

# The Crystal Structures of $Zr_3Al_3C_5$ , $ScAl_3C_3$ , and $UAl_3C_3$ and Their Relation to the Structures of $U_2Al_3C_4$ and $Al_4C_3$

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Single crystals of  $Zr_3Al_3C_5$ —a carbide previously reported with the formula  $ZrAlC_{2-x}$ —were isolated from a sample prepared by reaction of  $ZrC$  with an excess of aluminum. The carbides  $ScAl_3C_3$  and  $UAl_3C_3$  were synthesized from the elemental components by arc-melting. The crystal structures of these three compounds were redetermined from four-circle X-ray diffractometer data. In the original structure determination of  $ZrAlC_{2-x}$ , the metal positions were found to form close-packed layers in the space group  $P6_3/mmc$ , while the carbon atoms were assumed to occupy 5/6 of the octahedral voids at random. The present structure determination in the space group  $P6_3/mc$  ( $R = 0.024$  for 519 structure factors and 23 variable parameters) shows that all carbon positions are fully occupied and one has a trigonal bipyramidal aluminum coordination. The structures of  $ScAl_3C_3$  and  $UAl_3C_3$  also have originally been determined in the space group  $P6_3/mmc$ . The present structure refinements in the space group  $P6_3/mc$  ( $ScAl_3C_3$ :  $R = 0.031$  for 282  $F$  values and 16 variables;  $UAl_3C_3$ :  $R = 0.029$  for 217  $F$  values and 16 variables) essentially confirms the structures with the exception of one aluminum site. In all of these structures the metal atoms are arranged in close-packed layers and together with the previously reported structure of  $U_2Al_3C_4$  they form a homologous series with the general formula  $T_{1+n}Al_3C_{3+n}$ , where  $n = 0, 1, 2$  for  $ScAl_3C_3$ ,  $U_2Al_3C_4$ , and  $Zr_3Al_3C_5$ , respectively. The packing of the metal atoms is represented by the Zhdanov symbols  $(4)_2$ ,  $(5)_2$ , and  $(6)_2$ . The arrangement of the aluminum atoms is very similar to that of the binary carbide  $Al_4C_3$ , while the other metal atoms form a cubic stacking sequence, as it is found in the binary carbides  $TC$  with NaCl type structure. © 1998 Academic Press

## INTRODUCTION

In the ternary carbide  $U_2Al_3C_4$  the metal atoms form a close-packed arrangement, while most of the carbon atoms occupy octahedral voids formed by the uranium and the aluminum atoms or only by uranium atoms. One

carbon site has a trigonal bipyramidal environment of aluminum atoms (1). A similar close-packed structure for the metal atoms has been reported for the isotopic compounds  $ZrAlC_{2-x}$  and  $HfAlC_{2-x}$ . The carbon atoms in these structures were again assumed to occupy octahedral voids, and 5/6 of these voids were assumed to be filled statistically (2). In the present paper we show that the ideal composition of the zirconium compound is  $Zr_3Al_3C_5$ , the carbon atoms are fully ordered, and one carbon site has a trigonal bipyramidal aluminum coordination similar to the one found in  $U_2Al_3C_4$  (1).

The isotopic carbides  $ScAl_3C_3$  (3) and  $UAl_3C_3$  (4) also have a close-packed arrangement of metal atoms. Their structures were refined in the high-symmetry space group  $P6_3/mmc$  with a very large displacement parameter for one aluminum site (3) or with a statistical distribution of aluminum atoms on two adjacent sites (4), respectively. Here we show that both structures can be refined with full occupancy of the corresponding aluminum site with a normal displacement parameter in the lower symmetry space group  $P6_3/mc$ .

