

A Neutron-Diffraction Study of the Tetragonal–Monoclinic Crystal Structures of Some Uranium–Thorium Dicarbides

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Crystal-structure line profile refinements have been made for neutron powder diffraction data collected at room temperature from the ternary uranium–thorium dicarbide $U_{0.1}Th_{0.9}C_2$ and the two binary dicarbides UC_2 and ThC_2 . $U_{0.1}Th_{0.9}C_2$ is monoclinic, with unit cell dimensions $a = 6.630(2)$, $b = 4.183(1)$, $c = 6.690(2)$ Å, $\beta = 103.86(1)^\circ$, isostructural with ThC_2 , $a = 6.684(2)$, $b = 4.220(1)$, $c = 6.735(2)$ Å, $\beta = 103.91(1)^\circ$. The tetragonal structure for UC_2 is confirmed, with $a = 3.522(1)$, $c = 5.988(1)$ Å. $U_{0.1}Th_{0.9}C_2$ contains discrete C–C groups 1.297(8) Å long; more precise values for C–C lengths have been determined for UC_2 (1.322(4) Å) and ThC_2 (1.304(6) Å). © 1987 Academic Press, Inc.

1. Introduction

Binary and ternary carbides of the actinides, like those of the transition metals and lanthanides, are of both structural and technological interest, partly because of composition-dependent phase transitions and unusual mechanical and electrical properties. Discrete C_2^{2-} structural units, which commonly occur when the ratio of carbon to metal is greater than one, lengthen slightly (because of $C_2\pi^*$ interactions with cation orbitals) as the cationic charge increases. Neutron diffraction is preferable to X-ray diffraction for the determination of such carbon–carbon distances in the presence of actinide elements which scatter X-rays strongly, and the Rietveld neutron powder refinement method (1) is especially advantageous for symmetries lower than cubic when individually resolved Bragg reflections are few.

Uranium dicarbide, known from X-ray measurements to be tetragonal (2, 3), has a unit cell somewhat smaller than those of the $Y_xHo_{1-x}C_2$ series (4). Early neutron measurements (5–9), based on integrated intensities of Bragg reflections and isotropic thermal parameters, confirmed that the calcium-dicarbide structure prevails over a temperature range 5–2000 K (cubic at 2200 K (8)) with dimensions slightly dependent on heat treatment.

For thorium dicarbide, monoclinic symmetry has been established but appreciably different cell dimensions (and hence C–C bond distances) have been reported (10–12) from X-ray and neutron-diffraction studies. Although the intermediate ternary uranium–thorium dicarbides $U_xTh_{1-x}C_2$ form small crystallites so that diffraction lines are broadened, there is nevertheless some X-ray powder diffraction evidence that the monoclinic ThC_2 structure persists over the

range $x = 0.1$ to 0.55 before giving place to an enlarged tetragonal UC_2 structure (13). Interpretation of powder data is complicated by lines from the free carbon that persists whatever the preparative route.

In view of the lack of comparable neutron profile estimates of C-C dimensions for two binary dicarbides of different symmetries from a system having the same formal cation charge of M^{4+} and of the absence of any neutron-diffraction studies of the intermediate ternary dicarbides, we have prepared thorium-rich carbides $U_xTh_{1-x}C_2$ and report anisotropic profile refinements for $U_{0.1}Th_{0.9}C_2$ and for the two dicarbides UC_2 and ThC_2 .

2. Experimental

2.1. Sample Preparation

UC_2 and the three ternary dicarbides $U_xTh_{1-x}C_2$ ($x = 0.1, 0.3,$ and 0.5) were prepared by direct high-temperature synthesis from stoichiometric quantities of the constituent elements in a small argon-arc furnace as described previously (4). The actinide metals (minimum purity 99.9%) were supplied as arc-melted rods by Koch-Light

Limited. The ThC_2 sample was donated by the Metallurgy Group, D.E.R.E., Caithness.

