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UCr_4C_4 with Filled $MoNi_4$ Type Structure

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The title compound was prepared by arc melting coldpressed pellets of the elemental components with subsequent annealing at both 800 °C or 1 100 °C. UCr_4C_4 crystallizes tetragonal, space group I4/m, $a = 0.79363(4)$ nm, $c = 0.30754(3)$ nm, $V = 0.19370$ nm^3 with $Z = 2$ formula units per cell. The structure was determined from single-crystal X-ray data and refined to a residual of $R = 0.027$ for 16 variable parameters and 279 structure factors. The positions of the metal atoms correspond to those of the $MoNi_4$ type structure. The carbon atoms occupy octahedral voids formed by four chromium and two adjacent uranium atoms. Chemical bonding in UCr_4C_4 and in other interstitial compounds is briefly discussed. The average valence electron number of the metal atoms is usually greater for the unfilled (host) structure than for the corresponding filled structure.

(Keywords: Crystal chemistry; Crystal structure; Interstitial carbides; UCr_4C_4*)*

UCr_4C_4 *mit gefüllter* $MoNi_4$*-Struktur*

Die Titelverbindung wurde hergestellt durch Schmelzen kaltgepreßter Pillen der elementaren Komponenten im Lichtbogen mit anschließendem Tempern bei 800 °C oder 1 100 °C. UCr_4C_4 kristallisiert tetragonal in der Raumgruppe I 4/m, $a = 0.79363(4)$ nm, $c = 0.30754(3)$ nm, $V = 0.19370$ nm^3 mit $Z = 2$ Formeleinheiten pro Zelle. Die Struktur wurde aus Einkristall-Röntgendaten bestimmt und zu einem Restwert von $R = 0.027$ für 16 variable Parameter und 279 Strukturfaktoren verfeinert. Die Lagen der Metallatome entsprechen denen der $MoNi_4$-Struktur. Die Kohlenstoffatome besetzen oktaedrische Lücken, die von vier Chrom- und zwei benachbarten Uranatomen gebildet werden. Die chemische Bindung in UCr_4C_4 und in anderen Interstitialverbindungen wird kurz diskutiert. Die durchschnittliche Valenzelektronenzahl der Metallatome ist meist höher für die ungefüllte (Wirts-)Verbindung als für die entsprechende gefüllte Verbindung.

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* Dedicated to Prof. Dr. *Kurt Komarek* and to Prof. Dr. *Adolf Neckel* on the occasion of their 60th birthdays.

Introduction

The phase equilibria of the ternary actinoid transition metal carbon systems have been subject to numerous investigations because of their importance for the development of materials for nuclear reactors [1]. In their investigation of the uranium—chromium—carbon system *Briggs, Dutta,* and *White* [2] observed two ternary carbides: $UCrC_2$ with $UMoC_2$ type structure [3, 4] and another compound with the approximate composition $\sim U_3Cr_2C_4$. An uranium chromium carbide with unknown composition, which is in equilibrium with graphite, was reported also by *Farr* and *Bowman* [5]. It was described by these authors with a body centered tetragonal cell [$a = 0.3636(6)$ nm, $c = 1.5739(8)$ nm], but no further details were given. More recently *Alekseeva* and *Ivanov* [6] reported—besides the well established compound $UCrC_2$—two ternary phases. One of these with the approximate composition $\sim UCr_2C_4$ is in equilibrium with carbon. For the other they report a composition close to $U_{10}Cr_{45}C_{45}$ and the tetragonal lattice constants $a = 0.7933$ nm, $c = 0.3073$ nm. In the course of our studies of ternary lanthanoid and actinoid transition metal carbides [4, 7–12] we report here on the crystal structure of UCr_4C_4 which obviously corresponds to the tetragonal carbide described earlier by *Alekseeva* and *Ivanov* [6]. A preliminary report of our work was given before [13].

Experimental and Results

Sample Preparation

Starting materials for the preparation of UCr_4C_4 were fillings of uranium (Merck, "nuklearrein" and NUKEM), chromium powder (99.99%, 150 mesh), and graphite flakes (99.5% C, 20 mesh). The filings of uranium were kept under dried paraffin oil, which was washed away by repeated treatment with dried methylene chloride under argon. Stoichiometric mixtures of the elemental components were cold pressed to pellets of about 0.5 g and reacted in an arc-melting furnace. They were annealed at 800 °C or 1 100 °C. The major reaction product was UCr_4C_4 in the as cast as well as in the annealed samples. Only minor amounts of the only impurity $UCrC_2$ were observed on the *Guinier* powder patterns of the samples.