## SAMPLE PREPARATION AND LATTICE CONSTANTS

Starting materials were powders of zirconium (Ventron, 99.9%), uranium (Merck, "nuklearrein"), filings of scandium (Kelpin, 99.9%) and aluminum (KCL Koch Chemicals, 99.999%), and graphite flakes (Alpha, 99.5%). The uranium platelets were cleaned with concentrated nitric acid to remove oxide impurities. Single crystals of  $Zr_3Al_3C_5$  were isolated from a sample, where an excess of aluminum was used as a flux. A powder sample of the carbide  $ZrC$  was prepared first by arc-melting a pellet of a stoichiometric mixture of zirconium and graphite. The resulting button was then crushed and ground to powder. A mixture of this  $ZrC$  powder was then reacted with aluminum in the weight ratio 1:5 in a graphite crucible under argon for 2 days at 1500°C. After quenching, the crucible was crushed and adhering graphite layers were removed. The clean ingot was ductile, indicating a large proportion of elemental

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TABLE 1  
Some Data and Results of the Structure Determinations of  $Zr_3Al_3C_5$ ,  $ScAl_3C_3$ , and  $UAl_3C_3$ <sup>a</sup>

Composition	$Zr_3Al_3C_5$	$ScAl_3C_3$	$UAl_3C_3$
Structure type	$Zr_3Al_3C_5$	$ScAl_3C_3$	$ScAl_3C_3$
Space group	$P6_3mc$	$P6_3mc$	$P6_3mc$
Lattice constants from Guinier powder data			
<i>a</i> [pm]	334.6(1)	335.5(1)	338.9(1)
<i>c</i> [pm]	2764.9(6)	1677.6(3)	1739.4(3)
<i>V</i> [nm <sup>3</sup> ]	0.2681	0.1635	0.1730
Lattice constants from single-crystal data			
<i>a</i> [pm]	334.3(1)	335.2(1)	338.7(1)
<i>c</i> [pm]	2760.9(5)	1677.8(2)	1739.3(2)
<i>V</i> [nm <sup>3</sup> ]	0.2672	0.1633	0.1728
Formula units/cell, <i>Z</i>	2	2	2
Formula mass	414.7	161.9	355.0
Calculated density [g/cm <sup>3</sup> ], $\rho$	5.14	3.29	6.82
Crystal size [ $\mu\text{m}^3$ ]	$25 \times 25 \times 10$	$10 \times 13 \times 25$	$25 \times 100 \times 200$
Radiation	MoK $\alpha$	MoK $\alpha$	AgK $\alpha$
$\theta/2\theta$ -scan up to $2\theta$	80°	85°	50°
Range in <i>hkl</i>	$\pm 6, \pm 6, \pm 49$	$\pm 6, \pm 6, \pm 30$	$\pm 4, \pm 1, \pm 25$
Total number of reflections	5979	4734	1268
Unique reflections	712	537	269
Inner residual, $R_i$	0.109	0.050	0.038
Reflections with $F_o > 2\sigma(F_o)$	519	282	217
Highest/lowest transmission	1.03	1.37	1.48
Number of variables	23	16	16
Conventional residual, <i>R</i>	0.024	0.031	0.029

<sup>a</sup>Standard deviations in the positions of the least significant digits are given in parentheses throughout the paper.

aluminum. This was dissolved in a 10N solution of sodium hydroxide. The resulting product consisted of almost globular  $ZrAl_3$  crystals and crystals of  $Zr_3Al_3C_5$  in the form of hexagonal plates.

$ScAl_3C_3$  and  $UAl_3C_3$  were synthesized from the elemental components by arc-melting. The scandium compound was obtained in well crystallized form already after the arc-melting. The sample of  $UAl_3C_3$  was wrapped in a tantalum foil and annealed in an evacuated, sealed silica tube at 900°C for 2 weeks. The crystal used for the structure refinement was isolated from this annealed ingot.

Lattice constants (Table 1) were determined by least-squares fits of Guinier powder data using Cu  $K\alpha_1$  radiation and  $\alpha$ -quartz ( $a = 491.30$  pm,  $c = 540.46$  pm) as an internal standard. To prevent the reaction of the samples with the humidity of the air, the powdered samples were covered by dried paraffin oil.