2.2. Collection of Neutron-Diffraction Data

Neutron-diffraction patterns of the samples, contained in thin-walled cylindrical vanadium cans, were recorded at room temperature on three diffractometers at the High Flux Reactor (HFR) of the Institut Laue-Langevin, Grenoble, and at AERE, Harwell, with instrumental details as given in Table I. Since patterns recorded on D2 for $U_{0.3}Th_{0.7}C_2$ and $U_{0.5}Th_{0.5}C_2$ were weak and contained some reflections which could be indexed only as graphite contaminants, these data were judged inadequate for refinement.

2.3. Structure Refinement

All the structure refinements were carried out with a version of the Rietveld program, modified (14) to allow refinement of anisotropic temperature parameters.

The individual refinement procedures differed in detail as follows, according to the crystal symmetry and source of the data.

(1) UC_2 . The starting point for the profile

TABLE I
INSTRUMENTAL DETAILS FOR COLLECTIONS OF NEUTRON DIFFRACTION DATA

	UC_2 and $U_xTh_{1-x}C_2$ ($x = 0.3, 0.5$)	$U_{0.1}Th_{0.9}C_2$	ThC_2
Reactor	HFR, Grenoble	PLUTO, AERE	DIDO, AERE
Diffractometer	D2	PANDA	CURRAN (5 counters at 10° intervals)
Wavelength [\AA]	1.119	1.536	1.378
2θ range [$^\circ$]	10–120	5–104	5–57 and 55–107
Step increment (2θ)	0.1°	0.1°	0.1°
Counting time point ⁻¹ [min]	0.7	1.5	3.0
Recording time [hr]	12	24	13
Sample can diam [mm]	5	5	10

Note. For run 1 on CURRAN, counter 1 covered $2\theta = 5\text{--}17^\circ$; counter 2, $2\theta = 15\text{--}27^\circ$; and so on (i.e., 2° overlap) to encompass $5\text{--}57^\circ$ in all; similarly in run 2, counter 1 ranged from 55 to 67° so that the overall range was $55\text{--}107^\circ$, again with 2° overlap between consecutive counters. Corrections for differing counter efficiencies were made before refinement.

refinement was the body-centered tetragonal unit cell, space group $I4/mmm$, with the following 13 crystal-structural and instrumental parameters as variables:

- (a) the unit-cell parameters a and c ,
- (b) the anisotropic temperature parameters B_{ij} for the uranium and carbon atoms, subject to the constraints (15) $B_{11} = B_{22}$ and $B_{12} = B_{13} = B_{23} = 0$,
- (c) the z -coordinate for the carbon atom (carbon atoms are located at $0, 0, \pm z$ and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2} \pm z$),
- (d) an overall scale factor, k ,
- (e) the three peak-width parameters U , V , and W in the equation

$$H^2 = U \tan^2\Theta + V \tan \Theta + W$$

where H is the full-width at half-height of the Gaussian curve for the reflection at Bragg angle Θ (16),

- (f) a counter zero-point parameter, Z (1),
- (g) a peak-asymmetry parameter, P (1).

Initial values for these parameters were:

- (a) unit-cell parameters from (5),
- (b,c) atomic positional and thermal parameters from (7),
- (d,e) k and U , V , and W determined as described previously (4),
- (f,g) Z and P zero.

The neutron scattering amplitudes used were $b_U = 8.5$ fm and $b_C = 6.65$ fm (17). Some oscillation in the B_{ij} shifts at the start of refinement was overcome by applying only one-tenth of the calculated shift in each cycle. With this constraint, the refinement converged after about 30 cycles to the parameters in Table II. (Use of refined values of the unit-cell, peak-width, and zero-point parameters to recalculate the profile for further refinement (18) had negligible effect).

The correlation matrix from the final refinement cycle indicated some significant correlations between shifts for parameters within the following groups:

- (1) B_{ij} (coefficients up to 0.8),
- (2) U , V , and W (coefficients > 0.9),
- (3) a , c , Z , and P (coefficients up to 0.8)

(Shifts in k and z_C were not significantly correlated with those of any other parameter). Parameter shifts in the final cycles of refinement were all less than one percent of the estimated standard deviations (ESDs).