Structure Determination

Single crystals of UCr_4C_4 were isolated from the crushed samples. *Weißenberg* diffraction patterns showed a body centered tetragonal cell with the *Laue* symmetry 4/m and no further systematic extinctions. Thus the space groups I4, $I\bar{4}$, and I4/m are possible of which the centrosymmetric group I 4/m was found to be correct during the structure determination. The lattice constants (with standard deviations in the positions of the least significant digits in parentheses) were obtained by a least-squares fit of the powder data (Table 1): $a = 0.79363(4)$ nm, $c = 0.30754(3)$ nm, $V = 0.19370\,nm^3$. There are $Z = 2$ formula units UCr_4C_4 in this body centered cell (calculated density $\rho_c = 8.47\,g/cm^3$).

Table 1. *Powder pattern of* UCr_4C_4

hkl	Q_0	Q_c	I_c	I_0	hkl	Q_0	Q_c	I_c	I_0
110	317	318	55	s	002	4 231	4 229	9	w
200	636	635	15	m	112	4 550	4 547	4	vw
101	1 215	1 216	28	s	202	4 865	4 864	3	vw
220	1 270	1 270	21	m	431	5 027	5 027	25	s
310	1 588	1 588	70	vs	501			17	
211	1 850	1 851	100	vs	440	5 081	5 081	5	vw
301	2 486	2 486	16	m	530	5 399	5 398	8	w
400	2 541	2 540	1	vw	222	5 496	5 499	7	w
330	—	2 858	<1	—	521	5 663	5 662	13	w
321	3 122	3 121	18	m	600	5 717	5 716	6	w
420	3 176	3 175	25	m	312	5 815	5 817	25	m
411	3 757	3 756	19	m	620	6 348	6 351	6	w
510	4 127	4 128	7	w	402	—	6 770	1	—

The pattern was recorded in a *Guinier* camera with $Cu\,K\alpha_1$ radiation. The Q values are defined by $Q = 100/d^2$ (nm^{-2}). Observed intensities I_0 are abbreviated by vs (very strong), s (strong), m (medium), w (weak), vw (very weak).

The crystal used for the collection of the intensity data had elongated prismatic shape with the dimensions $6 \times 10 \times 40\,\mu m^3$. 3 166 reflections were recorded in the whole reciprocal space up to $2\theta = 90°$ in an automated four-circle diffractometer with graphite monochromated Mo Kα radiation, a scintillation counter, and a pulse-height discriminator. The background was determined at both ends of each θ—2θ scan. An empirical absorption correction was made from ψ scan data. The averaging of equivalent reflections resulted in 376 intensity data of which 279 were greater than three standard deviations of the intensities.

The positions of the metal atoms were deduced from a *Patterson* synthesis and the carbon atoms were located on a difference *Fourier* map. For the structure refinement a full-matrix least-squares program was used with atomic scattering factors [14], corrected for anomalous dispersion [15]. The weighting scheme was based on counting statistics. A parameter optimizing the secondary extinction correction was also refined. In one series of least-squares cycles the scale factor was held constant and the occupancy parameters of all atoms were allowed to vary. Only insignificant deviations from full occupancies (with standard deviations in parentheses) were obtained: U: 100.1 (0.2) %, Cr: 100.1 (0.5) %, C: 98.7 (3.0) %. The final residual is $R = 0.027$ (weighted residual $R_w = 0.029$) for a refinement with ellipsoidal thermal parameters (Table 2), a total of 16 variable parameters and 279 structure factors. A final difference *Fourier* analysis showed as highest peaks the values of $2.8 \cdot 10^3\,e/nm^3$ and $2.2 \cdot 10^3\,e/nm^3$, both too close to the positions of the uranium atoms to be occupied by additional atoms at the same time. The structure and the coordination polyhedra are shown in Fig. 1, interatomic distances are listed in Table 3. A listing of calculated and observed structure factors can be obtained from the authors.

