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Carbides with Filled Re_3B-Type Structure

Anne M. Witte and Wolfgang Jeitschko

Anorganisch-Chemisches Institut, Universität Münster, Wilhelm-Klemm-Strasse 8, D-48149 Münster, Germany

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The new compounds AFe_2SiC (A = Y, Sm, Gd, Tb, Ho, Er, Tm, Lu, Th, U) were prepared by arc-melting cold-pressed pellets of the elemental components. They are isotypic with the orthorhombic $DyFe_2SiC$-type structure, which was refined from single-crystal X-ray data of $ThFe_2SiC$: $Cmcm$, a = 386.32(6) pm, b = 1080.6(1) pm, c = 695.0(1) pm, Z = 4, R = 0.020 for 559 structure factors and 17 variable parameters. The polyanionic iron–silicon–carbon network is three-dimensionally infinite. The carbon atoms are situated in octahedral voids formed by four thorium and two iron atoms. The hydrolysis of $ErFe_2SiC$ with diluted hydrochloric acid yields mainly methane besides C_2 and C_3 hydrocarbons. A large number of compounds can be classified to crystallize with a filled-up version of the Re_3B-type structure. They are isotypic with V_3AsC, where the positions of the vanadium and arsenic atoms correspond to the atomic positions of Re_3B and the carbon atoms fill octahedral voids formed by the vanadium atoms. The $DyFe_2SiC$-type structure also can be described as a filled-up Re_3B structure; however, the carbon atoms of $DyFe_2SiC$ occupy different octahedral voids.

INTRODUCTION

We have recently reported on the two silicide carbides $U_3Si_2C_2$ and $U_{20}Si_{16}C_3$ (1). While the silicon and carbon atoms of $U_3Si_2C_2$ form anionic Si–C units derived from methyl silane $H_3C–SiH_3$, most silicon atoms of $U_{20}Si_{16}C_3$ form planar Si_6 rings. In addition the latter compond contains isolated silicon and carbon atoms. This is also the case for the compound $DyFe_2SiC$, which was communicated by Paccard *et al.* (2) some years ago. We have explored the stability range of this structure type and report 10 isotypic compounds as well as hydrolysis results and a structure refinement of the isotype $ThFe_2SiC$.

SAMPLE PREPARATION, PROPERTIES, AND LATTICE CONSTANTS

Starting materials were filings of the rare-earth metals (>99.9%), thorium ingots (nominal purity 99.9%), uranium platelets (Merck: "nuklearrein"), iron powder (Alpha, 99.9%, 325 mesh), silicon powder (Fluka, >99.9%, 100 mesh), and graphite flakes (Alpha, >99.5%, 20 mesh). The uranium platelets were cleaned with concentrated nitric acid to remove oxide impurities. Filings of thorium were prepared under dried paraffin oil. They were washed with dried cyclohexane under argon. The uranium platelets and the thorium filings were not allowed to come into contact with air prior to the reactions.

The samples were prepared by arc-melting of small (~0.5 g) cold-pressed pellets of the elemental components of the ideal compositions in an argon (99.996%) atmosphere. The argon was further purified by repeatedly melting a titanium button prior to the reactions. The samples were then wrapped in tantalum foil and annealed in evacuated silica tubes for 30 days at 1000°C.

The quaternary silicide carbides are all stable in air for several months. Single crystals are gray with metallic luster; powdered samples are dark gray. Energy-dispersive analyses of the new silicide carbides in a scanning electron microscope were compatible with the ideal composition and did not reveal any impurity elements heavier than sodium.

The powdered samples were characterized by Guinier powder diagrams with $CuK\alpha_1$ radiation using α-quartz (a = 491.30 pm, c = 540.46 pm) as a standard. Indices were assigned on the basis of the cell found by the single-crystal investigation. The identification of the diffraction lines was facilitated by intensity calculations (3) using the positional parameters of $DyFe_2SiC$. The lattice contants obtained by least-squares fits are listed in Table 1.