(2) ThC_2 . The starting point for the refinement was the C -centered monoclinic unit cell, space group $C2/c$, with the following 24 crystal-structural and instrumental parameters as variables:

- (a) the unit-cell parameters a, b, c , and β ,
- (b) the anisotropic temperature parameters B_{ij} for the thorium and carbon atoms, subject (for the thorium atom) to the constraint (15) $B_{12} = B_{23} = 0$,
- (c) the atomic positional coordinates, y_{Th} for thorium and x_C, y_C , and z_C for carbon; x_{Th} and z_{Th} are fixed by crystallographic symmetry at $x = 0.0$ and $z = 0.25$,

- (d,e,f,g) as for UC_2 .

Initial values were:

- (a,b,c) unit-cell, atomic positional, and thermal parameters from (12),
- (d,e,f,g) as for UC_2 .

TABLE II
RESULTS OF NEUTRON POWDER PROFILE
REFINEMENT FOR UC_2

a	3.522(1)	μ	0.05
c	5.988(1)	ΔB	< 0.001
z_C	0.3897(3)	R	0.134
$B_{11}(U)$	0.36(8)	R_w	0.143
$B_{33}(U)$	0.14(16)	R_E	0.071
$B_{11}(C)$	0.25(8)	C–C	1.322(4)
$B_{33}(C)$	1.12(16)	U–C	2.333(4)

Note. Unit-cell dimensions a and c (Å); fractional coordinates of carbon, z_C ; thermal parameters, $B_{ij} = 8\pi^2 U_{ij}$ (Å²); absorption coefficients μ (cm⁻¹); absorption correction ΔB to B ; unweighted (R), weighted (R_w), and expected (R_E) agreement factors; C–C and U–C bond lengths (Å) (ESDs of least significant figures in parentheses).

The neutron scattering amplitudes used were $b_{\text{Th}} = 10.5$ fm (19) and $b_{\text{C}} = 6.65$ fm (17).

A tendency in the early stages for some thermal parameters to become nonpositive definite was overcome by applying only one-hundredth of the calculated shift to each of the thermal parameters, by holding the off-diagonal elements constant in some cycles, and by extending the refinement to about 50 cycles. Use of refined values of the unit-cell, peak-width, and zero-point parameters to recalculate the profile for further refinement reduced the R_w value from 0.145 to 0.140. Repetition of this procedure gave no further improvement so that the final parameter values are as in Table III. Again, there were significant correlations between shifts for parameters within the groups:

- (1) B_{ij} (coefficients ≤ 0.7),
- (2) U , V , and W (coefficients > 0.9),
- (3) a , c , Z , and P (coefficients up to 0.5).

Shifts in k and in the atomic positional parameters were not significantly correlated, either with each other or with those of any other parameter. Parameter shifts in the final cycles of refinement were all less than the ESDs and, in most cases, were less than one-tenth of the ESD.

(3) $U_{0.1}\text{Th}_{0.9}\text{C}_2$. The starting point for this profile refinement was the structure of ThC_2 , with the same initial values as above for the crystal structural parameters; starting values for the instrumental parameters were determined in the same way as for UC_2 and ThC_2 . The diffraction pattern showed no evidence of ordering of the metal atoms, and the neutron scattering amplitude used for the metal atom was the weighted mean of those for uranium and thorium.

Since, with these starting values, R did not reduce below 0.50, the profile was recalculated with unit-cell parameters derived from the preliminary cycles of refine-