Table 2. *Atomic parameters of* UCr_4C_4

Atom	U	Cr	C
I4/m	2a	8h	8h
x	0	0.8246 (2)	0.406 (1)
y	0	0.6348 (2)	0.267 (1)
z	0	0	0
U_{11}	0.0017 (1)	0.0054 (5)	0.009 (3)
U_{22}	0.0017 (1)	0.0041 (4)	0.006 (3)
U_{33}	0.0023 (2)	0.0067 (5)	0.007 (3)
U_{12}	0	—0.0006 (4)	0.000 (3)
U_{13}	0	0	0
U_{23}	0	0	0
B	0.00152 (5)	0.0043 (2)	0.006 (1)

Standard deviations in the positions of the least significant digits are given in parentheses. The anisotropic thermal parameters are of the form $exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots 2U_{12}hk\,a^* b^* + \ldots)]$. The last line lists the equivalent isotropic thermal parameter $B[nm^2]$.

Table 3. *Interatomic distances (pm) in* UCr_4C_4

U:	8C	252.0	Cr:	1C	195.8	C:	1Cr	195.8
	2U	307.5		2C	196.9		2Cr	196.9
	8Cr	318.5		1C	198.7		1Cr	198.7
	4Cr	321.5		2Cr	266.6		2U	252.0
				4Cr	292.1			
				2Cr	307.5			
				2U	318.5			
				1U	321.5			

All distances shorter than 380 pm, 350 pm, and 280 pm for the U, Cr, and C atoms respectively are listed. Standard deviations are all equal or less than 0.3 pm for the metal—metal distances and 0.9 pm for the metal—carbon distances.

Discussion

The crystal structure of UCr_4C_4 is of a new type. It can be derived from that of $MoNi_4$ [16], which is a tetragonal superstructure ($a = a'\sqrt{5}$, $c = a'$) arising through the ordering of the Mo and Ni atoms on the atomic positions of the cubic body centered subcell (with the lattice constant a'). The positions of the U and Cr atoms in UCr_4C_4 correspond to the positions of the Mo and Ni atoms in $MoNi_4$, which also has the same space group symmetry. The carbon atoms occupy distorted octahedral voids formed by four Cr and two adjacent U atoms.

The Cr—C distances in UCr_4C_4 vary between 195.8 pm and 198.7 pm with an average of 197.1 pm. This is in good agreement with the value of 199 pm found in Cr_2AlC [17], Cr_2GaC [18], Cr_2GeC [18], and the average value of 198.1 pm in Cr_3GeC [19], where the C atoms are in octahedral Cr coordination. In Cr_3C_2 [20], where the C atoms are in monocapped (coordination number CN = 7) and dicapped (CN 8) trigonal prismatic coordination the average Cr—C distances are larger (208.0 pm and 217.7 pm). This is also true for $Cr_{23}C_6$ [21] where the C atoms have square antiprismatic coordination with an average Cr—C distance of 212.3 pm.

The U—C distance of 252.0 pm in UCr_4C_4 compares rather well with the corresponding distance of 248 pm in UC [22] where the carbon atoms have octahedral U environment. In U_2NiC_3 [11], where the C(1) atom is in octahedral coordination of four U and two Ni atoms, the average U—C(1) distance is 243.7 pm.

The assessment of the U—Cr interactions is difficult, because no binary U—Cr phases and no reliable U—Cr distances in ternary alloys are known. However, in comparing the U—Cr distances of 318.5 and 321.5 pm in UCr_4C_4 with the sum of the CN 12 radii [23] of 292 pm, the U—Cr interactions can only be considered as weak. On the other hand the U—U distances of 307.5 pm and the Cr—Cr distances of 266.6 pm must be considered as bonding.

A more thorough discussion of chemical bonding in UCr_4C_4 is difficult. Since carbon is the most electronegative element in the compound, it can be assumed that the 2s and 2p orbitals fully participate in the formation of the band structure. Thus the carbon atoms can be assigned oxidation number —4. In aiming for integral numbers (which is not a requirement for a band structure) we can tentatively assign oxidation numbers according to $U^{+4}Cr_4^{+3}C_4^{-4}$. Thus both the uranium and the chromium atoms retain some of their valence electrons which are available for the formation of U—U, Cr—Cr, and U—Cr bonding bands.