### CRYSTAL STRUCTURES

The single crystals of  $Zr_3Al_3C_5$ ,  $ScAl_3C_3$ , and  $UAl_3C_3$  used for the structure refinements were sealed into thin-walled silica tubes to prevent hydrolysis. Intensity data of the crystals of  $Zr_3Al_3C_5$  and  $ScAl_3C_3$  were recorded on a four-circle diffractometer with graphite-monochromated

MoK $\alpha$  radiation, a scintillation counter, and a pulse height discriminator. Background counts were taken at both ends of each  $\theta/2\theta$  scan. Empirical absorption corrections were made from  $\psi$  scan data. In the case of  $UAl_3C_3$  the data collection was carried out with an Image Plate Detector System (IPDS), using graphite-monochromated AgK $\alpha$  radiation to reduce the absorption effects, which had been observed earlier (4). Further details are given in Table 1.

The previous structure determinations of " $ZrAlC_{2-x}$ " (2),  $ScAl_3C_3$  (3), and  $UAl_3C_3$  (4) were all carried out in the higher symmetry space group  $P6_3/mmc$  with statistical distribution of all carbon positions (2), with a large cigar-shaped displacement parameter for one aluminum position (3), or with a split aluminum position (4), respectively. For the present structure refinements in the lower symmetry space group  $P6_3mc$  the metal positions as obtained in the original structure determinations were transformed to the lower symmetry. The carbon positions were obtained by difference Fourier syntheses. The structures were refined by the full-matrix least-squares program SHELXL-93 (5) using atomic scattering factors, corrected for anomalous dispersion, as provided by that program. Since the structures are very close to the higher symmetry space group  $P6_3/mmc$ , we expected inversion twins. The twin domain ratios refined by

TABLE 2  
Atomic Parameters of  $Zr_3Al_3C_5$ ,  $ScAl_3C_3$ , and  $UAl_3C_3$ <sup>a</sup>

	$P6_3mc$	$x$	$y$	$z$	$B$
$Zr_3Al_3C_5$					
Zr(1)	2b	1/3	2/3	0.59551(5)	0.21(6)*
Zr(2)	2b	1/3	2/3	0.90504(5)	0.21*
Zr(3)	2a	0	0	0	0.22(7)
Al(1)	2b	1/3	2/3	0.1776(2)	0.32(2)*
Al(2)	2b	1/3	2/3	0.3236(2)	0.32*
Al(3)	2a	0	0	0.2448(1)	0.29(3)
C(1)	2b	1/3	2/3	0.0510(5)	0.32(4)*
C(2)	2b	1/3	2/3	0.2511(9)	0.09(7)
C(3)	2b	1/3	2/3	0.4510(5)	0.32*
C(4)	2a	0	0	0.1508(5)	0.45(6)*
C(5)	2a	0	0	0.3472(5)	0.45*
$ScAl_3C_3$					
Sc	2a	0	0	0	0.34(2)
Al(1)	2b	1/3	2/3	0.1297(2)	0.41(2)*
Al(2)	2b	1/3	2/3	0.3706(2)	0.41*
Al(3)	2b	1/3	2/3	0.7582(2)	0.54(4)
C(1)	2b	1/3	2/3	0.2504(9)	0.40(6)
C(2)	2b	1/3	2/3	0.5848(4)	0.52(5)*
C(3)	2b	1/3	2/3	0.9103(5)	0.52*
$UAl_3C_3$					
U	2a	0	0	0	0.32(2)
Al(1)	2b	1/3	2/3	0.1361(9)	0.41(5)*
Al(2)	2b	1/3	2/3	0.3667(9)	0.41*
Al(3)	2b	1/3	2/3	0.7608(7)	0.17(9)
C(1)	2b	1/3	2/3	0.2488(25)	0.1(3)
C(2)	2b	1/3	2/3	0.5985(24)	0.7(2)*
C(3)	2b	1/3	2/3	0.9114(31)	0.7*

Note. (\*) The displacement parameters of those atoms which occupy the same atomic position in the higher symmetric space group  $P6_3/mmc$  were constrained to be equal.