HYDROLYSIS RESULTS

While the samples do not visibly react with water, hydrolysis with hydrochloric acid proceeds rather fast. A sample of $ErFe_2SiC$ was hydrolyzed with 2 N hydrochloric acid at room temperature. The emerging gaseous products were analyzed in a mass spectrometer (CH5, Varian MAT, 70 eV, 20°C). Besides a nonaccounted amount of hydrogen, the reaction product consisted of about 80% methane, and even though the compound contains only isolated carbon atoms, some 20% of C_2 and C_3 hydrocarbons were observed. The occurrence of these higher hydrocarbons can be ascribed to catalytic effects of the

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TABLE 1
Lattice Constants of the Carbides with Orthorhombic $DyFe_2SiC$-Type Structure[a]

Compound	a (pm)	b (pm)	c (pm)	V (nm^3)
YFe_2SiC	372.6(1)	1057.2(2)	686.3(1)	0.2703
$SmFe_2SiC$	380.3(1)	1061.4(2)	688.6(1)	0.2779
$GdFe_2SiC$	376.7(1)	1056.7(3)	686.9(1)	0.2734
$TbFe_2SiC$	374.0(1)	1055.2(2)	685.4(1)	0.2705
$DyFe_2SiC$	372.1(1)	1055.5(2)	685.2(1)	0.2691
$DyFe_2SiC$[b]	371.2(1)	1053.1(3)	686.3(1)	0.2683
$HoFe_2SiC$	370.6(1)	1054.4(1)	684.7(1)	0.2676
$ErFe_2SiC$	368.6(1)	1053.7(3)	683.5(1)	0.2655
$TmFe_2SiC$	366.2(1)	1053.7(2)	682.6(1)	0.2634
$LuFe_2SiC$	363.6(1)	1053.7(2)	681.4(1)	0.2611
$ThFe_2SiC$	386.3(1)	1080.6(2)	695.0(1)	0.2901
UFe_2SiC	368.9(1)	1071.1(2)	678.0(1)	0.2679

[a] Standard deviations in the positions of the least-significant digits are given in parentheses throughout the paper.
[b] Data taken from Ref. (2).

TABLE 2
Crystallographic Data for $ThFe_2SiC$

Lattice constants	Table 1
Formula units/cell	$Z = 4$
Space group	*Cmcm* (No. 63)
Formula weight	383.8
Calculated density (g/cm^3)	$\rho_c = 8.79$
Crystal dimensions (μm^3)	$20 \times 20 \times 60$
$\theta/2\theta$ scans up to	$2\theta = 80°$
Range in hkl	$\pm 7, \pm 18, \pm 12$
Total no. of reflections	4262
Absorption correction	From psi scans
Transmission coefficient (highest/lowest)	1.33
Unique reflections	869
Inner residual	$R_i = 0.033$
Reflections with $I > 3\sigma(I)$	559
No. of variables	17
Extinction correction value, g[a]	$8.7(3) \times 10^{-7}$
Conventional residual (on F values)	$R = 0.020$
Weighted residual	$R_w = 0.020$

[a] The extinction correction value g is defined by correction factor = $1/(1 + g \cdot I_c)$.

iron atoms. Similar mixtures of hydrolysis products were observed for various ternary carbides containing transition metals (4), while CaC_2 and Al_4C_3 are well known to yield solely acetylene and methane, respectively.

STRUCTURE REFINEMENT OF $ThFe_2SiC$

Single crystals of this compound were isolated from the annealed, crushed sample. Precession photographs showed the Laue symmetry *mmm*. They were fully compatible with the space group *Cmcm* established for $DyFe_2SiC$ (2). Intensity data were collected on an automated four-circle diffractometer with graphite monochromated Mo$K\alpha$ radiation and a scintillation counter with pulse-height discrimination. The crystallographic data and some results are summarized in Table 2.

