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The Crystal Structure of $U_5Re_3C_8$

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$U_5Re_3C_8$ crystallizes tetragonal in space group P4/mbm with the lattice constants $a = 1\,131.3(1)$ pm, $c = 330.29(7)$ pm, $V = 0.4227\,\mathrm{nm}^3$ and $Z = 2$ formula units per cell. The structure was determined from single-crystal counter-data and refined to a residual of $R = 0.032$ for 649 structure factors and 24 variable parameters. It is of a new type with carbon atoms on three different sites with approximately octahedral environment of five uranium and one rhenium or four uranium and two rhenium atoms. The positions of the metal atoms correspond to those of a (slightly distorted) cubic body centered structure as is also found for $Ho_2Cr_2C_3$, UCr_4C_4, $UMoC_2$, YCoC, and U_2IrC_2.

(Keywords: Crystal structure; Interstitial carbides; $U_5Re_3C_8$*)*

Die Kristallstruktur von $U_5Re_3C_8$

$U_5Re_3C_5$ kristallisiert tetragonal in der Raumgruppe P4/mbm mit den Gitterkonstanten $a = 1\,131.3(1)$ pm, $c = 330.29(7)$ pm, $V = 0.4227\,\mathrm{nm}^3$ und $Z = 2$ Formeleinheiten pro Zelle. Die Struktur wurde aus Einkristall-Diffraktometerdaten bestimmt und zu einem Restwert von $R = 0.032$ für 649 Strukturfaktoren und 24 veränderliche Parameter verfeinert. In diesem neuen Strukturtyp haben die Kohlenstoffatome annähernd oktaedrische Umgebungen, die aus fünf Uran- und einem Rhenium- bzw. vier Uran- und zwei Rheniumatomen gebildet werden. Die Positionen der Metallatome entsprechen denen einer kubisch raumzentrierten Packung. Dies gilt auch für die Strukturen von $Ho_2Cr_2C_3$, UCr_4C_4, $UMoC_2$, YCoC und U_2IrC_2.

Introduction

Three ternary carbides are reported for the system uranium-rhenium-carbon [1]. $UReC_2$ and $U_2Re_2C_3$ have $UMoC_2$ [2] and $Ho_2Cr_2C_3$ [3] type structure, respectively. For the third carbide of this system *Alekseeva* [4] determined the composition $U_5Re_3C_8$ and tetragonal lattice constants, which we confirm. We have now determined the crystal structure of this compound. A preliminary account of this work was given before [5].

Experimental Results

A well crystallized sample of $U_5Re_3C_8$ was prepared by arc melting the elemental components (all of purity 99.5% or better) in the atomic ratio 8:5:12 as reported before [4]. The sample was almost single phase $U_5Re_3C_8$ in the as cast condition, nevertheless, it was annealed in an evacuated silica tube at 900 °C for two days.

The compound is black with metallic luster and not sensitive to air. A check for superconductivity using the *ac* inductivity method was negative down to 1.7 K.

The tetragonal lattice constants $a = 1\,131.3\,(1)$ pm, $c = 330.29\,(7)$ pm, and $V = 0.4227\,\mathrm{nm}^3$ were obtained by a least-squares fit of the *Guinier* powder data using α-quartz ($a = 491.30$ pm, $c = 540.46$ pm) as a standard. They agree rather well with those determined earlier ($a = 1\,130.6$ pm, $c = 329.2$ pm) by *Alekseeva* [4]. With $Z = 2$ formula units per cell the calculated density is $14.49\,\mathrm{g\,cm^{-3}}$. This compares well with the observed density of $14.4\,\mathrm{g\,cm^{-3}}$ [4].

The crystal used for the structure determination had the dimensions $25 \times 20 \times 15\,\mu\mathrm{m}^3$. Precession diagrams showed the *Laue* symmetry 4/mmm and the systematic extinctions—reflections $0\,k\,l$ were observed only with $k = 2n$—led to the space groups P4bm, P$\bar{4}$b2, and P4/mbm of which the one with the highest symmetry P4/mbm-D_{4h}^5 was found to be correct during the structure determination.