TABLE III
RESULTS OF NEUTRON POWDER PROFILE
REFINEMENTS FOR ThC_2 AND $U_{0.1}\text{Th}_{0.9}\text{C}_2$

	ThC_2	$U_{0.1}\text{Th}_{0.9}\text{C}_2$
a	6.684(2)	6.630(2)
b	4.220(1)	4.183(1)
c	6.735(2)	6.690(2)
β	103.91(1)	103.86(1)
y_M	0.2022(9)	0.2050(11)
x_C	0.2986(7)	0.3001(9)
y_C	0.1305(8)	0.1320(11)
z_C	0.0513(7)	0.0522(9)
$B_{11}(M)$	0.37(29)	0.40(28)
$B_{22}(M)$	0.90(21)	1.05(33)
$B_{33}(M)$	0.84(32)	0.62(31)
$B_{13}(M)$	0.0(14)	0.13(18)
$B_{11}(C)$	0.94(27)	1.23(33)
$B_{22}(C)$	0.56(23)	1.29(33)
$B_{33}(C)$	0.40(18)	1.32(34)
$B_{12}(C)$	-0.09(15)	-0.32(28)
$B_{13}(C)$	0.08(15)	0.48(22)
$B_{23}(C)$	0.46(19)	0.21(28)
μ	0.04	0.04
ΔB	0.002	0.002
R	0.130	0.179
R_w	0.140	0.196
R_E	0.069	0.132

Note. Unit-cell dimensions a and c (Å) and angle β (degrees); fractional y coordinates of metal atoms y_M ; fractional coordinates of carbon atoms x_C , y_C , and z_C ; thermal parameters $B_{ij} = 8\pi^2 U_{ij}$ (Å²) of metal and carbon atoms; absorption corrections ΔB to B ; unweighted (R), weighted (R_w) and expected (R_E) agreement factors (ESDs of least significant figures in parentheses).

ment, in which only the unit cell parameters and scale factor were varied. Refinement now proceeded smoothly, without problems of either parameter oscillation or nonpositive definite thermal parameters, to give the final parameter values in Table III. The correlation matrix from the final cycle of refinement had a similar pattern to that of ThC_2 . Parameter shifts in the final cycles of refinement were all less than one percent of the ESDs.

Lists of observed and calculated intensi-

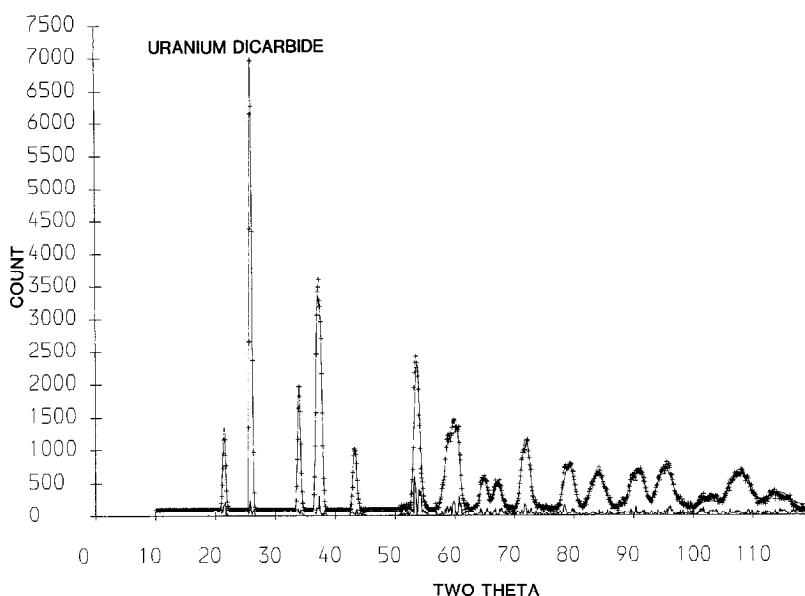


FIG. 1. Neutron powder diffraction diagram for UC_2 : solid line, calculated profile; crosses, experimental intensities; differences between these are shown at the bottom.

ties for all points for the three structures have been deposited.¹

3. Results and Discussion

For all three structures, application of the absorption correction for thermal parameters (coefficients μ in Tables II and III, calculated from mass absorption coefficients U, 0.005; Th, 0.01; C, 0.00015 $cm^2 g^{-1}$) in accordance with the Hewat procedure (20) produced corrections ΔB smaller than the apparent ESDs. Thermal vibration

corrections (which would tend to increase the estimates of the C–C bond lengths) were not applied, since none of the usual models (21) seemed appropriate.

3.1. UC_2 (Fig. 1)

Although the final ESDs of the refined parameters are similar to those with our data for structures on the same diffractometer (4), the agreement indices (Table II) are somewhat higher, probably because of inferior counting statistics (maximum peak height ~ 7000 counts for UC_2 compared with 13,000 to 20,000 counts for the analogous peaks in $Y_xHo_{1-x}C_2$ (4)).