Starting with the positional parameters of $DyFe_2SiC$, full-matrix least-squares refinements were carried out with atomic scattering factors (5), corrected for anomalous dispersion (6). The weighting scheme was based on the counting statistics. To check for deviations from the ideal composition, in one series of least-squares cycles the scale factor was held constant and all occupany parameters were allowed to vary along with the thermal parameters. No significant deviations from the full occupancies were found and in the final least-squares cycles the ideal occupancies were resumed. The metal and silicon atoms were refined with anisotropic and the carbon atoms with isotropic thermal parameters. The final conventional and weighted residuals are $R = 0.020$ and $R_w = 0.020$ for 559 structure factors and 17 variable parameters. A final difference Fourier analysis showed the value of 1.39 $e/Å^3$ as highest residual density, too small and too close to the thorium site to be suitable for an additional atomic position. The atomic parameters and interatomic distances are listed in Tables 3 and 4. A drawing of the structure and the coordination polyhedra is shown in Fig. 1. The structure factor tables and the anisotropic thermal parameters are available from the authors.

TABLE 3
Atomic Parameters of $ThFe_2SiC$[a]

Atom	*Cmcm*	Occupancy	x	y	z	B
Th	4*c*	1.002(1)	0	0.05275(3)	1/4	0.327(3)
Fe	8*f*	0.977(2)	0	0.66585(7)	0.5611(1)	0.466(9)
Si	4*c*	0.96(1)	0	0.7719(2)	1/4	0.55(3)
C	4*b*	0.97(2)	0	1/2	0	0.50(8)

[a] The last column contains the isotropic thermal parameter of the carbon atoms and the equivalent isotropic thermal parameters (×100, in units of nm^2) of the other atoms. The occupancy parameters were refined in separate least-squares cycles. In the final cycles the ideal occupancies were assumed.

TABLE 4
Interatomic Distances (pm) in the Structure of $ThFe_2SiC$[a]

Th:	4 C	266.0(1)	Fe:	1 C	184.2(1)	Si:	4 Fe	243.0(1)
	1 Si	303.5(2)		2 Si	243.0(1)		2 Fe	244.7(1)
	2 Si	305.6(2)		1 Si	244.7(1)		1 Th	303.5(2)
	4 Fe	314.7(1)		1 Fe	262.5(1)		2 Th	305.6(2)
	2 Fe	331.2(1)		2 Fe	278.6(1)			
	4 Fe	332.2(1)		2 Th	314.7(1)	C:	2 Fe	184.2(1)
	2 Th	365.7(1)		1 Th	331.2(1)		4 Th	266.0(1)
	2 Th	386.3(1)		2 Th	332.2(1)			

[a] All distances shorter than 395 pm (Th neighbors) and 340 pm (Fe, Si,C) are listed.

DISCUSSION

The cell volumes of the $DyFe_2SiC$-type compounds (Fig. 2) show the usual lanthanoid contraction. The cell volume of the yttrium compound is similar to that of the terbium compound as is frequently the case for ternary rare-earth carbides (7). As could be expected, the cell volume of the thorium compound is larger than that of the uranium compound; however, at first sight the difference of these two cell volumes appears to be rather high (8%). Nevertheless, this difference seems to be reasonable considering that the cell volumes of ThC and UC (8) differ by 24%.

It is known that the carbon positions in binary and ternary transition metal carbides are not always fully occupied. Some recently reported structures with partially occupied carbon positions include $LaMn_{11}C_{2-x}$ (9), $Pr_2Mn_{17}C_{3-x}$ (10), $Tb_2Mn_{17}C_{3-x}$ (11), and $Ce_2Ni_{22}C_{3-x}$ (12). Interestingly, these structures would have a low carbon content even if all carbon positions were fully occupied. In carbides with higher carbon contents there are usually no defects at the carbon positions, e.g., $Gd_3Mn_2C_6$ (13), $La_{3.67}FeC_6$ (14), Er_2MnC_4 (15), $U_3Si_2C_2$ (1), and also $U_{20}Si_{16}C_3$ (1). The present structure refinement of $ThFe_2SiC$ shows that the carbon positions are fully occupied and in this sense that compound may be considered as belonging to this latter class of carbides.

