	22
1 0 1	0.0404	0.0403	38
1 1 0	0.0689	0.0689	39
1 0 3	0.0864	0.0865	140
1 1 2 0 0 4	0.0919	0.0920 0.0925	134
2 0 0	0.1379	0.1379	48
2 0 2 1 1 4	0.1617	0.1610 0.1612	10
2 1 1 1 0 5	0.1789	0.1779 0.1789	76
0 0 6	—	0.2077	—
2 1 3	0.2242	0.2240	60
2 0 4	0.2297	0.2300	14
2 2 0 1 1 6	0.2763	0.2753 0.2766	42
2 2 2	—	0.2984	—
3 0 1 2 1 5 1 0 7	0.3164	0.3155 0.3163 0.3172	44
3 1 0	0.3445	0.3442	10
2 0 6	0.3455	0.3454	6
3 0 3	0.3617	0.3617	20

h k l	$\sin^2\Theta_o$	$\sin^2\Theta_c$	I_o
3 1 2	0.3672	0.3672	34
2 2 4	0.3692	0.3677	34
0 0 8		0.3693	
3 1 4	0.4377	0.4365	18
1 1 8		0.4381	
3 2 1	0.4543	0.4532	20
3 0 5		0.4540	
2 1 7		0.4548	
2 2 6	—	0.4831	—
3 2 3	0.4991	0.4993	16
1 0 9	0.5016	0.5019	10
2 0 8	0.5068	0.5069	24
4 0 0	0.5517	0.5507	14
3 1 6		0.5519	
4 0 2	—	0.5737	—
0 0 10	—	0.5770	—
4 1 1	0.5911	0.5908	18
3 2 5		0.5917	
3 0 7	—	0.5925	—
3 3 0	—	0.6195	—
4 1 3	0.6358	0.6370	14
2 1 9	0.6392	0.6396	14
3 3 2	—	0.6426	—
4 0 4	—	0.6430	—
2 2 8	0.6448	0.6446	30
1 1 10		0.6459	

the very same behaviour, but with smaller absolute values of magnetic moments, for the isomorphous silicides. We hope that the anticipated study of temperature-dependent magnetic behaviour and neutron diffraction data will enable us to clarify the magnetic structure of these compounds.

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REFERENCES

1. Z. Ban and M. Sikirica, to be published.
2. B. Kamenar, Z. Ban, and M. Dadić, *Croat. Chem. Acta* **31** (1959) 159.
3. *International Tables for X-ray Crystallography*, Birmingham, 1952.
4. J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Oxford University Press, London, 1959, p. 243 and 285.

IZVOD

Ternarni germanidi torija s prelaznim metalima

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Nađeni su novi ternarni germanidi. Opća im je formula ThM_2Ge_2. Rendgenska strukturna analiza Debye-Scherrerovom metodom pokazala je da je to niz spojeva koji su izostrukturni s ranije otkrivenim ternarnim silicidima analognoga sastava. Varijabilni parametar, koji definira položaj atoma germanija u elementarnoj ćeliji, određen je računanjem raspodjele elektronske gustoće uzduž osi c.

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