<sup>a</sup>The positional parameters were standardized by the program STRUCTURE TIDY (6). The last column contains the equivalent isotropic  $B$  values of the metal atoms and the isotropic  $B$  values of the carbon atoms in units of  $10^4 \text{ pm}^2$ .

this program resulted in the values 12(25)/88, 63(21)/37, and 61(11)/39 for  $Zr_3Al_3C_5$ ,  $ScAl_3C_3$ , and  $UAl_3C_3$ , respectively. The displacement parameters of those pairs of atoms, which occupy one atomic site in  $P6_3/mmc$  were constrained (Table 2).

As checks for the proper compositions we refined occupancy parameters together with the displacement parameters. They varied between the values of 0.98(1) for the C4 position in  $Zr_3Al_3C_5$  and 1.01(1) for the Al(1) position in  $UAl_3C_3$ . Thus, no significant deviations from the full occupancies were observed, and in the final least-squares calculations the ideal occupancies were assumed. The atomic parameters and interatomic distances are given in the Tables 2–4. Listings of the anisotropic displacement parameters and the structure factors are available from the authors (7).

TABLE 3  
Interatomic Distances in  $Zr_3Al_3C_5$ <sup>a</sup>

Zr(1):	3C(1)	229.1(7)	Al(2):	1C(2)	201(3)
	3C(4)	246.3(8)		3C(5)	203.9(5)
	3Al(1)	298.1(3)		3Al(3)	291.0(4)
	3Zr(3)	327.2(1)		3Zr(2)	296.8(4)
	6Zr(1)	334.6(1)		6Al(2)	334.6(1)
Zr(2):	3C(3)	231.2(8)	Al(3):	3C(2)	194.0(2)
	3C(5)	250.9(9)		1C(4)	260(1)
	3Al(2)	296.8(4)		3Al(1)	268.0(4)
	3Zr(3)	326.0(1)		1C(5)	283(1)
	6Zr(2)	334.6(1)		3Al(2)	291.0(4)
Zr(3):	3C(3)	236.0(8)		6Al(3)	334.6(1)
	3C(1)	239.1(8)	C(1):	3Zr(1)	229.1(7)
	3Zr(2)	326.0(1)		3Zr(3)	239.1(8)
	3Zr(1)	327.2(1)	C(2):	3Al(3)	194.0(2)
	6Zr(3)	334.6(1)		1Al(2)	201(3)
Al(1):	1C(2)	203(3)		1Al(1)	203(3)
	3C(4)	207.0(5)	C(3):	3Zr(2)	231.2(8)
	3Al(3)	268.0(4)		3Zr(3)	236.0(8)
	3Zr(1)	298.1(3)	C(4):	3Al(1)	207.0(5)
	6Al(1)	334.6(1)		3Zr(1)	246.3(8)
				1Al(3)	260(1)
			C(5):	3Al(2)	203.9(5)
				3Zr(2)	250.9(9)
				1Al(3)	283(1)

<sup>a</sup>All distances shorter than 400 pm (metal–metal) and 320 pm (metal–carbon, carbon–carbon) are given.

## DISCUSSION

The presently reported structure refinements of the carbides  $Zr_3Al_3C_5$ ,  $ScAl_3C_3$ , and  $UAl_3C_3$  in the space group  $P6_3/mmc$  show that all atomic positions are fully occupied, and all atoms have satisfactory displacement parameters. In the previous work on “ $ZrAlC_{2-x}$ ” (2) the arrangement of the metal atoms has correctly been determined. The positions of the carbon atoms, however, could not be located on the Fourier maps obtained from limited single-crystal film data. The metal/carbon ratio was estimated to be close to 6/5 in perfect agreement with the formula  $Zr_3Al_3C_5$  established during the present structure determination. Since carbon atoms frequently occupy octahedral voids formed by metal atoms, the authors of the previous investigation had assumed that the carbon atoms randomly occupy 5/6 of the octahedral voids formed by the close packed metal atoms. In the present investigation we found that all octahedral voids formed by six zirconium atoms or by three zirconium and three aluminum atoms are fully occupied, while the octahedral voids formed only by aluminum atoms are empty. Instead, one carbon site was found to have a trigonal bipyramidal aluminum coordination, as is known for the structure of  $Al_4C_3$  (1,8,9). Interestingly, these five-coordinated carbon atoms—C(2) of  $Zr_3Al_3C_5$ , C(1) of  $ScAl_3C_3$ , and C(1) of  $UAl_3C_3$ —have the lowest displacement