It has already been noted (16) that the structure of $DyFe_2SiC$ can be derived from that of Re_3B (17). The dysprosium and iron atoms occupy the positions of the rhenium atoms in an ordered manner, while the positions of the silicon atoms correspond to those of the boron atoms. The carbon atoms occupy octahedral interstitial voids formed by the metal atoms. Interestingly, the structure of the carbide V_3AsC was also described as a filled-up version of the Re_3B-type structure (18, 19). However, the two structures are different, as is demonstrated in Fig. 3. The difference arises from the positions of the carbon atoms, even though in both structures, $ThFe_2SiC$ and V_3AsC, the carbon atoms occupy voids formed by the corresponding metal atoms (Dy, Fe, and V, respec-

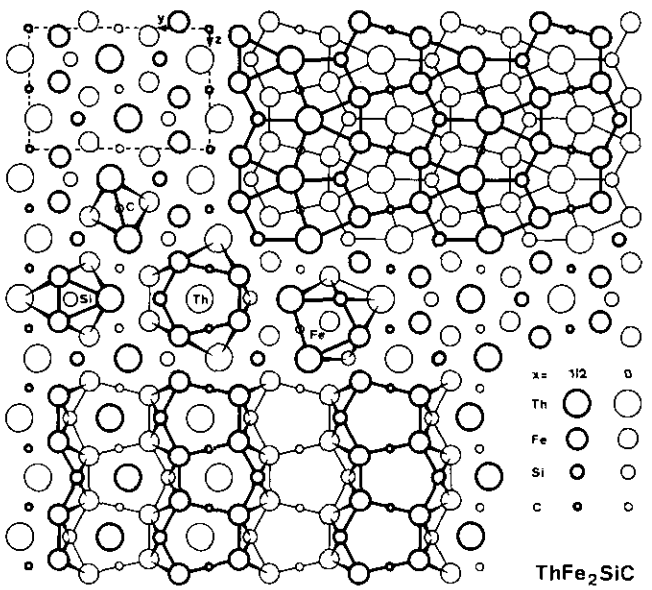

FIG. 1. Crystal structure and coordination polyhedra of $ThFe_2SiC$. All atoms are situated on mirror planes, which are perpendicular to the projection direction. Atoms at $x = 0$ and $x = \frac{1}{2}$ are connected by thin and thick lines, which do not necessarily correspond to chemical bonds. The bonds within the three-dimensionally infinite $[Fe_2SiC^{4-}]_n$ polyanion are emphasized, and the thorium atoms are omitted in the middle of the bottom part of the drawing.

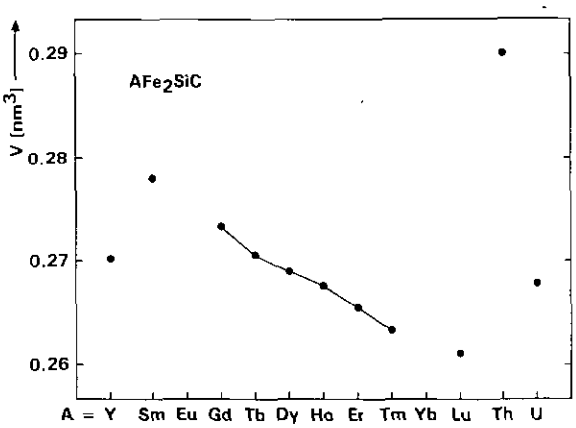

FIG. 2. Cell volumes of the isotypic series of the quaternary silicide carbides AFe_2SiC.

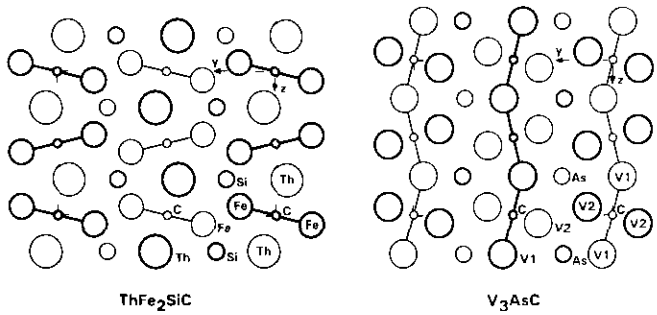

FIG. 3. The structure of the $DyFe_3SiC$-type compound $ThFe_2SiC$ as compared to that of V_3AsC. Atoms at $x = 0$ and $\frac{1}{2}$ are drawn with thin and thick lines. The structures differ in the positions of the carbon atoms; this is emphasized by the lines, which connect their near neighbors at the same height.