The unit-cell dimension c is significantly smaller than the most recent published (9) value of 6.000(1) Å for the room-temperature structure but both a and c agree well with the X-ray determinations (2) for slowly cooled samples. The C–C distance of 1.322(4) Å is the most accurate determination that has been made (though formally it does not differ significantly from earlier

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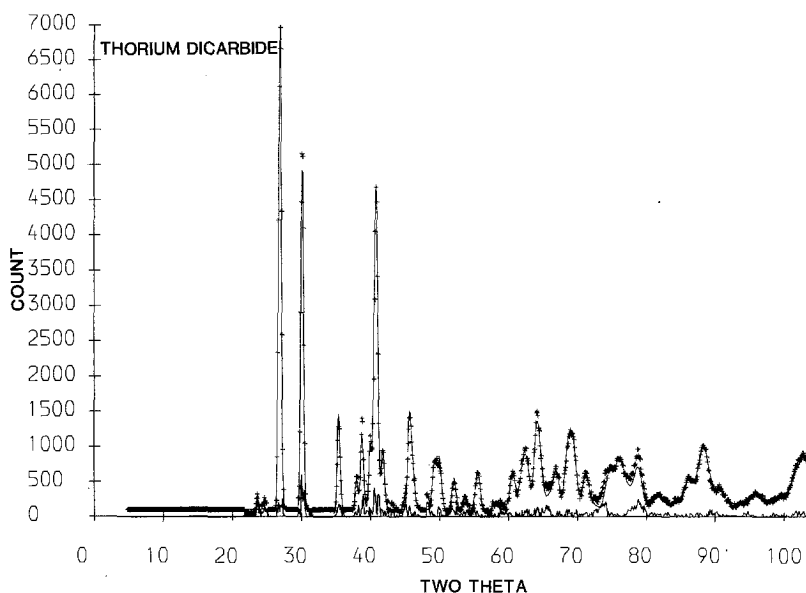


FIG. 2. Neutron powder diffraction diagram for ThC_2 ; details as for Fig. 1.

measurements (5–9) because of their larger standard deviations). For the carbon atom, the anisotropic thermal parameters show B_{33} larger than B_{11} , i.e., thermal vibration is greater along than perpendicular to the C–C bond; the reverse is the case for the dicarbides of yttrium and holmium (4) which have shorter C–C bond lengths. The refined half-height width parameters were close to those for other measurements from the same diffractometer (4).

3.2. ThC_2 (Fig. 2).

Although the final R indices (Table II and III) and counting statistics (maximum peak height ~ 7000 counts) are similar for the ThC_2 and UC_2 refinements, the ESDs of the final parameters (Table III) are somewhat larger for the ThC_2 refinement (with more variables) than for that of UC_2 .

The unit-cell dimensions a and c (Table III) are marginally smaller, and the β angle is slightly larger, than found in the earlier neutron study (12); the C–C bond length (Table IV) of 1.304(6) Å agrees closely with

the previously reported value (12). The metal–carbon distances have been determined more accurately than before; some of the differences in metal–metal distances are significant. Some anisotropy in the thermal motions of both thorium and carbon atoms may be inferred from the refined aniso-

TABLE IV
INTERATOMIC DISTANCES IN ThC_2 AND $\text{U}_{0.1}\text{Th}_{0.9}\text{C}_2$

Bond	ThC_2			$\text{U}_{0.1}\text{Th}_{0.9}\text{C}_2$
	(10)	(12)	Present work	Present work
C–C	1.47	1.315(41)	1.304(6)	1.297(8)
M–C A	2.43	2.66(11)	2.674(11)	2.658(13)
B	2.38	2.44(8)	2.453(9)	2.420(10)
C	2.92	2.78(11)	2.783(11)	2.755(13)
D	2.89	2.90(16)	2.848(15)	2.847(17)
E	2.86	2.94(7)	2.922(8)	2.901(9)
M–M	3.70	3.800(5)	3.771(3)	3.759(3)
	3.90	3.957(2)	3.952(3)	3.920(4)
	4.14	4.181(8)	4.207(3)	4.157(4)
	4.24	4.223(3)	4.220(6)	4.183(7)

Note. Distances are in Å; the nomenclature for the M–C bonds is that of Hunt and Rundle (10).