**TABLE 4**  
**Interatomic Distances in the Isotypic Carbides  $ScAl_3C_3$**   
**and  $UAl_3C_3$ <sup>a</sup>**

Sc/U:	3C(2)	240.3(4)/260(3)	Al(3):	3C(1)	194.1(1)/196.8(4)	
	3C(3)	245.3(5)/249(3)		1C(3)	255.1(8)/262(5)	
	3Al(2)	290.9(3)/303(1)		3Al(2)	270.3(2)/268.7(9)	
	3Al(1)	291.3(3)/307(1)		1C(2)	290.9(7)/282(4)	
	6Sc/U	335.5(1)/338.9(1)		3Al(1)	289.8(3)/292(1)	
Al(1):	1C(1)	202(2)/196(4)	C(1):	6Al(3)	335.5(1)/338.9(1)	
	3C(2)	207.9(3)/206(1)		3Al(3)	194.1(1)/196.8(4)	
	3Al(3)	289.8(3)/292(1)		1Al(1)	202(2)/196(4)	
	3Sc/U	291.3(3)/307(1)		1Al(2)	202(2)/205(4)	
	6Al(1)	335.5(1)/338.9(1)		C(2):	3Al(1)	207.9(3)/206(1)
Al(2):	1C(1)	202(2)/205(4)	C(2):	3Sc/U	240.3(4)/260(3)	
	3C(3)	204.8(3)/211(2)		1Al(3)	290.9(7)/282(4)	
	3Al(3)	270.3(2)/268.7(9)		C(3):	3Al(2)	204.8(3)/211(2)
	3Sc/U	290.9(3)/303(1)		3Sc/U	245.3(5)/249(3)	
	6Al(2)	335.5(1)/338.9(1)		1Al(3)	255.1(8)/262(5)	

<sup>a</sup>All distances shorter than 400 pm (metal–metal) and 320 pm (metal–carbon, carbon–carbon) are given

parameters of all carbon atoms in their respective compounds.

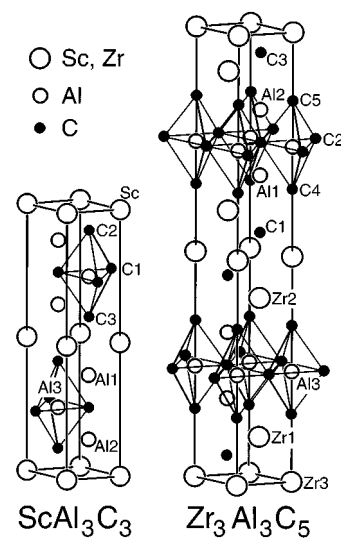
The interatomic distances in  $Zr_3Al_3C_5$  compare well with those of corresponding binary compounds. The three different zirconium atoms in  $Zr_3Al_3C_5$  are all octahedrally coordinated by six carbon atoms with average Zr–C distances of 237.7, 241.0, and 237.5 pm for the Zr(1), Zr(2), and Zr(3) atoms, with an overall average of 238.7 pm, which is close to the Zr–C distance of 234.9 pm calculated from the lattice constant of ZrC with NaCl-type structure (10). In addition, these zirconium atoms have 12 metal neighbors [3 Al + 9 Zr for Zr(1) and Zr(2); 12 Zr for Zr(3)]. The average Zr–Zr distance of 331.4 pm in  $Zr_3Al_3C_5$  is again close to the Zr–Zr distance of 332.2 pm in ZrC. The average Zr(1)–C and Zr(3)–C distances of 237.7 and 237.5 pm are shorter than the average Zr(2)–C distance of 241.0 pm. Hence, the Zr(2) atoms are not as strongly bonded to the carbon atoms as the Zr(1) and Zr(3) atoms. The somewhat weaker Zr–C bonds of the Zr(2) atoms are compensated by somewhat stronger (shorter) Zr(2)–Al and Zr(2)–Zr bonds (cf. Table 3). This clearly demonstrates the bonding character of the Zr–Zr and Zr–Al interactions. It is well known that the high stability of binary transition metal (*T*) carbides *TC* is due to both strong *T*–C and strong *T*–*T* bonding (11–13).