tively). In the structure of $ThFe_2SiC$ the carbon atoms are at the same height (x) as the iron atoms of the corresponding octahedron, while in V_3AsC the carbon atoms are at the height of the V1 atoms. Several other ternary compounds are reported in the literature, which may be considered as filled-up versions of the Re_3B-type structure. Those which were determined from single-crystal data or neutron powder data are listed in Table 5. To facilitate the comparisons we have standardized the settings using the program STRUCTURE TIDY (20). It can be seen that all of the previously determined structures are isotypic with V_3AsC and not with $DyFe_2SiC$. It should also be noted that several of these ternary compounds were classified (8) as isotypic with Pt_3Ge_2 (27). This, however, is not the case, since the germanium atoms in position 4*b* of Pt_3Ge_2 (which correspond to the carbon atoms of $DyFe_2SiC$ and $ThFe_2SiC$) have cubic and not octahedral metal coordination.

Strong chemical bonds in $ThFe_2SiC$ are certainly formed between the metal atoms on the one hand and the metalloids (Si, C) on the other hand, while the metal–metal interactions are less important. There are no silicon–carbon bonds. The thorium atoms are situated in a capped trigonal prism formed by four carbon and three silicon atoms. The iron atoms are tetrahedrally coordinated by one carbon and three silicon atoms. The silicon

TABLE 5
Structures Derived by "Filling" of the Re_3B-Type Structure[a]

Compound	8*f*	4*c*	4*c*	4*a*/4*b*	Ref.
Re_3B	Re1 00/37/06	Re2 00/07/25	B 00/76/25	——	17
$ThFe_2SiC$	Fe 00/33/06	Th 00/05/25	Si 00/77/25	C 00/50/00	This work
V_3AsC	V2 00/37/05	V1 00/05/25	As 00/74/25	C 00/00/00	18, 19
Cr_2VC_2	Cr 00/36/07	V 00/09/25	C2 00/75/25	C1 00/00/00	21
Cr_7BC_4	Cr2 00/36/05	Cr1 00/09/25	C 00/75/25	(B, C) 00/00/00	22
Cr_3GeC	Cr2 00/37/04	Cr1 00/03/25	Ge 00/74/25	C 00/00/00	23
$(V, Cr)_3C_{2-x}$	(V, Cr)2 00/36/05	(V, Cr)1 00/09/25	C2 00/74/25	C1 00/00/00	24
Zr_3AlN	Zr2 00/37/04	Zr1 00/04/25	Al 00/75/25	N 00/00/00	25
$UScS_3$	S2 00/36/06	S1 00/08/25	U 00/75/25	Sc 00/00/00	26

[a] All structures are normalized by the STRUCTURE TIDY program (20). The positions $x/y/z$ of corresponding atoms are listed in hundredths. $ThFe_2SiC$ is not isotypic with the other ternary compounds, because of the difference in the carbon position (4*a* and 4*b*, respectively).

atoms have nine metal neighbors forming a tricapped trigonal prism. This is the most frequently found environment for silicon in silicides with a high metal content (28). The carbon atoms are situated in octahedra formed by four thorium and two iron atoms.

Since the thorium atoms are the most electropositive component of the structure the chemical bonding between the thorium and the other atoms is primarily ionic, while the bonding between the other atoms has mainly a covalent character. Therefore the compound may be expressed by the formula $Th^{4+}(Fe_2SiC)^{4-}$. The iron–silicon–carbon polyanion is three-dimensionally infinite (Fig. 1). Certainly the *s* and *p* orbitals of the carbon and silicon atoms will fully participate in the chemical bonding and in counting the corresponding bonding electrons at the carbon and silicon atoms the compound may also be represented by the formula $Th^{4+}Fe^{2+}Fe^{2+}Si^{4-}C^{4-}$, where the superscripts represent oxidation numbers (formal charges). Thus, the iron atoms have a d^6 system; i.e., they have six electrons which are either nonbonding or iron–iron bonding. Some iron–iron bonding is likely to occur considering that the Fe–Fe distances in the compound (262.5 and 278.6 pm) are only somewhat greater than the Fe–Fe distances of 258 pm in the face-centered cubic modification of iron (29).