Intensity data were recorded 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 $\theta/2\,\theta$ scan. 8 594 possible reflections were measured within the whole reciprocal sphere up to $2\,\theta = 74°$. An empirical absorption correction was applied from psi scan data and additionally a correction assuming spherical crystal shape was made (the linear absorption coefficient for Mo Kα radiation is very high: $1\,338\,\mathrm{cm}^{-1}$). An internal R-value of $R_i = 0.069$ was obtained for the 1 097 averaged reflections of which 649 with $F_0 > 2\,\sigma(F_0)$ were used for the structure determination.

The positions of the metal atoms were determined from a combination of the *Patterson* synthesis, direct methods, and difference *Fourier* syntheses. A least-squares refinement of these positions with isotropic thermal parameters, using atomic scattering factors [6], corrected for anomalous dispersion [7] resulted in a residual of $R = 0.054$. A difference *Fourier* synthesis and structure-chemical considerations led to the carbon positions. The weighting scheme was based on the counting statistics and a parameter which accounted for isotropic secondary extinction was refined as a least-squares parameter. In a least-squares refinement with ellipsoidal thermal parameters of the metal atoms the occupancy parameters of the carbon atoms were also varied. The results—occupancy parameters (in % with standard deviations in parentheses) of 89 (7), 81 (6), and 105 (5) for the C (1), C (2), and C (3) positions—did not reveal great deviations from the full occupancies considering the relatively large standards deviations. We therefore preferred to refine the structure with the ideal occupancies in the final (fullmatrix) least-squares cycles. The resulting unweighted and weighted residuals are R

Table 1. *Atomic parameters of* $U_5Re_3C_8$

Atom	U(1)	U(2)	Re(1)	Re(2)	C(1)	C(2)	C(3)
P4/mbm	2*d*	8*j*	2*a*	4*g*	4*g*	4*h*	8*i*
x	0	0.54354(5)	0	0.20327(6)	0.347(2)	0.116(2)	0.156(1)
y	1/2	0.27268(5)	0	0.70327(6)	0.847(2)	0.616(2)	0.100(1)
z	0	1/2	0	0	0	1/2	0
U_{11}	34(3)	34(2)	23(3)	43(2)	—	—	—
U_{22}	U_{11}	18(2)	U_{11}	U_{11}	—	—	—
U_{33}	38(4)	35(2)	73(5)	58(3)	—	—	—
U_{12}	− 7(4)	1(2)	0	5(3)	—	—	—
U_{13}	0	0	0	0	—	—	—
U_{23}	0	0	0	0	—	—	—
B	0.28(1)	0.230(7)	0.32(1)	0.378(9)	0.3(3)	0.3(3)	0.4(2)

The anisotropic thermal parameters U_{ij} (pm^2) are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots 2U_{12}hka^*b^* + \ldots)]$. The last line lists the isotropic thermal parameters B ($\times 100$ in units of nm^2) of the carbon atoms and the equivalent isotropic thermal parameters of the metal atoms. Standard deviations in the positions of the least significant digit are listed in parentheses

Table 2. *Interatomic distances (pm) in* $U_5Re_3C_8$

U(1):	2 C(1)	244.8	Re(1):	4 C(3)	209.6	C(1):	1 Re(2)	229.9
	4 C(2)	248.2		8 U(2)	309.6		1 U(1)	244.8
	2 Re(2)	325.2		2 Re(1)	330.3		4 U(2)	246.9
	2 U(1)	330.3						
	8 U(2)	353.4	Re(2):	2 C(3)	197.4	C(2):	2 Re(2)	216.5
				2 C(2)	216.5		2 U(1)	248.2
U(2):	2 C(3)	245.6		1 C(1)	229.9		2 U(2)	253.0
	2 C(1)	246.9		1 U(1)	325.2			
	1 C(2)	253.0		2 Re(2)	330.3	C(3):	1 Re(2)	197.4
	2 C(3)	253.0		4 U(2)	331.7		1 Re(1)	209.6
	2 Re(1)	309.6		4 U(2)	333.8		2 U(2)	245.6
	2 U(2)	330.3					2 U(2)	253.0
	2 Re(2)	331.7						
	2 Re(2)	333.8						
	2 U(1)	353.4						
	1 U(2)	366.6						
	2 U(2)	370.3						