The Al(1) and Al(2) atoms of  $Zr_3Al_3C_5$  have four carbon neighbors in tetrahedral arrangement with average Al–C distances of 206.0 and 203.2 pm, respectively. These distances compare well with the range of Al–C distances found in  $Al_4C_3$  (1, 8, 9) extending from 194.2(4) to 218.5(4) pm. Similarly, the Zr–Al distances of 296.8 and 298.1 pm in  $Zr_3Al_3C_5$  are close to the Zr–Al distances found in binary zirconium–aluminum compounds; e. g., in  $ZrAl_3$  (14, 15) the

Zr atoms are coordinated by 12 Al atoms with Zr–Al distances of 283.0 (4 ×), 286.7 (4 ×), and 302.3 pm (4 ×), with an average of 290.7 pm.

The Al(3) atoms of  $Zr_3Al_3C_5$  as well as the Al(3) atoms of  $ScAl_3C_3$  and  $UAl_3C_3$  are located in trigonal bipyramidal voids formed by five carbon atoms. In the previous structure determination of  $ScAl_3C_3$  (3) in space group  $P6_3/mmc$  these aluminum atoms were located on a mirror plane in the center of the trigonal bipyramid. In the previous structure determination of  $UAl_3C_3$  (4), the Al(3) atoms were refined with a split position, where they are located 16.3 pm above and below the mirror plane. In the present structure determinations in the lower symmetry space group  $P6_3mc$  the Al(3) atoms of all these structures are located off the center of the trigonal bipyramid formed by carbon atoms with three close carbon atoms at 194.0, 194.1, and 196.8 pm in  $Zr_3Al_3C_5$ ,  $ScAl_3C_3$ , and  $UAl_3C_3$ , respectively. A fourth carbon atom at 260, 255.1, and 262 pm completes the rather distorted carbon tetrahedron in the three compounds, while the fifth carbon neighbor of these three Al(3) atoms at 283, 290.9, and 282 pm completes the trigonal bipyramid, which is emphasized in Fig. 1.

In Fig. 2, the structures of  $ScAl_3C_3$  and  $Zr_3Al_3C_5$  are shown together with the closely related structures of  $U_2Al_3C_4$  and  $Al_4C_3$ . The structures of  $U_2Al_3C_4$  and  $Zr_3Al_3C_5$  may be viewed as intergrowth structures consisting of two kinds of layers. One kind of layers are the layers with carbon atoms in octahedral uranium or zirconium



**FIG. 1.** Crystal structures of  $ScAl_3C_3$  and  $Zr_3Al_3C_5$ . The trigonal bipyramidal carbon environments of the Al(3) atoms in both structures are emphasized. The aluminum atoms have trigonal bipyramidal coordination, when the structures are refined in the space group  $P6_3/mmc$ . They have tetrahedral carbon coordination, when the structures are refined in the correct space group  $P6_3mc$ .



$ThAl_3$  (18, 19) and  $TbAl_3$  (20) as well as the ternary carbides  $Ti_2AlC$  (21) and  $Ti_3SiC_2$  (22) are shown as further examples for closely related structures with similar compositions. Figure 3 also demonstrates that the metal positions in the structures of  $ScAl_3C_3$ ,  $U_2Al_3C_4$ , and  $Zr_3Al_3C_5$ , and the hypothetical carbide  $Hf_4Al_3C_6$  are represented by the Jagodzinski–Wykoff symbols  $(hccc)_2$ ,  $(hcccc)_2$ ,  $(hccccc)_2$ , and  $(hcccccc)_2$ , respectively. With the Zhdanov notation (23, 24) the stackings are simply described with  $(4)_2$ ,  $(5)_2$ ,  $(6)_2$ , and  $(7)_2$ .

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