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REFERENCES

1. R. Pöttgen, D. Kaczorowski, and W. Jeitschko, *J. Mater. Chem.* **3,** 253 (1993).
2. L. Paccard, D. Paccard, and C. Bertrand, *J. Less Common Met.* **135,** L5 (1987).
3. K. Yvon, W. Jeitschko, and E. Parthé, *J. Appl. Crystallogr.* **10,** 73 (1971).
4. W. Jeitschko, M. H. Gerss, R.-D. Hoffmann, and S. Lee, *J. Less Common Met.* **156,** 397 (1989).
5. D. T. Cromer and J. B. Mann, *Acta Crystallogr. Sect. A* **24,** 321 (1968).
6. D. T. Cromer and D. Liberman, *J. Chem. Phys.* **53,** 1891 (1970).
7. W. Jeitschko, G. Block, G. E. Kahnert, and R. K. Behrens, *J. Solid State Chem.* **89,** 191 (1990).
8. P. Villars and L. D. Calvert,"Pearson's Handbook of Crystallographic Data for Intermetallic Phases." Am. Soc. for Materials, Materials Park, OH, 1991.
9. W. Jeitschko and G. Block, *Z. Anorg. Allg. Chem.* **528,** 61 (1985).
10. G. Block and W. Jeitschko, *Inorg. Chem.* **25,** 279 (1986).
11. G. Block and W. Jeitschko, *J. Solid State Chem.* **70,** 271 (1987).
12. R. Pöttgen, W. Jeitschko, Ch. Evers, and M. A. Moss, *J. Alloys Compd.* **186,** 223 (1992).
13. G. E. Kahnert and W. Jeitschko, *Z. Allorg. Allg. Chem.* **619,** 93 (1993).
14. A. Witte, R. Pöttgen, and W. Jeitschko, *Z. Kristallogr. Suppl.* **7,** 222 (1993).
15. G. E. Kahnert, W. Jeitschko, and G. Block, *Z. Anorg. Allg. Chem.* **619,** 442 (1993).
16. L. Paccard and D. Paccard, *J. Less Common Met.* **136,** 297 (1988).
17. B. Aronsson, M. Bäckman, and S. Rundqvist, *Acta Chem. Scand.* **14,** 1001 (1960).
18. H. Boller and H. Nowotny, *Monatsh. Chem.* **98,** 2127 (1967).
19. H. Boller and H. Nowotny, *Monatsh. Chem.* **99,** 721 (1968).
20. L. M. Gelato and E. Parthé, *J. Appl. Crystallogr.* **20,** 139 (1987).
21. P. Ettmayer, G. Vinek, and H. Rassaerts, *Monatsh. Chem.* **97,** 1258 (1966).
22. Yu. D. Kondrashev, *Sov. Phys. Crystallogr.* **11,** 492 (1967).
23. H. Boller, *Monatsh. Chem.* **102,** 431 (1971).
24. W. Steurer, P. Rogl, H. Boller, B. Kunsch, and H. Nowotny, *J. Less Common Met.* **76,** 145 (1980).
25. J. C. Schuster, *Z. Kristallogr.* **175,** 211 (1986).
26. R. Julien, N. Rodier, and V. Tien, *Acta Crystallogr. Sect. B* **34,** 2612 (1978).
27. S. Bhan and K. Schubert, *Z. Metallkd.* **51,** 327 (1960).
28. E. Parthé and B. Chabot, *in* "Handbook on the Physics and Chemistry of Rare Earths" (K. A. Gschneidner, Jr., and L. Eyring, Eds.), Vol. 6, p. 113. North-Holland, Amsterdam, 1984.
29. J. Donohue, "The Structures of the Elements." Wiley, New York, 1974.