An interesting relation exists for the average valence electron number of the metal atoms AVENOMA of the filled (interstitial) and that of the related unfilled (host) structure. For the transition elements we count all electrons outside the inert gas shell as valence electrons; for the main group elements the valence electron number corresponds to the group number. The AVENOMA of the host structure is then almost always greater than the AVENOMA of the corresponding filled structure, i.e. the

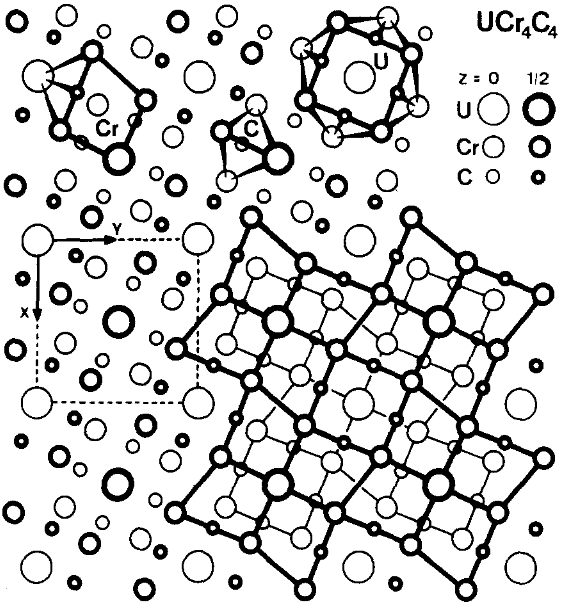

Fig. 1. Crystal structure and coordination polyhedra of UCr_4C_4

metal components of the filled structures are usually situated in the periodic system to the left of the elements of the unfilled host structures. Examples are $MoNi_4$ with AVENOMA $(6+4\cdot10)/(1+4)=9.2$ and UCr_4C_4 with AVENOMA $(6+4\cdot6)/(1+4)=6.0$, Cu_3Au (AVENOMA 11) and Mn_3CuN (AVENOMA 8) [24], Mn_5Si_3 (5.9) and Mo_5Si_3C (5.2) [25], β-Mn (7) and Mo_3Al_2C (4.8) [26], Re_3B (6) and V_3AsC (5) [27], $BaCd_{11}$ (11.2) and $LaMn_{11}C_2$ (6.7) [7], Th_2Zn_{17} (11.2) and $Pr_2Mn_{17}C_3$ (6.6) [8], Th_2Ni_{17} (9.4) and $Tb_2Mn_{17}C_3$ (6.6) [28]. This regularity is striking, although there are some exceptions, as for instance Cr_3AsN (AVENOMA 5.75) with filled U_3Si (AVENOMA 5.5) structure [29].

The assumption of a rigid band model for the host structure and the corresponding filled structure is certainly too simplistic for a rationalization of this regularity. Nevertheless one is reminded of a similar correlation which exists for the maxima in the cohesive energy of the transition elements and their carbides. The transition elements with the highest melting and boiling points are those of the fifth and sixth group of the periodic system, whereas the carbides with the highest melting points are those of the group four transition metals. The high melting point of tungsten can be rationalized by assuming optimal filling of bonding bands and minimal filling of antibonding bands. By going to rhenium and osmium the additional electrons fill mainly antibonding bands; by going to tantalum and hafnium the electrons are taken out mainly of the bonding bands. Thus in both cases the melting points decrease.

In the carbides some of the atomic orbitals of the transition elements (*T*), which are available for *T*—*T* bonding in the element, are utilized to build up the *T*—C bonding bands [30, 31]. The bands of the carbide are then filled not only by the valence electrons of the *T* element, but also by those of the carbon atoms. Thus fewer electrons of the transition elements can optimally be accommodated in the carbide and the maximum in cohesive energy is shifted to the carbides of the earlier transition metals. Similarily the optimal atomic arrangement found for the Mo and Ni atoms in the $MoNi_4$ structure is found for transition metals with fewer valence electrons in the corresponding filled carbide UCr_4C_4.

For some of the examples cited above this rationalization does not seem to be very plausible, especially for those examples where the corresponding compounds differ greatly in their AVENOMA values and where the number of interstitial atoms is relatively small, as for instance in the pairs $BaCd_{11}$ (AVENOMA 11.2)—$LaMn_{11}C_2$ (6.7), Th_2Zn_{17} (11.2)—$Pr_2Mn_{17}C_3$ (6.6), and Th_2Ni_{17} (9.4)—$Tb_2Mn_{17}C_3$ (6.6). However the $BaCd_{11}$ type structure is also adopted by $TbCo_9Si_2$ (7.7), the Th_2Zn_{17} structure is also found for Gd_2Fe_{17} (7.5), and the Th_2Ni_{17} structure occurs also for Er_2Fe_{17} (7.5) [32]. The AVENOMA values of the latter compounds are much closer to the AVENOMA values of the corresponding filled structures and the rationalization may very well be valid in these cases. Nevertheless we admit that in some cases the correlation may be accidental.

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