All distances shorter than 400 pm (uranium), 380 pm (rhenium), and 270 pm (carbon atoms) are listed. Standard deviations are all equal or less than 0.1 pm for metal-metal distances; for the U—C- and Re—C-distances they are 1 pm and 2 pm respectively

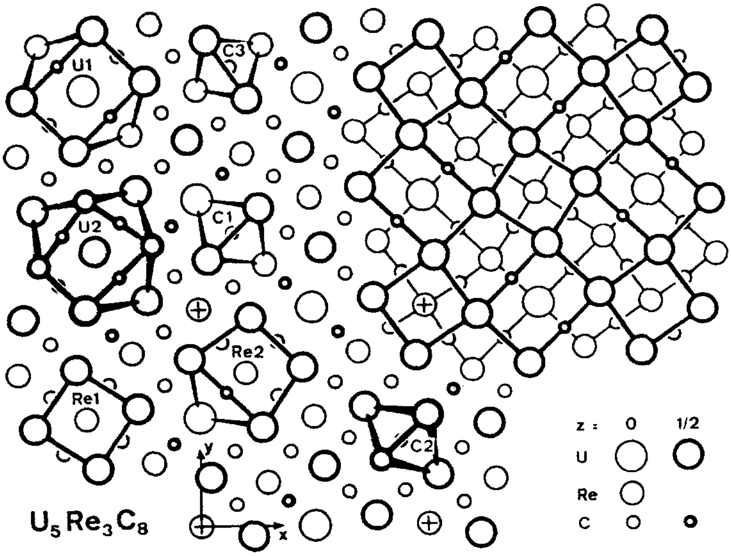


Fig. 1. Crystal structure and coordination polyhedra of $U_5Re_3C_8$

= 0.032 and $R_w = 0.028$ for 24 variable parameters and 649 structure factors. The atomic parameters and the interatomic distances are listed in Tables 1 and 2. Figure 1 shows a projection of the structure and the coordination polyhedra. A listing of the observed and calculated structure factors can be obtained from the authors [8].

Discussion

The crystal structure of $U_5Re_3C_8$ represents a new structure type, which may be derived from the CsCl structure. The positions of the metal atoms correspond to those of cesium and chlorine. The uranium : rhenium ratio deviates from 1 : 1, because one quarter of the rhenium positions is occupied by uranium atoms (the uranium atoms of the *Wykoff* position 2d). The CsCl structure has six octahedral voids per cell: 6/2 = 3 at the six faces and 12/4 = 3 at the twelve edges. They are grossly distorted with (from the center of the octahedron to the six corners) four corners at $a/\sqrt{2}$ forming a square and two more at $a/2$, where a is the lattice constant of the CsCl cell. In $U_5Re_3C_8$ one third of all these voids is filled by carbon atoms. To optimize the interatomic distances the CsCl-type subcells are somewhat distorted as is demonstrated in Fig. 2. In Fig. 3 we show some of the octahedral voids of the CsCl structure together with the structures of YCoC [9], $Ho_2Cr_2C_3$ [3], $UMoC_2$ [2], U_2IrC_2 [10], UCr_4C_4 [11], and $U_5Re_3C_8$, all of which can be derived from a body-centered arrangement of metal atoms with carbon atoms filling octahedral voids.