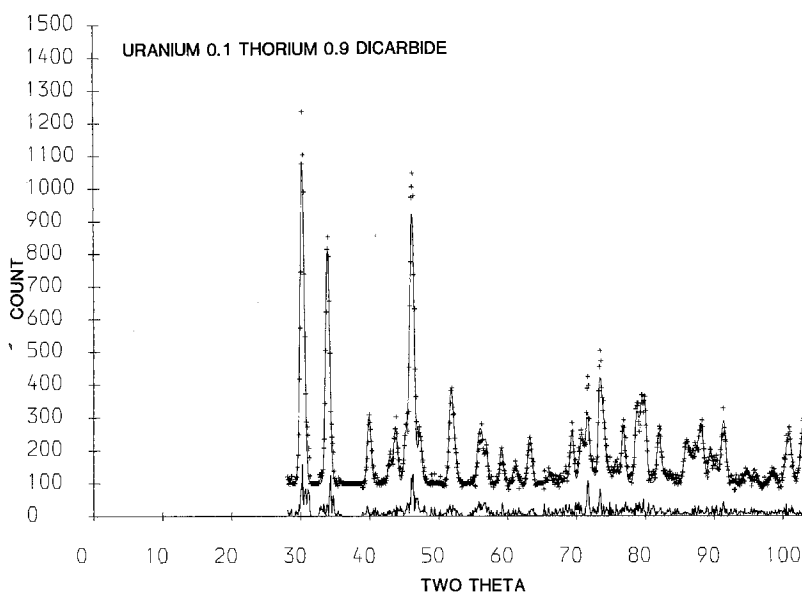


FIG. 3. Neutron powder diffraction diagram for $U_{0.1}Th_{0.9}C_2$; details as for Fig. 1.

tropic thermal parameters. The refined half-height width parameters were again close to those for other refinements on data from the same instrument (22).

3.3. $U_{0.1}Th_{0.9}C_2$ (Fig. 3)

The ESDs of the unit-cell parameters and the atomic positional coordinates are similar to those obtained for ThC_2 ; those of the thermal parameters are somewhat larger (Table III). The higher agreement indices than for UC_2 and ThC_2 may be a reflection of poorer counting statistics (maximum peak height ~ 1500 counts for $U_{0.1}Th_{0.9}C_2$, compared with ~ 7000 for UC_2 and ThC_2).

The unit-cell dimensions (Table III) are significantly smaller than those of ThC_2 , as was evident from the X-ray measurements (13). The C–C bond lengths in ThC_2 and $U_{0.1}Th_{0.9}C_2$ (Table IV) are the same within experimental error; only B and C of the metal–carbon distances have differences on the verge of significance, but all the metal–metal distances are significantly smaller in $U_{0.1}Th_{0.9}C_2$ than in ThC_2 . This is consistent with a decrease in the effective

ionic radius of the metal atom as thorium is replaced by even a small proportion of uranium.

For the metal atom, thermal parameters are similar to those for ThC_2 ; the absence of detectable anisotropy for the carbon atom may be because of data limitations (longer wavelength and more restricted $\sin \Theta/\lambda$ range).

4. Conclusions

Incorporation of 10 atom percent uranium in the room-temperature thorium dicarbide structure induces an appreciable contraction of the unit cell but monoclinic symmetry is retained in $U_{0.1}Th_{0.9}C_2$. At this composition there is no perceptible increase in the length of the discrete C–C dimers (close to 1.30 \AA , i.e., longer than in the $Y_xHo_{1-x}C_2$ series) toward the C–C separations of 1.32_2 \AA determined in the tetragonal structure of UC_2 . Crystallite problems prevented a fuller examination of the role of volume contraction on C–C length in the monoclinic $U_xTh_{1-x}C_2$ structures.

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