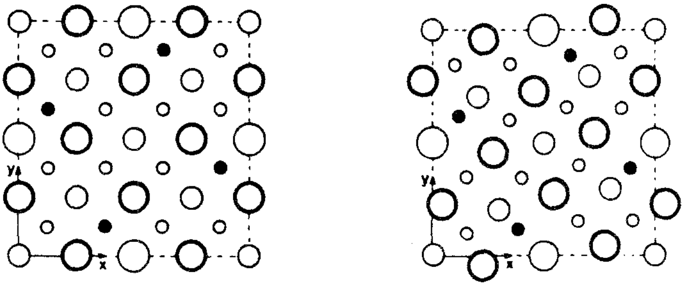
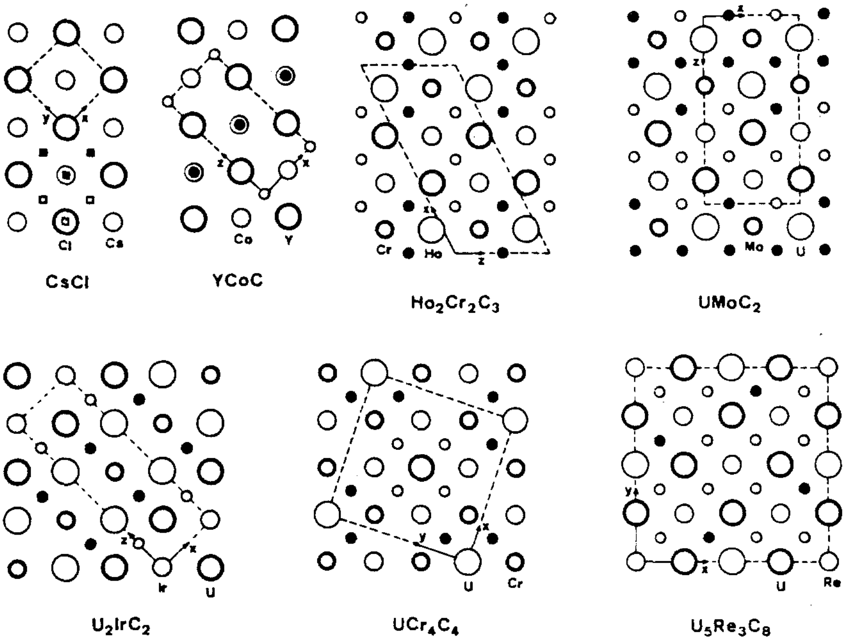


Fig. 2. The crystal structure of $U_5Re_3C_8$ as derived from a cubic body-centered structure of metal atoms by filling of certain interstitial octahedral voids by carbon atoms. Large, medium sized, and small circles represent uranium, rhenium, and carbon atoms at $z = 1/2$ (heavy) and $z = 0$ (light lines). On the left-hand side the structure is shown idealized with the carbon atoms occupying (distorted!) octahedral voids of metal atoms on the positions of a body-centered metal structure. At right the real atomic positions of $U_5Re_3C_8$ are shown for comparison



CsCl YCoC $Ho_2Cr_2C_3$ $UMoC_2$

U_2IrC_2 UCr_4C_4 $U_5Re_3C_8$

Fig. 3. Interstitial carbides which derive from a cubic body-centered arrangement of metal atoms by filling of octahedral voids by carbon atoms. The atom designations correspond to those of Figs. 1 and 2. In the CsCl structure (which corresponds to the metal atoms of YCoC) some of the (distorted) octahedral voids are indicated by squares. The structures are idealized to emphasize their correspondence

Of all known ternary rare earth metal and actinoid transition metal carbides with isolated carbon atoms (thus excluding carbides like Er_2FeC_4 [12], where the carbon atoms form pairs) the carbides $UMoC_2$ and $U_5Re_3C_8$ are those with the highest carbon content. Although a body-centered arrangement of metal atoms offers six (distorted) octahedral interstitial sites per two metal sites, not all of these can be occupied at the same time, because the octahedra interpenetrate each other. Thus, with the observed distribution of carbon atoms in $UMoC_2$ all possible octahedral sites are occupied in this structure. In $U_5Re_3C_8$ the pattern of occupied octahedral sites is such that one more octahedral site per formula unit (two per cell: at 0, 0, 0 and 1/2, 1/2, 1/2) is offered for a carbon atom, however, the distances of this site to the two rhenium atoms above and below are too short (165.1 pm = $c/2$) and we therefore can exclude the possibility of their occupation. Indicating unoccupied octahedral sites with a square the formulas of the ternary carbides of Fig. 3 are as follows: $YCoC\square_2$, $Ho_2Cr_2C_3\square$, $UMoC_2$, $U_2IrC_2\square_2$, $UCr_4C_4\square$, and $U_5Re_3C_8\square$. Of course the number of octahedral voids is larger, if we allow the interpenetration of octahedra (together the number of such occupied and unoccupied octahedral sites is always three times the number of the metal atoms forming the body-centered host structure). In such interpenetrating occupied octahedral voids two carbon atoms come quite close to each other (~ 190 pm). If we allow the carbon atoms to move towards each other, they could form a C-C bond (~ 150 pm). In such an arrangement each carbon atom would have four metal neighbors in common with the other carbon atom, in addition to the two metal neighbors of its own octahedron. Although such environments for C_2-pairs are known (e.g. in the Pu_2C_3-type structure, where the metal atoms also correspond to a body-centered arrangement [13]), so far they were not observed in ternary lanthanoid or actinoid transition-metal carbides.

The weighted average ratio of uranium atoms to rhenium atoms forming the octahedral environment of the C (1), C (2), and C (3) atoms in $U_5Re_3C_8$ is $(5/1 + 4/2 + 2 \times 4/2)/4 = 2.75$. It is thus greater than the ratio of uranium to rhenium $5/3 = 1.67$ in the compound. Similar results are obtained by comparing the corresponding lanthanoid and uranium to transition metal ratios for all carbides of Fig. 3. Also in the carbides with $LaMn_{11}C_{2-x}$ [14], $Pr_2Mn_{17}C_{3-x}$ [15], and $Tb_2Mn_{17}C_{3-x}$ [16] type structure, which do not derive from a body-centered arrangement of metal atoms, the octahedra around the carbon atoms contain two rare earth atoms, far more than what could be expected from the small percentage of rare earth metal atoms in these compounds. A remarkable exception to this regularity is the structure of $Ce_2Ni_{22}C_3$ [17], where the carbon atoms have only nickel neighbors.

As is the case for most intermetallic compounds, a thorough discussion of chemical bonding in $U_5Re_3C_8$ is difficult. Since the carbon atoms are the most electronegative components of the compound, we can assume that their 2 s and 2 p orbitals fully participate in the formation of bonds to the metal atoms, and since the uranium atoms are more electropositive than the rhenium atoms, the bonding bands will have considerable 5 d character. It is more difficult, however, to estimate the valency of the uranium atoms in the ternary uranium transition metal compounds. Thus, using the formalism of oxidation numbers* at first glance everything between $(U^{+6})_5(Re^{+0.67})_3(C^{-4})_8$ and $(U^{+2.2})_5(Re^{+7})_3(C^{-4})_8$ seems possi-

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* We assume familiarity with the concept of oxidation numbers. It can be used for band structures as well as for molecular compounds and salts. It does not imply ionic bonding at all, although, in the hypothetical extreme case of 100% ionic bonding it corresponds to that.

ble. The latter formulation excludes the possibility of rhenium-rhenium bonding (because rhenium atoms with oxidation number + 7 do not have any valence electrons which solely belong to them). Since the rhenium atoms have only two rhenium neighbors at the relatively large distance of 330.3 pm this formulation may come close to the real situation. Thus, a relatively low oxidation number of about + 3 can be assumed for the uranium atoms.

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